Side-Chain Polyacrylates with 4-(Dimethylamino)-4′-stilbenecarboxylic Ester Mesogens

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ABSTRACT: ω-(Acryloxy)alkyl 4-(dimethylamino)-*trans*-stilbene-4′-carboxylates with $(CH_2)_n$ spacer chains having n = 2, 4, 6, 8, and 10 have been synthesized and polymerized to give side-chain liquid-crystal polymers with M_n = 2800–13 300 relative to polystyrene standards by GPC. DSC and polarizing microscopy show that the polymers have glass and isotropization transition temperatures that decrease with increasing length of the spacer chain to T_g = 79 °C and T_i = 128 °C for the $(CH_2)_{10}$ polymer of M_n = 13 300. Low isotropization enthalpies of ≤1.2 cal/g and polarizing microscopic textures indicate a low degree of order in the liquid-crystal phases. The solubilities and the NMR spectra of the polymers give no indication of significant cross-linking through the stilbene double bond, and the trans configuration of the stilbene was maintained throughout the syntheses.

Introduction

The incorporation of mesogenic structures into flexible side chains of flexible main-chain polymers often produces polymers with liquid-crystalline phases, in some cases even when the analogous low molar mass compound does not exhibit a liquid-crystalline phase.[1-5] The resulting side-chain liquid-crystalline polymers (SCLCPs) have mesophases at ambient or moderately higher temperatures and harden to glasses with retention of liquid-crystalline order when cooled from the liquid-crystalline phase. Polyacrylates, polymethacrylates, and poly(methylsiloxane)s usually serve as the flexible main chains, the flexible side chains are usually polymethylene with 2–12 carbon atoms, and the mesogen is usually a rod-shaped structure attached at the end of the side chain. This structural scheme allows the synthesis of a wide variety of SCLCPs.

The phase transition temperatures of SCLCPs are influenced by the backbone, the side chain, the mesogen structure, and the polymer molecular weight. A more flexible backbone lowers the glass transition temperature. A longer and more flexible side chain lowers the T_g, increases the probability of side-chain crystallization at temperatures above the glass transition, and increases the probability of the appearance of smectic phases. Transition temperatures increase with polymer molecular weight, presumably reaching a high molecular weight limit.[6,7] Traces of residual monomer depress the transition temperatures.[8]

SCLCPs with polarizable aromatic mesogens are attractive candidates for thin-film second-order nonlinear optical (NLO) materials.[9-13] A commonly studied second-order NLO property is second harmonic generation (SHG), the doubling of the frequency of a laser beam. Second-order NLO polarizability requires a noncentrosymmetric structure, and the strength of the SHG effect is enhanced by a chromophore with a large transition moment.[14] Most single crystals of achiral polar organic compounds have centrosymmetric structures, and there is no way to predict which ones will not. Consequently polymer films for SHG investigations have been prepared by using compounds with large transition moments dissolved in glassy polymers, the solute dipoles have been aligned with a strong dc electric field at temperatures near or above T_g, and the aligned materials have been hardened into the glassy state with the field still on. Three types of glassy polymer films have been prepared for second-order NLO studies: (1) Polar aromatic dyes such as 4-(dimethylamino)-4′-nitrostilbene (DANS) dissolved in poly(methyl methacrylate) and in Bisphenol A polycarbonate and oriented in a dc field near T_g give strong SHG but lack temporal stability in the glassy state at room temperature.[15-18] Dyes dissolved in SCLCPs are more orientationally stable than those in PMMA or polycarbonate.[16,19] Incorporation of the dyes into a highly cross-linked epoxy network retards but does not prevent entirely decay of the SHG with time.[20] (2) Polar aromatic compounds such as *N*-(4-nitrophenyl)-L-prolinol and a 4-(dialkylamino)-4′-nitroazobenzene derivative have been covalently bound to functional polystyrenes, poled at high temperature, and hardened to ordered glasses at room temperature.[21,22] Such compounds are not inherently liquid crystal forming, and if the poled sample relaxes in the glassy state, the molecular orientation will become more nearly isotropic. (3) SCLCPs containing mesogens with large transition moments have thermodynamically stable anisotropic glassy states.[23-35] When formed in a dc field, that state is noncentrosymmetric. Side-chain LC copolymers, in which one kind of side chain contains a dye, are dichroic and have higher order parameters than dyes dissolved in SCLCPs.[23,24]

On the premise that inherently liquid-crystalline polymers will attain and retain a high degree of noncentrosymmetric order, we have prepared a series of side-chain polyacrylates with polarized 4-(dimethylamino)-4′-stilbenecarboxylic ester mesogens, which have the donor substituent at the end of the side chain and the acceptor in the spacer chain. Both the acrylate monomers (M-*n*) and the polymers (P-*n*) have LC phases at temperatures of 80 °C or higher. Other polymers that are known to form efficient SHG films have the donor substituent in the spacer chain and the acceptor at the end of the side chain.[26-37] Preliminary second- and third-order nonlinear optical measurements of films of P-10 are reported elsewhere.[38]

Experimental Section

Materials. 4-(*N*,*N*-Dimethylamino)benzaldehyde was recrystallized from ether. Acryloyl chloride and triethylamine were distilled under argon. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. Tetrahydrofuran (THF) and 1,4-dioxane were refluxed over sodium and distilled under nitrogen. All of the other reagents and solvents were used as received.

Analytical Methods. NMR spectra were recorded on a Varian XL-300 instrument at 300 MHz for ^1H or 75.43 MHz for ^{13}C. All spectra were recorded in $CDCl_3$ solution with TMS as internal standard unless otherwise specified. IR spectra were taken on a Perkin-Elmer 681 instrument with KBr disks. UV-visible spectra were taken on a Varian DMS 200 instrument.

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Elemental analyses were done at Desert Analytics (Tucson, AZ). TLC was performed with silica gel GF thin-layer chromatography plates (Analtech Inc.) with mixtures of petroleum ether and ethyl acetate as solvents. High-pressure liquid chromatographic (HPLC) analyses were performed with a Waters 590 pump equipped with a normal-phase 5-μm silica column (length × i.d. = 250 mm × 4.6 mm, Whatman PARTISIL 5), a Rheodyne injector with a 20-μL sample loop, a Beckman 153 analytical 254-nm UV detector, and an Interactive Microwave data station. The eluent was 9/1 (v/v) hexane/ethanol. Molecular weights were determined by gel permeation chromatography (GPC) with the same instrument at 25 °C using three PL gel columns of 10^2, 10^3, and 10^4 Å (particle size 10 μm, length × i.d. = 300 mm × 7.5 mm, Polymer Laboratories, Ltd.). THF was the solvent at a flow rate of 3 mL/min (this flow rate was needed because of limitations of the Interactive Microwave software), and polystyrenes of $M_n = (0.8–600) \times 10^3$ were the standards for calibration using the cubic fit values. Solutions were filtered through a 0.5-μm Millipore PTFE membrane before injection into the chromatograph. Some preliminary GPC analyses were performed with only the 10^3- and 10^4-Å columns at a flow rate of 1 mL/min with $M_n = (0.8–233) \times 10^3$ polystyrene standards. The transition temperatures and enthalpies were determined with a Perkin-Elmer DSC-2C differential scanning calorimeter equipped with a TADS 3600 data station. Temperatures reported are the maxima of the endothermic and exothermic peaks. After the first heating and cooling scans, the polymer sample was annealed at about 10 °C below the isotropization temperature for about 30 min, cooled to 25 °C at 20 K/min, and scanned for the reported data. Glass transition temperaures (T_g) were read at the midpoint of the change in the heat capacity. The temperatures and heats of transitions were calibrated with indium as the standard. The thermal transitions and anisotropic textures were observed with a Nikon 104 optical polarizing microscope fitted with an Instec hot stage (Instec, Inc., Boulder, CO) that was controlled by an Apple IIe computer.

Methyl 4-(Chloromethyl)benzoate (MCB). Method A. Thionyl chloride (83.3 g, 700 mmol) was added dropwise to methyl 4-(hydroxymethyl)benzoate (83.1 g, 500 mmol) cooled in an ice/water bath. The reaction mixture was heated slowly and refluxed for 10 h. The solution was poured into 500 mL of cold water and stirred, and the mixture was extracted with two 150-mL portions of ether. The combined ether extracts were washed twice with 150 mL of saturated aqueous sodium bicarbonate and once with 150 mL of water. The washed extracts were dried over 25 g of anhydrous sodium sulfate and concentrated with a rotary evaporator. The residue was distilled [bp 109 °C (10 mmHg)]. After recrystallization from hexane, 74.1 g (80%) of colorless needle crystals was obtained: mp 38–39 °C (lit.[39] mp 39–40 °C).

Method B. 4-(Chloromethyl)benzoic acid (80.0 g, 580 mmol) and concentrated sulfuric acid (64 mL) were dissolved in 900 mL of methanol. The solution was refluxed for 1.5 h under an argon atmosphere. The reaction mixture was poured into 1 L of water, stirred, and extracted twice with 350 mL of benzene. The organic layer was washed with water and with two 350-mL portions of saturated sodium bicarbonate, and dried over sodium sulfate. The organic solution was evaporated to an oil, which was distilled [bp 109 °C (10 mmHg)] to give 83.0 g (96%) of colorless needle crystals: mp 38–39 °C.

Diethyl [*p*-(Carbomethoxy)benzyl]phosphonate. Methyl 4-(chloromethyl)benzoate (36.9 g, 200 mmol) and triethyl phosphite (36.6 g, 220 mmol) were stirred and refluxed for 1 h under argon. Elimination of ethyl chloride started at about 130 °C, and as the reaction proceeded the solution temperature rose to 187 °C. At reduced pressure, the excess triethyl phosphite was distilled out, and 52.5 g (92%) of colorless viscous liquid was distilled at 185 °C (5 mmHg). ^{1}H NMR: δ 1.26 (t, 6 H, OCH_2CH_3), 3.24 (d, 2 H, PCH_2Ph), 3.90 (s, 3 H, CH_3O), 4.04 (m, 4 H, OCH_2CH_3), 7.4, 8.0 (m, 4 H, aromatic). ^{13}C NMR: δ 16.4 (OCH_2CH_3), 33.9 ($PhCH_2P$), 52.0 (CH_3O_2C–), 62.2 (OCH_2CH_3), 128.8, 129.8, 137.3 (aromatic) 166.8 (CH_3O_2C).

4-(Diethylamino)-4′-carbomethoxy-*trans*-stilbene (*trans*-CMS). In the dark in an argon atmosphere a solution of 4-(*N*,*N*-dimethylamino)benzaldehyde (3.0 g, 20 mmol) and diethyl [*p*-(carbomethoxy)benzyl]phosphonate (5.7 g, 20 mmol) in 30 mL of THF was added dropwise to a stirred slurry of sodium hydride (0.70 g, 30 mmol) in 60 mL of THF-containing 15-crown-5 ether (30 mg) at 0 °C. Hydrogen evolved rapidly, and a yellow precipitate formed. The suspension was stirred for 2 h at 25 °C and poured into 400 mL of ice water. The precipitate was filtered and washed with ether. Afer recrystallization from dimethylformamide, 4.4 g (78%) of luminescent yellow crystals was obtained: mp 220–222 °C (lit.[40] mp 217–218 °C). DSC data are in Table I. ^{1}H NMR: δ 3.00 (s, 6 H, NCH_3), 3.91 (s, 3 H, OCH_3), 6.71 (d, 2 H, ortho to N), 6.92 (d, 1 H, J = 16.4 Hz), 7.16 (d, 1 H, J = 16.2 Hz), 7.43 (d, 2 H, meta to N), 7.51 (d, 2 H, meta to C=O), 7.99 (d, 2 H, ortho to C=O). ^{13}C NMR: δ 40.4 (NCH_3), 52.0 (OCH_3), 112.3 (ortho to N), 123.0, 125.0, 126.0, 127.8, 128.0, 130.0, 131.4, 142.8 (para to C=O), 150.5 (aromatic C_N), 167.0 (C=O). IR 1710 (C=O), 960 cm^{-1} (CH). UV-vis: in $CHCl_3$, λ_{max} = 384 nm (ϵ = 35 700 M^{-1} cm^{-1}); in hexane, λ_{max} = 372 nm; in methanol, λ_{max} = 380 nm. Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.96; H, 6.82; N, 4.92.

4-(Dimethylamino)-4′-carbomethoxy-*cis*-stilbene (*cis*-CMS). The cis isomer was prepared by photoisomerization of the trans isomer. *trans*-CMS (0.30 g) was dissolved in 50 mL of chloroform and exposed to normal room fluorescent lights for 2 days. Two spots were detected by TLC by using 7% ethyl acetate and 93% petroleum ether as the solvent (*cis*-CMS, R_f = 0.27; *trans*-CMS, R_f = 0.20). The ^{1}H NMR spectrum showed that the solution was composed of 74% *cis*-CMS and 26% *trans*-CMS. The solution was chromatographed over silica gel (2.5 × 50 cm, Grade 62, 60–200 mesh, EM Science), and the *cis*-CMS was eluted with 7/93 (v/v) ethyl acetate/petroleum ether. After evaporation and crystallization from benzene, 0.10 g of crystals obtained, which contained 94% *cis*-CMS and 6% *trans*-CMS as determined from the ^{1}H NMR spectrum. ^{1}H NMR: δ 2.93 (s, 3 H, NCH_3), 6.39 (d, 1 H, J = 12.1 Hz), 6.55 (d, 2 H, ortho to N), 6.58 (d, 1 H, J = 11.9 Hz), 7.43 (d, 2 H, meta to N), 7.51 (d, 2 H, meta to C=O), 7.99 (d, 2 H, ortho to C=O). ^{13}C NMR: δ 40.3 (NCH_3), 52.0 (OCH_3), 111.7 (ortho to N), 124.4, 125.6, 128.0, 128.0, 128.7, 129.5, 130.0, 132.3, 143.3 (aromatic para to C=O), 149.8 (NC), 167.1 (C=O), IR: 1720 (C=O), 715 cm^{-1} (CH). UV-vis ($CHCl_3$): λ_{max} = 375 nm (ϵ = 13 700 M^{-1} cm^{-1}).

ω-Hydroxyalkyl 4-(Dimethylamino)-*trans*-stilbene-4′-carboxylates (A-*n*). All alcohols A-*n* were synthesized by the transesterification of *trans*-CMS with excess diol in the presence of concentrated sulfuric acid. A typical procedure is illustrated with the synthesis of A-8. *trans*-CMS (11.2 g, 40 mmol), 1,8-octanediol (200 g, 1.37 mol), and concentrated sulfuric acid (3.5 mL) were stirred at 90 °C for 36 h under argon in the dark. The reaction was monitored by TLC using 1/1 ethyl acetate/petroleum ether as the solvent. The solution was poured into 2 L of water and stirred. The yellow precipitate was filtered and recrystallized from methanol to yield 9.8 g (62%) of yellow product with a purity of 99% (HPLC). IR: 3520–3440 cm^{-1} (OH). The ^{1}H NMR and ^{13}C NMR spectra were nearly identical with those of *trans*-CMS with the expected additional signals from the C_8 chain. UV-vis (A-10, $CHCl_3$): λ_{max} = 384 nm (ϵ = 45 900 M^{-1} cm^{-1}). Yields and thermal analyses are reported in Table II. A-8 and A-10 had C, H, and N analyses within 0.2% of the calculated values. The other A-*n* compounds were not analyzed.

ω-(Acryloxy)alkyl 4-(Dimethylamino)-*trans*-stilbene-4′-carboxylates (M-*n*). The acrylate monomers were synthesized by esterification of the alcohols A-*n* with acryloyl chloride. For

Table I
Thermal Transition Temperatures and Enthalpies from DSC[a] of Monomers

compd	yield, %	T_m, °C	ΔH_m, kcal/mol (cal/g)	T_i, °C	ΔH_i, kcal/mol (cal/g)
trans-CMS	78	229	8.78 (31.2)		
A-2	69	216	5.14 (23.3)		
A-4	74	191	5.09 (15.0)		
A-6	69	170	5.07 (13.8)		
A-8	65	159	4.94 (12.5)		
A-10	61	149	5.00 (11.8)		
M-2	49	178	3.76 (10.3)	196	0.04 (0.1)
M-4	34	153	3.42 (8.7)	181	0.43 (1.1)
M-6	72	142	3.79 (9.0)	175	0.55 (1.3)
M-8	86	133	3.96 (8.8)	166	0.22 (0.5)
M-10	90	126	3.87 (8.1)	159	0.29 (0.6)

[a] Heating at 20 K/min.

Table II
Molecular Weights and Thermal Transitions[a] of Polymers

polymer	yield,[b] %	$M_n \times 10^{-3}$	M_w/M_n	monomer,[c] %	T_g, °C	T_i, °C	ΔH_i, kcal/mol (cal/g)
P-2	48	5.7	2.5		129	139	0.09 (0.25)
P-4	20	2.8	2.5		119	130	0.28 (0.72)
P-6	26	3.9	2.5		109	125	0.41 (0.98)
P-6[c,d]		8.1	50	1.0	86	138	0.84 (1.99)
P-8	24	3.4	2.7		91	121	0.52 (1.16)
P-8B	31	11.0	2.5		96	130	0.18 (0.41)
P-8B[c,e]		12.3	12	2.0			
P-10	27	5.2	2.0		81	117	0.58 (1.21)
P-10B	41	10.9	3.4		83	125	0.43 (0.89)
P-10B[c,e]		13.3	14	2.0	79	128	0.35 (0.73)

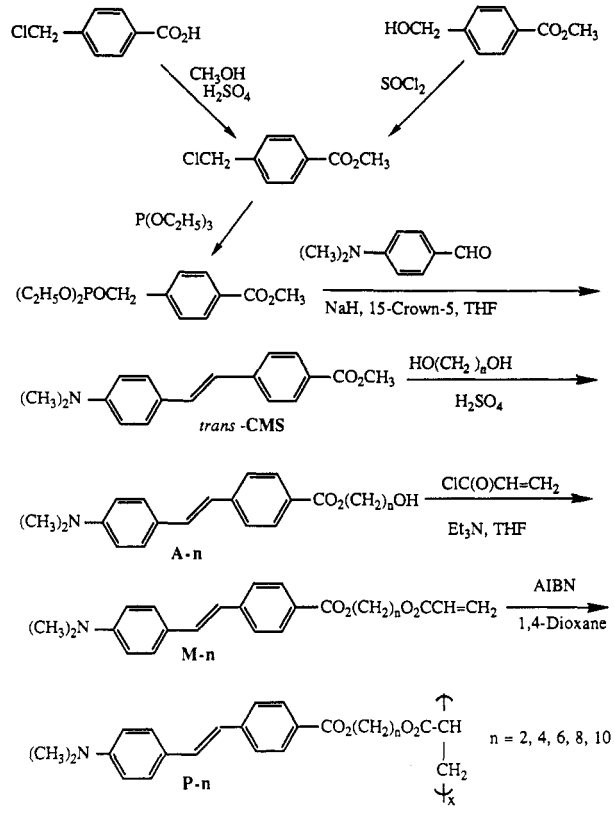
[a] DSC second heating at 20 K/min. [b] After reprecipitation. [c] Percent monomer could be determined only from later experiments in which a 10^2-Å column was used. The small amounts of monomer are included in the calculations of M_n and M_w. [d] A second sample was prepared by method A (Experimental Section). [e] Second analyses were performed after the samples were reprecipitated again more than 1 year after preparation.

example, M-8 was prepared as follows. Under argon in the dark A-8 (9.20, 23 mmol), triethylamine (5.10 g, 50 mmol) and 300 mL of THF were stirred at 0 °C. Acryloyl chloride (4.80 g, 50 mmol) was added dropwise. The mixture was allowed to warm to 25 °C and stirred for 12 h. The reaction was monitored by TLC with 1/1 ethyl acetate/petroleum ether as the solvent. The yellow suspension was poured into 2 L of water and stirred. The precipitate was filtered and recrystallized from methanol to give 9.0 g (86%) of yellow crytsals with a purity higher than 99.0% (HPLC). IR: 1715 cm^{-1} (C=O); there was no O–H stretching band. the ^1H NMR and ^{13}C NMR spectra were nearly identical with those of *trans*-CMS and the A-*n* compounds except for the expected ^1H acrylate signals (for M-8) at δ 5.81 (d, J = 10.2 Hz), 6.12 (dd, J = 17.4, 10.5 Hz), and 6.40 (d, J = 10.5 Hz) and ^{13}C acrylate signals (for M-8) at δ 128.2, 130.5, and 166.4 (C=O). UV–vis (M-10, $CHCl_3$): λ_{max} = 384 nm (ϵ = 38 400 M^{-1} cm^{-1}). Yields and DSC data are reported in Table II. M-8 and M-10 had C, H, and N analyses within 0.2% of the calculated values. The other M-*n* compounds were not analyzed.

Acrylate Polymers (P-*n*). Method A (for P-2, P-4, P-6, P-8, and P-10). The acrylate monomers (M-*n*), each 0.50 g, were polymerized as 10% (w/v) solutions in 1,4-dioxane with 1.0 wt % (2.2–2.8 mol %) AIBN as initiator. The solution in a glass tube was degassed by freeze–pump–thaw cycles under vacuum, sealed, and held in a water bath at 60 °C for 60 h. The solution was poured into methanol to precipitate the polymer. The polymer was filtered, dried under vacuum, and reprecipitated from THF into methanol. Small amounts of insoluble yellow solid were filtered out of the P-2, P-4, and P-6 solutions in THF before reprecipitation. Qualitatively the solubilities of the polymers in THF increased with increasing spacer chain length. The yields and DSC and GPC analyses of the polymers are reported in Table II.

Method B (for P-8B and P-10B). The monomers M-8 (8.40 g) and M-10 (12.50 g) was separately dissolved with 1 wt % (2.2–2.3 mol %) of AIBN into 76 and 104 mL of 1,4-dioxane in 200-mL flasks equipped with condensers. The solutions were purged with argon for 2 h, heated at 65 °C for 96 h, and poured into methanol to precipitate the polymers. The polymers were filtered and dried under vacuum to yield 5.47 g (65%) and 7.8 g (62%) of crude products. After reprecipitation from THF into methanol, 2.63 g (31%) of P-8B and 5.11 g (41%) of P-10B were obtained. GPC and DSC characterizations are reported in Table II. The ^1H NMR spectrum of P-10 ($CDCl_2CDCl_2$, 90 °C) has broad bands in both the aromatic and aliphatic regions that account for about half of the signal area, and lines as little as 8 Hz wide at half-height, which account for the other half of the signal area. The narrow line part of the spectrum was like that of M-10, including doublets at δ 6.93 and 7.15 (J = 16 Hz), lacking the vinyl H signals, and with additional broad bands at δ 1.3 and 1.7 (backbone CH_2) and 2.9 (backbone CH). The ^{13}C NMR spectrum of P-10 ($CDCl_2CDCl_2$, 90 °C) was nearly identical with that of M-10. The signal-to-noise ratio was too low to detect peaks from backbone or acrylic ester carbonyl carbons. There was no sign of broad bands like those in the ^1H NMR spectrum. UV–vis (P-10, $CHCl_3$): λ_{max} = 384 nm (ϵ = 20 200 M^{-1} cm^{-1}). Anal. of P-8B. Calcd for $C_{28}H_{35}NO_4$: C, 74.80; H, 7.85; N, 3.12. Found: C, 74.54; H, 7.93; N, 3.24. Anal. of P-10B. Calcd for $C_{30}H_{39}NO_4$: C, 75.44; H, 8.23; N, 2.93. Found: C, 75.45; H, 7.97; N, 2.99. The polymers made by method A were not analyzed.

Scheme I



Results

The monomers and polymers were synthesized as shown in Scheme I. The key double-bond-forming step was performed by a Wadsworth-Emmons reaction using 15-crown-5 ether as a catalyst to provide 78% yield of 4-(dimethylamino)-4′-carbomethoxy-*trans*-stilbene (*trans*-CMS) from *p*-(dimethylamino)benzaldehyde. *trans*-CMS was prepared before in low yield via hydrolysis of 4-(dimethylamino)-4′-cyanostilbene.[40] The ^1H NMR spectra of *trans*-CMS and all of the alcohols A-*n* and acrylate monomers M-*n* showed only the *trans*-stilbene isomer. *trans*-CMS, the alcohol A-10, the monomer M-10, and the polymer P-10 all have a bright yellow color and identical absorption maxima at 384 nm in $CHCl_3$. Thus the entire synthesis proceeded without detectable isomerization of the stilbene double bond.

In an early experiment the color of an NMR sample of *trans*-CMS in $CDCl_3$ turned red during a few days in fluorescent light, and new peaks for *cis*-CMS appeared in

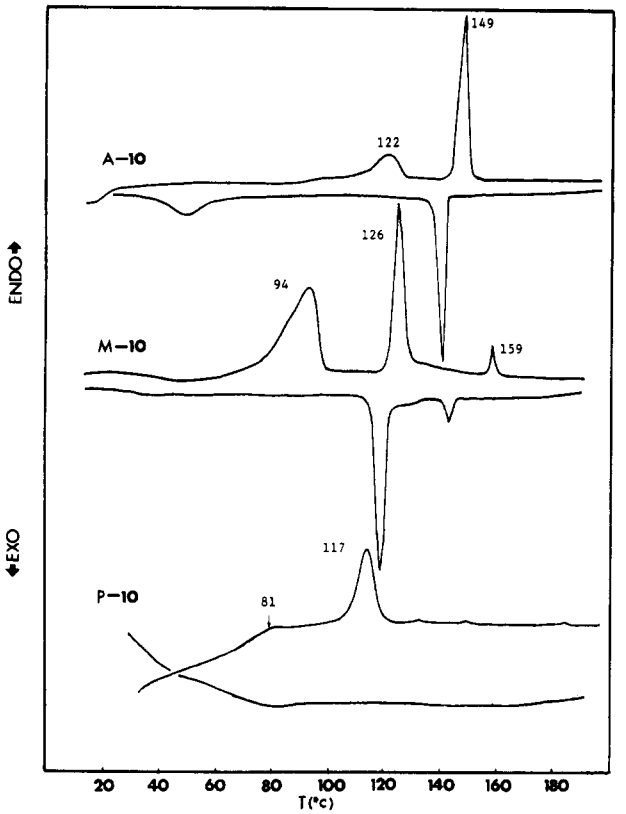


Figure 1. DSC thermograms of A-10, M-10, and P-10 at 20 K/min.

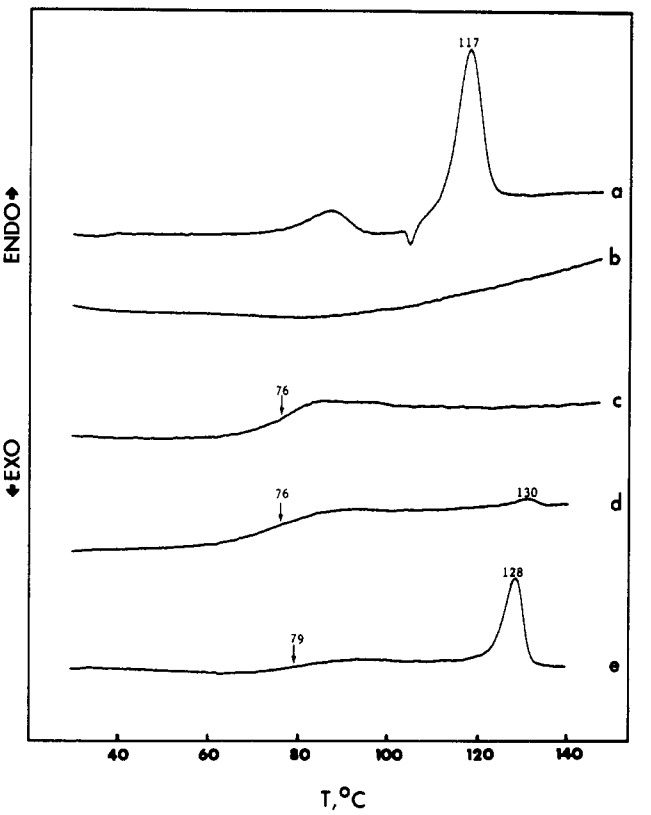


Figure 2. DSC analyses of P-10B at 20 K/min: (a) first heating; (b) first cooling; (c) second heating immediately after first cooling; (d) heating after 30 min of annealing at 110 °C during the preceding cooling cycle; (e) heating after 24 h of annealing at 110 °C during the preceding cooling cycle.

the ^{1}H NMR spectrum. From such a photoisomerized mixture on a larger scale 94% pure *cis*-CMS was isolated chromatographically. The mixtures of *cis*-CMS and *trans*-CMS are analyzed easily by the relative areas of the NCH_3 signals in their ^{1}H NMR spectra. *cis*-CMS is yellow too but not as intensely colored as *trans*-CMS.

The phase transition temperatures of alcohols A-*n* and acrylate monomers M-*n* determined by DSC are reported in Table I. Only a melting transition was observed for each of the alcohols. The acrylates all had a melting transition with a large ΔH_m and a mesophase to isotropic transition with $\Delta H_i < 0.6$ kcal/mol. Typical DSC thermograms of the C_{10} compounds are shown in Figure 1. The transition temperatures decrease systematically, and the temperature range of the liquid-crystalline phase increases, with increasing length of the polymethylene chain. Polarizing microscopic examination of each compound showed transitions at about the same temperatures observed by DSC.

The monomers M-*n* were polymerized with AIBN initiator in dioxane solutions. All polymers were precipitated from the reaction mixtures and reprecipitated once from THF into methanol. Yields were low due to separation of much monomer during the reprecipitation process. GPC analyses of the molecular weights based on polystyrene standards and DSC analyses of the phase transitions of the polymers P-*n* are reported in Table II. The samples prepared from 0.5 g of monomer had M_n = 2800–6600, whereas P-8B and P-10B, prepared from about 10 g of monomer, had M_n = 12 300–13 300. The initial GPC analyses were done with only 10^3- and 10^4-Å columns. Later GPC analyses using also a 100-Å column showed resolved monomer fractions in the samples of 1–2 area %. Some of the samples had very broad molecular weight distributions, which could be attributed to branched or cross-linked components or to partial aggregation in solution. Broad bands in the ^{1}H NMR spectrum of P-10B also were consistent with cross-linking or aggregation. However, the P-6, P-8B, and P-10B samples that had the greatest polydispersity were completely soluble in THF and in chloroform.

After the first DSC scan no isotropization endotherm appeared unless the samples were annealed for long times in the liquid-crystalline temperature range, as shown for P-10B in Figure 2. The higher molecular weight samples of P-6, P-8, and P-10 had higher isotropic transition temperatures. No other transitions were found for any annealed polymer in the temperature range between 0 °C and the T_g reported in Table II. Repeated DSC scans after the first showed approximately the same phase transitions, but, after many cycles and long annealing times between repeated heating scans, the peaks became smaller as shown for P-8 in Figure 3.

Polarizing microscopy of the polymers showed no recognizable texture until the samples were annealed for long times. The textures of P-8B and P-10B are shown in Figure 4. The shorter spacer chain polymers gave less well-defined textures.

Discussion

The apparent molecular weights of the P-*n* samples from GPC correspond with DP_n = 7–25. However, GPC with polystyrene standards underestimates the molecular weights of SCLCPs because the hydrodynamic volume of a comblike polymer is smaller than that of polystyrene of the same molecular weight.[41] Although the true molecular weights must be greater than those shown in Table II, some of the samples are still best described as oligomers. The incomplete polymerizations of M-*n* even after 96 h at 65 °C indicate low monomer reactivity and short kinetic chain lengths.

One possible reason for the broad molecular weight distributions is a branched structure due to polymerization

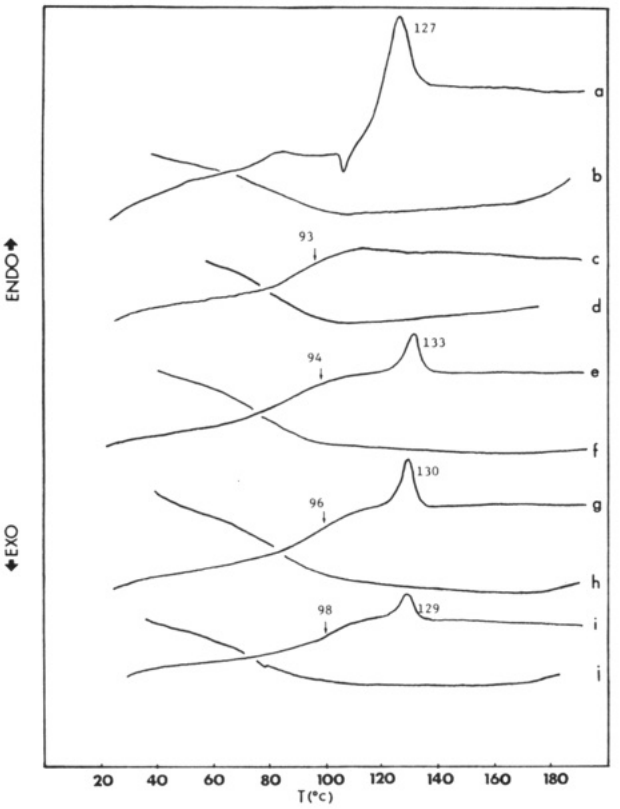


Figure 3. Repeated DSC analyses of P-8B at 20 K/min: (a) first heating, ΔH_i = 0.45 cal/g; (b) first cooling, after 2 min at 180 °C; (c) second heating, after 5 min at 25 °C; (d) second cooling, after 2 min at 180 °C; (e) third heating, after 26 h at 100 °C and cooling to 25 °C, ΔH_i = 0.38 cal/g; (f) third cooling, after 2 min at 180 °C; (g) fourth heating, after 60 h at 100 °C and cooling to 25 °C, ΔH_i = 0.45 cal/g; (h) fourth cooling, after 2 min at 180 °C; (i) fifth heating, after 100 h at 100 °C and cooling to 25 °C, ΔH_i = 0.29 cal/g; (j) fifth cooling, after 2 min at 180 °C.

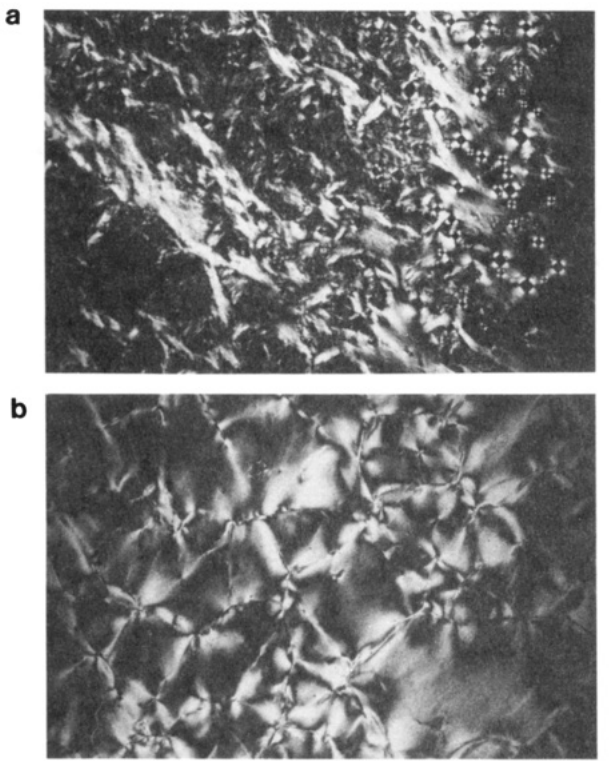


Figure 4. (a) P-8B and (b) P-10B between crossed polarizers (30×) after 10 h at 125 °C.

through the stilbene double bond or to chain transfer of a hydrogen atom from a methyl carbon of the dimethylamino group. Extensive branching would give a cross-linked polymer. There are reports of insoluble stilbene side-chain polymers prepared by free-radical polymerization.[42] However, a nonpolarized stilbene double bond does not polymerize with AIBN initiator.[43] We detected no peaks due to either type of chain branching in ^{1}H NMR spectra of P-10B, the highest molecular weight sample, and also no evidence of methyl end groups from the AIBN initiator. The solubilities of P-*n* increased with increasing spacer chain length, which is more consistent with greater solvation of the mesogens attached to longer spacer chains than with cross-linking.

The T_g's of the P-*n* with the longer spacer chains are unusually high for SCLCPs. We attribute this to strong aggregation of the dipolar stilbene mesogens, which is also consistent with high viscosity in the isotropic phase discussed below. Similarly high T_g's have been reported for other polarized stilbene[29,42] and aryl benzoate[44] side-chain polyacrylates.

Usually the T_i of a SCLCP is higher than that of the corresponding monomer.[6] That is not true for the polymers reported here, perhaps because of the broad molecular weight distributions including significant amounts of monomer, dimer, trimer, etc. As reported in Table II, T_i was consistently higher for the higher M_n samples. The isotropic phases and birefringent liquid-crystal phases reported from DSC data in Table II were observed by polarizing microscopy. Shearing of P-10B at 130 °C in the isotropic phase did not create birefringence.

The appearance of the isotropic transition of P-10B depends on sample history as shown in Figure 2. Since P-10B requires such a long time to develop liquid-crystalline order, the viscosity of the isotropic phase must be much greater than that of side-chain polyacrylates having less polarized mesogens. The high viscosities of the isotropic phase are consistent with the high T_g values of this entire family of polymers.

Transition temperatures of SCLCPs increase with increasing molecular weight up to limiting values. The molecular weights required for limiting values of T_g and T_i depend on the polymer backbone, spacer chain, and mesogen. The closest analogy to our P-*n* samples is the family of α-methylstilbene SCLCPs reported by Percec, Tomazos, and Pugh.[45] They found limiting values of T_g and T_i at $M_n > 10\,000$ based on GPC with polystyrene standards. Our data for different molecular weight samples (P-8 vs P-8B and P-10 vs P-10B in Table II) show that M_n = 3400–5100 lies below the M_n required for high limiting values of T_g and T_i. It is possible that the values for P-8B and P-10B are at the maxima, but samples with narrower molecular weight distributions would be needed to determine the maxima.

What are the liquid-crystalline phases of the polymers? All of the polyacrylates P-*n* have small ΔH_i indicative of a liquid-crystal phase of a low degree of order. The ΔH_i data in Table II were obtained with samples that were annealed briefly before the DSC heating scan, but only P-8B and P-10B were scanned repeatedly, as shown in Figures 2 and 3. The ΔH_i data in Figure 3 show ΔH_i = 0.45 cal/g for one scan after a short annealing time and ΔH_i = 0.38, 0.45, and 0.29 cal/g for three scans after long annealing times, which suggests that the other SCLCP ΔH_i data are probably reliable to within about 0.2 cal/g of the reported values in Table II. Typically, ΔH_i for polymer nematic phases are <1.0 cal/g, whereas the least ordered smectic phases, S_A and S_C, typically have ΔH_i of >1.0 cal/g.[2,3] (There are exceptions.) The ΔH_i includes contributions from the loss of order of both the spacer chains and the mesogens. Longer spacer chains give larger ΔH_i. The small ΔH_i values of our annealed polymers indicate a low degree of order of both the mesogens and

the spacer chains in the liquid-crystalline states. The microscopic textures of P-8 and P-10 in Figure 4 do not allow unambiguous assignments of the phases, but they are consistent with nematic or S_A phases.

The monomers M-*n* also have low ΔH_i values of ≤1.3 cal/g indicative of nematic or S_A phases. M-10 showed three phase transitions, but the other M-*n* compounds showed only two. The first transition of M-10 at 94 °C (Figure 1) occurred without change in its polarizing microscopic texture and without flow, which suggests that it may be a solid–solid transition, although we cannot rule out the possibility of a highly ordered mesophase at 94–126 °C.

Stilbenes are known to isomerize and dimerize photolytically. Photodimerization of stilbene double bonds, either of the monomers before polymerization or of the polymers during or after polymerization, could give crosslinked polymers. Photoisomerization of stilbenes is much faster than photodimerization in homogeneous solutions, but dimerization may be favored in the solid state[46] and in ordered assemblies such as bilayers.[47] After we observed photoisomerization of *trans*-CMS to *cis*-CMS in solution in fluorescent lighting, we stored all stilbene samples out of light and observed no other evidence of photoisomerization.

P-10 and related stilbenes have large second-order NLO polarizabilities due to the large transition moments of the donor–acceptor-substituted conjugated aromatic structures.[38,48-50] Preliminary experiments have shown also degenerate four-wave-mixing third-order nonlinear optical response from films of P-10B, and further nonlinear optical experiments are in progress.[38]

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