Molecular engineering of liquid crystal polymers by living polymerization: 9. Living cationic polymerization of 5-[(4-cyano-4'-biphenyl)oxy]pentyl vinyl ether and 7-[(4-cyano-4'-biphenyl)oxy]heptyl vinyl ether, and the mesomorphic behaviour of the resulting polymers

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The synthesis and living cationic polymerization of 5-[(4-cyano-4'-biphenyl)oxy]pentyl vinyl ether (6-5) and 7-[(4-cyano-4'-biphenyl)oxy]heptyl vinyl ether (6-7) are presented. The influence of molecular weight on the mesomorphic behaviour of poly(6-5) and poly(6-7) is discussed and compared to that of 5-[(4-cyano-4'-biphenyl)oxy]pentyl ethyl ether (8-5) and 7-[(4-cyano-4'-biphenyl)oxy]heptyl ethyl ether (8-7) which are models of the monomeric structural units of poly(6-5) and poly(6-7). Both (8-5) and (8-7) exhibit a monotropic nematic mesophase. Poly(6-5) with degrees of polymerization equal to and lower than six exhibit an enantiotropic nematic mesophase. Poly(6-5)s with higher degrees of polymerization display both smectic A and nematic enantiotropic mesophases. Poly(6-7) exhibits an enantiotropic smectic A mesophase over the entire range of molecular weights.

(Keywords: liquid crystal polymers; cationic polymerization; mesomorphism)

INTRODUCTION

There are several reports on the influence of molecular weight on the phase transitions of side chain liquid crystalline polymers[1-10]. However, to our knowledge the present series of publications is the first which attempts to provide a comprehensive study on the influence of molecular weight on the mesomorphic transitions of a series of polymers with spacer lengths varying from two to 11 methylenic units, and narrow molecular weight distribution. The polymers investigated by us are obtained through the living cationic polymerization of ω-[(4-cyano-4'-biphenyl)oxy]alkyl vinyl ethers. In all cases, their phase behaviour was compared to that of the model compound of their monomeric structural unit, i.e. ω-[(4-cyano-4'-biphenyl)oxy]alkyl ethyl ether. So far, we have investigated the poly(vinyl ether)s based on the following alkyl spacers: ethyl, propyl and butyl[11], hexyl and octyl[12], and undecanyl[13]. The trend observed on studying the influence of the molecular weight on the mesomorphic behaviour was strongly dependent on the spacer length.

These living polymerization experiments also allowed us to investigate the influence of copolymer composition on the phase behaviour, at a constant molecular weight

of the copolymer[14,15]. The trend which was most frequently encountered and which is generally accepted consists of the enlargement of the temperature range of the mesophase with the increase of the polymer molecular weight[1-13]. This dependence was recently explained based on thermodynamic principles assuming that the phase behaviour of the polymer is dictated by that of the monomeric structural unit[16,17]. When the mesophases exhibited by the monomeric structural unit and by the polymers with various molecular weights are identical, the overall dependence of phase transitions on molecular weight could be easily explained[16,17]. However, there are situations when the mesophases of the polymer are different at different molecular weights and are also different from those of the monomeric structural unit[4,7,9,10,12,13]. This last trend could not be yet explained. A collection of experimental data which can provide a complete understanding of the dependence of the mesomorphic behaviour as a function of both spacer length and polymer molecular weight is thus required.

This paper will describe the synthesis, the living cationic polymerization, and the phase behaviour of the resulting polymers of the penultimate two monomers from the series of ω-[(4-cyano-4'-biphenyl)oxy]alkyl vinyl ethers, i.e. 5-[(4-cyano-4'-biphenyl)oxy]pentyl vinyl ether (6-5) and 7-[(4-cyano-4'-biphenyl)oxy]heptyl vinyl ether (6-7).

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EXPERIMENTAL

Materials

4-Cyano-4'-hydroxybiphenyl of higher purity than 99.9% and 1,10-phenanthroline palladium (II) diacetate were synthesized as described previously[13,18]. Methyl sulphide (anhydrous, 99%, Aldrich) was refluxed over 9-borabicyclo[3.3.1]nonane (crystalline, 98%, Aldrich) and then distilled under argon. Dichloromethane (99.6%, Aldrich) used as polymerization solvent was first washed with concentrated sulphuric acid, then with water, dried over magnesium sulphate, refluxed over calcium hydride and freshly distilled under argon before each use. Trifluoromethanesulphonic acid (triflic acid, 98%, Aldrich) was distilled under vacuum. 7-Bromoheptanol (95%, Aldrich), 5-bromovaleric acid (97%, Aldrich) and the other reagents were used as received.

Techniques

^{1}H-n.m.r. (200 MHz) spectra were recorded on a Varian XL-200 spectrometer. TMS was used as internal standard. A Perkin–Elmer DSC-4 differential scanning calorimeter, equipped with a TADS data station was used to determine the thermal transitions which were reported as the maxima and minima of their endothermic or exothermic peaks respectively. In all cases, heating and cooling rates were $20°C\,min^{-1}$. Glass transition temperatures (T_g) were read at the middle of the change in the heat capacity. First heating scans sometimes differ from second and subsequent heating scans. However, second and subsequent heating scans are identical. Although in the present case both sets of data are identical, they will be reported. A Carl-Zeiss optical polarized microscope (magnification: $100 \times$) equipped with a Mettler FP 82 hot stage and a Mettler FP 800 central processor was used to observe the thermal

transitions and to analyse the anisotropic textures[19,20]. Molecular weights were determined by gel permeation chromatography (g.p.c.) with a Perkin–Elmer series 10 LC instrument equipped with LC-100 column oven, LC-600 autosampler and a Nelson analytical 900 series integrator data station. The measurements were made at 40°C using the u.v. detector. A set of Perkin–Elmer PL gel columns of 10^4 and $500\,Å$ with $CHCl_3$ as solvent ($1\,ml\,min^{-1}$) and a calibration plot constructed with polystyrene standards was used to determine the molecular weights. High pressure liquid chromatography (h.p.l.c.) experiments were performed with the same instrument.

Synthesis of monomers

Scheme 1 outlines the general methods used in the synthesis of monomers and model compounds.

### Synthesis of 4-cyano-4'-(7-hydroxyheptan-1-yloxy)-biphenyl (7-7)

4-Cyano-4'-hydroxybiphenyl (5.0 g, 0.0256 mol) and potassium carbonate (10.61 g, 0.0768 mol) were added to a mixture of acetone-DMSO (10:1) (110 ml). 7-Bromoheptan-1-ol (5 g, 0.0256 mol) was added to the resulting solution which was heated to reflux for 24 h. After cooling, the mixture was poured into water and then filtered. The obtained solid was recrystallized from methanol and then benzene, to yield 5.5 g (69.4%) of white crystals, m.p., 76.9°C, T_{n-i}, 103.2°C (d.s.c.). ^{1}H-n.m.r. ($CDCl_3$, TMS, δ, ppm): 1.10–1.95 (10 protons, $-(CH_2)_5-$, m), 3.67 (2 protons, $-CH_2OH$, t), 4.00 (2 protons, $PhOCH_2-$, t), 7.02 (2 aromatic protons, o to alkoxy, d), 7.52 (2 aromatic protons, m to alkoxy, d), 7.67 (4 aromatic protons, o and m to –CN, d of d).

Synthesis of 7-[(4-cyano-4'-biphenyl)oxy]heptyl vinyl ether (6-7)

4-Cyano-4'-(7-hydroxyheptan-1-yloxy)biphenyl (3.0 g, 9.7 mmol) was added to a mixture of 1,10-phenanthroline palladium (II) diacetate (0.39 g, 0.97 mmol), n-butyl vinyl ether (52.9 ml) and dry chloroform (14 ml). The mixture was heated to 60°C for 6 h. After cooling and filtration (to remove the catalyst) the solvent was distilled in a rotavapor and the product was purified by column chromatography (silica gel, CH_2Cl eluent) and then recrystallized from n-hexane to yield 2.8 g (86.2%) of white crystals. Purity: 99.5% (h.p.l.c.). M.p., 58.7°C (d.s.c.). ^{1}H-n.m.r. ($CDCl_3$, TMS, δ, ppm): 1.10–1.95 (10 protons, $-(CH_2)_5-$, m), 3.69 (2 protons, $-CH_2O-$, t), 4.01 (3 protons, $-OCH=CH_2$ trans and $PhOCH_2-$, m), 4.14 and 4.21 (1 proton, $-OCH=CH_2$ cis, d), 6.53 (1 proton, $OCH=CH_2$, q), 7.01 (2 aromatic protons, o to alkoxy, d), 7.51 (2 aromatic protons, m to alkoxy, d), 7.66 (4 aromatic protons, o and m to –CN, d of d).

Synthesis of 7-[(4-cyano-4'-biphenyl)oxy]heptyl ethyl ether (8-7)

4-Cyano-4'-(7-hydroxyheptan-1-yloxy)biphenyl (1.0 g, 3.23 mmol) was added to a solution containing potassium t-butoxide (0.36 g, 3.23 mmol), a catalytic amount of 18-crown-6 and dry tetrahydrofuran (20 ml). Diethyl sulphate (0.44 ml, 3.35 mmol) was added and the reaction mixture was refluxed for 4 h under argon. After cooling, the reaction mixture was poured into chloroform. The chloroform solution was extracted with 10% aqueous
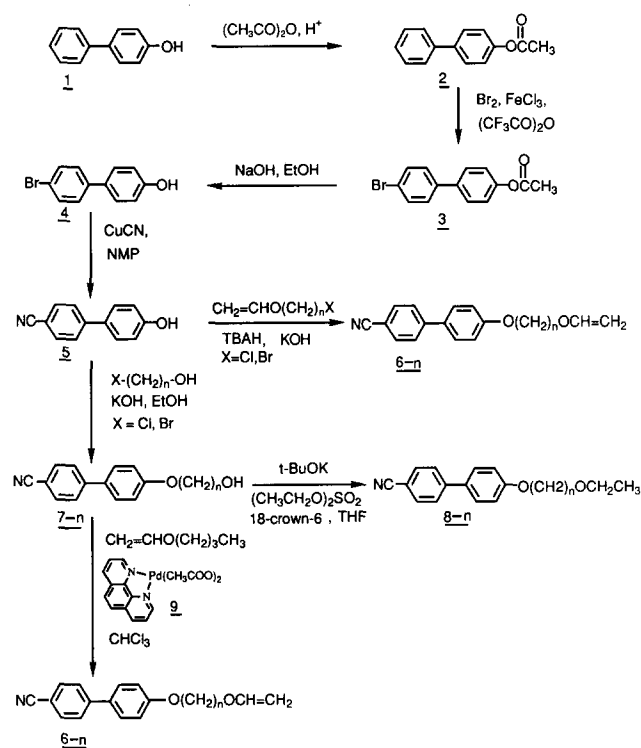
Scheme 1 Synthesis of 5-[(4-cyano-4'-biphenyl)oxy]pentyl vinyl ether (6-5) and 7-[(4-cyano-4'-biphenyl)oxy]heptyl vinyl ether (6-7)

KOH, washed with water, dried over magnesium sulphate and the solvent was removed in a rotavapor. The resulting product was purified by column chromatography (silica gel, CH_2Cl_2 eluent) and then was recrystallized from methanol to yield 0.62 g (52.8%) of white crystals. Purity: 99% (h.p.l.c.). M.p., 56.0°C (d.s.c.). ^{1}H-n.m.r. ($CDCl_3$, TMS, δ, ppm): 1.20 (3 protons, $-OCH_2CH_3$, t), 1.26–1.90 (10 protons, $-(CH_2)_5-$, m), 3.48 (4 protons, $CH_2OCH_2CH_3$, m), 4.02 (2 protons, $PhOCH_2$, t), 7.01 (2 aromatic protons, o to alkoxy, d), 7.50 (2 aromatic protons, m to alkoxy, d), 7.67 (4 aromatic protons, o and m to –CN, d of d).

Synthesis of 5-bromopentan-1-ol

A solution of 1-bromovaleric acid (15.0 g, 0.083 mol) in dry tetrahydrofuran (190 ml) was added dropwise into an ice-cooled solution of borane/THF complex (1 M) (155 ml). The reaction mixture was stirred at 0°C for 4 h and at room temperature for another 16 h, and the mixture was again cooled with ice. Water was added dropwise to the ice-cooled reaction mixture. Afterwards, a saturated aqueous K_2CO_3 solution was added to the reaction mixture which separates into two layers. The aqueous layer was extracted two times with tetrahydrofuran, the organic layers were combined, dried over anhydrous magnesium sulphate and the solvent was removed on a rotavapor to yield 13.3 g (96%) of liquid. Purity: 100% (i.r. and n.m.r.). ^{1}H-n.m.r. ($CDCl_3$, TMS, δ, ppm): 1.57 (4 protons, $BrCH_2CH_2CH_2-$, m), 1.90 (2 protons, $-CH_2CH_2OH$, m), 3.43 (2 protons, $BrCH_2-$, t), 3.67 (2 protons, $-CH_2OH$, t).

4-Cyano-4'-(5-hydroxypentan-1-yloxy)biphenyl (7-5)

Sodium metal (1.229 g, 0.0534 mol) was dissolved in 305 ml of absolute ethanol, then 4-cyano-4'-hydroxy-biphenyl (10.43 g, 0.0534 mol) was added, and the mixture was stirred for 45 min at room temperature. The ethanol was removed in a rotavapor to leave the salt. Dried N-methyl-pyrrolidinone (25 ml) and 5-bromo-1-pentanol (8.93 g, 0.0535 mol) were added, and the mixture was heated at 110°C for 30 h. After cooling, the reaction mixture was poured into water and the precipitate was washed with dilute NaOH and water. It was purified by column chromatography (silica gel, ethyl acetate/hexanes 6/4 eluent), and then it was recrystallized from chloroform to yield 7.53 g (50.1%) of white crystals. Purity: 99.9% (h.p.l.c.). M.p., 95.4°C (d.s.c.). ^{1}H-n.m.r. ($CDCl_3$, TMS, δ, ppm): 1.64–1.86 (6 protons, $-(CH_2)_3-$, m), 3.71 (2 protons, $-CH_2OH$, t), 4.03 (2 protons, $PhOCH_2-$, t), 6.99 (2 aromatic protons, o to alkoxy, d), 7.54 (2 aromatic protons, m to alkoxy, d), 7.66 (4 protons, o and m to –CN, d of d).

5-[(4-Cyano-4'-biphenyl)oxy]pentyl vinyl ether (6-5)

4-Cyano-4'-(4-hydroxypentan-1-yloxy)biphenyl (2.80 g, 9.95 mmol) was added to a mixture of 1,10-phenanthroline palladium (II) diacetate (0.193 g, 4.77 mmol), n-butyl vinyl ether (45 ml, 0.348 mol), and dry chloroform (15 ml). The mixture was heated to 60°C for 18 h. After cooling and filtration (to remove the catalyst) the solvent was distilled in a rotavapor and the product was purified by column chromatography (silica gel, CH_2Cl_2 and then petroleum ether/ethyl ether = 6/4 eluent) to yield 2.80 g (91%) of white crystals. Purity: 99% (h.p.l.c.). M.p., 52.4°C (d.s.c.). ^{1}H-n.m.r. ($CDCl_3$, TMS, δ, ppm): 1.57–1.93 (6 protons, $-(CH_2)_3-$, m), 3.73 (2 protons,

$-CH_2OCH=CH_2$, t), 4.03 (3 protons, $-OCH=CH_2$ *trans* and $PhOCH_2-$, m), 4.15 and 4.22 (1 proton, $OCH=CH_2$ *cis*, d), 6.49 (1 proton, $OCH=CH_2$, q), 6.99 (2 aromatic protons, o to alkoxy, d), 7.53 (2 aromatic protons, m to alkoxy, d), 7.66 (4 aromatic protons, m and o to –CN, d of d).

5-[(4-Cyano-4'-biphenyl)oxy]pentyl ethyl ether (8-5)

4-Cyano-4'-(5-hydroxypentan-1-yloxy)biphenyl (0.4974 g, 1.77 mmol), potassium t-butoxide (0.2105 g, 1.782 mmol) were refluxed in dry THF (20 ml) for 75 min. A few crystals of 18-crown-6 and diethyl sulphate (0.3017 g, 1.918 mmol) (98%, Aldrich) were added, and the reaction mixture was refluxed for 4 h. After cooling, the reaction mixture was poured into chloroform. The chloroform solution was extracted with 10% aqueous KOH, washed with water, dried over magnesium sulphate and the solvent was removed in a rotavapor. The resulting product was purified by column chromatography (silica gel, CH_2Cl_2 eluent) and then was recrystallized from methanol to yield 0.26 g (48%) white crystals. Purity: 99.85% (h.p.l.c.). M.p., 53.5°C (d.s.c.). ^{1}H-n.m.r. ($CDCl_3$, TMS, δ, ppm): 1.21 (3 protons, OCH_2CH_3, t), 1.60–1.92 (6 protons, $-(CH_2)_3-$, m), 3.48 (4 protons, $CH_2OCH_2CH_3$, m), 4.02 (2 protons, $PhOCH_2$, t), 6.99 (2 aromatic protons, o to alkoxy, d), 7.53 (2 aromatic protons, m to alkoxy, d), 7.66 (4 aromatic protons, o and m to –CN, d of d).

Cationic polymerizations

The cationic polymerization of **6-n** was performed with the initiating system $CF_3SO_3H/(CH_3)_2S$ in methylene chloride at 0°C[21] and is outlined in *Scheme 2.* Polymerizations were carried out in glass flasks equipped with Teflon stopcocks and rubber septa under argon atmosphere at 0°C for 1 h. All glassware was dried
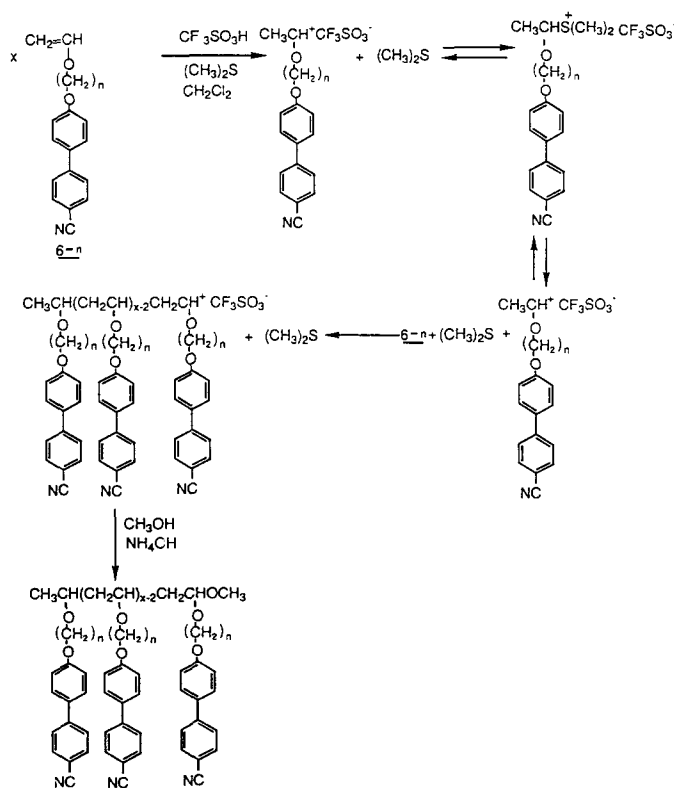
Scheme 2 Cationic polymerization of **6-5** and **6-7**

Table 1 Cationic polymerization of 5-[(4-cyano-4'-biphenyl)oxy]pentyl vinyl ether (**6-5**) (polymerization temperature, 0°C; polymerization solvent, methylene chloride; $[M]_0 = 0.325$; $[(CH_3)_2S]_0/[I]_0 = 10$; polymerization time, 1 h) and characterization of the resulting polymers. Data on first line are from first heating and cooling scans. Data on second line are from second heating scan

Sample no.	$[M]_0/[I]_0$	Polymer yield (%)	G.p.c.			Phase transitions (°C) and corresponding enthalpy changes (kcal mru^{-1})	
			$M_n \times 10^{-3}$	M_w/M_n	D.p.	Heating	Cooling
1	4	75.8	1.38	1.10	4.5	g 19.2 n 95.2 (0.11) i	i 91.1 (0.13) n 13.2 g
						g 18.7 n 94.3 (0.15) i	
2	6	79.2	1.85	1.11	6.0	g 24.7 n 98.3 (0.14) i	i 93.2 (0.15) n 16.5 g
						g 22.2 n 97.7 (0.14) i	
3	9	82.3	3.05	1.21	9.9	g 29.8 s$_A$ 80.1 n 100.8 (0.11)* i	i 96.5 (0.14)* n 76.0 s$_A$ 21.4 g
						g 27.5 s$_A$ 78.2 n 100.8 (0.12)* i	
4	13	87.1	3.94	1.13	12.8	g 33.8 s$_A$ 90.1 n 104.4 (0.14)* i	i 101.4 (0.14)* n 84.2 s$_A$ 28.2 g
						g 33.2 s$_A$ 89.1 n 103.2 (0.13)* i	
5	18	82.3	5.19	1.15	16.9	g 35.4 s$_A$ 95.0 n 112.3 (0.12)* i	i 107.1 (0.10)* n 93.3 s$_A$ 30.4 g
						g 33.8 s$_A$ 95.6 n 112.0 (0.13)* i	
6	23	85.0	7.50	1.21	24.4	g 38.2 s$_A$ 99.1 n 113.6 (0.14)* i	i 109.6 (0.11)* n 96.3 s$_A$ 35.0 g
						g 36.8 s$_A$ 102.7 n 113.8 (0.14)* i	
7	30	88.0	9.49	1.12	30.9	g 39.3 s$_A$ 104.9 n 115.4 (0.12)* i	i 111.7 (0.11)* 101.8 s$_A$ 34.2 g
						g 37.5 s$_A$ 104.4 n 115.5 (0.10)* i	

*Overlapped peaks

Table 2 Cationic polymerization of 7-[(4-cyano-4'-biphenyl)oxy]heptyl vinyl ether (**6-7**) (polymerization temperature, 0°C; polymerization solvent, methylene chloride; $[M]_0 = 0.298$; $[(CH_3)_2S]_0/[I]_0 = 10$; polymerization time, 1 h) and characterization of the resulting polymers. Data on first line are from first heating and cooling scans. Data on second line are from second heating scan

Sample no.	$[M]_0/[I]_0$	Polymer yield (%)	G.p.c.			Phase transitions (°C) and corresponding enthalpy changes (kcal mru^{-1})	
			$M_n \times 10^{-3}$	M_w/M_n	D.p.	Heating	Cooling
1	2	44.2	1.10	1.12	3.3	g 5.3 s$_A$ 89.5 (0.43) i	i 85.8 (0.43) s$_A$ 0.1 g
						g 5.1 s$_A$ 89.7 (0.44) i	
2	4	31.0	1.69	1.18	5.1	g 10.8 s$_A$ 108.0 (0.42) i	i 104.6 (0.40) s$_A$ 7.1 g
						g 10.8 s$_A$ 108.8 (0.80) i	
3	6	55.9	2.32	1.14	6.9	g 13.2 s$_A$ 116.0 (0.39) i	i 111.3 (0.39) s$_A$ 8.6 g
						g 13.0 s$_A$ 116.0 (0.40) i	
4	8	61.6	2.43	1.09	7.3	g 14.3 s$_A$ 120.1 (0.39) i	i 115.6 (0.39) s$_A$ 9.2 g
						g 14.1 s$_A$ 120.6 (0.39) i	
5	10	68.0	2.85	1.05	8.5	g 15.6 s$_A$ 123.1 (0.36) i	i 117.7 (0.39) s$_A$ 10.6 g
						g 15.6 s$_A$ 123.5 (0.74) i	
6	13	63.3	4.36	1.16	13.0	g 17.6 s$_A$ 131.3 (0.36) i	i 127.7 (0.36) s$_A$ 12.4 g
						g 17.6 s$_A$ 132.0 (0.37) i	
7	18	65.3	5.41	1.34	16.1	g 19.5 s$_A$ 133.0 (0.37) i	i 128.7 (0.36) s$_A$ 14.7 g
						g 18.8 s$_A$ 133.5 (0.37) i	
8	23	69.3	7.90	1.20	23.6	g 20.4 s$_A$ 137.3 (0.38) i	i 132.2 (0.36) s$_A$ 14.9 g
						g 20.1 s$_A$ 137.6 (0.35) i	
9	30	74.3	8.84	1.15	26.4	g 21.2 s$_A$ 140.3 (0.34) i	i 134.0 (0.34) s$_A$ 15.0 g
						g 20.8 s$_A$ 140.8 (0.35) i	

overnight at 130°C. The monomer was further dried under vacuum overnight in the polymerization flask. Then the flask was filled with argon, cooled to 0°C and the methylene chloride, dimethyl sulphide and triflic acid were added via a syringe. The monomer concentration was about 10 wt% of the solvent volume and the dimethyl sulphide concentration was 10 times larger than that of the initiator. The polymer molecular weight was controlled by the monomer/initiator ($[M]_0/[I]_0$) ratio. After quenching the polymerization with ammoniacal methanol, the reaction mixture was precipitated into methanol. The filtered polymers were dried and precipitated from methylene chloride solutions into methanol until g.p.c. traces showed no traces of monomer. *Tables 1* and *2* summarize the polymerization results. Although the polymer yields are lower than expected due to losses during the purification process, the conversions were almost quantitative in all cases.

RESULTS AND DISCUSSION

Figure 1a and *b* plots the dependences of M_n and M_w/M_n versus $[M]_0/[I]_0$ ratio for poly(**6-5**) and poly(**6-7**). Both sets of data demonstrate that within this range of
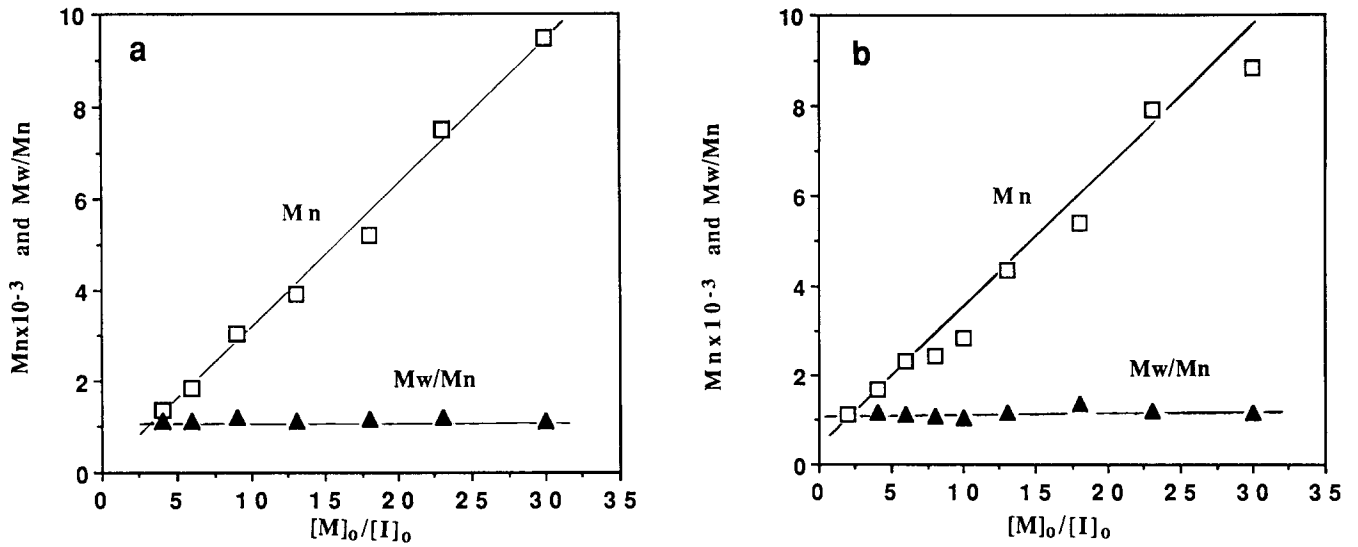
Figure 1 Dependence of the number average molecular weight (M_n) and of the polydispersity (M_w/M_n) of poly(6-5) (a) and poly(6-7) (b) on the $[M]_0/[I]_0$ ratio
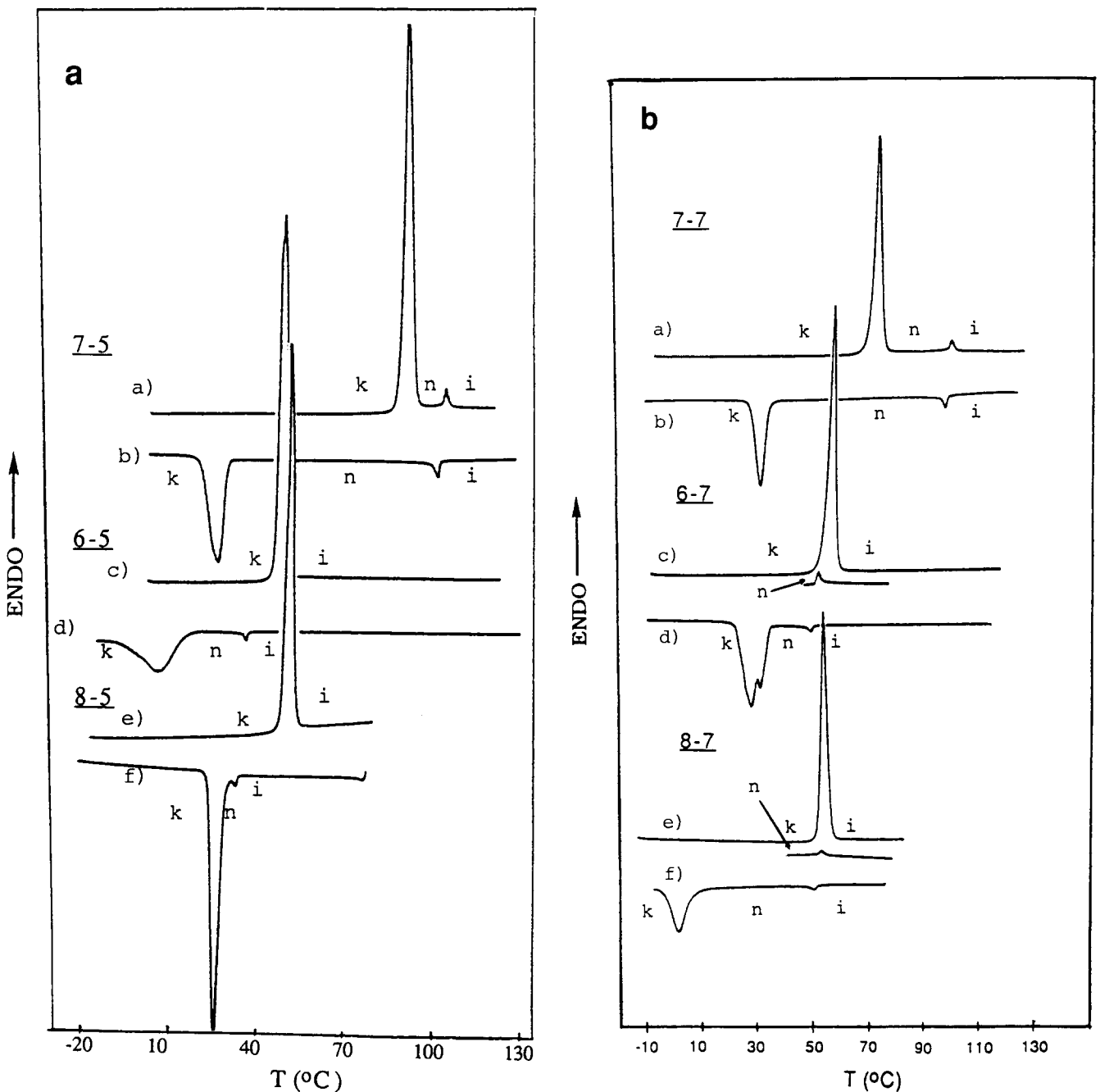

Figure 2 Heating and cooling d.s.c. scans of (a) 7-5 (A, B), 6-5 (C, D) and 8-5 (E, F); (b) 7-7 (A, B), 6-7 (C, D) and 8-7 (E, F)

molecular weights the polymerizations of **6-5** and **6-7** follow a living mechanism. The mechanism of this polymerization reaction is outlined in *Scheme 2*.

Figure 2 presents the heating and cooling d.s.c. traces of **7-5, 7-7, 6-5, 6-7, 8-5** and **8-7**. As we can observe from this figure, only the alcohol derivatives **7-7** and **7-5** display an enantiotropic nematic mesophase. Both the monomers (**6-5** and **6-7**) and the monomeric model compounds (**8-5** and **8-7**) exhibit a monotropic nematic mesophase. The phase transition temperatures and the corresponding thermodynamic parameters of these monomers and models are summarized in *Table 3*.

The d.s.c. traces obtained during the first and subsequent heating scans are identical for the case of poly (**6-5**) and poly(**6-7**). The experimental data collected from both scans are reported in *Tables 1* and *2*. However, only second heating and first cooling d.s.c. scans will be presented in more detail. *Figure 3* presents the d.s.c. traces of poly(**6-5**). Poly(**6-5**)s with degrees of polymerization below 10 exhibit an enantiotropic nematic mesophase

while **7-5**, which represents the 'polymer' with a degree of polymerization equal to one, displays only a monotropic nematic mesophase. Poly(**6-5**) with degrees of polymerization from 10 to 30 exhibit enantiotropic nematic and s_A mesophases. On the optical polarized microscope, the nematic mesophase of poly(**6-5**) exhibits a schlieren texture while the s_A mesophase a focal conic texture.

The dependence of glass transition and of mesomorphic transition temperatures of poly(**6-5**) are plotted in *Figure 4* as a function of the degree of polymerization. We can observe that the slope of the s_A-nematic *versus* molecular weight dependence is steeper than that of the nematic–isotropic *versus* molecular weight dependence. This trend provides a narrowing of the nematic range of poly(**6-5**) by increasing the degree of polymerization. Based on this trend, we can speculate that poly(**6-5**) with high molecular weights would have to exhibit only the s_A mesophase. So far, we do not have yet a polymer which does this.
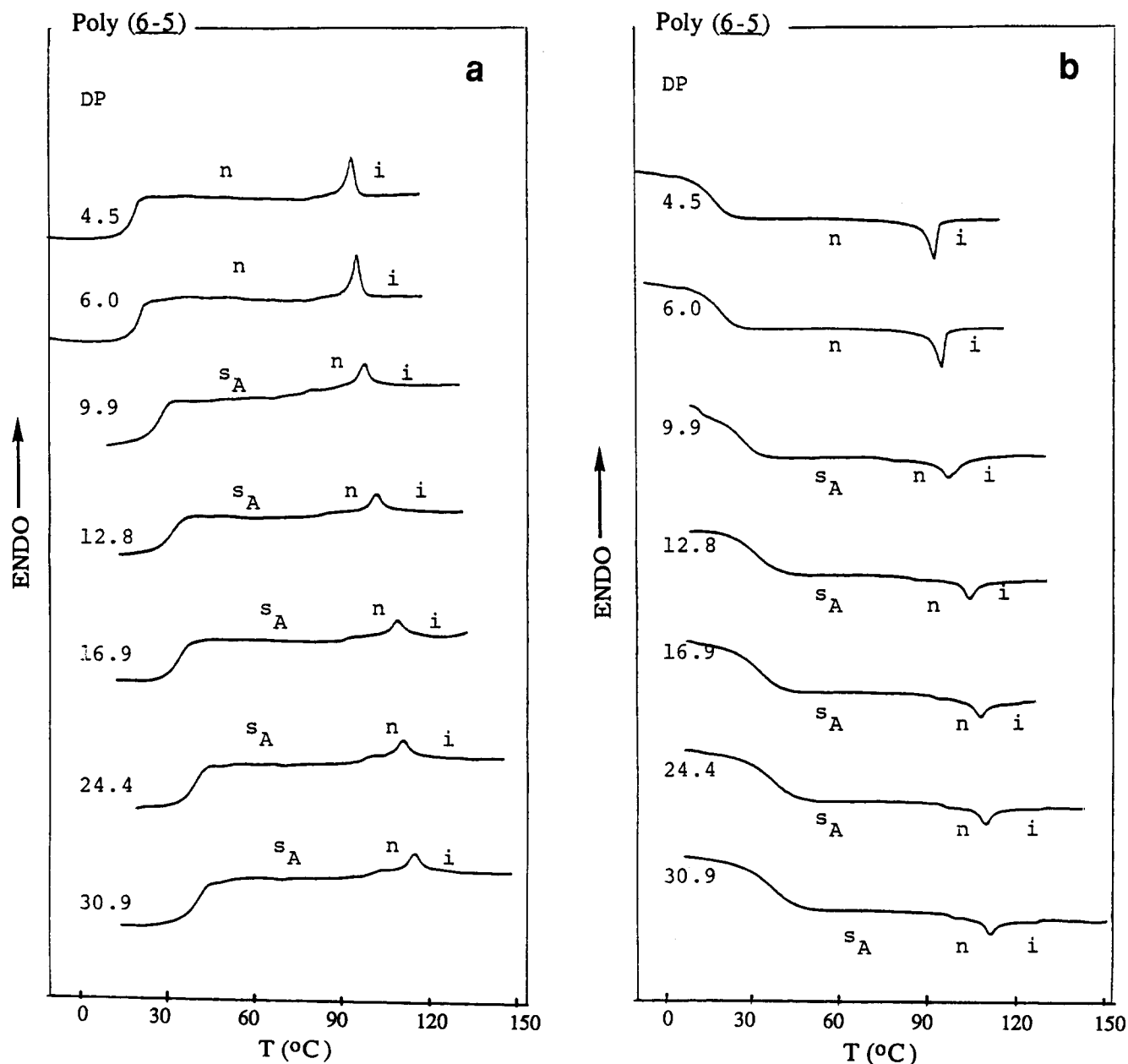

Figure 3 D.s.c. traces displayed during (a) the second heating scan and (b) the first cooling scan by poly(6-5) with different degrees of polymerization (d.p.). D.p. is shown on the left of each d.s.c. scan
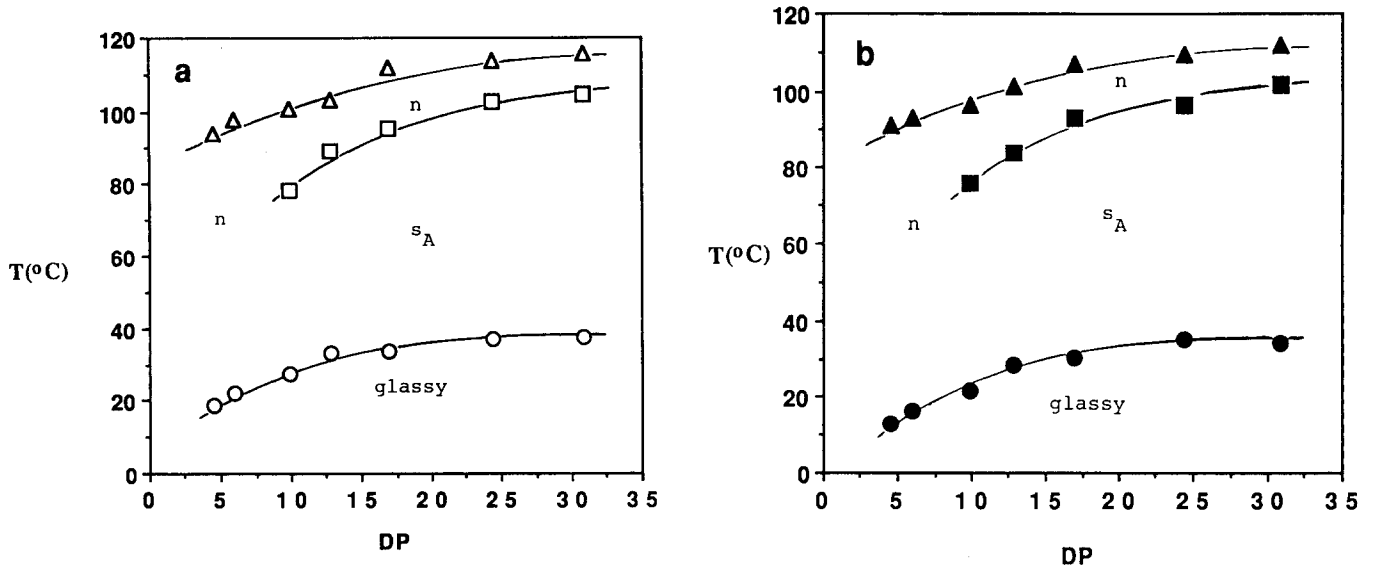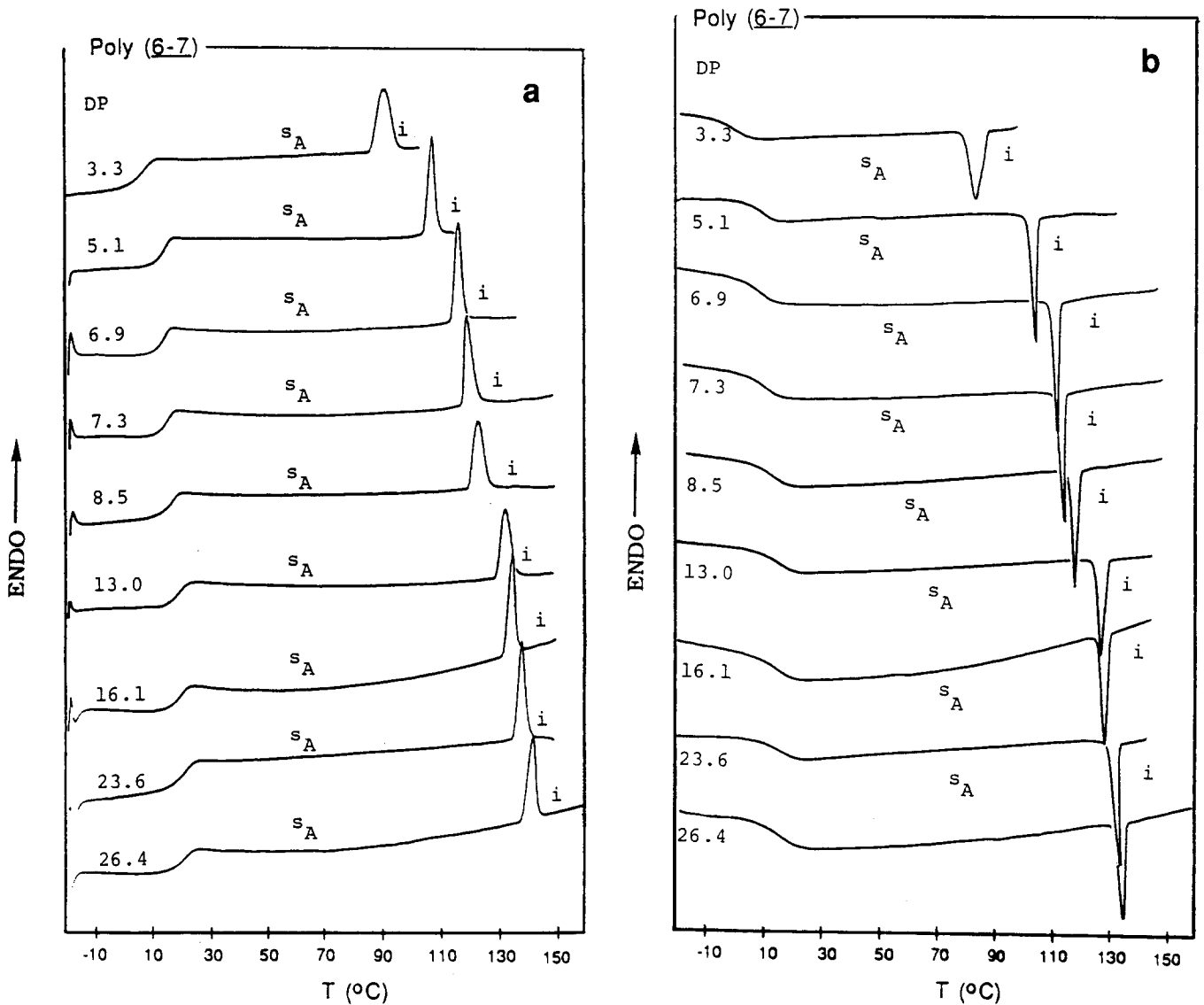
Figure 4 Dependence of phase transition temperature on the degree of polymerization of poly(6-5). (a) Data from second heating scan: ○, T_g, □, T_{s_A-n}, △, T_{n-i}; (b) data from first cooling scan: ●, T_g, ■, T_{n-s_A}, ▲, T_{i-n}

Figure 5 D.s.c. traces displayed during (a) the second heating scan and (b) the first cooling scan by poly(6-7) with different degrees of polymerization (d.p.). D.p. is shown on the left of each d.s.c. scan

Table 3 Thermal characterization of 4-cyano-4'(ω-hydroxyalkan-1-yloxy)biphenyls (**7-5**) and (**7-7**), ω-[(4-cyano-4'-biphenyl)oxy]alkyl vinyl ethers (**6-5**) and (**6-7**), and of ω-[(4-cyano-4'-biphenyl)oxy]alkyl ethyl ethers (**8-5**) and (**8-7**)

Com-pound	Phase transitions (0°C) and corresponding enthalpy changes (kcal mol^{-1})	
	Heating	Cooling
7-5	k 95.5 (7.59) n 108.1 (0.18) i	i 104.4 (0.27) n 28.6 (3.63) k
6-5	k 52.4 (7.94) i	i 38.6 (0.086) n 9.8 (6.20) k
8-5	k 53.5 (6.96) i	i 34.5 (0.050) n 27.6 (5.79) k
7-7	k 95.5 (9.67) n 108.1 (0.18) i	i 100.2 (0.27) n 33.0 (3.96) k
6-7	k 58.7 (9.9) i [n 54.5 (0.21) i]*	i 50.6 (0.17) n 29.4 (7.67) k
8-7	k 56.0 (9.7) i [n 55.4 (0.21)]†	i 50.9 (0.15) n 1.6 (5.56) k

*[ ] Virtual data
†Overlapped peaks

Figure 6 Dependence of phase transition temperature on the degree of polymerization of poly(**6-7**). (a) Data from second heating scan: ○, T_g, □, T_{s_A-i}; (b) data from first cooling scan: ●, T_g, ■, T_{i-s_A}

The d.s.c. traces collected from the second heating scan and first cooling scans of poly(**6-7**) are presented in *Figure 5*. The d.s.c. traces of the first, second and subsequent heating scans are identical over the entire range of molecular weights. Poly(**6-7**) exhibits only an enantiotropic s_A mesophase which exhibits a focal conic
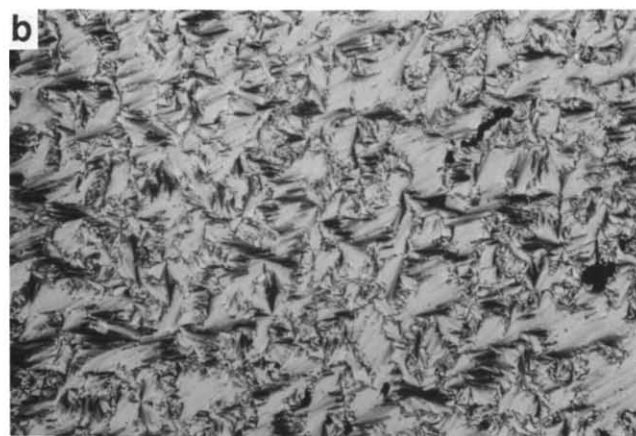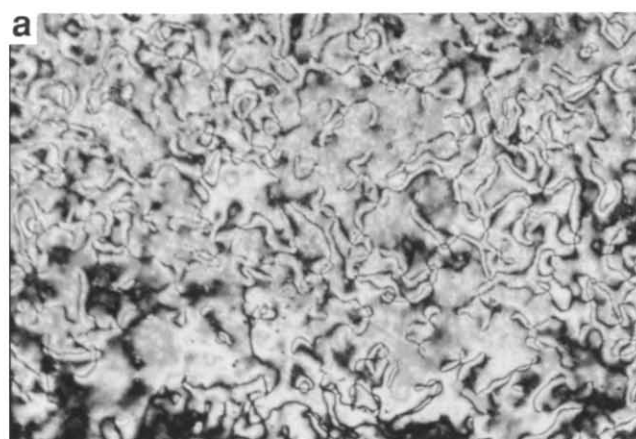
Figure 7 Representative optical polarized micrographs (100×) of: (a) the n mesophase displayed by poly(**6-5**) (d.p. = 24.4) at 105°C on the cooling scan; (b) the s_A mesophase displayed by poly(**6-5**) (d.p. = 24.4) at 70°C on the cooling scan; (c) the s_A mesophase displayed by poly(**6-7**) (d.p. = 26.4) at 120°C on the cooling scan
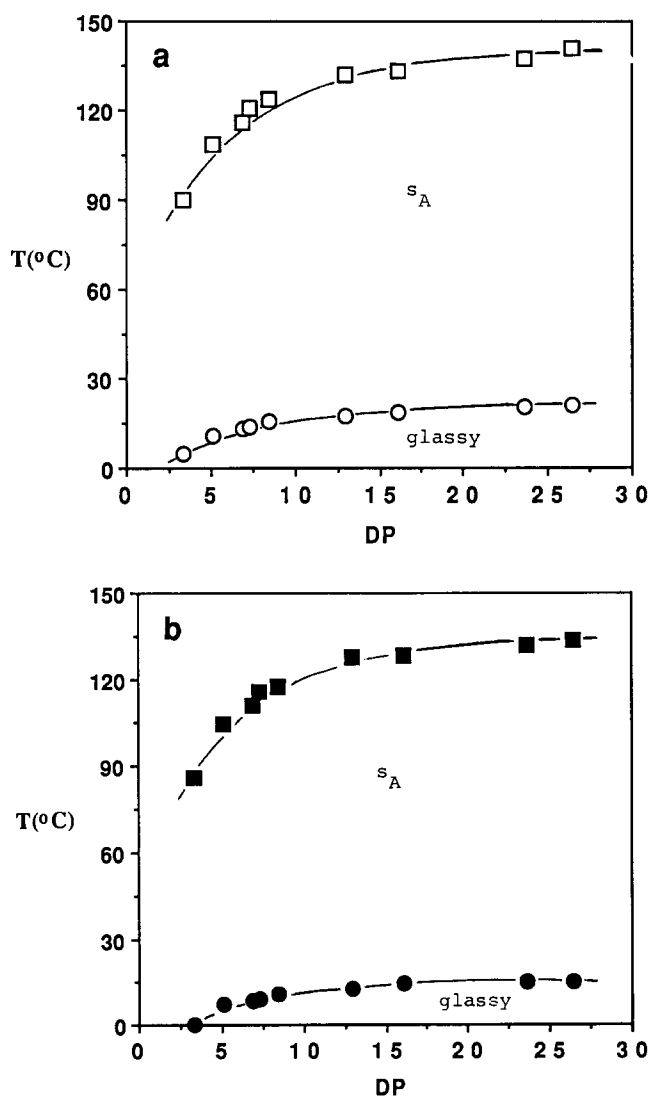
texture. The monomeric model compound **7-7** exhibits a monotropic nematic mesophase. Therefore, we can speculate that the change from nematic to s_A occurs at a degree of polymerization between one and 3.3. The dependences of T_g, T_{s_A-i} and T_{i-s_A} *versus* molecular weight obtained from the first and second heating, and first cooling scans are summarized in *Table 2*. The corresponding plots for the data obtained from the second heating and first cooling scans are presented in *Figure 6*. The plots from *Figures 4* and *6* demonstrate the strong influence of the spacer length on the overall dependence of polymer phase transitions on molecular

weight. This effect is particularly interesting for the case of poly(6-5) and poly(6-7) since these two polymers are based on odd spacers which have very similar lengths. *Figure 7* presents some representative textures exhibited by the nematic mesophase of poly(6-5) and by the s_A mesophase of poly(6-5) and poly(6-7).

The conclusion derived from these two experiments is that so far there is no general trend which is followed when studying the influence of molecular weight on the phase transitions of side chain liquid crystalline polymers. The observed trend is most probably determined both by the overall entropic change of the system as discussed previously[16,17] and by the anisotropy of the polymer backbone within its various mesophases[1,22-28].

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REFERENCES

1   Percec, V. and Pugh, C. in 'Side Chain Liquid Crystal Polymers', (Ed. C. B. McArdle), Chapman and Hall, New York, 1989, p. 30 and references cited therein
2   Kostromin, S. G., Talroze, R. V., Shibaev, V. P. and Plate, N. A. *Makromol. Chem., Rapid Commun.* 1982, **3**, 803
3   Stevens, H., Rehage, G. and Finkelmann, H. *Macromolecules* 1984, **17**, 851
4   Shibaev, V. *Mol. Cryst. Liq. Cryst.* 1988, **155**, 189
5   Uchida, S., Morita, K., Miyoshi, K., Hashimoto, K. and Kawasaki, K. *Mol. Cryst. Liq. Cryst.* 1988, **155**, 93
6   Percec, V. and Hahn, B. *Macromolecules* 1989, **22**, 1588
7   Percec, V., Tomazos, D. and Pugh, C. *Macromolecules* 1989, **22**, 3259
8   Sagane, T. and Lenz, R. W. *Polym. J.* 1988, **20**, 923
9   Sagane, T. and Lenz, R. W. *Polymer* 1989, **30**, 2269
10   Sagane, T. and Lenz, R. W. *Macromolecules* 1989, **22**, 3763
11   Percec, V. and Lee, M. *J. Macromol. Sci.-Chem.* 1991, **A28**, 651
12   Percec, V. and Lee, M. *Macromolecules* 1991, **24**, 1017
13   Percec, V., Lee, M. and Jonsson, H. *J. Polym. Sci., Polym. Chem. Edn.* 1991, **29**, 327
14   Percec, V. and Lee, M. *Polymer* in press
15   Percec, V. and Lee, M. *Polym. Bull.* 1991, **25**, 123 and *Polym. Bull.* 1991, **25**, 131
16   Percec, V. and Keller, A. *Macromolecules* 1990, **23**, 4347
17   Keller, A., Ungar, G. and Percec, V. in 'Advances in Liquid Crystalline Polymers' (Eds R. A. Weiss and C. K. Ober), ACS Symposium Series 435, Washington DC, 1990, p. 308
18   Rodenhouse, R., Percec, V. and Feiring, A. E. *J. Polym. Sci.: Part C: Polym. Lett.* 1990, **28**, 345
19   Demus, D. and Richter, L. 'Textures of Liquid Crystals', Verlag Chemie, Weinheim, 1978
20   Gray, G. W. and Goodby, J. W. 'Smectic Liquid Crystals, Textures and Structures', Leonard Hill, Glasgow, 1984
21   Feit, B. A., Cho, C. G. and Webster, O. W. *Macromolecules* 1990, **23**, 1918
22   Percec, V. and Tomazos, D. *Polymer* 1990, **31**, 1658 and references cited therein
23   Percec, V., Hahn, B., Ebert, M. and Wendorff, J. H. *Macromolecules* 1990, **23**, 2092 and references cited therein
24   Noel, C. in 'Side Chain Liquid Crystalline Polymers' (Ed. C. B. McArdle), Chapman and Hall, New York, 1989, p. 159
25   Warner, M. in 'Side Chain Liquid Crystalline Polymers' (Ed. C. B. McArdle), Chapman and Hall, New York, 1989, p. 7
26   Gray, G. W. in 'Side Chain Liquid Crystalline Polymers' (Ed. C. B. McArdle), Chapman and Hall, New York, 1989, p. 106
27   Pepy, G., Cotton, J. P., Hardouin, F., Keller, P., Lambert, M., Moussa, F., Noirez, L., Lapp, A. and Strazielle, C. *Makromol. Chem., Macromol. Symp.* 1988, **15**, 251 and references cited therein
28   Noirez, L., Cotton, J. P., Hardouin, F., Keller, P., Moussa, F., Pepy, G. and Strazielle, C. *Macromolecules* 1988, **21**, 2891