This article was downloaded by:
On: *26 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Nematic-nematic modification in side-on-fixed polysiloxanes

F. Hardouin[a]; S. Mery[a]; M. F. Achard[a]; M. Mauzac[a]; P. Davidson[b]; P. Keller[c]
[a] Centre de Recherche Paul Pascal, Université de Bordeaux I, Pessac, France [b] Laboratoire de Physique des Solides, Université Paris XI, Orsay Cedex, France [c] Laboratoire Léon Brillouin, CEA/CEN Saclay, Gif sur Yvette, France

To cite this Article Hardouin, F. , Mery, S. , Achard, M. F. , Mauzac, M. , Davidson, P. and Keller, P.(1990) 'Nematic-nematic modification in side-on-fixed polysiloxanes', Liquid Crystals, 8: 4, 565 — 575

To link to this Article: DOI: 10.1080/02678299008047371

URL: http://dx.doi.org/10.1080/02678299008047371

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

LIQUID CRYSTALS, 1990, VOL. 8, NO. 4, 565–575

Nematic–nematic modification in side-on-fixed polysiloxanes

by F. HARDOUIN, S. MERY, M. F. ACHARD and M. MAUZAC,
Centre de Recherche Paul Pascal, Université de Bordeaux I,
Avenue A. Schweitzer, F-33600 Pessac, France

P. DAVIDSON
Laboratoire de Physique des Solides, Université Paris XI, Bât. 510,
91405 Orsay Cedex, France

and P. KELLER
Laboratoire Léon Brillouin, CEA/CEN Saclay, 91191 Gif sur Yvette, France

(*Received 12 March 1990; accepted 4 May 1990*)

A series of side-chain liquid crystal polymers has been synthesized with mesogenic groups laterally branched to a polysiloxane backbone (the so-called side-on-fixed). An anomaly of the diamagnetic anisotropy in the nematic state was shown to be very sensitive to a number of structural parameters such as the length of the aliphatic tails, the length of the spacer and the fixation rate of the mesogenic groups on the backbone. On the basis of accurate density measurements, microscopic observations and X-ray diffraction experiments on aligned samples, the occurrence of a nematic–nematic transition connected to this anomaly is questionned.

1. Introduction

A new class of liquid-crystalline side chain polymers has been described in recent years: in these compounds the mesogenic groups are laterally attached (the so-called side-on-fixed) to a polymer main chain (see figure 1). Primarily reported in polymethacrylates (PMA) [1], this placement of the mesogenic units favours the existence of a nematic phase above the glassy state. By varying the nature of the backbone of these side-on-fixed polymers (polymethylsiloxanes (PMS) [2, 3], polyacrylates (PA) [4, 5], polychloroacrylates (PClA [5].), it has been confirmed that the lateral substitution of the mesogenic groups strongly promotes the nematic state.

On the basis of conoscopic observations on oriented samples, biaxial nematic phase behaviour has been claimed [6] for liquid-crystalline polymethacrylate polymers with long spacer ($n = 11$). Independently, by means of magnetic measurements we have provided evidence for a nematic–nematic modification in polysiloxanes with short spacers ($n = 4$) and with similar calamitic mesogenic groups laterally attached to the backbone. Only one nematic domain remained for long spacers [2].

We describe in this paper the influence of different structural parameters on the occurrence of such an anomaly, especially the length of the aliphatic tails, the length of the spacer and the fixation rate of the mesogenic pendants on the backbone. In addition, the nematic–nematic modification is confirmed by accurate density

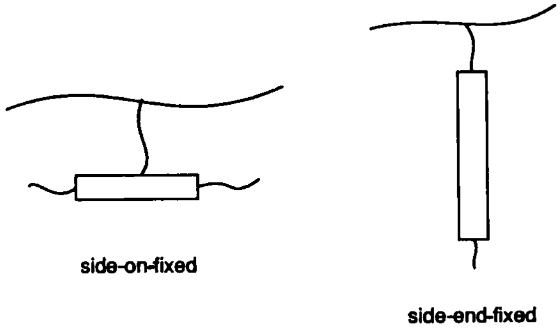
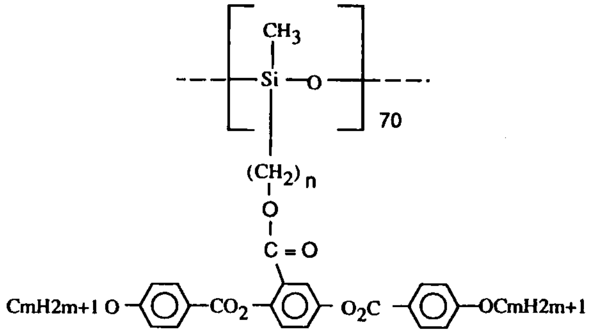


Figure 1. Schematic representation of side-on-fixed and side-end-fixed polymers.

measurements. The polymers investigated have the general formula:

$P_{n,m,m}$ for short



The synthesis of these side-on liquid-crystalline polysiloxanes has already been described [2]: the vinyl derivative corresponding to the side chain is fixed via a classical hydrosilylation reaction on a polymethylhydrogenosiloxane chain.

2. Results

The mesomorphic properties were first characterized by the usual methods: optical microscopy, DSC, and X-ray diffraction on powder samples (Guinier camera). All of these polysiloxanes exhibit nematic phases. The glass transition temperatures, the clearing temperatures and the enthalpies of transition are listed in table 1.

Table 1. Phase transition temperatures for the vinyl derivatives and the corresponding substituted polymethylsiloxanes. C = crystalline, g = glassy state, N = nematic, I = isotropic phase, [ ] indicates monotropic transition.

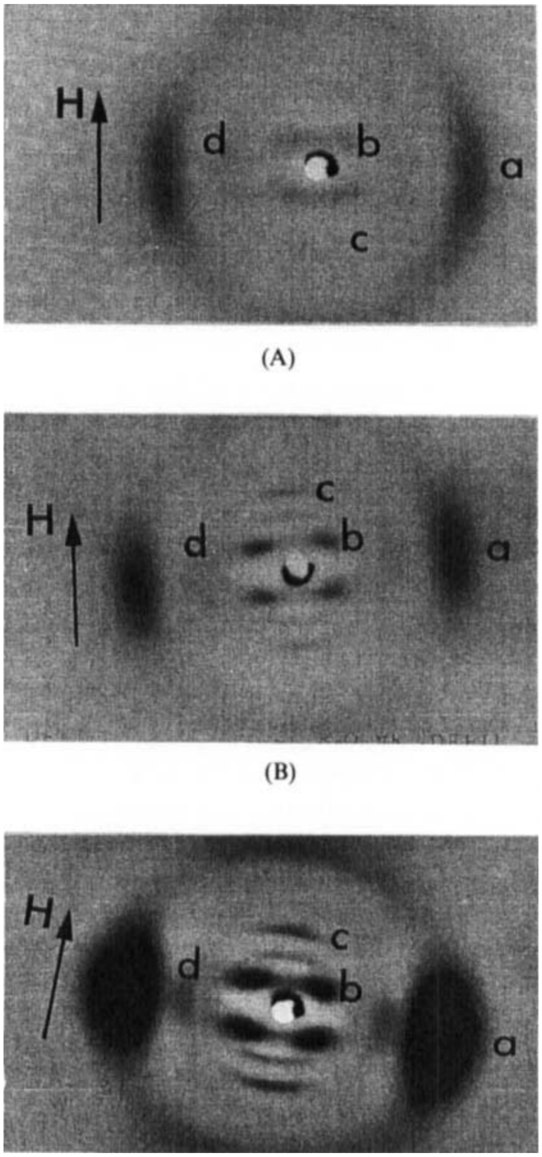
		Vinyl moiety					Homopolymer					
n	m	C		N		I	g		N		I	$\Delta H_{\mathrm{NI}}/\mathrm{J\,g^{-1}}$
4	1	●	135°C		[108°C]	●	●	53°C	●	154°C	●	1·7
4	2	●	136°C	●	[130°C]	●	●	36°C	●	158°C	●	2·7
4	3	●	105°C	●	[100°C]	●	●	48°C	●	130°C	●	2·1
4	4	●	100°C	●	113°C	●	●	36°C	●	120°C	●	2·1
4	6	●	107°C	●	[101°C]	●	●	18°C	●	99°C	●	1·6
4	8	●	96°C	●	[95°C]	●	●	24°C	●	93°C	●	1·7
10	3	●	77°C	●	[76°C]	●	●	7°C	●	93°C	●	1·4

These polysiloxanes do not differ in their behaviour from the PMA11,*m*,*m* series (using an analogous notation) [7]:

- they are nematic whatever the tail length,
- the nematic–isotropic transition enthalpy of the side-on-fixed polymers is about 2 J/g and corresponds to that of the side-end-fixed polymers,
- on average, T_C and T_g decrease as m increases.

In contrast with the usual side-end-fixed polymers, the stability of the mesophase is weakly improved from vinyl derivative to the side-on-fixed polymers. Moreover we confirm here that lateral substitution of mesogenic monomers strongly reduces the ability to form smectic phases independently of the nature of the polymer backbone (PMA, PA, PClA or PMS).

X-ray diffraction experiments on aligned samples of $P_{4,4,4}$ have been performed with the usual diffraction apparatus described elsewhere [8]. Because of the alignment procedure, the sample has a uniaxial symmetry around the magnetic field direction (i.e. the meridian). Figure 2 shows the X-ray diffraction patterns of $P_{4,4,4}$ at a temperature just below T_{NI} (see figure 2 (A)) and at room temperature (see figures 2 (B), (C)). The absence of any Bragg reflection together with the anisotropy of the pattern show that the sample is in a nematic state over the entire temperature range. Moreover, except for the usual contrast improvement with decreasing temperature, no sudden alteration of the pattern was observed. (The patterns were recorded every 5°C) Let us describe these X-ray diffraction patterns. The usual wide angle diffuse ring (*a*) shows that the mesogenic cores are oriented along the magnetic field (i.e. the director). From the extension of this diffuse ring, the behaviour of the orientational order parameter can be estimated qualitatively: it seems to increase monotonously as the temperature decreases, to reach a rather large value at room temperature. Several other diffuse elements can be seen on the patterns; they are due to several types of fluctuations already present just below T_{NI}. Their correlation lengths increase regularly as the temperature decreases. Firstly, four diffuse spots (*b*) located at small angles off the meridian show the presence of rather strong S_C fluctuations. Their coherence lengths range from approximately $\xi_\parallel \approx 50$ Å, $\xi_\perp \approx 30$ Å just below T_{NI} to about $\xi_\parallel \approx 100$ Å, $\xi_\perp \approx 50$ Å at room temperature. ($\xi_\parallel$ and $\xi_\perp$ refer to the correlation lengths along the meridian and perpendicular to it, respectively.) The tilt angle is about 50° and the projection of the wave vector along the director is $q_\parallel \approx 2\pi/28$ Å^{-1} (q is the momentum transfer vector, i.e. $(4\pi \sin\theta)/\lambda$ where 2θ is the scattering angle). Since the length of a side chain for $P_{4,4,4}$ measured on Dreiding stereomodels is about 29 Å, these S_C fluctuations are of the usual monolayer type. Along the meridian and perpendicular to it, a series of equidistant diffuse lines (*c*) can be seen. Their period is $2\pi/28$ Å^{-1} which means that they are due to the presence of periodic columns of molecules. The coherence length $\xi_\parallel$ of these columns varies from about 100 Å just below T_{NI} to the rather large value of about 250 Å at room temperature. The fluctuations (*b*) and (*c*) have already been seen together in several low molecular weight compounds [9, 10]. The last feature of the X-ray diffraction patterns is more original; a diffuse spot (*d*) can be detected on the equator (direction perpendicular to the meridian) at a wavevector $q_\perp \approx 2\pi/7$ Å^{-1}. The X-ray diffraction patterns of either conventional liquid crystals or side-end-fixed polymers usually do not show such diffuse scattering and therefore its origin is unclear. Actually, various types of rod-like mesogens complexed with transition metals, exhibit S_A phases. The diffraction patterns of these phases also display an additional diffuse scattering located on the equator [11]. Whatever its



(A)

(B)

(C)

Figure 2. X-ray diffraction patterns of a magnetically aligned sample of $P_{4,4,4}$. H is the magnetic field direction. Monochromatic (CuKα = 1·541 Å) radiation was used and the sample-film distance was 60 mm. (A) T = 115°C; (B) room temperature; and (C) room temperature, overexposed pattern.

origin, the intensity of this diffuse scattering increases smoothly over the whole temperature range.

Finally, it should be noted that keeping the samples at temperatures just above T_g for a few hours induces a slight crystallization which can be seen on the patterns since a few very faint but sharp diffraction lines appear.

X-ray diffraction experiments on aligned samples have been performed on $P_{4,4,4}$ only. Nevertheless, $P_{4,4,4}$ is representative of the whole series since all polymers of this series have the same type of powder pattern.

As already reported [2], we recall that in the nematic range an anomaly was detected in the thermal evolution of the diamagnetic anisotropy $\Delta\chi$. It has only been revealed for a polysiloxane backbone with a short spacer ($n = 4$). Indeed we showed that an increase of the spacer length leads to the disappearance of this anomaly [2]. One aim is now to appreciate, for the suitable spacer ($n = 4$), the influence on $\Delta\chi$ of the length of the aliphatic tails of the laterally attached mesogenic groups. The macroscopic parameter, $\Delta\chi$, is evaluated from the measurement, in the bulk, of the diamagnetic susceptibility in a direction parallel to the magnetic field $\chi_{\parallel B}$ (Faraday balance method [12]) in the nematic phase;

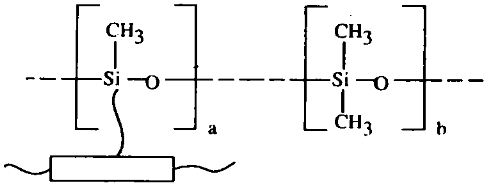
$$\Delta\chi = 3/2(\chi_{\parallel B} - \chi),$$

where χ is the scalar susceptibility measured in the isotropic state; $B = 1{\cdot}5\,\mathrm{T}$. In a uniaxial nematic phase this expression represents the macroscopic order parameter which is connected directly to the single orientational order parameter introduced in the Maier–Saupe theory [13]. This assumes that the molecules have cylindrical symmetry and the molecular shape does not change with temperature. The magnetic measurements were performed systematically as a function of temperature for the polymers with m varying from 1 to 8. The results are reported in figures 3 (*a*)–(*f*). An anomaly is detected for alkoxy chains containing one to six methylene groups; when we reach $m = 8$, the anomaly disappears (see figure 3 (*f*)).

Concerning the thermal stability of both nematic domains, figure 3 shows that the high temperature nematic domain is destabilized by long aliphatic chains. Thus the nematic–nematic anomaly is very sensitive to the molecular architecture. In this regard, we can also investigate the influence of the spacer length (n) for a given value of m ($m = 3$). As previous observed [2], increasing the spacer length leads to the disappearance of the magnetic anomaly (see figure 4 ($n = 10$) to be compared with figure 3 (*c*) ($n = 4$)).

We stress that the relaxation kinetics of the orientational order in these high molar mass systems prevent the reproducibility of the anomaly upon heating. Moreover the continuous evolution from zero of $\Delta\chi$ (see figures 3, 4 and 5) originates from the existence of an isotropic–nematic biphasic domain (over the temperature interval of about 5°C) which is always observed in polymers despite their low polydispersity index ($I = 1{\cdot}2$).

The scope of this study has been enlarged by considering another pertinent molecular parameter, i.e. the fixation rate of the mesogenic pendants [14]. Indeed copolymers have been synthesized by using copoly(methylhydrogeno-dimethyl) siloxane backbones (Petrach PS 123). The fixation rate of the mesogenic units depends on the number of dimethylsiloxane segments:



where $x = a/(a + b) = 0{\cdot}3$, $a + b = 30$ and is denoted by $\mathrm{P}_{\mathrm{n.m.m}}$ 30 per cent for short. These copolymers present nematic phases (see table 2) and, as usually observed for diluted polymers, both the glass transition temperature T_g and the nematic–isotropic

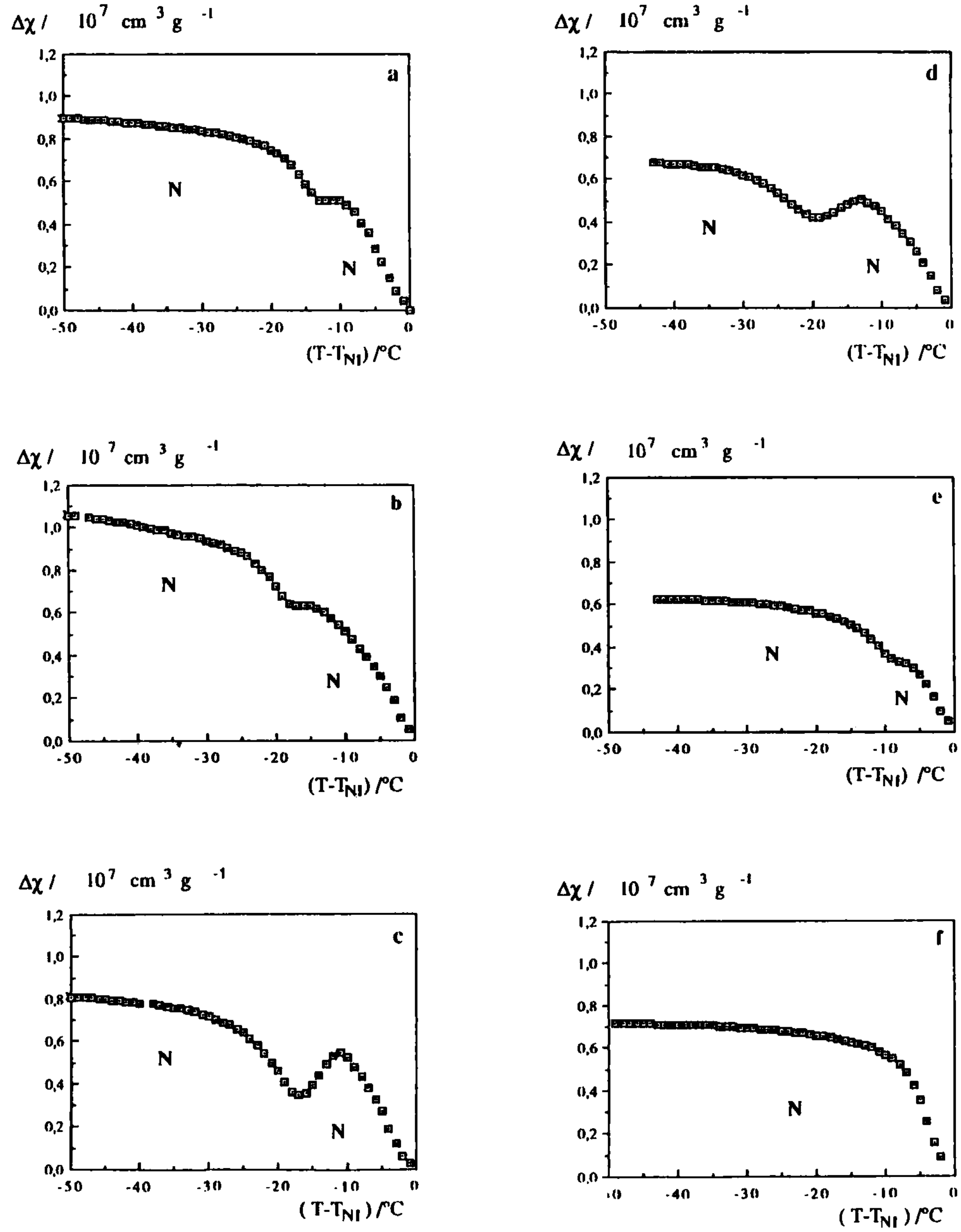


Figure 3. The temperature dependence of the diamagnetic anisotropy $\Delta\chi = 3/2\,(\chi_{\parallel B} - \chi)$ for several aliphatic tail lengths of $P_{4,m,m}$ (*a*) $m = 1$; (*b*) $m = 2$; (*c*) $m = 3$; (*d*) $m = 4$; (*e*) $m = 6$; (*f*) $m = 8$.

transition temperature T_{NI} decrease compared with those of the corresponding homopolymer. Nevertheless it should be noted the large amount of crystallinity of the copolymers (see the ΔH melting in table 2) whereas the homopolymers are essentially amorphous. Concerning the thermal evolution of the diamagnetic anisotropy $\Delta\chi$, no anomaly is detected in the copolymer series whatever the chain length m. An example is given in figure 5 for $P_{4,3,3}$ 30 per cent.

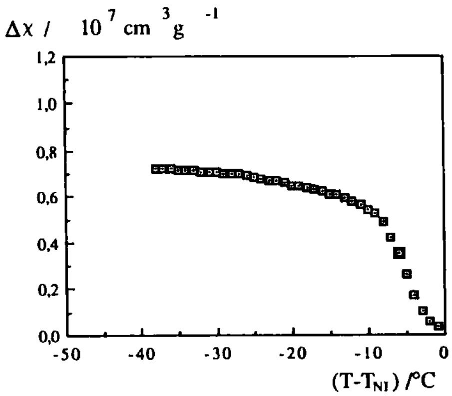


Figure 4. The temperature dependence the diamagnetic anisotropy $\Delta\chi = 3/2\,(\chi_{\parallel B} - \chi)$ for $P_{10,3,3}$.

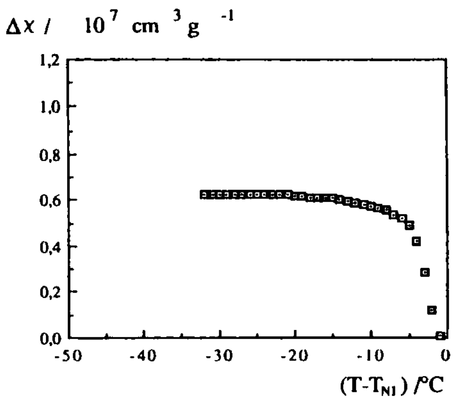


Figure 5. The temperature dependence of the diamagnetic anisotropy $\Delta\chi = 3/2\,(\chi_{\parallel B} - \chi)$ for $P_{4,3,3}$ 30 per cent.

Table 2. Phase transition temperatures for the copolymers with a fixation rate $x = 30$ per cent, C = crystalline, g = glassy state, N = nematic, I = isotropic phase.

		Copolymer $x = 0{\cdot}3$								
n	m	g		C		N		I	ΔH_m/J g^{-1}	ΔH_{NI}/J g^{-1}
4	1	●	8°C	●	64°C	●	[52°C]	●	14·5°C	0·7
4	2	●	12°C	●	104°C	●	[84°C]	●	19·3°C	0·7
4	3	●	10°C	●	66°C	●	[62°C]	●	14·9°C	0·7
4	4	●	10°C			●	74°C	●	–	0·7
4	6	●	– 3°C			●	63°C	●	–	0·7

Accurate and reliable density measurements as a function of temperature (carried out on cooling with an Anton Paar Density Meter DMA60–DMA602 [15] (accuracy ± 1 × 10^{-5} g cm^{-3})) also enable us to detect a nematic–nematic modification in the case without any applied external field. Indeed the temperature dependence of the density for $P_{4,3,3}$ reported in figure 6 shows a drastic change of slope over the temperature interval which is associated with the magnetic anomaly. We note that the

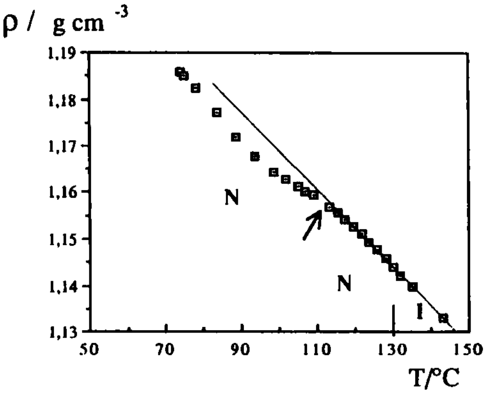


Figure 6. The temperature dependence of the density, ρ, for $P_{4,3,3}$.

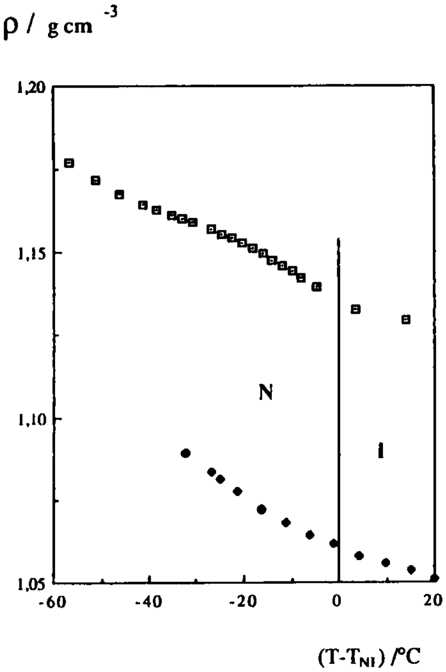


Figure 7. The temperature dependence of the density, ρ, for $P_{4,8,8}$ (◆) compared to that of $P_{4,3,3}$ (□).

thermal expansion coefficient does not remain constant in the low temperature nematic range while this coefficient is constant in the high temperature nematic domain. For $P_{4,8,8}$, which does not exhibit a magnetic anomaly (see figure 3(*f*), we do not detect a drastic change in the slope on decreasing the temperature in the nematic phase (see figure 7). This evolution shows a varying thermal expansion coefficient which resembles the behaviour of the low temperature nematic range of $P_{4,3,3}$. In contrast, for $P_{10,3,3}$ and of $P_{4,3,3}$ 30 per cent this coefficient is constant throughout the nematic domain (figure 8), which resembles the high temperature nematic behaviour of $P_{4,3,3}$. Finally, we note that the evolution of the density from the

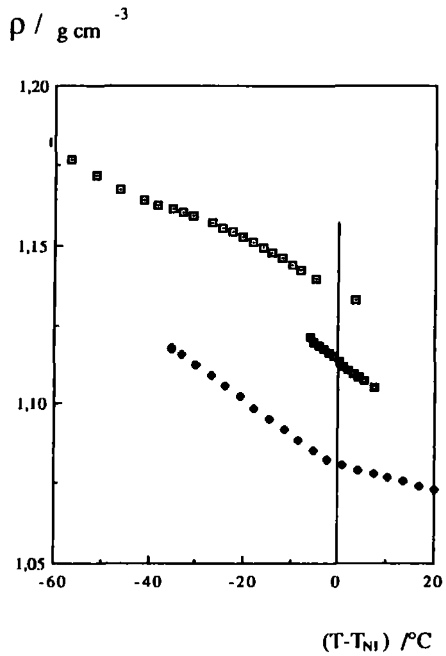


Figure 8. The temperature dependence of the density, ρ, for $P_{10,3,3}$ (◆) for the copolymer $P_{4,3,3}$ 30 per cent (□) and that of $P_{4,3,3}$ (□).

isotropic to the nematic phase appears continuous, as does $\Delta\chi$, owing to the existence of the biphasic region.

3. Discussion

The molecular structure of the side-on-fixed polymers favours orientational interactions between the main chain and the mesogenic parts. Therefore whatever the nature of the backbone these polymers give strong nematic tendencies.

The diamagnetic anomaly associated with the change of slope in the temperature dependence of the density could be interpreted as the effect of a phase transition between a high temperature nematic phase and a low temperature nematic phase.

The textural analysis of $P_{4,4,4}$ with a polarizing microscope supports this assumption: after annealing a droplet at high temperature we observe a typical schlieren texture for a uniaxial nematic (see figure 9 (*a*)). Unusual bright worm-like defects progressively develop everywhere in the free surface sample upon cooling (see figure 9 (*b*)) and subsequent heating makes them disappear. These modifications could be associated with a unaxial–biaxial symmetry breaking in the nematic phase. Indeed, such a symmetry breaking may not have been detected in the X-ray diffraction patterns of magnetically aligned samples since the pattern of a fibre (a two dimensional powder) of a biaxial nematic phase should not be very different from that of the usual uniaxial nematic phase. In fact the optically biaxial nematic phase involves three main axes. Thus the observations (e.g. conoscopic observations) of a single domain need an orientation imposed in two directions [16, 17] which unfortunately is not achieved by macroscopic homeotropic alignment. Nevertheless the lack of an excess specific heat detected by DSC at the temperature of the diamagnetic anomaly raises an objection. Moreover, the definition of a nematic–nematic phase transition can be subtle in

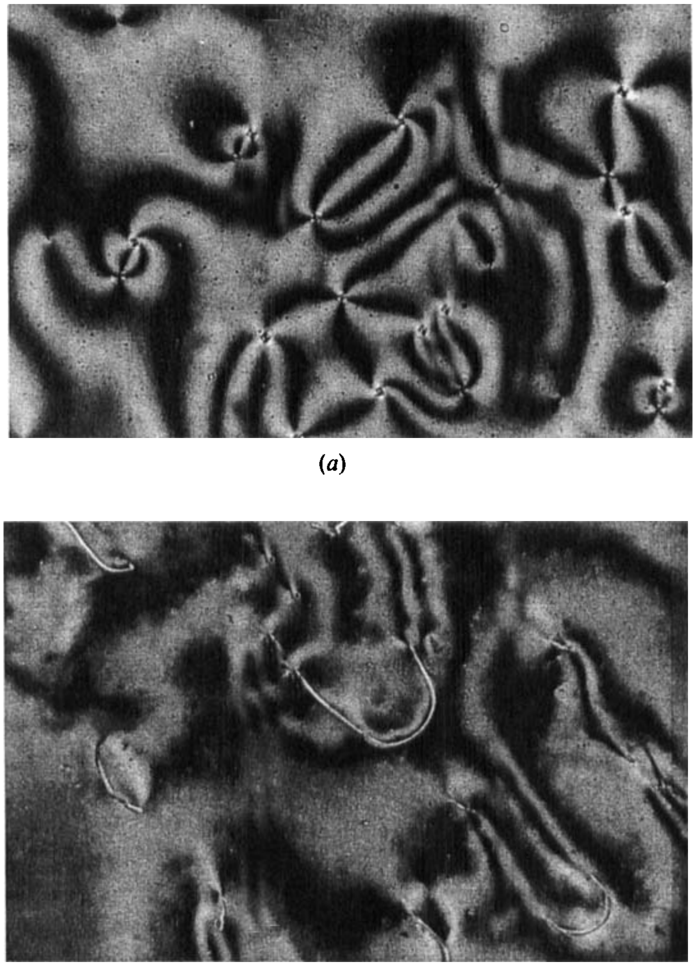


Figure 9. Microphotographs of $P_{4,4,4}$ under crossed polars. Magnification × 400. (a) 110°C; (b) 90°C.

polymers due to the change of the global shape (anisotropy of the giration radii) with temperature. Depending on the molecular characteristics such evolution can modify significantly the anisotropic interactions at short range. From this point of view a non-monotonous variation of $\Delta\chi$ with temperature could be expected even in a uniaxial nematic phase and even without a phase transition. The bending of the dilatometric curve would be considered as the signature of a conformational contraction of the chains.

More experiments are necessary therefore to specify whether the phenomenon observed in the nematic phase is a true thermodynamic event (i.e. a phase transition) or not. In the former assumption a careful analysis of the topological relevance of the defects described here seems of prime importance to test the validity of a uniaxial nematic–biaxial nematic phase transition. At any rate the terms in the equation for $\Delta\chi$ have to be taken into account in order to explain a non-monotonous variation with temperature. This behaviour could not be restricted to this kind of liquid crystal polymers. Additional results concerning structural and dynamic properties of these systems will be described in forthcoming papers.

References

[1] HESSEL, F., and FINKELMANN, H., 1985, *Polym. Bull. (Berlin)*, **14**, 375.
[2] KELLER, P., HARDOUIN, F., MAUZAC, M., and ACHARD, M. F., 1988, *Molec. Crystals liq. Crystals*, **155**, 171.
[3] GRAY, G. W., HILL, J. S., and LACEY, D., 1989, *Angew. Chem. Int. Engl. Adv. Mater.*, **28**, 1120.
[4] QI-FENG ZHOU, HUI-MIN LI and XIN-DE FENG, 1987, *Macromolecules*, **20**, 233; 1988, *Molec. Crystals liq. Crystals*, **155**, 73.
[5] HESSEL, F., and FINKELMANN, H., 1988, *Makromolek. Chem.*, **189**, 2275.
[6] HESSEL, F., and FINKELMANN, H., 1986, *Polym. Bull. (Berlin)*, **15**, 349.
[7] HESSEL, F., HERR, R., FINKELMANN, H., 1987, *Makromolek. Chem.*, **188**, 1597.
[8] DAVIDSON, P., KELLER, P., and LEVELUT, A. M., 1985, *J. Phys. Paris*, **46**, 939.
[9] USHA DENIZ, K., PARANJPE, A. S., AMRITHALINGAM, V. A., and MURALIDHARAN, K. V., 1989, *Molec. Crystals liq. Crystals Lett*, **49**, 265.
[10] LEVELUT, A. M., FANG, Y., and DESTRADE, C., 1989, *Liq. Crystals*, **4**, 441.
[11] LEVELUT, A. M., GHEDINI, M., BARTOLINO, R., NICOLETTA, F. P., and RUSTICHELLI, F., 1989, *J. Phys., Paris*, **50**, 113.
[12] REGAYA, B., and GASPAROUX, H., 1971, *C. r. hebd. Séanc. Acad. Sci., Paris* B, **272**, 724.
[13] MAIER, W., and SAUPE, A., 1959, *Z. Naturf. (a)*, **14**, 882; 1960, *Ibid.*, **15**, 287.
[14] HARDOUIN, F., SIGAUD, G., KELLER, P., RICHARD, H., NGUYEN, H. T., MAUZAC, M., and ACHARD, M. F., 1989, *Liq. Crystals*, **5**, 463, and references therein.
[15] ACHARD, M. F., HARDOUIN, F., SIGAUD, G., and MAUZAC, M., 1986, *Liq. Crystals*, **1**, 203.
[16] GALERNE, Y., and MARCEROU, J. P., 1983, *Phys. Rev. Lett.*, **51**, 2109.
[17] GALERNE, Y., 1988, *Molec. Crystals liq. Crystals*, **165**, 131.