Macromolecules **1995,** *28,* 5274–5279

Room Temperature Ferroelectric Terpolymers with Large Spontaneous Polarization

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Received February 14, 1995; Revised Manuscript Received April 12, 1995[⊗]

ABSTRACT: It is well-known that the mesomorphic range as well as the physical properties of low molecular weight mesogens can be tuned by mixing different types of monomers. We show here that a similar tuning can be achieved for side-chain liquid crystalline polymers by incorporating two different types of side groups in the backbone in different ratios. The transition temperatures of these terpolymers show a linear dependence on the ratio of the two mesogenic side groups, while their spontaneous polarization shows nonmonotonic dependence. Also, the spontaneous polarization of the terpolymers shows an unusual (linear) temperature dependence throughout the smectic C* phase.

Introduction

There is considerable current interest in liquid crystalline copolymers with a siloxane backbone for ferroelectric and electroclinic applications. These materials, while providing the inherent mechanical stability of polymers, exhibit fast response times due to the flexibility of the siloxane backbone and the decoupling of the mesogenic side group attached to the backbone, via an alkyl spacer. Of late, the importance of side chain liquid crystal polymers for nonlinear optic (NLO) applications has been well recognized.[1–4] The polar order, achieved spontaneously due to the noncentrosymmetric environment, can generate a second-order optical response if a NLO chromophore is suitably incorporated into the mesogenic group.

We have been investigating the ferroelectric properties of lactate-based side-chain liquid crystalline polymers (LCPs) with a siloxane backbone.[5–13] So far we have investigated two types of LCPs—homopolymers wherein a side group mesogen is attached to every available substituent of the siloxane backbone and copolymers wherein both mesogenic groups and (nonmesogenic) methyl groups are attached to the backbone. It was observed that while the polarizations of the homopolymer and the copolymer were nearly the same, the electrooptic switching time in the ferroelectric smectic C* phase was much faster for the copolymer than for the homopolymer. It was also observed that the copolymers exhibited a broader temperature range or higher temperature stability of the smectic C* than the homopolymer. In this paper we present our results on the synthesis and the ferroelectric properties of terpolymers containing *two* kinds of mesogenic side groups as well as the methyl group as the side-group substituents.

Experimental Section

Techniques. 300-MHz ^{1}H NMR spectra were recorded on a Bruker MSL300 spectrometer. All spectra were run in $CDCl_3$ or DMSO solutions. Infrared spectra were obtained by using an FT Perkin-Elmer 1800 spectrophotometer and KBr pellets. GC–MS chromatograms were recorded on a Finnegan ion-trap mass spectrometer connected to a Hewlett Packard 5890 GC (50 cm × 0.2 mm column, OV-101). The phases were identified by optical texture observations using a Nikon polarizing microscope equipped with a Mettler hot stage. The phase transition temperatures of the low molecular weight (unpolymerized) mesogenic groups and of the polymers were determined by using a Perkin-Elmer DSC-7 differential scanning calorimeter (scan rates 10 °C $min^{-}1$). Analytical TLC was conducted on Whatman precoated silica gel 60-F254 plates. The spontaneous polarization (P_s) was measured by the triangular wave method.[14] A 20–100-V amplitude triangular wave (frequency range 0.1–100 Hz) was applied across a 4-μm-thick sample, and the current was determined by measuring the voltage drop across a reference resistance with a storage oscilloscope.

Materials. All reagents were purchased from commercial sources and were used as received or further purified by conventional methods. Gel permeation chromatography was performed on Bio-Beads SX1 gel obtained from Bio-Rad. The initial polysiloxane poly[(30–35%)methylhydrosiloxane-*co*-(65–70%)dimethylsiloxane] ($\bar{M}_h$ = 2000–2100) was purchased from Huls America. The number-average molecular weights of the initial polysiloxane have been determined by osmometry,[15] and the values obtained were in agreement with the values given by the commercial source.

Synthesis. 4′-(9-Decenyloxy)biphenyl-4-carboxylic Acid Methyl Ester (1). To a nitrogen-flushed flask, kept at 0 °C, were added 960 mg (40 mmol) of oil-free sodium hydride, 7 g (30 mmol) of methyl (4-hydroxyphenyl)benzoate, and 150 mL of dry DMF. A solution of 6.57 g (30 mmol) of 10-bromo-1-decene in 20 mL of DMF was added dropwise to the suspension.[16] The resulting mixture was allowed to stir for 1 h at room temperature and 8 h at 80 °C. The solvent was removed by rotary evaporation in vacuo, and excess sodium hydride was quenched by addition of water. A 1 N HCl solution was poured into the mixture, and the resulting precipitate was filtered and washed with a 10% aqueous sodium bicarbonate solution and water. The crude product was recrystallized twice from ethanol to afford 8.7 g (79%) of **1**. ^{1}H NMR ($CDCl_3$, TMS): δ 1.2–2.08 (m, 14 H, (CH_2))), 3.98 (t, 2 H, CH_2O), 4.02 (s, 3 H,

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[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1995.

$\mathrm{OC}H_3$), 5.02 (m, 2 H, $\mathrm{CH{=}C}H_2$), 5.80 (m, 1 H, $\mathrm{C}H\mathrm{{=}CH_2}$), 6.95-8.1 (m, 8 H, ArH). Anal. Calcd for $C_{24}H_{30}O_3$: C, 78.68; H, 8.19. Found: C, 78.54; H, 8.08.

4′-(9-Decenyloxy)biphenyl-4-carboxylic acid (2) was obtained by hydrolysis of the ester derivative in the presence of KOH/ethanol.[17] The crude product was recrystallized from acetic acid to yield 90% of **2**. ^{1}H NMR (DMSO, TMS): δ 1.18–2.1 (m, 14 H, (CH_2)), 3.96 (t, 2 H, $\mathrm{C}H_2\mathrm{O}$), 5.02 (m, 2 H, $\mathrm{CH{=}C}H_2$), 5.75 (m, 1 H, $\mathrm{C}H\mathrm{{=}CH_2}$), 6.98–8.15 (m, 8 H, ArH). Anal. Calcd for $C_{23}H_{28}O_3$: C, 78.40; H, 7.95. Found: C, 78.80; H, 7.75.

1-(Benzyloxy)-4-[(*R*)-1-carbethoxyethoxy]benzene (3). To 4.48 g (38 mmol) of ethyl (*S*)-2-hydroxypropanoate, 10 g (50 mmol) of *p*-(benzyloxy)phenol, and 13.1 g (50 mmol) of triphenylphosphine was added 200 mL of dichloromethane. To this mixture was added dropwise a solution of 20 mL of dichloromethane and 8.14 mL (50 mmol) of diethyl azodicarboxylate (DEAD).[18] The reaction mixture was stirred overnight at room temperature. After evaporation of the solvent, the residue was subjected to column chromatography on silica gel with 1/4 ethyl acetate/hexane as the eluting solvent to yield 7 g (61%) of product **3** (mp 52 °C). ^{1}H NMR ($CDCl_3$, TMS): δ 1.2 (t, 3H, $\mathrm{CH_2C}H_3$), 1.63 (d, 3 H, $\mathrm{CHC}H_3$), 4.2 (q, 2 H, $\mathrm{C}H_2\mathrm{CH_3}$), 4.82 (q, 1 H, $\mathrm{C}H\mathrm{CH_3}$), 5.01 (s, 2 H, $\mathrm{ArC}H_2\mathrm{O}$), 6.88 (s, 4 H, OArO), 7.3–7.75 (m, 5 H, $ArCH_2$). Anal. Calcd for $C_{18}H_{20}O_4$: C, 72.00; H, 6.66. Found: C, 71.90; H, 6.72.

(*R*)-2-[(4-Benzyloxy)phenoxy]propanoic Acid (4). To a solution of benzyl ether **3** (6 g, 20 mmol) in 150 mL of methanol and 40 mL of water was added 3.75 g (90 mmol) of $LiOH{\cdot}H_2O$. The reaction mixture was stirred overnight at room temperature. After evaporation of the solvent, the residue was neutralized by HCl in water. The suspension was filtered and washed with cold water, and the crude product was recrystallized from an ethanol/water mixture. Yield: 5 g (91%). Mp: 96.6–97.6 °C. ^{1}H NMR (DMSO, TMS): δ 1.63 (d, 3 H, $\mathrm{CHC}H_3$), 4.82 (q, 1 H, $\mathrm{C}H\mathrm{CH_3}$), 5.01 (s, 2 H, $\mathrm{ArC}H_2\mathrm{O}$), 6.88 (s, 4 H, OArO), 7.3–7.75 (m, 5 H, $ArCH_2$). IR (KBr): 3000–2500 (br, COOH), 1779 (C=O), 1608 (C=C) cm^{-1}.

2,2,3,3,3-Pentafluoropropyl (*R*)-2-[(4-Benzyloxy)phenoxy]propanoate (5). To a suspension of carboxylic acid derivative **4** (3.5 g, 13 mmol) and 60 mL of benzene were added 2.8 mL (32 mmol) of oxalyl chloride and 2 drops of pyridine. After stirring the reaction mixture overnight at room temperature, the solvent was removed in vacuo. The acid chloride was dissolved in toluene and added dropwise to a solution of 2,2,3,3,3-pentafluoro-1-propanol (2.1 g, 14 mmol), 10 mL of pyridine, and a few crystals of DMAP in 80 mL of toluene. The mixture was heated for 1 h at 80 °C and left overnight at room temperature. The solvent was removed, and the residue was dissolved in dichloromethane, washed with water, a HCl solution, and sodium bicarbonate, and dried with Na_2SO_4. Evaporation of the solvent led to the final compound **5** which was purified by column chromatography with 1/4 ethyl acetate/hexane to give 3.71 g (75%) of a clear liquid. ^{1}H NMR ($CDCl_3$, TMS): δ 1.63 (d, 3 H, $\mathrm{CHC}H_3$), 4.5 (t, 2 H, $\mathrm{C}H_2\mathrm{CF_2}$), 4.81 (q, 1 H, $\mathrm{C}H\mathrm{CH_3}$), 5.01 (s, 2 H, $\mathrm{ArC}H_2\mathrm{O}$), 6.88 (s, 4 H, OArO), 7.3–7.75 (m, 5 H, ArH). IR (KBr): 1775 (C=O), 1608 (C=C) cm^{-1}. Anal. Calcd for $C_{19}H_{17}F_5O_4$: C, 56.43; H, 4.21. Found: C, 56.28; H, 4.0.

***p*-[(*R*)-1-[(2,2,3,3,3-Pentafluoro-1-propoxy)carbonyl]ethoxy]phenol (6).** Hydrogen was allowed to bubble through a stirred suspension of 10% palladium on carbon (0.4 g) in 40 mL of dichloromethane. After 15 min, 3 g (7.3 mmol) of benzyl ether **5** was added, and the reaction mixture was stirred overnight. After TLC (1/4 ethyl acetate/hexane) analysis showed no trace of the starting material, the suspension was filtered through a Celite pad. The solvent was removed by rotary evaporation, and the product **6** (white crystals, mp 81–82 °C, 90% yield) was used for the next step without further purification. ^{1}H NMR ($CDCl_3$, TMS): δ 1.62 (d, 3 H, $\mathrm{CHC}H_3$), 4.5 (t, 2 H, $\mathrm{C}H_2\mathrm{CF_2}$), 4.8 (q, 1 H, $\mathrm{C}H\mathrm{CH_3}$), 6.2 (br s, 1 H, OH), 6.75 (s, 4 H, ArH). IR (KBr): 3480 (OH), 1760 (C=O), 1608 (C=C) cm^{-1}. Anal. Calcd for $C_{12}H_{11}F_5O_4$: C, 45.85; H, 3.50. Found: C, 45.58; H, 3.40.

(*R*)-4-[1-[(2,2,3,3,3-Pentafluoropropoxy)carbonyl]ethoxy]phenyl 4-[4-(9-Decenyloxy)phenyl]benzoate (10PPBF2). To a mixture of **6** (1.9 g, 5.93 mmol), **2** (2.09 g, 5.93 mmol), and DMAP (61 mg, 0.49 mmol) in 100 mL of dichloromethane was added 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide methiodide ($EDC{\cdot}CH_3I$)[19] (2.43 g, 8.2 mmol). The mixture was stirred for 24 h at room temperature. After dilution with dichloromethane, the organic phase was washed with water, a saturated solution of sodium bicarbonate, and brine and finally dried over sodium sulfate. The solvent was evaporated, and the residue was purified by column chromatography on silica gel (1/4 ethyl acetate/hexane) followed by a recrystallization from ethanol to yield 2.44 g (61%). ^{1}H NMR ($CDCl_3$, TMS): δ 1.0–2.0 (m, 17 H), 3.98 (t, 2 H, $\mathrm{C}H_2\mathrm{O{-}}$), 4.5 (t, 2 H, $\mathrm{C}H_2\mathrm{CF_2}$), 4.8 (q, 1 H, $\mathrm{C}H\mathrm{CH_3}$), 5.0 (m, 2 H, $\mathrm{C}H_2\mathrm{{=}CH}$), 5.82 (m, 1 H, $\mathrm{C}H\mathrm{{=}CH_2}$), 6.85–8.2 (m, 12 H, ArH). Anal. Calcd for $C_{35}H_{37}F_5O_6$: C, 64.80; H, 5.71. Found: C, 64.70; H, 5.65.

4-Hydroxy-2-nitrophenyl Benzoate (8). To a solution of 4-hydroxyphenyl benzoate (**7**; 3.89 g, 18.2 mmol) in 70 mL of ether and 40 mL of dichloromethane was added dropwise a mixture of 22 mL of H_2O, 15 mL of HCl, 1.55 g of $NaNO_3$, and 0.08 g of catalyst $La(NO_3){\cdot}6H_2O$. The biphasic mixture was stirred vigorously at room temperature for 3 h until no starting material was detected by TLC. The organic phase was separated, and the aqueous layer was extracted with ethyl ether. The combined organic phases were dried over anhydrous $MgSO_4$, and the solvent was removed. The phenol derivative was purified by column chromatography with 1/4 ethyl acetate/hexane as the eluting solvent to give 4-hydroxy-2-nitrophenyl benzoate in 90% yield as a yellow crystal (mp 96 °C). ^{1}H NMR ($CDCl_3$, TMS): δ 7.24 (d, 1 H), 7.48 (dd, 1 H), 7.54–7.74 (m, 3 H), 8.02 (d, 1 H), 8.18 (dd, 2 H), 11 (s, 1 H). Anal. Calcd for $C_{13}H_9NO_5$: C, 60.23; H, 3.47; N, 5.4. Found: C, 60.43; H, 3.60; N, 5.6.

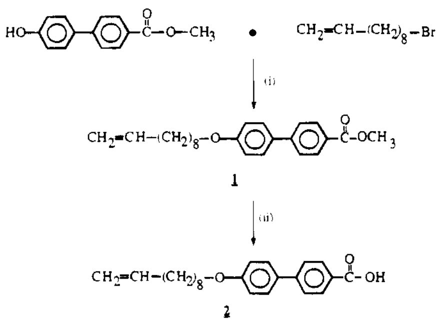
1-[(*R*)-1-(Butoxycarbonyl)ethoxy]-2-nitrophenyl Benzoate (9). To a nitrogen-flushed flask containing a mixture of butyl (*S*)-2-hydroxypropanoate (3 g, 20.5 mmol), 5.28 g (20.4 mmol) of **8** and 5.4 g (20.6 mmol) of triphenylphosphine in 50 mL of dry THF was added dropwise a solution of diethyl azocarboxylate (3.24 mL, 20.6 mL) in 20 mL of THF. The reaction mixture was stirred at room temperature for 24 h. After evaporation of the solvent, the residue was subjected to column chromatography on silica gel with 1/4 ethyl acetate/hexane as the eluting solvent to give the product **9** in 80% yield (6.34 g) as a yellow liquid. ^{1}H NMR ($CDCl_3$, TMS): δ 1.15 (t, 3 H, $\mathrm{CH_2C}H_3$), 1.25–1.40 (m, 4 H, $\mathrm{{-}C}H_2\mathrm{C}H_2\mathrm{{-}}$), 1.72 (d, 3 H, $\mathrm{{-}CHC}H_3$), 4.22 (m, 2 H, $\mathrm{{-}OC}H_2\mathrm{{-}}$), 4.9 (q, 1 H, $\mathrm{{-}C}H\mathrm{CH_3}$), 7.08 (d, 1 H, ArH), 7.4 (dd, 1 H, ArH), 7.5–7.7 (m, 3 H, ArH), 7.8 (d, 1 H, ArH), 8.2 (dd, 2 H, ArH). Anal. Calcd for $C_{20}H_{21}NO_7$: C, 62.0; H, 5.42; N, 3.62. Found: C, 62.15; H, 5.3; N, 3.60.

4-[(*R*)-1-(Butoxycarbonyl)ethoxy]-3-nitrophenol (10). The ester derivative **9** (2 g, 5.17 mmol) was dissolved in an excess of butanol, and a few drops of H_2SO_4 were added. The reaction mixture was refluxed for 40 h until no starting material was detected by TLC. The solvent was evaporated, and the crude product was purified by column chromatography with 1/4 ethyl acetate/hexane as the eluting solvent. The phenol was obtained in 90% yield as an orange oil. ^{1}H NMR ($CDCl_3$, TMS): δ 1.2 (t, 3 H, $-CH_2CH_3$), 1.27−1.38 (m, 4 H, $-CH_2CH_2-$), 1.75 (d, 3 H, $-CHCH_3$), 4.15 (m, 2 H, $-OCH_2-$), 4.92 (q, 1 H, $-CHCH_3$), 7.1 (d, 1 H, ArH), 7.3 (dd, 1 H, ArH), 7.45 (d, 1 H, ArH). Anal. Calcd for $C_{13}H_{17}NO_6$: C, 55.12; H, 6.0; N, 4.95. Found: C, 55.0; H, 5.85; N, 5.05.

4-[(*R*)-1-(Butoxycarbonyl)ethoxy]-3-nitrophenyl 4-[4-(9-Decenyloxy)phenyl]benzoate (10PPBN4). The procedure for the preparation of **10PPBN4** is the same as that for compound **10PPBF2**. The final crude product was purified by column chromatography (1/4 ethyl acetate/hexane) to give **10PPBN4** in 70% yield. The product was further purified by several recrystallizations from ethanol. ^{1}H NMR ($CDCl_3$, TMS): δ 1.2 (t, 3 H, $-CH_2CH_3$), 1.25−2.1 (m, 21 H), 4.0 (t, 2 H, $-CH_2Ar$), 4.25 (m, 2 H, $-OCH_2CH_2$), 4.85 (q, 1 H, $-CHCH_3$), 4.98 (m, 2 H, $CH_2{=}CH-$), 5.9 (m, 1 H, $CH_2{=}CH-$), 6.98−8.22 (m, 11 H, ArH). Anal. Calcd for $C_{36}H_{43}NO_8$: C, 70.0; H, 6.97; N, 2.27. Found: C, 70.2; H, 7.01; N, 2.20.

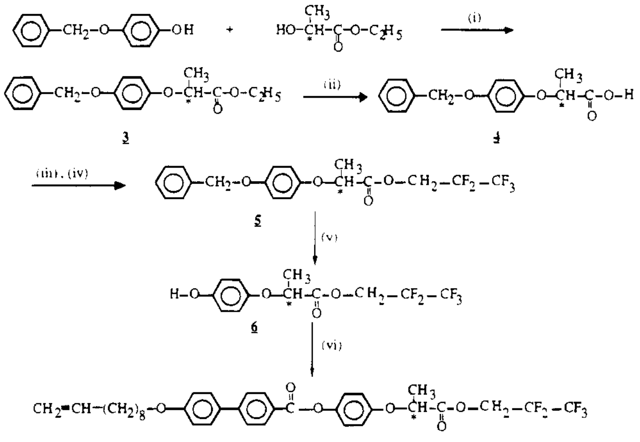
Synthesis of the Terpolymers. The synthesis of the terpolymers bearing the mesogenic groups **10PPBN4** and **10PPBF2** with $y_1 = 0.21$ and $y_2 = 0.09$ is given here as an example. All other copolymers with different y_1/y_2 ratios were made following the same procedure. To a solution of poly[(30−35%)methylhydrosiloxane-*co*-(65−70%)dimethylsiloxane] (0.36 mmol of SiH function) dissolved in 50 mL of dry toluene were added 241 mg (0.39 mmol) and 26.8 mg (0.04 mmol) of the vinyl derivatives **10PPBN4** and **10PPBF2**, respectively. The reaction mixture was heated to 100 °C under nitrogen, and 40 μL of a dicyclopentadienylplatinum(II) chloride catalyst[20] solution was then injected (1 mg/mL in dichloromethane). The mixture was refluxed under nitrogen for about 2 days. The polymer was purified by gel permeation chromtography eluting with toluene. The fractions containing the product were gathered, and the polymer was isolated by precipitation from a tetrahydrofuran solution into methanol. The pure polymer was obtained in 60% yield and dried under vacuum at 60 °C. The disappearance of the ^{1}H NMR peak of each of the polymers corresponding to the SiH groups (4.74 ppm, $CDCl_3$) and the ratios of the integrated areas of the various proton environments confirmed that virtually all of the Si−H bonds had been converted to Si−(mesogenic group) bonds.

Scheme 1



(i) NaH/DMF: H_3O^+ (ii) KOH/Ethanol; H_3O^+

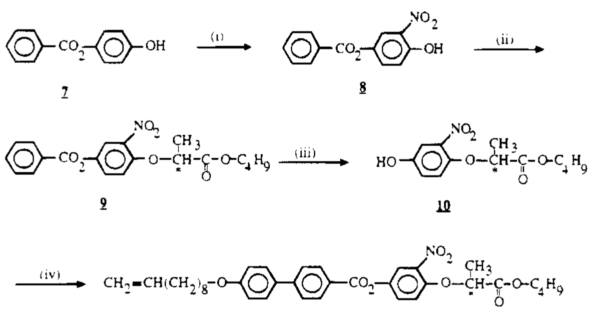
Scheme 2



10PPBF2

(i) DEAD/Ph_3P. (ii) LiOH, ethanol/water. (iii) ClCOCOCl, benzene. (iv) $C_2H_3F_5OH$, pyridine/DMAP. (v) H_2/Pd-C. (vi) $C_{10}H_{19}OC_{12}H_8COOH$, EDC.$CH_3I$/DMAP

Scheme 3



10PPBN4

(i) $NaNO_3$, $La(NO_3).6H_2O$. (ii) $HO\overset{*}{C}H(CH_3)COOC_4H_9$, DEAD/$Ph_3P$. (iii) HOC_4H_9/ H^+ (iv) $C_{10}H_{19}OC_{12}H_8COOH$, EDC.$CH_3I$/DMAP

Results and Discussion

Synthesis of the Materials. The synthesis steps leading to the preparation of the mesogenic side groups **10PPBF2** are shown in Schemes 1 and 2. 4′-(9-Decenyloxy)biphenyl-4-carboxylic acid (**2**) was prepared by reacting hydroxybiphenylcarboxylic acid methyl ester[16] with 10-bromo-1-decene in the presence of NaH, followed by hydrolysis. Compound **3** was synthesized by coupling ethyl (*S*)-2-hydroxypropanoate with *p*-(benzyloxy)phenol under standard Mitsunobu conditions[18] (diethyl azodicarboxylate (DEAD)/triphenylphosphine (Ph_3P)). The Mitsunobu coupling proceeds with inversion of the configuration at the chiral center. The acid derivative **4** was obtained by basic hydrolysis of **3** using LiOH in a methanol/water mixture. Coupling of the acid chloride of **4** with the fluoro alcohol derivative led to **5**, which upon treatment with palladium on activated carbon gave the phenol derivative **6**. The final product **10PPBF2** was obtained by a classical esterification of the carboxylic acid derivative **2** with **6** in the presence of 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide methiodide (EDC•CH_3I)[19] and (dimethylamino)pyridine (DMAP).

The synthesis scheme of **10PPBN4** is outlined in Scheme 3. 4-Hydroxy-2-nitrophenyl benzoate was prepared by reaction of a sodium nitrate/lanthanum nitrate reagent with 4-hydroxyphenyl benzoate. Compound **9** was synthesized by coupling butyl (*S*)-2-hydroxypropanoate with the nitrophenol derivative **8** under standard Mitsunobu conditions. Transesterification in an acidic medium of compound **9** in the presence of butanol led to the formation of the phenol derivative **10**. The

Scheme 4

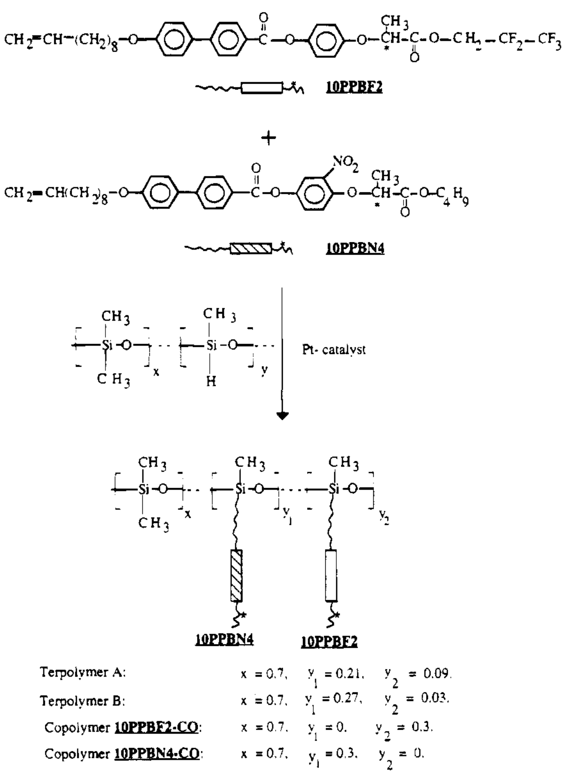


Table 1. Phase and Transition Temperatures Determined from a Combination of Optical Microscopy, DSC, and Spontaneous Measurement Techniques

material	phase sequence (°C)
10PPBF2	K 105 SmC* 137.2 SmA 152.1 Iso
10PPBN4	K 47.4 SmC* 54.7 SmA 74.4 Iso
10PPBN4/10PPBF2 (70/30)	K 30 SmC* 82.5 SmA 101 Iso
10PPBF2–CO	T_g 30[a] SmX 52 SmC* 139 SmA 156 Iso
10PPBN4–CO	T_g SmC* 37 SmA 148 Iso
terpolymer A	T_g 25 SmC* 70 SmA 150 Iso
terpolymer B	T_g SmC* 45.7 SmA 149 Iso

[a] High-ordered mesophase.

final product **10PPBN4** was obtained by reaction of (9-decenyloxy)benzoic acid with compound **4** in the presence of EDC•CH3I/DMAP reagents. The two mesogenic side groups were purified by silica gel chromatography, followed by several recrystallizations from ethanol.

The terpolymers consist of a flexible siloxane backbone to which a methyl group and the side groups **10PPF2** and **10PPBN4** are selectively attached (see Scheme 4). When one of the side group fractions (y_1 or y_2) is zero, we refer to it as the copolymer. In this notation for the copolymer **10PPF2-CO**, $x = 0.7$, $y_1 = 0$, and $y_2 = 0.3$; for the other copolymer **10PPBN4-CO**, $x = 0.7$, $y_1 = 0.3$, and $y_2 = 0$. The terpolymers were obtained through the classical hydrosilylation reaction[20] between the poly[(30–35%)methylsiloxane-*co*-(65–70%)-dimethylsiloxane] and the vinyl mesogenic side groups **10PPBF2** and **10PPBN4** in different ratios (see Scheme 4). They were purified by gel permeation chromatography followed by several precipitations from tetrahydrofuran into methanol.

Phase Transition Temperatures. The transition temperatures and the phases exhibited by the mesogens (**10PPBF2** and **10PPBN4**), their corresponding copolymers (**10PPBF2-CO** and **10PPBN4-CO**) and the terpolymers (A and B) are given in Table 1. In addition, we studied a 70/30 mixture of **10PPBN4** and **10PPBF2** (the same mesogenic ratio as in terpolymer A), which enables us to elucidate the effect of polymerization on the mixture.

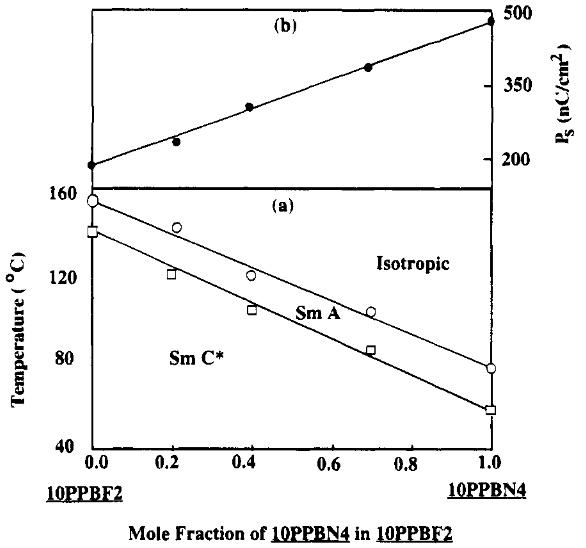


Figure 1. (a) Phase diagram for mixtures of the mesogenic side groups **10PPBF2** and **10PPBN4**. (b) Spontaneous polarization measured at a relative temperature of 20 °C below the SmA–SmC* transition.

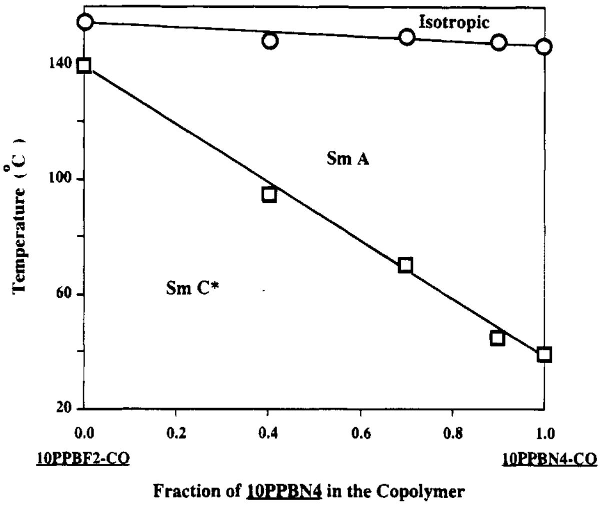


Figure 2. Phase diagram of the two copolymers **10PPBF2-CO** and **10PPBN4-CO**.

The phase diagram for the mixtures of the monomers **10PPBF2** and **10PPBN4** is given in Figure 1a. Both the isotropic–smectic A and smectic A–smectic C* transition temperatures for the mixtures vary linearly between those of the two pure components. This indicates that the two mesogens are completely miscible in all proportions. The phase transition temperatures for the copolymers (Figure 2) also show a linear dependence on the relative ratio of the two types of mesogenic groups (**10PPBN4/10PPBF2**) attached to the backbone. This linear dependence for the terpolymers, which is similar to that seen for the mixture of the unpolymerized side groups (Figure 1), shows that both types of side groups of the terpolymer are completely decoupled from the backbone. Another important aspect of the terpolymers needs to be pointed out. By virtue of the fact that the side groups are attached to the same backbone unit, the problem of phase separation, which is normally encountered while mixing a polymer with another polymer or monomer, does not appear to exist in the case of the terpolymer.

We shall now examine the effect of polymerization on the temperature stability of the smectic C* phase. In

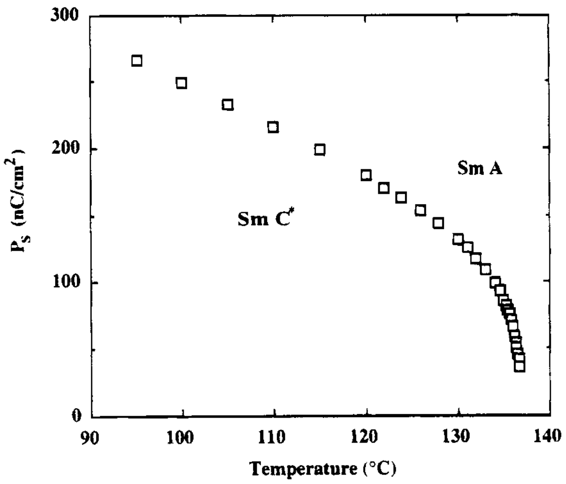


Figure 3. Temperature variation of the spontaneous polarization for the mesogenic side group **10PPBF2**.

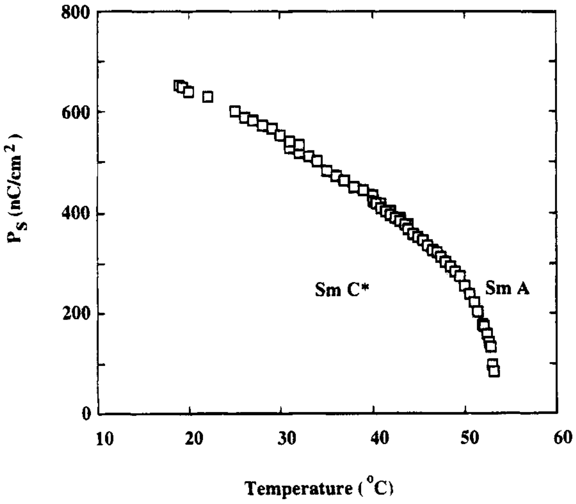


Figure 4. Temperature variation of the spontaneous polarization for the mesogenic side group **10PPBN4**.

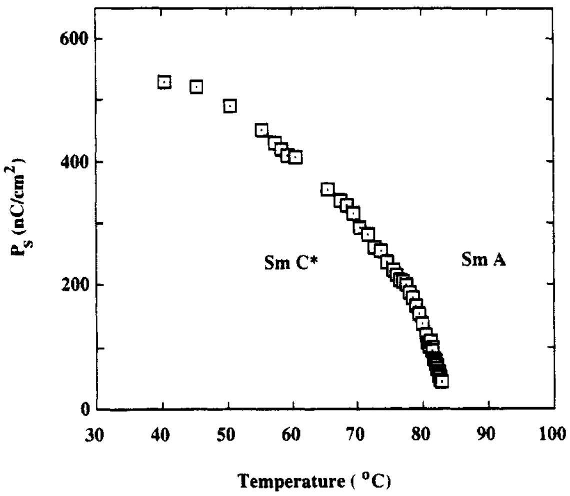


Figure 5. Temperature variation of P_s for the 70/30 mixture of **10PPBN4/10PPBF2** mesogenic groups.

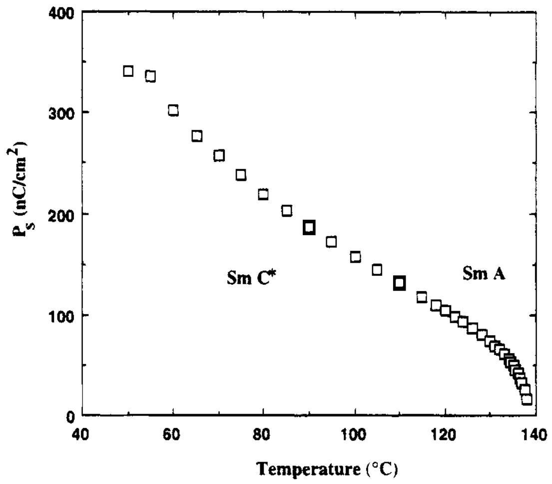


Figure 6. Temperature variation of the spontaneous polarization for the mesogenic side group **10PPBF2-CO**.

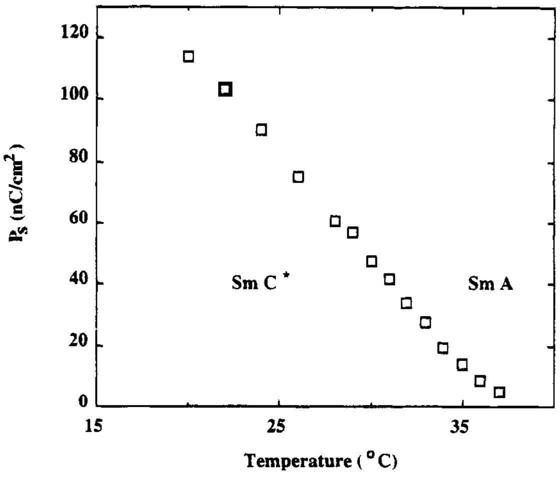


Figure 7. Temperature variation of the spontaneous polarization for the mesogenic side group **10PPBN4-CO**.

the case of **10PPBF2** and its corresponding copolymer, the SmA–SmC* transition temperatures are nearly the same. However, the range of the SmC* is considerably enhanced for the copolymer (≈87 °C) compared to the unpolymerized side group (≈32 °C). In comparison, in the case of **10PPBN2** and its corresponding copolymer, the value of the SmA–SmC* transition is considerably reduced for the copolymer with a concomitant increase in the range of the SmA phase. The enhancement of the thermal range of the mesophases on polymerization is similar to the results previously reported for other side-chain polymeric systems.[5,12] Thus, the terpolymers constitute a convenient way of tuning the phase transition temperatures as well as the thermal range of the ferroelectric phase of liquid crystalline polymers.

Polarization Studies. We have measured the temperature variation of spontaneous polarization P_s of the copolymers **10PPBF2-CO** and **10PPBN4-CO** and the terpolymers A and B (see Scheme 4). In addition, we have measured the P_s of the monomeric mesogens as well as a 70/30 mixture of the two monomers **10PPBF2** and **10PPBN4** for the sake of comparison (70/30 is also the ratio of the two mesogenic side groups in terpolymer A). The temperature variation of the spontaneous polarization for the mesogens and their 70/30 mixture is shown in Figures 3–5. The value of P_s in **10PPBN4** appears to be amongst the highest measured[21] so far in any ferroelectric liquid crystal. The pure mesogens as well as the mixture exhibit the usual power-law variation of polarization with temperature. We have also shown the relative value of P_s of the mixture at $T - T_{AC^*} = 20$ °C in Figure 1b. The value of P_s is seen to vary linearly between the two monomeric mesogens.

The temperature variation of the spontaneous polarization for the copolymers is shown in Figures 6 and 7 and for the terpolymers in Figures 8 and 9. Even though the highest value of the spontaneous polarization (340 nC/cm^2 at 50 °C) is achieved in the **10PPBF2-**

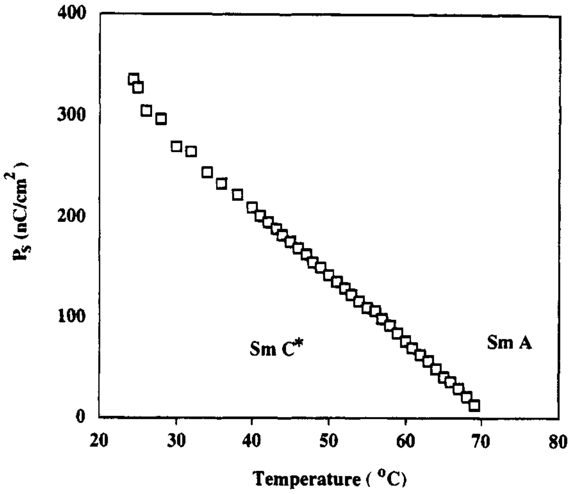


Figure 8. Temperature variation of the spontaneous polarization for terpolymer A.

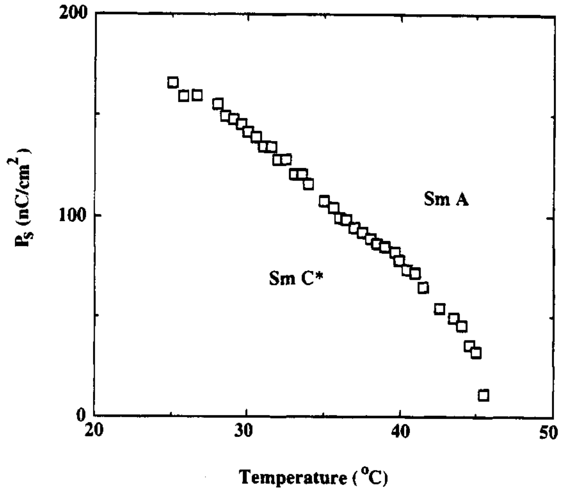


Figure 9. Temperature variation of the spontaneous polarization for terpolymer B.

CO (Figure 6), the smectic C* phase in this copolymer exists only at elevated temperatures between 52 and 139 °C (see Table 1). On the other hand, the **10PPBN4-CO** exhibits a smectic C* phase at room temperature, a feature that is attractive from the point of view of applications. But the value of P_s for this copolymer is relatively low (75 nC/cm^2 at 25 °C) (see Figure 7). Comparatively, both the terpolymers A and B show room temperature smectic C* phases with relatively large polarization values (300 nC/cm^2 for terpolymer A (Figure 8) and 160 nC/cm^2 for terpolymer B (Figure 9)). Thus, we have demonstrated that the beneficial trends of two polymers can be combined in a terpolymer. In fact, the effect of mixing the two mesogenic groups results in an enhancement of the spontaneous polarization, indicating that the intermolecular interaction between the two mesogens is very sensitive to the relative concentrations of the two mesogens.

Finally, it should be pointed out that terpolymer A exhibits an unusual temperature dependence of the spontaneous polarization: instead of showing the typical power law dependence, *P_s varies linearly with temperature throughout the smectic C* phase* (see Figure 8). The reason for this unusual behavior is still not clear to us. It is probably due to the competing effects of the temperature dependence of polarization for the two types of mesogenic groups attached to the backbone. An important aspect of this variation is that it leads to a temperature-independent pyroelectric coefficient ($p = dP_s/dT$). This might have important implications for infrared imaging applications.[22]

Conclusion

We have synthesized co- and terpolymers exhibiting large spontaneous polarizations. We have shown that, by incorporation of two kinds of mesogens into the siloxane backbone, it is possible to fine tune the physical properties of a polymer, in a way analogous to the monomer mixtures. One of the terpolymers studied exhibits an unusual linear temperature variation of spontaneous polarization, resulting in a constant pyroelectric coefficient (dP_s/dT) over a wide temperature range. Such a polymeric material can find application in IR or thermal detectors. Also, the presence of an electron acceptor unit ($-NO_2$ group) and an electron donor unit (*o*-nitroalkoxyl group) in one of the mesogens (**10PPBN4**) makes it a possible candidate for nonlinear optics applications. We are presently studying the second harmonic generation in these materials.

Acknowledgment. The authors thank Dr. Monique Mauzac, Centre de Recherche Paul Pascal, Université de Bordeaux I, for her assistance in the determination of the molecular weights of the polymers. We gratefully acknowledge the financial support of the Office of Naval Research.

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MA950184F