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Side-Chain Liquid Crystalline Alternating Copolymers of Mesogenic Monomers: Synthesis and Properties

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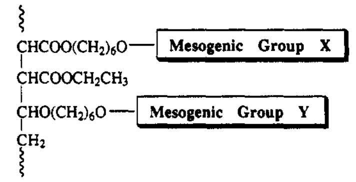
ABSTRACT: Seven new vinyl ether and fumarate monomers containing different mesogenic groups were synthesized and copolymerized to obtain three series of side-chain liquid crystalline copolymers. The free-radical copolymerization of the monomers led to copolymers with nearly alternating structures, although a preferential incorporation of fumarate units was always observed. Alternating tendency and composition behavior of the copolymers were interpreted in terms of a penultimate unit effect model. By appropriately adjusting the stoichiometry of the feed mixture, copolymers with a random distribution of mesogenic groups were also prepared. Comparison of the nematic-to-isotropic transition temperature and entropy (T_{NI},ΔS_{NI}) of alternating copolymers revealed that the randomization of mesogenic groups produces a moderate but definite increase in both the stability (T_{NI}) and degree of order (ΔS_{NI}) of the nematic mesophase.

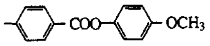
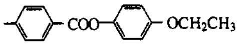
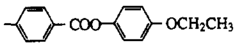
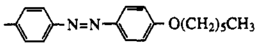
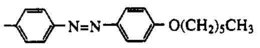
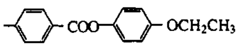
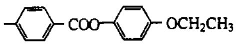
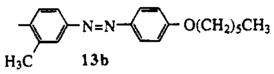
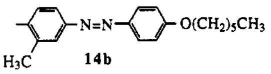
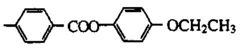
Introduction

Thermotropic side-chain liquid crystalline polymers are receiving considerable research interest for specialty applications, e.g., in data storage systems, in piezo-, pyro-, and ferroelectric devices, and in systems requiring non-linear optical characteristics.[1] For these precisely demanding applications it is essential to develop polymeric materials with optimized structures and well-defined architectures. The molecular design of monomers and subsequent synthesis of differently built polymeric systems have resulted in the establishment of reliable correlations between chemical structure and liquid crystalline properties. A very effective and fairly straightforward way of tailoring phase transitions and tuning the properties to desired levels is represented by the copolymerization of two or more monomers containing or not containing mesogenic groups.[2-4]

The principal route to the synthesis of side-chain liquid crystalline copolymers is the chain copolymerization, although polymer analog reactions and step copolymerization reactions have also been described. In chain copolymerization processes, the copolymer composition and sequence distribution are dictated by the inherent propensity of each monomer to enter the growing chain during the propagation reaction and are also dependent on the comonomer composition of the feed mixture. It is well established that the properties of synthetic copolymers in bulk and in solution are greatly affected by the primary and secondary structure of the macromolecular chain. It is also widely accepted that the mesophasic behavior of liquid crystalline copolymers may be influenced significantly by their chemical (and stereochemical) structure with major respect to the nature and relative amounts of comonomer units and their sequence distribution. For example, it has been recently shown[5,6] that by appropriate adjustment of the gross composition of random copolymers it is possible to predetermine their mesophase sequencing, including the onset of exotic polymorphic structures. However, while a large variety of copolymer combinations and compositions have been explored, no study is concerned with the effects of the sequence length and sequence distribution on the liquid crystalline phase transition behavior of side-chain copolymers.

Within the scope of elucidating this fundamental aspect inherent in the molecular engineering of side-chain liquid crystalline polymers, we have synthesized and studied three new classes of mesomorphic copolymers of general structures **I–III** as follows:



Copolymer	Fumarate (Mesogen X)	Vinyl Ether (Mesogen Y)
I	 **9a**	 **8b**
IIa	 **9b**	 **13a**
IIb	 **14a**	 **8b**
IIIa	 **9b**	 **13b**
IIIb	 **14b**	 **8b**
IIa/IIb	**9b/14a** (1:1 mix)	**8b/13a** (1:1 mix)
IIIa/IIIb	**9b/14b** (1:1 mix)	**8b/13b** (1:1 mix)

These copolymer systems were obtained by reacting vinyl ether and fumarate monomers containing different mesogenic groups. Copolymers **I** were prepared from vinyl

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ether and fumarate monomers containing the 4-ethoxyphenyl benzoate and the 4-methoxyphenyl benzoate groups, respectively. Copolymers **II** were prepared from monomers containing the 4-(hexyloxy)azobenzene and 4-ethoxyphenyl benzoate groups, while copolymers **III** were prepared from monomers containing the 4-(hexyloxy)-3′-methylazobenzene and 4-ethoxyphenyl benzoate groups. Accordingly, these copolymers are designated with the general acronym **X/Y(*n*)**, where **X** and **Y** are the reference marks of the fumarate and vinyl ether monomers, respectively, and ***n*** represents the mole fraction of the vinyl ether monomer in the feed mixture. Such monomer pairs easily participate in the formation of charge-transfer complexes in solution, owing to their opposite electron donor–acceptor characteristics[7] and consistently exhibit a strong tendency to alternating copolymerization.[8,9] A few other mesogenic side-chain alternating copolymers have been described, based on vinyl ether monomers and maleic anhydride[10–13] or α-olefins and sulfur dioxide[14,15] and mesogenic fumarate monomers.[16] By appropriately adjusting the monomer feed composition, the present copolymer systems could be prepared with either a nearly alternating distribution or a perfectly random distribution of mesogenic groups along the polymer chain. Comparison of the mesomorphic properties of these two series of topological isomers highlights the role played by monomer sequence distribution in affecting fine details of the liquid crystalline behavior of side-chain copolymers.

Experimental Section

Materials. Synthesis of Monomers. 4-[[(Benzyloxy)carbonyl]oxy]benzoic acid chloride (4) was prepared according to the procedure described in ref 14. 4-(Hexyloxy)-4′-hydroxyazobenzene (**12a**) and 4-(hexyloxy)-3′-methyl-4′-hydroxyazobenzene (**12b**) were prepared by the experimental procedure reported in a previous paper.[17] Monomers **8b–9b** and **13a–14b** were prepared according to the synthetic routes reported in Schemes I and II, respectively.

1-Chloro-6-(vinyloxy)hexane (2). A mixture of 20.0 g (0.146 mol) of 1-chloro-6-hydroxyhexane (1), 75.4 g (1.05 mol) of freshly distilled ethyl vinyl ether, and 7.8 g (0.024) mol) of mercuric acetate was heated and stirred at reflux for 6 h. Then 10.0 g (0.072 mol) of anhydrous potassium carbonate was added to the mixture, and the unreacted ethyl vinyl ether was distilled off. The residue was purified by distillation to give 7.1 g (yield 30%) of **2**: bp 65–67 °C (4 mbar).

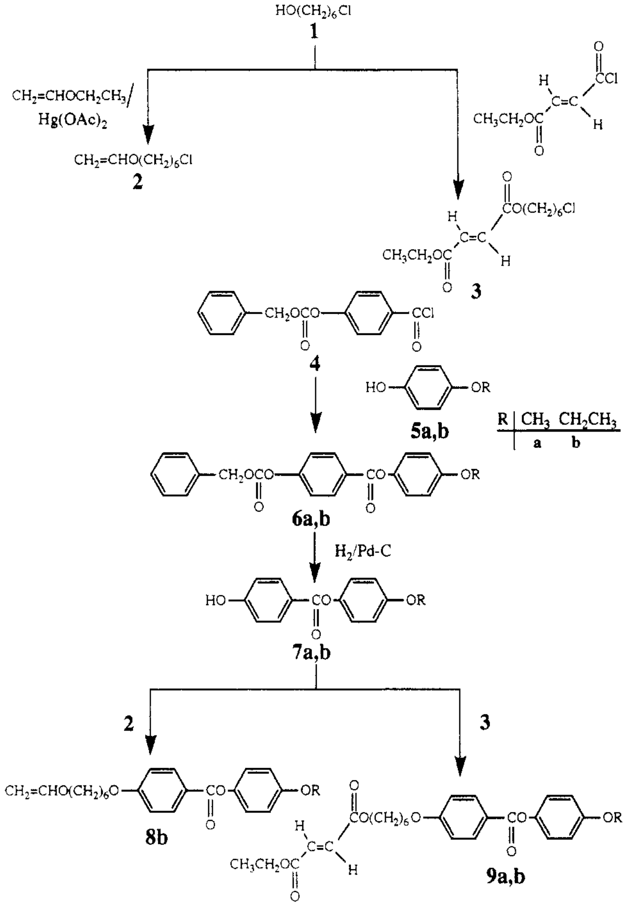
^{1}H NMR (CDCl$_3$): δ 6.4 (dd, H$_2$C=C*H*–); 4.1 (dd, H*H*C=CH–); 3.9 (dd, *H*HC=CH–); 3.6 (t, OCH$_2$); 3.5 (t, CH$_2$Cl); 1.8–1.3 (m, CH$_2$)$_4$).

6-Chlorohexyl Ethyl Fumarate (3). A solution of 7.0 g (0.043 mol) of monoethyl ester fumaric acid chloride in 20 mL of anhydrous 1,2-dichloroethane was added dropwise with vigorous stirring to a solution of 5.0 g (0.036 mol) of 1-chloro-6-hydroxyhexane, 7.3 g (0.072 mol) of triethylamine, and 0.1 g of 2,6-di-*tert*-butyl-4-methylphenol in 50 mL of the same solvent at room temperature, while a nitrogen stream was bubbled through the reaction mixture. After 2 h, the solution was filtered, washed successively with 2 × 50 mL of 1 M HCl and 2 × 100 mL of water, and dried over sodium sulfate, and the solvent was evaporated under vacuum. The product was purified by distillation to give 6.3 g (yield 71%) of **3**: bp 164–165 °C (4 mbar).

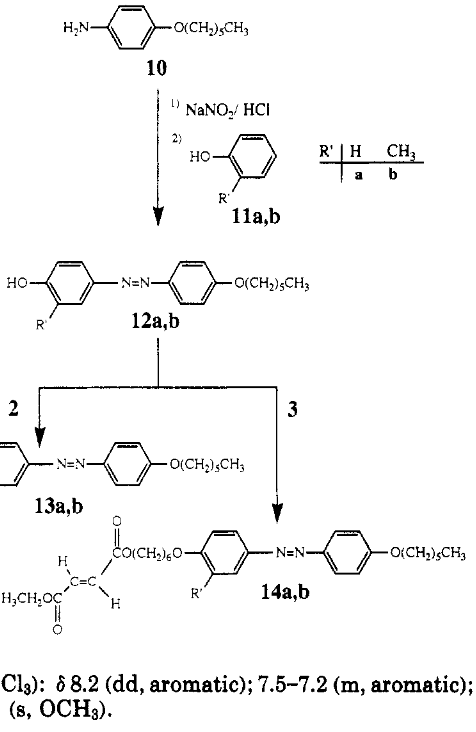
^{1}H NMR (CDCl$_3$): δ 6.9 (s, –CH=CH–); 4.2 (m, OCH$_2$); 3.6 (t, –CH$_2$Cl); 1.9–1.4 (m, (CH$_2$)$_4$); 1.3 (t, CH$_3$).

4-Methoxyphenyl 4-[[(Benzyloxy)carbonyl]oxy]benzoate (6a). A solution of 23.4 g (0.08 mol) of 4-[[(benzyloxy)carbonyl]oxy]benzoic acid chloride (4) in 40 mL of dry 1,2-dichloroethane was added at room temperature under vigorous stirring to a solution containing 10.0 g (0.08 mol) of 4-methoxyphenol (**5a**) and 1.0 g of benzyltributylammonium bromide in 100 mL of 1 M NaOH. After a 15-min reaction, the organic layer was separated, washed successively with 2 × 50 mL of 1 M NaOH and 2 × 50 mL of water, dried over sodium sulfate, and evaporated under vacuum. The solid product was crystallized from cyclohexane to give 19.8 g (yield 65%) of **6a**: mp 95–97 °C.

Scheme I



Scheme II



^{1}H NMR (CDCl$_3$): δ 8.2 (dd, aromatic); 7.5–7.2 (m, aromatic); 5.3 (s, CH$_2$); 3.8 (s, OCH$_3$).

4-Ethoxyphenyl 4-[[(Benzyloxy)carbonyl]oxy]benzoate (6b). It was prepared from 4-ethoxyphenol (**5b**) in a manner analogous to the preparation of **6a** and was crystallized from cyclohexane: mp 125–126 °C.

4-Methoxyphenyl 4-Hydroxybenzoate (7a). A suspension of 17.7 g (0.047 mol) of **6a** and 1.0 g of 10% Pd-C in dry tetrahydrofuran was treated with hydrogen in a Parr apparatus at 2.5 K g cm^{-2} pressure at room temperature until no more hydrogen was consumed. The reaction mixture was filtered and the solvent evaporated under vacuum. The solid product was

Table I. Characterization of Mesogenic Fumarate and Vinyl Ether Monomers

sample	cryst solvent	yield/%	T_m/K	T_{NI}/K	ΔH_{NI}/ (J mol^{-1})	ΔS_{NI}/ (J mol^{-1} K^{-1})
8b	ethanol	60	351	375	1830	4.9
9a	ethanol	65	368			
9b	methanol	35	363			
13a[a]	ethanol	48	348	382	2000	5.2
13b	ethanol	25	326	348	1640	4.7
14a	ethanol	73	352	(346)[b]	(8300)[b]	24.0
14b	ethanol	30	330			

[a] Additional smectic-to-nematic phase transition at 360 K (ΔH_{SN} = 700 J mol^{-1}, ΔS_{SN} = 1.9 J mol^{-1} K^{-1}). [b] Monotropic transition.

crystallized from ethanol/water (vol. ratio 1:1) to give 10.9 g (yield 95%) of **7a**: mp 194–196 °C.

^{1}H NMR (CDCl$_3$): δ 8.0 (dd, aromatic); 7.1 (dd, aromatic); 6.9 (dd, aromatic); 3.8 (s, OCH$_3$); 3.4 (b s, OH).

4-Ethoxyphenyl 4-Hydroxybenzoate (7b). It was prepared from **6b** in a manner analogous to the synthesis of **7a** and was crystallized from ethanol/water (vol. ratio 1:1): mp 204–205 °C.

4-Ethoxyphenyl 4-[[6-(Vinyloxy)hexyl]oxy]benzoate (8b). A mixture of 18.0 g (0.0697 mol) of **7b**, 11.3 g (0.0697 mol) of **2**, and 19.3 g (0.139 mol) of dry potassium carbonate in 70 mL of dry dimethyl sulfoxide was heated at 90 °C. After 2 h the mixture was poured into 200 mL of cold water under vigorous stirring and filtered. The residue was washed with 2 × 100 mL of 1 M NaOH and 2 × 100 mL of water. The solid product was crystallized from ethanol to give 16.1 g (yield 60%) of **8b**: mp 76–78 °C.

^{1}H NMR (CDCl$_3$): δ 8.2 (dd, aromatic); 7.1–6.9 (m, aromatic); 6.5 (dd, H$_2$C=C*H*–); 4.3 (dd, *H*HC=CH–); 4.2 (dd, *H*HC=CH–); 4.1 (m, ArOCH$_2$–); 3.7 (t, OCH$_2$); 1.9–1.5 (m, (CH$_2$)$_4$); 1.4 (t, CH$_3$).

Elem. anal. Calcd: C, 71.9; H, 7.3. Found: C, 71.5; H, 7.6.

4-Methoxyphenyl 4-[[6-[(Ethoxyfumaryl)oxy]hexyl]oxy]benzoate (9a). A mixture of 4.4 g (0.0168 mol) of **3**, 4.1 g (0.0168 mol) of **7a**, 4.6 g (0.0336 mol) of dry potassium carbonate, and 0.2 g of 2,6-di-*tert*-butyl-4-methylphenol in 40 mL of dry dimethyl sulfoxide was heated at 80 °C. After 5 h, the mixture was poured into 100 mL of cold water and the precipitate was filtered and washed with 2 × 50 mL of 1 M NaOH and 2 × 50 mL of water. The crude product was crystallized from absolute ethanol to give 5.1 g (yield 65%) of **9a**: mp 95–96 °C.

^{1}H NMR (CDCl$_3$): δ 8.1 (dd, aromatic); 7.1–6.9 (m, aromatic); 6.9 (s, –CH=CH–); 4.2–4.0 (m, OCH$_2$); 3.8 (s, OCH$_3$); 1.7–1.5 (m, (CH$_2$)$_4$); 1.3 (t, CH$_3$).

Elem. anal. Calcd: C, 66.4; H, 6.4. Found: C, 66.8; H, 6.5.

Vinyl ether monomers **13a** and **13b** were synthesized by reacting phenols **2a** and **12b** with **2**, while fumarate monomers **9b**, **14a**, and **14b** were synthesized by reacting phenols **7b**, **12a**, and **12b** with **3**, in a manner analogous to the above preparation of monomers **8b** and **9a**, respectively. Details about reaction yields and purification of these monomers are given in Table I.

Synthesis of Copolymers. In a typical copolymerization reaction, the required amounts of comonomers, adjusted to 2.0 g of total weight, were dissolved in 7 mL of dry benzene in the presence of 5.0 mg of AIBN. The reaction mixture was introduced into a Pyrex glass ampule, thoroughly freeze–thaw–degassed, and sealed under vacuum. After reacting 48 h at 60 °C the polymer was precipitated by addition of 100 mL of methanol, filtered, and purified by extraction with boiling methanol in a Kumagawa extractor. The copolymer was then dried under vacuum for 16 h. Reaction yields typically ranged from 20 to 30%.

In order to evaluate the reactivity ratios of monomers **8b** and **9a**, the polymerization reactions of these monomers were carried out to conversions lower than 5 wt %.

Characterization. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Gemini 200 spectrometer. The DEPT technique was used to generate the CH, CH$_2$, and CH$_3$ ^{13}C NMR subspectra. The composition of the copolymers was determined by ^{1}H NMR and confirmed by ^{13}C NMR from the relative areas of carbon atoms belonging to vinyl ether and fumarate units. Whereas the T_1 values of individual carbons were not measured, it was proved that the chosen carbon atoms had in fact similar relaxation times from their ^{13}C NMR spectra obtained with gated decoupling to remove NOE using an acquisition delay time of 5 min. Accordingly, the other spectra were then taken with gated decoupling to remove NOE using an acquisition delay time of 5 s (Figure 1).

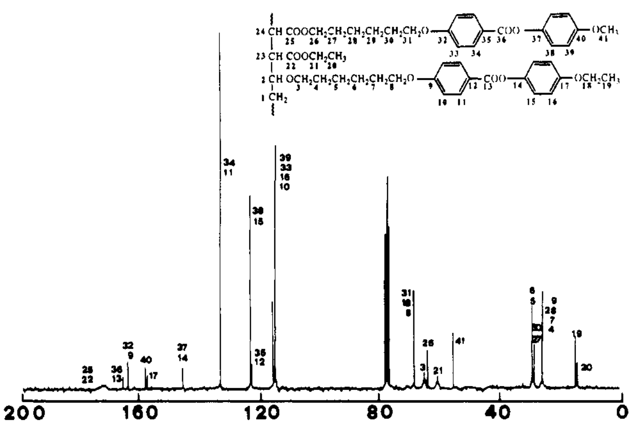


Figure 1. ^{13}C NMR spectrum of copolymer **9a/8b(0.7)**.

Average molecular weights were determined by SEC of chloroform solutions with a 590 Waters chromatograph equipped with a Shodex KF-804 column. Polystyrene standard samples were used for the universal calibration method. Differential scanning calorimetry (DSC) analyses were carried out under dry nitrogen flow with a Perkin-Elmer DSC 7 apparatus. Samples of 5–10 mg were employed. The temperature scale was calibrated against the melting temperature of indium. For the determination of the transition enthalpy, indium was used as a standard material. The transition temperatures were taken from the DSC traces of samples annealed by cooling from the isotropic melt, as corresponding to the maximum and to the onset point of the enthalpic peaks for polymers and low molar mass samples, respectively, at a heating rate of 10 K min^{-1}. Optical microscopy observations were performed on polymer films between glass slides by means of a Reichert Polyvar microscope equipped with a programmable Mettler FP52 heating stage at a scanning rate of 10 K min^{-1}.

Results and Discussion

Synthesis of Monomers. Monomers **8b**–**9b** and **13a**–**14b** were synthesized according to the general procedures outlined in Schemes I and II, respectively. 4-(Alkyloxy)phenyl 4-hydroxybenzoates (**7a,b**) were prepared by reacting the corresponding 4-(alkyloxy)phenols (**5a,b**) with 4-[[(benzyloxy)carbonyl]oxy]benzoic acid chloride (**4**) and removing the (benzyloxy)carbonyl group by catalytic hydrogenation. 4-(Hexyloxy)-4′-hydroxyazobenzene (**12a**) and 4-(hexyloxy)-3′-methyl-4′-hydroxyazobenzene (**12b**) were synthesized by coupling of the diazonium salt of 4-(hexyloxy)aniline (**10**) with phenol (**11a**) and *o*-cresol (**11b**), respectively. Vinyl ether monomers **8b** and **13a,b** with fumarate monomers **9a,b** and **14a,b** were obtained by reacting the corresponding compounds **7a,b** and **12a,b** with 1-chloro-6-(vinyloxy)hexane (**2**) and 6-chlorohexyl ethyl fumarate (**3**), respectively, in the presence of potassium carbonate and a small amount of free-radical inhibitor in dry dimethyl sulfoxide. Melting temperatures and reaction yields of monomers are collected in Table I.

Synthesis of Polymers. The copolymerization reaction between vinyl ether and fumarate monomers was studied in detail for copolymers I as a model system. All copolymerization runs of monomers **8b** and **9a** were carried out over a wide range of feed compositions, in dry benzene at 60 °C using 2,2′-azobis(isobutyronitrile) (AIBN) as the initiator, at conversions lower than 5% by weight, so that composition drifts with conversion may be neglected. The number-average molecular weight (M_n) values of the samples, as evaluated by SEC analysis, range from 6000

Table II. Molecular Weight and Composition data of Copolymers I

sample	M_n[a]	M_w/M_n[a]	f_v[b]	F_v[c]	$F_{v,calc}$[d]	$F_{v,calc}$[e]
9a/8b(0.1)	11 000	1.1	0.1	0.14	0.10	0.10
9a/8b(0.2)	6 000	1.1	0.2	0.19	0.17	0.17
9a/8b(0.3)	9 000	1.1	0.3	0.21	0.22	0.23
9a/8b(0.4)	11 000	1.1	0.4	0.25	0.26	0.28
9a/8b(0.5)	11 000	1.2	0.5	0.28	0.29	0.34
9a/8b(0.6)	12 000	1.2	0.6	0.32	0.32	0.37
9a/8b(0.7)	12 000	1.2	0.7	0.35	0.35	0.41
9a/8b(0.8)	12 000	1.1	0.8	0.42	0.38	0.44
9a/8b(0.9)	12 000	1.3	0.9	0.47	0.43	0.47

[a] By SEC, in chloroform at 25 °C. [b] Mole fraction of vinyl ether monomer in the feed mixture. [c] Mole fraction of vinyl ether units in the copolymer, evaluated with ^{1}H and ^{13}C NMR. [d] Mole fraction of vinyl ether units in the copolymer, calculated from eq 1 using r_{PF} = 0.81 and r_{PV} = 4.03. [e] Mole fraction of vinyl ether units in the copolymer, calculated from the terminal model.

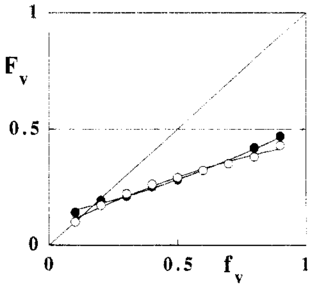


Figure 2. Copolymer composition curve for vinyl ether **8b** and fumarate **9a** copolymerization (F_v = mole fraction of vinyl ether in the copolymer; f_v = mole fraction of vinyl ether in the feed mixture): (●) experimental data; (○) penultimate model data.

to 12 000, corresponding to number-average degrees of polymerization in the 15–30 range, with polydispersity indexes (M_w/M_n) included between 1.1 and 1.3 (Table II). Note that, in attempted homopolymerization experiments under the same conditions of free-radical initiation, none of the present monomers gave appreciable amounts of polymer or oligomer products in accordance to their general very limited tendency to homopropagation. The cationic polymerization of these vinyl ether monomers is currently being investigated in a separate work.

The structure and composition of copolymers **I** were determined by ^{1}H and ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of copolymer sample **9a/8b(0.7)** is reported, together with relevant assignments, in Figure 1 as a typical example. Assignment of the various signals was made by combined chemical shift calculations,[18] DEPT technique, and comparison with the spectrum of monomers and relevant low molar mass intermediate compounds. The signals relevant to carbons 1, 2, 23, and 24 belonging to the main polymer chain are very broad and could not be precisely located in the spectrum. The composition of copolymers **I** was determined by ^{1}H NMR and, because of the partial overlap of the proton resonance signals, was confirmed by ^{13}C NMR from the relative areas of the signals at 14.7 and 15.3 ppm relevant to carbons 20 and 19, belonging to the fumarate and vinyl ether units, respectively (Table II). While their individual T_1 values were not measured, our inversion–recovery experiments showed that the selected carbon atoms had in reality comparable relaxation times, thus making them suitable for reliable calculations. The variation of the mole fraction of vinyl ether units from **8b** in copolymers **I** (F_v) as a function of the mole fraction of the monomer **8b** in the feed mixture (f_v) is illustrated in Figure 2. An overall preferential incorporation of fumarate units into the copolymer chain is clearly observed. The penultimate unit effect model[19] was used as a more adequate one to describe the composition diagram of this system than the more conventional terminal model. According to the scheme adopted, the propagation steps are as follows:[7]

$$\mathrm{FF} + \mathrm{V} \xrightarrow{k_1} \mathrm{FV}$$

$$\mathrm{FF} + \mathrm{F} \xrightarrow{k_2} \mathrm{FF}$$

$$\mathrm{VF} + \mathrm{V} \xrightarrow{k_3} \mathrm{FV}$$

$$\mathrm{VF} + \mathrm{F} \xrightarrow{k_4} \mathrm{FF}$$

$$\mathrm{FV} + \mathrm{F} \xrightarrow{k_5} \mathrm{VF}$$

$$\mathrm{FV} + \mathrm{V} \xrightarrow{k_6} \mathrm{VV}$$

where V and F represent the vinyl ether and fumarate monomers or repeat units, respectively.

Considering the very low tendency, if any, of vinyl ether monomers to free-radical homopolymerization, the last reaction was neglected. Complex fumarate derivatives exhibit some propensity to give homopolymers of relatively low degree of polymerization.[16] The instantaneous copolymer composition expressed as the ratio of fumarate to vinyl ether units [f/v] has the form:

$$[\mathrm{f/v}] = 1 + r_{PV}[\mathrm{F/V}]\,\frac{1 + r_{PF}[\mathrm{F/V}]}{1 + r_{PV}[\mathrm{F/V}]} \qquad (1)$$

where [F/V] is the ratio of fumarate to vinyl ether monomers in the feed and the reactivity ratios are defined as $r_{PF} = k_2/k_1$ and $r_{PV} = k_4/k_3$. The composition data reported in Table II were fitted to this model, using a nonlinear least-squares optimization procedure,[20] to yield r_{PF} = 0.81 and r_{PV} = 4.03 as optimum reactivity ratio values. The calculated data, expressed as mole fraction on the vinyl ether unit (F_v), are presented in Table II, and the experimental and calculated copolymerization curves are illustrated in Figure 2. The calculated points are distributed within the range of analytical uncertainty (about 2%), showing no systematic trend. A standard error Sy = 0.027 was evaluated in the measurements of copolymer compositions obtained from the fit of the model to the data. In contrast, the values of F_v calculated according to the terminal model (Table II) resulted in an Sy = 0.046. This indicates that the composition of the present copolymerization system would better conform to the penultimate unit effect model within the experimental error. Therefore, due to the tendency of the fumarate comonomer to enter in sequences, it appears that a large excess of the vinyl ether monomer is necessary to obtain copolymers with an essentially alternating distribution of comonomer units.

Copolymers **II** were prepared by reacting vinyl ether **8b** with fumarate **14a** (copolymers **IIb**) and vinyl ether **13a** with fumarate **9b** (copolymers **IIa**) (Table III) in the same experimental conditions adopted for copolymers **I**. These reactions were allowed to proceed to the maximal yield using initial monomer ratios vinyl ether/fumarate 3:1 and 6:1 for each copolymerization system. Copolymers **III** were prepared in exactly the same manner as copolymers **II**, starting from vinyl ether **8b** and fumarate **14b** (copolymers **IIIb**) and vinyl ether **13b** and fumarate **9b** (copolymers **IIIa**) (Table IV). Reaction yields of 20–30% were obtained in each series. Number-average molecular weight values ranged from M_n = 6200 to 9000, corresponding to number-average degrees of polymerization in

Table III. Physicochemical Properties of Copolymers II

sample	F_v[a]	F_{azo}[b]	M_n[c]	M_w/M_n[c]	T_g/K	T_{NI}/K	ΔS_{NI}/(J mol^{-1} s^{-1})
9b/13a(0.75)	0.38	0.38	8500	1.5	287	360	3.4
9b/13a(0.86)	0.49	0.49	8000	1.3	291	355	2.5
14a/8b(0.75)	0.38	0.62	8600	1.3	285	362	2.8
14a/8b(0.86)	0.48	0.52	8100	1.3	291	355	2.3
9b:14a/8b:13a(0.86)	0.50	0.50	6200	1.7	282	360	3.3

[a] Mole fraction of vinyl ether units in the copolymer, evaluated by ^{1}H and ^{13}C NMR spectroscopy. [b] Mole fraction of azobenzene-containing units in the copolymer, evaluated by ^{1}H and ^{13}C NMR spectroscopy. [c] By SEC, in chloroform at 25 °C.

Table IV. Physicochemical Properties of Copolymers III

sample	F_v[a]	F_{azo}[b]	M_n[c]	M_w/M_n[c]	T_g/K	T_{NI}/K	ΔS_{NI}/(J mol^{-1} K^{-1})
9b/13b(0.75)	0.40	0.40	9000	1.4	290	345	2.8
9b/13b(0.86)	0.46	0.46	8600	1.5	290	335	2.3
14b/8b(0.75)	0.38	0.62	7900	1.3	288	329	2.3
14b/8b(0.86)	0.46	0.54	8400	1.7	287	327	2.0
9b:14b/8b:13b(0.86)	0.50	0.50	8200	1.6	289	333	2.5

[a] Mole fraction of vinyl ether units in the copolymer, evaluated by ^{1}H and ^{13}C NMR spectroscopy. [b] Mole fraction of methyl-substituted azobenzene-containing units in the copolymer, evaluated by ^{1}H and ^{13}C NMR spectroscopy. [c] By SEC, in chloroform at 25 °C.

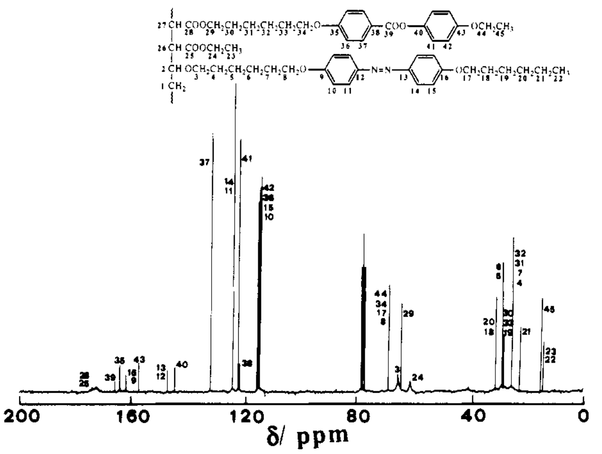


Figure 3. ^{13}C NMR spectrum of copolymer **9b/13a(0.86)**.

the 15–20 range, with M_w/M_n between 1.3 and 1.7. The structure and composition of copolymers **II** and **III** were analyzed by ^{13}C NMR spectroscopy, and a typical spectrum is reported in Figure 3 for copolymer **9b/13a(0.86)** together with relevant assignments. Also for these copolymers, the signals relevant to carbons 1, 2, 26, and 27 belonging to the main polymer chain are very broad and could not be precisely identified in the spectrum. From the intensities of the signals at 14.1, 14.3 and 15.0 ppm relevant to carbon atoms 22, 23, and 45 it was possible to determine the fraction of vinyl ether units in the copolymer. The composition values for copolymers **II** and **III**, expressed as mole fraction of the vinyl ether unit (F_v) (Tables III and IV), are very close to those calculated from eq 1 using the reactivity ratio values determined for copolymers **I**. Accordingly, the copolymerization behavior can be modeled under the same assumptions, and the composition of this copolymer system does not appear to depend significantly on the specific nature of the mesogenic groups present in the monomers.

In order to evaluate the effect of the sequence distribution on the mesomorphic behavior, one copolymer sample **IIa/IIb** was prepared by reacting a 1:1 mixture of vinyl ethers **8b** and **13a** with a 1:1 mixture of fumarates **9b** and **14a**, and analogously one copolymer sample **IIIa/IIIb** was prepared starting from a 1:1 mixture of vinyl ethers **8b** and **13b** and a 1:1 mixture of fumarates **9b** and **14b**, using a monomer ratio in the feed mixture vinyl ether/fumarate 6:1. Consistent with the above results, the backbones of these two copolymer samples, designated as **9b:14a/18b:13a(0.86)** (Table III) and **9b:14b/8b:13b(0.86)** (Table IV), should consist of a nearly regular alternating sequence of vinyl ether and fumarate repeat units, whereas the mesogenic groups are randomly distributed.

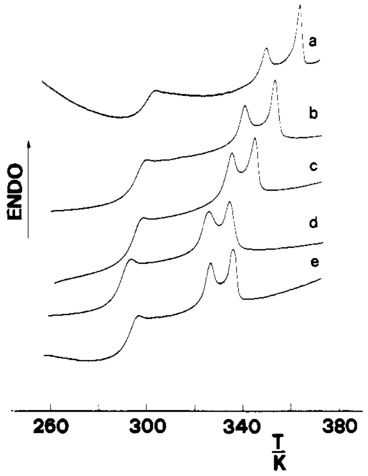


Figure 4. DSC second heating curves (10 K min^{-1}) for copolymers **I**: a, **9a/8b(0.8)**; b, **9a/8b(0.6)**; c, **9a/8b(0.4)**; d, **9a/8b(0.3)**; e, **9a/8b(0.1)**.

It should be observed that although the liquid crystalline phase transition parameters of side-chain polymers are known[21] to depend on their molecular weight characteristics, all the copolymer of series **I–III** possess very similar number-average molecular weight and dispersity index values. Accordingly, it appears reasonable to compare directly the phase transition parameters of the various samples as directly related to the different structural features of the polymer samples.

Liquid Crystalline Properties. The phase transition temperatures and relevant thermodynamic parameters were determined by DSC measurements and polarizing microscopy. The nature of the liquid crystalline phases was investigated by qualitative observations of the optical textures on the hot stage of a polarizing microscope and confirmed by preliminary X-ray diffraction experiments. The liquid crystalline properties of the prepared vinyl ether and fumarate monomers are summarized in Table I. No mesophases were observed for monomers **9a**, **9b**, and **14b**. Monomers **8b**, **13a**, and **13b** displayed one enantiotropic nematic mesophase. Additionally, **13a** exhibited an enantiotropic smectic A mesophase. A monotropic smectic A mesophase was only shown by monomer **14a**.

Copolymers **I–III** are noncrystalline and accordingly the liquid crystalline behavior extended from the glass transition up to the isotropization point. The DSC heating and cooling curves, following annealing by cooling at 10 K min^{-1} from the isotropic melt, of representative copolymers **I** are reported in Figures 4 and 5. On heating (Figure 4), all samples showed a step due to the glass transition and two partly overlapping endothermic peaks. On cooling (Figure 5), the reverse transitions occurred due to the formation of two thermotropic mesophases. By optical microscopy, the higher temperature mesophase was recognized as nematic by the appearance of a schlieren pattern with various types of singularity points,[22] whereas the lower temperature mesophase was identified as smectic from the observation of focal conic textures. A detailed X-ray diffraction study is in progress to characterize precisely the structure of the smectic mesophase and will be the subject of a forthcoming paper.[23] The phase transition

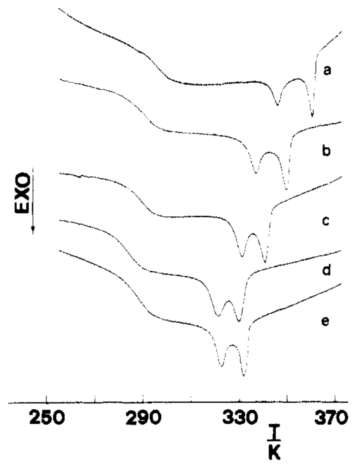


Figure 5. DSC second cooling curves (10 K min^{-1}) for copolymers I: a, **9a/8b(0.8)**; b, **9a/8b(0.6)**; c, **9a/8b(0.4)**; d, **9a/8b(0.3)**; e, **9a/8b(0.1)**.

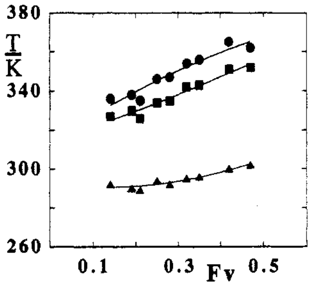


Figure 6. Trends of the glass (▲), smectic-to-nematic (■), and nematic-to-isotropic (●) transition temperatures as function of the mole fraction of vinyl ether unit F_v in copolymers I.

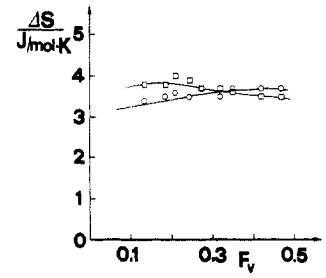


Figure 7. Trends of the smectic-to-nematic (□) and nematic-to-isotropic (○) transition entropies as function of the mole fraction of vinyl ether unit F_v in copolymers I.

Table V. Phase Transition Parameters of Copolymers I

sample	T_g/K	T_{SN}/K	T_{NI}/K	ΔS_{SN}/ (J mol^{-1} K^{-1})	ΔS_{NI}/ (J mol^{-1} K^{-1})
9a/8b(0.1)	292	327	336	3.8	3.4
9a/8b(0.2)	290	330	338	3.7	3.5
9a/8b(0.3)	289	326	335	4.0	3.6
9a/8b(0.4)	294	334	346	3.9	3.5
9a/8b(0.5)	292	335	347	3.7	3.7
9a/8b(0.6)	295	342	354	3.7	3.5
9a/8b(0.7)	296	343	356	3.6	3.7
9a/8b(0.8)	300	351	365	3.5	3.7
9a/8b(0.9)	302	352	362	3.5	3.7

temperatures and entropy changes of copolymers I are collected in Table V. The temperatures relevant to the nematic-to-isotropic (T_{NI}), smectic-to-nematic (T_{SN}), and glass (Tg) transitions gradually increase with increasing mole fraction of vinyl ether units in the copolymer (F_v) (Figure 6). The nematic-to-isotropic and smectic-to-nematic transition entropies (ΔS_{NI}, ΔS_{SN}) are of the same order of magnitude and a slightly pronounced rising trend of ΔS_{NI} is observed with increasing F_v, whereas the opposite trend is shown by ΔS_{SN} (Figure 7). So we can conclude that the phase transition parameters vary in a more or less linear fashion with the copolymer composition.

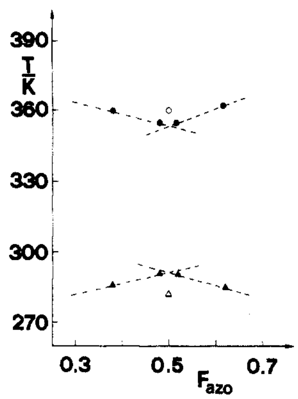


Figure 8. Trends of the glass (▲,△) and nematic-to-isotropic (●,○) transition temperatures as a function of the mole fraction of the azobenzene unit F_{azo} in copolymers II. Full symbols refer to copolymers of **9b/13a(*n*)** and **8b/14a(*n*)**, while open symbols refer to copolymer **8b:13a/9b:14a(0.86)**.

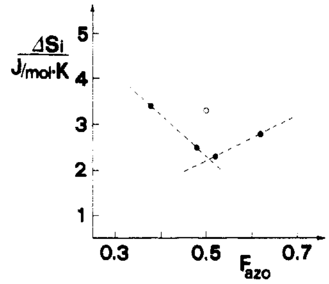


Figure 9. Trend of the nematic-to-isotropic transition entropies (●,○) as a function of the mole fraction of the azobenzene unit F_{azo} in the copolymers II. Full symbols refer to copolymers **9b/13a(*n*)** and **14a/8b(*n*)**, while the open symbol refers to copolymer **9b:14a/8b:13a(0.86)**.

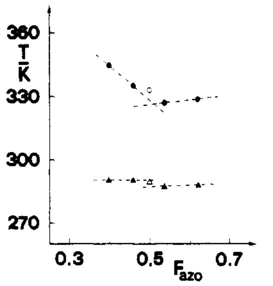


Figure 10. Trends of the glass (▲,△) and nematic-to-isotropic (●,○) transition temperatures as a function of the mole fraction of the methyl-substituted azobenzene unit F_{azo} in copolymers III. Full symbols refer to copolymers **9b/13b(*n*)** and **14b/8b(*n*)**, while open symbols refer to copolymer **9b:14b/8b:13b(0.86)**.

Copolymers II and III exhibited similar phase transition behaviors. In the DSC heating curves, all copolymers II and III show a step due to the glass transition and an endothermic peak attributed to the nematic-to-isotropic phase transition, in agreement with the unequivocal observations of schlieren textures in the relevant temperature ranges. Both transitions are reversible on cooling. The phase transition temperatures and relevant thermodynamic parameters of copolymers II and III are collected in Tables III and IV, respectively. The trends of the phase transition temperatures and entropy changes as a function of the content of the azobenzene-containing comonomer unit (F_{azo}) are illustrated in Figures 8 and 9 for copolymers II and in Figures 10 and 11 for copolymers III. The dashed lines joining the data points relevant to copolymer samples with a nearly alternating distribution of vinyl ether and fumarate monomers intersect at a composition of 1:1 molar ratio of comonomeric units, corresponding to the perfectly alternating copolymer structure, for which minimum values of both T_{NI} and ΔS_{NI} are observed in both II and

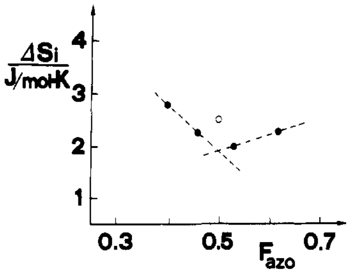


Figure 11. Trend of the nematic-to-isotropic transition entropies (●,○) as a function of the mole fraction of the methyl-substituted azobenzene unit F_{azo} in the copolymers **III**. Full symbols refer to copolymers **9b/13b(*n*)** and **14b/8b(*n*)**, while the open symbol refers to copolymer **9b:14b/8b:13b(0.86)**.

III copolymer systems. Accordingly, the nematic-to-isotropic transition temperature and entropy change of the perfectly alternating **II** and **III** copolymers may be estimated as T_{NI} = 353 K and ΔS_{NI} = 2.3 J mol^{-1} K^{-1} for **II** and T_{NI} = 326 K and ΔS_{NI} = 1.9 J mol^{-1} K^{-1} for **III**. In Figures 8–11 are also reported the data (open symbols) referring to the copolymers which possess a nearly alternating sequence of vinyl ether and fumarate units along the polymer chain and statistical distribution of mesogenic groups. Comparing these data with those estimated for the perfectly alternating copolymers, it appears that the randomization of the mesogenic groups causes an increase in T_{NI} by 6–7 K in both **II** and **III** copolymers and an increase in ΔS_{NI} by 1.1 J mol^{-1} K^{-1} for copolymer **II** and 0.6 J mol^{-1} K^{-1} for copolymer **III**.

Concluding Remarks

Seven new vinyl ether and fumarate monomers containing different mesogenic groups were synthesized and used to prepare three series of side-chain liquid crystalline copolymers. Their free-radical copolymerization led to copolymers with nearly alternating structures, although a preferential incorporation of fumarate units into the copolymers was observed practically over the whole range of feed compositions. To obtain an alternating structure, a very large excess of the vinyl ether monomer has to be used. The alternating tendency and composition behavior for copolymers **I** was described in terms of the penultimate unit effect model. The reactivity ratio values obtained for copolymers **I** were found to be extensible to copolymers **II** and **III**, independent of the mesogenic core structure.

By appropriately adjusting the stoichiometry of the feed mixture, copolymers of structures **II** and **III** with a nearly alternating sequence of vinyl ether and fumarate units and a perfectly random distribution of mesogenic groups were prepared.

The liquid crystalline behavior of monomers and copolymers was investigated by combined differential scanning calorimetry and optical microscopy. Although the substantial difference in the structure of the monomers prevented reliable comparisons of their thermotropic properties, a greater propensity of the vinyl ether monomers to give rise to stable and persistent mesophases was recognized.

Copolymers **I** showed two liquid crystalline mesophases recognized as nematic and smectic. The phase transition parameters were found to change rather regularly with composition. A rising trend of the phase transition temperatures as well as the nematic-to-isotropic entropy change, with increasing mole fraction of vinyl ether monomers containing the 4-ethoxyphenyl benzoate mesogenic group, was observed. The opposite trend was shown by the smectic-to-nematic entropy change.

Copolymers **II** and **III** possess only a nematic mesophase. The phase transition parameters in both series varied with composition, exhibiting minimal values corresponding to the 1:1 mole ratio of the different mesogenic groups. Extrapolation of the transition temperatures and entropy change to this composition value allowed estimation of the phase transition parameters relevant to the perfectly alternating copolymers. For the same alternating fumarate–vinyl ether co-unit sequencing in the polymer backbone, comparison of the extrapolated transition parameters of the copolymers with alternating distribution of unlike mesogenic groups with the corresponding parameters of copolymers with random distribution of like and unlike mesogenic groups reveals that the randomization of mesogenic groups produced a moderate but definite increase in the stability (T_{NI}) and degree of order (ΔS_{NI}) of the nematic mesophase. These results indicate that in these copolymers the distribution of mesogenic groups on adjacent monomeric units is playing a role in affecting the values of the mesophase transition parameters.

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