Molecular engineering of liquid crystal polymers by living polymerization:
5. Synthesis and mesomorphic behaviour of poly{2-[(4-cyano-4′-biphenyl)oxy]ethyl vinyl ether-*co*-8-[(4-cyano-4′-biphenyl)oxy]octyl vinyl ether}*

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(*Received 21 May 1990; revised 3 August 1990; accepted 7 September 1990*)

The synthesis and characterization of poly{2-[(4-cyano-4′-biphenyl)oxy]ethyl vinyl ether} [poly(**6-2**)], poly{8-[(4-cyano-4′-biphenyl)oxy]octyl vinyl ether) [poly(**6-8**)] and of poly(**6-2**-*co*-**6-8**)X/Y (where X/Y is the molar ratio of the two monomeric structural units) with degrees of polymerization of about 10 and narrow molecular weight distribution are described. Both homopolymers and copolymers were prepared by the living cationic polymerization and copolymerization of **6-2** and **6-8**. During the first heating scan poly(**6-2**) presents an inverse monotropic s_C mesophase. During subsequent heating and cooling scans, this polymer is amorphous regardless of the thermal history of the sample. Poly(**6-8**) exhibits an enantiotropic s_A mesophase. During both the first and subsequent heating and cooling scans, the phase diagram which plots the dependence of mesomorphic transition temperatures as a function of copolymer composition is continuous. In the case of poly(**6-2**-*co*-**6-8**) 3/7, which exhibits a triple point in its phase behaviour, the highest temperature mesophase changes from nematic to s_A. During the first heating scan, poly(**6-2**-*co*-**6-8**)X/Y with $X/Y = 10/0$ to 6/4 represents an inverse s_C monotropic mesophase. Poly(**6-2**-*co*-**6-8**)X/Y with $X/Y = 8/2$ to 6/4 show in addition to the s_C phase an enantiotropic nematic mesophase. Poly(**6-2**-*co*-**6-8**)5/5 exhibits only an enantiotropic nematic mesophase, while poly(**6-2**-*co*-**6-8**)4/6 displays both a nematic and a s_A enantiotropic mesophase. Poly(**6-2**-*co*-**6-8**)X/Y with $X/Y = 3/7$ to 0/10 present an enantiotropic s_A mesophase. The second and subsequent heating scans and first and subsequent cooling scans provide an identical phase behaviour with that obtained from the first heating scan, except that the s_C mesophase is absent.

(Keywords: side chain liquid crystalline polymers; ethers; copolyethers; living cationic polymerization; synthesis; mesomorphism)

INTRODUCTION

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

A general classification of side chain liquid crystalline copolymers was recently discussed in a review article[1]. There are two main classes of side chain liquid crystalline copolymers. The first refers to copolymers containing pairs of structural units with and without mesogenic units[1–4,6–12]. 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. These are at least four different categories which 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; and (d) copolymers from monomer pairs containing constitutional isomeric mesogenic 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 is provided in ref. 15.

The following general trends were observed when

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* For Part 4 of this series see reference 27

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copolymers from the second class of type (a), (b) and (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 non-isomorphic 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[16]. Copolymers synthesized by classic polymerization reactions exhibit a heterogeneous composition unless they are prepared at low conversions[16]. At the same time, there is no single example in the literature in which the molecular weights of statistical copolymers prepared by chain copolymerization have been reported[1,3,5,17–19]. Since mesomorphic transitions are molecular weight dependent[1,11,20–28] 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 which follow an azeotropic copolymerization and 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[23–29]. The living cationic polymerization of 2-[(4-cyano-4′-biphenyl)oxy]ethyl vinyl ether[25], 11-[(4-cyano-4′-biphenyl)oxy]undecanyl vinyl ether[26], 8-[(4-cyano-4′-biphenyl)oxy]octyl vinyl ether[27], 6-[(4-cyano-4′-biphenyl)oxy]hexyl vinyl ether[27], 9-[(4-cyano-4′-biphenyl)oxy]nonyl vinyl ether[28] and of 10-[(4-cyano-4′biphenyl)oxy]decyl vinyl ether[28] as well as the characterization of the resulting polymers as a function of molecular weight have already been investigated.

The first goal of this paper is to present the synthesis of the copolymers of 2-[(4-cyano-4′-biphenyl)oxy]ethyl vinyl ether and 8-[(4-cyano-4′-biphenyl)oxy]octyl vinyl ether with different compositions and a degree of polymerization of 10. The second goal is to describe the phase behaviour of these copolymers as a function of copolymer composition. Poly{2-[(4-cyano-4′-biphenyl)oxy]ethyl vinyl ether} with a degree of polymerization equal to 10 displays a s_C mesophase only during the first heating scan[26]. Cooling and subsequent heating scans provide only an amorphous polymer[25]. Poly{8-[(4-cyano-4′-biphenyl)oxy]octyl vinyl ether} with a degree of polymerization equal to 10 displays an enantiotropic s_A phase, regardless of the thermal history of the sample[27]. Therefore, it is expected that the investigation of this copolymer, during the first heating scan, will provide information about the isomorphism of the two structural units whose homopolymers display s_C and s_A mesophases respectively.

Alternatively, the investigation of this copolymer, during the cooling and second and subsequent heating scans, will provide information about the isomorphism of the two structural units whose parent homopolymers display a glassy and a s_A phase respectively. Both structural units of this copolymer contain the same mesogenic group but different spacer lengths.

EXPERIMENTAL

Materials

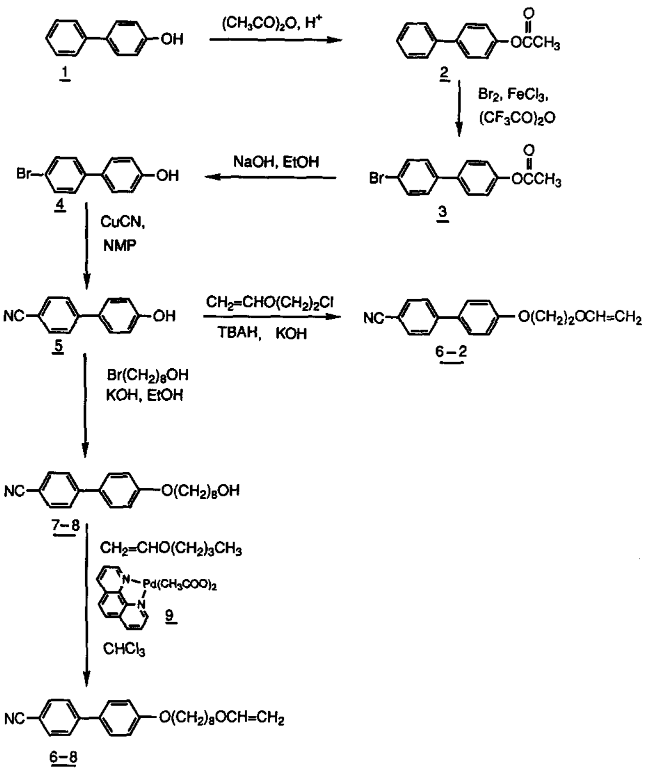
4-Phenylphenol (98%), 1,10-phenanthroline (anhydrous, 99%) palladium(II) acetate (all from Lancaster Synthesis), ferric chloride anhydrous (98%), copper(I) cyanide (99%), n-butyl vinyl ether (98%), 9-borabicyclo-[3.3.1]nonane (9-BBN, crystalline, 98%), 8-bromo-1-octanol (95%) (all from Aldrich), 2-chloro ethyl vinyl ether (Polysciences, b.p. 109–110°C) and the other reagents were used as received. Methyl sulphide (anhydrous, 99%, Aldrich) was refluxed over 9-BBN 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 anhydrous magnesium sulphate, refluxed over calcium hydride and freshly distilled under argon before each use. *N*-Methyl-2-pyrrolidone (98%, Lancaster Synthesis) was dried by azeotropic distillation with benzene, shaken with barium oxide, filtered, and fractionally distilled under reduced pressure. Trifluoromethane sulphonic acid (triflic acid, 98%, Aldrich) was distilled under argon.

Techniques

^{1}H n.m.r. (200 MHz) spectra were recorded on a Varian XL-200 spectrometer. Tetramethylsilane (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 which 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^{-1} unless otherwise specified. Glass transition temperatures (T_g) were read at the middle of the change in the heat capacity. For certain samples, first heating scans differ from second and subsequent heating scans. However, second and subsequent heating scans are identical. The first heating scans can be reobtained after proper thermal treatment of the polymer sample. 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 analyse the anisotropic textures[30,31]. 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 chloroform as solvent (1 ml min^{-1}) and a calibration plot constructed with polystyrene standards was used to determine the molecular weights. High pressure chromatography experiments were performed with the same instrument.

Synthesis of monomers

Scheme 1 outlines the synthesis of 2-[4-cyano-4′-biphenyl)oxy]ethyl vinyl ether (**6-2**) and of 8-[(4-cyano-4′-biphenyl)oxy]octyl vinyl ether (**6-8**). 1,10-Phenanthroline palladium (II) diacetate (**9**) and 4-cyano-4′-hydroxybiphenyl (**5**) were synthesized as described previously[26–28].



Scheme 1 Synthesis of 2-[(4-cyano-4'-biphenyl)oxy]ethyl vinyl ether (**6-2**) and 8-[(4-cyano-4'-biphenyl)oxy]octyl vinyl ether (**6-8**)

2-[(4-Cyano-4'-biphenyl)oxy]ethyl vinyl ether (**6-2**). A mixture of 2 g (10.25 mmol) 4-cyano-4'-hydroxybiphenyl, 3.16 ml (32.8 mmol) 2-chloroethyl vinyl ether, 0.45 g (11.07 mmol) of powdered NaOH, 0.176 g of tetrabutylammonium hydrogen sulphate (0.533 mmol), 10.5 ml toluene and 2 ml dimethyl sulphoxide was stirred at 90°C for 6 h. After cooling, the reaction mixture was washed with dilute NaOH, water, and dried over $MgSO_4$. The solvent was evaporated in a rotavapor and the resulting solid was recrystallized from methanol to yield 2.3 g (87%) of white crystals which were further purified by column chromatography (silica gel, CH_2Cl_2 eluent). Purity: 99% (h.p.l.c.). M.p. 104–105°C (lit 25, m.p. 105°C). ^1H n.m.r. ($CDCl_3$, TMS, δ, ppm): 4.07 (3 protons, $-\underline{CH_2}OCH{=}\underline{CH_2}$ *trans*, m), 4.27 (3 protons, $PhO\underline{CH_2}$ and $-OCH{=}\underline{CH_2}$ *cis*, m), 6.55 (1 proton, $-OC\underline{H}{=}CH_2$, q), 7.02 (2 aromatic protons, *o* to alkoxy, d), 7.53 (2 aromatic protons, *m* to alkoxy, d), 7.69 (4 aromatic protons, *o* and *m* to –CN, d of d).

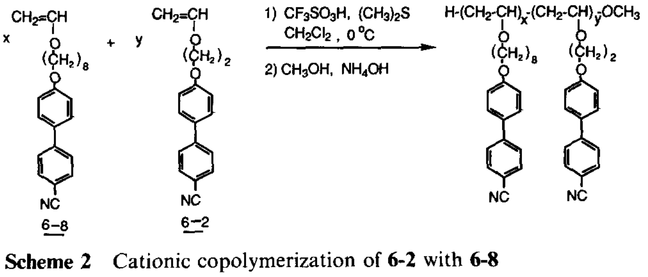
8-[(4-Cyano-4'-biphenyl)oxy]octyl vinyl ether (**6-8**). **6-8** was synthesized by the transetherification of 4-cyano-4'-(8-hydroxyoctan-1-yloxy)biphenyl (**7-8**) with n-butyl vinyl ether by using 1,10-phenanthroline palladium (II) diacetate as catalyst. Its detailed synthesis was presented in a previous publication[27]: Purity: 99.9% (h.p.l.c.). $T_{k-n} = 54.0$°C, $T_{n-i} = 70.8$°C.

Cationic polymerizations

Polymerizations and copolymerizations 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(s) was further dried under vacuum overnight in the polymerization flask. Then the flask was filled with argon, cooled to 0°C and the required amounts of methylene chloride and triflic acid were added using 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 molecular weight was controlled by the monomer/initiator ratio. At the end of the polymerization, the reaction mixture was precipitated in methanol containing a few drops of NH_4OH. The filtered polymers were dried and precipitated from methylene chloride solutions into methanol until g.p.c. traces showed no trace of monomer. *Table 1* summarizes the polymerization and copolymerization 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

Scheme 2 presents the living cationic copolymerization of 2-[(4-cyano-4'-biphenyl)oxy]ethyl vinyl ether (**6-2**) with 8-[(4-cyano-4'-biphenyl)oxy]octyl vinyl ether (**6-8**). An extensive study on the living cationic polymerization of **6-8** and on the characterization of the mesomorphic phase behaviour of poly(**6-8**) as a function of molecular weight was presented in a previous publication[27]. All copolymerization experiments described in this paper were performed under experimental conditions where the resulting poly(**6-2**), poly(**6-8**) and poly(**6-2**-*co*-**6-8**) have a degree of polymerization of about 9–10 (*Table 1*). We prefer to use the initiating system[32] $CF_3SO_3H/(CH_3)_2S$ since it initiates the living cationic polymerization of vinyl ethers in CH_2Cl_2 at 0°C. The yields reported in *Table 1* are lower than 80% due to polymer losses during the purification process. However, the conversions were quantitative and therefore the copolymer composition is identical to that of the monomer feed. ^1H n.m.r. spectra (200 MHz) of the copolymer samples support this statement. Poly(**6-8**) with degree of polymerization of 10 displays an enantiotropic s_A mesophase[27] (*Table 1*, *Figure 1*). Poly(**6-2**) was previously synthesized and characterized by Sagane and Lenz[25]. Poly(**6-2**) with a degree of polymerization of 10 displays only in the first heating scan an inverse monotropic s_C phase[25]. During the first and subsequent cooling scans and second and subsequent heating scans, poly(**6-2**) displays only a glass transition temperature (*Table 1*, *Figure 1*). Our results agree with those reported by Sagane and Lenz[25]. Therefore the investigation of copolymers based on the monomer pair **6-2** and **6-8** provides a unique system which can give information about the phase behaviour of a copolymer based on a structural unit whose homopolymer exhibits a s_C mesophase and a structural unit whose homopolymer exhibits a s_A mesophase when the data are collected from the first heating scan. Alternatively, when the data are collected from the second heating scan, the same copolymer system consists of a



Scheme 2 Cationic copolymerization of **6-2** with **6-8**

Table 1 Cationic polymerization of **6-2** with **6-8** (polymerization temperature, 0°C; polymerization solvent, CH_2Cl_2; $[M]_0 = [$**6-2** + **6-8**$] = 0.285–0.377$ M; $[M]_0/[I]_0 = 10$; $[(CH_3)_2S]_0/[I]_0 = 10$; polymerization time, 1 h and characterization of the resulting copolymers. First heating scan on first line. Second heating scan on second line

Sample no.	[**6-2**]/[**6-8**] (mol/mol)	Polymer yield (%)	G.p.c. $M_n \times 10^{-3}$	M_w/M_n	DP	Phase transitions (°C) and corresponding enthalpy changes (kcal/mru) Heating	Cooling
1	10/0	73.1	2.87	1.10	10.8	s_{C} 86.0 (0.18) *i* *g* 72.8 *i*	*i* 63.8 *g*
2	9/1	72.7	2.81	1.16	10.3	s_{C} 66.3 (0.38) *i* *g* 57.4 *i*	*i* 49.8 *g*
3	8/2	77.5	2.98	1.10	10.6	s_{C} 60.8 (0.41) *n* 75.2 (0.045) *i* *g* 48.3 *n* 74.8 (0.038) *i*	*i* 70.8 (0.042) *n* 41.0 *g*
4	7/3	81.3	2.87	1.13	9.8	s_{C} 54.6 (0.46) *n* 82.7 (0.049) *i* *g* 41.4 *n* 83.1 (0.061) *i*	*i* 80.2 (0.053) *n* 30.0 *g*
5	6/4	64.2	2.79	1.15	9.3	s_{C} 45.2 (0.39) *n* 94.1 (0.096) *i* *g* 36.0 *n* 93.8 (0.092) *i*	*i* 90.3 (0.087) *n* 27.8 *g*
6	5/5	65.1	2.82	1.17	9.2	*g* 33.7 *n* 102.3 (0.092) *i* *g* 31.5 *n* 102.5 (0.110) *i*	*i* 98.7 (0.110) *n* 22.6 *g*
7	4/6	71.8	3.09	1.15	9.3	*g* 24.9 s_{A} 98.1 (–)[a] *n* 106.5 (0.16)[a] *i* *g* 21.3 s_{A} 94.6 (–)[a] *n* 104.2 (0.21)[a] *i*	*i* 100.7 (0.18)[a] *n* 90.8 (–)[a] s_{A} 13.7 *g*
8	3/7	75.4	3.33	1.13	10.3	*g* 20.8 s_{A} 109.3 (0.28) *i* *g* 18.2 s_{A} 109.1 (0.26) *i*	*i* 104.8 (0.27) s_{A} 12.5 *g*
9	2/8	70.0	3.26	1.10	9.8	*g* 18.2 s_{A} 118.1 (0.32) *i* *g* 16.3 s_{A} 117.0 (0.34) *i*	*i* 110.5 (0.35) s_{A} 10.1 *g*
10	1/9	71.1	3.66	1.10	10.7	*g* 14.9 s_{A} 121.3 (0.41) *i* *g* 14.3 s_{A} 120.2 (0.43) *i*	*i* 115.2 (0.39) s_{A} 10.8 *g*
11	0/10	62.3	3.64	1.15	10.4	*g* 11.6 s_{A} 127.5 (0.43) *i* *g* 11.6 s_{A} 127.3 (0.45) *i*	*i* 122.8 (0.46) s_{A} 7.8 *g*

[a] Overlapped peaks

DP = Degree of polymerization

g = Glassy; *n* = nematic; *i* = isomorphic

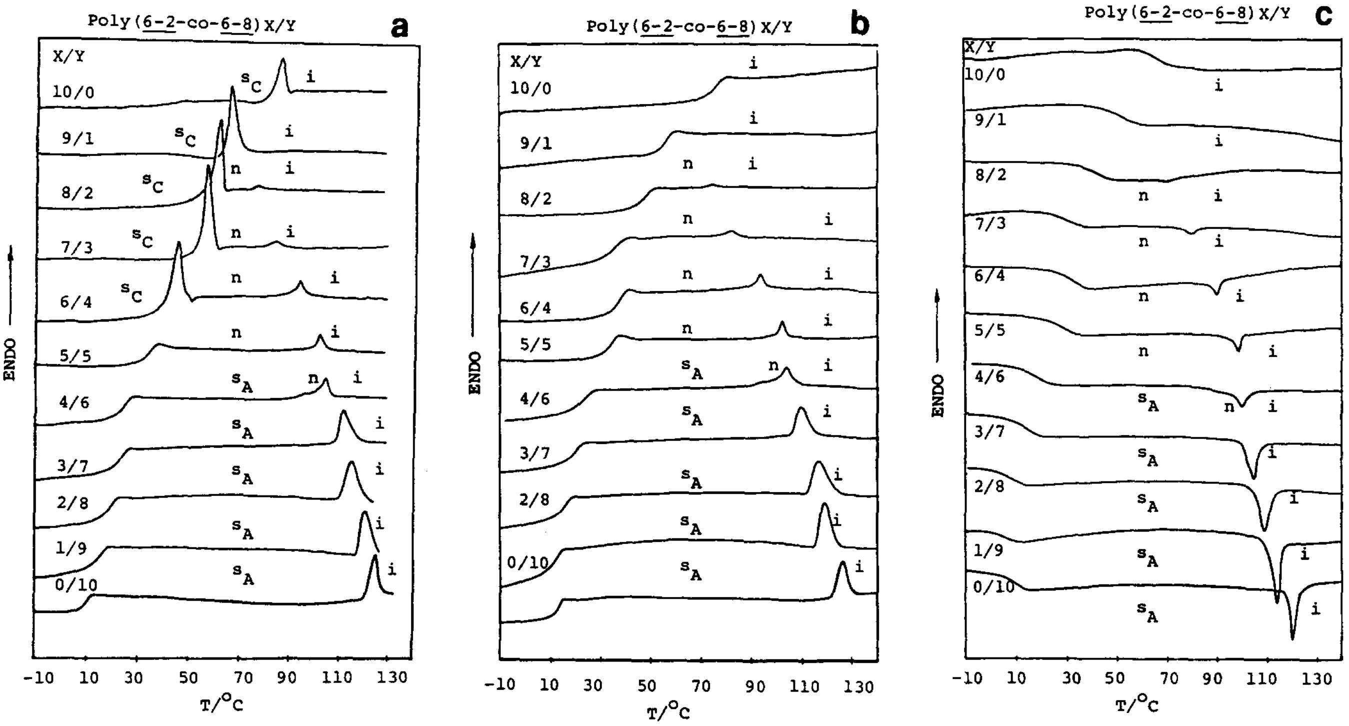


Figure 1 Differential scanning calorimetric traces displayed during the first heating scan (a), second heating scan (b), and first cooling scan (c) of poly(**6-2**), poly(**6-8**) and of poly(**6-2**-*co*-**6-8**)*X*/*Y*

structural unit whose homopolymer is amorphous and a structural unit whose homopolymer exhibits an enantiotropic s_A mesophase. Consequently, poly(**6-2**-*co*-**6-8**) represents a unique copolymer which, from a single series of experiments, provides information about the phase behaviour of two different binary copolymers.

Let us first discuss the behaviour of this copolymer as determined from the first d.s.c. heating scans. The first d.s.c. heating scans of poly(**6-2**-*co*-**6-8**) are presented in *Figure 1a*, which shows the nature of the mesophase displayed by various copolymers. Poly(**6-2**) displays a s_C phase which overlaps the glass transition temperature (*Table 1*). Upon copolymerization, the temperature associated with the s_C–isotropic phase transition decreases. Copolymers poly(**6-2**-*co*-**6-8**)5/5 to poly(**6-2**-*co*-**6-8**)0/10 do not exhibit the s_C phase. Therefore, the structural units derived from the monomers **6-2** and **6-8** are isomorphic within the s_C phase only over a very narrow range of compositions. A similar behaviour can be observed for the s_A phase displayed by poly(**6-8**). Poly(**6-2**-*co*-**6-8**)X/Y with compositions from $X/Y=$ 0/10 to 4/6 display a s_A phase. The temperature transition associated with this phase decreases by increasing the concentration of structural units derived from monomer **6-2**. Poly(**6-2**-*co*-**6-8**)4/6 exhibits both a nematic and a s_A mesophase. Poly(**6-2**-*co*-**6-8**)X/Y with X/Y from 5/5 to 8/2 exhibits a nematic phase.

The phase behaviour of poly(**6-2**-*co*-**6-8**)X/Y determined from the first heating scan is plotted in *Figure 2a*. This figure demonstrates that both the s_A and s_C phases exhibit continuous dependences of copolymer composition. However, the phase diagram of this copolymer exhibits a triple point at $X/Y=3/7$. The very interesting result consists in the ability to prepare copolymers exhibiting a nematic mesophase from structural units derived from two homopolymers which both display a smectic mesophase. This may result because within the s_A phase the backbone conformation of poly(**6-8**) is confined to the smectic layers[12]. Simultaneously, since the spacer of poly(**6-2**) is short, the backbone of this polymer may exhibit an extended conformation within the s_C phase[1]. Based on this account, the structural units of this copolymer are isomorphic in each of the two mesophases only over the range of compositions where the polymer backbone can get distorted to accommodate either the s_C or s_A mesophases. Morphological experiments are required to support this speculative explanation. The newly formed nematic mesophase extends over a broad range of copolymer composition (*Figure 2a–c*). The glass transition temperature of these copolymers decreases as expected by increasing the amount of **6-8** in the copolymer (*Figure 2a*).

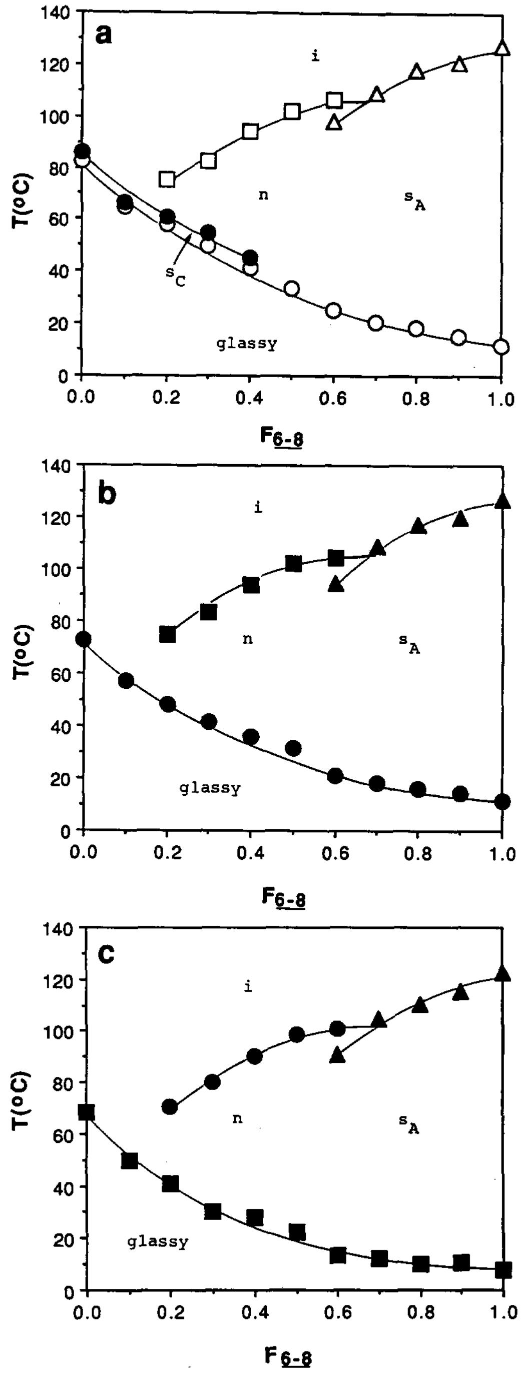


Figure 2 Dependence of phase transition temperatures on the composition of poly(**6-2**-*co*-**6-8**) copolymers. (a) Data from first heating scan: ○, T_g; ●, T_{s_C-i}(n); □, T_{n-i}; △, $T_{s_A-n(i)}$; (b) data from second heating scan; ●, T_g; ■, T_{n-i}; △, $T_{s_A-n(i)}$; (c) data from first cooling scan: ■, T_g; ●, T_{i-n}; ▲, $T_{n(i)-s_A}$

The d.s.c. traces of the second heating scans of poly(**6-2**-*co*-**6-8**)X/Y are presented in *Figure 1b*. They are identical to those from the first heating scans from *Figure 1a*, except that the s_C phase is missing and the change in the ΔC_p at the glass transition temperatures of poly(**6-2**-*co*-**6-8**)X/Y from $X/Y=10/0$ to 6/4 is larger. The thermal transition temperatures collected from *Figure 1b* are plotted in *Figure 2b*. This plot demonstrates that poly(**6-2**-*co*-**6-8**) displays a discontinuous dependence of the s_A and nematic phases on copolymer composition. The absence of the s_C phase in the second heating scans is most probably the result of a kinetic effect which is due to the close proximity of the s_C phase to the glass transition. Therefore this s_C phase forms only when the polymers are precipitated from solution. If the polymer sample is redissolved and reprecipitated, the s_C phase reappears. Alternatively if poly(**6-2**) and poly(**6-2**-*co*-**6-8**)9/1 are sheared above the glass transition temperature on the optical polarized microscope, an anisotropic texture forms. This behaviour can be easily explained by thermodynamics[33,34].

The cooling d.s.c. scans of poly(**6-2**-*co*-**6-8**)X/Y are presented in *Figure 1c*. They provide the same conclusion as derived from the second heating scans. The phase diagram of poly(**6-2**-*co*-**6-8**) obtained from the cooling d.s.c. scans is plotted in *Figure 2c* and agrees very well with that from *Figure 2b*.

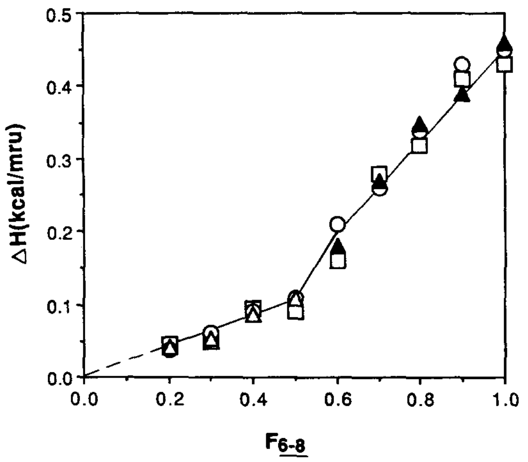


Figure 3 Dependence of the enthalpy changes associated with the mesomorphic–isotropic and isotropic–mesomorphic phase transitions on the composition of poly(**6-2**-*co*-**6-8**). □, $\Delta Hn(s_A)$–i (data from the first heating scan); ○, $\Delta Hn(s_A)$–i (data from second heating scan); △, ΔHi–n and ▲, ΔHi–s_A (data from first cooling scan)

The dependence of the enthalpy changes associated with nematic–isotropic, isotropic–nematic, s_A–isotropic and isotropic–s_A is plotted in *Figure 3*. The enthalpy changes of the nematic–s_A and s_A–isotropic as well as their reversed values of poly(**6-2**-*co*-**6-8**)4/6 could not be separated and were therefore plotted as the sum of both transitions (*Table 1*, *Figure 3*). Even so, *Figure 3* demonstrates that both the enthalpy changes associated with the s_A-phase and with the nematic phase transitions are located on straight lines. However, these lines have a different slope. These data prove that the structural units derived from **6-2** and **6-8** are isomorphic over a certain range of copolymer composition within the nematic phase and over a different range of composition within the s_A phase. A classification of the various classes of homopolymer and copolymer isomorphism within liquid crystalline phases was presented in a previous publication[35]. The plot from *Figure 3* shows that the mesomorphic phase behaviour of poly(**6-2**-*co*-**6-8**)X/Y *versus* copolymer composition is continuous. An attempt to extrapolate the linear dependence of the enthalpy change associated with the nematic–isotropic and isotropic–nematic phase transition to poly(**6-2**) leads to a value of $\Delta H = 0$. This result demonstrates that poly(**6-2**) with a degree of polymerization of 10 does not exhibit a nematic mesophase as already unequivocally seen in *Figure 1a–c*. The same conclusion can be derived if we try to extrapolate the dependences of the temperature transition of nematic–isotropic (*Figure 1a,b*) and isotropic–nematic (*Figure 1c*) *versus* copolymer composition corresponding to poly(**6-2**). We would obtain a virtual nematic mesophase which is located below the glass transition temperature of poly(**6-2**). However, since the enthalpy change of this virtual mesophase as determined from *Figure 3* is equal to zero, we can safely conclude that poly(**6-2**) with a degree of polymerization of 10 does not display a virtual nematic mesophase.

Finally, *Figure 4* shows some representative textures characteristic for the s_A and nematic phases exhibited by poly(**6-2**-*co*-**6-8**)X/Y copolymers and by poly(**6-8**). A characteristic texture could not be obtained for the s_C phase of poly(**6-2**) because this phase overlaps the glass transition temperature of the polymer and therefore the polymer is very viscous within its s_C phase. This result is in agreement with the data reported by Sagane and Lenz[25].

CONCLUSION

The experimental results described in this paper provide the first series of quantitative copolymerization experiments performed with mesogenic vinyl ethers. Since these monomers can be polymerized by living cationic polymerization, both the molecular weight, molecular weight distribution and the composition of these copolymers can be conveniently controlled. The most important conclusions obtained from the copolymerization of **6-2** with **6-8** are as follows. Although the two structural units of these copolymers lead to homopolymers which, depending on the thermal history of the sample, exhibit either a monotropic s_C or a glassy phase

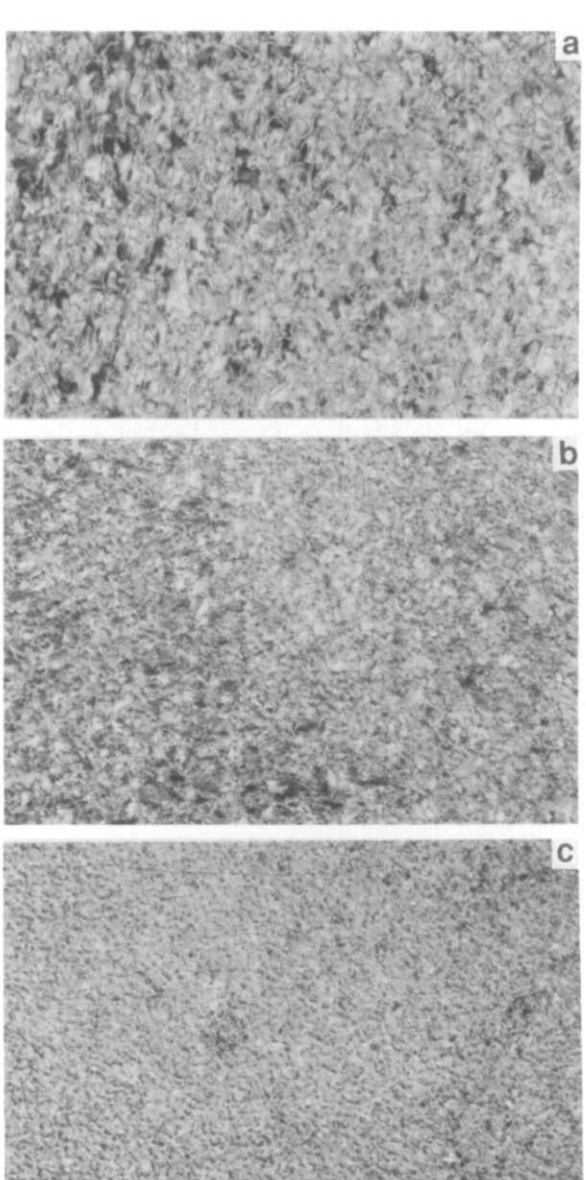


Figure 4 Representative optical polarized micrographs (100×) of: (a) the nematic phase displayed by poly(**6-2**-*co*-**6-8**)4/6 at 100°C on the cooling scan; (b) the s_A mesophase displayed by poly(**6-2**-*co*-**6-8**)4/6 at 90°C on the cooling scan; (c) the nematic mesophase displayed by poly(**6-2**-*co*-**6-8**)1/1 at 90°C on the cooling scan

and an enantiotropic s_A phase, respectively, the resulting copolymers display a nematic mesophase over a quite broad range of copolymer compositions. In addition, the dependence of mesomorphic phase transitions on copolymer composition is continuous and exhibits a triple point at a certain copolymer composition. The generation of a nematic polymer by copolymerization of two monomers containing dissimilar spacer lengths provides a simple technique for the synthesis of nematic polymers containing 4-cyanobiphenyl mesogenic groups. Very few examples of side chain liquid crystalline polymers containing a cyano substituent and displaying a nematic phase are available[1,36]. Most frequently, nematic polymers containing cyano groups are synthesized by inserting a lateral substituent into the structure of the mesogenic unit[37] by using laterally attached mesogenic units[38], and by copolymerization of mesogenic units containing laterally and terminally attached mesogenic side groups[39].

ACKNOWLEDGEMENT

Financial support of this work by the Office of Naval Research is gratefully acknowledged.

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