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Temperature Dependence of the Conformation of a Comblike Liquid Crystalline Polymer in a N_I Nematic Phase

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ABSTRACT: The backbone conformation of a comblike polymethacrylate, PMA-CH_3, was studied by small-angle neutron scattering in the nematic phase. The backbone is perpendicular to the mesogenic side chain moieties, corresponding to the oblate ellipsoid of the N_I phase of Wang and Warner's theory. We have measured the temperature dependence of the conformation of the polymer backbone on five well-defined molecular weights. In the direction perpendicular to the hanging groups, the backbone adopts a weakly confined random walk conformation, compared to that of the isotropic phase. In the direction of the nematic field, the chain conformation is extended: the exponents of the scaling laws vary between 0.60 and 0.50. At low temperature, smectic fluctuations freeze the backbone anisotropy. When increasing the temperature, the nematic order exerts a weaker force on the polymer backbone, which tends to an isotropic Gaussian conformation. The scaling laws for the backbone conformation and their variations with temperature are compared to the theoretical predictions.

A comblike liquid crystalline polymer (CLLCP)[1] is made of a flexible polymer (the backbone) with mesogenic moieties attached to each monomer via a flexible spacer. Because of the long-range orientation properties of the liquid crystal molecules and the mechanical properties of the polymer, these materials have many potential applications.[2] A fundamental question raised by CLLCP is the competition between the entropy of the polymeric part, which tends to adopt a random coil conformation, and the orientational ordering of the liquid crystalline side chains. Many theoretical predictions have been proposed to describe the nematic[3,4] and smectic[5,6] phases. In particular, Wang and Warner[4a] proposed an expression for the temperature dependence of the backbone conformation in the nematic phase. Because of the polymolecularity of CLLCP generally studied and the narrow temperature range of the nematic phase, the Wang and Warner model has never been evaluated experimentally. In this work, and in order to compare it with the theoretical predictions, we have measured precisely the backbone conformation of a CLLCP at different temperatures in its nematic phase and for several molecular weights.

Wang and Warner based their calculations on the mean field theory, using the Maier−Saupe expression,[7] to describe the dependence of the nematic order parameter on temperature. They defined five coupling parameters between the backbone and the mesogenic groups via the flexible spacers and two order parameters (for the side group and for the backbone). The backbone order parameter (S_B) gives the type of anisotropy ($S_B > 0$ in the prolate case and $S_B < 0$ for the oblate case). Concerning the polymeric aspect, the key problem is based on the competition between the increasing of entropy of chains and the decreasing of the bending energy (modulus ϵ) by avoiding highly contorted configurations. This last component, inherited from the theory of nematic main chain polymers,[4b] is temperature-dependent. The model predicts the existence of three backbone conformations called N_I, N_{II}, and N_{III}, which simply differ by the orientations of the backbone and mesogenic moieties with respect to the ordering direction. Transitions between the different phases are also predicted.[3,8]

The most likely situation occurs when the side chains order strongly and when the backbone prefers to be perpendicular to the side chains (like in a comb); this gives the oblate conformation (N_I phase). In this case, the authors give expressions for the chain radii of gyration in the directions parallel ($R_{\|}$) and perpendicular ($R_{\perp}$) to the director.[4a] In the case of strong nematic order (low T), where both the order parameters of side chains and of backbones saturate, this leads to

$$\langle R_{\perp}^2 \rangle \propto L/T \tag{1}$$

$$\langle R_{\|}^2 \rangle \propto TL \tag{2}$$

where L is the total length of the polymer. One may note that, in this model, the chains remain Gaussian ($R_i^2 \propto L$). As temperature is lowered, chains should shrink in the $\|$ direction, whereas in the $\perp$ direction, they should expand. This latter variation is due to the increase of effective step length of the random walk and not to a change in the nature of this walk.

Today, a great number of experimental studies have established some general rules for the anisotropy of CLLCPs backbone.[2,9−11] In the smectic phase, the segregation between the aliphatic and aromatic moieties of the mesogens leads to the confinement of the backbone in the aliphatic part of the smectic layers: an oblate conformation is adopted, confirming what was stated by theoretical models.[5,6] In the nematic phase, the situation is not so clear. Oblate or prolate type for the backbone anisotropy can be obtained[3,4] depending on the symmetry and on the nature of the fluctuations that take place.[12,13] In one special case of a reentrant nematic phase, the two kinds of backbone anisotropy have even been observed[14] by varying the temperature. The anisotropy ($R_{\|}$ smaller than $R_{\perp}$) has been observed several times,[11,12−14] but, as already mentioned, Wang and Warner's predictions for temperature dependence have never been evaluated experimentally.

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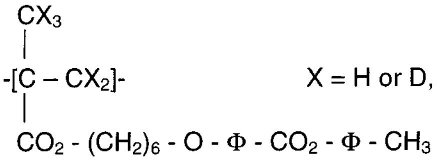
Table 1. Characteristics of PMA-CH$_3$ Samples of Different Average Molecular Weights M_w[a]

M_w (g/mol)[b]	x	M_{wH} (g/mol)	M_{wD} (g/mol)	$R_g/\sqrt{3}$ (Å)
43 000	0.50	47 000	40 000	17 ± 1
79 500	0.50	87 000	77 000	23 ± 1
131 000	0.40	139 000	126 000	31 ± 1
255 000	0.60	214 000	264 000	42 ± 2
620 000	0.55			65 ± 3

[a] x is the ratio of deuterated polymers. M_{wD} and M_{wH} are the weight-average molecular weights of respectively deuterated and hydrogenated polymers measured by size exclusion chromatography–light scattering. R_g is the radius of gyration obtained by SANS (ref 17) in the isotropic phase. [b] The molecular weight is determined by SANS.

Experimental Details

The polymer studied here displays a nematic phase over a large temperature range, between T_g = 44 °C, the glass transition temperature, and T_{NI} = 83 °C, the nematic-to-isotropic transition temperature. It is a polymethacrylate called PMA-CH$_3$; its chemical formula is



$$-[\overset{\displaystyle CX_3}{\overset{|}{C}} - CX_2]- \atop \underset{\displaystyle CO_2 - (CH_2)_6 - O - \Phi - CO_2 - \Phi - CH_3}{|}$$

X = H or D, Φ = phenyl group

Its backbone conformation is determined by small-angle neutron scattering (SANS) on mixtures of polymers with deuterated (X = D) and regular (X = H) backbones. Such experiments are well-known[15] to give the form factor of the backbone of one polymer chain dispersed among the others. The polymers are obtained from free radical polymerization of corresponding methacrylate monomers.[16] They have been fractionated using a precipitation method in order to obtain narrow fractions[17] of different weight-average molecular weights, M_w. M_w is determined from size exclusion chromatography coupled with small-angle light scattering.

Mixtures of about half and half H and D polymers with similar M_w values ($M_{wD} \cong M_{wH}$) were prepared following a method described in a previous paper.[17] Five M_w samples, ranging from 43 000 to 620 000, have been studied (see parameters in Table 1).

Before the SANS experiments, PMA-CH$_3$ samples were aligned in the nematic phase using a magnetic field of 1.4 T. The temperature was slowly decreased from T_{NI} to T_g (during about 70 h) in order to obtain an aligned sample. Under these conditions, the samples are known to be quenched in a N$_I$ nematic state containing weak smectic A fluctuations:[17] $R_{||} < R_\perp$.

Small-angle experiments were performed with the PAXY spectrometer[18] at the Orphée reactor (LLB, Saclay), in two configurations. This allowed us to explore the scattering vector ranges [$10^{-2} < q < 10^{-1}$ Å^{-1}] for the smallest molecular weight sample and [$7 \times 10^{-3} < q < 7 \times 10^{-2}$ Å^{-1}] for the others. The aligned sample was put inside an oven, itself placed between the poles of the magnet in order to maintain the nematic orientation. The temperature is within a precision of 0.2 °C. We started the SANS measurements at 318 K, thus close to T_g, and then increased the temperature up to 355 K, close to T_{NI}. The efficiency of detectors was corrected using the flat intensity delivered by a Plexiglas lamella. The incoherent background was determined from the intensities scattered by pure hydrogenated and pure deuterated samples. The absolute intensity, $I(q)$ in cm^{-1}, was obtained from the determination of the neutron flux in the incident beam.[19] It is directly proportional to the form factor of the backbone, which allows us to verify M_w.

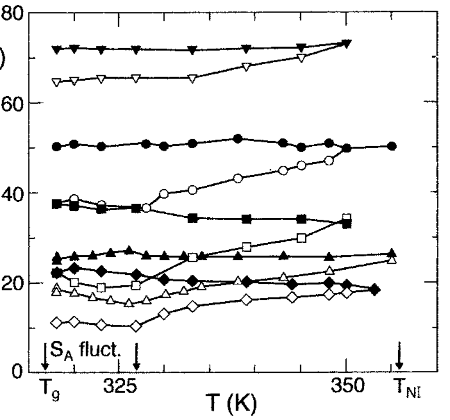


Figure 1. Variations of the inertial radii of the polymer backbone in the directions parallel (open symbols) and perpendicular (full symbols) to the director vs temperature for different molecular weights (from the top M_w = 620 000, 255 000, 131 000, 79 500, and 43 000) of PMA-CH$_3$ in the nematic phase. The lines are guides for the eyes.

Results and Discussion

The values of inertial radii[9,20] $R_\perp$ and $R_{||}$ of polymer backbones were obtained from Zimm plots of the data in the directions perpendicular and parallel to the field, using

$$\frac{1}{I_i(q)} = \frac{1}{kM_w}(1 + q^2 R_i^{\,2}) \quad qR_i < 1,\ i = \perp, || \qquad (3)$$

The prefactor k for the PMA-CH$_3$ polymers is[17] 3×10^{-5} g^{-1} cm^{-1}. $R_\perp$ and $R_{||}$ were determined, according to eq 3, from the slopes of the best linear fits in the Guinier range, $qR_i < 1$, simultaneously for both directions in order to be sure of $I(0)$, i.e., M_w. Thus, the error bars were less than 5% of the values of the inertial radii.

Figure 1 shows the evolution of the backbone anisotropy for each molecular weight species as a function of the temperature. The general features are the following:

(i) As already observed, the backbone anisotropy $R_{||} < R_\perp$, typical of the N$_I$ phase, is obtained whatever the molecular weight and temperature: the polymer backbone tends to be perpendicular to the director.

(ii) As temperature increases, the nematic interaction is getting weaker. The parallel dimension $R_{||}$ increases significantly, whereas the perpendicular dimension $R_\perp$ slightly decreases or remains almost constant for the higher molecular weights. Thus, the anisotropy factor, $\alpha = (R_\perp/R_{||})^2$, decreases as resulting from a weaker coupling between the mesogens and the backbone. Just below T_{NI}, where the nematic interaction becomes negligible, both sizes are merged. These common values are nevertheless systematically slightly higher (a few percent) than the corresponding inertial radii ($R_g/\sqrt{3}$) (see Table 1), deduced from previous measurements[17] in the isotropic phase.

(iii) Whatever the temperature, the smaller the molecular weight, the higher is the anisotropy factor. For example at 330 K, α = 2.54 for M_w = 43 000 and α = 1.74 for M_w = 255 000. This behavior, clearly visible in Figure 1 for the low temperatures, disagrees with the predictions. As a matter of fact, combining eqs 1 and 2 leads to a ratio ($R_\perp/R_{||}$) independent of L, i.e., of M_w.

(iv) Finally, by varying the temperature, two different regimes are clearly identified (see Figure 1). At low temperatures, the polymer dimensions show very weak

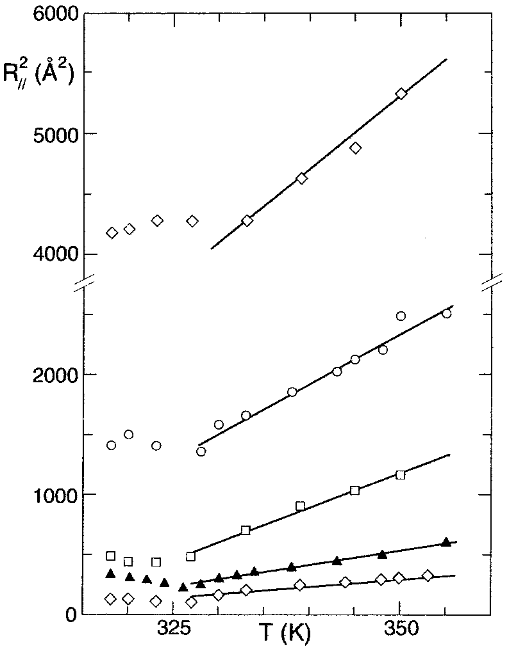


Figure 2. Representations of $R_{||}^2$ vs temperature for different molecular weights (from the top M_w = 620 000, 255 000, 131 000, 79 500, and 43 000) of PMA-CH$_3$ in the nematic phase.

variations. It is only above 328 K that $R_{||}$ significantly increases while $R_\perp$ still does not vary much. We can compare these variations with the predictions of Wang and Warner's model. In the $\perp$ direction, $R_\perp$ should decrease as a function of $\sqrt{1/T}$ (eq 1). Such a variation is not observed for the highest molecular weights, 620 000 and 255 000, and a slight decrease of $R_\perp$ is measured for the lower M_w values. In the $||$ direction, theoretical predictions are better verified since $R_{||}^2$ is linearly increasing with temperature, but only above 328 K (see Figure 2). We can see in this figure that the variation is more pronounced for higher M_w (i.e., L), as expected from eq 2. However, the slopes do not vary as M_w (i.e., L), as predicted.

A classical way to describe the chain conformation is to establish the relationship between the radius of gyration and the molecular weight: $R_g \propto M_w^v$. The value of the exponent ν indicates the nature of the chain walk. For a Gaussian chain, $\nu = {}^1/_2$. Preliminary experiments[17] have already shown that in the isotropic phase $\nu = 0.51 \pm 0.02$. Here, a complete set of ν exponents has been obtained for various temperatures between 318 and 355 K (see Figure 3). Once again, two different regimes clearly appear. At low temperature, roughly constant exponents are measured: $\nu_\perp \approx 0.46 \pm 0.02$ and $\nu_{||} \approx 0.66 \pm 0.02$, confirming our previous results,[17] $R_\perp \propto M_w^{0.48\pm0.03}$ and $R_{||} \propto M_w^{0.63\pm0.05}$, measured at 295 K in the glassy nematic state. When increasing the temperature, $\nu_\perp$ slowly increases from 0.46 up to 0.51, while $\nu_{||}$ decreases from 0.60 to 0.53 close to T_{NI}. Therefore, at $T \cong T_{NI}$, the chains come back to a Gaussian conformation, as observed in the isotropic phase. We can therefore wonder why both inertial radii are a bit larger than the isotropic value, as stressed in point ii, whereas no difference was observed[17] between the isotropic and the nonoriented nematic phases. It seems that the suppression of the defects of the nematic phase during the alignment process has some influence on the local backbone conformation. This peculiar point should be confirmed with further experiments. In fact, we wonder whether this characteristic parameter of the backbone conformation can change or not upon annealing in the isotropic phase.

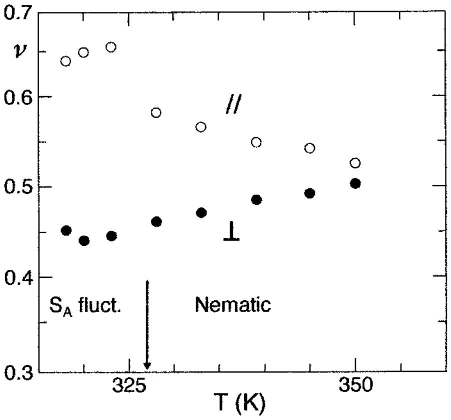


Figure 3. Temperature variations of the exponents of the scaling laws in the directions parallel (○) and perpendicular (●) to the director for PMA-CH$_3$ in its nematic phase. At low temperature, smectic fluctuations effects are visible.

At this point of the discussion, we have clearly demonstrated two different behaviors as regards temperature. Now, the question is, what is the origin of such a difference? Since we know that smectic fluctuations take place at low temperature, we can imagine that they govern the chain conformation below 328 K. Smectic fluctuations tend to segregate side-chain mesogens in planes perpendicular to them, but there is no long-range correlation between these planes. It is thus tempting to consider the model proposed by Rieger[6] for smectic CLLCP to describe the chain conformation at low temperature. One advantage of this model is to predict a Gaussian conformation in the perpendicular direction, without temperature variation, which is roughly what we have measured here. Another interesting specificity is the rodlike conformation of the backbone through the smectic layers. This specific tendencies of the smectic order are nevertheless not very marked here. For the high molecular weights (620 000 and 255 000), the smectic fluctuations just freeze the backbone anisotropy. For the low molecular weights, both dimensions ($R_{||}$ and $R_\perp$) seem to be slightly extended when the smectic fluctuations are stronger. The weak increase of $R_\perp$ probably arises from the enhancement of the tendency of the backbone to be perpendicular to the side groups. But, the other dimension $R_{||}$ does not decrease abruptly, when the smectic fluctuations become stronger. A weak increase is even observed for the low molecular weights: values of $R_{||}$ are 2 or 3 Å (depending on M_w) higher at 318 K than at 327 K. We can assume that this discrepancy is due to the length of the polymer: when $R_{||}$ is smaller than one typical layer (of size 23 Å), the backbone is not long enough to go through one smectic layer. Thus, when the smectic fluctuations are increasing, the backbone cannot shrink but simply tends to better align itself with respect to the mesogenic moieties. An increase of $R_{||}$ could also arise from a higher strength of the nematic coupling between the directions of the side and main chains, which tend to be parallel. But in this case, an increase of $R_{||}$ should occur for all the molecular weights, a fortiori for the higher M_w. In fact, the nematic coupling is competing with the segregation tendency between the backbone and the side groups: the first one leads to increase the parallel dimension, whereas the second one tends to shrink this dimension. This antagonism allows us to qualitatively explain the observed variations.

Concerning the exponents measured at low temperature, they are far from 1, the value obtained from a rodlike conformation. But here, just as regards the small dimensions of the backbones, we can assume that there are few crossings per chain (perhaps even fewer than for a LC polymer in a smectic phase[21]). Thus, the inertial radii $R_{||}$ have two components. The major component corresponds to interlayer distances, where the backbone adopts a random walk. The second component, less important, arises from few crossings with a rod trajectory for the backbone. With such a picture of the polymer backbone, we can understand why the exponents of the scaling laws are close to 0.5 and not 1.

When increasing the temperature, we clearly see a change in the variations of the backbone dimensions (see Figures 1 and 2). Above 328 K, the smectic fluctuations have vanished, and a pure nematic phase takes over. When increasing the temperature, the values of measured $\nu_\perp$ increase, little by little, going from 0.46 to 0.50, the characteristic value for a random coil. In this direction, the backbone conformation is no more strictly Gaussian, and it does not depend on temperature as predicted in the Wang and Warner model. This latter result means that the coupling between the mesogenic moieties and the backbone through the spacers is very weak in this nematic PMA-CH_3. The spacer, $-(CH_2)_6-$, can be considered as a flexible hinge. Furthermore, values of $\nu_\perp$ smaller than 0.5 would indicate that the segment density of the backbone is increased compared with the isotropic one. Indeed, we are tempted to propose the appearance of a weak confinement of the backbone in the plane perpendicular to the mesogenic moieties. At the same time, in the || direction, the backbone conformation is extended, since values of $\nu_{||}$ up to 0.6 are reached. The deviation from the ideal case is more pronounced here.

An alternative model to account for the exponents of the scaling laws in the || direction would be an excluded-volume model. Such a problem is generally not important in a polymer melt since the dense environment of other chains leads to screening of interactions, and the chains adopt an ideal conformation. The case of a polymer confined to two dimensions by the nematic field was evoked by Wang and Warner.[4a] They mentioned that in a highly oriented system the excluded-volume interaction cannot for topological reasons be screened. But in their predictions of the chain conformation for the N_I phase, the authors have ignored this problem. Here, we can give an insight into the order parameters: on similarly aligned PMA-CH_3 samples, the side chain order parameter, S_A, measured by X-ray diffraction was between 0.50 and 0.68.[17] These values are smaller than those calculated and discussed by Wang and Warner. Concerning the degree of orientation of the backbone, the SANS data are difficult to relate to the order parameter S_B of the model. In regard to the backbone dimensions, we can hardly say that the chain is compressed down toward a disk shape. Thus, we do not believe that the PMA-CH_3 polymers fulfill the drastic conditions where excluded-volume statistics must prevail.

The whole set of results measured in this temperature range allows us to state that the conformation of the nematic comblike polymer cannot be well described with ideal chain statistics as proposed in Wang and Warner's model, at least in the molecular weight range studied.

Finally, if we extrapolate to the high molecular weights the variations of the backbone conformations, we would expect a change of anisotropy of conformation, $R_{||} > R_\perp$. Such a transition remains to be observed and discussed. Another possible scenario would be to recover for infinite chains an isotropic conformation, even in the presence of a nematic interaction.

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