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Molecular Engineering of Liquid Crystal Polymers by Living Polymerization. VIII. Influence of Molecular Weight on the Phase Behavior of Poly {ω-[(4-Cyano-4'-biphenyl)-oxy]alkyl Vinyl Ether}s with Ethyl, Propyl, and Butyl Alkyl Groups

Virgil Percec[a]; Myongsoo Lee[a]
[a] Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio

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MOLECULAR ENGINEERING OF LIQUID CRYSTAL POLYMERS BY LIVING POLYMERIZATION. VIII. INFLUENCE OF MOLECULAR WEIGHT ON THE PHASE BEHAVIOR OF POLY{ω-[(4-CYANO-4′-BIPHENYL)-OXY]ALKYL VINYL ETHER}S WITH ETHYL, PROPYL, AND BUTYL ALKYL GROUPS

VIRGIL PERCEC* and MYONGSOO LEE

Department of Macromolecular Science
Case Western Reserve University
Cleveland, Ohio 44106

ABSTRACT

The synthesis and living cationic polymerization of 2-[4-cyano-4′-biphenyl)oxy]ethyl vinyl ether (6-2), 3-[4-cyano-4′-biphenyl)oxy]-propyl vinyl ether (6-3), and 4-[4-cyano-4′-biphenyl)oxy]butyl vinyl ether (6-4) are described. The mesomorphic behaviors of poly(6-2), poly(6-3), and poly(6-4) with different degrees of polymerization and narrow molecular weight distributions were compared to those of 6-2, 6-3, and 6-4 and of 2-[(4-cyano-4′-biphenyl)oxy]ethyl ethyl ether (8-2), 3-[(4-cyano-4′-biphenyl)oxy]propyl ethyl ether (8-3), and 4-[4-cyano-4′-biphenyl)oxy]butyl ethyl ether (8-4) which are model compounds of the monomeric structural units of poly(6-2), poly(6-3), and poly(6-4). In the first heating scan, all three polymers exhibit an *x* (unidentified) mesophase which overlaps the glass transition temperature, and an enantiotropic nematic mesophase. In the second and subsequent heating and cooling scans, poly(6-3) and poly(6-4) display only the enantiotropic nematic mesophase.

Both in the first and subsequent scans, only poly(6-2) with degrees of polymerization lower than 4 exhibits an enantiotropic nematic mesophase.

INTRODUCTION

Previous publications from this series and from other laboratories demonstrated that group transfer polymerization of mesogenic methacrylates [1] and cationic polymerization of mesogenic vinyl ethers [2–8] can be performed under living polymerization conditions. Our investigations on the polymerization of mesogenic vinyl ethers were performed with the initiating system $CF_3SO_3H/(CH_3)_2S$ which induces a living polymerization at 0°C in methylene chloride [9]. Presently, we are performing experiments which provide a complete understanding of the influence of molecular weight on the phase behavior of poly{ω-[(4-cyano-4′-biphenyl)oxy]alkyl vinyl ether}s with flexible spacers containing from 2 to 11 methylene units.

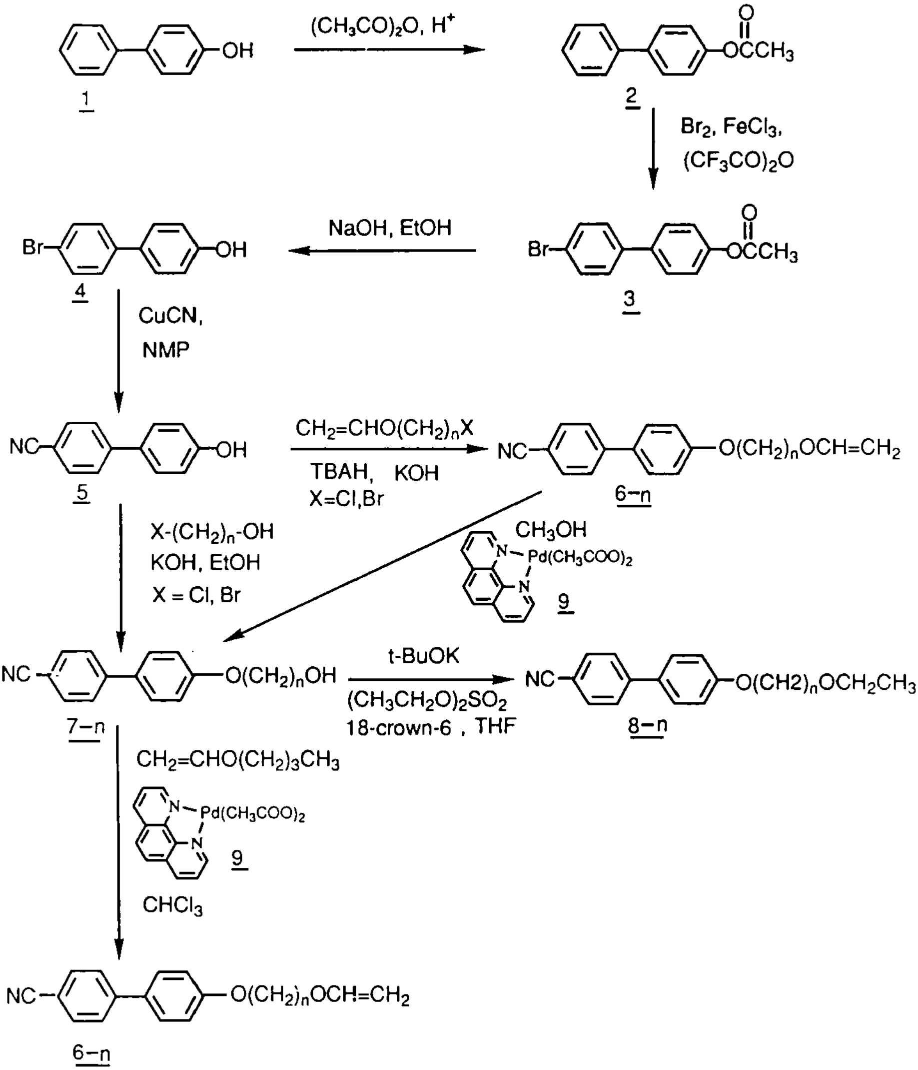
This paper describes our results on the influence of molecular weight on the behavior of poly{2-[4-cyano-4′-biphenyl)oxy]ethyl vinyl ether} (6-2), poly{3-[4-cyano-4′-biphenyl)oxy]propyl vinyl ether} (6-3), and poly{4-[4-cyano-4′-biphenyl)oxy]butyl vinyl ether} (6-4). Their phase behaviors will be compared to those of the model compounds of their monomeric structural units.

EXPERIMENTAL

Scheme 1 outlines the synthesis of monomers and model compounds.

Materials

3-Bromo-1-propanol (95%, Aldrich) and 4-chloro-1-butanol (94%, Lancaster Synthesis) were used as received. 2-[4-Cyano-4′-biphenyl)-oxy]ethyl vinyl ether (6-2) [5], 4-cyano-4′-hydroxybiphenyl [3, 10] of purities higher than 99.5%, and 1,10-phenanthroline palladium(II) diacetate [10] were synthesized as described previously. Methyl sulfide was refluxed over 9-borabicyclo[3,3,1]nonane (crystalline, 98%, Aldrich) and then distilled under argon. Dichloromethane (99.6%, Aldrich), used as the polymerization solvent, was first washed with concentrated H_2SO_4



SCHEME 1. Synthesis of 2-[(4-cyano-4′-biphenyl)oxy]ethyl vinyl ether (6-2), 3-[(4-cyano-4′-biphenyl)oxy]propyl] vinyl ether (6-3), and 4-[4-cyano-4′-biphenyl)oxy]butyl vinyl ether (6-4).

and then with water, dried over magnesium sulfate, refluxed over calcium hydride, and freshly distilled under argon before each use. Trifluoromethane sulfonic acid (triflic acid, 98%, Aldrich) was distilled under vacuum.

Techniques

^{1}H-NMR (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 unless otherwise specified. Glass transition temperatures (T_g) were read at the middle of the change in the heat capacity. First heating scans differ from second and subsequent heating scans. However, second and subsequent heating scans are identical. In the present case, both sets of data are reported. A Carl-Zeiss optical polarized microscope (magnification: 100×) equipped with a Mettler FP 82 hot stage and a Metter 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 an LC-100 column oven, LC-600 autosampler, and a Nelson analytical 900 series integrator data station. The measurements were made at 40°C by using the UV detector. A set of Perkin-Elmer PL get columns of 10^4 and 500 Å with $CHCl_3$ as solvent (1 mL/min) and a calibration plot constructed with polystyrene standards were used to determine the molecular weights. High pressure liquid chromatography (HPLC) experiments were performed with the same instrument.

Synthesis of 4-Cyano-4′-(2-hydroxyethan-1-yloxy)biphenyl (7-2)

2-[(4-Cyano-4′-biphenyl)oxy]ethyl vinyl ether (0.5 g, 1.885 mmol) was added to a mixture of 1,10-phenanthroline palladium(II) diacetate (0.038 g, 0.094 mmol) and methanol (15 mL). The mixture was refluxed for 12 h. After cooling and filtration (to remove the catalyst), the solvent was distilled in a rotary evaporator and the product was recrystallized from a 1:9 mixture of acetone and *n*-hexane to yield 0.38 g of white crystals (84.2%) which were further purified by column chromatography (silica gel, $CHCl_3$ eluent). mp: 128.7°C (DSC). ^1H-NMR ($CDCl_3$, TMS, δ, ppm), 4.02 (2 protons, $-C\underline{H}_2OH$, t), 4.16 (2 protons, $PhOC\underline{H}_2-$, t), 7.06 (2 aromatic protons, *o* to alkoxy, d), 7.53 (2 aromatic protons, *m* to alkoxy, d), 7.67 (4 aromatic protons, *o* and *m* to $-CN$, d of d).

Synthesis of 2-[(4- Cyano-4′-biphenyl)oxy]ethyl Ethyl Ether (8-2)

4-Cyano-4′-(2-hydroxyethan-1-yloxy)biphenyl (0.35 g, 1.463 mmol) was added to a solution containing potassium *t*-butoxide (0.164 g, 1.463 mmol), a catalytic amount of 18-crown-6, and dry tetrahydrofuran (7 mL). Diethyl sulfate (0.21 mL, 1.61 mmol) was added, and the reaction mixture was refluxed for 5 h under argon. After cooling, the reaction mixture was poured into chloroform. The chloroform solution was extracted with 10% aqueous KOH, washed with water, dried over magnesium sulfate, and the solvent was removed on a rotary evaporator. The resulting product was purified by column chromatography (silica gel, CH_2Cl_2 eluent) and then was recrystallized from methanol to yield 0.17 g (42.7%) of white crystals. Purity: 99% (HPLC). mp: 68.9°C (DSC). ^1H-NMR ($CDCl_3$, TMS, δ, ppm): 1.26 (3 protons, $-CH_2C\underline{H}_3$, t), 3.65 (2 protons, $-C\underline{H}_2CH_3$, q), 3.83 (2 protons, $-C\underline{H}_2OCH_2CH_3$, t), 4.18 (2 protons, $PhOC\underline{H}_2-$, t), 7.05 (2 aromatic protons, *o* to alkoxy, d), 7.52 (2 aromatic protons, *m* to alkoxy, d), 7.66 (4 aromatic protons, *o* and *m* to $-CH$, d of d).

Synthesis of 4-Cyano-4′-(3-hydroxypropan-1-yloxy)biphenyl (7-3)

4-Cyano-4′-hydroxybiphenyl (1.47 g, 7.53 mmol), sodium hydride (0.3 g, 7.59 mmol), and tetrabutylammonium hydrogen sulfate (0.24 g, 0.71 mmol) were added to a mixture of toluene–DMSO (5:1) (22.1 mL). 3-Bromo-1-propanol (1.05 g, 7.55 mmol) was added to the resulting solution which was heated to 80°C for 28 h. After cooling, the mixture was poured into water and then filtered. The obtained solid was dissolved in ethyl ether and then extracted with dilute aqueous NaOH, washed with water, dried over magnesium sulfate, and then the solvent was removed in a rotavapor. The resulting product was recrystallized from methanol and then purified by column chromatography (silica gel, 1:1 ethyl acetate–hexane eluent) to yield 1.52 g (83%) of white crystals. mp: 114.6°C (DSC). Purity: 99.6% (HPLC). ^1H-NMR ($CDCl_3$, TMS, δ, ppm); 2.09 (2 protons, $-CH_2C\underline{H}_2CH_2-$, m), 3.90 (2 protons, $-C\underline{H}_2OH$, t), 4.19 (2 protons, $PhOC\underline{H}_2-$, t), 7.02 (2 aromatic protons, *o* to alkoxy, d), 7.54 (2 aromatic protons, *m* to alkoxy, d), 7.66 (4 aromatic protons, *o* and *m* to —CN, d of d).

Synthesis of 3-[(4-Cyano-4′-biphenyl)oxy]propyl Vinyl Ether (6-3)

4-Cyano-4′-(3-hydroxypropan-1-yloxy)biphenyl (2.0 g, 7.9 mmol) was added to a mixture of 1,10-phenanthroline palladium(II) diacetate (0.31 g, 0.79 mmol), *n*-butyl vinyl ether (43.1 mL), and dry chloroform (10.78 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 rotary evaporator and the product was purified by column chromatography (silica gel, CH_2Cl_2 eluent) and then was recrystallized from *n*-hexane to yield 1.83 g (83.0%) of white crystals. Purity: 99.9% (HPLC). mp: 78.7°C (DSC). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 2.18 (2 protons, $-CH_2C\underline{H}_2CH_2-$, m), 3.90 (2 protons, $-C\underline{H}_2O-$, t), 4.01 and 4.05 (1 proton, $-OCH=C\underline{H}_2$ *trans*, d), 4.14 (2 protons, $-C\underline{H}_2OPh$, t), 4.19 and 4.27 (1 proton, $-OCH=C\underline{H}_2$ *cis*, d), 6.50 (1 proton, $-OC\underline{H}=CH_2$, q), 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 3-[(4-Cyano-4′-biphenyl)oxy]propyl Ethyl Ether (8-3)

4-Cyano-4′-(3-hydroxypropan-1-yloxy)biphenyl (0.5 g, 1.975 mmol) was added to a solution containing potassium *t*-butoxide (0.22 g, 1.975 mmol), a catalytic amount of 18-crown-6, and dry tetrahydrofuran (10 mL). Diethyl sulfate (0.284 mL, 2.17 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 KOH, washed with water, dried over magnesium sulfate, and the solvent was removed in a rotary evaporator. The resulting product was purified by column chromatography (silica gel, CH_2Cl_2 eluent) and then was recrystallized from methanol to yield 0.34 g (58.0%) of white crystals. Purity: 99.0% (HPLC). mp: 64.9°C (DSC). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.21 (2 protons, $-OCH_2C\underline{H}_3$, t), 2.08 (2 protons, $-CH_2C\underline{H}_2CH_2-$, m), 3.50 (2 protons, $-OC\underline{H}_2CH_3$, q), 3.62 (2 protons, $-C\underline{H}_2OCH_2CH_3$, t), 4.13 (2 protons, $PhOC\underline{H}_2-$, t), 7.02 (2 aromatic protons, *o* to alkoxy, d), 7.52 (2 aromatic protons, *m* to alkoxy, d), 7.66 (4 aromatic protons, *o* and *m* to —CN, d of d).

Synthesis of 4-Cyano-4′-(4-hydroxybutan-1-yloxy)biphenyl (7-4)

4-Cyano-4′-hydroxybiphenyl (4.2 g, 0.0215 mol) and potassium carbonate (39 g, 0.3 mol) were added to a mixture of acetone–DMSO (10:1) (110 mL). 4-Chloro-1-butanol (11.67 g, 0.1075 mol) was added to the resulting reaction mixture which was heated to reflux for 3 days. After cooling, the mixture was poured into water and the separated solid was filtered. The obtained solid was recrystallized first from methanol and then from toluene to yield 2.82 g (49.1%) of white crystals. mp: 126.4°C (DSC). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.55–2.15 (4 protons, $-(C\underline{H}_2)_2-$, m), 3.75 (2 protons, $-C\underline{H}_2OH$, t), 4.07 (2 protons, $PhOC\underline{H}_2-$, t), 7.02 (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 4-[4-Cyano-4′-biphenyl)oxy]butyl Vinyl Ether (6-4)

4-Cyano-4′-(4-hydroxybutan-1-yloxy)biphenyl (2.0 g, 7.48 mmol) was added to a mixture of 1,10-phenanthroline palladium(II) diacetate (0.29 g, 0.75 mmol), *n*-butyl vinyl ether (40.85 mL), and dry chloroform (10.2 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 rotary evaporator, the product was purified by column chromatography (silica gel, CH_2Cl_2 eluent), and then was recrystallized first from ethanol and then from *n*-hexane to yield 1.82 g (82.9%) of white crystals. Purity: 99.8% (HPLC). mp: 73.3°C. T_{n-i}, 77.1°C (DSC). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm); 1.91 (4 protons, $-(C\underline{H}_2)_2-$, m), 3.78 (2 protons, $-C\underline{H}_2OCH{=}CH{=}CH_2$, t), 4.06 (3 protons, $-OCH{=}C\underline{H}_2$ *trans* and $PhOC\underline{H}_2-$, m), 4.16 and 4.23 (1 proton, $OCH{=}C\underline{H}_2$ *cis*, d), 6.50 (1 proton, $OC\underline{H}{=}CH_2$, q), 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 4-[4-Cyano-4′-biphenyl)oxy]butyl Ethyl Ether (8-4)

4-Cyano-4′-(4-hydroxybutan-1-yloxy)biphenyl (0.5 g, 1.67 mmol) was added to a solution containing potassium *t*-butoxide (0.20 g, 1.67 mmol), a catalytic amount of 18-crown-6, and dry tetrahydrofuran (10 mL). Diethyl sulfate (0.25 mL, 1.9 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 KOH, washed with water, dried over magnesium sulfate, and the solvent was removed in a rotary evaporator. The resulting product was purified by column chromatography (silica gel, CH_2Cl_2 eluent) and then was recrystallized from methanol to yield 0.32 g (57.9%) of white crystals. Purity: 99% (HPLC). mp: 64.7°C (DSC). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.22 (3 protons, $-OCH_2\underline{CH_3}$, t), 1.65-2.11 (4 protons, $-(\underline{CH_2})_2-$, m), 3.50 (4 protons, $-\underline{CH_2}O\underline{CH_2}CH_3$, m), 4.05 (2 protons, $PhO\underline{CH_2}-$, t), 7.02 (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).

Cationic Polymerizations

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 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 sulfide, and triflic acid were added via a syringe. The monomer concentration was about 10 wt% of the solvent volume, and the dimethyl sulfide 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 GPC 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

Polymerization results are reported in Tables 1, 2 and 3. All polymers have number-average molecular weights which show a linear dependence of $[M]_0/[I]_0$, and narrow molecular weight distributions. Figure 1 presents representative plots which demonstrate the living polymerization character for the case of monomers $\underline{6\text{-}2}$, $\underline{6\text{-}3}$, and $\underline{6\text{-}4}$. The polymerization mechanism is outlined in Scheme $\underline{2}$ [9]. The thermal characterization of

TABLE 1. Cationic Polymerization of 2-[4-Cyano-4′-biphenyl)oxy]ethyl Vinyl Ether (6-2) (polymerization temperature, 0ºC; polymerization solvent, methylene chloride; $[M]_0 = 0.387$; $[(CH_3)_2S]_0/[I]_0 = 10$; 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

			GPC			Phase transitions (ºC) and corresponding enthalpy changes (kcal/mru)	
Sample	$[M]_0/[I]_0$	Polymer yield, %	$M_n \times 10^{-3}$	M_w/M_n	*DP*	Heating	Cooling
1	3.0	34.7	0.54	1.22	2.1	*g* 34.5 *x* 37.5 (0.21) *n* 79.2 (0.061) *i* *g* 33.5 *n* 79.8 (0.061) *i*	*i* 76.3 (0.072) *n* 29.5 *g*
2	4.0	57.3	0.74	1.11	2.8	*g* 53.7 *x* 56.7 (0.29) *n* 81.1 (0.034) *i* *g* 51.0 *n* 80.2 (0.037) *i*	*i* 77.1 (0.040) *n* 43.5 *g*
3	5.0	54.7	0.86	1.21	3.4	*g* 60.1 *x* 66.7 (0.37) *n* 81.4 (0.008) *i* *g* 55.6 *n* 71.8 (0.027) *i*	*i* 70.8 (0.033) *n* 49.7 *g*
4	7.0	73.3	1.78	1.08	6.7	*g* 68.6 *x* 71.6 (0.34) *i* *g* 61.9 *i*	*i* 54.7 *g*
5	10.0	73.1	2.87	1.10	10.8	*g* 78.5 *x* 86.0 (0.18) *i* *g* 72.8 *i*	*i* 63.8 *g*
6	20.0	64.8	4.56	1.18	17.2	*g* 81.0 *x* 85.7 (0.25) *i* *g* 78.3 *i*	*i* 70.5 *g*

TABLE 2. Cationic Polymerization of 3-[4-Cyano-4′-biphenyl)oxy]propyl Vinyl Ether (6-3) (polymerization temperature, 0°C; polymerization solvent, methylene chloride; $[M]_0 = 0.358$; $[(CH_3)_2S]_0/[I]_0 = 10$; 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

		Polymer	GPC			Phase transitions (°C) and corresponding enthalpy changes (kcal/mru)	
Sample	$[M]_0/[I]_0$	yield, %	$M_n \times 10^{-3}$	M_w/M_n	*DP*	Heating	Cooling
1	6	80.0	1.57	1.06	5.6	*g* 38.2 *x* 41.3 (0.17) *n* 79.6 (0.10) *i* *g* 36.3 *n* 77.3 (0.11) *i*	*i* 72.3 (0.083) *n* 30.8 *g*
2	10	88.0	2.55	1.14	9.1	*g* 41.3 *x* 46.6 (0.18) *n* 84.9 (0.067) *i* *g* 40.1 *n* 83.5 (0.065) *i*	*i* 79.1 (0.071) *n* 38.5 *g*
3	13	87.3	3.29	1.20	11.8	*g* 45.1 *x* 49.6 (0.19) *n* 88.8 (0.078) *i* *g* 45.0 *n* 87.0 (0.095) *i*	*i* 82.5 (0.083) *n* 42.7 *g*
4	18	83.3	5.08	1.18	18.2	*g* 59.5 *x* 64.5 (0.26) *n* 97.8 (0.094) *i* *g* 56.4 *n* 95.9 (0.070) *i*	*i* 90.8 (0.078) *n* 50.3 *g*
5	23	82.0	6.04	1.11	21.6	*g* 61.7 *x* 66.4 (0.23) *n* 102.7 (0.078) *i* *g* 59.4 *n* 102.3 (0.086) *i*	*i* 97.6 (0.078) *n* 52.1 *g*
6	30	79.3	8.09	1.21	28.9	*g* 64.4 *x* 68.4 (0.21) *n* 104.5 (0.070) *i* *g* 63.0 *n* 104.3 (0.081) *i*	*i* 100.3 (0.075) *n* 54.1 *g*

TABLE 3. Cationic Polymerization of 4-[4-Cyano-4′-biphenyl)oxy]butyl Vinyl Ether (6-4) (polymerization temperature, 0ºC; polymerization solvent, methylene chloride; $[M]_0 = 0.341$; $[(CH_3)_2\overline{S]_0}[I]_0 = 10$; 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

			GPC			Phase transitions (ºC) and corresponding enthalpy changes (kcal/mru)	
Sample	$[M]_0/[I]_0$	Polymer yield, %	$M_n \times 10^{-3}$	M_w/M_n	*DP*	Heating	Cooling
1	5	71.5	1.16	1.20	3.9	*g* 15.4 *n* 77.1 (0.056) *i* *g* 15.2 *n* 76.7 (0.067) *i*	*i* 72.3 (0.047) *n* 10.3 *g*
2	7	80.0	1.52	1.10	5.2	*g* 24.5 *n* 75.2 (0.032) *i* *g* 24.0 *n* 74.8 (0.026) *i*	*i* 67.8 (0.026) *n* 16.9 *g*
3	10	59.5	2.93	1.20	10.0	*g* 30.2 *x* 45.4 (0.29) *n* 83.3 (0.019) *i* *g* 28.4 *n* 77.2 (0.029) *i*	*i* 69.5 (0.035) *n* 23.9 *g*
4	14	63.5	3.73	1.16	12.7	*g* 34.8 *x* 48.8 (0.49) *n* 85.5 (0.0029) *i* *g* 33.1 *n* 74.5 (0.003) *i*	*i* 67.3 (0.009) *n* 23.2 *g*
5	18	80.7	5.03	1.22	17.1	*g* 35.7 *x* 52.2 (0.30) *n* 84.7 (0.0079) *i* *g* 34.3 *n* 83.2 (0.003) *i*	*i* 69.5 (0.012) *n* 23.1 *g*
6	24	86.7	6.99	1.23	23.8	*g* 39.1 *x* 52.8 (0.39) *n* 87.4 (0.0058) *i*	*i* 70.1 (0.003) *n* 28.0 *g*
7	30	89.3	8.45	1.18	28.8	*g* 47.2 *x* 58.2 (02) *n* 86.2 (0.015) *i* *g* 44.3 *n* 88.7 (0.011) *i*	*i* 71.9 (0.003) *n* 36.4 *g*

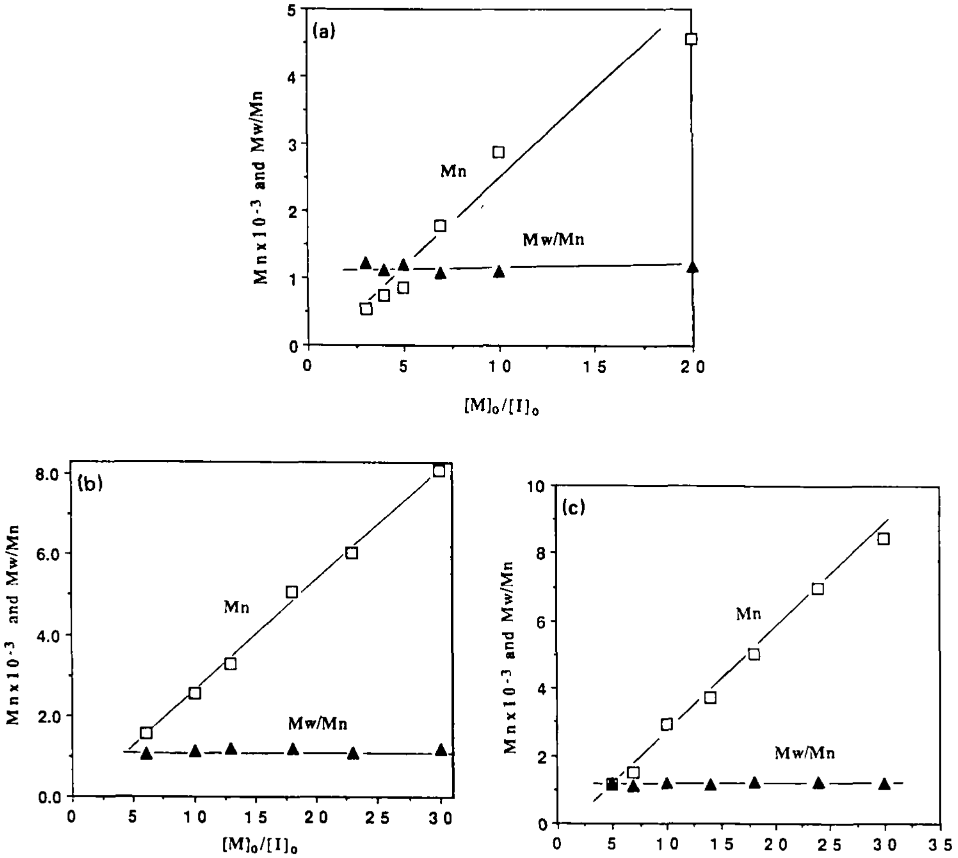
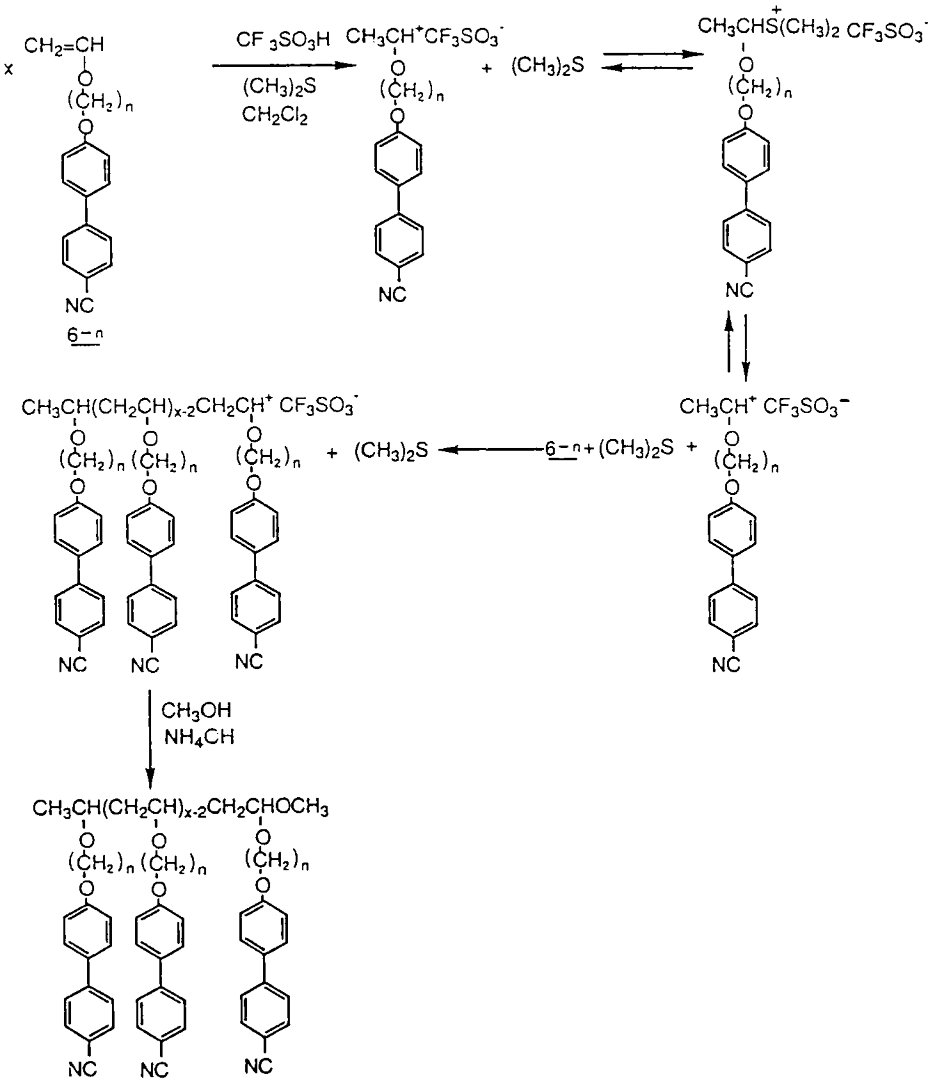


FIG. 1. The dependence of the number-average molecular weight (M_n) and of the polydispersity (M_w/M_n) of poly(6-2) (a), poly(6-3) (b), and poly(6-4) (c) on the $[M]_0/[I]_0$ ratio.

all intermediary alcohols, monomers, and model compounds is summarized in Table 4. The alcohol derivatives 7-2, 7-3, and 7-4 exhibit a monotropic nematic mesophase. 6-2 is crystalline, 6-3 exhibits a monotropic nematic mesophase, while 6-4 exhibits an enantiotropic nematic phase. The model compounds 8-2 and 8-3 are only crystalline. 8-4 displays a monotropic nematic mesophase.

Figure 2 presents the DSC traces of poly(6-2) with different molecular weights. The polymerization of 6-2 was investigated previously by Sa-



SCHEME 2. Cationic polymerization of 6-2, 6-3, and 6-4.

TABLE 4. Thermal Characterization of 4-Cyano-4′-(ω-hydroxyalkan-1-yloxy)biphenyls (7-2, 7-3, and 7-4), ω[(4-Cyano-4′-biphenyl)oxy]-alkyl Vinyl Ethers (6-2, 6-3, and 6-4) and ω-[(4-Cyano-4′biphenyl)oxy]-alkyl Ethyl Ethers (8-2, 8-3, and 8-4)

	Phase transitions (0^0C) and corresponding enthalpy changes (kcal/mol)	
Compound	Heating	Cooling
7-2	*k* 128.7 (6.84) *i*	*i* 123.4 (0.31) *n* 105.4 (3.85) *k*
	[*n* 126.5 (0.25) *i*][a]	
6-2	*k* 118.5 (8.21) *i*	*i* 83.4 (6.70) *k*
8-2	*k* 68.9 (5.46) *i*	*i* 13.3 (3.56) *k*
7-3	*k* 114.6 (7.45) *i*	*i* 112.7 (0.30) *n* 67.5 (2.87) *k*
	[*n* 115.3 (0.26) *i*]	
6-3	*k* 78.74 (9.02) *i*	*i* −10.4 (0.08) *n* −51.4 (2.30) *k*
8-3	*k* 64.9 (7.83) *i*	*i* −5.9 (4.13) *k*
7-4	*k* 126.4 (5.95) *i*	*i* 121.7 (0.31) *n* 99.3 (5.24) *k*
	[*n* 124.8 (0.32) *i*][a]	
6-4	*k* 73.3 (7.82) *n* 77.1 (0.22) *i*	*i* 73.4 (0.29) *n* 48.4 (6.37) *k*
8-4	*k* 64.7 (7.87) *i*	*i* 47.4 (0.094) *n* 33.1 (5.38) *k*
	[*n* 50.5 (0.062)] *i*	

[a][ ] = virtual data.

gane and Lenz [8c]. Our present data do not agree completely with their results. In the first DSC heating scan (Fig. 2a), poly(6-2) presents an endothermic transition which overlaps the glass transition temperature. This transition does not appear on the second heating (Fig. 2b) or on the cooling scans (Fig. 2c). Since we could not yet assign this phase, we will label it with *x* (Table 1). Irrespective of the thermal history of the sample, when the degree of polymerization of poly(6-2) is lower than 4.0, the polymer also presents an enantiotropic nematic mesophase. Poly(6-2) with higher degrees of polymerization does not present this nematic phase. The disappearance of this phase at higher polymer molecular weights is due to the steep increase of the dependence of the glass transition temperature versus polymer molecular weight with the increase of polymer molecular weight. At degrees of polymerization of about 7 and higher, the glass transition of poly(6-2) is very close to the nematic-

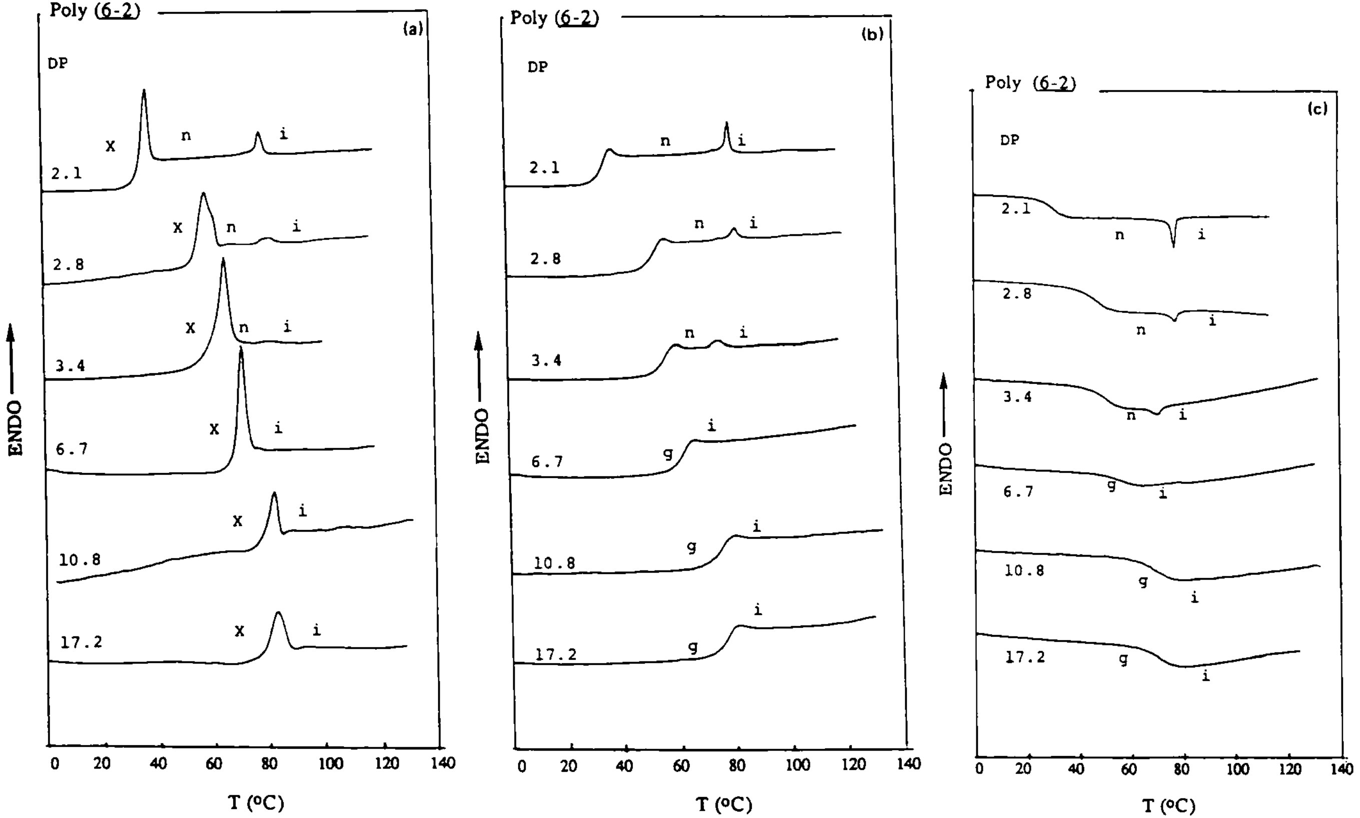


FIG. 2. DSC traces displayed during the first heating scan (a), second heating scan (b), and first cooling scan (c) by poly(6-2) with different degrees of polymerization (*DP*). *DP* is printed above each DSC scan.

isotropic transition temperature. Therefore, the mesophase becomes kinetically controlled, and due to its close proximity to glass transition, it cannot be observed by DSC. Upon shearing the polymer sample on the optical polarized microscope just above its T_g, we see the formation of the nematic phase. Figure 3 presents the dependence of glass transition, of the nematic-isotropic, and of the x-nematic transition temperatures on molecular weight. This figure demonstrates that the slope of the T_g - M_n is higher than that of T_{n-i}-M_n and, as a consequence, at higher polymer molecular weights the nematic mesophase becomes kinetically controlled.

The first and second heating and the cooling DSC traces of poly(6-3) are presented in Fig. 4. This polymer presents an enantiotropic nematic mesophase. However, on the first heating scan it also shows that x phase which overlaps the glass transition temperature (Fig. 4a, Table 2). Figures 4 and 5 show the dependence of glass transition and nematic-isotropic transition temperatures on molecular weight. The slopes of both dependences are almost identical. In the case of poly(6-2) the slope of

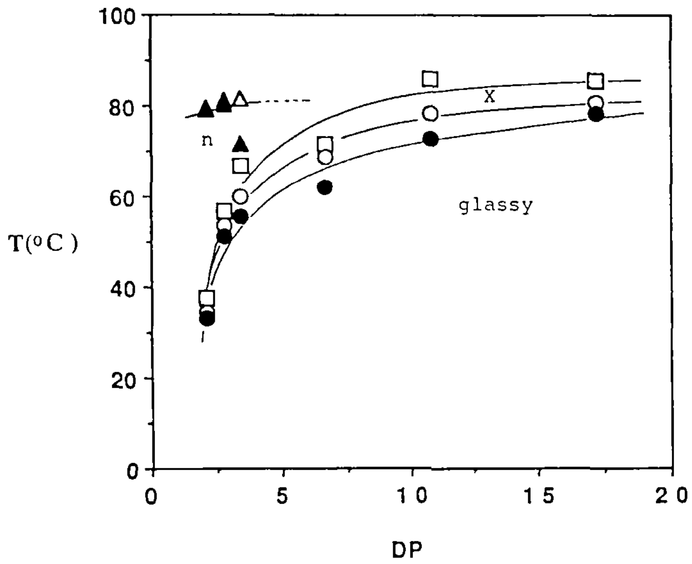


FIG. 3. The dependence of phase transition temperatures on the degree of polymerization of poly(6-2). Data from first heating scan (fh) and second heating scan (sh): (△) T_{n-i}(fh); (□) T_{x-n}(fh); (○) T_g(fh); (▲) T_{n-i}(sh); (●) T_g(sh).

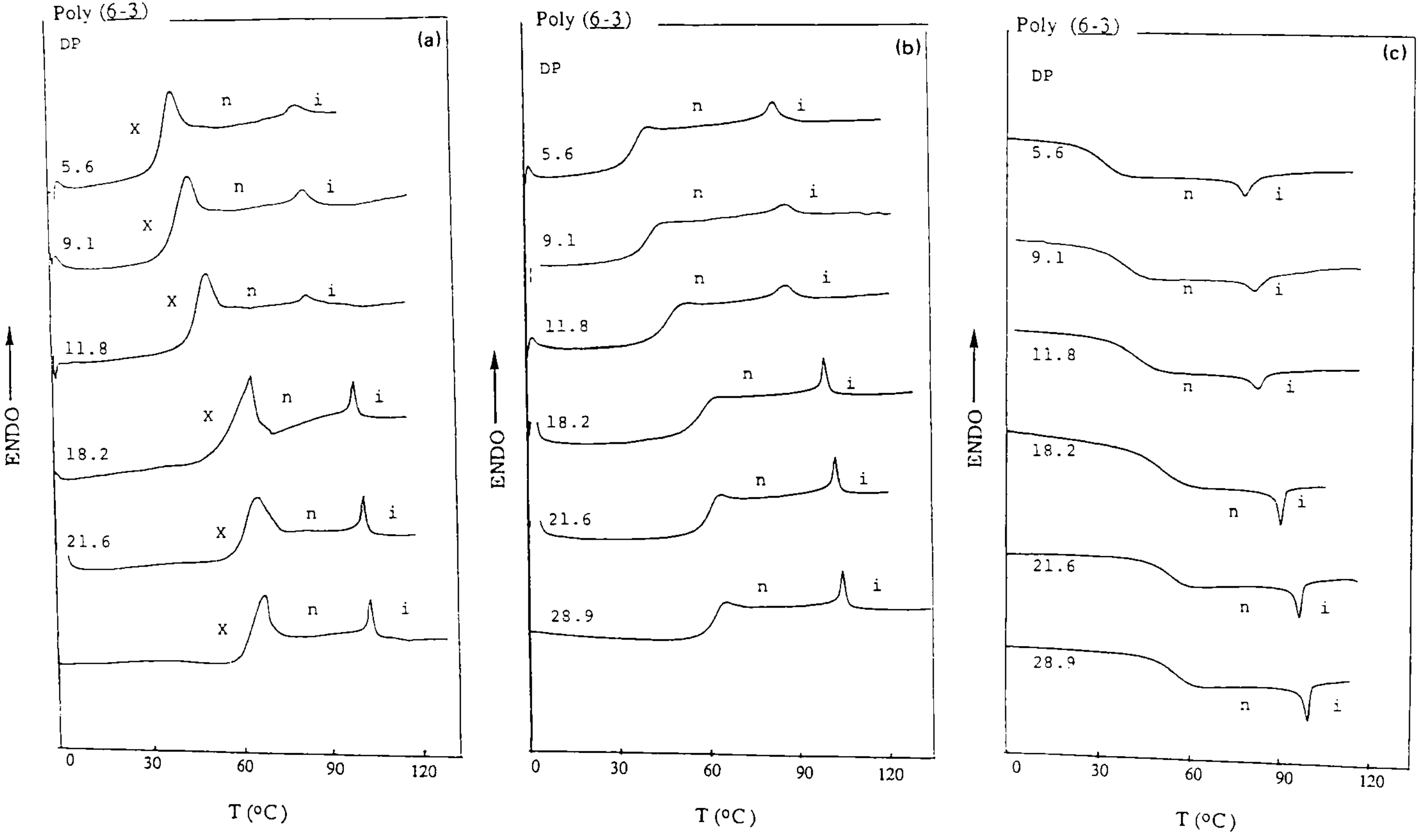


FIG. 4. DSC traces displayed during the first heating scan (a), second heating scan (b), and first cooling scan (c) by poly(6-3) with different degrees of polymerization (*DP*). *DP* is printed above each DSC scan.

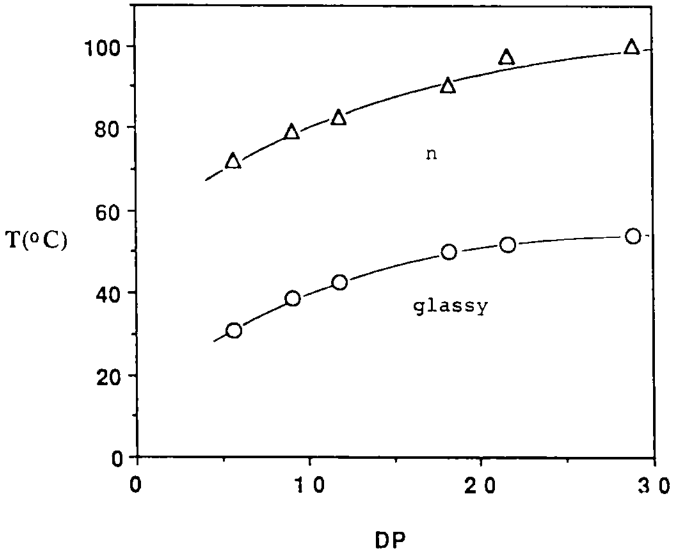


FIG. 5. The dependence of phase transition temperatures on the degree of polymerization of poly(6–3). Data from first cooling scan: (△) $T_{n\text{-}i}$; (○) T_g.

T_g–M_n was higher than that of T_{n-i}–M_n. At the same time, in the case of polymers with longer spaces, the slopes of the mesomorphic–isotropic phase transition temperatures versus M_n are higher than that of T_g–M_n [2, 3].

In the first heating scan, poly(6-4) with degrees of polymerization below 5 exhibits an enantiotropic nematic mesophase (Fig. 6a, Table 3). Polymers with higher molecular weights exhibit the *x* phase followed by the enantiotropic nematic mesophase. The *x* phase cannot be observed on the second heating and cooling scans (Figs. 6b and 6c). The dependences of the phase transition temperatures of poly(6-4), collected from the first heating scans versus M_n, are plotted in Fig. 7. Again we can observe similar slopes for the T_g–M_n and T_{n-i}–M_n dependences. It is very interesting to observe that the enthalpy changes associated with the nematic–isotropic transitions of poly(6-4) are very low.

In conclusion, mesomorphic poly(vinyl ether)s with long spacers exhibit smectic mesophases although their corresponding monomers and model compounds display nematic mesophases [2, 3]. The corresponding polymers with short flexible spacers exhibit nematic mesophases. Their

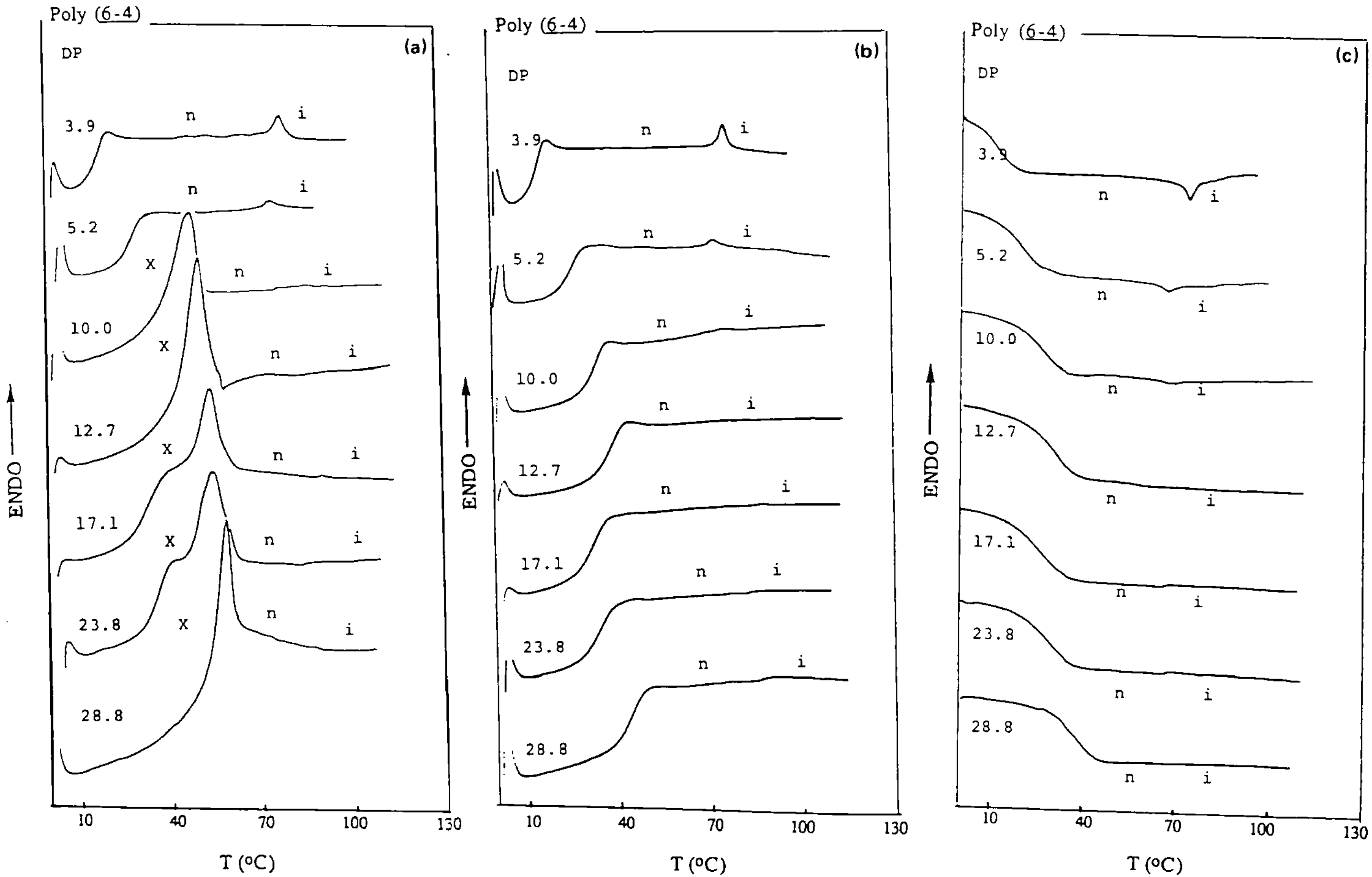


FIG. 6. DSC traces displayed during the first heating scan (a), second heating scan (b), and first cooling scan (c) by poly(6-4) with different degrees of polymerization (*DP*). *DP* is printed above each DSC scan.

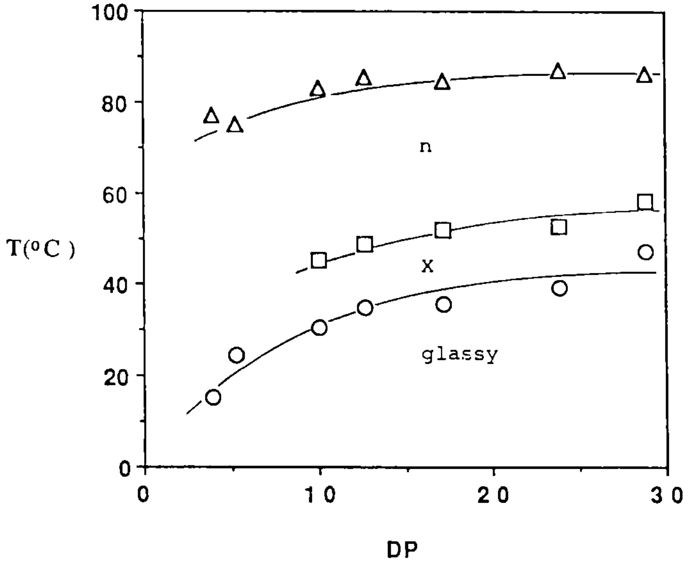


FIG. 7. The dependence of phase transition temperatures on the degree of polymerization of poly(6-4). Data from first heating scan: (△) $T_{n\text{-}i}$; (□) $T_{x\text{-}n}$; (○) T_g.

monomers and model compounds also exhibit nematic mesophases. In the case of polymers with short flexible spacers, the slopes of the T_g–M_n and T_{n-i}–M_n dependences are about equal, and therefore these two dependences do not intercept each other. An exception is provided by poly(6-2) whose T_g–M_n slope is steeper than that of T_{n-i}–M_n dependence. Consequently, at a certain degree of polymerization the T_g–M_n dependence intercepts the T_{n-i}–M_n dependence, and therefore above this molecular weight the nematic phase becomes virtual. In the case of polymers with long flexible spacers, the slope of T_{s-i}–M_n is much steeper than that of T_g–M_n. In this case the smectic mesophase is virtual below the molecular weight which corresponds to this interception and becomes enantiotropic above it. Last but not least, it is interesting to mention that the dimers and trimers of poly(6-2) as well as the low molecular weight oligomers of poly(6-3) have glass transition temperatures above room temperature and therefore provide an interesting new approach to nematic glasses with fast dynamics. They may have the same potential applications as low molar mass glassy nematic liquid crystals [11].

matic glasses with fast dynamics. They may have the same potential applications as low molar mass glassy nematic liquid crystals [11].

The experiments described in this series of publications, together with previous results on the same topic provided both by us [12] and by others [13-17], demonstrate the complexity of the influence of molecular weight on the phase transitions of side-chain liquid crystal polymers. The only case explained so far refers to systems in which the virtual or monotropic mesophase of the monomer or of the monomeric structural unit transforms into a monotropic or enantiotropic mesophase after polymerization [18, 19]. The same explanation holds for situations when the monomeric structural unit exhibits an enantiotropic mesophase and the resulting polymer exhibits a broader range of temperatures of its mesophase. However, the mechanism which changes the nature of the mesophase upon increasing the degree of polymerization is not yet known.

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