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Small-Angle Neutron Scattering from Diblock Copolymer Poly(styrene-d_8)-*b*-poly(γ-benzyl L-glutamate) Solutions: Rod−Coil to Coil−Coil Transition

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ABSTRACT: The elastic properties of rod−coil diblock copolymer poly(styrene-d_8)-*b*-poly(γ-benzyl L-glutamate) (PS*d*-*b*-PBLG) rod−coil diblock copolymer solutions were investigated using small-angle neutron scattering (SANS). PBLG is known to undergo a transition from a rodlike α-helical secondary structure to a random coil conformation under specific solvent conditions: the PBLG is (i) rodlike in dioxane and (ii) random coil in dioxane/trifluoroacetic acid (80/20). For the PS*d*-*b*-PBLG diblock copolymer, this conformational transition results in a topological change from a rod−coil to a coil−coil type structure. SANS results indeed show the presence of the expected scattering peaks—copolymer signature—for both conformational topologies. The position and the height of these scattering peaks are found in good agreement with a recent theoretical model that describes the conformational change in rod−coil diblock copolymer solutions. Circular dichroism experiments confirmed the change in secondary structure in the peptide block that accompanies the topological transition observed by SANS.

I. Introduction

Diblock copolymers consisting of two chemically incompatible and amorphous segments (coil−coil diblock copolymers) are well-known for their ability to self-organize in a variety of phase-separated morphologies with length scales between 10 and 100 nm. These structures are well understood, both experimentally and theoretically.[1] Replacing one of the blocks of a coil−coil diblock copolymer by a rigid segment significantly changes the microphase behavior. The self-organization of such rod−coil diblock copolymers is no longer solely determined by a microphase segregation of the constituent blocks, but is also influenced by the tendency of the rigid segments to aggregate. This competition process between microphase separation and aggregation of the rigid blocks leads to morphologies that are distinctly different from those commonly observed in classical coil−coil diblock copolymers.[2] Recently, rod−coil diblock copolymers have been extensively studied as building blocks for the development of self-assembled nanostructured materials.[3] In previous work, it was shown that the solid-state supramolecular organization of peptide-based rod−coil diblock oligomers PS-*b*-PBLG is not only sensitive to variations in the block length ratio but also can be influenced by thermally induced conformational changes in the peptide segment.[4] In contrast to these examples on bulk properties of rod−coil diblocks, where the self-assembly was the target, not much work has yet been done on the solution properties (disordered state). In this respect, we recently developed[5] a model based on the random phase approximation (RPA) describing the static and the dynamic properties of diblock copolymers having different architecture of the blocks (rigid, flexible, cyclic, once-broken rod) in solution. We specifically calculated the scattering intensity of rod−coil and coil−coil diblock copolymers, for instance under different solvent conditions and particularly in a solvent satisfying the zero average contrast condition (ZAC).[5]

In this paper, our aim was to investigate the solution properties of poly(styrene-d_8)-*b*-poly(γ-benzyl L-glutamate) (PS*d*-*b*-PBLG) rod−coil system, using small-angle neutron scattering (SANS) and circular dichroism (CD) techniques. For this purpose, deuterated polystyrene diblock copolymers (PS*d*-*b*-PBLG) were synthesized. PBLG is known to undergo a transition from rod to coil conformation under specific solvent conditions.[6] To gain more understanding of the effect of these conformational changes on the block copolymer topology, we have carried out SANS experiments both in dioxane, where the peptide block possesses an α-helical secondary structure and the block copolymer has a rod−coil architecture, and in dioxane−trifluoroacetic acid (TFA) mixtures, in which the peptide block adopts a random coil conformation and the copolymer behaves as a conventional coil−coil diblock copolymer.[7] For comparison, complementary experiments were carried out on the PS*d*/PBLG mixtures having the same molecular weights and concentrations.

Let us first recall the expression of the scattering intensity, under zero average contrast conditions, for the relatively simple case of a linear coil−coil diblock copolymer chain where the two blocks A and B have the same degree of polymerization ($N_A = N_B = N/2$), the same radius of gyration $R_{gA} = R_{gB} = R_g$, the same excluded volume parameter $v_{AA} = v_{BB} = v$, and a slight

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incompatibility ($\chi \neq 0$) introduced through the interaction parameter $\chi = v_{AB} - v$:[5]

$$\frac{I_{ZAC}(q)}{\Phi N} = \left(\frac{a_0 - b_0}{2}\right)^2 \frac{P_{half}(q) - P_t(q)}{1 - \left(\frac{\chi \Phi N}{2}\right)[P_{half}(q) - P_t(q)]} \quad (1)$$

where $P_t(q)$ and $P_{half}(q)$ are the usual Debye functions for the form factors. $P_t(q)$ and $P_{half}(q)$ correspond respectively to the total form factor and the form factor of one block (symmetrical coil–coil copolymer):

$$P_{t,lin}(q) = \frac{2}{u^4}(e^{-u^2} + u^2 - 1) \quad (2)$$

$$P_{half,lin}(q) = \frac{8}{u^4}\left(e^{-u^2/2} + \frac{u^2}{2} - 1\right) \quad (3)$$

with $u = qR_{gt}$ and R_{gt} is the total radius of gyration of the whole block copolymer. Φ is the copolymer concentration, and a_0 and b_0 are the contrast factors.

Replacing one coil block by a rod block [$P_{block,coil}(q) \neq P_{block,rod}(q)$] modifies the scattering intensity as follows:[5]

$$\frac{I_{ZAC}(q)}{\Phi N} = \left(\frac{a_0 - b_0}{2}\right) \times$$

$$\frac{[P_{half,rod}(q) + P_{half,coil}(q)]/2 - P_{t,rod-coil}(q) + \left(\frac{\Phi N}{4}\right)\left(v + \frac{\chi}{2}\right)\Delta P_{rod-coil}(q)}{1 + v\Phi N P_{t,rod-coil}(q) - \left(\frac{\chi \Phi N}{2}\right)\left[P_{rod,coil}(q) + \left(\frac{\Phi N}{4}\right)\left(v + \frac{\chi}{2}\right)\Delta P_{rod-coil}(q)\right]} \quad (4)$$

with

$$P_{t,rod-coil}(q) = \frac{1}{4}[P_{half,rod}(q) + P_{half,coil}(q) + 2P_{rod-coil}(q)] \quad (5)$$

and

$$\Delta P_{rod-coil}(q) = P_{rod}(q)\, P_{coil}(q) - P_{rod-coil}{}^2(q) \quad (6)$$

This theoretical development evidenced that the replacement of a coil block by a rigid one changes the copolymer peak position from characteristic values $qR_g = 2$ to $qR_g = 2.2$, indicating a smaller scale microphase separation in the case of rod–coil diblock copolymers. Moreover, the height of the scattering intensity has been shown to be higher in rod–coil systems, indicating a stronger tendency for rod–coil diblock to segregate.

II. Sample Preparation and Experimental Techniques

Materials. γ-Benzyl L-glutamate *N*-carboxyanhydride (Bn-Glu NCA) was prepared according to a published procedure.[8] *N*,*N*′-Dimethylformamide (DMF) was distilled from CaH_2 under reduced pressure and subsequently stored over molecular sieves (4 Å) under an argon atmosphere. All other reagents and solvents were obtained from commercial suppliers and used as received.

Methods. Molecular weight analysis was performed on two setups with different mobile phases. For the first setup, THF was used as the mobile phase, and GPC analysis was carried out at room temperature using a Jasco 880-PU pump system and a PSS–SDV column (8 × 300 mm) with a pore size of 50 Å. In this case, sample elution was monitored by UV (absorbance detector model UV-C–Rainin Dynamax) and RI detection (refractive index detector: RI-4). The second setup consisted of a Jasco PU-1580 Intelligent HPLC pump and a series of a three Tosohaas Bioseparation Specialistes TSK gel (3 × 7.8 × 300 mm) columns with a pore size of 50 Å. DMF was used as the mobile phase, and the elution of the samples was monitored by a Jasco RI-1530 Intelligent RI detector. ^1H NMR spectra were obtained at room temperature on a Bruker 250 spectrometer. ^{13}C NMR spectra were recorded at 80 °C on a Bruker AMX 500 using DMSO-d_6 as the solvent. The spectra were recorded inverse gated proton decoupled to allow integration of the ^{13}C NMR signals.

Procedures. a. Synthesis of PS*d*$_8$–NH$_2$. The ω-aminopolystyrene-d_8 (PSd_8–NH$_2$) was prepared by anionic polymerization of styrene-d_8 at room temperature in cyclohexane, using *sec*-BuLi as initiator. After 1 day, the polymerization was terminated by the addition of 1-(3-chloropropyl)-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane. The protective groups were removed using a THF/HCl(aq) mixture (90:10), providing the crude PSd_8–NH$_2$ in 80% yield. Finally, nonfunctionalized polystyrene was removed by flash chromatography on silica gel with dichloromethane–methanol mixture as eluent. The polymer was characterized using GPC analysis and ^1H NMR. The analysis indicated a degree of polymerization (DP) of 44 for PSd_8–NH$_2$ and a degree of functionalization close to 100%.

b. Synthesis of the Poly(styrene-*d*$_8$)-*b*-poly(γ-benzyl L-glutamate) Block Copolymer. A Schlenk flask fitted with a drying tube and a stir bar was charged with a solution of PSd_8–NH$_2$ in dry DMF. After that, a calculated amount of Bn–Glu NCA dissolved in dry DMF (~0.2 g/mL) was added, and the reaction mixture was stirred at room temperature under the exclusion of moisture. After 5 days, the diblock copolymer was isolated by precipitation in diethyl ether in 70% yield. The number-average degree of polymerization (DP) for the poly(γ-benzyl L-glutamate) (PBLG) block determined by ^{13}C NMR was found to be 54. The polydispersity of PS(d_8)$_{44}$-*b*-PBLG$_{54}$ deduced from GPC in DMF was 1.27.

Experimental Techniques. Small-angle neutron scattering experiments were performed on the D11 spectrometer at the Max Von Laue-Paul Langevin Institute (ILL-Grenoble). Using different sample-to-detector distances, the range of scattering vectors covered was $7.33 \times 10^{-3} \leq q \leq 3.33 \times 10^{-1}$ Å^{-1} ($q = (4\pi/\lambda)/\sin(\theta/2)$, where λ is the neutron wavelength and θ the scattering angle). The solutions were prepared with a proper choice of contrast H or D (polymer/solvent) to satisfy the ZAC conditions in dioxane and in dioxane:TFA mixture (80:20) in the concentration ranges from 5 to 40 wt %. All the data were treated according to standard procedures to correct the transmission, thickness, and normalization. CD measurements were carried out at 57 °C on a Jobin Yvon SpexCD6 spectropolarimeter in a cuvette with a path length of 1 mm and a sample concentration of 2.5 mg/mL. The temperature was controlled by means of a Haak F3-Fisions bath.

III. Results and Discussion

The study of a rod–coil to coil–coil transition for PS-(d_8)$_{44}$-*b*-PBLG$_{54}$ diblock copolymer was investigated using SANS and CD experiments. Figure 1 shows typical scattering intensities of the PS/PBLG mixture in solution (ZAC conditions and $C = 20\%$ (w/w)) at the same molecular weight and composition of the studied diblock copolymer. The curves present a monotonic decrease of $I(q)/C$ as a function of q in both studied solvents: dioxane and dioxane/TFA (80/20 (v/v)), which is typical for a homopolymer mixture. In Figure 2 is illustrated the SANS intensity profiles at different concentrations, ranging from $C = 5$ to 40% (w/w), for the diblock copolymer PS(d_8)$_{44}$-*b*-PBLG$_{54}$ in dioxane satisfying the ZAC conditions. As opposed to the PS/PBLG homopolymer mixture in the dioxane case (at the same molecular weight and composition), the SANS intensity profiles for the diblock copolymer show the existence of a scattering peak (copolymer signature). The peak positions remain at the same q value for the different investigated concentrations, and the scattering intensity increases with the diblock copolymer concen-

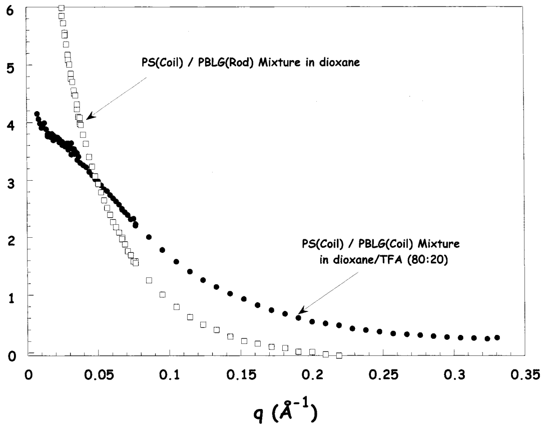

Figure 1. SANS intensities of PS/PBLG mixtures in ZAC conditions, $T = 53$ °C, $C = 20\%$ (w/w) solvent: (□) dioxane and (●) dioxane/TFA (80/20).

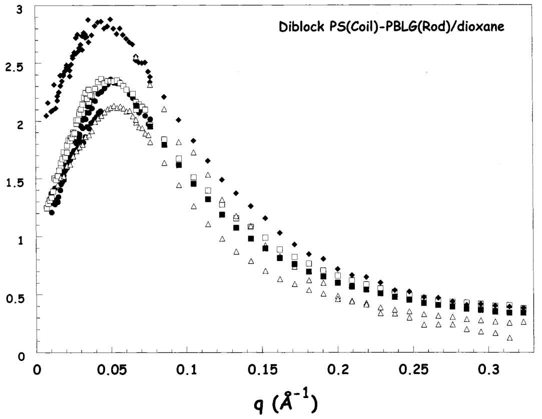

Figure 2. SANS intensities of PS(d_8)$_{44}$-*b*-PBLG$_{54}$ in ZAC conditions, $T = 53$ °C, in dioxane at the concentrations (●) 40%, (□) 30%, (◆) 20%, (△) 10%, and (■) 5% (w/w).

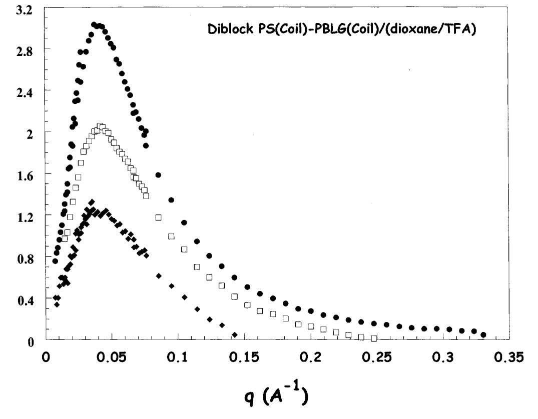

Figure 3. SANS intensities of PS(d_8)$_{44}$-*b*-PBLG$_{54}$ in ZAC conditions, $T = 53$ °C, in dioxane/TFA (80/20) at the concentrations (●) 35%, (□) 20%, and (◆) 10% (w/w).

tration. The same diblock copolymer PS(d_8)$_{44}$-*b*-PBLG$_{54}$ in the ZAC condition was studied in dioxane/TFA at different concentrations where a transition from rod to coil for the PBLG is expected to occur. The results are illustrated in Figure 3 where the variation of $I(q)/C$ is plotted as a function of q at different investigated concentrations. One observes also in this case that the scattering intensities exhibit a scattering peak (copolymer signature) whose position is independent of the concentration.

As mentioned above, we have recently developed an RPA model[5] that describes the scattering intensity for block copolymer systems having different architectures for the block. Figure 4a illustrates these theoretical predictions for two systems: coil–coil and rod–coil satisfying the ZAC conditions. It is clearly seen in this calculation that the architecture of the blocks (in this case the rigidity) plays an important role and induces a change in the variation of the scattering profile $I(q)$ vs q. Two important features can be highlighted: the peak position is modified as well as the height of $I(q)$ in both systems. The coiling of one block in rod–coil diblock copolymer shifts the peak position to lower q values and at the same time decreases the scattered intensity. Figure 4b illustrates the experimental results obtained for the same diblock copolymer PS(d_8)$_{44}$-*b*-PBLG$_{54}$ in dioxane (rod conformation of the PBLG) and in dioxane/TFA (coil conformation of the PBLG). Qualitatively, the results are in good agreement with the RPA model;[5] namely, the peak position is shifted to lower q values accompanied by a decrease of the scattered intensity in the whole q range.

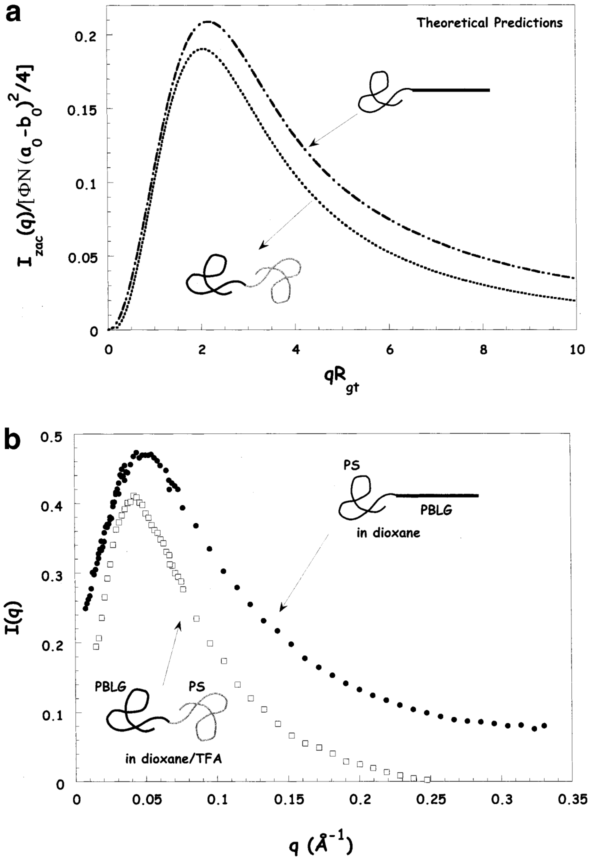

Figure 4. (a) Variation of the intensity in the zero average contrast conditions $I_{\mathrm{ZAC}}(q)/[\Phi N(a_0 + b_0)^2/4]$ as a function of qR_{gt} for (- - -) coil–coil and (• - - •) rod–coil at $(\chi\Phi N) = 8.2$ (see ref 5 for more detail). (b) Effect of solvent on PS(d_8)$_{44}$-*b*-PBLG$_{54}$. Transition rod–coil, $T = 53$ °C, $C = 20\%$ (w/w) in (●) dioxane and (□) dioxane/TFA (80/20).

The conformational changes that induce the topological transition from a coil–coil to a rod–coil diblock copolymer could also be monitored by circular dichroism (CD) experiments. Various experimental techniques have shown that, in mixed solvent systems containing between 10 and 30 vol % TFA, PBLG undergoes a transition from a rigid-rod-like α-helical secondary structure to a flexible, random coil polymer.[6] Circular dichroism experiments indeed show that in dioxane the peptide segment of the PS(d_8)$_{44}$-*b*-PBLG$_{54}$ block copolymer adopts an α-helix conformation, as evidenced by a

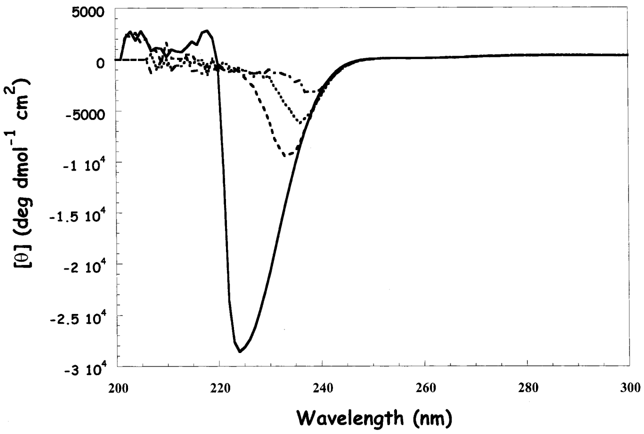

Figure 5. CD spectra of PS(d_8)$_{44}$-*b*-PBLG$_{54}$: (—) dioxane, (- - -) dioxane/TFA 10%, (• • •) dioxane/TFA 15%, and (• - - •) dioxane/TFA 20%. $C = 2.5$ mg mL^{-1}.

negative signal at ~222 nm in the CD spectrum shown in Figure 5. The intensity of this signal progressively disappears upon addition of TFA at different contents, namely 10%, 15%, and 20%, indicating a change from a predominantly α-helical secondary structure to a random coil conformation and supporting the results from the SANS experiments.

IV. Conclusion

In this paper, we have described the solution properties of poly(styrene-d_8)-*b*-poly(γ-benzyl L-glutamate) (PS*d*-*b*-PBLG) rod–coil diblock copolymers. The objective of this study was to probe the topological transition from a rod–coil to a coil–coil type diblock copolymer that is associated with the unfolding of the α-helical peptide segment by means of small-angle neutron scattering. In dioxane the PBLG adopts a rod conformation, and the scattering as well the CD results that were obtained are typical for rod–coil diblock copolymer solutions. SANS results showed the presence of a scattering peak (“copolymer signature”), and the CD experiments present the characteristic band of the α-helix conformation (≈222 nm) of the PBLG. In the dioxane/TFA mixture (80/20), the PBLG block undergoes a transition from rod to coil conformation. The SANS and CD results strongly support this change in the conformation. The position and the height of the scattering peak are found in good agreement with a recent theoretical model that describes the conformational change in rod–coil diblock copolymer solutions. This transition is also confirmed by circular diochroism experiments, where the characteristic band of the α-helix conformation at ≈222 nm in the CD spectrum of the block copolymer disappears progressively as the content of TFA is increased up to 20%. The topological transition from a rod–coil to a coil–coil copolymer has been also observed when investigating using SANS and dynamic light scattering other molecular weights and volume fractions of PS–PBLG under different conditions. We are currently comparing quantitatively our experimental results with the RPA model in order to extract, for instance, the Flory χ-parameter in the rod–coil and coil–coil conformations which will be published in a forthcoming paper.

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