Poly[(ω-hydroxyalkyl)thio-α-cyanocinnamates]. Linear Polyesters with NLO-Phores in the Main Chain

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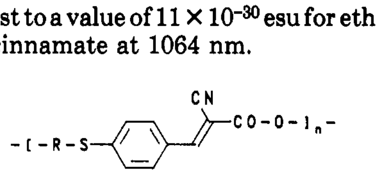
ABSTRACT: To obtain optically clear (amorphous), processable, film-forming polymers with high concentrations of nonlinear optically active units ("NLO-phores") distributed in the same direction along a polymer chain and possessing high glass transition temperatures, *p*-[(ω-hydroxyalkyl)thio]-α-cyanocinnamates were synthesized and polymerized. The key steps in the syntheses were nucleophilic displacement by ω-hydroxyalkane thiols on *p*-fluorobenzaldehyde, followed by Knoevenagel condensation with methyl cyanoacetate. When the alkyl group was ethyl, 1,6-hexyl, or *trans*-cyclohexyldimethyl, the homopolymers were highly crystalline and insoluble in spin-coating solvents. Copolymerization with methyl 12-hydroxydodecanoate gave amorphous, dichloromethane-soluble copolymers with T_g's below room temperature. A "copolymer" containing *cis*- and *trans*-1,4-cyclohexyldimethyl units was optically clear and dichloromethane-soluble, had T_g = 102 °C, and was our best material for future studies of NLO activity.

Introduction

The synthesis and characterization of polymers containing nonlinear optically active structures continue to be topics of current interest. The goal of the present work was to synthesize colorless, optically clear linear polyesters with high concentrations of NLO-phores in the main chain, which were soluble in spin-coating solvents, and which had high glass transition temperatures. We have previously reported the first linear AB polyesters containing NLO-phores in the main chain.[1] We showed that donor–acceptor quinodimethane[1] and *p*-oxy-α-cyanocinnamate[2] derivatives could be successfully incorporated into an AB polyester chain with all the dipoles lined up in the same direction along the polymer chain. The donor groups of those structures were based on nitrogen and oxygen. However, the resulting homopolymers were soluble only in highly polar solvents such as *m*-cresol, which are not suitable for spin-coating. The copolymers with methyl 12-hydroxydodecanoate were more soluble, but had T_g's below room temperature.

In a different approach we have used sulfur as a donor with the thought that sulfur might provide excited-state polarizability (high β value) with a relatively nonpolar ground state (ready solubility and processability)[3]. Methyl *p*-[(2-hydroxyethyl)thio]-α-cyanocinnamate has been shown to have a substantial β value by a solvatochromic method.[4,5] A value of 150×10^{-30} esu was obtained for β_{xxx}, in contrast to a value of 11×10^{-30} esu for ethyl *p*-methoxy-α-cyanocinnamate at 1064 nm.

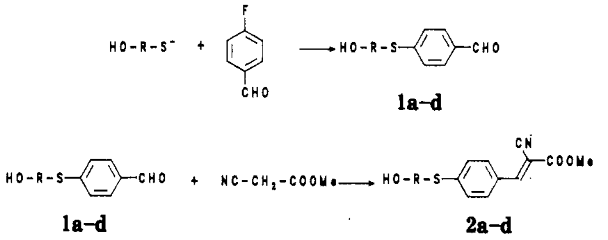


In this article, we describe the syntheses and properties of several *p*-[(ω-hydroxyalkyl)thio]-α-cyanocinnamate monomers and their homo- and copolymers. An overview of our work in this field, including some of the data in this paper, has appeared previously.[6]

Results

Synthesis of Monomers. The synthesis of the AB monomer unit is based on the aromatic nucleophilic displacement on *p*-fluorobenzaldehyde by the anions of ω-hydroxyalkanethiols (Chart I).

Chart I



a, R = $(CH_2)_2$ c, R = $CH_2C_6H_{10}CH_2$, trans
b, R = $(CH_2)_6$ d, R = $CH_2C_6H_{10}CH_2$, cis–trans

Of the ω-hydroxyalkanethiols required, 2-hydroxyethanethiol is commercially available. 6-Hydroxyhexanethiol and [4-(hydroxymethyl)cyclohexane]methanethiol are not commercially available and were synthesized from the ω-hydroxyalkyl bromides. 6-Hydroxyhexyl bromide was commercially available, while 4-(bromomethyl)cyclohexanemethanol was obtained from 1,4-cyclohexanedimethanol in 48% hydrobromic acid at 90 °C following the procedure described by Degerin and Boatright.[7] The bromohydrin formed in situ was continuously extracted with heptane. This reaction was rather slow, and low but reliable yields (25–36%) resulted.

Because of the expected water solubility of the ω-hydroxyalkanethiols, the nonaqueous procedure using thiourea, reported by Cossar et al.[8] seemed appropriate. This method involves cleavage of the isothiuronium salt with tetraethylenepentamine, a high-boiling amine, in triethylene glycol, and isolation of the thiol by distillation from the reaction mixture. Although these authors applied this method only to simple alkyl bromides, we obtained good yields of 6-hydroxyhexanethiol and 4-(hydroxymethyl)cyclohexanemethanethiol. Because of the expected higher boiling point of 4-(hydroxymethyl)cyclohexanemethanethiol, tetraethylene glycol was used instead of triethylene glycol.

2-Hydroxyethyl thiolate reacts readily with *p*-fluorobenzaldehyde in *N,N*-dimethylformamide at room temperature to form the corresponding *p*-[(2-hydroxyethyl)thio]benzaldehyde (**1a**) in 89% yield. The reactions between other ω-hydroxyalkanethiolates and *p*-fluorobenzaldehyde gave similar high yields of *p*-[(ω-hydroxyalkyl)thio]benzaldehydes **1b–d**. Knoevenagel condensa-

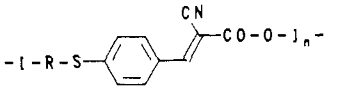
Table I
Synthesis and Characterization of Homopolymers

polymer	stage 1, h/°C	stage 2, h/°C	yield, %	inherent viscos, dL·g^{-1}	T_g, °C	T_m, °C	solubility[a]
3, C_2	1/160	2/185	93	--	86	200	soluble HFIP,[b] low solubility *m*-cresol, insoluble THF, dichloromethane
4, C_6	1/160	1/200	100	--	45	130	swells in dichloromethane
5, 97% trans	1/160	16/160 0.5/200	100	0.34[c]	113	226–251	soluble pentafluorophenol, chlorobenzene/phenol (1:1)

[a] Solubilities were determined on 0.5% (w/v) solutions. [b] 1,1,1,3,3,3-Hexafluoro-2-propanol. [c] Measured in chlorobenzene/phenol (1:1).

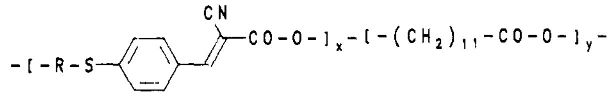
Chart II

Homopolymers



3, R = $(CH_2)_2$
4, R = $(CH_2)_6$
5, R = $CH_2C_6H_{10}CH_2$, trans

Copolymers



6, R = $(CH_2)_2$ ($x = y = 1$)
7, R = $(CH_2)_2$ ($x = 2$, $y = 1$)
8, R = $(CH_2)_2$ ($x = 3$, $y = 1$)
9, R = $(CH_2)_6$ ($x = y = 1$)
10, R = $(CH_2)_6$ ($x = 2$, $y = 1$)
11, R = $(CH_2)_6$ ($x = 3$, $y = 1$)
12, R = $CH_2C_6H_{10}CH_2$, cis–trans ($y = 0$)

tion of the latter with methyl cyanoacetate using the procedure of Hall and co-workers[2] led to the cinnamate derivatives **2a–d**. As previously, only one of the two possible geometric isomers of the *p*-thio-α-cyanocinnamates **2a–c** were observed (by NMR), namely, the *E* isomer.[2]

During the synthesis of trans monomer **2c**, which started from a mixture of isomers of 1,4-cyclohexanedimethanol, the cis/trans isomeric ratio changed from 27:73 to 3:97, respectively. This was probably due to selective crystallization during purification of the monomer **2c** rather than epimerization.

In order to prepare monomer **2d**, with a higher cis content, the mixed diols were benzoylated according to Haggis and Owen.[9] Recrystallization from methanol and debenzoylation afforded 1,4-cyclohexanedimethanol with a cis/trans isomeric ratio of 82:18. The monomer **2d** synthesized from this starting material had a cis/trans isomeric ratio of 42:58.

Polymeric Synthesis and Properties. The homopolycondensations of monomers **2a–c** were carried out by the two-stage, high-temperature polyesterification procedure in the presence of 2 mol % tributyltin acetate following the method of Hall and co-workers[2] (Table I).

Homopolymers **3** and **4** (Chart II), which differ only in the length of the alkyl spacer group, formed brittle, yellow, optically clear glasses, **3** having a T_g at 86 °C and **4** showing T_g at 45 °C. Crystallization could be induced by treating these amorphous polymers with either dichloromethane or methanol at room temperature. Thermal analysis of such treated samples revealed T_m, but amorphous homopolymer was obtained again when these oriented polymers were heated above T_m, followed by rapid cooling.

The homopolycondensation of **2c** (97% trans) resulted in crystalline homopolymer **5** with $T_m > 200$ °C. Crystallization was observed even during the synthesis of this polymer. To complete this solid-state polymerization, a longer reaction time in the second stage of the polymerization procedure was helpful in giving higher molecular weights (Table I). The obtained homopolymer had a moderate inherent viscosity of 0.34 dL·g^{-1}. After heating to T_m, followed by rapid cooling, an amorphous polymer having a T_g at 113 °C was obtained.

All homopolymers were insoluble in common solvents such as dichloromethane or THF, but were soluble in highly polar solvents such as hexafluoro-2-propanol or pentafluorophenol.

To improve solubility, monomers **2a–c** were copolymerized with methyl 12-hydroxydodecanoate. The data are summarized in Table II. These copolycondensations led to dichloromethane-soluble copolymers in most cases, except when monomer **2a** was used at ratios 2:1 or 3:1 with methyl 12-hydroxydodecanoate leading to copolymers **7** and **8**, which were only soluble in *m*-cresol. For copolymer **6**, carrying out the second stage at 160 °C for 4 h was less effective than heating to 200 °C for 1 h. Under the latter conditions, the resulting polymer had a higher molecular weight (MW 33 000).

Increasing the length of the alkyl chain in the spacer group from ethyl to the 1,6-hexyl group led to copolymers with higher molecular weight, over 60 000. The copolymer composition generally corresponded to the feed ratio. ^{1}H NMR suggested that the dipole to comonomer molar ratio was 1 for copolymer **9** and 2 for copolymer **10**. Only copolymer **11** with a monomer molar ratio of 3 showed a changed ratio in the polymer of 3.8. Finally, we synthesized a larger amount of copolymer **10** (~20 g). The prepared copolymer had an inherent viscosity of 0.53 dL·g^{-1} and an average molecular weight of 62 000.

We think that the polycondensation of **2d** cis/trans = 42:58 should be considered a copolymerization of the cis and trans isomers. It led to an optically clear polymer **12**. This amorphous polymer had a T_g of 102 °C.

All the obtained copolymers except **12** were yellow and opaque, the latter suggesting crystallinity. This was confirmed by thermal analysis (DSC) and the ability of thin films of the copolymer to rotate the plane of polarized light, as observed by polarized light microscopy. For all copolymers with methyl 12-hydroxydodecanoate, except **8**, T_m's were observed. As expected, decreasing the concentration of the *p*-thio-α-cyanocinnamate dipoles in the polymer chain decreased T_m. This tendency is clearly observed in the series of copolymers **9**, **10**, and **11**. Further, the copolymers, with the exception of the "copolymer" **12** of cis and trans isomers, lacked a T_g above room temperature. Films were cast from copolymer solutions in dichloromethane and could be drawn to twice their original length at room temperature.

Conclusions

A new family of linear AB dipolar polyesters with high concentrations of a novel sulfur-containing NLO-phore, has been synthesized. Compositions suitable for spin-

Table II
Synthesis and Characterization of Copolymers with Methyl 12-Hydroxydodecanoate

polymer	stage 1, h/°C	stage 2, h/°C	yield, %	inherent viscos, dL·g^{-1}	MW[a]	T_g, °C	T_m, °C	solubility[b]
6, C_2, 1:1	1/60	4/160	91	0.25[c]	19 000			dichloromethane
6, C_2, 1:1	1/160	1/200	100	0.33[c]	33 000		38	dichloromethane
7, C_2, 2:1	1/160	1/200	73	0.26[d]			58, 123	*m*-cresol
8, C_2, 3:1	1/160	1/200	56	0.29[d]				*m*-cresol
9, C_6, 1:1	2/160	0.75/200	91		64 000		33, 65	dichloromethane
10, C_6, 2:1	2/160	1/200	91	0.68[c]	62 000		88	dichloromethane
11, C_6, 3:1	1/160	1/200	72	0.69[c]	64 000		109	dichloromethane
12, (cis/trans = 42:58)	2/160	3/160	10			102		chlorobenzene/phenol

[a] Measured by SEC. [b] Solubilities were determined on 0.5% (w/v) solutions. [c] Inherent viscosity measured in dichloromethane. [d] Inherent viscosity measured in *m*-cresol.

coating thin films from dichloromethane are described. Melt-spinning may also be feasible. The most interesting sample for clear films, polymer **12**, has T_g of 102 °C, is optically clear, and is soluble in 1:1 chlorobenzene/phenol. 12-Hydroxydodecanoic units in the copolymers gave T_g values below room temperature.

In the accompanying paper,[10] we describe the incorporation of the same NLO-phore in the side chain of a polymer. Comparing the optical properties of these polymers should lead to information about the influence of the assembly of the NLO-phores on the NLO activity.

Experimental Section

Methods. Melting points were recorded with a Mel-Temp melting point apparatus and are corrected. Gas chromatographic analyses (GC) were obtained with a Varian 3300 gas chromatograph (FID detector) connected with a Hewlett-Packard HP 3392A integrator. T_m and T_g were measured with a Perkin-Elmer differential scanning calorimeter, Model DSC-4.

Inherent viscosities were determined with a Cannon-Fenske viscometer on 0.5% (w/v) polymer solutions in the indicated solvents at 30.0 °C. Number-average molecular weights were measured by size exclusion chromatography (SEC) on Du Pont Zorbax PSM 60S, Du Pont Zorbax PSM 300S, and IBM GPC/SEC pore type A columns calibrated with polystyrene standards with chloroform as eluent and a Spectra Physics detector at 254 nm.

Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were taken on a Bruker WM250 nuclear magnetic resonance spectrometer at 250 MHz.

Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Synthesis of Cis-Enriched 1,4-Cyclohexanedimethanol. A cis-enriched 1,4-cyclohexanedimethanol was prepared according to Haggis and Owen.[7] 1,4-Cyclohexanedimethanol (Aldrich, isomeric mixture) was benzoylated in pyridine. The dibenzoates were recrystallized twice from methanol to yield a mixture that contained ~80% of the cis isomer and 20% of the trans isomer (by ^{1}H NMR; mp 79–86 °C). The dibenzoate was debenzoylated to yield 1,4-cyclohexanedimethanol, isomeric ratio cis/trans = 82:18 (by GC, Carbowax 20M).

Synthesis of 4-(Bromomethyl)cyclohexanemethanol. Into a continuous liquid–liquid extractor was placed a solution of 1,4-cyclohexanedimethanol (20.35 g, 0.141 mol; Aldrich, isomeric mixture) in 16.1 mL of 48% hydrobromic acid and heated to 90 °C. The mixture was then continuously extracted with heptane for 5 days. Heptane was evaporated and the oily residue vacuum distilled: yield, 7.23 g (25%); bp 78–81 °C (0.15 Torr); IR (film) 3335, 1035 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.0–1.39 (m, 12 H), 3.30 and 3.39 (2 d, 2 H, equatorial and axial CH_2Br, respectively); isomeric ratio cis/trans = 19:81 (by ^{1}H NMR).

The reaction of 1,4-cyclohexanedimethanol (20.5 g, 0.142 mol; isomeric ratio cis/trans = 82:18) with 32 mL of 48% hydrobromic acid by the same method as described above yielded after 3.5 days 10.45 g (36%) of 4-(bromomethyl)cyclohexanemethanol: bp 78–81 °C (0.15 Torr); isomeric ratio cis/trans = 76:24 (GC, Carbowax 20M).

Synthesis of 6-Hydroxyhexanethiol. This thiol was prepared by following the reported literature procedure.[11] Thus, the reaction of 6-bromo-1-hexanol (17.77 g, 0.098 mol) with thiourea (8.21 g, 0.108 mol), dissolved in 13 mL of triethylene glycol at 75 °C, formed the isothiuronium salt, which after cleaving with tetraethylenepentamine (18.55 g, 0.098 mol) at 75 °C yielded 9.12 g (69%) of 6-thio-1-hexanol: bp 70 °C (0.7 Torr) [lit.[11] bp 121–122 °C (15 Torr)].

Synthesis of 4-(Hydroxymethyl)cyclohexanemethanethiol. To a solution of thiourea (2.92 g, 38.4 mmol) dissolved in 5 mL of tetraethylene glycol was added at 75 °C a solution of 4-(bromomethyl)cyclohexanemethanol (7.23 g, 34.9 mmol; isomeric ratio cis/trans = 19:81) in 2 mL of tetraethylene glycol. This mixture was stirred for 6 h at 80 °C. The flask was connected with a 5-cm Vigreux column and a distillation head. Then vacuum (0.5 Torr) was applied and tetraethylenepentamine (6.61 g, 34.9 mmol) was added dropwise at 80 °C. When the addition was complete, the temperature was slowly raised. The formed thiol distilled at 95 °C (0.3 Torr). The crude thiol was redistilled in a Kugelrohr apparatus at 80–85 °C (0.1 Torr): yield 3.67 g (66%); IR (film) 3349, 2556 cm^{-1}.

A thiol with a high cis content was prepared by the same method starting from 4-(bromomethyl)cyclohexanemethanol with a cis/trans ratio of 76:24: yield 82%; bp 94–96 °C (0.3 Torr); isomeric ratio cis/trans = 73:27 (GC, Carbowax 20M).

Syntheses of *p*-[(ω-Hydroxyalkyl)thio]benzaldehydes 1. General Method. To a suspension of sodium hydride (3.0 g, 0.1 mol, 80% dispersion in mineral oil) in 150 mL of dry DMF was added dropwise 2-mercaptoethanol (7.81 g, 0.1 mol) at 0 °C. The mixture was stirred at the same temperature until a solution was obtained (2 h). To this solution was rapidly added *p*-fluorobenzaldehyde (12.4 g, 0.1 mol) at 0 °C and stirring was continued for 15 h at room temperature. The reaction mixture was poured onto ice and stirred well with a blender. The white solid was filtered, washed with water, and vacuum dried, yield 16.08 g (98%) of **1a**. The product was recrystallized from hexanes/ethyl acetate: mp 62–63.5 °C; IR (KBr) 3314, 1651 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.6 (br, 1 H), 3.2 (t, 2 H), 3.8 (t, 2 H), 7.4 and 7.7 (2 d, 4 H, ArH), 9.9 (s, 1 H).

1b: yield 94%; mp 51–53 °C; IR (KBr) 3470, 2750, 1687, 1671 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.9–2.0 (m, 9 H), 2.75–3.15 (m, 2 H), 3.4–3.8 (m, 2 H), 7.3 and 7.7 (2 d, 4 H, ArH), 9.9 (s, 1 H).

1c (the thiol with high trans content described above was used): yield 51%; mp 93–99 °C; IR (KBr) 3477, 2743, 1691, 1670 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85–2.1 (m, 11 H), 2.94 and 3.05 (2 d, 2 H, equatorial and axial CH_2S, respectively), 3.49 and 3.59 (2 d, 2 H, equatorial and axial CH_2O, respectively), 7.4 and 7.8 (2 d, 4 H, ArH), 9.98 (s, 1 H); isomeric ratio cis/trans = 7:93 (by ^{1}H NMR).

Syntheses of the *p*-Thio-α-cyanocinnamates 2. General Method. To a solution of the benzaldehyde derivative **1a** (14.58 g, 0.08 mol) and methyl cyanoacetate (7.93 g, 0.08 mol) in 150 mL of toluene was added a mixture of β-alanine (285 mg) and glacial acetic acid (1.0 g). The mixture was heated under reflux until the theoretical amount of water was removed. The solvent was evaporated under vacuum. The obtained yellow solid was recrystallized from hexanes/ethyl acetate.

2a: yield 73%; mp 116–118 °C; IR (KBr) 3296, 2221, 1719 cm^{-1}; ^{1}H NMR ($CDCl_3$ and D_2O) δ 3.25 (t, J = 6.0 Hz, 2 H), 3.87 (t, J = 6.0 Hz, 2 H), 3.93 (s, 3 H), 7.4 and 7.9 (2 d, 4 H, ArH), 8.19 (s, 1 H). Anal. Calcd for $C_{13}H_{13}N_{13}NO_3S$: C, 59.29; H, 4.99; N, 5.32. Found: C, 59.15; H, 5.06; N, 5.23.

2b: yield 76%; mp 78–81 °C; IR (KBr) 3370, 2217, 1719 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.4–1.8 (m, 8 H), 2.06 (br, 1 H), 3.00 (t, J = 7.3 Hz, 2 H), 3.63 (t, J = 6.4 Hz, 2 H), 3.92 (s, 3 H), 7.3 and 7.9 (2 d, 4 H, ArH), 8.16 (s, 1 H); ^{13}C NMR (CDCl$_3$) δ 25.1 (t), 28.3 (t), 28.4 (t), 31.3 (t), 32.2 (t), 53.1 (q), 62.3 (t), 100.0 (s), 115.7 (s), 126.0 (d), 127.3 (s), 131.2 (d), 146.3 (s), 154.2 (d), 163.1 (s). Anal. Calcd for $C_{17}H_{21}NO_3S$: C, 63.92; H, 6.63; N, 4.39. Found: C, 64.11; H, 6.56; N, 4.40.

2c: isomeric ratio (by ^{1}H NMR) 3% cis, 97% trans; yield 85% (recrystallized from hexanes/toluene); mp 139 °C (DSC); IR (KBr) 3339, 2218, 1716 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.9–2.06 (m, 11 H), 2.91 (d, J = 6.75 Hz, 2 H), 3.47 (br, 2 H), 3.93 (s, 3 H), 7.3 and 7.9 (2 d, 4 H, ArH), 8.18 (s, 1 H). Anal. Calcd for $C_{19}H_{23}NO_3S$: C, 66.06; H, 6.71; N, 4.06. Found: C, 66.14; H, 6.66; N, 4.06.

Synthesis of a cis-enriched *p*-thio-α-cyanocinnamate **2d**. A cinnamate derivative containing 42% *cis*-**2c** and 58% *trans*-**2c** was prepared from 4-(hydroxymethyl)cyclohexanemethanethiol (isomeric ratio cis/trans = 73:27) as described above. The aldehyde derivative **1c**, which was obtained as a viscous oil, was used without further purification. The Knoevenagel condensation resulted in a monomer, **2c**, containing 42% of the cis isomer and 58% of the trans isomer, respectively: yield 20%; mp 100–128 °C; IR (KBr) 3448, 2219 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.9–2.1 (m, 11 H), 2.91 and 2.99 (2 d, equatorial and axial CH$_2$S, respectively), 3.46 and 3.56 (2 t, equatorial and axial CH$_2$O, respectively), 3.93 (s, 3 H), 7.3 and 7.9 (2 d, 4 H, ArH), 8.18 (s, 1 H).

Polymerization. Into a glass flask fitted with a capillary and a distillation head were placed the cinnamate monomer **2** (2–7 mmol) and the comonomer methyl 12-hydroxydodecanoate[2] (if used). Tributyltin acetate (2 mol %) was added and the apparatus was flushed with nitrogen. A homogeneous melt was obtained by heating to 160 °C. Nitrogen was bubbled through the melt and the temperature was kept at 160 °C for 0.5–2 h. To complete the polymerization, the melt (or the solid in case of polymer **5**) was placed under vacuum (0.1–0.2 Torr) and the temperature was raised to 185–200 °C. When the polymerization was complete, the viscous mixture was cooled to room temperature. Dichloromethane-soluble copolymers were purified by precipitation into petroleum ether. Dichloromethane-insoluble polymers were soaked several times in methanol.

3, C$_2$: yield 96%; T_g = 86 °C; T_m = 117 °C, 159–181 °C; IR (KBr) 2220, 1720 cm^{-1}. Anal. Calcd for $C_{12}H_9NO_2S$ (homopolymer repeat unit): C, 61.39; H, 3.87; N, 5.91. Found: C, 61.84; H, 3.92; N, 6.06.

4, C$_6$: yield 100%; T_g = 45 °C; T_m = 130 °C; IR (KBr) 2218, 1715 cm^{-1}. Anal. Calcd for $C_{16}H_{17}NO_2S$ (homopolymer repeat unit): C, 66.87; H, 5.96; N, 4.87. Found: C, 66.56; 5.80; N, 4.77.

5, 97% *trans*-**2c**: yield 100%; T_g = 113 °C, T_m = 226–251 °C; IR (KBr) 2219, 1714 cm^{-1}. Anal. Calcd for $C_{18}H_{19}NO_2S$ (values for the polymer repeat unit): C, 68.98; H, 6.11; N, 4.47. Found: C, 68.79; H, 5.91; N, 4.37.

6: yield 100%; T_m = 38 °C; MW 33 000; IR (film) 2221, 1727 cm^{-1}. Anal. Calcd for $C_{24}H_{31}NO_4S$, (values from a hypothetical copolymer repeat unit): C, 67.10; H, 7.28; N, 3.25. Found: C, 66.65; H, 7.33; N, 3.26.

7: yield 73%; T_m = 58, 123 °C; IR (KBr) 2221, 1728 cm^{-1}. Anal. Calcd for $C_{36}H_{40}N_2O_6S_2$ (values for a hypothetical copolymer repeat unit): C, 65.43; H, 6.10; N, 4.24. Found: C, 64.81; H, 5.94; N, 4.32.

8: yield 56%; IR (film) 2221, 1723 cm^{-1}. Anal. Calcd for $C_{48}H_{49}N_3O_8S_3$ (values for a hypothetical copolymer repeat unit): C, 64.62; H, 5.54; N, 4.71. Found: C, 64.40; H, 5.51; N, 4.86.

9: yield 91%; T_m = 33, 65 °C; MW 64 000; IR (film) 2219, 1729 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.2–1.9 (m), 2.29 (t), 2.95–3.1 (2 t), 4.0–4.1 (2 t), 4.25–4.35 (2 t), 7.3 (d), 7.9 (d), 8.15 (s). Anal. Calcd for $C_{28}H_{39}NO_4S$ (values for a hypothetical copolymer unit): C, 69.24; H, 8.10; N, 2.88. Found: C, 69.25; H, 7.93; N, 2.95.

10: yield 91%; T_m = 88 °C; MW 62 000; IR (film) 2219, 1724 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.2–1.9 (m), 2.3 (t), 2.95–3.1 (2 t), 4.0–4.1 (2 t), 4.25–4.35 (2 t), 7.3 (d), 7.9 (d), 8.15 (s). Anal. Calcd for $C_{44}H_{56}N_2O_6S_2$ (values for a hypothetical copolymer repeat unit): C, 68.36; H, 7.30; N, 3.62. Found: C, 68.13; H, 7.17; N, 3.69.

11: yield 72%; T_m = 109 °C; MW 64 000; IR (film) 2219, 1725 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.2–1.9 (m), 2.29 (t), 2.95–3.1 (2 t), 4.0–4.11 (2 t), 4.25–4.37 (m), 7.3 (d), 7.9 (d), 8.15 (s). Anal. Calcd for $C_{60}H_{73}N_3O_8S_3$ (values for a hypothetical copolymer repeat unit): C, 67.96; H, 6.94; N, 3.96. Found: C, 67.77; H, 6.88; N, 4.08.

12 (monomer **2d**, cis/trans isomeric ratio of 42:58 was used): yield 100%; T_g = 102 °C. Anal. Calcd for $C_{18}H_{19}NO_2S$ (values for a hypothetical copolymer repeat unit): C, 68.98; H, 6.11; N, 4.47. Found: C, 68.99; H, 6.07; N, 3.83.

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Registry No. **1a**, 53606-34-1; **1b**, 132492-87-6; **1c**, 132492-88-7; **2a**, 132492-89-8; **2b**, 132492-90-1; **2c**, 132492-91-2; **2d**, 132562-53-9; **3** (homopolymer), 132492-99-0; **3** (SRU), 132493-09-5; **4** (homopolymer), 132493-00-6; **4** (SRU), 132493-10-8; **5** (homopolymer), 132562-54-0; **5** (SRU), 132493-11-9; **6** (copolymer), 132512-98-2; **9** (copolymer), 132493-01-7; **12** (copolymer), 132616-87-6; *cis*-4-(bromomethyl)cyclohexanemethanol, 132492-85-4; *trans*-4-(bromomethyl)cyclohexanemethanol, 132492-92-3; *cis*-1,4-cyclohexanedimethanol, 28046-68-6; *trans*-1,4-cyclohexanedimethanol, 28046-69-7; hydrobromic acid, 10035-10-6; 6-hydroxyhexanethiol, 1633-78-9; 6-bromo-1-hexanol, 4286-55-9; thiourea, 62-56-6; *cis*-4-(hydroxymethyl)cyclohexanemethanethiol, 132492-86-5; *trans*-4-(hydroxymethyl)cyclohexanemethanethiol, 132492-93-4; 2-mercaptoethanol, 60-24-2; *p*-fluorobenzaldehyde, 459-57-4; methyl cyanoacetate, 105-34-0.