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Poly(meth)acrylates Containing the NLO-Phores *p*-Thio-α-cyanocinnamate and (*p*-Thiobenzylidene)malononitrile

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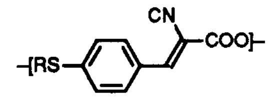
Introduction

Polymers with highly dipolar units have recently been the subject of much interest because of their exceptionally high second-order nonlinear optical (NLO) properties (high β value). In preceding papers, the synthesis of monomers and polymers containing nitrogen[1] and oxygen[2] donor–acceptor dipolar units in the main chain of polyesters, with all the dipolar units lined up in the same direction in a given chain, was described.

In the third paper of this series,[3] polyesters containing the *p*-thio-α-cyanocinnamate unit in the main chain were synthesized. NLO-phores containing sulfur should have a more polar excited state than the corresponding NLO-phore containing the alkoxy group, but may be less dipolar in the ground state. As a consequence, by a solvatochromic method, it has been shown that the sulfides have a higher β value than the corresponding ethers.[4] The introduction of sulfide linkages is also expected to increase solubility and processability of the polymers.



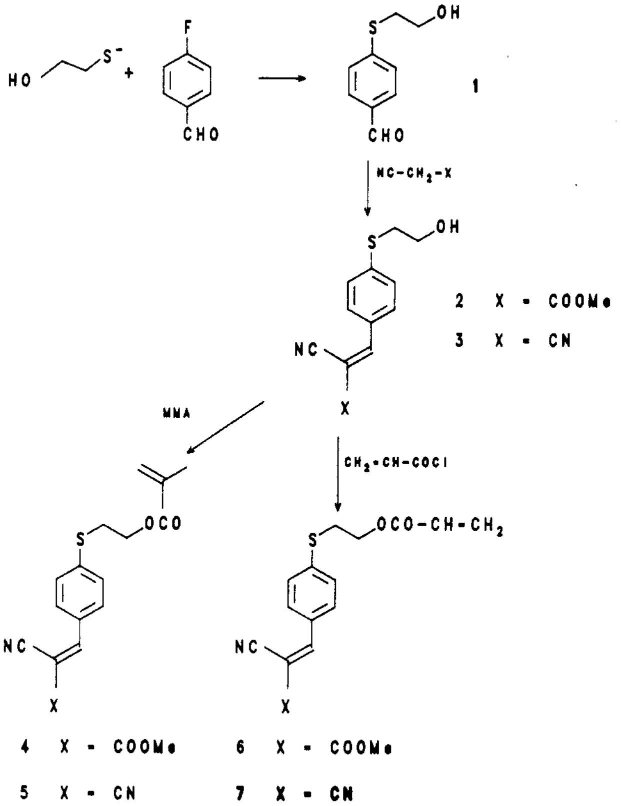
The question remains as to whether it is preferable to line up all the dipoles in the main chain, with accompanying processability problems but better mechanical properties, or whether these NLO-phores can be attached as side groups for equivalent activity. In this paper, the synthesis of (meth)acrylate monomers and polymers containing *p*-thio-α-cyanocinnamate and (*p*-thiobenzylidene)malononitrile units in the side chain is described. An overview of our research in this area, including some of the results described in this paper, has been described previously.[5]

Results

Synthesis. The new monomers were synthesized starting from *p*-[(2-hydroxyethyl)thio]benzaldehyde[3] (1), which was condensed with methyl cyanoacetate or malononitrile to yield *p*-[(2-hydroxyethyl)thio]-α-cyanocinnamate (2) and [*p*-[(2-hydroxyethyl)thio]benzylidene]malononitrile (3), respectively, as outlined in Scheme I.

Methacryloylations of 2 and 3 were carried out by ester interchange with an excess of methyl methacrylate to give methyl *p*-[[(methacryloyloxy)ethyl]thio]-α-cyanocinnamate (4) and [*p*-[[(methacryloyloxy)ethyl]thio]benzylidene]malononitrile (5), respectively. Magnesium/methanol and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) were used as reaction catalyst and polymerization inhibitor, respectively. Compound 2 has an active ester group, which can undergo self-transesterification to form a polyester,[3] so excess MMA was used. The conditions described in the Experimental Section are the preferred ones after various catalysts, inhibitors, solvents, and ratios of MMA to 2 were tried.

Scheme I



Acryloylation of 2 and 3 was done using acryloyl chloride. Methyl *p*-[[(acryloyloxy)ethyl]thio]-α-cyanocinnamate (6) and [*p*-[[(acryloyloxy)ethyl]thio]benzylidene]malononitrile (7) were prepared by the reaction of acryloyl chloride with 2 and 3, respectively. Monomers 6 and 7 were purified by recrystallization from toluene.

Monomer Characterization. The proposed monomer structures were completely in agreement with the analytical and spectroscopic data (see Experimental Section). On the basis of earlier NMR data,[6] the ester group is *E* relative to the phenyl substituent. The assignment of the peaks in the NMR spectra of the new monomer was made by comparison with the model compound *p*-[(β,β-dicyanovinyl)thio]anisole (8): the single peak around 8 ppm was assigned to the benzylidene proton, and the double peaks at 7.4 and 7.8 ppm were assigned to the aromatic protons. The peaks around 5.8 and 6.4 ppm were assigned to the acrylate vinyl protons. ^{13}C NMR spectra showed that the nitrile carbons absorbed around 115 ppm, and the aromatic carbons at 126, 128, 130, and 146 ppm, analogous to the resonances in 8. By comparison with the model compounds 8 and *p*-[(α,β,β-tricyanovinyl)thio]anisole (9), the resonances at 80 and 154 ppm in the monomer spectra can be assigned to the benzylidene β- and α-carbons, respectively. The IR spectra of the monomers 4–7 showed sharp peaks around 2224 cm^{-1}, which is common for monomers containing conjugated nitrile groups.

Polymerizations. As shown in Table I, monomers 4, 6, and 7 homopolymerized in benzene solution with AIBN as initiator at 60 °C. For monomer 5, DMF or chlorobenzene was used as solvent; in benzene only very low yields of poly-5 could be obtained (<10%). The monomer

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Table I
Homopolymerization of 4–7

monomer	solvent	[M]	AIBN, mol %	*T*, °C	*t*, h	yield, %	[η], dL/g	T_g, °C	solubility
4	benzene	0.48	6.2	60	16	50	0.40[a]	102	soluble in THF, CH_2Cl_2
4	benzene	0.56	4.4	60	24	70	0.21[a]		soluble in THF, CH_2Cl_2
4	benzene	1.0	5.5	65	20	68	0.22[a]		soluble in THF, CH_2Cl_2
4	benzene	2.0	4.8	65	20	68	0.22[a]		swelling in THF, CH_2Cl_2
5	DMF	0.31	7.5	60	48	66	0.9[b]	87	soluble in DMF
5	chlorobenzene	0.40	13.7	65	72	41	0.38[b]		soluble in THF, DMF
5	chlorobenzene	0.75	12.7	65	72	39			insoluble in THF, CH_2Cl_2
6	benzene	0.48	3.7	60	48	79	0.51[a]	67	soluble in THF, CH_2Cl_2
7	benzene	0.71	8.3	60	48	43	0.18[a]	16	soluble in THF

[a] In tetrahydrofuran. [b] In dimethylformamide.

Table II
Copolymerization of 4 with MMA in Benzene at 60 °C

4/MMA (mol/mol)	monomers/benzene (mol/1 L)	AIBN, mol %	*t*, h	yield, %	[η], dL/g	$(C_{17}H_{17}NO_4S)_y(C_5H_8O_2)$[a]	
4.8/95.2	0.92	10	14	95	0.47	0.03	0.97
30/70	0.84	6.2	24	68	0.54	0.39	0.61

[a] Calculated from analytical data.

concentrations of 4 and 5 determined whether soluble or swelling polymers were obtained. In concentrated monomer solution, polymerizations of 4 and 5 led only to swelling polymers (Table I).

Copolymerization of 4 with methyl methacrylate (MMA) without solvent led to swelling polymers, even when 4 was present at less than 5 mol % in the monomer mixture. In benzene solution, copolymerization of 4 with MMA at two different feed ratios resulted in optically clear polymers containing 4/MMA in the ratios of 0.39:0.61 and 0.03:97. These copolymers were readily soluble in methylene chloride and THF (Table II).

To investigate if the cross-linking was due to the terminal double bond (see Discussion), methyl methacrylate was polymerized by using AIBN in the presence of 5 mol % of either *p*-[(β,β-dicyanovinyl)thio]anisole (8) or *p*-(β,β-dicyanovinyl)anisole. The poly-MMA, obtained in each case in ~80% yield, was completely soluble, no aromatic protons were observed in the NMR, and the chemical analysis was in agreement with the calculated value for poly-MMA.

Physical Properties of Polymers. The polymers formed from dilute solutions of monomers 4–7 were soluble in common solvents such as THF and dichloromethane, but these polymers had low molecular weights, as indicated by their inherent viscosities and the SEC data (see Experimental Section). When higher monomer concentrations were used, insoluble polymers were obtained. Polymerizations of monomer 4 in bulk led to completely insoluble polymers, probably due to cross-linking.

The discrepancies between the inherent viscosity values and the SEC data suggest, according to a reviewer, that extensive branching occurs in these polymerizations. Any attempt at making films resulted in brittle films. Only the copolymer of 4 with MMA could be cast into films with good mechanical properties.

Discussion

The monomers in this study were readily accessible by standard organic synthesis procedures. However, the free-radical polymerizations did have some problems: low polymer yields, low molecular weights, and insoluble polymers, which only swelled in common solvents if high monomer concentrations were used. The dicyanovinyl or α-cyanoacrylate functionality in the para position of the phenyl is probably interfering with the polymerization, even though we did not observe any influence of model compounds on MMA polymerizations. It has been reported that ethyl α-cyanocinnamate and benzylidenemalononitrile do not homopolymerize, but the trisubstituted olefins copolymerize by radical initiation with vinyl acetate, styrene, acrylonitrile, or methyl acrylate.[7,8]

Mulvaney and Brand[8] reported that *p*-(β,β-dicyanovinyl)phenyl acrylate did not homopolymerize successfully. In contrast to that report, monomers 4–7 in this study did polymerize, but cross-linking occurred.

With the analogous linear polymers reported in the accompanying article, we have successfully synthesized matched pairs of polymers possessing the same NLO-phore in the side or the main chain. Measurement and comparison of the NLO activity of these polymers will be of interest.

Experimental Section

Methods. Melting points were determined on a Thomas-Hoover melting point apparatus and are corrected. Infrared spectra were determined with a Perkin-Elmer 983 spectrometer. ^1H and ^{13}C NMR spectra were determined with a Bruker WM 250. T_g were measured with a Perkin-Elmer Model DSC-4. Viscosities were determined with Ubbelohde-type viscometers. M_w and M_n were measured by SEC using a Shodex A804 column, chloroform as eluent, and polystyrene standards. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

***p*-[(2-Hydroxyethyl)thio]benzaldehyde (1) and Methyl *p*-[(2-Hydroxymethyl)thio]-α-cyanocinnamate (2).** These compounds were prepared in 75% and 86% yield according to Fuso.[3]

[*p*-[(2-Hydroxyethyl)thio]benzylidene]malononitrile (3). To 9.1 g (50 mmol) of *p*-[(2-hydroxyethyl)thio]benzaldehyde and 3.3 g (50 mmol) of distilled malononitrile in 150 mL of toluene was added 0.2 g of β-alanine and 2 mL of glacial acetic acid. The mixture was heated to reflux with a Dean–Stark trap until the theoretical amount of water was collected. The mixture was then cooled and filtered. The collected precipitate was recrystallized from THF/*n*-hexane to give 9.5 g (82%) of 3: mp 74–75 °C; IR (KBr) 3020, 2930, 2225, 1576 cm^{-1}; ^1H NMR ($CDCl_3$, δ ppm) 3.25 (m, 2 H, SCH_2), 3.9 (m, 2 H, OCH_2), 7.4 and 7.7 (2 d, 4 H, aromatic H), 7.8 (s, 1 H, PhCH=). Anal. Calcd for $C_{12}H_{10}N_2OS$: C, 62.59; H, 4.38; N, 12.16; S, 13.92. Found: C, 62.40; H, 4.26; N, 11.95; S, 13.91.

Methyl *p*-[[(Methacryloyloxy)ethyl]thio]-α-cyanocinnamate (4). A mixture of 0.2 g (8.2 mmol) of magnesium and 0.01 of iodine in 10 mL of anhydrous methanol was stirred until all the metallic magnesium reacted. To this mixture was added of 20 g (0.2 mol) of MMA, 1.32 g (5 mmol) of 2, and 0.01 g of TEMPO in 20 mL of diglyme. The oil bath temperature was raised to 120 °C to slowly distill out volatiles. The residue was diluted with

50 mL of THF and refluxed for 1 h. After being cooled, the mixture was filtered and the filtrate was concentrated, yielding the crude product. Recrystallization from toluene gave 1.2 g (75%) of **4**: mp 108–110 °C; IR (KBr) 3020, 2957, 2221, 1708, 1581 cm^{-1}; ^1H NMR ($CDCl_3$, δ, ppm) 1.93 (s, 3 H, CH_3), 3.31 (t, 2 H, SCH_2), 3.93 (s, 3 H, CO_2CH_3), 4.38 (t, 2H, OCH_2), 5.59 and 6.09 (2 d, 2 H, $H_2C=$), 7.4 and 7.9 (2 d, 4 H, aromatic H), 8.18 (s, 1 H, PhCH=); ^{13}C NMR ($CDCl_3$, δ, ppm) 18.3 (CH_3), 30.3 (SCH_2), 53.3 (OCH_3), 62.6 (OCH_2), 101.3 ($=C(CN)CO_2$), 115.7 (CN), 126.2, 128.5, 130.6, 144.4 (aromatic C), 131.9 (vinyl C), 154.2 (PhCH=), 163.2 (CO_2CH_3), 167.1 (CO_2CH_2). Anal. Calcd for $C_{17}H_{17}NO_4S$: C, 61.62; H, 5.17; N, 4.23; S, 9.68. Found: C, 61.85; H, 5.20; N, 4.05; S, 9.49.

[*p*-[[(Methacryloyloxy)ethyl]thio]benzylidene]malononitrile (5). A mixture of 0.2 g (8.2 mmol) of magnesium and 0.01 g of iodine in 10 mL of anhydrous methanol was stirred until all the metallic magnesium had reacted. To this mixture was added a solution of 20 g (0.2 mol) of MMA, 1.15 g (5 mmol) of **3**, and 0.01 g of TEMPO in 20 mL of diglyme. The bath temperature was raised to 120 °C to slowly distill out volatiles. The residue was added to 50 mL of THF and refluxed for 1 h. After being cooled, the mixture was filtered and the filtrate was concentrated, yielding the crude product. Recrystallization from toluene gave 0.9 g (64%) of **5**: mp 72 °C; IR (KBr) 3020, 2954, 2224, 1713, 1577, 1091, 820 cm^{-1}; ^1H NMR ($CDCl_3$, δ, ppm) 1.9 (s, 3 H, CH_3), 3.37 (m, 2 H, CH_2S), 4.38 (m, 2 H, CO_2CH_2), 5.6 and 6.1 (2 d, 2 H, $H_2C=$), 7.4 and 7.8 (2d, J = 8.6 Hz, 4 H, aromatic H), 7.6 (s, 1 H, PhCH=); ^{13}C NMR ($CDCl_3$, δ, ppm) 18.2 (CH_3), 30 (SCH_2), 62.4 (OCH_2), 80.9 ($=C(CN)_2$), 113, 114 (CN), 127.4, 128.7, 129.2, 147 (aromatic C), 131.2, 135.7 (vinyl C); 158.7 (PhCH=), 167.1 (CO_2); MS, M^+ 298. Anal. Calcd for $C_{16}H_{14}N_2O_2S$: C, 64.42; H, 4.69; N, 9.39; S, 10.73. Found: C, 63.81; H, 5.11; N, 9.32; S, 10.53.

Methyl *p*-[[(Acryloyloxy)ethyl]thio]-*α*-cyanocinnamate (6). To a well-stirred solution of 0.91 g (10 mmol) of acryloyl chloride in 100 mL of dry THF was added dropwise a solution of 2.63 g (10 mmol) of **2** and 1.1 g (11 mmol) of triethylamine in 100 mL of dry THF. The reaction mixture was kept between −20 and −10 °C by cooling with a dry-ice/2-propanol bath for 4 h. The reaction mixture temperature was allowed to rise to room temperature over a 16-h period, and the mixture was filtered. The filtrate was concentrated to collect the crude product. Recrystallization from toluene gave 2.5 g (79%) of **6**: mp 79–81 °C; IR (KBr) 3031, 2953, 2221, 1725, 1583 cm^{-1}; ^1H NMR ($CDCl_3$, δ, ppm) 3.31 (t, 2 H, SCH_2), 3.99 (s, 3 H, CO_2CH_3), 4.39 (t, 2 H, OCH_2), 5.86 and 6.42 (2 d, 2 H, $H_2C=$), 6.12 (m, 1 H, HC=), 7.4 and 7.9 (2 d, 4 H, aromatic H), 8.18 (s, 1 H, PhCH=); ^{13}C NMR ($CDCl_3$, δ, ppm) 30.2 (SCH_2), 53.4 (OCH_3), 62.4 (OCH_2), 101.2 ($=C(CN)CO_2$), 115.7 (CN), 126.6, 127.8, 128.4, 144.3 (aromatic C), 131.7, 132.4 (vinyl C), 154.2 (PhCH=), 163.2 (CO_2CH_3), 165.9 (CO_2CH_3). Anal. Calcd for $C_{16}H_{15}NO_4S$: C, 60.6; H, 4.8; S, 10.1. Found: C, 60.3; H, 4.9; N, 4.5; S, 9.9.

[*p*-[[(Acryloyloxy)ethyl]thio]benzylidene]malononitrile (7). The same procedure as described for **6** was performed using 0.91 g (10 mmol) of acryloyl chloride in 100 mL of dry THF and 2.3 g (10 mmol) of **3** and 1.11 g (11 mmol) of triethylamine in 100 mL of dry THF. Recrystallization from toluene gave 0.64 g (26%) of **7**: mp 70–72 °C; IR (KBr) 2961, 2222, 1720, 1571, 1091 cm^{-1}; ^1H NMR ($CDCl_3$, δ, ppm) 3.33 (t, 2 H, SCH_2), 4.4 (t, 2 H, OCH_2), 5.9 and 6.4 (2 m, 2 H, $H_2C=$), 6.1 (m, 1 H, HC=), 7.4 and 7.8 (2 d, J = 8.5 Hz, 4 H, aromatic H), 7.7 (s, 1 H, PhCH=); ^{13}C NMR ($CDCl_3$, δ, ppm) 30.3 (SCH_2), 62.2 (OCH_2), 80.9 ($=C(CN)_2$), 112.9 and 114 (CN), 126.8, 127.8, 131.1, 146.4 (aromatic), 131.7, 132.2 (vinyl C), 158.7 (PhCH=), 165.9 (CO_2); MS, M^+ 284.

Homopolymerization of Methyl *p*-[[(Methacryloyloxy)ethyl]thio]-*α*-cyanocinnamate (4) in Benzene. To a solution of **4** (0.33 g, 1 mmol) in 2 mL of freshly distilled benzene was added 9 mg of AIBN (6 mol % to monomer). The solution was degassed, put under a nitrogen atmosphere, and placed in a thermostated bath at 60 °C for 48 h. The resulting polymer was precipitated in methanol. Purification was done by successive dissolutions in THF and reprecipitation in methanol. The polymer was dried under reduced pressure to give 0.16 g (50% conversion): $[\eta]$ = 0.40 dL/g (30 °C, THF); M_w, 2.46 × 10^4; M_n, 9.5 × 10^3 (SEC); T_g, 102 °C; IR (KBr) 2995, 2951, 2221, 1726, 1582, 1087 cm^{-1}; ^1H NMR ($CDCl_3$, δ, ppm) 0.9–1.8 (br, 5 H, CH_2, CH_3), 3.2–3.3 (m, 2 H, SCH_2), 3.8–3.9 (br, 3 H, CO_2CH_3), 4.1–4.2 (m, 2 H, CO_2CH_2), 7.4 and 7.8 (br, 4 H, aromatic H), 8.1 (br, 1 H, PhCH=).

Homopolymerization of [*p*-[[(Methacryloyloxy)ethyl]thio]benzylidene]malononitrile (5) in *N,N*-Dimethylformamide (DMF). To a solution of **5** (0.30 g, 1 mmol) in 2 mL of freshly distilled DMF was added 11 mg of AIBN (7.5 mol % to monomer) and the resultant mixture was polymerized as described above. The polymer was dried under reduced pressure to give 0.2 g (66% conversion): $[\eta]$ = 0.90 dL/g (30 °C, DMF); T_g, 87 °C; IR (KBr) 2932, 2225, 2197, 1729, 1578, 1090 cm^{-1}; ^1H NMR (DMSO-d_6, δ, ppm) 1.1–1.8 (br, CH_2, CH_3), 3.1–3.3 (br, SCH_2), 4.1–4.3 (br, CO_2CH_2), 7.4 and 7.8 (br, Ar′H), 7.7 (br, PhCH=).

Homopolymerization of *p*-[[(Acryloyloxy)ethyl]thio]-*α*-cyanocinnamate (6) in Benzene. To a solution of **6** (0.31 g, 1 mmol) in 2 mL of freshly distilled benzene was added 5.5 mg of AIBN (3.8 mol % to monomer) and the resultant mixture was treated as described above. The resulting polymer was dried under reduced pressure to give 0.25 g (79% conversion): $[\eta]$ = 0.51 dL/g (30 °C, THF); M_w, 7.8 × 10^3; M_n, 5.0 × 10^3 (SEC); T_g, 67 °C; IR (KBr) 2953, 2851, 2221, 1729, 1582, 1085 cm^{-1}; ^1H NMR ($CDCl_3$, δ, ppm) 1.2–1.7 (br, CH_2), 2.1–2.4 (br, $CHCO_2$), 3.2–3.3 (br, SCH_2), 3.9 (s, CO_2CH_3), 4.1–4.3 (br, CO_2CH_2), 7.4 and 7.8 (br, aromatic H), 8.1–8.2 (br, PhCH=).

Homopolymerization of [*p*-[[(Acryloyloxy)ethyl]thio]benzylidene]malononitrile (7) in Benzene. To a solution of **7** (0.35 g, 1.2 mmol) in 2 mL of freshly distilled benzene was added 14.6 mg of AIBN (8.3 mol % to monomer) and the resultant mixture was treated as described above. The polymer was dried under reduced pressure to give 0.15 g (43% conversion): $[\eta]$ = 0.18 dL/g (30 °C, THF); M_w 1.3 × 10^3; M_n, 1.18 × 10^3 (SE); T_g 16 °C; IR (KBr) 2925, 2226, 1729, 1529, 1578, 1091 cm^{-1}; ^1H NMR ($CDCl_3$, δ, ppm) 1.2–1.7 (br, CH_2), 2.1–2.3 (br, $CHCO_2$), 3.1–3.3 (br, SCH_2), 4.2–4.4 (br, CO_2CH_2), 7.4–7.8 (br, aromatic H), 7.7 (br, PhCH=).

Copolymerization of 4 with MMA in Benzene. To a solution of **5** (0.167 g, 0.5 mmol) and MMA (1.0 g, 10 mmol) in 1.0 g (1.14 mL) of freshly distilled benzene was added 15 mg of AIBN (10 mol % to total monomers) and the resultant mixture was treated as described above. The polymer was extracted with methanol for 4 h and dried under reduced pressure to give 1.01 g (95% conversion): $[\eta]$ = 0.47 dL/g; T_g, 116 °C; IR (KBr) 3060, 2991, 2949, 2221, 1729, 1583, 1484, 1433, 1270, 1239, 1191, 1148, 989, 750 cm^{-1}; ^1H NMR ($CDCl_3$, δ, ppm) 0.85 and 1.02 (s, CH_3), 1.2–1.9 (br, CH_2), 3.2–3.3 (br, SCH_2), 3.6 and 3.95 (s, CO_2CH_3), 4.2 (br, CO_2CH_2), 7.4 and 7.8 (br, aromatic H), 8.2 (s, PhCH=). Anal. Found: C, 60.06; H, 7.61; N, 0.56; S, 1.22. Calcd for $(C_5H_8O_2)_x(C_{17}H_{17}NO_4S)_y$; x = 0.965, y = 0.035.

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Registry No. **1**, 53606-34-1; **2**, 132492-89-8; **3**, 132492-94-5; **4**, 132492-95-6; **4** (homopolymer), 132493-04-0; (**4**)(MMA) (copolymer), 132493-08-4; **5**, 132492-96-7; **5** (homopolymer), 132493-05-1; **6**, 132492-97-8; **6** (homopolymer), 132493-06-2; **7**, 132492-98-9; **7** (homopolymer), 132493-07-3; malononitrile, 109-77-3.