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Effect of the Molecular Weight on the Whole Conformation of a Liquid Crystalline Comb-like Polymer in Its Melt

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ABSTRACT: The whole conformation of a comb-like polymethacrylate (PMA-CH_3) has been determined by small-angle neutron scattering (SANS) in the isotropic and nematic phases. Its molecular weight dependence is obtained from six well-defined M values. In the isotropic phase, the persistence length is found to be $l_p = 10 \pm 1.5$ Å, and the relation between the radius of gyration, R_g, and M or N, the number of monomers, is $R_g = 0.143M^{1/2} = 2.85N^{1/2}$. Therefore, there is practically no difference between the conformation of the PMA-CH_3 backbone and that of the polystyrene. This result is striking since it appears that the backbone conformation of a polymer with a hanging group of 23 Å length every 2.5 Å along the chain is quite the same as that of the standard of linear polymers. In the unoriented nematic phase, the same values of l_p and R_g are found. This means that the l_p value remains unchanged in the nematic phase. In the oriented nematic phase, the values of the inertial radii of the chain, $R_\parallel$ and $R_\perp$, in the direction parallel and perpendicular to the nematic director have been measured as a function of M: $R_\perp = 0.12M^{0.48\pm0.03}$ and $R_\parallel = 0.015M^{0.63\pm0.05}$. These results are confirmed by the dependence of the form factor on the scattering vector in the intermediate range. They are discussed in term of smectic fluctuations.

I. Introduction

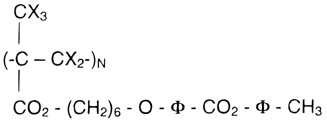
A comb-like liquid crystalline polymer[1] is made from mesogenic hanging groups linked to each monomer of a flexible polymer. Typically, the length of the hanging moieties is about 25 Å. These polymers are of interest because they combine the long-range orientation properties of the liquid crystal molecules and the mechanical properties of polymers. Their applications are numerous:[2] for instance, they may be used in optical data storage, in nonlinear optics, as stationary phases for gas or liquid chromatography, and as solid polymer electrolytes or conducting polymers.

There are currently a great number of studies available on the conformations of these polymers. A survey of them is given elsewhere.[3] They are obtained by small-angle neutron scattering (SANS) of samples made of mixtures of polymers with deuterated backbones and regular ones. Such an experiment is well known[3,4] to give the form factor of the backbone of a chain dispersed among the others.

Since most of the liquid crystalline polymers studied are obtained by a free radical polymerization, their polydispersity is large ($I_w = M_w/M_n > 2.5$). For this reason, the studies have essentially given important results concerning the mean values of the chain radius of gyration, R_g, in the different phases and their anisotropy in the aligned mesophases but nothing about their semi-local conformations. The form of a polymer can be obtained only from the variation of the chain form factor as a function of the scattering vector, q, in the intermediate range ($qR_g > 4$). In practice, such a range is very difficult to obtain with a large distribution of R_g values.

Thus, to our knowledge, nothing makes it possible to answer the following basic questions: Is the chain Gaussian in the isotropic phase? What is the value of the persistence length? How does the persistence length vary in the mesophases? Are the M variations of the chain sizes similar in both directions (parallel and perpendicular to the nematic director)?

In order to get experimental answers and also to improve on the results of other experiments[5] concerning the chain dynamics as observed from an uniaxial stretching of such polymers in the nematic phase, we have prepared polymers with six well-defined molecular weights. The polymer studied is a polymethacrylate, PMA-CH_3, of chemical formula



$$\underset{CO_2 - (CH_2)_6 - O - \Phi - CO_2 - \Phi - CH_3}{\overset{CX_3}{(\text{-}C}} - CX_2\text{-})_N$$

X = H or D

Of course, six polymers with deuterated backbones (X = D) of similar degree of polymerization, N, were also prepared.

Besides, since it is often admitted that short-range nematic interactions between mesogenic moieties remain in the isotropic phase, we want to test their influence on the chain conformation. With this aim, we prepared very similar polymers, PMA-MCH_3, of which the chemical formula differs from the above one only in the position of the terminal group -CH_3. It is here in the meta position on the last phenyl group, Φ, whereas it was in the para position in the preceding polymer. This small position change in the isomeric form is, nevertheless, sufficient to delete the nematic phase. The PMA-MCH_3 gives only an isotropic phase. Thus, it allows testing the effects of the nematic interactions on the polymer conformation.

In the following, the experimental details concerning the polymers and the SANS experiments will be described in section II. In section III will be given the

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results obtained in the isotropic phase, in the unoriented nematic phase, and in the oriented nematic phase. In the Conclusion, the most important results are discussed.

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

M_w (g/mol)	x	M_{wH} (g/mol)	I_{wH}	M_{wD} (g/mol)	I_{wD}
260 000	0.48	301 000	1.27	221 000	1.14
255 000	0.60	214 000	1.06	264 000	1.16
131 000	0.50	139 000	1.11	126 000	1.19
79 500	0.50	87 000	1.21	77 000	1.09
43 000	0.50	47 000	1.07	40 000	1.15
23 000	0.50	27 000	1.13	20 000	1.19

[a] x is the ratio of deuterated polymers. M_{wD}, M_{wH} are the weight average molecular weights and I_{wD}, I_{wH} the polydispersities of respectively deuterated and hydrogenated polymers measured by SEC-LS.

II. Experimental Details

II-1. Samples. The hydrogenated or deuterated polymers are obtained by free radical polymerization of corresponding methacrylate monomers in solution.[6] The polymers of large polydispersity, $I_w > 2.5$, are fractionated using a precipitation method with 1,2-dichloroethane as good solvent and methanol as bad solvent. The samples are then analyzed by size exclusion chromatography on line with small angle light scattering (SEC-LS) to obtain the molecular weight distribution characterized by the weight-average molecular weight, M_w, and the polydispersity, I_w. The results are reported in Table 1. Differential scanning calorimetry is used to obtain T_g (the temperature of the glass transition) and T_{NI} (the temperature of the nematic to isotropic transition). The heating rate is 15 °C/min for T_g and 2 °C/min for T_{NI}. The results are $T_g = 44 \pm 1$ °C and $T_{NI} = 83 \pm 2$ °C.

Mixtures of H and D polymers of similar M_w values containing x% (number or volume) of deuterated polymers are prepared. They are made by dissolving both species in chloroform under powerful mixing for 24 h in order to ensure a good homogeneity. After drying under vacuum at room temperature for at least 48 h, the calculated amount of powder is then deposed in the cell at 130 °C and put under vacuum until bubbles vanish. The parameters of the samples are given in Table 1.

II-2. X-ray Experiments. The X-ray diffraction experiments are carried out with an apparatus described elsewhere.[7] A rotating copper anode generator equipped with a microfocus produces the photon beam. A nearly parallel monochromatic ($\lambda_{\mathrm{Cu\ K\alpha}} = 1.541$ Å) beam is obtained by reflection from a bent graphite slab. The beam size is about 1 mm^2 at the sample level. The samples are those used in the SANS experiment, with thickness of about 1 mm. The scattered X-rays are collected with an image plate. The scattering vector range is $10^{-1} < q < 3$Å^{-1}. The nematic order parameter, S, is deduced from the crescent pattern using a recent analysis method[8] leading to the Leadbetter's integral equation and the Maier–Saupe distribution.

II-3. SANS Experiments. The small-angle experiments are done using the PAXY[9] spectrometer at the Orphée reactor (LLB, CEA Saclay). The distance between the XY detector (128 × 128 cells of s=5 × 5 mm^2) and the sample is $D = 2.50$ m. The incident collimation is obtained from two circular holes at 2 m distance, the first one of 16 mm diameter and the second one of 7.6 mm diameter. The corresponding scattering vector range is $1.2 \times 10^{-2} < q < 8 \times 10^{-2}$Å^{-1}. The sample is placed inside an oven whose temperature is known with a precision of 0.2 °C and regulated within 0.1 °C.

For the analysis of isotropic samples, the regrouping of data is annular around the center of the incident beam inside rings of 1 cm width. For the aligned samples in the nematic phase, the data are regrouped inside rectangles of 6 cm width perpendicular to the magnetic field and inside rectangles from 2.5 and 6 cm width (depending on the anisotropy of the scattered intensity) parallel to the field.

The efficiency of the detector cells is normalized by the flat intensity delivered by a Plexiglas lamella. The level of incoherent background is measured from the intensities scattered by two samples: the first one made of regular polymers and the second one made of polymers with deuterated backbones. Both samples give a flat intensity, except for a small central scattering due to defects occurring during the quenching. These defects are eliminated by using the totally flat intensity delivered by the Plexiglas lamella, whose level is restored to that of the incoherent background of the sample.

Absolute values of the scattering intensity are obtained[10] from the direct determination of the number of neutrons in the incident beam and the cell solid angle (s/D^2).

III. Results

III-1. Conformation in the Isotropic Phase. The measurements of the conformation of the polymer PMA-CH$_3$ have been performed at 90 °C (~7 °C above the nematic–isotropic transition). The absolute intensity, $I(q)$ in cm^{-1}, is directly proportional to the form factor, $s(q)$, of the polymer backbone, following the relation

$$I(q) = x(1 - x)n^2(a_D - a_H)^2(\rho_H N_A/m_H 2)M_w s(q) = kM_w s(q); \quad s(0) = 1 \quad (1)$$

where x is the ratio (volume/volume) of partially labelled chains, N_A Avogadro's number, $n(a_D - a_H)$ the contrast length between D and H monomers (here $n = 5$, $a_D = 0.667 \times 10^{-12}$ cm and $a_H = -0.374 \times 10^{-12}$ cm). The density of the H sample, $\rho_H = 1.17 \pm 0.03$ g cm^{-3}, was determined from masses and volumes of some samples at room temperature. $m_H = 396$ g/mol is the molecular weight of the H monomer. Thus, from the value of the intensity extrapolated to $q = 0$ and $k = 3 \times 10^{-5}$ cm^{-1} ($x = 0.5$), the value of M_w can be determined.

The SANS data have been fitted with the model of the Kratky–Porod chain.[11] This model describes a wormlike chain, which is Gaussian at large scale and evolves continuously to a rigid rod when decreasing the distance below the persistence length, l_p. Two parameters define the chain: its contour length L and l_p. The form factor of such a chain is not a simple function.[12–14] The simplest expression is obtained from merging[15] three functions; it is valid only for $L \geq 10l_p$. These functions are

$$ql_p \geq 4 \qquad s_1(q) = \frac{\pi}{qL} + \frac{2}{3q^2 l_p L} \qquad (2)$$

$$2 < ql_p < 4$$
$$q^2 l_p L s_2(q) = 6 + 0.5470(ql_p)^2 - 0.01569(ql_p)^3 - 0.002816(ql_p)^4$$

$$ql_p \leq 2 \qquad s_3(q) = \frac{2}{x^2}(e^{-x} - 1 + x) + \frac{2}{15u}\left[4 + \frac{7}{x} - \left(11 + \frac{7}{x}\right)e^{-x}\right]; \quad x = q^2 l_p L/3,\ u = L/l_p$$

$s_1(q)$ is the asymptotic form given by des Cloizeaux,[12] $s_2(q)$ is an approximation, better than 4×10^{-3}, of the tabulated data also given by des Cloizeaux in ref 12, and $s_3(q)$ is the approximation of Sharp and Bloomfield[13] for finite chains valid only for small q values, $ql_p \leq 2$. The radius of gyration of this chain is[16].

$$R_g^{\ 2} = l_p^{\ 2}\left(\frac{u}{3} - 1 + \frac{2}{u} - \frac{2}{u^2}(1 - e^{-u})\right) \qquad (3)$$

When u tends toward infinity, R_g^2 tends to $Ll_p/3$; thus, the statistical unit of the wormlike chain is $2l_p$.

In practice, the fit gives the best values of L, l_p, and $I(0)$. The consistency of each fit is verified from the values of M_w deduced from $I(0)$ with eq 1. Then the values of $I(0)$ were imposed in order to improve the precision on the other parameters. The quality of the fit is clearly shown in Figure 1 for $M_w = 255\ 000$, where the representations $I(q)$ in Figure 1a and $q^2I(q)$ in Figure 1b are used. The latter better shows the form factor behavior in the intermediate range. Similar good fits are obtained with the other polymers; another example, for the polymer $M_w = 43\ 000$, is given in Figure 1b. Thus, the model of a wormlike chain is well suited to the backbone form factor. The corresponding values for L and l_p are given in Table 2, where the R_g values deduced with eq 3 are also given. In Table 2, the M_L values are polymer molecular weights deduced from L values. They are obtained by multiplying the number of monomers, L/a (a is the monomer length, $a = 2.54$ Å), by m_H. These data are of interest to verify the consistency of the data treatment.

The persistence length determination is not very precise but seems to be really independent of M_w, and the following value,

$$l_p = 10 \pm 1.5 \text{ Å}$$

is adopted. Figure 2 shows the R_g values versus M_w in a log−log representation. The slope is found to be 0.51 ± 0.02. Thus, the chains can be considered as having a Gaussian conformation in the isotropic phase. Imposing an $M^{1/2}$ variation of R_g, the numerical relation is

$$R_g = (0.143 \pm 0.03)M_w^{\ 1/2} = 2.85N_w^{\ 1/2}$$

The prefactor 0.143 is smaller than the value of 0.17 we obtained[5] with a polydispersed polymer. This overestimated value led to $l_p = 14$ Å. The reason for this departure is that the latter values were obtained by direct measurement of R_g. In fact, it is easier to obtain a q range suitable to the determination of l_p than one suitable to the determination of R_g. The accuracy of R_g and l_p is better in the present article.

It is of interest to compare the l_p and R_g values to those of polystyrene. For the latter, the literature[15,17] gives $l_p = 9.2 \pm 0.3$ Å and $R_g = 0.279M^{1/2} = 2.85N^{1/2}$. This result is very striking, since it appears that the backbone conformation of a polymer with a hanging group of 23 Å length every 2.5 Å along the chain is quite the same as that of the standard linear polymers.

The same treatment has been applied to the data of the isomeric polymer, PMA-MCH3. With this polymer, the fits with the model of Kratky and Porod also give very good results (summarized in Table 3). Here also, the value of l_p is 10 Å, and the variation of R_g as a function of M obeys the same law, in the limit of the error bars, as the PMA-CH3 (see Figure 2). Thus, no conformation difference between both isomeric forms of the polymer can be observed in this SANS experiment.

III-2. Conformation in the Unoriented Nematic Phase. The samples of PMA-CH3 are studied by SANS in the unoriented nematic phase at two temperatures: 67.5 and 54 °C. No visible difference is found between the scattering curves obtained in the isotropic phase and in the nematic phase, even at the lower temperature. Thus, all results obtained in the isotropic phase remain unchanged in the unoriented nematic phase. Yet, at the semi-local scale (10−50 Å), where the persistence length l_p is measured, the nematic phase is totally aligned. Therefore, because the l_p value is not affected, this parameter is not sensitive to the nematic interaction.[18]

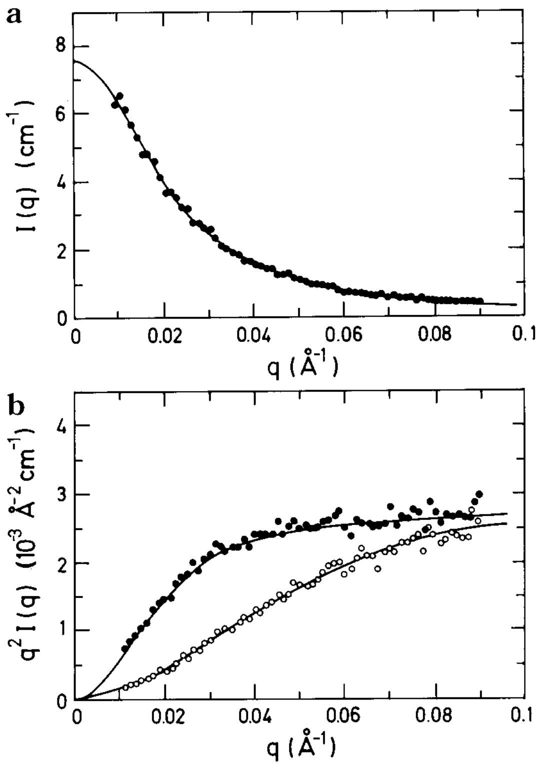

Figure 1. Two representations of the absolute scattering intensity $I(q)$ of PMA-CH3 in the isotropic phase for the sample $M_w = 255\ 000$. The lines are the best fits of the data to the model of a wormlike chain. (a) Direct intensity versus q. (b) Kratky representation $q^2I(q)$ for the same sample, $M_w = 255\ 000$ (●), and for the sample $M_w = 43\ 000$ (○). This representation is used to show the fit quality in the data curvature. The persistence length obtained is 10 Å.

Table 2. Values of the Persistence Length, l_p, the Contour Length, L, and the Radius of Gyration, R_g, of Different Molecular Weights, M_w, of PMA-CH3[a]

M_w (g/mol)[b]	L (Å)	l_p (Å)	R_g (Å)	M_L
620 000	3 800 ± 100	10 ± 1.5	113 ± 5	585 000 ± 15 000
260 000	1 650 ± 150	10 ± 1	74 ± 3	255 000 ± 20 000
255 000	1 600 ± 150	10 ± 1	72 ± 3	245 000 ± 20 000
131 000	790 ± 50	11 ± 2	53 ± 2	122 000 ± 8 000
79 500	500 ± 100	10 ± 0.5	40 ± 2	77 000 ± 10 000
43 000	260 ± 50	11 ± 2	29 ± 2	40 000 ± 8 000
23 000	190 ± 60	10 ± 5	23 ± 2	29 000 ± 9 000

[a] M_L is the molecular weight deduced from L ($M_L = m_HL/2.54$). [b] The molecular weight is only determined by SANS.

III-3. Conformation in the Aligned Nematic Phase. The alignment of PMA-CH3 samples in the nematic phase is rather difficult in a magnetic field of 1.4 T and is too long to be done in situ. The procedure used is the following: starting from the melt in the isotropic phase at a temperature T_{NI} + 3 °C, the temperature is slowly decreased (0.01 °C/min) and leveled for 15 min every 0.25 °C. It takes about 50 h to

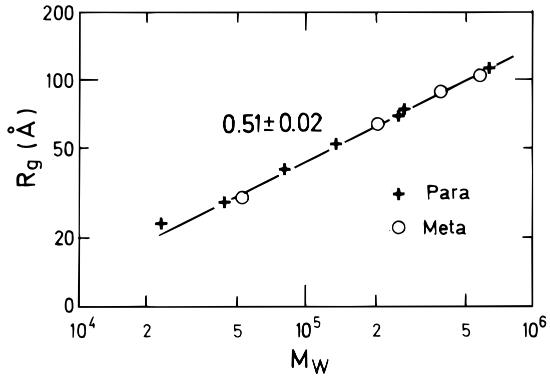

Figure 2. Log−log plot of the radii of gyration as function of weight-average molecular weight for PMA-CH_3 (+) and its isomeric form, PMA-MCH_3 (○), in the isotropic phase. The slope shows the Gaussian character of these polymers in the melt. The polymer of lower mass (M_w = 23 000) has only seven statistical units.

Table 3. Values of the Parameters of Table 2 for PMA-MCH_3, the Isomeric Form of PMA-CH_3[a]

M_w (g/mol)	L (Å)	l_p (Å)	R_g (Å)	M_L
565 000	3 300 ± 130	10 ± 1	105 ± 7	510000 ± 20 000
375 000	2 400 ± 100	10 ± 1	89 ± 6	370 000 ± 15 000
205 000	1 300 ± 50	10 ± 1	64 ± 5	200 000 ± 10 000
50 000	300 ± 60	10 ± 3	30 ± 2	46 000 ± 9 000

[a] The values of M_w are obtained from the SANS experiments.

obtain a glassy sample. The values of the order parameter S are obtained from the X-ray measurements described in section II. Since the samples are not perfectly aligned, the values of S are averages reflecting the quality of alignment of samples. These values lie between 0.50 and 0.68. The sample is quenched in a nematic phase containing smectic A fluctuations.[5] Under these conditions, it is known[19−21] that the chain size in the direction perpendicular to the director (or the field) is longer than that in the parallel direction.

Here, we have no model to fit the SANS data obtained in the directions parallel and perpendicular to the field. Thus, the Zimm plots,

$$I^{-1}(q) = kM_w(1 + q^2R_i^{\,2}) \qquad qR_i < 1,\ i = \perp \text{ or } \parallel \qquad (4)$$

have been used in order to determine the values of inertial radii[3,22] $R_\perp$ and $R_\parallel$ in the Guinier range. The slopes $R_\perp$ and $R_\parallel$ are obtained simultaneously in order to be sure to use the same value of $I(0)$, i.e., M_w, for both directions. Figure 3 shows an example of this plot for the polymer of mass M_w = 131 000. The values of $R_\perp$ and $R_\parallel$ are given in Table 4 with the corresponding values of the nematic order parameter S. The sizes of the two polymers, M_w = 255 000 and M_w = 260 000, are similar, whereas their S values are quite different, 0.50 and 0.64. This shows that the conformation is not very sensitive to the quality of the alignment.

The log−log plot of $R_\perp$ and $R_\parallel$ as a function of M_w is shown in Figure 4. A least-squares fit method gives the following results:

$$R_\perp = (0.12 \pm 0.04)M_w^{\,0.48\pm0.03}; \qquad R_\parallel = (0.015 \pm 0.01)M_w^{\,0.63\pm0.05} \qquad (5)$$

The chain seems Gaussian in the perpendicular direction and swollen in the parallel one, but due to a prefactor 10 times smaller, $R_\parallel$ is smaller than $R_\perp$.[23]

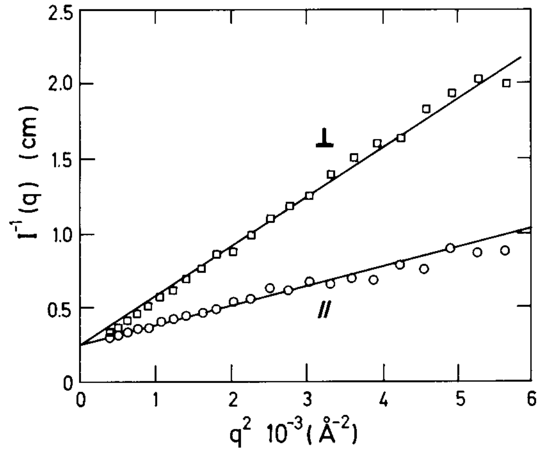

Figure 3. Zimm representation $I^{-1}(q)$ versus q^2 for the polymer M_w = 131 000 in the aligned nematic phase. The slopes of the straight lines are $R_\parallel$ and $R_\perp$, whereas their intercept at q = 0 gives M_w. The quenched sample shows a spurious central scattering whose influence is minored from the self-consistency of both curves.

Table 4. Values of the Inertial Radii, $R_\perp$ and $R_\parallel$, Obtained in the Aligned Nematic Phase[a]

M_w (g/mol)	S	$R_\perp$ (Å)	R_0 (Å)	$R_\parallel$ (Å)
260 000	0.50 ± 0.05	48 ± 3	43 ± 2	39 ± 3
255 000	0.64 ± 0.05	46 ± 3	42 ± 2	38 ± 3
131 000	0.56 ± 0.05	32 ± 2	31 ± 1	22 ± 2
79500	0.58 ± 0.05	26 ± 2	23 ± 1	20 ± 2
43 000	0.68 ± 0.05	20 ± 2	17 ± 1	12 ± 1
23 000	0.66 ± 0.05	13 ± 1	13 ± 1	9 ± 1

[a] S is the order parameter for different molecular weights M_w of PMA-CH_3. These values can be compared to R_0 ($R_g/3^{1/2}$) obtained in the isotropic phase.

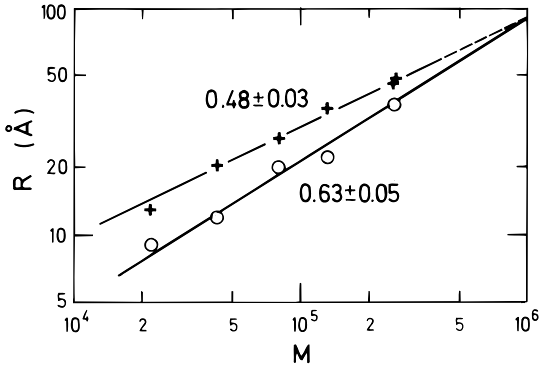

Figure 4. Plot of $R_\parallel$ (○) and $R_\perp$ (+) versus M_w in a log−log representation. The striking result is the difference found between exponents.

The difference of the exponents is the first striking result. This has to be verified in the intermediate range $qR > 4$ of the form factor $s(q)$. This test follows from the scaling concept that predicts[24] a $q^{-1/\nu}$ variation of $s(qR)$ if R varies as N^ν. Since the test needs a large intermediate range, it is realized with the longest polymer (M_w = 255 000). But even in this case, the chain length is not sufficient to have a wide enough intermediate range to get a good precision on the q exponent. Thus, only qualitative results are given. Figure 5a shows the $q^2I(q)$ variation. This figure clearly shows that $q^2I_\perp(q)$ is rather constant at large q whereas $q^2I_\parallel(q)$ is an increasing function. In the $q^{1.5}I(q)$ representation, Figure 5b, $q^{1.5}I_\parallel(q)$ is now rather constant, whereas $q^{1.5}I_\perp(q)$ is decreasing. Very similar behaviors are obtained with the M_w = 260 000 polymer. Thus,

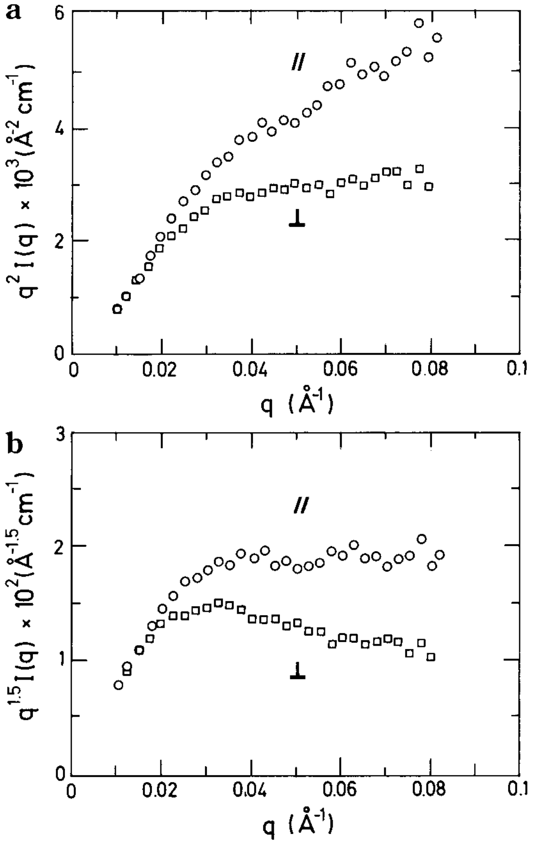

Figure 5. (a) Scattering data for the sample M_w = 255 000 in the aligned nematic phase. The representation $q^2I(q)$ shows that the scattering curve, perpendicular to the nematic director, is rather constant at large q. (b) The same data but plotted in the representation $q^{1.5}I(q)$, where the parallel scattering curve is rather constant at large q.

the differences found between both exponents are confirmed.

Let us now discuss the exponent 0.63 characteristic of the parallel direction. At first sight, it could be the excluded volume exponent,[24] $\nu = 0.59$, of the swelling of a chain in a good solvent. Such an assumption is not realistic, since $R_{\parallel}$ is smaller than $R_{\perp}$. In fact, it is probably due to the smectic fluctuations. It is well known[3] that, in the parallel direction, the polymer backbone has to cross the smectic layers (see Figure 6). Such a crossing of the polymer is predicted[25,26] to be energetically unfavorable since the hanging groups create defects in the layer. Figure 6 shows a schematic representation of the system as a succession of two layers, one containing essentially the hard cores and another of shorter thickness, where the spacers and the backbones are rather confined.[27] There is, of course, no long-range correlation between these layers. For the backbone conformation, in the perpendicular direction, the chain is a succession of usual steps. In the parallel direction, the chain is made of numerous steps of short length d (projection of the usual steps) and a few steps of large length D. This picture qualitatively explains the difference observed ($R_{\parallel} < R_{\perp}$).

The difference between the exponents is not easy to understand, even if we consider that a chain of infinite length has to be Gaussian. The difficulty lies in the existence of the two step lengths and especially in the determination of their numbers in the two directions. Let us notice that the two straight lines representing $R_{\perp}$ and $R_{\parallel}$ as a function of M_w have an intercept at a large value M^* of the molecular weight (see Figure 4). Here, the M^* value is about 10^6 g/mol, and its significance is not obvious.

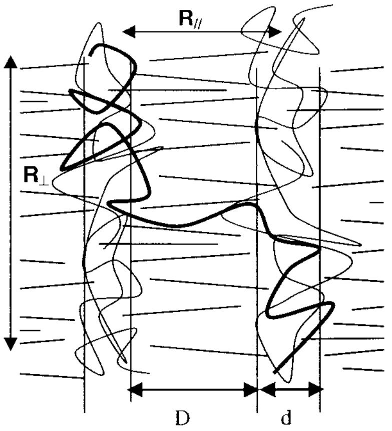

Figure 6. Schematic representation of the polymer in the nematic phase with smectic fluctuations. The greatest part of the backbone lies inside a thin layer (of thickness d) containing the backbones and spacers. Sometimes the backbone has to cross the layers (thickness D) containing essentially the mesogenic moieties, drawn as short, straight lines.

IV. Conclusion

The whole conformation of the liquid crystalline polymer PMA-CH$_3$ has been investigated by SANS. In the isotropic phase, it is found that there is no difference between the conformation of the backbone of this comb-like polymer and that of polystyrene. This probably derives from the very high flexibility of alkyl chains (the spacers) already encountered with the hairpin of the main-chain conformation.[28] Moreover, it is of interest to compare the dynamics of both polymer species. This has been realized by rheological measurements, and important differences are observed.[29]

In the unoriented nematic phase, it is shown that the nematic interactions have no visible influence on the whole chain conformation. This means that the number of crossings, discussed above in the oriented nematic phase, is too weak to modify the mean value of the persistence length and the Gaussian character of the chains.

In the aligned nematic phase, the simplest model consists of a Gaussian chain roughly confined inside planes perpendicular to the director. The chain is allowed to cross the perpendicular layer of mesogenic hard core. Nevertheless, in the plane, Rieger[26] has predicted three possible conformations: a random walk, a self-avoiding walk (SAW), and a compact SAW. Because the relation between M and $R_{\perp}$ ($R_{\perp} = (0.16/3^{1/2})M^{1/2}$) is not very different from that obtained in the isotropic phase, the first prediction, a Gaussian chain inside planes (or thin layers, see Figure 6), is well verified here. Concerning the parallel direction, the layer crossing corresponds to a step of length D roughly parallel to the director, since it has rather little influence, if any, on $R_{\perp}$. The number, N_c, of crossings per chain is predicted[25] to be $N \exp(-E/k_BT)$, where E is the crossing energy barrier. N_c appears to be very weak from the comparison of the prefactors in eq 5, the relations between $R_{\parallel}$ and $R_{\perp}$, and M. Nevertheless, the $M_w^{0.63}$ dependence of $R_{\parallel}$ is unpredicted. It could be a spurious effect due to the cross-over in the evolution of $R_{\parallel}$ from a rigid rod ($R_{\parallel} \sim M$) for low M values to a

Gaussian chain ($R_{\|} \sim M^{1/2}$) for large M values. But this assumption does not agree with the scaling also found in the intermediate range. Thus, this exponent remains a puzzling problem.

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References and Notes

(1) See, for instance: *Side Chain Liquid Crystal Polymers;* McArdle, C. B., Ed.; Blackie: London, 1989.
(2) Hsu, C. S. *Prog. Polym. Sci.* **1997**, *22*, 829.
(3) Cotton, J. P.; Hardouin, F. *Prog. Polym. Sci.* **1997**, *22*, 795.
(4) Higgins, J. S.; Benoît, H. C. *Polymers and Neutron Scattering*; Clarendon Press: Oxford, 1994.
(5) Brûlet, A.; Boué, F.; Keller, P.; Davidson, P.; Strazielle, C.; Cotton, J. P. *J. Phys. II (France)* **1994**, *4*, 1033.
(6) Portugall, M.; Ringsdorf, H.; Zentel, R. *Makromol. Chem.* **1982**, *43*, 589.
(7) Degert, C.; Davidson, P.; Megtert, S.; Petermann, D.; Mauzac, M. *Liq. Cryst.* **1992**, *12*, 779.
(8) Davidson, P.; Petermann, D.; Levelut, A. M. *J. Phys. II (France)* **1995**, *5*, 113.
(9) *Guide of neutron facilities at LLB,* available on request from LLB.
(10) Cotton, J. P. In *Neutron, X-Ray and Light Scattering*; Lindner, P., Zemb, T., Eds.; Elsevier: North-Holland, 1991; pp 1−31.
(11) Kratky, O.; Porod, G. *Recl. Trav. Chim.* **1949**, *68*, 1106.
(12) des Cloizeaux, J. *Macromolecules* **1973**, *6*, 403.
(13) Sharp, P.; Bloomfield, V. A. *Biopolymers* **1968,** *6*, 1201.
(14) Yoshizaki, T.; Yamakawa, H. *Macromolecules* **1980,** *13*, 1518.
(15) Brûlet, A.; Boué, F.; Cotton, J. P. *J. Phys. II (France)* **1996**, *6*, 885.
(16) Benoît, H.; Doty, P. M. *J. Phys. Chem.* **1953**, *87*, 958.
(17) Fetters, J.; Hadjichristidis, N.; Lindner, J. S.; Mays, J. W. *J. Phys. Chem.* **1994**, *23*, 619.
(18) One reviewer suggests the following quite different interpretation: the order is really defined by an order parameter tensor **S**, the anisotropy of which is ($S_{\|} - S_{\perp}$). The persistence length becomes a tensor, **T**, in an anisotropic phase. Expanding **S** in terms of **T**, after a constant value common to both the parallel and perpendicular components of **T**, the leading term is proportional to **S** itself (the only tensor available in the problem). Measuring R_g in an unaligned phase gives a result that is the trace of **T**. The first term of this isotropic average must then vanish since **S** is traceless. The result for an unaligned nematic phase must, at leading order beyond the constant, be the same as that for the isotropic phase. One expects the effect of nematic order to be small in such systems.
(19) Mitchell, G. R.; Davis, F. J.; Guo, W.; Lywinski, R. *Polymer* **1991**, *32*, 1347.
(20) Davidson, P.; Levelut, A. M. *Liq. Cryst.* **1992**, *11*, 469.
(21) Noirez, L.; Keller, P.; Cotton, J. P. *Liq. Cryst.* **1995**, *18*, 129.
(22) Guinier, A. *Théorie et Technique de la Radiocristallographie*; Dunod: Paris, 1964; p 645.
(23) During the data treatment, we learned that a similar exponent for $R_{\|}$ has been observed with another polymer where the terminal group CH$_3$ is replaced by OC$_4$H$_9$: Boeffel, C., Noirez, L., Daoud-Aladine, A., unpublished result.
(24) de Gennes, P. G. *Scaling concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(25) Renz, W.; Warner, M. *Phys. Rev. Lett.* **1986**, *56*, 1268.
(26) Rieger, J. *J. Phys., Fr.* **1988**, *49*, 1615.
(27) Noirez, L.; Davidson, P.; Schwarz, W.; Pépy, G. *Liq. Cryst.* **1994**, *16*, 1801.
(28) Li, M. H.; Brûlet, A.; Davidson, P.; Keller, P.; Cotton, J. P. *Phys. Rev. Lett.* **1993**, *70*, 2297.
(29) Fourmaux-Demange, V.; Brûlet, A.; Cotton, J. P.; Hiliou, L.; Martinoty, P.; Keller, P.; Boué, F., submitted to Macromolecules.

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