Registry No. sO-2,7-2 (copolymer), 119897-10-8; sO-2,7-2 (SRU), 119897-13-1; sO-1,5-2 (copolymer), 122847-43-2; sO-1,5-2 (SRU), 122847-51-2; sO-2,6-2 (copolymer), 122847-45-4; sO-2,6-2 (SRU), 122847-52-3; sO-1,6-2 (copolymer), 122847-47-6; sO-1,6-2 (SRU), 123001-64-9.

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Liquid Crystal Polymers Containing Macroheterocyclic Ligands. 2.† Side Chain Liquid Crystal Polysiloxanes and Polymethacrylates Containing 4-(ω-Alkan-1-yloxy)-4′-(4′-carboxybenzo-15-crown-5)biphenyl Side Groups

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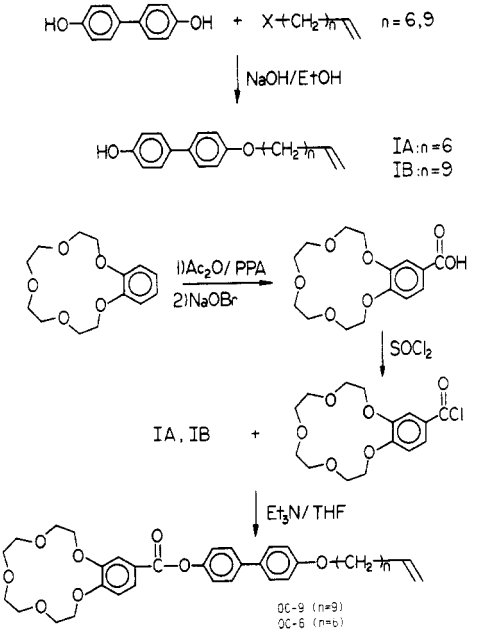
ABSTRACT: The synthesis and characterization of two poly(methylsiloxane)s containing 4-(ω-alkan-1-yloxy)-4′-(4′-carboxybenzo-15-crown-5)biphenyl side groups [where alkan = undecan (PSC-11) and octan (PSC-8)] and of poly[4-((11-methacryloylundecan-1-yl)oxy)-4′-(4′-carboxybenzo-15-crown-5)biphenyl] (PMC-11) are described. Both PSC-8 and PMC-11 display a nematic and a smectic enantiotropic mesophase, while PSC-11 displays a nematic and two smectic enantiotropic mesophases. Their parent monomers exhibit only monotropic mesophases. These polymers represent the first examples of side chain liquid crystal polymers containing macroheterocyclic ligands within their mesogenic side groups.

Introduction

The insertion of macroheterocyclic ligands capable of forming host–guest complexes within the structure of liquid crystalline compounds may lead to systems that combine the molecular features of the macroheterocyclic unit with the supramolecular arrangement of the units into a mesomorphic phase.[1] Liquid crystal macroheterocyclic ligands may add a new dimension to the field of host–guest chemistry that so far was performed either in an isotropic solution or in a three-dimensional crystalline phase.[1-3] They would represent the simplest examples of phase-dependent operating systems and could provide a new approach to systems that combine a highly selective recognition coupled with external thermal or electromagnetic regulation.[1,4]

So far, there are only two examples of low molar mass liquid crystals containing macroheterocyclic ligands. The first refers to disclike amide derivatives of macroheterocyclic polyamides that exhibit columnar mesophases.[1,5] The second refers to a series of rigid rodlike low molecular mass liquid crystals containing a benzocrown ether moiety. This second series of compounds exhibit calamitic mesophases.[6] To date, there is no example of side chain liquid crystal polymer containing crownlike ethers or any other kind of macroheterocyclic receptor.[7,8]

Scheme I
Synthesis of OC-6 and OC-11



The first example of main chain liquid crystalline polymer containing dibenzo-18-crown-6 based structural units was recently reported from our laboratory.[9]

† Part 1: Percec, V.; Rodenhouse, R. *Macromolecules* **1989**, *22*, 2043.

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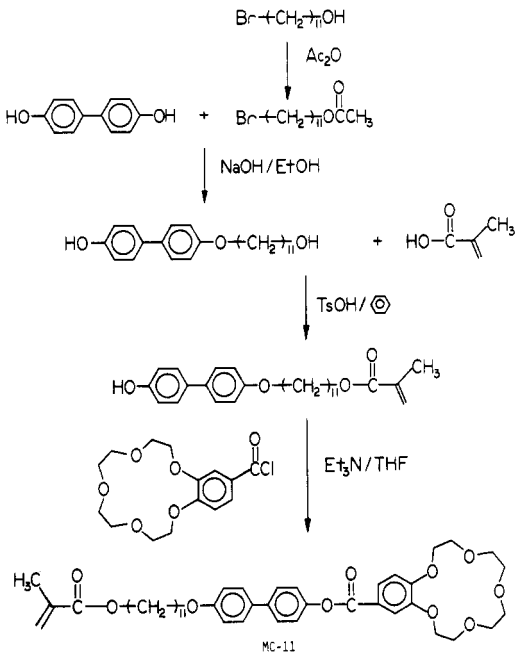
Scheme II
Synthesis of MC-11



This paper discusses the synthesis and characterization of the first examples of side chain liquid crystalline polymers containing benzo-15-crown-5 units in their mesogenic groups.

Experimental Section

Materials. All reagents were used as received or were synthesized and purified as previously described.[10,11]

Schemes I–III outline the synthesis of monomers and polymers.

Benzo-15-crown-5. Benzo-15-crown-5 was synthesized from catechol and 1,11-dichloro-3,6,9-trioxaundecane according to a literature method:[12] yield 60%; mp 78–79 °C (lit.[12] mp 79–79.5 °C); ^{1}H NMR ($CDCl_3$, TMS, δ, ppm) 3.77 (8 protons, OCH_2CH_2O, s), 3.92 (4 protons, $PhOCH_2CH_2O$, m), 4.12 (4 protons, $PhOCH_2CH_2O$, m), 6.90 (4 aromatic protons, s).

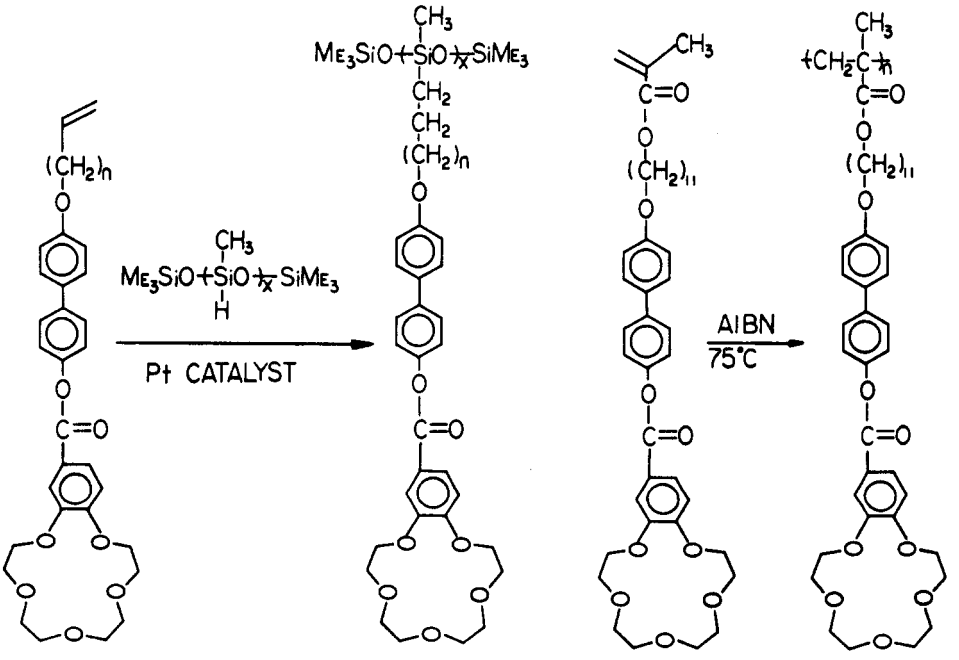
4′-Acetobenzo-15-crown-5. 4′-Acetobenzo-15-crown-5 was synthesized by acylation of benzo-15-crown-5 (5 g, 18.6 mmol) with acetic anhydride (2.5 mL) in a glacial acetic acid (4 mL) and polyphosphoric acid (55 g) mixture at 70 °C for 2 h.[13,14] The resulting dark red slurry was cooled to ~40 °C, and 400 mL of ice water was added. After 1 h of stirring, the product was extracted in $CHCl_3$, the solvent was evaporated, and the yellow solid was recrystallized from ethyl acetate/hexane to yield 5.2 g (90%) of white crystals: mp 94.5–95.5 °C (lit.[13] mp 95.5–96.5 °C); ^{1}H NMR ($CDCl_3$, TMS, δ, ppm): 2.56 (3 protons, $CH_3C(=O)$, s), 3.77 (8 protons, OCH_2CH_2O in crown ring, s), 3.94 (4 protons, OCH_2CH_2OPh in crown ring, br s), 4.20 (4 protons, OCH_2CH_2OPh in crown ring, br s), 6.88 (1 aromatic proton, d), 7.52 (1 aromatic proton, d of s), 7.57 (1 aromatic proton, d of d).

4′-Carboxybenzo-15-crown-5. It was synthesized by the oxidation of 4′-acetobenzo-15-crown-5 with NaOBr following the procedure described in ref 14: yield 88%; mp 180–181 °C (lit.[14] mp 180 °C); ^{1}H NMR ($CDCl_3$, TMS, δ, ppm) 3.78 (8 protons, OCH_2CH_2O, s), 3.93 (4 protons, $PhOCH_2CH_2O$, br s), 4.19 (4 protons, $PhOCH_2CH_2O$, br s), 6.88 (1 aromatic proton, d), 7.56 (1 aromatic proton, s), 7.69 (1 aromatic proton, d).

4-(10-Undecen-1-yloxy)-4′-hydroxybiphenyl (IB). IB was prepared by the monoalkylation of 4,4′-dihydroxybiphenyl (10 g, 53.7 mmol) with 10-undecen-1-yl tosylate[10] (17.5 g, 54.0 mmol) in ethanol (100 mL) by adding dropwise at reflux an aqueous (9 mL of H_2O) solution of KOH (3.29, 57.1 mmol). After 5 h, the reaction mixture was cooled to room temperature, excess base was added, and thereafter it was filtered. The solid was washed with hot ethanol, and the filtrate was rotovapped to yield a white solid that was washed with water, acidified, and recrystallized from methanol to yield 4.6 g (26%) of white crystals: mp 135–136 °C; ^{1}H NMR ($CDCl_3$, TMS, δ, ppm) 1.06–2.16 (16 protons, $(CH_2)_8$, m), 3.99 (2 protons, OCH_2, t), 4.85 (2 protons, $CH{=}CH_2$, m), 5.81 (1 proton, $CH{=}CH_2$, m), 6.71–7.05 (4 aromatic protons, m), 7.21–7.67 (4 aromatic protons, m).

4-(7-Octen-1-yloxy)-4′-hydroxybiphenyl (IA). IA was synthesized according to the procedure used in the preparation of 4-(10-undecen-1-yloxy)-4′-hydroxybiphenyl: yield 28%; mp 137–138 °C; ^{1}H NMR ($CDCl_3$, TMS, δ, ppm) 1.22–2.18 (10 protons, $(CH_2)_5$, m), 3.99 (2 protons, OCH_2, t), 4.86 (2 protons, $CH{=}CH_2$, m), 5.81 (1 proton, $CH{=}CH_2$, m), 6.72–7.07 (4 aromatic protons,

Scheme III
Synthesis of PSC-9, PSC-11, and PMC-11



OC-6 (n=6)
OC-9 (n=9)

PSC-8 (n=6)
PSC-11 (n=9)

MC-11

PMC-11

Table I
Characterization of Monomers and Polymers[a]

compd	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	phase transitions, °C (corresponding enthalpy changes, kcal/mru) heating	cooling
OC-6	590	1.0	k 147 (7.6) i	i 132 (0.12) n 107 (6.5) k
PSC-8	5300	1.5	g 61 s 152 (0.21) n 219 (0.20) i	i 213 (0.20) n 147 (0.35) s 52 g
OC-9	632	1.0	k 136 (3.6) i	i 134 (0.07) n 124 s 88 (2.9)[b] k
PSC-11	5700	1.3	g 50 s 106 (0.60) s 168 (0.80) n 216 (0.18) i	i 208 (0.18) n 159 (0.86) s 88 (0.64) s
MC-11	718	1.0	k 124 (12.1) i	i 114 (0.07) n 99 (0.03) s 78 (2.76) k
PMC-11	14600	2.8	g 50 s 129 (0.54) n 166 (0.37) i	i 160 (0.39) n 123 (0.57) s 49 g

[a] Abbreviations: g, glassy; k, crystalline; n, nematic; s, smectic. [b] Overlapped transitions; enthalpy change corresponds to the last two peaks.

m), 7.22–7.68 (4 aromatic protons, m).

4-(10-Undecen-1-yloxy)-4′-(4′-carboxybenzo-15-crown-5)-biphenyl (OC-9). To a mixture of 4′-carboxybenzo-15-crown-5 (2 g, 6.41 mmol) in dried $CHCl_3$ (20 mL) was added dropwise thionyl chloride (2 mL, 27.6 mmol). The mixture was refluxed for 3 h, followed by removal of solvent and excess thionyl chloride under vacuum. The resulting acid chloride was dissolved in a minimum amount of THF and added dropwise to 4-(10-undecen-1-yloxy)-4′-hydroxybiphenyl (2.17 g, 6.41 mmol) and triethylamine (0.65 g, 6.44 mmol) dissolved in THF (20 mL) at 0 °C. After the solution was stirred overnight at room temperature, THF was removed under vacuum and the remaining white solid was washed with water followed by recrystallization from ethanol, yielding 2.71 g (65%) of white crystals: mp 134 °C; purity (HPLC), 100%; ^{1}H NMR ($CDCl_3$, TMS, δ, ppm) 1.06–2.11 (16 protons, $(CH_2)_8$, m), 3.78 (8 protons, CH_2CH_2O in crown ring, s), 3.94 (6 protons, CH_2CH_2OPh in crown ring and biphenyl OCH_2, br s and t, respectively), 4.21 (4 protons, CH_2CH_2OPh in crown ring, br s), 4.96 (2 protons, CH=CH_2, m), 5.81 (1 proton, CH=CH_2, m), 6.95 (3 aromatic protons, biphenyl and aromatic crown, m), 7.24 (2 aromatic protons, biphenyl, d), 7.43–7.65 (4 aromatic protons, biphenyl, m), 7.68 (1 aromatic proton, crown, d of s), 7.86 (1 aromatic proton, crown, d of d).

4-(7-Octen-1-yloxy)-4′-(4′-carboxybenzo-15-crown-5)biphenyl (OC-6). This compound was synthesized according to the procedure used in the synthesis of 4-(10-undecen-1-yloxy)-4′-(4′-carboxybenzo-15-crown-5)biphenyl: yield 67%; mp 144 °C; ^{1}H NMR ($CDCl_3$, TMS, δ, ppm) 1.21–2.15 (10 protons, $(CH_2)_5$, m), 3.79 (8 protons, OCH_2CH_2O in crown ring, s), 3.97 (6 protons, OCH_2CH_2OPh in crown ring and biphenyl OCH_2, br s and t, respectively), 4.24 (4 protons, OCH_2CH_2OPh in crown ring, br s), 4.98 (2 protons, CH=CH_2, m), 5.82 (1 proton, CH=CH_2, m), 6.96 (3 aromatic protons, biphenyl and aromatic crown, m), 7.23 (2 aromatic protons, biphenyl, d), 7.45–7.64 (4 aromatic protons, biphenyl, m), 7.68 (1 aromatic proton, crown, d of s), 7.87 (1 aromatic proton, crown, d of d).

4-((11-Hydroxyundecan-1-yl)oxy)-4′-hydroxybiphenyl. To a refluxing mixture of 11-bromoundecan-1-yl acetate (synthesized from 11-bromoundecan-1-ol and acetic anhydride under acid-catalyzed conditions, 10.2 g, 34.9 mmol), 4,4′-dihydroxybiphenyl (6.5 g, 34.9 mmol), and ethanol (60 mL) was added dropwise a solution of ethanolic KOH (2.14 g, 38.2 mmol). The mixture was refluxed for 16 h followed by hot filtration. The filtrate was acidified and allowed to cool to room temperature at which time a precipitate forms. This solid was collected and recrystallized twice from slightly acidic methanol, yielding 3.32 g (27%) of white crystals: mp 144.5–146 °C; ^{1}H NMR (DMSO-d_6, TMS, δ, ppm) 1.09–1.81 (18 protons, $(CH_2)_9$, m), 3.35 (2 protons, CH_2OH, t), 3.96 (2 protons, OCH_2, t), 4.31 (1 proton, OH, br s), 6.82 (2 aromatic protons, d), 6.95 (2 aromatic protons, d), 7.31–7.49 (4 aromatic protons, m), 9.41 (1 proton, PhOH, br s).

4-((11-Methacryloylundecan-1-yl)oxy)-4′-hydroxybiphenyl. A mixture of 4-((11-hydroxyundecan-1-yl)oxy)-4′-hydroxybiphenyl (2.88 g, 8.09 mmol), methacrylic acid (8.5 mL), *p*-toluenesulfonic acid monohydrate (0.34 g, 1.75 mmol), and benzene (125 mL) was heated to reflux. Azeotropic removal of water was carried out by using a Dean-Stark trap, and the reaction was monitored until no more water of reaction was collected. After 22 h the reaction was cooled to room temperature and the benzene layer was removed under vacuum. The resulting white solid was recrystallized from ethanol to yield 2.13 g (62%): mp 86–87 °C; ^{1}H NMR ($CDCl_3$, TMS, δ, ppm) 1.19–1.90 (18 protons, $(CH_2)_9$, m), 1.95 (3 protons, $CH_3\dot{C}CO_2$, s), 3.99 (2 protons, OCH_2, t), 4.14 (2 protons, $CH_2OC(=O)$, t), 5.55 (1 proton, $CH_2\dot{C}CO_2$, br s), 6.11 (1 proton, CH_2=$\dot{C}CO_2$, br s), 6.82–7.00 (4 aromatic protons, m), 7.37–7.52 (4 aromatic protons, m).

4-((11-Methacryloylundecan-1-yl)oxy)-4′-(4′-carboxybenzo-15-crown-5)biphenyl (MC-11). To a mixture of 4′-carboxybenzo-15-crown-5 (0.87 g, 2.79 mmol) in dried $CHCl_3$ (15 mL) was added dropwise thionyl chloride (1 mL, 13.8 mmol). The mixture was refluxed for 3 h, followed by removal of solvent and excess thionyl chloride under vacuum. The resulting acid chloride was dissolved in a minimum amount of dried THF and added dropwise to 4-((11-methacryloylundecan-1-yl)oxy)-4′-hydroxybiphenyl (1.18 g, 2.78 mmol) and triethylamine (0.28 g, 2.78 mmol) at 0 °C. After the solution was stirred overnight at room temperature, the THF was removed under vacuum without heating. The remaining white solid was recrystallized from ethanol, yielding 1.42 (71%) of white crystals. The monomer was purified further by flash chromatography using neutral alumina with $CHCl_3$ as eluent: purity (HPLC), 99.7%; mp 124 °C, ^{1}H NMR ($CDCl_3$, TMS, δ, ppm) 1.18–1.88 (18 protons, $(CH_2)_9$, m), 1.95 (3 protons, $CH_3\dot{C}CO_2$, s), 3.79 (8 protons, OCH_2CH_2 in crown ring, s), 3.96 (6 protons, OCH_2CH_2OPh in crown ring and biphenyl OCH_2, br s and t, respectively, 4,15 (2 protons, $CH_2O\dot{O}C$, t), 4.23 (4 protons, OCH_2CH_2OPh in crown ring, br s), 5.55 (1 proton, CH_2=$\dot{C}CO_2$, br s), 6.11 (1 proton, CH_2=$\dot{C}CO_2$, br s), 6.96 (3 aromatic protons, biphenyl + aromatic crown, m), 7.25 (2 aromatic protons, biphenyl, d), 7.42–7.65 (4 aromatic protons, biphenyl, m), 7.69 (1 aromatic proton in crown, d of s), 7.86 (1 aromatic proton in crown, d. of d).

Synthesis of Polymers. The poly(methylsiloxane)s PSC-8 and PSC-10 were synthesized by the hydrosilation of OC-6 and OC-9 with a poly(methylsiloxane) (DP = 100) that was synthesized as described previously.[15] The reaction was performed by using dicyclopentadienylplatinum(II) chloride[10] or platinum divinyltetramethyldisiloxane in xylene[16] as catalysts. A typical procedure is as follows. The alkenic derivative (0.7570 g, 10 mol % excess versus the Si–H groups present in polysiloxane) was dissolved in 50 mL of Na-dry toluene together with the proper amount of poly(methylhydrosiloxane). The reaction mixture was heated to 110 °C under nitrogen, and 500 μL of dicyclopentadienylplatinum(II) chloride catalyst was then injected as a solution in CH_2Cl_2 (1 mg/mL). The reaction mixture was heated at 110 °C until both IR and ^{1}H NMR analyses showed that the hydrosilation reaction was complete. When the divinyltetramethyldisiloxane was used as the catalyst, the reaction was only heated to 60 °C and 1 drop of 3 wt % Pt catalyst in xylene was used. Purification was performed by several precipitations into CH_3OH.

Poly[4-((11-methacryloylundecan-1-yl)oxy)-4′-(4′-carboxybenzo-15-crown-5)biphenyl] (PMC-11) was synthesized by radical polymerization of MC-11 in toluene (8% wt/v), using AIBN as radical initiator (1 wt % versus monomer) at 75 °C for 24 h. The polymerization was carried out in a Schlenk tube under an argon atmosphere after the monomer solution was degassed by several freeze–pump–thaw cycles under vacuum. PMC-11 was purified by several precipitations into methanol until GPC measurements did not show any traces of unreacted monomer. Conversion was higher than 80%.

Techniques. ^{1}H NMR spectra (200 MHz) were recorded on a Varian XL-200 spectrometer. Thermal transitions and thermodynamic parameters were determined by using a Perkin-Elmer DSC-4 differential scanning calorimeter equipped with a TADS

3600 data station. Heating and cooling rates were 20 °C/min. Thermal transitions reported in Table I were collected during the second heating and cooling scans. A Carl Zeiss optical polarizing microscope (magnification 100×) equipped with a Mettler FP 82 hot stage and a Mettler FP 80 central processor was used to observe the thermal transitions and to analyze the anisotropic textures. Relative molecular weights were determined by gel permeation chromatography (GPC) with a Perkin-Elmer series 10 LC instrument equipped with LC-100 column oven, LC-600 autosampler, and Sigma 15 data station. High-pressure liquid chromatography (HPLC) determinations were performed with the same instrument. The measurements were made by using an UV detector, THF 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.

Results and Discussion

The synthesis of monomers and polymers containing benzo-15-crown-5 groups is outlined in Schemes I–III. These synthetic routes were selected to provide high yields and minimum number of reaction steps. An alternative synthesis of 4′-acetobenzo-15-crown-5, which consists of etherification of 3,4-dihydroxyacetophenone with 1,11-dichloro-3,6,9-trioxaudecane (45%),[17] was considered. However, 3,4-dihydroxyacetophenone has to be synthesized by Fries rearrangement of catechol diacetate (63%) which itself has to be synthesized from catechol (77%). Therefore this extensive synthetic route was replaced by a simple acylation procedure. We have surveyed a number of acylation procedures available in the literature on benzo and dibenzocrown ether derivatives,[9] and the most reliable method for the synthesis of 4′-acetobenzo-15-crown-5 is the one based on the acylation of benzo-15-crown-5 with acetic anhydride in a mixture of polyphosphoric acid and glacial acetic acid. We have to mention that slight deviations from the procedure described in the Experimental Section lead to lower yields and difficulties in the separation of the 4′-acetobenzo-15-crown-5. Particularly, larger amounts of acetic acid have led to lower acetylation yields.

Another recommendation we would like to make refers to the synthesis of 4-((11-hydroxyundecan-1-yl)oxy)-4′-hydroxybiphenyl by the monoetherification of 4,4′-dihydroxybiphenyl with 11-bromoundeca-1-yl acetate (Scheme II). This reaction can be performed by monoetherification of 4,4′-dihydroxybiphenyl with 11-bromoundecan-1-ol. However, when the acetate is used, the monoetherified derivative is less soluble in the reaction mixture than the 4-((11-hydroxyundecan-1-yl)oxy)-4′-hydroxybiphenyl and, once formed, precipitates. Although by the end of the reaction the acetate group is cleaved to alcohol, the difference in solubility between acetate and free alcohol enhances the overall yield of the monoetherification reaction.

Table I summarizes the characterization of both monomers and polymers. On the basis of our previous experience,[15] all relative molecular weights reported for side chain liquid crystalline polymers are lower than the real values.

All monomers and polymers synthesized display mesomorphic phases. OC-6 displays a monotropic nematic mesophase while OC-9 and MC-11 display monotropic nematic and smectic mesophases. OC-6 resembles the structure and the behavior of a previously synthesized low molar liquid crystal, i.e., 4-(*n*-octanyloxy)-4′-(4′-carboxybenzo-15-crown-5)biphenyl,[6] that was reported to melt into an isotropic liquid at 157 °C and exhibit a monotropic isotropic–nematic transition at 154 °C.[6] With the exception of PMC-11 that polymerizes during its thermal characterization, the phase behavior of all other monomers and polymers reported in Table I is independent of the heating or cooling DSC scan they were collected from. All data from Table I were determined from second heating and cooling DSC scans.

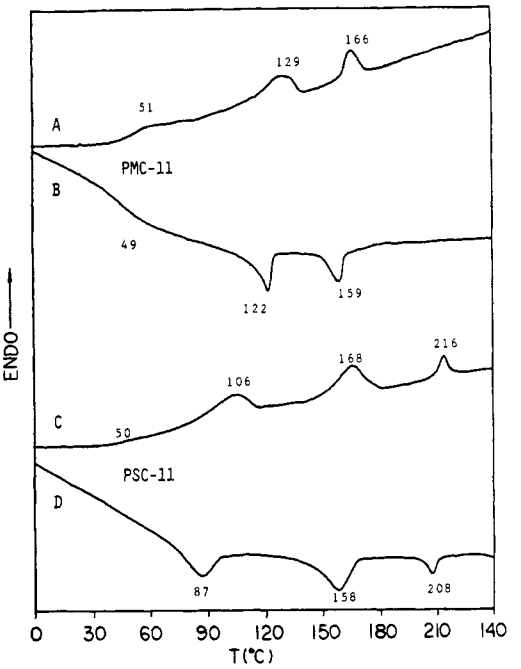


Figure 1. Normalized DSC traces (20 °C/min): (A) PMC-11, second heating scan; (B) PMC-11, second cooling scan; (C) PSC-11, second heating scan; (D) PSC-11, second cooling scan.

As expected, on going from monomer to polymer, the rate of crystallization decreases while the temperature of each mesomorphic phase transition increases.[8,12,20] Subsequently, certain monotropic or even virtual transitions become enantiotropic.[20] This is nicely illustrated by the phase behavior of the polymers reported in Table I. Both PSC-8 and PMC-11 display a nematic and a smectic enantiotropic mesophase. The phase behavior of PSC-11 and PMC-11 can be directly compared since the two polymers have identical mesogenic groups and spacer lengths and differ only through the nature of their polymer backbone. Representative heating and cooling DSC curves for PMC-11 and PSC-11 are presented in Figure 1. As demonstrated previously[21] for other side chain liquid crystal polymers, it is expected that the most flexible polymer backbone will provide the highest isotropization temperature. This is indeed the case. PMC-11 has a polymethacrylate backbone and undergoes isotropization at 166 °C while PSC-11 which has a polysiloxane backbone undergoes isotropization at 216 °C. In addition, PSC-11 displays a second highly ordered smectic mesophase. This last result agrees again with previous results concerning the influence of polymer backbone flexibility on mesomorphic phase transitions.[8,15,20,21]

On the optical polarized microscope all monomers and polymers display textures that are characteristic of low molar liquid crystals.[22,23] The monotropic nematic mesophases of all monomers are pseudohomeotropic. On cooling from the isotropic phase the monomers display for a very short time a Schlieren nematic mesophase that transforms into an isotropic liquid. Upon shearing the nematic texture reappears and subsequently on relaxation disappears. Probably this is because the crown ether moiety of the mesogenic unit interacts with the surface of the glass slide. All polymers display a nematic texture with a very high number of inversion lines. A representative texture is presented in Figure 2. However, the smectic phases are very viscous, and attempts to develop a char-

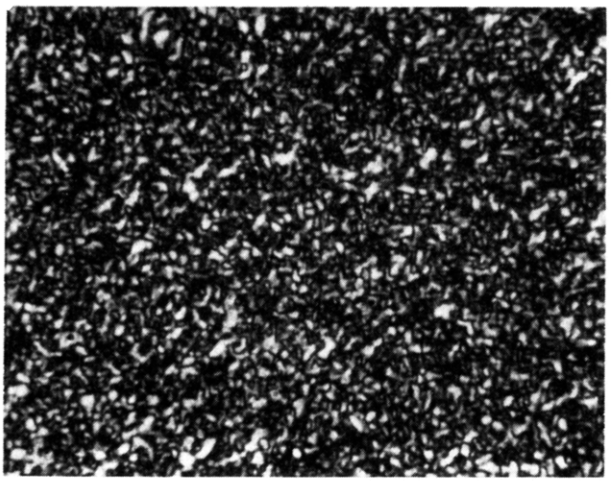


Figure 2. Representative optical polarization micrographs (100×) of the nematic texture displayed by PMC-11 after annealing at 162 °C (on cooling scan) for 30 min.

acteristic smectic mesophase upon annealing were unsuccessful so far.

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Registry No. IB, 123640-26-6; IA, 123640-27-7; OC-9, 123640-28-8; OC-6, 123640-29-9; MC-11, 123640-32-4; MC-11 (homopolymer), 123640-37-9; 4′-acetobenzo-15-crown-5, 41757-95-3; benzo-15-crown-5, 14098-44-3; acetic anhydride, 108-24-7; 4′-carboxybenzo-15-crown-5, 56683-55-7; 4,4′-dihydroxybiphenyl, 92-88-6; 10-undecen-1-yl tosylate, 51148-67-5; 4-(11-hydroxyundecan-1-yloxy)-4′-hydroxybiphenyl, 123640-30-2; 11-bromoundecan-1-yl acetate, 30295-23-9; 4-[(11-methacryloylundecan-1-yl)oxy]-4′-hydroxybisphenyl, 123640-31-3.

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Synthesis of Telechelic Poly(tetrahydrofuran) Having a Carboxyl Group Using Ketene Silyl Acetal as a Terminator

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ABSTRACT: Telechelic poly(tetrahydrofurans) (polyTHFs) having a carboxyl or an ester group were synthesized. The living polymerization of THF was achieved with trifluoromethanesulfonic anhydride ($(CF_3SO_2)_2O$) as initiator, and living propagating species thus formed were terminated with a nucleophile such as a ketene silyl acetal or a ketene bis(silyl acetal) without a catalyst. The structures of polymers were confirmed by IR and ^1H and ^{13}C NMR spectroscopy. Molecular weight was determined by vapor pressure osmometry and ^1H NMR. The functionality of these telechelic polyTHFs having two terminal ester groups was close to 2.0, as determined by ^1H NMR analysis. These telechelic polyTHFs of methyl and trimethylsilyl esters were converted to telechelic polyTHFs having carboxylic acid groups by alkaline hydrolysis.

Introduction

Telechelic polymers are those with reactive groups at both ends. They become increasingly important for practical use, e.g., as a prepolymer for block copolymers or a cross-linking agent. For the preparation of these telechelic polymers, living polymerizations can be most conveniently employed since functional groups are readily introduced via the termination of living propagating species.

Smith and Hubin described the polymerization of THF using trifluoromethanesulfonic anhydride ($(CF_3SO_2)_2O$) as a bifunctional initiator, which proceeds via living propagating species.[1] They obtained telechelic polyTHFs of glycol and diamine type by terminating the living species

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