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Synthesis and Characterization of Polymethacrylates, Polyacrylates, and Poly(Methylsiloxane)S Containing 4-[*S*(-)-2-Methyl-1-Butoxy]-4'-(ω-Alkanyl-1-OXY)-α-Methylstilbene Side Groups

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SYNTHESIS AND CHARACTERIZATION OF POLYMETHACRYLATES, POLYACRYLATES, AND POLY(METHYLSILOXANE)S CONTAINING 4-[*S*(−)-2-METHYL-1-BUTOXY]-4′-(ω-ALKANYL-1-OXY)-α-METHYLSTILBENE SIDE GROUPS

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ABSTRACT

The synthesis and characterization of polymethacrylates, polyacrylates, and poly(methylsiloxane)s containing 4-[*S*(−)-2-methyl-1-butoxy]-4′-(ω-alkanyl-1-oxy)-α-methylstilbene side groups with ω-alkanyl from 11-undecanyl to 2-ethyl are presented. According to both differential scanning calorimetry and thermal optical polarized microscopy analyses, the poly(methylsiloxane)s containing 1-octyl and 1-hexyl as ω-alkanyl groups exhibit enantiotropic S_A and S_C^* mesophases. All other polymers display only an enantiotropic S_A mesophase.

INTRODUCTION

Side-chain liquid crystalline polymers exhibiting chiral smectic C (S_C^*) mesophases are of interest for both theoretical and technological reasons which were reviewed recently [1]. So far there are only few examples of side-chain liquid crystalline polymers exhibiting S_C^* mesophases [2–12].

Previous experiments from our laboratory on the synthesis and characterization of side-chain liquid crystalline polymers containing chiral centers in the mesogenic groups [13, 14] led to polymers exhibiting S_A mesophases [13d, 14].

In an attempt to provide a systematic approach to the preparation of side-chain liquid crystalline polymers exhibiting S_C^* mesophases, we have decided to

investigate the synthesis and characterization of polymers containing 4-[*S*(−)-2-methyl-1-butoxy]-4′-(ω-alkanyl-1-oxy)-α-methylstilbene side groups and four different polymer backbones: polymethacrylate, polyacrylate, poly(methylsiloxane), and polyvinyl ether. The synthesis and characterization of polymethacrylate, polyacrylate, poly(methylsiloxane), and 1,3,5,7-tetramethylcyclotetrasiloxane containing 4-[*S*(−)-2-methyl-1-butoxy]-4′-(11-undecanyl-1-oxy)-α-methylstilbene side groups were reported in a previous publication [14]. All these polymers exhibit an enantiotropic S_A mesophase.

The goal of this paper is to report our results on the synthesis and characterization of polymethacrylates, polyacrylates, and poly(methylsiloxane)s containing 4-[*S*(−)-2-methyl-1-butoxy]-4′-(ω-alkanyl-1-oxy)-α-methylstilbene side groups whose alkanyl group varies from ethyl to undecanyl.

EXPERIMENTAL

Materials

Poly(methylhydrosiloxane) with a number-average degree of polymerization of 22 was synthesized as described elsewhere [13b]. *S*(−)-2-Methyl-1-butanol ($[\alpha]_D$ −7.3°, 95% from Fluka), methacryloyl chloride (Fluka), *p*-hydroxyphenyl acetic acid, 8-chloro-1-octanol, 6-chloro-1-hexanol, 3-chloro-1-propanol (all from Lancaster Synthesis), 11-bromoundecan-1-ol, 2-chloroethan-1-ol, 10-undecene-1-ol, 8-bromo-1-octene, 1,6-dibromo-hexane, allyl chloride, phenol, acryloyl chloride, 8-bromo-1-octanol (95%) (all from Aldrich), and platinum divinyltetramethyldisiloxane complex solution in xylene (from Petrarch) were used as received. Benzene used in radical polymerization reactions was first stirred with sulfuric acid, washed with water, dried over calcium hydride, and finally distilled from sodium. Toluene used in the hydrosilation reaction was first refluxed over sodium and then distilled under argon. All other reagents were used as received or were purified by standard methods, unless otherwise specified.

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 and minimum of their endothermic and 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 the heat capacity. Thermal transitions were collected from first, second, and further heating and cooling scans. 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. 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 chromatogra-

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

Synthesis of Monomers and Polymers

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

S(−)-2-Methyl-1-butyl Tosylate (2)

2 was synthesized by the tosylation of *S*(−)-2-methyl-1-butanol as described in a previous publication [14]. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.86 (m, 6H, CH_3−), 1.0-1.5 (m, 2H, −CH_2−), 1.69 (m, 1H, −CH−), 2.45 (s, 3H, Ph−CH_3), 3.85 (m, 2H, −CH_2−OPh), 7.37 and 7.77 (2d, 4H, ArH).

S(−)-2-Methyl-1-butoxy Benzene (4)

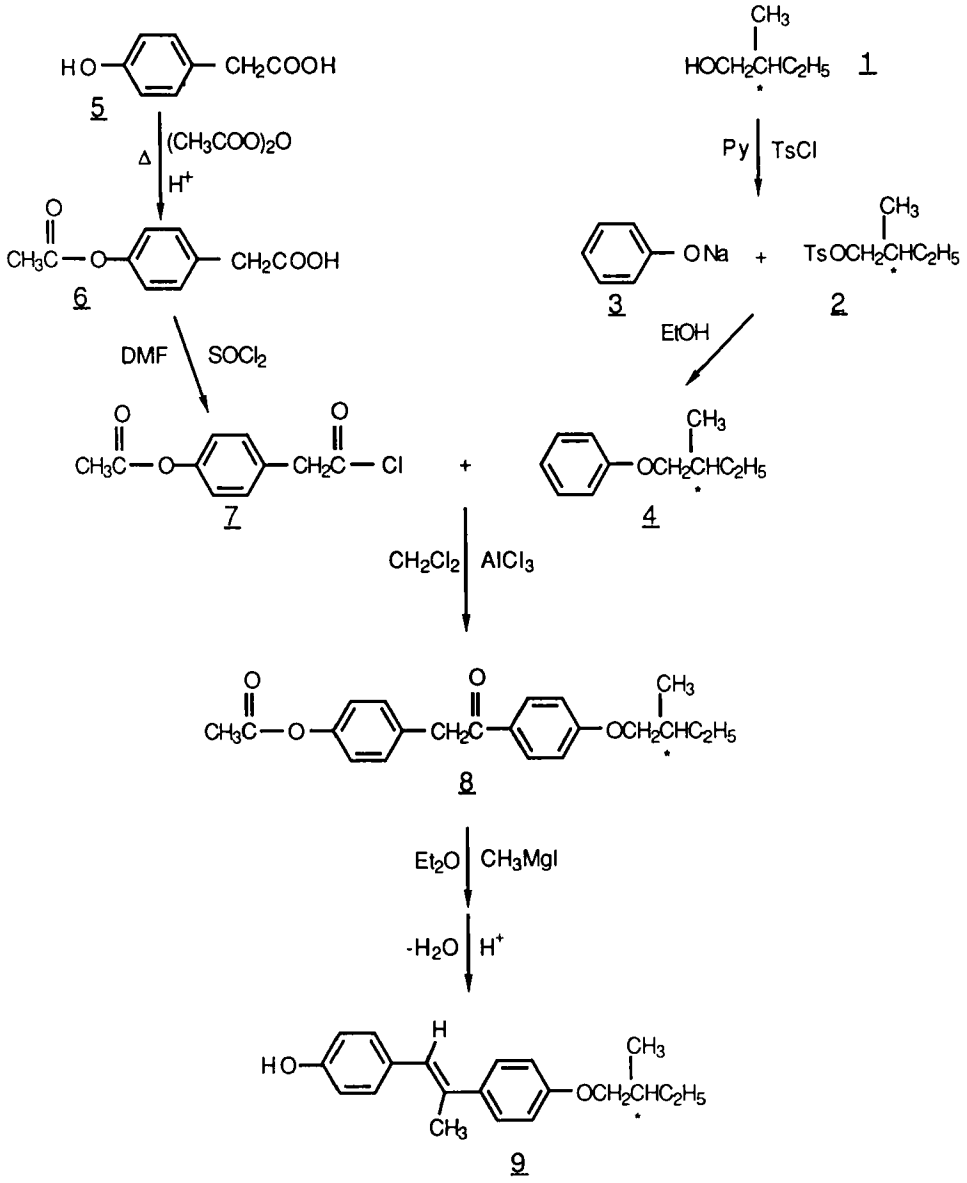
4 was synthesized by the alkylation of phenol with 2. The experimental procedure was described previously [14]. 4 is a colorless liquid (65-70°C/4 mmHg) ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.03 (m, 6H, CH_3−), 1.1-1.7 (m, 2H, CH_3−CH_2−), 1.84 (m, 1H, −CH−), 3.81 (m, 2H, −CH_2−OPh), 6.92 and 7.27 (2t, 5H, ArH).

p-Acetoxyphenyl Acetic Acid (6)

6 was synthesized as described previously [14]. mp 108-110°C. lit. 14, mp 108-110°C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 2.29 (s, 3H, CH_3−), 3.63 (s, 2H, Ph−CH_2−), 7.01 (d, 2H, ArH, ortho to acetoxy), and 7.28 (d, 2H, ArH, meta to acetoxy).

p-Acetoxybenzyl *p*-*S*(−)-2-Methyl-1-butoxyphenyl Ketone (8)

8 was synthesized by a modification of the procedure described previously [14]. To a round bottom flask containing 33 g (0.17 mol) *p*-acetoxyphenyl acetic acid, 14.3 mL (23.26 g, 0.19 mol) thionyl chloride followed by 2 drops of dry DMF were added and the slurry was stirred for 1 h. At this time it was shown by ^{1}H-NMR spectroscopy that complete transformation of the acid into the acid chloride took place: ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 2.30 (s, 3H, CH_3−), 4.13 (s, 2H, Ph−CH_2−), 7.12 and 7.26 (2d, 4H, ArH). After the acid reacted completely, 24.6 g (0.15 mol) *S*(−)-2-methyl-1-butoxybenzene dissolved in 250 mL dry CH_2Cl_2 was added. The resulting solution was flushed with nitrogen and cooled in a dry ice-acetone bath to −20°C. $AlCl_3$ (50 g, 0.37 mol) was then slowly added to the reaction mixture during 45 min, not allowing the temperature of the reaction to increase above −10°C. The reaction mixture was stirred for 15 min at −20°C, and then it was poured into 600 mL 50/50 (v/v) water/concentrated HCl mixture cooled with ice. The organic layer was separated, washed with water, 20% aqueous $NaHCO_3$, water, and then dried over anhydrous $MgSO_4$. The CH_2Cl_2 was removed on a rotavapor and the residue was recrystallized twice from ethanol to yield 28.5 g (49%) white crystals. mp 110°C. lit. 14 mp 106-108°C. ^{1}H-NMR ($CDCl_3$, TMS, δ,

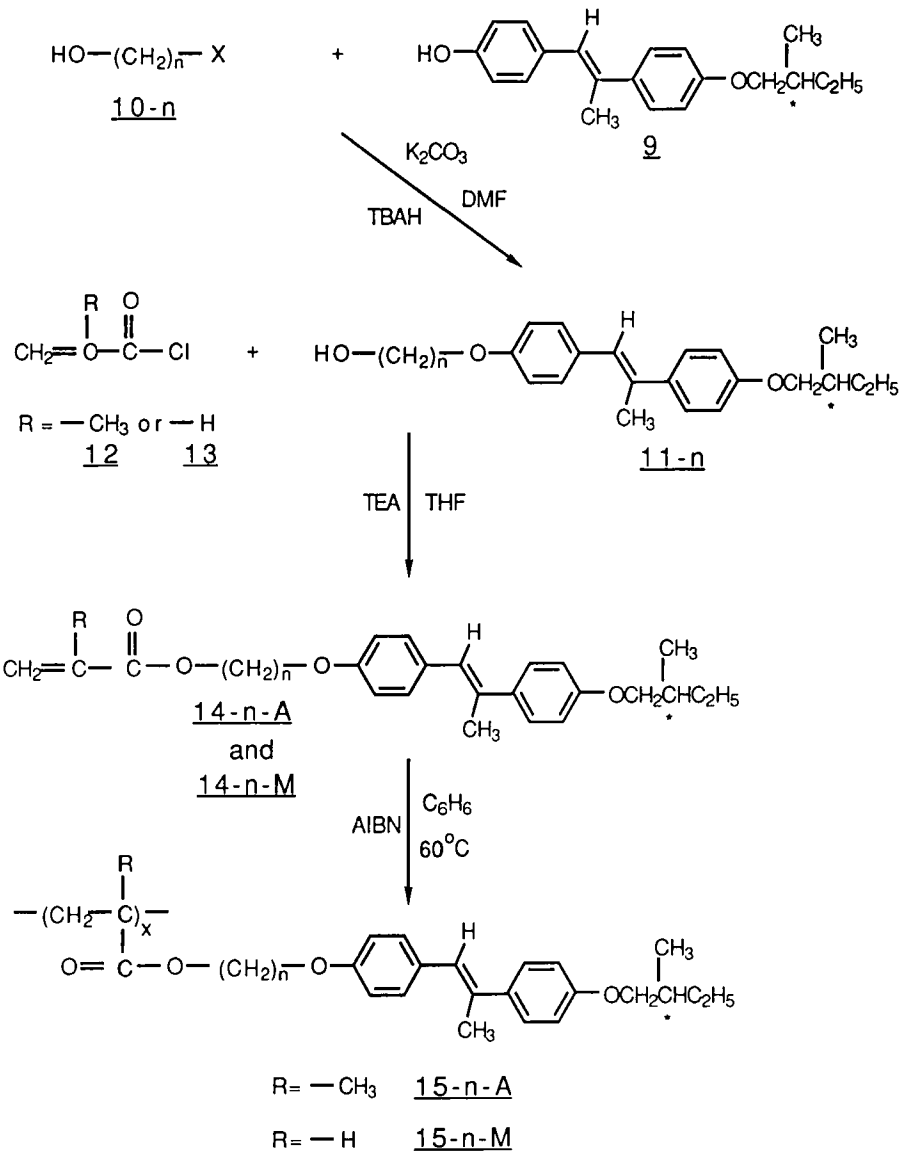


SCHEME 1. Synthesis of 4-[*S*(−)-2-methyl-1-butoxy]-4′-(hydroxy)-α-methylstilbene.

ppm): 0.9–1.1 (m, 6H, $C\underline{H}_3-$), 1.2–1.7 (m, 2H, $CH_3-C\underline{H}_2-$), 1.8–2.0 (m, 1H, $-C\underline{H}-$), 2.27 (s, 3H, $C\underline{H}_3COO-$), 3.82 (m, 2H, $-C\underline{H}_2-OPh$), 4.21 (s, 2H, $Ph-C\underline{H}_2-$), 6.9–8.0 (4d, 8H, ArH).

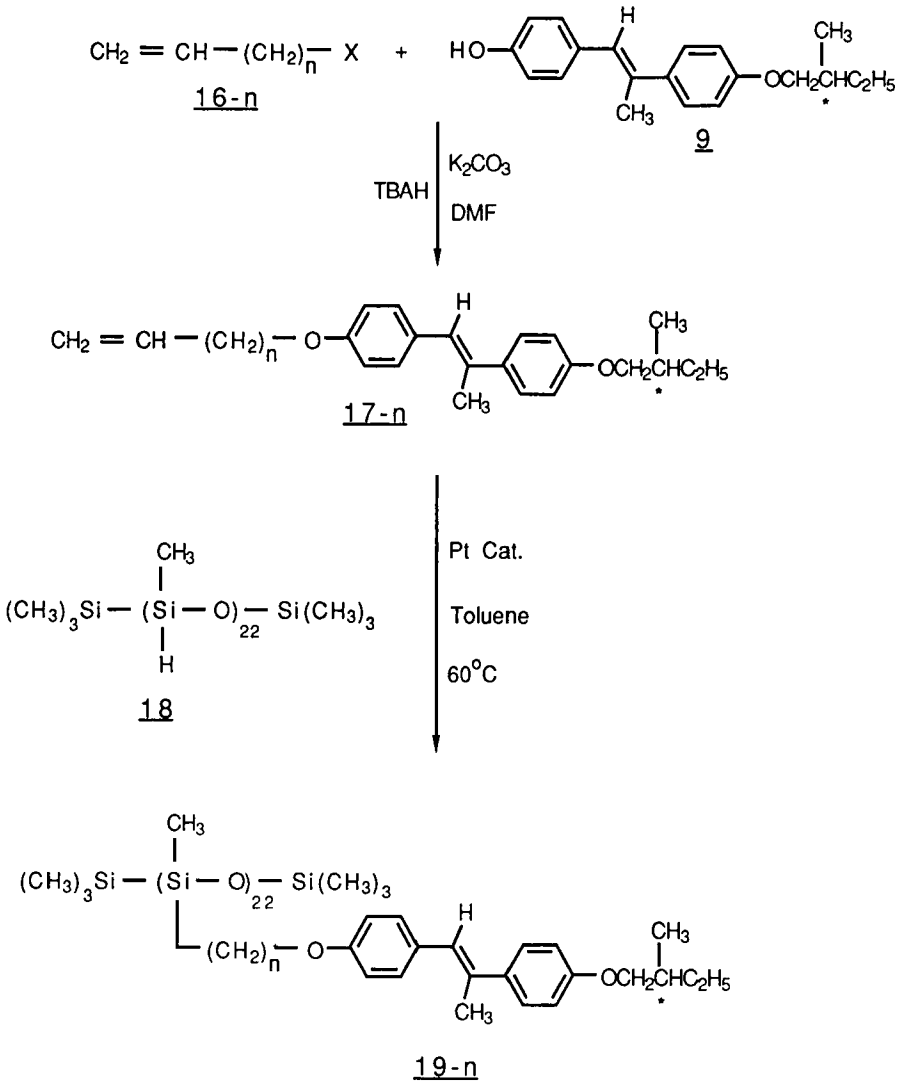
4-[*S*(−)-2-Methyl-1-butoxy]-4′-(hydroxy)-α-methylstilbene (9)

9 was synthesized by a modification of the procedure described previously [14]. To a flame-dried round bottom flask flushed with N_2 and containing 300 mL



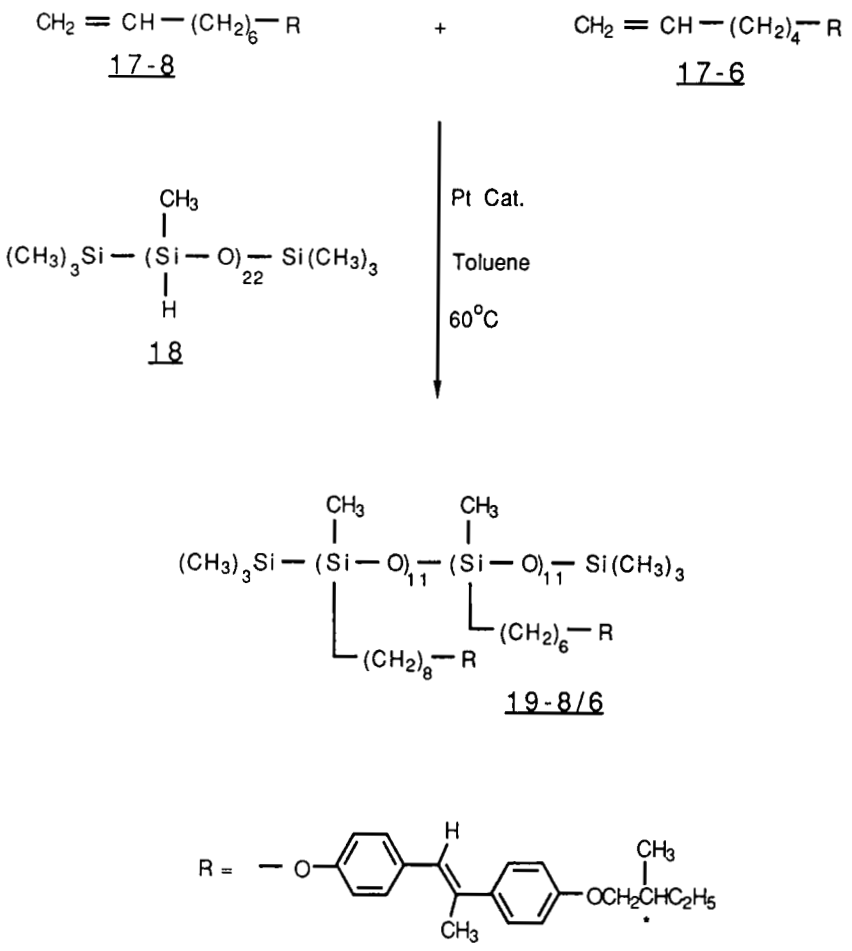
SCHEME 2. Synthesis of polymethacrylates and polyacrylates.

dry diethyl ether, 4.72 g (0.19 mol) magnesium turnings and a catalytic amount of I_2 were added. A few milliliters of CH_3I were then added to the reaction mixture. Once the reaction started, the rest of the CH_3I (27.6 g, 0.19 mol) was added dropwise under N_2 at a rate fast enough to maintain the reaction mixture under reflux. After all of the magnesium had been consumed (if not, the reaction mixture was warmed up until complete reaction took place), the *p*-acetoxybenzyl *p*-*S*(−)-2-methyl-1-butoxyphenyl ketone (16.5 g, 0.048 mol) dissolved in 200 mL of dry diethyl ether was added under vigorous stirring. A white precipitate formed immediately. All of the ketone was added to the reaction mixture, which was kept stirring



SCHEME 3. Synthesis of poly(methylsiloxane)s.

vigorously overnight. A dilute HCl solution in ice water was then flushed with N_2 and added dropwise to the reaction mixture until the pH of solution became neutral. After all the solid was dissolved, the ether layer was separated and washed with water, dried over $MgSO_4$, and the diethyl ether was removed on a rotavapor. The resulting product and a catalytic amount of *p*-toluenesulfonic acid were added into a round bottom flask equipped with a Dean-Stark trap. Dry toluene was added to maintain the product in solution. Water was azeotropically distilled. When no more water was collected in the trap (about 2 h), the remaining solvent was distilled on a rotavapor. The solid residue was recrystallized from methanol to yield 8.7 g (61.1%) colorless crystals. mp 121–122°C. lit. 14 (mp 120–122°C). Purity: 99% (HPLC). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.9–1.1 (m, 6H, CH_3—), 1.2–1.9 (m, 3H,



SCHEME 4. Synthesis of poly(methyl-*co*-dimethylsiloxane).

$CH_3-\underline{CH_2}-$, $-\underline{CH}-$), 2.23 (s, 3H, $\underline{CH_3}-C=C-Ph$), 3.81 (m, 2H, $-\underline{CH_2}-OPh$), 4.80 (s, 1H, $\underline{HO}-Ph$), 6.70 (s, 1H, $-\underline{HC}=C-Ph$), 6.81–7.45 (4d, 8H, ArH).

4-[*S*(−)-2-Methyl-1-butoxy]-4′-(11-hydroxyundecanyl-1-oxy)-α-methylstilbene (11-11)

Freshly cut sodium (0.19 g, 8.0 mmol) was added to a flask containing 50 mL absolute ethanol. After all sodium was dissolved, 2.0 g (6.76 mmol) 4-[*S*(−)-2-methyl-1-butoxy]-4′-(hydroxy)-α-methylstilbene was added, the reaction mixture was stirred for 30 min, and then 2.04 g (8.11 mmol) 11-bromo-1-undecanol and a catalyst amount of potassium iodide were added. The reaction mixture was heated to reflux overnight. The ethanol was removed on a rotavapor and the residue was mixed with water and extracted with diethyl ether. The ether layer was separated, washed with 10% aqueous K_2CO_3, water, dried over $MgSO_4$ and the ether was

removed on a rotavapor. The resulting solid was recrystallized from methanol to yield 1.94 g (61%) white crystals. Analytical data are presented in Table 1.

4-[*S*(−)-2-Methyl-1-butoxy]-4′-(8-hydroxyoctanyl-1-oxy)-α-Methylstilbene (11-8)

4-[*S*(−)-2-Methyl-1-butoxy]-4′-(hydroxy)-α-methylstilbene (2.0 g, 6.76 mmol), 1.87 g (13.52 mmol) potassium carbonate, a catalytic amount of tetrabutylammonium hydrogen sulfate, and 50 mL dry DMF were added into a flask and the mixture was stirred at 80°C under N_2. After 30 min, 1.33 g (6.76 mmol) 8-chloro-1-octanol was added and the solution was stirred at the same temperature for an additional 6 h. After that, the reaction mixture was added to 200 mL water with stirring. The resulting precipitate was filtered, dried, and recrystallized from methanol to yield 1.95 g (67.9%) white crystals. Analytical data are presented in Table 1.

4-[*S*(−)-2-Methyl-1-butoxy]-4′-(6-hydroxyhexanyl-1-oxy)-α-methylstilbene (11-6) and 4-[*S*(−)-2-methyl-1-butoxy]-4′-(3-hydroxypropanyl-1-oxy)-α-methylstilbene (11-3)

4-[*S*(−)-2-Methyl-1-butoxy]-4′-(hydroxy)-α-methylstilbene (2.0 g, 6.76 mmol)1nb and 1.02 g (7.44 mmol) 6-chloro-1-hexanol were reacted under the same conditions as those used for the synthesis of 11-8 to give 1.63 g (62%) 4-[*S*(−)-2-methyl-1-butoxy]-4′-(6-hydroxyhexanyl-1-oxy)-α-methylstilbene.

4-[*S*(−)-2-Methyl-1-butoxy]-4′-(hydroxy)-α-methylstilbene (2.0 g, 6.76 mmol) and 0.70 g (7.44 mmol) 3-chloro-1-propanol were reacted under a procedure similar to that used in the synthesis of 11-8 to give 1.60 g (67%) 4-[*S*(−)-2-methyl-1-butoxy]-4′-(3-hydroxypropanyl-1-oxy)-α-methylstilbene. Analytical data of both compounds are presented in Table 1.

4-[*S*(−)-2-Methyl-1-butoxy]-4′-(2-hydroxyethanyl-1-oxy)-α-Methylstilbene (11-2)

2-Chloro-1-ethanol (1.09 g, 13.6 mmol) was added at a rate of 4–5 drops per hour into a solution containing 4-[*S*(−)-2-methyl-1-butoxy]-4′-(hydroxy)-α-methylstilbene (2.0 g, 6.76 mmol) in 20 mL dry DMF during a period of about 24 h. After workup as in the previous cases, 0.85 g (37%) of the product was separated. Analytical data are presented in Table 1.

Methacrylate (14-11-M) and Acrylate (14-11-A) of 4-[*S*(−)-2-Methyl-1-butoxy]-4′-(11-undecanyl-1-oxy)-α-methylstilbene

The methacrylate and acrylate of 4-[*S*(−)-2-methyl-1-butoxy]-4′-(11-undecanyl-1-oxy)-α-methylstilbene were synthesized by esterification of 4-[*S*(−)-2-methyl-1-butoxy]-4′-(11-hydroxyundecanyl-1-oxy)-α-methylstilbene with methacryloyl and acryloyl chloride, respectively. An example for the synthesis of methacrylate is presented below.

A solution of 4-[*S*(−)-2-methyl-1-butoxy]-4′-(11-hydroxyundecanyl-1-oxy)-α-methylstilbene (1.94 g, 4.15 mmol), triethylamine (0.63 g, 6.2 mmol), and 100 mL dry THF was cooled to 5°C in an ice bath under N_2. Methacryloyl chloride

TABLE 1. Characterization of 4-[*S*(−)-2-Methyl-1-butoxy]-4′-(ω-hydroxyalkanyl-1-oxy)-α-methylstilbenes (11-n)

Compound	Yield, %	mp, °C	200 MHz ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm) chemical shifts
11-11	61	96–98	0.9–1.1 (m, 6H, $C\underline{H}_3-$), 1.2–1.9 (m, 21H, $CH_3-C\underline{H}_2-$, $-(C\underline{H}_2)_9-$, $-C\underline{H}-$), 2.24 (s, 3H, $C\underline{H}_3-C=C-Ph$), 3.64 (t, 2H, $-C\underline{H}_2OH$), 3.79 (m, 2H, $-C\underline{H}_2-OPh$), 3.97 (t, 2H, $-CH_2-C\underline{H}_2-OPh$), 6.71 (s, 1H, $-\underline{H}C=C-Ph$), 6.88–7.46 (3d, 8H, ArH)
11-8	68	89–91	0.9–1.1 (m, 6H, $C\underline{H}_3-$), 1.2–1.9 (m, 15H, $CH_3-C\underline{H}_2-$, $-(C\underline{H}_2)_6-$, $-C\underline{H}-$), 2.24 (s, 3H, $C\underline{H}_3-C=C-Ph$), 3.65 (t, 2H, $-C\underline{H}_2OH$), 3.81 (m, 2H, $-C\underline{H}_2-OPh$), 3.97 (t, 2H, $-CH_2-C\underline{H}_2-OPh$), 6.71 (s, 1H, $-\underline{H}C=C-Ph$), 6.87–7.46 (3d, 8H, ArH)
11-6	62	92–94	0.9–1.1 (m, 6H, $C\underline{H}_3-$), 1.2–1.9 (m, 11H, $CH_3-C\underline{H}_2-$, $-(C\underline{H}_2)_4-$, $-C\underline{H}-$), 2.24 (s, 3H, $C\underline{H}_3-C=C-Ph$), 3.69 (t, 2H, $-C\underline{H}_2OH$), 3.79 (m, 2H, $-C\underline{H}_2-OPh$), 3.99 (t, 2H, $-CH_2-C\underline{H}_2-OPh$), 6.71 (s, 1H, $-\underline{H}C=C-Ph$), 6.87–7.46 (3d, 8H, ArH)
11-3	67	108	0.9–1.1 (m, 6H, $C\underline{H}_3-$), 1.2–1.9 (m, 5H, $CH_3-C\underline{H}_2-$, $-(C\underline{H}_2-$, $-C\underline{H}-$), 2.24 (s, 3H, $C\underline{H}_3-C=C-Ph$), 3.75–3.88 (m, 4H, $-C\underline{H}_2OH$, $-C\underline{H}_2-OPh$), 4.15 (t, 2H, $-CH_2-C\underline{H}_2OPh$), 6.71 (s, 1H, $-\underline{H}C=C-Ph$), 6.87–7.45 (4d, 8H, ArH)
11-2	37	97	0.9–1.1 (m, 6H, $C\underline{H}_3-$), 1.2–1.9 (m, 3H, $CH_3-C\underline{H}_2-$, $-C\underline{H}-$), 2.23 (s, 3H, $C\underline{H}_3-C=C-Ph$), 3.81 (m, 2H, $-C\underline{H}_2-OPh$), 3.98 (t, 2H, $-C\underline{H}_2OH$), 4.11 (t, 2H, $-CH_2-C\underline{H}_2-OPh$), 6.71 (s, 1H, $-\underline{H}C=C-Ph$), 6.82–7.45 (4d, 8H, ArH)

(0.87 g, 8.30 mmol) was added dropwise to the reaction mixture. A white precipitate formed after a few minutes. The reaction was allowed to slowly warm to room temperature and was left stirring overnight. The mixture was filtered through a column containing about 2 cm thick basic alumina to remove the Et_3NHCl and the excess methacryloyl chloride. The THF was removed on a rotavapor at room temperature. The oily residue was dried in vacuum until it crystallized. The resulting solid was then purified by column chromatography (neutral alumina, chloroform as eluent) and then recrystallized from methanol to yield 1.2 g (54%) white crystals. Analytical data are presented in Table 2.

The acrylate of 4-[*S*(−)-2-methyl-1-butoxy]-4′-(11-hydroxyundecanyl-1-oxy)-α-methylstilbene was synthesized in the same way as the corresponding methacrylate from 4-[*S*(−)-2-methyl-1-butoxy]-4′-(11-hydroxyundecanyl-1-oxy)-α-methylstilbene and acryloyl chloride in 51% yield. Analytical data are presented in Table 3.

Methacrylates and Acrylates of 4-[*S*(−)-2-Methyl-1-butoxy]-4′-(ω-alkanyl-1-oxy)-α-methylstilbene Containing 2, 3, 6, and 8 Methylene Units (14-n-M and 14-n-A)

Preparation and purification of all these monomers were performed by the same method as the one described above for the case of 14-11-A and 14-11-M. The yields and the analytical data of these methacrylates and acrylates are reported in Tables 2 and 3.

10-Undecen-1-yl Tosylate (16-11)

16-11 was prepared as described previously [13a].

6-Bromo-1-Hexene (16-8)

16-8 was synthesized according to a literature procedure [15]. The detailed synthesis was described previously [16].

4-[*S*(−)-2-Methyl-1-butoxy]-4′-(10-undecenyl-1-oxy)-α-methylstilbene (17-11)

A mixture of 4-[*S*(−)-2-methyl-1-butoxy]-4′-(hydroxy)-α-methylstilbene (2.0 g, 6.76 mmol), 2.0 g (14.8 mmol) potassium carbonate, a catalytic amount of tetrabutylammonium hydrogen sulfate, and 50 mL dry DMF was stirred at 80°C under N_2. After 30 min, 2.19 g (6.76 mmol) 10-undecen-1-yl tosylate was added to the reaction mixture which stirred for an additional 6 h. The reaction mixture was added dropwise to 200 mL water with stirring. The precipitate was filtered, dried, and recrystallized from methanol to yield 0.57 g (40%) white crystals. Analytical data are presented in Table 4.

4-[*S*(−)-2-Methyl-1-butoxy]-4′-(7-octenyl-1-oxy)-α-methylstilbene and 4-[*S*(−)-2-Methyl-1-butoxy]-4′-(5-hexenyl-1-oxy)-α-methylstilbene (17-8) and (17-6)

Both 17-8 and 17-6 were synthesized by the same procedure as the one described above for the synthesis of 17-11 except that 10-undecen-1-yl tosylate was replaced with 8-bromo-1-octene and 6-bromo-1-hexene, respectively. Analytical data are presented in Table 4.

TABLE 2. Characterization of Methacrylates of 4-[*S*(−)-2-methyl-1-butoxy]-4′-(ω-alkanyl-1-oxy)-α-methylstilbene (14-n-M)

Compound	Yield, %	mp, °C	200 MHz ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm) chemical shifts
14-11-M	54	55	0.9–1.1 (m, 6H, CH_3−), 1.2–1.8 (m, 21H, CH_3-CH_2-, $-(CH_2)_9-$, −CH−), 1.94 (s, 3H, $CH_3-C=C-COO-$), 2.24 (s, 3H, $CH_3-C=C-Ph$), 3.81 (m, 2H, $-CH_2-OPh$), 3.97 (t, 2H, $-CH_2-CH_2-OPh$), 4.14 (t, 2H, $-CH_2-OOC$), 5.55 and 6.10 (d, 2H, $H_2C=C-$), 6.71 (s, 1H, $-HC=C-Ph$), 6.87–7.46 (3d, 8H, ArH)
14-8-M	31	84	0.9–1.1 (m, 6H, CH_3−), 1.2–1.8 (m, 15H, CH_3-CH_2-, $-(CH_2)_6-$, −CH−), 1.95 (s, 3H, $CH_3-C=C-COO-$), 2.24 (s, 3H, $CH_3-C=C-Ph$), 3.81 (m, 2H, $-CH_2-OPh$), 3.97 (t, 2H, $-CH_2-CH_2-OPh$), 4.14 (t, 2H, $-CH_2-OOC$), 5.55 and 6.10 (d, 2H, $H_2C=C-$), 6.71 (s, 1H, $-HC=C-Ph$), 6.87–7.46 (3d, 8H, ArH)
14-6-M	31	4	0.9–1.1 (m, 6H, CH_3−), 1.2–1.8 (m, 11H, CH_3-CH_2-, $-(CH_2)_4-$, −CH−), 1.94 (s, 3H, $CH_3-C=C-COO-$), 2.24 (s, 3H, $CH_3-C=C-Ph$), 3.81 (m, 2H, $-CH_2-OPh$), 3.98 (t, 2H, $-CH_2-CH_2-OPh$), 4.17 (t, 2H, $-CH_2-OOC$), 5.55 and 6.10 (d, 2H, $H_2C=C-$), 6.71 (s, 1H, $-HC=C-Ph$), 6.87–7.46 (3d, 8H, ArH)
14-3-M	25	42	0.9–1.1 (m, 6H, CH_3−), 1.2–1.8 (m, 5H, CH_3-CH_2-, $-CH_2-CH_2-CH_2-CH-$), 1.95 (s, 3H, $CH_3-C=C-COO-$), 2.24 (s, 3H, $CH_3-C=C-Ph$), 3.81 (m, 2H, $-CH_2-OPh$), 4.09 (t, 2H, $-CH_2-CH_2-OPh$), 4.36 (t, 2H, $-CH_2-OOC$), 5.60 and 6.14 (d, 2H, $H_2C=C-$), 6.71 (s, 1H, $-HC=C-Ph$), 6.87–7.45 (3d, 8H, ArH)
14-2-M	19	−16	0.9–1.1 (m, 6H, CH_3−), 1.2–1.8 (m, 3H, CH_3-CH_2-, −CH−), 1.96 (s, 3H, $CH_3-C=C-COO-$), 2.24 (s, 3H, $CH_3-C=C-Ph$), 3.81 (m, 2H, $-CH_2-OPh$), 4.25 (t, 2H, $-CH_2-CH_2-OPh$), 4.51 (t, 2H, $-CH_2-OOC$), 5.59 and 6.15 (d, 2H, $H_2C=C-$), 6.71 (s, 1H, $-HC=C-Ph$), 6.87–7.46 (3d, 8H, ArH)

TABLE 3. Characterization of Acrylates of 4-[*S*(−)-2-Methyl-1-butoxy]-4′-(ω-alkanyl-1-oxy)-α-methylstilbenes (14-n-A)

Compound	Yield, %	mp, °C	200 MHz ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm) chemical shifts
14-11-A	51	54	0.9–1.1 (m, 6H, $C\underline{H}_3-$), 1.2–1.8 (m, 21H, $CH_3-C\underline{H}_2-$, $-(C\underline{H}_2)_9-$, $-C\underline{H}-$), 2.24 (s, 3H, $C\underline{H}_3-C{=}C-Ph$), 3.79 (m, 2H, $-C\underline{H}_2-OPh$), 3.97 (t, 2H, $-CH_2-C\underline{H}_2-OPh$), 4.15 (t, 2H, $-C\underline{H}_2-OOC$), 5.79–6.45 (m, 3H, $\underline{H}_2C{=}CH-$, $H_2C{=}C\underline{H}-$), 6.71 (s, 1H, $-\underline{H}C{=}C-Ph$), 6.87–7.46 (3d, 8H, ArH)
14-8-A	41	58	0.9–1.1 (m, 6H, $C\underline{H}_3-$), 1.2–1.8 (m, 15H, $CH_3-C\underline{H}_2-$, $-(C\underline{H}_2)_6-$, $-C\underline{H}-$), 2.24 (s, 3H, $C\underline{H}_3-C{=}C-Ph$), 3.79 (m, 2H, $-C\underline{H}_2-OPh$), 3.97 (t, 2H, $-CH_2-C\underline{H}_2-OPh$), 4.16 (t, 2H, $-C\underline{H}_2-OOC$), 5.79–6.46 (m, 3H, $\underline{H}_2C{=}CH-$, $H_2C{=}C\underline{H}-$), 6.71 (s, 1H, $-\underline{H}C{=}C-Ph$), 6.87–7.46 (3d, 8H, ArH)
14-6-A	32	48	0.9–1.1 (m, 6H, $C\underline{H}_3-$), 1.2–1.8 (m, 11H, $CH_3-C\underline{H}_2-$, $-(C\underline{H}_2)_4-$, $-C\underline{H}-$), 2.24 (s, 3H, $C\underline{H}_3-C{=}C-Ph$), 3.81 (m, 2H, $-C\underline{H}_2-OPh$), 3.98 (t, 2H, $-CH_2-C\underline{H}_2-OPh$), 4.16 (t, 2H, $-C\underline{H}_2-OOC$), 5.79–6.47 (m, 3H, $\underline{H}_2C{=}CH-$, $H_2C{=}C\underline{H}-$), 6.71 (s, 1H, $-\underline{H}C{=}C-Ph$), 6.87–7.46 (3d, 8H, ArH)
14-3-A	39	59	0.9–1.1 (m, 6H, $C\underline{H}_3-$), 1.2–1.8 (m, 5H, $CH_3-C\underline{H}_2-$, $-C\underline{H}_2-C\underline{H}_2-CH_2$, $-C\underline{H}-$), 2.24 (s, 3H, $C\underline{H}_3-C{=}C-Ph$), 3.81 (m, 2H, $-C\underline{H}_2-OPh$), 4.09 (t, 2H, $-CH_2-C\underline{H}_2-OPh$), 4.38 (t, 2H, $-C\underline{H}_2-OOC$), 5.28–6.49 (m, 3H, $\underline{H}_2C{=}CH-$, $H_2C{=}C\underline{H}-$), 6.71 (s, 1H, $-\underline{H}C{=}C-Ph$), 6.88–7.46 (3d, 8H, ArH)
14-2-A	24	66	0.9–1.1 (m, 6H, $C\underline{H}_3-$), 1.2–1.8 (m, 3H, $CH_3-C\underline{H}_2-$, $-C\underline{H}-$), 2.24 (s, 3H, $C\underline{H}_3-C{=}C-Ph$), 3.84 (m, 2H, $-C\underline{H}_2-OPh$), 4.24 (t, 2H, $-CH_2-C\underline{H}_2-OPh$), 4.54 (t, 2H, $-C\underline{H}_2-OOC$), 5.85–6.51 (m, 3H, $\underline{H}_2C{=}CH-$, $H_2C{=}C\underline{H}-$), 6.72 (s, 1H, $-\underline{H}C{=}C-Ph$), 6.88–7.46 (3d, 8H, ArH)

TABLE 4. Characterization of 4-[*S*(−)-2-Methyl-1-butoxy]-4′-(ω-alkenyl-1-oxy)-α-methylstilbenes (17-n)

Compound	Yield, %	Phase transition temperature (°C) and enthalpy changes (kcal/mol)	200 MHz ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm) chemical shifts
17-11	40	*K* 91[a] S_A 102[a] (12.76) *I* *I* 68[a] S_A 60[a] *K* 51[a] (6.92) *K*	0.9–1.1 (m, 6H, $C\underline{H}_3-$), 1.2–1.8 (m, 21H, $CH_3-C\underline{H}_2-$, $-(C\underline{H}_2)_8-$, $-C\underline{H}-$), 2.24 (s, 3H, $C\underline{H}_3-C\equiv C-Ph$), 3.80 (m, 2H, $-C\underline{H}_2-OPh$), 3.97 (t, 2H, $-CH_2-C\underline{H}_2-OPh$), 5.00 (t, 2H, $\underline{H}_2C=CH-$), 5.81 (m, 1H, $H_2C=C\underline{H}-$), 6.71 (s, 1H, $-\underline{H}C\equiv C-Ph$), 6.87–7.45 (3d, 8H, ArH)
17-8	35	*K* 54[a] S_A 57[a] (8.58) *I* *I* 47[a] S_A 42[a] (0.79) S_X[b] 32 (5.36) *K*	0.9–1.1 (m, 6H, $C\underline{H}_3-$), 1.2–1.8 (m, 13H, $CH_3-C\underline{H}_2-$, $-(C\underline{H}_2)_5-$, $-C\underline{H}-$), 2.24 (s, 3H, $C\underline{H}_3-C\equiv C-Ph$), 3.80 (m, 2H, $-C\underline{H}_2-OPh$), 3.97 (t, 2H, $-CH_2-C\underline{H}_2-OPh$), 4.97 (t, 2H, $\underline{H}_2C=CH-$), 5.80 (m, 1H, $H_2C=C\underline{H}-$), 6.71 (s, 1H, $-\underline{H}C\equiv C-Ph$), 6.87–7.45 (3d, 8H, ArH)
17-6	62	*K* 61 (8.50) *I* *I* 44[a] S_A 42[a] (5.44) *K*	0.9–1.1 (m, 6H, $C\underline{H}_3-$), 1.2–1.8 (m, 9H, $CH_3-C\underline{H}_2-$, $-(C\underline{H}_2)_3-$, $-C\underline{H}-$), 2.24 (s, 3H, $C\underline{H}_3-C\equiv C-Ph$), 3.81 (m, 2H, $-C\underline{H}_2-OPh$), 3.98 (t, 2H, $-CH_2-C\underline{H}_2-OPh$), 5.00 (t, 2H, $\underline{H}_2C=CH-$), 5.82 (m, 1H, $H_2C=C\underline{H}-$), 6.71 (s, 1H, $-\underline{H}C\equiv C-Ph$), 6.87–7.45 (3d, 8H, ArH)
17-3	37	*K* 85 (7.10) *I* *I* 64 (5.89) *K*	0.9–1.1 (m, 6H, $C\underline{H}_3-$), 1.2–1.8 (m, 3H, $CH_3-C\underline{H}_2-$, $-C\underline{H}-$), 2.24 (s, 3H, $C\underline{H}_3-C\equiv C-Ph$), 3.81 (m, 2H, $-C\underline{H}_2-OPh$), 4.57 (t, 2H, $-CH_2-C\underline{H}_2-OPh$), 5.31–5.48 (q, 2H, $\underline{H}_2C=CH-$), 6.12 (m, 1H, $H_2C=C\underline{H}-$), 6.71 (s, 1H, $-\underline{H}C\equiv C-Ph$), 6.85–7.45 (3d, 8H, ArH)

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

TABLE 5. Thermal Transitions and Thermodynamic Parameters of the Liquid Crystalline Polymethacrylates, Polyacrylates, and Poly(methylsiloxane)s as Obtained from First and Second Heating and Cooling DSC Scans

Polymer			Transition temperatures (°C) and corresponding enthalpy (kcal/mru[b]) and entropy (cal/°K·mru) changes	
	GPC			
No.	M_n	M_w/M_n	Heating	Cooling
15-11-M	56,000	1.93	*K* 55 (1.33/4.05) S_A 99 (1.09/2.93) *I* *g* 4 S_A 96 (1.08/2.93) *I*	*I* 89 (1.07/2.96) S_A 0 *g* *I* 83 (1.02/2.87) S_A 1 g
15-8-M	31,000	1.49	*g* 18 S_A 71 (0.70/2.03) *I* *g* 13 S_A 72 (0.71/2.06) *I*	*I* 66 (0.72/2.12) S_A 12 *g* *I* 66 (0.69/2.04) S_A 11 *g*
15-6-M	17,000	2.74	*g* 33 S_A 90 (0.67/1.85) *I* S_A 89 (0.71/1.96) *I*	*I* 77 (0.67/1.91) S_A *I* 73 (0.61/1.76) S_A
15-3-M	25,000	1.88	*K* 63 (0.16/0.47) S_A 151 (0.99/2.33) *I* S_A 148 (1.03/2.45) *I*	*I* 132 (0.79/1.95) S_A *I* 130 (0.78/1.94) S_A
15-2-M	18,000	1.55	*K* 68 (0.54/1.37) S_A 116 (0.73/1.88) *I* S_A 118 (0.67/1.71) *I*	*I* 106 (0.54/1.39) S_A *I* 103 (0.53/1.41) S_A
15-11-A	5,700	1.49	*K* 50[a] S_A 64[a] (5.56/–) *I* *K* 38[a] S_A 68[a] (4.47/–) *I*	*I* 48 (3.56/11.09) S_A *I* 48 (3.82/11.90) S_A
15-8-A	6,500	1.63	S_A 53 (3.04/9.33) *I* *g* 4 S_A 56 (0.99/3.01) *I*	*I* 51 (0.22/0.68) S_A 0 *g* *I* 51 (0.23/0.71) S_A −1 *g*

15-6-A	5,100	1.18	S_A 60 (1.38/4.14) I g 4 S_A 58 (0.23/0.69) I	I 55 (0.21/0.64) S_A 0 g I 55 (0.24/0.73) S_A −1 g
15-3-A	9,900	1.29	S_A 71 (0.51/1.48) I S_A 76 (0.68/1.95) I	I 73 (0.52/1.49) S_A I 75 (0.58/1.67) S_A
15-2-A	3,700	1.20	K 60 (0.22/0.66) S_A 78 (0.11/0.30) I S_A 78 (0.22/0.63) I	I 72 (0.24/0.70) S_A I 73 (0.22/0.64) S_A
19-11	13,000	3.19	K 60[a] K 70[a] (4.80/−) S_A 116 (1.55/3.98) I K 64[a] K 72[a] (3.84/−) S_A 116 (1.52/3.91) I	I 109 (1.36/3.56) S_A 46 (3.59/11.25) K I 108 (1.33/3.49) S_A 46 (3.54/11.10) K
19-8	14,000	3.08	K 51[a] K 68[a] S_C^* 83[a] (2.12/−) S_A 120 (0.97/2.48) I K 70 (2.53/7.38) S_C^* 85 S_A 120 (0.99/2.51) I	I 113 (0.89/2.30) S_A 81 S_C^* 59 (2.44/7.36) K I 113 (0.88/2.28) S_A 81 S_C^* 59 (2.45/7.37) K
19-6	14,000	3.19	K 58 (2.14/6.47) S_C^* 69 (1.15/3.36) S_A 106 (0.99/2.61) I	I 99 (0.93/2.50) S_A 70 S_C^* 49 (2.00/6.21) K
			K 59 (1.99/5.99) S_C^* 70 (0.82/2.39) S_A 105 (1.04/2.75) I	I 98 (0.97/2.61) S_A 68 S_C^* 49 (2.04/6.34) K
19-3	13,000	2.76	g −8 K 61 (0.65/1.95) S_A 102 (0.68/2.29) I g −1 K 24 (0.34/1.14) S_A 102 (0.85/2.27) I	I 93 (0.77/2.10) S_A 11 (0.32/1.13) K I 93 (0.82/2.24) S_A 15 (0.25/0.87) K
19-8/6	11,000	1.94	K 57[a] K 66[a] S_C^* 70[a] (2.05) S_A 121 (0.71/1.80) I	I 115 (0.87/2.24) S_A 71 (0.04/0.11) S_C^* 51 (1.99/6.13) K
			K 64[a] S_C^* 72[a] (2.34/−) S_A 120 (0.88/2.25) I	I 115 (0.87/2.25) S_A 71 (0.04/0.11) S_C^* 51 (1.99/6.15) K

[a]Overlapped transitions, enthalpy change corresponds to the sum of both transitions.
[b]mru = mole repeat unit.

4-[S(−)-2-Methyl-1-butoxy]-4′-(2-propenyl-1-oxy)-α-methylstilbene (17-3)

17-3 was synthesized by the same procedure as that used for 17-11 except that one equivalent of 10-undecen-1-yl tosylate was replaced with two equivalents of allyl chloride which were added to the reaction mixture at the very beginning of the reaction and an additional equivalent amount of allyl chloride which was added after 8 h. Analytical data are presented in Table 4.

Radical Polymerization of Monomers

The polymerizations of acrylates and methacrylates were carried out under N_2 in Schlenk tubes equipped with septa. The polymerization tube containing the benzene solution of the acrylate or methacrylate (10%, w/v) and the initiator AIBN (1 wt% vs monomer) was degassed by several freeze–pump–thaw cycles under vacuum and then filled with nitrogen. The polymerizations were carried out at 60°C for 24 h. The resulting polymers were then precipitated into methanol containing a few drops of hydrochloric acid, filtered, and reprecipitated from THF solutions into methanol/acetone 70/30 (v/v). No unreacted monomers were detected in the purified polymers by HPLC analysis. The data of polymer molecular weights and thermal transitions are presented in Table 5.

Poly(methylsiloxane)s and Copoly(methylsiloxane)

The poly(methylsiloxane)s (19-n) were prepared by the hydrosilation reaction of 4-[S(−)-2-methyl-1-butoxy]-4′-(ω-alkenyl-1-oxy)-α-methylstilbene (17-n) and a poly(methylhydrosiloxane) (18) having a number-average degree of polymerization of 22. The copoly(methylsiloxane) (19-8/6) was prepared by the same procedure described above except that a 1:1 ratio of the two different monomers (i.e., 17-8 and 17-6) was used (Scheme 4). An example of the hydrosilation reaction is given below.

A solution of 0.36 g (0.81 mmol, 20% excess) 4-[S(−)-2-methyl-1-butoxy]-4′-(10-undecenyl-1-oxy)-α-methylstilbene, 0.04 g poly(methylhydrosiloxane), and a catalytic amount of platinum divinyltetramethyldisiloxane complex in 5 mL dry toluene was heated to 60°C under N_2 overnight. After IR analyses showed that the hydrosilation reaction was complete (no residual Si—H peak at 2150 cm^{-1} was observed), the polymer was separated by precipitation into methanol. The polymer was further purified by dissolving it in THF, filtering it through fluted filter paper, and precipitating it in methanol/acetone 70/30 (v/v). No unreacted olefin derivative was observed in the resulting polymer by HPLC analysis. The molecular weights and the thermal transitions of the resulting polymers are presented in Table 5.

RESULTS AND DISCUSSION

Scheme 1 outlines the synthesis of 4-[S(−)-2-methyl-1-butoxy]-4′-(hydroxy)-α-methylstilbene (9). During this sequence of reactions the optical purity of the starting material is not affected and therefore is not reported [13a]. The main improvement versus the previously reported procedure [14] consists of the acylation of 4 with 7 to give 8. When this reaction is performed between −20 and −10°C, 8 is obtained with a higher purity than that which resulted from the previous method.

Schemes 2–4 describe the synthesis of polymers and copolymers. The synthesis and characterization of 15-11-A, 15-11-M, and 19-11 were reported previously [14]. However, they were again prepared in order to confirm their mesomorphic behavior by comparing it with that of the previously synthesized polymers as well as with that of the new polymers reported for the first time in this paper.

All polymers and monomers were characterized by a combination of differential scanning calorimetry and thermal optical polarized microscopy.

The overall yields of the methacrylates 14-n-M (Table 2) and acrylates 14-n-A (Table 3) decrease due to their decreasing spacer lengths. This is due to larger losses of material at each purification by recrystallization because of the higher solubility of monomers and intermediary compounds containing shorter spacers. The molecular weights of polyacrylates 15-n-A are lower than those of the corresponding polymethacrylates 15-n-M since the acrylates undergo more chain transfer reactions than do the methacrylates.

All the methacrylates 14-n-M and acrylates 14-n-A are only crystalline. Some of the alkanyl derivatives 17-n exhibit mesomorphic phases. 17-11 displays an enantiotropic S_A phase and 17-6 a monotropic S_A mesophase. 17-8 displays an enantiotropic S_A phase and an unidentified monotropic smectic mesophase (S_X). The monotropic mesophase could not be identified by optical polarized microscopy since 17-8 crystallized during characterization. The S_A mesophase of compounds 17-11, 17-8, and 17-6 exhibits a focal conic texture.

All polyacrylates and polymethacrylates exhibit an enantiotropic S_A mesophase (Table 5) which displays a characteristic focal conic texture. The polymers with long (eleven methylenic units) and short (three and two methylenic units) flexible spacers give rise to side-chain crystallization. Their ability to crystallize is determined by the flexibility of their polymer backbones. 15-11-M, 15-3-M, 15-2-M, and 15-2-A display a melting transition only on their first DSC heating scan while 15-11-A shows melting and crystallization transitions on each scan regardless of the thermal history of the sample. The crystalline phase of 15-11-M can be obtained either by precipitation from solution or by annealing above the polymer glass transition temperature. This behavior agrees with that observed previously for other series of polymers containing α-methylstilbene-based side groups [14, 19, 20], and it can be explained by the polymer backbone effect [21]. In the liquid crystalline phase the random-coil conformation of the polymer backbone becomes distorted [23–26]. This distortion is higher in the smectic phase than in the nematic phase, and it is strongly dependent on polymer backbone flexibility [25]. Since flexible polymer backbones undergo the change from the random-coil to the distorted conformation much faster than do rigid backbones, the former show a faster rate of mesophase formation and a much higher ability to undergo side-chain crystallization [25]. In a smectic phase, polymers with very short flexible spacers should probably adopt an extended conformation [24].

Due to their very flexible backbones, poly(methylsiloxane)s containing mesogenic side groups show a much higher tendency toward mesophase formation and side-chain crystallization than do the corresponding polymethacrylates and polyacrylates [13d, 19–21, 25].

This behavior is indeed observed in the case of poly(methylsiloxane)s 19-n. Regardless of the thermal history of the samples, 19-11 and 19-3 exhibit S_A phase and side-chain crystallization (Table 5). The phase behavior of 19-8, 19-6, and the copolymer containing a 1/1 ratio of their structural units, i.e., 19-8/6, will be discussed on

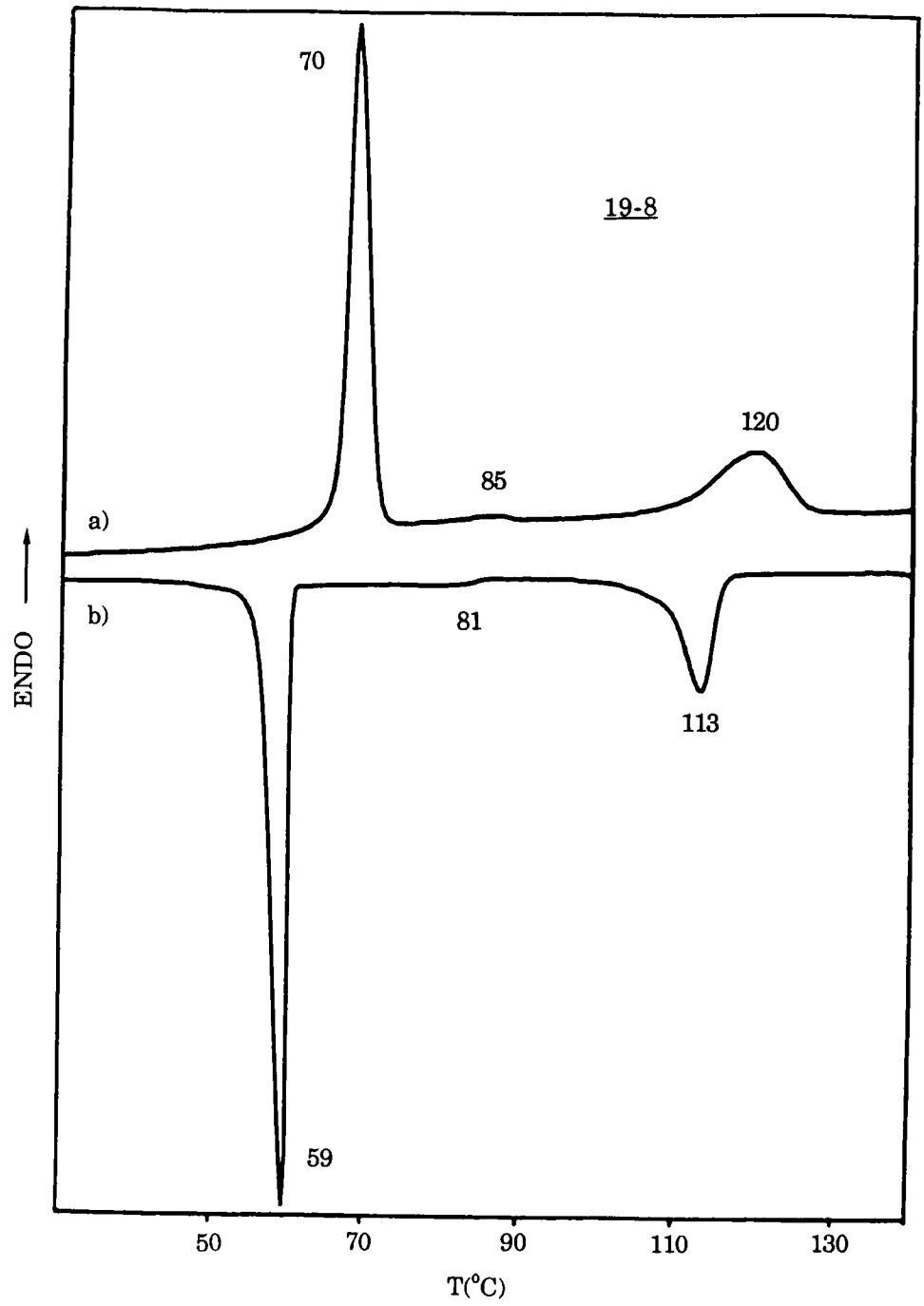


FIG. 1. DSC thermograms (20°C/min) of: a) second heating scan of 19-8; b) cooling scan of 19-8.

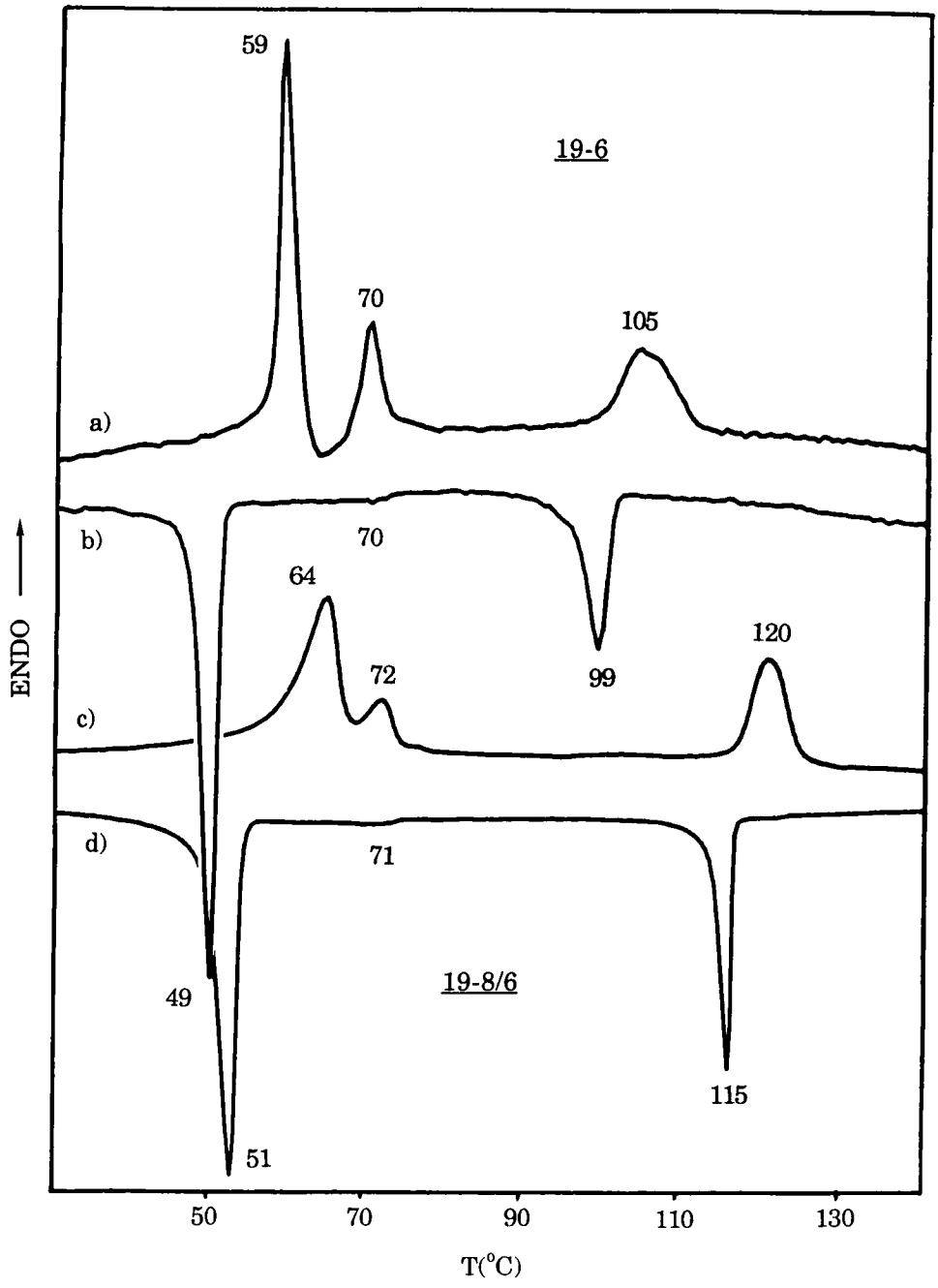
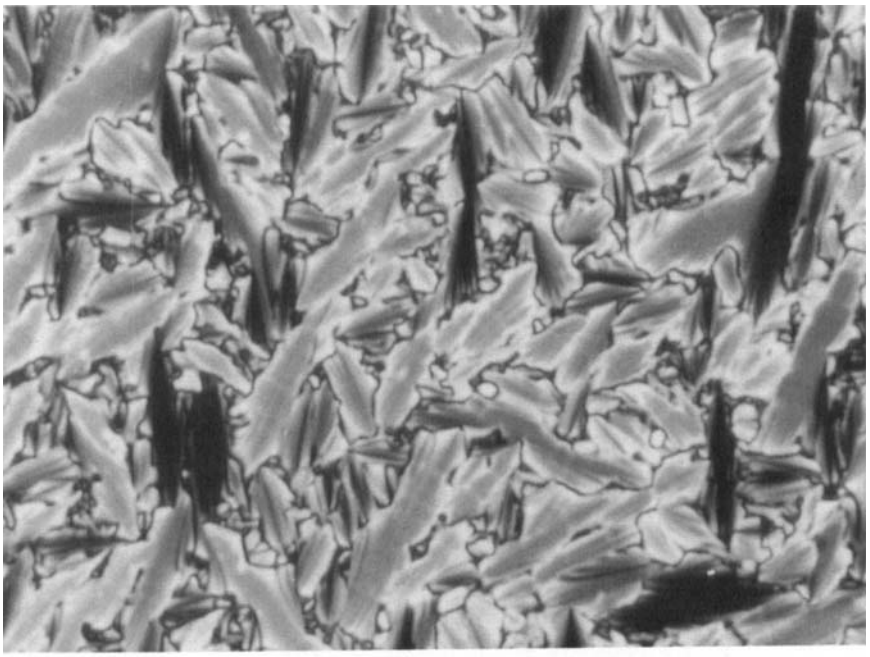
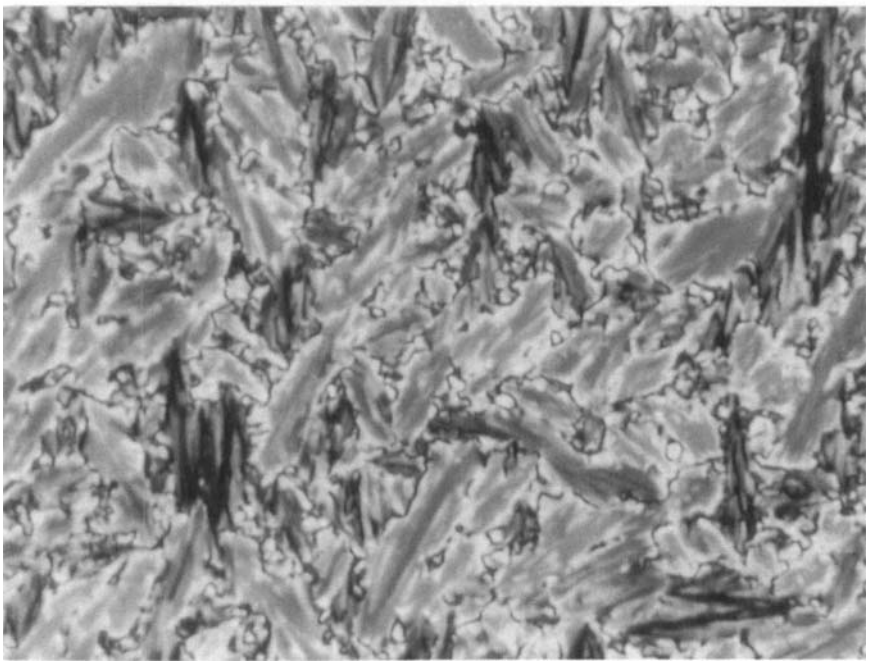


FIG. 2. a) Second heating scan of 19-6; b) cooling scan of 19-6; c) second heating scan of 19-8/6; d) cooling scan of 19-8/6.



a)



b)

the basis of their DSC traces which are available in Fig. 2. Their phase behavior is summarized in Table 5. Regardless of the DSC scan, 19-8, 19-6, and their copolymer exhibit two enantiotropic mesophases and side-chain crystallization (Figs. 1 and 2 and Table 5). The first enantiotropic mesophase is an S_A phase which in all cases exhibits a focal conic texture. Figure 3a shows a characteristic texture of the S_A phase of 19-6. On cooling from the S_A phase, 19-8 undergoes a transition from S_A to S_C^* at about 85°C. On the DSC scan this phase transition can be observed only with difficulty (Figs. 1a and 1b). However, the transition is observable on an optical polarized microscope both on heating and cooling. In the case of 19-6, the transition from S_A to S_C^* can be observed both on heating and cooling DSC scans (Figs. 2a and 2b). However, the enthalpy change associated with the $S_A \rightarrow S_C^*$ phase transition is smaller than the one associated with the $S_C^* \rightarrow S_A$ transition (Figs. 2a and 2b, Table 5). The DSC traces of the copolymer 19-8/6 (Figs. 2c and 2d) look like a combination of those of 19-8 (Figs. 1a and 1b) and 19-6 (Figs. 2a and 2b). A representative texture of the S_A phase is shown in Fig. 3(a) and of the S_C^* phase in Fig. 3(b). The S_A phase exhibits a focal conic texture. The more stable phase has been tentatively assigned as an S_C by a combination of photomicrography [3b, 5, 7, 18] (Fig. 3b) and x-ray scattering. A detailed characterization will be given in a future publication [26].

The formation of an S_C^* phase only by poly(methylsiloxane)s represents a characteristic example of the polymer backbone effect [21]. An additional example of the polymer backbone effect is the reentrant nematic mesophase N_{re} formed by certain polyacrylates but not by the corresponding polymethacrylates [27]. In both cases the more flexible poly(methylsiloxane) and polyacrylate backbone can probably adopt the required change in conformation at the $S_A \rightarrow S_C^*$ and $S_A \rightarrow N_{re}$ phase transitions. At the same time, the more rigid polymer backbones cannot undergo the required conformational change within the necessary time scale, and therefore these polymers do not exhibit S_C^* and N_{re} mesophases. Quantitative experimental data on this conformational change are required to confirm this assumption.

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FIG. 3. a) Typical optical polarized micrograph (100×) of the focal conic texture exhibited by the S_A phase of 19-6 at 89.6°C; b) typical optical polarized micrograph (100×) of the focal conic texture with equidistant lines exhibited by S_C^* phase of 19-6 at 68.6°C.

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