Supporting Information

Exploration of the Versatility of Ring Opening Metathesis Polymerization: an Approach for Gaining Access to Low Density Polymeric Aerogels

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Synthesis of cyclic olefin monomers

Norbornene-based crosslinker (2)

The norbornene-based crosslinker, 1,4-di(*exo*-bicyclo[2.2.1]hept-5-en-2-yl)benzene (**2**), was prepared as previously reported (Scheme 1a).[1] Purification was carried out by column chromatography (ethyl acetate/hexanes) followed by re-crystallization in ethyl acetate.

Norbornene monomers with a different length of alkyl groups (4-7)

Several norbornene monomers with a different length of alkyl group were prepared similarly to the synthesis of 5-methoxymethylbicyclo[2.2.1]hept-2-ene (**4**) (Scheme 1b).[2,3] Norbornene-based monomers **5-7** were synthesized by reacting 5-norbornene-2-methanol (**3**) with the corresponding alkyl halide in the presence of sodium hydride. Purification of monomers was carried out by extraction followed by silica gel flash column chromatography.

The synthesis of the hexyl modified norbornene monomer (**5**) was carried out by alkylating the diastereomeric mixture of norbornene alcohol **3** (2.11 g, 16.9 mmol, 1.40 equiv.) with 1-bromohexane (2.00 g, 1.70 mL, 12.1 mmol, 1.00 equiv.) in the presence of 95% NaH (0.88 g, 34.5 mmol, 2.85 equiv.) in anhydrous THF (50 mL) at 0°C. The suspension was refluxed at 90°C for 48 hours, at the end of which time the mixture was cooled to ambient temperature and partitioned between 1 M HCl (200 mL) and ethyl ether (300 mL). The organic phase was washed with saturated $NaHCO_3$ (200 mL), brine (200 mL), and water (200 mL), dried ($MgSO_4$), and evaporated *in vacuo* to give a crude mixture. The mixture was purified by flash column chromatography on silica gel (hexanes → 2:8 ethyl acetate:hexanes) to furnish the *n*-hexyl norbornene adduct **5** as a colorless liquid. R_f = 0.93 (ethyl acetate:hexanes 2:8); ^{1}H-NMR (600 MHz in $CDCl_3$): δ 6.14-5.94 (m, 4H), 3.49-3.31 (m, 6H), 3.16-3.13 (m, 1H), 3.02 (t, J = 9.2

Hz, 1H), 2.93-2.76 (m, 4H), 2.35 (br s, 1H), 1.85-1.81 (m, 1H), 1.70-1.58 (m, 1H), 1.62-1.54 (m, 4H), 1.45-1.42 (m, 1H), 1.39-1.23 (m, 16H), 1.14-1.10 (m, 1H), 0.91 (t, J = 7.1 Hz, 6H), 0.52-0.49 (m, 1H).

The synthesis of the dodecyl-modified norbornene monomer **6** was carried out by alkylating norbornene alcohol **3** (3.00 g, 24.2 mmol, 1.40 equiv.) with 1-bromododecane (4.30 g, 17.3 mmol, 1.00 equiv.) in the presence of 95% NaH (0.87 g, 72.6 mmol, 3.99 equiv.) in anhydrous THF (70 mL) at 0°C. The suspension was refluxed at 90°C for 48 hours, at the end of which time the mixture was cooled to ambient temperature and partitioned between 1 M HCl (200 mL) and ethyl ether (300 mL). The organic phase was washed with saturated $NaHCO_3$ (200 mL), brine (200 mL), water (200 mL), dried ($MgSO_4$), and evaporated *in vacuo* to give a crude mixture. The mixture was purified by flash column chromatography on silica gel (hexanes → 1:9 ethyl acetate:hexanes) to furnish the dodecyl norbornene adduct **6** as a colorless liquid (3.02 g, 60%). R_f = 0.89 (ethyl acetate:hexanes 1:9); ^{1}H-NMR (600 MHz in $CDCl_3$): δ 6.11-5.93 (m, 4H), 3.50-3.30 (m, 6H), 3.13-3.01 (m, 2H), 2.91-2.74 (m, 4H), 2.34 (br s, 1H), 1.85-1.81 (m, 1H), 1.68 (br s, 1H), 1.60-1.52 (m, 4H), 1.45-1.10 (m, 42H), 0.88 (t, J = 7.1 Hz, 6H), 0.52-0.46 (m, 1H).

In a similar fashion, the synthesis of the benzyl modified norbornene monomer **7** was carried out by alkylating **3** (2.16 g, 17.4 mmol, 1.20 equiv.) with benzyl bromide (3.00 g, 17.5 mmol, 1.00 equiv.) in the presence of 95% NaH (0.67 g, 27.8 mmol, 1.50 equiv.) in anhydrous THF (30 mL) at 0°C. The suspension was refluxed at 90°C for 48 hours, at the end of which time the mixture was cooled to ambient temperature and partitioned between 1 M HCl (200 mL) and ethyl ether (300 mL). The organic phase was washed with saturated $NaHCO_3$ (200 mL), brine (200 mL), water (200 mL), dried ($MgSO_4$), and evaporated *in vacuo* to give a crude mixture. The mixture was purified by flash column chromatography on silica gel (hexanes → 2:8 ethyl acetate:hexanes) to furnish the benzyl norbornene adduct **7** as a colorless liquid (1.50 g, 40%). R_f = 0.25 (hexanes only); ^{1}H-NMR (600 MHz in $CDCl_3$): δ

7.39-7.31 (m, 10H), 6.15-5.91 (m, 4H), 4.57-4.51 (m, 4H), 3.56-3.09 (m, 4H), 2.99 (br s, 1H), 2.81 (br s, 3H), 2.43 (br s, 1H), 1.87-1.83 (m, 1H), 1.46-1.16 (m, 6H), 0.53-0.51 (m, 1H).

Tosyl- and Iodo-Norbornene monomers (8, 9, 11, and 12)

Iodo-norbornene monomers were prepared and used as a typical example of functional co-monomers. The synthesis of the iodo-norbornene monomers was accomplished by initially tosylating the corresponding norbornene alcohol in the presence of 4-(dimethylamino)pyridine (DMAP) followed by tosyl displacement using sodium iodide.[4-6]

For the synthesis of the tosyl modified norbornene monomer (**8**), the norbornene alcohol **3** (3.00 g, 24.2 mmol, 1.20 equiv.) and DMAP (5.90 g, 48.4 mmol, 2.40 equiv.) were dissolved in dichloromethane (50 mL) and cooled to 0 °C. *p*-Toluenesulfonyl chloride (TsCl, 3.84 g, 20.2 mmol, 1.00 equiv.) was slowly added to the flask over 30 min and stirred at 0 °C for 1 h. The mixture was warmed to room temperature and stirred for 2 days. At the end of reaction, the salt was filtered out, and the filtrate was partitioned between 1 M HCl (200 mL) and ethyl ether (300 mL). The organic phase was washed with saturated $NaHCO_3$ (200 mL), brine (200 mL), water (200 mL), dried ($MgSO_4$), and evaporated *in vacuo* to give a crude mixture. The mixture was purified by flash column chromatography on silica gel (hexanes → 4:6 ethyl acetate:hexanes) to furnish the tosyl norbornene adduct **8** as a colorless liquid (3.90 g, 70%), which then slowly solidified to a white solid upon cooling. R_f = 0.41 (1:9 ethyl acetate:hexanes); ^{1}H-NMR (600 MHz in $CDCl_3$): δ 7.83-7.80 (m, 4H), 7.38-7.36 (m, 4H), 6.12-5.71 (m, 4H), 4.12-3.58 (m, 4H), 2.45 (br s, 6H), 2.40 (br s, 1H), 1.83-1.79 (m, 1H), 1.75 (br s, 1H), 1.46-1.08 (m, 6H), 0.48-0.45 (m, 1H).

For the synthesis of the iodo-norbornene monomer **9**, The acquired tosyl norbornene monomer **8** (1 g, 3.59 mmol, 1.00 equiv.) was dissolved in dry acetone (20 mL) and treated with NaI (0.97 g, 6.5 mmol,

1.80 equiv.). The resulting suspension was refluxed at 70 °C overnight. The following day, the mixture was cooled to room temperature, and the salt was filtered out. The filtrate was dissolved in ether, washed with aqueous sodium thiosulfate (0.2 M, 200 mL), water (200 mL), brine (200 mL), and dried over $MgSO_4$. The mixture was purified by flash column chromatography on silica gel (hexanes) to furnish the iodo-norbornene adduct **9** as a colorless liquid (0.30 g, 36%). R_f = 0.77 (hexanes); ^{1}H-NMR (600 MHz in $CDCl_3$): δ 6.26-6.02 (m, 4H), 3.26-3.24 (m, 2H), 3.03-2.75 (m, 6H), 2.56 (br s, 1H), 2.04-1.92 (m, 2H), 1.53-1.19 (m, 6H), 0.62-0.60 (m, 1H).

As a practical way to double the number of chemical functionalities in one monomer, the dimethanol norbornene monomer **10** was used to synthesize the bis-tosylated norbornene monomer **11**. For the synthesis of **11**, 5-norbornene-2-exo,3-exo-dimethanol (**10**) (5.00 g, 32.4 mmol, 1.0 equiv.) and DMAP (15.84 g, 129.6 mmol, 4.0 equiv.) were dissolved in dichloromethane (150 mL) and cooled to 0 °C. Tosyl chloride (TsCl, 18.53 g, 97.2 mmol, 3.0 equiv.) was slowly added to the flask over 30 min and stirred at 0 °C for 1 h. The mixture was warmed to room temperature and stirred for 2 days. At the end of the reaction, the salt was filtered out. Additional DCM (200 mL) and 1 M HCl (200 mL) were added to the residue and partitioned. The DCM layer was washed with saturated $NaHCO_3$ (200 mL), brine (200 mL), and water (200 mL), dried ($MgSO_4$), and evaporated *in vacuo* to yield a residue. The residue was taken up in diethyl ether and the resulting precipitate was washed copiously with ether and dried in a vacuum oven overnight. The bis-tosylated adduct **11** was obtained as a white powder and used without further purification. ^{1}H-NMR (600 MHz in $CDCl_3$): δ 7.80 (d, J = 8.3 Hz, 4H), 7.39 (d, J = 7.9, 4H), 6.13 (s, 2H), 4.11-3.89 (m, 4H), 2.71 (s, 2H), 2.49 (br, 6H), 1.86 (br s, 2H), 1.31 (s, 2H).

For the synthesis of the bisiodo-norbornene monomer **12**, bis-tosylated compound **11** (1.40 g, 3.0 mmol, 1.0 equiv.) was dissolved in dry acetone (30 mL) and treated with NaI (1.82 g, 12.1 mmol, 4.0 equiv.). The resulting suspension was refluxed at 70 °C for two days at the end of which time, the

mixture was cooled to room temperature, and concentrated under reduced pressure. The residue was dissolved in ether, washed with aqueous sodium thiosulfate, water, brine, and dried over $MgSO_4$. The mixture was purified by flash column chromatography on silica gel (hexanes) to furnish the bisiodo-norbornene adduct **12** as a colorless liquid (0.82 g, 73%). R_f = 0.50 (hexanes); ^{1}H-NMR (600 MHz in $CDCl_3$): δ 6.22 (br s, 2H), 3.59-3.56 (m, 2H), 3.07-3.04 (m, 4H), 2.07-2.06 (m, 2H), 1.45 (d, J = 9.4 Hz, 1H), 1.38 (d, J = 9.4 Hz, 1H).

Procedure to Determine Molar Ratios of NB-R to DCPD in Copolymer Gels

From the assumption of the chemical structure of P(DCPD-*r*-**12**) (Fig. 5c), the RBS result is related to the composition of sample, as follows:

$$\frac{N_C}{N_I} = \frac{10 \times x + 10 \times (1-x) + 9a'}{2a'} = \frac{C_{RBS,C}}{C_{RBS,I}} \quad (1)$$

$$a' = \frac{10}{\left(2 \times \frac{C_{RBS,C}}{C_{RBS,I}} - 9\right)} = \frac{10}{\left[2 \times \frac{(100 - C_{RBS,I}) \times \frac{10}{22}}{C_{RBS,I}} - 9\right]} \quad (2)$$

$$\frac{m_{NB-R,12}}{m_{DCPD}}(\%) = \frac{a' \times 374.0}{1 \times 132.2} \times 100 \quad (3)$$

where N_i is the number of the specific atom in the polymer; x is the degree of crosslinking; a and a' are the molar ratios of NB-R to DCPD, in the precursor solution and polymer gels, respectively; $C_{RBS,i}$ is the concentration of the specific atom measured by RBS; and the ratio of $m_{NB\text{-}R,\mathbf{12}}$ to m_{DCPD} is the normalized value of NB-R to DCPD by weight. The iodine concentrations in P(DCPD-*r*-**12**) (100/20) and (100/100) samples were determined to be about 0.63 and 1.90 (at.%), respectively. From the combined calculation with eq. 1 to eq. 3, the compositions, a', in polymers were determined to be about

0.074 and 0.26 for P(DCPD-*r*-**12**) (100/20) and (100/100), respectively. These values correspond to (100/21) and (100/75) by weight, respectively.

Table S1 Gelation time of P(DCPD-*r*-NB-R) gels

Monomers	Ratio of DCPD to NB-R co-monomer[a]			
	100:10	100:20	100:30	100:40
DCPD+**4**	4 h	N/A	N/A	N/A
DCPD+**5**	2 h	4h	4 h	4 h
DCPD+**6**	3 h	1 d	1 d	1d
DCPD+**7**	2 h	19 h	N/A	N/A
DCPD+**8**	1 h	3 h	3 h	3 h
DCPD+**9**	1 h	1 d	1 d	1 d
DCPD+**12**	45 min	2 h	2 h	3 h

[a] The gelation time of a solution of DCPD and NB-R in toluene at 50 mg/cc was determined by tilting or shaking the vial, and the sample with a gel time longer than 2 days was notified as N/A.

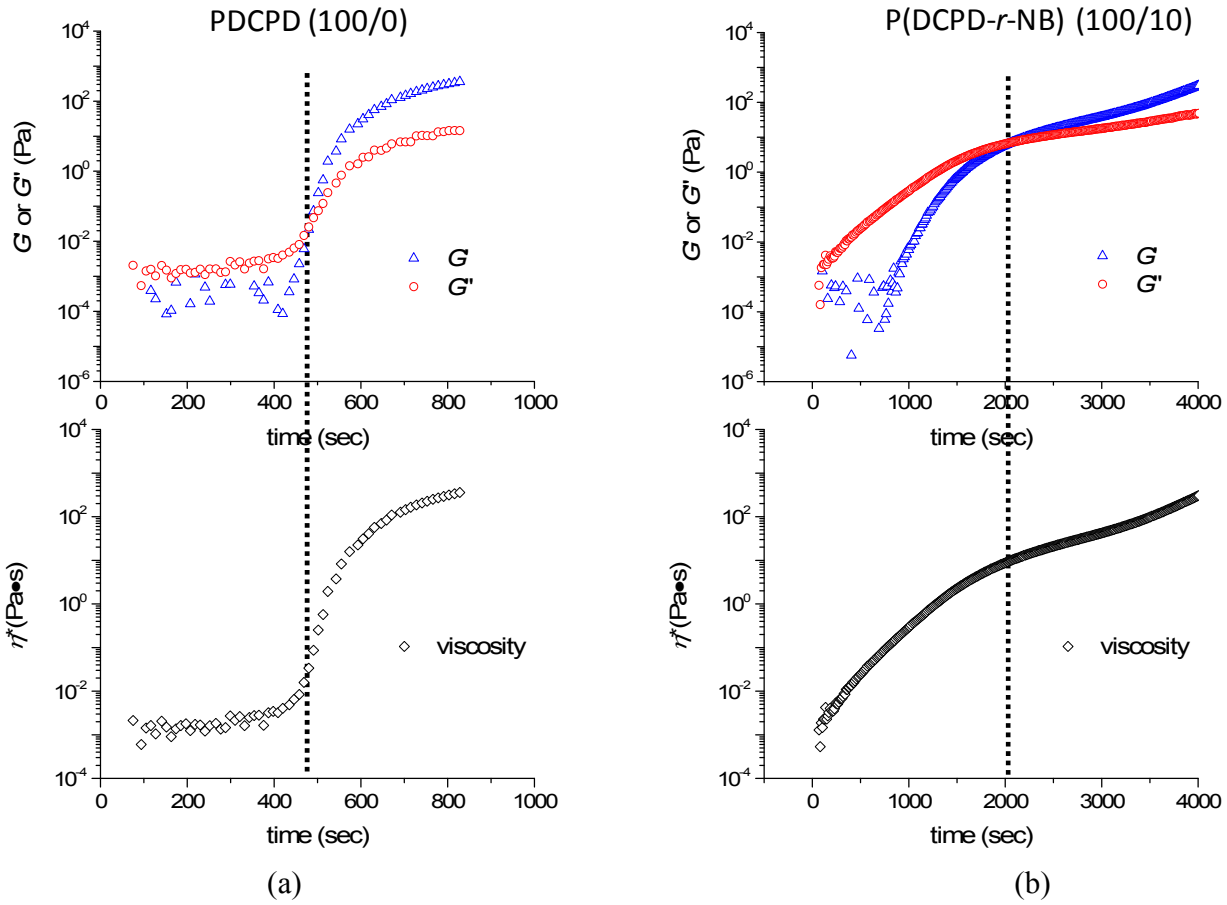
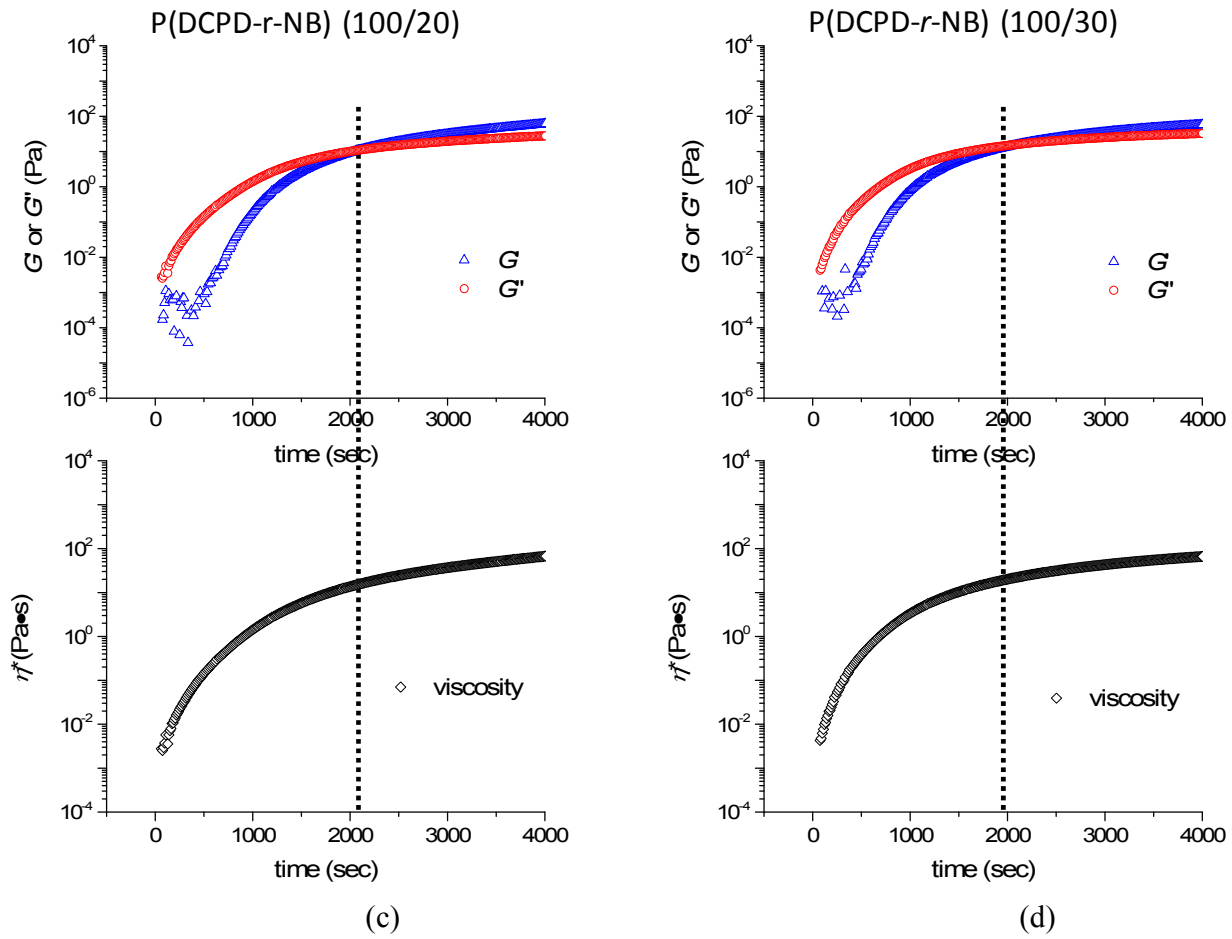
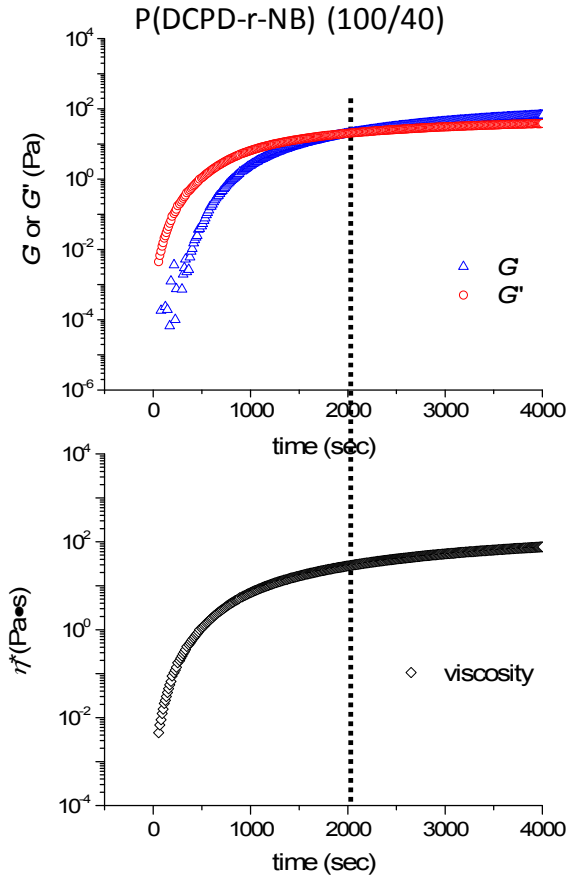


Fig. S1 (continued)



(c) (d)

Fig. S1 (continued)



(e)

Fig. S1 Plots of storage shear modulus, G', loss shear modulus, G'', and complex viscosity, η^* for P(DCPD-r-NB) (100/x) (wt/wt) samples with a different NB ratio, x, of (a) 0, (b) 10, (c) 20, (d) 30, and (d) 40.

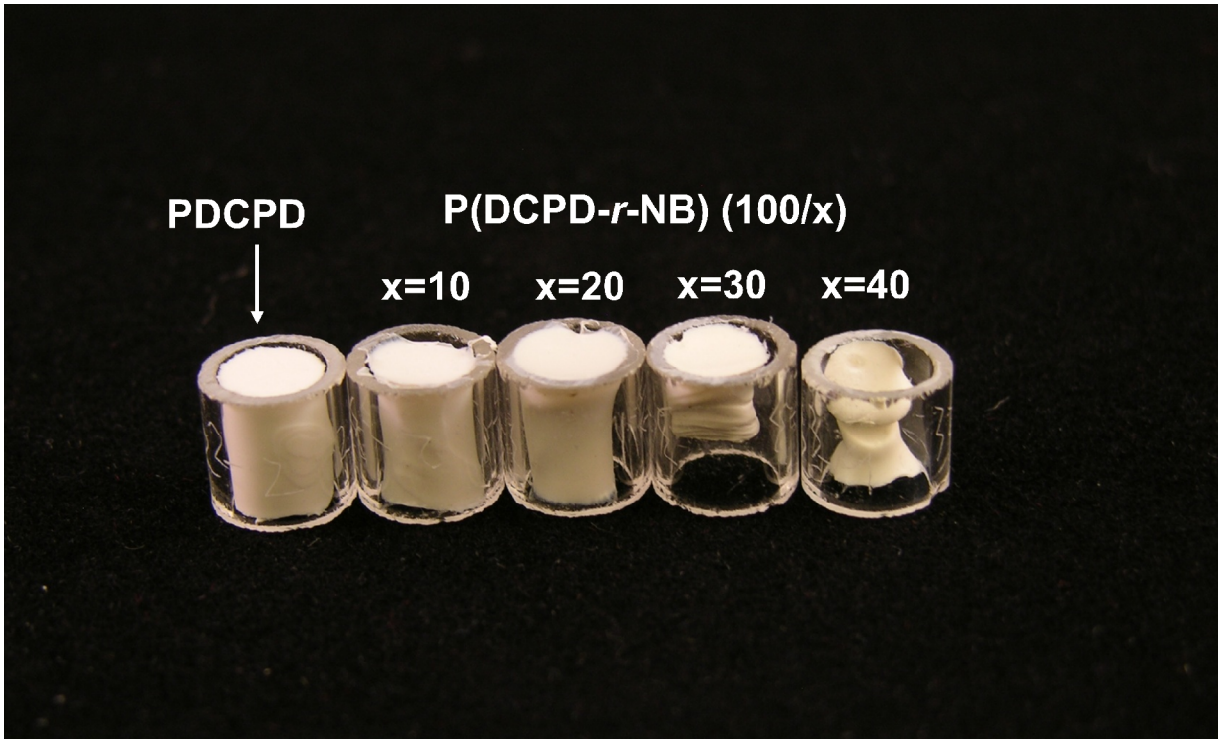


Fig. S2 Photos of dried P(DCPD-*r*-NB) (100/*x*) (wt/wt) aerogels with a different NB ratio, *x*, of 0 to 40. Wet gels are prepared in a glass mold (with a diameter×height of ~ 6 mm×8 mm), placed into an acetone bath for 2-3 days and dried using supercritical CO_2 drying technique.

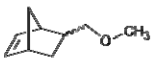
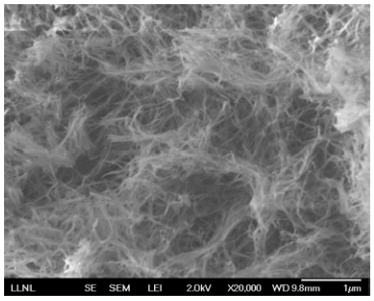
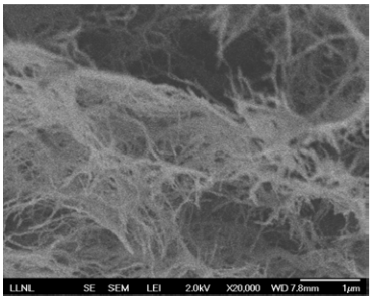
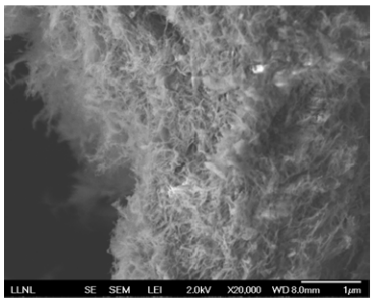
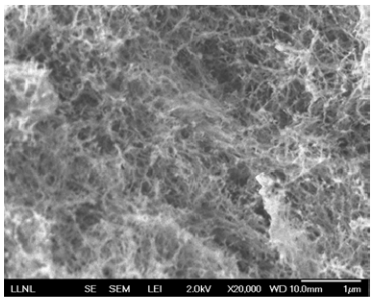
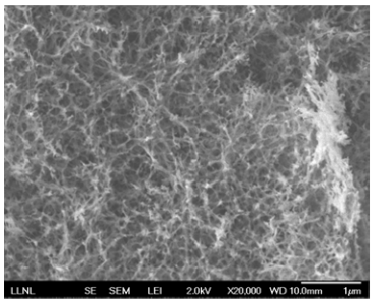
Ratio of DCPD to NB-R (w/w)	(a) DCPD + NB	(b) DCPD +  **4**
100:10		
100:20		N/A
100:30		N/A
100:40		N/A

Fig. S3. (continued)

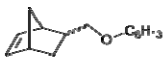
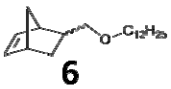
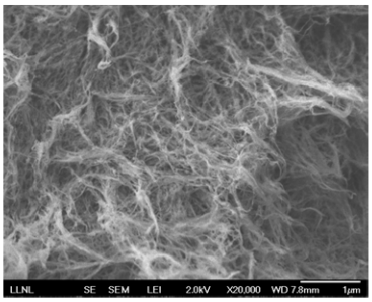
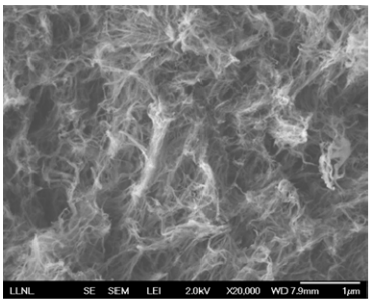
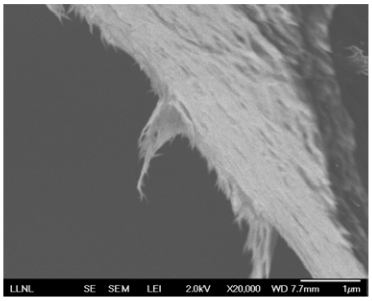
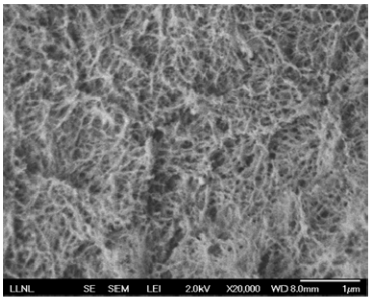
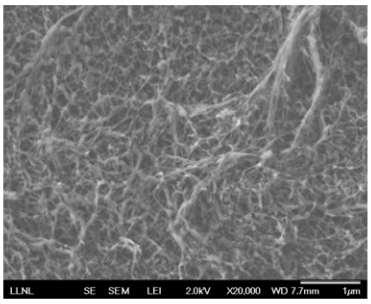
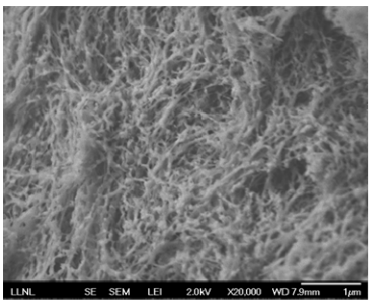
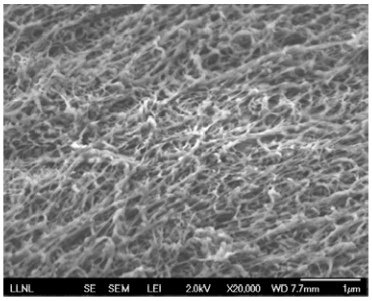
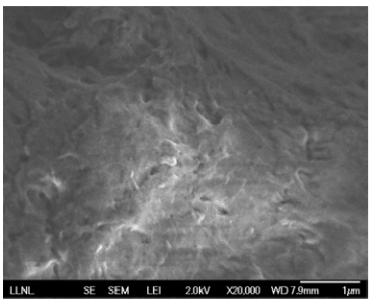
Ratio of DCPD to NB-R (w/w)	(c) DCPD +  5	(d) DCPD +  6
100:10		
100:20		
100:30		
100:40		

Fig. S3 (continued)

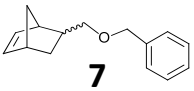
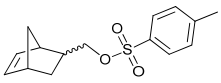
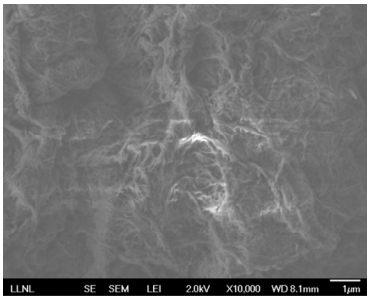
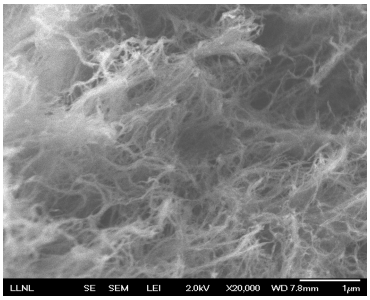
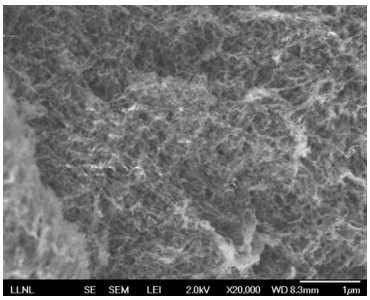
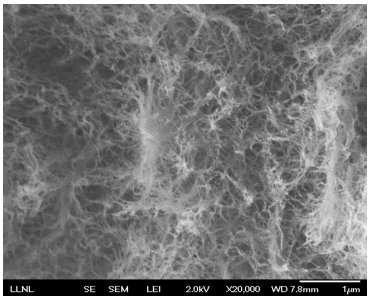
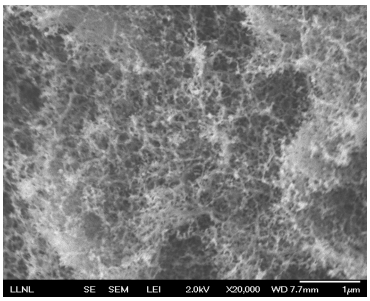
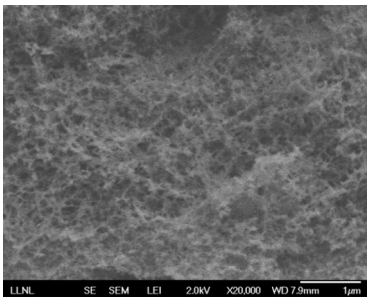
Ratio of DCPD to NB-R (w/w)	(e) DCPD +  **7**	(f) DCPD +  **8**
100:10		
100:20		
100:30	N/A	
100:40	N/A	

Fig. S3 (continued)

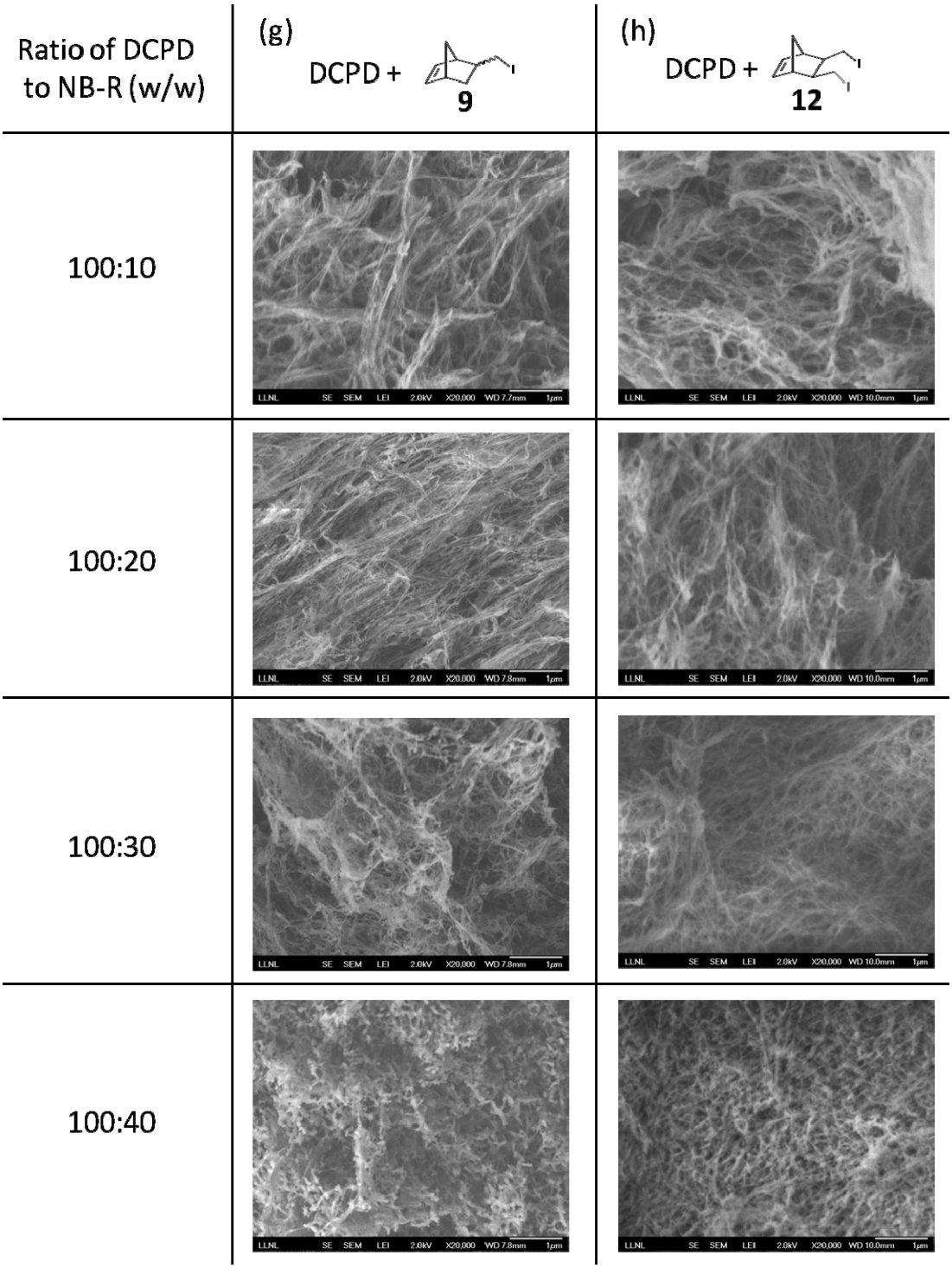


Fig. S3 Morphologies of P(DCPD-*r*-NB-R) aerogels prepared from a mixture of DCPD with a different composition of co-monomer such as (a) NB, (b) **4**, (c) **5**, (d) **6**, (e) **7**, (f) **8**, (g) **9**, and (h) **12**.

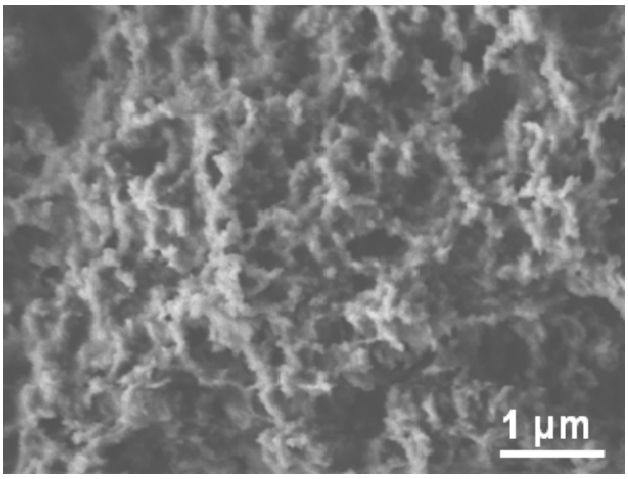


Fig. S4 SEM image of the aerogel prepared from norbornene-based crosslinker **2**.

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