

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>

### Neutron scattering study and discussion of the backbone conformation in the nematic phase of a side chain polymer

P. Davidson<sup>a</sup>; L. Noirez<sup>b</sup>; J. P. Cotton<sup>b</sup>; P. Keller<sup>b</sup>

<sup>a</sup> Laboratoire de Physique des Solides associé au CNRS, Bat. 510, Université Paris XI, Orsay Cédex, France <sup>b</sup> Laboratoire Léon Brillouin (CEA-CNRS), CEN Saclay, Gif-sur-Yvette Cédex, France

**To cite this Article** Davidson, P. , Noirez, L. , Cotton, J. P. and Keller, P.(1991) 'Neutron scattering study and discussion of the backbone conformation in the nematic phase of a side chain polymer', *Liquid Crystals*, 10: 1, 111 – 118

**To link to this Article:** DOI: 10.1080/02678299108028234

**URL:** <http://dx.doi.org/10.1080/02678299108028234>

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.

## Neutron scattering study and discussion of the backbone conformation in the nematic phase of a side chain polymer

by P. DAVIDSON\*†, L. NOIREZ‡, J. P. COTTON‡  
and P. KELLER‡

† Laboratoire de Physique des Solides associé au CNRS,  
Bat. 510, Université Paris XI, 91405 Orsay Cédex, France

‡ Laboratoire Léon Brillouin (CEA-CNRS),  
CEN Saclay, 91191 Gif-sur-Yvette Cédex, France

(Received 9 November 1990; accepted 2 January 1991)

A small angle neutron scattering study of a mesomorphic side chain polyacrylate in the nematic phase shows that the backbone adopts a prolate conformation. This observation is discussed in relation to the previous determinations of backbone anisotropy in the nematic phase of other side chain polymers. On the basis of the comparison with these previous determinations and also with the results obtained on other related systems, the assumption is made that, provided that the spacers are long enough, the natural tendency of the backbones is to adopt a prolate shape in any nematic phase devoid of smectic fluctuations.

### 1. Introduction

Mesomorphic side chain polymers made of mesogenic cores linked by one end to a polymeric backbone via flexible spacers (see figure 1) have been known for a long time [1]. The question of the global backbone conformation has become a central issue for this class of compounds [2]. Small angle neutron scattering (SANS) on mixtures of unlabelled and labelled polymers has proved to be a very efficient method to study this point experimentally. This technique has clearly established in several cases that the backbone adopts an oblate conformation in the smectic A phase [3-7]. This can be understood by considering the confinement effect exerted by the smectic field on the backbones [8]: since the existence of the  $S_A$  phase usually proceeds from the tendencies of the aromatic and aliphatic moieties to segregate, then the backbones should be preferentially located in the aliphatic part of the smectic layers. No exception to this rule has been reported so far.

The situation in the nematic phase is not as clear: the symmetry of the nematic phase alone in no way determines the type (prolate or oblate) of the backbone anisotropy. Indeed, early experiments showed in a few cases [3, 7, 9, 10] that in this phase, the anisotropy of the backbone is slightly oblate. However in the special case of a reentrant nematic phase, a prolate shape was observed [11]. This observation raised two questions.

- (i) Is this prolate conformation only due to the specific character of the  $N_{re}$  phase?
- (ii) Is it related to the  $S_C$  fluctuations of small amplitude but large correlation lengths which affect this  $N_{re}$  phase?

\* Author for correspondence.

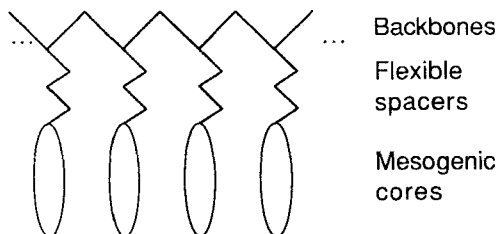
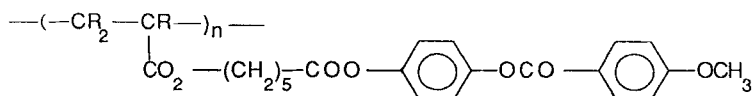


Figure 1. Schematic representation of a mesomorphic comb-like polymer.

Meanwhile, it was demonstrated by small angle X-ray scattering [12, 13] that the polymer backbone of a mesomorphic side chain polymer dissolved in a usual nematic phase (displayed by a low molecular weight mesogen) adopts a prolate conformation. Though it is not quite sure whether this behaviour should be that of the backbone for the pure polymer, this new observation was difficult to reconcile with the first SANS experiments upon the regular (i.e. non-reentrant) nematic phase. Finally, it was then noticed that the first SANS results were obtained from nematic phases which all have strong  $S_A$  fluctuations [14]. Such fluctuations might have affected the global backbone conformations.

From the theoretical point of view, Wang and Warner [15] have shown on the basis of a mean field theory involving two order parameters, that three kinds of nematic phases called  $N_I$ ,  $N_{II}$  and  $N_{III}$  should indeed exist according to the strength of the coupling between the backbone and mesogenic cores via the spacers. These kinds of nematic phases differ simply by the orientations of the backbone and mesogenic cores with respect to the director. Moreover this type of theory, which has also been developed by other groups [16, 17], predicts transitions between the different nematic phases. However, since the coupling constants involved in the theory are, *a priori*, unknown, the type of backbone conformation cannot yet be predicted by using this kind of approach.

In order to try to shed some light on this complicated situation, we have undertaken a study by SANS of a mesomorphic side chain polymer which displays a nematic phase over a large temperature range. This compound, called in the following  $PA_5(H, D)$  was first synthesized and characterized by Freidzon *et al.* [18] and has the formula



where  $R = \text{H}$  or  $\text{D}$ . In order to perform SANS studies, the hydrogenated compound and its homologue deuteriated on the backbone have been synthesized at the Laboratoire Léon Brillouin. The polymorphism is  $g$   $29^\circ\text{C}$   $N$   $129^\circ\text{C}$   $I$  where  $g$ ,  $N$  and  $I$  stand for the glassy nematic state, the nematic phase and the isotropic liquid, respectively. According to Freidzon *et al.* a transition was detected around  $60^\circ\text{C}$  between the usual nematic phase and a low temperature nematic phase called  $N_B$  of hexagonal symmetry. We have, therefore, performed X-ray diffraction experiments on  $PA_5(H)$  using an already well described apparatus [14]. The X-ray diffraction patterns obtained were characteristic of the usual nematic phase over the whole temperature range. At low temperatures ( $T < 70^\circ\text{C}$ ) very weak  $S_C$  fluctuations of quite short ( $\approx 5\text{--}20 \text{ \AA}$ ) correlation lengths may be detected. The discrepancy between the present observations and those of Freidzon *et al.* might be due to a difference in polymer molecular weight. The molecular weights of our polymers  $PA_5(H)$  and  $PA_5(D)$  were measured by light scattering and gel

permeation on line [19]. The hydrogenated polymer PA<sub>5</sub>(H) has a molecular weight  $\bar{M}_w$  (weight average) of 27000 and a polydispersity of 2.8. The deuteriated polymer PA<sub>5</sub>(D) is about 5 times larger than the hydrogenated one with a molecular weight of 120000 and a polydispersity of 2.9. X-ray diffraction experiments have also been performed on samples of polymer PA<sub>5</sub>(D). The X-ray patterns are identical to those of PA<sub>5</sub>(H) except that slow crystallization takes place at temperatures below 65°C. In order to get rid of this phenomenon, SANS experiments were only performed at temperatures above 65°C.

## 2. Experimental

The SANS experiments have been performed by following a well described procedure [3, 4, 7]. Mixtures in equal parts of the hydrogenated polymer PA<sub>5</sub>(H) and its counterpart PA<sub>5</sub>(D) deuteriated on the backbone were obtained by evaporation of a solution of these polymers in CHCl<sub>3</sub>. Under these conditions, the SANS signal only corresponds to the backbone conformation.

A disc-like cell (of thickness 1 mm and diameter 15 mm) was filled with the molten mixture and set in an oven (temperature stability of 0.2°C) itself placed in the neutron beam (diameter 7.6 mm). Aligned samples could be obtained by cooling them slowly (5°C/h) through the nematic-isotropic phase transition in a magnetic field of 1.4 T oriented perpendicular to the neutron beam. The neutrons scattered by the sample are collected on the SANS *xy* position multidetector PAXY (Orphée reactor, CEN Saclay). The sample-multidetector distance ( $d = 2m$ ) is such that using a wavelength  $\lambda = 10 \text{ \AA}$ , the scattering vector  $\mathbf{q} = 4\pi\theta/\lambda$  ( $2\theta$  is the scattering angle) takes values between  $0.01 \text{ \AA}^{-1} < \mathbf{q} < 0.1 \text{ \AA}^{-1}$ . The linear dependence of the inverse of the intensity  $I^{-1}(\mathbf{q})$  versus  $\mathbf{q}^2$  is obtained in the first half of this  $\mathbf{q}$  range. In this range, we have applied an extension of the Guinier approximation which takes into account the difference in molecular weight of the two polymers PA<sub>5</sub>(H) and PA<sub>5</sub>(D) [20]. This scattering law assumes that no specific interaction occurs between labelled and unlabelled parts. This can be checked experimentally by following the value of the intensity extrapolated at the origin for each temperature. Indeed, this value is directly related to the molecular weight (see the subsequent formula). If an isotopic segregation had taken place, polymers of the same isotopic species would form together scattering objects of higher molecular weight which should change the extrapolated value of the intensity. Since this is not the case here, we conclude that PA<sub>5</sub>(H, D) constitutes an ideal isotopic mixture from the isotropic phase down to 65°C after which partial crystallization occurs.

Let us call  $\mathbf{q}_i$  the component of the vector  $\mathbf{q}$  in the  $i$  direction, we then have

$$I^{-1}(\mathbf{q}_i) = A \left[ \frac{1}{M_H \Phi_H} + \frac{1}{M_D \Phi_D} \right] (1 + \mathbf{q}_i^2 R_{i\text{app}}^2),$$

where  $A$  is a constant,  $\Phi_H$  and  $\Phi_D$  are the volume fractions,  $M_H$ ,  $M_D$  the molecular weights of the hydrogenated chains and the deuteriated chains respectively.  $R_{i\text{app}}$  is an apparent quadratic size in the direction  $\mathbf{q}_i$  which appears because the two polymers do not have the same molecular weights. It is related to the real size  $R_{iD}$  of the deuteriated chains by [20]

$$R_{i\text{app}}^2 = R_{iD}^2 \left[ 1 + \frac{\Phi_D}{\Phi_H + \frac{M_D}{M_H - M_D}} \right].$$

These relations are valid in the Guinier range ( $\mathbf{q} \cdot R_i \leq 1$ ). The deuterated polymer has a higher molecular weight than the hydrogenated one and then the corresponding Guinier range is narrower. We have, nevertheless, used a larger domain (up to  $\mathbf{q} = 5.6 \cdot 10^{-2} \text{ \AA}^{-1}$ ) to achieve a better accuracy. This is correct since the large polydispersity of the polymers increases the Guinier range and since we have checked the linearity of  $I^{-1}(\mathbf{q})$  versus  $\mathbf{q}^2$  in all the  $\mathbf{q}$  range used. Through this correction, the obtained  $R_{iD}$  values are 1.66 times larger than the  $R_{iapp}$  values. This correction is, therefore, important but it does not change the type of backbone anisotropy. In the following,  $R_{iD}$  will be called  $R_{//}(R_{\perp})$  if  $\mathbf{q}_i$  is parallel (perpendicular) to the magnetic field.

### 3. Results

Figure 2 displays the scattered intensity distribution ( $\lambda = 10 \text{ \AA}$ ,  $d = 2m$ ) in the  $xy$  plane of the multidetector PAXY. Figure 2(a) corresponds to the isotropic phase at  $135^\circ\text{C}$  and, as expected, no anisotropy can be detected in the intensity distribution. Figure 2(b) corresponds to the nematic phase at  $93^\circ\text{C}$  and the shape of the scattering is clearly anisotropic. Qualitatively speaking, the scattering in reciprocal space is essentially perpendicular (i.e. it extends further in the perpendicular direction) to the magnetic field direction. This immediately indicates that, in direct space, the backbones present a prolate shape.

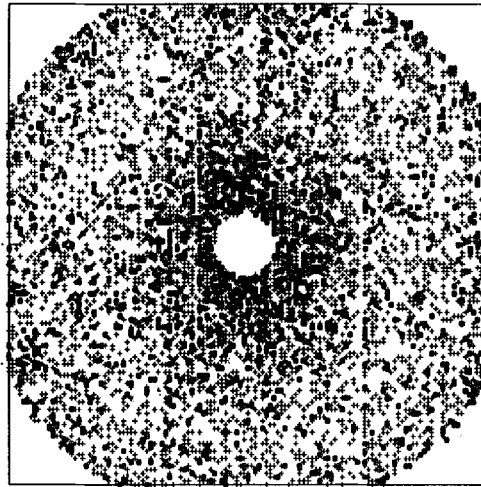
Figure 3 now shows the quantitative  $R_i$  values of the gyration radii of the polymer backbone along ( $R_{//}$ ) and perpendicular ( $R_{\perp}$ ) to the director. In the isotropic phase,  $R_{//}$  and  $R_{\perp}$  are both equal to  $35.5 \pm 1 \text{ \AA}$ . On decreasing temperature, at the nematic-isotropic transition,  $R_{//}$  jumps to about  $40.5 \pm 3 \text{ \AA}$  while  $R_{\perp}$  remains fairly constant at  $35.5 \pm 2 \text{ \AA}$ . On the contrary, within the nematic phase and by still decreasing temperature,  $R_{//}$  increases only slightly to reach a value of  $44 \pm 3 \text{ \AA}$  while  $R_{\perp}$  decreases significantly down to about  $27 \pm 2 \text{ \AA}$ . The reproducibility of these results was checked by measuring several times the same sample of polymer PA<sub>5</sub> using different thermal histories.

### 4. Discussion

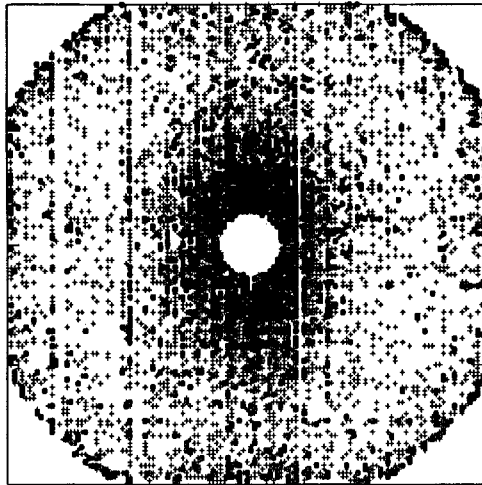
In this section we discuss the type of polymer backbone anisotropy (oblate or prolate) rather than the detailed thermal behaviour of  $R_{//}$  and  $R_{\perp}$  for which we have, so far, no explanation.

The SANS experiments described clearly demonstrate that the backbone of polymer PA<sub>5</sub> adopts a prolate shape in the nematic phase. In addition, the X-ray diffraction experiments show that the smectic fluctuations are negligible in this phase. We can also reasonably assume that the spacers here are long enough [21, 22] to efficiently decouple the backbone from the mesogenic cores (this means that there are little correlations between backbone and mesogenic cores due only to the chemical structure, i.e. the weak coupling assumption). If the spacers were too short, the backbone should be rigidly kept roughly perpendicular to the mesogenic cores and its conformation would probably be oblate.

Boeffel *et al.* [1, 22] have suggested that the backbone stiffness should determine its type of anisotropy: they have performed nuclear magnetic resonance experiments on two kinds of mesomorphic side chain polymers: polyacrylate and polymethacrylate. They have shown that the local orientation of the acrylate unit is roughly parallel to the nematic director whereas the methacrylate unit is roughly perpendicular to it. From these observations, they argue that the acrylate backbone should have a prolate shape



(a)



(b)

Figure 2. Transverse section of the intensity scattered by the backbone. Each cross represents a cell of the PAXY multidetector. The white disk in the centre is due to the beam trap. The magnetic field is horizontal. (a) Isotropic liquid ( $T = 135^{\circ}\text{C}$ ). The backbone conformation is isotropic. (b) Nematic phase ( $T = 93^{\circ}\text{C}$ ). The scattering in reciprocal space presents an oblate shape which means that the backbone adopts a prolate conformation in direct space.

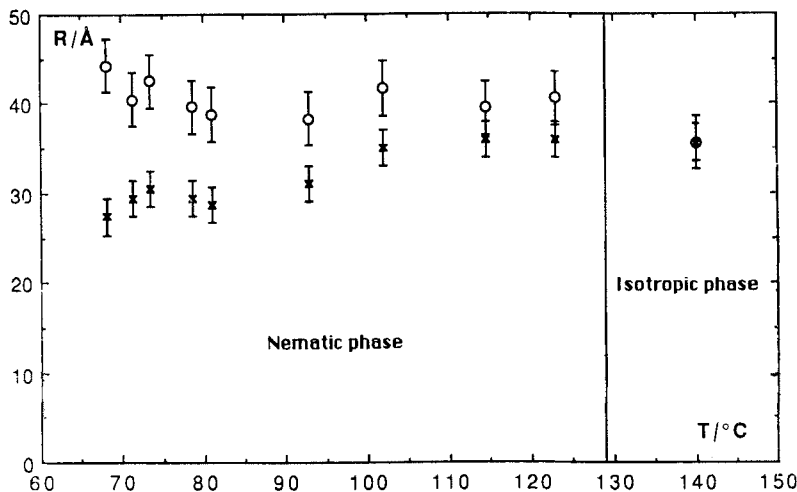


Figure 3. Values of the gyration radii (○)  $R_{\parallel}$  (along the director) and (×)  $R_{\perp}$  (perpendicular to the director) of the polymer backbone as functions of temperature. Just below the nematic–isotropic transition, though the absolute error bars overlap for the first two points, the relative backbone anisotropy is prolate.

and the methacrylate backbone an oblate shape. However, SANS studies [4] have shown that the same polyacrylate studied by Boeffel *et al.* rather adopts a globally oblate shape. Moreover the polymer called PA-CN [11] displays both types of anisotropy, oblate and prolate, in the N and  $N_{re}$  phases, respectively. Therefore, the chemical nature of the backbone alone does not by itself determine the type of backbone anisotropy; the nature of the mesophase plays a role too.

The SANS results described here, in the limit of the weak coupling assumption, imply that the natural tendency for the backbone in this nematic phase is to adopt a prolate shape [12, 13]. On the microscopic scale, this means that the densest packing would be obtained when the backbone is parallel to the mesogenic cores. Such a tendency indeed prevails in related systems. First, let us examine the polymer–mesogenic core interactions: the example of mesomorphic main chain polymers is not really significant because the mesogenic cores naturally impose their nematic order on the backbone since they are part of it [23]. The case of oligomers dissolved in a usual nematic phase [24, 25] is more interesting: though any anisotropy of the chain conformation could hardly be detected by SANS, a slight anisotropy was indeed observed by NMR. However, in neither of these papers [24, 25] is the type of anisotropy clearly stated. The same kind of ideas apply to polymer–polymer interactions too: a small nematic effect affecting the polymer chains was recently demonstrated by NMR not only in elastomers but also in polymer melts [26, 27]. In these experiments it was clearly shown that the chains tend locally to slightly align together creating a nematic field. This effect was interpreted by a steric condition which makes the polymer chains locally parallel to improve the packing [28].

In a next step it remains to understand why a few mesomorphic side chain polymers display an oblate backbone shape in the nematic phase. In these experiments [3, 7, 9, 10], the nematic phase had [14] strong smectic fluctuations with correlation lengths larger or comparable to the backbone gyration radius  $R_{\perp}$ . Then the polymer coil feels locally a smectic field and it was several times demonstrated by SANS that the backbone adopts an oblate conformation in the  $S_A$  phase. We are therefore inclined to

think that these backbone anisotropy determinations could be affected by the smectic fluctuations and might not be representative of the backbone behaviour in the nematic phase.

Finally, let us now formulate two assumptions [29] for the backbone conformation of comb-like polymers:

- (i) Because of the confinement effect, the backbone adopts a globally oblate conformation in the  $S_A$  phase.
- (ii) The backbone, if the spacers are long enough (the weak coupling assumption), should adopt a globally prolate shape in the nematic phase provided that the smectic fluctuations are negligible.

This last assumption may be qualitatively justified in terms of local close packing of the backbone among the pendant groups. However, we stress that these hypotheses are only based on the extrapolation to a global scale of microscopic considerations. (Such an extrapolation may indeed be hazardous [22, 25]). Of course, SANS studies of the backbone conformation of other mesomorphic side chain polymers in the nematic phase are needed to test the validity of these assumptions. In particular, it would be interesting to study the anisotropy of the backbone conformation as a function of the spacer length. In addition, in order to obtain a microscopic explanation of the backbone behaviour, it seems necessary to compare the local information given by NMR and the global information given by SANS.

We are indebted to M. Buzier for her help during the SANS experiments, to B. Deloche and A. M. Levelut for helpful discussions, to A. Rameau and C. Strazielle for the determination of the molecular weights and to M. F. Achard for the DSC study.

### References

- [1] For a general outline of the field of side chain liquid crystal polymers, see McARDLE, C. B. (editor), 1989, *Side Chain Liquid Crystals Polymers* (Blackie).
- [2] STRZELECKI, L., and LIÉBERT, L., 1973, *Bull. Soc. Chim. Fr.*, **2**, 597.
- [3] KELLER, P., CARVALHO, B., COTTON, J. P., LAMBERT, M., MOUSSA, F., and PÉPY, G., 1985, *J. Phys. Lett., Paris*, **46**, L1065.
- [4] NOIREZ, L., COTTON, J. P., HARDOUIN, F., KELLER, P., MOUSSA, F., PÉPY, G., and STRAZIELLE, C., 1988, *Macromolecules*, **21**, 2889.
- [5] OHM, H. G., KIRSTE, R. G., and OBERTHÜR, R. C., 1988, *Makromolek. Chem.*, **116**, 1387.
- [6] KALUS, J., KOSTROMIN, S. G., SHIBAEV, V. P., KUNCHENKO, A. B., OSTANEVICH, YU. M., and SVETOGORSKY, D. A., 1988, *Molec. Crystals liq. Crystals*, **155**, 347.
- [7] NOIREZ, L., Ph.D. Thesis, Université Paris XI-Orsay, 9/1/89 No. 798.
- [8] RENZ, W., and WARNER, M., 1986, *Phys. Rev. Lett.*, **56**, 1268.
- [9] KIRSTE, R. G., and OHM, H. G., 1985, *Makromolek. Chem. Rap. Commun.*, **6**, 179.
- [10] HARDOUIN, F., NOIREZ, L., KELLER, P., LAMBERT, M., MOUSSA, F., PÉPY, G., and RICHARD, H., 1988, *Molec. Crystals liq. Crystals*, **155**, 389.
- [11] NOIREZ, L., KELLER, P., DAVIDSON, P., HARDOUIN, F., and COTTON, J. P., 1988, *J. Phys., Paris*, **49**, 1993.
- [12] MATOUSSI, H., OBER, R., VEYSSIÉ, M., and FINKELMANN, H., 1986, *Europhysics Lett.*, **2**, 233.
- [13] MATOUSSI, H., and OBER, R., 1990, *Macromolecules*, **23**, 1809.
- [14] DAVIDSON, P., KELLER, P., and LEVELUT, A. M., 1985, *J. Phys., Paris*, **46**, 939 and also unpublished results.
- [15] WANG, X. J., and WARNER, M., 1987, *J. Phys. A*, **20**, 713.
- [16] RENZ, W., 1988, *Molec. Crystals liq. Crystals*, **155**, 549.
- [17] VASILENKO, S. V., SHIBAEV, V. P., and KHOKHLOV, A. R., 1985, *Makromolek. Chem.*, **186**, 1951.
- [18] FREIDZON, Y. S., BOIKO, N. I., SHIBAEV, V. P., and PLATÉ, N. A., 1985, *Dokl. AN SSSR*, **282**, 922.



- [19] BELTZUNG, L., and STRAZIELLE, C., 1984, *Makromolek. Chem.*, **185**, 1145.
- [20] BOUE, F., NIERLICH, M., and LEIBLER, L., 1982, *Polymer*, **23**, 319.
- [21] OULYADI, H., LAUPRÊTRE, F., MONNERIE, L., MAUZAC, M., RICHARD, H., and GASPAROUX, H., 1990, *Macromolecules*, **23**, 1965.
- [22] BOEFFEL, C., SPIESS, H., HISGEN, B., RINGSDORF, H., OHM, H., and KIRSTE, R., 1986, *Makromolek. Chem. Rapid. Comm.*, **7**, 777.
- [23] MARTINS, A. F., FERREIRA, J. B., VOLINO, F., BLUMSTEIN, A., and BLUMSTEIN, R. B., 1983, *Macromolecules*, **16**, 279.
- [24] SAMULSKI, E. T., 1985, *Polymer*, **26**, 177.
- [25] DUBAULT, A., OBER, R., VEYSSIÉ, M., and CABANE, B., 1985, *J. Phys. Paris.*, **46**, 1227.
- [26] DELOCHE, B., and SAMULSKI, E. T., 1981, *Macromolecules*, **14**, 575.
- [27] DELOCHE, B., DUBAULT, A., HERZ, J., and LAPP, A., 1986, *Europhysics Lett.*, **1**, 629.
- [28] SOTTA, P., DELOCHE, B., and HERZ, J., 1988, *Polymer*, **29**, 1171.
- [29] By the time this paper was refereed, we received a preprint of G. R. Mitchell *et al.* who independently formulated the same kind of assumptions: MITCHELL, G. R., DAVIS, F. J., GUO, W., and CYWINSKI, R., *Polymer* (in the press).