Macromolecules
Volume 23, Number 3 February 5, 1990

Synthesis and Characterization of the Liquid-Crystalline Side-Chain Polymer 4′-Cyano-4-(pentyloxy)stilbene Polysiloxane

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Received July 18, 1988; Revised Manuscript Received May 30, 1989

ABSTRACT: The liquid-crystalline side-chain polymer 4′-cyano-4-(pentyloxy)stilbene polysiloxane has been synthesized via direct condensation polymerization of the dichlorosilane monomer. Likewise, the synthesis of the starting silane, 4′-cyano-4-[[5-(dichloromethylsilyl)pentyl]oxy]stilbene as well as 4′-cyano-4-[[5-(chlorodimethylsilyl)pentyl]oxy]stilbene, which was used to terminate the reaction is reported. The mesogenic properties of the polymer, the side-chain liquid-crystal precursor, and the respective dichlorosilane monomer are discussed.

Introduction

The synthesis of liquid-crystalline side-chain polymers, especially polysiloxanes, has become an active research area because of the potential use of these materials in electrooptical devices.[1-4] Siloxane polymers enjoy a unique position due to their lower glass transition temperatures and flexibility.

Although polysiloxanes with various mesogenic side-chain units (biphenyl,[5,6] phenyl benzoates,[7] and steroids[8]) have been synthesized and used as stationary phases in gas chromatography, only a few have had cyano functional groups.[9-11] Usually mesogens with a terminal cyano group are strongly polar nematic compounds with positive dielectric anisotropy and display a twisted nematic effect. However, they can also give rise to a large number of smectic phases.[12]

Attempts have been made to produce polymeric cyano polysiloxanes, which can be used in display devices. To date, they have been prepared via polyhydrosilylation reaction[5] of poly(hydrogen methylsiloxane) (PHMS; commercially available) with appropriate vinylic mesogens using a wide variety of catalysts. The most commonly employed catalyst is chloroplatinic acid, H_2PtCl_6. Often problems are encountered in this conventional synthesis of polysiloxanes which include nonreproducibility, discoloration, and cross-linking of the resulting polymer.

Since the cause of these probelems has been attributed to the use of platinum during the polymeric addition reaction,[11] a way of minimizing them is elimination of Pt during the polymerization. This can be accomplished by first preparing the silyl monomer from the vinylic mesogen followed by direct condensation.

The current paper describes the synthesis and characterization of a liquid-crystalline side-chain polysiloxane polymer which bears the fluorescent cyanostilbene pendant. The material is prepared via condensation of the dichlorosilane monomer.

Experimental Section

Materials and Techniques. Most chemicals were purchased from the Aldrich Chemical Co. (Milwaukee, WI) and used as received. The starting silanes, which also were used as received, were from Petrarch (Levittown, PA). The microscopic studies were made in triplicate at heating rates of either 2 °C or 10 °C/min using a Leitz–Wetzler Ortholux polarizing instrument fitted with a modified Mettler FP-2 heating stage. Photographs were taken with a Leitz Microscopic 35-mm camera using Kodak Ektrachrome film (160 ASA). The DSC measurements were carried out on a Perkin-Elmer Model DSC-2 differential scanning calorimeter at a heating rate of 2.5 °C/min under nitrogen. The weight and number average molecular weight of the polymer were determined on a Waters liquid chromatograph equipped with a refractive index detector and GPC column. Polystyrene standards were used as calibration materials. ^1H and ^{13}C NMR spectra were recorded on a General Electric GN-300 spectrometer. Infrared spectra were recorded on IBM Instruments Model IR-32 FTIR spectrometer.

Synthesis. 4-(Pentenyloxy)benzaldehyde (1). A mixture of *p*-hydroxybenzaldehyde (24.2 g, 0.2 mol), 5-bromo-1-pentene (25 g, 0.17 mol), acetone (200 mL), and anhydrous potassium carbonate (35.5 g, 0.25 mol) were refluxed for 24 h with mechanical stirring. The reaction mixture was poured into water, the acetone removed, and the aqueous layer extracted with ether (60 mL, 4×). The ether layer was washed with aqueous potassium hydroxide (2 M, 50 mL, 4×), water (50 mL, 4×), and saturated brine (50 mL, 2×) and then dried using anhydrous sodium sulfate. Removal of the ether gave a yellow oil, which was puri-

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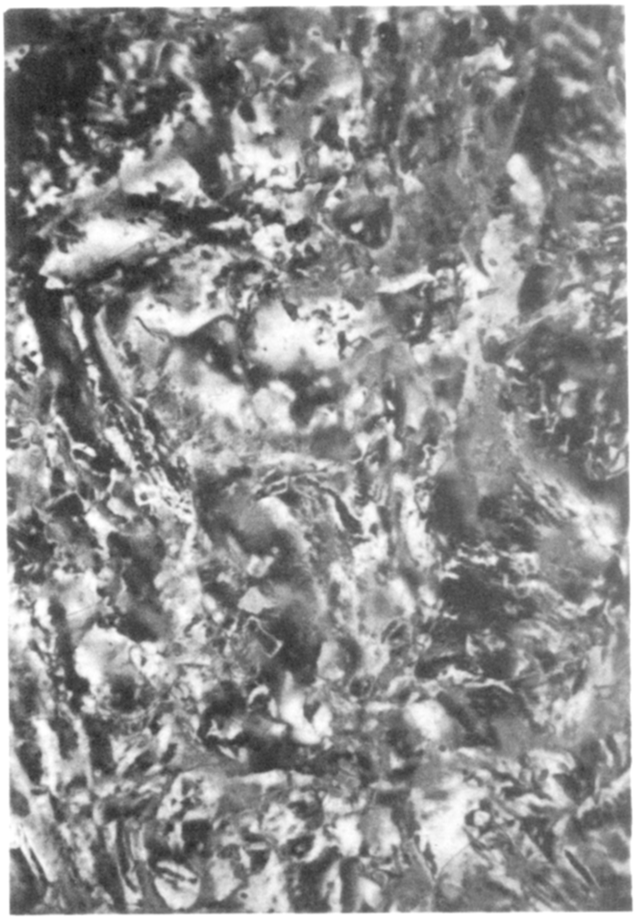


Figure 1. Typical optical polarization micrograph of 4′-cyano-4-(pentenyloxy)stilbene showing nematic marble texture. (Magnification 20 × 10.)

fied by distillation at reduced pressure; bp 135–140 °C (0.35 mm), yield 80.6%. IR (neat): 1690, 1600, 1500, 1260, 1160, 920, 830, 655, 615 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 9.86 (s, 1 H, –CHO), 7.80–6.96 (AA′ BB′, 4 H, aromatic), 5.85, 5.08–5.01 (m, 3 H, –vinyl), 4.02 (t, 2 H –OCH_2), 2.23, 1.90 (m, 4 H, –CH_2CH_2). ^{13}C NMR ($CDCl_3$): δ 190.60, 164.13, 137.40, 131.93, 129.86, 115.49, 114.73, 67.48, 30.00, 28.20.

4′-Cyano-4-(pentenyloxy)stilbene (2). Ethanolic solutions of **1** (32.5 g, 0.17 mol) and lithium ethoxide (0.2 M, 855 mL) were added to a stirred solution of (4-cyanobenzyl)triphenylphosphonium chloride (75 g, 0.18 mol) and absolute ethanol (200 mL). The solution was stirred for 3 days at room temperature. Subsequently, water (795 mL) was added, and the precipitate that formed was filtered, washed with absolute ethanol, and dried. The product was purified by recrystallization from a mixture of toluene and petroleum ether. A yield of 20% was obtained; mp (cp) 123–125 °C. IR (diffused reflectance; solid): 2200, 1600, 1500, 1450, 1160, 1100, 975, 925, 830, 650, 585, 550, 475 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.57–7.41 (m, 6 H, aromatic), 7.14–7.09 (d, 1 H, –CH=), 6.9–6.86 (m, 3 H, aromatic), 5.85–5.80, 5.08–4.98 (m, ABX, vinyl), 3.96 (t, 2 H, –OCH_2), 2.24, 1.87 (m, 4 H, –CH_2CH_2–). ^{13}C NMR ($CDCl_3$) δ 159.40, 142.08, 137.54, 132.25, 131.84, 128.77, 128.13, 126.38, 124.23, 119.01, 115.15, 114.71, 109.81, 67.13, 29.94, 28.24.

4′-Cyano-4-[[5-(dichloromethylsilyl)pentyl]oxy]stilbene (3). A mixture of **2** (1.45 g, 0.005 mol), chloroplatinic acid (THF solution 0.122 M, 3 drops), toluene (5 mL), and dichloromethylsilane (0.52 mL, 0.005 M) was heated at 40–50 °C for 16 h. The reaction mixture was cooled, and the resulting solid was redisolved in boiling toluene, filtered (under N_2), concentrated, and allowed to crystallize. A pale yellow solid was obtained at a yield of 90%; mp 191–192 °C. ^{1}H NMR ($CDCl_3$) δ 7.63–7.45 (m, 6 H, aromatic), 7.19–7.13 (d, 1 H, –CH=), 6.97–6.89 (m, 3 H, aromatic), 3.99 (m, 2 H, –OCH_2), 1.83 (m, 2 H, –CH_2), 1.6 (m, 4 H, –CH_2CH_2), 1.17 (m, 2 H, –CH_2), 0.79 (3 H, –CH_3). ^{13}C NMR ($CDCl_3$) δ 159.59, 142.25, 132.39, 132.01, 129.01, 128.23, 126.52, 124.48, 119.04, 114.87, 110.07, 67.79, 28.90, 28.73, 22.24, 21.53, 5.18.

4′-Cyano-4-[[5-(chlorodimethylsilyl)pentyl]oxy]stilbene (4). It was prepared via the same procedure as **3** with a yield of 77%; mp 90–91 °C. ^{1}H NMR ($CDCl_3$) δ 7.52–7.35 (m, 6 H, aromatic), 7.1–7.04 (d, 1 H, –CH=) 6.87–6.81 (m, 3 H, aromatic), 3.9 (t, 2 H, –OCH_2), 1.73 (m, 2 H, –CH_2), 1.45 (m, 4 H, –CH_2CH_2), 0.78 (m, 2 H, –CH_2), 0.35 (s, 6 H, $SiCH_3$). ^{13}C NMR ($CDCl_3$) δ 159.49, 142.11, 132.27, 131.66, 128.73, 128.15, 126.40, 124.22, 119.03, 116.70, 109.80, 67.78, 29.19, 28.14, 22.11, 18.78, 1.56.

Polysiloxane (5). Water (0.5 mL) was slowly added to a stirred solution of THF (8 mL), which contained **3** (0.8 g, 0.0019 mol). An immediate exothermic reaction was noted. After 15 min, pyridine (0.4 mL) was added and the mixture refluxed for 22 h followed by the addition of 4′-cyano-4-[[5-(chlorodimethylsilyl)pentyl]oxy]stilbene (0.5 g, 5% by weight). The mixture was refluxed for another 5 h. The resulting polymer was precipitated by the addition of methanol and was purified from chloroform by addition of methanol. This latter process was carried out three times. A yield of 75% was obtained for the cream-colored polymer.

Results and Discussion

Synthesis. The 4′-cyano-4-(pentyloxy)stilbene polysiloxane polymer was prepared by the four-step synthesis shown in Scheme I. All steps, except the Wittig reaction, proceeded with yields of 75–90%. However, in the latter case, only 20% of the mesogenic *trans*-stilbene could be isolated. The final polymer after purification was granular and cream colored. Its weight average and number average molecular weights were 5.56×10^3 and 3.17×10^3, respectively. The polydispersity ratio was 1.75.

The molecular weight of the polysiloxane obtained via direct condensation is similar to that obtained by traditional polyhydrosilylation reactions.[13–16] Although a relatively low molecular weight polymer was produced (M_n 3200), higher degrees of polymerization should be achievable with increased reaction times.

An important advantage of direct polymerization over polyhydrosilylation procedures is that the method assures the presence of consecutive mesogenic pendants over the polymer's entire length. When the latter method is carried out, NMR is often used to monitor the progress of hydrosilylation. The inherent limitation of this technique is detection of the Si–H resonance, which is approximately 20 mol %.[17] Hence, the abence of the Si–H peak in NMR spectrum does not guarantee complete addition. The direct condensation method does not suffer from this disadvantage. Additional problems of cross-linking (by the hydrosilylation cyano function) and discoloration (usually shades of gray and black) were not encountered via direct polymerization. Even though H_2PtCl_6 is used as a catalyst, it is used in a step (third step; monohydrosilylation) where purification is more easily accomplished.

Mesogenic Properties. The mesogenic properties of the precursors, **2** and **3**, and the polymer, **5**, were studied by polarized microscopy and differential scanning calorimetry.

Microscopy. The vinylic stilbene, **2**, showed three transitions on heating: a crystal to crystal change at ~70 °C, a crystal to nematic change at 94.5 °C, and a nematic to isotropic change at 124.8 °C. The second transition was reproducible both on heating and on cooling whereas supercooling occurred for the nematic to crystal change. The nematic nature of the mesophase was confirmed by a characteristic marble–Schlieren texture and by nematic droplets which formed near the isotropic temperature. A representative photomicrograph is reproduced in Figure 1.

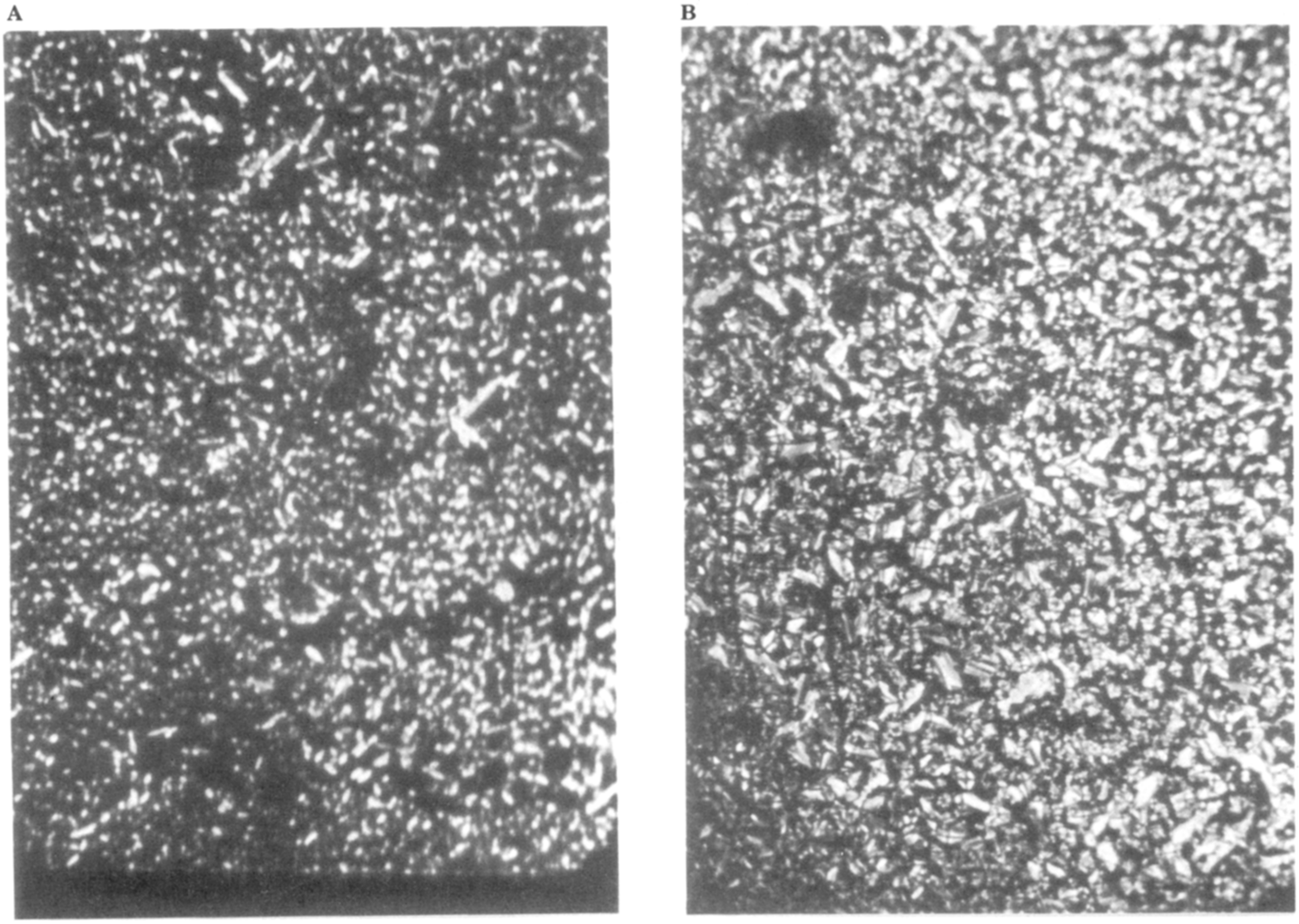
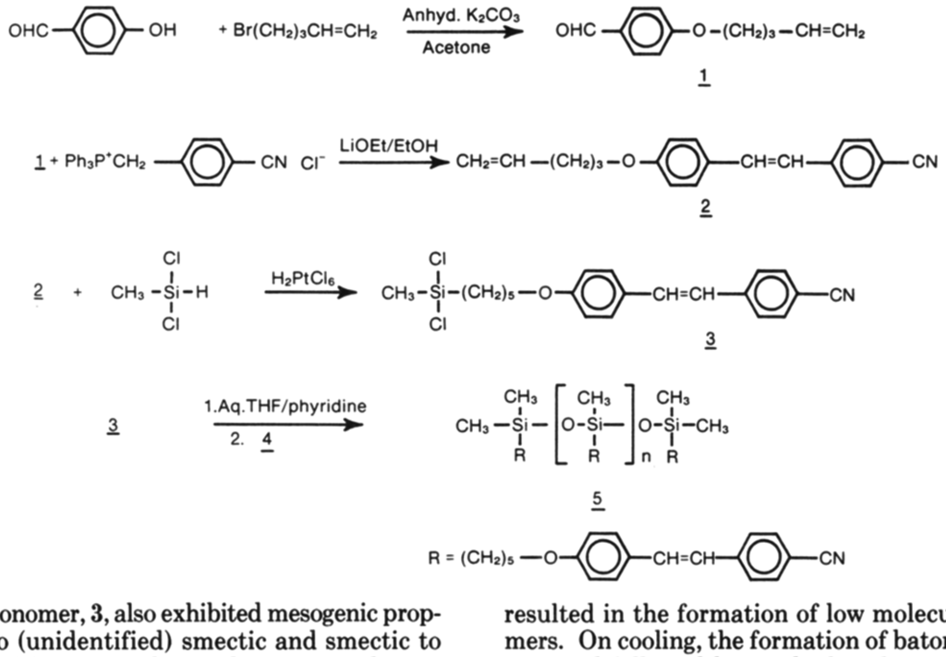


Figure 2. Optical polarization micrograph of 4′-cyano-4-[[5-(dichloromethylsilyl)pentyl]oxy]stilbene: (A) batonnet formation; (B) broken fan texture. (Magnification 20 × 10.)

Scheme I



The dichloro monomer, **3**, also exhibited mesogenic properties. Crystal to (unidentified) smectic and smectic to homeotropic transitions were observed at 119.4 and 191.4 °C, respectively. A homeotropic texture formed readily on heating, suggesting that **3** probably reacted with the glass slide forming a surface-aligned monolayer with an average perpendicular orientation. Since **3** is also hydrolytically unstable, it is likely that a small amount of reaction occurred during the microscopic examination, which resulted in the formation of low molecular weight oligomers. On cooling, the formation of batonnets (Figure 2A) occurred followed by gradual coalescence into tiny broken fans (Figure 2B). The viscosity and the texture obtained on cooling confirmed that **3** had smectogenic properties.

The polysiloxane polymer underwent a smectic transition at 115 °C with a texture similar to that of **3** at 119.4 °C. With further heating, more fluidity was observed.

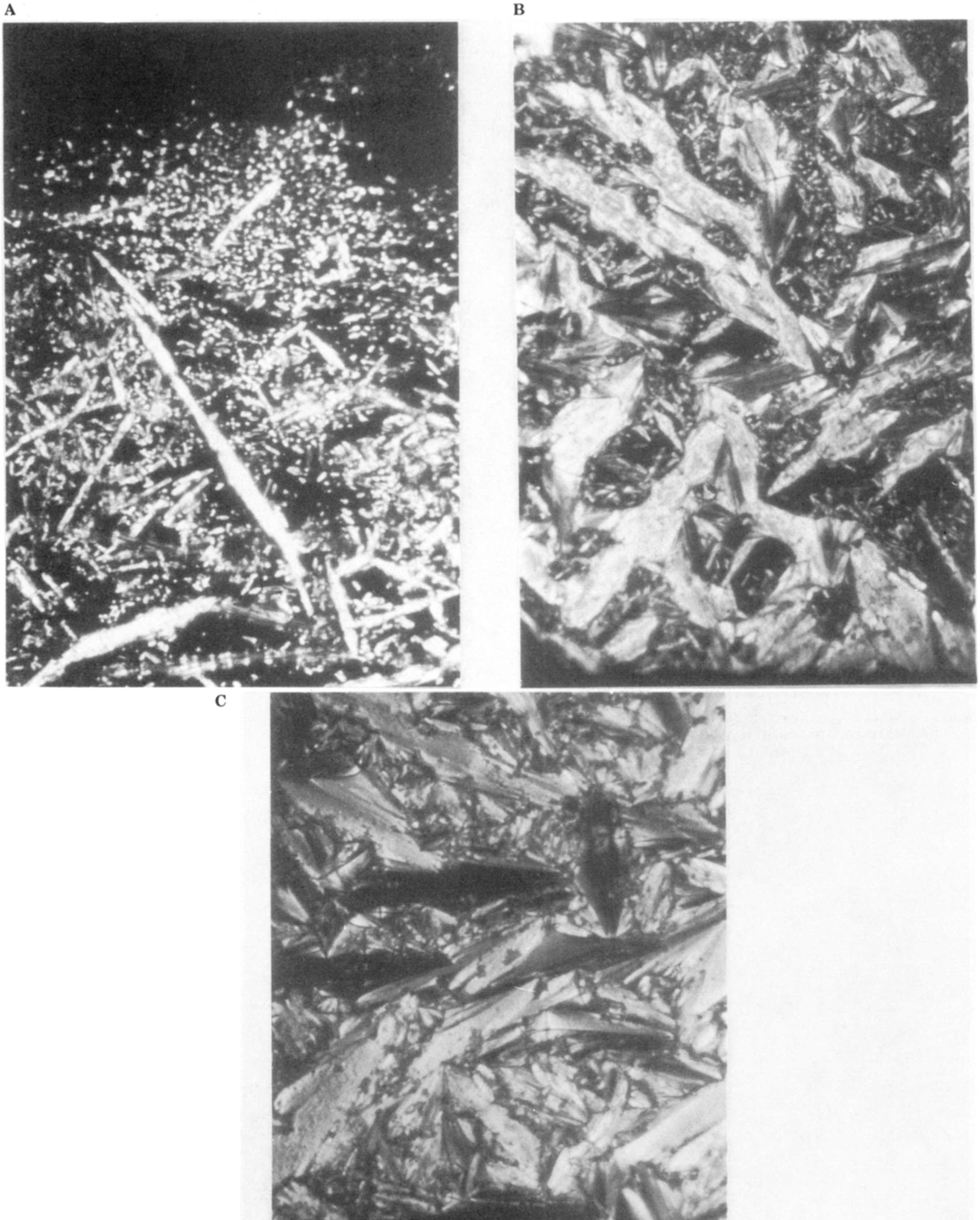


Figure 3. Optical polarization micrograph of polysiloxane: (A) batonnet formation; (B) fan texture of S_A developing, showing biphasic regions; (C) fully developed fan texture. (Magnification 20 × 10.)

Table I
DSC Data for the Precursors, 2 and 3[a]

	temp, °C (ΔH, J/g)		
compd	C-C	C-N,S	N,S-I
2	73.4 (10.8)	93.6 (68.3)	125.1 (1.34)
3		116.2 (12.0)	

[a] C denotes crystal phase; N denotes nematic phase; S denotes smectic phase; I denotes isotropic phase.

Table II
Thermal Transitions and Thermodynamic Parameters of Polymer 5

no.	T_1, °C	ΔH, J/g	ΔS, J/deg·g	T_2, °C	ΔH, J/g	ΔS, J/deg·g
			Heating Scans			
1	111.1	19.0	0.050			
2	111.3	24.0	0.063	9.84	0.018	0.0042
3	110.6	15.1	0.038			
			Cooling Scans			
1	92.1	-25.2	0.067			
2	88.8	-19.7	0.054			
3	63.5	-11.1	0.033			

At approximately 161 °C focal conic fans formed, which changed to a homeotropic texture (i.e., confirmed by conoscopic observations) with light and dark gray shades at 170.8 °C. On cooling, formation of batonnets occurred (Figure 3A) which coalesced to form well-developed focal conic fans against a gray background (Figure 3B). Further cooling resulted in the growth of tiny fans from the remainder of the dark pseudoisotropic phase (Figure 3C). This texture persisted even after cooling to -7 °C.

Differential Scanning Calorimetry. The DSC data of the vinylic precursor, **2**, and the monomer, **3**, are presented in Table I. The results for **2** agreed with that obtained by microscopy. The crystal to crystal transition, although barely observable by microscopy, was seen clearly by DSC. Crystal to nematic and nematic to isotropic changes were observed at 93.6 and 125.1 °C, respectively.

The DSC scan of the monomer, **3**, showed only one major transition at 116.2 °C. The second transition observed by microscopy was not detected. No other transitions were seen even up to a temperature of 252 °C. The magnitude of ΔH indicates a first-order transition. The cooling scan showed only a poorly defined exotherm at 68.7 °C. The temperatures and heats of transition of the polysiloxane, **5**, are summarized in Table II. Data from three heating and cooling cycles are given. The first cycle data were obtained from purified material directly precipitated from the solution. The second cycle data were obtained after an annealing period of 1 mo and the third cycle data collected immediately following the second cycle. The final temperature for the first heating cycle was 192 °C whereas the second and third cycles were heated to 252 °C. The lower limit was 27 °C for all experiments. The scan rate was 2.5 °C/min for all heating and cooling scans except for the third cooling scan (rate of cooling 40 °C/min).

The DSC scans of the polymer showed a reproducible transition at approximately 111 °C irrespective of the thermal history. The second heating scan also showed the onset of a second broad transition between 167 and 187 °C which was not detected in the first and third scans. A sharp endotherm at 226 °C was also seen in the second scan. These latter transitions were not visible in the third scan.

The enthalpy of the first transition varied between scans. The highest value was obtained on the annealed sample (i.e., second scan) indicative of a more ordered crystalline polymer. The lower value of the third scan may reflect an insufficient amount of annealing time between scans for the polymer chains to relax.

All cooling scans show only one major transition. However, the shape of the peak from the first scan reflects two closely occurring phase changes (i.e., cooling scan): smectic mesophase formation immediately followed by crystallization. The higher ΔH value also is consistent with this possibility. Lower ΔH values from the second and third scans probably are due to partial crystallization. Supercooling was observed in the third scan due to the extremely rapid rate of cooling used. Similarity in the thermal behavior of the monomer and the polymer suggests that the siloxane backbone does not dramatically influence the packing of the pendant groups for the polymer studied.

Acknowledgment. Support from DARPA-ONR Contract N0014-86-0772 is acknowledged.

References and Notes

(1) Ringsdorf, H.; Zentel R. *Makromol. Chem.* **1982**, *183*, 1245.
(2) Shibaev, V. P.; Talrose, R. V.; Kostromin, S. G.; Plate, N. A.; Kresse, H.; Sauer, K.; Demus, D. *Makromol. Chem. Rapid Commun.* **1981**, *2*, 305.
(3) Finkelmann, H.; Ringsdorf, H.; Naegle, D. *Makromol. Chem.* **1979**, *180*, 803.
(4) Finkelmann, H.; Kiechle, U.; Rehage, G. *Mol. Cryst. Liq. Cryst.* **1983**, *94*, 343.
(5) Finkelmann, H.; Apfel, M. A.; Janini, G. M.; Laub, R. J.; Luhmann, B. H.; Price, A.; Roberts, W. L.; Shaw, T. J.; Smith, C. A. *Anal. Chem.* **1984**, *57*, 651.
(6) Bradshaw, J. S.; Schregenberger, C.; Karen, H.; Chang, C.; Markides, K. E.; Lee, M. L. *J. Chromatogr.* **1986**, *358*, 95.
(7) Nishioka, M.; Jones, B. A.; Tarbet, B. J.; Bradshaw, J. S.; Lee, M. L. *J. Chromatogr.* **1986**, *357*, 79.
(8) Adams, N. W.; Bradshaw, J. S.; Bayona, J. M., Markides, K. E., Lee, M. L. *Mol. Cryst. Liq. Cryst.* **1987**, *147*, 43.
(9) Shibaev, V. P.; Kostromin, S. G.; Plate, N. A. *Eur. Polym. J.* **1982**, *18*, 651.
(10) Grammell, P. A.; Gray, G. W.; Lacey, D. *Mol. Cryst. Liq. Cryst.* **1985**, *122*, 205.
(11) Gray, G. W.; Lacey, D.; Nester, G.; White, M. S. *Makromol. Chem. Rapid. Commun.* **1986**, *7*, 71.
(12) Hardouin, F.; Achard, A. M.; Sigaud, G. *J. Chim. Phys.* **1983**, *80*, 53.
(13) Markides, K. E.; Nishioka, M.; Tarbet, B. J.; Bradshaw, J. S.; Lee, M. L. *Anal. Chem.* **1985**, *57*, 1296.
(14) Finkelmann, H.; Rehage, G. *Makromol. Chem. Rapid Commun.* **1980**, *1*, 31.
(15) Hahn, B.; Percec, V. *Macromolecules* **1987**, *20*, 2962.
(16) Hsu, C. S.; Percec, V. *J. Polym. Sci., Part A* **1987**, *25*, 2909.
(17) Janini, G. M.; Laub, R. J.; Pluyter, G. L.; Shaw, T. J. *Mol. Cryst. Liq. Cryst.* **1987**, *153*, 479.

Registry No. **1**, 124201-59-8; **2**, 124201-60-1; **3**, 124201-61-2; **4**, 124201-62-3; $Br(CH_2)_3CH{=}CH_2$, 1119-51-3; $CH_3SiH(Cl)_2$, 75-54-7; *p*-hydroxybenzaldehyde, 123-08-0; (4-cyanobenzyl)triphenylphosphonium chloride, 20430-33-5.