²H NMR study of phase transitions and orientational order in a side chain liquid crystal polymer: Evidence of a nematic-nematic transition

R. Muzzalupo[a]; G. A. Ranieri[a]; D. Catalano[b]; G. Galli[b]; C. A. Veracini[b]

[a] Dipartimento di Chimica, Universitá della Calabria, Arcavacata di Rende, Italy [b] Dipartimento di Chimica e Chimica Industriale, Universitá di Pisa, Pisa, Italy

PLEASE SCROLL DOWN FOR ARTICLE

^{2}H NMR study of phase transitions and orientational order in a side chain liquid crystal polymer: Evidence of a nematic–nematic transition

by R. MUZZALUPO, G. A. RANIERI

Dipartimento di Chimica, Universitá della Calabria,

87036 Arcavacata di Rende, Italy

D. CATALANO, G. GALLI and C. A. VERACINI*

Dipartimento di Chimica e Chimica Industriale, Universitá di Pisa,

56126 Pisa, Italy

We have investigated the mesomorphic behaviour of a partially deuteriated side chain LC polymethacrylate, poly[4-[6-methacryloyloxyhexyl-oxy]-4′-methoxyazobenzene], by means of ^{2}H NMR, DSC and optical microscopy. Evidence for a phase transition occurring in the middle of the nematic phase has been found.

1. Introduction

A wide variety of different side chain liquid crystal (LC) polymers has already been synthesized and characterized [1]. In particular, there is a growing interest in the properties of azobenzene-containing side chain LC polymers, because of their photoresponsive properties and their potential application in electro-optics and non-linear optics [2]. ^{2}H NMR has proven to be a successful technique in the study of the molecular order, phase transitions and dynamics of LC polymers [3]. In this paper we report preliminary results of a ^{2}H NMR investigation of a side chain LC polymethacrylate, poly[4-[6-methacryloyloxy-hexyl-1-oxy]-4′-methoxyazobenzene], deuteriated as sketched in figure 1.

2. Results

The mesophasic behaviour of this polymer sample ($\bar{M}_n = 50\,000$, $\bar{M}_w/\bar{M}_n = 2\cdot8$ by SEC) was followed by DSC and optical microscopy and by ^{1}H transverse-relaxation measurements (T_2^*). The phase transition temperatures (with enthalpies in kJ (mol repeat unit)$^{-1}$) were determined by DSC on heating (see figure 2) and are summarized as follows:

g 75°C S$_A$ 91°C (1·4) X 112°C ($\approx 0\cdot5$) N 132°C (1·2) I
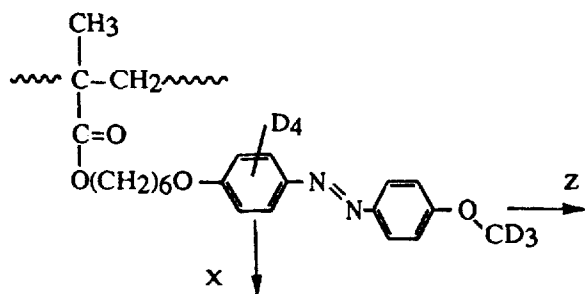
Figure 1.   Polymer structure and reference axis system.

* Author for correspondence.
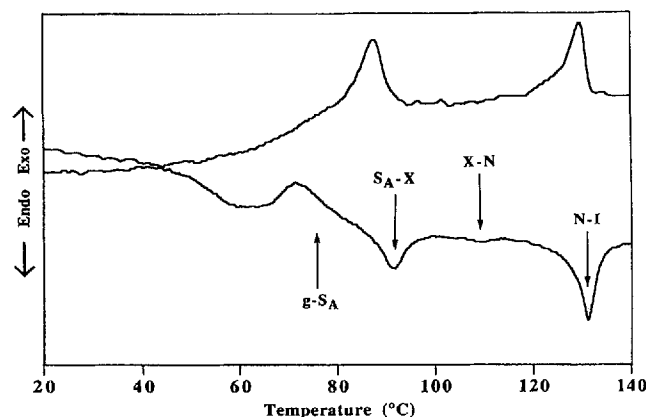

Figure 2.   DSC heating and cooling curves (10 K min^{-1}) for the deuteriated polymethacrylate (g: glass; S$_A$: smectic A; X: provisionally unidentified mesophase; N: nematic; I: isotropic).

The existence of smectic A and nematic mesophases ($S_A \approx 95°C$ N $\approx 140°C$ I) had already been established by various techniques for analogous polymethacrylates, either non-deuteriated or deuteriated at different positions [4]. In the present polymer sample, an additional transition to a provisionally unidentified mesophase X was detected at 112°C. There was a rather low enthalpy change associated with this transition (≈ 0.5 kJ (mol repeat unit)$^{-1}$), suggesting that there may be only a small variation in the order of the two phases. However, this could not be confirmed by polarizing optical microscopy observations, as no specific optical textures were developed by the polymer samples event after annealing for long periods of time. The above transitions were reversible on cooling, the formation of the smectic phase occurring with limited supercooling at 88°C. This is due to the close proximity of this transition to the glass temperature ($T_g = 75°C$) A detailed X-ray diffraction investigation of the deuteriated sample is in progress.
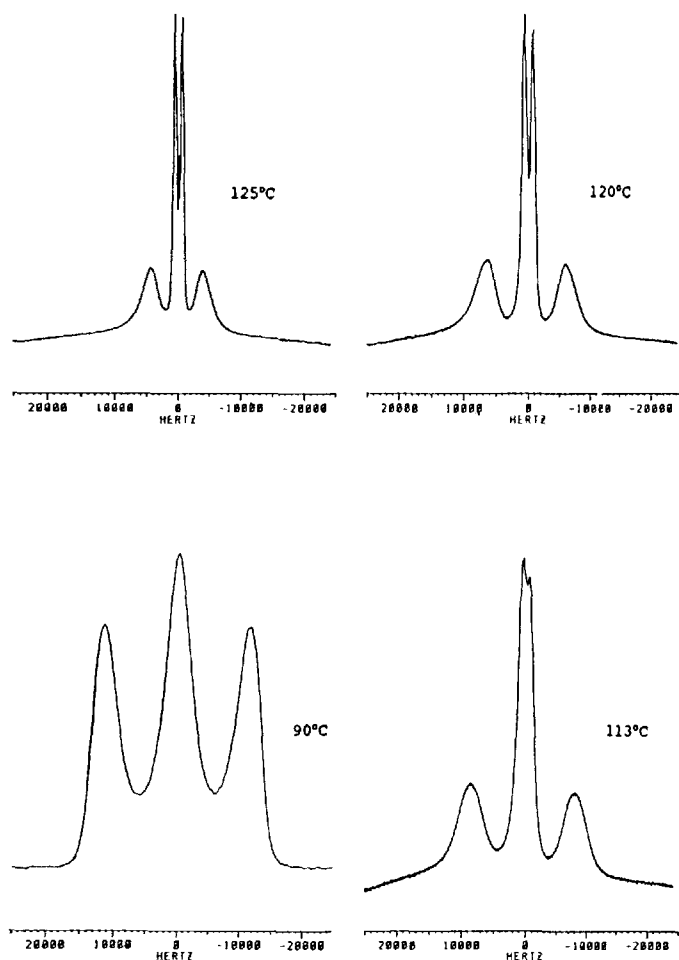
In figure 3, some ^2H NMR spectra recorded for the polymer sample at various temperatures are shown as typical examples; in figure 4 the quadrupolar splittings attainable from the recorded spectra are plotted versus temperature. The sample displays an isotropic phase above 130°C. On cooling to 89°C a marked jumped in the aromatic deuteron splitting corresponds with the X–S_A transition. Below 67°C, the splitting does not increase further, as the order degree of the smectic phase is locked in. The small splitting of the methoxy deuterons presents a maximum at 117°C. Below this temperature, the splitting rapidly decreases until, at 107°C, the relevant quadrupolar doublet collapses into one single, broad peak. This behaviour is reminiscent of that found for the quadrupolar splittings of the terminal methyl deuterons of 4-n-octyl-4'-cyanobiphenyl at the N–S_A transition [5]. The main peculiarity of the trends in figure 4, however, is the discontinuity detected at 112°C for both the aromatic and methoxy deuteron splittings. This is particularly evident in the latter case. Such discontinuities occurring in the middle of the nematic range could point to the presence of a phase transition X–N, as also revealed by DSC at the same temperature. Before discussing the nature of this transition, we will analyse the quadrupolar splittings in terms of the order parameters of the mesogenic moiety. The procedure that we follow is necessarily approximate; a detailed discussion of the determination of the
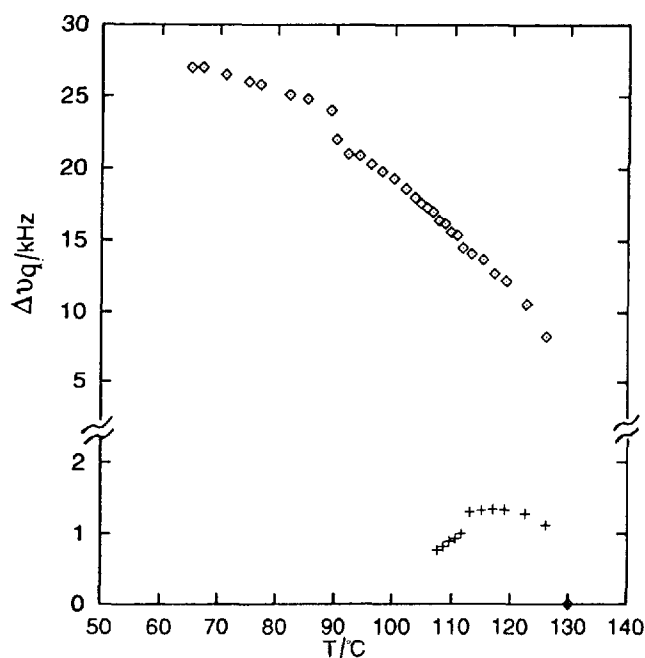

Figure 3. ^2H NMR spectra of the polymer at various temperatures.

Figure 4. Quadrupolar splittings of aromatic ($\Diamond$) and (+) methoxy deuterons versus temperature. Different vertical scales are used.
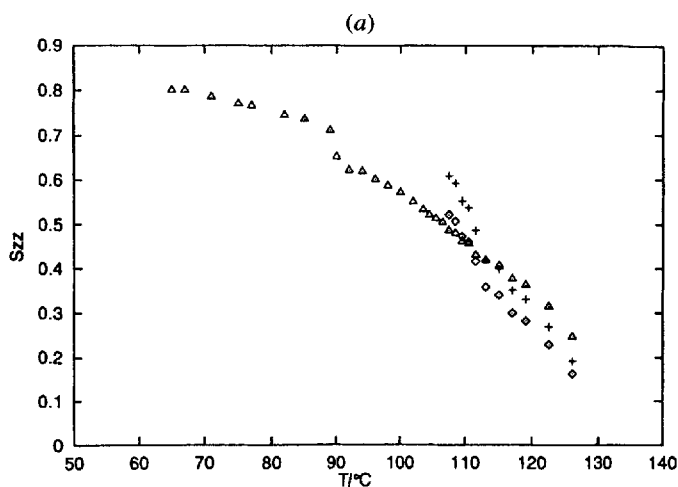
Figure 5. (*a*) The order parameter S_{zz} versus temperature. S_{zz} of the deuteriated ring, as computed from equation (1) with the assumptions of negligible η^{ar} and biaxiality (△); S_{zz} of the methoxyazobenzene fragment, as computed from equations (1) and (2) with $\alpha = 0$ (◇) and $\alpha = 1$ (+). (*b*) The order biaxiality $S_{yy} - S_{xx}$ of the methoxyazobenzene fragment versus temperature, as computed from equations (1) and (2) with $\alpha = 0$ (◇) and $\alpha = 1$ (+). (*c*) The biaxiality $S_{yy} - S_{xx}$ as a function of S_{zz} as computed with $\alpha = 0$ (◇) and $\alpha = 1$ (+).
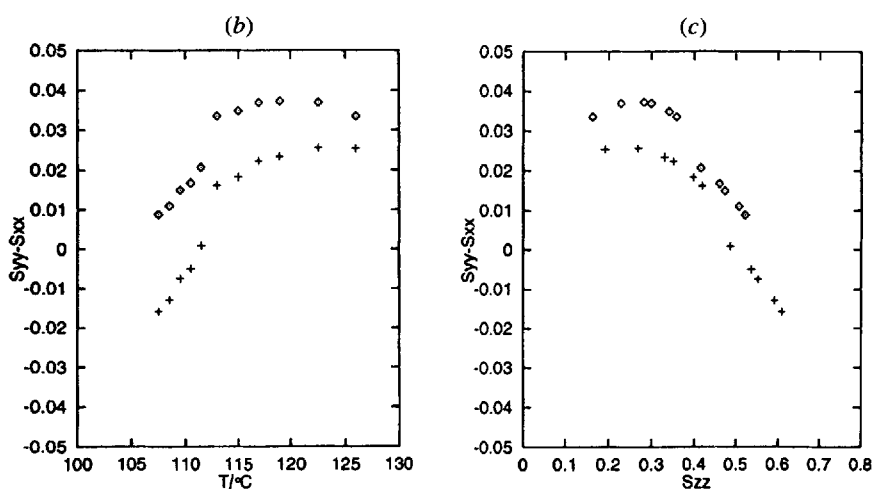
orientational order in LC phases is reported, for instance, in [6].

The data relative to the aromatic deuterons can be used to estimate the order parameter, S_{zz}, of the *para*-axis of the ring by means of equation (1), if we assume a vanishingly small asymmetry parameter η^{ar} for the quadrupolar interaction and the order biaxiality S_{xx}-S_{yy} (see figure 1 for the reference frame); the Δv_q^{ar} values must be negative to implement positive S_{zz} values. Of course, the trend of S_{zz}, plotted in figure 5 (*a*) against the temperature, closely reflects that of the quadrupolar splitting.

The data relative to the aromatic and methoxy deuterons can be used together (see equations (1) and (2)) to evaluate the principal order parameter S_{zz} and the order biaxiality S_{yy}-S_{xx} for the methoxyazobenzene moiety. In fact, all the rotations around single bonds are fast and produce an averaging of the spectra of symmetry-related conformations, for which a reliable geometry can be assumed [7–10]. The aromatic fragment is presumably planar, with

regular hexagonal structures and parallel *para*-axes of the rings (a single splitting has been found for deuterons on different rings in the selectively deuteriated poly-methacrylate, which indicates that the orientational order of the two rings is the same [8]). Moreover, as far as the rotation around the phenyl-OCD_3 bond is concerned, the only populated conformations are those with the C–O bonds in the plane of the rings [9]. Altogether, with the obvious choice of the reference frame shown in figure 1, both experimental splittings depend on the two order parameters S_{zz} and S_{yy}-S_{xx}. The splitting of the methoxy deuterons in principle also depends on the S_{xz} value, which is most probably small, but not necessarily vanishing. We cannot determine three order parameters from two experimental sets of data but we can estimate the importance of neglecting S_{xz} by assuming a rotation of some degree, α for the principal reference frame of S in the xz plane and by expressing S_{xz} as a function of S_{zz}, S_{yy}-S_{xx} and α. The equations we have used are

the following:

$$\Delta v_q^{ar} = (3/4)q^{ar}\{S_{zz}[(3\cos^2\beta^{ar} - 1) + \eta^{ar}\sin^2\beta^{ar}]$$
$$- (S_{yy} - S_{xx})[\sin^2\beta^{ar} + (\eta^{ar}/3)(1 + \cos^2\beta^{ar})]\} \quad (1)$$

$$\Delta v_q^{met} = (3/4)q^{met}\{S_{zz}[(3\cos^2\beta^{met} - 1)$$
$$- (3/4)\sin 2\beta^{met}\tan 2\alpha] - (S_{yy} - S_{xx})[\sin^2\beta^{met}$$
$$+ (1/4)\sin 2\beta^{met}\tan 2\alpha]\} \quad (2)$$

In equation (1), β^{ar} is the angle between the C–D aromatic bond and the z-axis, fixed at 60°; q^{ar} and η^{ar} are assumed to be 180 kHz and 0·04, respectively, two suitable values for aromatic deuterons [11]. The methoxy deuteron quadrupolar splitting can be referred to the threefold rotation axis of the group, with a proper reduction of the quadrupolar coupling constant [12]. Therefore, in equation (2), β^{met} is the angle between the z-axis and the axis of the methyl group, fixed at 124·8° as determined for the C–O–C angle in alkyloxybenzenes [10]; q^{met} is 57 kHz and η^{met} is 0·0. Both experimental splittings have to be chosen negative, in order to obtain a trend in S_{zz} consistent with that found using only Δv_q^{ar}.

The behaviour of S_{zz} and $S_{yy} - S_{xx}$ with varying temperature is reported in figures 5 (a) and (b), respectively, for the two cases of $\alpha = 0$ and 1°; in figure 5 (c) the relationship between S_{zz} and $S_{yy} - S_{xx}$ is shown. The three plots are similar to those typical of low molar mass LCs or of small molecules dissolved in LC phases [13,14], except of the discontinuities at 112°C. At 91°C, there is a jump in the order, typical of the N–S$_A$ first order phase transition. It is evident from figures 5 (a) and (b), as from direct inspection of equations (1) and (2), that the experimental value of Δv_q^{ar} is mainly determined by S_{zz} while Δv_q^{met} is dominated by the small biaxiality $S_{yy} - S_{xx}$. When $\alpha = 1°$ is assumed instead of $\alpha = 0°$, the order parameter trends are shifted, but not substantially varied, and the jump in $S_{yy} - S_{xx}$ at 112°C corresponds to a change of sign of this parameter. Eventually, we can conclude that the discontinuities found for the experimental quadrupolar splittings at 112°C are easily ascribable to jumps in the order parameters, the biaxiality in particular, of the mesogenic moiety at this temperature.

The trends in Δv_q^{ar} (see figure 4) and S_{zz} (see figure 5 (a)) are typical of specific liquid crystal phases. In nematic phases, both $|\Delta v_q^{ar}|$ and S_{zz} rapidly increase with decreasing temperature, whereas in smectic phases they vary much more slowly. Therefore, it might be consistent to associate these results with a phase transition within the nematic phase of the polymer—that is, to identify the X mesophase as a nematic phase. The possible existence of different nematic phases has been claimed with respect to the problem of uniaxial/biaxial nematics [15, 16]. Very recently, a simple model within the molecular field approximation has been proposed to explain the unusual

transitional behaviour of LC dimers; this is also able to predict the occurrence of a first-order nematic-to-nematic transition [17]. The possibility of the existence of various levels of nematic order has also been discussed theoretically for side chain LC polymers [18], and it was suggested that a side chain LC polymer that had been uniaxially oriented under mechanical stress gave rise to two different nematic structures [19]. Examples of nematic-to-nematic transitions have also been theoretically predicted [20] and experimentally provided for completely different main chain LC polymers [21, 22]. Therefore, this question appears to be of very general relevance and further work on this line is in progress.

References

[1] McArdle, C. B., 1989, *Side Chain Liquid Crystal Polymers* (Blackie).
[2] See for instance (a) Anderle, K., Birenheide, R., Eich, M., and Wendorff, J. H., 1989, *Makromolek. Chem., rap. Commun.*, **10**, 477. (b) Ikeda, T., Saski, T., Kurihara, S., and Tazuke, S., 1990, *Molec. Crystals liq. Crystals*, **188**, 235; (c) Ivanov, S., Yakovlev, I., Kostromin, S., Shibaev, V., Lásker, L., Stumpe, J., and Keysig, D., 1991, *Makromolek Chem. rap. Commun.*, **12**, 709.
[3] Böffel, C., and Spiess, H. W., in [1], p. 224.
[4] (a) Colby, R. H., Gillmor, J. R., Galli, G., Laus, M., Ober, C. K., and Hall, E., 1993, *Liq. Crystals*, **13**, 233; (b) Hall, E., Ober, C. K., and Galli, G., 1993, *Liq. Crystals*, **14**, 1351.
[5] Boden, N., Clark, L. D., Bushby, R. J., Emsley, J. W., Luckhurst, G. R., and Stockley, C. P., 1981, *Molec. Phys.*, **42**, 565.
[6] Zannoni, C., 1985, *Nuclear Magnetic Resonance of Liquid Crystals*, NATO ASI series C Vol. 141, edited by J. W. Emsley (D. Reidel), p. 1.
[7] Brown, C. J., 1966, *Acta Crystallogr.*, **21**, 146.
[8] Chiellini, E., and Veracini, C. A., (unpublished results).
[9] Catalano, D., and Celebre, G., Longeri, M., and Veracini, C. A., 1985, *Gazz. Chim. Ital.*, **115**, 233.
[10] Emsley, J. W., Wallington, D., Catalano, D., Veracini, C. A., Celebre, G., and Longeri, M., 1993, *J. phys. Chem.*, **97**, 6518.
[11] Ambrosetti, R., Catalano, D., Forte, C., and Veracini, C. A., 1986, *Z. Naturf.* (a), **41**, 431.
[12] Hoadson, G. L., Tse, T. Y., and Vold, R. L., 1992, *J. magn. Reson.*, **98**, 342.
[13] Emsley, J. W., 1985, *Nuclear Magnetic Resonance of Liquid Crystals*, NATO ASI series C Vol. 141, edited by J. W. Emsley (D. Reidel), p. 379.
[14] Catalano, D., Forte, C., Veracini, C. A., Emsley, J. W., and Shilstone, G. N., 1987, *Liq. Crystals*, **2**, 345.; ibid., 357.
[15] Galerne, Y., 1988, *Molec. Crystals liq. Crystals*, **165**, 131.
[16] Chandrasekhar, S., Ratna, B. R., Sadashiva, B. K., and Raja, V. N., 1988, *Molec. Crystals liq. Crystals*, **165**, 123.
[17] Ferrarini, A., Luckhurst, G. R., Nordio, P. L., and Roskilly, S. J., 1993, *Chem. Phys. Lett.*, **214**, 409.
[18] Warner, M., in [1], p. 7.

[19] FREIDZON, Y. S., TALROZE, R. V., BOIKO, N. I., KOSTROMIN, S. G., SHIBAEV, V. P., and PLATE, N. A., 1988, *Liq. Crystals*, **3**, 127.

[20] VASILENKO, S. V., KHOKHLOV, A. R., and SHIBAEV, V. P., 1984, *Macromolecules*, **17**, 2270.

[21] UNGAR, G., PERCEC, V., and ZUBER, M., 1992, *Macromolecules*, **25**, 75.

[22] FRANCESCANGELI, O., YANG, B., LAUS, M., ANGELONI, A. S., GALLI, G., and CHIELLINI, E., 1995, *J. polym. Sci. B, Polym. Phys.*, **33**, 6.