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F. Volino, A.F. Martins, R.B. Blumstein, A. Blumstein. Evidence by proton NMR of the alignment of a thermotropic nematic polymer by a magnetic field of ~ 1 tesla. *Journal de Physique Lettres*, 1981, 42 (13), pp.305-307. 10.1051/jphyslet:019810042013030500 . jpa-00231933

HAL Id: jpa-00231933

<https://hal.science/jpa-00231933>

Submitted on 1 Jan 1981

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Classification

Physics Abstracts

61.16N — 61.30 — 61.40

Evidence by proton NMR of the alignment of a thermotropic nematic polymer by a magnetic field of ~ 1 tesla (*)

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(Reçu le 27 mars 1981, accepté le 7 mai 1981)

Résumé. — On étudie un polymère nématogène thermotrope dans les phases solide et nématique, par RMN du proton. On montre que ce polymère s'aligne dans un champ magnétique de ~ 1 T. On estime le paramètre d'ordre nématique correspondant.

Abstract. — A thermotropic polymer is studied by proton NMR in the solid and in the nematic phases. It is shown that this polymer macroscopically aligns in a magnetic field of ~ 1 T. The corresponding nematic order parameter is estimated.

Investigations in the field of liquid crystalline polymers have come to the forefront of industrial and academic research [1]. Current work is focused primarily on linear polymers in which the mesogenic units are incorporated into the main chain. Polymers in which the mesogenic elements are separated by flexible spacer groups such as

can give thermotropic mesophases in which the tran-

sition temperatures are well below the range of thermal degradation of the macromolecule. A variety of smectic, nematic [2-8] and cholesteric [9-11] polymers have been prepared by condensation of mesogenic diols, diphenols or diacid chlorides with flexible diols or diacid chlorides. However, it is difficult to obtain macroscopic alignment of these systems in magnetic fields of ~ 1 tesla [12], as it is the case for low molecular weight liquid crystals.

In this letter, we present one of the first examples of a thermotropic nematic polymer which presents such an alignment [13].

This polymer, called DDA9-L, whose chemical formula is the following

(*) La version française de cet article a été proposée et acceptée pour publication aux Comptes Rendus de l'Académie des Sciences.
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is prepared by condensation of 4-4'-(2, 2'-methyl) azoxybiphenol with the acid chloride of dodecanedioic acid [14]. Its average molecular weight is 7 000, corresponding to an average degree of polymerization

of 15 [15]. The nematic phase extends from 98 to 135 °C between the solid and the isotropic phases.

The proton NMR spectra were recorded as a function of temperature with a Brüker C×P100 pulsed spectrometer, in a magnetic field of 1.17 tesla. We have found that :

1. Between room temperature and 70 °C, the absorption spectrum is a simple broad line whose shape is intermediate between a gaussian and a lorentzian shape and whose width decreases with increasing temperature. Between 70 °C and the solid-nematic transition, two shoulders, distant of $2\delta_i$, appear in the spectrum (Fig. 1a). The distance $2\delta_i$, which has been measured rather accurately on the

Fig. 1. — Proton NMR absorption spectra of DDA9-L at 50 MHz a) in the solid phase, b) in the nematic phase.

dispersion spectra, is found to be practically constant in this temperature range whereas the average width of the spectrum still decreases with increasing temperature (Fig. 2).

2. At the solid-nematic transition, the spectrum suddenly broadens and is better resolved (Fig. 1b). In particular, it appears a well defined doublet $2\Delta_N$ such that $2\Delta_N \approx 4\delta_i$. The splitting $2\Delta_N$ decreases as the temperature increases in a manner which resembles that of a nematic order parameter (Fig. 2).

These results can be interpreted as follows : first, the broadening of the spectrum at the solid-nematic transition, and the fact that $2\Delta_N \approx 2\delta_i$ show unambiguously that the spectrum has transformed from a

Fig. 2. — Evolution of the full width at half maximum $2\Delta_{1/2}$ and at a quarter of maximum $2\Delta_{1/4}$ of the NMR spectra, and of the splittings $2\delta_i$ and $2\Delta_N$, as a function of temperature.

« powder » spectrum to an « aligned » spectrum along the field [16] and consequently, that an alignment of the molecules has occurred at the transition. A detailed interpretation of this aligned spectrum is *a priori* very complicated, due to the large number of protons in the molecule, which are magnetically non equivalent. We can however clearly distinguish a central part of the spectrum and an external part which contains the doublet $2\Delta_N$. If we suppose that the amplitude of the motions associated with the flexible spacers of the molecule is larger than for the mesogenic groups, we can reasonably assume that the protons of flexible spacers contribute more to the intensity in the central part of the spectrum than the protons of the mesogenic groups. By comparing the spectra 1a and 1b it is observed that not only the external part but also the central part of the spectrum is broader in the nematic phase than in the solid phase. This result suggests that not only the mesogenic groups but also the flexible groups are aligned in the field. This result agrees well with the model proposed for the structure of a similar nematic polymer, on the basis of X-ray diffraction results [13]. However, our results concerning the degree of order S are different. We have indeed approximately simulated the NMR spectrum of the protons of the mesogenic groups of DDA9-L, at 120 °C, for the two most probable configurations, i.e. with the methyl groups, either on the same side, or in opposite sides. The approximation consists in reducing, in each case, the total system of protons in two weakly coupled sub-systems, in such a way that they can be approximately superposed. In these conditions, the experimental spectrum can be reproduced only for values of S which are relatively high compared e.g. to the case of PAA [17, 18]. At 120 °C, a value of $S \approx 0.85$, and the configuration where the two methyl groups are on the same side, and where the two phenyl rings form a certain dihedral angle, are the most likely. In this way, we could estimate that for DDA9-L S varies from ~ 0.88 to ~ 0.72 over the whole nematic range. This is definitely larger than the values deduced by X-rays for the polymer of reference [13] (0.64, 0.54). It should be noted however

that these latter values concern the average order of the molecule (mesogenic plus flexible groups), while our values of S for DDA9-L concern only the mesogenic groups. Moreover, the temperatures for DDA9-L are significantly lower ($\sim 120^\circ\text{C}$ compared to $\sim 200^\circ\text{C}$ for reference [13]). NMR experiments on partially deuteriated samples are needed to confirm

these results, in particular the alignment of the flexible spacers.

Acknowledgments. — Two of us (R.B.B. and A.B.) acknowledge support of this work by the National Science Foundation, under grant DMR-79-17397.

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