Conformation of Polystyrene Chain in Ultrathin Films Obtained by Spin Coating

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ABSTRACT: This article reports a study of the chain conformation in thin films of amorphous polymer prepared by spin coating. Polystyrene chains of two molecular weights M_w, 230 000 and 660 000, are confined in layers of thickness equal to either 1000 Å, thus greater than their unperturbed radii of gyration R_g, or 100 Å, thus smaller than R_g. The form factor of the chain inside the layer is measured by small-angle neutron scattering. Changes of the scattering are observed as a function of the film thickness in the intermediate scattering vector range. We analyze the data in the frame of the wormlike model. In the 1000 Å films, the chain has the same Gaussian conformation as in the bulk. In the films of 100 Å, the persistence length of the chain is increased (compared to 9.2 Å the value in the bulk) up to 45 Å, for both M_w values. However, the corresponding scattering intensity is higher than expected for such an extended chain.

Little is known about the conformation of polymer chains included in a thin film. Pioneering experiments[1−4] have measured the SANS (small-angle neutron scattering) of blends of polystyrene (PSH) and deuterated polystyrene (PSD) in films of very low thickness, between 150 and 1700 Å. In one case,[1,2] the films were obtained by successive water casting and piled up until a macroscopic thickness was obtained. In other cases, the measurements were done on films prepared by spin coating.[3,4] Even with such a low scattering volume, the authors were able to extract the form factor of one chain in the bulk, which is usually obtained[5] with a sample of thickness greater than several tenths of a millimeter. Shuto et al.[1,2] reported that when the film thickness was lower than $2R_g$, the radius of gyration of a chain along the direction parallel to the film surface was evaluated to be larger than the radius of gyration of an unperturbed chain. With the help of wide-angle X-ray measurements, the authors concluded that interpenetration of the chains was weaker than in bulk.[1,2] A contradictory result has been recently published by Jones et al.[4] on a series of thin films prepared by spin coating. They observe an excess of scattering observed when decreasing the thickness of the films, which they explain by lateral correlations of interfacial roughness between the polymer and the wafer or the air. Accounting for this phenomenon in analysis of the experimental SANS data for thin films, their conclusion is that both R_g and χ (the interaction parameter between H and D monomers) values have almost their bulk values for thicknesses down to $R_g/2$.

Here, a complementary experiment is reported using the SANS technique on thin films prepared by spin coating. Instead of measuring the radius of gyration, we want to observe the internal conformation of polystyrene chains of two molecular weights M_w, 230 000 and 660 000, confined in layers of two different thicknesses: 1000 Å, thus greater than the radius of gyration R_g of each chain; 100 Å, thus smaller than R_g. These experimental results can be compared with previous results[1,2,4] and with theoretical predictions.[6]

Polystyrene is an amorphous polymer. In molten or glassy state, it displays a well-known[7] Gaussian conformation, with a rigidity only at short scale characterized[8,9] by a persistence length $l_p = 9.2$ Å. We will see how this is modified in thin films.

Experimental Details

Polymers. We have prepared mixtures of 50 vol % of deuterated and regular polystyrene chains of molecular weights as close as possible. The characteristics of the polymers are given in Table 1. The lowest molecular weight sample is designated 230K and the other one 660K.

Thin films of polymer mixtures were prepared by spin coating toluene solutions onto 5 cm diameter silicon wafers (100 μm thickness, double side polished). Solutions of 0.21×10^{-2} and 1.41×10^{-2}g cm^{-3} have been used to coat 95 ± 5 and 1000 ± 50 Å films. The film thicknesses were measured by neutron reflectometry on the spectrometer EROS[10] (LLB, Saclay).

SANS experiments were performed on the as-cast films and after specific annealing. The conditions of the thermal treatment were chosen in order to have an annealing time a little greater than the terminal relaxation time τ_{ter} of the chains. The value of τ_{ter} was calculated using the following relationship[11] for the shift factor of the time/temperature superposition law established[12] at 160 °C:

$$\tau_{ter}(T) = \frac{a_T}{a_{T_0}}\tau_{ter}(T_0) \qquad \ln(a_T) = 1620\left(\frac{1}{T-49} - \frac{1}{T_0-49}\right) \tag{1}$$

At T_0 = 160 °C, $\tau_{ter}(T_0) = 2.75 \times 10^{-18} M_w^{3.44}$. Therefore, the 660K films were heated at 150 °C for 1 h under vacuum, meanwhile for the 230K films, the heating at only 130 °C was applied for 35 min. Such a limited annealing deserves two comments. First, we cannot be sure that chains in thin films are relaxed: in bulk they would be, but for $D < R_g$, confinement may slow the relaxation. We will see later that chains are totally relaxed when the film thickness D is larger than R_g. Second, short annealing leads us to think that the films did not dewet: dewetting is frequently observed,[13,14] but after much longer annealing. In addition, neutron reflectometry shows that annealing has not modified the thickness of the films or their apparent scattering density. Finally, the film surfaces have been observed with an optical microscope of 1

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Table 1. Composition of Polystyrene Samples[a]

designation	x	PSH $M_w - M_w/M_n$	PSD $M_w - M_w/M_n$	R_g (Å)
230K	0.5	245000−1.18	229000−1.05	131
660K	0.5	760000−1.15	620000−1.16	223

[a] x is the ratio of deuterated polymers. M_w is the weight-average molecular weight of regular (PSH) and deuterated (PSD) polymers. M_n is the number-average molecular weight. The designation recalls the average weight-average molecular weight of the sample. R_g is the value of the unperturbed radius of gyration in the bulk.

μm resolution. They display homogeneous and flat profiles very different from those observed for dewetted films.[13,14]

SANS Experiments. The experiments were performed on the PACE[10] spectrometer at the Orphée reactor (LLB, Saclay) using neutrons with wavelength of 15 Å. The sample-to-detector distance was 1.5 m. The incident collimation was obtained with the rectangular aperture 20 × 30 mm² of the incoming neutron guide and a 10 mm diameter hole (near the sample), a distance of 2 m from each other. The corresponding scattering vector range is $8 \times 10^{-3} < q$ (Å^{-1}) $< 8 \times 10^{-2}$. To increase the scattering intensities, wafers with 1000 Å films were cut into four pieces, stacked together, and put perpendicular to the neutron beam. For the wafers with 100 Å films, the stacking was made of 16 pieces. The electronic background was measured with a boron carbide sheet at the sample position. The predominant background is delivered by the empty beam. It is weakly modified by the intensity scattered by naked silicon wafers. The scattering obtained from blank samples, one coated with pure 1000 Å PSH polymer and another one with pure 1000 Å PSD polymer, was found to be identical to the one of naked wafers. Therefore, the incoherent background correction is at least of second order for the scattering intensities of the different ultrathin samples. Thus, we subtract simply the intensity delivered by eight wafers corrected in order to correspond to the exact number of wafer pieces (4 or 16). Such a procedure remains consistent because with high fractions of deuterated species, the incoherent scattering is not an important contribution compared to the coherent scattering of the PSH/PSD blend.

The efficiency of the detector cells was normalized by the flat intensity delivered by a Plexiglas lamella. Absolute values of the scattering intensity $I(q)$, in cm^{-1}, were obtained[15] from the direct determination of the number of neutrons in the incident beam and the cell solid angle.

Results and Discussion

The chain conformation is obtained from the absolute scattering intensity following the relation

$$I(q) = \phi_D(1 - \phi_D)(b_D - b_H)^2 \frac{\rho N_{av}}{m_H^{\ 2}} M_w S_1(q) \qquad (2)$$

where ϕ_D is the ratio (number) of deuterated chains, b_H and b_D are the scattering lengths of H and D monomers, N_{av} is Avogadro's number, ρ is the density of the H sample ($\rho = 1.06$ g cm^{-3}), and $m_H = 104$ is the molecular weight of the H monomer. $S_1(q)$ is the form factor and M_w the molecular weight of the polymer chains. For wormlike chains, $I(q)$ writes,[18] in the intermediate range $l_p^{-1} \gg q \gg R_g^{-1}$,

$$I(q) = \phi_D(1 - \phi_D)(b_D - b_H)^2 \frac{\rho N_{av}}{m_H}\left[\frac{12N}{2q^2 N_{l_p} l_p^{\ 2}} = \frac{6L}{q^2 L l_p a}\right] \sim \frac{6}{q^2 l_p a} \qquad (3)$$

where N is the number of monomers of length a, L the contour length ($L = Na$), and N_{l_p} the number of persistence length ($L = N_{l_p} l_p$). We can see in eq 3 that $I(q)$ is inversely proportional to l_p.

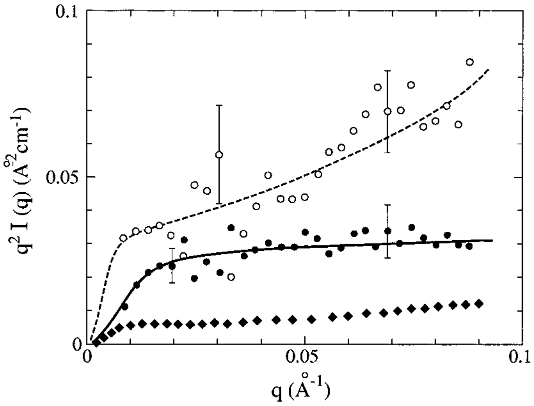

Figure 1. Kratky plot, $q^2I(q)$ versus q, of the absolute intensities scattered by samples 230K in the as-cast 1000 Å film (●) and in the annealed 100 Å film (○). The lines are the best fits to a scattering function of wormlike chains[9] of polystyrene. The full line correspond to Gaussian coil with a persistence length $l_p = 9.2$ Å. The dashed line is the fit obtained by using a prefactor of the scattering intensity (see text). Here, the prefactor is 5.9; the l_p value is 45 Å. ◆ corresponds to the calculated curve for wormlike chains of polystyrene with 45 Å of persistence length.

In the case of a mixture of chains, according to the random phase approximation, $S_1(q)$ is obtained from:[16]

$$\frac{1}{\phi_D(1 - \phi_D)N_w S_1(q)} = \frac{1}{\phi_D N_{wD} S_{1D}(q)} + \frac{1}{(1 - \phi_D)N_{wH} S_{1H}(q)} - 2\chi \qquad (4)$$

where χ is the interaction parameter between D and H monomers and $S_{1D}(q)$ and $S_{1H}(q)$ are the form factor of the two types of chains. N_w is the weight-average degree of polymerization. Equation 4 remains valid as long as the molecular weight distributions of polymers are narrow. For χ, we have taken the value 2×10^{-4} from earlier literature.[17]

Finally, let us recall some characteristics of polystyrene measured in the bulk state. The radius of gyration follows the relation $R_g = 0.275 M^{1/2}$. This gives $R_g = 131$ Å for a 230K bulk sample and $R_g = 223$ Å for a 660K bulk sample. In the intermediate q range, the Kratky representation $q^2I(q)$ leads to a plateau of value 0.0285 Å^{-2} cm^{-1}.

Results for Sample 230K. Let us start with the 1000 Å film. For this thickness, the scattering intensities of the as-cast and annealed films are identical. Figure 1 shows the Kratky representation. For the as-cast film, we obtain a plateau, characteristic of Gaussian chains. The full line corresponds to the scattering function calculated (eq 4) for a mixture of wormlike chains[18−20] in the bulk ($l_p = 9.2$ Å). We estimate the contour lengths of PSH and PSD chains, from their number-average molecular weights, to 5100 and 4900 Å, respectively. We can see, in Figure 1, that there is no difference between the experimental points of the 1000 Å film and the scattering function in the bulk. Therefore, the 230K polymer chain in the 1000 Å film exhibits the unperturbed Gaussian coil conformation of the bulk. This result shows that the background subtraction procedure performed for the thin films is correct and that the incoherent scattering is negligible with respect to the

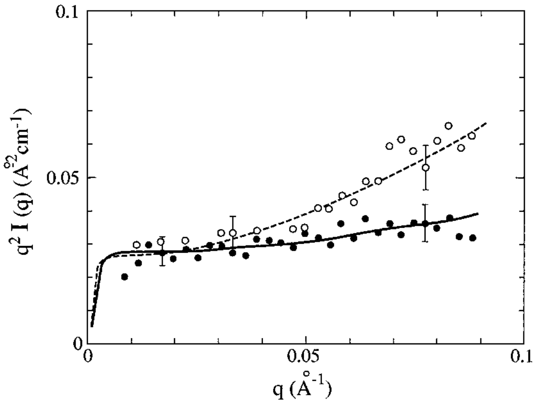

Figure 2. Kratky plot, $q^2I(q)$ versus q, of the absolute intensities scattered by samples 660K in the as-cast 1000 Å film (●) and in the 100 Å annealed film (○). The full line is the fit (see caption of Figure 1) obtained with a prefactor 2.9; l_p is 25 Å. The dashed line is the fit obtained with $l_p = 53$ Å by using a prefactor 5.6.

coherent one. It makes us confident in our measurements, in particular at large q values for the following results.

The 100 Å films behave differently. The as-cast film presents some central scattering and a rod behavior at large q values i.e., $I(q) \sim q^{-1}$. After annealing (130 °C for 35 min), the central scattering disappears, but the rod behavior remains (see Figure 1). We have adjusted the data of the annealed film (using a nonlinear fit method) with the scattering function of a wormlike chain. We find a l_p value of 45 ± 10 Å, but the prefactor of the form factor (eq 2) has to be multiplied by 5.9 as if the linear density of the chain was greatly increased. Both results are striking. From l_p, we can calculate a radius of gyration[21] $R_{g,calc}$ of 305 Å. Let us note at this stage that the scattering cross section for this film is higher than for 1000 Å, since the decrease at high q is slower ($1/q$ instead of $1/q^2$). The error due to incoherent scattering is therefore lower than for the 1000 Å film.

We have also used another method to determine l_p. From the position, q^*, of the crossover between the q^{-2} and q^{-1} variations, a persistence length can be obtained using the relation[18,22] $q^*l_p = 1.7$. This procedure leads also to a value near 45 Å, i.e., much higher than 9.2 Å obtained in the bulk or in the 1000 Å film here.

Thus, the local rigidity of the chains seems to be increased in the thin film made by spin coating, and it is not modified by the performed annealing.

The value of the plateau, in the Kratky representation, is estimated here of about 0.035 ± 0.005 Å^{-2} cm^{-1}. As just said above, this value is 5.9 times greater than 0.0058 Å^{-2} cm^{-1} expected for wormlike chains of 45 Å persistence length since it has to be proportional to $1/l_p$ (see eq 3). The form factor of the latter is also drawn in Figure 1, and one can see that it lies well below the experimental curve of the 100 Å film.

Results for Sample 660K. Let us first look at data for the 1000 Å film. The intensity, $q^2I(q)$, of the as-cast film is shown in Figure 2. It seems that the plateau is slightly higher than that of the Gaussian coil of the PS melt in bulk. These data have also been fitted, fixing here 18 600 and 14 100 Å for the contour lengths of PSH and PSD chains. For such high molecular weights, the χ parameter has now an effect, but only for the low q values (Guinier regime) which are not reached in these experiments. Here, as for the 100 Å film of sample 230K, a good fit can be obtained (see Figure 2), but the prefactor in eq 2 has to be multiplied by 2.8. This best fit is obtained with a l_p value of 20 ± 10 Å, i.e., twice that of a chain in the bulk. Thus, the conformation of this long chain is now sensitive to the 1000 Å thickness of the layer. The calculated radius of gyration becomes now 600 Å.

For the 100 Å films, the scattering intensities before and after annealing are similar. Both curves present, at large q values, a rod behavior clearly seen on the Kratky plot (Figure 2). For this 660K sample, the plateau is more visible than for the 230K film, which is normal since the plateau is expected for $1/R_g < q$, and here $1/R_g$ is lower. Thus, the crossover q^{-2}, q^{-1} is better defined; it leads to a persistence length of 50 ± 5 Å. Let us note that this value is very similar to 45 Å measured for the sample 230K of the same thickness. Such high values have never been observed neither in solutions of PS with deuteriation of different hydrogens inside the monomer[8] nor with stretched samples.[23] Here also, the plateau value (0.028 ± 0.004 Å^{-2} cm^{-1}) is 5.6 times too high to correspond to a mixture of wormlike chains of 50 Å of persistence length. The calculated value $R_{g,calc}$ is 870 Å.

Discussion. We have observed changes, as a function of thickness of the film, of the scattering of films in the intermediate scattering vector range. When the thickness becomes close to the radius of gyration, and even more when it is lower than R_g, the decrease of the scattering becomes slower than the q^{-2} variation found in bulk for such mixtures of H and D chains. In our interpretation, we use the model of a wormlike Gaussian chain, inherited from the three-dimensional case. As a matter of fact, a plateau in the Kratky representation—of same height as in bulk—was observed at our low q range, while a more pronounced rigid rod behavior appeared at large q only in thin films. At the first sight, the results were not so different from that obtained in the bulk. However, the interpretation of data with this model leads to an increase of the persistence length l_p, contradictory with the lack of change in the height of the $q^2I(q)$ plateau, which represents the linear density of the chain. We discuss first on the experimental level, then compare to former experiments, and finally evoke different physical mechanisms.

Experimental Point of View. On the experimental point of view, the results show a rather systematic dependence over the degree of confinement, which we can characterize by the ratio D/R_g. When $D = 100$ Å, D/R_g is lower than 1 for 230K ($R_g \sim 130$ Å) and lower than 0.5 for 660K ($R_g \sim 220$ Å), l_p reaches a constant value of 45 Å. For $D = 1000$ Å and for $D/R_g \sim 10$, all confinement effects vanish, and we recover the bulk value 9 Å; strikingly, for $D/R_g \sim 5$, l_p (20 ± 10 Å) is still larger by may be as much as a factor of 2. This would be less surprising if we took D/L (L the extended chain length) as the relevant parameter, assuming that confinement acts first on extended chain configurations.

However, we are faced with a paradox: in the frame of the wormlike chain model, if l_p is larger, the height of the $q^2I(q)$ plateau, which varies as $1/l_p$, should decrease. In practice, we find a height that is close to the one found in bulk for the usual persistence length. Obviously, the effect observed could be due to unaccounted flat background, being more and more visible at large q. A systematic error on all samples would affect more the usual bulk behavior observed for 230K at 1000 Å since its scattered intensity (which decreases as $1/q^2$)

is lower at large q than those of all the other samples (where it decreases more slowly as $1/q$). Since for this sample we recover the well-known value of about 9 Å for l_p in the bulk, we are confident in our results. Other possible sources of discrepancy are a wrong estimate of the volume (complications may arise from dewetting, but the latter is not observed optically or by neutron reflectometry) or of the density in confined geometry (see below).

Comparison with Former Experiments. There are few direct experimental studies of chain conformation in confined geometry, partly because of the weak signal and partly because of other complications such as dewetting, possible demixing, or surface enrichment. Actually, reports on these processes are much more numerous. Until now, we can compare our experiments to the results of Shuto et al.[2] and to the very recent but contradictory results of Jones et al.[4]

Shuto et al.[2] find an increase of R_g, by around 1.5 at the highest, for D values slightly larger than 100 Å. For wormlike chains, R_g varies as $N^{1/2}l_p^{1/2}$. Thus, if we assume that chains remain Gaussian, an increase of l_p from 10 to 45 Å should increase the radius of gyration by more than a factor of 2. This is more than observed[2] but comparable (we note that their measured R_g varies as $N^{1/2}$). The latter authors also observed by wide-angle X-ray measurements that the local arrangement of chains was looser in confined films. This could be correlated with a local change in the radial radius R_c, visible at high q.

Jones et al.[4] have examined the role of interfacial roughness on the scattering by looking at pure PSD films over a wide range of thickness. The thin films of PSD scatter significantly, and scattering surprisingly increases strongly with decreasing thickness. The authors attribute this signal to lateral correlations of interface roughness between PSD and Si or (and) air. It has a Debye Bueche variation, i.e., $1/(1 + q^2r^2)^2$, with a constant $r = 148$ Å. In the case of films, made of a mixture of H and D polymers, they show that a similar contribution (same correlation length r) to the scattering data manifests itself at low q values. Then, subtracting the Debye Bueche contribution to the data for thin films, they find values of R_g and χ similar to their bulk values for all thicknesses, down to 150 Å. Here, we also mention some excess scattering at low q for the as-cast sample 220K of 100 Å thickness, but it has disappeared after annealing. This excess scattering could be reasonably due to some roughness problem studied by Jones et al.[4] In Figure 3, we show the roughness contribution of a pure PSD film of 150 Å thickness using the data of ref 4. It is an overestimate for a PSD/PSH film, which has a lower contrast with respect to vacuum. Let us compare it to the scattering of the sample 230K (a 50/50 blend of PSH/PSD) of 100 Å thickness. It is clear from Figure 3, inset, the Kratky plot of the scattering intensities, that even if the roughness contribution is important at low q, it becomes negligible in the q domain where the rigid rod behavior is observed here. Unfortunately, we cannot directly compare our experimental curves to those given in ref 4: their highest q value is 0.035 Å^{-1}, and the deviation to the Gaussian conformation of the bulk which we observe is at higher q (see Figures 1 and 2).

Physical Models. The basic model for confined chains is for Gaussian chains.[6] Since the three directions of space are independent, observation along the plane should be the same as for the three-dimensional case. In the real case, chains are not Gaussian, and we must use the wormlike chain model. But in a confined geometry, there is no obvious reason for a change in the persistence length. In particular, there is no reason for more change at large q than at small q. Assuming external constraints, Gaussian chains should change at the global scale, but at small distances the effect of macroscopic deformation is generally lost. Similarly, if we assume that the violent acceleration of spin coating stretches the chains, the level of the $q^2I(q)$ plateau at low q should be lower, and the usual value should be recovered at large q. In addition, the chains should relax during annealing, which generally occurs first at small scales. In other words, it is unusual that l_p would remain stretched, except if the relaxation is frozen by confinement.

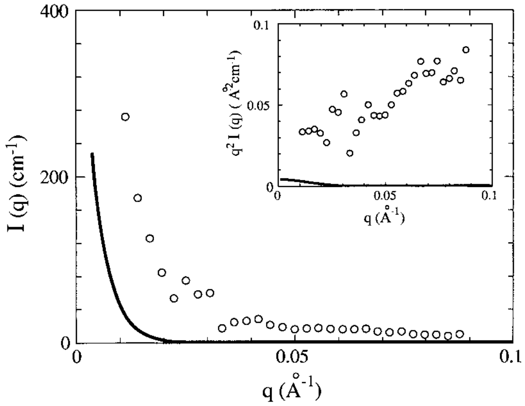

Figure 3. Absolute intensity scattered by the sample 230K in the annealed 100 Å film (○). The full line is the Debye Bueche variation of the intensity delivered by a pure PSD film of 150 Å thickness (data of ref 4). It arises from lateral correlations of interfacial roughness, which affect the scattering of thin films in the low q domain. In the inset, we can see that this roughness term has no more influence at large q values, where the rigid rod behavior is observed for the thin films.

One can at this stage take into account that real chains are not Gaussian, each monomer having a volume. From the point of view of scaling, in three dimensions, excluded volume is screened in bulk, but this screening may vanish in lower dimensionality since keeping the other directions constant increases the effective filling ratio. In one dimension,[24] the effect remains small except for very strong confinement ($D/R_g \sim N^{-1/2}$, estimated less than 10 Å). In two dimensions, confinement is marginal since the fractal dimension of Gaussian chains is also two. From the practical point of view, the apparent shape may however change to that of a disk, but the form factor of compact disks parallel to a surface is different from the one observed here.

Many other possible origins leading to original chain conformation in thin films could be imagined: cooling due to the solvent evaporation during the coating process, stress-induced enhancement of separation, or collapse. Some of them meet the inconsistencies discussed above. Segregation may occur in polymer blends also between H chains and D chains. From eq 4, which accounts for this phenomenon, we can infer that a weak segregation ($\chi N < 0.1$, say) induces an increase of the scattering intensity at small q values and has no influence in the intermediate q range observed here. Besides, a theoretical study[25] of the phase behavior of thin polymer blend films predicts a reduction of the effective interaction parameter χ. For PS chains, χ is well-known to be weak (2×10^{-4} in bulk[17]). The only strong effect could be due to specific enrichment in one type of chain at a surface. In such a case, the thin layer of one type of chains would have modified the neutron reflectivity profile at large q. (A 10 Å layer can be measured by this method.) We do not observe such an effect on the as-cast films or on the annealed films. Let us remember that annealing performed here is especially short compared to those used in the numerous studies of dewetting, demixing, etc. In the case of strong segregation, the SANS signal recorded would not represent anymore the form factor of a single chain, but it would not vary as observed here at large q.

Finally, one possible source of apparent change of persistence length at identical level of the plateau would be a change in the effective radial radius of gyration R_c of the chain filament. Such a transverse form factor would be modified if the benzene rings distribution around the chain axis was strongly modified. This has been observed for drastic modifications of the labeled object such as deuteriation of only the outer benzene ring.[8] It is however surprising that, compared to this case, the effects here are even more important.

Summary. The apparently systematic effects of confinement on the scattering—the fact that it occurs at large q and the fact that we can only describe it as an increase of rigidity or a change of shape at the local scale—are not contradictory with other observations in the low q range but are difficult to explain.

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