

# Influence of molecular structure on the nematic-nematic transition in polyethers based on 1-(4-hydroxyphenyl)-2-(2-R-4-hydroxyphenyl)ethane where R=CH<sub>3</sub> and Cl, and flexible spacers with an odd number of methylene units

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## Abstract

In a previous paper (reference 1b) we reported that flexible main chain liquid crystalline copolymers based on various molar ratios between the flexible mesogenic groups 1-(4-hydroxyphenyl)-2-(2-R-4-hydroxyphenyl)ethane (RBPE) where R = F, Cl, CH<sub>3</sub> and several different molar ratios between flexible spacers containing odd numbers of methylenic units, i.e. 5, 7, and 9 display two enantiotropic uniaxial nematic mesophases. The homopolymers RBPE-X (where R = -CH<sub>3</sub> and -Cl) and X = number of methylenic units in the flexible spacer, i.e. X = 5, 7, 9, 11, and 13) display also two nematic ( $n_1$ ,  $n_2$ ) mesophases which are however, monotropic or virtual. This paper will discuss the dependence of the phase transition temperatures between these two nematic mesophases ( $T_{n_1n_2}$ ), the isotropization temperature ( $T_{in_1}$ ), and of their associated thermodynamic parameters of the MBPE-X (M = CH<sub>3</sub>) and ClBPE-X homopolyethers as a function of spacer length X. These results will be compared with the predictions of the only available theory which predicts the existence of two uniaxial nematic mesophases in flexible main chain liquid crystalline polymers (reference 6).

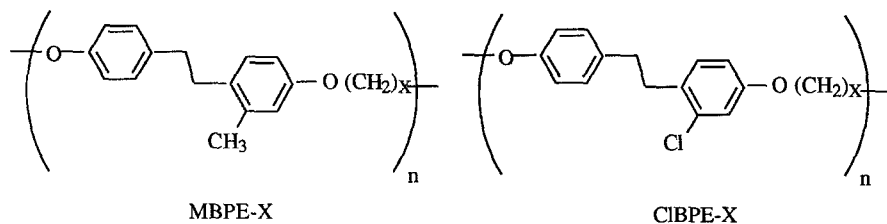
## Introduction

In a previous paper (1b) we reported a first-order thermotropic phase transition occurring within the nematic temperature range in a class of main-chain liquid crystalline copolyethers based on 1-(4-hydroxyphenyl)-2-(2-R-4-hydroxyphenyl) ethane where R = F, Cl, and CH<sub>3</sub>, and flexible spacers containing an odd number of methylene units (RBPE-X where X is the number of methylene units in the flexible spacer; i.e., X = 5, 7, 9, 11, 13). The transition endo- and exotherms, recorded respectively on heating or cooling, are notable for their sharpness and low hysteresis. These copolymers show almost identical birefringent optical textures both above and below the transition. Careful X-ray diffraction experiments on oriented and unoriented specimens failed to detect any sharp diffraction features in either of the phases. It was thus concluded that the phases above and below the transition are both nematic, denoted respectively  $n_1$  and  $n_2$ .

Apart from a few lyotropic systems, where phase separation between two nematic phases can occur due to limited miscibility of nematogenic components (2), a clear nematic-nematic phase transition has not been reported previously, except where the still somewhat controversial biaxial nematic phase is involved (3). Interesting anomalies in the temperature dependencies of diamagnetic anisotropy and bulk density have been reported for nematic polymers with laterally attached mesogenic side-groups (4), but no  $c_p$  singularity, indicative of a true thermodynamic transition, could be detected. More generally, in the case of end-linked side-group polymers different nematic phases have been theoretically predicted on the basis of separate ordering tendencies of side group and the backbone (5); again, however, no thermodynamic transitions between such phases have so far been reported.

In the present case of RBPE-X type polyethers there are no evident signs of biaxiality in either of the nematic phases, nor would biaxiality be expected on the basis of molecular geometry. A uniaxial-uniaxial  $n_1n_2$  transition involves no change of symmetry and hence must be first order, as indeed observed.

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Scheme 1. Structure of MBPE-X and CIBPE-X

In this paper we discuss the influence of chemical structure of the RBPE-X (with R = CH<sub>3</sub> = M and Cl), i.e. mesogen type and spacer length, on the  $n_{1n_2}$  transition temperature ( $T_{n_1n_2}$ ) and on its associated thermodynamic parameters, as well as on those of the similar parameters associated with the isotropization ( $T_{n_1i}$ ) transition. The results are compared with the predictions of the theory of main-chain nematics by Vasilenko, Khokhlov and Shibaev (6).

### Experimental

The synthesis and characterization of the polyethers based on 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane (MBPE) and flexible spacers containing from four to twenty methylenic units ( $X = 4 - 20$ ) (MBPE-X) are summarized elsewhere (7a, b). The synthesis and preliminary characterization data on a few polyethers based on 1-(4-hydroxyphenyl)-2-(2-chloro-4-hydroxyphenyl)ethane (CIBPE) and flexible spacers were also reported (8). The synthesis and characterization of CIBPE-X with  $X = 4 - 20$  is available elsewhere (9). Both  $T_{n_1i}$  and  $T_{n_1n_2}$  are monotropic in MBPE-X and CIBPE-X with  $X = 5$  and 9, while in the polymers with  $X = 11$   $T_{n_1i}$  is monotropic and  $T_{n_1n_2}$  is virtual. In the polymers with  $X = 7$  and 13 both nematic phases are virtual. All virtual thermal transition temperatures and their associated thermodynamic parameters were determined by a combination of copolymerization experiments and differential scanning calorimetry measurements (20°C/min) following standard procedures developed in our laboratory (7a-d).

### Discussion

Table I summarizes the  $T_{n_1i}$ ,  $T_{n_1n_2}$ , and the corresponding thermodynamic parameters collected from previous publications (7a, b, 9).

The main calorimetric results on  $n_{1n_2}$  and  $i_{n_1}$  transitions in MBPE-X and CIBPE-X polymers can be summarized as follows:

1. The difference  $T_{n_1i} - T_{n_1n_2}$  decreases by a small amount with increasing spacer length. (Table I, Figure 1a, b)

Table I: Phase Transition Temperatures (°C) and the Corresponding Enthalpy (kcal/mru) and Entropy (cal/°K mru) changes of MBPE-X and CIBPE-X Polyethers.

RBPE-X	$T_{n_1i}/^{\circ}\text{C}$	$\Delta H_{in_1}$ (kcal/mru)	$T_{n_1n_2}/^{\circ}\text{C}$	$\Delta H_{n_1n_2}$ (kcal/mru)
MBPE-5	51	0.57	37	0.1
MBPE-7	61 ± 1	0.76 ± 0.004	57 ± 2	0.16 ± 0.05
MBPE-9	69	1.05	58	0.06
MBPE-11	72	1.09	66 ± 3	0.11 ± 0.04
MBPE-13	70 ± 3	1.63 ± 0.24	60 ± 6	1.03 ± 0.03
CIBPE-5	43	0.54 ± 0.03	25 ± 3	0.04
CIBPE-7	66	0.8 ± 0.2	49 ± 3	0.05 ± 0.01
CIBPE-9	72	1.23	54	0.04
CIBPE-11	76	1.75	64	0.15 ± 0.04
CIBPE-13	73	2.1 ± 0.3	63 ± 4	1.03 ± 0.01

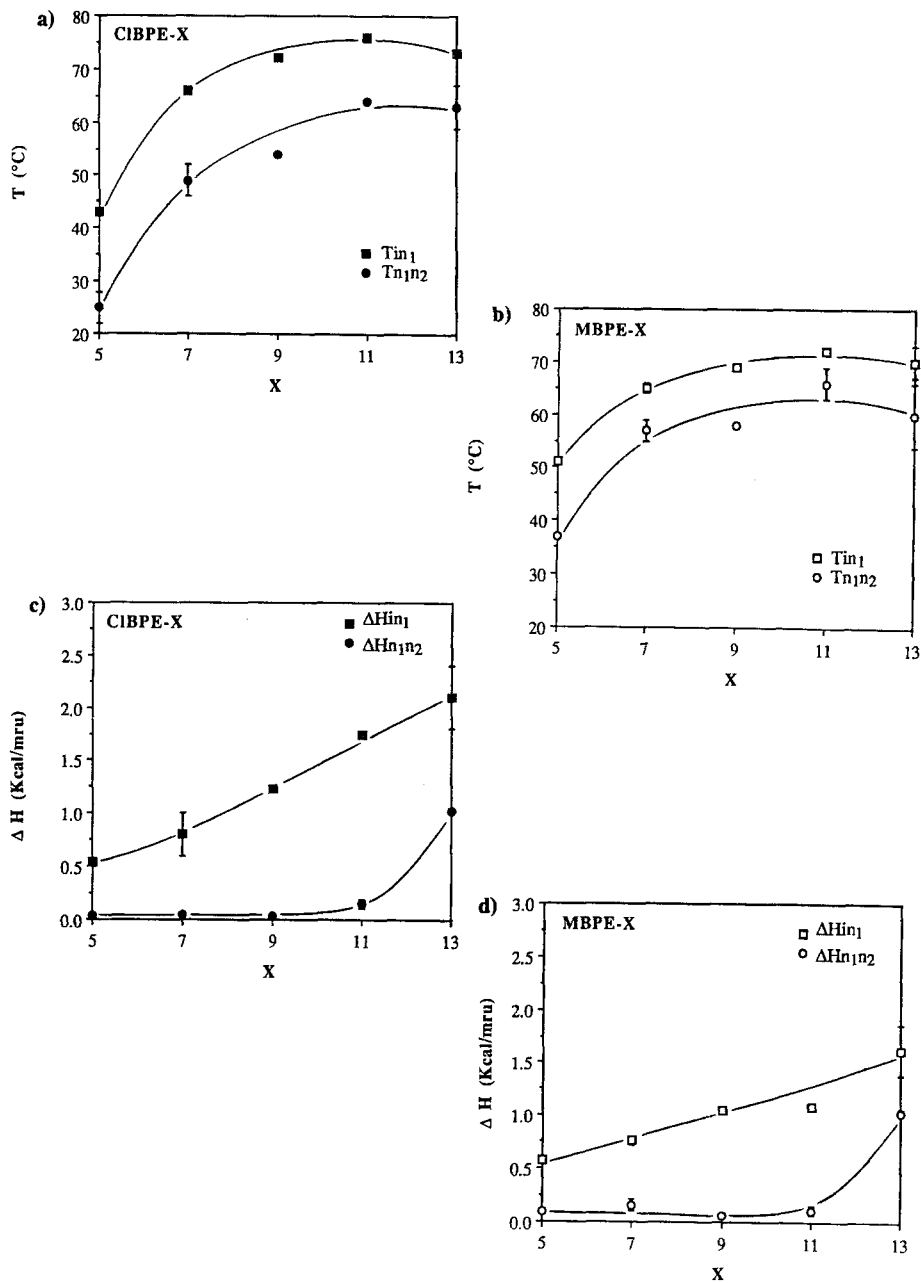


Figure 1. The dependence of  $T_{in1}$  and  $T_{n1n2}$  on spacer length ( $X$ ) for CIBPE-X (a) and MBPE-X (b) and of their corresponding  $\Delta H_{in1}$  and  $\Delta H_{n1n2}$  parameters (c, CIBPE-X; d, MBPE-X).

2. On the whole, both  $T_{in1}$  and  $T_{n1n2}$  increase moderately with increasing spacer length  $X$ , to reach a maximum around  $X = 11$  after which they decrease. (Figure 1a, b)
3.  $\Delta H_{in1}$  values are, to a fair approximation, increasing linearly with the number of methylene groups in the spacer ( $X$ ) for  $X = 1$  (Figure 1c, d).
4. Both for MBPE- $X$  and CIBPE- $X$  with  $X = 5, 7, 9$ , and  $11$   $\Delta H_{n1n2}$  values are, to a fair approximation, independent of  $X$ . However,  $\Delta H_{n1n2}$  values for RBPE-13 are higher. We have to consider these last data with more caution since they are virtual and therefore, determined by extrapolation from copolymerization experiments (7) (Figure 1c, d).

### Isotropic-Nematic Transition

The spacer length dependence of the clearing temperature ( $T_{in1}$ ) for MBPE- $X$  polymers, both with  $X$ =odd and  $X$ =even, has been discussed previously (7a, b). The present data show that, at least in the limited region of odd spacers between  $X = 5$  and  $X = 13$ , the behavior of CIBPE- $X$  (7b, 9) polymers is very similar to that of MBPE- $X$  polymers, and the similarity in  $T_{in1}$  vs.  $X$  dependencies was also observed for longer spacers, including also for  $X =$  even. For comparison, we recall that for short spacers  $T_{in1}$  starts off considerably higher for even spacer MBPE- $X$  polymers than for odd spacer ones. However,  $T_{in1}$  for  $X =$  even decreases monotonically with increasing  $X$  and the clearing temperatures for even and odd spacer polymers converge for large  $X$ . Decreasing  $T_{in1}$  with increasing  $X$  has also been observed for other main chain polymers (7a, b, 10) and this is generally attributed to an overall increase in chain flexibility.

The low  $T_{in1}$  for short odd spacers ( $X = 5$ ) and the maximum in  $T_{in1}$  around  $X = 11$ , observed for MBPE- $X$  and now CIBPE- $X$  polymers, is thought to be a consequence of the competing tendencies for maximum orientational order of the RBPE group and for maximum conformational/orientational order of the spacer. Whereas a number of nearly or fully extended conformations of an *even* spacer are compatible with parallel alignment of the adjoined mesogens, an extended *odd* spacer leaves the two successive mesogens considerably tilted with respect to the main director axis; a tilt of  $30^\circ$  has been calculated by Yoon et al (11) on the basis of the rotational isometric state model. With increasing spacer length, however, the restriction on mesogen orientation imposed by the spacer can be relaxed, as more spacer conformations become accessible, including those departing from the strict rotational isometric states. Thus, with increasing  $X$ ,  $T_{in1}$  moves progressively closer to the values for  $X =$  even polymers, which for  $X < 11$  involves an increase and for  $X > 11$  a decrease in the transition temperature.

$\Delta H_{in1}$  and  $\Delta S_{in1}$  data for MBPE polymers, including extrapolation to zero spacer length, were dealt with in references 7a, b, and 10b, while those of CIBPE are in references 7b, 9, and 10b. A comparison of these data is available in 7b and 10b. Suffice to say that, beside some differences for larger  $X$  values, the data for CIBPE- $X$  show the same trend as for MBPE- $X$ , and hence the conclusions of references 7a, b equally apply to CIBPE- $X$  polymers (9, 10b).

### Nematic-Nematic Transition

Regarding the  $n_{1n2}$  transition, the new information provided by the present work is that  $\Delta H_{n1n2}$  and  $\Delta S_{n1n2}$  as well as the interval of the high-temperature nematic phase,  $T_{in1}$ - $T_{n1n2}$ , are, within the accuracy of our experiments, independent of spacer length (points 2 and 4 above). While the underlying reasons for the occurrence of the  $n_{1n2}$  transition are not yet understood, this experimental information may help narrow the choice of possibilities. We proposed earlier (1) that the  $n_{1n2}$  transition might possibly be interpreted in terms of the lattice theory of molten semi-flexible polymers by Vasilenko et al (6). This theory predicts the existence of two uniaxial nematic phases for polymers with a sufficiently high flexibility parameter of the spacer  $f_0$ . For such polymers phase diagrams in terms of coordinates  $x$  and  $\alpha$  contain a triple point. The chains consist of freely jointed monomer units, with  $x = x' + x''$  being the extended length of the repeat unit,  $x'$  and  $x''$  the respective lengths of the flexible and rigid parts, and  $\alpha = x''/(x'+x'')$ . When the monomers are comparatively short, increasing the spacer length fraction  $\alpha$  produces a single transition from the usual highly anisotropic

nematic phase (at low  $\alpha$ ) to the isotropic phase (at high  $\alpha$ ). However, for  $x > x_{\text{triple point}}$  the theory predicts the existence of another nematic phase, of low anisotropy, for intermediate values of  $\alpha$ .

With regard to the present discussion it is significant that the range of existence of the low-anisotropy nematic phase broadens with increasing  $x$  and/or  $\alpha$ . Although the theory (6) does not specifically deal with temperature induced transitions, it can be easily seen that the phase diagram having temperature as one coordinate axis would have certain features qualitatively similar to those of the  $\alpha$ - $x$  diagram. In particular, the low anisotropy phase would be the high-temperature nematic, and its temperature range would increase with increasing  $x$  and/or  $\alpha$ . However, this prediction of the theory is not born out by the present experiments (point 2). By increasing the number of methylene groups in the spacer, while keeping the mesogen length constant, we effectively increase both  $x$  and  $\alpha$ ; nonetheless, the temperature range of our high-temperature nematic phase is found to decrease slightly or, at best, it remain constant. Thus the observed spacer length dependence of transition temperatures in MBPE-X and ClBPE-X polymers appears to contradict the theoretical predictions in reference 6.

The second point on which the agreement between the present results and the theory by Vasilenko et al. can be tested involves the enthalpy change associated with the transitions. The fact that  $\Delta H_{in_1}$  increases markedly with spacer length  $X$ , while  $\Delta H_{n_1n_2}$  remains constant (points 3 and 4 above) (Figure 1c, d), is a strong indication that the main ordering of the spacer occurs at the  $in_1$  transition and not at the  $n_1n_2$  transition. It would appear that the  $n_1n_2$  transition is associated to a greater degree with the mesogen or the spacer-mesogen link. On the contrary, according to the theory (6), the main change in the order parameters  $S_f$ , identified with the flexible moiety, occurs at the  $n_1n_2$  transition; the  $in_1$  transition is, according to reference 6, mostly limited to a change in  $S_r$ , the order parameter of the rigid units.

It ought to be said that the theory in reference 6 allows for considerable variation in  $n_1n_2$  transition entropy, and even predicts a critical point for sufficiently low  $f_0$ . Thus the difference between the high-anisotropy and low-anisotropy nematic phase, and hence the magnitude of  $\Delta S_{n_1n_2}$  may, under certain conditions, become very small. However, the increase in  $\Delta S_{n_1n_2}$  with spacer length remains an implicit feature of the theory.

Judging by the above, it seems unlikely that the nematic-nematic transition in RBPE-X polymers can be explained by the theory of Vasilenko et al., although the latter is to our knowledge the only theory that predicts the existence of two thermotropic nematic phases in main chain polymers. In view of the fact that only polymers with odd spacers exhibit this transition, an approach that takes account of some specific details of the polymer structure may be a more appropriate starting point for explaining the observed phenomenon.

Further work on physical characterization of the  $n_1n_2$  transition is in progress.

### Acknowledgments

Financial support by the National Science Foundation (DMR-9122227 and DMR-9206781) and NATO are gratefully acknowledged.

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Accepted January 19, 1994      K