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Liquid Crystalline Polymers

Monotropic Liquid Crystalline Poly(β-Thioester)s Containing Bis (*p*-Oxybenzoate) Mesogenic Units

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Summary

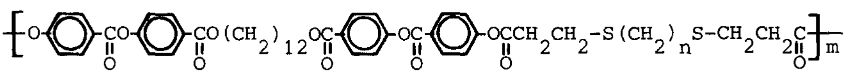
A new series of thermotropic liquid crystalline poly(β-thioester)s was prepared by a Michael-type polyaddition of α,ω-polymethylenedithiols of different length to a mesogenic diacrylate containing two bis(p-oxybenzoate) units symmetrically connected through a dodecamethylene segment. The thermotropic behaviour was studied by combined DSC and thermal-optical analyses. All the poly(β-thioester)s investigated exhibited quite unusual monotropic mesomorphism.

Introduction

The thermotropic, liquid crystalline behaviour of polymers having rigid mesogenic cores interconnected by flexible spacers within the main chain is well documented. By varying the structural components of the repeating unit, a great number of nematic, cholesteric, and smectic polymers has been prepared (1). Normally, such mesophases are enantiotropic in character, i.e., they establish both on heating above the melting temperature and on cooling below the isotropization point, whereas monotropic phases, i.e., those detectable only on supercooling of the isotropic melt, appear to be a few exceptions.

We have recently addressed our attention to functional liquid crystalline polymers (2,3), which incorporate in the flexible portion of the repeating unit reactive heteroatoms, viz. amino or sulphide groups, suitable for further transformation to modified liquid crystalline polymers.

In this paper we present some results on the mesophase behaviour of a new class of thermotropic liquid crystalline poly(β-thioester)s based on bis(p-oxybenzoate) units interconnected by two different flexible segments sequenced in an alternating fashion along the polymer backbone:



All the members of the investigated series surprisingly showed monotropic properties.

The bis(p-oxybenzoate) unit can be indicated as a new mesogenic moiety

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for structurally ordered polyesters. When connected to a terephthaloyl group, it previously served to promote liquid crystalline properties in aromatic co-polyesters derived from poly(ethylene terephthalate) and p-acetoxybenzoic acid (1,4). Sulphur-containing segments, that have been inserted for the first time only very recently in mesogenic polymers (3), can constitute a novel structural parameter of interest in the assessment of the structure-property relationship in mesomorphic semiflexible polymers.

Experimental Part

The synthesis of the diacrylate precursor and of the corresponding poly(β-thioester)s will be described in detail in a forthcoming paper (5). Commercially available α,ω-polymethylenedithiols were purified by distillation immediately prior to use.

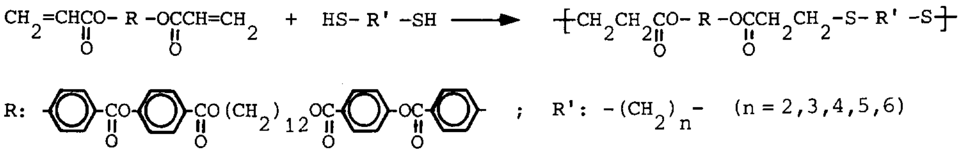
Average molecular weights of polymers were determined by gel permeation chromatography by a Perkin-Elmer 2/2 liquid chromatograph equipped with Shodex A802/S and A803/S columns and a Perkin-Elmer LC75 spectrophotometric detector. Monodisperse polystyrene samples were used for calibration.

Differential scanning calorimetry (DSC) analysis was performed by a Perkin-Elmer DSC-2 apparatus under dry nitrogen flow at a heating/cooling rate of 10 K/min. Higher cooling rates (20-80 K/min) were used to further supercool the transition from the isotropic liquid to the solid. Indium standards were employed for temperature calibration and enthalpy change evaluation.

Observations of liquid crystal textures were carried out by a Reichert Polyvar polarizing microscope equipped with a Mettler hot stage at a scanning rate of 10 K/min.

Results and Discussion

Polymer samples were prepared from 1,12-bis(4'-acryloyloxybenzoyloxy-4-benzoate)-dodecane and different α,ω-polymethylene bisthiols by a polymerization reaction involving a base-catalyzed Michael-type nucleophilic addition of the bisthiols to the bisacrylic ester:



$$CH_2{=}CH\underset{\overset{\|}{O}}{C}O-R-O\underset{\overset{\|}{O}}{C}CH{=}CH_2 + HS-R'-SH \longrightarrow \left[CH_2CH_2\underset{\overset{\|}{O}}{C}O-R-O\underset{\overset{\|}{O}}{C}CH_2CH_2-S-R'-S\right]$$

R: ; R': $-(CH_2)_n-$ (n = 2,3,4,5,6)

The polymer samples will be designated as DS-n, where n is the number of methylene groups in the dithiol spacer. Polymer DS-05 was obtained from the 3-oxa-1,5-pentanedithiol precursor.

The polyaddition reaction took place at room temperature in the presence of catalytic amounts of triethylamine with nearly quantitative yields. From a structural point of view these polymers have to be regarded as rigorously alternating copolymers in respect both of the relative orientational placement of the bis(p-oxybenzoate) units and of different flexible segments (α,ω-dodecamethylenediol and α,ω-polymethylenedithiol). The polymeric products were soluble in most common organic solvents. The intrinsic viscosity values in chloroform at 30°C were typically greater than 0.20 dl/g, to which values average molecular weights in the range 5,000-6,500 corresponded.

All the polymers examined by differential scanning calorimetry showed on heating an intense endotherm, which in all cases was associated with a transformation from the solid to the isotropic liquid. Such melting transition was structured by several endothermic peaks, whose temperatures and relative magnitudes were dependent upon thermal history. Reproducible values were obtained on samples first heated approximately 20 K above their solid-to-isotropic liquid transition temperature and then cooled to room temperature. The values of melting temperature, T_m, isotropization or clearing temperature, T_i, and crystallization temperature, T_c, collected in Table 1 were taken on annealed samples in correspondence of the maximum of the respective DSC enthalpic peaks.

The melting temperatures decreased smoothly on lengthening the bisthiol spacer according to a progressively greater main chain flexibility (Figure 1). On cooling at 10-20 K/min, all samples exhibited a sharp crystallization exotherm that was characterized by a relatively small degree of supercooling, more or less independent of chemical structure ($T_m - T_c = 13\text{-}26$ K).

Quite interestingly, samples DS-3, DS-4, and DS-5 showed on cooling an additional high temperature exothermic peak which preceded the crystallization exotherm, with no counterpart in the heating curves. Such a transition corresponded to the onset of a liquid crystal phase, that had therefore a monotropic character. The mesophasic range was in all cases rather narrow ($T_i - T_c = 6\text{-}14$ K), the maximum value being detected in poly(β-thioester) DS-4 (Table 1). The DSC heating and cooling profiles of sample DS-4

Table 1. Thermal properties of thermotropic poly(β-thioester)s containing the bis(p-oxybenzoate) unit.

Sample	n	$\bar{M}_n$	$[\eta]$ a)	Phase transitions (in K) b)			
			(dl/g)	T_m	T_i c)	T_c	$T_i - T_c$
DS-2	2	5100	0.20	424	408 d)	398 d)	10
DS-3	3	6500	0.25	413	404	397	7
DS-4	4	5200	0.20	410	407	393	14
DS-5	5	5800	0.22	405	398	392	6
DS-05	5 e)	-	0.23	404	388 d)	381 d)	7
DS-6	6	6400	0.24	404	394 d)	388 d)	6

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a) In chloroform, at 30°C. b) By DSC, at a scanning rate of 10 K/min, unless indicated otherwise. c) Monotropic transition. d) Cooling rate of 20 K/min. e) 3-oxa-1,5-pentanedithiol.

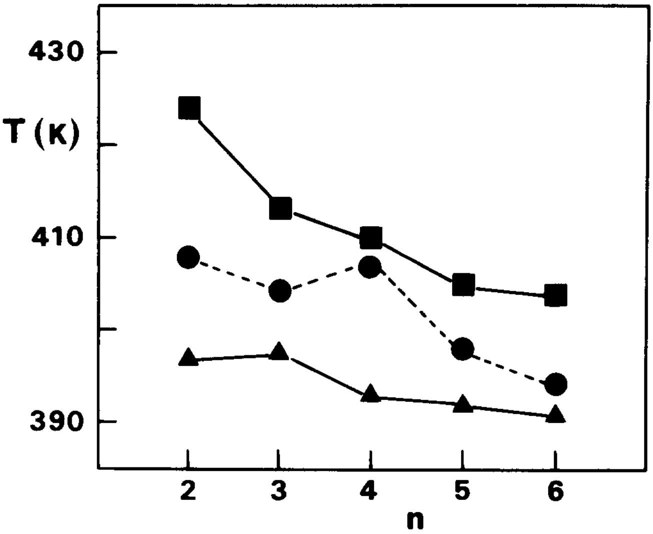


Figure 1. Trend of phase transition temperatures with dithiol spacer length n :
-■- melting, -●- isotropization, and
-▲- crystallization.

are reported in Figure 2, as typical examples.

In conventional low molar mass liquid crystals, the liquid crystal-to-isotropic liquid transition is completely reversible, while some supercooling characterizes the transformations from the isotropic liquid, or anisotropic liquid, to the solid. Such a behaviour can allow for the identification of monotropic mesophases. Variably high degrees of supercooling (up to 50 K) have been observed in mesogenic main chain polymers (6-9), probably due to the great loss of entropy in the process of reordering of the entangled polymer chains from the isotropic phase. However, such circumstances do not hold in the present case where all the processes appear to be quite reversible with practically no hysteresis phenomena. In all cases, the exotherm corresponding to the isotropic liquid-to-liquid crystal transition was narrow (5-10 K), but overlapped to some extent the crystallization exotherm. The isotropization enthalpies could be measured with some accuracy only in the case of DS-4 ($\Delta H_i = 2.6$ cal/g) and DS-5 ($\Delta H_i = 1.9$ cal/g). Samples DS-2, DS-6, and DS-O5 were cooled at 20 K/min to allow to split the overlapping signals in the individual components. For the last sample a $\Delta H_i = 1.2$ cal/g was found.

The isotropization temperatures follow a descending trend with increasing length of the bisthiol spacer, and there exists indication, at least for the first four members of the series, of alternation in the clearing temperature (Figure 1), in analogy with low molecular weight mesogens (10). Odd-even effects have been previously discussed in enantiotropic liquid crystalline polyesters (7,11), and our results suggest that they likely

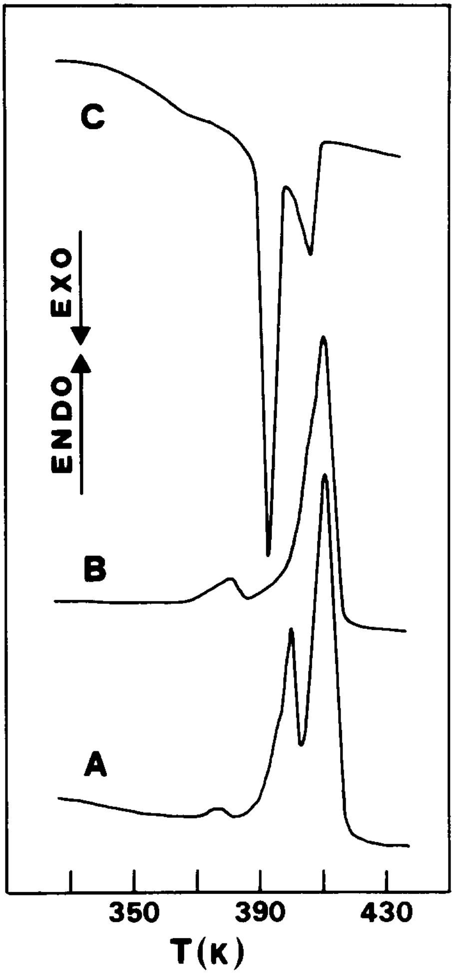


Figure 2. DSC curves of polymer DS-4 (n = 4): A, first heating run; B, successive heating runs; and C, cooling runs.

extend even to monotropic liquid crystalline polymers.

Observations on the hot stage of the polarizing microscope confirmed the attribution of the high temperature DSC transition to the melting process. All samples were characterized by a high birefringence in the semicrystalline phase, but not in the isotropic liquid phase. On cooling of the isotropic melt of samples from DS-3 to DS-5, a mesophase was seen to nucleate at 408, 409, and 400 K, respectively, thus indicating the occurrence of a very narrow biphasic isotropic liquid/liquid crystal region. Due to instrumental limitations, the transition from the isotropic melt to the solid could not be sufficiently supercooled in poly(β-thioester)s DS-2, DS-6, and

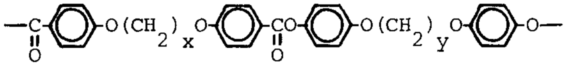
DS-05, and no mesophase was visually observed above crystallization that was seen to begin at 418, 402, and 396 K, respectively. We could not identify specific textures of the polymer liquid crystal phases, also because of the limited thermal persistence, and unambiguous assignment was not possible. However, in account for the low values of the isotropization enthalpies determined, we may suggest a nematic-type structure for such mesophases.

Monotropic mesomorphism rather rarely occurs in main chain liquid crystalline polymers and typically is shown by polyester samples of homologous series containing either very short trimethylene segments (7) or rather long decamethylene (12) or dodecamethylene (13) spacers, in general agreement with what is observed in low molar mass mesogens (10). Monotropic mesophases may be more common in side chain liquid crystal polymers (14), in which however the pendant mesogenic moieties behave independently of the polymer backbone, provided that their motions are decoupled from the main chain by flexible segments of sufficient length (15).

It is remarkable that all the poly(β-thioester)s described in the present work are monotropic independent of the spacer nature and length, and they represent, to the best of our knowledge, the first homologous series of polymers that display liquid crystalline properties of monotropic type.

The effect of molecular weight on the transition temperatures of mesogenic polymers is documented (16-18), and it has been shown that above a certain critical length the melting and clearing temperatures reach a plateau value. The disappearence of the enantiotropic mesophase does not take place even for a degree of polymerization as low as six, even though the transition temperatures are severely depressed (16). It might be conceived that isotropization and melting temperatures could be affected to a different extent at fairly low molecular weights. Preliminary results on structurally related poly(β-thioester)s containing the bis(p-oxybenzoate) mesogenic unit do not corroborate such conclusions (5). The reported peculiar liquid crystal behaviour should be imputed, in fact, to structural features independent of molecular weight.

Structurally related polymers consisting of hydroquinone p-oxybenzoate units were previously studied for their thermotropic characteristics (8,19):



It may be observed that the three polyester samples having x = 12 and y = 6,8,10 show enantiotropic nematic phases of rather high stability and persistence in the temperature ranges 474-486.5, 455-478, and 448-466 K, respectively (8). If we take the nematic-to-isotropic liquid transition temperature as a qualitative index of the thermal stability of the mesophase in the two classes of polymers, it appears that the bis(p-oxybenzoate) unit is comparatively scarcely effective in promoting stable and persistent phases. This finding suggests that the bis(p-oxybenzoate) mesogenic core is characterized by a lower polarity and/or polarizability with respect to the hydroquinone p-oxybenzoate unit, in accordance with previous suggestions on related low molar mass mesogens (20). On the other hand, it is possible that the simultaneous introduction of two sulphur atoms in the flexible part of the repeating unit can inhibit the ordering process in the nematic phase by steric and/or conformational effects with a consequent lowering of the clearing temperature.

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References

1. C.K.Ober, J.-I.Jin, R.W.Lenz, Adv.Polym.Sci. 59, 103 (1984)
2. G.Galli, M.Laus, A.S.Angeloni, P.Ferruti, E.Chiellini, Makromol.Chem., Rapid Commun. 4, 681 (1983)
3. M.Laus, A.S.Angeloni, G.Galli, P.Ferruti, E.Chiellini, J.Polym.Sci., Polym.Lett.Ed. 22, 587 (1984)
4. W.J.Jackson, Jr., H.F.Kuhfuss, J.Polym.Sci., Polym.Chem.Ed. 14, 2043 (1976)
5. M.Laus, A.S.Angeloni, G.Galli, E.Chiellini, in preparation
6. A.Roviello, A.Sirigu, J.Polym.Sci., Polym.Lett.Ed. 13, 455 (1975)
7. A.Blumstein, O.Thomas, Macromolecules 15, 1264 (1982)
8. A.C.Griffin, S.J.Havens, J.Polym.Sci., Polym.Phys.Ed. 19, 951 (1981)
9. E.Chiellini, G.Galli, C.Malanga, N.Spassky, Polym.Bull. 9, 336 (1983)
10. G.W.Gray, in "The Molecular Physics of Liquid Crystals", ed. by G.R. Luckhurst and G.W.Gray, Academic Press New York, 1 (1979)
11. A.Roviello, A.Sirigu, Makromol.Chem. 183, 895 (1982)
12. C.K.Ober, R.W.Lenz, G.Galli, E.Chiellini, Macromolecules 16, 1034 (1983)
13. A.Roviello, A.Sirigu, Makromol.Chem. 180, 2543 (1979)
14. See for instance H.Finkelmann, G.Rehage, Makromol.Chem., Rapid Commun. 3, 859 (1982)
15. H.Finkelmann, H.Ringsdorf, J.H.Wendorff, Makromol.Chem. 179, 273 (1978)
16. A.Blumstein, S.Vilasagar, S.Ponrathnam, S.B.Clough, R.B.Blumstein, G.Maret, J.Polym.Sci., Polym.Phys.Ed. 20, 877 (1982)
17. R.B.Blumstein, E.M.Stickles, A.Blumstein, Mol.Cryst.Liq.Cryst.Lett. 82, 205 (1982)
18. A.S.Angeloni, M.Laus, C.Castellari, P.Ferruti, G.Galli, E.Chiellini, Makromol.Chem. in press (1985)
19. D.vanLuyen, L.Strzelecki, Eur.Polym.J. 16, 303 (1980)
20. M.J.S.Dewar, R.S.Goldberg, J.Org.Chem. 35, 2711 (1970)

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