

Molecular Engineering of Liquid-Crystal Polymers by Living Polymerization. 14.[†] Synthesis and Characterization of Binary Copolymers of ω -[(4-Cyano-4'-biphenyl)oxy]alkyl Vinyl Ethers Containing Undecanyl and Hexyl, Pentyl and Propyl, and Undecanyl and Propyl Pairs of Alkyl Groups

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ABSTRACT: The synthesis and characterization of poly[11-[(4-cyano-4'-biphenyl)oxy]undecanyl vinyl ether-co-6-[(4-cyano-4'-biphenyl)oxy]hexyl vinyl ether] X/Y (poly[(6-11)-co-(6-6)] X/Y) (where X/Y represents the molar ratio of the two structural units), poly[5-[(4-cyano-4'-biphenyl)oxy]pentyl vinyl ether-co-3-[(4-cyano-4'-biphenyl)oxy]propyl vinyl ether] X/Y (poly[(6-5)-co-(6-3)] X/Y), and poly[11-[(4-cyano-4'-biphenyl)oxy]undecanyl vinyl ether-co-3-[(4-cyano-4'-biphenyl)oxy]propyl vinyl ether] X/Y (poly[(6-11)-co-(6-3)] X/Y) with degrees of polymerization of about 20 and molecular weight distributions of about 1.10 are described. The mesomorphic behavior of all copolymers determined from both the first and the second and subsequent differential scanning calorimetric (DSC) scans was discussed as a function of composition. As determined from the second DSC scans, poly(6-11) and poly(6-6) exhibit enantiotropic smectic A (s_A) and s_X (unidentified) mesophases and poly(6-5) exhibits enantiotropic nematic (n) and s_A , while poly(6-3) exhibits n mesophases. The temperature transitions and the corresponding enthalpy changes associated with the s_A phase of poly[(6-11)-co-(6-6)] X/Y and the n phase of poly[(6-5)-co-(6-3)] X/Y exhibit continuous almost linear dependences of copolymer composition. Both the temperature transitions and the enthalpy changes of the s_A and n mesophases of poly[(6-11)-co-(6-3)] X/Y exhibit continuous dependences of copolymer composition. The highest temperature mesophase of these copolymers changes from n to s_A in the case of poly[(6-11)-co-(6-3)] $4/6$, which exhibits a triple point in its phase behavior. In addition, poly[(6-11)-co-(6-3)] $3/7$ displays enantiotropic n , s_A , and reentrant nematic (n_{re}) mesophases. These results demonstrate that when the structural units of a copolymer are isomorphic within a certain mesophase, both the thermal transition temperatures and the enthalpy changes associated with this mesophase display continuous or even linear dependences of copolymer composition. The preparative implications of these results are discussed.

Introduction

Copolymerization represents the simplest synthetic technique that can be used to tailor make phase transitions of both main-chain^{1a} and side-chain^{1b} liquid-crystalline polymers. Indeed, copolymerization was frequently employed to manipulate the phase transitions of side-chain liquid-crystalline polymers.¹⁻⁵ However, most of the results reported in the literature can be considered only in a qualitative way, since there are only very few cases in which information about both copolymer composition and molecular weight are available.^{1b-6}

A general classification of side-chain liquid-crystalline copolymers⁵ was recently discussed in a review article.^{1b} There are two main classes of side-chain liquid-crystalline copolymers. The first one refers to copolymers containing pairs of structural units with and without mesogenic units.^{1b-4,8-12} This class of copolymers was extensively investigated. The second class refers to copolymers based on pairs of structural units containing mesogenic units in each one. There are at least four different groups that should be considered in this second class: (a) copolymers from monomer pairs containing identical mesogens and polymerizable groups but different spacer lengths; (b) copolymers from monomer pairs containing identical mesogens and spacer lengths but different polymerizable groups; (c) copolymers from monomer pairs containing dissimilar mesogens but either similar or different spacer lengths and polymerizable groups; (d) copolymers from

monomer pairs containing constitutional isomeric units and similar or dissimilar spacers and polymerizable groups. Presently, there is a relatively good understanding of the last class of copolymers.^{13,14} When the structural units of these copolymers are isomorphic in their liquid-crystalline phase but not in their crystalline phase, copolymerization could be used to transform virtual or monotropic mesophases into enantiotropic mesophases. A general discussion considering the isomorphism in liquid-crystalline polymers and copolymers was published elsewhere.¹⁵

The following general trends were observed so far when copolymers from the second class of types a-c were investigated. When the structural units of the copolymer were isomorphic within the liquid-crystalline phase, a continuous or even linear dependence of the phase-transition temperature versus copolymer composition was observed.¹⁶ When the structural units of the copolymer were nonisomorphic within the mesophase, a discontinuous dependence of phase transitions versus composition was observed.¹⁶⁻¹⁹

Although the compositions of these copolymers were reported, molecular weight information was not presented. Liquid-crystalline copolysiloxanes are prepared by hydrosilation reactions. They are considered to be statistical copolymers with a random distribution of their structural units.^{1b,18} Copolymers synthesized by chain copolymerization reactions exhibit a heterogeneous composition unless they are prepared at low conversions.^{1b,21} At the same time, there is no single example in the literature in which the molecular weights of statistical side-chain liquid-crystalline copolymers prepared by chain copolymerizations were reported.^{1b,3,5,17-19} Since mesomorphic tran-

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Table I
Cationic Copolymerization of 6-11 with 6-6 (Polymerization Temperature, 0 °C; Polymerization Solvent, Methylene Chloride; [M]₀ = [6-11] + [6-6] = 0.256–0.312 M; [M]₀/[I]₀ = 20; [(CH₃)₂S]₀/[I]₀ = 10; Polymerization Time, 1 h) and Characterization of the Resulting Polymers^a

sample no.	[6-11]/[6-6], mol/mol	polymer yield, %	GPC			phase transitions (°C) and corresponding enthalpy change (kcal/mru)			
			$\overline{M}_n \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$	DP	heating		cooling	
1	0/10	85	6.1	1.10	19	g 31.3 s _X 68.9 (0.30) s _A 127.3 (0.19) i	i 120.3 (0.17) s _A 57.4 (0.34) s _X 25.9 g		
2	1/9	86	7.0	1.09	21	g 29.1 s _X 67.7 (0.31) s _A 126.9 (0.18) i	i 123.1 (0.22) s _A 41.0 (0.30) s _X 21.4 g		
3	2/8	88	5.9	1.09	18	g 25.6 s _X 55.7 (0.21) s _A 130.4 (0.20) i	i 132.0 (0.33) s _A 15.4 g		
4	3/7	80	6.7	1.14	20	g 25.9 s _X 53.5 (0.19) s _A 130.2 (0.22) i			
5	4/6	84	6.9	1.16	19	g 22.2 s _X 48.9 (0.25) s _A 137.7 (0.32) i			
6	5/5	82	6.4	1.15	18	g 18.9 s _A 137.1 (0.30) i			
7	6/4	82	6.3	1.15	17	g 19.7 s _X 37.4 (0.22) s _A 140.4 (0.42) i			
8	7/3	74	7.0	1.13	19	g 17.7 s _A 140.5 (0.41) i			
9	8/2	75	6.8	1.15	18	g 16.5 s _A 144.9 (0.52) i			
10	9/1	80	8.1	1.12	21	g 15.4 s _A 144.7 (0.56) i			
11	10/0	81	8.2	1.12	19	g 15.4 s _A 148.1 (0.54) i			
						g 14.7 s _A 147.7 (0.56) i			
						g 14.8 s _A 151.7 (0.62) i			
						g 17.5 s _A 151.5 (0.61) i			
						g 14.3 s _A 153.7 (0.68) i			
						g 11.0 s _A 153.3 (0.71) i			
						g 12.6 k 47.5 (0.19) s _A 154.3 (0.74) i			
						g 10.8 s _A 154.2 (0.76) i			
						g 12.8 k 53.6 (2.18) s _A 155.8 (0.84) i			
						g 12.1 s _A 155.3 (0.82) i			
						g 14.5 k 57.1 (3.45) s _A 157.2 (0.90) i			
						g 14.0 s _X 44.2 (0.93) s _A 156.4 (0.87) i			

^a Data on the first line are from the first heating and cooling scans. Data on the second line are from the second heating scan.

Table II
Cationic Copolymerization of 6-5 with 6-3 (Polymerization Temperature, 0 °C; Polymerization Solvent, Methylene Chloride; [M]₀ = [6-5] + [6-3] = 0.326–0.358 M; [M]₀/[I]₀ = 20; [(CH₃)₂S]₀/[I]₀ = 10; Polymerization Time, 1 h) and Characterization of the Resulting Polymers^a

sample no.	[6-5]/[6-3], mol/mol	polymer yield, %	GPC			phase transitions (°C) and corresponding enthalpy changes (kcal/mru)			
			$\overline{M}_n \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$	DP	heating		cooling	
1	0/10	80	5.9	1.09	21	g 61.3 s _X 68.8 (0.19) n 102.9 (0.12) i	i 97.6 (0.10) n 51.9 g		
2	1/9	89	4.8	1.11	17	g 60.0 n 102.9 (0.10) i			
3	2/8	84	4.9	1.09	18	g 55.9 s _X 62.8 (0.14) n 101.4 (0.10) i	i 95.5 (0.09) n 46.8 g		
4	3/7	84	5.2	1.15	18	g 554.9 n 101.7 (0.09) i			
5	4/6	86	5.3	1.10	19	g 51.2 s _X 58.5 (0.17) n 103.1 (0.10) i	i 97.2 (0.10) n 42.1 g		
6	5/5	71	5.3	1.12	18	g 50.8 n 103.4 (0.09) i			
7	6/4	82	5.3	1.09	18	g 47.9 s _X 55.1 (0.17) n 103.3 (0.10) i	i 97.4 (0.10) n 38.1 g		
8	7/3	78	5.2	1.10	18	g 47.5 n 103.5 (0.11) i			
9	8/2	84	5.1	1.11	17	g 45.2 s _X 53.4 (0.18) n 104.9 (0.10) i	i 99.3 (0.45) n 37.1 g		
10	9/1	85	4.8	1.11	16	g 44.5 n 105.1 (0.11) i			
11	10/0	80	5.4	1.13	18	g 42.3 s _X 46.9 (0.15) n 106.9 (0.11) i	i 101.4 (0.10) n 34.8 g		
						g 42.1 n 107.1 (0.09) i			
						g 39.4 s _X 42.9 (0.14) n 107.3 (0.12) i	i 101.7 (0.11) n 32.1 g		
						g 38.8 n 107.4 (0.11) i			
						g 33.4 s _X 41.1 (0.18) n 110.6 (0.11) i	i 103.4 (0.11) n 31.5 g		
						g 34.2 n 110.7 (0.12) i			
						g 32.2 s _X 39.3 (0.12) n 111.6 (0.09) i	i 106.9 (0.12) n 28.7 g		
						g 31.4 n 111.7 (0.11) i			
						g 27.3 s _A 89.2 (-) n 112.6 (0.10) i	i 107.8 (0.11) n 81.7 (-) s _A 25.7 g		
						g 27.7 s _A 88.4 (-) n 112.8 (0.12) i			
						g 28.1 s _A 102.3 (-) n 113.2 (0.14) i	i 108.9 (0.12) n 90.3 (-) s _A 25.5 g		
						g 28.5 s _A 102.1 (-) n 113.5 (0.13) i			

^a Data on the first line are from the first heating and cooling scans. Data on the second line are from the second heating scan.

sitions are molecular weight dependent,^{1b,11,21–31} the synthesis of copolymers with both well-defined compositions and molecular weights is required. The ideal solution to the synthesis of copolymers by chain reactions would be to select monomer pairs that follow an azeotropic copolymerization and that can be prepared by a living polymerization mechanism. Such systems require $r_1 = r_2 = 1$ and are encountered mainly for comonomer pairs of almost similar structure.

Vinyl ethers containing an identical mesogenic group but different spacer lengths are presently the most suitable monomers for these investigations.^{24–32} The living cationic polymerization of ω -(4-cyano-4'-biphenyl)oxyalkyl vinyl ethers with ethyl, propyl and butyl,²⁷ pentyl,²⁸ hexyl,²⁹

heptyl,²⁸ octyl,²⁹ nonyl,³⁰ decanyl,³⁰ and undecanyl³¹ alkyl groups and the characterization of the resulting polymers as a function of molecular weight were investigated. The availability of these data and monomers provides access to a quantitative investigation of side-chain liquid-crystalline copolymers.

Two previous papers from our laboratory reported the first examples of such quantitative experiments. They refer to the synthesis and characterization of poly[2-[(4-cyano-4'-biphenyl)oxy]ethyl vinyl ether-co-8-[(4-cyano-4'-biphenyl)oxy]octyl vinyl ether]X/Ys³³ and poly[11-[(4-cyano-4'-biphenyl)oxy]undecanyl vinyl ether-co-2-[(4-cyano-4'-biphenyl)oxy]ethyl vinyl ether]X/Ys³⁴ with constant degrees of polymerization, narrow molecular

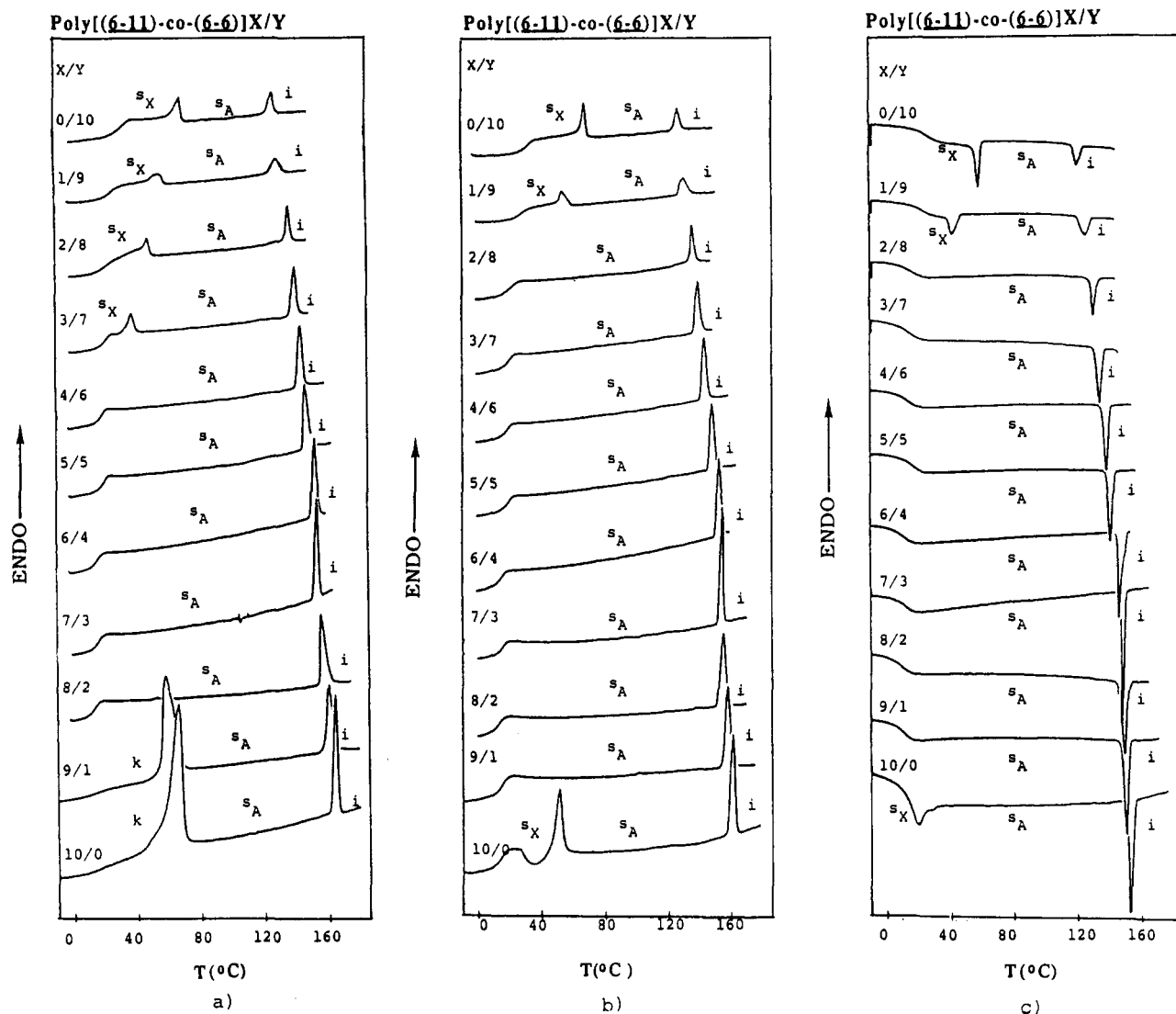


Figure 1. DSC traces displayed during the first heating (a), the second heating scan (b), and the first cooling scan (c) by poly(6-11), poly(6-6), and poly[(6-11)-co-(6-6)]X/Y.

weight distributions, and variable composition. At the degree of polymerization investigated (i.e., DP = 10 and, respectively, 15), both copolymers belong to a special case of class a. That is, both copolymers are prepared from monomer pairs containing identical mesogens and polymerizable groups but different spacer lengths. As determined from the second differential calorimeter (DSC) scans, poly[2-[(4-cyano-4'-biphenyl)oxy]ethyl vinyl ether] [poly(6-2)] does not exhibit any mesophase^{27,33,34} (i.e., is an amorphous polymer), poly[8-[(4-cyano-4'-biphenyl)oxy]octyl vinyl ether] [poly(6-8)] exhibits an enantiotropic smectic A mesophase,^{29,33} and poly[11-[(4-cyano-4'-biphenyl)oxy]undecanyl vinyl ether] [poly(6-11)] displays both enantiotropic s_X and s_A mesophases.^{31,34}

Depending on copolymer composition, both poly[(6-2)-co-(6-8)]X/Ys³³ and poly[(6-2)-co-(6-11)]X/Ys³⁴ exhibit as the highest temperature phase glassy, enantiotropic nematic, enantiotropic nematic and smectic A, and smectic A mesophases. In other words, the highest temperature mesophase exhibited by these copolymers displays a continuous dependence of copolymer composition with a triple point at which the nematic, smectic A, and glassy phases merge.

The goal of this paper is to describe the synthesis and characterization of the following copolymers: poly[11-[(4-cyano-4'-biphenyl)oxy]undecanyl vinyl ether-co-6-[(4-

cyano-4'-biphenyl)oxy]hexyl vinyl ether]X/Y [poly[(6-11)-co-(6-6)]X/Y], poly[5-[(4-cyano-4'-biphenyl)oxy]pentyl vinyl ether-co-3-[(4-cyano-4'-biphenyl)oxy]propyl vinyl ether]X/Y [poly[(6-5)-co-(6-3)]X/Y], and poly[11-[(4-cyano-4'-biphenyl)oxy]undecanyl vinyl ether-co-3-[(4-cyano-4'-biphenyl)oxy]propyl vinyl ether]X/Y [poly[(6-11)-co-(6-3)]X/Y]. All copolymers were synthesized with degrees of polymerization of about 20 and molecular weight distributions of about 1.10. The mesomorphic phases exhibited by the parent polymers with a degree of polymerization of 20 as determined from the second DSC scans are as follows: poly(6-11) and poly(6-6), enantiotropic s_A and s_X ; poly(6-5) enantiotropic s_A and n, and poly(6-3), enantiotropic nematic. Therefore, the investigation of these three pairs of copolymers will elucidate the phase behavior of copolymers derived from pairs of homopolymers exhibiting the high-temperature mesophases s_A and s_A , n and n, and s_A and n and thus will provide a complete characterization of the class of copolymers a.

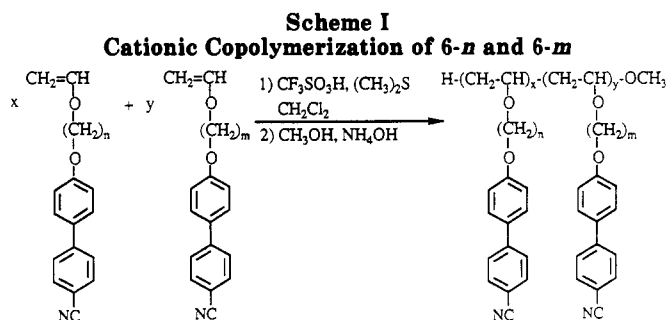
Experimental Section

Materials. All materials were commercially available and were used as received or purified as described previously.^{27-29,31} Methyl sulfide (anhydrous, 99%; Aldrich) was refluxed over 9-borabicyclo[3.3.1]nonane (9-BBN, crystalline, 98%; Aldrich) and then distilled under argon. Dichloromethane (99.6%; Al-

Table III
Cationic Copolymerization of 6-11 with 6-3 (Polymerization Temperature, 0 °C; Polymerization Solvent, Methylene Chloride; [M]₀ = [6-11] + [6-3] = 0.256–0.358 M; [M]₀/[I]₀ = 20; [(CH₃)₂S]₀/[I]₀ = 10; Polymerization Time, 1 h) and Characterization of the Resulting Polymers^a

sample no.	[6-11]/[6-3], mol/mol	polymer yield, %	GPC			phase transitions (°C) and corresponding enthalpy changes (kcal/mru)	
			$\overline{M}_n \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$	DP	heating	cooling
1	0/10	80	5.9	1.09	21	g 61.3 s _X 68.8 (0.19) n 102.9 (0.12) i g 60.0 n 102.9 (0.10) i	i 97.6 (0.10) n 51.9 g
2	1/9	78	5.7	1.12	18	g 54.1 s _X 61.3 (0.26) n 106.1 (0.13) i g 52.8 n 106.0 (0.14) i	i 100.7 (0.12) n 44.2 g
3	2/8	86	6.0	1.10	19	g 44.7 s _X 51.8 (0.33) n 110.2 (0.17) i g 44.2 n 110.4 (0.16) i	i 104.9 (0.15) n 36.7 g
4	3/7	74	5.6	1.08	17	g 37.9 s _X 43.6 (0.42) s _A 98.3 (0.019) n 114.2 (0.20) i	i 108.5 (0.22) n 91.8 (0.026) s _A 27.8 g
5	4/6	79	6.0	1.08	18	g 34.8 s _A 98.2 (0.022) n 114.5 (0.19) i g 29.8 s _X 36.4 (0.18) s _A 121.1 (0.44) i	i 116.1 (0.45) s _A 22.5 g
6	5/5	82	6.6	1.10	19	g 27.7 s _A 121.0 (0.45) i g 23.1 s _A 128.7 (0.56) i	i 122.8 (0.54) s _A 17.9 g
7	6/4	76	6.7	1.10	19	g 22.5 s _A 129.0 (0.55) i g 18.5 s _A 134.0 (0.63) i	i 129.2 (0.59) s _A 13.9 g
8	7/3	65	6.3	1.07	17	g 17.5 s _A 134.5 (0.61) i g 16.5 s _A 139.4 (0.66) i	i 135.0 (0.67) s _A 10.5 g
9	8/2	70	7.6	1.10	20	g 15.6 s _A 140.2 (0.70) i g 14.6 k 47.4 (0.12) s _A 144.3 (0.76) i	i 139.9 (0.74) s _A 9.8 g
10	9/1	67	7.5	1.09	19	g 14.0 s _A 144.9 (0.74) i g 14.8 k 50.6 (2.15) s _A 150.8 (0.84) i	i 144.3 (0.80) s _A 9.0 g
11	10/0	81	8.2	1.12	19	g 14.1 s _A 150.3 (0.81) i g 14.5 k 57.1 (3.45) s _A 157.2 (0.90) i	i 149.4 (0.89) s _A 18.9 (0.63) s _X 8.8 g

^a Data on the first line are from the first heating and cooling scans. Data on the second line are from the second heating scan.



drich) used as a polymerization solvent was first washed with concentrated sulfuric acid and then with water, dried over anhydrous magnesium sulfate, refluxed over calcium hydride, and freshly distilled under argon before each use. Trifluoromethanesulfonic acid (triflic acid, 98%; Aldrich) was distilled under argon.

Techniques. ¹H 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 3600 data station, was used to determine the thermal transitions that were reported as the maxima and minima of their endothermic and 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. For certain polymer samples, the first heating scans sometimes differ from the second and subsequent heating scans. At the proper place, this difference will be mentioned. However, the second and subsequent heating scans are identical. The first heating scans can be reobtained after proper thermal treatment of the polymer sample. Both the first and the second DSC heating scans will be reported and discussed. A Carl-Zeiss optical polarized microscope (magnification: 100×) equipped with a Mettler FP 82 hot stage and a Mettler FP 800 central processor was used to observe the thermal transitions and to analyze the anisotropic textures.^{35,36} Molecular weights were determined by gel permeation chromatography (GPC) with a Perkin-Elmer Series 10 LC instrument equipped with an LC-100 column oven, an LC-600 autosampler, and a Nelson analytical 900 series integrator data station. The measurements were made at 40 °C using the UV detector. A set of Perkin-Elmer PL gel columns

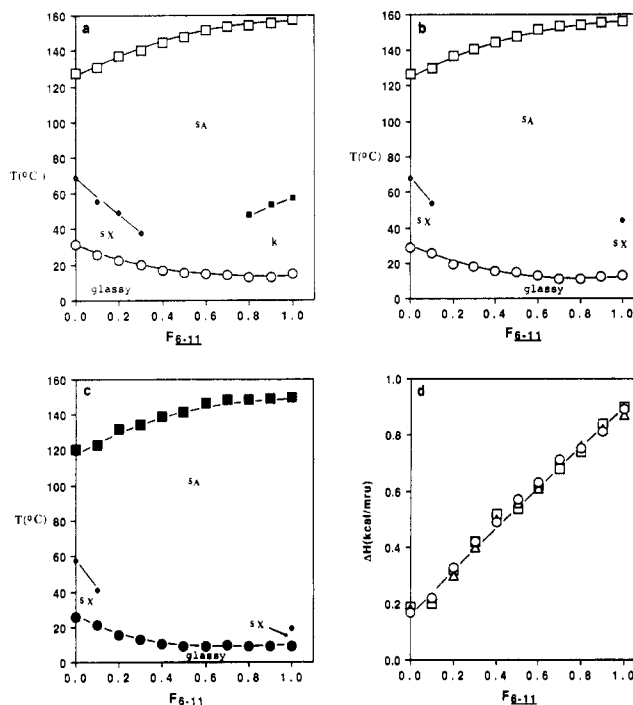


Figure 2. Dependence of phase-transition temperatures on the composition of poly[(6-11)-co-(6-6)]X/Y. (a) Data from the first heating: (○) *T_g*; (◇) *T_g→SA*; (■) *T_g→SX*; (□) *T_g→SX→SA*. (b) Data from the second heating scan: (○) *T_g*; (◇) *T_g→SA*; (□) *T_g→SA*. (c) Data from the first cooling scan: (■) *T_g→SA*; (◆) *T_g→SX→SA*; (●) *T_g*. (d) Dependence of the enthalpy changes associated with the mesomorphic-isotropic and isotropic-mesomorphic phase transitions on the composition of poly[(6-11)-co-(6-6)]X/Y: (□) ΔH_{SA-i} (data from the first heating scan); (Δ) ΔH_{SA-i} (data from the second heating scan); (○) ΔH_{SA-i} (data from the first cooling scan).

of 10⁴ and 500 Å with CHCl₃ as solvent (1 mL/min) and a calibration plot constructed with polystyrene standards were used to determine the molecular weights. Therefore, all molecular weights discussed in this paper are relative to polystyrene. High-pressure liquid chromatography (HPLC) experiments were performed with the same instrument.

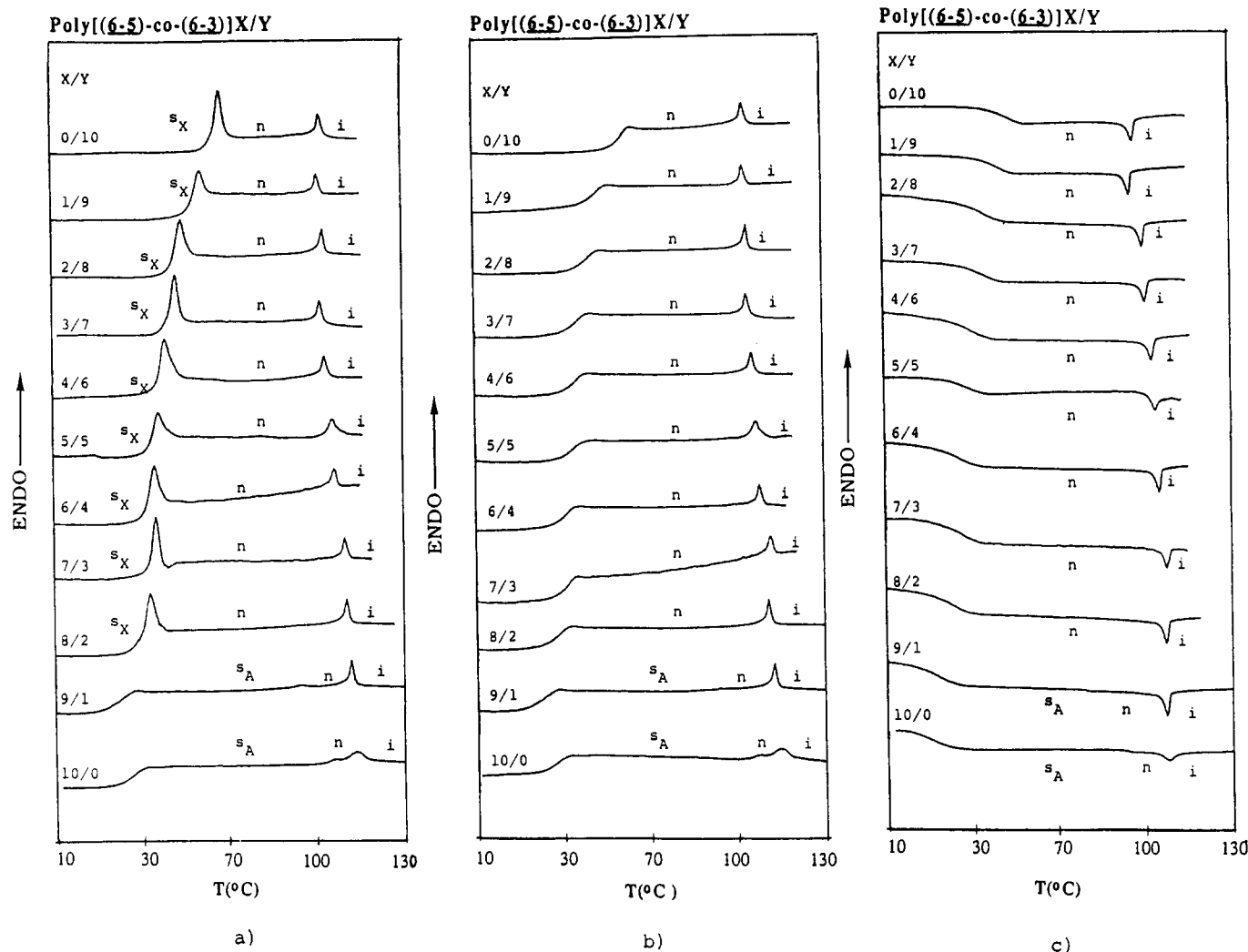


Figure 3. DSC traces displayed during the first heating (a), the second heating scan (b), and the first cooling scan (c) by poly(6-5), poly(6-3), and poly[(6-5)-co-(6-3)]X/Y.

Synthesis of Monomers. 11-[(4-Cyano-4'-biphenyl)oxy]undecanyl vinyl ether (6-11),³¹ 6-[(4-cyano-4'-biphenyl)oxy]hexyl vinyl ether (6-6),²⁹ 5-[(4-cyano-4'-biphenyl)oxy]pentyl vinyl ether (6-5),²⁸ and 3-[(4-cyano-4'-biphenyl)oxy]propyl vinyl ether (6-3)²⁷ were synthesized and purified as described in previous publications. Their purity was higher than 99% (HPLC). Their detailed characterization is described in the previous publications.

Cationic Polymerizations and Copolymerization. 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 and 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. When necessary, the polymers were reprecipitated until their GPC and HPLC traces showed complete absence of unreacted monomers. Tables I–III summarize the polymerization results. Although polymer yields are lower than expected due to losses during the purification process, conversions determined by HPLC and GPC analysis before polymer purification were almost quantitative in all cases.

Results and Discussion

The synthesis, characterization, and living cationic polymerization of ω -(4-cyano-4'-biphenyl)oxyalkyl vinyl

ethers with alkyl groups from ethyl to undecanyl were described in the previous papers.^{27–31} Our preferred initiating system is $\text{CF}_3\text{SO}_3\text{H}/\text{S}(\text{CH}_3)_2$ ³⁷ since it can be used to perform living cationic polymerizations in CH_2Cl_2 at 0 °C. In addition, we have shown that this system can be used to initiate the living cationic polymerization and cyclopolymerization of monomers containing a variety of functional groups.^{38–41}

The copolymerization of these monomer pairs is outlined in Scheme I. As discussed in the Experimental Section, the copolymer composition is equal to the monomer feed. Some ^1H NMR experiments were used to test this assumption, which is based on the following additional experimental data. All copolymerizations lead to almost quantitative conversions (determined by HPLC and GPC), although the yields reported in Tables I–III are lower than 100%. This is due to polymer losses during the purification experiments. The GPC traces of all copolymers show a monomodal molecular weight distribution characterized by a polydispersity of about 1.10 (Tables I and III). A previous experiment from our laboratory has demonstrated that for the case of poly[(6-2)-co-(6-8)]X/Y with X/Y = 1/1 the copolymerization follows a living character.⁴² Attempts were made to synthesize all copolymers investigated in this study with degrees of polymerization of about 20.

According to the nature of the highest temperature mesophase exhibited by the pair of homopolymers generated

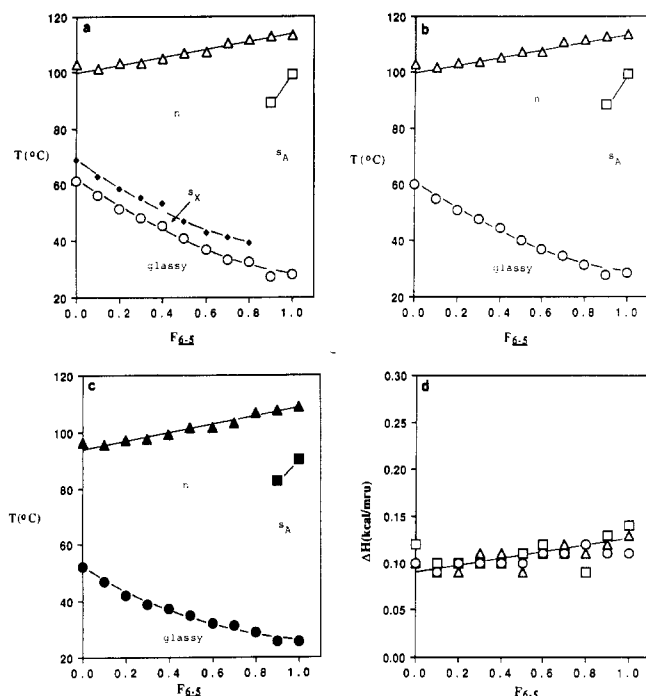


Figure 4. Dependence of phase-transition temperatures on the composition of poly[(6-5)-co-(6-3)]X/Y. (a) Data from the first heating: (○) T_g ; (◇) T_{n-i} ; (□) T_{sA-n} ; (Δ) T_{n-i} . (b) Data from the second heating scan: (○) T_g ; (□) T_{sA-n} ; (Δ) T_{n-i} . (c) Data from the first cooling scan: (Δ) T_{n-i} ; (■) T_{n-sA} ; (●) T_g . (d) Dependence of the enthalpy changes associated with the mesomorphic-isotropic and isotropic-mesomorphic phase transitions on the composition of poly[(6-5)-co-(6-3)]X/Y: (□) ΔH_{n-i} (data from the first heating scan); (Δ) ΔH_{n-i} (data from the second heating scan); (○) ΔH_{i-n} (data from the first cooling scan).

from the pair of monomers used in the synthesis of copolymers, we can classify these experiments in two classes. Copolymers based on monomer pairs whose parent homopolymers exhibit identical mesophases and copolymers based on monomer pairs whose parent homopolymers exhibit different mesophases. Poly[(6-11)-co-(6-6)]X/Y and poly[(6-5)-co-(6-3)]X/Y copolymers belong to the first class. The first copolymer is derived from a monomer pair whose parent homopolymers exhibit enantiotropic s_A phases as their highest temperature mesophase, while the second copolymer is derived from a monomer pair whose parent homopolymers exhibit enantiotropic n phases as their highest temperature mesophase. Copolymers poly[(6-11)-co-(6-3)]X/Y are based on a monomer pair whose parent homopolymers exhibit enantiotropic s_A and, respectively, enantiotropic n phases as their highest temperature mesophase. The phase behavior of these copolymers will be presented in the order discussed above. The phase behavior of all these copolymers will be discussed as obtained from their first and second heating and first cooling DSC scans.

Poly[(6-11)-co-(6-6)]X/Y. The synthesis and characterization of poly[(6-11)-co-(6-6)]X/Y copolymers are summarized in Table I. The first and the second heating and the first cooling DSC traces of all homopolymers and copolymers are presented in Figure 1a–c. As determined from the first DSC scans, poly(6-11) with a degree of polymerization of 19 exhibits an enantiotropic s_A mesophase and a crystalline melting.³¹ When the phase behavior of the same poly(6-11) is determined from second and subsequent DSC scans, it exhibits enantiotropic s_A and s_X (i.e., an unidentified smectic) mesophases³¹ (Figure 1a–c). Regardless of the thermal history of the sample, poly-

(6-6) with a degree of polymerization of 19 exhibits enantiotropic s_A and s_X mesophases (Figure 1a–c).²⁹

The dependence of the temperatures associated with the s_A -isotropic and isotropic- s_A transitions can be easily observed from the DSC traces presented in Figure 1a (for the first heating scans), Figure 1b (for the second heating scans), and Figure 1c (for the first cooling scans). This transition temperature shows a continuous, almost linear, dependence of copolymer composition, regardless of the DSC scan the temperature transitions are collected from. However, the temperature transitions associated with s_X - s_A and k - s_A from the first heating scans (Figure 1a), s_X - s_A and s_X - s_A from the second heating scans (Figure 1b), and s_A - s_X from the first cooling scans (Figure 1c) show an abrupt decrease of copolymer composition.

The phase-transition temperatures collected from the first heating scans are plotted in Figure 2a, those from the second heating scans in Figure 2b, and those from the first cooling scans in Figure 2c. The upward curvature of the s_A -isotropic and isotropic- s_A dependences versus copolymer composition (Figure 2a–c) can be explained by the Schroeder-van Laar equation.^{43a} This upward curvature was calculated by using the Schroeder-van Laar equation and qualitatively agrees with that obtained experimentally. Thus, the phase diagram of these copolymers can be regarded as close to what is expected for an ideal solution resulting from the structural units of the copolymer.^{43a,b} The enthalpy changes associated with the s_A -isotropic phase transitions determined from the first and second DSC scans and the isotropic- s_A phase transitions (Table I) are plotted in Figure 2d as a function of copolymer composition. This dependence is linear, thus demonstrating a weight average dependence of copolymer composition.

The conclusion derived from these results is as follows. Over the entire range of compositions, the structural units of the poly[(6-11)-co-(6-6)]X/Y copolymers are isomorphic within the s_A mesophase.¹⁵ However, the same two structural units are not isomorphic within the crystalline phase of poly(6-11) (Figure 2a) and are isomorphic only over a very narrow range of composition into the s_X mesophase of poly(6-6) (Figures 1a–c and 2a–c). As a consequence, poly[(6-11)-co-(6-6)]X/Y copolymers with X/Y = 2/8 to 9/1 exhibit only an enantiotropic s_A phase over a very large range of temperatures.

From the preparative point of view, the results of this experiment provide a technique that can be used to molecular engineer noncrystallizable copolymers that exhibit a s_A mesophase over a very large range of temperatures. At the same time, it teaches us how to tailor make the degree of order of the s_A mesophase by living copolymerization experiments (Figure 2d) (i.e., how to design a polymer exhibiting a s_A mesophase with a well-established enthalpy change associated with the s_A -isotropic phase transition).

Poly[(6-5)-co-(6-3)]X/Y. Table II summarizes the synthesis and characterization of poly[(6-5)-co-(6-3)]X/Y. The DSC traces of the first heating scans are presented in Figure 3a, those of the second heating scans in Figure 3b, and those of the first cooling scans in Figure 3c. Poly-(6-5) with a degree of polymerization of 18 exhibits enantiotropic s_A and n mesophases both in the first and second DSC scans.²⁸ As characterized from the first DSC heating scan, poly(6-3) with a degree of polymerization of 21 exhibits monotropic s_X and enantiotropic n mesophases.²⁷ However, when the same polymer is characterized from the second DSC heating scan, it exhibits only an enantiotropic n mesophase (Figure 3a–c).²⁷ Let us investigate

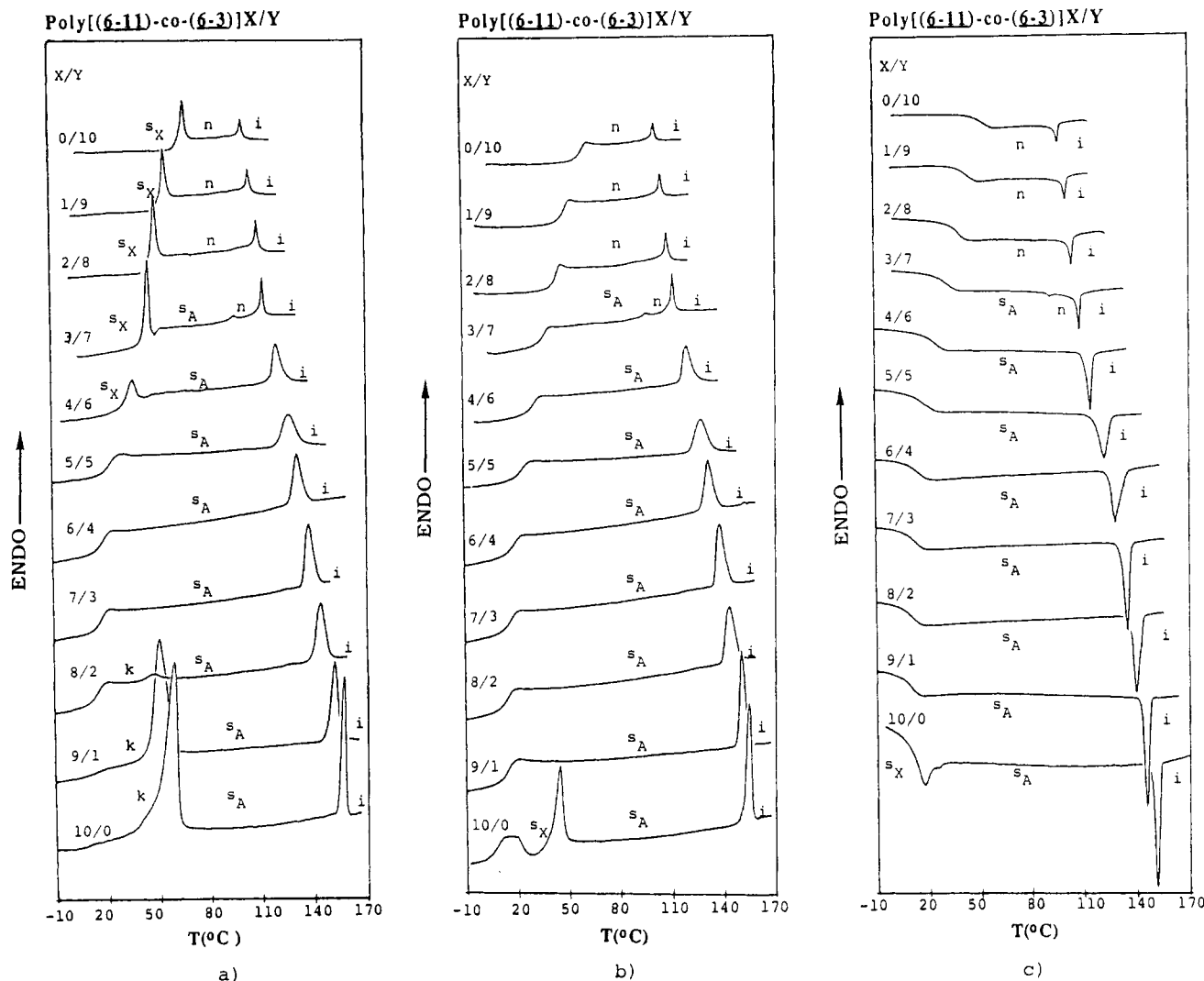


Figure 5. DSC traces displayed during the first heating (a), the second heating scan (b), and the first cooling scan (c) by poly(6-11), poly(6-3), and poly[(6-11)-co-(6-3)]X/Y.

the phase behavior of poly[(6-5)-co-(6-3)]X/Y as obtained from the first DSC heating scans (Figure 3a). The *n* mesophase exhibits a linear dependence of copolymer composition. That is, the structural units of both poly(6-5) and poly(6-3) are isomorphic within the *n* phase over the entire range of compositions. The *s_X* mesophase is also showing a continuous dependence of copolymer composition over the range of compositions from X/Y = 0/10 to 8/2. Poly[(6-5)-co-(6-3)]9/1 does not exhibit this mesophase.

The *s_A* mesophase appears also over a narrow range of copolymer composition, i.e., in the case of copolymer poly[(6-5)-co-(6-3)]9/1. In the second DSC heating scan, the *s_X* mesophase does not appear, while the *s_A* and *n* mesophases follow the same trend as the one observed in the first DSC heating scans (Figure 3a,b). The *s_X* mesophase does not form during the second heating scan since this phase is almost overlapping the glass transition temperature of these copolymers, and, therefore, it is strongly kinetically controlled. The cooling DSC scans (Figure 3c) are following the same pattern as the second heating DSC scans (Figure 3b). The phase behavior of poly[(6-5)-co-(6-3)]X/Y determined from the first heating, the second heating, and the first cooling DSC scans is plotted in Figure 4a-c. All these plots show linear dependences of the *n*-*i* and *i*-*n* phase transition temperatures versus copolymer composition.

Figure 4d plots the dependence of the enthalpy change associated with the *n*-*i* phase transition from the first and the second DSC heating scan and *i*-*n* phase transition, as a function of copolymer composition. The values of these enthalpy changes are much lower than those of the values associated with the *s_A*-*i* phase transition from Figure 2d and, therefore, are subjected to a larger experimental error. Nevertheless, the plot from Figure 4a shows a linear dependence of copolymer composition.

In conclusion, the *n* mesophase of poly[(6-5)-co-(6-3)]X/Y exhibits, as the *s_A* mesophase of poly[(6-11)-co-(6-6)]X/Y, a linear dependence of composition over the entire range of copolymer compositions. From a preparative point of view, the results of the investigation of the copolymers poly[(6-5)-co-(6-3)]X/Y teach us how to design noncrystallizable nematic polymers containing a cyano group in the mesogen and a very broad range of temperature of the mesophase. There are very few examples of side-chain liquid-crystalline polymers containing cyano groups and exhibiting nematic mesophases.^{1b,2} Most frequently, nematic polymers containing cyano groups are synthesized by inserting a lateral substituent within the structure of the mesogenic unit and by using combinations of laterally and terminally attached mesogenic side groups.⁴⁴⁻⁴⁶

Poly[(6-11)-co-(6-3)]X/Y. This copolymer system is different from the two systems described above since the

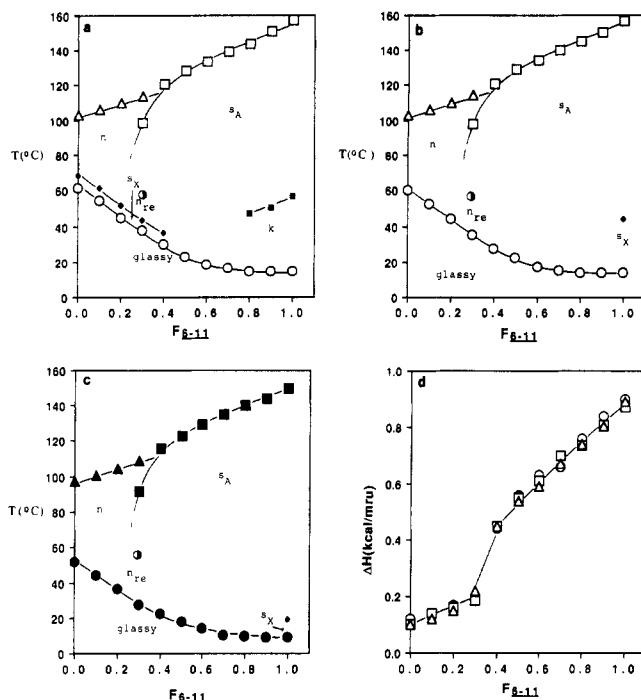


Figure 6. Dependence of phase-transition temperatures on the composition of poly(6-11)-co-(6-3)]X/Y. (a) Data from the first heating: (O) T_g ; (◊) $T_{n \rightarrow s_A}$; (■) $T_{s_A \rightarrow i}$; (Δ) $T_{n \rightarrow i}$. (b) Data from the second heating scan: (O) T_g ; (◊) $T_{s_X \rightarrow s_A}$; (□) $T_{s_A \rightarrow i}$; (Δ) $T_{n \rightarrow i}$. (c) Data from the first cooling scan: (▲) $T_{i \rightarrow n}$; (■) $T_{i \rightarrow s_A}$; (◆) $T_{s_A \rightarrow s_X}$; (●) T_g . (d) Dependence of the enthalpy changes associated with the mesomorphic-isotropic and isotropic-mesomorphic phase transitions on the composition of poly[(6-11)-co-(6-3)]X/Y: (□) $\Delta H_{s_A(n) \rightarrow i}$ (data from the first heating scan); (Δ) $\Delta H_{s_A(n) \rightarrow i}$ (data from the second heating scan); (O) $\Delta H_{i \rightarrow s_A(n)}$ (data from the first cooling scan).

higher temperature mesophase of poly(6-11) is s_A , while that of poly(6-3) is nematic. Table III summarizes the experimental data of the copolymer poly[(6-11)-co-(6-3)]X/Y.

Let us start by investigating the DSC traces of the first heating scan (Figure 5a). The s_X phase of poly(6-3) shows a linear dependence of copolymer composition up to a value of $X/Y = 4/6$. Copolymers with $X/Y = 5/5$ to $7/3$ exhibit a single s_A mesophase. Only copolymers with $X/Y = 10/0$ to $8/2$ exhibit the s_A mesophase and a crystalline phase. Copolymers with $X/Y = 0/10$ to $3/7$ exhibit the n and the s_X mesophases. All copolymers from $X/Y = 3/7$ to $10/0$ exhibit the s_A mesophase. Only the copolymer with $X/Y = 3/7$ exhibits both a n and a s_A mesophase. Figure 6a plots all the phase transitions from the first DSC heating scan as a function of copolymer composition. As we can observe from Figure 6a, both the n and the s_A phases are showing linear dependences of copolymer composition. However, the phase diagram of this copolymer exhibits a triple point at $X/Y = 4/6$. Poly[(6-11)-co-(6-3)] $3/7$ exhibits both enantiotropic nematic and s_A mesophases. On the optical polarized microscope, this copolymer exhibits a reentrant nematic (n_{re}) mesophase, which appears both on heating and cooling at 58.6°C . A detailed characterization of the n_{re} phase of this copolymer as well as the ability to molecular engineer n_{re} mesophases by living cationic polymerization and copolymerization will be described in a separate publication.⁴⁷ To our knowledge, so far n_{re} mesophases were observed only in polyacrylates with cyano side groups and spacers containing six methylenic units.⁴⁸

In the second DSC heating scan (Figure 5b), the s_X mesophase does not appear. This is again due to its close

proximity to the glass transition temperature of the copolymers. Only poly(6-11) exhibits on the second heating DSC scan a crystalline phase. The cooling DSC traces of these copolymers resemble those of the second heating scan (Figure 5b,c). The data collected from the second DSC heating scans and the first cooling scans are plotted in Figure 6b,c.

Finally, the enthalpy changes associated with the highest temperature mesophase of these copolymers are plotted in Figure 6d. Data collected from the first and the second heating and the first cooling DSC scans are plotted together. This plot shows very clearly the continuous character of the dependence of enthalpy change versus copolymer composition.

From a preparative point of view, these copolymerization experiments provide a very simple technique that can be used to design a copolymer exhibiting two enantiotropic mesophases, by starting from two monomers whose parent homopolymers exhibit these two mesophases, and suggest a technique for the preparation of polymers displaying n_{re} mesophases.

In conclusion, the series of experiments described in this paper, and the two experiments described previously,^{33,34} are providing a complete and quantitative picture of the class of side-chain liquid-crystalline copolymers prepared from monomer pairs containing identical mesogens and polymerizable groups but a different spacer length. This quantitative relationship can be summarized as follows: over the range of copolymer compositions where the two structural units of the copolymer are isomorphic within a certain mesophase, both the phase-transition temperature and the enthalpy changes associated with this mesophase display a continuous or even linear dependence of composition. Alternatively, when the two structural units are nonisomorphic within a certain mesophase, a continuous dependence of both transition temperatures and enthalpy changes with a triple point at a certain copolymer composition is observed. This dependence is in complete agreement with the rules of isomorphism of monomer structural units (copolymer isomorphism), which were extensively investigated for the case of crystalline copolymers^{49,50} and low molar mass liquid-crystal mixtures.^{15,43a} A detailed discussion of the isomorphism of crystalline polymers, low molar mass liquid crystals, and liquid-crystalline polymers and copolymers was presented in detail elsewhere.¹⁵ The results described in this paper will allow the molecular engineering of side-chain liquid-crystalline copolymers exhibiting one and more than one mesophase with a well-defined degree of order.

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Registry No. 6-3 (homopolymer), 131896-12-3; (6-3)(6-5) (copolymer), 134847-56-6; (6-3)(6-11) (copolymer), 134847-57-7; 6-5 (homopolymer), 131930-49-9; 6-6 (homopolymer), 131896-16-7; (6-6)(6-11) (copolymer), 134847-55-5; 6-11 (homopolymer), 130712-85-5.