Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Nematic and Cholesteric Thermotropic Azoxy Polyesters with Moderately Low Transition Temperatures

A. Blumstein [a] & S. Vilasagar [a]
[a] Polymer Program, Department of Chemistry, University of Lowell, Lowell, Massachusetts, 01854

Version of record first published: 21 Mar 2007.

To cite this article: A. Blumstein & S. Vilasagar (1981): Nematic and Cholesteric Thermotropic Azoxy Polyesters with Moderately Low Transition Temperatures, Molecular Crystals and Liquid Crystals, 72:1, 1-8

To link to this article: http://dx.doi.org/10.1080/01406568108084029

Mol. Cryst. Liq. Cryst. Vol. 72 (Letters), pp. 1-8
0140-6566/81/7201-0001$06.50/0

NEMATIC AND CHOLESTERIC THERMOTROPIC AZOXY POLYESTERS WITH MODERATELY LOW TRANSITION TEMPERATURES

A. BLUMSTEIN AND S. VILASAGAR

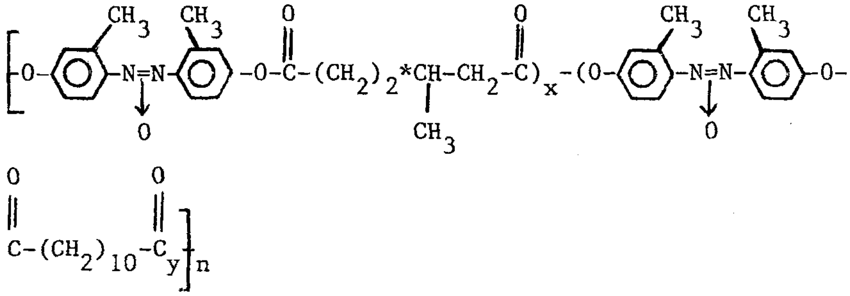
Polymer Program, Department of Chemistry, University of Lowell, Lowell, Massachusetts 01854

(Submitted for Publication February 9, 1981)

ABSTRACT

The synthesis and properties of a new nematic and twisted nematic polyester system based on 4,4'azoxy-2,2'methylphenyl moiety separated by flexible spacers with an asymmetric center in the backbone is described. The polymers of the system have moderately low transition temperatures and are well soluble in various solvents. The polyesters described flow easily and give characteristic textures of nematic and cholesteric fluids including selective reflections of light. The thermal properties of these polyesters indicate an increase of isotropisation entropy with the increase of average spacer length.

We have described recently (1,2) the synthesis and properties of some linear smectic, nematic and novel cholesteric thermotropic polyesters. A large number of papers have recently appeared in the literature describing similar systems (see for example 3-9). The identification of polymeric mesophases is often not easy to establish. Due to high viscosity, broad molecular weight distributions, coexistance of poly-crystalline and amorphous material microscopic observation of specific textures can be misleading. Differential scanning colorimetry is also complicated by the very same factors. These factors make the interpretation of D.S.C. traces much more difficult for mesomorphic polymers than for the corresponding low molecular liquid-crystals. X-ray patterns may be of help in the case of smectic mesophases. They are, however, often too diffuse to be used for unoriented nematic or cholesteric phases. A need exists, therefore, to synthesize polymers with non-equivocal mesophase behavior. Aliphatic polyesters based on 4,4'azoxyphenol, give on heating textures characteristic of nematic and cholesteric phases (2). Their synthesis and characterization are easy. The systems described previously (2) have high transition temperatures which makes their study difficult. In this paper the synthesis and some preliminary studies are described for low-melting polyesters based on the 2,2'methylazoxybenzene moiety (this mesogenic group is being denoted as n°9 in our mesogenic series) and flexible spacers composed of (+3)methyladipic (MAA*) and dodecanedioic (DDA) acids. The repeat unit is as follows:



Three polymers are described below:

(a) x = 0; y = 1

(b) x = 1; y = 0

(c) x = .5; y = .5

EXPERIMENTAL:

The 4,4'hydroxy, 2,2'methylazoxybenzene was prepared according to literature procedures (10,11). The acid chlorides were prepared from corresponding acids and thionyl chloride. The diols were obtained from commercial sources.

In a typical interfacial polyesterification reaction, 1 mol of bisphenol and 2 mol of NaOH were dissolved in water. Benzyltriethylammoniumchloride, in amounts of about 10 wt % of the theoretically expected polymer, was added and the contents were stirred vigorously. Diacid chloride (1 mol) dissolved in dichloroethane was then added very rapidly and the stirring continued at room temperature for one hour. The slurry was poured into an excess of methanol and the precipitated polymer was filtered and washed with methanol. The polymer was purified by extraction with methanol in a Soxhlet apparatus for 24 hours and dried in vacuo at 60°C. Yields of the polymers ranged from 90 to 95%.

Elemental Analysis:

		Calculated:			Found:		
	Polymer	C	H	N	C	H	N
(a)	DDA-9	69.00	7.13	6.19	68.77	7.20	6.09
(b)	MAA*-9	65.95	5.80	7.33	66.03	5.87	7.30
(c)	MAA*/DDA-(50/50)-9	67.62	6.53	6.71	67.75	6.59	5.68

Textures of polymers were studied between slide and coverslip using a Leitz Ortholux polarizing microscope equipped with a hot stage and a Mettler FP-52 temperature programmer. The polymers were characterized by intrinsic viscosity in 1:1 (wt) m-cresol:chloroform at 30°C and by number average molecular weight $\overline{M}_n$ determined with a vapor pressure osmometer using a Knauer V.P.O. apparatus. The thermal properties were investigated by means of a Perkin Elmer B-1 Differential Scanning calorimeter.

RESULTS AND DISCUSSION:

As we have pointed out previously (2), the polyesters derivatives of azoxyphenol display spontaneously typically nematic and cholesteric textures between slide and cover-glass. However, the high transition temperatures characterizing these polymers infringing on their partial decomposition led us to synthesize the 2,2'methyl derivative of the azoxyphenyl moiety, which is characterized by significantly lower transition temperatures as it can be seen in Table 1.

TABLE 1 PROPERTIES OF MAA*/DDA-9 POLYESTERS

Composition	Trans-itions °C	ΔH_1 $\frac{\text{Kcal}}{\text{mru}}$	ΔH_2 $\frac{\text{Kcal}}{\text{mru}}$	ΔS_2 $\frac{\text{cal}}{\text{mole °K}}$	$[\eta]$ $\frac{\text{dl}}{\text{g}}$	$\bar{M}_n$
(a) DDA-9	K118N162I	1.39	1.37	3.19	0.62	11,700
(b) MAA*-9	K151N210I	0.41	0.73	1.51	0.42	7,800
(c) MAA*/DDA-9	K76N178I	0.25	0.95	2.11	0.58	10,800

While the values of ΔH_1 and ΔH_2 depend on the thermal history of the sample (as it is frequently observed in polymers) the position of peaks does not. The entropy of isotropisation ΔS_2 is very high in comparison with ΔS_2 values for low molecular nematic compounds and decreases consistently with the average spacer length (14 spacer atoms for DDA-9, 11 for MAA*/DDA-9 and 8 for MAA*-9).

Chirality and Formation of Cholesteric Phases:

As we have noted previously (2) the chiral system MAA*/DDA-8 (where MAA* symbolizes the (+)3,methyladipic acid unit in the flexible spacer) induces cholesteric behavior characterized by irridescence due to selective reflexions of light. We have also indicated that the pitch of the cholesteric helix decreases with the increase in the content of the chiral MAA* units. This is in agreement with previous results of Finkelmann (12) for polymers containing mesogenic and chiral elements in the side group.

As has been pointed out (2,13), the MAA*/DDA-8 system displays at about 230°C for 70/30 - 60/40 composition a blue irridescence which passes for 50/50 to yellow green, than for 40/60 to orange-red. Other compositions on both sides of this interval do not give any visible selective reflexions but present under slide and cover glass "oily streak" textures characteristic of cholesteric mesophases.

The system MAA*/DDA-9 is also irridescent in blue for 50/50 at 140-160°C (see Fig. 1), but unlike in the system 8 the irridescence can be "locked in" by cooling.

Orientation:

As has been pointed out in a recent paper (13) the racemic system 8 orients easily in a field of 12-16 Tesla in its nematic state whilst the chiral system 8 in its cholesteric state does not orient. The system 9 also orients well in magnetic fields in its nematic state, whereas the cholesteric system does not orient (14). Both systems give X-ray patterns characteristic of polycrystalline materials at room temperature. Table 2 gives some representative X-ray spacings.

TABLE 2

	Polymer	Spacings Å
(a)	DDA-9	3.70;4.08;4.38;4.62;7.28;11.64
(b)	MAA*-9	3.94;4.95
(c)	MAA*/DDA-9	3.70;4.04;4.36;4.59;7.03;11.28

Above the first transition temperature all polymers gave diffuse halos around 4.9-5.3Å indicating the absence of a smectic order. The DDA component of the flexible spacer has the predominant tendency to crystallize.

In this work a new cholesteric and nematic polyester system is described with moderately low transition temperatures. In spite of substantial molecular weights the polymers flow easily and give characteristic textures of nematic and twisted nematic systems. The system -9 can be studied in solution and isotropic melt. The results of such studies are reported elsewhere (15). The study of thermal properties indicate a high value of isotropisation entropy ΔS_2 in agreement with recent results on another mesogenic system (4). The value of ΔS_2 increases consistently with the average length of the methylene sequence (and decreases with the MAA* content). This result does not favor a totally random conformation of the spacer chains in the nematic state such as proposed in (4). The X-ray diffraction of a melt extruded fiber (4) indicates an extended conformation for this type of polymers. The fiber period found by us on the MAA-8 polymer oriented in the magnetic field indicates also an extended chain conformation in the crystallites (14). On the other hand, the measurements of the Cotton-Mouton constant of isotropic melts performed on similar systems (15) indicate a random coiled chain conformation at temperatures beyond the N/I transition. The conformation in the nematic state is probably between both extremes and our results favor a partial orientation of the flexible spacer in the unoriented nematic state. A more detailed description of mesogenic polymers with azoxyphenyl moieties will be given elsewhere.

ACKNOWLEDGEMENT:

The support of the National Science Foundation's Polymer Program under Grant DMR-7925059 is gratefully acknowledged.

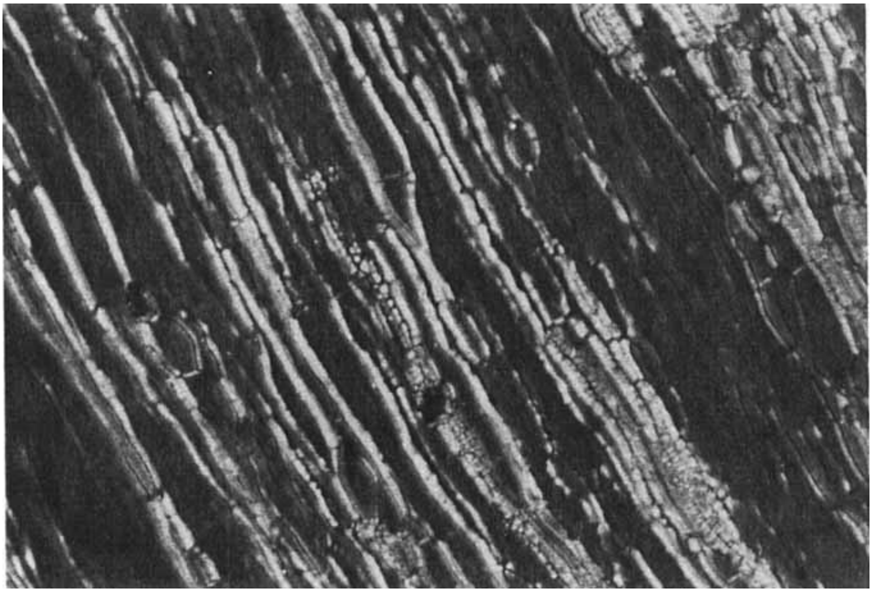


FIGURE 1 Polymer MAA*/DDA-9 cholesteric mesophase blue irridescent background with "oily streaks" t° 160°C Magn. 320X.

REFERENCES:

1. A. Blumstein, K.N. Sivaramakrishnan, S.B. Clough, and R.B. Blumstein, Polymer Preprints, 19, 2, (1978); Mol. Cryst. Liq. Cryst. (letters) 49, 255 (1979).
2. S. Vilasagar and A. Blumstein, Mol. Cryst. Liq. Cryst. 56, 263 (1980).
3. A. Roviello and A. Sirigu, Europ Polymer J., 15, 61 (1979).
4. A. Roviello and A. Sirigu, Makromol. Chem., 181, 1799 (1980).
5. D. Guillon and A. Skoulios, Mol. Cryst. Liq. Cryst. (letters) 119 (1978).

6. B. Millaud, A. Thierry, C. Stratielle and A. Skoulios, Mol. Cryst. Liq. Cryst., 49, 299 (1979).
7. L. Strzelecki and D. van Luyen, Europ. Polym. J., 16, 299, 303 (1980).
8. B. Fayolle, C. Noel and J. Billard, J. Phys. (Colloque C3) Suppl. 40, 485 (1979).
9. A.C. Griffin and S.J. Hasens, Mol. Cryst. Liq. Cryst. (letters), 49, (1979).
10. N.J. Leonard and J.W. Curry, J. Org. Chem., 17, 1071 (1952).
11. R.A. Raphael and E. Vogel, J. Chem. Soc., Pt. 2, 1958 (1952).
12. Finkelmann, J. Kaldehoff and H. Ringsdorf, Angew. Chem. Int. Ed. Encl., 17, 935 (1978).
13. G. Maret, A. Blumstein and S. Vilasagar, Polymer Preprints, 22, 1 (1981).
14. G. Maret and A. Blumstein, Macromolecules (in preparation).
15. A. Blumstein, G. Maret and S. Vilasagar, Macromolecules (in print).