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

4. Side chain liquid crystalline polymethylsiloxanes containing hemiphasmidic mesogens based on 4-[3,4,5-tri-(alkan-1-yloxy)benzoate]biphenyl groups

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SUMMARY

The synthesis and characterization of the hemiphasmidic monomers 4-{3,4,5-tri-[S(-)-2-methylbutan-1-yloxy]benzoate}-4'-(10-undecenoate)biphenyl (13), 4-[3,4,5-tri-(n-pentan-1-yloxy)benzoate]-4'-(10-undecenoate)biphenyl (14), 4-[3,4,5-tri-(n-dodecan-1-yloxy)benzoate]-4'-(10-undecenoate)biphenyl (15), 4-[3,4,5-tri-(n-dodecan-1-yloxy)benzoate]-4'-(10-undecen-1-yloxy)biphenyl (16) and of the polymethylsiloxanes derived from them (i.e. 17, 18, 19, and 20) are described. Monomers 13 to 16 are only crystalline. Polymer 17 is crystalline, 18 displays an unidentified mesophase, while 19, and 20 exhibit enantiotropic, most probably hexagonal columnar phasmidic mesophases.

INTRODUCTION

Low molar mass liquid crystals based on various combinations of disc-like and rigid rod-like moieties[1-10] form either columnar hexagonal (Φ_h) or biaxial nematic (N_b)[7,8] mesophases. Hemiphasmidic liquid crystals are obtained from a half-disc and a rod-like moieties.

There are relatively few examples of polymeric structures containing hemiphasmidic mesogens.[11-15] We are presently exploring various mesogenic groups containing combinations of half-disc and rod-like moieties in which the half-disc is based on the 3,4,5-tri-(alkoxybenzyloxy)benzoate and 3,4,5-tri(alkoxy)benzoate groups for the synthesis of side chain liquid crystalline polymers exhibiting hexagonal columnar (Φ_h) mesophases.[11-14] The polymers described in this communication i.e., 17, 18, 19, and 20 are obtained by the hydrosilation of poly(methylsiloxane)s with 13, 14, 15, and 16 respectively. They will provide information on the influence of the length of the alkyl groups from the disc-like moiety and of the interconnecting group between the spacer and the meogen on the mesomorphic phase transitions of the polymers.

EXPERIMENTAL

Materials

The origin and the purification of the starting materials have been described previously.[14] The polymethylsiloxane (M_n=1500 from Petrarch) was found to have a DP=42.8 (M_n=2735) as determined by 200 MHz ^{1}H-NMR spectroscopy.[16]

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), high pressure liquid chromatography (HPLC), and thermal optical polarized microscopy] have been described elsewhere.[16,17]

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Monomers and Polymers

Scheme I outlines the synthesis of the monomers and polymers.

4-Hydroxy-4'-(10-undecenoate)biphenyl (4)

A solution containing 10g (50 mmol) of 10-undecenoic acid (2), 11g (60 mmol) of 4,4'-dihydroxybiphenyl (3) and 100 ml dry THF was cooled to 0°C and 4 ml (60 mmol) of thionyl chloride followed by dry pyridine (10 ml, 120 mmol) were added dropwise. The mixture was stirred at 0°C for 30 min, at room temperature for 4 hrs, and at 50°C for 4 hrs. The mixture was then cooled and poured into H_2O. The resulting precipitate was filtered, redissolved in THF, precipitated into H_2O, filtered, and allowed to dry in air. The product was then purified twice by flash chromatography. The first purification was done on neutral alumina with $CHCl_3$ as eluent. The second purification was done on basic alumina. A first fraction which was eluted with CH_2Cl_2 was discarded (mostly the diester). A second fraction was eluted with THF. The THF was evaporated to yield 5g (28 %) of a white solid. Purity: 80% (HPLC). mp, 116-118°C. ^{1}H-NMR ($CDCL_3$, TMS, δ, ppm): 1.34 (m, 10H, $-(C\underline{H}_2)-$), 1.72 (m, 2H, $-C\underline{H}_2-CH_2-COO-$), 2.05 (m 2H, $-C\underline{H}_2-CH=CH_2$), 2.58 (t, 2H, $-C\underline{H}_2-COO-$), 4.93 (d, 1H, $-CH=C\underline{H}_2$ trans), 5.00 (d, 1H, $-CH=C\underline{H}_2$ cis), 5.82 (m, 1H, $-C\underline{H}=CH_2$), 6.84 (d, 2H, biphenyl ortho from -OH), 7.10 (d, 2H, biphenyl ortho from -OOC-), 7.39 (d, 2H, biphenyl meta from -OH), 7.50 (d, 2H, biphenyl meta from -OOC-). IR (KBr plate): 1760 cm^{-1} sharp (ν-C=O), 1735 cm^{-1} sharp (ν-C=O).

4-Hydroxy-4'-(10-undecen-1-yloxy)biphenyl (5)

The synthesis of 5 was described previously.[12]

3,4,5-Tri-[S(-)-2-methylbutan-1-yloxy]benzoic acid (10)

A mixture containing 22g (90 mmol) of S(-)-2-methylbutan-1-tosylate (7) (prepared from S(-)-2-methyl-1-butanol as described previously[18]), 6.1g (29 mmol) of propyl-3,4,5-trihydroxybenzoate (6), 50g (360 mmol) anhydrous K_2CO_3 and 200 ml of dry DMF was purged with N_2, heated at 80°C under N_2 for 16 hrs, and then allowed to cool to room temperature. The reaction mixture was poured into 1500 ml H_2O and the solution was acidified with dilute HCOOH. CH_2Cl_2 (150 ml) was added and the organic layer was separated, dried over $MgSO_4$, filtered, and the solvent was evaporated. The product was purified by flash chromatography (basic alumina, CH_2Cl_2 eluent) and the CH_2Cl_2 was evaporated. A solution (200 ml) of 0.5 M KOH in EtOH + 5% H_2O was added and the mixture was refluxed for 1hr and allowed to cool to room temperature. The solution was acidified with dilute HCOOH and precipitated into H_2O. The solid was filtered and dried under vacuum to yield 7.5g (68 %) of a white solid. Purity: 99% (HPLC). mp, 87°C (DSC, 20°C/min). ^{1}H-NMR ($CDCL_3$, TMS, δ, ppm): 0.96 (t, 9H, $C\underline{H}_3-CH_2-CH^*$), 1.05 (d, 9H, $C\underline{H}_3-CH^*$), 1.30, 1.59, 1.87 (3 m, 9H, $CH_3-C\underline{H}_2-C\underline{H}^*$), 3.87 (overlapped t, 6H, $-C\underline{H}_2-O-$), 7.32 (s, 2H, Ph$\underline{H}$). IR (KBr plate): 1680 cm^{-1} (ν-C=O).

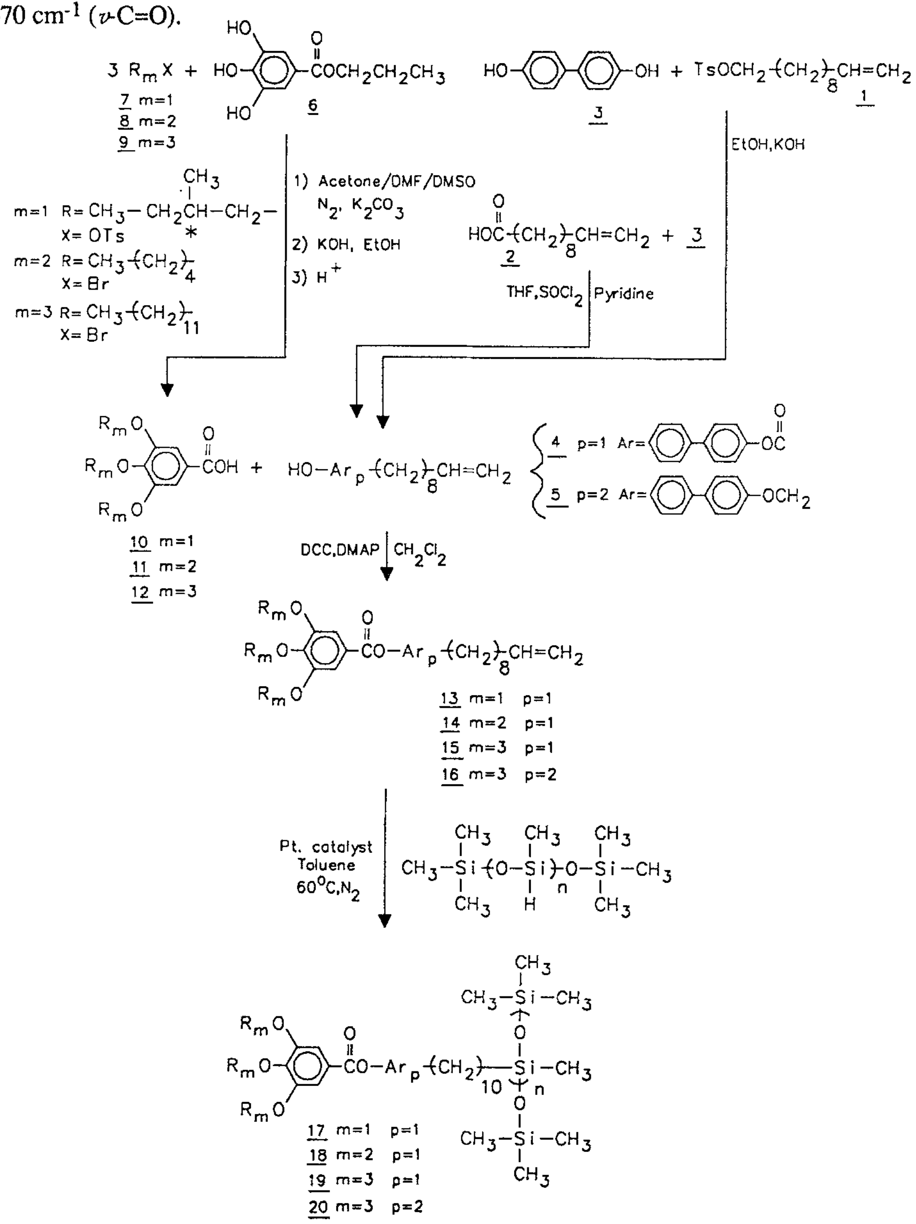
3,4,5-Tri-(n-pentan-1-yloxy)benzoic acid (11)

Compound 11 was synthesized and purified according to the same procedure as 10 with the following modifications: 1) the etherification solvent was acetone + 10% dry DMSO; 2) the reaction was performed at reflux for 10 hrs. From 14.0g (66 mmol) propyl-3,4,5-trihydroxybenzoate (6) and 30g (200 mmol) of bromopentane (8) were obtained 17.0g (68%) of a tan solid. Purity: 99% (HPLC). mp, 51°C (DSC, 20°C/min). ^{1}H-NMR ($CDCL_3$, TMS, δ, ppm): 0.93 (t, 9H, $C\underline{H}_3-$), 1.40 (m, 12H, $-(C\underline{H}_2)-$), 1.78 (m, 6H, $-C\underline{H}_2-CH_2-O-$), 4.01 (overlapped t, 6H, $-C\underline{H}_2-O-$), 7.24 (s, 2H, Ph$\underline{H}$). IR (KBr plate): 1680 cm^{-1} (ν-C=O).

3,4,5-Tri-(n-dodecan-1-yloxy)benzoic acid (12)

Compound 12 was synthesized and purified according to the same procedure as compound 10 with the following modifications: 1) the etherification solvent was acetone +

10% dry DMSO; 2) the reaction was performed at reflux for 10 hrs. From 8.5g (40 mmol) propyl-3,4,5-trihydroxybenzoate (6) and 30g (120 mmol) of bromododecane (9) were obtained 15.5g (57 %) of a white solid. Purity: 99% (HPLC). mp, 64°C (DSC, 20°C/min). ^{1}H-NMR (CDCL$_3$, TMS, δ, ppm): 0.85 (t, 9H, C$\underline{H}_3$-), 1.27 (m, 54H, -(C$\underline{H}_2$)-), 1.74 (m, 6H, -C$\underline{H}_2$-CH$_2$-O-), 3.97 (overlapped t, 6H, -C$\underline{H}_2$-O-), 7.27 (s, 2H, Ph$\underline{H}$). IR (KBr plate): 1670 cm^{-1} (ν-C=O).



Scheme I: Synthesis of polymethylsiloxanes based on 4-[3,4,5-tri-(alkan-1-yloxy)benzoate]biphenyl groups decoupled from the main chain by a flexible spacer containing eleven methylenic units and an ether group, or ten methylenic units and an ester group.

4-{3,4,5-Tri-[S(-)-2-methylbutan-1-yloxy]benzoate}-4'-(10-undecenoate)biphenyl (13)

A solution of 1.0g (2.6 mmol) of 3,4,5-tri-[S(-)-2-methylbutan-1-yloxy]benzoic acid (10), 0.9g (2.6 mmol) 4-hydroxy-4'-(10-undecenoate)biphenyl (4), 0.52g (2.5 mmol) of dicyclohexylcarbodiimide (DCC), 0.1g (1 mmol) of N,N-dimethylaminopyridine (DMAP) in 50 ml dry CH_2Cl_2 was stirred for 6 hrs at room temperature. The resulting precipitate was filtered and 2 ml of EtOH and 1 ml HCOOH were added to the filtrate. The solution was allowed to stir for 18 hrs. The solvents were evaporated on a rotovapor. The remaining product was purified by flash chromatography (basic alumina, CH_2Cl_2 eluent) and then by column chromatography (silica gel, hexane + 15% ethyl acetate eluent) to yield 1.09g (59%) of a slightly yellow solid. Purity: 99% (HPLC). mp, 49.3°C (DSC, 20°C/min). ^1H-NMR ($CDCL_3$, TMS, δ, ppm): 0.96 (t, 9H, $C\underline{H}_3$-CH_2-CH*), 1.06 (d, 9H, $C\underline{H}_3$-CH*), 1.20-2.20 (overlapped m, 23H, CH_3-$C\underline{H}_2$-C$\underline{H}$* and -($C\underline{H}_2$)-), 2.59 (t, 2H, -$C\underline{H}_2$-COO-), 3.90 (overlapped t, 6H, -$C\underline{H}_2$-O-), 4.96 (d, 1H, -CH=$C\underline{H}_2$ trans), 5.05 (d, 1H, -CH=$C\underline{H}_2$ cis), 5.82 (m, 1H, -C$\underline{H}$=CH_2), 7.16 (d, 2H, biphenyl ortho from -OOC-CH_2-), 7.26 (d, 2H, biphenyl ortho from -OOC-Ph), 7.41 (s, 2H, Ph$\underline{H}$-COO-), 7.57,7.62 (2 d, 4H, biphenyl meta from -OOC-). IR (KBr plate): 1750 cm^{-1} (ν-C=O aliphatic), 1730 cm^{-1} (ν-C=O aromatic).

4-[3,4,5-Tri-(n-pentan-1-yloxy)benzoate]-4'-(10-undecenoate)biphenyl (14)

A solution of 1.0g (2.6 mmol) of 3,4,5-tri-(n-pentan-1-yloxy)benzoic acid (11), 0.9g (2.6 mmol) 4-hydroxy-4'-(10-undecenoate)biphenyl (4), 0.52g (2.5 mmol) of DCC, 0.2g (2 mmol) of DMAP in 50 ml dry CH_2Cl_2 was stirred for 16 hrs at room temperature. The resulting precipitate was filtered and the CH_2Cl_2 was evaporated on a rotovapor. THF (20 ml) was added and the solution was poured into 300 ml of H_2O that was slightly acidified with HCl. The solution was allowed to stir for 20 hrs. CH_2Cl_2 (100 ml) was added and the organic layer was separated, dried over Na_2SO_4, filtered, and the CH_2Cl_2 was evaporated. The product was purified by flash chromatography (basic alumina, CH_2Cl_2 eluent) and the CH_2Cl_2 evaporated to yield 0.96g (52%) of a viscous yellow liquid. Purity: 99% (HPLC). mp, 18.1°C (DSC, 20°C/min). ^1H-NMR ($CDCL_3$, TMS, δ, ppm): 0.93 (t, 9H, $C\underline{H}_3$-), 1.38 (m, 22H, -($C\underline{H}_2$)-), 1.82 (m, 8H, -$C\underline{H}_2$-CH_2-O-Ph and -$C\underline{H}_2$-CH_2-COO-), 2.04 (m, 2H, -$C\underline{H}_2$-CH=CH_2), 2.58 (t, 2H, -$C\underline{H}_2$-COO-), 4.06 (overlapped t, 6H, -$C\underline{H}_2$-O-), 4.96 (d, 1H, -CH=$C\underline{H}_2$ trans), 5.05 (d, 1H, -CH=$C\underline{H}_2$ cis), 5.81 (m, 1H, -C$\underline{H}$=CH_2), 7.15 (d, 2H, biphenyl ortho from -OOC-CH_2-), 7.26 (d, 2H, biphenyl ortho from -OOC-Ph), 7.42 (s, 2H, Ph$\underline{H}$-COO-), 7.58,7.60 (2 d, 4H, biphenyl meta from -OOC-). IR (KBr plate): 1750 cm^{-1} (ν-C=O aliphatic), 1730 cm^{-1} (ν-C=O aromatic).

4-[3,4,5-Tri-(n-dodecan-1-yloxy)benzoate]-4'-(10-undecenoate)biphenyl (15)

A solution of 1.71g (2.5 mmol) of 3,4,5-tri-(n-dodecan-1-yloxy)benzoic acid (12), 0.9g (2.5 mmol) of 4-hydroxy-4'-(10-undecenoate)biphenyl (4), 0.52g (2.5 mmol) of DCC, and 0.2g (1.6 mmol) of DMAP in 50 ml dry CH_2Cl_2 was stirred for 16 hrs at room temperature. The resulting precipitate was filtered and the CH_2Cl_2 was evaporated on a rotovapor. THF (20 ml) was added and the solution was precipitated into 300 ml H_2O. The precipitated solid was filtered, dissolved in 30 ml of THF and precipitated into 300 ml MeOH. The solid was filtered and allowed to dry in air. The product was then purified by flash chromatography (basic alumina, CH_2Cl_2 eluent) and the CH_2Cl_2 was evaporated. THF (20 ml) was added and the solution was precipitated into 300 ml MeOH. The solid was filtered and allowed to dry in air giving 1.6g (63 %) of a white solid. Purity: 99% (HPLC). mp, 59.5°C (DSC, 20°C/min). ^1H-NMR ($CDCL_3$, TMS, δ, ppm): 0.86 (t, 9H, $C\underline{H}_3$-), 1.26 (m, 64H, -($C\underline{H}_2$)-), 1.77 (m, 8H, -$C\underline{H}_2$-CH_2-O-Ph and -$C\underline{H}_2$-CH_2-COO-), 2.02 (m, 2H, -$C\underline{H}_2$-CH=CH_2), 2.54 (t, 2H, -$C\underline{H}_2$-COO-), 4.01 (overlapped t, 6H, -$C\underline{H}_2$-O-), 4.93 (d, 1H, -CH=$C\underline{H}_2$ trans), 5.00 (d, 1H, -CH=$C\underline{H}_2$ cis), 5.81 (m, 1H, -C$\underline{H}$=CH_2), 7.10 (d, 2H, biphenyl ortho from -OOC-CH_2-), 7.24 (d, 2H, biphenyl ortho from -OOC-Ph), 7.41 (s, 2H, Ph$\underline{H}$-COO-), 7.57,7.60 (2 d, 4H, biphenyl meta from -OOC-). IR (KBr plate): 1750 cm^{-1} (ν-C=O aliphatic), 1730 cm^{-1} (ν-C=O aromatic).

4-[3,4,5-Tri-(n-dodecan-1-yloxy)benzoate]-4'-(10-undecen-1-yloxy)biphenyl (16)

Compound 16 was synthesized by the same procedure as compound 15. From 1.54g (2.3 mmol) of 3,4,5-tri-(n-dodecan-1-yloxy)benzoic acid (12) and 0.8g (2.4 mmol) of 4-hydroxy-4'-(10-undecen-1-yloxy)biphenyl (5) were obtained 1.26g (56%) of a tan solid. Purity: 98% (HPLC). mp, 51.2°C (DSC, 20°C/min). ^{1}H-NMR ($CDCL_3$, TMS, δ, ppm): 0.88 (t, 9H, $C\underline{H}_3$-), 1.34 (m, 66H, -($C\underline{H}_2$)-), 1.82 (m, 8H, -$C\underline{H}_2$-CH_2-O-), 2.02 (m, 2H, -$C\underline{H}_2$-CH=CH_2), 4.13 (overlapped t, 8H, -$C\underline{H}_2$-O-), 4.98 (d, 1H, -CH=$C\underline{H}_2$ trans), 5.04 (d, 1H, -CH=$C\underline{H}_2$ cis), 5.88 (m, 1H, -C$\underline{H}$=CH_2), 6.97 (d, 2H, biphenyl ortho from -O-CH_2-), 7.22 (d, 2H, biphenyl ortho from -OOC-), 7.41 (s, 2H, Ph$\underline{H}$-COO-), 7.51,7.58 (2 d, 4H, biphenyl meta from -O-). IR (KBr plate): 1720 cm^{-1} (ν-C=O).

Polymethylsiloxanes (17, 18, 19, 20)

The hydrosilation of polymethylsiloxane and their purification were performed as described previously[14] except that the polymethylsiloxane 18 was purified by two precipitations into MeOH. The characterization results are summarized in Table I.

Table I Characterization of Polysiloxanes 17, 18, 19,and 20 (g=glassy phase, k=crystalline phase, Φ=phasmidic mesophase: data on the first line are from the first heating and cooling scans, with data on the second line from the second heating scan).

Polymer. #	Mn (GPC)	M_w/M_n (GPC)	Purity % (HPLC)	Yield %	Phase transitions (°C) and corresponding enthalpy changes (kcal/mru)[a] heating	cooling
17	22,000	1.8	98	75	g 17 k 32(0.16) i g 16 k 29(0.14) i	i 15 g
18	30,000	2.9	98	83	g 12 k 38 lc[b] 48(1.0)[c] i g 12 k 38 lc 48(0.9)[c] i	i 38(0.8) lc[c] 3 g
19	28,000	1.6	99	45	k 40(4.1) Φ 98(0.10) i g 10 k 40(0.01) Φ 99(0.11) i	i 90(0.9) Φ 9 g
20	26,000	1.6	99	55	k 47 k 64(5.41)[c] Φ 79(0.04) i k 15(2.1) Φ 65,78(0.3)[c] i	i 68,50(0.6)[c] Φ 3(1.2) k

[a] mru=mole repeat unit ; [b] lc=unidentified liquid crystalline phase; [c] combined enthalpy for overlapped transitions

RESULTS AND DISCUSSION

Scheme I outlines the synthesis of 13, 14, 15, and 16 and of the polymers 17, 18, 19 and 20. The synthetic procedures and the purification techniques are similar to those reported previously for the synthesis of other related monomers and polymers.[12-14] Changes made here represent our efforts to find optimum general procedures that can be used to synthesize hemiphasmidic mesogens and intermediates of varying structural architectures

The characterization of monomers 13, 14, 15, and 16 by both differential scanning calorimetry (DSC) and thermal optical polarized microscopy showed that all displayed only crystalline phases.

The heating and cooling DSC traces of the polymers 17 to 20 are presented in Figure 1. 17 exhibits only a crystalline phase. In addition to the glass transition temperature, 18 exhibits two endotherms on heating and one exotherm on the cooling DSC traces. On the optical polarized microscope above the first endotherm 18 shows an anisotropic texture which dissapears above the second endotherm. On cooling from the isotropic phase the anisotropic phase does not form. Additional characterization experiments are required to confirm the anisotropic mesophase exhibited by 18. Both 19 and 20 display enantiotropic mesophases. On the DSC thermograms 19 exhibits one enantiotropic mesophase. (The exotherm at 40°C from Figure 1f is the result of an electronic spike from the DSC instrument). On the optical polarized microscope this mesophase exhibits a focal conic fan shaped texture (Figure 2a) which is characteristic to hexagonal columnar mesophases. Heating and cooling DSC thermograms of 20 show two enantiotropic mesophases and a crystalline phase (Figure 1). However, optical polarized microscopy reveals only one texture (Figure 2b) for both mesophases. Most probably, in the case of 20 the formation of one single texture is the result of the high viscosity of the polymer.

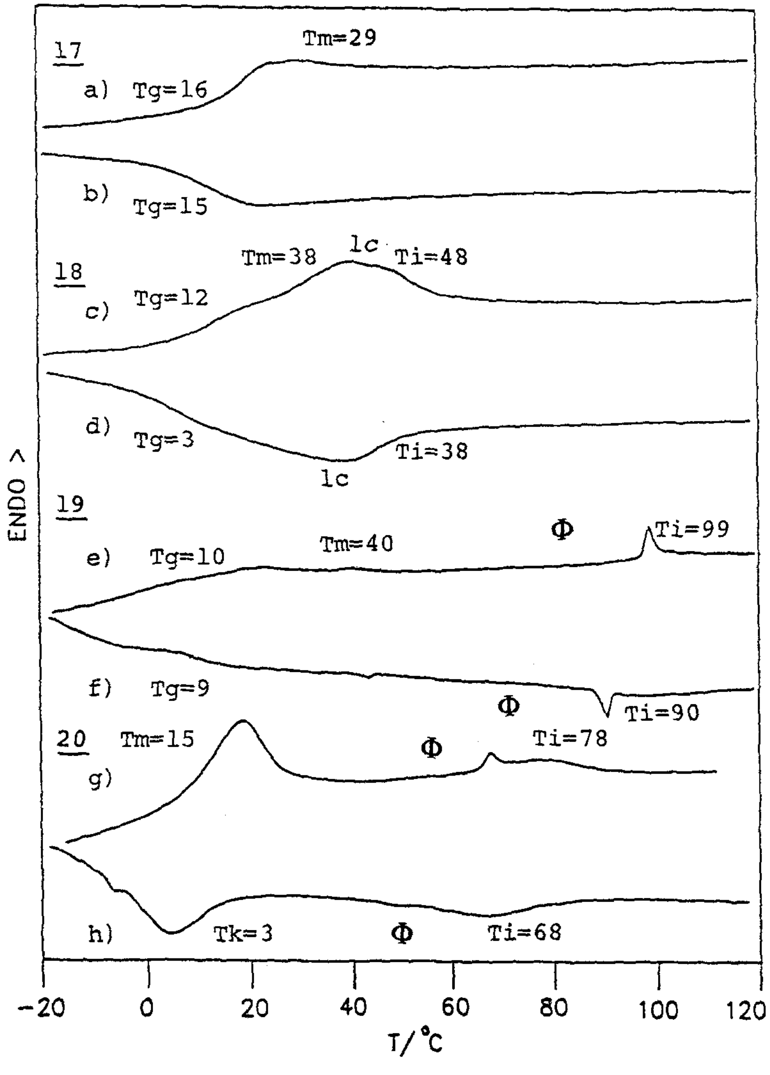


Figure 1: Heating and cooling traces of: 17 (a, second heating scan ; b, first cooling scan); 18 (c, second heating scan ; d, first cooling scan); 19 (e, second heating scan ; f, first cooling scan); 20 (g, second heating scan ; h, first cooling scan).

From the results summarized in Table 1 we observe that the isotropization temperature of 19 is higher than that of 20. This is due to the difference in the interconnecting group between the spacer and the rigid rod-like mesogen i.e., ester in the case of 19 versus ether in the case of 20. The ester bond increases the rigidity of the mesogen and therefore decreases the entropy and increases the isotropization temperature[19] of the polymer 19. Polymers 17 and 18 have their isotropization temperatures greatly depressed due to their shorter alkyl groups present in their disc-like moieties. Presently we do not have any definitive explanation for this behaviour.

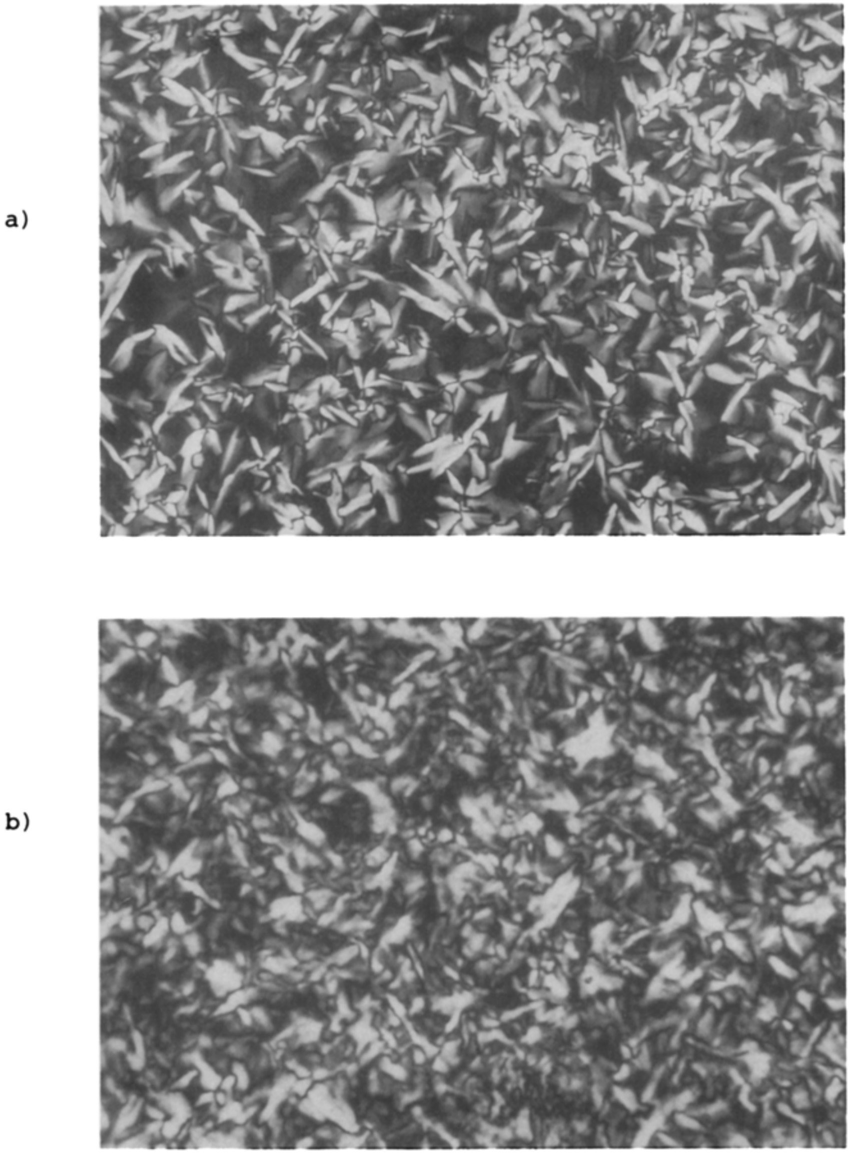


Figure 2: Representative optical polarized micrographs (100x) of the focal conic fan shaped texture displayed by : a) 19 after annealing at 95°C for 20 min; b) 20 after annealing at 61°C for 14 hrs.

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REFERENCES

1) J. Malthete, A. M. Levelut, and N. H. Tinh, J. Phys. Lett., 46, L-875(1985)
2) J. Malthete, L. Liebert, A. M. Levelut and Y. Galerne, C. R. Acad. Sci. Paris, 303, Series II, 1073(1986)
3) J. Malthete, N. H. Tinh and A. M. Levelut, J. Chem. Soc., Chem. Commun., 1986, p. 1548
4) A. M. Levelut, J. Malthete, C. Destrade and N. H. Tinh, Liq. Cryst., 2, 877(1987)
5) D. Guillon, A. Skoulios and J. Malthete, Europhys. Lett., 3, 67(1987)
6) J. Malthete, A. Collet and A. M. Levelut, Liq. Cryst., 5, 123(1989)
7) D. Demus, Liq. Cryst., 5, 75(1989)
8) K. Praefcke, B. Kohne, B. Gundogan, D. Demus, S. Diele, and G. Pelzl, Mol. Cryst. Liq. Cryst., Lett., 7, 27(1990)
9) S. Chandrasekhar, B. R. Ratna, B. K. Sadashiva and V. N. Raja, Mol. Cryst. Liq. Cryst., 165, 123(1988)
10) S. Chandrasekhar and G. S. Ranaganath, Rep. Prog. Phys., 53, 57(1990)
11) V. Percec and J. Heck, Am. Chem. Soc. Polym. Chem. Div. Polym. Prepr., 30(2), 450(1989)
12) V. Percec and J. Heck, Polym. Bull., 24, 255(1990)
13) V. Percec and J. Heck, J. Polym. Sci.: Polym. Lett. Ed., in press
14) V. Percec and J. Heck, Polym. Bull., in press
15) C. Liu, H. Ringsdorf, M. Ebert, R. Kleppinger and J. H. Wendorff, Liq. Cryst., 5, 1841(1989)
16) V. Percec and B. Hahn, Macromolecules, 22, 1588(1989)
17) V. Percec and R. Rodenhouse, Macromolecules, 22, 4408(1989)
18) V. Percec and B. Hahn, J. Polym. Sci: Part A: Polym. Chem., 27, 2367(1989)
19 V. Percec and A. Keller, Macromolecules, 23, 4347(1990)

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