Liquid crystalline polymers containing mesogenic units based on half-disc and rod-like moieties

3. Synthesis and characterization of polymethylsiloxanes and copolymethylsiloxanes based on 4-[3,4,5-tri(*p-n*-dodecan-1-yloxybenzyloxy)benzoate]-4'-(*p*-allyloxybenzoate)biphenyl and 4-[3,4,5-tri(*p-n*-dodecan-1-yloxybenzyloxy)benzoate]-4'-(*p*-allyloxybenzoate)thiodiphenyl side groups

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SUMMARY

The synthesis and characterization of the hemiphasmidic monomers 4-[3,4,5-tri(p-n-dodecan-1-yloxybenzyloxy)benzoate]-4'-(p-allyloxybenzoate)biphenyl (10) and 4-[3,4,5-tri(p-n-dodecan-1-yloxybenzyloxy)benzoate]-4'-(p-allyloxybenzoate)thiodiphenyl (11) and of the polymethylsiloxanes and copolymethylsiloxanes [13(X/Y)] containing side groups derived from 10 and 11 are described. Both 10 and 11 are only crystalline. However, 13(100/0), 13(0/100), and the corresponding copolymers exhibit enantiotropic, most probably phasmidic mesophases.

INTRODUCTION

Liquid crystals based on combinations of two half-disc and a rod-like moiety display either columnar oblique (Φ_{ob}), hexagonal (Φ_h) phasmidic[1-7], or biaxial nematic (N_b)[7,8] mesophases. Half phasmids or hemiphasmidic liquid crystals are combinations of a half-disc and a rod-like moieties[7] and so far seem to provide the most successful architectural approach to the synthesis of liquid crystals displaying N_b mesophases.[2,6,7,9]

The first examples of liquid crystalline polymers containing phasmidic and half phasmidic mesogens were reported from our[10-12] and from Ringsdorf's[13] laboratories. In the first two publications from this series we reported the synthesis and characterization of side chain liquid crystalline polysiloxanes containing 4-(11-undecan-1-yloxy)-4'-[3,4,5-tri(p-n-dodecan-1-yloxy)benzyloxy]biphenyl[12] and 2-[3,4,5-tri(p-n-dodecan-1-yloxy)benzyloxy]benzoate-7-[p-(11-undecan-1-yloxy)benzoate]naphthalene[11] side groups. While the first hemiphasmidic mesogen[12] represents a classic combination of a half-disc and a rigid rod-like group, the second one[11] represents a combination of a half-disc and a kinked-rigid moiety. The first goal of this paper is to extend the structural concept of hemiphasmidic mesogens to combinations based on a half-disc and a non-rigid-kinked moiety. The second goal is to demonstrate the ability to molecular engineer phase transitions of side chain liquid crytalline polymers containing hemiphasmidic mesogens by copolymerization. The experiments which demonstrate these two concepts will be performed with polymethylsiloxanes and copolymethylsiloxanes containing mesogenic side groups derived from 4-[3,4,5-tri(p-n-dodecan-1-yloxybenzyloxy)benzoate]-4'-(p-allyloxybenzoate)biphenyl and 4-[3,4,5-tri(p-n-dodecan-1-yloxybenzyloxy)benzoate]-4'-(p-allyloxybenzoate)thiodiphenyl.

EXPERIMENTAL

Materials

THF was distilled from LiAlH₄. CH₂Cl₂ was distilled from CaH₂. DMSO and DMF were stirred overnight at 100°C over CaO and then distilled from CaO under vacuum. Pyridine was heated overnight at 100°C over KOH, distilled from KOH, and then stored over KOH. N,N-dicyclohexylcarbodiimide (DCC) was dissolved in hexanes, filtered, and the solvent

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evaporated. Toluene and xylene were both washed with 50 ml portions of H_2SO_4 until the portions were relatively uncolored, washed with water until neutral pH, dried over $MgSO_4$, filtered, allowed to reflux overnight with Na metal and then distilled from Na metal. The platinum divinyltetramethyldisiloxane catalyst (solution in xylene from Petrarch) was purified by placing it in a clean flamed dried round bottom flask with gas inlet adapter which was attached to a vacuum line under vacuum (0.2 mm Hg). A beaker of warm tap water was placed up under the flask so as to partially submerge it. The tap water was replaced as it cooled and the vacuum maintained for 8 hrs, after which the remaining catalyst was diluted to 30 times its original volume with the previously dried xylene, sealed, and stored in a desicator. The benzoic acids and phenols used in the esterifications and the monomers used in hydrosilations were dried under vacuum in a desicator for 24 hrs prior to use. All other materials were commercially available and were used as received.

Techniques
    The techniques used in the characterization of intermediary derivatives and polymers [200 MHz ^{1}H-NMR spectroscopy, IR spectroscopy, differential scanning calorimetry (DSC, 20°C/min), gel permeation chromatography (GPC, with polystyrene standards) and high pressure liquid chromatography (HPLC), and thermal optical polarized microscopy] have been described elsewhere.[14,15]

Monomers and Polymers
    Scheme I outlines the synthesis of the monomers and polymers.
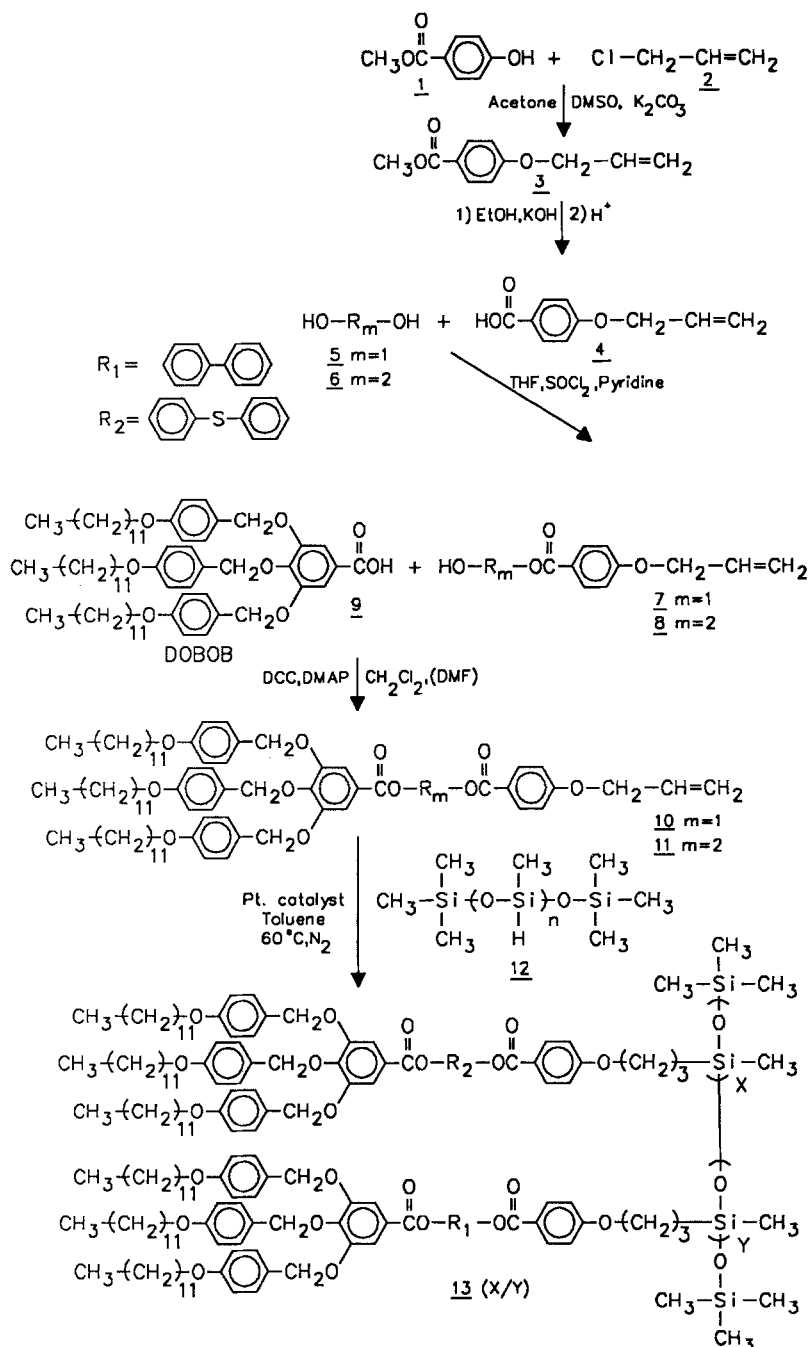
Methyl-p-allyloxybenzoate (3)
    A mixture containing 40g (0.52 mol) of allyl chloride, 41g (0.27 mol) methyl-4-hydroxybenzoate (1), 45g (0.33 mol) anhydrous K_2CO_3 and 300 ml acetone with 5% dry DMSO was heated at 50°C for 20 hrs. The acetone and residual allyl chloride were then evaporated, water was added and the product was extracted with hexanes. Some of the hexane was evaporated to reduce the volume. The product was then purified by flash chromatography (neutral alumina, hexanes eluent) and the solvent evaported to give 51g (98%) of a yellow oil. Purity: >99% (HPLC). ^{1}H-NMR (CDCl$_3$, TMS, δ, ppm): 3.84 (s, 3H, CH$_3$), 4.56 (d, 2H, -CH$_2$-O-Ph), 5.31 (d, 1 H, CH$_2$=CH-CH$_2$- trans), 5.38 (d, 1H, CH$_2$=CH-CH$_2$- cis), 6.02 (m, 1H, -CH=CH$_2$), 6.89 (d, 2H, -O-PhH-COOH ortho from -O-), 7.93 (d, 2H, -O-PhH-COOH meta from -O-). IR (KBr plate): 1703 cm^{-1} (v-C=O)

p-Allyloxybenzoic acid (4)
    A mixture containing 51g (0.26 mol) of methyl-p-allyloxybenzoate (3), 23g (0.41 mol) KOH, and 250 ml EtOH with 40% H_2O was refluxed 8 hrs and then allowed to cool to room temperature. The solution was acidified with dilute formic acid and the resulting precipitate was filtered. The solid was then dissolved in acetone and slightly acidified with dilute formic acid to ensure complete protonation. The acetone solution was poured into H_2O and the precipitate filtered and allowed to air dry on the filter to give 47g (99%) of white flakes. Purity was not determined because of low solubility of 4 in CHCl$_3$. mp, 159°C. ^{1}H-NMR (CD$_3$COCD$_3$, TMS, δ, ppm): 4.67 (d, 2H, -CH$_2$-O-Ph), 5.30 (d, 1H, CH$_2$=CH-CH$_2$-trans), 5.38 (d, 1H, CH$_2$=CH-CH$_2$- cis), 6.05 (m, 1H, -CH=CH$_2$), 7.01 (d, 2 H, -O-PhH-COOH ortho from -O-), 7.95 (d, 2H, -O-PhH-COOH meta from -O-). IR (KBr plate): 1664 cm^{-1} (v-C=O)

4-Hydroxy-4'-(p-allyloxybenzoate)biphenyl (7)
    To a solution containing 14g (0.086 mol) of 4 in 100 ml dry THF at 0°C was added dropwise 12ml (0.16 mol) of SOCl$_2$. The solution was then allowed to stir 5 hrs at room temperature after which the solvent, HCl, and residual thionyl chloride were evaporated on a rotovapor at reduced pressure. 50 ml dry THF was added and the resulting solution was added dropwise to a solution of 75 ml dry THF and 25g (0.13 mol) of 4,4'-

Scheme I: Synthesis of copolymethylsiloxanes 13(X/Y) based on 4-[3,4,5-tri(p-n-dodecan-1-yloxybenzyloxy)benzoate]-4'-(p-allyloxybenzoate)biphenyl and 4-[3,4,5-tri(p-n-dodecan-1-yloxybenzyloxy)benzoate]-4'-(p-allyloxybenzoate)thiodiphenyl side groups.

dihydroxybiphenyl (5) at room temperature. Then 15 ml (0.19 mol) of dry pyridine and 0.2 g (0.002 mol) 4-dimethylamino-pyridine were added. The solution was allowed to stir 1.5 hrs after which 1 ml (0.01 mol) of additional $SOCl_2$ was added and the solution allowed to stir for an additional 0.5 hrs. The mixture was filtered, quenched with H_2O, poured into H_2O and allowed to stir 16 hrs. The precipitate was filtered and washed with water. The precipitate was placed in a beaker with MeOH and allowed to stir 0.25 hrs, filtered, and air dried on the filter. The solid was purified by flash chromatography (neutral alumina, acetone eluent) and the solvent was evaporated. The resulting solid was dissolved in acetone and the precipitate was filtered and discarded. The solvent was evaporated and the remaining solid was stirred in hot MeOH for 0.5 hrs, cooled to room temperature, and filtered. This was repeated three times, after which the solid was stirred in hot CH_2Cl_2 for 0.5 hrs, cooled to room temperature, and filtered, to afford 7.24 g (24%) of a white solid. Purity was not determined because of low solubility of 7 in $CHCl_3$. mp, 205ºC. ^{1}H-NMR (CD_3COCD_3, TMS, δ, ppm): 4.72 (d, 2H, -C$\underline{H}_2$-O-Ph), 5.31 (d, 1H, C$\underline{H}_2$=CH-CH$_2$- trans), 5.40 (d, 1H, C$\underline{H}_2$=CH-CH$_2$- cis), 6.07 (m, 1H, -C$\underline{H}$=CH$_2$), 6.92 (d, 2H, biphenyl ortho from -OH), 7.11 (d, 2H, -O-Ph$\underline{H}$-COO- ortho from -O-), 7.28 (d, 2H, biphenyl ortho from -OOC-Ph), 7.45 (d, 2H, biphenyl meta from -OH), 7.63 (d, 2H, biphenyl meta from -OOC-Ph), 8.12 (d, 2H, -O-Ph$\underline{H}$-COOH meta from -O-). IR (KBr.pellet): 1691 cm^{-1} (v-C=O), 3200 cm^{-1} (v-OH)

4-Hydroxy-4'-(p-allyloxybenzoate)thiodiphenyl (8)

To a solution of 4.2 ml (0.058 mol) $SOCl_2$, 4.7 ml (0.058 mol) dry pyridine, and 50 ml dry THF was added dropwise a solution of 10.0 g (0.056 mol) 4 in 50 ml dry THF at room temperature. The resulting mixture was added dropwise to a solution of 20 g (0.092 mol) 4,4'-thiodiphenol (6) in 100 ml dry THF at room temperature. Then 5.0 ml (0.062 mol) dry pyridine were added dropwise and the solution was heated at 40ºC for 18 hrs. The solution was poured into H_2O, extracted with $CHCl_3$, and the solvent was evaporated. The mixture was stirred with hot petroleum ether, allowed to cool, most of the solvent was decanted and the residue was evaporated. The resulting solid was recrystallized from MeOH over a 10 hr period. The crystals formed in the first 30-45 min. were discarded since they contained mostly disubstituted thiodiphenyl. The crystals were filtered, air dried, and then purified by flash chromatography (neutral alumina, $CHCl_3$ eluent). The solvent was evaporated to yield 4.69 g (22%) of a white solid. Purity: 96% (HPLC). mp, 139ºC. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 4.62 (d, 2H, -C$\underline{H}_2$-O-Ph), 5.34 (d, 1H, C$\underline{H}_2$=CH-CH$_2$- trans), 5.42 (d, 1H, C$\underline{H}_2$=CH-CH$_2$- cis), 6.04 (m, 1H, -C$\underline{H}$=CH$_2$), 6.75 (d, 2H, thiodiphenyl ortho from -OH), 6.98 (d, 2H, -O-Ph$\underline{H}$-COO- ortho from -O-), 7.06 (d, 2H, thiodiphenyl ortho from -OOC-Ph), 7.20 (d, 2H, thiodiphenyl meta from -OH), 7.34 (d, 2H, thodiphenyl meta from -OOC-Ph), 8.12 (d, 2H, -O-Ph$\underline{H}$-COOH meta from -O-). IR (KBr plate): 1708 cm^{-1} (v-C=O), 3300 cm^{-1} (v-OH)

3,4,5-Tri[p-(n-dodecan-1-yloxy)benzyloxy]benzoic acid (DOBOB) (9)

The synthesis of compound 9 has been reported previously.[12]

4-{3,4,5-Tri[p-(n-dodecan-1-yloxy)benzyloxy]benzoate}-4'-(p-allyloxybenzoate)biphenyl (10)

A solution containing 4.3g (4.3 mmol) of 9, 1.5g (4.3 mmol) of 7, 0.9g (4.3 mmol) of DCC and 0.2g (2 mmol) of 4-dimethylamino-pyridine in 50 ml dry CH_2Cl_2 with 5% dry DMF was stirred for 18 hrs at room temperature. The resulting precipitate was filtered and the CH_2Cl_2 was evaporated. THF and 1 ml of H_2O were added and the solution was stirred for 1 hr, then poured into H_2O and the product was extracted with $CHCl_3$. The $CHCl_3$ was evaporated, CH_2Cl_2 was added and the resulting solution was precipitated into MeOH. The precipitate was filtered and allowed to dry in the air. The product was purified by flash chromatography (basic alumina, CH_2Cl_2 eluent), the volume of the solvent reduced, and again precipitated into MeOH, filtered, and allowed to dry in air, yielding 3.4 g (59%) of a white solid. Purity: >98% (HPLC). mp, 97.8ºC (DSC, 20ºC/min). ^{1}H-NMR ($CDCl_3$,

TMS, δ, ppm): 0.87 (t, 9H, -CH₃), 1.30 (m, 54H, -(CH₂)-), 1.77 (m, 6H, -CH₂CH₂OPh-), 3.93 (2 overlapped t, 6H, -CH₂OPh-CH₂O-), 4.64 (d, 2H, -CH₂-CH=CH₂), 5.05 (s, 2H, -OPh-CH₂OPh-COO- from para position), 5.08 (s, 4H, -OPh-CH₂OPh-COO- from 3 and 5 positions), 5.36 (d, 1H, CH₂=CH-CH₂- trans), 5.42 (d, 1H, CH₂=CH-CH₂- cis), 6.07 (m, 1H, -CH=CH₂),6.77 (d, 2H, -OPhH-CH₂OPh-COO- ortho from -O- of internal benzylic unit), 6.89 (d, 4H, -OPhH-CH₂OPh-COO- ortho from -O- of external benzylic units), 7.01 (d, 2H, -CH₂CHOPhH-COO- ortho from -O-), 7.27 (2 overlapped d, 6H, -OPhH-CH₂OPh-COO- meta from -O- of internal benzylic unit and biphenyl protons meta from -O-), 7.34 (d, 4H, -OPhH-CH₂OPh-COO- meta from -O- of external benzylic units), 7.52 (s, 2H, -Ph-CH₂OPhH-COO- ortho from -COO-), 7.63 (d, 4H, biphenyl protons meta from -O-), 8.16 (d, 2H, -CH₂CH₂OPhH-COO- meta from -O-). IR (KBr plate): 1718 cm⁻¹ (ν-C=O).

4-{3,4,5-Tri[p-(n-dodecan-1-yloxy)benzyloxy]benzoate}-4'-(p-allyloxybenzoate)thiodiphenyl (11)

Compound 11 was synthesized by a similar procedure to that used in the preparation of 10 with the following exceptions: (1) the reaction mixture contained no DMF, and (2) the precipitations were done from a CH₂Cl₂ solution into MeOH which was maintained at less than -10°C. Starting from 4.4g (4.5 mmol) of 9 and 1.7g (4.4 mmol) of 8 we attained 3.4g (57%) of a white solid. Purity: >99% (HPLC). mp, 70.7°C (DSC, 20°C/min). ¹H-NMR (CDCl₃, TMS, δ, ppm): 0.87 (t, 9H, -CH₃), 1.29 (m, 54H, -(CH₂)-), 1.76 (m, 6H, -CH₂CH₂OPh-), 3.92 (2 overlapped t, 6H, -CH₂OPh-CH₂O-), 4.63 (d, 2H, -CH₂-CH=CH₂), 5.04 (s, 2H, -OPh-CH₂OPh-COO- from para position), 5.07 (s, 4H, -OPh-CH₂OPh-COO- from 3 and 5 positions), 5.34 (d, 1H, CH₂=CH-CH₂- trans), 5.41 (d, 1H, CH₂=CH-CH₂- cis), 6.05 (m, 1H, -CH=CH₂), 6.76 (d, 2H, -OPhH-CH₂OPh-COO- ortho from -O- of internal benzylic unit), 6.88 (d, 4H, -OPhH-CH₂OPh-COO- ortho from -O- of external benzylic units), 6.99 (d, 2H, -CH₂CH₂OPhH-COO- ortho from -O-), 7.15 (2 overlapped d, 4H, thiodiphenyl protons ortho from -O-), 7.26 (d, 2H, -O-PhH-CH₂OPh-COO- meta from -O- of internal benzylic unit), 7.33 (d, 4H, -OPhH-CH₂OPh-COO- meta from -O- of external benzylic units), 7.41 (d, 4H, thiodiphenyl protons meta from -O-), 7.48 (s, 2H, -Ph-CH₂OPhH-COO- ortho from -COO-), 8.12 (d, 2H, -CH₂CH₂OPhH-COO- meta from -O-). IR (KBr plate): 1725 cm⁻¹ (ν-C=O).

Copolymethylsiloxanes containing 4-[3,4,5-tri(p-n-dodecan-1-yloxybenzyloxy)benzoate]-4'-(p-allyloxybenzoate)biphenyl and 4-[3,4,5-tri(p-n-dodecan-1-yloxybenzyloxy)benzoate]-4'-(p-allyloxybenzoate)thiodiphenyl side groups (13)

All the hydrosilations and purifications were performed in the same way. A summary of the results is presented in Table I. An example is given below. To a flame dried 5 ml test tube containing a microstirring bar were added 0.246g (0.182 mmol) of 11, 0.360 (0.272 mmol) of 10, 0.027g (0.45 mmol) poly(hydrogenmethylsiloxane) (Mn=1500 from Petrarch), 2-3 ml dry toluene, and five drops (about 0.1g) of purified platinum divinyltetramethyldisiloxane complex. The reaction was purged with nitrogen and the tube was sealed with a cork stopper covered with teflon tape. The reaction mixture was heated for 24 hr at 60°C, after which 0.04g (0.4 mmol) of 1-octene and two additional drops (about 0.04g) of catalyst were added and the mixture heated 2 hrs. The solution was then cooled and precipitated into methanol. The precipitate was filtered, dissolved in CH₂Cl₂ and precipitated in acetone cooled to <-10°C to yield 0.43g (71%) of a white solid. Purity: >99% (HPLC). Mn=27000, Mw/Mn=1.6 (GPC)

RESULTS AND DISCUSSION

Scheme I outlines the synthesis of the monomers 10 and 11 and of the polymers 13 containing various X/Y ratios; ie. 13(X/Y). A detailed synthesis of 9 was reported previously.[12] Both 10 and 11 are only crystalline. However, we may expect that they exhibit virtual mesophases. Simple thermodynamic considerations demonstrate that upon increasing the degree of polymerization, the virtual mesophase of the original monomer unit becomes

either monotropic or enantiotropic.[16,17] This effect was experimentally observed in many cases of side chain liquid crystalline polymers containing rigid-rod like mesogenic groups.[14,18-20]

We did expect the same trend to be observed in the case of side chain liquid crystalline polymers containing hemiphasmidic side groups. This is the case indeed. Both 13(100/0) and 13(0/100) exhibit enatiotropic mesophases (Table I) although the parent monomers were only crystalline. On the optical polarized microscope, when cooling from the isotropic phase, 13(100/0), 13(0/100), and the 13(X/Y) copolymers exhibit a fan shaped focal conic texture which is representative for a phasmidic (Φ) mesophase (Figure 1).

Table I Characterization of Copolysiloxanes (13) (g=glassy phase, k=crystalline phase, Φ=phasmidic mesophase)

Mole Ratio X /Y	Mn (GPC)	M_w/M_n	Purity % (HPLC)	Yield %	Phase transitions($^{\circ}$C)and corresponding enthalpy changes(kcal/mru)[a] heating[b]	cooling
100/0	21,000	1.6	>99	22	k 51(4.4) Φ 74(0.08) i g 36 Φ 74(0.04) i	i 64(0.01) Φ 31 g
80/20	23,000	1.5	>99	54	k 52(1.5) Φ 81(0.07) i g 39 Φ 81(0.03) i	i 78(0.07) Φ 31 g
60/40	26,000	1.6	>98	59	g,k 49(0.4)[c] Φ 108(0.04) i g 41 Φ 110(0.05) i	i 94(0.05) Φ 38 g
40/60	27,000	1.6	>99	70	g,k 52,57(0.4)[c] Φ 135(0.05) i g 45 Φ 137(0.03) i	i 111(0.04) Φ 43 g
20/80	23,000	1.7	>99	58	g,k 58(0.6)[c] k 111(1.1) Φ 170(0.13) i g 46 Φ 168(0.05) i	i 151(0.05) Φ 45 g
0/100	25,000	1.6	>99	43	g,k 95(0.6)[c] Φ 199,205(0.16)[c] i g 59 Φ 196(0.08) i	i 180(0.05) Φ 44 g

[a]average mole repeat unit based on composition; [b]first and second heating scan;[c]combined enthalpy for overlapped transitions

a)

Figure 1: Representative optical polarized micrographs (100x) of the focal conic fan shaped texture displayed by : a) 13(0/100) upon cooling at 5°C/min from the isotropic phase to 164°C; b) 13(20/80) upon cooling at 5°C/min from the isotropic phase to 159°C and annealing for 5 minutes.

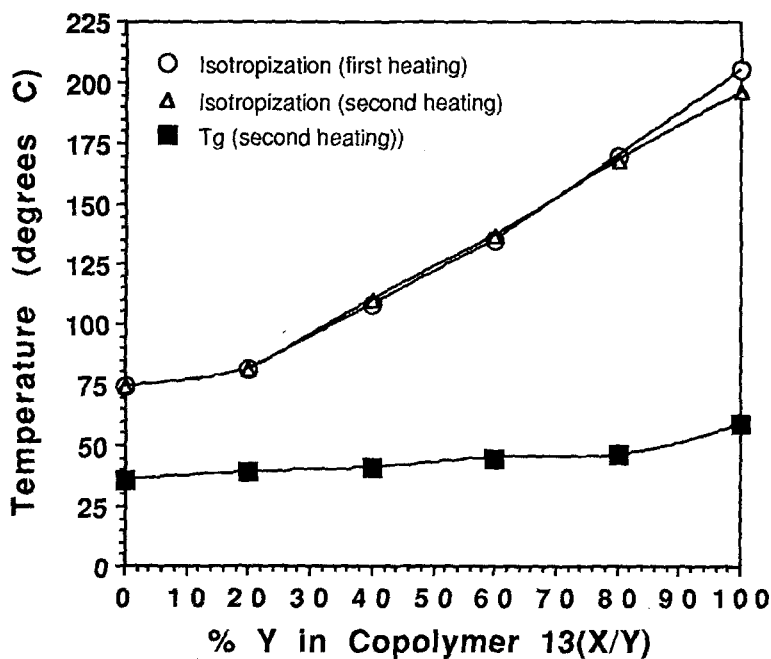Figuire 2: The dependence of glass transition (T_g) and isotropization temperatures (from first and second heating scans) on copolymer 13(X/Y) composition.

Such a mesophase would have been expected for the case of polymer 13(0/100) since its mesogenic unit is based on a combination of rigid rod-like and half-disc groups. However, in the case of 13(100/0) the linear part of the mesogen contains a flexible diphenyl sulfide group which can freely rotate, and therefore its hemiphasmidic character is not trivial, As we can observe from Table I, the main difference between these two polymers consists in the lower isotropization transition temperature observed for the case of 13(100/0). The copolymers 13(X/Y) exhibit phase transition temperatures which show a continuous dependence on copolymer composition (Table I, Figure 2). Therefore, we can consider that the two structural units of these copolymers are isomorphic within their phasmidic mesophase.

These copolymerization experiments have demonstated that mesomorphic phase transitions temperatures of polymers containing hemiphasmidic side groups can be engineered by copolymerization in the same way as in the case of polymers containing rigid rod-like mesogenic side groups.[18] Additional research on the characterization of the mesophases exhibited by 13(X/Y) is in progress.

ACKNOWLEDGEMENT

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