# Polydicyclopentadiene Aerogels Grafted with PMMA: I. Molecular and Interparticle Crosslinking

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## **Electronic Supplementary Information**

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# <u>Appendix I.</u> <sup>1</sup>H NMR and GC-MS controls for probing possible modes of crosslinking in **pDCPD-xx** and in **pDCPD-xx-X-MMA-yy** aerogels

#### **Figure S.1** dhDCPD + GC-II in toluene-d<sub>8</sub>

Shows that the cyclopentene ring of DCPD does not undergo ROMP even under much harsher conditions than those involved in the gelation and aging process of DCPD.

#### **Figure S.2** DCPD (low concentration) + **GC-II** in toluene- $d_8$

Shows that during ROMP of DCPD at low concentrations (corresponding to hypothetical **pDCPD-05** aerogels) the cyclopentene ring is not involved quantitatively in reaction.

#### **Figure S.3** DCPD (high concentration) + **GC-II** in toluene- $d_8$

Shows that during ROMP of DCPD at high concentrations (corresponding to the **pDCPD-30** aerogels) cyclopentene might be involved in reaction. (However, IR and solids <sup>13</sup>C NMR in Figures 4 and 5 of the main article, indicate that cyclopentene is not involved in reaction quantitatively. Hence, the extent of crosslinking is small.)

## **Figure S.4** and **Table S.1** DCPD + AIBN in benzene- $d_6$

Shows that all vinylic and allylic positions of DCPD are potential reaction cites in free radical reactions.

## Figure S.5 GC-MS analysis of the reaction mixture in Figure S.4

Due to overlap of aliphatic protons, products from the reaction probed in Figure S.4 are intractable by <sup>1</sup>H NMR. Hence, the reaction mixture at the end of the heating period in Figure S.4 was analyzed by GC-MS.

## **Figure S.6 and Table S.2** pNB + MMA + AIBN in benzene-d<sub>6</sub>

Control showing that under the free radical conditions used for the preparation of **pDCPD-xx-X-MMA-yy** aerogels, at least the skeletal double bonds formed via ROMP are engaged in the process. Engagement of the allylic positions is ambiguous from these data.



**Figure S.1** Liquid <sup>1</sup>H NMR as a function of time during attempted ROMP of a 30% w/w **dhDCPD** solution in toluene-d<sub>8</sub> at 70 °C using **GC-II** (0.025 mol% vs. **dhDCPD**). Spectrum at 0 h was taken before the addition of **GC-II**. Naphthalene (50% mol/mol vs. **dhDCPD**) was used as internal standard. Spectra were recorded using the same number of scans (4) and at the same attenuation. Peak assignment by simulation. Signal integration:

		U	5	<u> </u>	
reaction time (h)	vinyl : H <sub>a</sub>		allylic : H <sub>a</sub>		
	H <sub>8</sub> : H <sub>a</sub>	H <sub>9</sub> : H <sub>a</sub>	$H_{10a}$ : $H_a$	H <sub>5</sub> : H <sub>a</sub>	
0 h	0.52	0.52	0.50	0.50	
1 h	0.52	0.51	0.50	0.51	
2 h	0.52	0.51	0.51	0.52	
3 h	0.52	0.51	0.50	0.51	
12 h	0.52	0.51	0.50	0.51	



**Figure S.2** Liquid <sup>1</sup>H NMR as a function of time during ROMP of a <u>low-concentration</u> (5% w/w) DCPD solution in toluene-d<sub>8</sub> at room temperature using **GC-II** (0.05 mol% vs. DCPD) as catalyst. Bottom spectrum is before addition of **GC-II**. In the pDCPD structure on top, cyclopentene rings are shown unreacted, consistent with the surviving of resonances '8,9'. The *cis* and *trans* assignment for the backbone double bonds was based on R-S.1 and R-S.2.

- R-S.1. Vargas, J.; Martínez, A.; Santiago, A. A.; Tlenkopatchev, M. A.; Gaviño, R.; Aguilar-Vega, M. J. *Fluorine Chem.* **2009**, *130*, 162-168.
- R-S.2. Díaz, K.; Vargas, J.; Del Castillo, L. F.; Tlenkopatchev, M. A.; Aguilar-Vega, M. *Macromol. Chem. Phys.* 2005, 206, 2316-2322.



**Figure S.3** Liquid <sup>1</sup>H NMR as a function of time towards gelation via ROMP of a <u>high-concentration</u> (30% w/w) DCPD solution in toluene-d<sub>8</sub> at room temperature using **GC-II** (0.025 mol% vs. DCPD) as catalyst. Bottom spectrum is before addition of **GC-II**. With the passage of time, peaks become broader and their intensity decreases, consistent with polymerization. At the end, cyclopentene resonances '8,9' are either buried underneath the polymer resonance, or the 8,9 double bond has reacted. However, based on Figure S.1, that double bond is unreactive towards ROMP. Also, by IR (Figure 4 of the main article) at least some of the cyclopentene double bonds are to participate in crosslinking, that will have to be according to an olefin addition mechanism as suggested by Wagener (and shown in the structure above).



**Figure S.4** Liquid <sup>1</sup>H NMR of a 35% w/w DCPD solution in benzene-d<sub>6</sub> in the presence of AIBN (1:1 mol/mol vs. DCPD). Bottom spectrum is immediately after making the solution at room temperature and top spectrum is after heating the NMR tube at 80 °C for 10 h. Data summary and conclusions in Table S.1. GC-MS analysis after heating: Figure S.5.

reaction	norbornene vinyl : H <sub>4</sub>	cyclopentene vinyl : H <sub>4</sub>	norbornene allylic : H <sub>4</sub>		cyclopentene allylic : H <sub>4</sub>		ne 4
time (n)	$H_{1,2}: H_4$	$H_{8,9}: H_4$	$H_6$ : $H_4$	$H_3$ : $H_4$	$H_5$ : $H_4$	H <sub>10a</sub> : H <sub>4</sub>	$H_{10b}$ : $H_4$
0	1.96	2.00	0.97	0.98	0.96	1.00	b
2	1.49	1.56	0.89	0.85	0.90	1.41	b
4	1.45	1.55	0.86	0.84	0.86	1.41	b
10	1.44	1.55	0.87	0.87	0.88	1.45 <sup>c</sup>	b

Integration of <sup>1</sup>H NMR data of Figure S.4 above, as shown.<sup>a</sup> Table S.1

<sup>a</sup> <sup>1</sup>H NMR peak assignment according to R-S.3. Proton H<sub>4</sub> is well separated from everything else, and not prone to be involved in radical reactions as it is not in a vinylic, nor in an allylic position. Hence, it was used as an internal standard. As it can be seen from the integrals included in the spectra of Figure S.4, as well as from the data summarized in this Table, both double bonds as well as all allylic positions are prone to react. In fact, the vinylic positions are more prone to radical attack. Due to merging of aliphatic protons, product formation is intractable in the <sup>1</sup>H NMR of Figure S.4. Therefore, radical addition was confirmed with GC-MS (Figure S.5 below).

<sup>b</sup>  $H_{10b}$  could not be integrated as it merges with  $H_{7a}$ . <sup>c</sup> Ratio increases probably due to overlapping resonances from product protons.

R-S.3. Yang, Y.-S.; Lafontaine, E.; Mortaigne, B. J. Appl. Polym. Sci. 1996, 60, 2419-2435.



**Figure S.5** GC-MS analysis of the peak marked with the asterisk of the sample shown in Figure S.4 after the end of the heating period. The other peaks in the cluster show the same spectra with different peak intensities, most probably reflecting different isomers. Addition of the AIBN fragment across the double bond is observed directly (m/z=268). Allylic addition is inferred from the products of inverse Diels-Alder reaction (m/z=200 and m/z=131).



**Figure S.6** Liquid <sup>1</sup>H NMR of a 5% w/w polynorbornene (pNB) solution in benzene-d<sub>6</sub> in the presence of MMA (53% w/w vs. pNB) and AIBN (10% w/w vs. MMA). Bottom spectrum is immediately after making the solution at room temperature and top spectrum is after heating the solution in NMR tube at 80 °C for 10 h. Peak assignment according to R-S.1 and R-S.2.

**Table S.2** Integration <sup>1</sup>H NMR data of Figure S.6 above. Vinyl Hs are reacting.

time (h)	Vinyl Hs ( <i>cis+trans</i> ): allylic Hs (2 & 2')
0	0.89
2	0.83
4	0.81
10	0.79

# Appendix II. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) data

## Figure S.7 DSC of selected pDCPD aerogels

Glass transitions are observed for both **pDCPD-xx** and **pDCPD-xx-X-MMA-yy** aerogels, suggesting substantial linear character for both polymeric components (pDCPD and PMMA). First and second heating cycles are shown. Inset Table summarizes the data.

## Figure S.8 DSC of selected pNB aerogels

As expected, glass transitions are observed for all formulations of this linear polymer.

Figure S.9 TGAs are shown for the pDCPD-30 and all pDCPD-30-X-MMA-yy aerogels in air and under  $N_2$ 

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**Figure S.7** DSC data under  $N_2$  (see Experimental section) for selected pDCPD aerogels. Exotherms between 100-200 °C in the first heating cycles are due to crystallization. The exotherm in the second heating cycle of **pDCPD-30** is associated with decomposition (see also TGA data in Figure S.9 [R-S.3]. The glass transition at 77 °C is assigned to linear pDCPD [R-S.4] and it is taken as indication that the polymer is only partially crosslinked.

- R-S.3. Dimonie, D.; Dimonie, M.; Munteanu, V.; Iovu, H.; Couve, J.; Abadie, M. J. *Polymer Degradation and Stability* **2000**, *70*, 319-324.
- R-S.4 Abadie, M. J.; Dimonie, M.; Couve, C.; Dragutan, V. European Polymer Journal 2000, 36, 1213-1219.



Figure S.8 DSC data under  $N_2$  (see Experimental section) for selected pNB aerogels. Only the pNB-30(50:50) sample shows crystallization in the first heating cycle



**Figure S.9** TGA data for all pDCPD aerogels. (For experimental details see Experimental section.)

<u>Appendix III.</u> SEMs before and after compression (SHPB) of pDCPD-30-X-MMA-50 and of pNB-30(0:100) aerogels.



**Figure S.10** SEM of representative samples before and after compression testing as shown. pDCPD samples loose all their porosity, while pNB samples keep some porosity, but particles are flattened and fused.



Appendix IV. Gel permeation chromatography data for the pNB-30-(zz:ww) samples

**Figure S.11** GPC data of polynorbornene aerogels (A) and a polynorbornene wet-gel right after aging in the mold (B). (Polynorbornene wet-gels were made in toluene, hence the name: **pNB-30(100:0)**. For other pertinent information see Experimental section.) Peaks at low retention times (longer polymers) are cut off abruptly at around 5 min, because of the resolution of the column. Data analysis by fitting as shown by dotted lines. Data for the lower molecular weight polymer are summarized in Table S.3. (In (B), the black line shows the actual chromatogram, the red line is the fitted chromatogram and the red dashed line is the de-convoluted fitted chromatogram.)

sample	N	M <sub>n</sub>	$M_{_{W}}$	$M_{w}/M_{n}$
pNB-30(100:0) <sup>a</sup> wet-gel	192	2968	18047	6
pNB-30(50:50)	143	1023	13480	13
pNB-30(30:70)	112	1317	10567	8
pNB-30(10:90)	209	1681	19722	12

Table S.3 GPC data analysis by fitting the broad peak at higher retention times.

<sup>a</sup> Note, this sample (also shown in Figure S.11B) was made in toluene, which is a good solvent for pNB. Therefore, this was not a colloidal gel but rather a linear polymer gel (see Section 2.1 in the main article), readily soluble in larger amounts of toluene or THF.