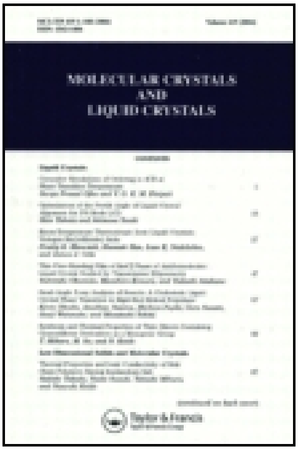

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G. Torquati [a], O. Francescangeli [a], M. Laus [b], A. S. Angeloni [c], C. Carlini [c], D. Caretti [c], G. Galli [d] & E. Chiellini [d]

[a] Dipartimento Scienza dei Materiali, Università di Ancona, Pisa, Italy
[b] Dipartimento Ingegneria Meccanica, Università di Brescia, Pisa, Italy
[c] Dipartimento Chimica Industriale, Università di Bologna, Pisa, Italy
[d] Dipartimento Chimica e Chimica Industriale, Università di, Pisa, Italy

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AN X-RAY INVESTIGATION OF THERMOTROPIC POLYMALONATES CONTAINING THE AZOBENZENE MESOGEN

G.Torquati[1]†, O.Francescangeli[1], M.Laus[2], A.S.Angeloni[3], C.Carlini[3], D.Caretti[3], G.Galli[4], E.Chiellini[4]*

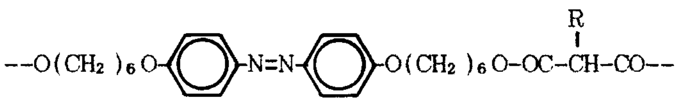
[1]Dipartimento Scienza dei Materiali, Università di Ancona,
[2]Dipartimento Ingegneria Meccanica, Università di Brescia,
[3]Dipartimento Chimica Industriale, Università di Bologna,
[4]Dipartimento Chimica e Chimica Industriale, Università di Pisa, Italy

Abstract The structure of three main chain poly[(α,ω-alkylene) monoalkylmalonate]s containing the azobenzene mesogen was investigated by X-ray diffraction. The mesogenic properties of the samples are compared with those of related side chain or combined polymeric systems

INTRODUCTION

Liquid crystalline polymers containing photosensitive groups are nowadays attracting a great interest for their potential applications in (electro)optics[1-4].

Within this scope, we are studying[5,6] liquid crystalline polymers incorporating the photochromic *trans*-azobenzene mesogen either in the side chains or in the main chain, such as polymalonates **1-3**.



	1	**2**	**3**
R :	n-C_3H_7	n-C_4H_9	(S)-$CH_2\overset{*}{C}H(CH_3)C_2H_5$

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† G.Torquati is suddenly deceased when the manuscript was in preparation

*To whom correspondence should be addressed

Other examples are known of thermotropic polymalonates based on the azobenzene group, including the so-called combined polymers, linear or crosslinked[7-9].

The synthesis, mesomorphic properties, and photoisomerization behaviour in solution of polymers **1–3** were previously described[5]. In this work the mesophase structure was studied by X-ray diffraction on unoriented polymer samples.

EXPERIMENTAL PART

Polymers **1–3** were prepared by a polycondensation reaction of 4,4'-bis(6-hydroxyhexyloxy)azobenzene with the appropriate alkylmalonyl chloride in 1,2-dichloroethane in the presence of triethylamine[5]. The mesomorphic properties were studied by thermal analysis (DSC) and polarizing microscopy. The mesophase structure was investigated by X-ray diffraction with a conventional diffractometer using the CuKα radiation (λ = 1.54 Å) and a heating device with an accuracy of ±1°C.

RESULTS AND DISCUSSION

Polymalonates **1–3** exhibit thermotropic properties (Tab.I), but no significant effect of the substituent R can be noted on the mesophase stability. The relatively high values of the isotropization enthalpies and entropies are consistent with the occurrence of a smectic-isotropic transition.

The structure of the different phases was investigated by X-ray diffraction. The three samples display a somewhat similar behaviour with varying temperature, and the X-ray diagrams of polymer **3** are reported in Figure 1, as a typical example. The thermal evolutions of the structure of polymers **1–3** are illustrated in Figure 2.

The as-received sample **3** shows a lamellar crystalline structure (Fig.1a), which on heating above 55°C gives rise to a new crystalline structure characterized by slightly different

Table I Mesomorphic properties of polymalonates 1-3

Sample	$\overline{M}_n$	T_m[a]	T_{SI}[a]	ΔH_{SI}	ΔS_{SI}
	$\cdot 10^{-3}$	°C	°C	kJ·mol^{-1}	J·mol^{-1}·K^{-1}
1	14.6	33(44)	127(130)	9.6	23.9
2	7.2	64(71)	129(145)	8.6	21.4
3	14.3	61(68)	121(122)	9.8	24.9

[a] By DSC and X-ray diffraction (values in parentheses).

periodicities (Fig.1b). This high temperature modification is thermodynamically more stable, and is also regained on slowly cooling from the melt. An analogous behaviour is observed for sample 2, whereas in sample 1 only one semicrystalline phase appears to exist (Fig.2). This last, however, is not recovered on cooling from the melt, and the mesophase remains frozen-in at room temperature.

Above melting, all of the samples exhibit a disordered smectic phase with a layer thickness d ≈ 37-38 Å and an interchain distance D ≈ 4.4 Å (Fig.1c). The smectic interlayer distance is in any case a little longer than the length of the fully stretched repeating unit (L = 36 ±1 Å), and the mesophase must be of the A type. The relatively low intensity and sharpness of the small angle peak indicate the existence of a small concentration of packed layers of structural units with a short-range positional correlation in the smectic phase[10]. On the other hand, one may note the diffuse signal corresponding to a periodicity of about 9 Å (Fig.1c), which originates from domains consisting of laterally paired polymeric segments stabilized by interlocking alkyl substituents.

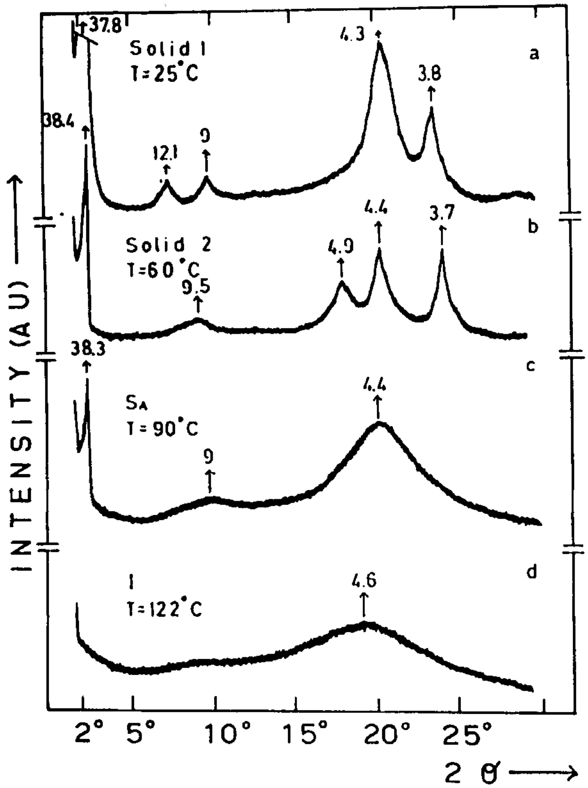

FIGURE 1 X-ray diffraction diagrams with Bragg periodicities of polymalonate 3 at different temperatures

The smectic A phase is stable up to the isotropic melt (Fig.1d), the mesophase range being particularly broad for sample 1 (80-90°C) (Fig.2). Differences are only observable in the distinct thermal changes of the mesophase structure of the polymers with reference to the smectic layer thickness d (Fig.2). In particular, d monotonously decreases, with increasing temperature of sample 1, from 37.0 to 35.5 Å, indicating a progressive deviation of the polymer repeating unit from its fully extended conformation. The transition temperatures in Fig.2 and Tab.I refer to the completed phase transitions as revealed by X-ray analysis and consistently are higher than those determined by DSC[5]. This also shows that relatively broad biphasic intervals exist at the various phase

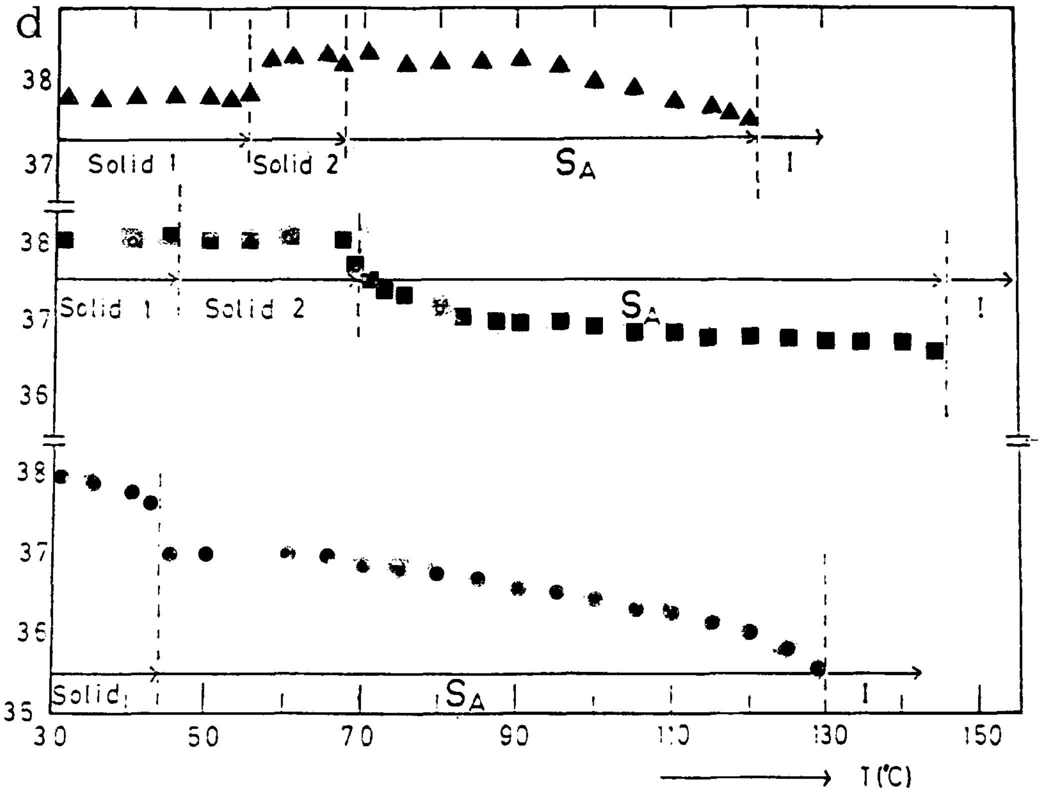

FIGURE 2 Variation of the layer thickness d/Å with increasing temperature of polymalonates 1 (●), 2 (■), and 3 (▲)

transitions of the polydisperse samples, with the most evident biphasic gap being detected at the isotropization of polymalonate 2.

CONCLUSIONS

The three polymalonates investigated exhibit one broad smectic A phase, even in spite of the prevalent chirality of the malonyl residue in sample 3. This is in contrast with what is found with various side chain polyacrylates and polymethacrylates for which minor structural changes in the terminal alkyloxy substituent on the azobenzene mesogens resulted in significant variations of the mesomorphic properties[5,6]. The smectogenic tendency of the molecular system should be maximized in combined polymalonates[7], in which the fixation of mesogenic side groups to the flexible main chain spacers favours peculiar packings of both types of mesogens[11,12].

REFERENCES

1. M.Eich, J.H.Wendorff, B.Reck, and H.Ringsdorf, Makromol.Chem., Rapid Commun., **8**,59(1987).
2. I.Cabrera, V.Krongauz, and H.Ringsdorf, Angew.Chem., Int.Ed.Engl., **26**,1178(1987).
3. D.Creed, A.C.Griffin, J.R.D.Gross, C.E.Hoyle, and K.Venkataram, Mol.Cryst.Liq.Cryst., **155**,57(1988).
4. K.Ichimura, Y.Suzuki, T.Seki, Y.Kawanishi, and K.Aoki, Makromol.Chem., Rapid Commun., **10**,5(1989).
5. A.S.Angeloni, D.Caretti, C.Carlini, E.Chiellini, G.Galli, A.Altomare, and R.Solaro, M.Laus, Liq.Cryst., **4**,513(1989).
6. A.S.Angeloni, D.Caretti, C.Carlini, M.Laus, E.Chiellini, G. Galli, A.Altomare, and R.Solaro, Gazz.Chim.Ital, in press.
7. B.Reck and H.Ringsdorf, Makromol.Chem., Rapid Commun., **6**, 291(1985).
8. B.Reck and H.Ringsdorf, Makromol.Chem., Rapid Commun., **7**, 389(1986).
9. R.Zentel and G.Reckert, Makromol.Chem., **187**,1915(1986).
10. V.V.Shilov, V.V.Tsukruk, and Yu.S.Lipatov, J.Polym.Sci., Polym.Phys.Ed., **22**,21(1984).
11. R.Zentel, G.F.Schmidt, J.Meyer, and M.Benalia, Liq.Cryst., **2**,651(1987).
12. I.G.Voigt-Martin and H.Durst, Macromolecules, **22**,168(1989).

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