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Phase Behavior of Sulfur-Containing Polymers: Polythioesters

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ABSTRACT: Three polythioesters containing the 4,4′-dithiobiphenyl group have been synthesized by reaction under interfacial conditions of 4,4′-dimercaptobiphenyl with 1,5-pentanedicarbonyl dichloride (polymer P5), 1,10-decanedicarbonyl dichloride (polymer P10), or 1,13-tridecanedicarbonyl dichloride (polymer P13). They were characterized by FT-IR, ^{1}H NMR, and GPC methods, and their phase behavior was investigated by DSC, polarizing microscopy, and X-ray diffraction techniques. The DSC heating curve of each polymer shows two endothermic signals that are almost coalescent in the case of P13, indicating that the second phase transition occurs in addition to melting. The X-ray diffraction evidence suggests that for polymers P5 and P10 the first phase transition is a solid–solid one. These polymers melt to an isotropic liquid. Some birefringence may reversibly be induced by mechanical shear of this phase whose X-ray diffraction pattern is typical of an amorphous structure. The first phase transition observed for P13 is the melting. An optically anisotropic liquid is produced whose morphological features are indicative of a nematic liquid crystal. This phase has a narrow thermal stability range. Possible effects of molecular weight on the phase behavior are not taken into account; they could play some role in the case of P10.

Introduction

The liquid crystal properties of some polyalkanoates of 4,4′-dihydroxybiphenyl have been investigated by several authors[1,2] and particularly by Krigbaum et al.[3,4] Their nematogenic or smectogenic character, depending on the odd or even number of methylene groups contained in the flexible spacer, has been discussed.

This article reports the results of an investigation of the phase behavior of three polythioesters containing 4,4′-dithiobiphenyl groups. Some results of an investigation on the possible consequences of replacing with sulfur atoms oxygen atoms of ester groups are available for some low molecular weight mesogenic thiobenzoates[5-7] or for several cholesteric mesogens such as 3β-(n-alkanoylthio)-5α-cholestene[8] or 3β-((ω-phenylalkanoyl)thio)-5α-cholestene;[8-11] in addition, the effect of the substitution has been discussed for polymeric liquid crystals containing ether or thioether groups.[12] As a general trend, sulfur-containing compounds have higher mesophase stability than the oxygenated homologues.

Results and Discussion

Polythioesters were obtained by reacting 4,4′-dimercaptobiphenyl (DMB) with aliphatic acid dichlorides under interfacial conditions in the presence of benzyltriethylammonium chloride (BTEAC) as the catalyst,

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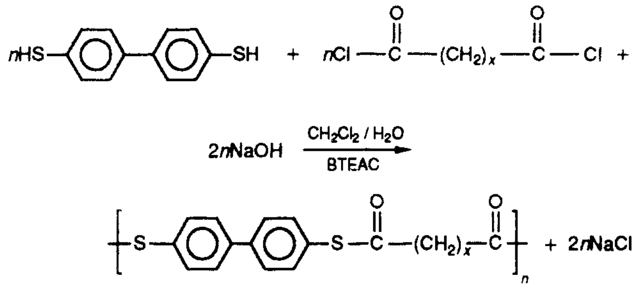
using water and dichloromethane as solvents:



p5, x = 5
p10, x = 10
p13, x = 13

The various syntheses were performed at room temperature under a nitrogen atmosphere with mechanical stirring.

The polymers, obtained as white powders by precipitation from CH_2Cl_2 solution into methanol (see Experimental Section), were characterized by FT-IR and ^{1}H NMR spectroscopy and by GPC analysis. The data discussed below are reported in Table I. The FT-IR spectra of the three polymers show a strong band in the region 1692–1695 cm^{-1}, typical of the thioester group;[8] the IR spectrum of polymer P13 is presented in Figure 1.

The ^{1}H NMR spectra are also consistent with the proposed structures. In fact, the aromatic/aliphatic proton ratios calculated for all the polymers are correct, and in the aromatic region they present a typical AA′BB′ system approaching an AB system; the ^{1}H NMR spectrum of polymer P13 is presented in Figure 2.

Finally, from GPC traces, using polystyrene standards for the linear calibration, the peak molecular weights were found at 20 000, 75 000, and 4500 for P13, P5, and P10, respectively. We attribute the low molecular weight of P10 to the fact that this polymer is partially insoluble in CH_2Cl_2 and, during the polymerization, it tends to precipitate; all the reported values are relative to the insoluble fraction of this polymer after purification (see Experimental Section).

It is well-known that liquid crystal properties, particularly isotropization temperature and molar enthalpic change, of a polymer depend on molecular weight. However, this dependence is, in general, rather weak for molecular weights >5 × 10^3. Therefore, the following discussion does not take into account possible effects of molecular weight although some minor influence on the thermal data concerning P10 should not be ruled out.

The interpretation of the phase behavior of the polymers reported in this article is not a straightforward matter. The phase transition temperatures and enthalpies obtained, discussed below, are reported in Table II. Of the three polymers, P13 is the only one exhibiting unambiguous evidence of liquid crystalline behavior. Polarizing microscopy analysis and DSC analysis together show that melting and isotropization, as well as the reverse transitions, occur within temperature intervals that overlap partially. A better although not a complete resolution is achieved at the second DSC heating run with melting and isotropization endotherms peaked at 410 and 417 K, respectively. A total 42 J g^{-1} transition enthalpy was measured. About 80% of this quantity should be attributed to the isotropization. However, the partial overlap of the DSC endotherms prevents a more precise evaluation. The occurrence of marbled and schlieren textures suggests the nematic nature of the mesophase. No further calorimetric signal was detected up to 573 K. Annealing the polymer for 2 h at 402 K narrows to some extent the temperature range of the melting + isotropization transition but has hardly any influence on the peak temperature (416 K) and no influence at all on the upper temperature limit of the isotropization transition. This feature is in favor of an enantiotropic character for the liquid crystal phase.

Table I
Yields and Characteristic Data of Polythioesters

polymer	yield,[a] %	MW[c]	IR,[d] cm^{-1}	^{1}H NMR,[e] ppm
P5	70	75 000	1692	1.48–1.66 (m, 2 H) 1.75–1.95 (m, 4 H) 2.74 (t, 4 H) 7.54, 7.70 (2d, 8 H, arom)
P10	30[b]	4 500	1693	1.35 (br s, 12 H) 1.65–1.85 (m, 4 H) 2.72 (t, 4 H) 7.50, 7.66 (2d, 8 H, arom)
P13	70	20 000	1695	1.35 (br s, 18 H) 1.65–1.85 (m, 4 H) 2.72 (t, 4 H) 7.52, 7.68 (2d, 8 H, arom)

[a] After purification. [b] Based on the insoluble fraction. [c] Molecular weights by GPC analysis using polystyrene standards for the linear calibration. [d] Carbonyl stretching band. [e] In $CDCl_3$, downfield from TMS. s = singlet, d = doublet, t = triplet, m = multiplet, br = broad.

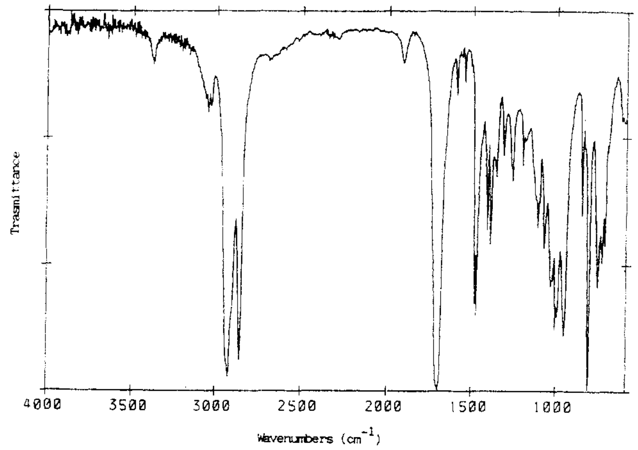


Figure 1. IR spectrum of polymer P13 obtained on a thin film cast on a sodium chloride plate from CH_2Cl_2 solution.

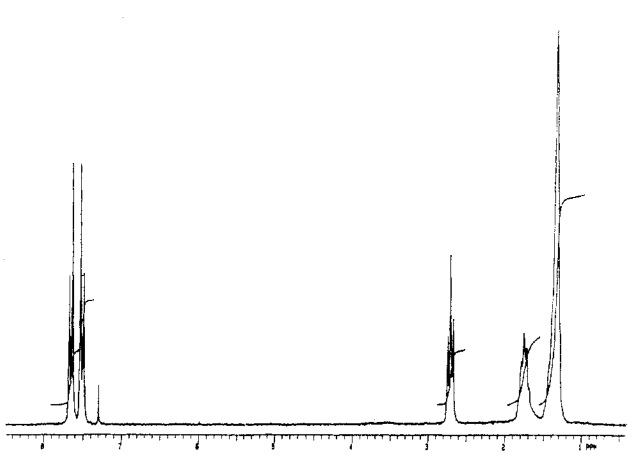


Figure 2. ^{1}H NMR (200 MHz) spectrum of polymer P13 recorded from deuteriochloroform solution (2%).

Polymer P5 as obtained by solution precipitation has virtually zero crystallinity. The X-ray diffraction pattern is characterized essentially by a diffuse halo around θ = 10°. No low-angle Bragg diffraction signal was detected within the 55-Å lattice distance.

Crystallinity develops during DSC heating at a 10 K/min scanning rate. No single exothermic DSC single signal

Table II
Phase Transition Temperatures (T/K) and Enthalpies ($\Delta H/(\mathrm{J\ g^{-1}})$)

	P5				P10				P13	
run	T_1	ΔH_1	T_2	ΔH_2	T_1	ΔH_1	T_2	ΔH_2	T	ΔH
1[a]	462	7.2	493	20	447	24	477	32	415	52
2[b]	430	2	498	26	455	58	483	34	410–417	42
3[c]	439	7.5	501	28	459	66	488	39		

[a] First DSC heating run, polymer as prepared. [b] Second heating run. [c] Sample previously annealed at $T_1 < T < T_2$.

was detectable to indicate the abrupt occurrence of crystallization, which, starting at $T_g = 338$ K, takes place apparently in a continuous way. The DSC curve is characterized by two endotherms with maxima at 462 and 492 K. At ~570 K a small endothermic signal followed by an irregular fluctuation of the base line indicates the beginning of appreciable thermal decomposition. Softening becomes detectable at the polarizing microscope at ~485 K (this temperature lies within the range of the second transition endotherm), and the viscous liquid that progressively forms is optically isotropic. Complete isotropy is attained at ~500 K. This corresponds to the upper limit of the second transition endotherm. The X-ray diffraction spectrum recorded at 513 K is typical of an amorphous structure.

Optical birefringence may be induced by shearing the isotropic liquid. The recovery of isotropy by relaxation is immediate. This behavior is similar to what one would expect for a nematic liquid taking a homeotropic texture. However, no way was found to produce stable birefringence by acting on the glass surface. Therefore, we should conclude that the observed optical anisotropy is a feature mechanically induced on a truly isotropic liquid.

The polymer crystallizes on cooling, with ~30 K supercooling of the isotropic liquid, as indicated by a sharp DSC exothermic signal at 465 K. The X-ray diffraction pattern recorded at room temperature is unmistakably typical of a semicrystalline polymer.

An identical diffraction pattern was recorded with a sample that was previously brought to 473 K at a 10 K/min heating rate (i.e., in the same dynamic condition of the DSC heating run) and then rapidly cooled to room temperature. This is additional evidence demonstrating that a partial crystallization of the originally amorphous phase does intervene during heating.

The X-ray diffraction pattern of the phase stable between ~462 and ~497 K (phase II) was recorded at 473 K. It is characterized by a few sharp Bragg lines. Two of them, at 4.57- and 17.6-Å lattice distance, are by far the strongest. The same basic feature is observed in the spectrum of the crystal form (phase I) stable at room temperature (4.41 and 18.0 Å, respectively) although many more Bragg lines of lower intensity are also present.

The thermal behavior exhibited at the first heating run is not entirely reproducible in the following thermal cycles. This is presumably related to the amorphous structure of the solution-precipitated samples. Thermal annealing (1 h at 473 K) of a previously untreated sample increases the melting temperature from 493 to 501 K and the corresponding enthalpic change from ~20 to 28 J g^{-1}. However, what appears to be particularly significant is that the thermal parameters of phase I are influenced, too. This indicates that the polymer fraction that constitutes phase I is essentially the same that was formed as phase II during the annealing process. Therefore, although the X-ray diffraction spectrum is in itself compatible with a highly ordered smectic, phase II is very likely a crystal phase.

The phase behavior of polymer P10 is to some extent similar to that of P5. The solution-precipitated polymer has very low crystallinity. The X-ray diffraction spectrum is essentially characterized by two strong Bragg lines at 3.75 and 16.4 Å and by a faint line at ~4.5 Å superimposed on a diffuse halo. As for P5, even a mild annealing enhances crystallinity. The first DSC heating curve is characterized by two endothermic signals with maxima at 447 and 447–483 K. The seemingly composite structure of the second endotherm is not reproducible in the successive thermal cycles or if the polymer is first annealed at $T < 477$ K. On the polarizing microscope, melting to an isotropic liquid is clearly detectable at ~475 K, and complete isotropy is attained at ~490 K. Above this temperature optical birefringence is only obtained by shearing the liquid, this effect decreasing with increasing temperature. As for P5, isotropy is rapidly restored by relaxation. The X-ray diffraction pattern recorded at 503 K is typical of an amorphous structure. No significant DSC signal is detectable up to the beginning of thermal decomposition at ~579 K.

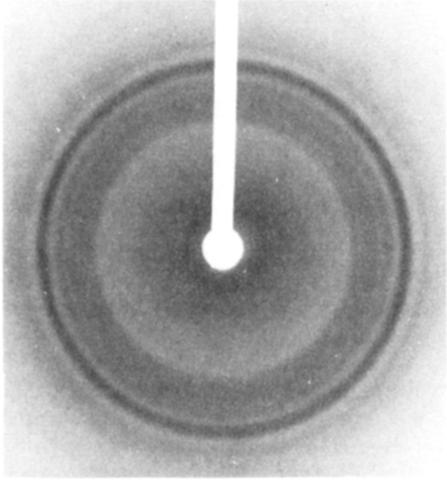


Figure 3. X-ray diffraction spectrum of P10 recorded at room temperature. The sample was previously annealed for 2 h at 471 K.

Two exothermic DSC signals with maxima at 463 and 426 K are detected on cooling the polymer from the liquid phase. Only one exothermic transition at 429 K occurs on cooling the polymer after annealing at 471 K. The X-ray diffraction spectra recorded at room temperature with polymer samples that were previously melted or annealed are identical and both indicative of increased crystallinity (Figure 3). The set of diffraction lines includes those observed for a previously untreated sample. The X-ray diffraction pattern recorded at 471 K is characterized by two strong Bragg lines at 4.57 and 15.0 Å (Figure 4). Several other lines of less intense diffraction are detectable. A comparison of the spectra unambiguously indicates that the intense Bragg lines characterizing the high-temperature form (phase II) are not included among those observed for the form stable at room temperature (phase I).

As for P5, transition temperatures and enthalpies depend

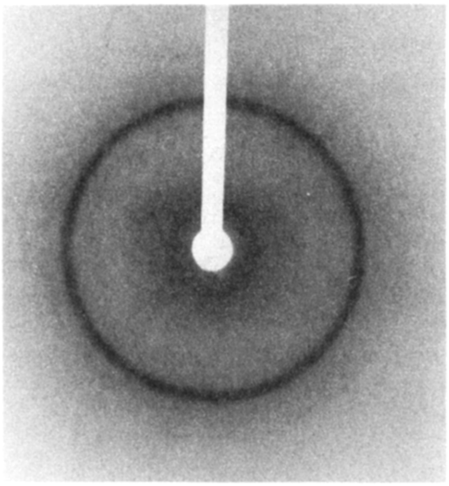


Figure 4. X-ray diffraction spectrum of P10 recorded at 471 K.

on the thermal history. The phase transitions of a melt-crystallized sample take place at 455 and 483 K with enthalpies of 58 and 34 J g^{-1}, respectively. The corresponding values for a sample that was previously annealed for 1 h at 471 are 459 K, 488 K, 66 J g^{-1} and 39 J g^{-1}. The ratio $\Delta H_1/\Delta H_2$ is fairly constant.

In conclusion, all of the evidence suggests a crystal nature of phase II.

It is worth recalling that polyalkanoates of 4,4′-dihydroxybiphenyl have been reported by Krigbaum et al.[4] as nematogenic within a narrow temperature interval when the number of methylene groups of the spacer is odd, while they are smectogenic over fairly large temperature intervals for even numbers. The smectic phase was defined to be S_H by X-ray diffraction analysis. Only P13 is found to behave coherently with this trend with melting and isotropization temperatures presumably lower than those of the corresponding oxygen-containing homologue (actually, polymers containing 5–12 methylene groups in the spacers were examined by Krigbaum et al., but extrapolation of their results to a ~473 K melting temperature for $n = 13$ appears quite reasonable).

On the contrary, polymers P5 and P10 have melting temperatures that are comparable to those found for the oxygen-containing homologues but considerably lower than the isotropization temperatures measured for the latter compounds. Indeed, it is tempting, at least for P10, to compare phase II with the S_H phase of the oxygenated homologues. They have qualitatively very similar X-ray diffraction spectra, and only a very accurate line-shape analysis might indicate whether the coherence lengths are substantially different. As to P5, any further comparison should take into account the previous elucidation of the nature of the phase characterizing the oxygenated homologue[3] between 403 and 418 K. In connection with this, Krigbaum and co-workers[4] have shown that the polymer containing seven methylene groups in the spacer is also smectogenic, although in a monotropic way.

Experimental Section

IR spectra were recorded on a FT-IR Bruker IFS 48 instrument. ^1H NMR spectra were recorded on a Varian XL-200 spectrometer.

The GPC analysis was performed on a Perkin-Elmer Series 2 liquid chromatography instrument, using a set of 5 μm PL gel columns (mixed plus 2 × 10^3, 300 × 7.5 length/i.d., mm) under the following operating conditions: THF as mobile phase, flow rate of 1.0 mL/min, column temperature of 40 °C, and UV detection at 260 nm.

The calorimetric analysis of the phase transition was performed by using a Perkin-Elmer DSC-2 apparatus. Samples were kept under a dry nitrogen atmosphere, and a 10 K/min scanning rate was generally used. For the optical analysis a Leitz polarizing microscope was used together with a Mettler FP5 microfurnace for temperature control. Cu Kα X-ray diffraction spectra were photographically recorded at both high and room temperature with a flat-film camera. Samples were sealed inside Lindemann capillaries under a nitrogen atmosphere, and a small furnace with a ±1 K temperature control was employed for high-temperature measurements.

Aliphatic acid dichlorides were prepared by reaction of the corresponding diacids with thionyl chloride according to the standard procedure.[14] They were distilled under vacuum immediately before use. 4,4′-Dimercaptobiphenyl was synthesized according to Marvel and Caesar.[15] Solvents were reagent grade and were used without further purification.

The procedure followed for the syntheses of polythioesters is now described in some detail for P13 as an example.

A 250-mL three-necked round-bottom flask was charged with 0.35 g (1.6 mmol) of DMB, 0.240 g (6.0 mmol) of sodium hydroxide, 0.05 g (0.22 mmol) of BTEAC as catalyst, 10 mL of CH_2Cl_2, and 20 mL of water. 1,13-Tridecanedicarbonyl dichloride (0.494 g (1.6 mmol)) dissolved in 30 mL of CH_2Cl_2 was added dropwise to the rapidly stirred mixture.

The reaction was allowed to continue at room temperature for 1 h. The mixture was then washed with dilute hydrochloric acid (2 × 50 mL, 10%) and with distilled water (3 × 100 mL). The polymer was recovered, after separating the organic phase, by precipitation into methanol. Purification was then performed by chromatography on silica gel using chloroform as eluant and by successive precipitation (twice) into methanol from CH_2Cl_2 solution. P5 was obtained and purified in the same way.

After this treatment P5 and P13 were found to be completely free from the oligomeric fractions present in the polymers before purification. During the synthesis of P10 a partial precipitation of the polymer occurs; in the soluble fraction only low molecular weight oligomers were present. The insoluble fraction, which has been used for the characterization of the polymer, was purified only by precipitation (two times) because we did not find any acceptable condition for performing a purification by chromatography.

The yields and characteristic data of the polymers are reported in Table I.

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