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Microphase Structure of Block Ionomers. 2. Nonionic Segment Conformation in Molded Styrene–4-Vinylpyridinium ABA Copolymers

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I. Introduction

A recent investigation by small-angle X-ray scattering (SAXS) of the structure of polystyrene-based ABA block ionomers containing long polystyrene blocks and terminated by 10–50 ionic monomers[1] has shown that these associate in spherical microdomains organized on a distorted cubic lattice, i.e., in a manner very similar to what would be expected of nonionic copolymers. More specific of these materials is the fact that, for such short A lengths, the ionic segments are fully extended and the number of chains emanating from an ionic domain is quite high (more than 100). In doing so, the polymer reduces its total interfacial energy. It seemed interesting to probe the effect of such tight binding of many chain ends on the conformation of the polystyrene middle chain in the spherical microphase morphology. The results of a small-angle neutron scattering (SANS) investigation using contrast variation techniques will be reported in this paper. The samples of (methyl 4-vinylpyridinium)-*b*-styrene-*b*-(methyl 4-vinylpyridinium) are the same as for the SAXS investigation.[1]

While block ionomers of the type discussed here have been the subject of several recent studies,[2-7] the question of chain conformation in these systems has not been considered so far. Apart from their intrinsic interest as new materials, these block copolymers are adequate model compounds to investigate both the importance of molecular architecture on ionic aggregation in ionomers and the effect of an attractive interaction on the final structure of the block polymers.

II. Experimental Section

Materials. ABA block copolymers of structure 4-vinylpyridine-*b*-styrene-*b*-4-vinylpyridine were synthesized by sequential anionic copolymerization according to a procedure described elsewhere[6] that provides samples with identical midblock lengths and various end-block lengths. Two series were prepared with either hydrogenated or perdeuterated PS of about 500 units and 10–50 VP units.

The vinylpyridine content of the resulting copolymers was determined by FTIR for the hydrogenated samples containing less than 10 mol % of vinylpyridine. Nonaqueous titration of the vinylpyridine segments by perchloric acid was done for all samples. The molecular weight of the polystyrene midblock was determined by gel permeation chromatography (GPC). The resulting precision on the number of repeat units per block is on the order of 5%. The polydispersity index was found to vary from 1.2 to 1.3.

Blends of a various proportion of deuterated and hydrogenated materials of the same architecture were prepared in THF. The resulting solutions were stirred overnight, then precipitated in water, dried at 70 °C in vacuum, compression molded at about 130 °C, and soaked in 80/20 (v/v) absolute ethanol/methyl iodide solution for 3 days under reflux in order to fully quaternize the 4-VP units. Under these conditions the polystyrene matrix is swollen by methyl iodide. The samples were then dried and remolded at about 140 °C into disks, ca. 1 mm thick. The disappearance of the 1414-cm^{-1} 4-VP IR band was taken as evidence of complete quaternization. Phase separation of the resulting samples was tested by SAXS. A description of the samples is given in Table I.

Scattering Experiments. SANS experiments were conducted at Laboratoire Léon Brillouin (LLB), Saclay, France, on the PACE spectrometer. A mechanical selector provided neutrons of 7 Å wavelength with a 10% distribution. The distance was chosen such that the angular range varied from $q = 0.011$ to 0.12 Å^{-1} ($q = 2\pi \sin(\theta/\lambda)$ with 2θ the scattering angle). The absence of a preferred orientation in our samples permitted the use of an annular detector with 30 concentric rings. Hence radially averaged patterns are directly collected. The resulting I vs q curves are corrected for incident beam intensity, sample thickness and transmittance, and empty beam scattering. Inhomogeneity of the detector cell response is accounted for by normalization of the resulting curves with the flat incoherent background of a water sample.

Because of the high concentration of hydrogen atoms in our samples, an incoherent q-independent background is superposed to the coherent signal. For the totally hydrogenated samples, the constant intensity at the largest angles was used as a first estimate of that background. Alternatively the scattering curves were plotted as Iq^4 vs q^4,[8] and the slope was taken as a measure of the incoherent background. Both estimates agreed to within 1%. A constant intensity value was thus removed from each scattering curve based on the knowledge of the hydrogen content of the corresponding material and assuming the intensity of the incoherent scattering to be a linear function of the hydrogen concentration.

III. Results and Discussion

For each sample, the coherent scattering pattern obtained after the standard corrections mentioned above is the sum of two contributions: (1) a phase scattering of the ionic domains (4-VP chain ends) in the PS matrix and (2) the scattering signal due to the contrast between labeled and unlabeled PS segments. Only the latter contribution contains the desired information about chain dimension. Hence, it is necessary to remove the part of the scattered signal arising from the ionic domains. This was done by the "subtraction method" described by Koberstein.[9] It takes into account the fact that, for each deuterium composition of the PS matrix, the domain scattering retains the same shape and the intensity is simply scaled by a contrast factor, which expresses the change in the average scattering density of the PS matrix when a fraction of the chains are deuterated. Formally, it is given by

$$KP_{\mathrm{B}}(q) = I_{\mathrm{L}}(q) - \left[\frac{\beta_{\mathrm{A}} - x\beta_{\mathrm{BD}} - (1-x)\beta_{\mathrm{BH}}}{\beta_{\mathrm{A}} - \beta_{\mathrm{BH}}}\right]^2 I_{\mathrm{U}}(q) \qquad (1)$$

where $I_{\mathrm{L}}(q)$ and $I_{\mathrm{U}}(q)$ are the intensities of the partially labeled and unlabeled samples, respectively; $P_{\mathrm{B}}(q)$ is the single segment scattering for the chains in phase B (polystyrene in this study); the β's are the coherent scattering length densities of pure ionic segments (A), pure deuterated polystyrene segments (BD), and pure protonated polystyrene segments (BH); x is the fraction of polystyrene chains that are deuterated; K is a constant containing various molecular parameters which was not calculated here since no absolute measurements were used.

The resulting $P_{\mathrm{B}}(q)$ curves contain all the information about the configuration of the polystyrene chain and were

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Table I
Sample Description and SANS Results

sample[a] VP/PS$_H$/VP + VP/PS$_D$/VP	PS$_D$ content, mol/L	R_g, Å	$R_g(c=0)$, Å	R_g^{corr}, Å	$R_g^{corr}(c=0)$, Å
9/480/9 +	2.99	68	73	70	75
10/530/10	3.94	66		68	
	4.99	65		67	
	5.96	63		65	
17/480/17 +	2.65	61	69	65	73
22/530/22	3.63	58		63	
	4.52	57		63	
	5.28	53		57	
48/480/48 +	2.40	51			
53/530/53	3.11	59			
	3.97	42			
	4.64	33			

[a] Polymers represented by the number of VP units/number of styrene units/number of VP units; the first chain is the hydrogenated one, and the second one has the perdeuterated polystyrene block.

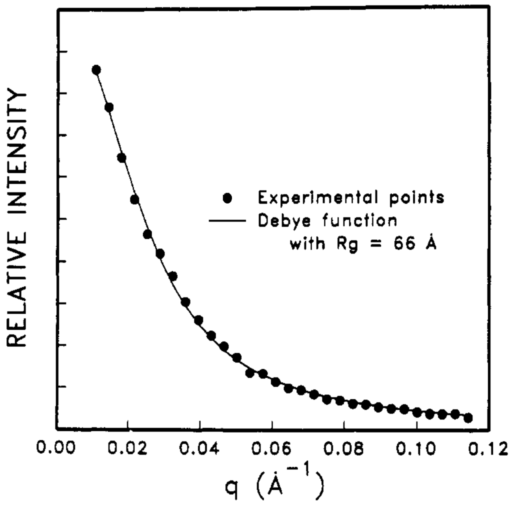

Figure 1. Fit of the single PS segment profile to a Debye function for sample 10–530–10 containing 3.98 mol/L of perdeuterated PS.

fitted using a least-squares regression with a Debye scattering function for Gaussian coils

$$I_{\mathrm{Debye}}(q) = (2/t)(e^{-t} + t - 1) \qquad (2)$$

where $t = q^2R_g{}^2$ and R_g is the radius of gyration of the coil.

A fit is shown in Figure 1, and the values of R_G determined for each sample are listed in Table I. It can be seen that for the 10–530–10 and 22–530–22 series R_g decreases as the deuterium content increases and that no reasonable fit could be found for the 53–530–53 samples. Close examination of the curves shows that, in some cases, there is a remnant of domain scattering in the experimental data. Indeed, it is known that this method can lead to incomplete subtraction of domain scattering and that small errors in the correction can lead to large errors in single chain scattering data.[10] Because this investigation was no exception, the reliability of the results will be discussed in more detail. It must be stressed that a key factor for achieving a good correction is the relative importance of the chain scattering and domain scattering.[11] For our materials it was found that, within each architectural series, both the domain scattering and the labeled chain scattering decreased as the content of deuterated PS chains decreased. Furthermore, estimates of the scattering power of each species indicate that the relative importance of the contributions of the domain over the deuterated chain in the total scattering increases as the concentration of the deuterated chains increases. Thus the best correction should be obtained with the lowest concentration of deuterated chains compatible with a sufficiently intense chain signal, and indeed it was found that the quality of the fits to a Debye function decreased with increasing deuteration. The corresponding values of R_g are noted in the table. The importance of domain scattering also increases with the volume fraction of ionic aggregates, i.e., with the length of the 4-VP segment. Indeed no reasonable fit could be obtained for the materials with 50 ionic monomers at each chain end whatever the corrections applied, and thus the values in the table are only indicative. For the 10 and 20 VP series, it was found that R_g decreases as the content of deuterated polymer increases. If some phase scattering is still present, there is an excess intensity in the 0.03–0.05-Å^{-1} range with no change in the smaller angle region. The apparent single chain scattering function dampens more slowly in the region where the fit is performed, leading to an underestimated value of R_g. In order to take this effect into account, the experimental values of R_g were extrapolated to zero deuterium concentration (Figure 2) and are reported as $R_g(c=0)$ in the table.

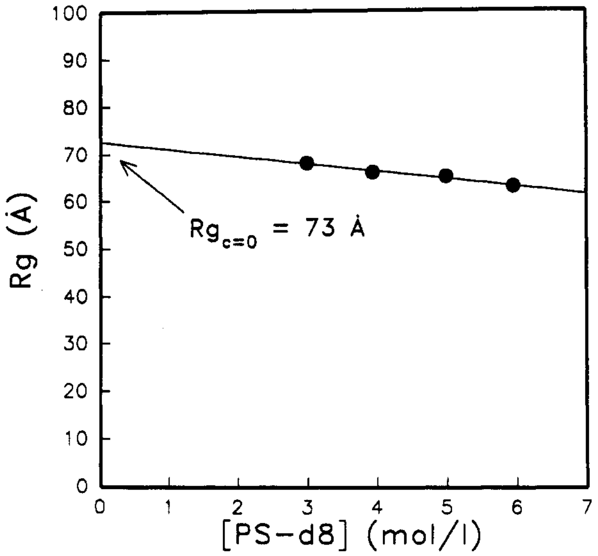

Figure 2. Variation of the radius of gyration obtained with the fits as a function of the concentration of the deuterated chains for the architecture 10–530–10. The curve extrapolates to 73 Å at zero concentration.

In a further attempt to minimize the influence of the imperfection of the subtraction of the domain scattering on the final results, the data points of the resulting single segment scattering curves where some domain scattering could be visually detected have been simply omitted. The values of the radius of gyration and their extrapolation to zero deuterium concentration are denoted R_g^{corr} and $R_g^{corr}(c=0)$, respectively. As expected, they are larger. The remaining slight dependence on the deuterium content could be due to more subtle effects such as a molecular weight mismatch between proto- and deuterocopolymers. For the 50 VP series too many points would have had to be omitted, and this procedure was not possible. Therefore, for both series containing 10 or 20 VP units $R_g^{corr}(c=0)$ is constant within experimental error and close to the value of 75 Å for the unperturbed dimension of a polystyrene chain of the same length as the deuterated chain.[12] It should be remarked, however, that SANS gives access to the chain conformation averaged over all orientations and therefore an affine deformation of the chain could not be detected with this geometry.

The difficulties encountered with the subtraction method in this study are undoubtedly related to the strong dependence of the position of the domain scattering to the end-block length[1] and its polydispersity.[13] A difference in the length of the end blocks for the copolymers containing deutereated and protonated polystyrene is unavoidable since they were obtained in different syntheses. The control of that length and its dispersion is known to be difficult.[6] Matching of the average scattering length density of the domains to that of the partially deuterated matrix should in principle, lead to more precise measurements. However, it requires labeling also of the VP units and still involves problems of reproducibility of the polymers. It was not attempted here.

IV. Conclusion

It has been possible to determine by SANS the conformation of the polystyrene midblock of an ABA block ionomer in the spherical morphology. It has been shown that for two architectures with short end blocks (10 and 20 units) the average radius of gyration of a midblock containing about 500 units is constant and close to the value of a PS chain of the same length would have in the melt. These data rule out an appreciable chain extension as that observed previously for some more classical ionomers[14] and agree with a recent similar investigation of the chain conformation of a telechelic ionomer; in that case no difference was found between a sodium carboxylate terminated polystyrene containing about 70 monomers and its nonionic precursor.[15]

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