Electronic Supplementary Information

Facile Synthesis of Soluble Nonlinear Polymers with Glycogen-Like Structures and Functional Properties from "Simple" Acrylic Monomers

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Synthesis and Characterization

The synthetic procedures for monomer **1**, **2** and **3** are shown in Scheme 1. Detailed experimental procedures are given below.

1,1-Bis(4-acryloyloxyphenyl)-2,2-diphenylethene (1) and 1,1,2,2-Tetra(4-acryloyloxyphenyl)ethene (3). Into a 500 mL two-necked round-bottom flask with a reflux condenser were placed 7.17 g (109.7 mmol) of zinc dust. The flask was evacuated under vacuum and flushed with dry nitrogen three times. Then, 80 mL of THF was added. The mixture was cooled to −78 °C and 6.03 mL (54.9 mmol) of $TiCl_4$ was slowly added. The mixture was slowly warmed to room temperature, stirred for 0.5 h and then refluxed for 2.5 h. The mixture was again cooled to −5–0 °C, charged with 1.20 mL of pyridine and stirred for 10 min. Then, 40 mL of THF solution of 5.87 g (27.4 mmol) of 4,4'-dihydroxylbenzophenone and 5.00 g (27.4 mmol) of benzophenone was added slowly. The mixture was refluxed overnight. The reaction was quenched with 10% aqueous K_2CO_3 solution. The mixture was extracted with dichloromethane three times and the collected organic layer was washed by brine twice.

The mixture was dried over anhydrous Na_2SO_4. After filtration and solvent evaporation, the crude product was purified by silica gel chromatography using petroleum ether/ethyl acetate (4:1 v/v) as eluent to give **6** and **7**.

To a solution of compound **6** and 5 mL of triethylamine in 30 mL of THF at −30 °C, 4.43 mL (54.8 mmol) of acryloyl chloride was added dropwise over 20 min. After stirring the mixture for 2 h, the reaction mixture was concentrated under vacuum. The residue was dissolved in ethyl acetate and the resulting solution was washed with water and brine, dried with Na_2SO_4 and concentrated. The crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (4:1 v/v) as eluent to give 4.21 g (overall yield 33%) of **1** as white solid. IR (KBr), υ (cm^{-1}): 3052 (w, CH_2=CH), 1738 (s, C=O), 1634, 1598, 1501, 1403, 1294, 1248, 1202, 1155, 982, 900. ^1H NMR (300 MHz, CD_2Cl_2), δ (TMS, ppm): 7.14 (m, 6H, Ar–H), 7.06 (m, 8H, Ar–H), 6.90 (m, 4H, Ar–H), 6.52 (dd, 2H, CH_2=C–H), 6.25 (dd, 2H, CH=CH–H), 5.96 (dd, 2H, CH=CH–H). ^{13}C NMR (75 MHz, CD_2Cl_2), δ (TMS, ppm): 164.83, 149.77, 144.05, 141.66, 139.65, 132.83, 131.69, 128.45, 128.35, 127.19, 121.38. HRMS (MALDI-TOF): *m*/*z* 472.2757 (M^+, calcd 472.1675).

Monomer **3** was prepared from compound **7** and 4.43 mL (54.8 mmol) of acryloyl chloride. The procedures were similar to those for monomer **1**. White solid; overall yield 10% (0.86 g). IR (KBr), υ (cm^{-1}): 3079 (w, CH_2=CH), 1736 (s, C=O), 1655, 1597, 1500, 1401, 1307, 1256, 1213, 1167, 1022, 981, 932, 904, 852, 801, 762. ^1H NMR (300 MHz, CD_2Cl_2), δ (TMS, ppm): 7.87 (d, 8H, Ar–H), 7.29 (d, 8H, Ar–H), 6.63 (dd, 4H, CH_2=C–H), 6.35 (dd, 4H, CH=CH–H), 6.07 (dd, 4H, CH=CH–H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 163.98, 153.85, 134.98, 133.35, 131.60, 127.54, 121.57.

1,2-Bis(4-acryloyloxyphenyl)-1,2-diphenylethylene (2). Into a 250 mL two-necked round-bottom flask with a reflux condenser were placed 5.00 g (25.2 mmol) of 4-hydroxylbenzophenone and 3.30 g (50.4 mmol) of zinc dust. The flask was evacuated under vacuum and flushed with dry nitrogen for three times. Then, 100 mL of THF was added. The mixture was cooled to −78 °C and 2.77 mL (25.2 mmol) of $TiCl_4$ was added dropwise by a syringe. The mixture was slowly warmed to room temperature, stirred for 0.5 h and then refluxed for 24 h. The reaction was quenched with 10% aqueous K_2CO_3 solution and the resulting mixture was filtered. The filtrate was extracted with dichloromethane three times and the organic layer was washed with water and dried over Na_2SO_4. After filtration and solvent evaporation, the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (4:1 v/v) as eluent to give **9** as white solid.

Using the same procedures described above, monomer **2** was prepared from compound **9**, 5.28 mL (37.9 mmol) of triethylamine and 2.55 mL (31.6 mmol) of acryloyl chloride in 30 mL of THF solution. White solid; overall yield 38% (2.28 g). IR (KBr), υ (cm^{-1}): 3053 (w, CH_2=CH), 1734 (s, C=O), 1505, 1405, 1252, 1204, 1167. ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.12 (m, 6H, Ar–H), 7.03 (m, 8H, Ar–H), 6.90 (m, 4H, Ar–H), 6.57 (d, 2H, CH_2=C–H), 6.27 (q, 2H, CH=CH–H), 5.98 (d, 2H, CH=CH–H). HRMS (MALDI-TOF): *m*/*z* 472.3200 (M^+, calcd 472.1675).

All the polymerization reactions and manipulations were carried out under nitrogen using Schlenk techniques in a vacuum-line system except for the purification of the resulting polymers, which was done in an open atmosphere. Typical experimental procedures for the polymerization of monomer **1** in THF using azobisisobutyronitrile as initiator are given below as an example. In a 20-mL Schlenk tube with a side arm was placed 50 mg of monomer **1** and 10 mg of azobisisobutyronitrile. The tube was evacuated under vacuum and then flushed with nitrogen three times through the side arm. 1 mL of THF was then injected. The reaction mixture was stirred and refluxed under nitrogen for 10 h. The resulting mixture was diluted with 2 mL of THF and added dropwise through a cotton filter to 200 mL methanol under stirring. The precipitate was allowed to stand for 24 h and then filtered with a Gooch crucible. The polymer was washed with methanol three times and dried in a vacuum oven at 40 ^{o}C to a constant weight. A white powder was obtained in 97% yield. P**1**: White solid; yield 97%. M_w 87100; M_w/M_n 6.11 (Table 1, no.2). IR (KBr), υ (cm^{-1}): 2962, 1755, 1597, 1501, 1200, 1164, 1137. ^{1}H NMR (300 MHz, CD_2Cl_2), δ (TMS, ppm): 7.12, 7.03, 6.85, 3.81, 3.68, 2.60, 1.98, 1.82. ^{13}C NMR (75 MHz, CD_2Cl_2), δ (TMS, ppm): 149.98, 144.08, 141.44, 132.74, 131.67, 128.35, 127.16, 121.45, 68.17, 31.74, 31.21, 26.14. P**2**: White solid; yield 99%. M_w 19600; M_w/M_n 4.25 (Table 4, no. 2). IR (KBr), υ (cm^{-1}): 2932, 1755, 1505, 1200, 1165. ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.08, 7.01, 6.91, 6.83, 6.81, 3.86, 3.71, 2.62, 1.88. P**3**: White solid; yield 99%. M_w 33400; M_w/M_n 6.05 (Table 4, no. 4). IR (KBr), υ (cm^{-1}): 2960, 1759, 1658, 1598, 1502, 1277, 1203, 1159, 930, 760. ^{1}H NMR (300 MHz, CD_2Cl_2), δ (TMS, ppm): 7.81, 7.69, 7.21, 3.83, 3.71, 2.78, 2.67, 1.90. ^{13}C NMR (75 MHz, CD_2Cl_2), δ (TMS, ppm): 194.49, 174.01, 172.22, 171.36, 162.79, 154.45, 135.37, 132.00, 122.18, 78.58, 68.22, 36.75, 31.89, 31.75, 31.17, 26.31.

The procedures for the polymerization of **1** in toluene were similar to those carried out in THF. The reaction was carried out under nitrogen for 1 h to avoid gelation and added into hexane under stirring for precipitation of the polymeric products. White powder; yield 82%. M_w 1000; M_w/M_n 1.14. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.18, 7.11, 7.02, 6.89, 6.55, 6.26, 5.97, 1.87.

Oligo(phenyl acrylate) was prepared from 100 mg of phenyl acrylate and 3 mg of azobisisobutyronitrile in reflux THF for 24 h using similar procedures as described above. No precipitates were obtained when the mixture was precipitated into hexane. After solvent evaporation, the residue was dried in a vacuum oven. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.36, 7.22, 7.08, 3.95, 3.87, 2.97, 2.73, 1.94.

Table S1. Crystal data and structure refinement for compound **1**.

Empirical formula	$C_{32}H_{24}O_4$
Formula weight	472.51
Temperature	173(2) K
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 8.9570(2) Å = 80.558(2)^{o}.
	b = 11.1473(3) Å = 89.540(2)^{o}.
	c = 12.7782(4) Å = 86.557(2)^{o}.
Volume	1256.30(6) Å^{3}
Z	2
Density (calculated)	1.249 mg/m^{3}
Absorption coefficient	0.654 mm^{-1}
F(000)	496
Crystal size	0.40 × 0.35 × 0.32 mm^{3}
Theta range for data collection	3.51 to 67.46^{o}.
Index ranges	-10<=h<=8, -13<=k<=13, -15<=l<=15
Reflections collected	11051
Independent reflections	4445 [R(int) = 0.0371]
Completeness to theta = 66.50^{o}	98.1%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00 and 0.82
Refinement method	Full-matrix least-squares on F^{2}
Data / restraints / parameters	4445/0/345
Goodness-of-fit on F^{2}	1.046
Final R indices [I>2sigma(I)]	R1 = 0.0375, wR2 = 0.1020
R indices (all data)	R1 = 0.0423, wR2 = 0.1048
Largest diff. peak and hole	0.185 and -0.186 e.Å^{-3}

Table S2. Crystal data and structure refinement for compound *E*–**2**.

Empirical formula	$C_{32}H_{24}O_4$
Formula weight	472.51
Temperature	173(2) K
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 9.5026(11) Å = 98.109(7)^{o}.
	b = 12.2523(14) Å = 110.976(8)^{o}.
	c = 12.4543(8) Å = 105.891(10)^{o}.
Volume	1255.2(2) Å^{3}
Z	2
Density (calculated)	1.250 mg/m^{3}
Absorption coefficient	0.655 mm^{-1}
F(000)	496
Crystal size	0.40 × 0.30 × 0.04 mm^{3}
Theta range for data collection	3.94 to 67.48^{o}.

Index ranges	-11<=h<=11, -14<=k<=14, -11<=l<=14
Reflections collected	6598
Independent reflections	4371 [R(int) = 0.0285]
Completeness to theta = 66.50°	96.6%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00 and 0.75
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4371/0/324
Goodness-of-fit on F^2	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0505, wR2 = 0.1425
R indices (all data)	R1 = 0.0637, wR2 = 0.1498
Largest diff. peak and hole	0.306 and -0.330 e.Å^{-3}

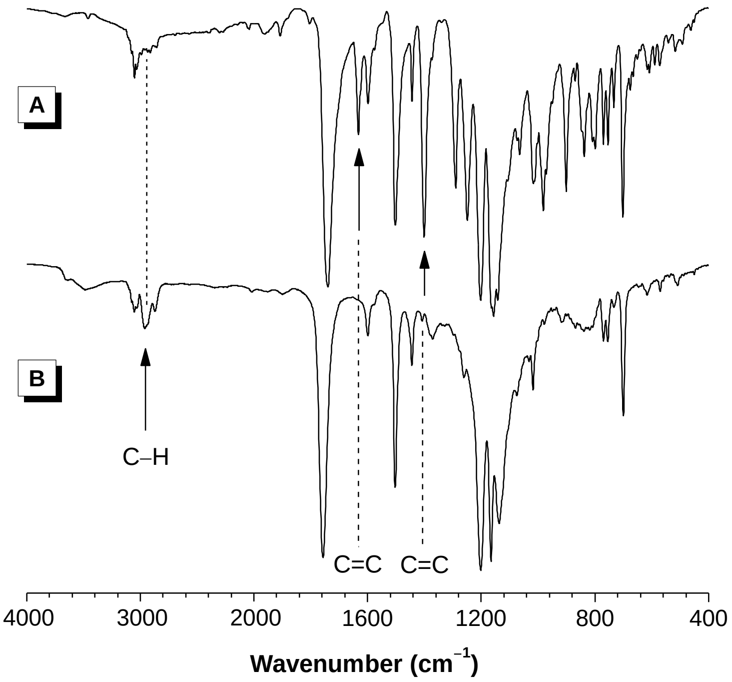

Fig. S1 IR spectra of (A) monomer **1** and (B) polymer P**1** (sample taken from Table 1, no. 2).

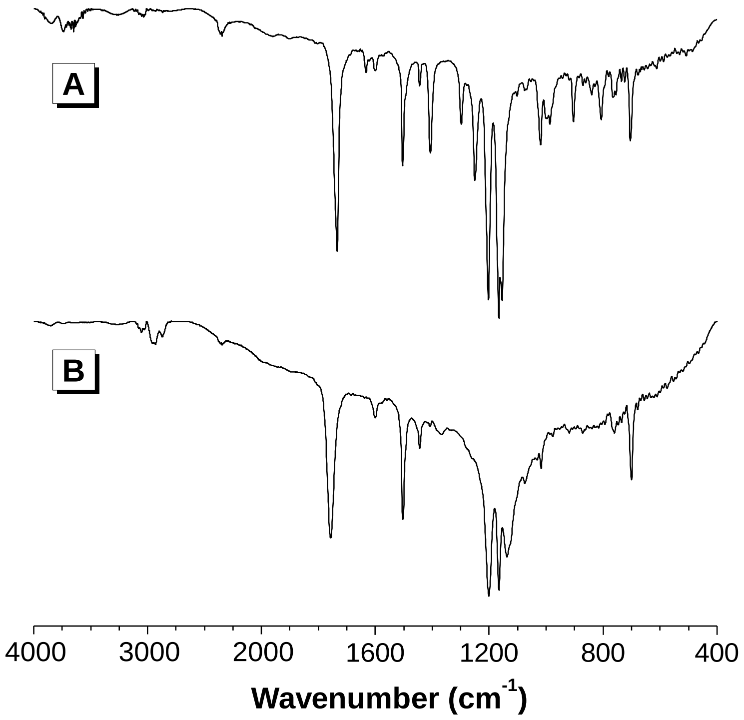

Fig. S2 IR spectra of (A) **2** and (B) P**2** (sample taken from Table 4, no. 2).

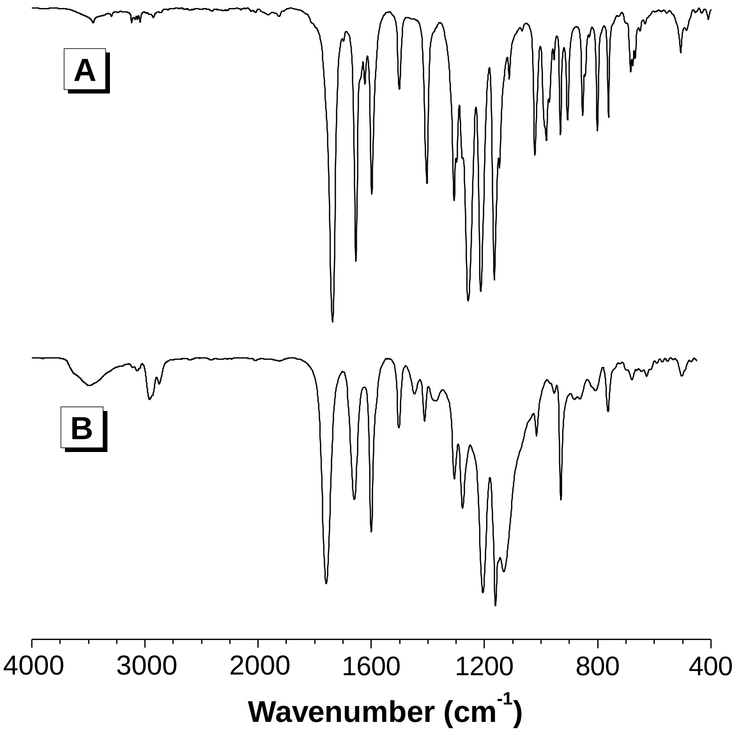

Fig. S3 IR spectra of (A) **3** and (B) P**3** (sample taken from Table 4, no. 4).

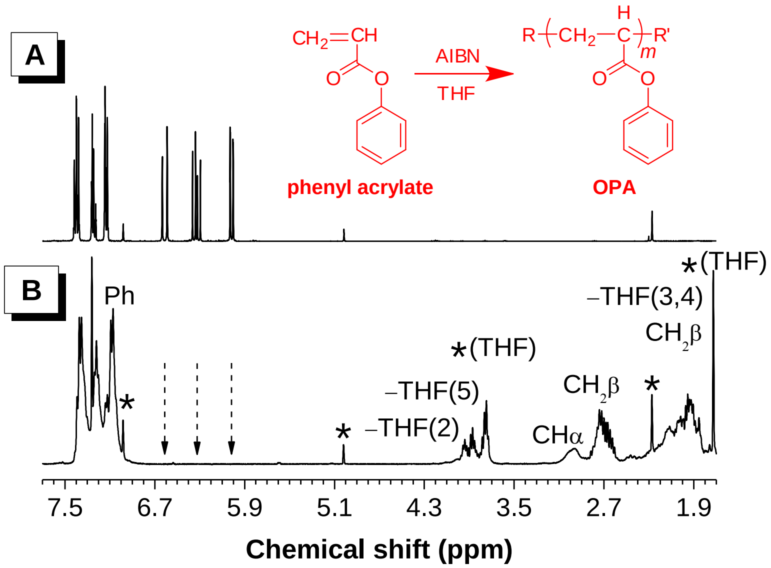

Fig. S4 ^{1}H NMR spectrum of chloroform-*d* solution of (A) phenyl acrylate and (B) oligo(phenyl acrylate) (OPA) obtained by radical polymerization of phenyl acrylate in THF. The solvent peaks were marked with asterisks (*).

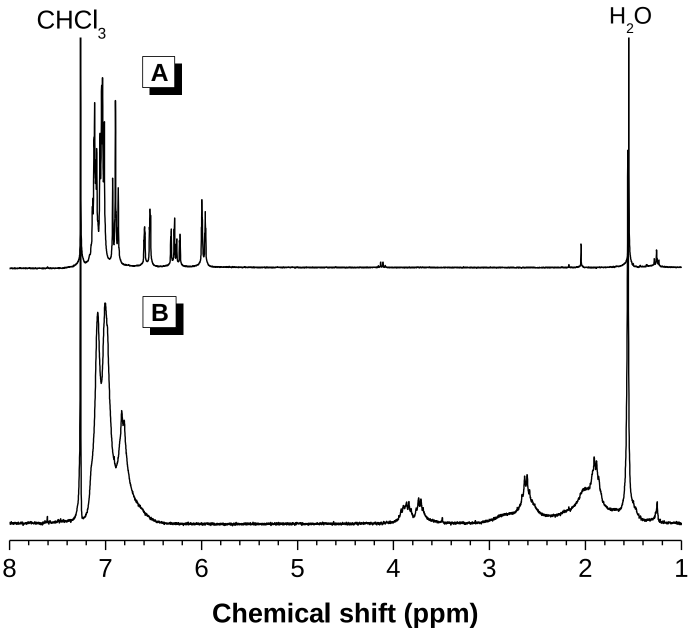

Fig. S5 ^{1}H NMR spectra of (A) **2** and (B) its polymer P**2** (sample taken from Table 4, no. 2) in chloroform-*d*.

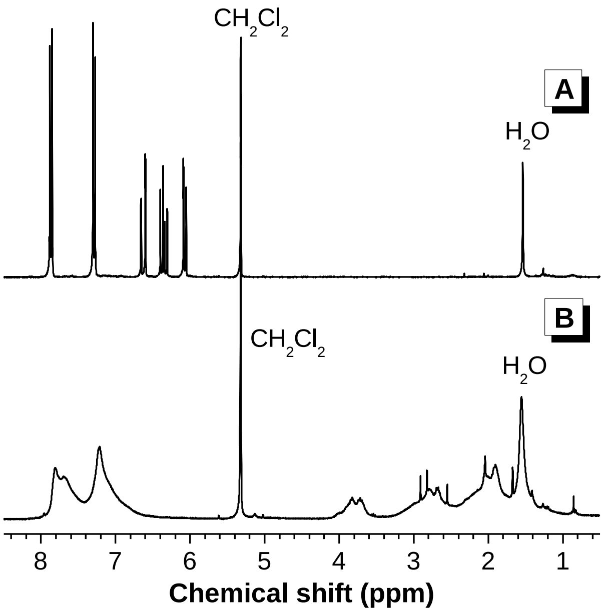

Fig. S6 ^{1}H NMR spectra of (A) **3** and (B) its polymer P**3** (sample taken from Table 4, no. 4) in dichloromethane-*d*$_2$.

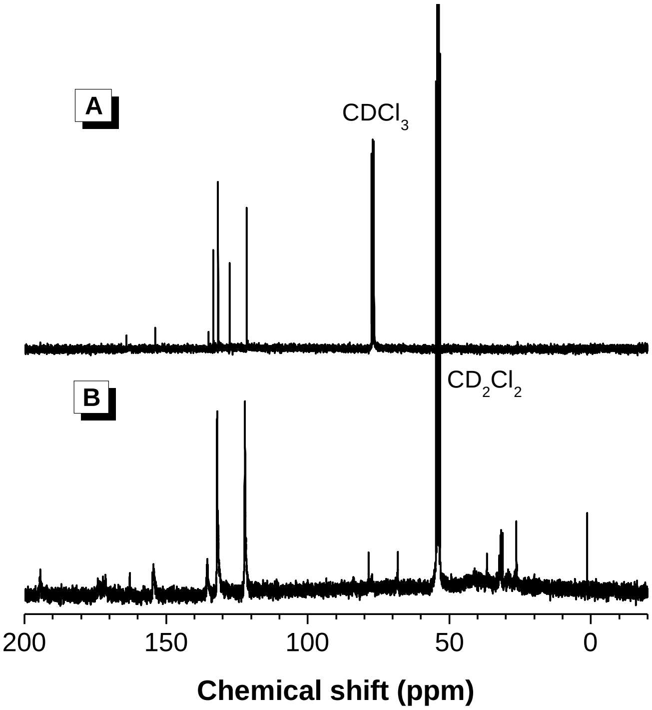

Fig. S7 ^{13}C NMR spectra of (A) **3** and (B) its polymer P**3** (sample taken from Table 4, no. 4) in chloroform-*d* and dichloromethane-*d*$_2$.

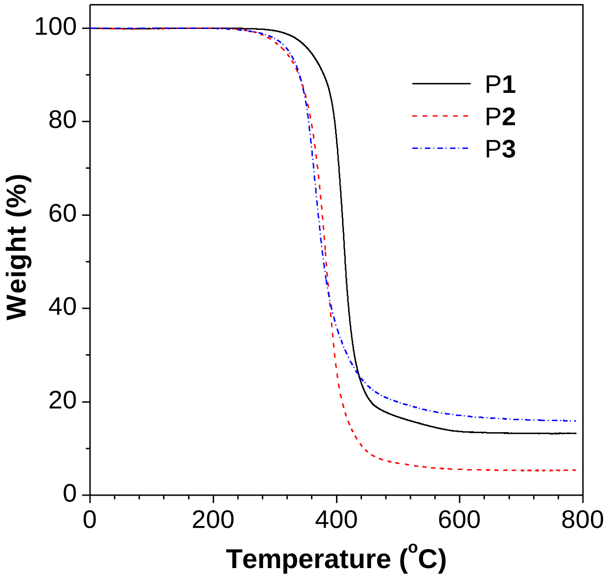

Fig. S8 TGA thermograms of P**1**, P**2** and P**3** recorded under nitrogen at a heating rate of 20 °C/min.

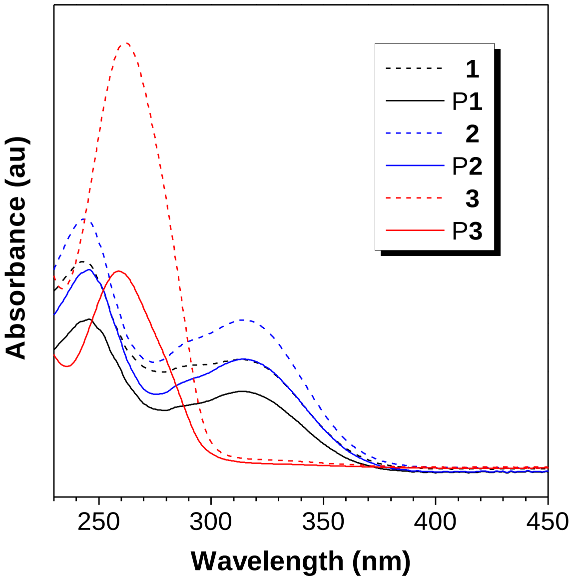

Fig. S9 UV spectra of **1**–**3** and P**1**–P**3** in THF solutions. Concentration: 10 µM.

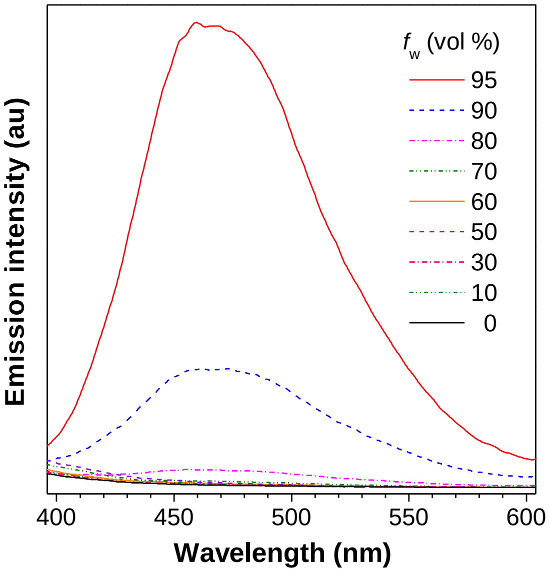

Fig. S10 PL spectra of monomer **1** in THF/water mixtures with different water fractions (f_w). [**1**] = 10 μM; excitation wavelength: 313 nm.

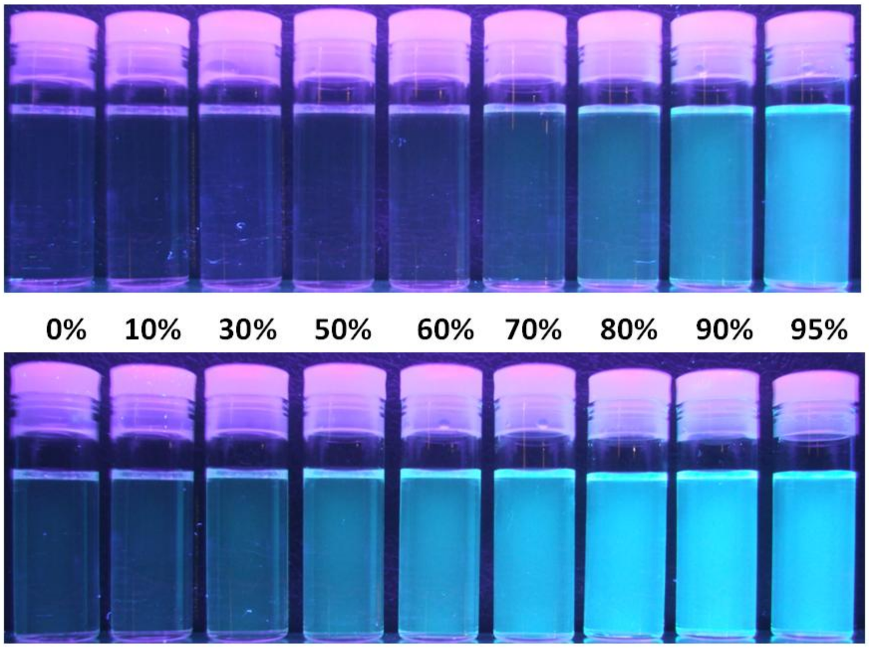

Fig. S11 Photographs of **2** (upper) and P**2** (bottom) (sample taken from Table 4, no. 2) taken under UV illumination from a hand-held UV lamp in THF/water mixtures with different water contents.

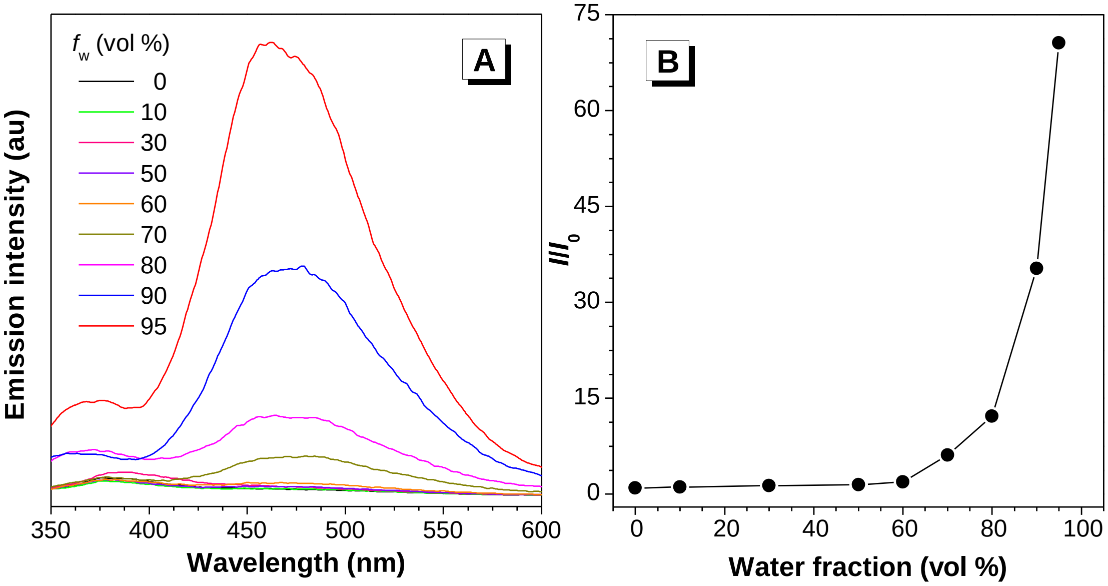

Fig. S12 (A) PL spectra of **2** in THF/water mixtures with different water contents (f_w). (B) Dependence of relative emission intensities on the solvent compositions of THF/water mixtures of **2**. Concentration: 10 μM; excitation wavelength: 314 nm.

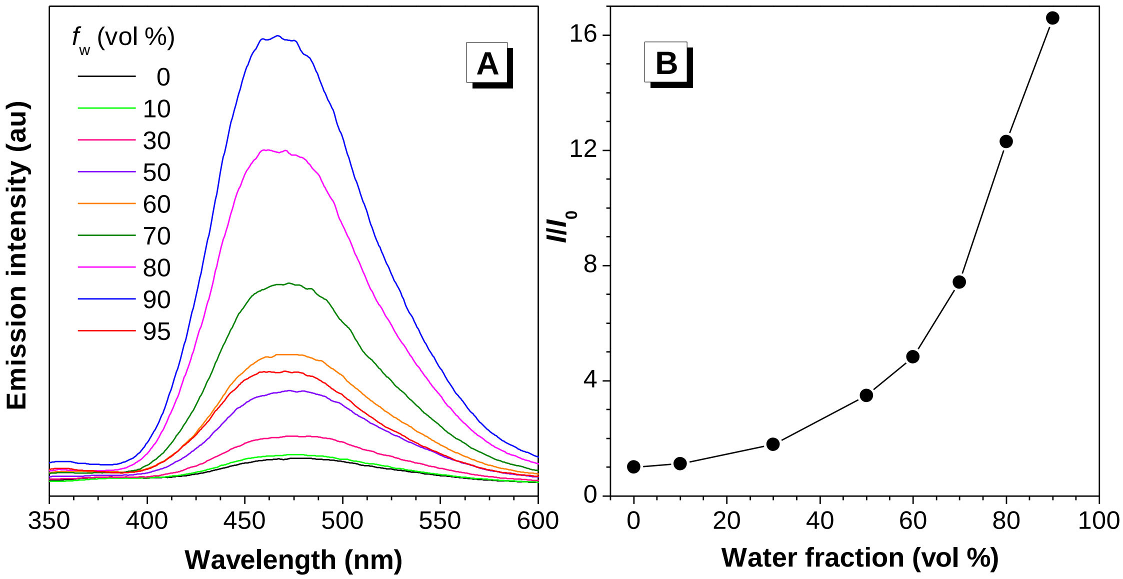

Fig. S13 (A) PL spectra of P**2** in THF/water mixtures with different water contents (f_w). (B) Dependence of relative emission intensities on the solvent compositions of THF/water mixtures of P**2**. Concentration: 10 μM; excitation wavelength: 314 nm.

Table S3. Particle sizes of P**1** and P**2** in THF/water mixtures with different water fractions. [a]

f_w (vol %)	d_{P1} (nm)	d_{P2} (nm)
0[b)]		
10		
30	490	400
50	190	130
60	170	150
70	150	120
80	120	110
90	90	110
95	80	100

[a]Measured by a zeta-potential particle size analyzer. [b]Pure THF solution.

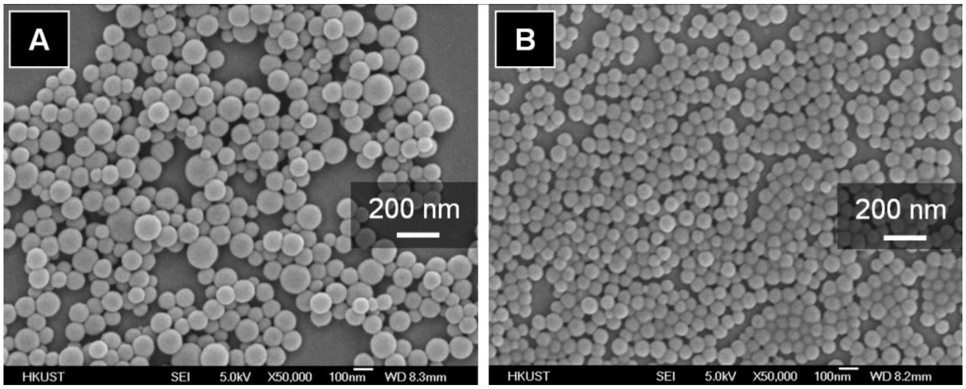

Fig. S14 SEM images of nanoparticles of P**2** formed by deposition of (A) THF solution and (B) THF/water mixture (1:9 v/v) of P**2** on silicon wafer.

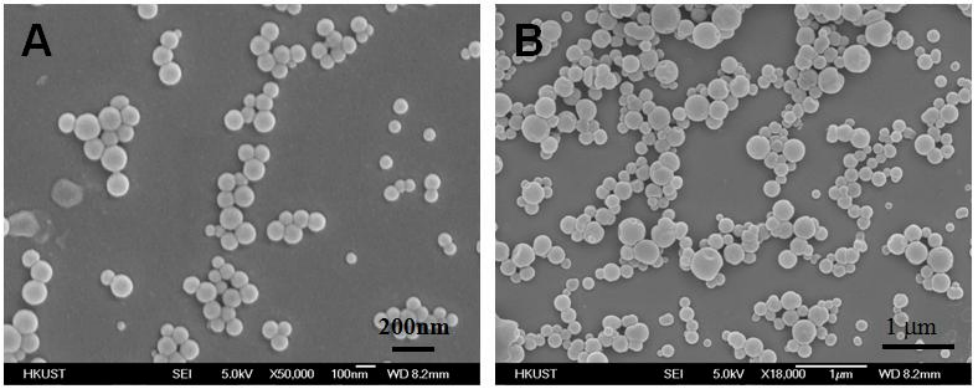

Fig. S15 SEM images of nanoparticles of (A) P**1** and (B) P**3** formed in THF solutions.

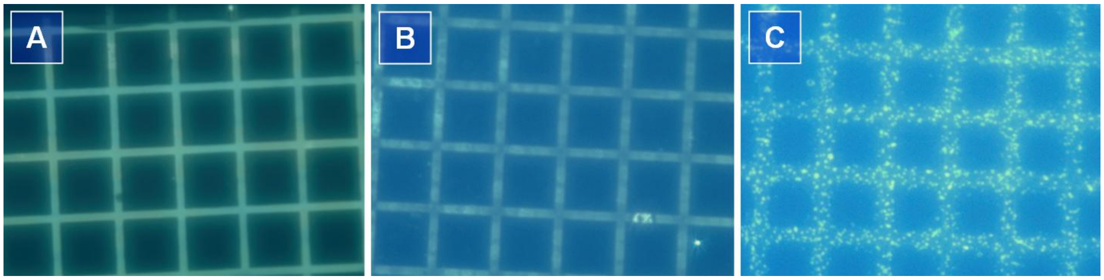

Fig. S16 Negative-tone photoresist patterns generated by photo-crosslinking of thin films of (A) **1**, (B) **2** and (C) **3**. The photographs were taken under UV illumination from a hand-held UV lamp.

Table S4. Crystal data and structure refinement for compound **16**.

Empirical formula	$C_{31} H_{22} O_4$	
Formula weight	458.49	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 17.330(8) Å	α= 90°.
	b = 9.333(4) Å	β= 99.064(6)°.
	c = 13.964(6) Å	γ = 90°.
Volume	2230.2(17) $Å^3$	
Z	4	
Density (calculated)	1.366 mg/m^3	
Absorption coefficient	0.090 mm^{-1}	
F(000)	960	
Crystal size	0.35 × 0.20 × 0.18 mm^3	
Theta range for data collection	2.38 to 26.00°.	
Index ranges	-21<=h<=18, -11<=k<=11, -17<=l<=17	
Reflections collected	6479	
Independent reflections	2159 [R(int) = 0.0507]	
Completeness to theta = 25.00°	98.3%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.89	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2159/0/159	
Goodness-of-fit on F^2	1.031	
Final R indices [I>2sigma(I)]	R1 = 0.0527, wR2 = 0.1109	
R indices (all data)	R1 = 0.0635, wR2 = 0.1159	
Largest diff. peak and hole	0.266 and -0.206 $e.Å^{-3}$	

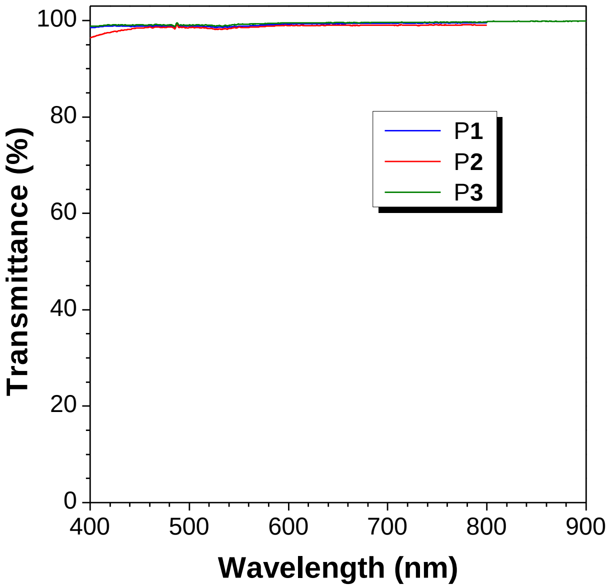

Fig. S17 Light transmission spectra of THF solutions of P**1** (sample from Table 1, no. 2), P**2** (sample from Table 4, no. 2) and P**3** (sample from Table 4, no. 4). Polymer concentration: 1.0×10^{-4} M.