

Electronic supplementary information

12th December 2016

Note added after first publication: This Supplementary Information file was uploaded after the publication of the article on 26th October 2016.

Experimental

Materials

Maleic anhydride (Sigma-Aldrich) was sublimed before use (mp 51-52 °C). 4-Hydroxybenzaldehyde 98 % wt. (Fluka) was recrystallized twice from water (mp. 117-119 °C). Thionyl chloride and styrene were freshly distilled before use. 2,2'-Azobis(2-methylpropionitrile) (AIBN) was recrystallized from methanol (mp 103-104 °C), acetic anhydride, 4-aminoazobenzene, *N,N'*-dicyclohexylcarbodiimide, dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), triethylamine (TEA), all Sigma-Aldrich, were used as received.

Measurements

Infrared spectra were recorded with a Specord M-80 spectrophotometer by using KBr pellets. The ¹H-NMR spectra were recorded on a BRUKER Advance DRX 400 MHz spectrometer, in DMSO-d₆ as solvent with tetramethylsilane (TMS) as internal reference. Chemical shifts are reported in parts per million (ppm). Gel permeation chromatography (GPC) measurements were performed on THF solution, using a PL-EMD 950 evaporative mass detector equipped with 2xPLgel 5 mm MIXED-C, 300x7.5 mm columns and polystyrene standard. Wide-angle X ray diffraction measurements were obtained on powder samples, at room temperature, on a Bruker D8 ADVANCE diffractometer using the nickel filtered copper K_α radiation (λ 0.1541 nm), in the range of 1.5-40 (2θ) at room temperature. Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere by using a TG-DSC-FTIR-MS complex system analysis instrument composed from the following modules coupled each other: TG/DSC instrument, model STA 449F1 Jupiter (Netzsch, Germany); The temperature corresponding to 10 % wt. loss (T₁₀) was considered as criteria of thermal stability., at a heating rate of 12 °C/min. The initial decomposition temperature (IDT) was considered as the temperature at which the sample achieves a 5% wt. loss. Polarizing Optical Microscopy (POM) measurements were performed with an Olympus BH-2 polarized light microscope fitted with a THMS 600/HSF9I hot stage, magnification 200x. Differential scanning calorimetry (DSC) was performed under a nitrogen atmosphere with a Mettler TA Instrument DSC 12E at a heating rate of 10 °C/min. Endothermal and exothermal transition temperatures have been read at the top of the peaks. Heat flow versus temperature scans from the second heating run were plotted and used to measure the glass transition temperature. The mid-point of the inflexion curve resulting from the second heating scan, was assigned as the glass transition temperature of the respective polymer. Electronic absorption spectra were made on an Analytik Jena SPECORD 200 spectrophotometer in dimethylformamide. Irradiation experiments were performed using a medium-pressure mercury lamp in 10 mm path length quartz cells fitted with polytetrafluoroethylene stoppers. The initial absorbance in the *trans* azo absorption band was chosen between 0.8 and 1.0 for all samples. Glass band-pass filters were utilized for the selection of the irradiation wavelength.

Monomer synthesis

4-Maleimido-benzoic acid (**M1**)

The monomer was obtained by the reaction between maleic anhydride and *p*-amino-benzoic acid, in dried acetone, at ambient temperature, followed by chemical cyclodehydration with sodium acetate and acetic anhydride (Scheme 1), according to a previous method.¹⁹ Yield 76%; mp 241 °C (lit. 244 °C;²⁰ Anal. calcd. for C₁₁H₇NO₄: C 60.83, H 3.25, N 6.45; found: C 60.48, H 2.84, N 5.97; ¹H-NMR (400 MHz, DMSO-d₆, δ): 12.36 (s, 1H, COOH), 7.93 (d, 2H, ortho to COOH), 7.49 (d, 2H, ortho to -N<), 7.15 (s, 2H, olefinic); IR (KBr, cm⁻¹) 3500-2500 (broad, O-H), 1777 (C=O free imide I), 1710 (overlapping of imide I and carboxylic acid C=O), 1600, 1510 (C=C, aromatic), 1390 (imide II), 1215 (C-O, COOH), 1145 (imide III), 820 (1,4-phenylene ring), 820, 690 (imide IV).

4-Maleimido-benzoyl chloride (**M2**)

The monomer was synthesized by the reaction of 4-maleimido-benzoic acid with thionyl chloride, according to the procedure.²¹ Yield 81%; mp 168-169 °C (lit. mp. 170 °C²¹) Anal. calcd. for C₁₁H₆ClNO₃: C 56.07, H 2.57, N 5.94, Cl 15.05; found: C 56.51, H 2.79; N 6.34, Cl 15.63; ¹H-NMR (400 MHz, DMSO-d₆, δ): 8.12 (d, 2H, ortho to COCl), 7.49 (d, 2H, ortho to -N<), 7.20 (s, 2H, olefinic); IR (KBr, cm⁻¹) 3120 (w, olefin C-H), 3080 (w, aromatic C-H), 1776 (s, acyl chloride C=O), 1718 (s, imide I), 1390 (imide II), 1145 (imide III), 890 (COCl), 845, 830 (1,4-phenylene ring), 720 (imide IV).

N-(4-formyl-phenoxy-4'-carbonylphenyl)maleimide (**M3**)

The maleimide monomer was prepared by a Schotten-Baumann type-reaction from maleimido-benzoyl chloride and *p*-hydroxy-benzaldehyde (Scheme 1). In a nitrogen-purged flask containing a solution of 2.58 g (0.023 mol) *p*-hydroxybenzaldehyde and 2.34 g (0.023 mol) triethylamine (TEA) in dried acetone, were added gradually 5.429 g (0.023 mol) of **M2** dissolved in dry acetone and the reaction mixture was stirred for 30 minutes at room temperature. The obtained product was filtered, washed several times with aqueous sodium carbonate and acetone to remove the unreacted reagents, and dried under vacuum at 50 °C. Yield 84.6%, mp 224-225 °C;^{19, 22} Calcd. for C₁₈H₁₁NO₅: C 67.28, H 3.42, N 4.36; found: C 68.42, H 4.02, N 3.85; ¹H-NMR (400 MHz, DMSO-d₆, δ): 9.74-9.62 (s, 1H, CHO); 8.06-7.41 (m, 8H, aromatic); 7.12 (s, 2H, vinyl); IR (KBr, cm⁻¹): 3105 (=C-H), 2870, 2780, 1660 (CH=O), 1780, 1720 (C=O imide I), 1755 (C=O ester), 1380 (C=O imide II), 1150 (C=O imide III), 1270, 1070 (C-O-C ester), 690 (CH=CH).

N-[4-(carbonylaminoazobenzene)-phenylene]-maleimide (**M4**)

The maleimide model compound was prepared by the condensation reaction between 4-maleimido-benzoyl chloride (**M2**) and *p*-amino-azobenzene (**4**) (Scheme 1). A nitrogen-purged flask containing a solution of 2.35 g (0.01 mol) **M2** and triethylamine (TEA), 1.02 g (0.01 mol) in chloroform, was cooled in an ice bath. An equimolar solution of **4** 1.82 g (0.01 mol) in dry THF was gradually added to the flask and the mixture was stirred at room temperature for 2 h. The precipitated product was filtered, washed with water, dried and then recrystallized from methanol/water. Yield 61%, mp 217-220 °C; Anal. calcd. for C₂₃H₁₇N₄O₃: C 69.69, H 4.04, N 14.14; found: C 68.72, H 3.81, N 13.59; ¹H-NMR (400 MHz, DMSO-d₆, δ): 7.24 (s, 2H, CH=CH); 7.57-8.10 (m, 13H aromatic); 10.68 (s, 1H, CONH); IR (KBr, cm⁻¹): 3400-3300 (N-H), 1527, 1511, (CONH), 1660 (CONH), 1774, 1710 (CONCO), 1439 (Ar-N), 1403 (C-N), 1157 (imide III), 762 (imide IV), 687 (CH=CH).

N-[4-(4-benzylideneiminoazobenzene)-benzoate]-maleimide (**M5**)

The maleimide monomer was obtained by solution condensation reaction between **M3** and *p*-aminoazobenzene (Scheme 1). In a nitrogen-purged flask containing 3.21 g. (0.01 mol) of **M3** in DMSO, 1.97 g. (0.01 mol) of 4-aminoazobenzene dissolved in DMSO, were gradually added. The reaction mixture was stirred at 80 °C for 10 h. The resulting product was washed three times with ethanol and acetone to remove the unreacted monomers, then dried under vacuum at 50 °C. Yield 72%, mp 214–215 °C; Anal. calcd. for C₃₀H₂₀N₄O₄: C 71.99, H 4.03, N 11.19; found: C 71.52, H 4.38, N 10.69; ¹H NMR (400 MHz, DMSO-d₆, δ): 8.64 (s, 1H, CH=N), 8.27-7.42 (m, 17 H, aromatic), 7.12 (s, 2H, vinyl); IR (KBr, cm⁻¹): 3100 (=C-H), 1770, 1720 (C=O imide I), 1735 (C=O ester), 1623 (CH=N), 1402 (C-N), 1160 (imide III), 1270, 1070 (C-O-C), 760 (imide IV), 680 (CH=CH).

Copolymer synthesis

Copolymer P1 of N-(4-carboxyphenyl)maleimide (**M1**) and styrene (**5**)

In a Pyrex glass tube, 1.352 g (6.23 mmol) **M1**, 0.72 ml (6.23 mmol) styrene and 0.0061 g (0.0374 mmol) of AIBN as radical initiator were dissolved in 16 mL of THF. The tube was sealed under vacuum. Copolymerization was performed at 60 °C, for 48 h. After copolymerization, the content of the tube was poured into a large amount of methanol to precipitate the copolymer. After washing with methanol, the copolymer was dried *in vacuo* at 40 °C for 48 h. The copolymer composition determined by ¹H-NMR spectroscopy indicated that the molar ratio between *N*-(4-carboxyphenyl)maleimide and styrene units in **P1** was 1.0/1.5. White solid, yield 89 %. Anal. calcd.: N 4.02; found: 3.75; ¹H-NMR (400 MHz, DMSO-d₆, δ): 12.56, 6.87-7.62, 7.85-8.23, 3.41-3.18, 2.18. IR (KBr, cm⁻¹): 3500-2500, 1780, 1720, 1610, 1510, 1380, 1225, 1175, 1110, 840, 705.

Copolymer P3 of N-(4-formylphenoxy-4'-carbonylphenyl)maleimide (**M3**) and styrene (**5**)

In a Pyrex glass tube, 1.510 g (4.70 mmol) **M3**, 0.55 mL (4.70 mmol) styrene (**5**) and 0.0046 g (0.0282 mmol) AIBN were dissolved in 30 mL of DMSO. Copolymerization was performed at 60 °C, for 168 h. Purification of the resulting polymer **P3** was carried out similarly as described for **P1** synthesis. The copolymer composition determined by ¹H-NMR spectroscopy indicated that molar ratio between *N*-(4-formylphenoxy-4'-carbonylphenyl)maleimide/styrene units in **P3** is 1.0/1.0, which is an alternating copolymer²³ (Table 1). White solid, yield 30 %. Anal. calcd.: N 2.93; found: 3.29; ¹H NMR (400 MHz, DMSO-d₆, δ): 9.80, 6.78-8.23, 4.12, 3.71, 2.18. IR (KBr, cm⁻¹): 2875, 2760, 1775, 1750, 1725, 1660, 1610, 1530, 1390, 1275, 1220, 1170, 1070, 840, 705.

Copolymer P2 by chemical modification of copolymer P1 with p-aminoazobenzene (**4**)

The copolymer **P2** was synthesized from 0.6 g (1.6 mmol of **M1** moiety) of **P1**, (dissolved in 7 mL of dry DMF), 0.32 g (1.6 mmol) **4** and 0.43 g (2 mmol) of DCC, separately dissolved in a minimum amount of dry DMF. After addition, the reaction was continued for 86 h at room temperature under inert atmosphere. The dicyclohexylurea (DCU) formed during reaction was filtered off. The remaining solution was precipitated in a water/methanol mixture 1/1(v/v). To remove the remaining DCU traces, the resulting crude product was washed several times with water and methanol, dried, and then stirred one hour with acetic acid, washed with water and dried again. Finally, it was extracted with ethanol and dried under vacuum. The content in *p*-aminoazobenzene moieties of the copolymer **P2**, estimated by ¹H-NMR spectroscopy, was about 62 % (mol) to *N*-(4-carboxyphenyl)maleimide moieties. Orange solid, yield 73 %. ¹H NMR (400 MHz, DMSO-d₆, δ): 8.27, 7.85, 7.75, 7.42, 6.82, 6.73, 3.70, 3.57, 3.07, 3.02. IR (KBr, cm⁻¹): 3480, 3400, 1778, 1740, 1635, 1605, 1520, 1380, 1270, 1210, 1170, 1070, 703.

*Copolymer **P4** by chemical modification of copolymer **P3** with *p*-aminoazobenzene (**4**)*

The copolymer **P4** was synthesized from 0.6 g (1.41 mmol of **M3** moiety) **P3** and 0.278 g of **4** (1.41 mmol) in 8 mL DMSO with the use of acetic acid as catalyst. The reaction was performed under inert atmosphere for 10 h at 80 °C. The reaction mixture was poured into a 1/1 (v/v) water/methanol mixture. The resulting product was washed with ethanol several times then dried under vacuum at 50 °C. The content of *p*-aminoazobenzene moieties of the copolymer **P4**, estimated by ¹H-NMR spectroscopy, was 100 % mol to N-(4-formylphenoxy-4'-carbonylphenyl)-maleimide moiety. Orange solid, yield 85 %. ¹H-NMR (400 MHz, CDCl₃, δ): 8.30-6.73 (m, 1H –CH=N–, 22 H aromatic), 3.70-2.02 (m, 2H >CH-CO, 2H –CH₂–, 1H >CH-Ph). IR (KBr, cm⁻¹): 3480, 3400, 1778, 1740, 1635, 1605, 1520, 1380, 1270, 1210, 1170, 1070, 705.