Effect of Dense Grafting on the Backbone Conformation of Bottlebrush Polymers: Determination of the Persistence Length in Solution

S. Lecommandoux,* F. Chécot, R. Borsali, M. Schappacher, and A. Deffieux

Laboratoire de Chimie des Polymères Organiques (LCPO), École Nationale Supérieure de Chimie et Physique de Bordeaux, Université Bordeaux 1, 16 Avenue Pey-Berland, 33607 Pessac Cedex, France

A. Brûlet and J. P. Cotton

Laboratoire Léon Brillouin (CEA-CNRS), CEA-Saclay, 91191 Gif-sur-Yvette Cedex, France

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ABSTRACT: The effect of dense grafting on the polymer brush's conformation is studied by small-angle neutron scattering on well-defined branched copolymers. We have determined the persistence length l_p of the backbone of poly(chlorovinyl ether) grafted with polystyrene (PCEVE-*g*-PS) copolymers. In a good solvent, this length l_p can be directly obtained from the scattering vector q^* at which the polymer chain locally behaves as a rod; i.e., its form factor enters the q^{-1} variation regime. This method is first applied to a linear PCEVE polymer, as reference. Then, we compare to the branched copolymers by using the matching condition for the PS branches in order to only measure the form factor of the PCEVE backbone. From the flexible linear chain to the bottlebrush-like polymer, the persistence length increases from 12 to 110 Å.

Introduction

The chemical and topological chain complexity of macromolecules play an important role in the intra- and intermolecular interactions as well as in the structure formation and rheological properties of solutions and melts of such molecules. In this respect, the dense grafting of side chains onto a main polymer chain should lead to a drastic change in the main chain conformation. In the past decades, chemists have been able to control the topology and the degree of branching, making well-defined branched, dendritic, or hyperbranched polymers.[1,2] The synthesis of so-called bottlebrush polymers has been mainly developed by two methodologies referred to “grafting onto”[3−5] and “polymacromonomer”[6] methods.

Studies of polymacromonomers of different backbones and branches (polystyrene (PS), poly(methyl methacrylate) (PMMA), polyfluorenes, etc.), varying functionality, and/or molecular mass have been performed recently in order to determine the structure and dynamics in solutions[7−9] or in melts.[10] It was shown by different scattering techniques that high molecular weight polymacromonomers, for example PMMA grafted with PS, had in dilute solutions the structure of wormlike cylindrical brushes.[7,8] Increasing the side chain length, the whole chains adopt stiff conformations,[8] characterized by large persistence length values. The cross-section radii of such cylindrical brushes measured by X-ray scattering showed[8b] no clear evidence of expansion of the side chains resulting from some expected steric interaction. Besides, increasing the polymer brushes concentration was observed to yield spontaneous orientational ordering.[11−13]

Such macromolecules with flexible side chains have been also considered in theoretical[14−16] and simulation[17−19] works. Macromolecular bottlebrushes have been described theoretically on the basis of scaling concepts[20] and mean-field analysis.[14,15] Depending on the side chain length, the conformation of comb polymers would change from a spherical toward a wormlike chain, observed[7,8,11] with a persistence length of the order of the whole main chain.[14,15] Such an enhancement of the main chain rigidity would be controlled by the steric interaction of the side chains. Aside from these theoretical predictions, computer simulations were performed[17−19] to study the effects of the side chain length and rigidity on the whole main-chain conformation. Their results roughly suggest that the description of the backbone conformation requires to separate the flexible behavior at short scale from that more elongated at large scale.

These models predicting sizes and shapes of branched polymers however fail to describe the dependence of the intrinsic viscosity with molecular weight. One reason might be that the relation between the sizes and the degrees of polymerization of both the main chain and side chain is not well understood. If static light scattering gives information about the size as well as the shape of a branched polymer, the separate contributions to the scattering intensity from the backbone and the side chains remain unknown. In principle, small-angle neutron scattering (SANS) can be used to measure these contributions, but this technique requires partially deuterated molecules and synthesis of such complex molecules is still difficult. A recent neutron scattering study[21] on polynorbornene-*g*-polystyrene polymacromonomers seems to describe these objects as stiff rods, with very elongated branches. In principle, this latter result can be clarified by SANS or X-rays measurements of cross-section radii of polymacromonomers.[8b,10] They should be also faced with theoretical predictions.[16]

In this article, our purpose is to determine the persistence length of the backbone of poly(chloroethylvinyl ether)-*g*-polystyrene (PCEVE-*g*-PS)[4] comblike polymers using the SANS technique. In the following, we describe the SANS experiments performed on solutions of PCEVE-*g*-PS of different degree of polymerization

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* Corresponding author: e-mail s.lecommandoux@enscpb.fr.

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(DP) for the PCEVE backbone and the same DP for the PS side chain. The branched polymer solutions were prepared in a mixture of hydrogenated and deuterated tetrahydrofuran (THF/THF$_{D8}$) in contrast matching conditions for the polystyrene in order to obtain only the scattering function of the backbone. We thus compared the persistence length of the branched polymers to that of the linear PCEVE polymer.

Experimental Determination of the Persistence Length

SANS has been widely used[22] for measurements of form factors of polymer chains in different environments. In the case of a semiflexible polymer, its conformation is well explained by the wormlike chain model of Kratky and Porod.[23] In this model, the polymer chain is a Gaussian chain, which evolves continuously to a rigid rod when looking at short distance. The notion of persistence length l_p has been introduced in order to describe the local chain stiffness. Experimentally, it is observed in the asymptotic range, i.e., at large scattering wave vector q values. In this q range, the form factor $P(q)$ as a function of q has been calculated by Des Cloizeaux[24] for an infinitely long chain

$$P(q) = \frac{\pi}{qL} + \frac{2}{3q^2 l_p L} \tag{1}$$

where L is the contour length of the polymer chain. Following eq 1, at $ql_p > 1$ the form factor $P(q)$ displays the q^{-1} scattering behavior of a rodlike molecule. The determination of the persistence length l_p is related to the value q^* at which $qP(q)$ is reaching the plateau. Let us note that other methods[25] can be used to obtain l_p, including a fit of the whole scattering curve to the theoretical expression of the form factor of a flexible polymer chain.

In good solvent, the effect of excluded volume drastically increases the chain dimensions. Recently, Monte Carlo simulations of wormlike chains with excluded volume were performed[26] in order to obtain semianalytic expressions of scattering functions of semiflexible chains. These results are however deeply modified by chain concentration effects. Indeed, in dilute solution, the concentration and scattering vector dependence of the coherent scattering intensity $I(q)$ is given by[27]

$$\frac{1}{I(q)} \propto \frac{1}{M_w P(q)} + 2A_2 c + ... \tag{2}$$

where c is the concentration, M_w the weight-average molecular weight of the polymer, and A_2 the second osmotic virial coefficient. The intermolecular signal is not negligible especially in the small q range and represents a significant part of the scattering intensity (eq 2). So, a fit of the scattering signal to the analytic expression[26] of the form factor of a semiflexible chain without taking into account the second term of eq 2 would lead to erroneous values of L or l_p. Another complication of this problem, which is not a trivial experimental point, is the q dependence of A_2.[28] Thus, in good solvent, the method to determine l_p described in ref 26 cannot be directly used for dilute solutions in good solvent.

Let us come back to the Θ solvent case. It was shown[25b] that the internal structure of statistical or wormlike chains was not important at high q values, at least when the chain cross section effects are negligible. Thus, for different kinds of linear chains, the q^{-1} behavior is observed beyond

$$q^* l_p \sim 3.5 \tag{3}$$

In practice, q^* is the q value at which the function $qP(q)$ becomes constant. Even if other models to determine l_p exist (see refs 25 and 26 and references therein), this simple approximation can be used to estimate the l_p value.

In good solvent, we can emphasize that the excluded volume effects are no more important at the local scale of the chain, i.e., around q^*. This point has been verified[26] by Monte Carlo simulations of scattering functions of wormlike chains. The simulations were performed for chains with different contour lengths L and statistical segment lengths b ($b = 2l_p$). The results have shown that the scattering functions with and without excluded volume effects were superimposed perfectly at high q range. Therefore, eq 3 can be used whatever the solvent quality to determine the persistence length of a wormlike chain.

Experimental Details

Synthesis and Characterization of PCEVE-*g*-PS.[4] The bottlebrush polymers studied here have been synthesized by combining different types of controlled living polymerizations, cationic for the backbone and anionic for the side chains. The synthesis of the PCEVE-*g*-PS comblike polymers was performed as described elsewhere.[4] Such a technique allowed to obtain well-controlled architectures characterized by narrow molecular weight distribution and extremely high branching density, branching regularly distributed along the main PCEVE backbone.

PCEVE-*g*-PS Samples. For this study, the PCEVE-*g*-PS polymers were obtained from the same PSLi batch and thus have the same branch length, whereas the PCEVE backbone DP was varied. The weight-average molecular weight of the PS branches is 3000; the DP values of the PCEVE backbone of the samples studied are 36, 134, 764, and 1042 (see Table 2 in ref 4a).

Solutions have been prepared in a mixture of THF/THF$_{D8}$ containing a THF$_{D8}$ volume fraction $x_D = 0.201$, so that the scattering length density of the PS branches is equal to that of the solvent. In such a mixture, the scattering intensity only gives the form factor of the backbone (PCEVE). The concentration (c) is 10^{-1} g/cm^3. We must stress that, among the different polymer solutions studied, only the comb polymer of DP = 1042 gave a significant signal. Unfortunately, for this polymer, the concentration is above the overlap concentration c^*. This concentration value was chosen in order to increase the scattering signal because of the weak contrast imposed by the matching condition of the branches. We also prepared a mixture of solvents containing a THF$_{D8}$ volume fraction $x_D = 0.250$ in order to mimic the incoherent background[29] given by the PCEVE-*g*-PS solutions.

PCEVE Samples. Two dilute solutions of a linear PCEVE polymer have been prepared in pure THF$_{D8}$, a good solvent of this polymer. The molecular weight characteristics have been measured by SEC on the basis of PCEVE calibration (see ref 4a). The weight-average molecular weight is 90 000 (DP ~ 850). The concentrations are 5×10^{-3} and 10^{-2} g/cm^3, i.e., in the dilute regime. The incoherent signal scattered by respectively a pure THF$_{D8}$ solvent and a mixture of solvents containing $x_D = 0.97$ has been subtracted from the corresponding dilute solutions.

SANS Experiments. Small-angle experiments are carried out with the PACE spectrometer[30] at the Orphée reactor (LLB, Saclay) using different configurations (neutron wavelength/

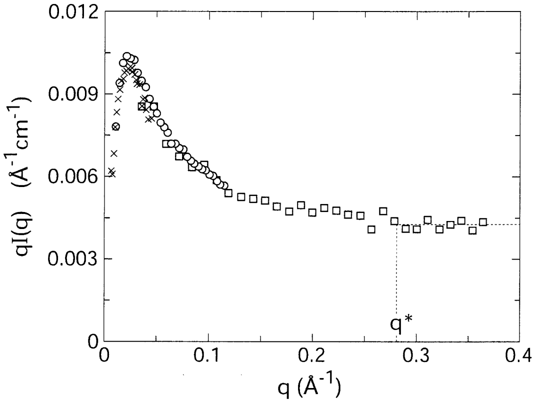

Figure 1. Representation $qI(q)$ as a function of the scattering vector q for a linear polymer PCEVE in dilute THF_{D8} solution ($c = 10^{-2}$ g/cm^3). At high q values, the plateau observed beyond q^* is characteristic of the local rodlike conformation. It indicates a persistence length of the PCEVE chain of 12 ± 1 Å (see text).

sample to detector distance): 15 Å/2.9 m, 6 Å/2.9 m, 6 Å/0.86 m. This allows us to measure the chain conformation of the linear PCEVE polymer on a wide scattering vector range. Measurements on the matched solutions of PCEVE-*g*-PS are done with the spectrometer configuration 6 Å/2.9 m, i.e., in the intermediate q range [$10^{-2} < q < 1.2 \times 10^{-1}$ Å^{-1}]. The efficiency of the detector cells is normalized by the incoherent signal delivered by 1 mm water cell.[31] Absolute values of the scattering intensity ($I(q)$ in cm^{-1}) are obtained[32] from the direct determination of the number of neutrons in the incident beam and the detector cell solid angle.

In absolute units, the scattering intensity $I(q)$ (eq 3) can be written

$$\frac{Kc}{I(q)} = \frac{1}{M_w P(q)} + 2A_2 c + ... \qquad (4)$$

$$K = \frac{1}{m^2} N_{av}\left(b_m - b_s \frac{v_m}{v_s}\right)^2 \qquad (5)$$

where K is the contrast parameter and N_{av} Avogadro's number. The K parameter can be calculated knowing the molar mass of the monomer (m), the scattering lengths of the repetitive unit and of the solvent (b_m, b_s), and their respective partial molar volumes (v_m, v_s). Here, the partial molar volume of the PCEVE repetitive unit in the linear polymer has been estimated from its molar mass and the density ρ_m of the pure monomer.[33] We assume that the density of the polymer is 15% higher; thus, $\rho_m = 1.15 \times 1.05 = 1.20$ g/cm^3 and $K = 3.16 \times 10^{-3}$ cm^2 g^{-2}.

Results and Discussion

Linear PCEVE. The scattering intensity of the solution 10^{-2} g/cm^3 of the linear PCEVE polymer (our reference solution) has been measured using three spectrometer configurations. A good superposition of the scattering curves is obtained in a wide q range as shown in Figure 1, using the representation $qI(q)$ vs q. Such a curve is typical of what is expected for the form factor of long enough wormlike chains.[25]

At high q values we see a plateau, in good agreement with the expected rod conformation. This plateau appears at $q^* = 0.28$ Å^{-1}, and its value is 4.25×10^{-3} Å^{-1} cm^{-1}; thus, according to eq 3, the persistence length of the linear PCEVE is $l_p = 12 \pm 1$ Å. Another parameter of the polymer chain can be measured in the asymptotic q range. In this range, we know that intermolecular correlations are negligible. Thus, by combining the asymptotic form of $P(q)$ (eq 1) and the expression of the scattering intensity (eq 4), we get

$$qI(q) = Kc\pi M_L \qquad (6)$$

where M_L is the linear density of the polymer. Here, from the plateau value we find $M_L = 43$ Da/Å. This value is in a very good agreement with that of the PCEVE monomer. Indeed, by taking the monomer mass (106.5 g/mol) and for the monomer distance the typical −C−C− length (2.52 Å), we find 42 Da/Å for the linear density of the monomer.

Besides the persistence length, we have estimated the radius of gyration of this linear PCEVE polymer. We have performed scattering measurements in the Guinier range ($qR_g < 1$) for the two different concentrations to determine R_g. From the Zimm plot thus obtained we get $R_g = 80 \pm 7$ Å, $M_w = 40\,000 \pm 5000$, and $A_2 = 5 \pm 3 \times 10^{-4}$ cm^3 g^{-2} mol. We have compared the measured radius of gyration to the calculated one for a polymer chain of $M_w \sim 40\,000$ with excluded volume effects. The latter is given by[26]

$$R_g = \alpha(L/2l_p)R_{g\Theta} \qquad (7)$$

where $R_{g\Theta}$ is the radius of gyration of the Gaussian chain $(Ll_p/3)^{1/2}$ and $\alpha(L/2l_p)$ the expansion factor in good solvent. The empirical expression of $\alpha(L/2l_p)$ is given in ref 26:

$$\alpha(x) = (1 + (x/3.12)^2 + (x/8.67)^3)^{(2\nu-1)/6} \qquad (8)$$

It depends on L, l_p, and ν the excluded volume exponent (0.588 in a three-dimensional space). If we apply eq 7 to a PCEVE chain of $M_w = 40\,000$, i.e., $L = (40000/106.5) \times 2.52 \cong 950$ Å, with a persistence length $l_p = 12$ Å, we find $R_g = 72 \pm 5$ Å. This calculated value is very closed to the measured one. Finally, let us note, without being able to explain it, that the molecular weight 40 000 is very different from 90 000 obtained from SEC experiments (estimated R_g, 115 Å).

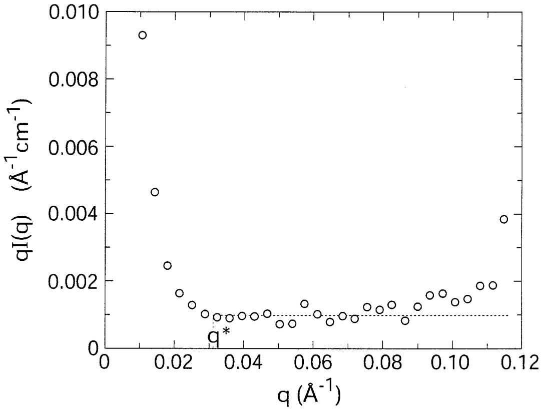

Figure 2. Representation $qI(q)$ as a function of the scattering vector q for a solution of PCEVE-*g*-PS bottlebrush polymer in the matching condition for the PS branches. The concentration is $c = 10^{-1}$ g/cm^3. The plateau observed beyond q^* now indicates a persistence length of 110 ± 15 Å for the PCEVE backbone (see text).

Grafted PCEVE-*g*-PS. As mentioned above, whereas several samples with different degree of polymerization have been measured, only the highest molecular weight sample (DP = 1042) gave a meaningful scattering signal. Such a result is not surprising since the scattering intensity is proportional to the chain molecular weight. Moreover, this unfavorable condition is magnified by the matching condition of PS branches since the contrast factor of the backbone monomer with respect to the matching solvent mixture is dramatically reduced. The intensity scattered by the PCEVE-*g*-PS polymer with DP = 1042 is shown in Figure 2, using the representation $qI(q)$ vs q. We also see a plateau, characteristic of a rod conformation, but in this case it appears at $q^* = 0.03$ Å^{-1}. According to eq 3, the persistence length of this polymer is then $l_p = 110 \pm 15$ Å. Compared to the linear PCEVE, the dense grafting of flexible PS chains produces a huge increase of the local rigidity of the copolymer backbone. We do not believe that the concentration, higher than c^*, is responsible for such an increase.

Conclusion

In this work, we have shown using small-angle neutron scattering and matching techniques that the effect of branching dramatically increases the intrinsic persistence length of linear polymer chain. We mention, however, that this increase of the persistence length from 12 Å (linear flexible PCEVE) to 110 Å (PCEVE-*g*-PS) is monitored by the number of grafted branches on the backbone. We therefore expect that reducing the degree of branching may reduce the persistence length. Moreover, more experiments are currently in progress in order to determine the relative importance of the degree of polymerization of the PCEVE backbone on the increase of the persistence length and also to measure the conformation of the side chains.

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