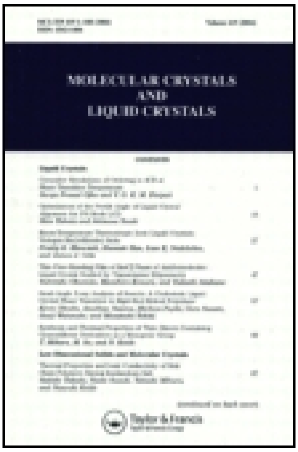

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Synthesis and Characterization of Chiral Smectic Side-Chain Liquid Crystalline Polysiloxanes Containing 2,5-Disubstituted-1,3-Dioxane Based Mesogenic Side Groups

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Synthesis and Characterization of Chiral Smectic Side-Chain Liquid Crystalline Polysiloxanes Containing 2,5-Disubstituted-1,3-Dioxane Based Mesogenic Side Groups

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The synthesis of three liquid crystalline polysiloxanes containing 4-[(S)-2-methyl-1-butoxycarbonyl]phenyl 4-(trans-5-alkanyl-1,3-dioxan-2-yl]benzoates side groups is presented. The phase behavior of both monomeric and polymeric liquid crystals was characterized by optical polarizing microscopy, differential scanning calorimetry and X-ray diffraction measurements. The monomer which contains eleven methylene units in the spacers is the only one to exhibit the enantiotropic smectic A and chiral smectic C phases. The polymer containing six methylene units in the spacers presents an enantiotropic smectic A phase while the polymer containing eleven methylene units in the spacers shows an enantiotropic smectic A and a monotropic smectic B phase.

Keywords: ferroelectric liquid crystal, side-chain liquid crystalline polymer, trans-1,3-dioxane-based mesogen, polysiloxane backbone

1. INTRODUCTION

The potential application of ferroelectric liquid crystals (FLCs) in fast-switching, high resolution electroptical devices is well documented.[1–3] Besides low molar mass FLCs, a number of ferroelectric liquid crystalline side-chain polymers have been successfully prepared during the past few years.[4–13] This field has been reviewed by P. Le Barney and J. C. Dubois.[14] However the detailed structure property relationship of ferroelectric liquid crystalline polymers (LCPs) has not been very clear up until now. It seems necessary to introduce additional functional groups to the mesogenic units, spacers and polymer backbone of side-chain liquid crystalline polymers to create some new property combinations in order to achieve these goals.

Recently, we reported on systematic investigations concerning the replacement of aromatic structures from mesogenic side groups of side-chain LCP by hetero-

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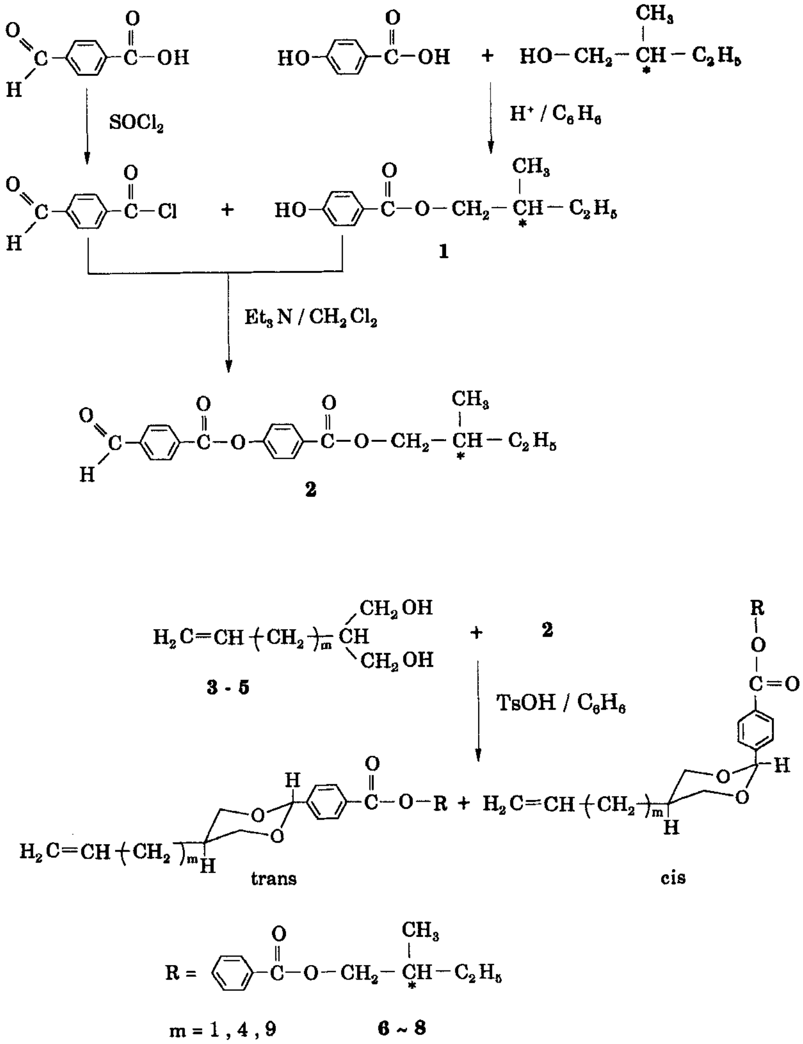
cycloalkane units, e.g., the trans-1,3-dioxane rings.[15–20] We have demonstrated that mesogenic units based on the trans-1,3-dioxane ring can be used to synthesize noncrystallizable side-chain LCPs even when the polymers contain up to eleven methylene units in the spacers. The conformational isomers of the trans-1,3-dioxane-based mesogens are in a dynamic equilibrium and this depresses their crystallization when they are attached as polymeric side chains. B. Hahn and V. Percec reported the synthesis and characterization a series of chiral smectic polysiloxanes containing 2,5-disubstituted-1,3-dioxane- and 2,5-disubstituted-1,3,2-dioxaborinane-based mesogenic groups.[21,22]

In 1988, Y. Haramoto prepared a series of new low molar mass ferroelectric



SCHEME I Synthesis of 4-[(S)-2-methyl-1-butoxycarbonyl]phenyl 4-(trans-5-ω-alkenyl-1,3-dioxan-2-yl)benzoates.

liquid crystals containing 2,5-disubstituted-1,3-dioxane-based mesogens.[23,24] The goal of this study is to present the synthesis and characterization of some new chiral smectic liquid crystalline polysiloxanes containing 4-[(S)-2-methyl-1-butyloxycarbonyl]phenyl 4-(trans-5-alkanyl-1,3-dioxan-2-yl)benzoate side groups. Their characterizations by differential scanning calorimetry, optical polarizing microscopy and X-ray diffraction have been presented.

2. RESULTS AND DISCUSSION

The synthetic routes for the preparation of 4-[(S)-2-methyl-1-butyloxycarbonyl]phenyl 4-[trans-5-(ω-alkenyl)-1,3-dioxan-2-yl]benzoates (6–8) are outlined in Scheme I. The chiral group was inserted into these mesogenic monomers starting with the commercially available (−)-2-(S)-methyl-1-butanol. This was done by a sequence of reactions which avoided its racemerization. The monomers were characterized by differential scanning calorimetry and optical polarizing microscopy. The thermal transitions and thermodynamic parameters of monomers 6–8 are summarized in Table IV. Monomer 6, containing three methylene units in the spacers, presents an enantiotropic smectic A phase and a monotropic cholesteric phase while monomer 7, containing six methylene units in the spacers, presents only an enantiotropic smectic A phase. Figure 1 illustrates the representative DSC

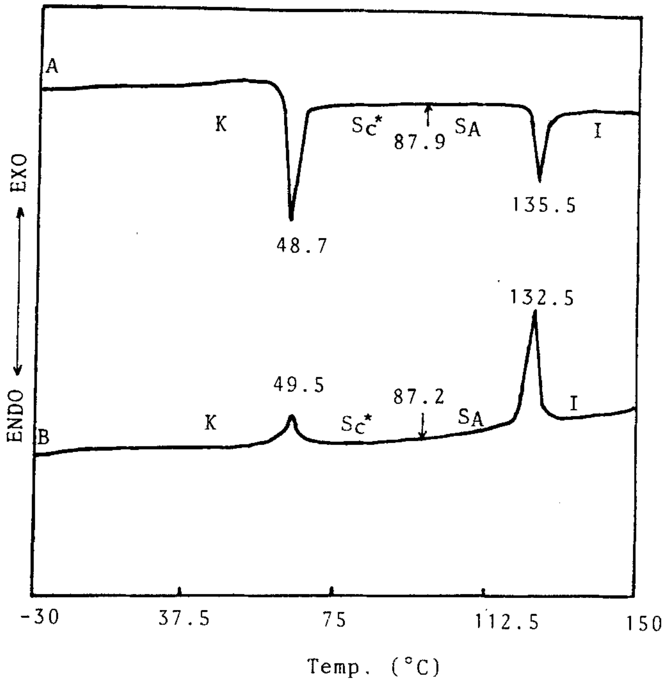


FIGURE 1 DSC thermograms of monomer 8: A) heating scan; B) cooling scan.

heating and cooling traces of monomer 8 which contains eleven methylene units in the spacers. The heating scan shows a melting transition at 48.7°C, a chiral smectic C to smectic A transition at 87.9°C, and a smectic A to isotropic phase transition at 135.5°C. The cooling scan presents an isotropic to smectic A phase transition at 132.5°C, a smectic A to chiral smectic C phase transition at 87.2°C, and a crystallization transition at 49.5°C. The smectic A to chiral smectic C phase transition on both heating and cooling scans was determined by optical polarizing microscopy. Figures 2A and 2B display respectively the typical smectic A and chiral smectic C textures exhibited by monomer 8. The results demonstrate that the

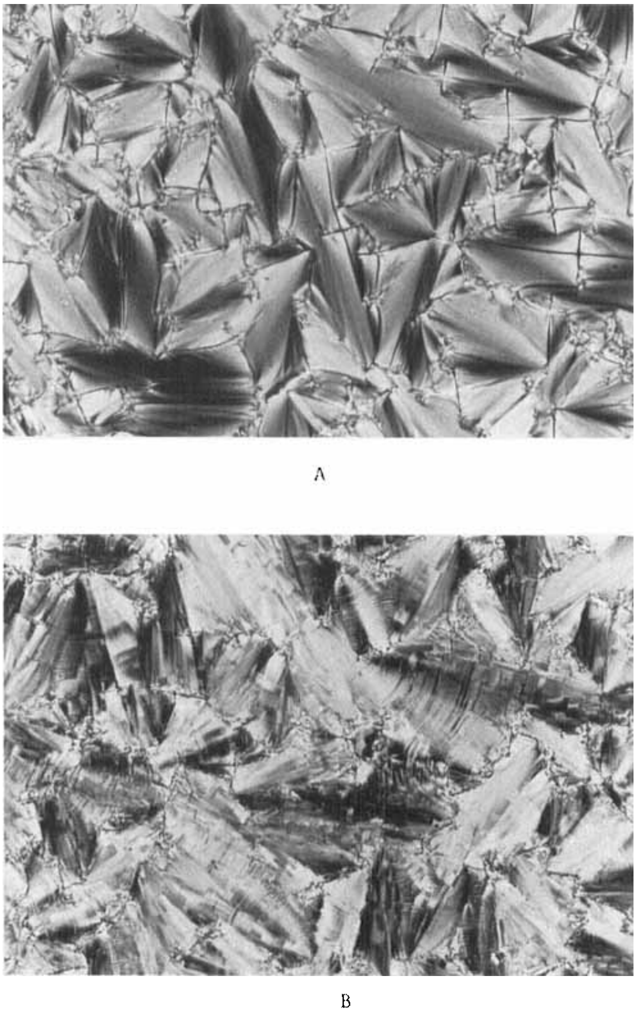
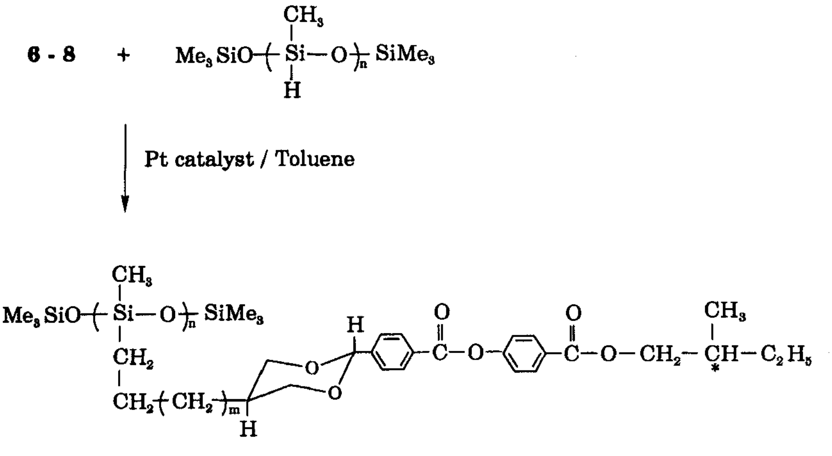


FIGURE 2 Typical optical polarizing micrographs of 8 monomer: A) S_A texture obtained after cooling from isotropic phase to 103°C; See Color Plate XII; B) Sc* texture obtained after cooling to 85°C.

tendency toward chiral smectic C mesomorphism increases by increasing the length of the flexible spacer.

The synthesis of polysiloxanes 9–11 is described in Scheme II. An excess amount of olefinic monomers was usually used to carry the hydrosilation reaction to completion. The unreacted monomers were removed by several reprecipitations from THF solution into methanol and by preparative GPC. Therefore the polymers were isolated with high purity. Table II summarizes the thermal transitions and thermodynamic parameters of the obtained polymers 9–11. Polymer 9 shows no mesophase while both polymers 10 and 11 present smectic mesomorphism. Figure 3 illustrates the DSC traces for polymers 10 and 11. Polymer 10 shows a glass transition temperature at 16°C and a S_A to isotropic phase transition at 132°C on the heating scan (Curve A) and a isotropic to S_A phase transition present at 129.6°C on the cooling scan (Curve B). Heating and cooling DSC scans for polymer 11 are presented as Curves C and D in Figure 3. Above the glass transition temperature (14.4°C) the polymer exhibits a S_A mesophase which undergoes isotropization at 202.2°C. The cooling scan presents first a S_A mesophase which transfers into a S_B phase at 32.8°C. Figure 4 presents the temperature-dependent X-ray diffraction diagrams obtained from the powder sample of 11 at 160, 130, 80, 50°C and room temperature. A broad reflection at wide angles (associated with the lateral packing) and two sharp reflections at low angles (associated with the smectic layers) are respectively shown by all curves. Curve E, obtained at a measuring temperature of 160°C, presents a diffuse reflection at about 4.83 Å, which corresponds to the lateral spacing of two mesogenic side groups, a sharp first-order reflection at 35.03 Å and a second-order reflection at 17.52 Å, which corresponds to the smectic layers. The optical polarizing micrograph (Figure 5) reveals a focal-conic fan texture for



m = 1, 4, 9 **9 - 11**

SCHEME II Synthesis of polysiloxanes.

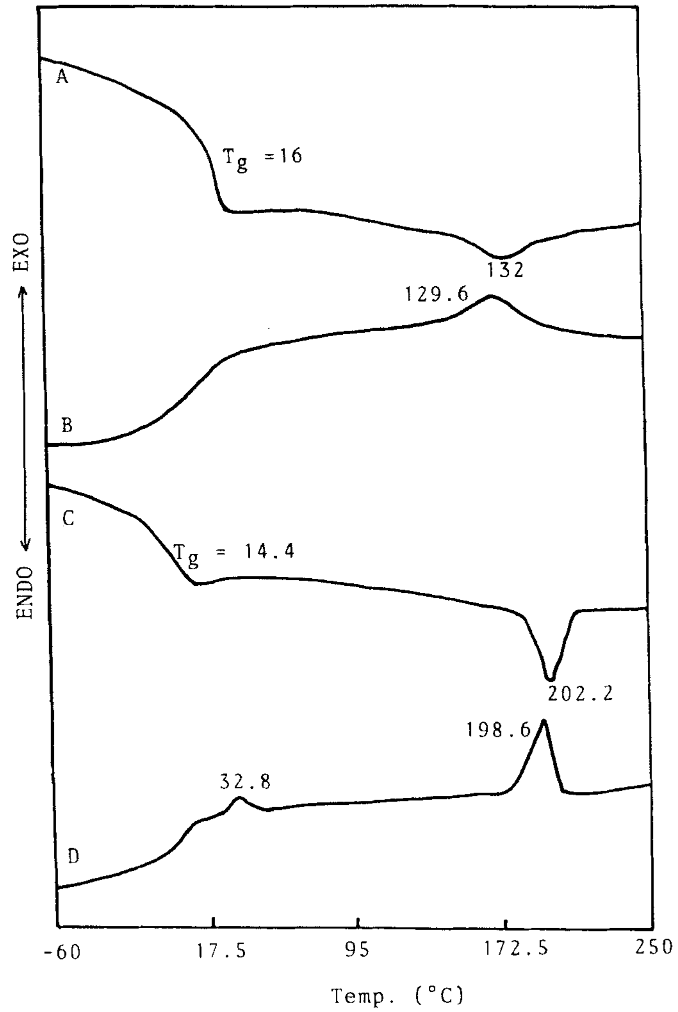


FIGURE 3 DSC thermograms of polymers 10 and 11: A) heating scan of 10; B) cooling scan of 10; C) heating scan of 11; D) cooling scan of 11.

polymer 11 at this temperature range. Both results are consistent with a smectic A structure. When the measuring temperature has been lowered from 160°C to 130,100, 80 or 50°C (Curves B ~ D), the d-spacings of first-order reflections and second-order reflections do not change and only the wide-angle reflection becomes sharper. The results indicate that the polymer also presents the smectic A phase at these temperatures. When the measuring temperature has been lowered to room temperature (Curve A), the d-spacings of the first-order reflections and second-order reflections show respectively 36.03 Å and 18.02 Å. The wide-angle diffraction shows at 4.51 Å and the peak becomes very sharp. This result indicates the formation of the smectic B phase.

Upon comparison of the thermal behavior of three polymers to that of their

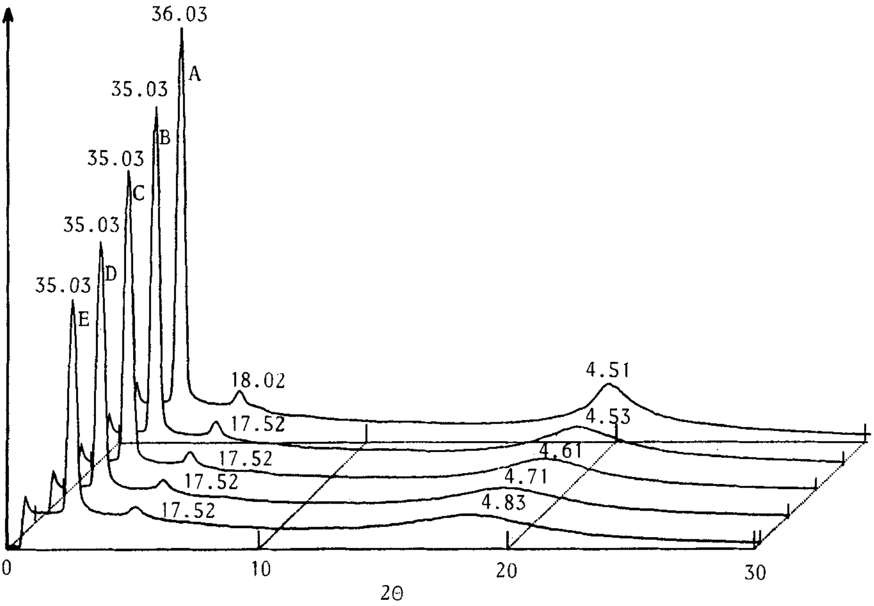


FIGURE 4 Temperature dependent X-ray diffraction diagrams of polymer 11: A) room temperature, B) 50°C, C) 80°C, D) 130°C, E) 160°C.

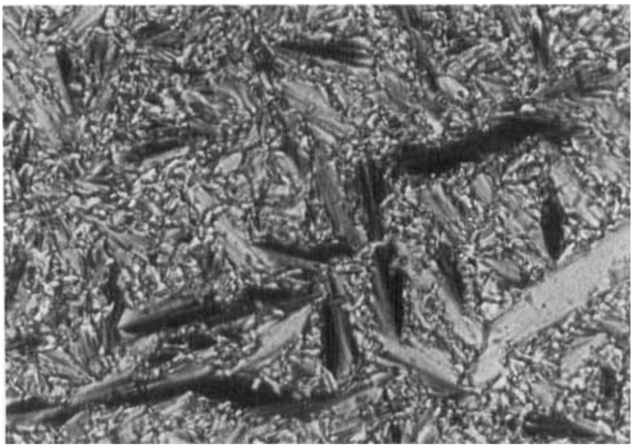


FIGURE 5 Typical optical polarizing micrographs of polymer 11: S_A texture obtained at 178°C. See Color Plate XIII.

corresponding monomers, it demonstrates that polymer 10 is the only one which shows the same mesophase with its corresponding monomer. According to our previous reports in the literature (15–20), we have demonstrated that 1,3-dioxane-based mesogens could form several conformational isomers which are in dynamic equilibrium. As can be seen from Tables I and II, polymer 9 reveals no mesophase

TABLE I

Phase Transitions and Phase Transition Enthalpies for Monomers 6 ~ 8

Monomers	n	Phase transitions, °C (Corresponding enthalpy changes, Kcal/mol) Heating Cooling
6	3	K 79.1 (28.82) S_A 102.9 (0.31) I I 101.4 (0.26) N^* 77.2 (0.01) S_A 0.3 (13.16) K
7	6	K 77.4 (18.08) S_A 133.7 (3.91) I I 131.4 (4.15) S_A 35.7 (12.48) K
8	11	K 48.7 (11.32) S_C^* 87.9 (-)[a] S_A 135.5 (5.46) I I 132.5 (5.69) S_A 87.2 (-)[a] S_C^* 49.5 (0.83) K

[a] Enthalpy is very small and the transition was observed from optical

TABLE II

Phase Transitions and Phase Transition Enthalpies for Polymers 9 ~ 11

Polymers	n	Phase transitions, °C (Corresponding enthalpy changes, Kcal/mol) Heating Cooling
9	3	g 24 I —
10	6	g 16 S_A 132 (0.28) I I 129.6 (0.31) S_A
11	11	g 14.4 S_A 202.2 (1.33) I I 198.6 (1.24) S_A 32.8 (0.17) S_B

while its corresponding monomer 6 exhibits cholesteric and smectic A phases. The possible reason is that the spacer length is too short for the mesogenic side groups to form a mesophase. In the case of polymers 11, it presents smectic A and smectic B phases while its corresponding monomer 8 shows smectic A and chiral smectic C phase. The reason that polymer 11 exhibits no chiral smectic C phase, could be due to the existence of several conformers for the mesogenic side groups. The conformers impede the formation of tilted chiral smectic C phase.

In conclusion, the synthesis of liquid crystalline polysiloxanes containing 4-[(S)-2-methyl-1-butoxycarbonyl]phenyl 4-(trans-5-alkanyl-1,3-dioxan-2-yl]benzoate side groups is presented. The monomer which contains eleven methylene units in the spacers is the only one to exhibit the enantiotropic smectic A and chiral smectic

C phases. Among the obtained polymers, one containing six methylene units in the spacers presents an enantiotropic smectic A phase while the other one containing eleven methylene units in the spacers shows an enantiotropic smectic A and a monotropic smectic B phase.

3. EXPERIMENTAL

Materials

Poly(methylhydrogensiloxane) ($\overline{Mn}$ = 2270) and divinyltetramethylsiloxane platinum catalyst were obtained from Patrarch System Inc., and used as received. (S)-(−)-2-Methyl-1-butanol, $[\alpha]_D^{25} = -6.5°$ (from Merck), 4-formylbenzoic acid and all other reagents (from Aldrich) were used as received. Toluene used in the hydrosilation reaction was first refluxed over sodium and then distilled under nitrogen.

Techniques

Experimental techniques used in the characterization of intermediary compounds and of polymers are identical to those previously reported [25].

(S)-2-Methyl-1-butyl 4-hydroxybenzoate ($\underline{1}$). 4-Hydroxybenzoic acid (4.9 g, 0.036 mol), and (S)-2-methyl-1-butanol (8.1 g, 0.092 mol) were dissolved in dried benzene. Four drops of conc. sulfuric acid completely dissolved and water was collected in a Dean-Stark trap. The reaction mixture was cooled to room temperature and extracted with diethyl ether (100 ml). The ether solution was washed with 2% aqueous solution of NaHCO$_3$, water and dried over anhydrous MgSO$_4$. The oily product, obtained after solvent was evaporated, was distilled at 170°C/1.33 mbar. Yield 6.5 g (93%); $[\alpha]_D^{25} = +7.63$. ^{1}H-NMR (CDCl$_3$): δ = 0.80–1.10 (m, 6H, two —C$\underline{H}_3$), 1.20–1.58 (m, 2H, —C$\underline{H}_2$—), 1.78–1.91 [m, 1H, —C$\underline{H}$(CH$_3$)—], 4.14 (q, 2H, —COOC$\underline{H}_2$—), 6.90–7.90 (m, 4H, Ar$\underline{H}$), 7.15 (s, 1H, ArO$\underline{H}$).

4-[(S)-2-Methyl-1-butyloxycarbonyl]phenyl 4-formylbenzoate ($\underline{2}$). 4-Formylbenzoic acid (4.13 g, 0.028 mol) was reacted at room temperature with excess thionyl chloride containing a drop of dimethylformamide in 10 ml of methylene chloride for 2 h. The solvent and excess thionyl chloride were removed under reduced pressure to give the crude acid chloride. The product was dissolved in 10 ml of methylene chloride and slowly added to a cold solution of $\underline{1}$ (5.7 g, 0.025 mol), triethylamine (3.03 g, 0.03 mmol) in 50 ml of methylene chloride. The solution was stirred at room temperature for 2 h, washed with water and dried over anhydrous MgSO$_4$. The crude product, obtained after the solvent was evaporated, was purified by column chromatography (silica gel, ethyl acetate/n-hexane = 1:1 as eluent) to yield 6.7 g (82%), $[\alpha]_D^{25} = +7.63$. ^{1}H-NMR (CDCl$_3$): δ = 0.80–1.10 (m, 6H, two —C$\underline{H}_3$), 1.20–1.60 (t, 2H, —C$\underline{H}_2$—), 1.78–1.91 [m, 1H, —C$\underline{H}$(CH$_3$)—], 4.14 (q, 2H, —COOC$\underline{H}_2$—), 7.28–8.39 (m, 8H, Ar$\underline{H}$), 10.14 (s, 1H, —C$\underline{H}$O)

2-Allylpropan-1,3-diol ($\underline{3}$), *2-(5-Hexane-1-yl)propan-1,3-diol* ($\underline{4}$), *2-(10-undecen-1-yl)propen-1,3-diol* ($\underline{5}$). Compounds $\underline{3}$–$\underline{5}$ were prepared by reduction of corresponding diethyl 2-(w-alkenyl)malonates with $LiAlH_4$ in diethyl ether according to a literature procedure reported previously.[26,27]

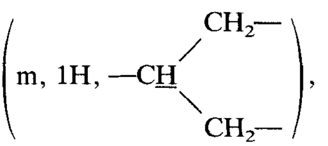
3 Yield 84%; b.p. 45 ~ 47°C/4.0 m bar; ^1H-NMR($CDCl_3$): δ = 1.78–1.91 [m, 1H, $-C\underline{H}(CH_2OH)_2$], 2.00–2.10 (m, 2H, $=CH-C\underline{H}_2-$), 3.00 (s, 2H, two $-O\underline{H}$), 3.60–3.85 (m, 4H, two $-C\underline{H}_2OH$), 5.02–5.11 (m, 2H, $C\underline{H}_2=$), 5.72–5.86 (m, 1H, $=C\underline{H}-$).

4 Yield 92%; b.p. 92 ~ 93°C/4.0 m bar; ^1H-NMR ($CDCl_3$): δ = 1.14–1.15 (m, 6H, $-(C\underline{H}_2)_3-$), 1.69–1.82 [m, 1H, $-C\underline{H}(CH_2OH)_2$], 1.91–2.20 (m, 2H, $=CH-C\underline{H}_2-$), 2.85 (s, 2H, two $-O\underline{H}$), 3.52–3.97 (m, 4H, two $-C\underline{H}_2OH$), 4.88–5.07 (m, 2H, $C\underline{H}_2=$), 5.70–5.87 (m, 1H, $=C\underline{H}-$).

5 Yield 88%; m.p. 58 ~ 59°C; ^1H-NMR ($CDCl_3$): δ = 1.20–1.40 (m, 16H, $-(C\underline{H}_2)_8-$), 1.72–1.83 [m, 1H, $-C\underline{H}(CH_2OH)_2$], 2.00–2.10 (m, 2H, $=CH-C\underline{H}_2-$), 2.23 (s, 2H, two $-O\underline{H}$), 3.61–3.78 (m, 4H, two $-C\underline{H}_2OH$), 4.95–5.05 (m, 2H, $C\underline{H}_2=$), 5.78–5.90 (m, 1H, $=C\underline{H}-$).

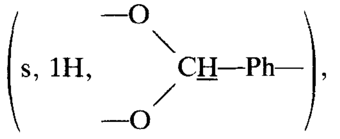
4-[(S)-2-Methyl-1-butyloxycarbonyl]phenyl 4-(trans-5-allyl-1,3-dioxan-2-yl)benzoate (6), *4-[(S)-2-Methyl-1-butyloxycarbonyl]phenyl 4-[trans-5-(5-hexen-1-yl)-1,3-dioxan-2-yl]benzoate* (7), *4-[(S)-2-Methyl-1-butyloxycarbonyl]phenyl 4-[trans-5-(10-undecen-1-yl)-1,3-dioxan-2-yl]benzoate* (8). All three compounds were prepared according to a same method. The synthesis of compound 8 is described below. 2-(10-Undecen-1-yl)propan-1,3-diol (2.0 g, 8.7 mmol), 4-[(S)-2-methyl-1-butyloxycarbonyl)phenyl 4-formyl-benzoate (3.0 g, 8.7 mmol) and p-toluenesulfonic acid (10.45 mg) was dissolved in 50 ml of benzene. The solution was refluxed under nitrogen atmosphere until the equivalent amount of water was collected in a Dean-Stark trap. After the reaction mixture was cooled to room temperature, 50 ml of diethyl ether was added. The solution was washed with 2% aqueous solution of $NaHCO_3$ and water, and dried with anhydrous $MgSO_4$. The crude product, obtained after the solvent was evaporated, was recrystallized several times from n-hexane until pure trans-isomer was isolated. Yield 3.26 g (78%).

6 Yield 73.2%; $[\alpha]_D^{25}$ = +2.92; ^1H-NMR($CDCl_3$): δ = 0.89–1.06 (m, 6H, two $-C\underline{H}_3$), 1.21–1.93 [m, 5H, $=CH-C\underline{H}_2-$ and $-C\underline{H}(CH_3)-C\underline{H}_2-$],

2.18–2.30 

$$\left(m, 1H, -C\underline{H}\begin{matrix} \nearrow CH_2- \\ \searrow CH_2- \end{matrix} \right),$$

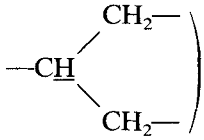
3.52 and 4.20 (m, 6H, two $-C\underline{H}_2O-$ and $-COOC\underline{H}_2-$), 5.04–5.10 (m, 2H, $C\underline{H}_2=$),

5.48 

$$\left(s, 1H, \begin{matrix} -O \searrow \\ -O \nearrow \end{matrix} C\underline{H}-Ph- \right),$$

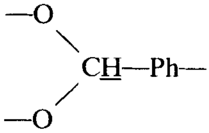
5.69–5.80 (m, 1H, $=C\underline{H}-$), 7.22–8.20 (m, 8H, $Ar\underline{H}$).

7 Yield 68%; $[\alpha]_D^{25} = +6.91$; ^{1}H-NMR ($CDCl_3$): δ = 0.89–0.99 (m, 6H, two $—C\underline{H}_3$), 1.08–1.93 [m, 11H $—(C\underline{H}_2)_4—$ and $—C\underline{H}(CH_3)—C\underline{H}_2—$ and $—C\underline{H}(CH_3)—$],



$$2.18\text{–}2.30\left(\text{m, 1H, }—C\underline{H}\begin{matrix} / CH_2— \\ \\ \backslash CH_2— \end{matrix}\right),$$

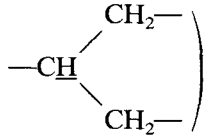
3.55 and 4.20 (m, 6H, two $—C\underline{H}_2O—$ and $—COOC\underline{H}_2—$), 4.92–5.04 (m, 2H, $C\underline{H}_2{=}$),



$$5.48\left(\text{s, 1H, }\begin{matrix} —O \backslash \\ \\ —O / \end{matrix} C\underline{H}—Ph—\right),$$

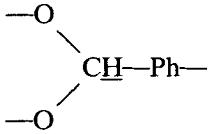
5.72–5.86 (m, 1H, $=C\underline{H}—$), 7.22–8.20 (m, 8H, Ar$\underline{H}$).

8 Yield 78%; $[\alpha]_D^{25} = +2.57$; ^{1}H-NMR ($CDCl_3$): δ = 0.89 – 1.06 (m, 6H, two $—C\underline{H}_3$), 1.07–2.06 [m, 21H $—(C\underline{H}_2)_9—$ and $—C\underline{H}(CH_3)—C\underline{H}_2—$]



$$2.10\text{–}2.19\left(\text{m, 1H, }—C\underline{H}\begin{matrix} / CH_2— \\ \\ \backslash CH_2— \end{matrix}\right),$$

3.55 and 4.20 (m, 6H two $—C\underline{H}_2O—$ and $—COOC\underline{H}_2—$), 4.90–5.02 (m, 2H, $C\underline{H}_2{=}$),



$$5.48\left(\text{s, 1H, }\begin{matrix} —O \backslash \\ \\ —O / \end{matrix} C\underline{H}—Ph—\right),$$

5.74–5.87 (m, 1H, $=C\underline{H}—$), 7.20–8.21 (m, 8H, Ar$\underline{H}$).

6: $C_{26}H_{30}O_6$ (438.5)	Calc.	C 71.22	H 6.90
	Found	C 72.18	H 6.88
7: $C_{29}H_{36}O_6$ (480.6)	Calc.	C 72.48	H 7.55
	Found	C 72.45	H 7.52
8: $C_{34}H_{46}O_6$ (550.7)	Calc.	C 74.16	H 8.42
	Found	C 74.14	H 8.36

Synthesis of Polysiloxanes (9 ~ 10)

The olefinic derivative 1.0 g (10 mol% excess versus the Si—H groups present in polysiloxane) was dissolved in 100 mL of dry, freshly distilled toluene together with the proper amount of poly(methylhydrogensiloxane). The reaction mixture was heated to 110°C under nitrogen and 100 mg of divinyltetramethyldisiloxane platinum catalyst was then injected with a syringe as a solution in toluene (1 mg/mL). The reaction mixture was refluxed (110°C) under nitrogen for 24 h. After this reaction time the FT-1R analysis showed that the hydrosilation reaction was complete. The polymers were separated and purified by several reprecipitations from tetrahydrofuran solution into method and further purified by preparative GPC, and then dried under vacuum.

Acknowledgment

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References

1. N. A. Clark and S. T. Lagerwall, *Appl. Phys., Lett.*, **36**, 899 (1980).
2. S. T. Lagerwall and I. Dahl, *Mol. Cryst. Liq. Cryst.*, **114**, 151 (1984).
3. S. T. Lagerwall, B. Otterholm, and K. Skarp, *Mol. Cryst. Liq. Cryst.*, **152**, 503 (1987).
4. V. P. Shibaev, M. V. Kozlovsky, L. A. Beresnev, L. M. Blinov and N. A. Plate, *Polym. Bull.*, **12**, 299 (1984).
5. S. Esselin, L. Bosio, C. Noel, G. Decobert, and J. C. Dubois, *Liq. Cryst.*, **2**, 505 (1987).
6. R. Zentel, G. Rekert, and B. Reck, *Liq. Cryst.*, **2**, 83 (1987).
7. S. Bualek, H. Kapitza, J. Meyer, G. F. Schmidt and R. Zentel, *Mol. Cryst. Liq. Cryst.*, **155**, 47 (1988).
8. S. Esselin, C. Noel, G. Decobert and J. C. Dubois, *Mol. Cryst. Liq. Cryst.*, **155**, 371 (1988).
9. H. Kapitza and R. Zental, *Makromol. Chem.*, **189**, 1793 (1988).
10. R. Zentel, G. Reckert, S. Bualek and H. Kapitza, *Makromol. Chem.*, **190**, 2869 (1989).
11. V. P. Shibaev, M. V. Kozlovsky and N. A. Plate, *Liq. Cryst.*, **8**, 1281 (1990).
12. H. R. Brand and H. Pleiner, *Makromol. Chem. Rapid. Commun.*, **11**, 607 (1990).
13. H. Kapitza and R. Zentel, *Makromol. Chem.*, **192**, 1859 (1991).
14. P. LeBarny and J. C. Dubois, In "Side Chain Liquid Crystal Polymers," C. B. McArdle Eds., Blackie: Glasgow and London, p. 130 (1989).
15. C. S. Hsu, J. M. Rodriguez-Parada and V. Percec, *Makromol. Chem.*, **188**, 1017 (1987).
16. C. S. Hsu, J. M. Rodriguez-Parada and V. Percec, *J. Polym. Sci. Polym. Chem.*, Ed., **25**, 2425 (1987).
17. C. S. Hsu and V. Percec, *Makromol. Chem. Rapid Commun.*, **8**, 331 (1987).
18. C. S. Hsu and V. Perced, *Polym. Bull.*, **17**, 49 (1987).
19. B. Hahn and V. Percec, *Macromolecules*, **20**, 2961 (1987).
20. C. S. Hsu and V. Percec, *Makromol. Chem.*, **189**, 1147 (1988).
21. V. Percec and B. Hahn, *Macromolecules*, **22**, 1588 (1989).
22. V. Percec, B. Hahn, M. Ebert and J. H. Wendorff., *Macromolecules*, **23**, 2092 (1990).
23. Y. Haramoto, K. Kawashiman and H. Kamogawa, *Bull. Chem. Soc. Jpn.*, **61**, 431 (1988).
24. Y. Haromoto and H. Kamogawa, *Mol. Cryst. Liq. Cryst.*, **173**, 89 (1989).
25. C. S. Hsu, J. H. Lin, L. R. Chou and G. H. Hsiue, *Macromolecules*, in press.
26. C. S. Hsu and V. Percec, *Polym. Bull.*, **17**, 49 (1987).
27. C. S. Hsu and V. Percec, *Makromol. Chem., Rapid Commun.*, **8**, 331 (1987).