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# Catalytic polymerization of cycloolefins and isocyanates with transition metal complexes

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## PhD THESIS

Catalytic polymerization of cycloolefins and isocyanates with transition metal complexes

Καταλυτικός πολυμερισμός κυκλοολεφινών και ισοκυανικών εστέρων με σύμπλοκα των στοιχείων μεταπτώσεως

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# ABSTRACT

In this thesis two types of metal-mediated polymerization have been studied: (a) metathesis polymerization, including alkyne metathesis polymerization and ring opening metathesis polymerization (ROMP) for the synthesis of unsaturated polymers; and, (b) condensation polymerization for the synthesis of polyurea.

Metathesis polymerization. The kinetics of the polymerization of phenylacetylene, norbornene and some of its derivatives with the catalytic system  $(Ph_4P)_2[W_2(\mu-Br)_3Br_6]/AgBF_4$  (1;  $\{W_{2.5}^{2.5}W\}^{7+}$ ,  $a^{-2}e^{-3}$ ) has been studied. The catalytic system Na[W<sub>2</sub>( $\mu$ -Cl)<sub>3</sub>Cl<sub>4</sub>(THF)<sub>2</sub>]·(THF)<sub>3</sub>/PA (**2**; {W- $\frac{3}{2}$ W}<sup>6+</sup>,  $a'^{2}e''^{4}$ ; PA: phenylacetylene) was used for the synthesis of highly crosslinked poly(dicyclopentadiene) (PDCPD) xerogels, which showed extreme swelling. This behavior is unique compared to polymeric and carbon-based adsorbents from the literature, and is directly related to the use of the ditungsten catalyst.  $Na[W_2(\mu-CI)_3CI_4(THF)_2] \cdot (THF)_3/NBD$  (3; NBD: norbornadiene) was also used as a catalytic system for the synthesis of PDCPD xerogels and aerogels. Those materials are very robust and show high and fast solvent uptake, which renders them excellent candidates for sensors. Finally, those catalytic systems not only provide cost-efficient alternatives to well-established W- and Ru-based catalysts, but also provide polymeric materials with unique properties via facile synthetic routes, rendering them attractive for environmental remediation applications.

*Condensation polymerization.* The synthesis of polyurea aerogels using transition metal compounds (M: Cr, Fe, Co, Ni, Cu, Mo, W) as catalysts has been studied. The resulting aerogels were doped with metal ions homogeneously throughout their entire network. Those metal-doped aerogels were pyrolyzed providing metal-doped porous carbons.

**SUBJECT AREA**: Catalysis

**KEYWORDS**: aerogels, metal-metal bonds, polyurea, polydicyclopentadiene, ROMP

## ΠΕΡΙΛΗΨΗ

Στην παρούσα διατριβή εξετάζονται δύο τύποι αντιδράσεων πολυμερισμού καταλυόμενων από μεταλλικές ενώσεις: (α) ο πολυμερισμός μετάθεσης, που περιλαμβάνει τον μεταθετικό πολυμερισμό αλκινίων και τον μεταθετικό πολυμερισμό αλκινίων και τον μεταθετικό πολυμερισμό, για τη σύνθεση ακόρεστων πολυμερών, και (β)ο πολυμερισμός συμπύκνωσης για τη σύνθεση πολυουρίας.

Πολυμερισμός μετάθεσης. Μελετήθηκαν τρία καταλυτικά συστήματα. Η κινητική του πολυμερισμού φαινυλακετυλενίου (PA), νορβορνενίου και παραγώγων αυτού μελετήθηκε με (Ph<sub>2</sub>P)<sub>2</sub>[W<sub>2</sub>(μ-Br)<sub>3</sub>Br<sub>6</sub>]/AgBF<sub>4</sub> (**1**: {W<sup>2.5</sup>W}<sup>7+</sup>, a<sup>2</sup>e<sup>3</sup>). Χρησιμοποιήθηκε το Na[W<sub>2</sub>(μ-Cl)<sub>3</sub>Cl<sub>4</sub>(THF)<sub>2</sub>] (THF)<sub>3</sub>/PA (**2**: {W<sup>3</sup>W}<sup>6+</sup>, a<sup>2</sup>e<sup>2</sup>) για τη σύνθεση πηκτωμάτων (πολυ)δικυκλοπενταδιενίου (PDCPD) με υψηλό βαθμό δικτύωσης, τα οποία παρουσίασαν πολύ μεγάλη διόγκωση και προσρόφηση οργανικών διαλυτών. Αυτή η συμπεριφορά είναι μοναδική σε σύγκριση με άλλα υλικά της βιβλιογραφίας, και σχετίζεται άμεσα με τη χρήση του καταλύτη **2**. Επίσης, το Na[W<sub>2</sub>( $\mu$ -Cl)<sub>3</sub>Cl<sub>4</sub>(THF)<sub>2</sub>] (THF)<sub>3</sub>/NBD (**3**, NBD: νορβορναδιένιο) χρησιμοποιήθηκε για τη σύνθεση πηκτωμάτων και αεροπηκτωμάτων PDCPD, τα οποία είναι πολύ ανθεκτικά και παρουσιάζουν υψηλή και γρήγορη πρόσληψη διαλύτη. Τα παραπάνω καταλυτικά συστήματα δεν παρέχουν μόνο οικονομικά αποδοτικές εναλλακτικές λύσεις σε σύγκριση με καθιερωμένους καταλύτες W και Ru, αλλά επίσης παρέχουν πολυμερικά υλικά με μοναδικές ιδιότητες μέσω εύκολων συνθετικών οδών, καθιστώντας τα κατάλληλα για εφαρμογές που αφορούν στην προστασία του περιβάλλοντος.

Πολυμερισμός συμπύκνωσης. Μελετήθηκε η παρασκευή αεροπηκτωμάτων πολυουρίας χρησιμοποιώντας ως καταλύτες ενώσεις μετάλλων μετάπτωσης (M: Cr, Fe, Co, Ni, Cu, Mo, W). Τα συγκεκριμένα αεροπηκτώματα (Mαεροπηκτώματα) φέρουν μεταλλικά ιόντα ομογενώς κατανεμημένα σε ολόκληρο το δίκτυο τους και με την πυρόλυσή τους παράγονται πορώδεις άνθρακες με μεταλλικές ενώσεις.

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**ΛΕΞΕΙΣ ΚΛΕΙΔΙΑ**: αεροπηκτώματα, δεσμοί μετάλλου-μετάλλου, πολυουρία, πολυδικυκλοπενταδιένιο, ROMP

... to the memory of my beloved father,

... to my family and fiancé

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## **CHAPTER 1**

# **RING OPENING METATHESIS POLYMERIZATION (ROMP)**

#### 1.1 Introduction

An important class of olefin metathesis reactions which induce the cleavage and formation of carbon-carbon double and triple bonds (Scheme 1), allowing for the one-step synthesis of complex functional molecules, involves ring opening metathesis polymerization (ROMP). ROMP provides polyalkenamers<sup>1–</sup> <sup>3</sup> and it is considered as one of the most important tools in polymer and materials science. The importance of this reaction has been acknowledged by the 2005 Nobel Prize in Chemistry,<sup>4</sup> awarded to Y. Chauvin, R. H. Grubbs and R. R. Schrock "for the development of the metathesis method in organic synthesis". The mechanism of ROMP is similar to that of any olefin metathesis reaction. Initiation and propagation occur by formation of an open coordination site and by formation of a metallacyclobutane intermediate, respectively. After termination, the unsaturated polymer is formed.



Scheme 1. Mechanism of olefin metathesis reaction.

A wide range of unsubstituted and substituted cycloolefins have been used as monomers for ROMP reaction. Cycloolefins have one or more degrees of unsaturation and may be monocyclic, bicyclic or polycyclic. Depending on the ligands of the cycloolefins, such as alkyl, cycloalkyl or aryl groups and also with functional groups, the monomers can be classified as monocyclic, bicyclic and polycyclic and monomers with functional groups.<sup>5,6</sup>

In the past few decades, there has been a growing interest in dicyclopentadiene (DCPD) as a monomer for ROMP because of its low cost, high reactivity and ability to give highly crosslinked materials.<sup>7–10</sup> As shown in Scheme 2, two mechanisms of crosslinking contribute to the formation of crosslinked poly(dicyclopentadiene) (**PDCPD**) either *via* metathesis or *via* radical addition on the double bond of the pendant cyclopentene ring.<sup>11</sup> ROMP-derived crosslinked **PDCPD** is a rigid polymer with excellent mechanical, chemical and physical properties.<sup>12–14</sup> **PDCPD** aerogels combine the unique properties of aerogels with those of **PDCPD** polymer.<sup>12,13,15–17</sup> Thus, thermally stable and mechanically strong **PDCPD** aerogels can find applications as thermal and acoustic insulators,<sup>12</sup> or as low-density coatings.<sup>15</sup>



Scheme 2. ROMP of DCPD.

#### 1.2 Catalytic systems for ROMP reaction

The first catalysts that were active for ROMP reaction were reported by H. S. Eleuterio in 1957.<sup>18</sup> From this discovery, the development of catalysts for ROMP reaction was rapid over the last few decades due to their unprecedented potential to create new polymers having industrial and technological applications.

ROMP can be catalyzed with a wide range of catalytic systems consisting of one, two or more components, based on transition metal mononuclear complexes along the periodic table (Ti, Nb, Ta, Cr, Mo, W, Re, Co, Ru, Os).<sup>6,19,20</sup> Among those, the protagonists are those of ruthenium, molybdenum and tungsten, which are discussed in Sections 1.3-1.5. On the other hand, only a few examples of catalytic systems with bimetallic clusters have been developed for this reaction. In these clusters, the metal centers are linked with bridging ligands and/or directly with a metal-metal bond. Those bimetallic complexes are used for ROMP and metathesis reactions and in most cases their activity is limited to a monomer or requires strictly defined conditions.<sup>21</sup>

The activity of the catalysts for a particular monomer depends to some extent on the exothermic ROMP reaction. Rings with high strain can be activated by catalytic systems based on titanium, vanadium, ruthenium, osmium and iridium complexes, whereas rings with lower strain require more reactive catalytic systems (based on ruthenium, molybdenum, tungsten), used at strictly controlled conditions. Polymerization times can vary from a few seconds to several days. The activity of the catalytic systems depends most of the times on the ratio of the components, the order of mixing, whether the monomer is added at the end or beginning (catalyst-cocatalyst incubation time). For example, [WCl<sub>6</sub>]/EtAlCl<sub>2</sub>/EtOH with molar ratio 1/4/1, exhibits maximum activity immediately after the reactants are mixed. Under these conditions it is preferable for the monomer to be added before EtAlCl<sub>2</sub>. Another catalytic system, [WCl<sub>6</sub>]/Me<sub>4</sub>Sn, takes some time to develop maximum activity. In this case the monomer must be added last.<sup>22</sup>

Catalytic systems for ROMP reactions can be divided in two general classes:

(i) well-defined metal carbenes, such as  $[(C_6H_5)_2C=W(CO)_5]$ , (PCy<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>Ru=CHCH=CPh<sub>2</sub>, Mo(NAr)CHC(CH<sub>3</sub>)<sub>2</sub>R){OC(CH<sub>3</sub>)(CF<sub>3</sub>)<sub>2</sub>}<sub>2</sub>, and

(ii) ill-defined systems, in which the active metal carbene is formed from the reaction of the monomer with the metallic center (*in situ* formation).<sup>23</sup>

An effective catalyst, in general, should:

- convert the growing chains of polymers quantitatively and rapidly (ie rapid start from kinetic aspect);
- have the ability to control the molecular weight and molecular weight distribution of the polymer (especially important for linear polymers);

- have such activity as to maintain the living-polymerization;
- exhibit good solubility in common organic solvents; and
- for practical reasons, be stable at ambient temperature, air, humidity and common functional groups.<sup>24</sup>

Particular attention should be paid to the study of two groups, R.H. Grubbs<sup>25</sup> and R.R. Schrock,<sup>26</sup> who together with Y. Chauvin<sup>27</sup> were honored with Nobel prize in Chemistry in 2005. The Grubbs and Schrock investigations led in the development of the well-defined transition metal carbenes, which quickly prevailed over all others. Below, the Grubbs and Schrock catalysts will be discussed in more detail.

#### 1.3 Schrock-type catalysts

The synthesis of well-defined metal carbenes of molybdenum was first reported by R. R. Schrock *et al.* in 1990.<sup>28,29</sup> The above and the tungsten carbene analogs are now known as Schrock-type catalysts. Catalysts of this type have the general formula [M(NAr')(OR')<sub>2</sub>(CHR)L] (Scheme 3), wherein M = Mo or W, Ar = Ph or substituted phenyl, R = Et, Ph, SiMe<sub>3</sub>, CMe<sub>2</sub>Ph or <sup>*t*</sup>Bu, R' = CMe<sub>3</sub>, CMe<sub>2</sub>CF<sub>3</sub>, CMe(CF<sub>3</sub>)<sub>2</sub>, C(CF<sub>3</sub>)<sub>2</sub> or aryl, L = cuminidine, trialkylphosphine or tetrahydrofuran (THF). The complexes commonly used and commercially available have a neopentylidene, neophenylidene, etc. as ligand. Schrock-type catalysts are very difficult to synthesize and this is a very serious disadvantage compared to the other catalytic systems.<sup>30–32</sup>



Scheme 3. Examples of Schrock-type metal carbenes.

#### 1.4 Grubbs-type catalysts

Scheme 4 shows the first, second and third generation Grubbs catalysts. They are tolerant to olefin functional groups. A large number of Grubbs-type catalysts that promote ROMP have been synthesized. Their basic structure consists of a ruthenium atom, two halides, and two neutral molecules. However, modern catalysts are significantly more active, more stable in air and soluble in more organic solvents.<sup>33,34</sup>



Scheme 4. 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> generation Grubbs catalysts.

RuCl<sub>2</sub> (PPh<sub>3</sub>)<sub>2</sub>(CH=CH=CPh<sub>2</sub>)] complex was shown to satisfactorily catalyze the polymerization of norbornene and substituted norbornenes *via* ROMP, although the  $k_i/k_p < 1$  ( $k_p$ : polymerization rate constant;  $k_i$ : initiation rate constant). The first generation Grubbs catalyst is also precursor for other Grubbs-type catalysts. In August 1999, R.H. Grubbs reported the secondgeneration catalyst, based on a saturated N-heterocyclic carbene [1,3bis(2,4,6-trimethylphenyl)dihydroimidazole].<sup>35</sup>

#### 1.5 Bimetallic clusters with metal-metal bonds

The synthesis of compounds containing metal-metal bonds was first reported in 1844 when E.M. Peligot published the synthesis of a highly air-sensitive compound, without knowing the existence of metal-metal bond.<sup>36</sup> M–M bonds and their chemistry are known for many decades, but several publications are dedicated to recent advances in chemistry.<sup>37–40</sup> Moreover, metal-metal bonded systems are finding increasing applications in various fields, such as molecular electronics,<sup>41</sup> catalysis,<sup>10,42,43</sup> or enzyme-mediated transformations.<sup>44</sup> Bimetallic complexes that are of interest to us in this work, can be classified, based on the metal center, in the following three categories:<sup>21,45,46</sup> (a) clusters of group 6 (Mo and W); (b) clusters of group 8 (Ru, Os); and (c) heterometallic clusters.

#### (A) Clusters of group 6 (Mo and W)

Several neutral and ionic clusters of Mo have been reported, in the form of  $[Mo_2L_4]$  or  $[Mo_2L_2X_4]_n$ , including a core with a quadrapole metal-metal bond and a plurality of ligands. These clusters are reactive in the ROMP of norbornene at ambient temperature, most of which require activation by AIEt<sub>2</sub>CI.<sup>46</sup> Same behavior is also observed with the cluster [{Mo<sub>2</sub>(µ- $O_2C(CH_2)_2CO_2)(NCMe)_6_2](BF_4)_4 \cdot 3MeCN (Scheme 5, I).$  When  $[MO_2(\mu - O_2CR)_4]$ (R= Me, CF<sub>3</sub>) (Scheme 5, II) and K<sub>4</sub>[Mo<sub>2</sub>Cl<sub>8</sub>] (Scheme 5, III) clusters are activated by AIEt<sub>2</sub>CI, they promote the ROMP of 1-methylnorbornene<sup>47</sup> and the reaction is rapid and exothermic. In all cases, the different ligands almost do not affect the stereoselectivity of the reaction.<sup>46</sup>



Scheme 5. Bimetallic Mo clusters that have been used as ROMP catalysts.

The first reference for ROMP catalyzed with a cluster was made in 1970. A twocomponent system consisting of  $[W_2(\pi-C_3H_5)_4]$  ({W-4-W}<sup>4+</sup>) and  $[WCl_6]$  was found to be active towards the ROMP of cyclopentene, giving high yields with a 60% *trans*-content.<sup>48</sup> The cluster  $[W_2(NAr)_2(\mu-OCMe_2CF_3)_3(C_2H_4)]$  ({W-1-W}<sup>10+</sup>, Scheme 6, I) slowly polymerizes norbornene.<sup>49</sup> Also, the bimetallic cluster Na<sub>4</sub>[W<sub>2</sub>Cl<sub>8</sub>]•(THF)<sub>x</sub> ({W-4-W} }<sup>4+</sup>,  $\sigma^2\pi^4\delta^2$ ) (Scheme 6, II) selectively polymerizes several cycloolefins, such as norbornene and norbornadiene, to yield polymers with high molecular weights and high *cis*-content.<sup>21,50,51</sup> A major disadvantage of this system is its sensitivity to oxygen, humidity and thermal instability. The Na[W<sub>2</sub>( $\mu$ -Cl<sub>3</sub>)Cl<sub>4</sub>(THF)<sub>2</sub>].(THF)<sub>3</sub> (**2**; {W<sup>3</sup>W}<sup>6+</sup>,  $\alpha$ <sup>2</sup>e<sup>4</sup>) (Scheme 6, III) catalyzes effectively the ROMP of several cycloolefins providing polymers with a high *cis*-content (80%).<sup>42,43</sup> The reactivity of the perbromo-complex (Ph<sub>4</sub>P)<sub>2</sub>[W<sub>2</sub>( $\mu$ -Br)<sub>3</sub>Br<sub>6</sub>] (**1**; {W<sup>2.5</sup>W}<sup>7+</sup>,  $\alpha$ <sup>2</sup>e<sup>3</sup>) towards the ROMP of norbornene and some of its derivatives as well as towards the mechanistically related polymerization of phenylacetylene has also been explored (Scheme 6, IV). **1** is easily accessible, moderately air-stable, bears labile ligands and higher nuclear charge compared to **2**. The results showed that addition of a silver salt (AgBF<sub>4</sub>) is required in order to activate the ditungsten complex.<sup>10,52</sup>



Scheme 6. Bimetallic W clusters that have been used as ROMP catalysts.

#### (B) Clusters of group 8 (Ru, Os)

Among the first catalysts used for ROMP, about 50 years ago, are RuCl<sub>3</sub> and OsCl<sub>3</sub>. Those systems are very active under reflux in alcohol solutions.<sup>53</sup> Although mononuclear catalytic systems of Ru are in abundance, there are very few examples of binuclear systems. Clusters of the form [Ru<sub>2</sub>L<sub>4</sub>] ({Ru<sup>2</sup>-Ru}<sup>4+</sup> L = acetates, benzoates, etc., Scheme 7, I) are inactive for initiating ROMP in a non-alcohol environment, even in the presence of strong Lewis acids.<sup>54</sup> The [Cp\*<sub>2</sub>Ru<sub>2</sub>Cl<sub>4</sub>] ({Ru<sup>3</sup>-Ru}<sup>6+</sup>; Scheme 7, II) promotes the ROMP of norbornene and norbornadiene by refluxing in ethanol, but at low yields. Higher activity is observed in the osmium complex [Cp\*<sub>2</sub>Os<sub>2</sub>Br<sub>4</sub>] ({Os<sup>3</sup>-Os}<sup>6+</sup>,  $\sigma^2 \pi^4 \delta^2 \delta^{*2}$ , Scheme 7, IV), which upon activation by methylaluminoxane polymerizes norbornene to

give polymers insoluble in organic solvents and with a moderate *cis*-content.<sup>55</sup> Finally, the trinuclear cluster  $Os_3(\mu-H)_2(CO)_{10}]$  ({ $Os_3$ }<sup>2+</sup>, Scheme 7, III) has been reported to promote the norbornene ROMP reaction.<sup>56</sup>



Scheme 7. Ru and Os clusters used as ROMP catalysts.

#### (C) Heterometallic clusters

All of those clusters carry a simple metal-metal bond and are structurally unsaturated, which allows the cycloolefin to be easily attached. Clusters  $[M_2(\mu-Cl)_3(CO)_7(M'Cl_3)]$  and  $[M(\mu-Cl)(CO)_3(M'Cl_3)]$  (Scheme 8) are catalyst precursors for the ROMP of norbornene and norbornadiene.<sup>57</sup> The second cluster (Scheme 8, II; M = Mo or W, M' = Sn or Ge) polymerizes substituted cycloolefins too.<sup>58</sup> It is worth noting that the choice of transition metal determines the stereochemistry of the polymer produced.



Scheme 8. Heterometallic clusters with single M-M bond that have been used as ROMP catalysts.

# CHAPTER 2 AEROGELS

## 2.1 Definition and historical notes

According to IUPAC Gold Book aerogel is a gel comprised of a microporous solid in which the dispersed phase is a gas.<sup>59</sup> More accurately, they can be defined as solid colloidal or polymeric networks of particles expanded throughout their entire volume by a gas.<sup>60,61</sup> Aerogels were invented by S. S. Kistler in the 1930s in order to study the structure of wet-gels.<sup>62</sup> The first aerogels were produced from silica gels. The silica gel powder was marketed in 1940 by Monsanto Corporation under the name SANTOCEL (used as a coagulant for colors, makeup or in cigarette filters).<sup>63,64</sup> Later, S. S. Kistler expanded into alumina, chromium and tin dioxide aerogels. In 1980, he introduced safer techniques for producing aerogels, which were 30 times lighter than previously achieved. Big pieces of silica aerogels were commercially available (Hamburg/DESY and Lund) for application to high-energy Cerenkov detectors.<sup>65</sup>

#### 2.2 Properties of aerogels

As we have already mentioned, aerogels are porous solids consisting of a network of interconnected particles. Aerogels can be microporous, mesoporous, or macroporous; usually they are mesoporous. Microporous materials have pores <2 nm in diameter and mesoporous materials have pores in the range of 2 to 50 nm in diameter. Aerogels usually have high porosities, sometimes as high as 99 % v/v. As a result, aerogels can be extremely lightweight materials.<sup>66–68</sup> Therefore, the term aerogel does not refer to a particular substance, but to the morphology of the substance. Aerogels can be derived from a wide variety of substances, such as:

- Silicon oxide
- Main group metal oxides (e.g., tin oxide)
- Transition metal oxides (e.g., iron oxide)
- Lanthanide and actinide oxides

36
- Organic polymers (e.g., polyureas, polyacrylates, polystyrenes, polyurethanes, polyamides, polyimides, ROMP-derived polymers)
- Biopolymers (e.g., pectin, cellulose, alginate)
- Carbon
- ✤ •Metals (e.g., copper, gold)

Aerogels have a combination of impressive properties that other materials do not have. For example, the lowest density of any material known today, the lowest dielectric constant of any solid material, the highest specific surface area, but also the slower sound propagation through any other solid material. In addition, aerogels are considered as excellent thermal insulators, since they almost prevent two of the three heat transfer methods.<sup>68,69</sup>

Moreover, it should be noted that by adjusting the gelation process of wet-gels, many of their properties can be adjusted. For example, their density can be adjusted by increasing or decreasing the concentration of the initial gelation solution. Similarly, thermal conductivity can also be adjusted in this way, since it is related to density. Typically, aerogels have densities in the range of 0.5 to 0.01 g cm<sup>-3</sup> and surface areas ranging from 100 to >2000 m<sup>2</sup> g<sup>-1</sup>. Other properties such as transparency, color, mechanical strength, etc. are primarily dependent on the composition of the aerogel.

### 2.3 Applications of aerogels

Aerogels are finding more and more applications in today's industry, due to their spectacular properties.<sup>70</sup> Briefly, they have become attractive candidates for a wide range of applications including thermal insulators,<sup>71,72</sup> batteries,<sup>73,74</sup> hydrogen storage,<sup>75</sup> absorbents,<sup>76,77</sup> catalysts and catalyst supports.<sup>78–80</sup> Some of those applications are described below.

Because of their significant heat-insulating and sound-insulating properties, as well as their low weight, they can replace conventional insulating materials in constructions or industrial insulation. This is the biggest market for aerogels at the time; around \$500 million since 2013.<sup>81</sup>

Because of their high surface area and porosity, many of those materials have also been used as filter media to remove heavy metals, or as absorbents for cleaning various leaks.<sup>82</sup> For example, aerogels derived from copper alloys such as sulfur, selenium, tellurium, etc., have shown promising data for the adsorption of heavy metals (mercury, lead and cadmium) from water.<sup>83</sup>

In 2000, a commercial production of aerogel blankets was made of silica gel reinforced with fibers. This product had a variety of mechanical and thermal properties depending on the choice of reinforcing fibers. Something similar was also used by the US Navy in divers suits as passive thermal protection.<sup>84</sup>

Many bio-aerogels have also been tested for medical applications. They have been used as drug delivery systems due to their biocompatibility. The high surface area and porous structure of those aerogels allow the drugs to be adsorbed while the rate of drug release can then be adjusted by changing the properties of those aerogels.<sup>70</sup>

### 2.4 Organic aerogels

The first organic aerogel, prepared by S. Kistler, was made of gel consisting of organic pectin heteropolysaccharide. S. Kistler also produced gelatin and rubber aerogels from organic polymers. Organic aerogels have very different properties than inorganic ones (such as metal oxide aerogels). In general, organic aerogels are less fragile than inorganic aerogels when compressed.<sup>66</sup>

Organic aerogels can be derived from polyurethanes,<sup>85,86</sup> polyureas,<sup>87–89</sup> polyamides,<sup>90</sup> polyimides,<sup>91</sup> phenol-formaldehyde resins (RF),<sup>92</sup> etc. Although organic aerogels existed since the first aerogel, they had not been developed until the 1980's when L. Livermore's laboratory began to produce organic phenol resin aerogels. R. Pekala and J. Satcher, synthesized the first polymeric resorcinol-formaldehyde aerogel (RF aerogels, resorcinol-formaldehyde aerogels), which depending on their density, have light orange to dark red-black color and are translucent or completely opaque. The microstructure of these RF polymer aerogels is largely controlled by the [resorcinol]/[catalyst] ratio.<sup>93–96</sup>

Organic aerogels are prepared through a "sol-gel" process, starting from a solution containing small molecules that will bind to each other (polymerize) and form larger molecular aggregates that will be developed into nanoparticles throughout the solution. These nanoparticles will then form a continuous

network of interconnected particles throughout the volume of the liquid, i.e., a gel, which will then be washed and dried by using supercritical CO<sub>2</sub> to give the corresponding aerogel.<sup>93,95</sup>

In general, organic aerogels are known for their unique physical, chemical and electrochemical properties. Organic aerogels can be used in capacitors, batteries, thermal insulation, acoustic insulation, adsorbents/filters, plastics, etc. Nanosized pores and the particles that aerogels consist of are responsible for their very low thermal conductivity. Thus, organic aerogels exhibit lower conductivity and higher IR constant (good infrared radiation scattering, 80-90%) than silica aerogels, resulting in lower total thermal conductivity (~ 0.012 W/m\*K).<sup>97</sup>

### 2.4.1 ROMP-derived aerogels

ROMP-derived aerogels (ROMP: Ring Opening Metathesis Polymerization) belong to the class of organic aerogels. This category mainly includes polydicyclopentadiene (PDCPD) and polynorbornene (PNBE)<sup>98</sup> aerogels, as well as norbornene derivatives such as dendritic urethane-norbornene monomers.<sup>99,100</sup> The materials resulting from the above monomers are highly hydrophobic since they are pure hydrocarbons. Depending on the catalyst used, for example, first or second generation Grubbs catalysts (Ru-I or Ru-II, respectively), the double bonds along the polymer backbone can be either *trans* or *cis*.<sup>9,98,101</sup>

Such porous polymers, which have equally very low densities, have led to many interesting new applications such as super hydrophobic surfaces, chromatographic columns, or porous polymeric membranes.<sup>98</sup>

### 2.4.2 Polyurea (PUA) aerogels

At the mid 1990s, Biesmans and co-workers reported the preparation of polyurea (PUA) aerogels for the first time.<sup>102</sup> PUAs are a class of polymers that can be defined as the product of the reaction between an isocyanate and an amine, as shown in Scheme 9, top. Alternatively, PUA aerogels can be synthesized from isocyanates and water (Scheme 9 middle),<sup>103</sup> or isocyanates and mineral acids (e.g. boric acid, Scheme 9 bottom).<sup>89</sup> PUAs can be good

elastomers, with good mechanical properties, chemical stability, thermal shock abrasion resistance, flexibility and water repellency. Those properties depend on the chemical identity and structure of isocyanates and amines, the hydrogen bonding and the polymerization conditions.



Scheme 9. Formation of urea from isocyanates and amines (a), isocyanates and water (b), or isocyanates and boric acid (c).

The isocyanate, -N=C=O, is one of the most reactive organic groups. Due to both oxygen and nitrogen atoms exhibiting electron withdrawing ability, the carbon atom has a much smaller electron density than in a typical carbonyl group (Scheme 10, top). Therefore, the isocyanate group is susceptible to nucleophilic attack (Scheme 10, bottom). The reactivity of the isocyanate group can be modified by electron-withdrawing or electron-donating groups attached to the nitrogen atom. The most commonly used isocyanate molecules are di- or triisocyanates. Consequently, the nature of the isocyanate component affects the properties of the PUA aerogel. The reaction between isocyanates and amines is fast and catalyst-free, which are advantages for the production of aerogels using sol-gel processing. Aromatic isocyanates generally show higher reactivity than aliphatic ones.<sup>104</sup> Electron-withdrawing substituents on aromatic isocyanates also increase the positive charge on the carbon atom, further increasing the reactivity of the isocyanate towards nucleophilic attack.<sup>105,106</sup> On the contrary, electron-donating groups reduce the reactivity of the -N=C=O group.<sup>104</sup> Isocyanates can react with various functional groups and can undergo self-addition reactions.<sup>107</sup>



Scheme 10: Top: Possible resonance structures of the isocyanate group. Bottom: addition of nucleophiles to the isocyanate group.

Some reactions of isocyanates with specific nucleophiles relative to the synthesis of PUA aerogels are presented below.

*Reaction of Isocyanates with Amines.* Nucleophilic addition of the amine group to the isocyanate electrophilic carbonyl yields urea (Scheme 9 top). The reaction is fast and exothermic, with no catalyst addition required. Aromatic amines react slower than aliphatic ones due to resonance delocalization of the amine electron pair in the aromatic ring.<sup>108</sup>

*Reaction of Isocyanates with Water.* Water can attack the isocyanate carbonyl to form an unstable carbamic acid, which decomposes to form an amine and carbon dioxide. The *in situ* generated amine can then react rapidly with yet unreacted isocyanate to form urea as illustrated in Scheme 11.<sup>109,110</sup>



Scheme 11: (a) Nucleophilic addition of water to an isocyanate yields an unstable carbamic acid, which decomposes to amine. (b) Reaction of that amine with a new isocyanate forms urea.

The two synthetic ways above have both led to the preparation of PUA aerogels, not only in the form of monoliths but also in the form of beads, or powders, with very good properties.<sup>87–89,103,111</sup>

The polymerization mechanism for the synthesis of PUA using transition metal compounds as catalysts can be explained through the hypothesis that the metal compounds have the ability to form intermediate compounds with the starting materials (isocyanates or/and amines). In some cases, for the synthesis of polyurethane, such compounds have been isolated and characterized.<sup>112–114</sup> A general mechanistic scheme has been proposed (Scheme 12).



Scheme 12. General proposed mechanism for the synthesis of polyurethane using metal compounds as catalysts.

Little is known about the organometallic chemistry of isocyanates, in particular about their coordination ability toward one or more metallic centers. Complexes with coordinated isocyanates are thought to be intermediates in Pt-catalyzed conversion of nitro-compounds to urea derivatives.<sup>115</sup> In the literature, there are many examples of insertion reactions of isocyanates into a M-carbon, M-oxygen, M-nitrogen, or M-chloride bond.<sup>116,117</sup>

### 2.4.3 Metal-doped aerogels

Shortly after the invention of aerogels, Kistler himself pointed out that some of the unique aerogel properties, (in particular their high porosity, high specific surface area, and thermal stability) would render them good candidates for use as catalysts.<sup>118</sup> In fact, he went on to demonstrate the first aerogel catalyst, a thoria aerogel from reaction of thorium nitrate with ammonia in water, which catalyzed the conversion of organic acids to ketones. Unfortunately, preparation of those thoria aerogels was extremely lengthy, taking more than 12 days (!) to make just a few grams. That hindered further development of aerogel catalysts until the mid-1970's with only a handful of relevant reports in the literature. The first systematic group of papers using aerogels in catalysis

dealt with alumina aerogels for the hydrogenation of ethylene to ethane.<sup>119</sup> In 1975 a brief review described aerogel catalysts for partial oxidation of olefins, hydrogenolysis ethylbenzene, and selective hydrogenation of of cyclopentadiene; catalytic fixed-bed all tests were performed in microreactors.120

The major boost in using aerogels in catalysis came from shifting attention from catalytic aerogels (like thoria and alumina) to chemically inert frameworks that would host finely dispersed catalytic nanoparticles. In that configuration the open pore structure provides fast mass transfer within the aerogel bulk, and easy accessibility of gas-phase reactants to the catalytic nanoparticles. In fact, the most common type of aerogels, those based on silica, fits that bill exactly.<sup>121,122</sup> Metal-containing (e.g., Cu, V, Zr, W, Nb, Ta, Ti, Co, Ni, Pt, Fe) silica aerogels have become promising materials for a number of catalytic applications including NO<sub>x</sub> reduction,  $^{123,124}$  volatile organic compounds (VOCs) oxidation,<sup>125</sup> methane partial oxidation,<sup>126</sup> Fischer-Tropsch synthesis,<sup>127</sup> H<sub>2</sub> production,<sup>128</sup> selective oxidation of CO in hydrogen-rich fuels,<sup>129</sup> nitroxidation of hydrocarbons into unsaturated nitriles,<sup>130</sup> conjugate additions,<sup>131</sup> low temperature EtOH<sup>132</sup> or MeOH<sup>133</sup> steam reforming. Several metal-doped carbon aerogels have also found applications in catalysis, including isomerization of alkenes, oxidation of toluene, hydrogenation of ethylene or cinnamaldehyde,<sup>134</sup> and aromatization of hexane.<sup>135</sup>

Nevertheless, all catalytic systems using inorganic oxide aerogels either as the catalyst itself or as a support have one major drawback: fragility.<sup>122</sup> That issue has been addressed with polymer-crosslinked aerogels, whereas the dangling –OH groups of silica wet-gels play the role of a chemical template that directs reaction with isocyanates and accumulation of a nano-thin conformal polymer coating over the entire skeletal framework.<sup>136</sup>

Polymer-crosslinked aerogels redirected the way of thinking about robust aerogels: since the exceptional mechanical strength of those materials came from the polymer coating over the inorganic (oxide) skeletal framework, pure polymers with the same nanostructure and interparticle connectivity should have similar mechanical properties. Indeed, that hypothesis has been verified by a large variety of organic (polymeric) aerogels, including aerogels based on phenolic resins (e.g., resorcinol-formaldehyde),<sup>137,138</sup> polyureas,<sup>103</sup> polyimides,<sup>103,139</sup> polyamides (Kevlar<sup>TM</sup>-like),<sup>140</sup> polybenzoxazines,<sup>141</sup> polyurethanes,<sup>142</sup> polynorbornene and polydicyclopentadiene.<sup>143</sup>

It is therefore evident that organic polymer aerogels are good candidates for robust catalyst supports, as they combine the advantages of inorganic aerogels (high porosity, large pore volumes, thermal stability, etc.) with greatly enhanced mechanical strength. Furthermore, the subset of carbonizable organic polymer aerogels are also good candidates for the preparation of metal-impregnated carbon aerogels.

### **CHAPTER 3**

### SWELLING AND HANSEN SOLUBILITY PARAMETERS

#### 3.1 Introduction

Organic pollutants in water, and in particular chlorinated solvents, present a serious threat to human health. For example, dichloromethane shows toxicity for the liver and kidneys and is harmful to the nervous and reproductive systems,<sup>144,145</sup> chloroform is carcinogenic and causes liver damage,<sup>146</sup> while carbon tetrachloride can cause tissue damage.<sup>147–149</sup> The low water solubility of chlorinated solvents leads to long life spans that increase their concentration above the regulatory levels for drinking water.<sup>150</sup> Although in recent years the focus is mainly on destructive removal of chlorinated solvents, non-destructive physicochemical methods are still employed, due to their reliability and, sometimes, the recovery of the pollutants.<sup>151</sup> The materials that have been used to absorb solvents include graphene<sup>152–155</sup> and other carbon-based materials, 152, 156, 157 polymers,<sup>158–167</sup> organic polyelectrolytes,<sup>168,169</sup> polymethylsilsesquioxanes,<sup>170</sup> poly(alkoxysilanes)<sup>171</sup> and sol-gel silica substrates.<sup>172</sup>

Dearomatization of oil is also of great importance,<sup>173</sup> both because of the hazardous effects of aromatic compounds toward the environment and human health,<sup>174–176</sup> and also due to their role as inhibitors in the desulfurization of oil.<sup>177–181</sup> The main methods applied for the dearomatization and desulfurization of oil involve selective solvent extraction<sup>173</sup> and hydrogenation,<sup>182</sup> while selective absorption, using carbon aerogels<sup>183</sup> or zeolites<sup>184</sup> has also been reported.

Similarly, it is also known that many organic polymers may absorb solvents selectively and swell, thus becoming reservoirs that can be harvested, drained and reused. For example, materials based on polydicyclopentadiene (PDCPD) have been studied for their swelling behavior<sup>185–190</sup> and their potential use in separation membranes.<sup>185,190,191</sup>

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#### 3.2 Hansen solubility parameters

The swelling of insoluble polymers in various solvents can be related to the Hansen Solubility Parameters (HSP) of the solvents.<sup>192,193</sup> J. H. Hildebrand introduced the concept of the solubility parameter, defining it as the square root of the cohesive energy density,<sup>194</sup> and later C. M. Hansen introduced a three-dimensional solubility parameter by splitting the Hildebrand parameter into three components,<sup>195</sup> thus taking into consideration three major types of interactions between molecules: dispersion (or Van der Waals; D), dipole-dipole (P) and hydrogen bonding (H). The total solubility parameter ( $\delta_{T}$ ) can be calculated *via* Equation 1, where  $\delta_{D}$ ,  $\delta_{P}$  and  $\delta_{H}$  are the parameters representing dispersion (D), dipole-dipole (P) and hydrogen bonding (H).

 $\delta T^2 = \delta D^2 + \delta P^2 + \delta H^2$  (1)

A significant advantage of the HSP theory is that it allows the study of polymersolvent interactions. During swelling, the solvent resides within regions of the polymer bulk that are chemically and energetically similar to it; in other words, in this case the principle "like dissolves like" can be interpreted as "like seeks like".<sup>192</sup> Thereby, if a solvent is found homogeneously distributed throughout the polymer, the solubility parameters of that solvent will reflect the properties of the whole polymer itself.<sup>192</sup> In the case of crosslinked polymers, such as PDCPD, the swelling behavior does not depend only on the polymer-solvent interactions, but also on the crosslinking density, as described in the Flory-Rehner theory.<sup>196</sup>

### 3.3 Application of swelling in chemical sensors

The research on synthesis of polymers led to the development of a new class of polymers, which respond to their environment by changing their physical and/or chemical properties. Polymer gels can be used for sensor or actuator applications depending also on their swelling behavior.

Those polymers are referred to as "smart" or "intelligent" polymers and they respond under several external excitations (temperature,<sup>197</sup> pH, etc). This application is a rapidly expanding field of a live process monitoring and

controlling in food industry, water treatment, pharmaceutical industry, process chemistry, environmental measuring technology, controlled drug delivery, and artificial muscles etc.<sup>197–199</sup>

This unique feature of such intelligent materials, mostly reported for hydrogels, is that when they used as sensors and actuators- at the same time, they do not require any measuring devices or power supplies. Sensors are increasingly being used for monitoring changes in environmental conditions in a fully automated manner.<sup>200</sup>

The identification of an appropriate material for a specific application may be intricate, since different measures for swelling are used in literature.<sup>198</sup> The main principles for the response-applications of smart polymer gels that swell in organic solvents are the automatic size change of the polymer and the fast response between an effector (i.e. organic solvent) and the polymer.

### CHAPTER 4 EXPERIMENTAL

### 4.1 Materials and methods

All starting materials were purchased from Sigma-Aldrich and are of the highest available purities.

For kinetic studies and ROMP reactions, all operations were performed under a pure dinitrogen or argon atmosphere, using Schlenk techniques on an inert gas/vacuum manifold or in a drybox ( $O_2$ ,  $H_2O < 1$  ppm).

 $(Ph_4P)[W(CO)_5Br]$  is the starting material for the synthesis of  $(Ph_4P)_2[W_2(\mu-Br)_3Br_6]$ . Both of the complexes were synthesized according to literature procedures.<sup>201,202</sup> For the synthesis of both compounds, Ph<sub>4</sub>PBr was used instead of nPr<sub>4</sub>NBr. Na[W<sub>2</sub>( $\mu$ -Cl)<sub>3</sub>Cl<sub>4</sub>(THF)<sub>2</sub>]·(THF)<sub>3</sub> <sup>203</sup> was also prepared according to literature procedures.

PA (phenylacetylene) was passed through an  $AI_2O_3$  column and was distilled under vacuum. NBE (norbornene) was dissolved in the solvent used for the reaction, was dried by stirring with CaH<sub>2</sub> under argon, and was distilled under vacuum prior to use. NBD (norbornadiene), VNBE (5-vinyl-2-norbornene), and DCPD were dried by stirring with CaH<sub>2</sub> and was distilled under vacuum. Dichloromethane (DCM) was distilled under inert atmosphere over P<sub>4</sub>O<sub>10</sub> and was degassed by three freeze-pump-thaw cycles. All solvents were distilled in an inert atmosphere, and were degassed by three freeze-pump-thaw cycles. Solvents for washings of wet-gels (tetrahydrofuran (THF), pentane and acetone) were used as received.

For all swelling experiments, organic solvents were used as received.

For PUA-M experiments, all reagents and solvents were used as received. Desmodur RE tris(4-isocyanatatophenyl)methane (TIPM; 27% w/w solution in ethyl acetate, EA) were kindly provided by Covestro Deutschland GA (Leverkusen, Germany).

Size exclusion chromatography (SEC) experiments were carried out at the Laboratory of Industrial Chemistry, Department of Chemistry, N.K.U.A., Greece

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with a modular instrument consisting of a Waters model 600 pump, a Waters model U6K sample injector, a Waters model 410 differential refractometer and a set of 4  $\mu$ -Styragel columns with a continuous porosity range of 106–103 Å. The columns were housed in an oven thermostated at 40 °C. THF was the carrier solvent at a flow rate of 1 mL/min. The instrument was calibrated with PS standards covering the molecular weight range of 4000–900,000.

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were carried out as follows:

(a) on free-surface, gold- or carbon-coated dried aerogel filings, adhered on conductive double sided adhesive carbon tape using a Jeol JSM 5600 SEM instrument, Department of Geology and Geoenvironment, N.K.U.A., Athens; (b) on free-surface, platinum-coated samples, using a Jeol JSM 5600 SEM instrument, equipped with an Oxford ISIS 300micro analytical device at the Institute of Geology and Mineral Exploration, Athens (accelerating voltage was 20 KV, the beam current 0.5 nA and the beam diameter <2 $\mu$ m; and,

(c) on free-surface, palladium-coated samples, using a Zeiss EVO MA 25 instrument, equipped with a Bruker Quantax EDX-System with 123 eV beam releasing (Mn Ka), IFEM Institute, Hamburg, Germany.

The thermal stability of the materials was studied with TGA, employing a Mettler-Toledo TGA (Schwerzenbach, Switzerland). Samples were placed in alumina crucibles. An empty alumina crucible was used as a reference. Samples were heated from ambient temperatures to 800 °C in a 50 mL/min flow of N<sub>2</sub> at a heating rate of 10 °C/min.

ATR-FTIR spectra were obtained with an FTIR Cary 630 spectrometer with a diamond ATR accessory (Agilent, Santa Clara, CA, USA).

<sup>1</sup>H-NMR spectra were obtained with a 300 Unity Plus spectrometer (Varian, Palo Alto, CA, USA) in deuterated acetone at room temperature. Solid-state NMR spectra were obtained with a 600 MHz Varian spectrometer (Palo Alto, CA) operating at 150.80 MHz for <sup>13</sup>C. For <sup>1</sup>H-<sup>13</sup>C ramped CPMAS (Cross-Polarization Magic Angle Spinning) spectra the spinning rate used was 5 kHz and the temperature run the experiment was 25 °C.

The determination of the crystalline phases was achieved using powder X-Ray Diffraction (PXRD) (Siemens D5005 instrument, with Cu radiation operating at 40kV and 40mA) in 2-theta range from 3 to 45°, step 0.01°/sec and evaluation was conducted using the DIFRAC PLUS v2.2 software by Siemens.

N<sub>2</sub>-sorption and CO<sub>2</sub>-sorption measurements were made on a Micromeritics Tristar II 3020 surface area and porosity analyzer (Micromeritics, Norcross, GA, USA). Skeletal densities ( $\rho_s$ ) were determined with He pycnometry, using a Micromeritics AccuPyc II 1340 pycnometer (Micromeritics, Norcross, GA, USA). Bulk densities ( $\rho_b$ ) of the samples were calculated from their weight and natural dimensions.

SCF drying was carried out in an autoclave (E3100, Quorum Technologies, East Sussex, UK). Wet-gels were placed in the autoclave at 12 °C and were covered with acetone. Liquid CO<sub>2</sub> was allowed in the autoclave; acetone was drained out as it was being displaced by liquid CO<sub>2</sub> (5×; 1 per 30 min). Afterwards, the temperature of the autoclave was raised to 45 °C and was maintained for 1h. Finally, the pressure was gradually released, allowing SCF CO<sub>2</sub> to escape as a gas, leaving dry-gels (aerogels).

Pyrolysis of PUA-W and PUA-Mo aerogels was carried out at a MTI GSL1800X-KS60 tube furnace (alumina >99.9% pure, 54/60 mm inner/outer diameters, 300 mm heating zone). The desired temperature was raised at a 2.5 °C min<sup>-1</sup> rate, under flowing N<sub>2</sub> or Ar (150 mL min<sup>-1</sup>) for a given time. At the end of the heating period the temperature was returned to room temperature at 2.5 °C min<sup>-1</sup> under constant flow of Ar.

For fitting the material properties of PUA aerogels the statistical software Design-Expert (Version 11, 2019) was used. For Hansen sphere simulations and calculations of Hansen Solubility Parameters HSPiP 5.1.02 software (2018) was used.

# 4.2 Kinetic studies using (Ph<sub>4</sub>P)<sub>2</sub>[W<sub>2</sub>(μ-Br)<sub>3</sub>Br<sub>6</sub>]/ AgBF<sub>4</sub> (1) as catalytic system

The polymerization reactions with the catalytic system **1** has been described elsewhere.<sup>10,52</sup> All polymers were synthesized *via* ROMP reaction of the monomers used for the kinetic studies.<sup>52</sup> The progress of reaction of each monomer, with the exception of NBE polymerization, which was very rapid, was monitored by measuring the polymerization yield gravimetrically, and the molecular characteristics (number average molecular weight distribution) using SEC analysis.

## 4.3 Swelling studies of PDCPD xerogels, synthesized using Na[W<sub>2</sub>(μ-Cl)<sub>3</sub>Cl<sub>4</sub>(THF)<sub>2</sub>]·(THF)<sub>3</sub>/PA (2) as catalytic system

2-PDCPD wet-gels were prepared via ROMP of DCPD in methylene dichloride using the catalytic system Na[W<sub>2</sub>( $\mu$ -Cl)<sub>3</sub>Cl<sub>4</sub>(THF)<sub>2</sub>]·(THF)<sub>3</sub>/PA (**2**) and it has been described elsewhere.<sup>9</sup> In brief, PA (450 µL, 4.18 mg, 4.10 mmol) was added to a solution of Na[W<sub>2</sub>( $\mu$ -Cl)<sub>3</sub>Cl<sub>4</sub>(THF)<sub>2</sub>]·(THF)<sub>3</sub> (**W**<sub>2</sub>; 210.0 mg, 0.210 mmol) in DCM (30.0 mL), followed by DCPD (10.0 mL, 9.8 g, 74 mmol) ([DCPD] = 20% w/w). The resulting mixture was stirred vigorously for 30 min at room temperature and was poured into polypropylene molds (Wheaton polypropylene OmniVials, 1.1 cm in diameter). Gelation was observed within 18 h. Wet-gels were aged for 6 h in their molds at room temperature. Afterwards, wet-gels were washed with toluene (4×, 8 h per wash cycle), using 4× the volume of each wet-gel for each washing. Toluene was exchanged out of the pores with pentane (4×, 8 h per wash cycle, 4× the volume of the gel), and wet-gels were dried in an oven at 50 °C under atmospheric pressure.

The concentration of DCPD was 20% w/w. The resulting gels will be referred to as **2-PDCPD**. Those materials have been chemically characterized with ATR-FTIR, solid-state <sup>13</sup>C CPMAS NMR, and thermogravimetric analysis (TGA). <sup>9</sup> Those data confirm the mostly-*cis* configuration of the polymeric chain. Furthermore, TGA supported a high degree of crosslinking and <sup>13</sup>C CPMAS NMR showed that crosslinking occurred mainly *via* metathesis (approximately 70%; Scheme 17b). Cylindrical **2-PDCPD** xerogels of initial volume 1-1.5 cm<sup>3</sup> were sanded and were immersed in a solvent. At selected time intervals gels were taken out and their height and diameter were measured, to determine their volume. Gels were re-immersed in the respective solvents immediately to continue swelling. The maximum volume degree of swelling ( $q_{max}$ ) was calculated as the ratio of the volume of swollen gels to the volume of dry gels (xerogels), according to Equation 2.

$$q_{\max} = \frac{\text{Volume of swollen gel}}{\text{Volume of dry gel}}$$
 (2)

The same procedure was followed for the swelling of **3-PDCPD** xerogels and aerogels.

## 4.4 Synthesis of 3-PDCPD xerogels with catalytic system Na[W<sub>2</sub>(μ-Cl)<sub>3</sub>Cl<sub>4</sub>(THF)<sub>2</sub>]·(THF)<sub>3</sub>/NBD (3)

**3-PDCPD** wet-gels were prepared *via* ROMP of DCPD in methylene dichloride using the catalytic system Na[W<sub>2</sub>( $\mu$ -Cl)<sub>3</sub>Cl<sub>4</sub>(THF)<sub>2</sub>]·(THF)<sub>3</sub>/NBD (**W**<sub>2</sub>/NBD, 3) In a typical procedure, **NBD** was added to a solution of the ditungsten cluster (**W**<sub>2</sub>) with DCM, followed by the addition of **DCPD**. The mixture was stirred vigorously at room temperature for 1 min and then was poured into polypropylene molds. All solutions gelled within 15 min. The resulting wet-gels were aged in their molds for 24-28 h at room temperature. Consequently, wet-gels were removed from their molds and were transferred into THF and washed 4× 8 h per wash cycle, using 4× the volume of the gels. Then, wet-gels were solvent-exchanged with pentane and were washed 4× 8 h per wash cycle, using 4× the volume of the gels. The wet-gels were air-dried in the oven at 50 °C. The resulting xerogels are referred to as **3-PDCPD** xerogels.

### 4.5 Synthesis of 3-PDCPD aerogels with catalytic system 3

**3-PDCPD** wet gels were synthesized according to the previously described protocol. Then, wet-gels were solvent-exchanged with acetone and were washed 4× 8 h per wash cycle, using 4× the volume of the gels. Finally, wet-gels were dried from scf CO<sub>2</sub> to give aerogels. The resulting aerogels are referred to as **3-PDCPD** aerogels. All formulations for the synthesis of **3-PDCPD** xerogels and aerogels are summarized in Table 1.

Table 1. Formulations of 3-PDCPD xerogels and aerogels obtained using catalytic system (3) in 12mL DCM prepared with 20% w/w of DCPD.

W <sub>2</sub> /NBD/DCPD (molar ratio)	Catalyst (mg) [mmol]	NBD (μL) [mmol]	DCPD (mL) [mmol]	Gelation time (min)
1/5/350		10.2 [0.1]		_a
1/10/350	21.50	20.4 [0.2]	1.00	15
1/20/350	[0.02]	40.8 [0.4]	[7.0]	10
1/30/350		61.2 [0.6]		5

<sup>a</sup> no gelation was observed within 72 h.

### 4.6 Swelling studies for 3-PDCPD aerogels

Thin disks of **3-PDCPD** aerogels of 0.1 mL initial volume were immersed in 5 mL of various organic solvents (toluene, DCM, chloroform, chlorobenzene, bromobenzene, THF, 1-bromobutane, ethyl bromide, ethylene dichloride, m-xylene, p-xylene and mesitylene) in graduated closed glass vials. Gels were kept in the solvent for 2 hours in total. The volume increase of gels in each solvent was measured every 10 minutes – for 1 hour in total – and it was determined by the volume decrease of each solvent when gel was taken out from the graduated glass vial.

# 4.7 Synthesis of PUA aerogels using first-row transition metal compounds as catalysts

Polyurea aerogels were synthesized from the aromatic triisocyanate Desmodur RE (TIPM, 27% w/w in ethyl acetate, Scheme 13) with water and various metal compounds as catalysts.



Scheme 13. Structure of the triisocyanate monomer used in this study, Desmodur RE (TIPM).

The resulting aerogels are referred to as **PUA-M-X**, whereas M indicates the metal compound that was used as catalyst and X denotes the percent weight

of the monomer in the sol. The quantity of anhydrous DMF was varied depending upon the desirable weight percent of the monomer in the sol. Several hydrated metal salts have been utilized as catalysts (CuSO<sub>4</sub>·5H<sub>2</sub>O, CuCl<sub>2</sub>·2H<sub>2</sub>O, FeCl<sub>3</sub>·xH<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, CrCl<sub>3</sub>·6H<sub>2</sub>O, CoCl<sub>2</sub>·6H<sub>2</sub>O) for the reaction of Desmodur RE with water, according to Scheme 11a.

The synthetic procedure of **PUA-M-X** aerogels is illustrated in Scheme 19 and it was based on a typical sol-gel process, at which two solutions are mixed to give the gelation sol. The first solution was containing the metal compound dissolved in a certain amount of DMF and the second one was containing Desmodur RE and water. All data for the synthesis of PUA-M-X aerogels are summarized in Table 2 and Table 3. The resulting sol was stirred for a few seconds at room temperature and then it was transferred to molds. After gelation, all wet gels were left for aging for 24h. The aged wet-gels were solvent exchanged with acetone (10 washes / 8 h each wash), and finally dried to aerogels from supercritical fluid (SCF) CO<sub>2</sub>.

Sampla	TIPM/M	De	smodur	RE	H <sub>2</sub>	0	C	Catalyst		Solv (DI	vent MF)	Gelation time
Sample	mol/mol	g	mL	TIPM (mmol)	g	mmol	g	mmol	% w/w	g	mL	min
	1/0.1	1.36	1.33	1.0	0.054	3.0	0.010	0.1	0.1	9.1	9.6	15
DIIA_4_EtaN	1/0.5	1.36	1.33	1.0	0.054	3.0	0.050	0.5	0.5	9.1	9.6	12
FUA-4-LUIN	1/1.5	1.36	1.33	1.0	0.054	3.0	0.150	1.5	1.4	9.0	9.5	3
	1/3	1.36	1.33	1.0	0.054	3.0	0.300	3.0	2.9	8.8	9.3	8
	1/0.1	1.36	1.33	1.0	0.054	3.0	0.029	0.1	0.3	9.1	9.6	13
PLIA-Ni-4	1/0.5	1.36	1.33	1.0	0.054	3.0	0.145	0.5	1.4	9.0	9.5	25
104-11-4	1/1.5	1.36	1.33	1.0	0.054	3.0	0.436	1.5	4.1	8.7	9.2	3
	1/3	1.36	1.33	1.0	0.054	3.0	0.872	3.0	8.3	8.2	8.7	8
	1/0.1	1.36	1.33	1.0	0.054	3.0	0.027	0.1	0.3	9.1	9.6	10
PUA-Cr-4	1/0.5	1.36	1.33	1.0	0.054	3.0	0.133	0.5	1.3	9.0	9.5	13
104-01-4	1/1.5	1.36	1.33	1.0	0.054	3.0	0.400	1.5	3.8	8.7	9.2	3
	1/3	1.36	1.33	1.0	0.054	3.0	0.800	3.0	7.6	8.3	8.8	10
	1/0.1	1.36	1.33	1.0	0.054	3.0	0.016	0.1	0.2	9.1	9.6	13
PUA-Fe-4	1/0.5	1.36	1.33	1.0	0.054	3.0	0.081	0.5	0.8	9.0	9.6	10
	1/1.5	1.36	1.33	1.0	0.054	3.0	0.243	1.5	2.3	8.9	9.4	10
	1/3	1.36	1.33	1.0	0.054	3.0	0.486	3.0	4.6	8.6	9.1	5
	1/0.1	1.36	1.33	1.0	0.054	3.0	0.024	0.1	0.2	9.1	9.6	4
BUA-Co-4	1/0.5	1.36	1.33	1.0	0.054	3.0	0.120	0.5	1.1	9	9.5	10
FUA-C0-4	1/1.5	1.36	1.33	1.0	0.054	3.0	0.360	1.5	3.4	8.8	9.3	7
	1/3	1.36	1.33	1.0	0.054	3.0	0.720	3.0	6.8	8.4	8.9	8
	1/0.1	1.36	1.33	1.0	0.054	3.0	0.017	0.1	0.2	9.1	9.6	9
PUA-Cu-4	1/0.5	1.36	1.33	1.0	0.054	3.0	0.085	0.5	0.8	9	9.6	10
1 0A-0u-4	1/1.5	1.36	1.33	1.0	0.054	3.0	0.256	1.5	2.4	8.8	9.4	9
	1/3	1.36	1.33	1.0	0.054	3.0	0.511	3.0	4.9	8.6	9.1	5

Table 2. Formulations for the synthesis of PUA-M-4 aerogels and gelation times.

Comple	TIPM/M	De	esmod	ur RE	H <sub>2</sub>	0		Catalyst		D	ИF	Gelation time
Sample	mol/mol	g	mL	TIPM (mmol)	g	mmol	g	mmol	% w/w	g	mL	min
	1/0.1	1.36	1.33	1.0	0.054	3.0	0.010	0.1	0.3	2.1	2.2	2
PIIΔ_12_Ft₂N	1/0.5	1.36	1.33	1.0	0.054	3.0	0.050	0.5	1.4	2.0	2.2	5s
	1/1.5	1.36	1.33	1.0	0.054	3.0	0.150	1.5	4.3	1.9	2.1	2s
	1/3.0	1.36	1.33	1.0	0.054	3.0	0.300	3.0	8.6	1.8	1.9	1s
	1/0.1	1.36	1.33	1.0	0.054	3.0	0.029	0.1	0.8	2.1	2.2	5
PUA-Ni-12	1/0.5	1.36	1.33	1.0	0.054	3.0	0.145	0.5	4.1	1.9	2.1	5
	1/1.5	1.36	1.33	1.0	0.054	3.0	0.436	1.5	12.4	1.7	1.8	0.5
	1/0.1	1.36	1.33	1.0	0.054	3.0	0.027	0.1	0.8	2.1	2.2	8
PUA-Cr-12	1/0.5	1.36	1.33	1.0	0.054	3.0	0.133	0.5	3.8	2.0	2.1	12
	1/1.5	1.36	1.33	1.0	0.054	3.0	0.400	1.5	11.4	1.7	1.8	0.2
	1/0.1	1.36	1.33	1.0	0.054	3.0	0.016	0.1	0.5	2.1	2.2	6
PUA-Fo-12	1/0.5	1.36	1.33	1.0	0.054	3.0	0.081	0.5	2.3	2.0	2.1	9
FUA-Fe-12	1/1.5	1.36	1.33	1.0	0.054	3.0	0.243	1.5	6.9	1.9	2.0	4
	1/3.0	1.36	1.33	1.0	0.054	3.0	0.486	3.0	13.9	1.6	1.7	8
	1/0.1	1.36	1.33	1.0	0.054	3.0	0.024	0.1	0.7	2.1	2.2	4
PUA-Co-12	1/0.5	1.36	1.33	1.0	0.054	3.0	0.120	0.5	3.4	2.0	2.1	14
	1/1.5	1.36	1.33	1.0	0.054	3.0	0.360	1.5	10.3	1.7	1.8	2
	1/0.1	1.36	1.33	1.0	0.054	3.0	0.017	0.1	0.5	2.1	2.2	3
PUA-Cu-12	1/0.5	1.36	1.33	1.0	0.054	3.0	0.085	0.5	2.4	2.0	2.1	2
	1/1.5	1.36	1.33	1.0	0.054	3.0	0.256	1.5	7.3	1.8	1.9	1

Table 3. Formulations for the synthesis of PUA-M-12 aerogels and gelation times.

### 4.8 Synthesis of PUA aerogels using W and Mo compounds as catalysts

Polyurea (PUA) aerogels were synthesized from the aromatic triisocyanate Desmodur RE (TIPM, 27 % w/w in ethyl acetate, Scheme 13) with water and various W and Mo compounds as catalysts. Various W and Mo based compounds were used for the synthesis of PUA aerogels:

- ➤ WO<sub>3</sub>
- ➢ H<sub>2</sub>WO<sub>4</sub> (WO<sub>3</sub>⋅H<sub>2</sub>O)
- Peroxypolytungstic Acid Solution (WO<sub>3</sub> precursor solution)
- $\rightarrow$  H<sub>3</sub>[P(W<sub>3</sub>O<sub>10</sub>)<sub>4</sub>] × H<sub>2</sub>O (12WO<sub>3</sub>·H<sub>3</sub>PO<sub>4</sub> × H<sub>2</sub>O)
- ➢ Na₂WO₄·2H₂O
- ➢ WCl<sub>6</sub>
- ➢ (NH₄)<sub>6</sub>W<sub>12</sub>O<sub>39</sub> × H<sub>2</sub>O
- ➢ H₂MoO₄ × H₂O
- Na<sub>2</sub>MoO<sub>4</sub>× 2H<sub>2</sub>O

In Table 21 are shown all W and Mo used for the synthesis of PUA, along with their abbreviations. The polymerization reactions took place in EA and/or DMF. The synthetic procedure can be described in Scheme 14. Briefly, in a

polypropylene mold, a certain amount of M compound is added, followed by the addition of Desmodur RE, water and the solvent of choice. The mold was sealed, shaken and left for gelation. All wet gels were aged for 24 h, were solvent-exchanged with acetone and dried with SCF CO<sub>2</sub>. The resulting aerogels are referred to as **PUA-X-M**, whereas M indicates the W or Mo compound that was used as catalyst and X denotes the percent weight of the monomer in the sol.



Scheme 14. Synthetic procedure of PUA-X-M aerogels.

Comple	TIPM/WO	D	esmodur	RE	H₂O		WO <sub>3</sub>			Sol	vent	Gelation time
Sample	mol/mol	g	mL	TIPM (mmol)	g	mmol	g	mmol	% w/w	g	mL	min
					Solve	ent: EA						
PUA-4-WO	1/0.1	1.36	1.33	1.0	0.10	6.0	0.0232	0.1	0.2	10.3	11.4	300
PUA-4-WO	1/0.5	1.36	1.33	1.0	0.10	6.0	0.116	0.5	1.0	10.3	11.4	240
PUA-8-WO	1/0.1	1.36	1.33	1.0	0.05	3.0	0.0232	0.1	0.4	3.8	4.2	270
PUA-8-WO	1/0.1	1.36	1.33	1.0	0.10	6.0	0.0232	0.1	0.4	4.3	4.8	240
PUA-12-WO	1/0.1	1.36	1.33	1.0	0.05	3.0	0.0232	0.1	0.7	2.1	2.3	180
PUA-12-WO	1/0.1	1.36	1.33	1.0	0.10	6.0	0.0232	0.1	0.6	2.4	2.7	180
PUA-16-WO	1/0.1	1.36	1.33	1.0	0.05	3.0	0.0232	0.1	0.9	1.2	1.3	120
PUA-16-WO	1/0.1	1.36	1.33	1.0	0.10	6.0	0.0232	0.1	0.8	1.4	1.6	120
PUA-30-WO	1/0.1	1.36	1.33	1.0	0.5	30	0.0232	0.1	0.9	0.8	0.9	60
PUA-30-W	1/0.2	2.72	2.66	2.0	0.1	3.0	0.0700	0.3	2.4	-	-	ovr
PUA-45-WO	1/0.2	2.72	2.66	2.0	1.0	30.0	0.0700	0.3	1.8	-	-	ovr
				-	Solve	nt: DMF			-	-		-
PUA-4-WO	1/3	1.36	1.33	1.0	0.05	3.0	0.695	3.0	6.6	8.4	8.9	25
PUA-12-WO	1/6	2.72	2.66	2.0	0.11	6.0	1.39	6.0	20.1	2.7	2.9	6
PUA-16-WO	1/4.5	3.06	3.00	2.2	1.0	60	2.31	10.0	20.9	4.7	5.0	0.2

Table 4. Formulations for the synthesis of PUA-WO aerogels and gelation times.

Sample	TIPM/HW	De	esmodu	r RE	H <sub>2</sub> O		H <sub>2</sub> WO <sub>4</sub>			Solv	Gelation time	
Cample	mol/mol	g	mL	TIPM (mmol)	g	mmol	g	mmol	% w/w	g	mL	min
					Solver	nt: EA						
PUA-4-HW	1/0.1	1.36	1.33	1.0	0.10	6.0	0.0250	0.1	0.2	10.3	11.4	ovr
					Solvent	t: DMF			-			
PUA-4-HW	1/0.1	0.34	0.33	0.25	0.02	1.2	0.006	0.02	0.2	2.3	2.4	10
PUA-4-HW	1/3	1.36	1.33	1.0	0.05	3.0	0.750	3.0	7.2	8.3	8.8	24
PUA-12-HW	1/3	1.36	1.33	1.0	0.05	3.0	0.750	3.0	21.7	1.3	1.4	12

### Table 5. Formulations for the synthesis of PUA-HW aerogels and gelation times.

#### Table 6. Formulations for the synthesis of PUA-PAS aerogels and gelation times.

Comple	TIPM/W	D	esmodur	RE	H	20		PAS		E	EA	Gelation time
Sample	mol/mol	g	mL	TIPM (mmol)	g	mmol	mL	g W	% w/w <sup>a</sup>	g	mL	min
PUA-16-PAS	1/0.02	2.72	2.66	2.0	0.1	5.6	0.1	0.007	0.13	2.4	2.7	50
PUA-20-PAS	1/0.06	2.72	2.66	2.0	0.3	17	0.3	0.021	0.40	1.8	2.0	25
PUA-24-PAS	1/0.04	2.72	2.66	2.0	0.2	11	0.2	0.014	0.30	1.3	1.4	30
PUA-28-PAS	1/0.1	2.72	2.66	2.0	0.7	39	0.7	0.049	0.97	1.6	1.8	20
PUA-46-PAS	1/0.3	2.72	2.66	2.0	1.5	83	1.5	0.105	2.2	0.5	0.6	15

<sup>a</sup> Content (% w/w) of W in gelation sol.

### Table 7. Formulations for the synthesis of PUA-NaW aerogels in EA and gelation times.

Samala	TIPM/NaW	De	esmodu	r RE	F	I2O	Na <sub>2</sub> V	VO₄·2⊦	l2 <b>O</b>	E	A	Gelation time
Sample	mol/mo I	g	mL	TIPM (mmol)	g	mmol	g	mmol	% w/w	g	mL	min
			Р	rotocol (a	ı): NaV	V in gela	ation sol					
PUA-4-NaWa	1/1	1.36	1.33	1.0	0.2	12	0.3290	1.0	2.3	12.6	14.0	ovr
PUA-14-NaWa	1/0.1	1.36	1.33	1.0	-	-	0.0300	0.1	1.2	1.2	1.4	ovr
PUA-20-NaWa	1/0.1	1.36	1.33	1.0	0.1	6.0	0.0450	0.1	1.9	0.9	1.0	ovr
PUA-20-NaWa	1/0.2	0.68	0.67	0.5	0.1	6.0	0.0470	0.1	3.3	0.6	0.6	ovr
			Pro	tocol (b):	NaW o	dissolve	d in wate	ər				
PUA-4-NaWb	1/0.5	0.33	0.32	0.2	0.1	6.0	0.0394	0.1	1.4	2.4	2.7	no gelation
PUA-10-NaWb	1/1	0.33	0.32	0.2	0.3	17	0.0788	0.2	2.6	2.4	2.7	150
PUA-10-NaWb	1/2	0.33	0.32	0.2	0.3	17	0.1182	0.4	3.8	2.4	2.7	90
PUA-12-NaWb	1/3	0.33	0.32	0.2	0.3	17	0.1965	0.6	6.1	2.4	2.7	150
PUA-16-NaWb	1/0.6	2.11	2.07	1.6	0.5	28	0.3280	1.0	5.8	2.7	3.0	140
PUA-16-NaWb	1/5	0.33	0.32	0.2	0.5	28	0.3275	1.0	9.2	2.4	2.7	120
PUA-16-NaWb	1/3	0.07	0.25	0.2	0.6	33	0.200	0.6	6.3	2.3	2.5	150
PUA-25-NaWb	1/0.1	1.36	1.33	1.0	0.3	18	0.0300	0.1	1.0	1.3	1.4	10
PUA-25-NaWb	1/0.7	3.96	3.88	2.9	1.0	56	0.6560	2.0	7.9	2.7	3.0	135
PUA-25-NaWb	1/10	0.33	0.32	0.2	1.0	56	0.6550	2.0	14.9	2.4	2.7	160
PUA-30-NaWb	1/3	0.14	0.50	0.4	0.3	17	0.400	1.2	17.9	1.4	1.5	60
PUA-30-NaWb	1/20	0.33	0.32	0.2	2.0	112	1.310	4.0	21.7	2.4	2.7	90

Sample	TIPM/NaW	Des	smodur	RE	н	l2 <b>O</b>	Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O			DN	IF	Gelation time
Sample	mol/mol	g	mL	TIPM (mmol)	g	mmol	g	mmol	% w/w	g	mL	min
				Protoco	l (a): Na	aW in gela	ation sol					
PUA-4-NaWa	1/1.5	2.72	2.66	2.0	0.1	6.0	0.9896	3.0	4.7	17.3	18.3	no gelation
PUA-12-NaWa	1/1.5	2.72	2.66	2.0	0.1	6.0	0.9896	3.0	13.9	3.3	3.5	6
PUA-12-NaWa	1/1	1.36	1.33	1.0	0.05	3.0	0.3299	1.0	9.9	1.6	1.8	1
PUA-14-NaWa	1/0.3	1.36	1.33	1.0	0.1	5.6	0.0999	0.3	3.2	1.6	1.8	1
PUA-14-NaWa	1/0.2	8.44	8.25	6.2	0.33	18	0.3299	1.0	1.6	12.0	13.4	1
PUA-30-NaWa	1/0.8	2.72	2.66	2.0	1.2	67	0.5000	1.5	9.6	0.8	0.9	3
PUA-30-NaWa	1/3	0.68	0.67	0.5	0.9	50	0.5000	1.5	14.4	1.4	1.5	film
PUA-35-NaWa	1/0.8	2.72	2.66	2.0	1.2	67	0.5000	1.5	9.1	1.1	1.2	3
			Pr	otocol (	b): NaW	/ dissolve	ed in wate	ər				
PUA-16-NaWb	1/3	0.07	0.25	0.2	0.3	17	0.200	0.6	6.5	2.4	2.5	1s
PUA-16-NaWb	1/0.8	0.92	0.90	0.7	0.3	17	0.1968	0.6	5.6	2.0	2.1	1s
PUA-25-NaWb	1/1.5	0.92	0.90	0.7	0.5	28	0.3280	1.0	8.5	2.0	2.1	1s
PUA-25-NaWb	1/2	0.92	0.90	0.7	0.5	28	0.4590	1.4	11.0	2.0	2.1	1s
PUA-25-NaWb	1/3	0.92	0.90	0.7	0.5	28	0.6560	2.0	14.0	2.0	2.1	1s
PUA-30-NaWb	1/3	0.14	0.50	0.4	0.6	33	0.400	1.2	15.2	1.4	1.5	1s
PUA-45-NaWb	1/3	1.36	1.33	1.0	2.0	111	0.9840	3.0	18.4	0.9	1	5s
PUA-60-NaWb	1/30	0.13	0.13	0.1	1.5	83	0.9840	3.0	17.5	2.8	3	1s

Table 8. Formulations for the synthesis of PUA-NaW aerogels in DMF and gelation times.

Table 9. Formulations for the synthesis of PUA-PW aerogels and gelation times.

Sample	TIPM/PW	Des	smodur	RE	СТАВ		H₂O			E	A	Gelation time	
Sample	mol/mo I	g	mL	TIPM (mmol)	g	g	mmol	g	mmol	% w/w	g	mL	min
PUA-10-PW	1/0.01	1.36	1.33	1.0	0.0150	0.1	6.0	0.0327	0.01	0.8	2.7	3.0	120
PUA-10-PW	1/0.1	0.34	0.33	0.25	-	0.1	6.0	0.0576	0.02	1.9	2.6	2.9	-
PUA-14-PW	1/0.2	0.34	0.33	0.25	-	0.2	11	0.1152	0.04	3.5	2.6	2.9	-
PUA-16-PW	1/0.2	0.34	0.33	0.25	-	0.3	17	0.1728	0.06	5.1	2.6	2.9	-
PUA-16-PW	1/0.3	0.34	0.33	0.25	-	0.3	17	0.2304	0.08	6.5	2.6	2.9	-
PUA-45-PW <sup>a</sup>	1/0.2	0.68	0.67	0.50	0.1092	1.5	83	0.2880	0.10	6.7	1.8	2.0	-

<sup>a</sup> PW was dissolved to ethyl acetate and then it was transferred to RE, H<sub>2</sub>O and CTAB.

Table 10. Formulations for the s	vnthesis of PUA-NHW aero	ogels and gelation times.
	J	· gele alle gelalet interes

Sample	TIPM/NHW	De	smodu	r RE	H	<u>2</u> 0			D	ИF	Gelation time	
Sample	mol/mol	g	mL	TIPM (mmol)	g	mmol	g	mmol	% w/w	g	mL	min
PUA-4-NHW	1/0.6	0.51	0.50	0.4	0.02	1.2	0.7350	0.25	18.1	2.8	3.0	3
PUA-4-NHW	1.0/0.25	1.36	1.33	1.0	0.05	3.0	0.7350	0.25	7.0	8.3	8.8	8

Samplo	TIPM/WCI	De	smodu	r RE	H <sub>2</sub> O		WCI6			So	Gelation time	
Sample	mol/mo I	g	mL	TIPM (mmol)	g	mmol	g	mmol	% w/w	g	mL	min
					Solver	it: EA						
PUA-4-WCI	1/0.1	0.68	0.67	0.5	0.05	3.0	0.0198	0.05	0.3	5.1	5.7	ovr
PUA-4-WCI	1/3	0.68	0.67	0.5	-	-	0.594	1.5	3.1	18.2	20.3	-
PUA-10-WCI	1/0.05	1.36	1.33	1.0	0.05	3.0	0.0198	0.05	0.5	2.7	3.1	ovr
PUA-20-WCI	1/0.05	1.02	1.00	0.8	0.1	6.0	0.0175	0.04	0.9	0.9	1.0	30
PUA-30-WCI	1/0.05	2.72	2.66	2.0	0.1	6.0	0.0500	0.1	1.7	-	-	180
PUA-35-WCI	1/0.05	2.04	2.00	1.6	1.0	55.6	0.0320	0.08	1.0	-	-	ovr
PUA-35-WCI	1/0.5	2.72	2.66	2.0	0.1	6.0	0.3970	1.0	12	-	-	-
PUA-75-WCI	1/0.04	1.02	1.00	0.8	2.0	111	0.0350	0.09	1.1	-	-	ovr
					Solvent	: DMF						
PUA-20-WCI	1/0.3	1.36	1.33	1.0	2.0	111	0.1180	0.3	1.1	7.6	8.0	-

### Table 11. Formulations for the synthesis of PUA-WCI aerogels and gelation times.

Table 12. Formulations for the synthesis of PUA-HMo and PUA-NaMo aerogels and gelation times.

Sample	TIPM/Mo	Desmodur RE			H <sub>2</sub> O		Mo compound			Solvent		Gelation time
	mol/mol	g	mL	TIPM (mmol)	g	mmol	g	mmol	% w/w	g	mL	min
Solvent: EA												
PUA-4-HMo	1/0.6	1.36	1.33	1.0	0.5	30	0.1000	0.6	5.1	-	-	60
PUA-4-HMo	1/1	1.36	1.33	1.0	0.2	12	0.1800	1.0	1.3	12.6	14.0	100
PUA-12-HMo	1/3	1.36	1.33	1.0	0.1	6.0	0.5400	3.0	13.8	1.9	2.1	10
PUA-20-NaMo	1/0.1	1.36	1.33	1.0	0.2	12	0.0242	0.1	0.8	1.3	1.4	10
Solvent: DMF												
PUA-12-HMo	1/0.6	1.36	1.33	1.0	0.1	6.0	0.1000	0.6	2.5	2.4	2.5	3
PUA-12-HMo	1/3	1.36	1.33	1.0	0.1	6.0	0.5400	3.0	13.8	1.9	2.0	3
PUA-4-NaMo	1/1.5	2.72	2.66	2.0	0.2	12	0.7258	3.0	3.4	17.6	18.6	10
PUA-12-NaMo	1/1.5	2.72	2.66	2.0	0.2	12	0.7258	3.0	10.3	3.4	3.6	5

### 4.8.1 Synthesis of Peroxypolytungstic Acid Solution (PAS)

PAS was prepared according to the literature procedure and it is described below.<sup>204</sup>

### **Materials**

6.5 g metallic tungsten powder

40 mL H<sub>2</sub>O<sub>2</sub> (30 %)

54 mL deionized H<sub>2</sub>O

### Procedure

In a 3-neck round bottom flask (200 mL), equipped with a condenser, 6.5 g of tungsten metallic powder was added. Then, 40 mL of hydrogen peroxide solution diluted with 4 mL deionized water were added gradually. The reaction was strongly exothermic, so for at least 2 h it was cooled in an iced-water bath (5 °C). The solution was kept under magnetic stirring for 72 h. After the reaction was finished, the solution was diluted with 40 mL of deionized water and was kept at least for 3 days to ensure that the excess hydrogen peroxide has decomposed. The final product had a light yellow color, with no visible oxygen bubbles. The reaction was quantitative.



Scheme 15. Schematic presentation for the synthetic procedure of PAS.

### CHAPTER 5 ROMP DERIVED POLYMERIC MATERIALS

### 5.1 Catalytic systems used in this chapter

In this chapter, different polymeric materials are discussed, which have been synthesized *via* ROMP using different catalytic systems. All relevant catalytic systems are shown in Scheme 16 along with their abbreviations.



Scheme 16. Catalytic systems reported in this chapter.

# 5.2 Kinetic studies using (Ph<sub>4</sub>P)<sub>2</sub>[W<sub>2</sub>(μ-Br)<sub>3</sub>Br<sub>6</sub>]/ AgBF<sub>4</sub> (1) as catalytic system

The catalytic system Na[W<sub>2</sub>( $\mu$ -Cl)<sub>3</sub>Cl<sub>4</sub>(THF)<sub>2</sub>]·(THF)<sub>3</sub>/PA (**2**) is already known that is catalytically active towards the metathesis polymerization of several terminal alkynes<sup>50</sup> and the ROMP of various cycloolefines, giving high-*cis* polymers.<sup>42</sup> The ditungsten complex (Ph<sub>4</sub>P)<sub>2</sub>[W<sub>2</sub>( $\mu$ -Br)<sub>3</sub>Br<sub>6</sub>] (**W**<sub>2</sub>**Br**<sub>9</sub>) is easily accessible, moderately air-stable, bears labile ligands and higher nuclear charge compared to **2**. **1** was successfully employed for the metathesis polymerization of phenylacetylene (PA) and the ROMP of norbornene (NBE) and some of its derivatives.<sup>10,52</sup> Addition of AgBF<sub>4</sub> as a co-catalyst was necessary for the activation of **W**<sub>2</sub>**Br**<sub>9</sub> *via* abstraction of bromide ligands. PA polymerization proceeded smoothly in a mildly coordinating solvent like THF (but not in MeCN, which is a stronger donor) quantitatively producing PPA with high molecular weight and very narrow molecular weight distribution (1.16).<sup>10</sup> The polymeric products featured high *cis* content (>80 %). On the contrary, in CH<sub>2</sub>Cl<sub>2</sub>, oligomers were formed, most likely due to PPA depolymerization, a

trend that was previously observed for the catalytic system Na[W<sub>2</sub>( $\mu$ -Cl)<sub>3</sub>Cl<sub>4</sub>(THF)<sub>2</sub>]·(THF)<sub>3</sub>/PA (**2**).<sup>50</sup>

NBE was significantly less reactive than PA, and as a result, ROMP of NBE did not take place in THF. In the latter case, a non-coordinating solvent, i.e.,  $CH_2Cl_2$ , was used, and PNBE and derivatives were formed in high yields, when the stoichiometric ratio was properly adjusted in order to avoid gelation of reaction mixtures. In comparison to  $W_2$ , which is an efficient and stereoselective catalyst (formation of polymers with high cis content was favored) for ROMP,<sup>42</sup> 1 was equally effective with respect to yields, but exhibited lower selectivity. However,  $W_2Br_9$  is less sensitive to moisture and oxygen and it can be prepared more easily.

Other notable features of 1 reactivity are:

(a) Short reaction times (15 min-3 h), of all monomers except for VNBE (23 h).

(b) PVNBE contained all pendant vinyl bonds intact, had low molecular weight ( $M_w = 8000$ ), but also narrow molecular weight distribution ( $M_w/M_n = 1.27$ ), the lowest reported so far.

(c) Polymerization of NBD could proceed in toluene without addition of cocatalyst (reflux, less than 5 h and 80 % yield). That result was important, because catalytic systems in which components may coexist and do not react unless the system is heated, are of particular industrial interest.

(d) PNBD and PDCPD were insoluble and highly cross-linked, as evidenced by thermogravimetric analysis. <sup>13</sup>C CPMAS spectra revealed the operation of two mechanisms (metathetic and radical) for cross-linking, with metathesis being the major pathway (~80 %).

The progress of reaction of each monomer, with the exception of NBE polymerization, which was very rapid, was monitored by measuring the polymerization yield gravimetrically, and the molecular characteristics (number average molecular weight and molecular weight distribution) using SEC analysis (Table 13). Results for PA polymerization in THF using a molar ratio  $W_2Br_9$ /AgBF<sub>4</sub>/PA equal to 1/3/350 are displayed in Figure 1. It is obvious that the yield increased more or less linearly with time up to quantitative conversion

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in 6 h. In the same time the molecular weight increased to high values, whereas the molecular weight distribution diminished rapidly. Longer polymerization times, up to 24 h, lead to scission of the produced polymeric chains and therefore to lower yields of polymerization along with lower molecular weights and broader distributions. This behavior is similar to that observed during the polymerization of PA with the triply bonded complex **2** in THF solutions.<sup>50</sup> In the present study, the maximum yield and molecular weight were observed in ~6 h of polymerization, whereas in the previous study in ~2 h. Therefore, **1** polymerized PA with a lower rate, but the reaction was more controlled, leading to products of higher molecular weight and considerably smaller molecular weight distributions.



Figure 1. Polymerization of PA (653  $\mu$ L, 608 mg, 6.0 mmol) with W<sub>2</sub>Br<sub>9</sub> (30.0 mg, 0.017 mmol), AgBF<sub>4</sub> (9.9 mg, 0.051 mmol) and 10 mL THF (25 °C); (a) % yield vs. time plot of PPA; (b)  $M_n \times 10-3$  vs. time plot.

Variation of polymerization yield with time for NBD is given in Figure 2, (a). Apparently, the system was characterized by an induction period, which was equal to a few minutes. This period was devoted to the complexation of the monomer to the catalyst and the initiation step of the polymerization process. After this period the yield increased linearly with time. Nearly quantitative yields were obtained after 90 min of reaction. This result indicates that both the polymerization reaction through the opening of the first double bond and the cross-linking reaction through the opening of the second double bond proceeded smoothly with time and simultaneously in the same manner leading to a controlled synthesis of crosslinked PNBD.



Figure 2. (a) Polymerization of NBD (0.8 mL, 725.0 mg, 8.5 mmol) with  $W_2Br_9$  (30mg, 0.017mmol), AgBF<sub>4</sub> (13.3 mg, 0.069 mmol) and 5 mL CH<sub>2</sub>Cl<sub>2</sub> (25 °C); time-% yield of PNBD plot. (b) Polymerization of VNBE (4.9 mL, 4.1 g, 34.0 mmol) with  $W_2Br_9$  (30mg, 0.017mmol), AgBF<sub>4</sub> (13.2 mg, 0.068 mmol) and 2 mL CH<sub>2</sub>Cl<sub>2</sub>; time-% yield of PVNBE plot.

The kinetics of polymerization of VNBE was studied in CH<sub>2</sub>Cl<sub>2</sub> solutions, as shown in Table 13 and Figure 2 (b). As in the case of NBD polymerization, an induction period was also observed for VNBE polymerization, indicating that the same mechanism took place in both cases. Compared to NBD, the initiation, as well as the propagation reaction, proceeded in a slower manner, probably due to the increased steric hindrance of VNBE. However, the yield scaled linearly with time, indicating that the polymerization reaction proceeded in a well-controlled way.



Figure 3. Polymerization of DCPD (0.6 mL, 552.0 mg, 4.2 mmol) with  $W_2Br_9$  (30.0 mg, 0.017 mmol), AgBF<sub>4</sub> (13.2 mg, 0.068 mmol) and 5.0 mL CH<sub>2</sub>Cl<sub>2</sub>; time-% yield of PDCPD plot.

The initiation reaction for DCPD was very fast, since the plot of yield *vs.* time passed through the origin, as shown in Figure 3. The polymerization rate was initially very fast without the presence of an appreciable induction period. However, upon progressing time, the rate of polymerization was substantially lowered. Compared to other monomers examined in this work, DCPD was the less reactive, probably due to the increased steric hindrance of this monomer. Retardation of the polymerization may be attributed to the increased time needed for the activation of the second double bond of the monomer leading to cross-linking products.

<i>t</i> (min)	Yield (%)	<i>M</i> <sub>n</sub> ×10 <sup>−3</sup>	<i>M</i> w/ <i>M</i> n					
PA <sup>a</sup>								
120	13	70.5	1.72					
240	40	82.4	1.62					
360	98	207	1.16					
480	79	54.2	1.61					
1440	59	16.0	2.07					
<i>t</i> (min)	Yield (%)	<i>t</i> (min)	Yield (%)					
NBD⁵		DCPD <sup>d</sup>	DCPD <sup>d</sup>					
15	12	30	0					
30	32	60	5					
45	34	90	11					
60	69	120	13					
75	74	150	14					
<b>VNBE</b> <sup>c</sup>		180	25					
60	5	210	48					
120	10	240	51					
180	28	270	52					
240	54	300	53					
300	66	330	56					
360	70	360	59					
420	87	390	59					
		420	61					
		450	62					
		480	67					
		600	79					
		720	81					
		840	91					
		960	95					

Table 13. Kinetic study of polymerization of all monomers with the catalytic system 1.

<sup>a</sup> Conditions: molar ratio **W<sub>2</sub>Br**<sub>9</sub>/AgBF<sub>4</sub>/PA equal to 1/3/350, 10 mL THF. <sup>b</sup> Conditions: molar ratio **W<sub>2</sub>Br**<sub>9</sub>/AgBF<sub>4</sub>/NBD equal to 1/4/500, 5 mL CH<sub>2</sub>Cl<sub>2</sub>. <sup>c</sup> Conditions: molar ratio **W<sub>2</sub>Br**<sub>9</sub>/AgBF<sub>4</sub>/VNBE equal to 1/4/2000, 2 mL CH<sub>2</sub>Cl<sub>2</sub>. <sup>d</sup> Conditions: molar ratio **W<sub>2</sub>Br**<sub>9</sub>/AgBF<sub>4</sub>/DCPD equal to 1/4/250, 5 mL CH<sub>2</sub>Cl<sub>2</sub>.

### 5.2.1 Conclusions

The kinetics of polymerization *via* ROMP of PA in THF, NBD, VNBE and DCPD in DCM solutions were studied, employing catalytic system **1** as catalyst.

Comparing with catalytic system 2, 1 polymerized PA with a lower rate but the products had higher molecular weights and narrower molecular weight distributions. In the case of polymerization of NBD, almost quantitative yields were obtained after 1.5 h of reaction. However, an induction period of a few minutes was observed, probably due to the complexation of the monomer to the catalyst and the initiation step of the polymerization process. The kinetics of polymerization of VNBE were studied, and as in the case of NBD, an induction period was also observed, indicating that the same mechanism took place in both cases. Compared to NBD, the initiation, as well as the propagation reaction, proceeded in a slower manner, probably due to the increased steric hindrance of VNBE. However, the yield scaled linearly with time indicating that the polymerization reaction proceeded in a well-controlled way. The initiation reaction for DCPD was very fast, since the plot of yield vs. time passed through the origin. Initially, the polymerization rate was very fast without the presence of an induction period. However, upon progressing time the rate of polymerization was reduced. Compared to other monomers examined in this work, DCPD was the less reactive, probably due to the increased steric hindrance of this monomer. Retardation of the polymerization may be attributed to the increased time needed for the activation of the second double bond of the monomer leading to crosslinked products.

### 5.3 Swelling of PDCPD xerogels and aerogels from various W-based catalytic systems

We have previously reported that *cis*-enriched **2-PDCPD** xerogels absorb toluene and swell, while mostly-*trans* PDCPD does not.<sup>9</sup> When swollen in toluene **2-PDCPD** wet-gels were kept in pentane, rapid shrinkage back to their original volume without any noticeable deformation was observed.<sup>9,205</sup>

In addition, by testing the swelling ability of PDCPD xerogels, obtained using various catalytic systems, in organic solvents we observed that both **2-PDCPD** and **3-PDCPD** xerogels swelled in various solvents (Table 14). Similar behavior was observed for other PDCPD materials, obtained from different W-based catalytic systems, although with different swelling rates and degrees of swelling.

Catalytic System	(1)	(2)	(3)	W <sub>2</sub> /Bu <sup>1</sup>	WCI <sub>6</sub>	WCI <sub>6</sub> /PA
Solvent						
toluene						
pentane						
acetone						
THF						
dioxane						
MeOH						
MeCN						
CH <sub>2</sub> Cl <sub>2</sub>						
CHCl <sub>3</sub>						
CCl <sub>4</sub>						
CS <sub>2</sub>						
DMF						
DMSO						
oil						
PhCI						
1,2-PhCl <sub>2</sub>						
PhCH <sub>2</sub> Cl						

Table 14. Swelling of PDCPD xerogels in selected solvents obtained using different catalytic systems.

color coding: extensive swelling, intermediate swelling, no swelling. <sup>1</sup> Bu: 1-Butene (as initiator).

In Dr. Raptopoulos' Thesis **2-PDCPD** xerogels were examined for their swelling ability towards 25 solvents.<sup>205</sup> In this work we expanded the study to 44 solvents. All swelling experiments were repeated at least three times. Swelling studies of **2-PDCPD** xerogels will be described in the next Chapter.

### 5.4 Swelling studies of 2-PDCPD xerogels

Mostly-*cis* **2-PDCPD** wet-gels were prepared in DCM *via* ROMP of dicyclopentadiene (DCPD; Scheme 17b) using the inexpensive dinuclear tungsten cluster Na[W<sub>2</sub>( $\mu$ -Cl)<sub>3</sub>Cl<sub>4</sub>(THF)<sub>2</sub>]·(THF)<sub>3</sub> ({W-<sup>3</sup>-W}<sup>6+</sup>, a'<sup>2</sup>e'<sup>4</sup>; Scheme 17a) together with small amounts of phenylacetylene (PA) as a co-initiator (Scheme 17c).<sup>9,206</sup>



Scheme 17. (a) Structure of dinuclear  $[W_2(\mu-CI)_3CI_4(THF)_2]^-$  (W<sub>2</sub>) used as a catalyst for Ring Opening Metathesis Polymerization (ROMP) of dicyclopentadiene (DCPD). (b) ROMP of DCPD including the modes of crosslinking. (c) Synthetic protocol for the preparation of 2-PDCPD xerogels.

The swelling behavior of such mostly-*cis* **2-PDCPD** xerogels toward toluene was quite dramatic (>100× v/v), exceeding by far the behavior of mostly-*trans*, or *cis*-enriched PDCPD, that were synthesized either with the 1<sup>st</sup> and 2<sup>nd</sup> generation Grubbs catalysts,<sup>207–209</sup> or the mononuclear tungsten-based catalytic system WCl<sub>6</sub>/PA,<sup>9</sup> probably because of poorer packing of the cis vs the trans configuration. The extreme uptake and swelling behavior of **2-PDCPD** xerogels in toluene is very relevant because toluene is used widely as a solvent, a coolant (e.g., in nuclear reactors), and as an octane booster in gasoline fuels. Furthermore, because of its low viscosity and density, runoffs of toluene enter easily water bodies causing pollution analogous to other oil-based organic pollutants.

The large swelling ability of mostly-*cis* **2-PDCPD** xerogels in toluene prompted an extensive investigation of the swelling behavior of that material in other organic solvents (a total of 44) of variable polarity, and ability to develop dispersion forces and hydrogen bonding.

Indeed, the swelling behavior of insoluble polymers in various solvents can be related to the Hansen Solubility Parameters (HSP) of the solvents.<sup>192,193</sup> HSPs

stemmed out of J. H. Hildebrand's concept of the solubility parameter, which was defined as the square root of the cohesive energy density.<sup>194</sup> C. M. Hansen introduced a three-dimensional solubility parameter by splitting the Hildebrand parameter into three components,<sup>195</sup> thus taking into consideration three major types of interactions between molecules: dispersion (or Van der Waals; D), dipole-dipole (P) and hydrogen bonding (H). The total solubility parameter ( $\delta \tau$ ) can be calculated *via* Equation 1, where  $\delta_D$ ,  $\delta_P$  and  $\delta_H$  are the parameters representing dispersion (D), dipole-dipole (P) and hydrogen bonding (H)

A significant advantage of the HSP theory is that it allows the study of polymersolvent interactions. During swelling, the solvent resides within regions of the polymer bulk that are chemically and energetically similar to it; in other words, in this case the principle "like dissolves like" can be interpreted as "like seeks like".<sup>192</sup> Thereby, if a solvent is found homogeneously distributed throughout the polymer, the solubility parameters of that solvent will reflect the properties of the whole polymer itself.<sup>192</sup> In the case of crosslinked polymers, such as PDCPD, the swelling behavior does not depend only on the polymer-solvent interactions, but also on the crosslinking density, as described in the Flory-Rehner theory.<sup>196</sup>

Thus, from a fundamental perspective, the most significant outcome of the analysis of the swelling behavior of **2-PDCPD** xerogels in a large array of solvents was the direct experimental estimation of the HSP of mostly-*cis* PDCPD, which is expected to become the point of departure for further development of efficient absorbers. From a practical perspective, we have shown the potential of mostly-*cis* PDCPD for removing organic solvents from water and/or oils.

After drying, resulting **2-PDCPD** xerogels were re-submerged in toluene and swelled up to the same volume, with the same rate, as the first time. The process was repeated three times with the same results. Similar behavior was observed in other organic solvents, although with different swelling rates and degrees of swelling.

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**2-PDCPD** xerogels had smooth external surfaces, and they were not porous materials, as discussed based on their skeletal and bulk densities above. This conclusion was also supported by SEM showing no internal pore structure (Figure 4e). When **W**<sub>2</sub>-**PDCPD** xerogels that had been swollen in toluene were dried with supercritical fluid (SCF) CO<sub>2</sub>, they shrunk a little, but they retained their shape (Figure 4a-d). However, those materials were not aerogels. SEM imaging of the SCF-dried samples showed the presence of big voids and collapsed dense walls (Figure 4 f,g).



Figure 4. (a, b) 2-PDCPD wet-gel in toluene right after immersion (a) and after 210 h (b). (c, d) Dry-gel obtained after drying the 2-PDCPD wet-gel of frame (b) with SCF CO<sub>2</sub>. (e) SEM image of a 2-PDCPD xerogel (before swelling in toluene). (f, g) SEM images of the 2-PDCPD dry-gel of frames (c) and (d).

What was even more interesting was that PDCPD xerogels prepared with different catalytic systems, i.e.,  $1^{st}$  and  $2^{nd}$  generation Grubbs catalyst (Ru-I and Ru-II, respectively), or WCl<sub>6</sub>, swelled less or did not swell at all. The degree of swelling was correlated to the *cis*-content of the polymer chain; both increased in the order Ru-I (*trans*) < Ru-II (high-*trans*) < WCl<sub>6</sub> (more-*cis*) < **2** (mostly-*cis*),<sup>9</sup> following the general trend of ROMP-derived polymers. That correlation was based on the fact that the only clear difference between those materials was in the configuration of the polymeric chains that varied from mostly-*trans* to mostly-*cis*. The degrees of crosslinking of those polymers were not calculated.

However, an estimation is possible from the FTIR-ATR spectra,<sup>9</sup> by calculating the ratio of the intensities of the band at 708 cm<sup>-1</sup> (assigned to the double bond of the cyclopentene ring) and the band at 1450 cm<sup>-1</sup> (assigned to the  $-CH_2-$  of the polymeric chain). This ratio is very similar for the four catalytic systems (in the range of 0.95 to 0.98), which shows that the degree of crosslinking is also very similar. This conclusion is also supported by the  $T_g$  values of PDCPD obtained using the four catalytic systems (142-144 °C for catalytic systems **W**<sub>2</sub>/**PA** (**2**), Ru-I, Ru-II and 129 °C for catalytic system WCl<sub>6</sub>/PA). In a previous study, Ru-II-derived fully cured PDCPD (from *endo*-DCPD) was reported to have higher swelling capacity in toluene than Ru-I-derived fully cured PDCPD (the weight of the swollen xerogels was ~4.5× vs ~2×, respectively, of the initial weight of the xerogel).<sup>210</sup> That behavior was attributed to the lower degree of crosslinking of GC-II-derived PDCPD, based on literature data,<sup>185</sup> mechanical testing and  $T_g$  values (145.0 vs 156.2 °C, respectively).

In order to study the swelling behavior of the **2-PDCPD** xerogels in organic solvents and understand the interactions of the polymer (mostly-*cis* PDCPD) with each solvent we used the Hansen Solubility Parameter (HSP) theory<sup>193</sup> and aspects of the Flory theory.<sup>196</sup> We selected 44 solvents covering a wide range of functional groups and properties, such as polarity, molar volume, surface tension, etc. The maximum volume ratios (degree) of swelling ( $q_{max}$ ) for all 44 solvents are summarized in Table 15. Figure 5 shows in bar graph format the  $q_{max}$  values for the 23 solvents in which swelling was observed. Representative plots of the volume degree of swelling (q) as a function of time and optical photographs of representative samples along different stages of swelling are shown in Supporting Information (Figure S2 to Figure S10).

Among the solvents considered, **2-PDCPD** xerogels swelled in aromatic hydrocarbons, halogenated solvents, cyclic ethers and carbon disulfide. They did not swell ( $q_{max} = 1$ ) in aliphatic hydrocarbons, ketones, amines, amides, nitriles, esters, alcohols, water and dimethylsulfoxide, with the exception of cyclohexane ( $q_{max} = 4$ ), cyclohexanone ( $q_{max} = 2$ ) and pyridine ( $q_{max} = 2$ ). It is also clear from the data of Table 15 that **2-PDCPD** xerogels swell in the various solvents not only to different extent, but also with different rates. During the swelling process the volume of the wet-gels increased linearly, or sometimes

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stepwise until wet-gels either reached a maximum volume, or they disintegrated. Interestingly, even in the "stepwise" volume increase, the overall trend was still linear. In that regard, it is noted that  $q_{max}$  represents the maximum volume measured experimentally. That means that  $q_{max}$  does not necessarily describe an equilibrium state, as in many cases the wet-gels disintegrated while they were still expanding (i.e., before they reached an equilibrium volume). Therefore,  $q_{max}$  may be different from the maximum-volume degree of swelling that **2-PDCPD** gels would have reached if they did not disintegrate. The highest degree of swelling was observed in toluene, in which gels expanded to more than 110× their original volume, before disintegrating.<sup>9</sup>

Table 15. Experimental maximum volume degree of swelling ( $q_{max}$ ) of 2-PDCPD xerogels in various solvents, scoring of the solvents according to their swelling capacity from "1" (maximum swelling observed) to "6" (no swelling observed), calculated Ra and RED values according to the Hansen theory, and Flory-Huggins  $\chi_{12}$  parameters.

Solvent	t <sup>a</sup> max (h)	<b>q</b> <sub>max</sub> <sup>b</sup>	score	Ra <sup>e</sup> (MPa <sup>1/2</sup> )	Ra <sup>2 e</sup> (MPa)	RED <sup>f</sup>	χ <sub>12</sub> <sup>g</sup> (α*=1)
toluene <sup>205</sup>	240 °	115	1	2.8	7.8	0.485	0.08
chloroform	228 °	54	2	2.3	5.3	0.389	0.04
bromobenzene	170°	24	3	2.8	7.8	0.491	0.09
carbon disulfide <sup>205</sup>	70 <sup>c</sup>	21	3	6.3	39.7	0.992	0.24
1,3-dichlorobenzene <sup>205</sup>	72	19	3	2.7	7.3	0.470	0.08
carbon tetrachloride <sup>205</sup>	82 °	16	3	4.8	23.0	0.820	0.22
chlorobenzene <sup>205</sup>	76 <sup>c</sup>	14	3	2.4	5.8	0.411	0.06
1,2-dibromoethane	190	13	3	5.5	30.3	0.922	0.26
tetrahydrofuran	100	12	3	5.6	31.4	0.931	0.26
benzene <sup>205</sup>	64	12	3	4.0	16.0	0.683	0.15
ethyl bromide	144	12	3	5.9	34.8	0.966	0.26
1-bromobutane	140	11	3	3.3	10.9	0.577	0.11
methylene dichloride <sup>205</sup>	90 <sup>c</sup>	10	4	5.6	31.4	0.891	0.20
1,3,5-trimethylbenzene	326 <sup>c</sup>	8	4	4.3	18.5	0.781	0.26
1,4-dimethylbenzene <sup>205</sup>	196 <sup>c</sup>	7	4	2.8	7.8	0.502	0.10
1,3-dimethylbenzene <sup>205</sup>	144 <sup>c</sup>	7	4	1.9	3.6	0.327	0.04
1,2-dichlorobenzene <sup>205</sup>	72	7	4	3.4	11.6	0.590	0.13
benzyl chloride <sup>205</sup>	119	5	4	3.8	14.4	0.665	0.17
cyclohexane	144	4	5	5.7	32.5	0.992	0.35
1,4-dioxane <sup>205</sup>	200	4	5	5.9	34.8	0.994	0.30
cyclohexanone	40	2	5	5.0	25.0	0.869	0.26
1,2-dichloroethane	210	2	5	5.6	31.4	0.624	0.46
pyridine	168	2	5	5.9	34.8	0.977	0.28
water <sup>205</sup>	_ d	1	6	41.0	1681.0	5.314	3.05
pentane <sup>205</sup>	_ d	1	6	8.9	79.2	1.576	0.93
N,N-dimethylformamide <sup>205</sup>	_ d	1	6	12.7	161.3	2.106	1.27
methanol <sup>205</sup>	_ d	1	6	21.8	475.2	3.228	1.94
dimethylsulfoxide <sup>205</sup>	_ d	1	6	14.4	207.4	2.339	1.48
diethyl ether <sup>205</sup>	_ d	1	6	7.4	54.8	1.289	0.58
acetonitrile <sup>205</sup>	_ d	1	6	15.6	243.4	2.421	1.30
acetone <sup>205</sup>	_ d	1	6	9.2	84.6	1.511	0.63
hexane	_ d	1	6	8.3	68.9	1.493	0.91
2-propanol	_ d	1	6	13.9	193.2	2.293	1.50
glycerol	_ d	1	6	24.9	620.0	4.076	4.59
ethylene glycol	- d	1	6	23.7	561.7	3.713	3.17
------------------------	-----	---	---	------	-------	-------	------
benzyl alcohol	_ d	1	6	10.5	110.3	1.821	1.15
N, N-dimethylacetamide	_ d	1	6	10.1	102.0	1.724	0.96
methyl-2-pyrrolidone	- d	1	6	9.4	88.4	1.603	0.85
triethylamine	_ d	1	6	6.7	44.9	1.229	0.64
diisopropylamine	_ d	1	6	7.0	49.0	1.278	0.70
aniline	- d	1	6	8.8	77.4	1.503	0.72
methyl methacrylate	_ d	1	6	5.8	33.6	1.007	0.36
propylene carbonate	_ d	1	6	14.8	219.0	2.482	1.88
ethyl acetate	_ d	1	6	6.2	38.4	1.061	0.38

<sup>a</sup> Time in which wet-gels reach maximum volume. <sup>b</sup> Experimental maximum volume degree of swelling of **2-PDCPD** gels at  $t_{max}$  (mean values of at least three measurements), calculated according to the equation  $q_{max} = V_{max}/V_{in}$ , where  $V_{max}$  is the volume of the wet-gel at  $t_{max}$  and  $V_{in}$  is the initial volume of the xerogel. <sup>c</sup> Last measurement before wet-gels disintegrated. <sup>d</sup> Wet-gels remained unaffected more than 6 months in that solvent. <sup>e</sup> Calculated from Equation (4) using the HSP that were calculated for **2-PDCPD**:  $\delta_D = 18.15$ ,  $\delta_P = 3.69$ ,  $\delta_H = 3.55$  MPa<sup>1/2</sup>. <sup>f</sup> Values calculated using the HSPiP 5.1.02 software. <sup>g</sup> Calculated from Equation (4). HSP for **2-PDCPD**:  $\delta_D = 18.15$ ,  $\delta_P = 3.69$ ,  $\delta_H = 3.55$  MPa<sup>1/2</sup>.



Figure 5. Swelling behavior of 2-PDCPD xerogels in various organic solvents. Colorcoding demotes the scores given to the various solvents according to the Hansen theory based on their ability to cause swelling (red, score: "1"; blue, score: "2"; green, score: "3"; orange, score: "4"; cyan, score: "5". See text).

According to the Hansen theory, if a polymer swells in a specific solvent, then the diffusivity of the solvent in the swollen polymer is much higher (by several orders of magnitude) than its diffusivity in the pure polymer.<sup>192</sup> A significant entry resistance may be found within the surface of a polymeric block and is due to the morphology of the polymer at the interface, wherein the mass transfer coefficient can be very low. Different surface morphology can be the result of rapid cooling after, for example, processing by injection molding, or be just a natural state of a given polymer, whereas larger and bulkier molecules have difficulty finding suitable absorption sites to anchor, hop and move into the bulk of the polymeric block. Surface/entry resistance has been described as a boundary condition for the diffusion equation. One should also take into consideration that not all segments of the polymer behave in the same way towards the same solvent. Characteristic examples are block copolymers or crosslinked polymers, which in many cases show different correlations of the different blocks/segments with the same solvents.<sup>192</sup>

In an obvious deviation from Fickian diffusion, Case II diffusion (as described in Hansen theory) is generally defined as a linear uptake of solvent in a plot of amount absorbed *vs* time (not the square root of time as in typical diffusion).<sup>192</sup> This behavior is described by appropriate solutions of the diffusion equation, and is encountered when the diffusion coefficient depends strongly on the solvent concentration. The diffusion coefficient of a solvent in rigid polymers typically increases by a factor of about 10 for each additional 3% by volume of solvent that is locally present. (By comparison, in elastomers the diffusion coefficient increases by a factor of approximately 10 for each additional 15% by volume of solvent.) There is a limit to this rule-of-thumb when the solvent concentration approaches 100% and the diffusion coefficient approaches the self-diffusion value.

In summary, the final element in understanding solvent diffusion in **2-PDCPD** xerogels is the surface effect that was described above. That is, if for any reason solvent molecules cannot penetrate quickly enough through the boundary of the polymer and the surrounding solvent, the rate of diffusion will be limited not by diffusion coefficients, but by the surface resistance that is applied in series to regular diffusion.

ROMP-derived polymers based on norbornene-terminated macromonomers,<sup>158</sup> as well as polyurethane foams based on poly(ethylene terephthalate),<sup>159</sup> have also been found to swell in toluene, although their  $q_{max}$  (36 and 28, respectively) was much lower than what we have observed with **2-PDCPD** xerogels ( $q_{max} = 115$ ). The swelling behavior of GC-I-derived PDCPD in various solvents has also been studied.<sup>185</sup> Although the authors reported

swelling as a weight ratio, thus prohibiting direct comparison with our volume degree of swelling data, it is evident, however, even *via* a crude calculation, that their absorption capacities were much lower than those reported here: specifically, the reported uptake of CHCl<sub>3</sub> did not exceed 3.38 g per g of absorber, while **2-PDCPD** xerogels, absorbed more than 10 g per g of DCM and THF, more than 80 g per g of CHCl<sub>3</sub> and more than 100 g per g of toluene. It is noted that the gooey and/or sticky texture of our swollen gels prohibits weighting, thus forcing us to measure swelling as a volume ratio instead of a mass ratio. Besides that, measuring the change in the dimensions of the gel is more accurate than measuring the mass, because in the latter case evaporation of the solvent may affect the measurement.<sup>211</sup>

To put overall swelling in perspective, it is noteworthy that the maximum uptake of solvents by **2-PDCPD** xerogels is comparable to or higher than the swelling reported by several well-known swellable hydrogels, for example those consisting of carbon nanotubes-doped poly(vinyl alcohol),<sup>212</sup> gelatin,<sup>213</sup> acrylamide/maleic acid copolymers<sup>214</sup> and graphene oxide/poly(*N*-isopropylacrylamide) hybrids.<sup>215</sup> Nevertheless, there are exceptions: for example the maximum absolute swelling of **2-PDCPD** xerogels is still much lower than that observed for certain graphene oxide hydrogel composites.<sup>216</sup>

Regarding comparison of specific solvent uptake with other materials, on per weight basis, **2-PDCPD** xerogels generally showed higher uptake of toluene and CHCl<sub>3</sub> than organic polymers including several photoresponsive copolymers,<sup>160</sup> copolymers of cinnamoyloxy ethyl methacrylate and octadecyl acrylate,<sup>161</sup> disulfide-linked polymeric networks,<sup>162</sup> porous polyurea monoliths derived from toluene diisocyanate,<sup>165</sup> *cis*-9-octadecenyl-based polymers,<sup>166</sup> mesogenic polyelectrolyte gels,<sup>168</sup> conjugated microporous (co)polymers,<sup>163</sup> polymethylsilsesquioxanes,<sup>170</sup> and poly(alkoxysilanes).<sup>171</sup> For a more detailed comparison of **2-PDCPD** xerogels with those classes of polymers see Table S1 in Appendix I.

Compared to carbon-based materials, on per weight basis again, **2-PDCPD** xerogels had almost half the uptake capacity for CHCl<sub>3</sub> of carbon nanotube sponges, which also showed high uptakes of DMF, ethanol, hexane and oils.<sup>156</sup> **2-PDCPD** xerogels also showed lower solvent uptake than graphene/carbon composite aerogels,<sup>152</sup> nitrogen-doped graphene,<sup>153</sup> and ultra-flyweight carbon aerogels.<sup>157</sup> Compared to spongy graphene, results were mixed, with **2-PDCPD** xerogels having higher uptake for toluene (~2×), almost equal for CHCl<sub>3</sub>, and lower for THF (> 4×) and 1,2- dichlorobenzene (> 6×).<sup>154</sup> Finally, **2-PDCPD** xerogels had a higher toluene uptake (> 7×) than graphene/FeOOH aerogels,<sup>155</sup> but it is pointed out that all those graphene-based materials also showed absorption capacity for alkanes and/or alcohols,<sup>152–155</sup> for which **2-PDCPD** xerogels did not.



Figure 6. Toluene and chloroform uptake on per weight basis (data directly from the literature), and on per volume basis (data calculated using reported densities – when available). Numerical labels of the horizontal axis refer to the materials: (1): WCl<sub>6</sub>-PDCPD<sup>9</sup>, (2): ROMP polymers from norbornene-terminated macromonomers,<sup>158</sup> (3): polyurethane foams,<sup>159</sup> (4): photoresponsive copolymers,<sup>160</sup> (5): cinnamoyloxy ethyl methacrylate/octadecyl acrylate copolymers,<sup>161</sup> (6): disulfide-linked polymeric networks,<sup>162</sup> (7): porous polyurea monoliths,<sup>165</sup> (8): *cis*-9-octadecenyl-based polymers,<sup>166</sup> (9): crosslinked lipophilic polyelectrolytes,<sup>169</sup> (10): poly(alkoxysilanes),<sup>171</sup> (11): graphene/carbon composite aerogels,<sup>152</sup> (12): nitrogen-doped graphene,<sup>153</sup> (13): spongy graphene,<sup>154</sup> (14): graphene/FeOOH aerogels,<sup>155</sup> (15): ultra-flyweight carbon aerogels,<sup>157</sup> (16): conjugated microporous (co)polymers,<sup>163</sup> (17): melamine formaldehyde sponges,<sup>164</sup>

(18): mesogenic polyelectrolyte gels,<sup>168</sup> (19): polymethylsilsesquioxanes,<sup>170</sup> (20): Ru-I-PDCPD,<sup>185</sup> (21): carbon nanotube sponges.<sup>156</sup> The first bar corresponds to the 2-PDCPD material of this work.

The toluene and CHCl<sub>3</sub> uptakes for all materials mentioned above are summarized in Table S1 and are compared in bar-graph form with the values from **2-PDCPD** xerogels in Figure 6 top. Although on per weight basis **2-PDCPD** xerogels seem to generally lag behind carbon-based materials, it must be pointed out that from a practical standpoint this perception is misleading because other materials do not swell. That is, for example, graphene/carbon composites may uptake 279 g of toluene per g of graphene/carbon composite, but given the low density of that material (0.003 g cm<sup>-3</sup>) in order to remove 1000 g of toluene, one needs 1.2 L of graphene/carbon composite. Clearly, for adsorption of large quantities of toluene that imposes severe issues related to the storage and transport of the absorber. On the contrary, because **2-PDCPD** xerogels swell a lot, one would need only 10 mL (0.01 L) of xerogel to absorb 1000 g of toluene. To account for that swelling effect, the data of Figure 6 top have been replotted on a mass-per-volume basis (Figure 6 bottom, and it is clear that **2-PDCPD** xerogels perform by far better than all competitors.

# 5.4.1 Hansen Solubility Parameters (HSP)

HSP theory takes into consideration three major types of interactions between molecules: dispersion (D), dipole-dipole interactions (P) and hydrogen bonding (H). The total solubility parameter ( $\delta_{T}$ ) can be calculated *via* Equation 1, where  $\delta_{D}$ ,  $\delta_{P}$  and  $\delta_{H}$  are the parameters representing dispersion (Van der Waals), dipole-dipole and hydrogen bonding interactions, respectively. HSP for all solvents used in this study along with the respective maximum volume degree of swelling ( $q_{max}$ ) of swollen **2-PDCPD** xerogels are given in Table S2. As discussed above,  $q_{max}$  does not necessarily describe an equilibrium state. Nevertheless, considering that HSP provide only a direction for solvent selection, rather than a precise determination of the relative ability of solvents to dissolve or swell a polymer, the plots of  $q_{max}$  vs HSP can be useful as a general guide in solvent selection. Plots of  $q_{\text{max}}$  vs  $\delta_T$ ,  $\delta_D$ ,  $\delta_P$  and  $\delta_H$  are shown in Figure S13. Solvents in which xerogels do swell are referred to as "good" and solvents in which gels do not swell are referred to as "bad." No clear correlation between swelling behavior and HSP can be seen. Although the "good" solvents can be found in a certain area, there are also always a couple of exceptions (i.e., "bad" solvents in that area). The "good" solvents were more scattered when  $\delta_P$  (0 – 8.8 MPa<sup>1/2</sup>, see Figure S13c) or  $\delta_{\rm H}$  (0.2 – 9 MPa<sup>1/2</sup>, see Figure S13d) were considered, and were concentrated in a much narrower area when  $\delta_D$  (16.5 – 20.2 MPa<sup>1/2</sup>, see Figure S13b) or  $\delta_T$  (17 – 22 MPa<sup>1/2</sup>, see Figure S13a) were considered. Those results suggest that the dispersion forces (Van der Waals interactions) are the most important parameters that affect the swelling behavior of 2-PDCPD xerogels. This conclusion is in agreement with the chemical composition and structure of PDCPD. On the other hand, the fact that always there are solvents that do not follow those trends serves as a reminder of the complexity of the matter, and suggests that the swelling behavior of **2-PDCPD** xerogels is a multivariable problem, whereas in addition to the usual polar, H-bonding and disperse force interactions of the solvent with the polymer, local association effects between the polymer and the solvent (for both "good" and "bad" solvents) have to be taken into account.<sup>211</sup>

#### 5.4.2 Surface tension and HSP

Surface tension (or specific free energy,  $\gamma$ ) is the elastic tendency of a fluid surface area that makes it acquire the least surface area possible. Surface tension can be correlated to the molar volume ( $V_m$ ) and the HSP of the solvent according to Equation 3.<sup>217</sup> The atomic dispersion interactions are differentiated by a constant from the molecular dipolar and hydrogen bonding interactions. Equation 3 is not valid for aliphatic alcohols and alkali halides.<sup>192</sup> The surface tension calculated for all solvents of this study, except for 2-propanol, methanol, glycerol and ethylene glycol (Table S2), was plotted *vs q*<sub>max</sub>. As shown in Figure 7a, **2-PDCPD** xerogels swell in solvents with  $\gamma$  ranging from 20 to 35 mN/m, with a few exceptions.

$$\gamma = 0.01709 \ V_{\rm m}^{1/3} \left[ \delta_{\rm D}^2 + 0.632 (\delta_{\rm P}^2 + \delta_{\rm H}^2) \right]$$
(3)



Figure 7. Relation between the experimental maximum volume degree of swelling ( $q_{max}$ ) of 2-PDCPD xerogels and: (a) the surface tension ( $\gamma$ ); (b) the Hansen Ra<sup>2</sup> of the solvents; (c) the Hansen RED.; and, (d) the Flory-Huggins parameter  $\chi_{12}$ , calculated using Equation 5 and setting  $\alpha^*$  equal to 1.

#### 5.4.3 Estimation of the HSP of 2-PDCPD

The HSP theory can be used to estimate the HSP of a polymer from the experimental swelling data of that polymer (i.e., **2-PDCPD**). To that end, a 3D plot of the individual solubility parameters for each solvent tested was drawn using the HSPiP 5.1.02 software.<sup>218</sup> Then a sphere is constructed with all "good" solvents inside the sphere, and all "bad" solvents outside the sphere. The HSP of the polymer are the coordinates of the center of the sphere. From a practical perspective, there are two methods to construct the sphere. According to the 1<sup>st</sup> method solvents are classified as "good" or "bad"; "good" are solvents that yield any degree of swelling, irrespective how small or large, and "bad" are solvents that give no swelling. According to the 2<sup>nd</sup> method solvents are given scores in the range of 1 to 6: "1" is given to the "best" solvents and "6" is given to the "worst" solvents, i.e., to the solvents in which **2-PDCPD** 

xerogels did not swell at all. In effect, the score "6" set is equivalent to the "bad" solvent set of the 1<sup>st</sup> method. In order to find the sphere that fits the experimental data best, we constructed different spheres, leaving successively outside solvents with scores "4", "5" and "6". Always, the center of the sphere represents the HSP of **2-PDCPD** xerogels. The radius of a sphere (R) defines the limit of "happiness," as stated in the software website.<sup>218</sup> In the case of crosslinked polymers, such as **2-PDCPD**, "happiness" is of course defined as "swelling." Solvents located closer to the center of any sphere would be expected to cause more extensive swelling.

Both methods have been applied to our system. For the 2<sup>nd</sup> method, all spheres considering all solvents with scores "1" up to "5" have been created successively, and the best fit was found when all solvents with scores "1" to "5" were considered to be inside the sphere (leaving outside all solvents in which **2-PDCPD** xerogels did not swell at all). Thereby, both the "good" / "bad" solvent method and the score method gave identical results. The 1<sup>st</sup> method is described in the Supporting Information (Table S3, Figure S14 and Figure S15); the 2<sup>nd</sup> method (the sphere with the best fit) is described below.

For the 2<sup>nd</sup> method, solvents were given scores according to the experimental  $q_{max}$  values as follows: "1" for  $q_{max} > 100$ , "2" for  $q_{max} \ge 50$ , "3" for  $q_{max} > 10$ , "4" for  $q_{max} = 5-10$ , "5" for  $q_{max} < 5$  and "6" for  $q_{max} = 1$  (Table 15). Figure 8 shows the generated sphere and without a single exception, **2-PDCPD** xerogels swell in a solvent if and only if the solvent is situated in the Hansen sphere. The 2D plots (Figure S16) of the individual HSP of the solvents under study provide a measure of reliability of the method. It is obvious that solvents covering the entire range of the three HSP have been used. The radius (R) of the sphere was 5.8 MPa<sup>1/2</sup>. The HSP of **2-PDCPD** were calculated from the center of the sphere:  $\delta_D = 18.15$ ,  $\delta_P = 3.69$ ,  $\delta_H = 3.55$  MPa<sup>1/2</sup>, and  $\delta_T = 18.86$  MPa<sup>1/2</sup>. Those values (that were used in all subsequent calculations) were calculated using molar volume ( $V_m$ ) correction, which modifies the fitting algorithm so that bigger 'good' molecules and smaller 'bad' molecules are accepted as 'out' and 'in', respectively, on the basis that their molar volume decreases and their solubility increases. Without molar volume correction, the radius of the sphere (6.1

MPa<sup>1/2</sup>) and the HSP of **2-PDCPD** xerogels had slightly higher values:  $\delta_D = 18.40$ ,  $\delta_P = 3.82$ ,  $\delta_H = 3.58$  MPa<sup>1/2</sup>, and  $\delta_T = 19.13$  MPa<sup>1/2</sup>.



Figure 8. 3D plot of the individual Hansen Solubility Parameters (HSP) for each solvent tested. Blue dots represent solvents in which 2-PDCPD xerogels swelled (23 "good" solvents – scores: "1"-"5"). Red squares represent solvents in which no swelling was observed (21 "bad" solvents – score: "6"). The green sphere, generated by the HSPiP 5.1.02 software, is the sphere with the minimum diameter that fits best the experimental data. The center of the sphere is a reasonable estimate of the HSP of 2-PDCPD, which is represented by the green dot. The sphere contains all "good" solvents and no "bad" solvents (referred to as wrong solvents), giving a fit value of 1.0, which is considered as a perfect fit.

The HSP of **2-PDCPD** have also been estimated using the group contribution method, which is a theoretical method that relies on the structure of the repeating units of polymers. Those values,  $\delta_D = 16.7$ ,  $\delta_P = 0.5$ ,  $\delta_H = 3.4$  MPa<sup>1/2</sup>, and  $\delta_T = 17.0$  MPa<sup>1/2</sup>, were significantly different from those calculated from the sphere. The HSP calculated from the sphere are considered more reliable for two reasons: (a) this method uses experimental data, while the theoretical method relies heavily on assumptions about the structure of the polymer; and, (b) **2-PDCPD** is not a linear polymer; its structure is complicated by random crosslinking *via* metathesis as well as *via* radical coupling (Scheme 17), thereby neither the repeat unit nor the molecular mass can be estimated with any measure of confidence.

HSP for the DCPD monomer have been calculated using the same software (DIY method, Figure S17):  $\delta_D = 17.2$ ,  $\delta_P = 2.4$ ,  $\delta_H = 3.0$  and  $\delta_T = 17.7$  MPa<sup>1/2</sup>. The location of DCPD was found inside the sphere (Figure S18). We note that the polymer and the monomer do not change functionality (both are hydrocarbons). Therefore, it is not surprising that their HSP were very similar.

Skaarup and Hansen<sup>219</sup> have developed an equation for a solubility parameter that is referred to as "distance" (Ra), and signifies the HSP distance between a solvent and the polymer. Ra is a measure of how alike the two molecules are and can be calculated using Equation 4, where in our case "1" refers to the 2-**PDCPD** and "2" refers to the solvent. The smaller the Ra value, the more likely for the two molecules to be compatible. Ra values for each solvent are shown on Table 15. For a "good" solvent Ra must not exceed the radius of the sphere  $(R = 5.8 \text{ MPa}^{1/2})$ , which is indeed the case. The  $q_{max} vs Ra^2$  plot is shown in Figure 7b. Nevertheless, a quantitative correlation of swelling to the Ra values is risky and was not attempted. The swelling behavior cannot be related to the HSP alone. In addition, in most of the "good" solvents, gels did not reach equilibrium-swelling at all. In another approach<sup>220</sup> to evaluate the correlation of the HSP of **2-PDCPD** xerogels with the HSP of the solvents and their effect on swelling, the magnitude differences ( $\Delta 2\delta_D$ ,  $\Delta \delta_P$ ,  $\Delta \delta_H$ ) between each of the components of HSP for the solvent and the 2-PDCPD xerogels were calculated (Table S4) and were plotted (Figure S19). That way, the effect of two of the three components can be observed simultaneously. Solvents in which 2-**PDCPD** xerogels swelled are located closer to the (0,0) point.

$$Ra2 = 4 (δD1 - δD2)2 + (δP1 - δP2)2 + (δH1 - δH2)2 (3)$$

Table 15 shows also the Relative Energy Difference (RED) values. RED is the ratio of the distance of solvent from the center of the sphere (Ra) over the radius of the sphere (R). In theory, the lower the RED value, the highest the affinity between the solvent and the "center of the sphere" (in our case **2-PDCPD**). In practice, RED < 1 shows a good affinity between the polymer and the solvent. RED is also important for relating the HSP approach to that of Flory-Huggins, as it will be discussed in the next Section. Plotting  $q_{max}$  vs RED (Figure 7c) shows a general trend in which solvent swelling is reduced as RED increases.

According to those results, toluene, for which we have observed the highest volume degree of swelling ( $q_{max} = 115$ ), is not the solvent closest to the center of the sphere (RED = 0.485); 1,3-dimethylbenzene ( $q_{max} = 7$ ), chloroform ( $q_{max} = 54$ ), chlorobenzene ( $q_{max} = 14$ ), 1,3-dichlorobenzene ( $q_{max} = 19$ ) are closer to the center of the sphere than toluene, thereby are predicted to be "better" solvents than toluene, i.e., **2-PDCPD** xerogels would have been expected to swell more in those solvents than in toluene. That inconsistency between the HSP theory and experiment may be attributed to the fact that in most of the "good" solvents gels disintegrated while they were still swelling, and therefore they did not reach equilibrium volumes. After all, as was stated above, this method is only a guideline for solvent selection.

# 5.4.4 The Flory-Huggins interaction parameter ( $\chi_{12}$ )

The polymer/solvent interactions can be described with the Flory-Huggins theory and the  $\chi$  parameter,<sup>221</sup> or the  $\chi_{12}$  parameter, which can be more easily calculated and is being currently accepted for general use.  $\chi_{12}$  can be derived from the Hildebrand solubility parameters of a non-polar solvent, a non-polar polymer and the solvent molar volume (V<sub>m</sub>).<sup>192</sup> Several methods have been developed for determining  $\chi_{12}$ , such as the corresponding states theories (CST),<sup>222</sup> Inverse Gas Chromatography (IGC),<sup>223-229</sup> vapor pressure depression, osmotic pressure effect, equilibrium swelling of polymer by liquid, and light scattering.<sup>230</sup> A very good estimation of the  $\chi_{12}$  parameter can be achieved from the HSP, according to Equation 5.<sup>192,231</sup> Parameter  $\alpha^*$  is a universal correction factor, which is equal to 0.6 for polymers bearing polar groups<sup>231</sup> and equal to 1 for systems where dispersion forces dominate over polar and hydrogen-bonding forces,<sup>192</sup> as is the case for **2-PDCPD** xerogels. Thus calculated  $\chi_{12}$  values are shown in Figure 4. Solvents with  $\chi_{12} \le 0.5$  are considered as "good" solvents, and this is observed for all the solvents in which gels swelled. Indeed, as shown in Figure 7d, 2-PDCPD xerogels swelled for  $\chi_{12}$ in the range  $0.04 \le \chi_{12} \le 0.46$ . Methyl methacrylate and ethyl acetate comprised exceptions with  $\chi_{12} < 0.5$ , yet no swelling was observed.

$$\chi_{12} = \alpha^* \frac{V_{\rm m} \, {\rm Ra}^2}{4 {\rm RT}}$$
 (5)

#### 5.4.5 Conclusions

Mostly-cis 2-PDCPD xerogels, synthesized with the catalytic system 2, swelled in various organic solvents, mainly aromatic, chlorinated, and brominated hydrocarbons. The small volume of material required (1/100 or even less) vs other literature absorbents including organic polymers or carbon-based materials, and the competitive technology for preparing 2-PDCPD xerogels (inexpensive starting materials and catalyst, room temperature synthesis, ambient pressure drying) render those xerogels superior materials in terms of solvent uptake. The swelling behavior of 2-PDCPD xerogels was rationalized with the Hansen Solubility Parameters (HSP) theory and the Flory theory, each of which provided insight into the swelling mechanism and the parameters that affected it. A correlation was made between the swelling behavior of the xerogels in each solvent and the solvent Hansen Solubility Parameters (HSP), leading to an estimation of the HSP of mostly-cis PDCPD. Based on those findings, many applications include separations of organic solvents from water, or the use thin layers of those xerogels in sensors and actuators by coupling volumetric swelling to optical or electrical signal transduction. From a fundamental perspective, the most significant outcome of this study was the direct experimental estimation of the HSP of mostly-cis PDCPD. From a practical perspective, we have shown the potential of mostly-cis PDCPD for separating organic solvents from water and/or oil.

# 5.5 3-PDCPD aerogels and xerogels obtained using the catalytic system Na[W<sub>2</sub>(μ-Cl)<sub>3</sub>Cl<sub>4</sub>(THF)<sub>2</sub>]·(THF)<sub>3</sub>/NBD (3)

The synthesis of **PDCPD** wet-gels was carried out at room temperature under Ar atmosphere (Scheme 18). All formulations are shown in Table 1. The weight percent of **DCPD** was the same for all samples (20 % w/w). Higher concentrations of the monomer provided materials with bulk densities > 1 g/cm<sup>3</sup>. Attempts to work with lower concentration sols (e.g., 10 or 5 % of **DCPD**) provided wet-gels (within 24 to 48 h), which were not very sturdy, and could not be handled easily during post-gelation solvent exchange. The most likely explanation of this behavior is the higher amount of linear **PDCPD**, which is soluble in common organic solvents. Previous research by both our group and others<sup>11,232,233</sup> has shown the formation of linear **PDCPD** in low **DCPD** concentrations. The soluble part of the wet-gels (i.e., linear oligomers, unreacted monomer, remained processing solvents) was dissolved away in THF during washes, as was confirmed with <sup>1</sup>H NMR spectroscopy (Figure S20). From this spectra, the most characteristic peaks are at 5.60 and 5.48 ppm and are assigned to linear PDCPD and linear PNBD respectevely.<sup>9,43</sup> Different molar ratios of **W**<sub>2</sub>/**NBD** were tested for a constant concentration of the monomer (20 % w/w): 1/5, 1/10, 1/20, 1/30 and 1/40. Specifically, experiments with 1/5 ratio did not gel, while the highest ratios gave rigid wet-gels. Regarding the material properties of **PDCPD** aerogels (Table 16), the optimal **W**<sub>2</sub>/**NBD** ratio was 1/10.



Scheme 18. Synthetic route for 3-PDCPD xerogels and aerogels (left) and representative photos of different procedure stages for the preparation of aerogels (right).

For comparison purposes, the configuration and the material properties of **3-PDCPD** xerogels and aerogels synthesized using the catalytic system **3** (W<sub>2</sub>/NBD) are compared to those of PDCPD xerogels and aerogels synthesized using W<sub>2</sub>/PA and Grubbs catalyst first generation (Ru-I), respectively. <sup>13,234,235</sup> Material properties of **3-PDCPD** aerogels are also compared with PDCPD derived from Grubbs catalyst second generation (Ru-II). All catalysts structures are shown in Scheme 16.

#### 5.5.1 Physicochemical characterization of PDCPD xerogels and aerogels

The structure and the configuration of the polymeric chain of **PDCPD** xerogels and aerogels were studied with spectroscopic techniques (FTIR-ATR, FT-Raman, <sup>13</sup>C CPMAS NMR) and their thermal stability with thermogravimetric analysis (TGA). As expected, xerogels and aerogels are chemically identical. Therefore, the characterization data for **3-PDCPD** aerogels are presented below, along with SEM and N<sub>2</sub>-sorption data which provided information about the porous network of the aerogels. For comparison purposes, along with the characterization data for **3-PDCPD** aerogels we present two additional extreme cases; **PDCPD** aerogels obtained with **Ru-I**, which have a mostly-*trans* structure, and **PDCPD** xerogels obtained with **W<sub>2</sub>/PA**, which have a mostly-*cis* 

FTIR-ATR spectra are presented in Figure 9. Stretching vibrations of *trans* and *cis* C=C bonds appear at 1660 cm<sup>-1</sup> and at 1650 cm<sup>-1</sup>, respectively, while deformation vibrations of C–H bonds on *trans* and *cis* double bonds appear at 972 and 750 cm<sup>-1</sup>, respectively. The shoulder at 710 cm<sup>-1</sup> shows the existence of unreacted pendant cyclopentene groups, pointing out the presence of linear **PDCPD** segments in the polymer backbone. The relative intensity of the bands related to *cis/trans* bonds, in comparison to the spectra of **PDCPD** obtained with catalytic systems **2** and **Ru-I**, suggested that **3** and **2** provided **PDCPD** with the same configuration, i.e., mostly-*cis*.



Figure 9. FTIR-ATR spectra (left: 1700-1590 cm<sup>-1</sup>; right: 1500-675 cm<sup>-1</sup>) of 3-PDCPD aerogels and xerogels obtained from ROMP of DCPD with three catalytic systems, as indicated.

Raman spectroscopy (Figure 10) which has been used in addition with FTIR-ATR spectra to give supplementary information. The most remarkable bands of this spectra were at 1650 and 1620 cm<sup>-1</sup>, which were attributed to acyclic *cis* double bonds of the polymer network and to cyclic *cis* cyclopentene double bonds, respectively. The latter is consistent with FTIR-ATR and confirms that not all cyclopentene rings were involved in crosslinking. A small shoulder at 1664 cm<sup>-1</sup> corresponds to the v(C=C) of the *trans* double bonds of the polymeric chain.<sup>9,236,237</sup> In agreement with the FTIR-ATR spectra, FT-Raman spectra of **PDCPD** from both catalytic systems **3** and **2** were almost identical (indicating high-*cis* polymers), while **PDCPD** from **Ru-I**-showed a more intense band at 1664 cm<sup>-1</sup> (high-*trans* polymer). Both FTIR-ATR and FT-Raman spectra provide qualitative evidence that **3** provides high-*cis* **PDCPD**.





The <sup>13</sup>C CPMAS NMR spectra (Figure 11), in agreement with the FTIR-ATR and FT-Raman spectra, confirmed the high-*cis* configuration of **3-PDCPD** xerogels and aerogels prepared in this study. The peak at 40 ppm was assigned to *cis* double bonds of the polymeric chain and prevailed over the peak at 44 ppm which was assigned to *trans* double bonds of the polymeric chain.<sup>9</sup> The exact determination of the cis/trans ratio was not possible due to overlapping of the two peaks. However, the stereoselectivity of each catalytic system is rather straightforward. The peak at 132 ppm, is assigned to the olefinic carbons while peaks in the 30–60 ppm region to aliphatic carbons.<sup>235</sup>



Figure 11. <sup>13</sup>C CPMAS NMR spectra of PDCPD aerogels and xerogels obtained from the ROMP of DCPD obtained from the ROMP of DCPD with three catalytic systems, as indicated.

The thermal stability of the **PDCPD** aerogels was investigated with thermogravimetric analysis (TGA) under nitrogen (Figure 12, left). TGA curves for materials obtained with the three catalytic systems were very similar and showed that the thermal decomposition can be divided in two steps. For the **PDCPD** aerogels of this study, a very small weight loss (2 %) was observed during the first step, from 25 to 420 °C, corresponding to the evaporation and decomposition of unreacted monomers and oligomers. The second and main degradation step happened after 460 °C and resulted in a residue of 18 %. As can be seen in differential thermogravimetry (Figure 12, right), a shoulder appeared at 470 °C and indicated a bimodal and more complex thermal decomposition mechanism than in the case of **PDCPD** obtained with **Ru-I**.



Figure 12. Weight loss with temperature (left) and derivative weight loss with temperature (right) of PDCPD aerogels and xerogels obtained from the ROMP of DCPD with three catalytic systems, as indicated.

The morphology of **PDCPD** xerogels and aerogels prepared with **3** was studied with SEM (Figure 13). **3-PDCPD** xerogels exhibited a smooth morphology with no internal structure (Figure 13, top). **PDCPD** aerogels exhibited a somewhat corrugated morphology, with an internal structure. Their morphology differs significantly from **PDCPD** aerogels which were synthesized using Grubbs 1<sup>st</sup> (**Ru-I**) and 2<sup>nd</sup> generation (**Ru-II**) catalysts.<sup>209</sup> Those aerogels were macroporous materials with common fibrous morphologies at the studied monomer concentration (20% w/w).<sup>235</sup> This difference in morphology may be relevant to the different cis/trans configuration of the polymers. Differences in morphologies that could be attributed to the configuration of the polymer chains have also been observed for norbornene/norbornadiene copolymers; high-cis copolymers, obtained using catalytic system **2**,<sup>238</sup> had different morphologies than copolymers with 50/50 cis/trans double bond ratio, obtained using Rubased catalysts.<sup>239–241</sup>



Figure 13. SEM images of 3-PDCPD xerogels (top) and aerogels (bottom) obtained from the ROMP of DCPD with 3.

The material properties for **PDCPD** aerogels synthesized with **3** are summarized in Table 16, and N<sub>2</sub>-sorption isotherms and pore size distributions are presented in Figure 14. Lower bulk density, higher porosity, higher BET surface area and smaller particle sizes were obtained for **PDCPD** aerogels synthesized using the lowest  $W_2/NBD$  molar ratio (1/10).

The skeletal density was also lower, compared to the higher **W**<sub>2</sub>/**NBD** molar ratios, as a result of the incorporation of more or longer **PNBD** segments in the polymer chain. The shape of the N<sub>2</sub>-sorption isotherms (i.e., no saturation, narrow hysteresis loop; Figure 14, left) and the fact that for **3-PDCPD** aerogels  $V_{\text{Total}} >> V_{1.7-300\text{nm}}$  (Table 16) indicate that our materials were macroporous, in agreement with the literature.<sup>235</sup> Average pore diameters were calculated using the  $4 V/\sigma$  method. *V* was set either as the maximum volume of N<sub>2</sub> adsorbed along the isotherm, or as the volume ( $V_{\text{Total}}$ ) calculated from the bulk and the skeletal density of the corresponding materials (Table 16). In all cases, average pore diameters using  $V_{\text{Total}}$  were higher and they increased with decreasing bulk density. From the BJH method, peak maxima showed larger pore diameters for the materials synthesized using the **W**<sub>2</sub>/**NBD** molar ratio 1/10.

Table 16 includes also the properties of **PDCPD** aerogels from the literature,<sup>209</sup> synthesized using **Ru-I** and **Ru-II**. All comparisons are made for aerogels from same concentration sols (20% w/w). **PDCPD** aerogels of this study (**W**<sub>2</sub>/**NBD** 1/10) have lower bulk density and higher porosity, but significantly lower BET surface area compared to **PDCPD** aerogels from **Ru-I**. On the other hand, they

have similar BET surface area (42 vs 38 m<sup>2</sup>/g) and particle size (63 vs 75 nm), and lower average pore diameter (11 vs 32 nm) compared to **PDCPD** aerogels from **Ru-II**. It seems that high-*cis* **PDCPD** aerogels (from **W**<sub>2</sub>/**NBD**) have similar properties with high-*trans* **PDCPD** aerogels (from **Ru-II**), and they have two advantages: they are sturdy and well-shaped, while **Ru-II**-derived aerogels deform significantly, the catalytic system used for their preparation is more costefficient.



Figure 14. N<sub>2</sub>-sorption isotherms (left) and pore size distributions by the BJH method (right) of W<sub>2</sub>/NBD-PDCPD aerogels (1<sup>st</sup> and 2<sup>nd</sup> entry, Error! Reference source not found.).

Table 16.	Material	properties	of 3-PD0	CPD aeroge	els obtained	from t	the	ROMP	of	DCPD
with three	e differen	t catalytic s	ystems.							

Catalyti c system	Linear shrinkage <sup>a</sup> (%)	Bulk density <i>p</i> ₀(g cm <sup>-3</sup> )	Skeletal density ∕∕s(g cm⁻³)	Porosity ♭ Π (% v/v)	BET surf. area σ (m <sup>2</sup> g <sup>-1</sup> ) [micropore surf. area] <sup>c</sup>	V <sub>Total</sub> d (V <sub>1.7</sub> . <sub>300nm</sub> ) <sup>e</sup> (cm <sup>3</sup> g <sup>-1</sup> )	Av. pore diameter <sup>f</sup> (4 V <sub>Total</sub> /σ) (nm)	Particle radius <sup>g</sup> (nm)
W <sub>2</sub> /NBD 1/10	15	0.135±0.009	1.128±0.005	89	42	7.0 (0.1)	11 (667)	63
W2/NBD 1/20	26	0.52±0.08	1.348±0.006	69	7 [4]	1.6 (0.009)	6.6 (914)	318
Ru-I <sup>h</sup>	12	0.28±0.07	1.136±0.003	75	186	2.7 (N/A)	21 (57)	14.2
Ru-II <sup>h</sup>	N/A	N/A	1.055±0.004	-	38	N/A (N/A)	32 (NA)	75

<sup>a</sup> Calculated according to formula:  $(y_1+y_2)/2$ , where  $y_1 = 100-[(h_{fin}/h_{st})\times100]$  and  $y_2 = 100-[(d_{fin}/d_{st})\times100$ . <sup>b</sup> Calculated according to formula:  $(\rho_s-\rho_b)/\rho_s$ , where  $\rho_s$ : skeletal density and  $\rho_b$ : bulk density. <sup>c</sup> Micropore surface area *via t*-plot analysis, according to the Harkins and Jura model. <sup>d</sup> Total pore volume calculated according to formula:  $1/\rho_b - 1/\rho_s$ . <sup>e</sup> Cumulative volume of pores between 1.7 and 300 nm from N<sub>2</sub>-sorption data and the BJH desorption method. <sup>f</sup> Calculated by the  $4 V/\sigma$  method; *V* was set equal to the maximum volume of N<sub>2</sub> adsorbed along the isotherm as  $P/P_0 \rightarrow 1.0$ . For the number in parentheses *V* was set equal to  $V_{Total}$  from the previous column. <sup>g</sup> Calculated according to formula:  $3/(\rho_s \times \sigma)$ . <sup>h</sup> Values from reference <sup>235</sup>.

# 5.5.2 Swelling studies of 3-PDCPD xerogels and aerogels

During washing of **PDCPD** wet-gels with THF we noticed that they absorbed a significant amount of solvent and swelled. The same behavior was observed also when **PDCPD** wet-gels (aerogels or xerogels) were immersed in a number of organic solvents (e.g., toluene (Figure 15), DCM, THF, chloroform). The same behavior had been observed for **PDCPD** xerogels synthesized with the catalytic system **W**<sub>2</sub>/**PA** (2).<sup>9,206</sup> Those xerogels have shown the best by far performance regarding solvent uptake compared to all other literature materials.<sup>206</sup>



#### Figure 15. Optical photos representing the swelling of 3-PDCPD aerogels in toluene.

In the literature, there is a growing interest for the use of crosslinked gels in chemical sensors.<sup>197</sup> For this kind of applications, the swelling behavior of those gels needs to be examined.<sup>242</sup> Swelling is essentially a chain rearrangement, resulting from interactions between the polymer and its environment.,<sup>243</sup> which, in this case, is the solvent. In order for a gel to be used as a sensor, it has to show a fast volume change when exposed to external stimuli. For this fast response to be achieved, the gel dimensions need to be small.

Therefore, **3-PDCPD** aerogels were cut in thin disks and immersed into various organic solvents to test their volume change in a certain time period. The volume change was studied in 12 different organic solvents (Table 17). **3-PDCPD** aerogels in the form of thin disks were immersed in 5 mL of various organic solvents (toluene, DCM, chloroform, chlorobenzene, bromobenzene, THF, 1-bromobutane, ethyl bromide, ethylene dichloride, m-xylene, p-xylene and mesitylene) in graduated glass tubes. The initial volume of the disks was 0.1 mL in all cases. Gels were kept in the solvent for 2 hours in total and for the first hour the volume increase ( $\Delta V$ ) of gels in each solvent was measured every

10 minutes.  $\Delta V$  was determined by the volume decrease of each solvent when gel was taken out from the graduated vial (Figure 16).

	Solvent											
	toluene	CH <sub>2</sub> Cl <sub>2</sub>	CHCI <sub>3</sub>	PhCI	PhBr	THF	1-Br	ethyl	ethylene	m-xylene	p-xylene	mesitylene
Time							butane	bromide	dichloride			
(min)						Volume	e increase	<u> </u>			•	
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10	0.25	0.15	0.30	0.05	0.05	0.30	0.10	0.20	0.00	0.10	0.10	0.10
20	0.30	0.35	0.40	0.20	0.20	0.40	0.20	0.20	0.00	0.10	0.15	0.10
30	0.30	0.40	0.40	0.30	0.20	0.45	0.20	0.25	0.10	0.10	0.25	0.15
40	0.30	0.40	0.45	0.30	0.25	0.50	0.20	0.30	0.10	0.20	0.25	0.15
50	0.40	0.40	0.50	0.30	0.30	0.50	0.20	0.30	0.10	0.20	0.25	0.20
60	0.45	0.50	0.55	0.40	0.30	0.50	0.30	0.35	0.10	0.25	0.25	0.20
120	0.45	0.60	0.65	0.40	0.40	0.65	0.30	0.40	0.10	0.35	0.40	0.30

Table 17. Volume increase of 3-PDCPD aerogel thin disks in various organic solvents.



Figure 16. Representative optical photos of graduated tubes containing PDCPD aerogel thin disks immersed into organic solvents at a certain time (top: t = 0 min; bottom: t = 60 min).

Figure 17 shows  $\Delta V$  of **PDCPD** aerogel thin disks in various organic solvents within 60 min. All plots (volume increase *vs* time) are provided in the Appendix Section II (Figure S21-Figure S32). **PDCPD** aerogel thin disks exhibit the higher volume increase in chloroform, THF, DCM and toluene. In most of the solvents, the volume increase after 2 h has not changed too much (Table 17; Figure 12).



Figure 17. Volume increase of PDCPD aerogel thin disks in various organic solvents within 60 min.





### 5.5.3 Conclusions

High-*cis* **3-PDCPD** aerogels were successfully synthesized using the  $W_2/NBD$  catalytic system. Compared to high-*trans*, 1<sup>st</sup> and 2<sup>nd</sup> generation Grubbs' catalyst-derived **PDCPD** aerogels described in literature, **3-PDCPD** aerogels had a much different morphology, possibly due to the different *cis/trans* configurations. Although analogous differences were not observed for the properties of the materials, the  $W_2/NBD$  (3) catalytic system is advantageous

due to its cost-effectiveness. **3-PDCPD** aerogels were able to swell in various organic solvents, with their fast response making them good candidates for use in chemical sensors.

# CHAPTER 6 POLYUREA AEROGELS

# 6.1 Synthesis of polyurea aerogels using first row transition metal compounds as catalysts

As reported in Chapter 2, PUA aerogels can be synthesized from isocyanates and water using triethylamine as catalyst (Scheme 9), or from isocyanates and mineral acids (e.g., boric acid; Scheme 9) in stoichiometric amounts.<sup>89,244</sup> In this work, we have utilized several hydrated metal salts as catalysts (i.e., CrCl<sub>3</sub>·6H<sub>2</sub>O, FeCl<sub>3</sub>·xH<sub>2</sub>O, CoCl<sub>2</sub>·6H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and CuCl<sub>2</sub>·2H<sub>2</sub>O) for the reaction of TIPM (Scheme 13) with water, according to Scheme 9.

Those **PUA-M** aerogels were prepared in the form of monoliths according to Scheme 19. A solution of the metal compound in DMF (solution A) and a solution of the triisocyanate monomer (TIPM) and water in ethyl acetate (EA) (solution B) were mixed. The resulting sol was poured into molds and allowed to gel. It is noted that TIPM is supplied as 27% w/w solution in EA and it is used as received. As a result, all experiments were carried out in a mixture of the two solvents (DMF/EA). All wet-gels were aged for 24 h, were solvent-exchanged with acetone and dried with SCF CO<sub>2</sub>. The resulting aerogels are referred to as **PUA-M-X**, whereas X denotes the concentration of the monomer in the sol (% w/w) and M indicates the metal of the metal compound used as catalyst. The monomers concentration (i.e., TIPM (Scheme 13) and water) was 4 and 12% w/w. The molar ratio of TIPM/water was consistent and equal to 1/3 for all experiments. Four molar ratios of TIPM/metal salt (abbreviated as TIPM/M) were studied: 1/0.1, 1/0.5, 1/1.5 and 1/3. In the first two cases, the amount of the metal compounds was catalytic. In the other two cases overstoichiometric amounts of the metal compounds were used, because we wanted to test how much of the metal can be retained in the polymer. For comparison purposes, native PUA aerogels were also synthesized, using Et<sub>3</sub>N as catalyst, at the same monomer concentrations and TIPM/Et<sub>3</sub>N ratios with PUA-M-X aerogels. PUA-**M-12** aerogels using a TIPM/M ratio of 1/3 were not synthesized, because the amount of DMF used could not dissolve the corresponding amount of the metal

compound. Only in the case of FeCl<sub>3</sub> (low molecular weight), we managed to synthesize **PUA-Fe-12** aerogels with TIPM/catalyst: 1/3.



Scheme 19. Top: synthetic procedure of PUA-M aerogels according to the sol-gel process. Bottom: optical photos of PUA-M aerogels.

**PUA-M-X** wet-gels were very sturdy and the corresponding aerogels were very rigid at all monomer concentrations. On the other hand, native PUA wet-gels were not as sturdy and they were removed from their molds with difficulty, especially at 4% w/w monomers concentration. The corresponding PUA aerogels were not as rigid as **PUA-M-X** aerogels and they underwent severe cracking in most cases. The cracking problem has been mentioned in the literature for these materials.<sup>89</sup> For the synthesis of **PUA-Cu-X** aerogels both CuCl<sub>2</sub>·2H<sub>2</sub>O and CuSO<sub>4</sub>·5H<sub>2</sub>O were tested as catalysts and the resulting **PUA-Cu** aerogels had completely different morphologies. CuSO<sub>4</sub>·5H<sub>2</sub>O-derived **PUA-Cu** aerogels were actually different from all other **PUA-M** aerogels; they were not rigid, they looked like a sponge, they showed elasticity, and their surface area was close to zero. Hence, only CuCl<sub>2</sub>·2H<sub>2</sub>O-derived aerogels were studied in detail and are reported here. All formulations are summarized in

Table 2 and Table 3 and the chemical characterization along with the properties of the new materials are described below. For the low monomer concentration (4% w/w), the gelation times where up to 25 min for all TIPM/M molar ratios, while at the high monomer concentration (12% w/w) gelation was faster reaching up to 14 min.

### 6.1.1 Characterization of PUA-M Aerogels

The characterization of **PUA-M-X** and native PUA aerogels was carried out using ATR-FTIR and <sup>13</sup>C CPMAS NMR spectroscopy, thermogravimetric analysis (TGA), N<sub>2</sub>-sorption porosimetry, He pycnometry, SEM, EDS spectroscopy, X-ray mapping, and PXRD.

The ATR-FTIR spectra of the **PUA-M** aerogels (Figure 19) were almost identical and in agreement with the expected chemical structure of PUA, as well as with similar materials from the literature.<sup>89</sup> All spectra showed the characteristic C=O stretch of urea at 1660 cm<sup>-1</sup>, while at 1506 and 1410 cm<sup>-1</sup> bands were assigned to aromatic C=C stretches. The N–H scissoring vibration appeared at 1590 cm<sup>-1</sup> and the C–H bending on the phenyl rings of TIPM was observed at 815 cm<sup>-1</sup>. No unreacted TIPM has been detected in the spectra. The unreacted –NCO would appear at 2264 cm<sup>-1</sup>.



Figure 19. ATR-FTIR spectra of native PUA and PUA-M aerogels, as indicated.

<sup>13</sup>C CPMAS NMR spectra of **PUA-M** (except for **PUA-Co**) and native PUA aerogels showed all characteristic peaks of TIPM-derived PUA.<sup>89,245</sup> Specifically, the urea carbonyl peak appeared at 154 ppm, the aromatic carbons appeared in the area 115-145 ppm and the central (aliphatic) carbon of TIPM (Scheme 13) appeared at 55 ppm. No spectrum could be recorded for **PUA-Co** aerogels, because the material was extremely hard and could not be pulverized.



Figure 20. <sup>13</sup>C CPMAS NMR spectra of all PUA-M and native PUA aerogels.

TGA showed that all **PUA-M-X** aerogels followed the same decomposition pattern as native PUA aerogel. All materials presented high thermal stability (>300 °C). Two significant weight loss events were observed in Figure 21 (**PUA-M** aerogels prepared with a TIPM/M molar ratio 1/0.5) apart from the small weight loss incurred due to loss of moisture and remaining solvents (1-6% weight loss at 100 °C). The first significant weight loss, about 30% of the initial weight, occurred at around 380 °C. A second weight loss also occurred from 390 °C to 430 °C, followed by another smaller weight loss event at temperatures between 500 and 550 °C. The residue of the samples ranged from 38-41% for all **PUA-M** aerogels, while for native PUA aerogels the residue was 48%. **PUA-**

**Ni** aerogel showed the highest residue (52%). Similar observations were made from the TGA of all other **PUA-M** aerogels prepared with various TIPM/M ratios (Figure S33).



Figure 21. Weight loss with temperature (left) and derivative weight loss with temperature (right) for PUA-M-4 and native PUA-4 aerogels prepared with TIPM/M molar ratio 1/0.5.

Selected material properties for all PUA aerogels are given in Table 18 and presented graphically in Figure 22, Figure 23 and Figure 24. Wet-gels exhibited substantial shrinkage during solvent exchanges (up to 45%) with acetone, suggesting a major reorganization of the nanostructure during that process. During SCF drying, shrinkage was less than during solvent exchanges and ranged between 10-30%. Total shrinkage from wet-gels to aerogels is shown in Table 18 and Figure 22 for all TIPM/M molar ratios and for both monomer concentrations. Comparing the two monomer concentrations (4 and 12 % w/w), shrinkage was higher for **PUA-M-4** aerogels, as expected. Native PUA and **PUA-M** aerogels showed very similar shrinkage for all TIPM/M molar ratios, except for ratio 1/3, for which native PUA and **PUA-Cu-4** aerogels showed the lowest shrinkage. **PUA-M-12** aerogels showed similar shrinkage, which was not much affected by the different TIPM/M molar ratios.

Although skeletal densities (Table 18) seemed to be very similar for **PUA-M-4** (1.27 to 1.40 g cm<sup>-3</sup>), **PUA-M-12** (1.23 to 1.34 g cm<sup>-3</sup>) and native PUA (1.26-1.35 g cm<sup>-3</sup>) aerogels, a more careful look at the values shown in Table 18 shows that the skeletal densities of **PUA-M** aerogels are higher compared to the skeletal density of native PUA aerogels prepared with the same TIPM/catalyst ratio. This observation is more obvious for CuCl<sub>2</sub>·2H<sub>2</sub>O-derived

aerogels, because CuCl<sub>2</sub>·2H<sub>2</sub>O has the highest density (2.51 g cm<sup>-3</sup>) among the metal precursors used (i.e., CrCl<sub>3</sub>·6H<sub>2</sub>O 1.76 g cm<sup>-3</sup>, FeCl<sub>3</sub>·xH<sub>2</sub>O 1.82 g cm<sup>-3</sup>, CoCl<sub>2</sub>·6H<sub>2</sub>O 1.92 g cm<sup>-3</sup>, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O 2.05 g cm<sup>-3</sup>). For native PUA aerogels bulk density (Figure 23) decreased when overstoichiometric amounts of Et<sub>3</sub>N were used. The same trend was observed for **PUA-Fe** aerogels. Bulk densities of all other **PUA-M** aerogels were almost the same for the same "M", irrespective of the TIPM/M ratio and they were similar to the higher values of bulk density of native PUA aerogels (i.e., prepared with TIPM/M molar ratio 1/0.1). Porosities of **PUA-M** aerogels were in general higher for the low monomer concentration, as expected, and similar or higher compared to native PUA aerogels of the same concentration.

BET surface areas of **PUA-M** aerogels were higher compared to native PUA aerogels (Figure 24) of the same monomer concentration. BET surface areas of **PUA-Cr**, **PUA-Co** and **PUA-Cu** aerogels were almost the same at both monomer concentrations and at all TIPM/M molar ratios. **PUA-Fe** and **PUA-Ni** aerogels have higher BET surface areas at low metal salt concentrations. Particle radii of **PUA-M** and native PUA aerogels (Figure 23) were very similar.

Sample	TIPM/M	Linear	Bulk	Skeletal	Porosity <sup>b</sup>	BET surf. area	<b>V</b> <sub>Total</sub> <sup>d</sup>	Av. pore	Particle
	(mol/mol)	shrinkage <sup>a</sup>	density	density	Π (% v/v)	σ (m² g <sup>-1</sup> )	( <i>V</i> 1.7-300nm) <sup>e</sup>	diameterf	radius <sup>g</sup>
		(%)	<i>ρ</i> ₀ (g cm⁻³)	ρ₅ (g cm⁻³)		[micropore	(cm³ g⁻¹)	(4 $V_{Total}/\sigma$ )	<i>r</i> (nm)
						surf. area] <sup>c</sup>		(nm)	
PUA-4	1/0.1	57±3	0.4±0.1	1.298±0.007	76	318 [30]	2.4 (0.6)	7.2 (31)	7.3
PUA-4	1/0.5	57±6	0.48±0.09	1.353±0.009	66	205 [20]	1.4 (0.4)	7.5 (28)	11
PUA-4	1/1.5	51±2	0.282±0.008	1.31±0.02	78	125 [11]	2.8 (0.2)	7.4 (89)	18
PUA-4	1/3	34±2	0.18±0.02	1.333±0.009	87	230 [24]	4.9 (0.4)	7.4 (85)	9.8
PUA-Cr-4	1/0.1	51±2	0.377±0.005	1.328±0.005	68	469 [55]	1.6 (0.9)	8.2 (14)	4.8
PUA-Cr-4	1/0.5	54±1	0.463±0.004	1.40±0.02	67	317 [30]	1.4 (1.1)	13 (18)	6.8
PUA-Cr-4	1/1.5	48.8±0.4	0.46±0.02	1.349±0.002	65	363 [40]	1.4 (0.7)	8.5 (15)	6.1
PUA-Cr-4	1/3	57±5	0.4±0.1	1.285±0.004	77	316 [30]	6.1 (1.0)	9.6 (77)	7.4
PUA-Fe-4	1/0.1	47±2	0.27±0.04	1.310±0.008	78	471 [42]	2.7 (0.7)	6.9 (23)	4.9
PUA-Fe-4	1/0.5	48±5	0.25±0.10	1.325±0.006	89	480 [30]	5.8 (1.1)	10 (49)	4.7
PUA-Fe-4	1/1.5	44±3	0.21±0.3	1.37±0.01	88	468 [28]	5.3 (0.9)	7.3 (46)	4.7
PUA-Fe-4	1/3	45.5±0.5	0.31±0.01	1.304±0.005	76	416 [27]	2.4 (1.6)	16 (23)	5.5
PUA-Co-4	1/0.1	50±4	0.34±0.08	1.29±0.02	78	345 [44]	2.8 (0.9)	12 (32)	6.7
PUA-Co-4	1/0.5	46±9	0.4±0.1	1.24±0.01	78	406 [53]	2.9 (0.9)	9.8 (29)	6.0
PUA-Co-4	1/1.5	54.5±0.1	0.389±0.005	1.300±0.006	70	360 [37]	1.8 (0.8)	10 (20)	6.4
PUA-Co-4	1/3	53.6±0.8	0.42±0.01	1.305±0.007	69	354 [37]	1.7 (0.8)	10 (19)	6.5
PUA-Ni-4	1/0.1	52±2	0.43±0.02	1.31±0.01	66	320 [42]	1.5 (1.1)	21 (18)	7.2
PUA-Ni-4	1/0.5	54±1	0.46±0.02	1.272±0.005	63	262 [32]	1.3 (0.6)	8.8 (20)	9.0
PUA-Ni-4	1/1.5	53.5±0.6	0.45±0.02	1.296±0.003	67	154 [28]	1.5 (0.4)	8.8 (40)	15
PUA-Ni-4	1/3	64±1	0.46±0.05	1.319±0.005	69	258 [40]	1.7 (0.5)	7.8 (26)	8.8
PUA-Cu-4	1/0.1	50±6	0.3±0.1	1.288±0.006	70	417 [45]	1.8 (0.6)	7.0 (17)	5.6
PUA-Cu-4	1/0.5	50±4	0.34±0.05	1.326±0.007	72	276 [40]	1.9 (0.6)	8.3 (28)	8.2
PUA-Cu-4	1/1.5	50±3	0.28±0.04	1.34±0.01	82	344 [36]	3.3 (0.7)	9.1 (39)	6.5
PUA-Cu-4	1/3	37±1	0.36±0.06	1.325±0.004	69	312 [32]	1.7 (0.6)	9.1 (22)	7.2
PUA-12	1/0.1	44±1	0.68±0.02	1.256±0.002	46	279 [16]	0.7 (0.4)	6.4 (9.6)	8.6
PUA-12	1/0.5	44±2	0.43±0.06	1.264±0.001	66	360 [20]	1.5 (0.9)	10 (17)	6.6
PUA-12	1/1.5	34.0±0.8	0.37±0.02	1.276±0.004	71	350 [24]	1.9 (1.5)	18 (22)	6.7
PUA-12	1/3	27±1	0.270±0.007	1.270±0.002	79	243 [28]	2.9 (0.8)	13 (48)	9.7
PUA-Cr-12	1/0.1	35.6±0.8	0.52±0.02	1.291±0.006	59	363 [45]	1.1 (0.7)	7.2 (12)	6.4
PUA-Cr-12	1/0.5	36.2±0.9	0.66±0.02	1.324±0.003	51	518 [32]	0.8 (0.08)	6.9 (6.1)	4.4
PUA-Cr-12	1/1.5	43±3	0.82±0.04	1.345±0.004	52	314 [25]	0.5 (0.4)	6.9 (6.3)	/.1
PUA-Fe-12	1/0.1	43±4	0.7±0.2	1.277±0.001	60	496 [40]	1.2(0.7)	7.0 (9.8)	4.9
PUA-Fe-12	1/0.5	30±2	$0.7\pm0.1$	1.278±0.001	53	292 [25]	0.9 (0.4)	0.4 (12)	8.0
PUA-Fe-12	1/1.0	32±0	0.3±0.1	$1.337 \pm 0.002$	77	341[17]	1.6 (0.6)	9.7(21)	0.0
PUA-Fe-12	1/0 1	$\frac{23\pm0}{132\pm01}$	$0.34\pm0.00$	1.303±0.004	57	249 [21]	2.3 (0.0)	72(11)	9.2
PUA-Co-12	1/0.1	43.2±0.1	0.092±0.007	1.202±0.002	67	386 [52]	1.0(0.0)	0.0(17)	6.3
PUA-Co-12	1/1.5	38 4+0 6	0.50+0.02	1 298+0 008	60	355 [42]	1.0 (0.3)	9.3 (13)	6.5
PUA-Ni-12	1/0 1	46+5	0 71+0 05	1 288+0 002	43	335 [34]	70(05)	67(14)	6.9
PUA-Ni-12	1/0.5	41+6	0.74±0.14	1.304+0.001	52	474 [30]	0.8 (0.6)	5.8 (3.4)	4.9
PUA-Ni-12	1/1.5	37±3	0.68±0.03	1.231±0.005	33	56 [9]	0.7 (0.07)	6.9 (48)	44
PUA-Cu-12	1/0.1	38.6±0.5	0.492±0.006	1.302±0.002	63	399 [42]	1.3 (0.7)	8.1 (13)	5.8
PUA-Cu-12	1/0.5	41.2±0.9	0.71±0.02	1.302±0.006	50	351 [39]	0.7 (0.7)	8.0 (7.7)	6.6
PUA-Cu-12	1/1.5	37±1	0.51±0.02	1.341±0.001	61	373 [38]	1.2 (0.9)	9.8 (12)	6.0

Table 18. Material properties of PUA-M-X aerogels.

<sup>a</sup> Calculated according to formula:  $(y_1+y_2)/2$ , where  $y_1 = 100-[(h_{fin}/h_{st})\times 100]$  and  $y_2 = 100-[(d_{fin}/d_{st})\times 100]$ . <sup>b</sup> Calculated according to formula:  $(\rho_s-\rho_b)/\rho_s$ , where  $\rho_s$ : skeletal density and  $\rho_b$ : bulk density. <sup>c</sup> Micropore surface area *via t*-plot analysis, according to the Harkins and Jura model. <sup>d</sup> Total pore volume calculated according to formula:  $1/\rho_b-1/\rho_s$ . <sup>e</sup> Cumulative volume of pores between 1.7 and 300 nm from N<sub>2</sub>-sorption data and the BJH desorption method. <sup>f</sup> Calculated by the  $4V/\sigma$  method; *V* was set equal to the maximum volume of N<sub>2</sub> adsorbed along the isotherm as  $P/P_0 \rightarrow 1.0$ . For the number in parentheses *V* was set equal to  $V_{Total}$  from the previous column. <sup>g</sup> Calculated according to formula:  $3/(\rho_s \times \sigma)$ .



Figure 22. Linear shrinkage (%) of native PUA and PUA-M aerogels at all TIPM/M molar ratios, as indicated.



Figure 23. Bar-graphs summarizing bulk density (left) and particle radii (right) of PUA-M-4 and PUA-M-12 aerogels, prepared with TIPM/M molar ratio 1/0.1.



Figure 24. Bar-graphs summarizing BET and micropore surface area of PUA-M-4 (left) and PUA-M-12 (right) aerogels prepared with all TIPM/M molar ratios.

Representative  $N_2$ -sorption isotherms are shown in Figure 25 top, together with pore size distributions for **PUA-M-4** synthesized using the molar ratio TIPM/M:

1/0.1. N<sub>2</sub>-sorption isotherms and pore size distributions of all materials are provided in the Appendix Section III (Figure S34-Figure S45). In agreement with the shape of the N<sub>2</sub>-sorption isotherms (i.e., no saturation, narrow hysteresis loop; Figure 25 left top and Figure S34-Figure S39), **PUA-M-4** aerogels as well as native PUA aerogels of the same monomer concentration gave  $V_{Total} > V_{1.7}$ . 300 nm (Figure 26, left), indicating macroporous materials. For the fraction of pores in the 1.7-300 nm range, average pore diameters (by the BJH desorption method; Figure 25 left bottom were in the range of 18-27 nm, for aerogels synthesized with a TIPM/M molar ratio of 1/0.1. For higher TIPM/M molar ratios the ranges were similar, except for the 1/3 ratio, for which average pore diameters by the BJH method were bigger, in the range of 26-33 nm (Figure S34 to Figure S39, right). **PUA-M-12** aerogels as well as native PUA aerogels of the same monomer concentration showed broader hysteresis loops and saturation plateaus (Figure 25 right top and Figure S40-Figure S45, left), indicating a higher percentage of mesoporosity compared to PUA-M-4 aerogels. For those materials  $V_{Total} > V_{1.7-300 \text{ nm}}$  (Figure 26 right), showing that pores larger than 300 nm did exist in all materials. For the fraction of pores in the 1.7-300 nm range, average pore diameters using the BJH desorption method, gave pore diameters in the ranges 8-11, 7-27 and 4-16 nm for PUA-M-12 aerogels synthesized with TIPM/M molar ratios of 1/0.1, 1/0.5 and 1/1.5, respectively. Average pore diameters were also calculated using the  $4V/\sigma$ method, whereas V was either the maximum volume of  $N_2$  adsorbed along the isotherm, or the volume (V<sub>Total</sub>) calculated from the bulk and the skeletal density of the materials (Table 18). For PUA-M-4 aerogels average pore sizes obtained using  $V_{\text{Total}}$  were higher, while for **PUA-M-12** aerogels average pore sizes obtained with the two methods were in good agreement. For the fraction of pores in the 1.7-300 nm range, average pore diameters (by the BJH desorption method; Figure 25 right bottom) were in the range of 7.3-11.2. However, the BJH method is not reliable for pore sizes below 10 nm.



Figure 25. Representative  $N_2$ -sorption diagrams (top) and pore size distributions by the BJH method (bottom) for PUA-M-4 (left) and PUA-M-12 aerogels (right) prepared with TIPM/M molar ratio 1/0.1.



Figure 26. Bar-graphs summarizing log(Vtotal/V1.7-300nm) of PUA-M-4 (left) and PUA-M-12 (right) aerogels, prepared with various TIPM/M molar ratios, as indicated.

Significantly, a fraction (5-43%) of their BET surface area was assigned to micropores. This appears to be an intrinsic characteristic of aerogels based on the rigid aromatic core of TIPM (Scheme 13), and has been observed with all polyurea,<sup>89,244</sup> polyurethane<sup>254–257</sup> and polyamide<sup>140,250</sup> aerogels. Microporosity was evaluated independently with CO<sub>2</sub> adsorption to 1 bar at 273 K and Table

19 summarizes data related to CO<sub>2</sub> adsorption. All aerogels adsorbed CO<sub>2</sub>, which signified the presence of free-volume microporosity,<sup>251,252</sup> which was related to the way polymer molecules are stacked together. Pore size distributions for pores <1 nm were calculated from the CO<sub>2</sub> adsorption isotherms using a DFT model<sup>253</sup> (Figure 27 right and Figure S46-Figure S50). Pore size distributions were very similar for all aerogels and showed at least three maxima. Micropores were distributed in the range of 0.51-0.86 nm.

Sample	TIPM/M (mol/mol)	Quan CO₂ adso	V <sub>&lt;7.97Å</sub> <sup>a</sup> (cm³ g⁻¹)		
		mmol g⁻¹	<b>c</b> m <sup>3</sup> g <sup>−1</sup>		
PUA-Cr-4	1/3	1.22	27	0.05	
PUA-Fe-4	1/0.5	1.34	30	0.06	
PUA-Fe-4	1/3	0.81	18	0.03	
PUA-Co-4	1/0.1	1.32	30	0.05	
PUA-Co-4	1/0.5	1.04	23	0.04	
PUA-Ni-4	1/0.1	1.30	29	0.05	
PUA-Ni-4	1/0.5	0.87	20	0.04	
PUA-Ni-4	1/3	1.14	26	0.05	
PUA-Cu-4	1/0.1	1.28	29	0.05	
PUA-Cu-4	1/0.5	1.11	25	0.06	
PUA-Cr-12	1/0.5	0.24	5.4	0.01	
PUA-Fe-12	1/0.5	1.10	25	0.04	
PUA-Fe-12	1/3	0.62	14	0.02	
PUA-Co-12	1/0.5	0.83	19	0.03	
PUA-Ni-12	1/0.5	0.70	16	0.03	

Table 19. Selected results from CO<sub>2</sub> porosimetry of PUA-M-X aerogels.

<sup>a</sup> Total pore volume of pores less than 7.97 Å from  $CO_2$  sorption data at 273 K using the single-point absorption method at *P*/*Po* = 0.03.





The morphology of all aerogels was investigated with SEM microscopy. Figure 28, Figure S62, Figure S52, Figure S55, Figure S57, Figure S59 and Figure S64, show SEM images of **PUA-M-4** aerogels synthesized with TIPM/M molar

ratios 1/0.5, 1/1.5 and 1/3 and Figure S63, Figure S53, Figure S56, Figure S61 and Figure S66 shows SEM images of **PUA-M-12** aerogels synthesized with TIPM/M molar ratios 1/0.5 and 1/1.5. The morphology of TIPM-derived PUA aerogels in the literature is fibrous at low densities and progressively turns particulate as the density increases.<sup>89</sup> **PUA-M** aerogels have uniform and dense morphology, the same for all metal precursors used, and at all molar ratios.

The composition of **PUA-M-4** aerogels and the metal content in them were determined *via* X-Ray mapping and EDS spectroscopy. Figure 28 to Figure 34 and Figure S51 to Figure S66 show SEM images, X-ray mapping and EDS of selected **PUA-M** aerogels. The most important finding of those studies is that the metal compound is homogeneously distributed in the polymer matrix, which means that those **PUA-M** aerogels are very promising precursors for metal-doped carbon aerogels.

The % w/w of the elements given from EDS spectra was compared to the theoretical % w/w calculated *via* Equation 6. It must be noted that peaks for carbon and nitrogen are overlapping.<sup>254</sup> Equation 6 was designed considering that only TIPM (polymerized) and the metal compound are present in the final polymer. In addition, because of the carbon dioxide produced from the reaction shown in Scheme 11, the corresponding mass of CO<sub>2</sub> was subtracted. Those results are summarized in Table 20. Interestingly, the % w/w of "M" retained in the PUA network increased when TIMP/M molar ratio increased from 1/0.5 to 1/1.5, but it remained the same or even decreased at TIMP/M molar ratio 1/3. Therefore, there is no need to use such a big amount of metal compound for the preparation of **PUA-M** aerogels.

% M (theor.) =  $\frac{\text{mass of M}}{\text{mass of TIPM + mass of meal salt - mass of CO}_2} \times 100$  (6)


Figure 28. X-Ray mapping of PUA-M-4 aerogels prepared with TIPM/M molar ratio 1/0.5.



Figure 29. SEM images of PUA-M-4 aerogels prepared with TIPM/M molar ratio 1/1.5.



Figure 30. (a) SEM image, (b) X-Ray mapping and (c) EDS spectrum of PUA-Cr-4 aerogels prepared with TIPM/Cr molar ratio 1/1.5.



Figure 31. SEM image (left) and EDS spectrum (right) of PUA-Fe-4 aerogels prepared with TIPM/Fe molar ratio 1/1.5.



Figure 32. (a) SEM image, (b) X-Ray mapping and (c) EDS spectrum of PUA-Co-4 aerogels prepared with TIPM/Co molar ratio 1/1.5.



Figure 33. (a) SEM image, (b) X-Ray mapping and (c) EDS spectrum of PUA-Ni-4 aerogels prepared with TIPM/Ni molar ratio 1/1.5.

(a)	cps/eV (C)	Element	Weight %
····	20	С	77.85±8.90
A CARACTER NON	18-	N	10.37±2.07
	16-	0	5.83±1.08
17 117	14	Р	0.09±0.03
	12-	S	0.21±0.04
	10-	CI	3.46±0.14
(b)		Cu	2.18±0.10
	8	Total	100.00
State of the second second	6		
	4		
A CONTRACTOR	2 <u>Cu</u>		
BSE C N O P S C	0 P S 1 2 3 4	5 6 7 keV	Cu Cu 8 9 10

Figure 34. (a) SEM image, (b) X-Ray mapping and (c) EDS spectrum of PUA-Cu-4 aerogels prepared with TIPM/Cu molar ratio 1/1.5.

Table 20. Theoretical and experimental metal composition (% w/w) of selected PUA-M aerogels.

Sample	TIPM/M (mol/mol)	M theoretical content (% w/w)	M content from EDS <sup>a</sup> (% w/w)
PUA-Cr-4	1/0.5	6.0	1.3
PUA-Cr-4	1/1.5	11	5.1
PUA-Cr-4	1/3	14	0.8
PUA-Fe-4	1/0.5	7.3	2.9
PUA-Fe-4	1/1.5	22	1.6
PUA-Fe-4	1/3	21	1.7
PUA-Co-4	1/0.5	13	1.9
PUA-Co-4	1/1.5	13	2.5
PUA-Co-4	1/3	17	1.9
PUA-Ni-4	1/0.5	6.6	3.1
PUA-Ni-4	1/1.5	12	3.3
PUA-Ni-4	1/3	15	0.5
PUA-Cu-4	1/0.5	8.2	3.7
PUA-Cu-4	1/1.5	17	2.1
PUA-Cu-4	1/3	24	1.9
PUA-Cr-12	1/1.5	11	4.6
PUA-Fe-12	1/1.5	22	7.7
PUA-Co-12	1/0.5	7.0	0.8
PUA-Co-12	1/1.5	13	2.6
PUA-Ni-12	1/1.5	12	5.1
PUA-Cu-12	1/1.5	17	6.1

 $^{\rm a}$  For routine EDS analysis, the detection limits are about 0.1% w/w.  $^{\rm 255}$ 

The degree of molecular order within the solid framework was investigated by powder X-ray diffraction (PXRD). PXRD of **PUA-M** aerogels (Figure S67)

showed broad, but well-defined diffractions indicating the presence of nanocrystallinity.<sup>89</sup>

## 6.1.2 Fitting material properties of PUA aerogels

Design Expert 11 was used for the fitting of selected material properties of native PUA and **PUA-M** aerogels to empirical models defining the effect of the independent variables on those properties. The two independent variables were: the molar ratio TIPM/M (x<sub>1</sub>; 10, 2, 0.7, corresponding to molar ratios of 1/0.1, 1/0.5 and 1/1.5) and the concentration of the monomers (4 and 12 % w/w, x<sub>2</sub>). Molar ratio 1/3 was not used for the fitting, because that molar ratio was used only for the low monomer concentration. Figure 35 displays the fitting of bulk density of all **PUA-M** and **PUA-native** aerogels reported in this Chapter. 3D surfaces shown in Figure 35 were generated using the quadratic fitting model (Equation 7). In all cases, R<sup>2</sup> is higher than 0.91 indicating an excellent correlation. In addition, the fittings of BET surface area and log( $V_{Total}/V_{1.7-300nm}$ ) are provided in Appendix III (Figure S68 and Figure S69), all showing excellent correlations.





**PUA-Cr** 

 $z=0.1063x_1^2+-0.0411x_1x_2-0.0981x_1+0.1072x_2+0.4403$ R<sup>2</sup> = 0.96

# $z = A^{2} x_{1}^{2} + B^{2} x_{2}^{2} + AB x_{1} x_{2} + A x_{1} + B x_{2} + C$ (7)

114



 $R^2 = 0.99$ 



Figure 35. Fitting bulk density of native PUA and PUA-M aerogels to the two exploratory variables  $x_1$  (TIPM/M molar ratio, mol/mol) and  $x_2$  (monomer concentration, %w/w) according to Equation 7. Red and pink dots indicate points above and below, respectively, the predicted values.

### 6.1.3 Conclusions

Metal-doped PUA (PUA-M) aerogels were synthesized from the reaction of TIPM (aromatic triisocyanate) with water using metal salts as catalysts (i.e., CrCl<sub>3</sub>·6H<sub>2</sub>O, FeCl<sub>3</sub>·xH<sub>2</sub>O, CoCl<sub>2</sub>·6H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and CuCl<sub>2</sub>·2H<sub>2</sub>O). The reactions were carried out with different TIPM/M molar ratios, varying from catalytic to overstoichiometric, in order to test how much "M" could be retained in the polymer network. All **PUA-M** aerogels had low bulk densities, moderate to high porosity, high BET surface area as well as microporosity (6-15%). The most important finding of those studies is that "M" was homogeneously distributed in the polymer matrix, which means that those **PUA-M** aerogels are very promising precursors for metal-doped carbon aerogels. Also, the metal content of **PUA-M** aerogels increased when TIMP/M molar ratio increased from 1/0.5 to 1/1.5, but it remained the same or even decreased at TIMP/M molar ratio 1/3. Therefore, there is no need to use such a big amount of metal compound for the preparation of **PUA-M** aerogels.

# 6.2 Synthesis of PUA aerogels using tungsten and molybdenum compounds as catalysts

Various W- and Mo-based compounds were used also as catalysts for the synthesis of metal-doped PUA aerogels from the reaction of TIPM (Scheme 13) and water.

The choice of tungsten, especially, as basis for catalytic activity relies on its low cost, high affinity to O-donor ligands<sup>256</sup> and the catalytic versatility of W-compounds. Tungsten oxides (WO<sub>x</sub>) show catalytic activity towards a number of organic transformations, such as alcohol dehydration, alkane dehydrogenation, olefin oligomerization, etc.<sup>257</sup>

The synthetic procedure was described in Scheme 14. All W and Mo compounds used in this Chapter are shown in Table 21 together with their abbreviations.

Table 21. W and Mo compounds used as catalysts for the synthesis of PUA-W and PUA-Mo aerogels, respectively.

W cor	npound	Abbreviation
(i)	WO <sub>3</sub>	WO
(ii)	$H_2WO_4$ ( $WO_3 \cdot H_2O$ )	HW
(iii)	Peroxypolytungstic Acid Solution (WO <sub>3</sub> precursor solution)	PAS
(iv)	H <sub>3</sub> [P(W <sub>3</sub> O <sub>10</sub> ) <sub>4</sub> ]·xH <sub>2</sub> O (12WO <sub>3</sub> ·H <sub>3</sub> PO <sub>4</sub> ·xH <sub>2</sub> O)	PW
(v)	Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O	NaW
(vi)	(NH4)6W12O39'XH2O	NHW
(vii)	WCl <sub>6</sub>	WCI
(viii)	H2MoO4·xH2O	HMo
(ix)	Na <sub>2</sub> MoO <sub>4</sub> ·2H <sub>2</sub> O	NaMo

Formulations and gelation times are reported in Table 4 -

Table 11. All wet gels were aged for 24 h, were solvent-exchanged with acetone and dried with SCF CO<sub>2</sub>. The resulting aerogels are referred to as **PUA-W-X** and **PUA-Mo-X** aerogels, where X denotes the concentration of the monomers in the sol (% w/w). The polymerization reactions took place in EA, because TIPM is provided as a solution in EA and is also environmental friendly, and/or DMF/EA, which has been used also in the literature for the synthesis of PUA aerogels.<sup>89,244</sup> The concentration of the monomers (TIPM and water) varied from low (4% w/w) to very high (>40% w/w). The amount of water added in the reaction did not affect the morphology or the material properties of the resulting aerogels, but it affected the gelation times. In some cases, with addition of larger amounts of water caused a faster gelation. The amount of "M" retained in the polymer network. In all cases "M" was retained in the polymer matrix. Those aerogels are excellent candidates as precursors for metal-doped carbons.

Materials prepared in EA had completely different properties compared to materials prepared in DMF/EA. PUA-W and PUA-Mo aerogels from EA were light pink or purple, soft and spongy, and in several cases showed some elasticity, while those from DMF/EA were dark purple, stiff and rigid. Wet-gels were also different: EA-derived wet-gels looked were spongy, while DMF/EAderived wet-gels were gelly and dense. This difference in appearance feeds back to certain material properties, such as bulk density and BET surface area. EA-derived aerogels were very light, with very low bulk densities (even at monomer concentrations higher than 40% w/w), high porosities and BET surface areas close to zero. On the other hand, DMF/EA-derived aerogels had higher BET surface areas, but also higher bulk densities. The synthetic procedure is described in Section 4.8. The characterization of PUA-M-X and native PUA aerogels was carried out using ATR-FTIR and <sup>13</sup>C CPMAS NMR spectroscopy, thermogravimetric analysis (TGA),  $N_2$ -sorption porosimetry, He pycnometry, SEM, EDS spectroscopy, X-ray mapping, and PXRD. Selected material properties are summarized in Table 22.

# 6.2.1 PUA aerogels synthesized using W compounds as catalysts

The W compounds used for the synthesis of **PUA-W** aerogels and their abbreviations are shown in Table 21. Compounds (i)-(iv) are all WO<sub>3</sub>-based, and compounds (v)-(vii) are a tungstate salt, a polyoxometalate and tungsten(VI) chloride, respectively.

Tungsten(VI) oxide (tungsten trioxide, WO<sub>3</sub>) is slightly soluble in DMF and EA. The resulting aerogels are referred to as **PUA-WO** aerogels. Figure 36 shows **PUA-WO** aerogels prepared in EA and in DMF/EA. All experimental details are shown in Table 4. In EA, at low monomer concentrations (4% w/w) gelation did not occur with the stoichiometric TIPM/H<sub>2</sub>O molar ratio (1/3); with TIPM/H<sub>2</sub>O molar ratio equal to 1/6 gelation was slow and complete within 5h. In the case of higher monomer concentrations (8 to 45% w/w), gelation occurred at all TIPM/H<sub>2</sub>O molar ratios, although at different gelation times. In DMF/EA gelation was faster for all experiments than in EA.

ethyl acet	DMF	
1º	21	
	20	
15 16		Ų

Figure 36. Optical photographs of PUA-WO aerogels prepared in EA (left) and DMF/EA (right).

Tungstic acid, H<sub>2</sub>WO<sub>4</sub>, is slightly soluble in EA and in DMF. Experimental details for **PUA-HW** aerogels are summarized in Table 5. At low monomer concentration (4% w/w) and any TIPM/HW molar ratio, all sols gelled, although with different gelation rates, which ranged from 10 min to 18 h. Gelation in DMF/EA was always faster compared to gelation in EA.

Peroxypolytungstic acid solution (PAS) is a WO<sub>3</sub>-precursor solution and was used because WO<sub>3</sub> and H<sub>2</sub>WO<sub>4</sub> were insoluble or slightly soluble in the solvents used for the polymerization of TIPM. PAS was prepared according to a literature method,<sup>204</sup> which is briefly described in Section 4.8.1. The solution is stable for

about one week after its preparation; afterwards, WO<sub>3</sub> precipitates. The W content in PAS solution is 5.5% w/w. Polymerization reactions were carried out only in EA. The monomer concentration varied from 20 to 46% w/w and the W concentration varied from 0.1 to 2.2% w/w. TIPM/PAS increased simultaneously with the concentration of monomers in the gelation sol, because PAS is an aqueous solution and water is one of two reaction monomers. Gelation times depended on the monomers concentration (Table 6); gelation was faster with increasing monomer concentration.

Phosphotungstic acid hydrate (12WO<sub>3</sub>·H<sub>3</sub>PO<sub>4</sub>·H<sub>2</sub>O or H<sub>3</sub>[P(W<sub>3</sub>O<sub>10</sub>)<sub>4</sub>]·H<sub>2</sub>O; Scheme 20) has been used in the literature as a homogeneous or heterogeneous catalyst due to its high acidity and thermal stability.<sup>258</sup> Herein, it was tested as a W-based catalyst together with cetyltrimethylammonium bromide (CTAB; Scheme 20) as a linker<sup>259</sup> to deposit PW onto the polymer structure probably by electrostatic interactions. First, PW was dissolved in water and then it was added to a solution of TIPM and CTAB in EA. PW was also tested without CTAB. Gelation occurred only in the presence of CTAB, and at low monomer concentration (10 % w/w) and low TIPM/PW molar ratio (1/0.01 mol/mol). All experimental details are summarized in Table 9.



Scheme 20. Structures of PW (top) and CTAB (bottom).

Sodium tungstate dihydrate (Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O) is slightly soluble in EA or DMF, but it is highly soluble in water. For that reason, two synthetic protocols were followed: (a) addition of Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O in the solution of TIPM and water in EA or DMF/EA, and (b) dissolution of Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O in water and addition of the aqueous solution into the solution of TIPM in EA or DMF/EA. All experimental details are described in Table 7 for experiments in EA and Table 8 for experiments in DMF. Experiments in EA under protocol (a) gave soft and very light-weight **PUA-NaW** aerogels, while under protocol (b) materials were also soft and showed some elasticity. At low monomer concentration (3% w/w) and TIPM/NaW molar ratio 1/0.5 no gelation occurred. At higher monomer concentrations all wet-gels were gelly and flexible. For higher molar ratios of TIPM/NaW (>1/3), the molds containing the reaction mixture were deposited in a sonicator for approximately 30 min to facilitate homogenization. Wet-gels prepared in DMF/EA were more rigid compared to wet-gels prepared in EA. Gelation was faster in DMF/EA than in EA; no gelation occurred for the 4% w/w monomer concentration. In DMF/EA under protocol (b) gelation occurred within seconds but wet-gels derived from low monomer concentrations were too difficult to handle, ending up like powders; at monomer concentrations higher than 30% w/w, the corresponding aerogels were spongy.

Ammonium metatungstate hydrate ((NH<sub>4</sub>)<sub>6</sub>W<sub>12</sub>O<sub>39</sub>·H<sub>2</sub>O) is also soluble in DMF at 50 °C. The resulting wet gels were transparent, but after SCF drying they became opaque (Figure 37). All experimental details are summarized in Table 9. In all cases gelation was fast and complete within minutes. A TIPM/NHW molar ratio of 1/0.25 gave steady and easy to handle wet-gels, while a TIPM/NHW molar ratio of 1/0.6 gave wet-gels that were too brittle. In an attempt to avoid extreme shrinkage and cracking during solvent exchange with acetone, the solvent exchange was carried out gradually, with acetone/DMF mixtures 30/70, 60/40 and 90/10 v/v, and then with pure acetone, but wet-gels behaved the same as when they were solvent-exchanged directly with acetone. Therefore, the gradual solvent exchange was not pursued further.



Figure 37. Optical photo of a PUA-NHW wet-gel (transparent, left) and aerogel (opaque, right).

Tungsten hexachloride (WCl<sub>6</sub>) is the last W-based compound used for the synthesis of **PUA-W** aerogels. WCl<sub>6</sub> is slightly soluble in DMF and EA. All experimental details are summarized in Table 11. The polymerization reaction with WCl<sub>6</sub> was very violent for all TIPM/WCl<sub>6</sub> molar ratios, even at low monomer concentrations. For that reason, the sol was kept in an ice bath until it was poured into the molds. In some cases, the sol seemed to gel but only powders could be isolated (e.g., monomer concentration: 4% w/w; TIPM/WCl molar ratio equal to 1/0.1). In DMF/EA the concentration of the monomers was high (22% w/w), and no gelation occurred, while in EA the reaction was vigorous and some of the wet-gels popped out of their molds.

Moving forward to the characterization of **PUA-W** aerogels, ATR-FTIR spectra (Figure 38) of all **PUA-W** materials is in agreement with the expected chemical structure of TIPM-derived PUA and with similar materials from the literature.<sup>89</sup> The characteristic urea C=O stretch appeared at 1670 cm<sup>-1</sup>, while aromatic C=C stretches appeared at 1500 and 1402 cm<sup>-1</sup>. The N–H scissoring vibration appeared at 1595 cm<sup>-1</sup>. Finally, The C–H bending on the phenyl rings of TIPM was observed at 822 cm<sup>-1</sup>. No unreacted TIPM has been detected in the spectra. The unreacted –NCO would appear at 2264 cm<sup>-1</sup>. ATR-FTIR spectroscopy also proved that materials obtained in DFM/EA or in EA had the same chemical composition. For example, Figure 39 shows the ATR-FTIR spectra of **PUA-NaW** aerogels prepared in DMF/EA and EA, which are identical.



Figure 38. ATR-FTIR spectra of PUA-W aerogels.



Figure 39. ATR-FTIR spectra of PUA-NaW aerogels prepared in DMF/EA or in EA, as indicated.

<sup>13</sup>C CPMAS NMR spectra (Figure 40) of all **PUA-W** aerogels showed all characteristic peaks of TIPM-derived PUA.<sup>89,245</sup> Specifically, the urea carbonyl peak appeared at 154 ppm, the aromatic carbons appeared in the area 115-

145 ppm and the central (aliphatic) carbon of TIPM (Scheme 13) appeared at 55 ppm. The peak at 30 ppm (**PUA-PW** and **PUA-NaW** spectra) was assigned to acetone and confirmed the tendency of PUA aerogels to retain small amounts of solvents.<sup>89</sup> No spectrum could be recorded for **PUA-NHW** aerogels, because the material was extremely hard and could not be pulverized. Materials prepared in DMF/EA and in EA were chemically identical, as shown, for example, in Figure 41 for **PUA-HW** aerogels.



Figure 40. <sup>13</sup>C CPMAS NMR spectra of all PUA-W and native PUA aerogels prepared in EA.



Figure 41. <sup>13</sup>C CPMAS NMR spectra of all PUA-HW aerogels prepared in EA (top) and DMF/EA (bottom).

TGA (Figure 42, left) showed that **PUA-W** aerogels followed similar, but not the same decomposition pattern compared to native PUA aerogels. Those materials were thermally stable up to ~370 °C and the residue at 800 °C ranged from 34% (for **PUA-WO** aerogels) to 60% w/w (for **PUA-PAS** aerogels). Two significant weight loss events were observed in the derivative weight change/temperature plot (Figure 42, right) in addition to the small weight loss incurred due to loss of moisture and remaining solvents (~3-9% weight loss up to 150 °C). The first significant weight loss occurred at around 357-377 °C, along with a small shoulder at ~430 °C in most cases, followed by a smaller peak at ~550-560 °C.



Figure 42. Weight loss with temperature (left) and derivative weight loss with temperature (right) for PUA-W aerogels prepared in EA.

Selected material properties for PUA-W aerogels are given in Table 22. In general, most **PUA-W** aerogels prepared in EA had very low bulk densities, lower shrinkage and higher porosities even at high monomer concentrations, compared to **PUA-W** aerogels prepared in DMF/EA and to native PUA aerogels prepared by us (Table 18) or from the literature.<sup>89</sup> Skeletal densities of **PUA-W** aerogels were, in most cases, higher compared to native PUA aerogels, consistent with the presence of W-compounds in the polymer network. BET surface areas of **PUA-W** aerogels prepared in EA were zero or close to zero, while BET surface areas of PUA-W aerogels prepared in DMF/EA were comparable to those of native PUA aerogels. This property, consistent with all W-based compounds studied, could be explained by the different solubility of the growing polymer in the two different solvents. Higher solubility of the polymer in EA led to the formation of big particles and therefore to very low BET surface area; lower solubility of the polymer in DMF/EA lead to faster precipitation, formation of small particles and therefore higher BET surface areas.

**PUA-WO** aerogels prepared in EA were highly porous, with the porosity being as high as 93% v/v. Bulk densities were very low, especially for low monomer concentrations; for monomer concentrations up to 16% w/w, bulk densities were lower than 0.2 g cm<sup>-3</sup>. **PUA-WO** aerogels prepared in DMF/EA were inhomogeneous and were not pursued further.

**PUA-4-HW** aerogels were prepared in EA or DMF/EA and with two different TIPM/H<sub>2</sub>WO<sub>4</sub> molar ratios: 1/0.1 and 1/3. In DMF/EA BET surface areas were high (272 and 185 m<sup>2</sup> g<sup>-1</sup>) and comparable to that of native PUA aerogels of the same concentration (Table 18). Higher surface areas and lower bulk densities were obtained with the TIPM/H<sub>2</sub>WO<sub>4</sub> molar ratio 1/0.1.

**PUA-PAS** aerogels had similar properties regardless of the monomer concentration or the TIPM/PAS molar ratio. Porosities were high, in the range of 79 to 85% v/v, and bulk densities ranged from 0.18 to 0.27 g cm<sup>-3</sup>. **PUA-PW** aerogels (also prepared in EA only) were highly porous (porosity 88% v/v) and very lightweight, with a bulk density of 0.149 g·cm<sup>-3</sup>.

**PUA-NaW** aerogels were prepared according to two different synthetic protocols: (a) addition of Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O in the solution of TIPM and water in EA or DMF/EA, and (b) dissolution of Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O in water and addition of the aqueous solution into the solution of TIPM in EA or DMF/EA. Protocol (b) in EA provided aerogels with very low bulk densities (0.09-0.24 g·cm<sup>-3</sup>), moderate BET surface areas (112-160 m<sup>2</sup> g<sup>-1</sup>) and porosities as high as 96% v/v (Table 22). This is the only case that non-zero BET surface areas appear for PUA-W aerogels prepared in EA. This behavior could be explained by the reduced solubility of the growing polymer in EA/H<sub>2</sub>O compared to EA. Protocol (a) in DMF/EA gave materials with higher BET surface areas, but also higher bulk density and lower porosity.

**PUA-4-NHW** aerogels underwent severe cracking during solvent-exchange with acetone. For that reason, wet-gels were solvent-exchanged with mixtures of acetone/DMF 10/90, 30/70, 50/50, 90/10 v/v and then with acetone. The resulting aerogels were also cracked, and they did not have any improved properties compared to aerogels resulting from wet-gels that were solvent-exchanged the normal way. Specifically, they showed higher linear shrinkage (52 vs 40%), lower BET surface area (117 vs 241 m<sup>2</sup>/g), higher bulk density (0.495 vs 0.333 g cm<sup>-3</sup>) and lower porosity (69 vs 77% v/v).

**PUA-WCI** aerogels were prepared in EA with monomer concentrations of 20 and 30% w/w. **PUA-WCI-30** showed low BET surface area ( $27 \text{ m}^2 \text{ g}^{-1}$ ). Skeletal

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density and porosity were almost the same for both 20 and 30% w/w monomer concentrations.

Sample	TIPM/W (mol/mol)	Linear shrinkageª (%)	Bulk density ρ <sub>b</sub> (g cm <sup>-3</sup> )	Skeletal density ρ <sub>s</sub> (g cm <sup>-3</sup> )	Porosity <sup>b</sup> Π (% v/v)	BET surf. area σ (m <sup>2</sup> g <sup>-1</sup> ) [micropore surf. area] <sup>c</sup>	V <sub>Total</sub> d ( V₁.ァ-₃₀₀nm) <sup>e</sup> (cm³ g⁻¹)	Av. pore diameter <sup>f</sup> (4 V <sub>Total</sub> /σ) (nm)	Particle radius <sup>9</sup> r (nm)
				WO3 / E	A				
PUA-4-WO	1/0.1	6.6±3.1	0.110±0.008	1.31±0.01	92	6 [9]	9.0 (0.7)	4.0 (-)	-
PUA-8-WO	1/0.1	7.2±1.8	0.108±0.004	1.500±0.007	93	<5	8.2 (0.2)	15 (-)	-
PUA-12-WO	1/0.1	12.4±4.7	0.18±0.03	1.345±0.006	89	<1	6.0 (-)	-	-
PUA-16-WO	1/0.1	6.4±2.1	0.18±0.01	1.262±0.003	84	<5	4.3 (0.2)	9.0 (-)	-
PUA-30-WO	1/0.2	8.6±2.4	0.45±0.06	1.624±0.004	68	8 [2]	1.3 (0.01)	1.0 (-)	-
PUA-45-WO	1/0.15	7.5±1.5	0.39±0.04	1.429±0.002	73	12 [5]	1.9 (0.01)	1.0 (-)	175
			•	H <sub>2</sub> WO <sub>4</sub> /	EA				•
PUA-4-HW	1/0.1	8.6±2.1	0.052±0.002	1.35±0.02	96	<5	15 (-)	2.0 (-)	-
			•	H <sub>2</sub> WO <sub>4</sub> / DI	MF/EA		•		
PUA-4-HW	1/0.1	53±4.5	0.37±0.04	1.374±0.008	73	272 [35]	2.0 (0.6)	8.2 (29)	8.0
PUA-4-HW	1/3	52±5.5	0.76±0.05	1.974±0.006	63	185 [20]	0.9 (0.4)	10 (19)	8.2
			Peroxy	/polytungstic A	cid Solutior	n / EA	•		
PUA-16-PAS	1/0.02	15±2.3	0.185±0.002	1.29±0.01	86	<2	4.6 (-)	-	-
PUA-20-PAS	1/0.06	16±2.1	0.27±0.05	1.273±0.004	79	<2	2.9 (-)	-	-
PUA-24-PAS	1/0.04	10±0.9	0.255±0.004	1.259±0.002	80	<2	3.1 (-)	-	-
PUA-28-PAS	1/0.1	13±1.1	0.25±0.03	1.643±0.008	85	<2	3.4 (-)	-	-
PUA-46-PAS	1/0.3	4.5±0.9	0.219±0.005	N/A	-	<2	-	-	-
				H3[P(W3O10)4]·	xH₂O / EA				
PUA-10-PW	1/0.01	11±1.2	0.149±0.007	1.291±0.005	88	<1	5.9 (-)	-	-
				Na <sub>2</sub> WO <sub>4</sub> ·2H	2 <b>0 / EA</b>				
PUA-14-NaWa	1/0.1	11±2.3	0.34±0.05	1.261±0.003	73	18 [0]	2.9 (0.04)	7.8 (644)	183
PUA-20-NaWa	1/0.2	12±2.3	0.24±0.03	N/A	-	<2	- (0.002)	2.0 (-)	-
PUA-25-NaWa	1/0.1	18±1.4	0.171±0.002	1.499±0.008	89	5 [4]	5.2 (0.01)	9.0 (-)	-
PUA-10-NaWb	1/1	19±0.8	0.134±0.005	1.434±0.007	91	140 [21]	6.7 (0.2)	6.4 (191)	15
PUA-10-NaWb	1/2	11±2.4	0.087±0.002	2.11±0.01	96	116 [16]	11 (0.2)	7.7 (379)	12
PUA-12-NaWb	1/3	9.5±1.7	0.12±0.06	1.774±0.008	93	112 [13]	7.7 (0.2)	6.9 (275)	15
PUA-16-NaWb	1/0.6	NA	0.19±0.08	3.53±0.06	94	51 [16]	- (0.1)	8.4 (-)	17
PUA-16-NaWb	1/3	19±2.2	0.27±0.03	1.41±0.01	83	160 [26]	3.4 (0.2)	6.4 (85)	13
PUA-16-NaWb	1/5	14±1.5	0.221	2.366±0.009	91	44 [5]	4.1 (0.08)	8.5 (373)	29
PUA-25-NaWb	1/0.7	12±3.0	0.186	3.04±0.03	94	22 [4]	5.0 (0.04)	8.4 (-)	45
PUA-30-NaWb	1/3	15±1.6	0.385	1.262±0.005	69	113 [14]	1.8 (0.2)	7.3 (64)	21
				Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O	/ DMF/EA				-
PUA-12-NaWa	1/1.5	39±3	1.01±0.05	1.292±0.002	25	195 [21]	0.3 (0.3)	6.8 (6.2)	12
PUA-12-NaWa	1/1	48±2	0.86±0.08	1.381±0.004	38	231 [15]	0.4 (0.4)	6.7 (6.9)	9.4
PUA-14-NaWa	1/0.3	48±2	0.8±0.1	1.373±0.002	42	258 [18]	0.5 (0.5)	7.4 (7.8)	8.5
PUA-30-NaWa	1/3	12±1	0.42±0.03	1.49±0.01	72	179 [27]	1.7 (0.4)	10 (38)	11
PUA-35-NaWa	1/0.8	15±2	0.35±0.05	1.511±0.003	77	260 [30]	2.2 (0.9)	15 (34)	7.6
PUA-25-NaWb	1/0.3	17±3	0.21±0.04	2.76±0.02	92	10 [5]	4.4 (0.04)	15 (-)	-
PUA-25-NaWb	1/2	18±4	0.20±0.06	1.72±0.01	88	171 [14]	4.4 (0.4)	10 (103)	10
			()	NH4)6W12O39·XH2	O / DMF/EA	<u> </u>			
PUA-4-NHW	1/0.25	40±1	0.333±0.006	1.483±0.007	77	241 [26]	2.3 (0.6)	10 (38)	8.4
				WCI <sub>6</sub> / I	EA				
PUA-20-WCI	1/0.05	1.1±0.7	0.25±0.01	1.300±0.004	82	<2	3.5 (0.001)	1.0 (-)	-
PUA-30-WCI	1/0.05	6.2±1.2	0.37±0.04	1.285±0.003	71	27 [7]	1.9 (0.04)	7.9 (284)	86.5

Fable 22. Selected materia	properties o	of PUA-W	aerogels.
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<sup>a</sup> Calculated according to formula:  $(y_1+y_2)/2$ , where  $y_1 = 100-[(h_{fin}/h_{st})\times 100]$  and  $y_2 = 100-[(d_{fin}/d_{st})\times 100]$ . <sup>b</sup> Calculated according to formula:  $(\rho_s-\rho_b)/\rho_s$ , where  $\rho_s$ : skeletal density and  $\rho_b$ : bulk density. <sup>c</sup> Micropore surface area *via t*-plot analysis, according to the Harkins

and Jura model. <sup>d</sup> Total pore volume calculated according to formula:  $1/\rho_b-1/\rho_s$ . <sup>e</sup> Cumulative volume of pores between 1.7 and 300 nm from N<sub>2</sub>-sorption data and the BJH desorption method. <sup>f</sup> Calculated by the  $4V/\sigma$  method; *V* was set equal to the maximum volume of N<sub>2</sub> adsorbed along the isotherm as  $P/P_o \rightarrow 1.0$ . For the number in parentheses *V* was set equal to  $V_{Total}$  from the previous column. <sup>g</sup> Calculated according to formula:  $3/(\rho_s \times \sigma)$ .

N<sub>2</sub>-sorption isotherms for all materials are shown in Appendix III, in Figure S70-Figure S77 together with pore size distributions. The N<sub>2</sub>-sorption isotherms of **PUA-W** aerogels showed hysteresis loops, indicating that the materials are mesoporous/macroporous. In EA the loop is narrower than in DMF. Microporosity of all **PUA-W** aerogels was evaluated with CO<sub>2</sub> adsorption to 1 bar at 273 K. Pore size distributions for pores smaller than 1 nm were calculated using the DFT model. The results proved that all PUA-W materials adsorbed CO<sub>2</sub>. Most of the micropores of all **PUA-W** materials were distributed in the range of 0.47-0.87 nm. CO<sub>2</sub> adsorption isotherms are shown in Figure S78-Figure S82 (Appendix Section III). All CO<sub>2</sub> sorption data are provided in Table 23. Highest uptakes were observed for **PUA-PAS** (1.12 mmol g<sup>-1</sup>; Figure 43 left) and **PUA-WO** (1.11 mmol g<sup>-1</sup>; Figure 43 right) aerogels, which were also higher from the reported values in the literature for native PUA aerogels with similar monomer concentrations (0.85 and 0.60 mmol g<sup>-1</sup>, respectively).<sup>89</sup> All other **PUA-W** aerogels adsorbed 0.8-0.9 mmol g<sup>-1</sup> of CO<sub>2</sub>, except for **PUA-PW** materials which showed the lowest adsorption (0.47 mmol  $g^{-1}$ ).

Sample	TIPM/W catalyst	Quantity of CO	D₂ adsorbed, P	V <sub>&lt;7.97Å</sub> <sup>a</sup> (cm³ g⁻¹)	Micropores range <sup>b</sup>	
	(mol/mol)	mmol g <sup>-1</sup>	cm³ g⁻¹		nm	
PUA-12-WO	1/0.1	1.11	24.9	0.05	0.47-0.87	
PUA-4-HW	1/0.1	0.78	17.4	0.03	0.58-0.87	
PUA-24-PAS	1/0.04	1.12	25.1	0.05	0.49-0.86	
PUA-10-PW	1/0.01	0.47	10.6	0.02	0.54-0.82	
PUA-35-NaWa	1/0.8	0.83	18.7	0.03	0.56-0.86	
PUA-4-NHW	1/0.25	0.86	19.3	0.04	0.56-0.84	
PUA-20-WCI	1/0.05	0.79	17.8	0.03	0.56-0.84	

Fable 23. Selected results from	CO <sub>2</sub> porosimetr	y of PUA-W	aerogels.
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<sup>a</sup> Total pore volume of pores less than 7.97 Å from CO<sub>2</sub> sorption data at 273 K using the single-point absorption method at *P*/*Po* = 0.03. <sup>b</sup> Calculated using the DFT method.



Figure 43. CO<sub>2</sub>-sorption isotherm of PUA-24-PAS (left) an PUA-12-WO (right) aerogel prepared in EA.

The structural morphology of **PUA-W** aerogels was investigated with SEM (Figure 44-Figure 55). SEM revealed that the morphology of **PUA-W** aerogels prepared in EA is different compared to those prepared in DMF/EA. **PUA-W** aerogels prepared in EA consisted of big particles, in the order of  $\mu$ m, while **PUA-W** aerogels prepared in DMF/EA showed a uniform, dense morphology. That difference in morphology is consistent with the different BET surface areas of those materials and with the different solubility of the growing polymer in the different solvents. EDS and X-Ray mapping (Figure 45-Figure 47 and Figure 50,Figure 52,Figure 53 and Figure 55) proved the presence of W in the polymer network. In most cases, the distribution of W was homogeneous. The experimental W content (% w/w), derived from EDS data is shown in Table 24, together with the theoretical values calculated according to Equation 6.

Representative SEM images and optical photos of **PUA-WO** materials are shown in Figure 44. SEM showed that **PUA-WO** aggregates were arranged in big particles with spherical shape. The concentration of the monomers did not seem to affect the morphology of the aerogels. Figure 45 shows SEM images of **PUA-WO** aerogels prepared in DMF/EA. The morphology of the polymers is completely different; it is uniform, dense and more compact compared to **PUA-WO WO** aerogels prepared in EA. EDS spectroscopy (Figure 45, bottom) confirmed the existence of W in the polymer network and its homogeneous distribution. Similarly, **PUA-HW** aerogels prepared in EA and in DMF/EA showed different morphologies (Figure 46): in EA big particles were formed, while in DMF/EA the morphology was uniform. X-Ray mapping (Figure 47 and Figure 48) of **PUA-HW** aerogels prepared in DMF/EA showed the presence of W in the polymer network and its homogeneous distribution.

Figure 49 (top) shows SEM images of **PUA-PAS** aerogels. Particles were about 2  $\mu$ m in diameter. The EDS spectrum (Figure 49, bottom) confirmed the presence of W in the polymer network. **PUA-PW** aerogels had a similar morphology (Figure 50) with slightly larger particles. Figure 53 reveals the morphology of the **PUA-NHW** aerogels, which can be characterized as dense.

SEM images of **PUA-NaW** aerogels (Figure 51) showed that preparation in EA using the two different synthetic protocols (a) and (b) provided aerogels with different morphologies, in agreement with the different BET surface areas and the different solubility of the developing polymer in EA and EA/H<sub>2</sub>O.

Figure 54 shows SEM images of **PUA-WCI** aerogels, which consist of spherical particles. **PUA-20-WCI** aerogels consist of micron-size particles, while **PUA-30-WCI** aerogels consist of sub-micron-size particles. The EDS spectrum (Figure 55) confirmed the presence of W in the polymer, but it was mostly located on the surface of the polymer.



Figure 44. Optical photographs and SEM images of PUA-WO aerogels prepared in EA.





Figure 45. SEM images (top) and EDS spectrum (bottom) of PUA-WO aerogels prepared in DMF/EA. Values shown in the table are average values from at least 5 measurements.



Figure 46. SEM images of PUA-4-HW aerogels prepared with TIPM/HW molar ratio 1/0.1 in EA (top) and DMF/EA (bottom).



Figure 47. X-ray mapping (left) and EDS spectrum (right) of PUA-4-HW aerogels prepared with TIPM/HW molar ratio 1/0.01 in DMF/EA.



Figure 48. Optical and SEM images (top) and EDS spectrum (bottom) of PUA-4-HW aerogels prepared with TIPM/HW molar ratio 1/3 in DMF/EA. Values shown in the table are average values from at least 5 measurements.



Figure 49. SEM images (top) and EDS spectrum (bottom) of PUA-46-PAS aerogels prepared with TIPM/PAS molar ratio 1/0.3 in EA.



Figure 50. SEM images (top) and EDS spectrum (bottom) of PUA-10-PW aerogels prepared with TIPM/PW molar ratio 1/0.01 in EA.



Figure 51. SEM images of PUA-NaW aerogels, synthesized under two different synthetic protocols in EA and in DMF/EA. Corresponding EDS spectra with element contents for (b), (c) and (d) are shown in Figure S83.



Figure 52. X-Ray mapping (left) and corresponding EDS spectrum (right) of PUA-12-NaW aerogel prepared with TIPM/NaW molar ratio 1/1.5 in DMF/EA.



Figure 53. (a) optical and SEM images, (b) X-ray mapping and (c) EDS spectrum of PUA-4-NHW aerogel.



Figure 54. SEM images of PUA-WCI aerogels prepared in EA.

cps/eV 20 - C		element	Weight %
18		С	73.91±8.45
16-		N	12.06±2.26
14-		0	8.81±1.46
12		Р	0.34±0.04
10		S	0.43±0.04
8		CI	2.93±0.13
6-		W	1.52±0.09
4-	Pd		
	Pd Pd Pd		ww
1 2	3 4 5 6 keV	7 8	9 10

Figure 55. EDS spectrum of PUA-20-WCI aerogel prepared with TIPM/WCI molar ratio 1/0.05 in EA.

Sample	TIPM/W (mol/mol)	W theoretical content (% w/w)	W content from EDS (% w/w)ª
PUA-4-HW	1/0.1	5.6	0.4
PUA-46-PAS	1/0.3	18	7.5
PUA-10-PW	1/0.01	19	4.7
PUA-12-NaW	1/1.5	35	0.6
PUA-16-NaWb	1/3	3.5	0.05 <sup>b</sup>
PUA-25-NaWb	1/0.3	8.0	1.7 <sup>b</sup>
PUA-35-NaWa	1/0.8	5.0	0.7 <sup>b</sup>
PUA-4-NHW	1/0.25	53	8.0
PUA-WCI	1/0.05	3.1	1.5

Table 24. Theoretical and experimental metal content (% w/w) of PUA-W aerogels.

<sup>a</sup> For routine EDS analysis, the detection limits are about 1% w/w.<sup>255</sup>. <sup>b</sup> Mean values of at least five measurements.

PXRD of **PUA-W** aerogels show broad, but well-defined diffractions in the range of  $\theta$  = 15-20°, indicating the presence of nanocrystallinity (Figure 56).<sup>249</sup>



Figure 56. PXRD patterns of PUA10-PW, PUA-14-NaW and PUA-20-WCI aerogels.

#### 6.2.2 PUA aerogels synthesized using Mo compounds as catalysts

H<sub>2</sub>MoO<sub>4</sub>·H<sub>2</sub>O (HMo) and Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O (NaMo) compounds were studied as catalysts for the polymerization of TIPM. Both those Mo compounds were slightly soluble in EA and in DMF/EA. All formulations along with gelation times for the synthesis of **PUA-HMo** and **PUA-NaMo** aerogels in EA and in DMF/EA are shown in Table 12. As observed for **PUA-W** aerogels, in DMF/EA gelation was faster at all monomer concentrations and molar ratios of TIPM/Mo. All **PUA-Mo** experiments were carried out at overstoichiometric ratios of TIPM/H<sub>2</sub>O (1/60 mmol/mmol), because at lower molar ratios (1/3, 1/6 mol/mol) no gelation was observed. In EA, **PUA-4-HMo** sols gelled faster when higher TIPM/HMo molar ratio was used (1/1, instead of 1/0.6 mol/mol). In DMF/EA **PUA-12-HMo** sols gelled within 3 min regardless of the TIPM/HMo molar ratios. **PUA-NaMo** aerogels were synthesized with TIPM/NaMo 1/1.5 mol/mol and the gelation was faster for the higher monomer concentration (12% instead of 4% w/w).

ATR-FTIR spectra (Figure 57) of **PUA-Mo** aerogels were in agreement with the expected chemical structure of TIPM-derived PUA and with similar materials from the literature.<sup>89</sup> All spectra showed the characteristic C=O stretch of urea

at 1668 cm<sup>-1</sup>, while at 1500 and 1402 cm<sup>-1</sup> bands were assigned to aromatic C=C stretches. The N–H scissoring vibration appeared at 1595 cm<sup>-1</sup> and the C–H bending on the phenyl rings of TIPM was observed at 818 cm<sup>-1</sup>. No unreacted TIPM has been detected in the spectra. The unreacted –NCO would appear at 2264 cm<sup>-1</sup>.



Figure 57. ATR-FTIR spectrum of PUA-HMo (left) and PUA-NaMo (right) aerogels.

<sup>13</sup>C CPMAS NMR spectra (Figure 58) of **PUA-Mo** aerogels showed all characteristic peaks of TIPM-derived PUA.<sup>89,245</sup> Specifically, the urea carbonyl peak appeared at 154 ppm, the aromatic carbons appeared in the area 115-145 ppm and the central (aliphatic) carbon of TIPM (Scheme 13) appeared at 55 ppm.



Figure 58. <sup>13</sup>C CPMAS NMR spectra of PUA-Mo and native PUA aerogels.

TGA curves (Figure 59) showed that **PUA-HMo** and **PUA-NaMo** aerogels followed similar decomposition patterns. In addition to the small weight loss up to 150 °C (~5% w/w), two main weight loss events were observed in the derivative weight loss/temperature graph (Figure 59, right). The first loss occurred at ~366 °C, together with a smaller shoulder at ~430 °C, as was also observed for **PUA-W** aerogels (Figure 42). The second smaller decomposition peak for **PUA-HMo** and **PUA-NaMo** aerogels was observed at 537 and 546 °C respectively.



Figure 59. Weight loss with temperature (left) and derivative weight loss with temperature (right) for PUA-HMo and NaMo aerogels.

Selected material properties for **PUA-Mo** aerogels are given in Table 25. In general, as in the case of **PUA-W** aerogels, aerogels prepared in EA had lower bulk densities and linear shrinkage, and higher porosities than aerogels prepared in DMF/EA and native PUA aerogels prepared by us (Table 18) or from the literature.<sup>89</sup> Moreover, **PUA-12-HMo** aerogels synthesized with TIPM/HMo molar ratio 1/3 had high values of bulk density (1.378 g cm<sup>-3</sup>) probably due to the heterogeneous distribution of the metal in the polymer matrix. Skeletal densities of **PUA-Mo** aerogels prepared in EA had also higher values than native PUA aerogels (Table 18), because of the presence of Mo in the structure of the final polymer. Moreover, experiments in EA gave aerogels with large particle sizes and consequently decreased surface areas. All **PUA-Mo** aerogels showed microporosity.

Comparing aerogels prepared in two different solvents, again in DMF/EA **PUA-HMo** and **PUA-NaMo** materials have better material properties, considering the BET surface area values and the smaller particle radii. The most important drawback of **PUA-Mo** aerogels prepared in DMF/EA is that they have high bulk density because of extensive linear shrinkage.

For the fraction of pores in the 1.7-300 nm range, average pore diameters (by the BJH desorption method; Figure S84, left) of **PUA-HMo** aerogels prepared in EA had higher values (42 nm for aerogels synthesized with TIPM/HMo molar ratio 1/0.6). For **PUA-HMo** aerogels prepared in DMF/EA, average pore diameters by the BJH method were much smaller, in the range of 12-14 nm

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(Figure S84, right). Average pore diameters were also calculated using the  $4 V/\sigma$  method, whereas *V* was either the maximum volume of N<sub>2</sub> adsorbed along the isotherm, or the volume (*V*<sub>Total</sub>) calculated from the bulk and the skeletal density of the materials (Table 25). For **PUA-12-HMo** aerogels from DMF/EA average pore sizes obtained using *V*<sub>Total</sub> were similar, for both TIPM/HMo molar ratios.

For **PUA-4-NaMo** aerogels prepared in DMF/EA average pore diameters (by the BJH desorption method; Figure S85) were 33 nm (for the fraction of pores in the 1.7-300 nm range), equal to average pore diameters calculated from  $V_{\text{Total}}$ . **PUA-12-NaMo** aerogels had average pore diameters from BJH desorption method equal to 13 nm, while from  $V_{\text{Total}}$ , those diameters were higher and equal to 64 nm.

Sample	TIPM/Mo (mol/mol)	Linear shrinkageª (%)	Bulk density ০♭ (g cm <sup>-3</sup> )	Skeletal density ρ <sub>s</sub> (g cm <sup>-3</sup> )	Porosity <sup>ь</sup> Π (% v/v)	BET surf. area $\sigma$ (m <sup>2</sup> g <sup>-1</sup> ) [micropore surf. area] <sup>c</sup>	V <sub>Total</sub> d ( <i>V</i> <sub>1.7-300nm</sub> ) <sup>e</sup> (cm³ g <sup>−1</sup> )	Av. pore diameter <sup>f</sup> (4 V <sub>Total</sub> /σ) (nm)	Particle radius <sup>g</sup> r (nm)
H2MoO4·H2O / EA									
PUA-4-HMo	1/0.6	3.8±1.1	0.238±0.004	1.64±0.01	80	8 [8]	- (0.01)	6.5 (-)	-
PUA-4-HMo	1/1	5.6±0.8	0.26±0.05	1.323±0.008	85	<1	-	-	-
PUA-12-HMo	1/3	4.5±2.2	0.275±0.003	2.341±0.0006	88	<1	3.2 (-)	- (-)	-
				H <sub>2</sub> MoO <sub>4</sub> ·H <sub>2</sub>	) / DMF/EA				
PUA-12-HMo	1/0.6	39±4.5	0.60±0.09	1.401±0.001	57	269 [28]	1.0 (0.7)	11 (15)	8.0
PUA-12-HMo	1/3	41±3.9	1.378±0.008	1.744±0.001	21	223 [25]	0.2 (0.5)	8.9 (3.6)	7.7
				Na <sub>2</sub> MoO <sub>4</sub> ·2	2H₂O / EA				
PUA-20-NaMo	1/0.1	10±2.8	0.17±0.05	1.251±0.003	86	<1	5.1 (-)	- (-)	-
				Na <sub>2</sub> MoO <sub>4</sub> ·2H;	₂O / DMF/EA				
PUA-4-NaMo	1/1.5	59.7±0.3	0.342±0.04	1.244±0.004	75	294 [24]	2.4 (1.2)	17 (33)	8.2
PUA-12-NaMo	1/1.5	37.6±5.9	0.6±0.2	2.142±0.007	80	118 [14]	1.9 (0.3)	10 (64)	12

Fable 25. Material	properties	of PUA-Mo	aerogels.
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<sup>a</sup> Calculated according to formula:  $(y_1+y_2)/2$ , where  $y_1 = 100-[(h_{fin}/h_{st})\times 100]$  and  $y_2 = 100-[(d_{fin}/d_{st})\times 100]$ . <sup>b</sup> Calculated according to formula:  $(\rho_s-\rho_b)/\rho_s$ , where  $\rho_s$ : skeletal density and  $\rho_b$ : bulk density. <sup>c</sup> Micropore surface area *via t*-plot analysis, according to the Harkins and Jura model. <sup>d</sup> Total pore volume calculated according to formula:  $1/\rho_b-1/\rho_s$ . <sup>e</sup> Cumulative volume of pores between 1.7 and 300 nm from N<sub>2</sub>-sorption data and the BJH desorption method. <sup>f</sup> Calculated by the  $4V/\sigma$  method; *V* was set equal to the maximum volume of N<sub>2</sub> adsorbed along the isotherm as  $P/P_0 \rightarrow 1.0$ . For the number in parentheses *V* was set equal to  $V_{Total}$  from the previous column. <sup>g</sup> Calculated according to formula:  $3/(\rho_s \times \sigma)$ .

Representative N<sub>2</sub>-sorption isotherms are shown in Figure S84 and Figure S85 together with PSDs. N<sub>2</sub> adsorption-desorption isotherms revealed the same pattern as in the case of **PUA-W** aerogels; hysteresis loops are present at all cases, indicating that materials are mesoporous/macroporous.

Microporosity of **PUA-Mo** aerogels was evaluated independently with CO<sub>2</sub> adsorption to 1 bar at 273 K. **PUA-HMo** aerogels derived from both solvents
had similar CO<sub>2</sub> uptake (~0.5-0.6 mmol/g, Figure 60). Pore size distributions for pores <1 nm were calculated from the CO<sub>2</sub> adsorption isotherms using a DFT model (Figure 60, inset). Most of the micropores were distributed in the range of 0.5-0.9 nm. **PUA-20-NaMo** aerogels from EA showed higher CO<sub>2</sub> uptake than **PUA-HMo** aerogels (1.17 mmol/g, Figure 61) and most of the micropores were distributed in the range of 0.6-0.9 nm.

Sample	TIPM/W (mol/mol)	Quantity of CC STI	V <sub>&lt;7.97Å</sub> <sup>a</sup> (cm³ g⁻¹)	
		mmol g⁻¹	cm³ g <sup>−1</sup>	
PUA-12-HMo (DMF)	1/3	0.56	12.57	0.02
PUA-12-HMo (EA)	1/3	0.51	11.35	0.02
PUA-20-NaMo	1/0.1	1.17	26.21	0.05

Table 26. Selected results from CO<sub>2</sub> porosimetry of PUA-Mo aerogels.

<sup>a</sup> Total pore volume of pores less than 7.97 Å from  $CO_2$  sorption data at 273 K using the single-point absorption method at *P*/*Po* = 0.03.



Figure 60. CO<sub>2</sub> sorption diagrams and pore size distribution diagrams using the DFT method (insets) of PUA-12-HMo aerogels prepared in EA (left) and DMF/EA (right).



Figure 61. CO<sub>2</sub> sorption diagram and pore size distribution diagram using the DFT method (inset) of PUA-20-NaMo aerogels prepared in EA.

The structural morphology of **PUA-Mo** aerogels was investigated with SEM (Figure 62-Figure 65). As was also observed for **PUA-W** aerogels, **PUA-Mo** aerogels prepared in EA had a particulate morphology, while those prepared in DMF/EA had a uniform morphology. EDS and X-Ray mapping (Figure 63 and Figure 65) proved the presence of Mo in the polymer network. In most cases, the distribution of Mo was homogeneous. The experimental Mo content (% w/w), derived from EDS data is shown in Table 27, together with the theoretical values calculated according to Equation 6.



Figure 62. SEM images of PUA-4-HMo and PUA-12-HMo aerogels prepared in EA or DMF/EA.



Figure 63. X-Ray mapping (left) and EDS spectrum (right) of PUA-12-HMo aerogels prepared with TIPM/HMo molar ratio 1/3 in EA.



Figure 64. SEM images of PUA-20-NaMo and PUA-4-NaMo aerogels prepared in EA (top) or DMF/EA (bottom).

		) ¢		Element	Weight %	
months and the print of				С	60.4	
				0	18.5	1
				Ν	1.5	
an a				Мо	19.6	The second second
Constraints and the second s second second sec second second sec second second sec		11		Na	0.1	MAR AND THE REAL
C C C C C C C C C C C C C C C C C C C	<u> </u>	cļ		Total	100.00	100 µm
Mo	Na		Mo Mo Mo Mo Mo Mo Mo Mo	4	5 6	7 6 9 10
		Fulls	Scale 5079 cts Cursor: 10.0	89 kev (0 cts)		keV

Figure 65. X-Ray mapping of PUA-20-NaMo aerogels prepared in EA.

Table 27. Theoretical and experimental metal composition (% w/w) of PUA-Mo aerogels.

Sample	TIPM/Mo (mol/mol)	Mo theoretical content (%w/w)	Mo content from eds (%w/w)
PUA-12-HMo	1/3	16	10
PUA-20-NaMo	1/0.5	3.0	19.6

<sup>a</sup> For routine EDS analysis, the detection limits are about 1% w/w.<sup>255 b</sup> Heterogeneous distribution of the metal in the polymer matrix.

### 6.2.3 Conclusions

Metal-doped PUA aerogels (**PUA-W** and **PUA-Mo**) were synthesized from the reaction of TIPM (aromatic triisocyanate) with water using several compounds of W (i.e., WO<sub>3</sub>, H<sub>2</sub>WO<sub>4</sub>, peroxypolytungstic acid solution, H<sub>3</sub>[P(W<sub>3</sub>O<sub>10</sub>)<sub>4</sub>]·xH<sub>2</sub>O, Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O, (NH<sub>4</sub>)<sub>6</sub>W<sub>12</sub>O<sub>39</sub>·xH<sub>2</sub>O, WCl<sub>6</sub>) and Mo (i.e., H<sub>2</sub>MoO<sub>4</sub>·H<sub>2</sub>O,

Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O) as catalysts. The reactions were carried out with different TIPM/M (M = W, Mo) molar ratios, varying from catalytic to overstoichiometric, in order to test how much "M" could be retained in the polymer network. The most important findings of those studies are:

(a) The morphology and related properties of **PUA-W** and **PUA-Mo** aerogels depend on the solvent of the reaction; aerogels are particulate when the reaction is carried out in EA and dense when the reaction is carried out in DMF/EA, as a result of the different solubility of the growing polymer in the different solvents. Particles are in most cases micron-sized and non-porous, therefore the BET surface area of those materials is close to zero.

(b) "W" or "Mo" were homogeneously distributed in the polymer matrix, which means that those **PUA-W** and **PUA-Mo** aerogels are very promising precursors for metal-doped carbon aerogels.

#### 6.3 Pyrolysis of PUA-W and PUA-Mo aerogels

It is already known that Pt has high catalytic activity. However, replacing this expensive metal would be desirable. Some Pt-like materials have attracted considerable attention as alternative catalysts for various applications, which sometimes even offer significant advantages over noble metals.<sup>260</sup> Among these, transition-metal carbides display remarkable catalytic activities, owing to their similar electronic and catalytic properties to Pt-group metals. Thus, by inducing carbon into the metal lattice they have been identified as the most promising candidates to replace or reduce Pt employment in catalytic reactions.

Tungsten carbide shows catalytic activity akin to Pt, that is tungsten carbide catalyzes the reaction of H<sub>2</sub> and O<sub>2</sub> to H<sub>2</sub>O at room temperature, the reduction of WO<sub>3</sub> by H<sub>2</sub> in the presence of water, and the isomerization of 2,2-dimethylpropane to 2-methylbutane.<sup>261,262</sup>

As it is already known, TIPM-derived PUA aerogels can be converted to carbon aerogels *via* pyrolysis, with a 56% w/w carbonization yield.<sup>245</sup> Catalytic and non-catalytic amounts have been studied for the synthesis of **PUA-W** and **PUA-Mo** aerogels, as described in Section 6.5, with the aim to prepare PUA aerogels doped with metal ions, which could potentially provide metal-doped carbons after pyrolysis and/or etching. Those metal-doped carbons are excellent candidates as catalysts to several reactions.

Table 28 shows all data for the pyrolyzed **PUA-W** and **PUA-Mo** aerogels under inert atmosphere. The temperatures of pyrolysis were in the range of 700 and 1200 °C, while the duration of the process was 3, 5 or 6 h. The yield of pyrolysis ( $\alpha$  %) was calculated by dividing the mass of pyrolyzed sample with the mass of the unpyrolyzed sample (×100). The resulting pyrolyzed samples are metal-doped carbons and they are referred to as **W-Carbon** or **Mo-Carbon** aerogels.

#### 6.3.1 Characterization of W-carbon and Mo-carbon aerogels

**W-Carbon** and **Mo-Carbon** aerogels were characterized with PXRD, SEM, EDS spectroscopy, X-Ray mapping, N<sub>2</sub> and CO<sub>2</sub> porosimetry and He pycnometry.

Table 28. Data for pyrolysis of selective PUA-W and PUA-Mo under inert atmosphere.

		Temperature	Pyrolysis		
Metal precursor	Material (TIPM/M, solvent)	of pyrolysis (°C)	time (h)	α (%)	xrd results
	PUA-4-WO (1/0.1, EA)	800	3	23	tungsten nitride oxide W <sub>0.62</sub> (N,O)
	PUA-8-WO (1/0.1, EA)	1200	3	24	tungsten carbide hexagonal (WC)
WO <sub>3</sub>	PUA-12-WO (1/0.1, EA)	800	3	10	small quantity
	PUA-12-WO (1/0.1, EA)	1200	3	20	tungsten carbide hexagonal (WC)
	PUA-30-WO (1/0.1, EA)	1200	3	22	tungsten carbide (WC) hexagonal
	PUA-4-HŴ (1/0.1, EA)	800	3	33	tungsten carbide (WC <sub>1-x</sub> )
H <sub>2</sub> WO <sub>4</sub>	PUA-4-HW (1/0.1, EA)	1200	3	25	tungsten carbide hexagonal (WC) W cubic
	PUA-4-HŴ (1/3, DMF/EA)	1200	3	20	tungsten carbide hexagonal (WC)
Peroxypolytungstic acid solution	PUA-46-PAS (1/0.3, EA)	1200	3	22	tungsten carbide (WC)
H <sub>3</sub> [P(W <sub>3</sub> O <sub>10</sub> ) <sub>4</sub> ]·xH <sub>2</sub> O	PUA-10-PW (1/0.01, EA)	1200	3	12	small quantity
	PUA-10-NaW (1/2, EA)	1000	6	9	small quantity
	PUA-12-NaW (1/1.5, DMF/EA)	1200	3	22	tungsten carbide hexagonal (WC) W cubic tungsten carbide orthorhombic
Na₂WO₄·2H₂O	PUA-25-NaW (1/0.1, EA)	800	3	30	no crystalline phase
	PUA-30-NaW (1/0.8, DMF/EA)	1200	3	27	tungsten carbide hexagonal (WC) W cubic tungsten carbide hexagonal (W <sub>2</sub> C)
	PUA-35-NaW (1/0.8, DMF/EA)	1200	3	22	no crystalline phases
	PUA-20-WCI (1/0.05, EA)	1200	3	11	small quantity
WCI <sub>6</sub>	PUA-30-WCI (1/0.05, EA)	800	3	54	tungsten nitride (W2N)
	PUA-35-WCI (1/0.05, EA)	700	5	40	tungsten carbide hexagonal
H2MoO4·H2O	PUA-4-HMo (1/0.6, EA)	800	3	28	molybdenum nitride (Mo <sub>2</sub> N) molybdenum oxide (MoO <sub>2</sub> )
	PUA-12-HMo (1/3, EA)	1200	3	44	molybdenum carbide (Mo <sub>18</sub> C <sub>7</sub> ) molybdenum oxide (MoO <sub>2</sub> ) Mo
	PUA-12-HMo (1/3, EA)	1200	3	25	molybdenum carbide (Mo <sub>18</sub> C <sub>7</sub> ) Mo

Polymeric systems under the melting temperatures give usually semicrystalline solids, where amorphous and crystalline phases coexist. PXRD patterns of most pyrolyzed samples (Figure 66 to Figure 70) indicated amorphous carbon, in equilibrium with crystalline phases. Few exceptions of pyrolyzed samples did not show crystallinity at all (Table 28, entries 13 and 15). In most cases **W**-carbons contained tungsten carbide in the crystalline phase of the material, even at temperatures relatively low (700 or 800 °C), which is important,

because there are not many reports in the literature that tungsten carbide can be formed at such low temperatures.<sup>263</sup> The usual temperature for the synthesis of tungsten carbide is over 1000 °C.<sup>264</sup> Figure 66 shows the PXRD patterns of **W-carbons** derived from **PUA-WO** aerogels at 1200 °C. In all cases of **PUA-WO** aerogels, WC (hexagonal) was formed except for entry 1 of Table 28 which gave tungsten nitride oxide (Figure 66, bottom), probably because pyrolysis was carried out at a lower temperature.



Figure 66. Top: PXRD patterns of the residue after pyrolysis of PUA-30-WO (left) and PUA-12-WO (right) aerogels at 1200 °C for 3 h under Ar. Bottom: PXRD pattern of the residue after pyrolysis of PUA-4-WO at 800 °C for 3 h under N<sub>2</sub>. All aerogels were prepared with TIPM/WO molar ratio 1/0.1 in EA.

PXRD patterns for pyrolyzed **PUA-HW** aerogels (Figure 67) revealed crystalline phases corresponding to WC (hexagonal) and W (cubic) in some cases. For **W-carbons** obtained from the pyrolysis of **PUA-NaW** aerogels at 1200 °C XPRD revealed three different crystalline phases: WC (hexagonal), W (cubic) and a third phase that depended on the solvent used for the polymerization, i.e., W<sub>2</sub>C (orthorhombic) for **PUA-NaW** aerogels prepared in DMF/EA (Figure

69) and W<sub>2</sub>C (hexagonal) for **PUA-NaW** aerogels prepared in EA. **W-carbons** from **PUA-PAS** aerogels at 1200 °C also revealed WC (hexagonal) and W<sub>2</sub>C (hexagonal) phases. Finally, pyrolysis of **PUA-WCI** aerogels under different conditions (temperature, pyrolysis duration) and atmosphere, yielded **W-carbons** with different crystalline phases (Figure 70).



Figure 67. Top: PXRD patterns of the residue after pyrolysis of PUA-4-HW (prepared with TIPM/HW molar ratio 1/0.1 in EA; left) and PUA-4-HW (prepared with TIPM/HW molar ratio 1/3 in DMF; right) at 1200 °C for 3 h under Ar. Bottom: PXRD patterns of the residue after pyrolysis of PUA-4-HW (prepared with TIPM/HW molar ratio 1/0.01 in EA) at 800 °C for 3 h under Ar.



Figure 68. PXRD pattern of the residue after pyrolysis of PUA-46-PAS (prepared with TIPM/W molar ratio 1/0.3 in EA) at 1200 °C for 3 h under Ar.



Figure 69. Top: PXRD patterns of the residue after pyrolysis of PUA-12-NaW (prepared with TIPM/NaW molar ratio 1/1.5 in DMF/EA; top left) and PUA-30-NaW (prepared with TIPM/NaW molar ratio 1/0.8 in DMF/EA; top right) at 1200 °C for 3 h under Ar. Bottom: PXRD pattern of the residue after pyrolysis of PUA-25-NaW (prepared with TIPM/NaW molar ratio 1/0.1 in EA) at 800 °C for 3 h under Ar.



Figure 70. PXRD patterns of the residue after pyrolysis of PUA-20-WCI aerogels at 800 °C for 3 h under N<sub>2</sub> and PUA-30-WCI (right) aerogels at 700 °C for 5 h under Ar. Both aerogels were prepared with TIPM/WCI molar ratio 1/0.05 in EA.

The formation of tungsten carbide is of interest to us, due to its resemblance, in terms of catalytic activity, to platinum.<sup>261</sup> Cubic WC<sub>1-x</sub>, in particular, is a very interesting phase of tungsten carbide. For many years, its study as a catalyst has not drawn much attention. However, theoretical calculations<sup>265</sup> have shown that its density of states near the Fermi level is much larger than those of WC and W<sub>2</sub>C, indicating that it may be the most catalytically active phase of tungsten carbide. WC<sub>1-x</sub> is stable above 2500 °C and metastable at room temperature.<sup>266</sup> Therefore, its pyrolytic formation has not been observed. Instead, cubic WC<sub>1-x</sub> is usually produced by non-conventional methods, i.e., sonochemically,<sup>267</sup> by sputtering,<sup>268</sup> by chemical explosion of tungsten wires in liquid paraffin,<sup>269</sup> or by pulsed plasma in liquid methods.<sup>270</sup>To our knowledge, formation of cubic WC<sub>1-x</sub> by such a convenient method as simple pyrolysis is unique, thus worth further studying.

SEM images (Figure 71-Figure 75) showed that **W-carbons** are macroporous. EDS spectra and X-Ray mapping of **W-carbons** showed the presence of C, O, N and W (Figure 71, Figure 73-Figure 75). Specifically, SEM images of the residue after pyrolysis of **PUA-WO** aerogels (Figure 71) revealed a fine primary structure with no presence of W in the inner phase, but rather on the surface of the monolith.



Figure 71. SEM images (top) and EDS spectrum (bottom) of the residue after pyrolysis of PUA-12-WO aerogels (prepared with TIPM/WO molar ratio1/0.1 in EA) at 800 °C for 3 h under  $N_2$ .



Figure 72. SEM images of the residue after pyrolysis of PUA-4-HW aerogels (prepared with TIPM/HW molar ratio 1/0.1 in EA) at 800 °C for 3 h under Ar.



Figure 73. X-Ray mapping and EDS spectrum of the residue after pyrolysis of PUA-35-NaW aerogels (prepared with TIPM/NaW molar ratio 1/0.8 in DMF/EA) at 1200 °C for 3h under Ar.



Figure 74. (a) SEM images, (b) X-Ray mapping and (c) EDS spectrum of the residue after pyrolysis of PUA-12-NaW aerogels (prepared with TIPM/NaW molar ratio 1/1.5, in DMF/EA) at 1200 °C for 3h under Ar.



Figure 75. SEM images (top) and EDS spectrum (bottom) of the residue after pyrolysis of PUA-34-WCI aerogels (prepared with TIPM/WCI molar ratio 1/0.06 in EA) at 700 °C for 3 h under Ar.

For **Mo-carbons** derived from pyrolysis of **PUA-HMo** aerogels at 1200 °C, PXRD showed the presence of molybdenum carbides (Mo<sub>18</sub>C<sub>7</sub> and Mo<sub>2</sub>C) along with amorphous carbon (Figure 76a and b). At lower pyrolysis temperature (800 °C) molybdenum nitride and molybdenum oxide were obtained (Figure 76c).

Molybdenum carbides are also highly active in catalysis, mostly for hydrogen production,<sup>271–273</sup> as well as other catalytic reactions, such as the hydrodenitrogenation of carbazole.<sup>274</sup> For the synthesis of Mo<sub>18</sub>C<sub>7</sub> there is only one report in the literature; the carbide was synthesized from the thermal decomposition of isopolymolybdates at 900 °C.<sup>275</sup> On the other hand, a number of preparation procedures has been reported for Mo<sub>2</sub>C. It has been prepared from Mo oxides or salts<sup>271,274,276,277</sup> under CH<sub>4</sub>/H<sub>2</sub> mixtures or inert atmosphere at different pyrolysis temperatures, ranging from 725 to 1000 °C. Alternatively, Mo<sub>2</sub>C has been prepared from organic precursors, i.e., resorcinol-formaldehyde aerogels, doped with Mo at 1000 °C, under H<sub>2</sub>/Ar flow.<sup>278</sup>



Figure 76. PXRD patterns of the residue after pyrolysis of PUA-12-HMo (prepared with TIPM/Mo molar ratio 1/3 in DMF/EA; left top), PUA-12-HMo (prepared with TIPM/HMo molar ratio 1/3 in EA; right top) at 1200 °C for 3 h under Ar. Bottom: PXRD pattern of the residue after pyrolysis of PUA-4-HMo (prepared with TIPM/HMo molar ratio 1/0.6 in EA) at 800 °C for 3 h under N<sub>2</sub> (left bottom).

Selected material properties of selected **W-** and **Mo-carbons** are summarized in Table 29. Bulk density, porosity and *V*<sub>Total</sub> are not displayed in the Table, because **W** and **Mo-carbons** are brittle and their cylindrical shape deformed easily. In most cases, BET surface area was higher or almost the same after pyrolysis, while in the case of PUA native aerogels surface area was decreased significantly. Skeletal densities of **M-carbons** were in the range of 1.9-2.8 g cm<sup>-3</sup>, which is higher than the range for amorphous carbon (1.8-2.0 g cm<sup>-3</sup>),<sup>245</sup> reflecting the presence of W and Mo crystalline phases in **W** and **Mo-carbons**.

Metal precursor	Starting Material (TIPM/M, solvent)	SkeletalBET surf. areadensity $\sigma$ (m² g⁻¹) $\rho_s$ (g cm⁻³)[micropore surf. area]		SkeletalBET surf. areaAv. poreJensity $\sigma$ (m² g⁻¹)diameterb $\rho_s$ (g cm⁻³)[micropore surf. area]a		V <sub>1.7-300nm</sub> c (cm³ g⁻¹)	Particle radius <sup>d</sup> r (nm)
			PUA-M	M-carbon			
Et <sub>3</sub> N (C1200)	PUA-12 (1/0.06, DMF)	1.42±0.03	290 [25]	3 [5]	1.3	0.0009	-
	PUA-4-WO (1/0.1, EA)	2.82±0.07	6 [9]	18 [27]	2.7	0.009	59
	PUA-8-WO (1/0.1, EA)	1.90±0.02	<0.5	<0.5	-	-	-
WO3	PUA-12-WO (1/0.1, EA)	2.11±0.02	367	313	2.1	0.001	4.5
	PUA-12-WO (1/0.1, EA)	2.17±0.04	<2	<2	-	-	-
	PUA-30-WO (1/0.1, EA)	7.2±0.1	<2	15 [11]	2.6	0.003	28
H <sub>2</sub> WO <sub>4</sub>	PUA-4-HW (1/0.1, EA)	2.00±0.01	<2	<2	4.1	0.0008	-
Peroxypolytungstic acid solution (PAS)	PUA-46-PAS (1/0.3, EA)	2.12±0.02	<2	22 [16]	2.7	0.75	64
WCL	PUA-29-WCI (1/0.05, EA)	1.924±0.006	27 [7]	14 [7]	11	0.04	-
WCl6	PUA-34-WCI (1/0.06, EA)	2.24±0.01	N/A	312 [233]	2.6	0.04	4.3
	PUA-4-HMo (1/0.6, EA)	2.088±0.004	8 [8]	7 [7]	8.1	0.01	-
	PUA-12-HMo (1/3, DMF/EA)	3.06±0.03	223 [25]	56 [26]	6.9	0.08	18

Table 29. Material properties of W-carbon and Mo-carbon aerogels.

<sup>a</sup> Micropore surface area *via* t-plot analysis, according to the Harkins and Jura model. <sup>b</sup> Calculated by the  $4V/\sigma$  method; *V* was set equal to the maximum volume of N<sub>2</sub> adsorbed along the isotherm as  $P/P_0 \rightarrow 1.0$ . For the number in parentheses *V* was set equal to  $V_{\text{Total}}$  from the previous column. <sup>c</sup> Cumulative volume of pores between 1.7 and 300 nm from N<sub>2</sub>-sorption data and the BJH desorption method. <sup>d</sup> Calculated according to formula:  $3/(\rho_s \times \sigma)$ .

**W-carbons** were tested for their ability to adsorb CO<sub>2</sub>, as they show microporosity. CO<sub>2</sub> porosimetry showed a high uptake of 3.52 mmol  $g^{-1}$  CO<sub>2</sub> (Figure 77), which gives the motivation for further study of those carbon materials in adsorption of other gases, e.g., methane. Moreover, pore size distribution using the DFT method showed that micropores were in the range of 0.5-0.9 nm.



Figure 77. CO<sub>2</sub> isotherm and pore size distribution (inset) of the residue after pyrolysis of PUA-12-WO prepared with TIPM/WO molar ratio 1/0.1 in EA.

## 6.3.2 Conclusions

The pyrolysis of **PUA-W** and **PUA-Mo** aerogels was studied at different temperatures and times. In most cases porous carbons were formed, which were doped with the corresponding metal carbides and nitrides and showed good CO<sub>2</sub> adsorption. Although further studies are required to determine the optimum conditions (in terms of yield and energy saving) of pyrolysis for the preparation of a particular metal carbide or nitride, this work has shown the potential to synthesize such carbides and nitrides *via* a novel and cost-efficient procedure.

## CONCLUSIONS

In this thesis two types of metal-mediated polymerization routes have been studied: (a) metathesis polymerization, including alkyne metathesis polymerization and ring opening metathesis polymerization (ROMP) for the synthesis of unsaturated polymers; and, (b) condensation polymerization for the synthesis of polyurea.

*Metathesis polymerization.* Catalytic systems based on ditungsten clusters with multiple metal-metal bonds have been studied for their activity and stereoselectivity towards metathesis reactions. The three catalytic systems were:  $Ph_4P_2[W_2(\mu-Br)_3Br_6]/AgBF_4$  (1;  $\{W_{-2.5}^{-}-W\}^{7+}$ ,  $a'^2e'^3$ ),  $Na[W_2(\mu-Cl)_3Cl_4(THF)_2]\cdot(THF)_3/PA$  (2;  $\{W_{-3}^{-}-W\}^{6+}$ ,  $a'^2e'^4$ ; PA: phenylacetylene) and  $Na[W_2(\mu-Cl)_3Cl_4(THF)_2]\cdot(THF)_3/NBD$  (3; NBD: norbornadiene). It is noted that the three catalytic systems have been invented, developed and studied previously at the Department of Chemistry NKUA. Our previous studies have shown that 1 and 2 are active towards metathesis polymerization of alkynes and ring opening metathesis polymerization (ROMP) of cycloolefins. In this work we studied the kinetics of polymerization of selected olefins with 1 and we explored the potential of 2 towards environmental remediation applications. Finally, the reactivity of 3 was explored towards the synthesis of selected polymeric materials. More specifically:

The kinetics of metathesis polymerization, induced by **1**, of phenylacetylene (PA), (NBD), 5-vinyl-2-norbornene norbornadiene (VNBE) and dicyclopentadiene (DCPD) were studied. By comparing with catalytic system 2, 1 polymerized PA with a lower rate, but resulting polymers had higher molecular weights and narrower molecular weight distributions. NBD was polymerized almost quantitatively within 1.5 h; the induction period was just a few minutes, probably due to complexation of the monomer to the catalyst at the initiation step of the polymerization process. Similar kinetics were found for VNBE, indicating that the mechanism remains the same in both cases, although polymerization of VNBE was slower, probably due to the increased steric hindrance. Nevertheless, the yield scaled linearly with time indicating that the polymerization reaction proceeded in a well-controlled manner. On the other hand, the initiation reaction for DCPD was very fast without an induction period as concluded by the fact that the plot of yield vs time passed through the origin. By the same token, however, the rate of polymerization was reduced with time. Compared to other monomers examined in this work, DCPD was the least reactive monomer, probably due to the highest degree of steric hindrance. Retardation of the polymerization may be attributed to the increased time needed for the activation of the second double bond of the monomer leading to crosslinked products.

Catalytic system 2 was used for the synthesis of highly crosslinked poly(dicyclopentadiene) (2-PDCPD) xerogels. Mostly-cis 2-PDCPD xerogels swelled in various organic solvents, mainly aromatic, chlorinated, and brominated hydrocarbons. The small volume of material required (1/100 or even less) vs other literature absorbents, including organic polymers or carbonbased materials, and the competitive technology for preparing 2-PDCPD xerogels (inexpensive starting materials and catalyst, room temperature synthesis, ambient pressure drying) render those xerogels superior materials in terms of solvent uptake. The swelling behavior of **2-PDCPD** xerogels was rationalized with the Hansen Solubility Parameters (HSP) theory and the Flory theory, each of which provided insight into the swelling mechanism and the parameters that affected it. A correlation was made between the swelling behavior of the xerogels in each solvent and the solvent Hansen Solubility Parameters (HSP), leading to an estimation of the HSP of mostly-cis PDCPD. Based on those findings, many applications include separations of organic solvents from water, or the use of thin layers of those xerogels in sensors and actuators by coupling volumetric swelling to optical or electrical signal transduction. From a fundamental perspective, the most significant outcome of this study was the direct experimental estimation of the HSP of mostly-cis PDCPD. From a practical perspective, we have shown the potential of mostlycis PDCPD for separating organic solvents from water and/or oil.

Catalytic system **3** was also used as a catalytic system for the synthesis of high*cis* PDCPD (**3-PDCPD**) xerogels and aerogels. Compared to high-*trans* **PDCPD** aerogels described in the literature with the use of 1<sup>st</sup> and 2<sup>nd</sup> generation Grubbs' catalysts, **3-PDCPD** aerogels had a much different nanomorphology, possibly due to the different *cis/trans* configurations. Interestingly, their material properties (e.g., BET surface area) were very similar with those of PDCPD aerogels obtained with 2<sup>nd</sup> generation Grubbs' catalyst, thus **3** provides a cost-effective alternative to the 2<sup>nd</sup> generation Grubbs' catalyst. In addition, **3-PDCPD** aerogels were able to swell in various organic solvents, with their fast response making them good candidates for use in chemical actuators.

*Condensation polymerization.* Metal-doped PUA (**PUA-M**) aerogels were synthesized from the reaction of TIPM (aromatic triisocyanate) with water using first-row transition metal salts as catalysts (i.e., CrCl<sub>3</sub>·6H<sub>2</sub>O, FeCl<sub>3</sub>·xH<sub>2</sub>O, CoCl<sub>2</sub>·6H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and CuCl<sub>2</sub>·2H<sub>2</sub>O). The reactions were carried out with different TIPM/M molar ratios, varying from catalytic to overstoichiometric, in order to test how much "M" could be retained in the polymer network. All **PUA-M** aerogels had low bulk densities, moderate to high porosities, high BET surface areas as well as microporosities (6-15%). The most important finding of those studies is that "M" was homogeneously distributed in the polymer matrix, which means that those **PUA-M** aerogels are very promising precursors for metal-doped carbon aerogels. Also, the metal content of **PUA-M** aerogels increased when TIMP/M molar ratio increased from 1/0.5 to 1/1.5, but it remained the same or even decreased at TIMP/M molar ratio 1/3. Therefore, there is no need to use such a big amount of metal compound for the preparation of **PUA-M** aerogels.

Tungsten- and molybdenum-doped PUA aerogels (**PUA-W** and **PUA-Mo**) were synthesized from the reaction of TIPM (aromatic triisocyanate) with water using several compounds of W (i.e., WO<sub>3</sub>, H<sub>2</sub>WO<sub>4</sub>, peroxypolytungstic acid solution, H<sub>3</sub>[P(W<sub>3</sub>O<sub>10</sub>)<sub>4</sub>]·xH<sub>2</sub>O, Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O, (NH<sub>4</sub>)<sub>6</sub>W<sub>12</sub>O<sub>39</sub>·xH<sub>2</sub>O, WCl<sub>6</sub>) and Mo (i.e., H<sub>2</sub>MoO<sub>4</sub>·H<sub>2</sub>O, Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O) as catalysts. The reactions were carried out with different TIPM/M (M = W, Mo) molar ratios, varying from catalytic to overstoichiometric, in order to test how much "M" could be retained in the polymer network. The most important findings of those studies are:

(a) The morphology and related properties of **PUA-W** and **PUA-Mo** aerogels depend on the solvent of the reaction; aerogels are particulate when the reaction is carried out in EA and dense when the reaction is carried out in

DMF/EA, as a result of the different solubility of the growing polymer in the different solvents. Particles are in most cases micron-sized and non-porous, therefore the BET surface area of those materials is close to zero.

(b) "W" or "Mo" were homogeneously distributed in the polymer matrix, which means that those **PUA-W** and **PUA-Mo** aerogels are very promising precursors for metal-doped carbon aerogels.

**PUA-W** and **PUA-Mo** aerogels were pyrolyzed at different temperatures and for different lengths of time. In most cases porous carbons were formed, which were doped with the corresponding metal carbides and nitrides and showed good CO<sub>2</sub> adsorption. Although further studies are required to determine the optimum pyrolytic conditions (in terms of yield and energy savings) for the preparation of a particular metal carbide or nitride, this work has shown the potential to synthesize such carbides and nitrides *via* a novel and cost-efficient procedure.

## **ABBREVIATIONS-ACRONYMS**

ATR-FTIR	Attenuated Total Reflection- Fourier-Transform Infrared spectroscopy
CPMAS	Cross Polarization Magic Angle Spinning
DCM	Dichloromethane
DFT	Density Functional Theory
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
EDS	Energy Dispersive X-Ray Spectroscopy
HSP	Hansen Solubility Parameters
MeOH	Methanol
MeCN	Acetonitrile
NMR	Nuclear Magnetic Resonance
PAS	peroxypolytundstic acid solution
(P)DCPD	(poly)dicyclopentadiene
(P)NBE	(poly)norbornene
(P)NBD	(poly)norbornadiene
(P)PA	(poly)phenylacetylene
PSD	Pore Size Distribution
PUA	Polyurea
(P)VNBE	(poly)5-vinyl-2-norbornene
PXRD	Powder X-Ray Diffraction
ROMP	Ring Opening Metathesis Polymerization
Ru-I	Grubbs Catalyst 1 <sup>st</sup> generation
Ru-II	Grubbs Catalyst 2 <sup>nd</sup> generation
scd or scf	Supercritical drying or Supercritical fluid
SEC	Size Exclusion Chromatography
SEM	Scanning Electron Microscopy
TIPM	Tris(4-isocyanatatophenyl)methane
THF	Tetrahydrofuran
TGA	ThermoGravimetric Analysis

# APPENDIX I SWELLING STUDIES OF 2-PDCPD XEROGELS



Figure S1. Swelling of a 2-PDCPD xerogel in chloroform with time.



Figure S2. Swelling of a 2-PDCPD xerogel in bromobenzene with time.



Figure S3. Swelling of a 2-PDCPD xerogel in 1,2-dibromoethane with time.



Figure S4. Swelling of a 2-PDCPD xerogel in tetrahydrofuran with time.



Figure S5. Swelling of a 2-PDCPD xerogel in ethyl bromide with time.



Figure S6. Swelling of a 2-PDCPD xerogel in 1-bromobutane with time.



Figure S7. Swelling of a 2-PDCPD xerogel in cyclohexane with time.



Figure S8. Swelling of a 2-PDCPD xerogel in cyclohexanone with time.



Figure S9. Swelling of a 2-PDCPD xerogel in 1,2-dichloroethane with time.



Figure S10. Swelling of a 2-PDCPD xerogel in pyridine with time.



Figure S11. Swelling of a 2-PDCPD xerogel in bromobenzene.



Figure S12. Swelling of a 2-PDCPD xerogel in 1,2-dibromoethane.

#### Table S1. Solvent uptake and density of 2-PDCPD xerogels and other materials from the

Matarial	Bulk density		Toluene up	otake	Chloroform uptake			
Wateria	(g cm⁻³)	(g g <sup>-1</sup> )	(g cm⁻³)	(cm <sup>3</sup> cm <sup>-3</sup> )	(g g <sup>-1</sup> )	(g cm <sup>-3</sup> )	(cm <sup>3</sup> cm <sup>-3</sup> )	
Polymeric materials								
2-PDCPD	0.9	111	100	115 <sup>9</sup>	89	80	54 <sup>this work</sup>	
polyurethane foams <sup>159</sup>	0.061	28	1.7	2				
WCl <sub>6</sub> -PDCPD <sup>9</sup>	0.9	4.3	3.9	4.5				
GC-II-PDCPD aerogels <sup>209</sup>	<1 <sup>b</sup>			1.5				
GC-I-PDCPD <sup>185</sup>					3.38			
GC-I-PDCPD aerogels	0.282 <sup>209</sup>	0	0	0 <sup>9</sup>				
ROMP polymers from norbornene-		36						
terminated macromonomers <sup>158</sup>								
porous polyurea monoliths <sup>279</sup>	0.093	10.14	0.94	1.1	15.02	1.40	0.94	
photoresponsive copolymer <sup>160</sup>	<1 <sup>b</sup>	15			19.5			
cinnamoyloxy ethyl	0.54	34	18	21				
methacrylate/octadecyl acrylate								
copolymers <sup>161</sup>								
cis-9-octadecenyl-based		3.69			8.5			
polymers <sup>166</sup>								
disulfide-linked polymeric		0.5			1.0			
networks <sup>162</sup>								
conjugated microporous	0.027				16	0.4	0.3	
(co)polymers <sup>163</sup>	0.04.00							
melamine formaldehyde	0.010 <sup>a</sup>				200	2.0	1.3	
sponges <sup>104</sup>					0.5			
mesogenic polyelectrolyte gels <sup>100</sup>		45			6.5			
crossiinked lipopnilic		15			75			
polyelectrolytes	0.10				15	1.0	1.0	
polymethylslisesquioxanes***	0.12	0.00			10	1.0	1.2	
Carbon materials		0.92						
carbon nanotubo anongoa <sup>156</sup>	0.005.0.010				175	0.0.1.75		
graphano/oarban composite	0.005-0.010	270	0.9	1.0	175	1.2	0.9	
aerogels <sup>152</sup>	0.003	279	0.8	1.0	400	1.2	0.8	
ultra-flyweight carbon aerogels <sup>157</sup>	0.00016	350	0.06	0.06	550	0.09	0.06	
nitrogen-doped graphene <sup>153</sup>	0.002	200	0.4	0.5	500	1.0	0.7	
spongy graphene <sup>154</sup>	0.012	55	0.7	0.8	85	1.0	0.7	
graphene/FeOOH aerogels <sup>155</sup>		15						

<sup>a</sup> The density of melamine formaldehyde sponges has not been measured, but ref. 8 states that similar

materials have densities below 0.010 g cm<sup>-3</sup>. <sup>b</sup> Polymers were floating on water.

Table S2. Experimental maximum volume degree of swelling (qmax) of 2-PDCPD xerogels in various solvents; Hansen Solubility Parameters (HSP),<sup>218</sup> molar volume  $(Vm)^{218}$  and surface tension ( $\gamma$ ) of the solvents used in this study.

Solvent	<b>q</b> <sub>max</sub> <sup>a</sup>	δ <sub>D</sub> (MPa <sup>1/2</sup> )	∂ <sub>P</sub> (MPa <sup>1/2</sup> )	<i>б</i> н (MPa <sup>1/2</sup> )	<i>δ</i> т (MPa <sup>1/2</sup> )	V <sub>m</sub> (cm³/mol)	γ <sup>ь</sup> (mN/m)
toluene	115	18.0	1.4	2.0	18.2	106.6	26.6
chloroform	54	16.8	5.7	8.0	19.5	80.5	25.3
bromobenzene	24	17.8	3.1	5.7	18.9	105.6	27.7
carbon disulfide	21	19.2	5.5	4.1	20.4	60.6	26.7
1,3-dichlorobenzene	19	20.2	0.0	0.6	20.2	114.5	33.9
carbon tetrachloride	16	19.2	5.1	2.7	20.0	97.1	30.6
chlorobenzene	14	19.0	4.3	2.0	19.6	102.1	30.0
1,2-dibromoethane	13	19.2	3.5	8.6	21.3	86.6	32.0
tetrahydrofuran	12	17.8	0.0	0.6	17.8	81.9	23.5
benzene	12	17.0	7.3	7.1	19.8	89.5	27.1
ethyl bromide	12	18.4	0.0	2.0	18.5	74.6	24.5
1-bromobutane	11	16.5	8.4	2.3	18.7	100.0	25.4
methylene dichloride	10	16.5	3.6	3.0	17.2	64.4	19.6
1,3,5-trimethylbenzene	8	18.0	0.6	0.6	18.0	139.5	28.8
1,4-dimethylbenzene	7	17.8	1.0	3.1	18.1	121.1	27.4
1,3-dimethylbenzene	7	18.0	2.3	2.3	18.3	100.0	26.2
1,2-dichlorobenzene	7	19.2	6.3	3.3	20.5	148.5	36.3
benzyl chloride	5	16.8	0.0	0.2	16.8	115.4	23.5
cyclohexane	4	18.8	7.1	2.6	20.3	108.9	31.8
1,4-dioxane	4	17.5	1.8	9.0	19.8	85.7	27.1
cyclohexanone	2	17.8	8.4	5.1	20.3	104.2	30.4
1,2-dichloroethane	2	17.0	7.3	7.1	19.8	148.5	32.1
pyridine	2	19.0	8.8	5.9	21.8	80.9	31.9
water	1	15.5	16.0	42.3	47.8	18.0	68.7
pentane	1	14.5	0.0	0.0	14.5	116.0	17.5
N,N-dimethylformamide	1	17.4	13.7	11.3	24.9	77.4	36.6
methanol	1	14.7	12.3	22.3	29.4	40.6	- c
dimethylsulfoxide	1	18.4	16.4	10.2	26.7	71.3	40.7
diethyl ether	1	14.5	2.9	4.6	15.5	104.7	18.4
acetonitrile	1	15.3	18.0	6.1	24.4	52.9	29.7
acetone	1	15.5	10.4	7.0	19.9	73.8	24.3
hexane	1	14.9	0.0	0.0	14.9	131.4	19.3
2-propanol	1	15.8	6.1	16.4	23.6	76.9	_ C
glycerol	1	17.4	11.3	27.2	34.2	73.4	_ C
ethylene glycol	1	17.0	11.0	26.0	33.0	55.9	- *
benzyl alconol	1	18.4	6.3	13.7	23.8	103.8	38.7
IV, IV-dimethylacetamide	1	16.8	11.5	9.4	22.4	93.0	32.6
methyl-2-pyrrolidone	1	18.0	12.3	1.2	23.0	96.6	35.5
	1	15.5	0.4	1.0	15.5	139.7	21.4
		14.8	3.1 5.0	1.5	15.3	141.9	20.4
	1	20.1	5.8	11.2	23.7	91.6	38.9
	1	15.8	0.5	5.4	17.9	106.7	23.9
propylene carbonate	1	20.0	18.0	4.1	27.2	85.2	46.3
etnyl acetate	1	15.8	5.3	1.2	18.2	98.6	23.7

<sup>a</sup> Experimental maximum volume degree of swelling of **2-PDCPD** gels at  $t_{max}$  (mean values of at least three measurements), calculated according to the equation  $q_{max} = V_{max}/V_{in}$ , where  $V_{max}$  is the volume of the wet-gel at  $t_{max}$  and  $V_{in}$  is the initial volume of the xerogel. <sup>b</sup> Surface tension ( $\gamma$ ) calculated from Beerbower's equation:  $\gamma = 0.01709 V_m^{1/3} [\delta_D^2 + 0.632(\delta_P^2 + \delta_H^2)]$ . <sup>c</sup> Beerbower's equation is not valid for aliphatic alcohols.



Figure S13. Relation between the experimental maximum volume degree of swelling  $(q_{max})$  of 2-PDCPD xerogels and the Hansen Solubility Parameters (HSP): total solubility parameter ( $\delta_T$ , a), D-component ( $\delta_D$ , b), P-component ( $\delta_P$ , c) and *H*-component ( $\delta_H$ , d) of the respective solvents.

#### 1<sup>st</sup> Method of HSPiP: Inside-Out Solvents

Table S3 shows the HSP of all solvents used in this study, their empirical classification as score "1" solvents (gels swelled) or score "0" solvents (gels did not swell) and the corresponding RED (Relative Energy Difference) values. RED values were calculated using the formula: RED = (distance of solvent from the center of the sphere) / (radius of the sphere). RED values close to 0 indicate higher, and RED values close to 1 indicate lower affinity of the solvent with the molecule under study (located at the center of the sphere).

Figure S14 shows the generated sphere (R = 5.9) and the HSP (in MPa<sup>1/2</sup>) for **2-PDCPD**:  $\delta_D = 18.15$ ,  $\delta_P = 3.69$ ,  $\delta_H = 3.55$  MPa<sup>1/2</sup>, and  $\delta_T = 18.86$  MPa<sup>1/2</sup>. The 2D plots (Figure S15) display the boundaries in HSP space and help visualize whether the solvents tested cover sufficiently the entire range of each solubility parameter ( $\delta_P$ ,  $\delta_D$ , and  $\delta_H$ ). It is obvious that solvents covering the entire range of the three HSPs have been used.

Table S3. Experimental maximum volume degree of swelling (qmax) of 2-PDCPD xerogels in various solvents, Hansen Solubility Parameters (HSP) of the solvents,<sup>218</sup> scoring according to whether they are "good" ("1") or "bad" ("0") solvents, and calculated Relative Energy Differences (RED).

Solvents	<b>q</b> _max <sup>a</sup>	<i>δ</i> ₀ (MPa <sup>1/2</sup> )	<i>δ</i> ⊦ (MPa <sup>1/2</sup> )	<i>б</i> н (MPa <sup>1/2</sup> )	score	RED <sup>b</sup>
1,3-dimethylbenzene	115	18.0	2.3	2.3	1	0.327
chloroform	54	17.8	3.1	5.7	1	0.389
chlorobenzene	24	19.0	4.3	2.0	1	0.411
1,3-dichlorobenzene	21	19.2	5.1	2.7	1	0.470
toluene	19	18.0	1.4	2.0	1	0.485
bromobenzene	16	19.2	5.5	4.1	1	0.491
1,4-dimethylbenzene	14	17.8	1.0	3.1	1	0.502
1-bromobutane	13	16.5	8.4	2.3	1	0.577
1,2-dichlorobenzene	12	19.2	6.3	3.3	1	0.590
1,2-dichloroethane	12	17.0	7.3	7.1	1	0.624
benzyl chloride	12	18.8	7.1	2.6	1	0.665
benzene	11	18.4	0.0	2.0	1	0.683
1,3,5-trimethylbenzene	10	18.0	0.6	0.6	1	0.781
carbon tetrachloride	8	17.8	0.0	0.6	1	0.820
cyclohexanone	7	17.8	8.4	5.1	1	0.869
methylene dichloride	7	1.7	7.3	7.1	1	0.891
1,2-dibromoethane	7	19.2	3.5	8.6	1	0.922
tetrahydrofuran	5	16.8	5.7	8.0	1	0.931
ethyl bromide	4	18.4	0.0	2.0	1	0.966
pyridine	4	19.0	8.8	5.9	1	0.977
carbon disulfide	2	20.2	0.0	0.6	1	0.992
cyclohexane	2	16.8	0.0	0.2	1	0.992
1,4-dioxane	2	17.5	1.8	9.0	1	0.994
methyl methacrylate	1	15.8	6.5	5.4	0	1.007

ethyl acetate	1	15.8	5.3	7.2	0	1.061
trimethylamine	1	15.5	0.4	1.0	0	1.229
diisopropylamine	1	14.8	3.7	1.5	0	1.278
diethyl ether	1	14.5	2.9	4.6	0	1.289
hexane	1	14.9	0.0	0.0	0	1.493
aniline	1	20.1	5.8	11.2	0	1.503
acetone	1	15.5	10.4	7.0	0	1.511
pentane	1	14.5	0.0	0.0	0	1.576
methyl-2-pyrrolidone	1	18.0	12.3	7.2	0	1.603
N,N-dimethyl acetamide	1	16.8	11.5	9.4	0	1.724
benzyl alcohol	1	18.4	6.3	13.7	0	1.821
dimethyl formamide	1	17.4	13.7	11.3	0	2.106
2-propanol	1	15.8	6.1	16.4	0	2.293
dimethyl sulfoxide	1	18.4	16.4	10.2	0	2.339
acetonitrile	1	15.3	18.0	6.1	0	2.421
propylene carbonate	1	20.0	18.0	4.1	0	2.482
methanol	1	14.7	12.3	22.3	0	3.228
ethylene glycol	1	17.0	11.0	26.0	0	3.713
glycerol	1	17.4	11.3	27.2	0	4.076
water	1	15.5	16.0	42.3	0	5.314

<sup>a</sup> Experimental maximum volume degree of swelling of **2-PDCPD** gels at  $t_{max}$  (mean values of at least three measurements), calculated according to the equation  $q_{max} = V_{max}/V_{in}$ , where  $V_{max}$  is the volume of the wet-gel at  $t_{max}$  and  $V_{in}$  is the initial volume of the xerogel. <sup>b</sup> Values calculated by the HSPiP 5.1.02 software.



Figure S14. 3D plot of the individual Hansen Solubility Parameters (HSP) for each solvent tested. Blue dots represent solvents in which 2-PDCPD xerogels swelled (23 "good" solvents – score: "1"). Red squares represent solvents in which no swelling was observed (21 "bad" solvents – score: "0"). The green sphere, generated by the HSPiP 5.1.02 software, is the sphere with the minimum diameter that fits best the experimental data. The center of the sphere is a reasonable estimate of the HSP of 2-PDCPD, which is represented by the green dot. The sphere contains all "good" solvents and no "bad"

solvents (referred to as wrong solvents), giving a fit value of 1.0, which is considered as a perfect fit.



Figure S15. 2D projections, generated by the HSPiP 5.1.02 software, of the individual Hansen Solubility Parameters (HSP) for each solvent tested at the three planes of the cube inscribing the sphere of Figure S14, as indicated. Blue dots represent solvents in which 2-PDCPD xerogels swelled ("good" solvents). Red squares represent solvents in which no swelling was observed ("bad" solvents). The green dot represents 2-PDCPD itself. The green circle contains all "good" solvents.



Figure S16. 2D projections, generated by the HSPiP 5.1.02 software, of the individual Hansen Solubility Parameters (HSP) for each solvent tested at the three planes of the cube inscribing the sphere of Figure 8 of Section 5.2, as indicated. Blue dots represent solvents in which 2-PDCPD xerogels swelled ("good" solvents). Red squares represent solvents in which no swelling was observed ("bad" solvents). The green dot represents 2-PDCPD itself. The green circle contains all "good" solvents.



Figure S17. Calculation of the Hansen Solubility Parameters (HSP) of dicyclopentadiene (DCPD) using the DIY method of the HSPiP 5.1.02 software.



Figure S18. Same as Figure 8 of Section 5.2, showing also the location of dicyclopentadiene (DCPD; orange dot; RED = 0.438).

Table S4. Calculated Hansen Solubility Parameters (HSP) of 2-PDCPD xerogels and solvents.

Solvent	Δ2δ <sub>D</sub> <sup>a</sup> (MPa <sup>1/</sup> <sup>2</sup> )	<i>∆δ</i> <sub>Р</sub> <sup>ь</sup> (MPa <sup>1/2</sup> )	<i>∆δ</i> <sub>H</sub> <sup>c</sup> (MPa <sup>1/2</sup> )
toluene	0.3	2.3	1.6
chloroform	0.7	0.6	-2.2
bromobenzene	-2.1	-1.8	-0.6
carbon disulfide	-4.1	3.7	3.7
1,3-dichlorobenzene	-2.1	-1.4	0.9
carbon tetrachloride	0.7	3.7	3.0
chlorobenzene	-1.7	-0.6	1.6
1,2-dibromoethane	-2.1	0.2	-5.1
tetrahyfrofuran	2.7	-2.0	-4.5
benzene	-0.5	3.7	1.6
ethyl bromide	3.3	-4.7	1.3
1-bromobutane	3.3	0.1	0.6
methylene dichloride	2.3	-3.6	-3.6
1,3,5-trimethylbenzene	0.3	3.1	3.0
1,4-dimethylbenzene	0.7	2.7	0.5
1,3-dimethylbenzene	0.3	1.4	1.3
1,2-dichlorobenzene	-2.1	-2.6	0.3
benzyl chloride	-1.3	-3.4	1.0
cyclohexane	2.7	3.7	3.4
1,4-dioxane	1.3	1.9	-5.5
cyclohexanone	0.7	-4.7	-1.6
1,2-dichloroethane	2.3	-3.6	-3.6
pyridine	-1.7	-5.1	-2.4
water	5.3	-12.3	-38.8
pentane	7.3	3.7	3.6
N,N-dimethylformamide	1.5	-10.0	-7.8
methanol	6.9	-8.6	-18.8
dimethylsulfoxide	-0.5	-12.7	-6.7
diethyl ether	7.3	0.8	-1.1
acetonitrile	5.7	-14.3	-2.6
acetone	5.3	-6.7	-3.5
hexane	6.5	3.7	3.6
2-propanol	4.7	-2.4	-12.9
glycerol	1.5	-7.6	-23.7
ethylene glycol	2.3	-7.3	-22.5
benzyl alcohol	-0.5	-2.6	-10.2
N,N-dimethylacetamide	2.7	-7.8	-5.9
methyl-2-pyrrolidone	0.3	-8.6	-3.7
triethylamine	5.3	3.3	2.6
diisopropylamine	6.7	0.0	2.1
aniline	-3.9	-2.1	-7.7
methyl methacrylate	4.7	-2.8	-1.9
propylene carbonate	-3.7	-14.3	-0.6
ethyl acetate	4.7	-1.6	-3.7

<sup>a</sup>  $\Delta 2 \delta_D = (2 \delta_{D1}) - (2 \delta_{D2})$ . <sup>b</sup>  $(\Delta \delta_P) = (\delta_{P1}) - (\delta_{P2})$ . <sup>c</sup>  $(\Delta \delta_H) = (\delta_{H1}) - (\delta_{H2})$ . "1" refers to 2-PDCPD xerogels and "2" refers to the solvent. Hansen Solubility Parameters (HSP) for 2-PDCPD:  $\delta_D = 18.15$ ,  $\delta_P = 3.69$ ,  $\delta_H = 3.55$  MPa<sup>1/2</sup>.



Figure S19. 2D plots of the magnitude differences between the solvent and 2-PDCPD xerogels:  $\Delta \delta_{P}$  vs  $\Delta 2 \delta_{D}$  (a) and  $\Delta \delta_{H}$  vs  $\Delta 2 \delta_{D}$  (b). Green dot shows point (0,0).
#### **APPENDIX II**



## **3-PDCPD AEROGELS AND XEROGELS**

Figure S20. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of the residue remaining after evaporation of THF from the 4 washes of a 3-PDCPD wet-gel.



Figure S21. Swelling of a 3-PDCPD aerogel in toluene versus time.



Figure S22. Swelling of a 3-PDCPD aerogel in DCM versus time.



Figure S23. Swelling of a 3-PDCPD aerogel in CHCl<sub>3</sub> versus time.



Figure S24. Swelling of a 3-PDCPD aerogel in PhCl versus time.



Figure S25. Swelling of a 3-PDCPD aerogel in PhBr versus time.



Figure S26. Swelling of a 3-PDCPD aerogel in THF versus time.



Figure S27. Swelling of a 3-PDCPD aerogel in 1-bromobutane versus time.



Figure S28. Swelling of a 3-PDCPD aerogel in ethyl bromide versus time.



Figure S29. Swelling of a 3-PDCPD aerogel in ethylene dichloride versus time.



Figure S30. Swelling of a 3-PDCPD aerogel in m-xylene versus time.



Figure S31. Swelling of a 3-PDCPD aerogel in p-xylene versus time.



Figure S32. Swelling of a 3-PDCPD aerogel in mesitylene versus time.

## **APPENDIX III**

# **PUA-M AEROGELS**



PUA-aerogels using as catalysts first row transition metal compounds

Figure S33. Weight loss with temperature (left) and derivative weight loss with temperature (right) for PUA-Cr-4 aerogels, as indicated.

N<sub>2</sub> sorption isotherms



Figure S34. N<sub>2</sub>-sorption diagrams (left) and pore size distributions using the BJH desorption method (right) of native PUA-4 aerogels at all TIPM/Et<sub>3</sub>N molar ratios, as indicated.



Figure S35. N<sub>2</sub>-sorption diagrams (left) and pore size distributions using the BJH desorption method (right) of PUA-Cr-4 aerogels at all TIPM/Cr molar ratios, as indicated.



Figure S36. N<sub>2</sub>-sorption diagrams (left) and pore size distributions using the BJH desorption method (right) of PUA-Fe-4 aerogels at all TIPM/Fe molar ratios, as indicated.



Figure S37. N<sub>2</sub>-sorption diagrams (left) and pore size distributions using the BJH desorption method (right) of PUA-Co-4 aerogels at all TIPM/Co molar ratios, as indicated.



Figure S38. N<sub>2</sub>-sorption diagrams (left) and pore size distributions using the BJH desorption method (right) of PUA-Ni-4 aerogels at all TIPM/Ni molar ratios, as indicated.



Figure S39. N<sub>2</sub>-sorption diagrams (left) and pore size distributions using the BJH desorption method (right) of PUA-Cu-4 aerogels at all TIPM/Cu molar ratios, as indicated.



Figure S40. N<sub>2</sub>-sorption diagrams (left) and pore size distributions using the BJH desorption method (right) of native PUA-12 aerogels at all TIPM/Et<sub>3</sub>N molar ratios, as indicated.



Figure S41. N<sub>2</sub>-sorption diagrams (left) and pore size distributions using the BJH desorption method (right) of PUA-Cr-12 aerogels at all TIPM/Cr molar ratios, as indicated.



Figure S42.  $N_2$ -sorption diagrams (left) and pore size distributions using the BJH desorption method (right) of PUA-Fe-12 aerogels at all TIPM/Fe molar ratios, as indicated.



Figure S43.  $N_2$ -sorption diagrams (left) and pore size distributions using the BJH desorption method (right) of PUA-Co-12 aerogels at all TIPM/Co molar ratios, as indicated.



Figure S44.  $N_2$ -sorption diagrams (left) and pore size distributions using the BJH desorption method (right) of PUA-Ni-12 aerogels at all TIPM/Ni molar ratios, as indicated.



Figure S45.  $N_2$ -sorption diagrams (left) and pore size distributions using the BJH desorption method (right) of PUA-Cu-12 aerogels at all TIPM/Cu molar ratios, as indicated.

## CO<sub>2</sub> sorption isotherms



Figure S46. CO<sub>2</sub>-sorption isotherms (left) and pore size distributions using the DFT method (right) for all PUA-Cr aerogels, as indicated.



Figure S47. CO<sub>2</sub>-sorption isotherms (left) and pore size distributions using the DFT method (right) for all PUA-Fe aerogels, as indicated.



Figure S48. CO<sub>2</sub>-sorption isotherms (left) and pore size distributions using the DFT method (right) for all PUA-Co aerogels, as indicated.



Figure S49. CO<sub>2</sub>-sorption isotherms (left) and pore size distributions using the DFT method (right) for all PUA-Ni aerogels, as indicated.



Figure S50. CO<sub>2</sub>-sorption isotherms (left) and pore size distributions using the DFT method (right) for all PUA-Cu aerogels, as indicated.



SEM Images, X-Ray Mapping and EDS spectra

Figure S51. Corresponding EDS spectrum of Figure 28 of PUA-Cr-4 aerogels prepared with TIPM/Cr molar ratio 1/0.5.



Figure S52. SEM images (top), X-Ray mapping (bottom, left) and EDS spectrum (bottom, right) of PUA-Cr-4 aerogels prepared with TIPM/Cr molar/ratio 1/3.



Figure S53. (a)SEM image, (b) X-Ray mapping and (c) EDS spectrum of PUA-Cr-12 aerogels prepared with TIPM/Cr molar ratio 1/1.5.

l ¢	Element	Weight%	
	СК	56.0	
	NK	17.7	
	OK	22.6	•
	CIK	0.8	
	Fe K	2.9	
	Total	100.00	30 μm
Fe O V Fe	ci	1	Fe N. Fe
0 1 2 Cull Carda 704 ata Cumanu 4	3 4	5 6	7 8 9 1

Figure S54. Corresponding EDS spectrum of Figure 28 of PUA-Fe-4 aerogels prepared with TIPM/Fe molar ratio 1/0.5.



Figure S55. SEM images of PUA-Fe-4 aerogels prepared with TIPM/Fe molar ratio 1/1.5.



Figure S56. (a)SEM image, (b) X-Ray mapping and (c) EDS spectrum of PUA-Fe-12 aerogels prepared with TIPM/Fe molar ratio 1/1.5.



Figure S57. SEM images of PUA-Fe-4 aerogels prepared with TIPM/Fe molar ratio 1/3.



Figure S58. Corresponding EDS spectrum of Figure 28 of PUA-Co-4 aerogels prepared with TIPM/Co molar ratio 1/0.5.



Figure S59. (a)SEM image, (b) X-Ray mapping and (c) EDS spectrum of PUA-Co-4 aerogels prepared with TIPM/Co molar ratio 1/3.



Figure S60. X-Ray mapping (left) and EDS spectrum (right) of PUA-Co-12 aerogels prepared with TIPM/Co molar ratio 1/0.5.



Figure S61. (a)SEM image, (b) X-Ray mapping and (c) EDS spectrum of PUA-Co-12 aerogels prepared with TIPM/Co molar ratio 1/1.5.



Figure S62. Optical photograph and SEM images (top), X-Ray mapping (bottom, left) and EDS spectrum (bottom, right) of PUA-Ni-4 aerogels prepared with TIPM/Ni molar ratio 1/3.



Figure S63. (a) SEM image, (b) X-Ray mapping and (c) EDS spectrum of PUA-Ni-12 aerogels prepared with TIPM/Ni molar ratio 1/1.5.



Figure S64. Optical photograph and SEM images (top), X-Ray mapping (bottom, left) and EDS spectrum (bottom, right) of PUA-Cu-4 aerogels prepared with TIPM/Cu molar ratio 1/3.



Figure S65. Corresponding EDS spectrum of Figure 28 of PUA-Cu-4 aerogels prepared with TIPM/Cu molar ratio 1/0.5.



Figure S66. (a)SEM image, (b) X-Ray mapping and (c) EDS spectrum of PUA-Cu-12 aerogels, synthesized with TIPM/Cu (mol/mol): 1/1.5.



Figure S67. PXRD pattern of PUA-Fe-4 aerogels prepared with TIPM/Cu molar ratio 1/1.5.

#### Fitting of material properties











PUA-Cr



 $z=-141.08x_{1}^{2}-40.83x_{1}x_{2}+41.14x_{1}-1.69x_{2}+515.94$ R<sup>2</sup>=0.46

**PUA-Co** 

**PUA-Cu** 



 $z= -79.63x_1^2 + 10.07x_1x_2 + 1.69x_1 + 2.64x_2 + 436.45$ R<sup>2</sup>=0.96

PUA-Ni



Figure S68. Fitting BET surface area of native PUA and PUA-M and aerogels to the two exploratory variables  $x_1$  (TIPM/M mol/mol) and  $x_2$  (monomer concentration, %w/w) according to Equation 7. Red and pink dots indicate points above and below, respectively, the predicted value.





PUA-Co



Figure S69. Fitting log( $V_{Total}/V_{1.7-300nm}$ ) of native PUA and PUA-M and aerogels to the two exploratory variables  $x_1$  (TIPM/M mol/mol) and  $x_2$  (monomer concentration, %w/w) according to Equation 7. Red and pink dots indicate points above and below, respectively, the predicted value.

#### PUA-aerogels using W and Mo compounds as catalysts

### N<sub>2</sub> sorption isotherms



Figure S70.  $N_2$ -sorption diagrams and pore size distributions using the BJH desorption method (insets) of PUA-WO aerogels, as indicated.



Figure S71. N<sub>2</sub>-sorption diagrams and pore size distributions using the BJH desorption method (insets) of PUA-HW aerogels, as indicated.



Figure S72.  $N_2$ -sorption diagrams of PUA-PAS aerogels, as indicated.



Figure S73. N<sub>2</sub>-sorption diagram of PUA-PW aerogels, as indicated.


Figure S74. N<sub>2</sub>-sorption diagrams and pore size distributions using the BJH desorption method (insets) of PUA-NaW aerogels, as indicated.



Figure S75.  $N_2$ -sorption diagrams and pore size distributions using the BJH desorption method (insets) of PUA-NaW aerogels, as indicated.



Figure S76.  $N_2$ -sorption diagram and pore size distribution using the BJH desorption method (inset) of PUA-HW aerogels, as indicated.



Figure S77.  $N_2$ -sorption diagrams and pore size distributions using the BJH desorption method (inset) of PUA-WCI aerogels, as indicated.





Figure S78. CO<sub>2</sub>-sorption isotherms (left) and pore size distributions using the DFT method (right) for PUA-4-HW aerogels, as indicated.



Figure S79. CO<sub>2</sub>-sorption isotherms (left) and pore size distributions using the DFT method (right) for PUA-10-PW aerogels, as indicated.



Figure S80. CO<sub>2</sub>-sorption isotherms (left) and pore size distributions using the DFT method (right) for PUA-35-NaW aerogels, as indicated.



Figure S81. CO<sub>2</sub>-sorption isotherms (left) and pore size distributions using the DFT method (right) for PUA-4-NHW aerogels, as indicated.



Figure S82. CO<sub>2</sub>-sorption isotherms (left) and pore size distributions using the DFT method (right) for PUA-20-WCI aerogels, as indicated.

SEM Images, X-Ray Mapping and EDS spectra



Figure S83. Corresponding EDS spectrum of Figure 51b, c and d.



Figure S84. N<sub>2</sub>-sorption diagrams and pore size distributions using the BJH desorption method (insets) of PUA-HMo aerogels, as indicated.



Figure S85. N<sub>2</sub>-sorption diagrams and pore size distributions using the BJH desorption method (insets) of PUA-NaMo aerogels, as indicated.

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