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Synthesis and Characterization of Poly(methylsiloxane)S Containing 4-[*S*(-)-2-Methyl-1 -Butoxy1-4' -[*p*-(ω-alkan-l-yloxy)benzoyloxy]-α-methylstilbene Side Groups

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SYNTHESIS AND CHARACTERIZATION OF POLY(METHYLSILOXANE)S CONTAINING 4-[*S*(−)-2-METHYL-1-BUTOXY]-4′-[*p*-(ω-ALKAN-1-YLOXY)BENZOYLOXY]-α-METHYLSTILBENE SIDE GROUPS

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ABSTRACT

The syntheses of poly(methylsiloxane)s containing 4-[*S*(−)-2-methyl-1-butoxy]-4′-[*p*-(ω-alkan-1-yloxy)benzoyloxy]-α-methylstilbene side groups containing 11-undecanyl (18), 8-octyl (19), 6-hexyl (20), and 3-propyl (21), of a poly[(50–55%)-methyl-*co*-(45–50%)-dimethylsiloxane] containing 4-[*S*(−)-2-methyl-1-butoxy]-4′-[*p*-(8-octan-1-yloxy)benzoyloxy]-α-methylstilbene side groups (22) and of a poly(methylsiloxane) containing a 1:1 molar ratio of 4-[*S*(−)-2-methyl-1-butoxy]-4′-[*p*-(8-octan-1-yloxy)benzoyloxy]-α-methylstilbene and 4-[*S*(−)-2-methyl-1-butoxy]-4′-[*p*-(6-hexan-1-yloxy)benzoyloxy]-α-methylstilbene side groups (23) are described. All polymers and copolymers were characterized by a combination of differential scanning calorimetry and thermal optical polarized microscopy techniques. 18 exhibits an enantiotropic s_A, while 19, 20, 21, and 23 display both enantiotropic s_A and s_C^* mesophases. 22 exhibits only an enantiotropic s_C^* mesophase. In addition, all polymers and copolymers exhibit sidechain crystallization. These results have demonstrated that extending the length of the rigid part of the mesogenic unit of 4-[*S*(−)-2-methyl-1-butoxy]-4′-(ω-alkan-1-yloxy)-α-methylstilbene to 4-[S(−)-2-methyl-1-butoxy]-4′-[p-(ω-alkan-1-yloxy)benzoyloxy]-α-methylstilbene increases the tendency of the resulting poly(methylsiloxane)s toward polymesomorphism.

INTRODUCTION

Previous publications from our laboratory reported the synthesis and characterization of polymethacrylates, polyacrylates, and poly(methylsiloxane)s containing 4-[S(−)-2-methyl-1-butoxy]-4′-(ω-alkan-1-yloxy)-α-methylstilbene side groups [1, 2] in which the alkanyl group contains two to eleven methylenic units. Although in the field of low molar mass liquid crystals there are some empirical rules which are used to design compounds displaying chiral smectic C (s_C^*) mesophases [3], such rules are not available for sidechain liquid crystalline polymers [4–15]. A classic example comes from our laboratory where repeated attempts to synthesize sidechain liquid crystalline polymers exhibiting a s_C^* mesophase [1, 16] led to polymers exhibiting a s_A mesophase. Therefore, we decided to perform a series of systematic investigations aimed at deriving some empirical rules useful for the molecular design of sidechain liquid crystalline polymers exhibiting s_C^* mesophases. Our approach uses various polymer architectures based on a single mesogenic unit which we decided to be 4-[S(−)-2-methyl-1-butoxy]-4′-(hydroxy)-α-methylstilbene, and polymethacrylate, polyacrylate, poly(methylsiloxane), poly(vinyl ether), and polyphosphazene backbones [1, 2]. This mesogenic unit was selected since we have accumulated previous experience with similar polymers based on the nonchiral 4-methoxy-4′-hydroxy-α-methylstilbene and 4-hydroxy-4′-methoxy-α-methylstilbene mesogenic groups [17–22]. From the previous series of investigations, only the poly(methylsiloxane)s containing 4-[S(−)-2-methyl-1-butoxy]-4′-(ω-alkan-1-yloxy)-α-methylstilbene, with ω-alkanyl being 8-octyl and 6-hexyl, exhibited enantiotropic s_C^* mesophases [2]. All other polymers displayed s_A mesophases [1, 2]. The goal of the present paper is to report the synthesis and characterization of poly(methylsiloxane)s containing 4-[S(−)-2-methyl-1-butoxy]-4′-[p-(ω-alkan-1-yloxy)benzoyloxy]-α-methylstilbene mesogenic groups with 11-undecanyl, 8-octyl, 6-hexyl, and 3-propyl ω-alkanyl groups.

EXPERIMENTAL

Materials

Poly(methylhydrosiloxane) with number-average degree of polymerization 65 was synthesized as described elsewhere [16b]. Poly(methylhydrosiloxane) with number-average degree of polymerization 43 (determined by ^{1}H-NMR spectroscopy (M_n = 1500, reported by Petrarch), poly[(50–55)-methylhydro-*co*-45–50%)-dimethylsiloxane] (M_n = 900–1000, *DP* = 12), platinum divinyltetramethyldisiloxane complex in xylene solution (all from Petrarch), 10-undecenoic acid (from Fluka), methyl *p*-hydroxybenzoate, 8-bromo-1-octene, 1,6-dibromohexane, allyl chloride, and 1-octene (all from Aldrich) were used as received. 4-[*S*(−)-2-Methyl-1-butoxy]-4′-(hydroxy)-α-methylstilbene was synthesized according to the procedure reported previously [2].

Methylene chloride used in the esterification reaction was first refluxed over CaH_2 and then distilled under nitrogen. Toluene used in the hydrosilation reaction was first refluxed over sodium and then distilled under nitrogen. All other reagents were used as received or were purified by standard methods.

Techniques

200 MHz ^{1}H-NMR spectra were recorded on a Varian XL-200 spectrometer. All spectra were recorded in $CDCl_3$ solution with TMS as internal standard, unless noted. A Perkin-Elmer DSC-4 differential scanning calorimeter, equipped with a TADS 3600 data station, was used to determine the thermal transitions which were read at the maximum or minimum of their endothermic or exothermic peaks. In all cases, heating and cooling rates were 20°C/min, unless otherwise specified. Glass transition temperatures (T_g) were read at the middle of the change in heat capacity. Thermal transitions were collected from second or further heating and cooling scans, unless otherwise specified. A Carl-Zeiss optical polarized microscope (magnification: 100 ×) equipped with a Mettler FP 82 hot stage and a Mettler FP 800 central processor was used to observe the thermal transitions and to analyze the anisotropic textures [23, 24]. Molecular weights were determined by gel permeation chromatography (GPC) with a Perkin-Elmer Series 10 LC instrument equipped with LC-100 column oven, LC-600 autosampler, and Sigma 15 data station. High pressure liquid

chromatography (HPLC) determinations were performed with the same instrument. The measurements were made by using a UV detector, $CHCl_3$ as solvent (1 mL/min; 40°C), a set of PL gel columns of 10^2, 5×10^2, 10^3, 10^4, and 10^5 Å, and a calibration plot constructed with polystyrene standards.

Synthesis of Monomers and Polymers

The synthesis of monomers and polymers is outlined in Schemes 1-4.

10-Undecen-1-ol ($\underline{2}$)

10-Undecenoic acid (30.7 g, 0.167 mol) was added dropwise to a stirred suspension of 7.6 g (0.200 mol) $LiAlH_4$ in 250 mL dry diethyl ether. The reaction mixture was heated under reflux with stirring overnight. Then it was cooled to room temperature, and the excess of $LiAlH_4$ was reacted with 40 mL ethyl acetate. The resulting mixture was treated with 40 mL HCl and extracted with chloroform. The chloroform layer was washed with water, dried over anhydrous $MgSO_4$, filtered, and the chloroform was evaporated to yield 23.7 g (83%) of a colorless liquid. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.34-2.10 (m, 16H, $-(C\underline{H}_2)_8-$), 3.70 (t, 2H, $-C\underline{H}_2O$), 5.10 and 5.80 (m, 3H, $C\underline{H}=C\underline{H}_2$)

10-Undecen-1-yl Tosylate ($\underline{4}$)

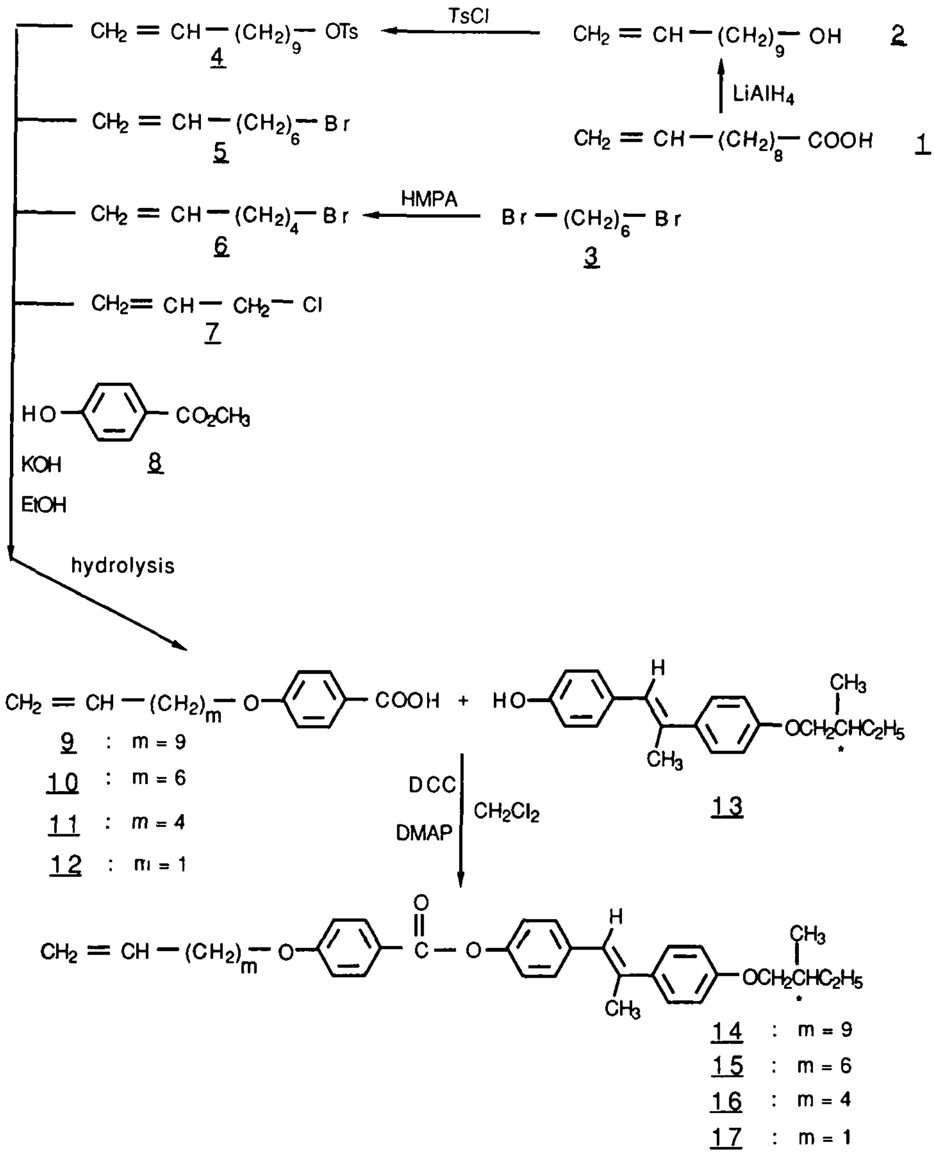
$\underline{4}$ was prepared as previously described [16a].

6-Bromo-1-hexane ($\underline{6}$)

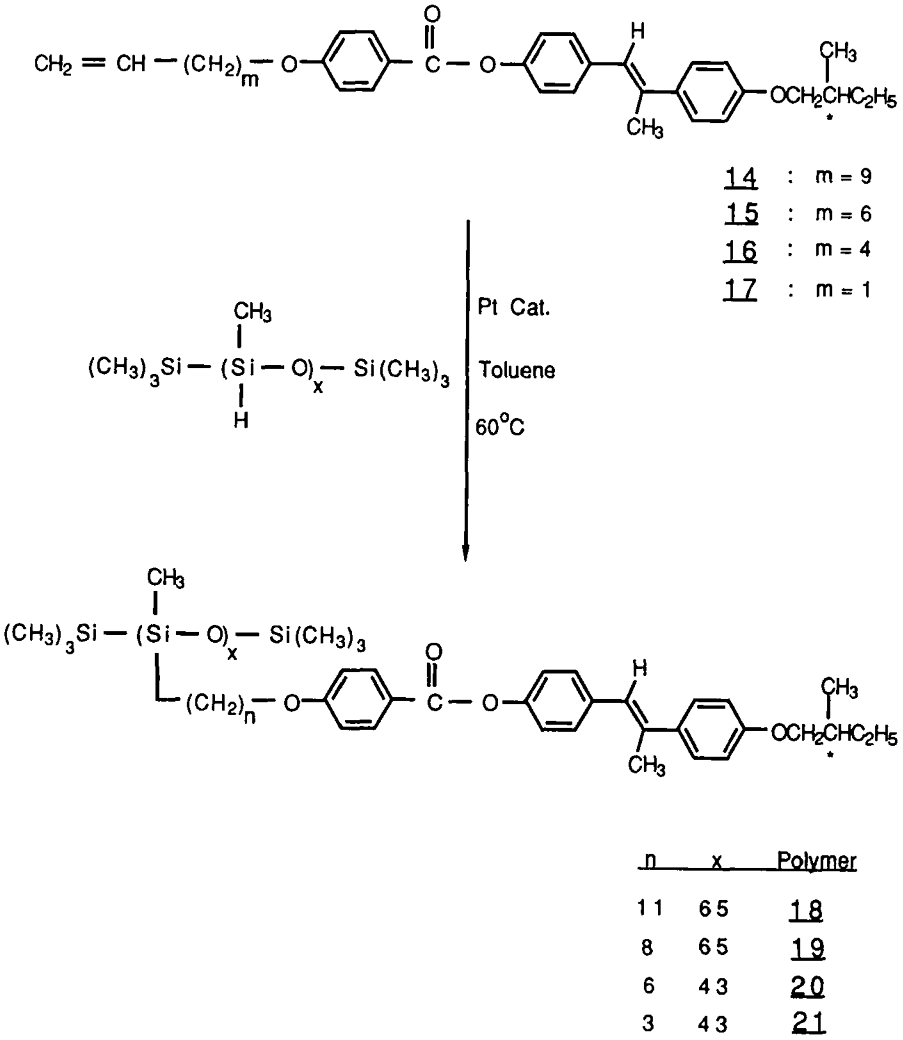
$\underline{6}$ was synthesized from 1,6-dibromohexane according to a literature procedure [25]. The detailed synthesis was previously described [17].

p-(10-Undecen-1-yloxy)benzoic Acid ($\underline{9}$)

Methyl *p*-hydroxybenzoate (10.0 g, 0.0658 mol) and 4.4 g (0.0790 mol) potassium hydroxide were dissolved in 100 mL of 95% ethanol. After stirring at room temperature for 30 min, 21.4 g (0.0658 mol) of 10-undecen-1-yl tosylate were added and the resulting solution was stirred at reflux temperature under nitrogen for 8 h, cooled to room temperature, and the solvent was removed on a rotavapor. The residue was taken up in 200 mL water, neutralized with dilute HCl, and extracted with diethyl ether. The

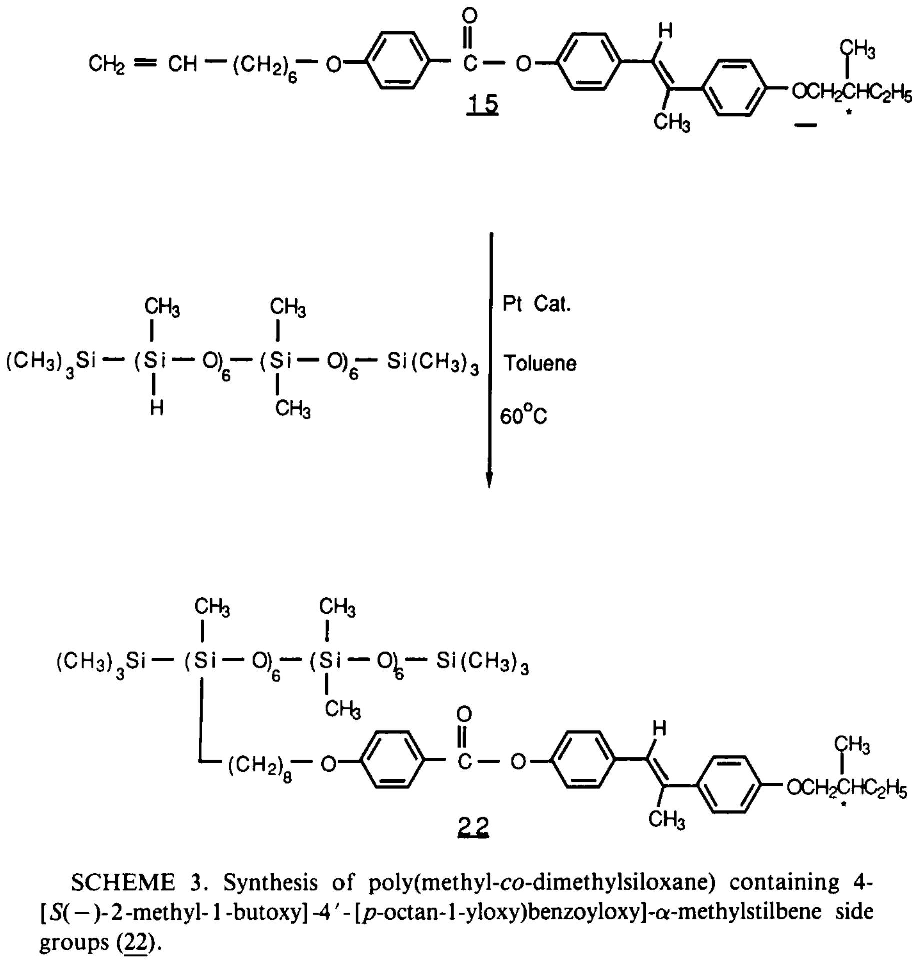


SCHEME 1. Synthesis of 4-[*S*(−)-2-methyl-1-butoxy]-4′-[*p*-(ω-alkan-1-yloxy)-benzoyloxy]-α-methylstilbene monomers (14, 15, 16, and 17).



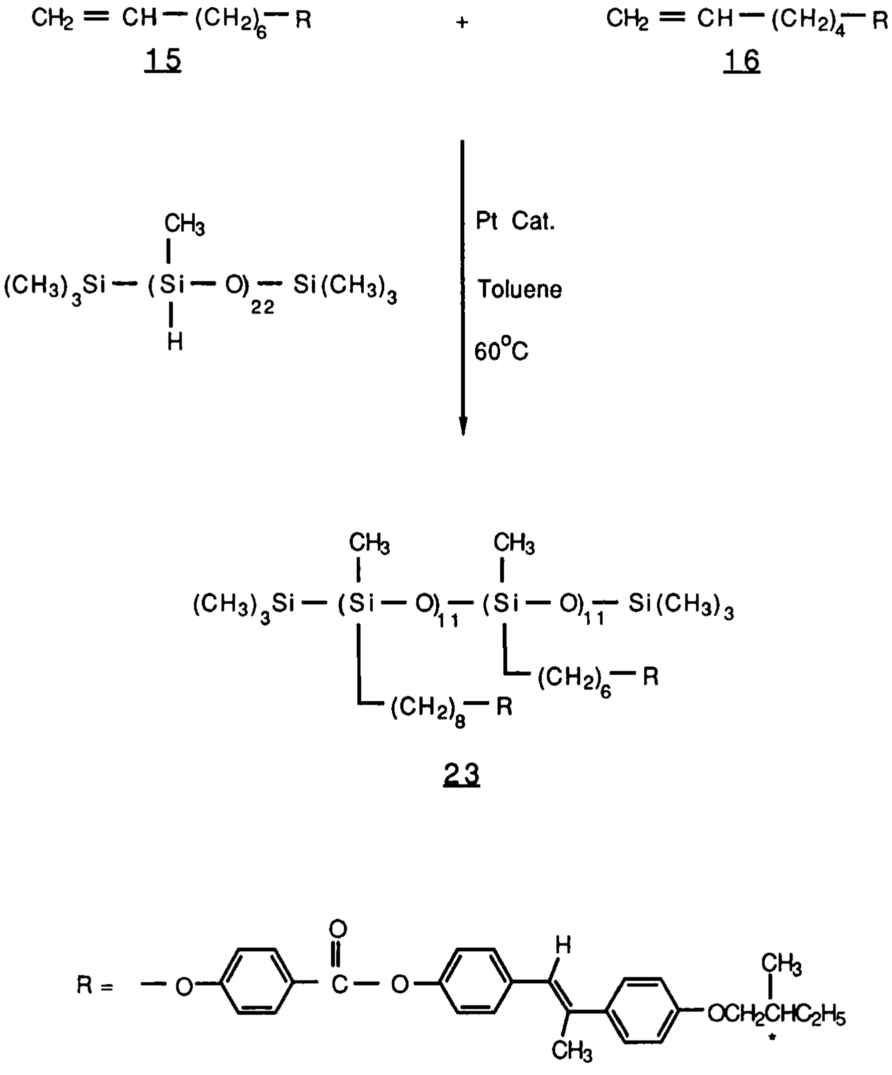
n	x	Polymer
11	65	18
8	65	19
6	43	20
3	43	21

SCHEME 2. Synthesis of poly(methylsiloxane)s containing 4-[*S*(−)-2-methyl-1-butoxy]-4′-[*p*-(ω-alkan-1-yloxy)benzoyloxy]-α-methylstilbene side groups (18, 19, 20, and 21).



SCHEME 3. Synthesis of poly(methyl-*co*-dimethylsiloxane) containing 4-[*S*(−)-2-methyl-1-butoxy]-4′-[*p*-octan-1-yloxy)benzoyloxy]-α-methylstilbene side groups (22).

ether layer was dried over anhydrous $MgSO_4$, filtered, and the solvent was distilled in a rotary evaporator to yield 16 g of a solid product. The solid was dissolved in 400 mL of 3*N* KOH solution in 95% EtOH. The resulting solution was stirred at reflux temperature under nitrogen overnight, cooled to room temperature, and acidified with dilute HCl. The solvent was removed on a rotavapor, and the resulting residue was dried in vacuum. After recrystallization from MeOH, 11.0 g (58%) of white crystals were obtained. Purity: 98% (HPLC). Characterization of 9 is presented in Table 1.



SCHEME 4. Synthesis of copoly(methylsiloxane) containing both 4-[*S*(−)-2-methyl-1-butoxy]-4′-[*p*-(8-octan-1-yloxy)benzoyloxy]-α-methylstilbene and 4-[*S*(−)-2-methyl-1-butoxy]-4′-[*p*-(6-hexan-1-yloxy)benzoyloxy]-α-methylstilbene side groups (23).

TABLE 1. Characterization and Thermal Transitions of *p*-(ω-Alken-1-yloxy)benzoic Acids

Compound	Yield, %	Phase transitions temperature, °C, and enthalpy changes, kcal/mol	^{1}H-NMR (CDCl$_3$, TMS, δ, ppm) chemical shifts
9	58	k 88 (5.61) $s_X{}^{b}$ 125 (0.19) s_A 137^{a} *n* 139^{a} (0.75) i i 135 (0.36) *n* 127 (0.15) s_A 122 (0.13) $s_X{}^{b}$ 106 (−) $s_X{}^{b}$ 69 (2.02) k	1.31–2.03 (m, 16H, $-(C\underline{H}_2)_8-$), 4.02 (t, 2H, $-C\underline{H}_2-O-$), 4.96 and 5.83 (m, 3H, $-C\underline{H}=C\underline{H}_2$), 6.95 and 8.07 (2d, 4H, ArH)
10	52	k 85 (5.31) s_A 97 (0.23) *n* 143 (0.43) i 138 (0.42) *n* 93 (0.21) s_A 70 (1.56) k 62 (0.74) k	1.42–2.05 (m, 10H, $-(C\underline{H}_2)_5-$), 4.02 (t, 2H, $-C\underline{H}_2-O-$), 4.97 and 5.80 (m, 3H, $-C\underline{H}=C\underline{H}_2$), 6.95 and 8.07 (2d, 4H, ArH)
11	59	k 102 (3.56) $s_X{}^{b}$ 109 (0.13) *n* 144 (0.46) i i 140 (0.35) *n* 91 (0.27) $s_X{}^{b}$ 87^{a} k 84^{a} (3.44) k	1.62–2.16 (m, 6H, $-(C\underline{H}_2)_3-$), 4.04 (t, 2H, $-C\underline{H}_2-O-$), 5.01 and 5.85 (m, 3H, $-C\underline{H}=C\underline{H}_2$), 6.95 and 8.08 (2d, 4H, ArH)
12	81	k 166 (5.42) *n* 176 (0.55) i i 159 (1.19) *n* 153 (3.74) k	4.63 (d, 2H, $-C\underline{H}_2-O-$), 5.40 and 6.08 (m, 3H, $-C\underline{H}=C\underline{H}_2$), 6.99 and 8.09 (2d, 4H, ArH)

[a] Overlapped transitions, enthalpy change corresponds to the sum of both transitions.
[b] Unidentified smectic phase.

p-(7-Octen-1-uloxy)benzoic Acid (10) and *p*-(5-Hexen-1-yloxy)benzoic Acid (11)

Both 10 and 11 were synthesized by the procedure used for the synthesis of *p*-(10-undecen-1-yloxy)benzoic acid, except that 8-bromo-1-octene and respectively, 6-bromo-1-hexene, were used instead of 10-undecen-1-yl tosylate. Table 1 contains the ^{1}H-NMR data and the thermal characterization of both compounds.

p-(2-Propen-1-yloxy)benzoic Acid (12)

12 was synthesized by a similar procedure to that used for the preparation of 9, 10, and 11 except that 2 equivalents of allyl chloride were used at the beginning of the reaction and an additional equivalent of allyl chloride was added after 8 h. Analytical data of 12 are available in Table 1.

4-[*S*(−)-2-Methyl-1-butoxy]-4′-(hydroxy)-α-methylstilbene (13)

13 was prepared as described in a previous publication from our laboratory [2].

4-[S(−)-2-Methyl-1-butoxy]-4′-[*p*-(10-undecen-1-yloxy)benzoyloxyl-α-methylstilbene (14)

p-(10-Undecen-1-yloxy)benzoic acid (0.98 g, 3.37 mmol), 1.05 g (3.54 mmol) of 4-[*S*(−)-2-methyl-1-butoxy]-4′-(hydroxy)-α-methylstilbene, 0.76 g (3.71 mmol) of dicyclohexylcarbodiimide and 0.082 g (0.67 mmol) of 4-dimethylaminopyridine were added into a 50-mL beaker containing 25 mL dry CH_2Cl_2. The beaker was sealed with parafilm and the solution was stirred at room temperature for 6 h. The reaction mixture was filtered to remove the white precipitate, mixed with some additional $CHCl_3$, and then was precipitated into 150 mL $MeOH/H_2O$ = 4/1 (v/v) mixture. The white precipitate was filtered, dried, and analyzed by IR spectroscopy. The precipitation was repeated until the IR spectrum showed no residual dicyclohexylcarbodiimide and dicyclohexylurea remaining in the sample. Then the residue was dried in vacuum to yield 1.4 g (70%) of white solid. Analytical data are presented in Table 2.

4-[*S*(−)-2-Methyl-1-butoxy]-4′-[*p*-(7-octen-1-yloxy)benzoyloxy]-α-methylstilbene (15), 4-[*S*(−)-2-Methyl-1-butoxy]-4′-[*p*-(5-hexen-1-yloxy)benzoyloxy]-α-methylstilbene (16), and 4-[*S*(−)-2-Methyl-1-butoxy]-4′-[*p*-(2-propen-1-yloxy)benzoyloxy]-α-methylstilbene (17)

All compounds were synthesized by a similar procedure with that used for the preparation of 4-[*S*(−)-2-methyl-1-butoxy]-4′-[*p*-(10-undecen-1-yloxy)benzoyloxy]-α-methylstilbene, except that the corresponding *p*-(ω-alken-1-yloxy)benzoic acid was used instead of *p*-(10-undecen-1-

yloxy)benzoic acid. Table 2 summarizes the characterization of compounds 15, 16, and 17.

Poly(methylsiloxane)s, Copoly(methylsiloxane), and Poly(methyl-*co*-dimethylsiloxane) Containing Mesogenic Side Groups

The poly(methylsiloxane)s and poly(methyl-*co*-dimethylsiloxane) were prepared by the hydrosilation reaction of 4-[*S*(−)-2-methyl-1-butoxy]-4′-[*p*-(ω-alken-1-yloxy)benzoyloxy]-α-methylstilbene with (14–17), a poly(methylhydrosiloxane) having a number-average degree of polymerization of 65 (or 43), and poly[(50–55%)-methylhydro-*co*-(45–50%)-dimethysiloxane], respectively. The copoly(methylsiloxane) was prepared by the hydrosilation reaction of a 1/1 ratio of monomers 15 and 16 with a poly(methylhydrosiloxane) with $DP = 43$. An example of the hydrosilation reaction is given below.

A solution of 0.70 g (1.23 mmol, 20% excess) of 4-[*S*(−)-2-methyl-1-butoxy]-4′-[*p*-(10-undecen-1-yloxy)benzoyloxy]-α-methylstilbene, 0.061 g poly(methylhydrosiloxane), and a catalytic amount of platinum divinyltetramethyldisiloxane complex in 10 mL dry toluene was heated to 60°C under N_2 until IR and NMR analyses showed that the Si—H peak (2150 cm^{-1}) disappeared. Then 1.0 g of 1-octene was added to the reaction mixture to consume the undetectable residual Si—H groups. After an additional 8 h of reaction, the resulting polymer was separated by precipitation into methanol. The polymer was purified by filtering its chloroform solution through fluted filter paper and precipitation into methanol/acetone: 70/30 (v/v). The purification was repeated several times until no unreacted monomer was observed in the resulting polymer by HPLC and GPC analyses. The analysis of all polymers by 200 MHz ^{1}H-NMR spectroscopy showed no detectable incorporation of 1-octene into the polymer structure (ratio of signals $-C\underline{H}_2-Si-$ at $\delta = 0.46$ ppm to $HC{=}C-C\underline{H}_3$ at $\delta = 2.04$ ppm to 2 aromatic protons ortho to $-C{=}O$ group from the benzoyloxy group at $\delta = 7.94$ ppm). Nevertheless, the addition of 1-octene was used in all cases to prevent the presence of any unreacted Si—H groups in the final polymer.

RESULTS AND DISCUSSION

The synthesis and characterization of polymethacrylates, polyacrylates, and poly(methylsiloxane)s containing 4-[*S*(—)-2-methyl-1-butoxy]-4′-(ω-alkan-1-yloxy)-α-methylstilbene side groups with ω-alkanyl con-

TABLE 2. Characterization and Thermal Transitions of 4-[*S*(−)-2-Methyl-1-butoxy]-4′-[*p*-(ω-alken-1-yloxy)benzoyloxy]-α-methylstilbene Monomers

Monomer	Yield, %	Phase transitions temperature, °C, and enthalpy changes, kcal/mol	^{1}H-NMR ($CDCl_3$, TMS, δ, ppm) chemical shifts
$\underline{14}$	70	k 84 (6.67) s_C^* 97 (0.06) s_A 158 (0.35) i i 153 (0.37) s_A 92 (0.09) s_C^* 47 (5.17) k	0.9–1.1 (m, 6H, $C\underline{H}_3-$), 1.3–2.1 (m, 19H, $CH_3-C\underline{H}_2-$, $-(C\underline{H}_2)_8-$, $-C\underline{H}-$), 2.27 (s, 3H, $C\underline{H}_3-C=$-$C-Ph$), 3.82 (m, 2H, $-C\underline{H}_2-OPh$), 4.05 (t, 2H, $-CH_2-C\underline{H}_2-OPh$), 4.96 and 5.84 (m, 3H, $-C\underline{H}=C\underline{H}_2$), 6.77 (s, 1H, $-\underline{H}C=C-Ph$), 6.89–8.17 (6d, 12H, ArH)
$\underline{15}$	86	k 71 (5.27) s_C^* 77 (0.21) s_A 170 (0.35) i i 166 (0.43) s_A 62 (0.20) s_C^* 47 (4.17) k	0.9–1.1 (m, 6H, $C\underline{H}_3-$), 1.3–2.1 (m, 13H, $CH_3-C\underline{H}_2-$, $-(C\underline{H}_2)_5-$, $-C\underline{H}-$), 2.26 (s, 3H, $C\underline{H}_3-C=$-$C-Ph$), 3.82 (m, 2H, $-C\underline{H}_2-OPh$), 4.05 (t, 2H, $-CH_2-C\underline{H}_2-OPh$), 4.98 and 5.81 (m, 3H, $-C\underline{H}=C\underline{H}_2$), 6.77 (s, 1H, $-\underline{H}C=C-Ph$), 6.89–8.17 (6d, 12H, ArH)

16	87	k 73 (0.09) k 92 (6.58) s_A 179 (0.34) i i 175 (0.35) s_A 65 (6.00) k	0.9-1.1 (m, 6H, $C\underline{H}_3-$), 1.2-2.2 (m, 9H, $CH_3-C\underline{H}_2-$, $-(C\underline{H}_2)_3-$, $-C\underline{H}-$), 2.27 (s, 3H, $C\underline{H}_3-C=C-Ph$), 3.80 (m, 2H, $-C\underline{H}_2-OPh$), 4.06 (t, 2H, $-CH_2-C\underline{H}_2-OPh$), 5.02 and 5.83 (m, 3H, $-C\underline{H}=C\underline{H}_2$), 6.78 (s, 1H, $-\underline{H}C=C-Ph$), 6.89-8.17 (6d, 12H, Ar$\underline{H}$)
17	31	k 107^a k 116^a (8.34) s_A 203 (0.43) i i 196 (0.38) s_A 86^a k 83^a (6.86) k	0.9-1.1 (m, 6H, $C\underline{H}_3-$), 1.2-2.0 (m, 3H, $CH_3-C\underline{H}_2-$, $-C\underline{H}-$), 2.27 (s, 3H, $C\underline{H}_3-C=C-Ph$), 3.82 (m, 2H, $-C\underline{H}_2-OPh$), 4.66 (d, 2H, $-CH_2-C\underline{H}_2-OPh$), 5.41 and 6.10 (m, 3H, $C\underline{H}=C\underline{H}_2$), 6.77 (s, 1H, $-\underline{H}C=$-$C-Ph$), 6.89-8.19 (6d, 12$\underline{H}$, ArH)

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[a] Overlapped transitions, enthalpy change corresponds to the sum of both transitions.

taining from two to eleven methylenic units were reported previously [1, 2]. Poly(methylsiloxane)s containing 6-hexyl and 8-octyl as ω-alkanyl groups exhibited enantiotropic s_A and s_C^* mesophases [2]. All other polymers exhibited only enantiotropic s_A mesophases. As a consequence, we decided to further investigate the synthesis of poly(methylsiloxane)s containing 4-[*S*(−)-2-methyl-1-butoxy]-4′-[*p*-(ω-alkan-yloxy)benzoyloxy]-α-methylstilbene side groups. Scheme 1 outlines the synthesis of *p*-(ω-alkan-1-yloxy)benzoic acid derivatives 9 to 12 and of the 4-[*S*(−)-2-methyl-1-butoxy]-4′-[*p*-(ω-alkan-1-yloxy)benzoyloxy]-α-methylstilbene derivatives 14 to 17. The mesophases displayed by compounds 9 to 12 are summarized in Table 1. Compounds 9 to 12 exhibit mesomorphism due to their dimeric structure obtained through the hydrogen bonding of their carboxylic groups. Representative DSC traces of compounds 14 to 17 are presented in Figs. 1, 2, and 3. Their mesomorphic behavior is summarized in Table 2. Their DSC traces will be discussed briefly since they resemble the behavior of their corresponding poly(methylsiloxane)s. 14, 15, 16, and 17 exhibit an enantiotropic $s_A$mesophase which displays a characteristic focal conic texture (Fig. 4a). As observed from Fig. 1, compounds 14 and 15 exhibit a second enantiotropic mesophase which on the optical polarized microscope is characterized by the appearance of equidistant lines on the fan-shaped texture. This texture suggests the existence of a typical structure of a s_C^* mesophase [6b, 8, 10, 24] (Fig. 4b). Therefore, we believe that the second enantiotropic phase exhibited by 14 and 15 is most probably a s_C^* mesophase (Table 2).

Scheme 2 describes the synthesis of poly(methylsiloxane)s 18 to 21. The DSC traces of the polymers 18 to 21 are presented in Figs. 5 and 6. Their mesomorphic behavior is summarized in Table 3. Some of these polymers were synthesized two times, and their phase transitions were in perfect agreement. Polymers 18, 19, 20, and 21 display two melting transitions on their first DSC heating scan (Fig. 5a, c and Fig. 6c, e), and one melting and crystallization transition on their second and subsequent heating and first and subsequent cooling DSC scans (Fig. 5b, d and Fig. 6d, f). Regardless of the thermal history of the sample, 18 displays only an enantiotropic s_A mesophase (Fig. 5a, b). Upon cooling from the isotropic phase on the optical polarized microscope, batonnets appear first. Then they are transformed into a focal conic texture. 19, 20, and 21 display both enantiotropic s_A and enantiotropic s_C^* mesophases. The droplet texture with fan-shaped domains in each droplet appears at the very beginning of the i→s_A transition, before the typical focal conic texture is generated.

After the i→s_A transition (at 213°C), 19 displays a characteristic s_A tex-

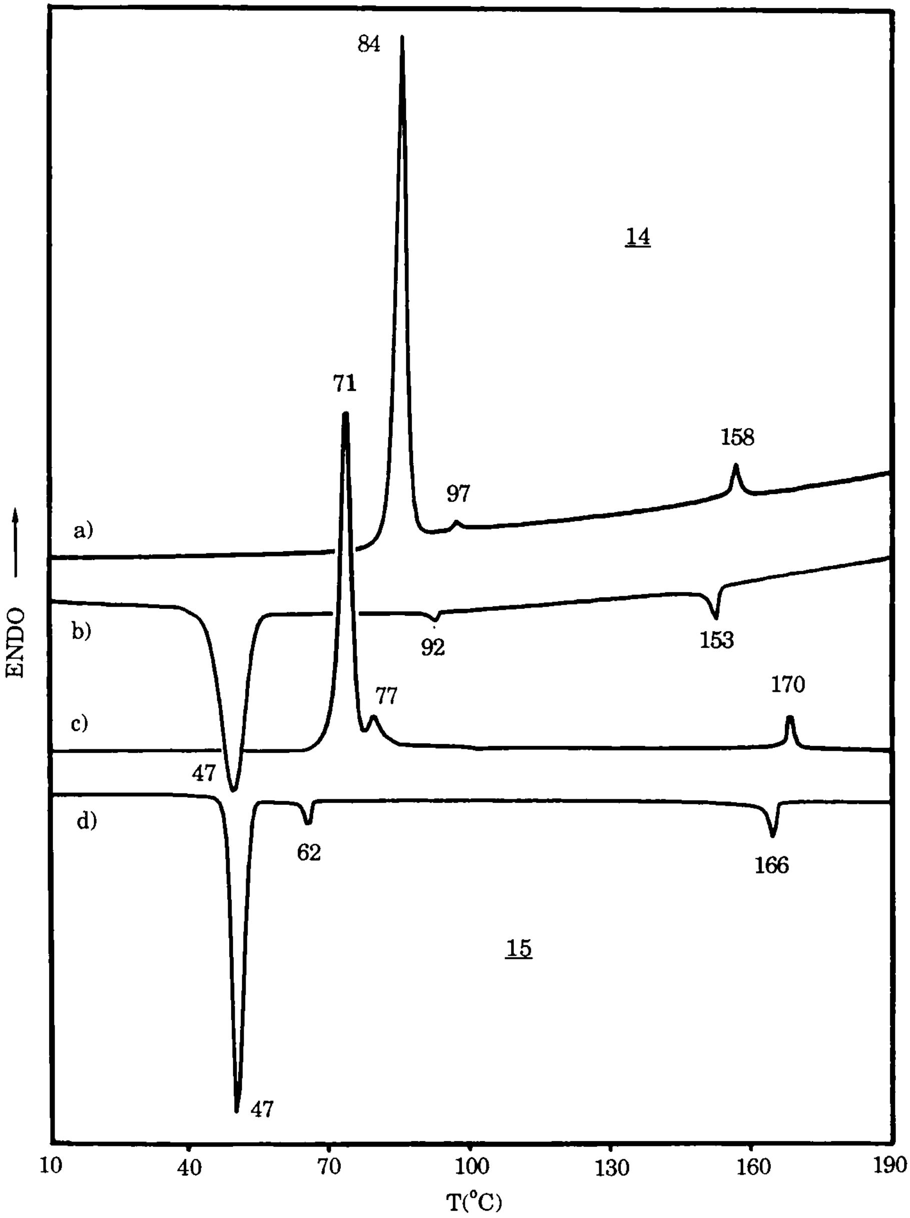

FIG. 1. DSC thermograms (20°C/min) of 4-[*S*(−)-2-methyl-1-butoxy]-4′-[*p*-(10-undecen-1-yloxy)benzoyloxy]-α-methylstilbene (<u>14</u>) [a) second heating scan; b) second cooling scan], and 4-[*S*(−)-2-methyl-1-butoxy]-4′-[*p*-(7-octen-1-yloxy)benzoyloxy]-α-methylstilbene (<u>15</u>) [c) second heating scan; d) second cooling scan].

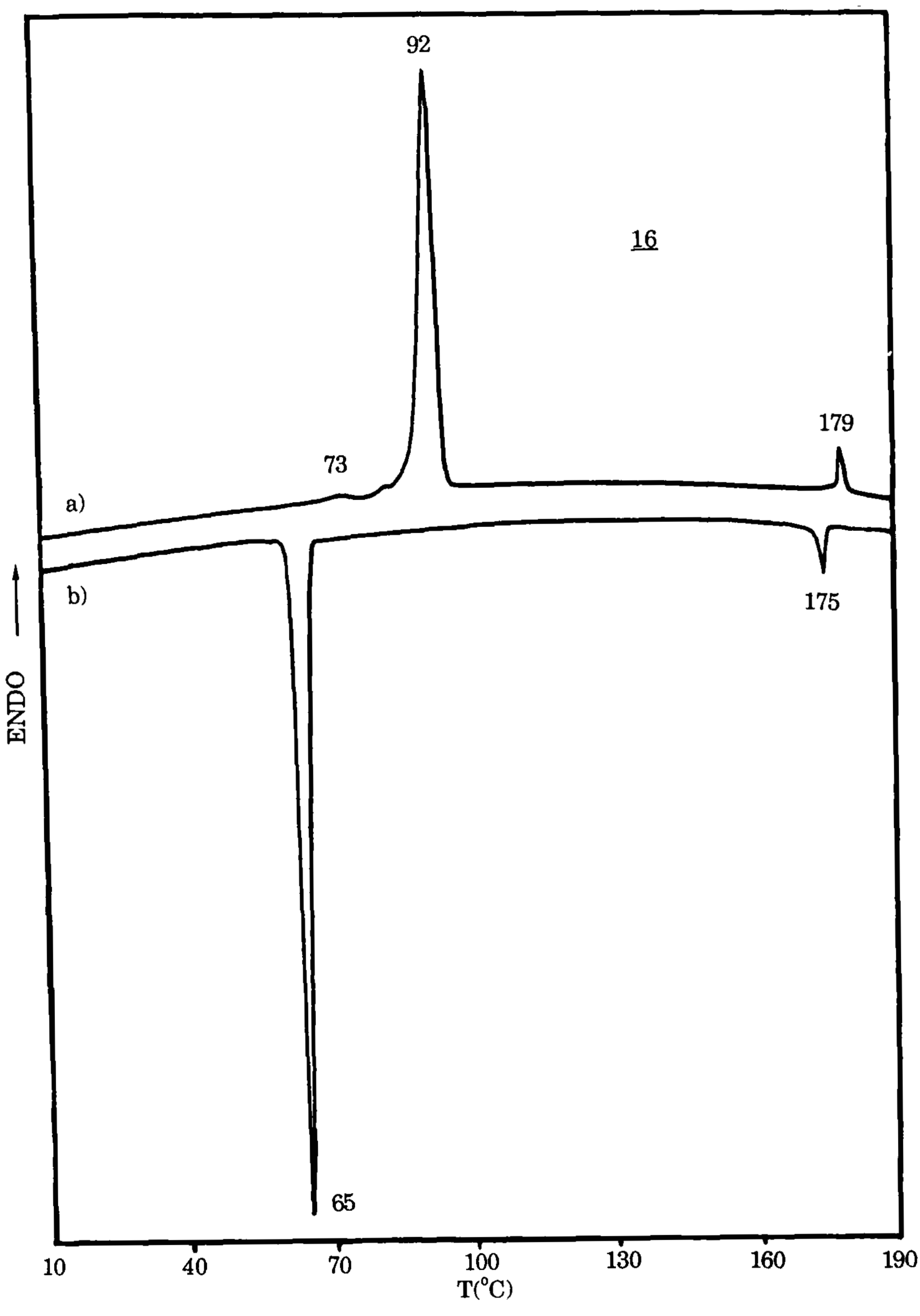

FIG. 2. Second heating (a) and first cooling (b) DSC thermograms (20°C/min) of 4-[S(−)-2-methyl-1-butoxy]-4′-[p-(5-hexen-1-yloxy)benzoyloxy]-α-methylstilbene (16).

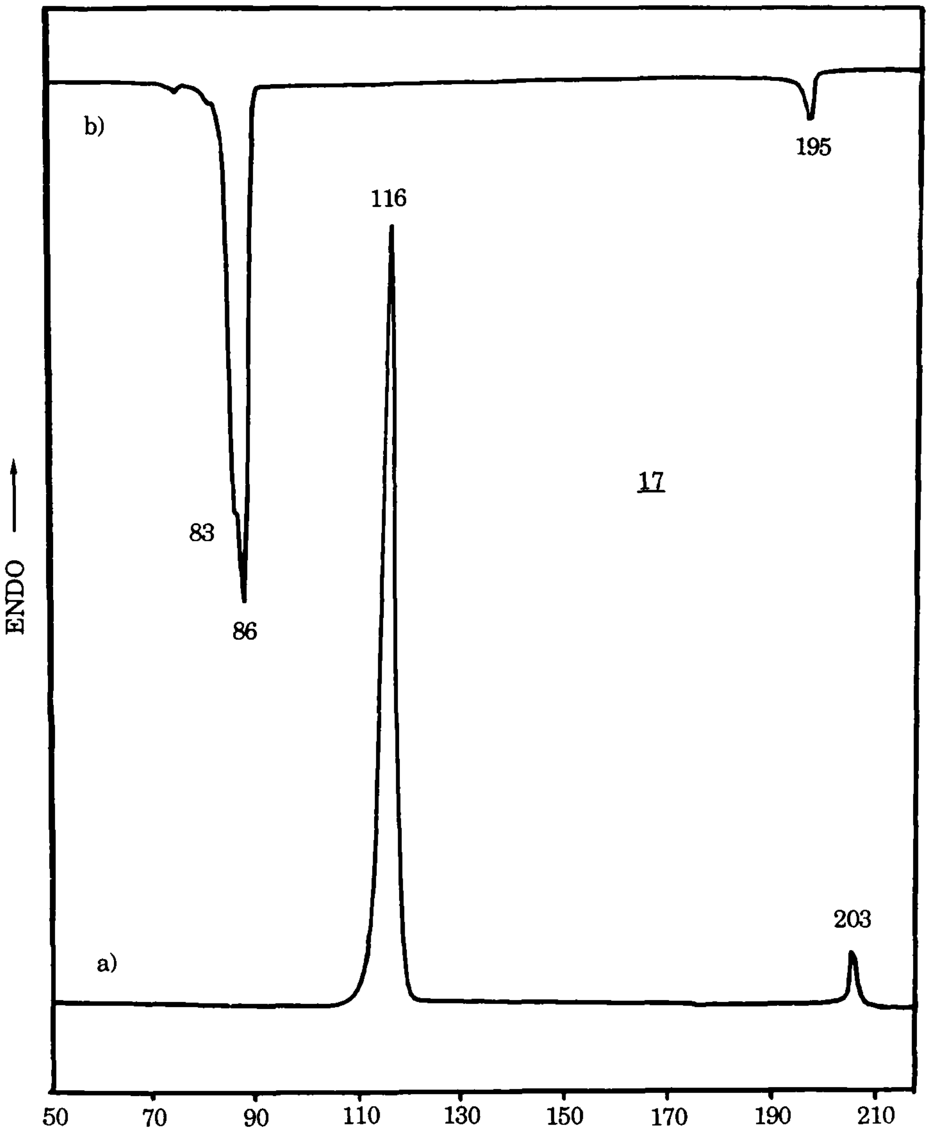

FIG. 3. First heating (a) and first cooling (b) DSC thermograms (20°C/min) of 4-[*S*(−)-2-methyl-1-butoxy]-4′-[*p*-(2-propen-1-yloxy)benzoyloxy]-α-methylstilbene (17).

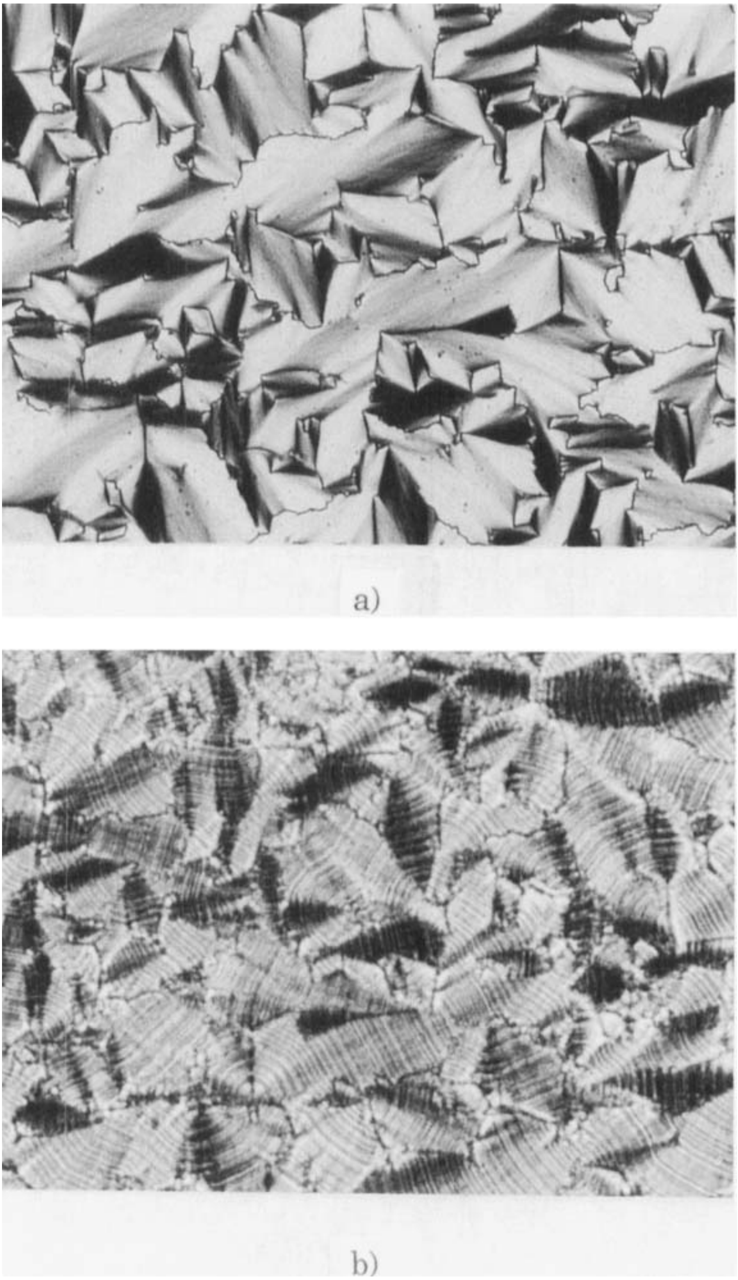

FIG. 4. a) Representative optical polarized micrograph (100 ×) of the focal conic texture of the s_A phase of 15 at 156.1 °C. b) Representative optical polarized micrograph (100 ×) of the focal conic texture with equidistant lines exhibited by the s_C^* phase of 15 at 60 °C. c) Representative optical polarized micrograph (100 ×) of the focal conic texture of the s_A phase of 19 at 212.7 °C. d) Representative polarized micrograph (100 ×) of the focal conic texture with equidistant lines of the s_C^* phase of 19 at 188.8 °C.

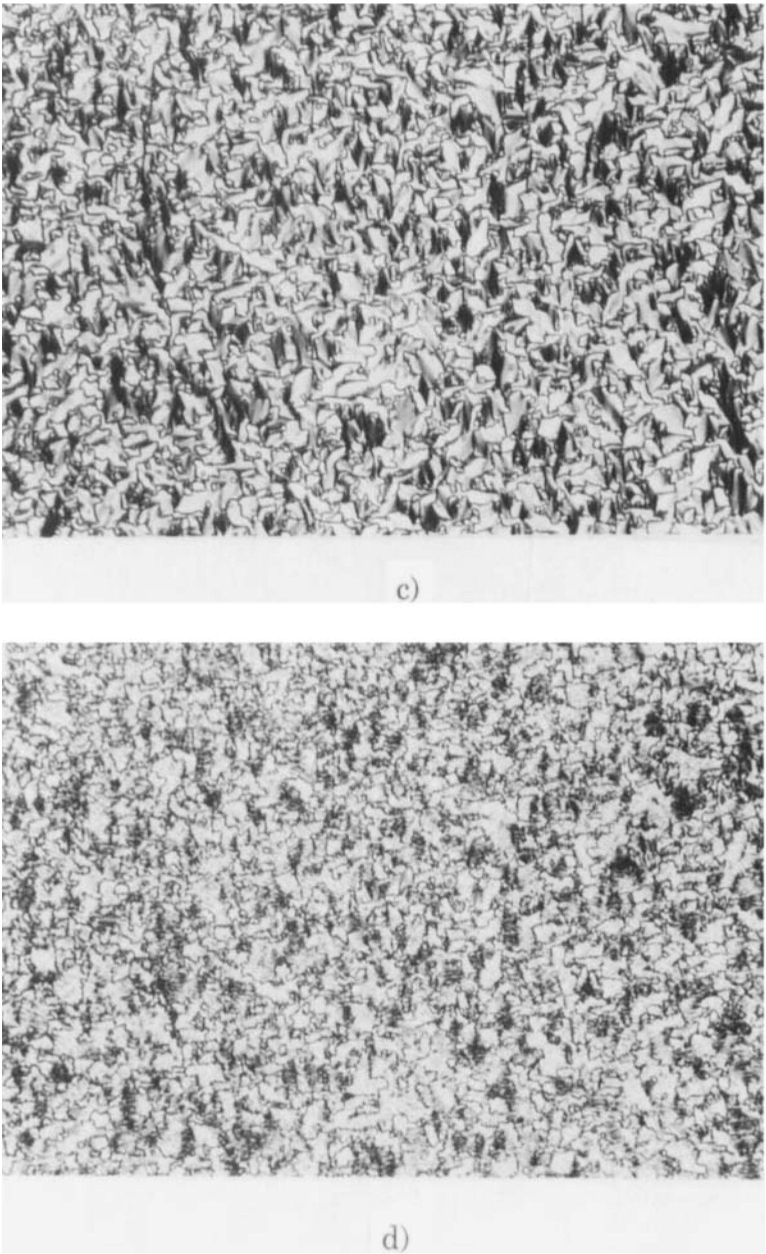

FIG. 4 (continued).

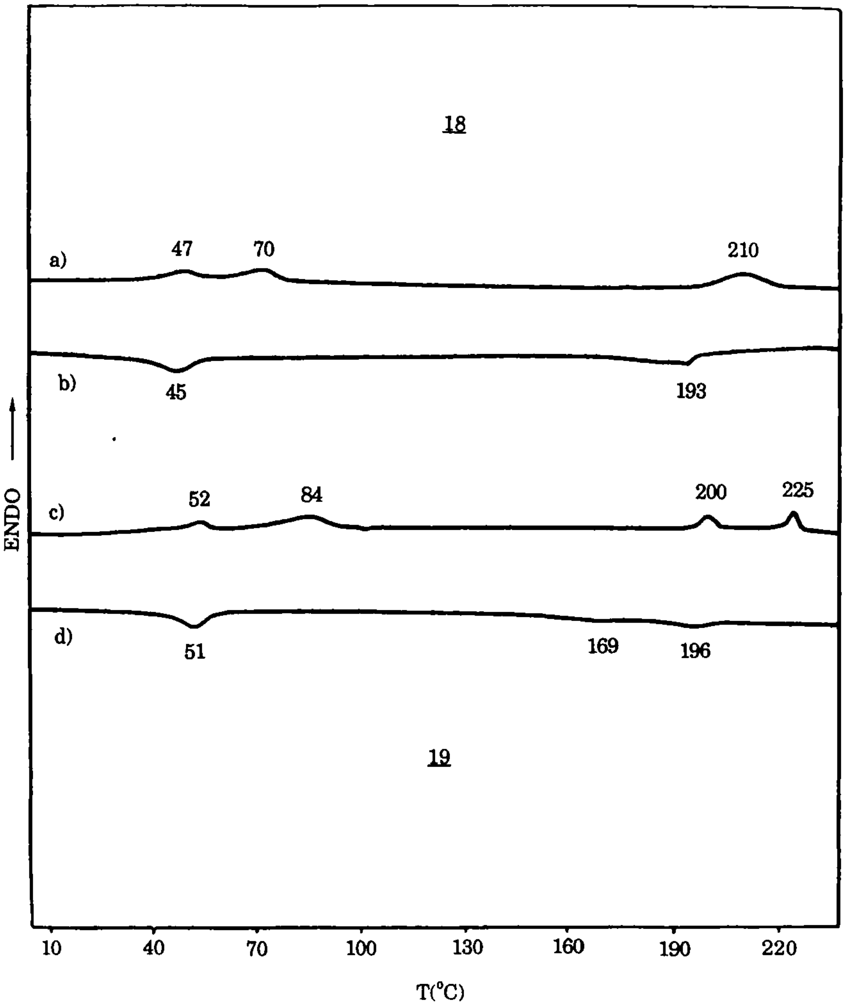

FIG. 5. DSC thermograms (20°C/min) of the poly(methylsiloxane) containing 4-[*S*(−)-2-methyl-1-butoxy]-4′-[*p*-(11-undecan-1-yloxy)benzoyloxy]-α-methylstilbene (18) [a) first heating scan; b) first cooling scan] and of the poly(methylsiloxane) containing 4-[*S*(−)-2-methyl-1-butoxy]-4′-[*p*-(8-octan-1-yloxy)benzoyloxy]-α-methylstilbene side groups (19) [c) first heating scan; d) first cooling scan].

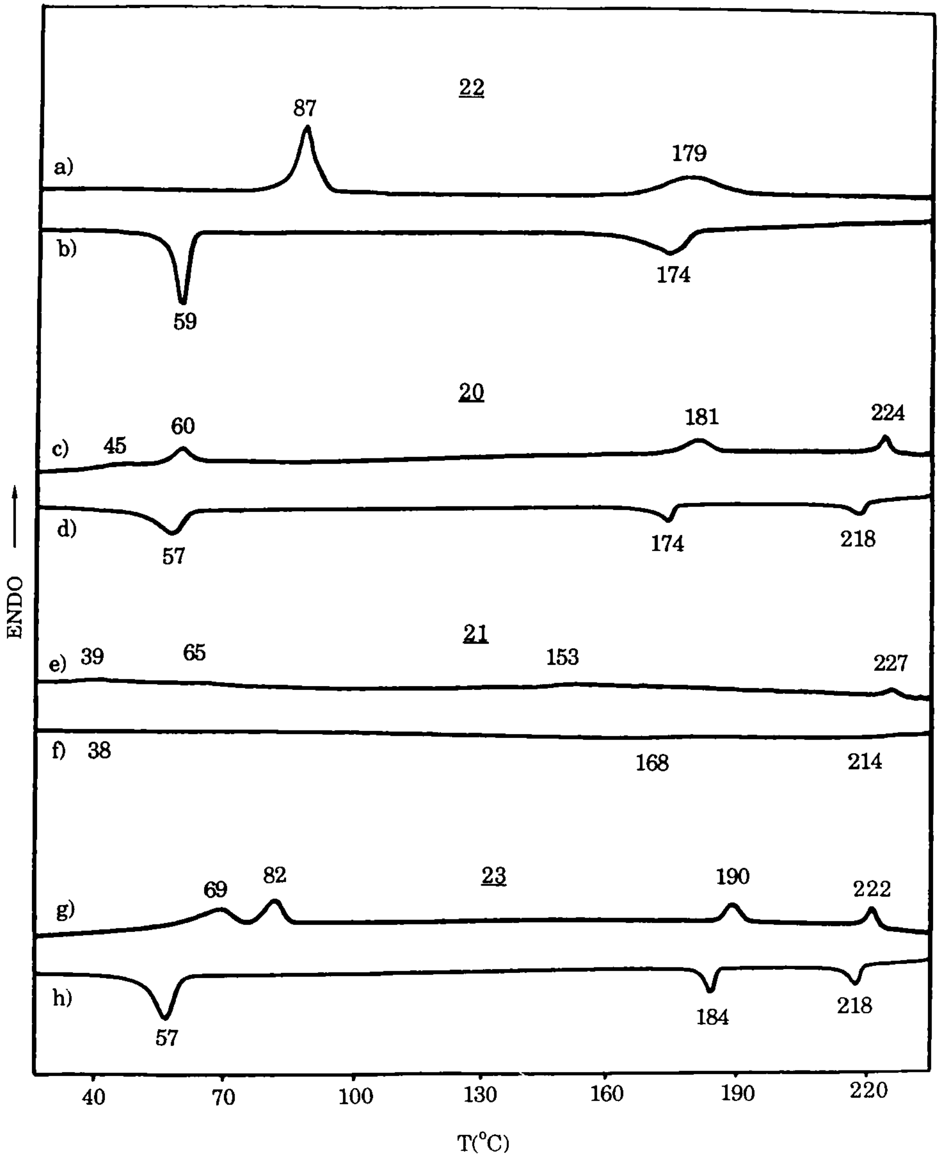

FIG. 6. DSC thermograms (20°C/min) of the poly(methyl-*co*-dimethylsiloxane) containing 4-[*S*(−)-2-methyl-1-butoxy]-4′-[*p*-(8-octan-1-yloxy)benzoyloxy]-α-methylstilbene side groups (22) [a) second heating scan; b) first cooling scan], the poly(methylsiloxane) containing 4-[*S*(−)-2-methyl-1-butoxy]-4′-[*p*-(6-hexan-1-yloxy)benzoyloxy]-α-methylstilbene (20) [c) first heating scan; d) first cooling scan], the poly(methylsiloxane) containing 4-[*S*(−)-2-methyl-1-butoxy]-4′-[*p*-(3-propan-1-yloxy)benzoyloxy]-α-methylstilbene side groups (21) [e) first heating scan; f) first cooling scan], and of the copoly(methylsiloxane) containing both 4-[*S*(−)-2-methyl-1-butoxy]-4′-[*p*-(8-octan-1-yloxy)benzoyloxy]-α-methylstilbene and 4-[*S*(−)-2-methyl-1-butoxy]-4′-[*p*-(6-hexan-1-yloxy)benzoyloxy]-α-methylstilbene side groups (23) [g) second heating scan; h) first cooling scan].

TABLE 3. Thermal Transitions and Thermodynamic Parameters of the Liquid Crystalline Poly(methylsiloxane)s, Poly(methyl-*co*-dimethylsiloxane), and Copoly(methylsiloxane)

Polymer				Transition temperatures, °C, and corresponding enthalpy, kcal/mru,[b] and entropy, cal/K·mru, changes	
	DP	M_n	M_w/M_n		
No.	NMR	GPC		Heating	Cooling
18	65	19,300	2.03	k 47[a] k 70[a] (1.80/ –) s_A 210 (1.13/2.34) i	i 193 (0.82/1.76) s_A 45 (0.70/2.20) k
				k 56[a] k 70[a] (1.57/ –) s_A 194 (1.03/2.21) i	i 165 (0.92/2.10) s_A 39 (0.69/2.21) k
19	65	22,900	2.86	k 52 (0.18/0.55) k 84 (0.99/2.77) s_C^* 200 (0.31/0.66) s_A 225 (0.38/0.76) i	i 196 (0.41/0.87) s_A 169 (0.24/0.54) s_C^* 51 (1.04/3.20) k
				k 76 (0.43/1.23) s_C^* 173 (0.21/0.47) s_A 202 (0.26/0.55) i	i 178 (0.24/0.53) s_A 140 (0.10/0.24) s_C^* 44 (0.88/2.78) k
20	22	13,600	2.21	k 45[a] k 60[a] (1.10/ –) s_C^* 181 (0.42/0.93) s_A 224 (0.33/0.66) i	i 218 (0.37/0.75) s_A 174 (0.39/0.87) s_C^* 57 (0.99/3.00) k
				k 70 (1.11/3.24) s_C^* 178 (0.39/0.86) s_A 222 (0.39/0.79)	i 217 (0.37/0.76) s_A 173 (0.37/0.83) s_C^* 57 (0.96/2.91) k

21	22	9,900	1.95	k 39 (0.12/0.38) k 65 (0.02/0.06) s_C^* 153 (0.10/0.23) s_A 227 (0.15/0.33) i	i 214 (0.26/0.53) s_A 168 (0.24/0.54) s_C^* 38 k
				k 37 (0.16/0.52) s_C^* 116 (0.27/0.69) s_A 184 (0.03/0.07) i	i 214 (0.26/0.53) s_A 146 (0.12/0.29) s_C^* 28 (0.12/0.40) k
22	12	7,400	1.65	k 54[a] k 83[a] k 90[a] (2.30/ –) s_C^* 179 (1.41/3.13) i	i 174 (1.55/3.48) s_C^* 59 (1.43/4.31) k
				k 87 (1.78/4.95) s_C^* 179 (1.41/3.13) i	i 174 (1.51/3.39) s_C^* 59 (1.40/4.21) k
				k 87 (1.76/4.89) s_C^* 178 (1.40/3.10) i	i 172 (1.47/3.31) s_C^* 59 (1.41/4.24) k
23	22	13,000	1.89	k 38[a] k 49[a] k 63[a] k 82[a] (1.08/ –) s_C^* 192 (0.34/0.73) s_A 223 (0.36/0.72) i	i 218 (0.41/0.84) s_A 184 (0.37/0.81) s_C^* 57 (1.39/4.22) k
				k 69[a] k 82[a] (1.68/ –) s_C^* 190 (0.33/0.72) s_A 222 (0.39/0.79) i	i 217 (0.39/0.79) s_A 183 (0.37/0.82) s_C^* 57 (1.37/4.15) k
				k 69[a] k 81[a] (1.72/ –) s_C^* 189 (0.32/0.69) s_A 221 (0.37/0.75) i	i 216 (0.38/0.78) s_A 183 (0.38/0.83) s_C^* 57 (1.27/3.84) k

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[a] Overlapped transitions, enthalpy change corresponds to the sum of both transitions.

[b] mru = mole repeat unit.

ture (Fig. 4c). On cooling from the s_A phase, 19 undergoes a transition from the s_A into a s_C^* phase at 189 °C. This transition is accompanied by the formation of equidistant lines on the focal conic texture (Fig. 4d). From the DSC traces of 19 (Fig. 5d), the i→s_A and s_A→s_C^* transition occur at 190 and 169 °C while on the optical polarized microscope they are observed at 213 and 189 °C. This difference is consistent with the difference between the two heating rates used and the reading of onset on the microscope versus minimum of the peak on the DSC trace. In addition, if extensive annealing is performed at about 200 °C, these polymers start to degrade. 20 and 21 also exhibit i→s_A→s_C^* phase transitions. These mesophases display characteristic textures, i.e., focal conic for the s_A and focal conic with equidistant lines for the s_C^* phase. 20 undergoes the i→s_A transition at 218 °C and the s_A→s_C^* transition at 174 °C. 21 undergoes the i→s_A transition at 214 °C and the s_A→s_C^* transition at 168 °C.

The synthesis of poly(methyl-*co*-dimethylsiloxane) 22 is presented in Scheme 3. The heating and cooling of DSC traces of 22 are presented in Fig. 6a, b. Table 3 summarizes its mesomorphic behavior. 22 undergoes an i→s_C^* phase transition at 174 °C. The s_C^* phase is characterized by the appearance of equidistant lines on the focal conic texture. The enthalpy change of phase transition associated with the i→s_C^* and s_C^*→i of 22 is much greater than that of its corresponding homopolymer 19, even when we compare it with the sum of enthalpy changes of i→s_A and s_A→s_C^* phase transitions of 19. A very small peak at 82 °C on each DSC cooling scan appears even though no texture change can be observed on an optical polarized microscope. In addition, copolymer 22 does not undergo thermal decomposition when it is annealed within its s_C^* mesophase. Therefore, insertion of dimethylsiloxane structural units within the structure of 19 seems to decrease the tendency toward the formation of a s_A phase more than that of a s_C^* phase and, consequently, copolymer 22 exhibits only an enantiotropic s_C^* phase. This statement has only a qualitative value since the molecular weights of homopolymer 19 and of copolymer 22 are different.

Scheme 4 outlines the synthesis of copoly(methylsiloxane) 23. The DSC traces and the mesomorphic behavior of 23 are also presented in Fig. 6g, h and in Table 3. The DSC traces of *23* look like a combination of the DSC traces of its corresponding homopolymers 19 and 20 with the exception of an additional small peak observed on the DSC traces at 113 °C on the heating scan and at 82 °C on the cooling scan. On the optical polarized microscope we could not observe any texture change associated with this phase transition of 23. 23 undergoes the i→s_A phase transition at 218 °C, and the s_A→s_C^* phase transition at 184 °C.

The results on the investigation of polymers containing 4-[*S*(–)-2-methyl-1-butoxy]-4′-[*p*-(ω-alkan-1-yloxy)-α-methylstilbene [2] and 4-[*S*(–)-2-methyl-1-butoxy]-4′-[*p*-(ω-alkan-1-yloxy)benzoyloxy]-α-methylstilbene side groups have provided the following conclusions. In the case of the polymers containing 4-[*S*(–)-2-methyl-1-butoxy]-4′-(ω-alkan-1-yloxy)-α-methylstilbene [2] the tendency toward s_C^* phase formation is highest for polymers containing intermediary flexible spacer length (i.e., containing eight and six methylenic units) and a very flexible poly(methylsiloxane) backbone. By increasing the length of the mesogenic group from 4-[*S*(–)-2-methyl-1-butoxy]-4′-(ω-alkan-1-yloxy)-α-methylstilbene to 4-[*S*(–)-2-methyl-1-butoxy]-4′-[*p*-(ω-alkan-1-yloxy)benzoyloxy]-α-methylstilbene and maintaining the poly(methylsiloxane) backbone, the ability of the polymer to display a s_C^* mesophase increases. These last polymers exhibit an enantiotropic s_C^* mesophase when their flexible spacers contain eight, six, and three methylenic units. In addition to the s_C^* mesophase, all polymers exhibited a s_A mesophase regardless of the nature of the polymer backbone and of the spacer length. Poly[(50–55%)-methyl-*co*-(45–50%)-dimethylsiloxane]s containing 4-[*S*(–)-2-methyl-1-butoxy]-4′-[*p*-(8-octan-1-yloxy)benzoyloxy]-α-methylstilbene exhibited only a s_C^* mesophase. Therefore, copolymers containing dimethylsiloxane and methylsiloxane units with mesogenic groups as structural units stabilize the s_C^* phase and destabilize the s_A mesophase. This last result is very rewarding since poly(methyl-*co*-dimethylsiloxane)s displaying smectic mesophases exhibit a microphase-separated morphology which displays a faster dynamic than that of their parent homopolymers [16, 20, 21, 22b].

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