Macromolecules
Volume 20, Number 12 December 1987

Liquid-Crystalline Polymers Containing Heterocycloalkane Mesogenic Groups. 5. Synthesis of Biphasic Chiral Smectic Polysiloxanes Containing 2,5-Disubstituted-1,3-dioxane- and 2,5-Disubstituted-1,3,2-dioxaborinane-Based Mesogenic Groups†

Bruce Hahn and Virgil Percec*

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106. *Received January 9, 1987*

ABSTRACT: The synthesis of side-chain liquid-crystalline polysiloxanes containing chiral mesogenic side groups, i.e., *trans*-2-[*p*-(11-undecanyloxy)phenyl]-5-[*p*-(2(*S*)-methyl-1-butoxy)phenyl]-1,3-dioxane, *trans*-2-[*p*-(2(*S*)-methyl-1-butoxy)phenyl]-5-(11-undecanyl)-1,3-dioxane, and polysiloxanes and copolysiloxanes containing 2-[4-(2(*S*)-methyl-1-butoxy)phenyl]-5-(11-undecanyl)-1,3,2-dioxaborinane is presented. Differential scanning calorimetry and optical polarization microscopy revealed chiral smectic mesomorphism for all polymers. The last two polymers present also a chiral smectic C (S^*_C) mesophase. All copolymers exhibit two glass transition temperatures; one due to the independent motion of the main chain, the other due to the cooperative but independent motion of the side groups. Therefore, these liquid-crystalline copolymers are biphasic systems resembling the behavior of phase-separated graft copolymers; i.e., they exhibit a microphase separated morphology containing main-chain and side-chain domains.

Introduction

In 1977, Meyer et al.[1,2] demonstrated the ferroelectricity of chiral smectic C and H phases (C* and H*). Since then, there is an increasing interest in the synthesis of low molar mass chiral smectic liquid crystals, particularly those exhibiting S^*_C phases. Both the theoretical and technological reasons for the interest in chiral smectic liquid crystals were recently reviewed.[3,4]

There are only a few published results concerning the synthesis of side-chain liquid-crystalline polymers exhibiting chiral smectic mesophases.[5-8]

Previous results from this laboratory have demonstrated that side-chain liquid-crystalline polymers containing 11 methylenic units in the flexibile spacer and trans 2,5-disubstituted-1,3-dioxane-based mesogenic groups do not undergo side-chain crystallization.[9,10] The conformational isomers of the 1,3-dioxane-based mesogens are in a dynamic equilibrium and this depresses their crystallization when they are attached as polymeric side chains. This is an important result since most of the side-chain liquid-crystalline polymers containing long spacers undergo side-chain crystallization.[11,12] At the same time, long spacers are required to provide a high degree of decoupling of the mobility of the main chain from that of the side groups.

A complete or a high degree of decoupling would suggest that a side-chain liquid-crystalline polymer would have to behave as a phase-separated graft copolymer, presenting a microphase-separated morphology containing main-chain and side-chain domains, and therefore would exhibit two glass transition temperatures, i.e., one due to the independent motion of the main chain and the other due to the cooperative but independent motion of the side groups. This would mean that although the side groups are connected to the main chain, the polymer behaves as two, semiindependent thermodynamic subsystems (i.e., main chain plasticized by part of the spacer and mesogenic unit stabilized by part of the spacer), interacting through a part of the flexible spacer.[13,14]

Recently, we have prepared the first example of side-chain liquid-crystalline polymers exhibiting two glass transition temperatures, i.e., biphasic side-chain liquid-crystalline polymers.[15,16]

The goal of this paper is to present the synthesis and preliminary data on the characterization of the first examples of biphasic side-chain chiral smectic liquid-crystalline polysiloxanes. The particular examples described here refer to polysiloxanes containing *trans*-2-[*p*-(11-undecanyloxy)phenyl]-5-[*p*-(2(*S*)-methyl-1-butoxy)-phenyl]-1,3-dioxane, *trans*-2-[*p*-(2(*S*)-methyl-1-butoxy)-phenyl]-5-(11-undecanyl)-1,3-dioxane, and 2-[4-(2(*S*)-methyl-1-butoxy)phenyl]-5-(11-undecanyl)-1,3,2-dioxaborinane and copolysiloxanes containing 2-[4-(2(*S*)-

† Paper 4 in this series: ref 16.

0024-9297/87/2220-2961$01.50/0

methyl-1-butoxy)phenyl]-5-(11-undecanyl)-1,3,2-dioxaborinane side groups.

Experimental Section

A. Materials. Poly(methylsiloxane) ($\bar{M}_n$ = 4500–5000) and poly[(30–35%)- or (15–18%)-methylsiloxane-*co*-(65–70%)- or (82–85%)-dimethylsiloxane] ($\bar{M}_n$ = 2000–2100) were obtained from Petrarch Systems and used as received. (–)-2(*S*)-methyl-1-butanol, $[\alpha]_D$ –7.3°, was obtained from Fluka and was used as received. Toluene used in the hydrosilation reaction was first refluxed over sodium and then distilled under argon. All other solvents and reagents were purified by standard methods.

B. Techniques. ^{1}H NMR spectra, 200 MHz, were recorded on a Varian XL-200 spectrometer. All spectra were recorded in $CDCl_3$ solution with TMS as internal standard unless noted otherwise. Thermal transitions 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. Glass transition temperatures (T_g) were read at the middle of the change in the heat capacity. After the first heating and cooling scans all the DSC scans gave reproducible data. The transitions reported were read during the second or third heating and cooling scans unless reported otherwise. 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. Optical rotations were measured at 25 °C on a Perkin-Elmer 241 polarimeter with absolute ethanol as solvent for all compounds except for IA, IB, and IC derivatives, which were measured from chloroform solutions.

C. Synthesis of Monomers. 2(*S*)-Methyl-1-butyl Tosylate. To a stirred solution of *p*-toluenesulfonyl chloride (112.5 g, 0.59 mol) in 200 mL of dry pyridine, 50 g (0.57 mol) of (–)-2(*S*)-methyl-1-butanol was added dropwise at 0 °C. The reaction mixture was stirred at 4 °C overnight. The resulting solution was poured into 400 mL of ice water and extracted with diethyl ether. The ether layer was washed with a 50/50 (v/v) water/hydrochloric acid mixture and water, dried over anhydrous $MgSO_4$, and filtered and the diethyl ether was removed on a rotavapor to yield 131 g (95%) of an oil: ^{1}H NMR ($CDCl_3$, TMS) δ 0.84 (m, 6 H, CH_3), 1.0–1.4 (m, 2 H, n-CH_2-n), 1.6 (m, 1 H, C*H*), 2.4 (s, 3 H, Ph–CH_3), 3.8 (m, 2 H, CH_2O), 7.2 and 7.7 (2 d, 4 H, Ar H); $[\alpha]_D$ +3.6° (89% optical purity).

***p*-(2(*S*)-Methyl-1-butoxy)phenylacetic Acid.** To a stirred solution of 15.2 g (0.38 mol) of sodium hydroxide in 150 mL of 95% ethanol was added 25 g (0.16 mol) of *p*-hydroxyphenylacetic acid. When dissolution was complete, 40 g (0.16 mol) of 2(*S*)-methyl-1-butyl tosylate was added. The solutions was heated under reflux with stirring under N_2 for 19 h. The solvent was removed and 100 mL of water was added to the residue. Dilute hydrochloric acid was used to acidify the solution which was extracted with diethyl ether. The ether layer was dried over anhydrous magnesium sulfate and filtered and the solvent was removed on a rotavapor. The resulting product was recrystallized from water containing 10% ethanol to yield 18 g (97%) of white crystals: mp 40–42 °C; ^{1}H NMR ($CDCl_3$, TMS) δ 0.93–0.98 (m, 6 H, CH_3), 1.2–1.4 (m, 2 H, CH_2), 1.9 (m, 1 H, C*H*), 3.5 (s, 2 H, PhCH_2COOH), 3.7 (m, 2 H, CH_2O), 6.8 and 7.2 (2 d, 4 H, Ar H); $[\alpha]_D$ + 4.8°.

Ethyl *p*-(2(*S*)-Methyl-1-butoxy)phenylacetate. To a stirred solution containing 15.0 g (0.07 mol) of *p*-(2(*S*)-methyl-1-butoxy)phenylacetic acid and 100 mL of dry methylene chloride, thionyl chloride (9.25 g, 0.078 mol) was added dropwise. The reaction mixture was stirred for 1 h. An excess of ethanol was then added to it. After 2 h the solvent was removed on a rotavapor to yield 14.95 g (76%) of a colorless oil: ^{1}H NMR ($CDCl_3$, TMS) δ 0.94–1.00 (m, 6 H, CH_3), 1.2 (t, 3 H, CH_3CH_2), 1.2–1.7 (m, 2 H, CH_2), 1.9 (m, 1 H, C*H*), 3.5 (s, 2 H, PhCH_2), 3.75 (m, 2 H, CH_2O), 4.1 (q, 2 H, $COOCH_2$), 6.8 and 7.2 (2 d, 4 H, Ar H).

Diethyl 2-[*p*-(2(*S*)-Methyl-1-butoxy)phenyl]malonate. To a solution of sodium ethoxide in ethanol, prepared from 1.45 g (0.06 mol) of sodium added to 100 mL of absolute ethanol, and 8.8 g (0.06 mol) of ethyl oxalate, 14.95 g (0.05 mol) of ethyl *p*-(2(*S*)-methyl-1-butoxy)phenylacetate was added. The solution was stirred at reflux overnight. The solvent was removed on a rotavapor. The pastelike residue was dissolved into diethyl ether and treated with dilute sulfuric acid. The ether layer was dried over anhydrous $MgSO_4$ and filtered and the ether was evaporated. The resulting oil was then heated to 170 °C for 6 h and then distilled under vacuum to yield 14.5 g (90%): ^{1}H NMR ($CDCl_3$, TMS) δ 0.98 (m, 6 H, CH_3), 1.2 (m, 6 H, CH_3CH_2O), 1.2–1.7 (m, 2 H, CH_2CH), 1.9 (m, 1 H, C*H*), 3.5 (s, 1 H, PhC*H*), 3.8 (m, 2 H, CH_2OPh), 4.2 (m, 4 H, CH_2COO), 6.8 and 7.3 (2 d, 4 H, Ar H).

2-[*p*-(2(*S*)-Methyl-1-butoxy)phenyl]propane-1,3-diol. A solution containing diethyl 2-[*p*-(2(*S*)-methyl-1-butoxy)-phenyl]malonate (14.5 g, 0.045 mol) in 50 mL of dry diethyl ether was added dropwise to a stirred mixture of 2.23 g (0.059 mol) of $LiAlH_4$ in 200 mL of dry diethyl ether. The reaction mixture was stirred at reflux for 20 h and then cooled to room temperature. The reaction mixture was treated with 50 mL of ethyl acetate to consume the excess $LiAlH_4$, followed by 50 mL water and 50 mL of 50% hydrochloric acid. The ether layer was separated, washed with 100 mL of water, dried over anhydrous $MgSO_4$, and filtered and the solvent was evaporated to yield 7.9 g (75%) of a colorless oil: ^{1}H NMR ($CDCl_3$, TMS) δ 1.9 (m, 6 H, CH_3), 1.2–1.7 (m, 2 H, CH_2CH), 1.9 (m, 3 H, C*H*, O*H*), 3.06 (m, 1 H, PhCH), 3.8 (m, 2 H, CH_2OPh), 3.97 (m, 4 H, CH_2OH), 6.8 and 7.3 (2 d, 4 H, Ar H).

10-Undecen-1-yl Tosylate. A mixture containing 50 g (0.29 mol) of 10-undecen-1-ol and 150 mL of dry pyridine was cooled to 0 °C. Nitrogen was bubbled through the mixture for 10 min. *p*-Toluenesulfonyl chloride (56 g, 0.29 mol) was then added to the reaction mixture which was stirred overnight at 4 °C. The solution was then poured into 500 mL of ice water, and the mixture was extracted with diethyl ether. The ether extract was washed with 50/50 water/hydrochloric acid and water, dried over anhydrous $MgSO_4$, and filtered and the ether evaporated to yield 90 g of a colorless oil (95%): ^{1}H NMR ($CDCl_3$, TMS) δ 1.2–2.0 (m, 16 H, $(CH_2)_8$), 2.38 (s, 3 H, PhCH_3), 3.84 (t, 2 H, CH_2O), 4.85 and 5.67 (m, 3 H, $CH{=}CH_2$), 7.2 and 7.7 (2 d, 4 H, Ar H).

***p*-(10-Undecen-1-yloxy)benzaldehyde.** To a stirred solution containing 1.5 g (0.037 mol) of NaOH, 95% ethanol (200 mL), and 3.8 g (0.03 mol) of *p*-hydroxybenzaldehyde (freshly recrystallized from water), 10 g (0.03 mol) of 10-undecen-1-yl tosylate was added. The resulting solution was stirred at reflux temperature under nitrogen atmosphere overnight and cooled to room temperature and the solvent was removed in a rotavapor. The residue was washed with water and extracted with diethyl ether. The ether layer was dried over anhydrous $MgSO_4$, filtered, and evaporated to yield 7.6 g (90%) of a colorless oil: ^{1}H NMR ($CDCl_3$, TMS) δ 1.29–2.02 (m, 16 H, $(CH_2)_8$), 3.94 (t, 2 H, OCH_2), 4.85 and 5.67 (m, 3 H, $CH{=}CH_2$), 6.83 and 7.62 (2 d, 4 H, Ar H), 9.9 (s, 1 H, $HC{=}O$).

***trans*-2-[*p*-(10-Undecen-1-yloxy)phenyl]-5-[*p*-(2(*S*)-methyl-1-butoxy)phenyl]-1,3-dioxane (IA).** *p*-(10-Undecen-1-yloxy)benzaldehyde (1.3 g, 5 mmol) and 1.1 g (5 mmol) of 2-[*p*-(2(*S*)-methyl-1-butoxy)phenyl]propane-1,3-diol were added to 150 mL of dry benzene. *p*-Toluenesulfonic acid (0.05 g) was then added, and the solution was heated under reflux for 3 h. During this time the theoretical amount of water was removed on a Dean-Stark trap. The reaction mixture was cooled to room temperature and washed with a 2% aqueous solution of sodium bicarbonate and water, dried over anhydrous $MgSO_4$, and filtered and the benzene was removed on a rotavapor. The resulting product was purified by column chromatography (silica gel, chloroform eluent) and recrystallized from hexanes to yield 0.26 g (11.6%). Thermal transitions (DSC): heating scan, $T_{C\text{-}S_B}$ = 91.4 °C, ΔH = 2.73 kcal/mol, ΔS = 7.5 cal/mol·K, $T_{S_B\text{-}I}$ = 120.2 °C, ΔH = 1.2 kcal/mol, ΔS = 3.05 cal/mol·K; cooling scan, $T_{I\text{-}S_B}$ = 118.4 °C, ΔH = 1.1 kcal/mol, ΔS = 2.73 cal/mol·K, $T_{S_B\text{-}S_E}$(monotropic) = 71.4 °C, ΔH = 0.1 kcal/mol, ΔS = 0.3 cal/mol·K, T_C = 66 °C, ΔH = 2.9 kcal/mol, ΔS = 8.55 cal/mol·K. ^{1}H NMR ($CDCl_3$, TMS) δ 0.7–2.1 (m, 25 H, $(CH_2)_8$, $CH(CH_3)C_2H_5$), 3.12 (m, 1 H, PhC*H*), 3.75 (m, 2 H, CH_2O axial), 3.9 (q, 4 H, CH_2OPh), 4.2 (q, 2 H, CH_2O equatorial), 4.95 (t, 2 H, $CH_2{=}CH$), 5.52 (s, 1 H, PhC*H*$(O)_2$), 5.80 (m, 1 H, $CH_2{=}CH$), 6.8–7.4 (m, 8 H, Ar H).

Diethyl 2-(10-Undecylenyl)malonate. A sodium ethoxide solution in ethanol was prepared by adding 3.3 g (0.14 mol) of freshly cut sodium to 200 mL of absolute ethanol. After the mixture was completely dissolved, 22.8 g (0.14 mol) of diethyl malonate was added and the resulting solution was stirred until

a white precipitate began to appear. 10-Undecen-1-yl tosylate (40 g, 0.13 mol) was added, and the reaction mixture was stirred at the reflux temperature for 14 h. The ethanol was removed on a rotavapor and 100 mL of water was added to the residue. The resulting mixture was extracted with diethyl ether. The ether layer was dried over anhydrous $MgSO_4$ and filtered and the ether was evaporated on a rotavapor to yield 34.93 g (87%) of colorless oil: ^1H NMR ($CDCl_3$, TMS) δ 0.7–1.5 (m, 20 H, CH_3CH_2, $(CH_2)_7$), 1.7–2.2 (m, 4 H, $CH_2C{=}C$, CH_2CH), 3.3 (t, 1 H, CH), 4.15 (q; 4 H, OCH_2), 4.9 and 5.8 (m, 3 H, $CH_2{=}CH$).

2-(10-Undecenyl)-1,3-propanediol. A solution of diethyl 2-(10-undecylenyl)malonate (34.0 g, 0.11 mol) in 50 mL of dried diethyl ether was added dropwise to a suspension of $LiAlH_4$ (6.3 g, 0.17 mol) in 200 mL of dried diethyl ether. The reaction mixture was heated under reflux with stirring for 20 h. It was cooled to room temperature, and the excess of $LiAlH_4$ was reacted with 50 mL of ethyl acetate. The resulting mixture was treated with 50 mL of hydrochloric acid and extracted with chloroform. The chloroform layer was washed with water, dried over anhydrous $MgSO_4$, and filtered and the chloroform was evaporated. The residue was recrystallized from diethyl ether at 0 °C to yield 12.6 g (50.2%) of white crystals: mp 44–47 °C; ^1H NMR ($CDCl_3$, TMS) δ 0.8–2.2 (m, 19 H, $(CH_2)_9CH$), 2.9–4.0 (m, 6 H, CH_2OH), 5.0 and 5.8 (m, 3 H, $CH_2{=}CH$).

***trans*-2-[*p*-(2(*S*)-Methyl-1-butoxy)phenyl]-5-(10-undecenyl)-1,3-dioxane (IB).** A solution containing 2-(10-undecenyl)-1,3-propanediol (3.4 g, 0.015 mol), *p*-(2(*S*)-methyl-1-butoxy)benzaldehyde (2.7 g, 0.015 mol), 150 mL of dry benzene, and *p*-toluenesulfonic acid (0.15 g) was heated to the reflux temperature until the theoretical amount of water of reaction was azeotropically removed on a Dean-Stark trap. The reaction mixture was cooled to room temperature, washed with a 2% aqueous sodium bicarbonate solution, and dried over anhydrous $MgSO_4$ and the solvent was removed on a rotavapor to yield 5.3 g (88%) of a mixture containing 23% cis and 77% trans isomers. The trans isomer was separated by repeated crystallizations from diethyl ether at −70 °C and further purified by column chromatography with chloroform as eluent and silica gel as stationary phase, to yield 0.65 g (10.8%) of white crystals: mp 48 °C; ^1H NMR ($CDCl_3$, TMS) δ 0.8–2.1 (m, 28 H, $(CH_2)_9CH$, $CH(CH_3)C_2H_5$), 3.07 (t, 2 H, CH_2O axial), 3.9 (t, 2 H, CH_2O), 4.18 (q, 2 H, CH_2O equatorial), 4.95 (t, 2 H, $CH_2{=}CH$), 5.36 (s, 1 H, $PhCH(O)_2$), 5.79 (m, 1 H, $CH_2{=}CH$), 6.84–7.40 (2 d, 4 H, Ar H); $[\alpha]_D$ +5.6°.

***p*-(2(*S*)-Methyl-1-butoxy)phenyl Bromide.** 2(*S*)-Methyl-1-butyl tosylate (31.7 g, 0.13 mol) was added to a solution containing 6 g (0.015 mol) of sodium hydroxide and 22.68 g (0.13 mol) of *p*-bromophenol in 200 mL of 95% ethanol. The reaction mixture was heated under reflux with stirring for 19 h. The ethanol was removed on a rotavapor. The resulting product was mixed with 100 mL of water and extracted with diethyl ether. The ether layer was dried over anhydrous $MgSO_4$ and filtered and the ether was evaporated. The remaining product was distilled at 110 °C (10 mmHg) to yield 24.9 g (84%) of a colorless liquid of 98% purity as determined by gas chromatography: ^1H NMR ($CDCl_3$, TMS) δ 1.9 (m, 6 H, CH_3), 2.2–2.7 (m, 2 H, CH_2CH), 2.8 (m, 1 H, CH), 3.7 (m, 2 H, CH_2O), 6.8 and 7.3 (2 d, 4 H, Ar H); $[\alpha]_D$ +5.1°.

Tri-*n*-butyl Borate. A mixture of 1-butanol (161.6 g, 2.18 mol) and boric acid (29.95 g, 0.48 mol) was heated until the boric acid dissolved. The resulting solution was heated under reflux until 25 mL of water was azeotropically removed with a Dean-Stark trap. The excess of butanol was then removed from the reaction mixture by distillation under nitrogen. The remaining product was then purified by vacuum distillation at 90 °C (14 mmHg) to yield 100 g (90.6%) of tri-*n*-butyl borate.

[*p*-(2(*S*)-Methyl-1-butoxy)phenyl]boronic Acid. To a mixture containing magnesium turnings (40.0 g, 0.16 mol), *p*-(2(*S*)-methyl-1-butoxy)phenyl bromide (5 g, 0.02 mol), and 100 mL of dried diethyl ether, was added a drop of methyl iodide to catalyze the reaction. To the refluxing mixture, 3.5 g (0.14 mol) of *p*-(2(*S*)-methyl-1-butoxy)phenyl bromide was added dropwise under a nitrogen atmosphere. The reaction mixture was held at reflux temperature overnight and then it was decanted from the unreacted magnesium and added dropwise to a cold (−70 °C) solution of tri-*n*-butyl borate (60 g, 0.2 mol) in dry diethyl ether, over a period of 2 h. This solution was allowed to warm to 0 °C and then was added to 100 mL of cold 10% sulfuric acid solution. The resulting mixture was extracted with diethyl ether, and the ether was evaporated on a rotavapor. The remaining product was treated with aqueous KOH until the pH was basic. Water was added and the *n*-butyl alcohol was evaporated on a rotavapor. The residue was acidified with sulfuric acid, heated to 100 °C, and filtered hot through fluted filter paper. [*p*-(2(*S*)-Methyl-1-butoxy)phenyl]boronic acid crystallizes from the water solution upon cooling, to yield 8.4 g (24.5%) of white crystals: mp 125–127 °C; ^1H NMR ($CDCl_3$, TMS) δ 1.1 (m, 6 H, CH_3), 1.2–1.7 (m, 2 H, CH_2CH), 1.6 (s, 2 H, $B(OH)_2$), 1.9 (m, 1 H, CH), 3.9 (m, 2 H, CH_2O), 7.1 and 8.2 (2 d, 4 H, Ar H).

2-[*p*-(2(*S*)-Methyl-1-butoxy)phenyl]-5-(10-undecenyl)-1,3,2-dioxaborinane (IC). A solution of 2-(10-undecenyl)-1,3-propanediol (1.6 g, 7 mmol), [*p*-(2(*S*)-methyl-1-butoxy)phenyl]-boronic acid (1.5 g, 7 mmol), and 100 mL of dry benzene was heated to reflux and the water formed was azeotropically removed with a Dean-Stark trap. After 16 h at reflux, the remaining benzene was removed in a rotavapor and the borinane derivative was crystallized from acetone at −70 °C. Column chromatography (silica gel, chloroform as eluent) was used to complete the purification: yield, 2.0 g (70.6%); mp 39 °C; ^1H NMR ($CDCl_3$, TMS) δ 0.7–2.1 (m, 28 H, $(CH_2)_9CH$, $CH(CH_3)C_2H_5$), 3.78 (m, 4 H, CH_2O axial), 4.1 (q, 2 H, CH_2O equatorial), 5.0 (t, 2 H, $CH_2{=}CH$), 5.8 (m, 1 H, $CH_2{=}CH$), 6.8–7.7 (2 d, 4 H, Ar H); $[\alpha]_D$ +5.7°.

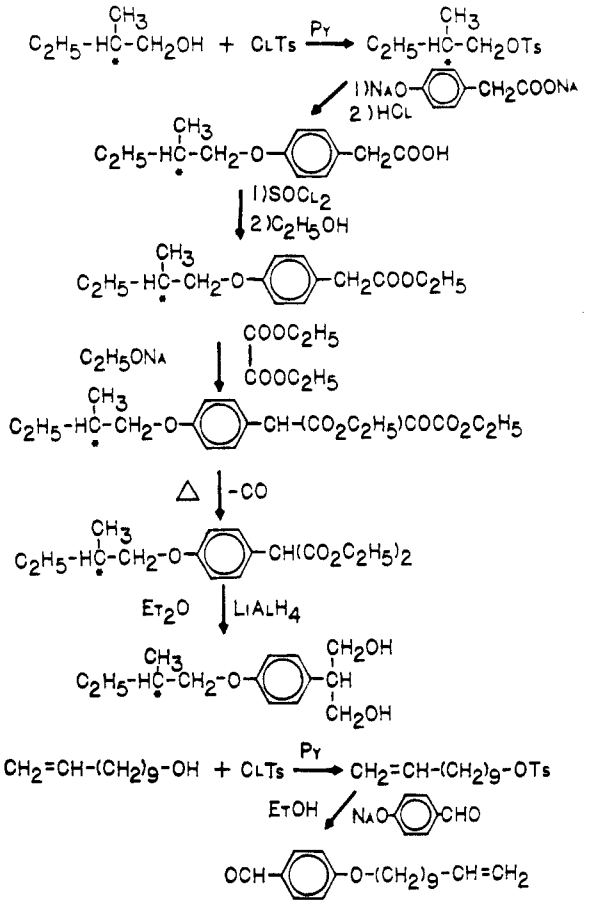
D. Synthesis of Polymers and Copolymers. Polysiloxanes and copolysiloxanes were synthesized by hydrosilation of the corresponding alkenic derivative (IA, IB, and IC) with poly(methylsiloxane), poly[(30–35%)-methylsiloxane-(65–70%)dimethylsiloxane], and poly[(15–18%)-methylsiloxane-(82–85%)-dimethylsiloxane], using dicyclopentadienylplatinum(II) chloride[10] as catalyst in toluene. A detailed procedure for complete hydrosilation free of side reactions is given as follows. The alkenic derivative (1.0 g, 10 mol % excess versus the Si–H groups present in polysiloxane) was dissolved in 100 mL of sodium-dried freshly distilled toluene together with the proper amount of poly(methylsiloxane) or a copolymer containing methylsiloxane and dimethylsiloxane units. The reaction mixture was heated to 110 °C under nitrogen, and 100 μL of dicyclopentadienylplatinum(II) chloride catalyst was then injected with a syringe as a solution in methylene chloride (1 mg/mL). The reaction mixture was heated under reflux (110 °C) under nitrogen until both IR and 200-MHz ^1H NMR analyses showed that the hydrosilation reaction was complete. The white (powder) or colorless (liquid) polymers were separated by precipitation in methanol and purified by several reprecipitations from chloroform solutions into methanol. When the resulting polymers were insoluble in hexane (all homopolymers) a final purification was done by precipitation from chloroform solution into hexane. Then the polymers were dried under vacuum at constant weight. We recommend only Teflon tape and Teflon gaskets to be used in the assemblage of the hydrosilation equipment. Rubber septa can poisson the catalyst, while traces of silicon grease or oil can contaminate the resulting polymer and therefore should be completely avoided. Silicon grease can be used only when the final purification of the polymer can be done by successive precipitations into hexane (good solvent for poly(dimethylsiloxane)).

Results and Discussion

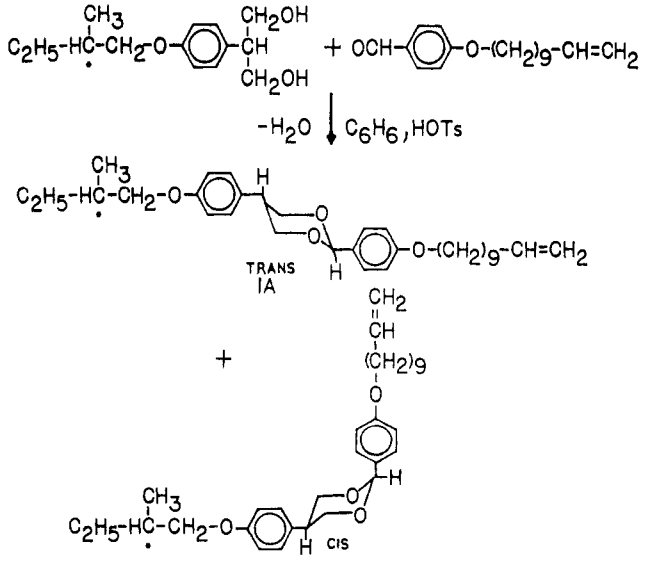
The synthetic route used for the preparation of *trans*-2-[*p*-(10-undecen-1-yloxy)phenyl]-5-[*p*-(2(*S*)-methyl-1-butoxy)phenyl]-1,3-dioxane (IA) is described in Schemes I and II. The chiral group was inserted into this mesogenic unit starting with the commercially available (−)-2(*S*)-methyl-1-butanol, by a sequence of reactions which avoids its racemization. Although the 1,3-dioxane derivative (Scheme II) was prepared by acetalyzation under thermodynamically controlled reaction conditions, the trans isomer is obtained in very high yield. It can be purified from traces of cis isomer by a combination of recrystallizations from hexanes and column chromatography.

trans-2-[*p*-(2(*S*)-Methyl-1-butoxy)phenyl]-5-(10-undecenyl)-1,3-dioxane (IB) was synthesized by the sequence

Scheme I
Synthesis of 2-[*p*-(2(*S*)-Methyl-1-butoxy)phenyl]propane-1,3-diol and *p*-(10-Undecen-1-yloxy)benzaldehyde

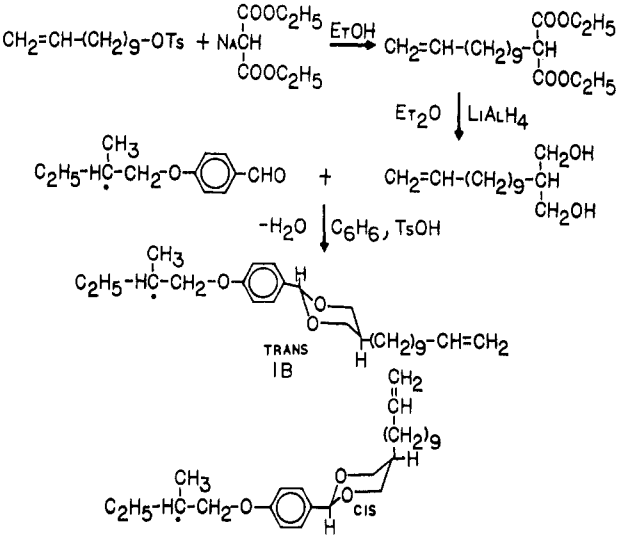


Scheme II
Synthesis of *cis*- and *trans*-2-[*p*-(10-Undecen-1-yloxy)phenyl]-5-[*p*-(2(*S*)-methyl-1-butoxy)phenyl]-1,3-dioxanes

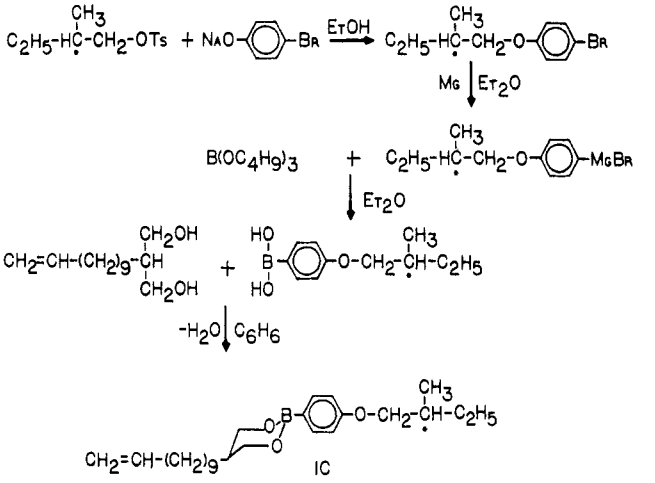


of reactions described in Scheme III. Although this 1,3-dioxane ring was prepared under similar reaction conditions as the previous ones, the amount of cis isomer obtained in this case is as high as 23%. Since the cis isomer is liquid and the trans isomer melts at low temperature (48 °C), the cis–trans mixture is liquid at room temperature. The separation of the trans isomer required multiple recrystallizations at −70 °C from diethyl ether followed by

Scheme III
Synthesis of *cis*- and *trans*-2-[*p*-(2(*S*)-Methyl-1-butoxy)phenyl]-5-(10-undecenyl)-1,3-dioxanes



Scheme IV
Synthesis of 2-[*p*-(2(*S*)-Methyl-1-butoxy)phenyl]-5-(10-undecenyl)-1,3,2-dioxaborinane (IC)



filtration at 0 °C. The final purification was accomplished by column chromatography.

Since the separation of the trans isomer from the cis represents the most difficult step in the preparation of *trans*-2-[*p*-(2(*S*)-methyl-1-butoxy)phenyl]-5-(10-undecenyl)-1,3-dioxane, we decided to replace carbon-2 from the 1,3-dioxane ring with a boron atom. The resulting 1,3,2-dioxaborinane ring does not exhibit cis–trans configurational isomerism because the boron atom is trivalent. Therefore, its synthesis does not require the separation of the two configurational isomers.

Scheme IV outlines the synthetic route used for the preparation of 2-[4-(2(*S*)-methyl-1-butoxy)phenyl]-5-(10-undecenyl)-1,3,2-dioxaborinane (IC). 2,5-Disubstituted-1,3,2-dioxaborinanes became of interest for the synthesis of low molar mass liquid crystals only recently.[17,18] To our knowledge this paper presents the first example of a liquid-crystalline polymer containing 2,5-disubstituted-1,3,2-dioxaborinane-based mesogens.

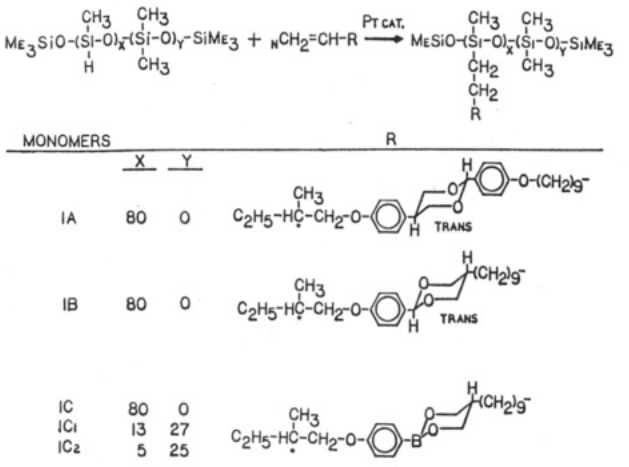
The synthesis of the liquid-crystalline polysiloxanes is described in Scheme V. It is well-known that hydrosilation is accompanied by a number of side reactions if traces of air–oxygen, water, or alcohols are present in the reaction mixture.[19] We have previously discussed some

Figure 1. Typical optical polarization micrographs (50×) of the *trans*-2-[*p*-(10-undecen-1-yloxy)phenyl]-5-[*p*-(2(*S*)-methyl-1-butoxy)phenyl]-1,3-dioxane (IA): (A) S_B, texture with lancets after cooling the isotropic melt at 118.5 °C; (B) S_B, same as in (A) but different region, showing pseudo-π-disclinations, dislocation lines, and parts of lancets; (C) S_E at 89 °C, cooling from S_B; (D) solid state as a paramorphosis from S_E (room temperature).

of these reactions.[20] In addition to the absence of impurities in the reaction mixture, it is essential to carry the hydrosilation to completion. Alternatively, particularly when the resulting polymers present a low glass transition temperature, we have encountered situations when cross-linking can occur during drying the polymer which was separated by precipitation into methanol. The hydrosilation reactions described in the Experimental Section have always provided only soluble polymers.

The monomeric compounds IA, IB, and IC from Scheme V were characterized both by differential scanning calorimetry and optical polarization microscopy. IB and IC melt directly into an isotropic liquid. IC exhibits a liquid-crystalline S_B mesophase (see Experimental Section) between 91.4 and 120.2 °C on the heating scan and between 118.4 and 71.4 °C on the cooling scan. A monotropic S_E appears between 71.4 and 66 °C. Optical polarization microscopy reveals very characteristic textures for both mesophases (Figure 1).

Scheme V
Synthesis of Polysiloxanes and Copolysiloxanes Containing IA, IB, and IC Side Groups



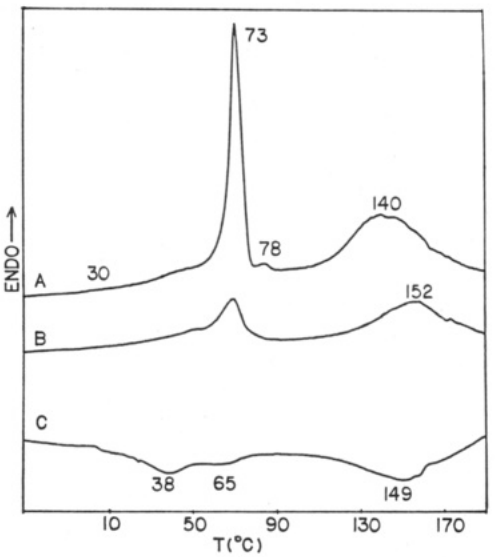


Figure 2. Normalized DSC thermograms (heating and cooling rates are 20 °C/min) of polysiloxane-containing IA side groups: (A) first heating scan; (B) second heating scan; (C) second cooling scan.

Some preliminary information on the phase behavior of the polysiloxanes was obtained by DSC[21] and optical polarization microscopy.[22]

Representative DSC traces of the polysiloxane containing IA side groups are presented in Figure 2. The first heating scan (Figure 2, curve A) reveals a glass transition temperature at 30 °C, followed by a melting transition at 73 °C. This transition was assigned to melting due to its lower enthalpy change obtained from the second heating (curve B) and cooling (curve C) scans and also due to the high degree of supercooling of the corresponding crystallization from the cooling scan (i.e., from 73 to 38 °C). This transition is followed by a very narrow smectic mesophase which undergoes an additional smectic–smectic transition at 78 °C. With the exception of the first scan, in all other cases the isotropization transition occur at 152 °C. It

Table I
Thermal Transitions[e] and Thermodynamic Parameters[b] of Polysiloxanes

		heating						cooling		
side group	scan	T_{g_1}	T_{m_1}/T_{m_2}	T_{g_2}	$T_1/(\Delta H_1/\Delta S_1)$	$T_2/(\Delta H_2/\Delta S_2)$	$T_i/(\Delta H_i/\Delta S_i)$	$T_i/(\Delta H_i/\Delta S_i)$	$T_2/(\Delta H_2/\Delta S_2)$	$T_1/(\Delta H_1/\Delta S_1)$
IA	1			30	73 (m)[b]	78[b]	140[b]			
					1.8/5.2[b]	0.005/0.014[c]	1.6/3.9[b]			
IA	2			30	69 (m)[d]		152	149	65[a]	38 (k)
					0.56/1.6		1.2/2.8	1.0/2.4	0.05/0.15	0.1/0.4
IB	1			4	50[b]		91[b]			
					0.4/1.2[b]		0.2/0.5[b]			
IB	2			4	50		97	97		48
					0.03/0.10		0.2/0.6	0.2/0.6		0.05/0.2
IC	2			−7	19		85	79		17
					0.1/0.4		1.5/4.3	1.5/4.2		0.1/0.4
IC_1	2	−87		−9	5.3		52	47		−0.3
	2				0.02/0.09		1.6/4.9	1.6/4.9		0.03/0.11
IC_2	2	−101	−41/−34	−37			29	24		
	2						0.93/3.0	0.97/3.3		
$-CH_3$	2	−123	−40/−27							
$-CH_3$ (60–65)										
−H (30–35%)	2	−132								

[a] Overlapped transitions. [b] After annealing above T_g. [c] Overlapped transitions, part of ΔH_2 is overlapped by ΔH_1. [d] Overlapped transitions: $\Delta H_i = \Delta H_1 + \Delta H_2$. [e] Degrees celsius. [f] ΔH in kcal/mru; ΔS in cal/(mru K); mru = mole of repeat units, consisting of mesogenic unit and ten methylene units; m, melting; k, crystallization.

seems that the broad isotropization peak is split both on heating and on cooling scans into two transitions (Figure 2, curves B and C). Both optical polarization microscopy and the enthalpy of isotropization (Table I) support a smectic mesophase. Optical polarization microscopy did not reveal a very characteristic smectic texture although the mesophase is pseudohomeotropic. Pseudohomeotropic petal textures are characteristic for S^*_C liquid crystals.[22] Even so, it is difficult at this time to make any assumptions concerning the type of smectic mesophase exhibited by this polymer.

Curves A–C from Figure 3 are typical DSC traces for the polysiloxane containing IB-type side groups. Above the glass transition temperature (4 °C) there is a smectic mesophase which undergoes a smectic–smectic transition at 50 °C. Although on subsequent scans the enthalpy of the transition at 50 °C changes (Table I), this is due to its close proximity to the T_g value. Support for the fact that this is a smectic–smectic and not a melting transition comes from its nonsupercooled transition on the cooling scan (curves A–C, Figure 3). The smectic phase between 50 and 97 °C resembles a pseudohomeotropic petal texture which is characteristic of a S^*_C mesophase. On increasing the temperature from 50 to 97 °C, the color of the mesophase changes from blue to red, i.e., the opposite of a cholesteric mesophase.[22] The weak point toward a final conclusion on this mesophase is its low enthalpy of isotropization (Table I), which according to the literature is within the range of enthalpies for a transition from a nematic or cholesteric mesophase into an isotropic liquid.[21] Evidence against a cholesteric mesophase between 50 and 97 °C is the split of the isotropization transition on the cooling scan into two peaks. If we have a cholesteric mesophase, the isotropic liquid would have to transform directly into the cholesteric mesophase. Additional support against a cholesteric mesophase is based on the lack of a typical texture for a cholesteric liquid-crystalline phase. We could not yet determinate between the two transitions from the cooling scan, i.e., 97 °C and the following one, although apparently the first could be assigned only between a cholesteric and a smectic A phase.

Heating and cooling DSC traces for the polymer containing IC side groups are presented as curves D and E in Figure 3. Above the glass transition temperature (−7 °C) the polymer exhibits a smectic mesophase which could not

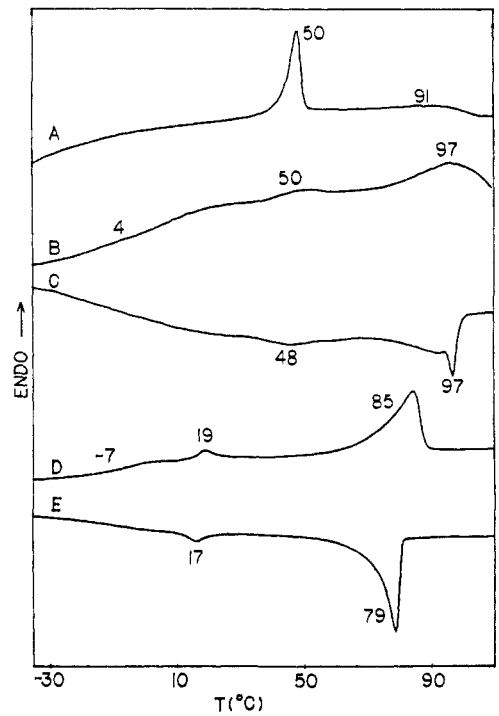


Figure 3. Normalized DSC thermograms (heating and cooling rates are 20 °C/min): (A) first heating scan of polymer IA; (B) second heating scan of polymer IB; (C) second cooling scan of polymer IB; (D) second heating scan of polymer IC; (E) second cooling scan of polymer IC.

be assigned. This smectic mesophase undergoes a smectic–S^*_C transition at 19 °C. S^*_C undergoes isotropization at 85 °C. The cooling scan presents first a very narrow S_A mesophase which transforms into S^*_C at 79 °C. DSC can hardly discriminate these two transitions (Figure 3E). Optical polarization microscopy reveals clearly the formation of bâtonnets just before 79 °C. Since the range of temperature is very narrow (about 1 °C on the optical microscope) the bâtonnets cannot form a focal-conic texture, but they undergo a direct transition into a pseudohomeotropic petal texture. Bâtonnets are representative of a S_A mesophase, as is the petal texture of a S^*_C mesophase.[22] Figure 4A presents a typical optical polarization micrograph for bâtonnets, while Figure 4B a typical S^*_C

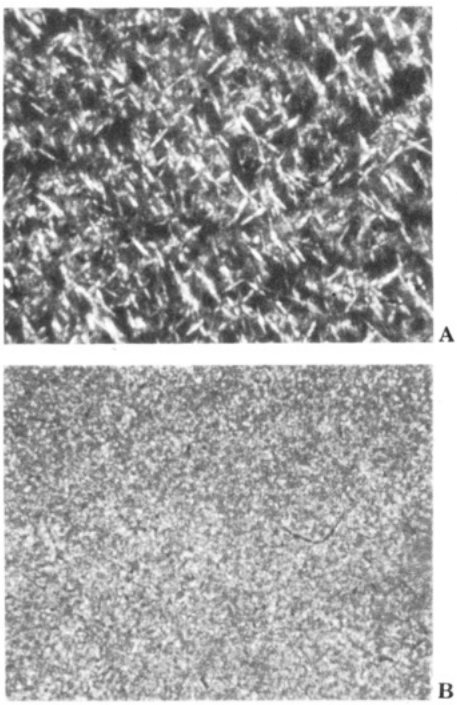


Figure 4. Typical optical polarization micrographs (50×) of the polysiloxane-containing pendant IC side groups: (A) S_A, bâtonnets formed on cooling from the isotropic melt at 82 °C; (B) S^*_C, pseudohomeotropic petal texture obtained on cooling the bâtonnets below 80 °C.

texture. At this time there is no doubt about a S^*_C phase, since the isotropization enthalpy is within the expected values for a smectic–isotropization transition (Table I).[21]

It is quite interesting to compare the DSC traces of the polymers containing IB and IC side groups (Figure 3 BC and DE). Although the only difference between these two polymers consists of the replacement of one carbon atom by a boron atom, their phase transitions are affected by this structural change quite a bit.

The phase transitions of the copolymer IC_1 appear at lower temperatures than those of the parent homopolymer IC. In the case of copolymer IC_2, the first liquid-crystalline transition T_1 does not appear at all (Table I).

Curve C in Figure 5 presents the low-temperature range of a typical DSC thermogram of a poly(dimethylsiloxane) with $\bar{M}_n = 5600$. This polymer exhibits typical transitions for a poly(dimethylsiloxane),[23] i.e., glass transition temperature at −123 °C, a crystallization transition at −79 °C, and two melting transitions at −40 and −27 °C. Curve D of Figure 5 presents a typical DSC thermogram for the poly(methylsiloxane-*co*-dimethylsiloxanes), the particular example displayed by this trace being for poly[(30–35%)-methylsiloxane-*co*-(65–70%)-dimethylsiloxane]. This copolymer exhibits only a glass transition temperature at −132 °C. Curve A of Figure 5 presents a typical DSC thermogram for the copolymer IC_1 while curve B a typical DSC thermogram for the copolymer IC_2, both from Scheme V. Both DSC thermograms present only the low-temperature range. The DSC thermograms of both copolymers containing mesogenic units present two well-defined glass transition temperatures. The heat capacity change of the low T_g is proportional to the weight fraction of the polymer backbone, while the heat capacity change of the high T_g is proportional to the weight fraction of the mesogenic groups. We can certainly conclude from these results that both copolymers present two glass transition temperatures. Therefore, T_{g_1} from Table I is due to the independent motion of the backbone, the upper T_g being

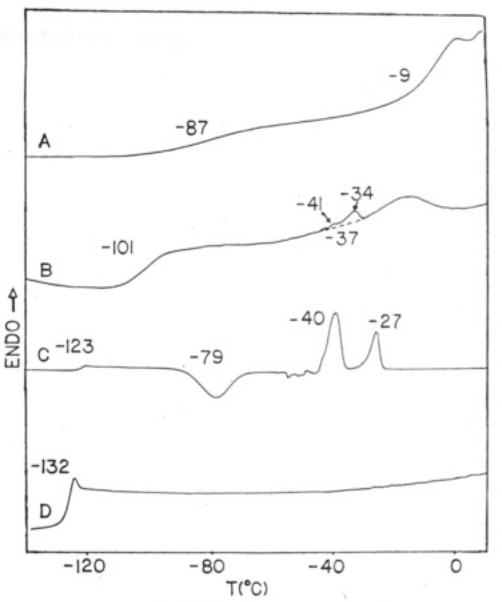


Figure 5. Normalized DSC thermograms (heating rate is 20 °C/min): (A) second heating scan of polymer IC_1; (B) second heating scan of polymer IC_2; (C) second heating scan of poly(dimethylsiloxane), $\bar{M}_n = 5600$; (D) second heating scan of the poly[(30–35%)-methylsiloxane-*co*-(65–70%)-dimethylsiloxane], $\bar{M}_n = 2000$–2100.

due to the cooperative but independent motion of the mesogenic units. It is quite rewarding to observe that copolymer IC_2 from Table I and Scheme V (curve B, Figure 5) exhibits in addition to the two T_g's also two melting transitions which overlap the second T_g. These meltings are not available in the starting copolymer (curve D) but resemble the two meltings exhibited by poly(dimethylsiloxane) (curve C) and therefore are due to the melting of the polymer backbone. The overlap of the melting of the backbone with the T_g of the side groups supports independent motion of these two subsystems. Since the weight fraction of the polymer backbone is very small for the case of the homopolymers, it is difficult to clearly assign a T_{g_1} for all three homopolymers on the basis of DSC experiments only. Therefore, at this time we will refrain from making additional comments on homopolymers. Table I summarizes the thermal transitions and the corresponding thermodynamic parameters for all polymers. Since the thermal transition temperatures for the backbone are similar to those of the pure poly(dimethylsiloxane), we consider that at least one methylenic unit of the spacer is part of the backbone. Therefore the mole repeat unit (mru) considered in these calculations contains the mesogenic part of the side group and 10 methylenic units.

These results confirm our previous findings,[15,16] i.e., that side-chain liquid-crystalline polymers can be either biphasic or monophasic systems. The biphasic systems resemble phase-separated block or graft copolymers, since although the two subsystems or domains are chemically interconnected, they behave as two semiindependent thermodynamic subsystems. Prior to our present and previous results,[15,16] biphasic systems obtained from comblike homopolymers were only seldom encountered in the literature.[24,25]

The difference between the behavior of biphasic versus monophasic side-chain liquid-crystalline polymers represents a fundamental problem for the entire field of side-chain liquid-crystalline polymers.

A complete characterization of the phase behavior of these polymers by X-ray diffraction is in progress and it will be reported.

Acknowledgment. Financial support from the National Science Foundation (Materials Research Group) and partial support from the Office of Naval Research is gratefully acknowledged.

Registry No. 1A, 110458-67-8; **1B**, 110458-68-9; **1C**, 110458-71-4; (*S*)-$C_2H_5CH(CH_3)CH_2OTs$, 38261-81-3; TsCl, 98-59-9; (*S*)-$C_2H_5CH(CH_3)CH_2OH$, 1565-80-6; (*S*)-$C_2H_5CH(CH_3)CH_2C_6H_4$-*p*-CH_2CO_2H, 110458-62-3; HOC_6H_4-*p*-CH_2CO_2H, 156-38-7; (*S*)-$C_2H_5CH(CH_3)CH_2OC_6H_4$-*p*-$CH_2CO_2C_2H_5$, 110458-63-4; (*S*)-$C_2H_5CH(CH_3)CH_2OC_6H_4$-*p*-$CH(CO_2C_2H_5)_2$, 110458-64-5; $H_5C_2O_2CCO_2C_2H_5$, 95-92-1; (*S*)-$C_2H_5CH(CH_3)CH_2OC_6H_4$-*p*-$CH(CH_2OH)_2$, 110458-65-6; $H_2C{=}CH(CH_2)_9OTs$, 51148-67-5; $H_2C{=}CH(CH_2)_9OH$, 112-43-6; $H_2C{=}CH(CH_2)_9OC_6H_4$-*p*-CHO, 110458-66-7; HOC_6H_4-*p*-CHO, 123-08-0; $H_2C{=}CH(CH_2)_9CH(CO_2C_2H_5)_2$, 52355-51-8; $C_2H_5O_2CCH_2CO_2C_2H_5$, 141-05-9; $H_2C{=}CH(CH_2)_9CH(CH_2OH)_2$, 108414-88-6; (*S*)-$C_2H_5CH(CH_3)CH_2OC_6H_4$-*p*-CHO, 55535-61-0; (*S*)-$C_2H_5CH(CH_3)CH_2OC_6H_4$-*p*-$BrBrC_6H_4$-*p*-OH, 106-41-2; $B(OC_4H_9)_3$, 688-74-4; H_3BO_3, 10043-35-3; (*S*)-$(HO)_2BC_6H_4$-*p*-$OCH_2CH(CH_3)C_2H_5$, 110458-70-3.

References and Notes

(1) Meyer, R. B.; Liebert, L.; Strzelecki, L.; Keller, P. *J. Phys.* **1975**, *36*, L-69.
(2) Meyer, R. B. *Mol. Cryst. Liq. Cryst.* **1977**, *40*, 33.
(3) Goodby, J. W. *Science (Washington, D.C.)* **1986**, *231*, 350.
(4) Walba, D. M.; Slater, S. C.; Thurmes, W. N.; Clark, N. A.; Handschy, M. A.; Supon, F. *J. Am. Chem. Soc.* **1986**, *108*, 5210.
(5) Shibaev, V. P.; Kozlousky, M. V.; Beresnev, L. A.; Blinov, M. L.; Plate, N. A. *Polym. Bull.* **1984**, *12*, 299.
(6) Decobert, G.; Soyer, F.; Dubois, J. C. *Polym. Bull.* **1985**, *14*, 179.
(7) Decobert, G.; Dubois, J. C.; Esselin, S.; Noel, C. *Liq. Cryst.* **1986**, *1*, 307.
(8) Guglielminetti, J. M.; Decobert, G.; Dubois, J. C. *Polym. Bull.* **1986**, *16*, 411.
(9) Hsu, C. S.; Rodriguez-Parada, J. M.; Percec, V. *Makromol. Chem.* **1987**, *188*, 1017.
(10) Hsu, C. S.; Rodriguez-Parada, J. M.; Percec, V. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 2425.
(11) Finkelmann, H.; Rehage, G. *Adv. Polym. Sci.* **1984**, *60/61*, 99.
(12) Shibaev, V. P.; Plate, N. A. *Adv. Polym. Sci.* **1984**, *60/61*, 173.
(13) Engel, M.; Hisgen, B.; Keller, R.; Kreuder, W.; Reck, P.; Ringsdorf, H.; Schmidt, H. W.; Tschirner, P. *Pure Appl. Chem.* **1985**, *57*, 1009.
(14) Cser, F. In *Liquid Crystals and Ordered Fluids*; Griffin, A. C., Johnson, J. F., Eds.; Plenum: New York, 1984; Vol. 4, p 945.
(15) Hsu, C. S.; Percec, V. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 331.
(16) Hsu, C. S.; Percec, V. *Polym. Bull.* **1987**, *17*, 49.
(17) Seto, K.; Takahashi, S.; Tahara, T. *J. Chem. Soc., Chem. Commun.* **1985**, 122.
(18) Seto, K.; Takahashi, S.; Tahara, T. *Mol. Cryst. Liq. Cryst. Lett.* **1985**, *2*, 197.
(19) Gray, G. W.; Lacey, D.; Nestor, G.; White, M. S. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 71.
(20) Auman, B. C.; Percec, V.; Schneider, H. A.; Jishan, W.; Cantow, H. J. *Polymer* **1987**, *28*, 119.
(21) Krigbaum, W. R. *J. Appl. Polym. Sci.: Appl. Polym. Symp.* **1985**, *41*, 105.
(22) Gray, G. W.; Goodby, J. W. *Smectic Liquid Crystals. Textures and Structures*; Leonard Hill: Glasgow and London, 1984; p 63. Demus, D.; Richter, L. *Textures of Liquid Crystals*; Verlag Chemie: Weinheim and New York, 1978.
(23) Clarson, S. J.; Dodgson, K.; Semlien, J. A. *Polymer* **1985**, *26*, 930.
(24) Cowie, J. M. J.; Hag, Z.; McEwen, I. J. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 771.
(25) Cowie, J. M. J.; Hag, Z.; McEwen, I. J.; Velickovic, J. *Polymer* **1981**, *22*, 327.

Protection and Polymerization of Functional Monomers. 10. Synthesis of a Well-Defined Poly(4-vinylbenzaldehyde) by the Anionic Living Polymerization of *N*-[(4-Ethenylphenyl)methylene]cyclohexamine

Akira Hirao* and Seiichi Nakahama

Department of Polymer Chemistry, Tokyo Institute of Technology, 2-12-1, Meguro-ku, Ohokayama, Tokyo 152, Japan. *Received February 17, 1987*

ABSTRACT: Anionic polymerization of *N*-[(4-ethenylphenyl)methylene]cyclohexamine (**1**), *N*-cyclohexylimine of 4-vinylbenzaldehyde, was investigated in THF at −78 °C with potassium naphthalenide, cumylpotassium, and oligo(α-methylstyryl)dialkali-metal salts. The polymerization of **1** proceeded without chain-transfer and termination reactions with each of the initiators to afford a stable living polymer. Yields of polymers were quantitative. The resulting polymers had predictable molecular weights and narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n$ = 1.05–1.15). Under mild acidic conditions (0.5 N HCl in 1,4-dioxane–water), cleavage of the *N*-cyclohexylimino group was completely achieved to give a well-defined poly(4-vinylbenzaldehyde) which still retained a narrow molecular weight distribution. The Mark–Houwink equation for poly(**1**), $[\eta] = 4.3 \times 10^{-4} M^{0.58}$ (in THF at 40 °C), was correlated.

Introduction

Recently we have investigated the synthesis of linear functional polymers having uniformity of chain length as well as predictable molecular weight.[1] Our approach involves the anionic living polymerization of monomers with suitably protected functional groups, followed by the complete removal of the protecting groups from the resulting polymers to regenerate the original functional groups.

In the previous paper,[2] we successfully synthesized linear poly(4-vinylbenzaldehydes) with controlled molecular weights and with narrow molecular weight distributions by means of the anionic living polymeriation of 1,3-dimethyl-2-(4-vinylphenyl)imidazolidine and subsequent removal of the imidazolidine ring from the resulting polymer. A triblock copolymer of a new type, poly[α-methylstyrene)-*b*-(4-vinylbenzaldehyde)-*b*-(α-methylstyrene)] was also prepared by the above living polymerization. Although this provides an excellent method for preparing well-defined poly(4-vinylbenzaldehydes), the disadvantage of this method is the use of an expensive *N*,*N*′-dimethylethylenediamine, equivalent to monomer for the protection of aldehyde function. Therefore, we have been interested in exploring an alternative group to have the ability of masking the aldehyde function under the conditions of anionic polymerization.

As a part of a series of studies on protection and polymerization of functional monomers,[3] we wish to report

0024-9297/87/2220-2968$01.50/0