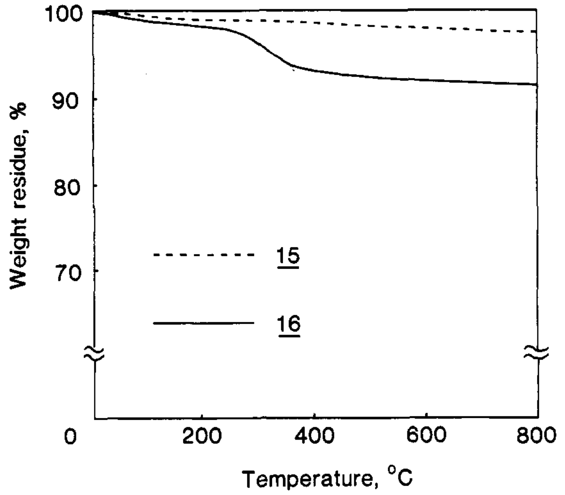

Figure 2. TGA of PAEI-modified silica gel (**16**, —) and untreated silica gel (**15**, - - -).

to 13.7 multiples of the weight of dried **16**. Thus, silica gel has been made more hydrophilic by a PAEI segment.

Figure 2 shows the result of thermogravimetric analysis, in which the weight loss of the resulting PAEI-modified silica gel (**16**, run 2 in Table III) started at 230 °C; the weight was nearly 90% above 400 °C under nitrogen. The amount of weight loss at 400 °C is comparable with the PAEI content of **16** determined from elemental analysis. In other words, **16** lost its PAEI moiety at 400 °C.

Conclusions

Two ways have been established for the preparation of trimethoxysilyl-terminated PAEIs. As mentioned in the Introduction, PAEI has useful characteristics, i.e., hydrophilicity and good compatibility with other organic commodity polymers. Taking account of these characteristics, the polymer obtained in the present study can be used as a novel type of silane coupling agent. In fact, silica gel was made more hydrophilic by these polymeric silane coupling agents. Generally, polyoxazolines have a wide spectrum from hydrophilic to lipophilic nature depending on the *N*-acyl groups. For example, the polymer from 2-methyl-2-oxazoline shows high hydrophilicity, and the polymers from higher alkyl derivatives (butyl or higher) show hydrophobicity (lipophilicity). Accordingly, trialkoxysilyl-terminated polymer from 2-alkyl-2-oxazoline can be used to modify lipophilic silica gel. The subject will be the next target of our research. Polyoxazolines also have high compatibility with organic commodity polymers such as poly(vinyl chloride). This property makes it possible to produce a new composite material, in which polyoxazoline reinforces the interface between organic polymers and inorganic materials. Reinforcement by polyoxazoline silane coupling agent is now under investigation.

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Registry No. 4, 4873-09-0.

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Liquid Crystal Polyethers Containing Macroheterocyclic Ligands. 1. Polyethers and Copolyethers Based on 4,4′-Dihydroxy-α-methylstilbene, Bis(8-bromooctyl)dibenzo-18-crown-6, and/or 1,11-Dibromoundecane

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ABSTRACT: The synthesis and characterization of the first examples of thermotropic main-chain liquid-crystalline polyethers and copolyethers containing macroheterocyclic ligands is described. The particular example presented in this paper refers to polyethers and copolyethers based on bis(8-bromooctyl)dibenzo-18-crown-6 and/or 1,11-dibromoundecane and 4,4′-dihydroxy-α-methylstilbene. The polyether based on 4,4′-dihydroxy-α-methylstilbene and 1,11-dibromoundecane displays an enantiotropic nematic mesophase while the one based on 4,4′-dihydroxy-α-methylstilbene and bis(8-bromooctyl)dibenzo-18-crown-6 is crystalline. Copolyethers containing up to as much as 60 mol % dibenzo-18-crown-6 structural units display a monotropic nematic mesophase. Both liquid-crystalline transition temperatures and the corresponding enthalpies of the copolymers are weight-averaged values of the parent homopolymers. Extrapolation of the monotropic nematic transition temperatures and their enthalpy changes have demonstrated that all copolymers and the homopolymer based on 4,4′-dihydroxy-α-methylstilbene and bis(8-bromooctyl)dibenzo-18-crown-6 exhibit a virtual monotropic nematic mesophase. The thermal transition temperatures and the enthalpy changes associated with the virtual nematic mesomorphic transitions of the homopolymer and the copolymer were determined.

Introduction

Since the discovery of crown ethers,[1] the field of host guest complex chemistry has received tremendous research interest[2] and recently definitive scientific recognition.[1,3] However, to our knowledge, there are only two examples of low molar mass liquid crystals containing macroheterocyclic ligands. The first one refers to disclike amide derivatives of macrocyclic polyamines which exhibit co-

Table I
Characterization of Polyethers Based on HMS and 1,11-Dibromoundecane (HMS-C11) and HMS and Bis(8-bromooctyl)dibenzo-18-crown-6 (HMS-DECE-8) and of Corresponding Copolyethers [HMS-C11/DECE-8 (*A*/*B*)]

copolymer HMS-C11/DECE-8 (*A*/*B*)				thermal transitns, °C (corresponding enthalpy changes, kcal/mru)	
C11/DECE-8 mol ratio	yield, %	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	heating	cooling
100/0	82	18800	2.03	g 18 k 114 n 138 (0.14)[a] i	i 117 (0.31) n 85 k 16 g
80/20	97	16200	2.00	g 22 k 107 i	i 95 (0.27) n 65 k 17 g
60/40	96	38100	1.84	g 29 k 88 i	i 80 (0.30) n 24 g
50/50	92	14800	1.79	g 29 k 89 i	i 73 (0.28) n 38 k 24 g
40/60	75	8300	1.95	g 30 k 93 i	i 65 (0.15) n 42 k 25 g
20/80	76	13500	1.80	g 34 k 96 i	i 54 k 31 g
0/100	77	16700	2.00	g 42 k 99 i	i 55 k 33 g

[a] Overlapped transitions.

lumnar mesophases.[4] The second one refers to a series of rigid rodlike low molar mass liquid crystals containing a benzo crown ether moiety. This second series of compounds exhibit calamitic mesophases.[5] To date, there is no example of a liquid crystal polymer containing crownlike ethers or any other kind of macroheterocyclic receptor.[6,7]

Thermotropic liquid crystals containing macroheterocyclic ligands may add a new dimension to the field of host guest complex chemistry from both a fundamental and applied points of view. They would represent the simplest examples of phase-dependent operating systems and can provide a new approach to systems which combine a highly selective recognition coupled with external regulation. Liquid crystals containing macroheterocyclic ligands can also lead to the generation of molecular ionic devices.[3]

The goal of this paper is to describe the synthesis and characterization of the first examples of main-chain liquid-crystalline polymers containing crown ethers within their structural units. The liquid-crystalline polymers referred to are polyethers and copolyethers obtained by phase transfer catalyzed polyetherification of bis(8-bromooctyl)dibenzo-18-crown-6 and/or 1,11-dibromoundecane with 4,4′-dihydroxy-α-methylstilbene as the mesogenic unit.

Experimental Section

Materials. Dibenzo-18-crown-6 (98%), 8-bromooctanoic acid (98%), polyphosphoric acid, triethylsilane (99%), tetrabutylammonium hydrogen sulfate (TBAH), *o*-dichlorobenzene (99%), 1,11-dibromoundecane (C11, 98%), and all other reagents (Aldrich) were used as received.

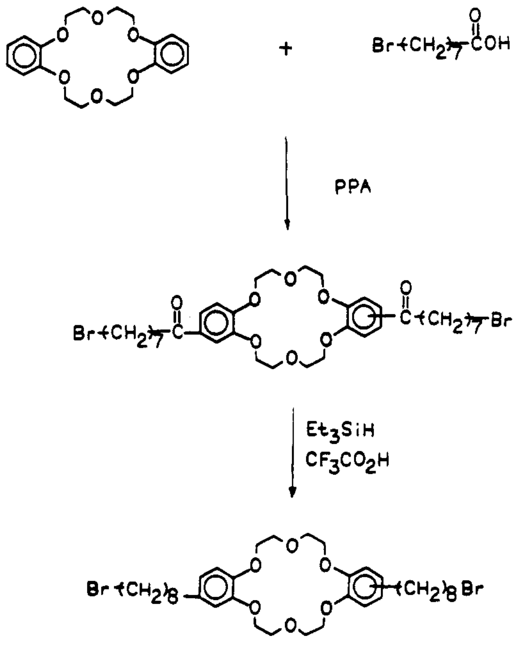
Techniques. ^{1}H NMR (200-MHz) spectra were recorded on a Varian XL-200 spectrometer. IR spectra were recorded from KBr pellets on a Perkin-Elmer Model 1320 IR spectrometer.

Molecular weights were determined by gel permeation chromatography (GPC). High-pressure chromatography (HPLC) and GPC analyses were carried out with a Perkin-Elmer Series 10 LC equipped with a LC-100 column oven, LC 600 auto sampler, and a Sigma 15 data station. The measurements were made by using the UV detector, tetrahydrofuran as solvent (1 mL/min, 40 °C) a set of PL gel columns of 10^2, 5×10^2, 10^3, 10^4, and 10^5 Å, and a calibration plot constructed with polystyrene standards.

Thermal transitions reported in Table I were determined with a Perkin-Elmer DSC-4 differential scanning calorimeter equipped with a TADS data station Model 3600. Heating and cooling rates were 20 °C/min in all cases unless stated. First-order transitions (crystalline–crystalline, crystalline–liquid crystalline, liquid crystalline–isotropic, etc.) were read at the maximum of the endothermic or exothermic peaks. Glass transition temperatures (T_g) were read at the middle of the change in the heat capacity. All heating and cooling scans after the first heating scan produced perfectly reproducible data. The transitions reported were taken from the second or third heating or cooling scans.

A Carl Zeiss optical polarizing microscope (magnification 70×) equipped with a Mettler FP 82 hot stage and a Mettler 800 central processor was used to observe the thermal transitions and to analyze the anisotropic textures.[8]

Scheme I
Synthesis of Bis(8-bromooctyl)dibenzo-18-crown-6

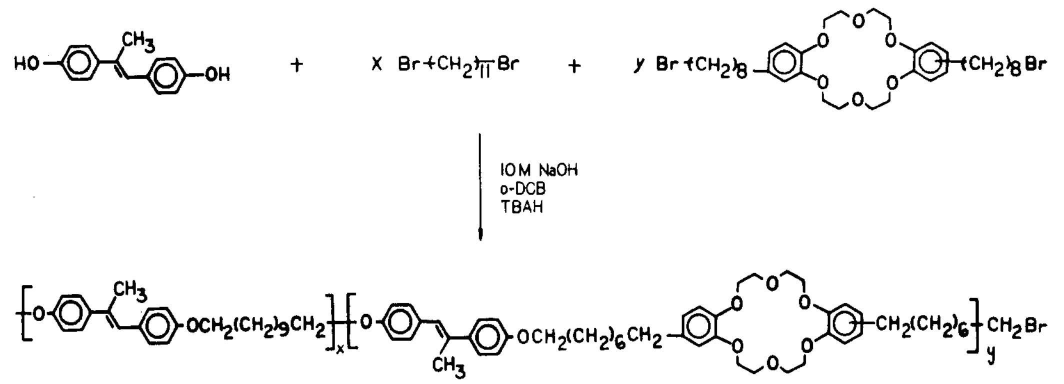


Synthesis of Monomers and Polymers. Synthesis of bis(8-bromooctyl)dibenzo-18-crown-6 is outlined in Scheme I.

Synthesis of Bis(8-bromooctanoyl)dibenzo-18-crown-6. A slurry of 8-bromooctanoic acid (5.7 g, 25.5 mmol) and dibenzo-18-crown-6 (4.0 g, 11.1 mmol) was added to polyphosphoric acid (40 g). The reaction mixture was then heated to 90 °C while stirring mechanically for 1 h. The reaction was worked up by slowly pouring the hot viscous solution into rapidly stirred ice cold H_2O. After stirring for several hours, the resulting precipitate was collected by filtration and recrystallized from EtOH to yield 8.0 g (93.6%) of white crystals: mp 112–114 °C; IR (KBr) 1660 cm^{-1} ($\nu_{C=O}$); ^{1}H NMR ($CDCl_3$, TMS, δ, ppm) 1.20–2.00 (20 protons, CH_2, β, γ, etc. to C=O, m), 2.83 (4 protons, CH_2CO, t), 3.34 (4 protons, CH_2Br, t), 3.96 (8 protons, CH_2O in crown ring, br s) 4.14 (8 protons, CH_2OPh, br s), 6.76 (2 Ar protons ortho to C=O and meta, para to O, d), 7.41–7.63 (4 Ar protons, ortho to each O, s + d).

Synthesis of Bis(8-bromooctyl)dibenzo-18-crown-6 (DECE-8). Et_3SiH (3.8 mL, 23.8 mmol) was added to a stirring solution of bis(8-bromooctanoyl)dibenzo-18-crown-6 (3.8 g, 4.9 mmol) in CF_3COOH (50 mL) and then stirred at room temperature until the reduction was completed. The progress of this reaction was monitored by NMR spectroscopy, which indicated that the reaction was over within about 2 h. The reaction mixture was then worked up by diluting with $CHCl_3$, followed by the slow addition of aqueous $NaHCO_3$ until no further exothermicity was evident. The organic layer was separated, washed with H_2O, and dried over $MgSO_4$ and the $CHCl_3$ was removed under vacuum. The resulting residue was triturated with EtOH to afford a precipitate which was dissolved in hot EtOH containing Darco

Scheme II
Synthesis of Polyethers and Copolyethers Based on 4,4′-Dihydroxy-α-methylstilbene, 1,11-Dibromoundecane, and/or Bis(8-bromooctyl)dibenzo-18-crown-6



G-60 activated carbon, hot filtered, and allowed to crystallize. An additional recrystallization from EtOH was usually sufficient to obtain about 99% purity. In the present case after the second recrystallization we obtained 2.8 g (76%) of white crystals: mp 68–70 °C; purity (HPLC), 98.6%; IR (KBr) no 1660-cm^{-1} absorbance due to C=O group was observed; ^{1}H NMR (CDCl$_3$, TMS, δ, ppm) 1.30–1.90 (24 protons, CH$_2$, β, γ, etc. to phenyl ring, m), 2.51 (4 protons, CH$_2$Ph, t), 3.40 (4 protons, CH$_2$Br, t), 4.03 (8 protons, CH$_2$O in crown ring, br s), 4.14 (8 protons, CH$_2$OPh, br s), 6.69–6.80 (6 Ar protons, m). This product contains a mixture of cis and trans isomers (HPLC). No attempts to separate these two isomers were made.

Synthesis of 4,4′-Dihydroxy-α-methylstilbene (HMS). HMS was synthesized and purified according to a previously described procedure:[9] mp (DSC) 182 °C; purity (HPLC), 99.3%.

Synthesis of Polyethers and Copolyethers. Synthesis of polyethers and copolyethers based on 4,4′-dihydroxy-α-methylstilbene, bis(8-dibromooctyl)dibenzo-18-crown-6, and 1,11-dibromoundecane is outlined in Scheme II. Both polyethers and copolyethers were synthesized by conventional liquid–liquid two-phase (organic solvent–aqueous NaOH solution) phase transfer catalyzed polyetherification conditions.[10-12] The polyetherifications were carried out under nitrogen atmosphere at 80 °C in *o*-dichlorobenzene–10 N NaOH water solution (10 times molar excess of NaOH versus phenol groups) in the presence of TBAH (10 mol % of phenol groups) as phase transfer catalyst. The molar ratio of nucleophilic to electrophilic monomers was 1.0/1.0 in every case.

An example of copolyetherification is as follows. To a 25-mL single-neck flask equipped with condenser, nitrogen inlet–outlet, and magnetic stirrer were successively added 0.226 g (1.0 mmol) of HMS, 2 mL of 10 N NaOH, 0.371 g (0.5 mmol) of bis(8-bromooctyl)dibenzo-18-crown-6, and 0.157 g (0.5 mmol) of 1,11-dibromoundecane dissolved in 2.3 mL of *o*-dichlorobenzene. The reaction vessel was then purged with dry N$_2$ before the addition of TBAH (0.068 g, 0.2 mmol). The reaction mixture was stirred at 1100 rpm with a magnetic stirrer at 80 °C under nitrogen. After 5 h of reaction, the organic and aqueous layers were diluted with chloroform and water, respectively, and the organic layer was washed 3 times with water and once with dilute HCl. The polymer was separated by precipitation of the chloroform solution into methanol to obtain 0.545 g (92%) of white fibrous precipitate. The polymer was further purified by an additional precipitation from chloroform solution into methanol.

Over the entire manuscript polyethers and copolyethers will be designated HMS-C11/DECE-8 (*A*/*B*) where *A*/*B* refers to the molar ratio of the two spacers, i.e., derived from 1,11-dibromoundecane (C11) and bis(8-bromooctyl)dibenzo-18-crown-6 (DECE-8), respectively.

Results and Discussion

Scheme I outlines the synthesis of bis(8-bromooctyl)dibenzo-18-crown-6. The first step consists in the acylation of dibenzo-18-crown-6 with 8-bromooctanoic acid using polyphosphoric acid as both solvent and acylating catalyst[13,14] to afford the bis(acylated)dibenzo-18-crown-6 free of side products. Eaton's reagent (methanesulfonic acid/phosphorous pentoxide) is a superior reagent for the acylation of benzo crown ether compounds;[13] however, this method leads to both acylation and glycol cleavage products. Similar results have previously been reported with other crown ether derivatives.[16] The acylation of benzo crown ether derivatives in the presence of AlCl$_3$ as catalyst is also known to lead to side products,[13] including strong complexes of the Lewis acid with the crown ether derivative.[17] Therefore, utilizing polyphosphoric acid as catalyst has been found to be the most suitable acylation procedure.

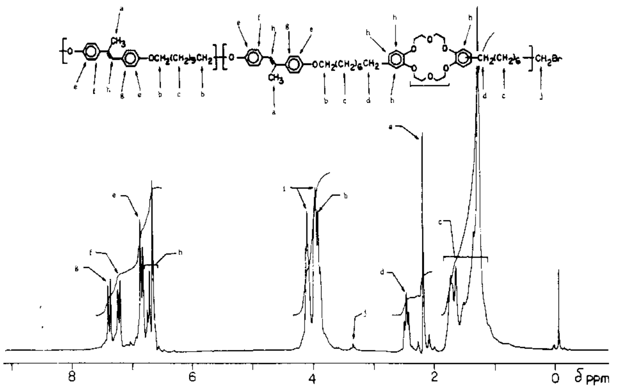


Figure 1. Representative 200-MHz ^{1}H NMR spectrum of HMS-C11/DECE-8 (50/50) copolyether (CDCl$_3$, TMS).

The reduction of the carbonyl groups of bis(8-bromooctanoyl)dibenzo-18-crown-6 to methylene was best accomplished with triethylsilane in trifluoroacetic acid.[18] A number of different methods were reported in the literature to selectively reduce the aryl ketone groups from acylated benzo crown ethers to methylene. However, all were less than satisfactory.[14] Our attempts to reduce the keto groups with LiAlH$_4$/AlCl$_3$/Et$_2$O reagent[19,20] under a variety of conditions have led to the formation of side products thought to be formed by the cleavage of the crown ether ring.[21]

The polyethers and copolyethers described in this paper were obtained in high yields (Table I) and are soluble in conventional solvents such as chloroform, tetrahydrofuran, etc. Due to the high conversions of the copolymerization reactions, copolymer compositions correspond to monomer feed compositions within about 5% error. This has been determined by ^{1}H NMR spectroscopy, by comparing the integrals of the signals a and d from Figure 1. The proton assignments from Figure 1 demonstrate that the copolymer's structure agrees with that depicted in Scheme II. The molecular weights of polyethers and copolyethers were determined by GPC using polystyrene as calibration standard and therefore have only a relative meaning.

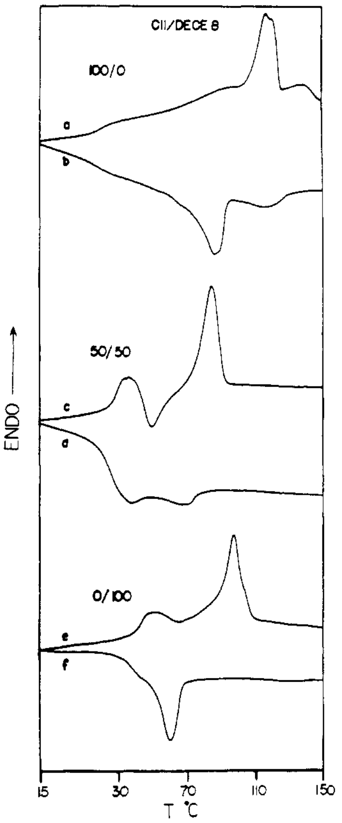


Figure 2. Representative normalized DSC traces (20 °C/min) of polyethers and copolyethers based on HMS, C11, and/or DECE-8: (a) HMS-C11, second heating scan; (b) HMS-C11, first cooling scan; (c) HMS-C11/DECE-8 (50/50), second heating scan; (d) HMS-C11/DECE-8 (50/50), first cooling scan; (e) HMS-DECE-8, second heating scan; (f) HMS-DECE-8, first cooling scan.

Nevertheless, they are useful in deciding whether phase transitions of different polymers can be compared. Previously, we have shown that for polyethers with number-average molecular weights larger than 12000 liquid-crystalline transitions are no longer dependent on their molecular weight.[10,11] However, they are kinetically controlled[22] and therefore equilibrium values are not straightforward enough to be determined. This manuscript will not be concerned with equilibrium data, and all the results reported (Table I) were collected from second heating and first or subsequent cooling DSC scans. The DSC traces of these scans are identical with those of subsequent scans.

Some representative DSC curves for both homopolymers and copolymers are presented in Figure 2. HMS-C11 is crystalline and upon melting exhibits an enantiotropic nematic mesophase (Figure 2a,b). The detailed characterization of the mesomorphic[10] and crystalline[23] phases of this polymer was already published, and these phase transitions are reported in Table I. Optical polarization microscopy reveals a typical schlieren nematic texture for HMS-C11. The DSC traces of HMS-DECE-8 are presented in Figure 2e,f, and the corresponding phase transitions are summarized in Table I. According to DSC traces, this polymer exhibits only a crystalline phase. However, if the polymer sample is sheared on the optical polarized microscope just below the isotropic–crystalline transition (at about 80 °C), HMS-DECE-8 seems to display an anisotropic texture resembling a nematic mesophase.

All HMS-C11/DECE-8 (*A*/*B*) copolymers, with the exception of HMS-C11/DECE-8 (20/80), exhibit a monotropic nematic mesophase. Representative DSC traces for HMS-C11/DECE-8 (50/50) are presented in Figure 2c,d. In the heating scans all polymers exhibit T_g followed by a small exotherm, which is due to the crystallization process, followed by melting of the crystalline phase (Figure 2c). In the cooling scans, all copolymers with the exception of HMS-C11/DECE-8 (20/80) exhibit a nematic mesophase followed by a crystallization exotherm (Figure 2d). HMS-C11/DECE-8 (20/80) is only crystalline. The melting and crystallization temperatures of the copolymers are highly depressed compared to the corresponding transitions of the parent homopolymers (Table I). This is best illustrated by Figure 3 which presents the plot of thermal transitions as a function of copolymer composition. In the case of copolymer HMS-C11/DECE-8 (60/40) the crystallization temperature is decreased to the extent that it does not occur upon cooling since it is situated in close proximity to the glass transition temperature.

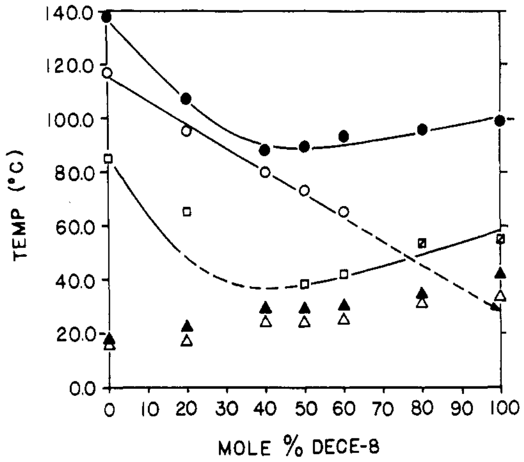


Figure 3. Thermal transitions for homopolymers (HMS-C11 and HMS-DECE-8) and copolymers [HMS-C11/DECE-8 (*A*/*B*)]: (●), T_{ki}; (○), T_{in}; (□), T_{nk}; (⊠), T_{ik}; (▲), T_g (heating); (△), T_g (cooling). Dotted lines represent extrapolations to virtual transitions which are pointed by arrows.

To understand and interpret the phase diagram from Figure 3 we have to consider some relationships between phase transitions and copolymer composition for the case of LC copolymers synthesized from two different flexible spacers and a single mesogenic unit. Recent work on this topic performed in different laboratories leads to the conclusion that copolymerization depresses crystallization and melting transition temperatures as well as their enthalpy changes determined in a dynamic way. At the same time, liquid-crystalline transitions and their enthalpy changes are weight averaged over those of the parent homopolymers.[10,12,24-28] This conclusion can be used as an important experimental tool to obtain further information about the phase behavior of both homopolymers and copolymers. First, by weight averaging liquid-crystalline transitions of copolymers and their enthalpy changes, we can obtain information about eventual virtual transitions and enthalpies of their parent homopolymers which displayed only crystalline transitions.[12,27]

A close inspection of the T_{in} transitions plotted in Figure 3 shows that these thermal transitions are situated on a straight line which by extrapolation leads to the determination of the virtual isotropic–nematic transitions of the copolymer HMS-C11/DECE-8 (20/80) and of the homopolymer HMS-DECE-8. The isotropic–nematic transition for HMS-C11/DECE-8 (20/80) is equal to 45 °C. This transition is below the copolymer crystallization temperature and is at the same time in close proximity of its glass transition. Therefore, due to the lack of mobility of the copolymer at this temperature, no exotherm appears on the DSC cooling scan. However, shearing this sample on

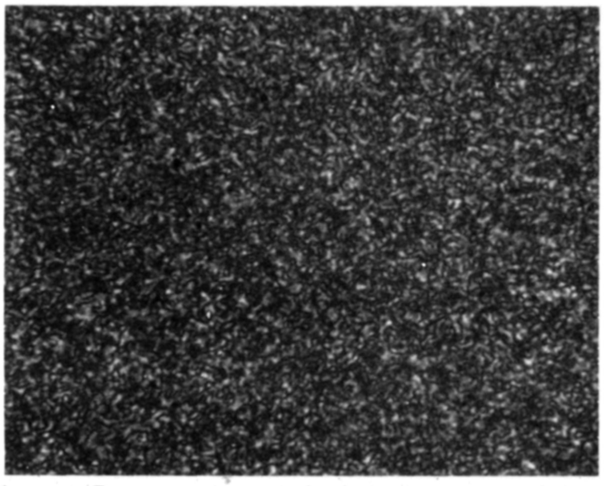


Figure 4. Representative optical polarization micrograph (70×) of the schliering nematic texture exhibited by the monotropic liquid-crystalline copolymers.

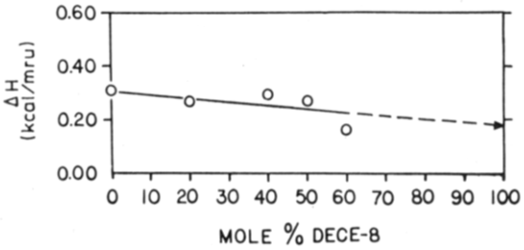


Figure 5. Enthalpy changes of isotropic–nematic transitions for homopolymers (HMS-C11 and HMS-DECE-8) and copolymers [HMS-C11/DECE-8 (*A*/*B*)]. Dotted line represents extrapolation to virtual transition enthalpy of the HMS-DECE-8 (pointed with arrow).

the optical polarized microscope just above the crystallization temperature induces a schlieren nematic texture which is similar to that exhibited by the monotropic copolymers (Figure 4). This suggests that indeed the isotropic–crystalline and crystalline–nematic transitions are overlapped. The virtual monotropic nematic mesophase for HMS-DECE-8 is 28 °C. This transition temperature is below both the crystallization and glass temperature of the homopolymer and therefore cannot be detected by DSC or optical polarized microscopy.

Figure 5 presents the plot of isotropic–nematic enthalpy changes as a function of copolymer composition. These data are also situated on a straight line. The extrapolation of this straight line leads to the calculation of the isotropic–nematic enthalpy for the HMS-C11/DECE-8 (20/80) copolymer (0.21 kcal/mru), and for the HMS-DECE-8 homopolymer (0.18 kcal/mru).

In conclusion, the polyether based on 4,4′-dihydroxy-α-methylstilbene and bis(8-bromooctyl)dibenzo-18-crown-6 presents a virtual liquid-crystalline mesophase, which is located below the glass transition of the homopolymer. However, the copolyethers based on 4,4′-dihydroxy-α-methylstilbene, bis(8-bromooctyl)dibenzo-18-crown-6, and 1,11-dibromoundecane led to copolymers exhibiting monotropic nematic mesophases. To our knowledge these copolymers represent the first examples of functional liquid-crystalline polymers containing crown ethers within their structural units. Research to synthesize liquid-crystal polymers containing crown ether structural units and exhibiting enantiotropic mesophases is currently in progress in our laboratory.

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Registry No. DECE-8, 117548-23-9; (C11)(HMS) (copolymer), 105117-12-2; (C11)(HMS) (SRU), 105005-93-4; (C11)(HMS)-(DECE-8) (copolymer), 117604-86-1; (DECE-8)(HMS) (copolymer), 117604-85-0; (DECE-8)(HMS) (SRU), 118473-64-6; bis(8-bromooctanoyl)dibenzo-18-crown-6, 117579-32-5; 8-bromooctanoic acid, 17696-11-6; dibenzo-18-crown-6, 14187-32-7.

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