structure is considered to be less stable than furan or its derivatives like **10**, due to its antiaromatic 4π system.

Conclusions. In this work we have prepared two new seven-membered SOCs and studied their cationic ring-opening polymerization in comparison with those of other SOCs. We have concluded that (i) SOCs bearing spiro[6.6]tridecane skeletons afford polycarbonate or poly(ether-carbonate) on cationic ring-opening polymerization, depending on the structure of SOC, but independent of solvent, temperature and catalyst; (ii) the attack of monomer on the ring methylene carbon adjacent to oxygen actually occurs; and (iii) the polymerization course may be determined by electrophilicity of the attacked site of the propagating species or leaving ability of the eliminated moiety. The examples described in this study are expected to contribute to designing more reactive SOCs.

Registry No. **7**, 103545-44-4; **7** (homopolymer), 112795-42-3; **8**, 103541-92-0; **5** (homopolymer), 112795-43-4; **10**, 4743-54-8; $C(OMe)_4$, 1850-14-2; 2-$HOCH_2C_6H_4CH_2OH$, 612-14-6; hexahydrophthalic anhydride, 85-42-7; 1,2-bis(hydroxymethyl)cyclohexane, 3971-29-7; phthalic anhydride, 85-44-9.

References and Notes

(1) Bailey, W. J.; Sun, R. R.; Katsuki, H.; Endo, T.; Iwama, H.; Tsushima, K.; Saigo, K.; Bitritto, M. M. *Ring-opening Polymerization with Expansion in Volume*; ACS Symposium Series 59; Saegusa, T., Goethals, E., Eds.; American Chemical Society: Washington DC, 1977; p 38.
(2) Endo, T.; Bailey, W. J. *Makromol. Chem.* **1975**, *176*, 2897.
(3) Endo, T.; Bailey, W. J. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 1735.
(4) Endo, T.; Katsuki, H.; Bailey, W. J. *Makromol. Chem.* **1976**, *177*, 3231.
(5) Bailey, W. J.; Endo, T. *J. Polym. Sci., Polym. Symp.* **1978**, *64*, 17.
(6) Sakai, S.; Fujinami, T.; Sakurai, S. *J. Polym. Sci., Polymn. Lett. Ed.* **1973**, *11*, 631.
(7) (a) Bailey, W. J.; No, K.; Pan, C.-Y.; Saigo, K.; Stansbury, J.; Tan, S.-R.; Zhou, J. *Polymn. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1985**, *26* (1), 50. (b) Bailey, W. J.; Amone, M. J.; Issari, B.; Lin, Y.-N.; No, K.; Pan, C.-Y.; Saigo, K.; Stansbury, J.; Tan, S.-R.; Wu, C.; Yamazaki, N.; Zhou, J. *Am. Chem. Soc., Div. Polym. Mater., Prepr.* **1986**, *54*, 23.
(8) Endo, T.; Arita, H. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 137.
(9) Endo, T.; Sato, H.; Takata, T. *Macromolecules* **1987**, *20*, 1416.
(10) Endo, T.; Maruoka, S.; Yokozawa, T. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 2925.
(11) Endo, T.; Maruoka, S.; Yokozawa, T. *Macromolecules* **1987**, *20*, 2690.
(12) Endo, T.; Uno, H. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 359.
(13) Endo, T.; Okawara, M. *Synthesis* **1984**, 873.
(14) Nystrom, R. F. *J. Am. Chem. Soc.* **1947**, *69*, 1197.
(15) Takata, T.; Endo, T. 8th IUPAC Conference on Physical Organic Chemistry, Tokyo, Aug 1986; abstract p 302.

A Reexamination of the Synthesis of Liquid Crystalline Side-Chain Polyacrylates via Liquid-Liquid Phase-Transfer Catalysis

S. H. Chen* and Y. F. Maa

Department of Chemical Engineering and Laboratory for Laser Energetics, University of Rochester, Rochester, New York 14627.

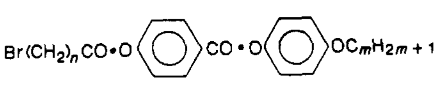
Received July 23, 1987

ABSTRACT: We have reexamined the synthesis of liquid crystalline side-chain polyacrylates under liquid-liquid phase-transfer conditions as first reported by Keller. Instead of the polymeric liquid crystals, the hydrolysis of the mesogen and a subsequent nucleophilic substitution reaction were found to predominate over the anticipated reaction between the carboxylate group and the mesogen. The present results are consistent with the high pH conditions prevailing in the poly(sodium acrylate) solution as determined previously. The control of the pH value in the reaction medium is perceived to be crucial in determining the reaction pathway.

I. Introduction

Chemical modification of functional polymers via phase-transfer catalysis has been an active area of research for the past several years because of the utility of the polymer products in the study of polymer-supported organic reactions.[1-3] More recently, Keller[4-7] has reported the first syntheses of mesomorphic polyacrylates and polymethacrylates in a liquid-liquid configuration by using tetrabutylammonium bromide as a phase-transfer catalyst. The idea originated from extensive research in the past on phase-transfer catalysis involving simple electrolytes.[8-10] Compared to direct polymerization of functional monomers, the chemical modification approach is attractive for its apparent simplicity.[11] However, Fréchet[12] also pointed out that the failure to perceive organic reactions involving polymeric substrates and that the lack of thorough characterization of polymer products have given rise to questionable results in the literature.

In the present work we reexamined the chemical modification of poly(sodium acrylate) with liquid crystal mesogens of the general structure



I

under liquid-liquid phase-transfer conditions. Our results suggest that the observations of mesomorphism alone (with polarized optical microscopy and differential scanning calorimetry) are not sufficient for the structural assignment of polymer liquid crystals derived from polymeric substrates. In fact, nuclear magnetic resonance (NMR) spectroscopy turned out to be very useful in the structural elucidation of the products.

II. Results and Discussion

Liquid crystal mesogens shown as I were prepared following the procedures reported by van Meter and Klanderman[13] and by Hassner and Alexanian[14] using p-hydroxybenzoic acid, p-alkoxyphenol, and ω-bromo-

Table I
Phase-Transition Temperatures for Reactants 1a, 2a, and 3a and Products 1b, 2b, and 3b

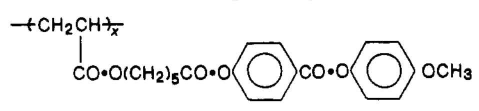
reactant[a]	phase transitn,[b] °C	product	phase transitn, °C
1a	C → I, 93 (84); I → N, 72 (82.5)	**1b**	C → N, 126; N → I, 219
2a	C → I, 112 (103)	**2b**	C → N, 195; N → I, 248
3a	C → N, 79 (74); N → I, 87 (91)	**3b**	C → S, 143; S → N, 221; N → I, 226

[a] **1a**, $n = 5$, $m = 1$; **2a**, $n = 1$, $m = 1$; **3a**, $n = 3$, $m = 4$. All based on structure I. [b] Abbreviations; C, crystal; S, smectic; N, nematic; I, isotropic. Transition temperatures given in parentheses are those reported by Keller in ref 4 and 5.

alkanoic acid. The phase transition temperatures of the three mesogens determined with differential scanning calorimetry (DSC) and hot-stage polarized optical microscopy are listed in Table I. Note that compound **2a** was selected for the present study because of its structural simplicity, compared to **1a** or **3a**, that may facilitate the molecular structure elucidation for the product. Compound **1a** was intended to permit us to compare our results with Keller's,[4] and compound **3a** should serve to demonstrate the generality of our observations on the reactions involving **1a** and **2a**.

Commercially available poly(acrylic acid) with average molecular weight 2000 g/mol was neutralized with sodium hydroxide solution on an equivalent basis;[4] the concentration of the carboxylate groups was 0.9 N. The reaction was carried out between poly(sodium acrylate) and compounds 1a–3a following Keller's[4] procedures under identical conditions. Although the products were precipitated from chloroform solution with methanol, it was found that they could be further recrystallized from acetone. The appearance of the carbonyl absorption due to the ester group (1730–1775 cm^{-1}) in place of the carboxylate group (1550–1610 cm^{-1}) was ascertained with IR spectroscopy. The mesomorphic properties of the three products, designated as **1b**, **2b**, and **3b**, are also reported in Table I. Compared to Keller's results (see Table I of ref 4), it is noted that product **1b** quenched at −320 °C/min from 250 to −50 °C does not exhibit glass transition, although Keller reported a T_g at 70–80 °C. Furthermore, product **1b** shows nematic threaded texture under polarized optical microscope between 125 and 219 °C. Keller[4] reported a clearing temperature of 210 °C.

In an attempt to verify the molecular structure of product **1b**, which was assigned by Keller[4] as



$$\underset{\mathrm{CO{\cdot}O(CH_2)_5CO{\cdot}O\text{-}C_6H_4\text{-}CO{\cdot}O\text{-}C_6H_4\text{-}OCH_3}}{\underset{|}{-\!\!\!+\!CH_2CH\!+_{\!x}}}$$

II

we obtained the NMR spectra for both **1a** and **1b** as presented in Figures 1 and 2, respectively. It is noted that the protons associated with the terminal $BrCH_2$– group in **1a** undergo a downfield shift from 3.4 to 4.1 as a result of the reaction. Furthermore, the numbers of protons designated as b through f relative to those designated as a or those on the benzene rings as shown in Figure 1 for **1a** are reduced by half as a result of the reaction. If the polymer product depicted as II had formed, such reduction in the relative numbers of protons should not have occurred and the signals associated with protons on the polymer backbone would have appeared besides those observed in Figure 2. The values of the chemical shifts for non-benzenoid protons are consistent with empirical values and those calculated with Shoolery's group contribution method.[15] On the basis of the information on chemical shift and integration before and after the reaction and on the basis of the perception of possible reaction paths involving **1a**, it seems reasonable for one to expect that product **1b** assumes the structure:

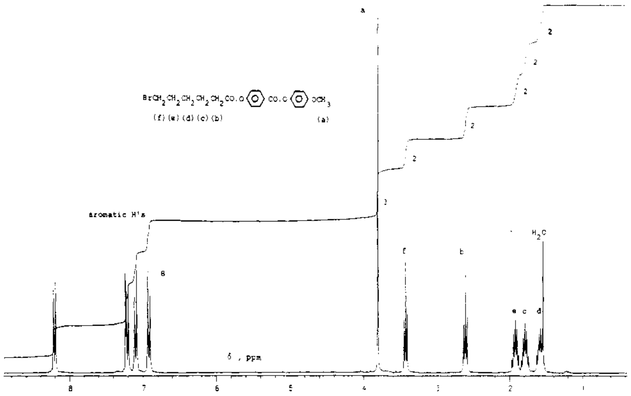


Figure 1. Proton NMR spectrum (2% in CDCl$_3$) of **1a**.

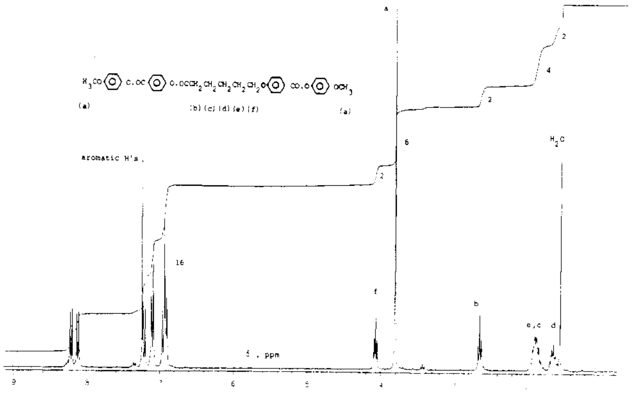
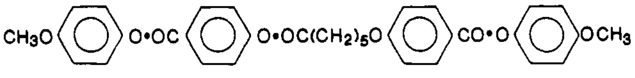


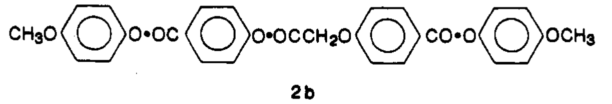
Figure 2. Proton NMR spectrum (2% in CDCl$_3$) of **1b**.



1b

We have conducted additional experiments in an effort to understand how the reaction between poly(sodium acrylate) and **1a** proceeds to yield **1b**. We first performed a reaction in the absence of poly(sodium acrylate) and then in the absence of tetrabutylammonium bromide, conditions and procedures being identical otherwise. We were unable to isolate any reaction product from either experiment. We have also performed a series of reactions where the chain length of poly(sodium acrylate) was varied from 28 to 556 corresponding to poly(acrylic acid) molecular weights from 2000 to 40 000 g/mol. It turned out that product **1b** was consistently obtained from the reaction.

In order to better understand the mechanism involved in the reaction under present investigation, one has to demonstrate its reproducibility as well as generality. With this objective in mind, let us examine the behavior of **2a**, which shows no mesophase upon heating or cooling, and **3a**, a typical liquid crystal, in addition to that of **1a**, a monotropic liquid crystal. The structure of **2b** can be identified as



2b

by comparing the NMR spectra given in Figures 3 and 4.

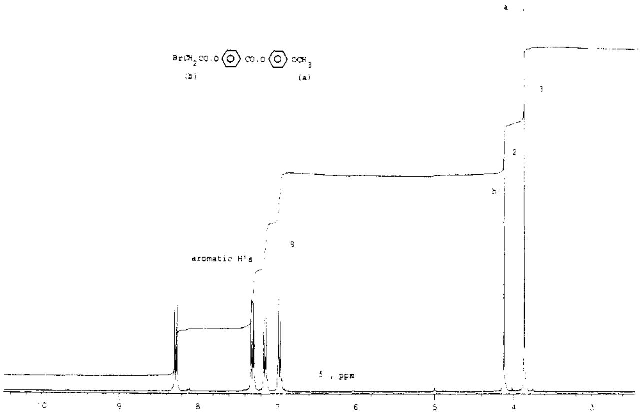


Figure 3. Proton NMR spectrum (2% in $CDCl_3$) of **2a**.

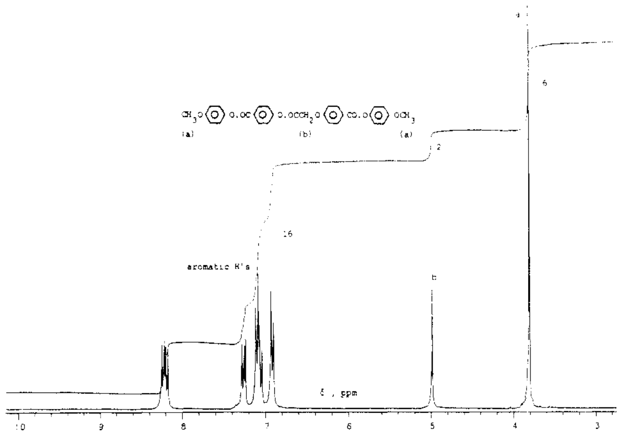
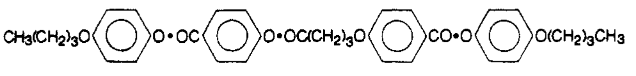


Figure 4. Proton NMR spectrum (2% in $CDCl_3$) of **2b**.

Similarly, on the basis of the NMR spectra the product from **3a** is most likely to assume the following structure:



3b

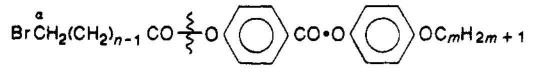
To provide further evidence that, instead of polymer product II, products **1b**–**3b** have resulted from the reaction, we have also carried out translational diffusivity measurements for **3a** and **3b** in *p*-dioxane at 50 °C using the extended Taylor dispersion method reported earlier.[16] The hydrodynamic radii were then calculated from the translational diffusivity and solvent viscosity using the Stokes–Einstein equation. The results are summarized in Table II. We make the following observations: (1) The dispersion curve for **3b** is Gaussian, giving no indication that polydispersity in molecular weight accompanies **3b** as a result of the broad molecular weight distribution poly(acrylic acid) with average molecular weight 2000 g/mol used to prepare poly(sodium acrylate). (2) The hydrodynamic radii for the products prepared from **3a** and a series of sodium salts of poly(acrylic acids) with molecular weight 2000, 5000, 24 000 and 40 000 g/mol are identical within an experimental uncertainty of ±1%. Poly(sodium acrylate) does not appear to be a part of the product. (3) The hydrodynamic radius of **3b** is only about 40% larger than that of **3a** and is 40% less than a polystyrene standard with molecular weight 2000 g/mol (PS2K). The molecular structure given as **3b** appears to be consistent with this observation. From the observations stated above, one could claim that polymer products II have not resulted from the reaction and that products **1b**–**3b** are most likely to be what one has obtained.

Table II
Hydrodynamic Radii of 3a, 3b, and PS 2K in *p*-Dioxane at 50 °C

solute	10^6D,[a] cm^2/s	R_h,[b] Å
3a	6.22	4.74
3b	4.39	6.71
PS 2K[c]	2.77	10.7

[a] Translational diffusivity (D) determined with the Taylor dispersion method presented in ref 16. [b] Hydrodynamic radius calculated from $R_h = kT/6\pi\mu_0 D$, where k is Boltzmann's constant and μ_0 is solvent viscosity. [c] Polystyrene standard with molecular weight 2000 g/mol; D and R_h values taken from ref 16.

We offer an explanation for the formation of products **1b**–**3b** instead of the anticipated polymeric liquid crystals with the general structure depicted as II. Poly(sodium acrylate) was prepared by the neutralization of poly(acrylic acid) with an equivalent amount of sodium hydroxide in aqueous solution. The hydrolysis of the resultant poly(sodium acrylate) gives rise to a basic solution in view of the fact that poly(acrylic acid) is a weak acid.[17] For the 0.9 N poly(sodium acrylate) solution used in the reaction, the pH value was determined to be around 13 with an Orion pH meter (Model 701A), confirming the above speculation. Such a high value of pH is not surprising in view of the dependence of pH on the degree of neutralization presented in Figure 4 of ref 18. Thus, the presence of poly(sodium acrylate) induces the formation of HO^-, which is then transferred to the liquid–liquid interface by tetrabutylammonium ion. The question of why HO^- is not transferred into the organic phase can be partially answered in terms of the extraction coefficient of tetrabutylammonium hydroxide, which is 4 orders of magnitude less than that of tetrabutylammonium bromide.[19] In any event, whether the reaction takes place at the liquid–liquid interface or in the bulk organic phase should be clarified with additional mechanistic studies. In the presence of HO^-, the labile ester linkage activated by the carboyl group at the para position undergoes cleavage as indicated below:



The phenoxide then undergoes nucleophilic substitution with I at the α position. The proposed mechanism also explains why no reaction proceeds in the absence of poly(sodium acrylate) *or* tetrabutylammonium bromide.

Finally, the proposed mechanism was substantiated by a series of experiments in which an aqueous solution of NaOH, instead of the solution of poly(sodium acrylate), was stirred with a chloroform solution of **3a** and tetrabutylammonium bromide under reflux over a period of 4 days. For the pH value of the starting NaOH solution at 8, 10, or 13, product **3b** was isolated. No product could be isolated at pH 3 or 6, where the poly(acrylic acid) in the aqueous solution was partially neutralized with NaOH solution.

III. Summary

We have reexamined the synthesis of liquid crystalline side-chain polymers based on the chemical modification of poly(sodium acrylate) under liquid–liquid phase-transfer conditions. It was found that the formation of polymer liquid crystals should not be claimed on the basis of the mesomorphic properties of the products alone. The classical approach to the determination of chemical structure should be followed to characterize the products. The results also suggest that more has to be learned about the reactions involving polymeric substrates; perception of organic reactions involving low molar mass reactants extended to polymeric systems might turn out to be misleading. The present study of the reaction between poly(sodium acrylate) and liquid crystal mesogens testifies to this observation. Instead of the mesomorphic polyacrylates as one might have anticipated from the reaction studied here, we have identified products with the NMR spectroscopy. The values for the hydrodynamic radii obtained from translational diffusivity and solvent viscosity appear to be consistent with the proposed structures. A possible explanation for the formation of the unexpected products is given on the basis of hydrolysis of poly(sodium acrylate) resulting in a basic solution and the relatively labile ester linkage susceptible to cleavage by HO^- followed by nucleophic substitution on the mesogen.

IV. Experimental Section

The synthesis of **1a**, **2a**, and **3a** was accomplished following the procedures reported in ref 13 and 14 using *p*-hydroxybenzoic acid (99.5%, Kodak), *p*-methoxyphenol (98+%, Fluka), *p*-butoxyphenol (99+%, Chemical Dynamics), bromoacetic acid (99+%, Aldrich), 4-bromobutyric acid (98%, Aldrich), and 6-bromohexanoic acid (98%, Aldrich). The purities of **1a**–**3a** were demonstrated to be at least 95% based on GC analysis (Hewlett-Packard, GC 5890). Poly(acrylic acid) with average molecular weight 2000 g/mol (65% solution in water, Aldrich Chemical Co.) and molecular weight standards 5000, 24 000, and 40 000 g/mol (Polysciences, Inc.) were all used as received. The preparation of poly(sodium acrylate) was achieved by neutralization of poly(acrylic acid) in sodium hydroxide solution following Keller's procedures[4] except for two higher molecular weight acids that are supplied as sodium salts. Compounds **1a**–**3a** and **1b**–**3b** were all repeatedly recrystallized to constant phase transition temperatures.

The reaction between poly(sodium acrylate) and **1a**–**3a** was performed in a liquid–liquid (aqueous/chloroform) configuration using tetrabutylammonium bromide (99%, Aldrich) as a phase-transfer agent under reflux over a period of 96 h. The reaction condition was identical with Keller's.[4] Keller's procedures[4] were also followed to achieve product isolation and purification. The products were precipitated from chloroform solution with methanol; the yield was 20–30%. Isocratic reverse phase LC analysis in acetonitrile at room temperature was followed to verify the purities of **1b**–**3b**. The column (RP-18 ODS, Hewlett-Packard) was packed with 10 μm silica particles whose surface was modified by octadecylsilane. No impurities were detectable on an ISCO system with a UV monitor (set at 254 nm), and **3b** doped with **3a** showed clear separation under the same chromatographic conditions.

The IR (in Nujol) spectra were obtained on a Perken-Elmer instrument (Model 710B) and the NMR (2% in $CDCl_3$) spectra on QE-300 (300 MHz, Nicolet). Perkin-Elmer DSC-4 was used to determine the thermograms of reactants **1a**–**3a** and products **1b**–**3b**. All samples were heated up to 250 °C and then rapidly quenched prior to thermal measurements. Mesophases were identified with a hot-stage polarized optical microscope (Leitz Orthoplan-Pol and Mettler FP52 Microthermal System). Finally, the translational diffusion measurements were conducted with a dispersion apparatus presented elsewhere.[16] The concentration of the injected pulse was around 0.05 wt % for **3a** and **3b** and 0.1 wt % for PS2K. Solvent *p*-dioxane (99.8%, Aldrich Chemical Co.) was used as received.

Acknowledgment. We appreciate the helpful discussion with Dr. Abraham Warshawsky of the Weizmann Institute of Science, Rehovot, Israel, and Professor Jacob Jorne for permitting them to use his pH meter. The technical assistance of K. L. Marshall at the Laboratory for Laser Energetics, University of Rochester, is also appreciated. They wish to acknowledge the support of this work by the National Science Foundation under Grant CBT-8714924 and by the New York State Center for Advanced Optical Technology at the University of Rochester and the Army Research Office. Such support does not imply endorsement of the content by any of the above parties.

Registry No. **1a**, 81877-54-5; **1b**, 113110-00-2; **2a**, 99542-60-6; **2b**, 113110-01-3; poly(acrylic acid) sodium salt, 9003-04-7.

References and Notes

(1) Hodge, P.; Sherrington, D. C. *Polymer-Supported Reactions in Organic Synthesis*; Wiley: London, 1980.
(2) Mathur, N. K.; Narang, C. K.; Williams, R. E. *Polymers as Aids in Organic Synthesis*; Academic: New York, 1980.
(3) Ford, W. T.; Tomoi, M. *Adv. Polym. Sci.* **1984**, *55*, 49.
(4) Keller, P. *Macromolecules* **1984**, *17*, 2937.
(5) Keller, P. *Mol. Cryst. Liq. Cryst.* **1985**, *2*, 101.
(6) Keller, P. *Macromolecules* **1985**, *18*, 2337.
(7) Keller, P. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 707.
(8) Starks, C. M.; Liotta, C. *Phase Transfer Catalysis: Principles and Techniques*; Academic: New York, 1978.
(9) Montanari, F.; Landini, D.; Rolla, F. *Top. Curr. Chem.* **1982**, *101*.
(10) Dehmlow, E. V.; Dehmolw, S. S. *Phase Transfer Catalysis*, 2nd ed.; Verlag Chemie: Weinheim, 1983.
(11) Fréchet, J. M. J. *J. Macromol. Sci., Chem.* **1981**, *A15*, 877.
(12) Fréchet, J. M. J. In *Crown Ethers and Phase Transfer Catalysis in Polymer Science*; Mathias, L. J., Carraher, C. E., Jr., Eds.; Plenum: New York, 1984.
(13) Van Meter, J. P.; Klanderman, B. H. *Mol. Cryst. Liq. Cryst.* **1973**, *22*, 285.
(14) Hassner, J.; Alexanian, V. *Tetrahedron Lett.* **1978**, 4475.
(15) Pasto, D. J.; Johnson, C. R. *Organic Structure Determination*; Prentice-Hall: Englewood, NJ, 1969; pp 168–170.
(16) Barooah, A.; Sun, C. K. J.; Chen, S. H. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 817.
(17) Morawetz, H.; Wang, Y. *Macromolecules* **1987**, *20*, 194.
(18) Kern, W. *Z. Phys. Chem.* **1938** *181*, 249.
(19) Brändström, A. *Adv. Phys. Org. Chem.* **1977**, *15*, 281.