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

The Existence of Two Distinct Levels of Order in Thermotropic Nematic Polyesters

A. Blumstein [a] , R. B. Blumstein [a] , M. M. Gauthier [a] , O. Thomas [a] & J. Asrar [a]
[a] University of Lowell, Department of Chemistry, Polymer Program

Version of record first published: 21 Mar 2007.

To cite this article: A. Blumstein , R. B. Blumstein , M. M. Gauthier , O. Thomas & J. Asrar (1983): The Existence of Two Distinct Levels of Order in Thermotropic Nematic Polyesters, Molecular Crystals and Liquid Crystals, 92:3, 87-97

To link to this article: http://dx.doi.org/10.1080/01406568308084524

Mol. Cryst. Liq. Cryst. Vol. 92 (Letters), pp. 87-97
0140-6566/83/9203-0087$18.50/0

Printed in the United States of America

THE EXISTENCE OF TWO DISTINCT LEVELS OF ORDER IN THERMOTROPIC NEMATIC POLYESTERS

A. BLUMSTEIN, R. B. BLUMSTEIN, M. M. GAUTHIER,
O. THOMAS AND J. ASRAR
University of Lowell, Department of Chemistry,
Polymer Program

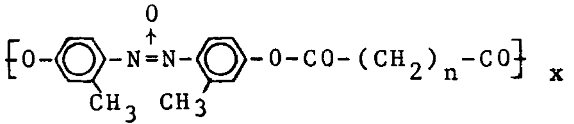
(Received for Publication June 8, 1983)

ABSTRACT

It is shown by means of x-ray diffraction and PMR broad line spectroscopy, that the structure of the flexible spacer drastically influences the order within the nematic phase of thermotropic polyesters based on the 4,4'-dioxy-2,2'-dimethyl azoxybenzene moiety. The existence of two distinct molecular arrangements is proposed: one is characterized by an unusually high degree alignment of macromolecules, the other by a lower degree of alignment. The former is displayed by spacers with an even number of methylene units in the alkanedioic acid moiety of the spacer (odd number of bonds); the latter by a certain number of flexible spacer moieties with an odd number of methylene groups (even number of bonds), as well as in mixed spacers irregularly alternating along the macromolecular chain (copolyesters).

The isotropic-nematic transition in linear thermotropic polymers composed of alternating rigid mesogenic and flexible "spacer" moieties is characterized by a degree of orientational and conformational ordering which has not yet been systematically investigated. Such studies would be desirable in view of the potential applications of these systems; they would also serve to check the validity of theoretical treatments developed for semiflexible nematic polymers. Influence of chain flexibility, molecular structure, chain length and chain length distribution on phase transitions and phase alignment requires investigation.

We have recently begun to carry out a detailed study of some of these factors through a synthesis and characterization of homologous series of nematic polyesters



$$\left[O-C_6H_3(CH_3)-\overset{O}{\overset{\uparrow}{N}}=N-C_6H_3(CH_3)-O-CO-(CH_2)_n-CO \right]_x$$

based on 4,4'-dioxy-2,2'-dimethyl azoxybenzene (mesogen 9) and alkanedioyls with spacer length n = 2 - 14 (1,2). The I → N transition of these polymers, a investigated by measurement of magnetic birefringenc (2,3) is characterized by drastic intramolecular conformational changes from randomly coiled chains to chains with a high degree of alignment.

For poly(4,4'-dioxy-2,2'-dimethylazoxybenzene dodecanedioyl)-polymer DDA9, with spacer length n = 10, chain extension in the nematic phase was demonstrated by the strong cooperative increase of both the isotropization entropy, $\Delta S_{IN}(\overline{M}_n)$, (4) and the nematic order parameter, $S(\overline{M}_n)$, (5) with increasing molecular weight. Development of a polymeric mesophase, as characterized by maximum local chain extension, appears to require cooperactivity between some 8 to 10 repeating units per chain (4,5). We have proposed for the nematic state of DDA9 a "cybotactic" nematic model (1) similar to that introduced by de Vries (6) for low molecular mass n-alkoxyazoxybenzenes. Evidence for this model was drawn from SAX data obtained for a quenched oriented nematic sample (1) and PMR lineshape analysis (7). In what follows we present evidence in support of the existence of two distinct degrees of ordering in polymeric mesophases based on mesogen 9: a cybotactic nematic phase similar to that described for DDA-9 (1), and an "ordinary" nematic phase characterized by a considerably smaller degree of order. The former molecular organization is observed for polymers containing an even number of methylene units, such as n = 4,6,8,10,12 and 14, the latter for n = 5,7,9 and 11, or copolymers of mesogen 9 with two spacers of different length and structure.

EXPERIMENTAL

The synthesis of polyesters and copolyesters I was described previously (1,2). Fractional precipitation using DMF-water solvent precipitant couple yielded fractions of polyesters used in this study. The orientation in the magnetic field of 10 Tesla was done as described in (1); in addition, the specimens were oriented in fields of 2.5T., x-ray photographs were taken at room temperature using a flat plate camera, Ni-filtered Cu-α radiation with a sample to film distance of 8 cm. The order parameters were determined from broad line PMR spectra using a Bruker CXP-100 instrument as described in (7). The thermal data were obtained by means of a Perkin Elmer 2C as described in (2) and (4).

Figs. 1 and 2 give x-ray diffraction pictures of two polyesters with n = 10 (DDA-9) and n = 7 (AZA-9) respectively. In both cases the molecular mass was low enough to procude an easy orientation of the thermotropic nematic phase by a field of 10 Tesla, but high enough to avoid crystallization on cooling. The x-ray patterns in Fig. 1 and Fig. 2 are different: while for n = 10 the pattern is similar to the patterns prevalent in the low molecular mass oriented "cybotactic" nematics (such as alkoxyazoxybenzenes (6)) the pattern for n = 7 is typical of an ordinary oriented nematic.

The pattern of Fig. 1 is typical of n = 6,8,12 and 14, while the pattern of Fig. 2 is typical of n = 5,7,9 and 11.

Fig. 1. DDA-9 (n = 10) polyester, T_{NI} = 123.6°C, $\overline{M}_n$ = 3,200, heated to 155°C in a magnetic field of 10 Tesla, and quenched at 118°C to room temperature at 100°/min. Picture is typical of n = 4,6,8,12,14.

Fig. 2. AZA-9 (n = 7), Polyester T_{NI} = 90°C, $\overline{M}_n$ = 2,000, heated to 90°C in a magnetic field of 10 Tesla and quenched at 73°C to room temperature at 100°/min. Picture is typical of n = 5,9 and 11.

Both types of polymeric nematics are totally miscible (8) as in the case of low molecular cybotactic and ordinary nematics. In contrast to low molecular weight alkoxyazoxybenzenes which displayed four maxima SAX patterns for n = 2,4,5,6,7,8,9,10, i.e. for odd <u>and</u> even number of bonds in the terminal chains (9), the pattern of four maxima is displayed in the polymer preferentially for even n (or an odd number of bonds in the spacer). This pattern of four SAX maxima can be disrupted by copolymerization of two spacers with widely differing structure and concomitant introduction of randomness in the chain, as it was shown in the case of a copolymer based on mixed spacers of 3,3 dimethylglutaric acid and dodecanedioic acid (14).

Fig. 3 shows the evolution of the dipolar splitting $2\delta_N$ upon cooling from the isotropic phase for a DDA-9 sample of $\overline{M}_n$ = 4,800 (sample DDA-9LII) and a AZA-9 fraction of $\overline{M}_n$ = 4,100. The double-headed arrows on Fig. 3 indicate the range of the nematic-isotropic biphasic region (N + I biphase). The DDA-9 sample has a dispersity index of $\sim$1.5, whereas AZA-9 is a narrow fraction, with a corresponding narrow N + I biphase. Both samples are completely aligned in the nematic phase. The nematic order parameter S associated with the mesogenic moiety was deduced from the value of $2\delta_n$ as described in reference (7). In the homogeneously oriented samples, values of S range from 0.75 to 0.85 for DDA-9LII and from 0.48 to 0.68 for AZA-9. Incipient crystallization destroys alignment of the supercooled nematic phase in both instances. The ondulations in the curves $2\delta_N$ (temp.) do not seem to be an artifact and will be discussed elsewhere.

The values of the order parameter S observed for polymer AZA-9 are comparable to those found in the case of low molecular mass LC; for PAA, for example, the values of S range from S_c = 0.405 at the nematic transition temperature T_c to S_{max} = 0.76 for the supercooled mesophase (10). Polymer DDA-9, on the other hand, displays a high degree of orientational order. This high degree of alignment extends to the spacer, as shown by PMR line shape analysis (7) and deuterium magnetic resonance (11).

Due to the existence of the biphasic region the exact location of the nematic-isotropic transition temperature T_c is difficult to establish in

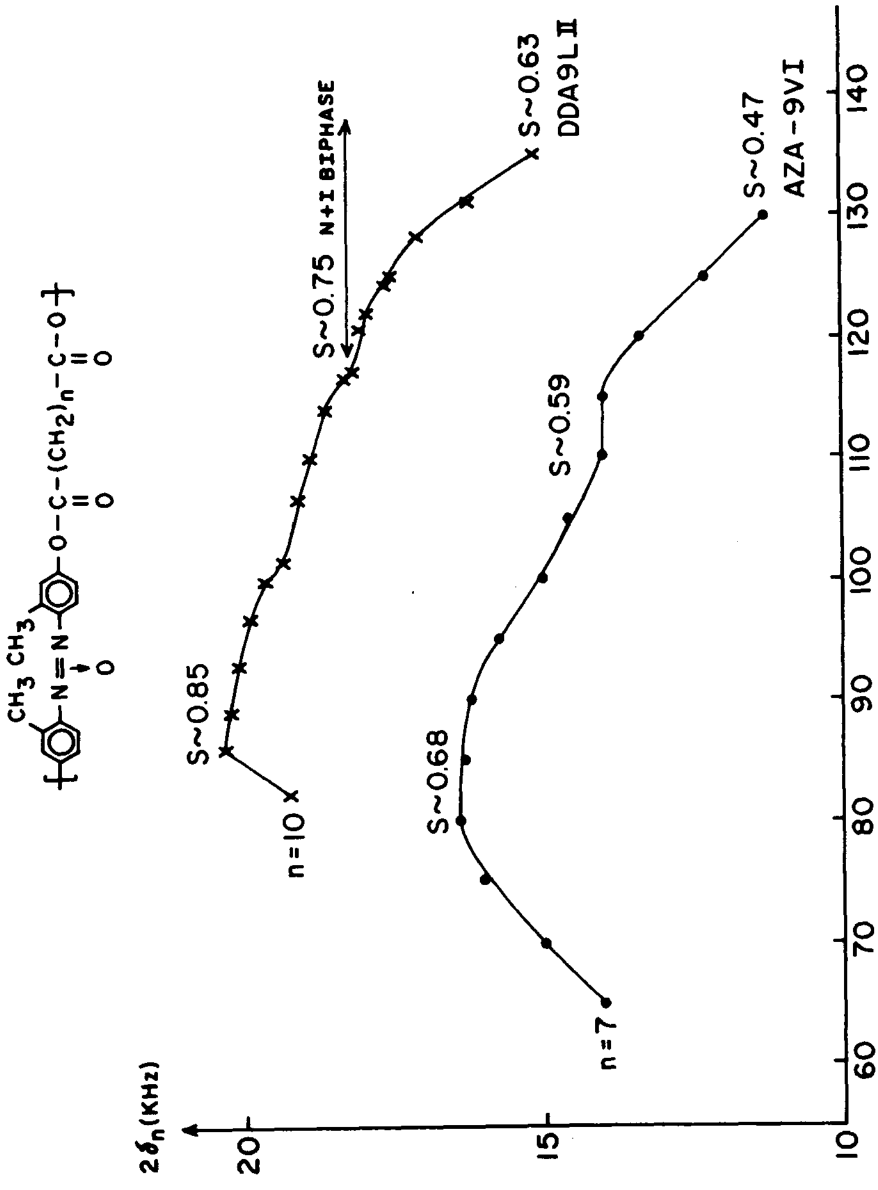

2δn (KHz)
20
15
10
60
70
80
90
100
110
120
130
140
n=10
S~0.85
S~0.75
N+I BIPHASE
S~0.63
DDA9L II
n=7
S~0.68
S~0.59
S~0.47
AZA-9VI
CH3 CH3
N=N
O
O-C-(CH2)n-C-O
O
O

Fig. 3.

the case of polymers, theoretically and experimentally. The value of the DSC peak maximum T_{NI}, which is located within the biphasic region, can be used as a reasonable first approximation (5). We can also determine T_c from magnetic birefringence measurements (12) as the temperature at which the optical transmission has decayed, on cooling through the pretransitional state, to half its maximum value. The values of S_c, calculated from the pretransitional temperature dependence of magnetic birefringence using the Landau de Gennes theory (13), are in excellent agreement with the values measured by PMR at $T = T_{IN}$, for DDA-9 and AZA-9.

Finally, the variation of $\Delta S_{IN}(\overline{M}_n)$ suggests a much smaller increase in conformational and orientational entropy and very little cooperactivity between repeating units in the case of AZA-9 (14), compared to DDA-9 (4). At saturation, the values of isotropization entropies are 12.9 and 35.9 J/Kg · degree, respectively; the former being comparable to the isotropization entropies of classical low molecular mass nematics.

A simple tentative explanation can be advanced if one considers that in an alkyl chain attached at one point to a mesogenic core the probability of trans/gauche $\pm$ conformers is significantly enhanced for the first 3 even bonds (15). If both ends of the chain are attached, this enhancement will propagate along the chain from the attachment points in opposite directions (11). Destructive interference can then be expected in the case of an even number of bonds (n odd) and hence a lowering of the average ratio of t/g ± conformers can be expected. A spacer with an odd number of bonds (n even) would conversely favor an enhancement of the t/g ± ratio with a concomitant increase in the tendency to align.

These data which point toward the existence of two distinct nematic arrangements of molecules with widely differing order parameters may explain the apparent discrepancy between the high order parameters reported for the polyester DDA-9 (7, 16) and the lower degree of alignment reported for a polyester based on 1,4-dihydroxyphenylbenzoate and pentanedioic acid (17).

We believe that the system described above is particularly well suited for the study of structure-property correlations because of low transition temperatures. Polyester systems with high transition temperatures such as derivatives of hydroxybenzoic-acid, for example, undergo within the mesophase a reorganization into block copolymers with concomitant chain randomness.

ACKNOWLEDGEMENT

This work was supported by the NSF Polymer Program under Grant DMR 7925059. Thanks are expressed to Dr. G. Maret for performing the orientation experiments in the magnetic field of 10 T.

REFERENCES

1. A. Blumstein, S. Vilasagar, S. Ponrathnam, S. B. Clough, G. Maret, R. B. Blumstein. J. Polymer Sci. Polym. Phys. Ed., 20, 877 (1983).

2. A. Blumstein and O. Thomas. Macromolecules, 15, 1264 (1982).
3. A. Blumstein, G. Maret, S. Vilasagar. Macromolecules, 14, 1543 (1981).
4. R. B. Blumstein, E. Stickles and A. Blumstein. Molec. Cryst. Liq. Cryst. (Letters), 82, 205 (1982).
5. R. B. Blumstein, E. M. Stickles, M. M. Gauthier, A. Blumstein and F. Volino. Macromolecules (in print).
6. A. de Vries, Mol. Cryst. Liq. Cryst., 10, 219 (1970).
7. A. F. Martins, J. B. Ferreira, F. Volino, A. Blumstein and R. B. Blumstein. Macromolecules, 16, 279 (1983).
8. J. Billard, A. Blumstein and S. Vilasagar. Mol. Cryst. Liq. Cryst. (Letters), 82, 205 (1982).
9. I. G. Chistyakov and W. M. Chaikovsky. Mol. Cryst. Liq. Cryst., 7, 269 (1969).
10. E. G. Hanson, Y. R. Shen. Mol. Cryst. Liq. Cryst. 231, 193 (1976).
11. E. T. Samulski, M. M. Gauthier, R. B. Blumstein and A. Blumstein. Macromolecules (submitted).
12. G. Maret, F. Volino, R. B. Blumstein, A. F. Martins and A. Blumstein. Proceedings of 27th IUPAC Strasborg, Vol. II, 973 (1981).
13. G. Maret. Polymer Preprints, ACS Meeting, Washington, D. C., August, 1983.
14. A. Blumstein, O. Thomas, J. Asrar, P. Makris, S. B. Clough and R. B. Blumstein. J. Polymer Sci. (Letters) (submitted).

15. E. T. Samulski and R. Dong. J. Chem. Phys., 77, 5090 (1982).

16. F. Volino, A. F. Martins, R. B. Blumstein and A. Blumstein. J. Physique (Letters), 42, L-305 (1981).

17. L. Liebert, L. Strzelecki, D. van Luyen and A. M. Levelut. Europ. Polymer J., 17, 71 (1981).