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Kinetics of Coil Overlap in Ionomer Blends by ^{1}H NMR in DMSO-d_6. 1. Effect of Electrolytes, Water, Molecular Weight, Ion Content, and Temperature

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ABSTRACT: ^{1}H nuclear magnetic resonance (NMR) studies were performed on solutions of mixtures of lightly sulfonated polystyrenes (PS-SSA), with poly(methyl methacrylate-*co*-4-vinylpyridine) (PMMA-4VP) copolymers. The PS-SSA (5-15 mol % sulfonation) had molecular weights (MW) ranging from 2×10^3 to 1×10^5, while the PMMA-4VP chains (5-11 mol %) had a MW of 1×10^5. The driving force for coil overlap was electrostatic attraction between the sulfonate anions and the pyridinium cations which were produced as a result of proton transfer from the sulfonic acid to the 4VP moieties. The coil overlap process was monitored as a function of time by the acquisition of proton spectra, which showed the gradual disappearance of the original (unshielded) methoxy signal and the appearance of a new signal originating from the shielded methoxy protons. In order to propose a complete model for the coil overlap process, it was first necessary to ascertain that the ionic species were, indeed, responsible for the interchain attraction rather than some other unsuspected mechanism. The electrostatic nature of the mechanism was confirmed by the addition of various electrolytes to the equilibrated blend solutions. The addition of electrolytes does, indeed, result in the disappearance of the shielded methoxy signal, confirming the electrostatic nature of the mechanism. In addition, the qualitative influence of other parameters on the electrostatic interaction was studied. These parameters were the water content of the solution, the ion content of the copolymers, the MW of the PS-SSA chains, and the temperature. The detailed kinetics and the mechanistic aspects of the coil overlap process are described in a subsequent paper.

1. Introduction

Since major improvements in polymer properties can be achieved by blending, this area has been the subject of increasing interest over the last few decades.[1-7] The potential of this approach can be appreciated when one considers the improvement in the properties of metallic alloys over those of pure metals. However, most polymer pairs are not miscible, and the blends formed from such pairs tend to phase separate. The lack of strong cohesive forces between the phases in many such blends gives rise to poor mechanical properties, which greatly limits the number of industrial applications of these materials. A few methods are described in the literature that lead to miscibility enhancement in polymer blends.[5] One such method, which has received considerable attention recently, involved introduction of appropriate ionic groups onto each polymer chain.[8]

Many techniques can be used to determine the extent of phase separation in polymer blends, and each of these methods is sensitive to domains of specific sizes. For instance, film transparency indicates homogeneity at a level of ca. 1000-10000 Å, while glass transition temperature measurements reveal homogeneity over dimensions of ca. 100 Å. Molecular level information can be obtained by spectroscopic techniques such as, IR,[9] NMR,[10] and fluorescence.[11-13]

In a previous study by A. Natansohn and A. Eisenberg, ^{1}H NMR spectroscopy was used to probe the miscibility of a blend of poly(methyl methacrylate-*co*-4-vinylpyridine) (PMMA-4VP) with poly(styrene-*co*-styrenesulfonic acid) (PS-SSA) in DMSO solution (see Figure 1).[14] This technique was useful because the methoxy proton signal of MMA is very sensitive to any aromatic shielding effect, in this particular case to the effect of the aromatic rings of the styrene units. It was previously demonstrated[15] that the proton transfer from the SSA group to the pyridine ring takes place very rapidly; by contrast, it was found[14] that the mixing of the two types of polymers is a slow process dictated by the segmental motion in solution. For a system containing ca. 11 mol % ionic groups on each polymer at a 2% total polymer concentration in DMSO, the coil overlap took ca. 1 h at 85 °C. The process could be followed by monitoring the chemical shift of the

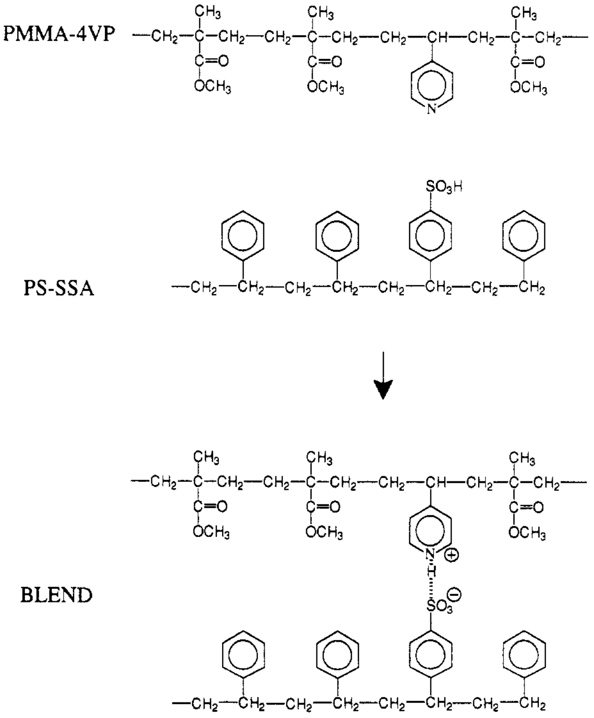

Figure 1. Illustration of the polymer structures and the proton transfer results for the PMMA-4VP and the PS-SSA.

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Table 1. Molecular Weight, Polydispersity Index, and SSA Content of the PS Samples

M_n	peak MW	M_w	polydispersity index	SSA content (mol %)	mean no. of SSA units per chain
2.0×10^3 [a]			1.2[a]	25.0	5
4.2×10^3	4.4×10^3	5.0×10^3	1.18	10.2	4
				14.9	6
				20.7	8
9.8×10^3	9.8×10^3	1.1×10^4	1.08	16.0	15
1.2×10^4	1.2×10^4	1.3×10^4	1.10	5.3	6
				8.3	10
				10.5	12
1.0×10^5	1.1×10^5	1.1×10^5	1.07	7.7	74
				10.0	96
				14.7	140

[a] Values from Pressure Chemicals.

methoxy signal in the proton spectra, or by measuring the area of the cross-peak that appears in the 2D-NOESY spectrum between the methoxy and aromatic signals. The one- and two-dimensional NOE-correlated spectra demonstrated the presence of dipolar coupling through space between the methoxy protons of the PMMA–4VP and the aromatic protons of the PS–SSA, and this requires an interchain distance of about 4 Å.

It is well known that due to the negligible entropic contribution on mixing of polymer, specific interactions between two dissimilar polymer chains are very helpful in order to achieve miscibility. Thus, in the previous paper, Natansohn and Eisenberg suggest that the blending process occurring between the PS–SSA and the PMMA–4VP is due to proton transfer that occurs between the SSA and the 4VP, which, in turn, generates the oppositely charged ions which are the driving force responsible for the miscibility of the PS–SSA and PMMA–4VP (see Figure 1). Therefore, it was proposed that the formation of those ion pairs should pull both chains close to one another.

If the Coulombic interaction is the driving force for the coil overlap process, the addition of microelectrolytes or possibly even water to the polymer solution should disrupt the process. Moreover, other experimental parameters should have an influence on the mechanism (e.g., temperature or molecular weight of the polymer chains). The purpose of this part of the investigation is to elucidate this aspect of the coil overlap mechanism in greater detail. The investigated parameters are the presence of microelectrolytes, the water content, the SSA and 4VP contents, the molecular weight, and the temperature. Establishing the nature and the influence of the parameters on the electrostatic interaction is a prerequisite for a detailed study of the mechanism of the shielding process, which is the subject of a subsequent paper.

2. Experimental Section

Copolymers of PMMA–4VP of 5, 7, and 11 mol % VP were synthesized as part of another project.[16] These polymers, prepared by radical bulk copolymerization, were found to have a viscosity-average molecular weight (M_v) of $\simeq 10^5$.

The PS sample ($M_n = 2.0 \times 10^3$) from Pressure Chemicals was used as received. The characterization of the monodisperse PS samples (Polyscience) was performed by size exclusion chromatography (SEC) on a Varian 5000 LC. The solvent used for the standardization curve was tetrahydrofuran (THF; Chemlab spectroscopic grade). The analyses were performed in duplicate and the results averaged. The peak of the molecular weight distribution curve, the weight-average MW (M_W), the number-average MW (M_n), and the polydispersity index for the samples are given in Table 1. The acid copolymers based on PS were synthesized according to an established procedure suggested by the patent of Makowski et al.[17] The extent of sulfonation varied between 5 and 25 mol % SSA units. The titration procedure for the determination of the sulfonic acid content in the copolymers was obtained from the literature.[18] The PS–SSA nonaqueous titrations, in benzene/methanol (90/10 v/v), were performed in triplicate, and the average deviation in the SSA content was less than 1%. These results are also given in Table 1.

Solutions of the blends were prepared using the following procedure: Equimolar quantities of the two dried copolymers were weighed separately to a total of 10 mg. The PMMA–4VP was then placed in a predried NMR tube, while the PS–SSA was kept in a predried vial. Subsequently, 0.25 mL of DMSO-d_6 was added to each copolymer. Both copolymer solutions were then placed for 15 min in a thermostated bath set at the experimental temperature. Subsequently, the PS–SSA solution was injected with a syringe into the NMR tube containing the PMMA–4VP solution, and the NMR tube was immediately placed in the probe at the experimental temperature.

All NMR spectra for the materials were obtained in a DMSO-d_6 solution on a Varian XL-300 spectrometer. Deuterated DMSO (Aldrich; 99.96% deuterated) was used as received. The ^{1}H NMR spectra were monitored over the spectral range included between 4.5 and 2.5 ppm. The pulse sequence employed was a standard S2PUL with 32 transients. The S2PUL sequence consisted of a 90° pulse with a width of 11 μs, followed by an acquisition time of 2.51 ms. The free induction decays (FIDs) were accumulated via 512 time-domain data points, with a pulse repetition delay of 1.5 s. Since the proton spin–lattice relaxation times for both polymers in the laboratory frame are much less than 1 s, this ensures that the proton spectra are fully relaxed, and that no signal distortion should be expected.

The deconvolution process involves the separation of a complex curve into a certain number of independent contributions, which, when added to the proper baseline, restructure the original line shape. The procedure used to achieve the deconvolution of the superposed ^{1}H NMR signal of the two methoxy groups, as well as the principles behind the deconvolution, was described elsewhere.[19] For convenience, in this paper, the methoxy group line shape was deconvoluted using two Lorentzian bands. In all cases, a correlation coefficient equal to or greater than 0.995 was achieved. Thus, it can be concluded that there is no significant difference between the experimental and the deconvoluted line shapes. Furthermore, the end value of the χ^2 obtained by the deconvolution process qualitatively indicates that the maximum error in the area of individual bands is of the order of ±2.5% (confidence level of 95%). However, it is important to note that, due to the pure PMMA–4VP line shape (without ionic interactions), this procedure only yields an approximation of the real area of the peaks. This point will be discussed in some detail in the second paper in this series, since precise area will be crucial in order to establish the concentration–time curves.

The procedure that was adopted for the mixture of the two copolymers consists of the following steps: The two peaks for the spectrum were deconvoluted into two Lorentzian bands, and then the relative area of the unshielded methoxy group signal to the total area of the methoxy signal was calculated. For a given spectrum, the concentration of the shielded methoxy groups (X) can then be calculated from the multiplication of the relative area of the signal by the initial copolymer concentration (a_0). Evidently, the ratio of the equilibrium concentration of the shielded methoxy groups, X_e, to a_0 ($=X_e/a_0$) is the relative contribution of the shielded methoxy signal at steady state. The X_e/a_0 parameter will be used as a comparison basis between the blends in which a shielded methoxy signal is present, enabling one to draw qualitative conclusions on the effects of the experimental parameter under study.

Another procedure was used for blends in which no resolvable shielded methoxy peak is seen. Since for these dilute mixtures no significant differences in viscosity were observed, a convenient way to determine whether aromatic shielding is present is to compare the width at half-height (Γ) of the main methoxy peak signal ($\simeq$3.6 ppm) for the homopolymer of PMMA–4VP at 85 °C with that obtained for the blend. If some shielding is present in the blend as seen in the methoxy group line shape, one can expect a greater Γ value, since for these mixtures the line shapes will contain an additional unresolved signal arising from the shielded methoxy groups. The Γ value for the main peak due

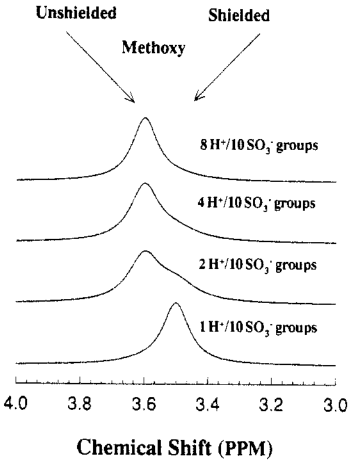

Figure 2. Spectra obtained after the addition of H_2SO_4 to the equilibrated polymer solution: elapsed time 60 min at T = 85 °C.

to the methoxy group of the homopolymer is 0.025 ± 0.001 ppm. One can subtract this value from the Γ value of the main blend peak and obtain the difference (ΔΓ), which is a qualitative indication of the extent of aromatic shielding.

3. Results and Discussion

3.1. Introduction. Before proposing a detailed mechanism for the coil overlap process, it is necessary, in view of the high polarity of DMSO, to confirm that the two polymer chains are, indeed, held together by electrostatic interactions. The subsequent sections will explore this aspect in detail. The first section describes the experiments performed in order to confirm the electrostatic nature of the interactions. These experiments involve the addition of microelectrolytes to the equimolar equilibrated blends (EQB). The second section describes an investigation of the effect of water content in the polymer solutions. Finally, in the last three sections, a discussion is given of the effects of varying the molecular weight of the PS–SSA chain, the SSA and 4VP contents, and the temperature.

3.2. Electrolyte Effect. As was mentioned earlier, if the electrostatic interactions have a major role in the process, the presence of small quantities of microelectrolytes should disrupt the ion pairing between the 4VP and the SSA moieties, while large quantities should lead to the complete disappearance of the shielded methoxy signal. This seems reasonable in view of the fact that microanions from the added electrolytes can now be paired with the pyridinium cations, and microcations with the sulfonate anions, thus eliminating the driving force which keeps the two polymer chains close to one another. To test this, varying small amounts of 0.5 N H_2SO_4 in DMSO-d_6 were added to an equimolar equilibrated blend (EQB), i.e., a polymer solution that had previously reached the equilibrium state. This EQB contained a total of 10 mg of PMMA–4VP, 11 mol % (MW $\simeq 10^5$), and PS–SSA, 10 mol % (MW = 10^5), in 0.5 mL of DMSO-d_6 at 85 °C. The solution was thus 0.1 M in each of the repeat units. The spectra were followed for 1 h.

As can be seen in Figure 2, after the first addition of 0.001 mL of the H_2SO_4 solution to the EQB (1 H^+ cation to 10 SO_3^- anions), no significant deshielding was observed. This was ascertained by the comparison of the X_e/a_0 values of the starting EQB (=0.95) with the one calculated for this mixture (=0.93). After the second addition of 0.001 mL, i.e., 2 H^+ cations to 10 SO_3^- anions, partial deshielding was observed (X_e/a_0 = 0.31). The deshielding process is rapid and the intensity of the shielded methoxy signal does not change with time after the first spectrum is obtained. After the third addition of 0.002 mL, i.e., a total of 4 H^+ cations to 10 SO_3^- anions, deshielding is almost complete (X_e/a_0 = 0.18). For a ratio of 8 H^+ cations to 10 SO_3^- anions, complete deshielding is observed (X_e/a_0 = 0.15). Thus, it is clear that addition of sulfuric acid can cause deshielding, even at low concentrations. The presence of trace quantities (<10% of the stoichiometric amount), however, will not weaken the electrostatic interaction between the SSA and 4VP moieties. It is noteworthy that 20% of the amount required for ion pairing is already enough to produce mostly deshielded methoxy groups. This does not mean, however, that the dissimilar chains are far apart. The only requirement is that the methoxy groups from the PMMA and the aromatic rings from the PS–SSA be at distances greater than 5 Å. Apparently, two H^+ per SO_3^- anion is enough to bring it to about 70% of the original unshielded methoxy group signal. However, when we reach a ratio of 8 H^+/10 SO_3^-, the chains seem to be far apart, since the original methoxy group signal is fully restored.

The deshielding experiment was repeated with other electrolytes such as NaOH or *p*-toluenesulfonic acid. Small quantities of solutions (0.1 M) of each electrolyte were added to the EQB, and as in the case of the sulfuric acid experiment, deshielding was again observed at similar concentrations, confirming that electrolytes can induce deshielding. These experiments clearly show that the electrostatic interaction between the pyridinium cation and the styrenesulfonate anion is necessary in order to observe the signal from the shielded methoxy groups, and that the electrostatic interactions are the primary step of the global coil overlap process.

3.3. Water Content. The second parameter to be explored is the presence of water. In the absence of polymer, it can be assumed that water, in small quantities, would be uniformly distributed throughout the DMSO. After polymer addition, it is likely that some of the water would concentrate in the vicinity of the ionic groups, and since water tends to solvate the ion pairs, an increased amount of water might be able to weaken the electrostatic interactions, resulting in an increased separation between the polymer chains. If this is the case, the intensity of the shielded methoxy signal should decrease, and furthermore, for freshly prepared mixtures, the shielding process should be slower with increasing water content. Thus, if the above considerations are correct, deshielding would be expected on addition of water to an EQB.

However, one should also keep in mind that the strength of the interaction between water and DMSO is high (ΔH_{hyd}(RSO_3^-/1000 H_2O) = 620 kJ/mol vs ΔH_{mix}(DMSO/1000 H_2O) = 350 kJ/mol),[20] and that a partition of the water will occur, since there is a competition between DMSO and the ions for the water. Moreover, since DMSO is present in much greater quantity than the ions, the total number of water molecules interacting with each ion pair might be small, even if the overall number of H_2O molecules per ion pair is large. Therefore, even if the interchain interaction is completely electrostatic, small quantities of H_2O may not lead to any observable deshielding.

Since it is known that the addition of even trace quantities of water produces a very intense NMR signal compared to that due to the polymer, D_2O was used instead. Chemically, the effect will be the same, but from the NMR point of view, one will detect only a very weak proton signal because of the small amount of H_2O in the D_2O. The experiments involved an EQB of PS–SSA, 10 mol %,

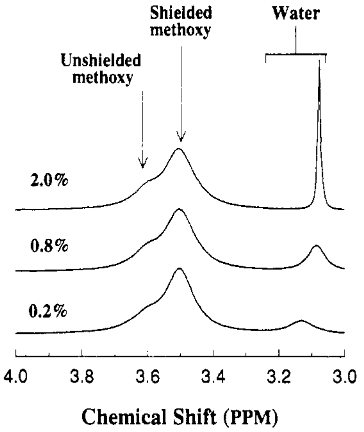

Figure 3. Spectra obtained after the addition of D_2O to the equilibrated polymer solution: elapsed time 1.5 h at $T = 85$ °C. The percentage figures refer to (volume of D_2O)/(volume of DMSO-d_6) × 100.

and PMMA–4VP, 11 mol %, in DMSO-d_6 at 85 °C. The samples, to which 0.001, 0.01, or 0.04 mL (0.2, 0.8, and 2% v/v or 10, 100, and 400 D_2O molecules/ion pair) of D_2O were added at $t = 0$, were allowed to reach equilibrium ($\simeq$100 min).

For the three blends, it was empirically observed that steady-state values of the intensity for the shielded methoxy signal were obtained in about 1 h, after which the signal remained constant. Figure 3 shows the EQB spectrum for the three shielding experiments. One can see three major peaks which are, respectively, the unshielded methoxy signal ($\simeq$3.6 ppm), the shielded methoxy signal ($\simeq$3.5 ppm), and the water peak (3.2–3.0 ppm region). This figure shows that shielding has occurred even in the presence of water. Further addition of D_2O (up to 5% v/v) to the previous EQB (not shown) did not induce deshielding. Additional confirmation was obtained from the determination of the X_e/a_0 ratio for these blends (0.81 ± 0.01), which was found to be identical within experimental error. From these results, one can conclude that the presence of small quantities of water in the solvent or the polymers does not weaken the electrostatic interaction. Furthermore, since the time required to reach the equilibrium concentration of the shielded methoxy (X_e) is independent of the water content, one can conclude that water does not have a major influence on the overall coil overlap process. This suggests that most of the water interacts with the DMSO.

3.4. Molecular Weight Ratio. Before describing in detail the molecular weight ratio effects, it should be recalled that even in presence of strong electrostatic interactions, aromatic shielding may not always be observed. A hypothetical example of such a situation would be the interaction between PS–SSA and a PMMA chain containing only one VP as the terminal group. After complete proton transfer, the pyridinium ion will be in proximity of the sulfonate ion. However, there would be no driving force for the rest of the PMMA chain to be close to the PS. Under those circumstances, no aromatic shielding should be expected.

To study the effects of the molecular weight on aromatic shielding, blends containing PS–SSA with MWs of 2.0×10^3, 4.2×10^3, 9.6×10^3, 1.2×10^4, and 1.0×10^5 with PMMA–4VP, 11 mol %, of MW $\simeq 10^5$ were investigated at 85 °C. Triplicate samples of the blend compositions listed in Table 2 were monitored for more than 1 h. The SSA/VP ratios ranged from 1.0 to 2.3; for each series, a near-stoichiometric sample was included. The meanings of Γ and ΔΓ were explained earlier.

Two observations can be made for the blends containing a PS–SSA chain with a MW ≥ 9.6×10^3, i.e., samples C, D, and E. First, a shielded methoxy group signal is observable for all three blends. Second, the shielded methoxy concentration at equilibrium (X_e) increases with increasing MW (see X_e/a_0 values in Table 2). Clearly, electrostatic interactions are present in these blends.

The decrease of X_e in parallel with the decrease in the MW of the PS–SSA chains can be attributed to two possible factors. First, the lower the MW of the PS–SSA chain, the larger the entropic penalty per mole of repeat unit for localizing it near the PMMA chain. For the very short chains (samples A and B) the total number of functional groups is also small. Therefore, the lower the MW of one of the segments, the greater is the thermodynamic penalty for localization. This factor must be kept in mind, since it may lead to a certain amount of dissociation of the chain even in the presence of proton transfer. For very high molecular weight chains, the entropic penalty becomes relatively small compared to the enthalpy payback. Second, it should be noted that, as the MW of the PS–SSA decreases, the mismatch in length between the dissimilar chains becomes more severe. Compared to blends in which the MW is similar ($\simeq 10^5$), the mismatch in length in the low MW blends leads to the reduction of the X_e value, since, at steady state, more defects (loops and/or dangling ends) will be present in the ladder-like complex. It should be noted that these two factors are interrelated and cannot be evaluated independently. Thus, the greater the mismatch between the chains, the lower the X_e value will be, since both factors contribute to its decrease.

For blends containing low MW PS–SSA chains (≤4.2×10^3), no shielding methoxy peak was observed experimentally. As mentioned in section 2, a convenient way to determine whether aromatic shielding is present in the low MW blends is to compare the width at half-height (Γ) of the main methoxy peak signal ($\simeq$3.6 ppm) for the homopolymer of PMMA–4VP at 85 °C with that obtained for the blend. If some shielding is present, one can expect a greater Γ value. The Γ value for the main peak due to the methoxy group of the homopolymer is 0.025 ± 0.001 ppm. Subtraction of this value from the Γ value of the main blend peak yields ΔΓ, which is a qualitative indication of the presence of aromatic shielding. Table 2 also gives the Γ and the ΔΓ values for the blends of the low MW PS–SSA samples, which were equilibrated for more than 3 h. From these ΔΓ values, one can see that some shielding is present in all these blends, which implies that proton transfer occurred at least to a certain extent, and that the electrostatic interaction is still present.

In the blends involving PS–SSA of MW = 2.0×10^3 with a 25% degree of sulfonation (A1 and A2), very little aromatic shielding is present. This is not surprising because the separation of the ionic groups is, on the average, 3 repeat units, while on the MMA chain that separation is 10 units. The contour mismatch is therefore severe, and the nonionic components of the chains would not be expected to be close to one another.

In the PS–SSA of MW = 4.2×10^3 system, the shielding effect is reasonably good for the B1 samples, in which the SSA and 4VP groups are present in approximately stoichiometric amounts, and in which the distances between ions are almost equal (no contour mismatch). In spite of this, the shielding in that sample is not nearly as high as in samples of comparable MW, because of the presence of a considerable amount of dangling PS chain material near the chain ends, i.e., not connected to two

Table 2. Effects of the Molecular Weights on the Shielded Methoxy Group Signals for Various Blends

	blend composition									
	PS-SSA			PMMA-4VP						
label	MW	ion content (mol %)	weight (mg)	MW	ion content (mol %)	weight (mg)	SSA/VP	Γ (ppm)	ΔΓ (ppm)	X_e/a_0
A1	2.0×10^3	25	2.2	$\simeq 10^5$	11	5.0	1.0	0.027	0.002	
A2	2.0×10^3	25	5.0	$\simeq 10^5$	11	5.0	2.3	0.030	0.005	
B1	4.2×10^3	10	5.1	$\simeq 10^5$	11	5.0	1.0	0.038	0.013	
B2	4.2×10^3	15	3.7	$\simeq 10^5$	11	5.0	1.0	0.032	0.007	
B3	4.2×10^3	15	5.0	$\simeq 10^5$	11	5.0	1.4	0.039	0.014	
B4	4.2×10^3	20	2.8	$\simeq 10^5$	11	5.0	1.0	0.031	0.006	
B5	4.2×10^3	20	5.0	$\simeq 10^5$	11	5.0	1.8	0.037	0.012	
C[a]	9.6×10^3	16	5.0	$\simeq 10^5$	11	5.0	1.4			0.58
D[a]	1.2×10^4	11	5.0	$\simeq 10^5$	11	5.0	1.0			0.75
E[a]	1.0×10^5	10	5.1	$\simeq 10^5$	11	5.0	1.0			0.88

[a] Indicates that a shielded methoxy peak is present.

Table 3. Effects of the Ion Content on the Shielded Methoxy Group Signals for Various Blends

	blend composition									
	PS-SSA			PMMA-4VP						
label	MW	ion content (mol %)	weight (mg)	MW	ion content (mol %)	weight (mg)	SSA/VP	Γ (ppm)	ΔΓ (ppm)	X_e/a_0
F1	1.0×10^5	10	3.2	$\simeq 10^5$	5	6.8	1.0	0.030	0.005	
F2	1.0×10^5	10	5.0	$\simeq 10^5$	5	5.0	2.0	0.032	0.007	
G1	1.0×10^5	10	4.3	$\simeq 10^5$	7	5.8	1.0	0.032	0.007	
G2	1.0×10^5	10	5.0	$\simeq 10^5$	7	5.0	1.4	0.035	0.010	
H1[a]	1.2×10^4	5.3	5.0	$\simeq 10^5$	11	5.0	0.5			0.33
H2[a]	1.2×10^4	8.6	5.0	$\simeq 10^5$	11	5.0	0.8			0.52
H3[a]	1.2×10^4	11	5.0	$\simeq 10^5$	11	5.0	1.0			0.75
I1[a]	1.0×10^5	7.7	5.0	$\simeq 10^5$	11	5.0	0.7			0.67
I2[a]	1.0×10^5	10	5.1	$\simeq 10^5$	11	5.0	1.0			0.88
I3[a]	1.0×10^5	15	5.0	$\simeq 10^5$	11	5.0	1.4			0.96

[a] Indicates that a shielded methoxy peak is present.

ionic groups. Any styrene involved in interchain bridging would also not be expected to contribute to aromatic shielding. As we increase the ion content from 10 to 15%, keeping the ion ratio constant at 1.0 (B1 to B2), aromatic shielding decreases due to increased contour mismatch. If we now increase the total quantity of styrene, so as to achieve stoichiometry in repeat units (B3), aromatic shielding increases, as would be expected. While we do not have pendant ion stoichiometry, we do have a match that leads to a level of aromatic shielding comparable to that for B1. As the ionic concentration reaches 20% (B4), overlap is again poor for the blend in which pendant ion stoichiometry is present; it improves again for the blend B5 which is stoichiometric in total repeat units. The ΔΓ value for these samples, containing a low MW PS-SSA, clearly shows that a certain quantity of aromatic shielding is present.

It appears that the greatest degree of shielding is achieved if both contour match and pendant ion stoichiometry are present (as in B1). However, if a series contour mismatch is present, pendant ion stoichiometry is not sufficient to yield a fair amount of shielded methoxy groups (see sample B1 vs B2 or B1 vs B4). Hence, for the sample with a serious contour mismatch, the situation can be improved by adding excess material of short ion spacing (samples B2 vs B3 and B4 vs B5).

3.5. SSA and 4VP Contents. The effects of the ion content on the aromatic shielding were studied for a range of copolymer blends containing 5–11 mol % 4VP and 5.3–15 mol % SSA in DMSO-d_6 at 85 °C. Duplicate samples of the blend compositions listed in Table 3 were monitored for more than 1 h. The SSA/VP ratios ranged from 0.7 to 2.0; for each species, a near-stoichiometric sample was included. It should be noted that, for all the samples, except for series H, no mismatch in total chain length is present, since both dissimilar chains have similar MWs ($\simeq 10^5$). Therefore, for samples F, G, and I used in this part of the study, factors other than contour length are required to rationalize any variation in the X_e values.

For blend series H and I (PS-SSA of 5.3-15 mol %, with PMMA-4VP of 11 mol %) two observations can be made. First, a shielded methoxy peak is present for all these mixtures. Second, the X_e value associated with the shielded methoxy peak increases with increasing SSA content. For the six samples of these series, the extent of overlap is good. However, the highest X_e value is achieved when an excess of SSA groups is present (sample I3). Moreover, at equivalent contour lengths, the X_e values observed for samples H are systematically lower than those for the I series. Evidently, as was pointed out in section 3.4, this is due to the mismatch in total length that exists for the H samples.

For blends with a PMMA-4VP ion content of less than 11 mol %, i.e., 5 and 7 mol % (samples F and G in Table 3), no resolvable shielded methoxy peak was observed. As was mentioned earlier, the absence of the shielded peak does not imply the absence of proton transfer or electrostatic interactions. Using the procedure described in section 3.4, the presence of the shielding effect was evaluated from the Γ and ΔΓ values. These two parameters are also included in Table 3.

The blends of series F and G will be treated together, since they exhibit the same behavior (trend). For these blends, very little aromatic shielding is present. As mentioned earlier, for blends which are stoichiometric in ion pendant groups, a closer match in contour length yields the highest X_e values, and this is, indeed, the case here (sample G1 vs F1). Moreover, as for the blends of series I, an excess of SSA pendant groups leads to the observation of higher X_e values (F2 vs F1 and G2 vs G1).

The fact that no shielding peak is present for sample F is not surprising, since the contour length mismatch is too severe to obtain a good overlap between the two chains, i.e., an average number of 20 segments between ionic sites for the PMMA chain vs 10 for the PS–SSA chain. However, for the G samples, the discrepancy in contour length (13 vs 10 segments for the PS–SSA chain) is not severe. Hence, the MW and the contour length mismatch for the G samples is quite mild compared to other mixtures in which a shielded methoxy peak is present (samples H1 and H2). This suggests the 4VP content of the PMMA chain has a strong influence on the formation of the ladder-like complex, and that a minimum quantity of 4VP units must be present to observe a shielded methoxy peak. This is reasonable, since after proton transfer, but before the ladder formation, the higher the 4VP content, the more severe the repulsion between the pyridinium cation in the coil will be. This repulsion will lead to the opening up of some regions of the PMMA–4VP coil.[21] These regions could then act as seeds which will favor the formation of a ladder-like complex. Thus, the mismatch in counter length is an important factor in order to obtain an optimal shielding effect. However, in order to observe the spatial reorganization between the two chains, it seems that a threshold number of 4VP groups must be present on the PMMA chain (≃11 mol %).

3.6. Temperature Effect and Reshielding at 80 °C for a Blend Equilibrated at 150 °C. Temperature can have two possible effects. On one hand, it favors molecular motion, and therefore would tend to increase the rate of the coil overlap process. However, an increase in temperature effectively decreases the importance of the Coulombic interactions between the ions, and therewith also the driving force for the mixing process relative to kT. For this reason, it is necessary to explore the temperature dependence of the shielding process, since we cannot predict the relative importance of these two effects.

For an equimolar mixture (0.10 M) containing PS–SSA, 10 mol % (MW = 10^5), with PMMA–4VP, 11 mol %, the first observation made at elevated temperature relates to deshielding. It was found that, for mixtures which were allowed to equilibrate at 85 °C, an increase in temperature to about 100 °C caused the size of the shielded methoxy peak to decrease. This shows that at 100 °C the thermal motion is sufficient to disrupt the shielding process partly. For temperatures higher than 100 °C, the deshielding rates increase monotonously with temperature. However, while complete deshielding could be achieved, this process is quite slow, taking more than 1 h at the highest temperature (150 °C).

Moreover, after deshielding, the mean $\Delta\Gamma$ value for the unshielded methoxy peak was not equal to 0, but to 0.005 ± 0.001 ppm. This result confirms that high temperatures effectively reduce the relative importance of the Coulombic interactions, but do not completely eliminate them.

Two extreme cases can be envisaged to rationalize the presence of the interactions at high temperatures (>100 °C). First, the two dissimilar chains could be far from one another; however, due to random collisions between the coils, interactions are present. Second, the chains could still be close to one another, forming a ladder-like complex, but with mean distances greater than 5 Å. In the first case, it is clear that the mechanism for the coil overlap process on cooling of the mixture will be quite similar to a standard shielding experiment; i.e., a similar time to reach the X_e value will be observed. By contrast, for the second case, since the chains are already involved in a complex, the shielding process will be independent of the concentration of the reactants (order zero) and the X_e value will be reached more rapidly than in the previous case.

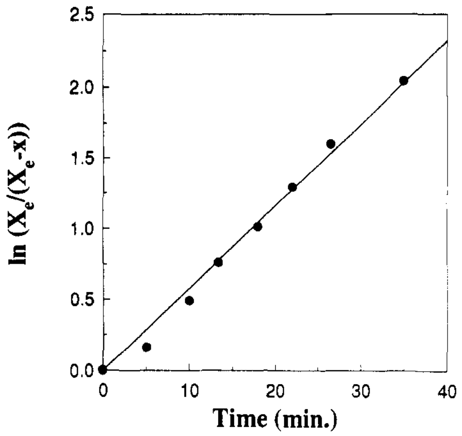

Figure 4. $\ln(X_e/(X_e-X))$ vs time for an EQB (0.10 M) containing PMMA–4VP, 11 mol % (MW ≃ 10^5), with PS–SSA, 10 mol % (MW ≃ 10^5), at 80 °C after equilibration at 150 °C.

In order to ascertain the origin of the interactions, the following experiment was performed in triplicate: ^{1}H NMR spectra of the previous mixture were acquired, using equimolar blends (0.10 M) containing PMMA–4VP, 11 mol % (MW ≃ 10^5), with PS–SSA, 10 mol % (MW = 10^5). The ^{1}H NMR spectra were observed at 80 °C until the X_e was reached (≃90 min). These blends were then removed from the NMR probe, and placed in a thermostated bath for 3 more h at 80 °C (EQB). These EQBs were then monitored at 150 °C until complete deshielding was obtained. The NMR probe temperature was then set back to 80 °C, followed immediately by the acquisition of spectra.

Experimentally, it was observed that the X_e concentration is reached in ≃45 min, i.e., half the time required for a standard shielding experiment at 80 °C. This qualitative observation implies that the coils are not far from one another.

In order to ascertain that the order of this process is zero, one can plot $\ln(X_e/(X_e-X))$ vs time, where X_e is the equilibrium concentration of the shielded methoxy groups and X the concentration of the shielded methoxy groups at a given time.[22] Both concentrations (X and X_e) were calculated using a correction factor that accounts for the "pure" PMMA–4VP line shape (discussed in a subsequent paper). Figure 4, which is an example of these plots, shows that a good correlation (0.996) can be obtained for a zero-order plot.

Thus, one may conclude that, even at 150 °C, the two dissimilar chains are close to one another. Furthermore, the zero-order process observed for the reshielding experiments at 80 °C indicates that the two dissimilar chains are still in a ladder-like complex.

4. Conclusion

In this paper, it was confirmed that the electrostatic interaction is responsible for the interchain attraction, since electrolyte concentrations of the order of the polymer ion content in solution could completely disrupt the interaction. Trace quantities of electrolytes did not affect the electrostatic interaction. It was also shown that the water content of the DMSO-d_6 solutions did not have a significant effect on the Coulombic interaction and the overall shielding process. Therefore, it can be concluded that the water molecules interact mostly with the DMSO.

Experiments were also performed to explore the influence of the SSA MW, as well as the SSA and 4VP contents on the shielding effect. It was observed that the value for the equilibrium concentration of the shielded methoxy groups (X_e) was sensitive to mismatch in the contour length between the two dissimilar polymer chains. With increasing total chain length mismatch or contour length mismatch, one observes a decreasing X_e value. For mixtures in which the mismatch is severe, the X_e value is reduced to the point where no resolvable shielded methoxy peak can be observed. The results also suggest that a threshold number of 4VP groups must be present on the PMMA chain ($\simeq$11 mol %) in order to induce the spatial reorganization between the two chains.

Deshielding was observed for temperatures above 100 °C, and this process was found to be fully reversible upon cooling. Reshielding experiments on EQB at 80 °C confirmed that high temperatures induced deshielding due to the slight pulling apart of the two dissimilar polymer chains, with the electrostatic interactions still present even in the absence of a resolvable shielded methoxy peak. Therefore, reshielding is a zero-order process.

The global mechanism of the coil overlap process still needs to be established. The detailed kinetics of the process will be investigated in greater detail in the second paper in this series.

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