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(14) In the CSCMBB experiment, two resonances similar to that displayed in Figure 4D were observed, but with much reduced intensity. Furthermore, we cannot on the basis of this analysis exclude the possibility of a high-order m-centered peak contributing to the r peaks and vice versa.

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Received July 9, 1985

Synthesis of Liquid Crystalline Side-Chain Polyitaconates via Phase-Transfer Catalysis

During recent years, increasing interest has been shown in thermotropic liquid crystalline polymers.[1-5] This interest is justified both by the potential technological applications of these materials and by the fundamental problems they give rise to.

Thermotropic liquid crystalline polymers are classified under two categories: "main-chain" and "side-chain" polymers. In the first, the liquid crystalline character is a property of the chain backbone; i.e., the mesogenic groups are linked to form the macromolecular chain. In the side-chain liquid crystalline polymers, with which this work deals, low molar mass mesogenic groups are linked to the polymeric chain as side chain directly or via flexible spacers.

The systematic synthesis of liquid crystalline side-chain polymers has become possible by applying the "flexible spacer concept" originally proposed by Finkelmann et al.[6], which postulates a partial decoupling of the motion of the polymer main chain from the motion of the anisotropically oriented mesogenic side chains. By this means, a few series of mesomorphic polymers have been prepared by varying the chemical constitution of the macromolecular backbone: polymethacrylates,[6] polyacrylates,[7] poly(chloroacrylates),[8] and polysiloxanes.[9-12] But even though mesogenic side-chain polymers have been synthesized and investigated for several years, the mutual interaction of polymeric and liquid crystalline properties is not well understood. Therefore, new series of liquid crystalline side-chain polymers are needed in order to diversify the structures of the compounds available. This might help to better understand the influence of the main chain on the liquid crystalline properties of the side-chain polymers.

We wish to present here the synthesis and the phase behavior of a new series of liquid crystalline polymers with a polyitaconate backbone.

Scheme I

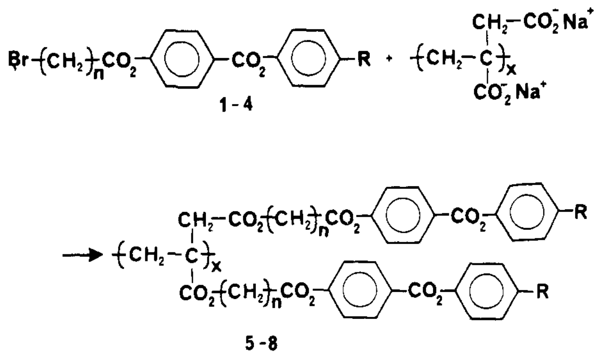

Table I
Mesomorphic Properties of ω-((Bromoalkanoyl)oxy) Esters 1-4

product	n	R	phase transitions[a]
1a	3	OCH_3	K 73 N 90 I
1b	4	OCH_3	K 66 N 78 I
1c	5	OCH_3	K 84 (N 82.5) I
2a	4	OC_3H_7	K 52 N 84 I
2b	5	OC_3H_7	K 71 N 95 I
3a	4	OC_4H_9	K 64 N 87 I
3b	5	OC_4H_9	K 47 N 85 I
4a	4	C_6H_5	K 114 N 138 I
4b	5	C_6H_5	K 133 N 141 I

[a] Transition temperatures in °C; K = crystal, N = nematic, I = isotropic.

Results and Discussion. Liquid crystalline side-chain polymers are usually prepared by the radical polymerization of appropriate mesogenic monomers such as acrylates,[7] methacrylates,[6] or chloroacrylates.[8] However, another synthesis route has been proposed, starting with "reactive polymers"[9-13,19] which can be modified to mesogenic side-chain polymers by using suitable reactive mesogenic compounds.

Following this route, we have recently described a new synthesis of mesomorphic polyacrylates[14] resulting from the reaction of sodium polyacrylates with mesogenic ω-((bromoalkanoyl)oxy) esters under phase-transfer conditions.

The synthesis of the liquid crystalline polyitaconates **5–8** is similar to this published procedure. It is achieved by displacement of bromide ion from ω-((bromoalkanoyl)oxy) esters **1–4** with sodium polyitaconates under phase-transfer conditions (Scheme I). The ω-((bromoalkanoyl)oxy) esters **1–4** are heated under reflux in water–chloroform solvent with sodium polyitaconates and tetrabutylammonium bromide as phase-transfer reagent. Mesomorphic polyitaconates are recovered from chloroform solution by precipitation with methanol as nonsolvent (see experimental part).

The melting and transition points for the ω-((bromoalkanoyl)oxy) esters **1–4** are reported in Table I, while Table II lists the polymers synthesized (**5–8**), with yields, inherent viscosities (in chloroform at 25 °C), and thermal properties.

In these experiments, we have not tried to optimize the parameters (solvents, structures of the phase-transfer reagents, and molar ratio between the ω-(bromoalkanoyl)oxy esters and the reactive groups of the polymer) with respect to yields. However, the completion of the alkylation reaction was confirmed by the IR spectra of the polymers. For example, a comparative study of the IR spectra of the starting polymer (Figure 1, curve A) and of the polyitaconates **6b** (Figure 1, curve B), **7b**, and **8a** (Figure 2, curves A and B) shows that only ester carbonyl

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Table II
Yields, Inherent Viscosities, and Transition Temperatures of Mesomorphic Polyitaconates 5-8

polymer	n	R	yield, %	η_{inh}, dL·g^{-1}	phase transitions^a
5a	3	OCH_3	30	0.07	g 75-85 N 190-210 I
5b	4	OCH_3	25	0.05	g 85-95 N 148-165 I
5c	5	OCH_3	36	0.046	g 55-65 N 170-185 I
6a	4	CO_3H_7	53	0.042	g 117-120 N 172-190 I
6b	5	OC_3H_7	26	0.061	g 137-140 N 208-220 I
7a	4	OC_4H_9	30	0.05	g 128-138 S 146-148 N 164-168 I
7b	5	OC_4H_9	25	0.09	g 118-125 S 150-153 N 198-206 I
8a	4	C_6H_5	26	0.051	g 125-135 S 166-170 N 219-225 I
8b	5	C_6H_5	60	0.059	g 105-115 S 139-145 N 210-230 I

^{a}Transition temperatures in °C; g = glass, S = smectic, N = nematic, I = isotropic.

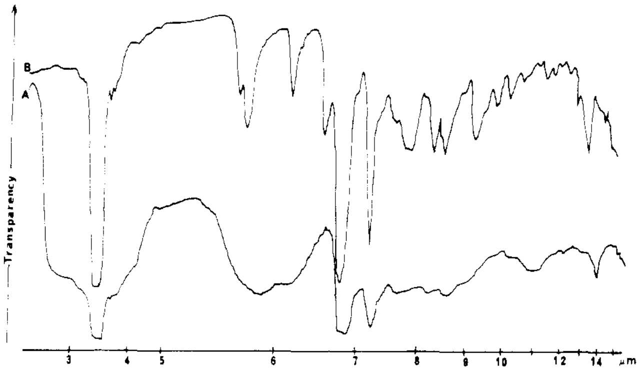

Figure 1. IR absorption spectra: (a) poly(itaconic acid); (b) polymer **6b**.

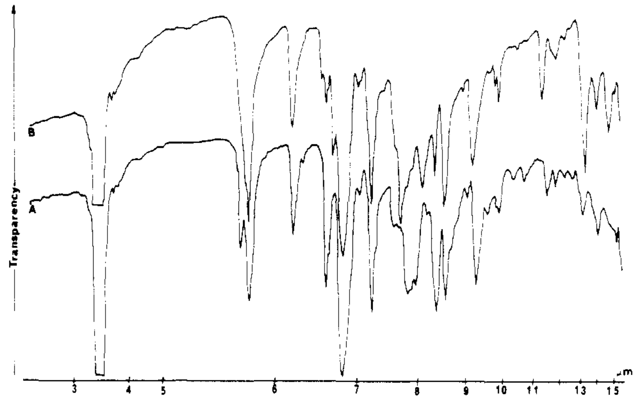

Figure 2. IR absorption spectra: (a) polymer **7b**; (b) polymer **8a**.

absorptions are present in the mesomorphic polyitaconates whereas peaks attributed to unreacted COOH are not seen.

All of the polyitaconates exhibit liquid crystalline behavior, and their transition temperatures could clearly be defined by either DSC or by hot-stage polarizing microscopy. Transition temperatures determined by these two techniques were found to be in reasonable agreement. Identification of the mesophases has been done by examination of the optical textures[15] exhibited by thin samples sandwiched between two glass slides. From the data given in Table II, it can be seen that the mesomorphism of the polyitaconates **5-8** is strongly influenced by the structure of the mesogenic side chain. Polymers with mesogenic groups bearing a short terminal chain (R = OCH_3 or OC_3H_7, polymers **5** and **6**) exhibit only a nematic phase. For polymers with mesogenic groups terminated with longer end chain (R = OC_4H_9 or C_6H_5, polymers **7** and **8**), the nematic is systematically preceded by a smectic phase (this behavior is commonly found in other thermotropic liquid crystalline side-chain polymer series[4,5]).

Further work needs to be done in order to identify much more thoroughly the mesophases exhibited by these polymers. X-ray diffraction experiments are in progress to clarify the structures of the smectic phases.

In conclusion, the possibility of obtaining liquid crystalline side-chain polymers based on the structurally "tortured" polyitaconate[16] backbone was not a priori predictable. In fact, it is difficult at present to predict the properties of the polymers from the chemical structure and properties of either the starting reactant polymers or the mesogenic monomers. Further systematic syntheses must be carried out in order to obtain more information concerning the mutual interaction of polymeric and liquid crystalline properties in liquid crystalline side-chain polymers.

Experimental Section. The thermal properties of the compounds were studied by optical microscopy using a polarizing microscope (Leitz Ortholux II Pol BK) fitted with a Mettler FP 82 heating stage and FP 80 control unit. They were checked by DSC (Mettler FP 85 TA cell and FP 80 control unit). Inherent viscosities of the polymers were determined at 25 °C using 0.5 g·dL^{-1} solutions in chloroform. KPG Ubbelohde microviscometers were used with an AVS 300 automatic viscometer assembly (Schott-Geräte). Structural checks were carried out with a Shimadzu IR-408 instrument for infrared spectra.

Materials. The poly(itaconic acid) used in the preparation of mesomorphic polymers was purchased commercially (Polysciences, Inc.) and was used as received. Other compounds and solvents were of commercial sources.

4′-(Methyloxy)phenyl 4-((5-Bromopentanoyl)oxy)benzoate (**1c**). Typical Procedure (after ref 17). A solution of 5-bromopentanoic acid (1.81 g, 0.01 mol), 4′-(methyloxy)phenyl 4-hydroxybenzoate[18] (2.7 g, 0.011 mol), *N,N*-dicyclohexylcarbodiimide (2.26 g, 0.011 mol), and 4-pyrrolidinopyridine (0.148 g, 0.001 mol) in dichloromethane (50 mL) was stirred for 24 h at room temperature. *N*,-*N′*-Dicyclohexylurea was filtered, and the filtrate was washed with water (2 × 100 mL), with 5% acetic acid (4 × 100 mL), and again with water (2 × 100 mL) and dried over sodium sulfate. The solvent was evaporated to give the ester, which was recrystallized from ethanol to a constant transition temperature (K 66 N 78 I) (26 g, 65%).

Mesomorphic Polyitaconate (**5b**). Typical Procedure. Poly(itaconic acid) (0.058 g, 4.8×10^{-4} mol) was dissolved in 1 N sodium hydroxide (2 mL, 2×10^{-3} mol), and the resulting solution, diluted with 3 mL of water, was mixed with 4′-(methyloxy)phenyl 4-((5-bromopentanoyl)oxy)benzoate (0.44 g, 1.08×10^{-3} mol) and tetrabutylammonium bromide (0.058 g, 1.8×10^{-4} mol) in 10 mL of chloroform. The mixture was refluxed in an oil bath for 96 h and, after cooling to room temperature, was diluted with 50 mL of chloroform. The organic layer was separated, washed with water (2 × 40 mL), and dried over sodium sulfate. The solvent was evaporated and the solid residue was dissolved in the minimum of chloroform (~5 mL). Addition of a large excess of methanol (100 mL) gave a precipitate, which was filtered off and dried under vacuum at room temperature (0.09 g, 25%).

Acknowledgment. The author is grateful to CNRS-PIRMAT for support of this work (ATP Mat 5 Polymères, 1983).

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Received June 13, 1985

Anisotropic Electrical Conductivity of Oriented Poly(diacetylene) Films

In recent publications,[1-4] we reported a series of studies on urethane-substituted poly(diacetylenes), $=(RC{-}C{\equiv}C{-}RC){=}_n$, with R = $(CH_2)_xOCONHCH_2COO(CH_2)_yCH_3$ ($x = 2$–4, $y = 1$ or 3), which are soluble in common organic solvents such as $CHCl_3$.[5] The electrical conductivity of $CHCl_3$-cast films of poly[4,6-decadiyne-1,10-diol bis([(*n*-butoxycarbonyl)methyl]urethane)] ($x = 3$, $y = 3$), abbreviated as poly(3BCMU), was enhanced from 10^{-12} to 10^{-5} S cm^{-1} by doping with an electron acceptor such as iodine.[2,4] For poly[5,7-dodecadiyne-1,12-diol bis([(*n*-butoxycarbonyl)methyl]urethane)] ($x = 4$, $y = 3$), abbreviated as poly(4BCMU), single crystals with fully extended chains were prepared by solid-state polymerization of its monomer single crystals. The anisotropy in conductivity, defined as the ratio of the conductivity along the chain axis to that along the chain stacking direction, was 6.5 [illegible] 0.4, independent of iodine concentration Y.[3] However, the poly(4BCMU) single crystals absorbed iodine only up to 3 × 10^{-4} mol %, and correspondingly, the enhancement in electrical conductivity was very low. Since as-cast films can be doped to a large extent, a study on the anisotropic conductivity of oriented poly(diacetylene) films, if available, should enable us to cover much wider ranges of dopant concentration and conductivity and, thus, is interesting to elucidate the condition mechanism of polymers with conjugated backbones. In this communication, we report the electrical conductivity of uniaxially stretched films of poly(3BCMU) as a function of iodine concentration and the degree of orientation. In this context, the anisotropy in conductivity was reported also for stretch-oriented films of polyacetylene[6] and poly(*p*-phenylenevinylene).[7,8]

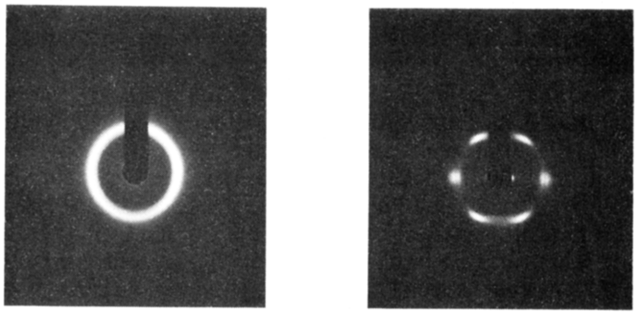
(a) (b)

Figure 1. X-ray diffraction photographs for (a) an as-cast film and (b) a stretched film of λ = 2.9. The X-ray incident beam is perpendicular to the film surface.

Preparation of poly(3BCMU) samples was conducted[1,2] by the method proposed by Patel.[5] In this study, we used a purified poly(3BCMU) sample with number- and weight-average molecular weights 7.7 × 10^4 and 6.4 × 10^7, respectively, determined by GPC using polystyrene standards. Poly(3BCMU) films ca. 0.1–0.3 mm thick were cast from 0.7–2.0% (w/v) $CHCl_3$ solution. Stretched films with various elongation ratios, $\lambda = l/l_0$ (where l and l_0 are the stretched and unstretched length, respectively) were prepared by the following procedures. An as-cast film was placed between two Teflon sheets, gripped by two cramps of an elongation device, and then heated to about 170 °C, near the melting temperature of poly(3BCMU). As soon as the purple-black film changed to yellowish red, it was drawn by the device together with the Teflon sheets and quenched immediately to the room temperature. The color of the film after stretching was green-black with a golden luster, slightly different from the unstretched film. This suggested some changes had taken place in the film morphology. However, the bulk density of the film was almost unchanged (typically 1.165 and 1.169 before and after stretching, respectively).

Wide-angle X-ray measurements were carried out to determine the degree of orientation of the stretched films. Figure 1 shows typical examples of X-ray photographs obtained with a cylindrical camera of radius 35 mm for an as-cast film and a stretched film of λ = 2.9. Both X-ray diffraction patterns show that the films are semicrystalline, but the degree of crystallinity is very low. The diffuse Debye rings observed for the as-cast film change to the diffuse spots for the stretched film. Poly(3BCMU) chains in the solid state are supposed to assume a planar flat ribbonlike conformation stabilized by hydrogen bondings between NH and C=O groups of the neighboring side chains.[9] In the stretched film, such ribbonlike poly(3BCMU) chains are partially oriented along the stretch direction. This was also confirmed from the difference in the intensities of the polarized infrared absorption for the NH stretching band at 3330 cm^{-1}. The spacing calculated from the meridional layer lines is 0.49 nm, corresponding to the length of the repeat unit of the polymer backbone. For stretched films, the intensity distribution of the spots on the equator (i.e., an azimuthal scan) was used to evaluate the orientation function $f = (3\langle\cos^2\alpha\rangle - 1)/2$, where α is the angle between the stretching direction and polymer chain axis.[10] The calculated f values scattered between 0.40 and 0.45 for all the stretched films, although the bulk stretch ratios λ varied from 1.7 to 3.0. This result