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Nuclear Magnetic Resonance Studies of Ionomers. 1. Interactions between Poly(methyl methacrylate-*co*-4-vinylpyridine) and Poly(styrene-*co*-styrenesulfonic acid) in Dimethyl Sulfoxide Solution

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ABSTRACT: Poly(methyl methacrylate (MMA)) and poly(styrene (S)) form immiscible blends. However, copolymers of MMA with 4-vinylpyridine (4VP) are miscible with sulfonated poly(S) because of proton transfer and the resulting ionic interaction. Both the proton transfer from the styrenesulfonic acid (SSA) group to the 4VP ring and the alignment of the chains that results from ion pair formation can be followed by NMR spectroscopy in dimethyl sulfoxide solutions at 85 °C. The proton transfer takes place very quickly. The process of coil overlap is demonstrated by the upfield shift of all poly(MMA-*co*-4VP) signals induced by the aromatic shielding effect of the poly(S-*co*-SSA) units. For a comonomer content of 11 mol %, the process is completed in ca. 2 h. One- and two-dimensional NOE-correlated spectra demonstrate the presence of dipolar coupling through space between the methoxy protons of poly(MMA-*co*-4VP) and the aromatic protons of poly(S-*co*-SSA). This indicates an interchain distance of about 4 Å.

Introduction

The study of miscibility in polymers depends on the utilization of probes that are sensitive to regions of different size. One popular technique, light scattering, probes dimensions of the order of the wavelength of light. If the refractive index of the homopolymer components of the blend is different and the blends are transparent, this is an indication that homogeneity is present down to a level of approximately 1000 Å.

The glass transition temperature is another way of probing polymer miscibility. Immiscible blends usually display two glass transition temperatures, while miscible systems show only one transition. Again, the glass transition phenomenon is not sensitive to dimensions much smaller than 100 Å, so that even polymers that show a single glass transition temperature can still show a considerable degree of heterogeneity over dimensions smaller than that.

In some cases, much more specific tools are available for the determination of the miscibility. A recent review[1] presents the use of instrumental methods in the study of polymer blends. Of the spectroscopic methods, FTIR studies have been utilized to probe the environment of a particular species by monitoring its absorption when it is surrounded by molecules of its own type or by the other material. NMR spectroscopy is still another method. Short-range interactions are studied by measuring the different relaxation times. Carbon chemical shifts of low molecular weight model compounds can also prove intermolecular interactions.[2] Solid-state spin diffusion pulse sequences offer an insight at a level of a few angstroms.[3]

The presence of aromatic groups is known to influence the chemical shift of protons in solution. This factor will be utilized in the present study to explore the miscibility of two polymers, the miscibility of which can be varied by the presence of ionic interactions.

Miscibility enhancement in a wide range of polymer pairs can be achieved by introducing appropriate ionic groups onto each polymer chain. A series of papers on ionomeric blends presented some examples of miscibility enhancement.[4–9] The first example[4] dealt with the immiscible pair poly(styrene) [poly(S)] and poly(ethyl acrylate). When a copolymer of ethyl acrylate with 4-vinylpyridine was mixed with a lightly sulfonated poly(S), the proton from the styrenesulfonic acid unit was transferred to the pyridine ring, forming an ion pair, which rendered this polymer pair miscible.

It is straightforward that the ratio of interacting groups has to be equimolar in order to obtain maximum interaction. Previous studies on diffferent polymer pairs suggest that a minimum of ca. 4 mol % of interacting groups was necessary in order to achieve miscibility in two polymer pairs,[5,10] i.e., to obtain a single glass transition temperature for the blend. The criterion for miscibility was the glass transition temperature measured by dynamic mechanical studies. This and similar methods were applied to improve miscibility of several polymer pairs.[4–9] One of the systems that can be rendered miscible is the mixture of poly(methyl methacrylate) [poly(MMA)] with poly(S). Methyl methacrylate and styrene copolymerize very easily, forming copolymers over the whole range of compositions. However, mixing poly(MMA) and poly(S) generates an incompatible blend.[11] No dynamic mechanical or DSC studies were performed on this system because the glass transition temperatures of the two components are too close. This applies also to copolymers. For example, poly(MMA-*co*-4VP) has a T_g of 126 °C (in the range 2–11% 4VP); when it is quaternized with methyl iodide, its T_g depends on the ion content (130 °C for 2% 4VP to 150 °C for 11% 4VP).[12] Poly(S-*co*-SSA) has a T_g that depends on the SSA content and on the degree of ionization (sodium salt); the T_g values are very close to those found for poly(MMA-*co*-4VP).[13] Therefore, the only proof that the mixture of poly(MMA-*co*-4VP) with poly(S-*co*-SSA) is compatible is obtained by analyzing the transparency of the film formed by the mixture, as will be described in the Experimental Section. It should be recalled, however, that this method probes homogeneity only above ca. 1000 Å. Scheme I presents the reaction of ion formation when the two polymers are mixed.

This paper will analyze the interactions that take place between poly(MMA-*co*-4VP) and poly(S-*co*-SSA) in dimethyl sulfoxide (Me_2SO) solution by ^1H NMR spectroscopy. It is the first paper of a series that will utilize extensively NMR spectroscopy to answer some unresolved structural problems of ionomers and ionomer blends. The first system to be analyzed was chosen, despite the lack of dynamic mechanical measurements, because the meth-

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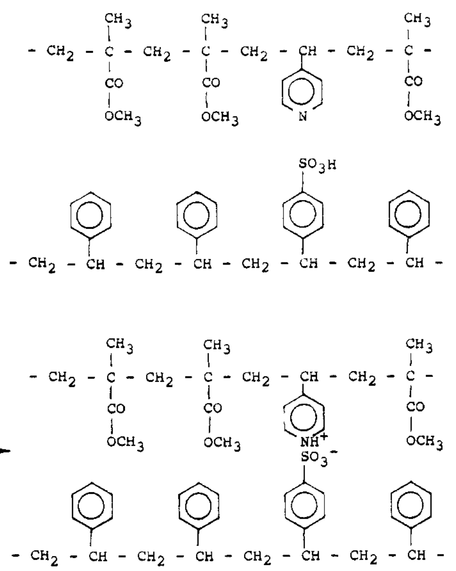
Scheme I



oxy protons of the MMA units are known to be very sensitive to the presence of aromatic rings (in this case S units on the other polymer chain). In a copolymer of MMA with S, the methoxy signal is split into three parts that can be roughly assigned to nonshielded OCH$_3$ groups, those that are shielded by one aromatic ring, and those that are shielded by two aromatic rings. This assignment was made by Ito and Yamashita[14] as early as 1965 and enabled the authors to determine the probability of coisotactic addition, i.e., the probability that a methoxy group and an aromatic ring will be on the same side of the main chain. In poly(MMA-*co*-S) the shielding of one aromatic ring shifts the methoxy signal upfield by ca. 0.5 ppm. However, if methyl acrylate is copolymerized with S, the shielding of a methoxy group by one aromatic ring is much lower (ca. 0.15 ppm) for the same configuration.[15] This was explained by differences in conformational probabilities.[16]

The precise assignment of the methoxy peak in poly(MMA-*co*-S) is still under discussion. More remote units seem to have an influence on the chemical shift of the central methoxy group, and different pentad assignments have been proposed.[17] However, it is clear that the main shielding effect arises from the influence of a near-neighboring aromatic ring. A recent paper[18] proves this with the help of two-dimensional NOE-correlated spectra.

The concepts presented above were the starting point of our work. If the methoxy protons are so sensitive to aromatic shielding, then in a compatibilized mixture, where poly(MMA) and poly(S) are forced to stay close to each other by Coulombic interactions, there might be an influence of the aromatic rings of poly(S) on the methoxy protons of poly(MMA). In addition, the nuclear Overhauser effect can be useful to confirm the existence of intermolecular interactions.

Experimental Section

Copolymers of methyl methacrylate with 4-vinylpyridine were synthesized as part of another project[12] by radical bulk copolymerization. Samples containing 1.8, 4.7, 7.3, and 11.1 mol % 4VP were used in the present study. Polystyrene was partly sulfonated to different levels of styrenesulfonic acid units also as part of another project.[10]

Mixtures of poly(MMA-*co*-4VP) with poly(S-*co*-SSA) were prepared by mixing 1% chloroform solutions of the two components. The amounts of polymer dissolved were calculated to correspond to molar equivalents of the interacting groups (4VP and SSA). Even at low interacting group contents (1.8%), mixing of the two solutions produced immediate precipitation. The precipitate was lighter than the solvent and floated freely. The mixtures were left at room temperature until complete evaporation of the solvent. A corresponding mixture of poly(MMA) with poly(S) did not produce any precipitate, but the film obtained by slow solvent evaporation was completely opaque. All other films (even at 1.8% interacting groups) were transparent, indicating homogeneity at the level of the wavelength of the visible light. NMR spectra were registered in Me$_2$SO solution at 85 °C. Deuteriated Me$_2$SO (Aldrich; 100% deuteriated) was used as received. Mixtures of poly(MMA-*co*-4VP) and poly(S-*co*-SSA) with high 4VP and SSA content, respectively, were not very soluble in Me$_2$SO at room temperature. Mixing the separately prepared solutions of the two polymers produced precipitation. Therefore the blend solution was generally prepared by weighing the two components in the NMR tube to a total amount of 12 mg and subsequently adding 0.5 mL of the solvent. Then the sample was either heated at ca. 90 °C for about 3 h (procedure A) or directly put in the NMR probe at the preset temperature (procedure B). The blends were soluble in Me$_2$SO at high temperatures. However, when the samples were cooled to room temperature, the solutions became cloudy again.

Regular spectra were registered on a Varian XL-300 spectrometer with a pulse width of 6 μs and no delay time between pulses. The acquisition time of ca. 4 s was long enough to ensure relaxation.

Two-dimensional spectra (COSY and NOESY) were obtained by using the Varian software (DQF and NOE2D sequences). DQF provided suppression of intense signals on the diagonal. It consisted of a sequence of three 90° pulses, the first two being separated by an increment delay time (evolution period). The last two pulses had no delay interval between them and were followed by immediate detection. The preparation delay had to be at least 3 times the average proton relaxation time.[19] The NOE2D sequence consisted of the well-known three 90° pulses separated by the evolution period (the first two) and the mixing time (the last two). A preparation delay of 2.5 s was also included. The mixing time was estimated at 0.4 s from T_1 measurements in blend samples.[20] Also, an increment in the mixing time was provided by the software and allowed for the *J*-correlated cross peaks to be spread while the position of NOE or exchange cross peaks was maintained.[19]

To avoid the presence of quadrature image peaks, which appear from the quadrature detection procedure, the spectral window was doubled so as to cover the whole spectrum in its right-side half. Consequently, the two-dimensional spectrum covers only one-quarter of the frequency area swept by the instrument. This procedure was previously reported by other authors[21] and had as a side effect a certain loss of resolution. The maximum capability of the spectrometer is a matrix of 1024 × 1024 points, only 512 × 512 of them being used for the spectrum. A total of 256 increments of 32 transients each were used for the 2D experiments for a total time of ca. 12 h for one 2D spectrum. The preparation interval for the DQF sequence was set at 5 s, and the spectral window was 5423 Hz.

The pulse sequence for measuring NOE on different signals was the one described in the literature.[22] The decoupler frequency was set at 7.0 ppm (for the aromatic meta and para protons of S), at 3.46 ppm (for the shielded methoxy protons of MMA), and at ca. 33 ppm (as a reference). A total of 32 scans were interleaved for each decoupler frequency. The decoupler was on during the initial delay (3 s) and off during the 90° pulse and the acquisition time.

Results and Discussion

Spectra of the two components of the blend and of the blend itself are shown in Figure 1. Poly(MMA-*co*-4VP) (Figure 1a) presents the following signals: Around 1 ppm there are the three α-methyl signals arising from syndiotactic (0.79 ppm), heterotactic (0.96 ppm), and isotactic (1.13 ppm) MMA triads. The shoulder at 0.64 ppm is a result of MMA–4VP sequences. Between 1.2 and 2.1 ppm there are the main-chain proton signals. At 3.0 ppm the peak is assigned to the methoxy protons that experience aromatic shielding from a neighboring 4VP aromatic ring in coisotactic configuration. This signal is partly over-

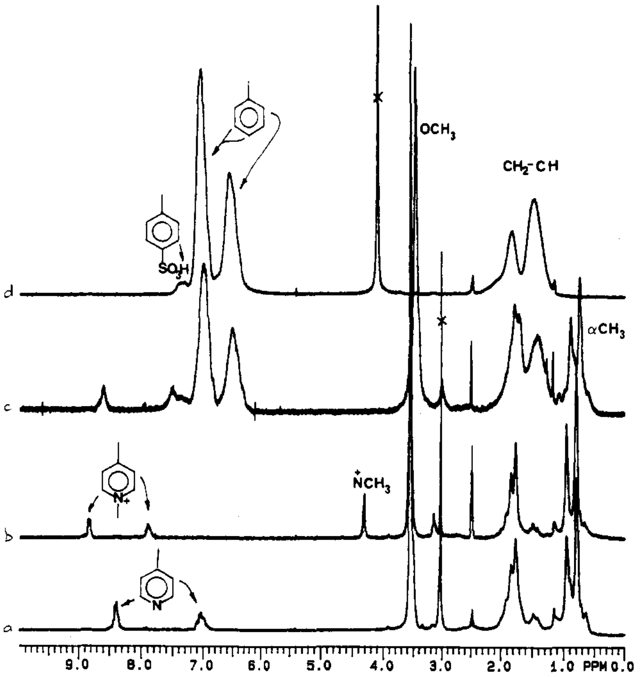


Figure 1. ^{1}H NMR spectra in Me$_2$SO-d_6 at 85 °C of (a) poly(MMA-*co*-4VP) (11 mol % 4VP units), (b) poly(MMA-*co*-4VP) quaternized with methyl iodide (7 mol % 4VP units), (c) a mixture of poly(MMA-*co*-4VP) and poly(S-*co*-SSA) with equivalent numbers of interacting groups (4VP and SSA, respectively; the mixture was prepared by procedure A), and (d) poly(S-*co*-SSA) (10 mol % SSA units). × = traces of water.

lapped in Figure 1a by a signal appearing from the water traces present in the solvent. The assignment of this signal was made in terms of pentads.[23] The main methoxy signal appears at 3.56 ppm and it is assigned to methoxy groups in MMA sequences and to those in cosyndiotactic MMA–4VP sequences. The pyridine resonances are situated at 7.02 ppm (ortho to the main chain) and at 8.38 ppm (ortho to the nitrogen). Detailed analysis in terms of copolymer microstructure, obtained from carbon–hydrogen heteronuclear correlation spectra, will be given elsewhere.[24]

Quaternization of 4VP structural units with methyl iodide produces an ionic copolymer whose spectrum is presented in Figure 1b. The main spectral changes can be noticed in the aromatic region. The two signals are shifted downfield by the appearance of the positive charge on the nitrogen atom to 7.89 and 8.22 ppm, respectively. The shielded methoxy signal is slightly shifted downfield to 3.1 ppm, probably due to a different chain conformation as compared to the nonionic copolymer.[24] A new signal appears at 4.25 ppm due to the methyl group bonded to the pyridinium nitrogen.

The spectrum of poly(S-*co*-SSA), presented in Figure 1d, consists of the main-chain resonances (about 1.4 ppm for the CH$_2$ protons and about 1.7 ppm for the CH protons) and of the aromatic resonances (about 6.5 ppm for the aromatic protons in the ortho position to the main chain, about 7.0 ppm for the aromatic protons of S units in meta and para positions to the main chain, and about 7.5 ppm for the aromatic protons of SSA units in ortho position to the sulfonic acid group).

Figure 1c presents the spectrum of the mixture of poly(MMA-*co*-4VP) (whose spectrum appears in Figure 1a) and poly(S-*co*-SSA) (whose spectrum is presented in Figure 1d). The blend was obtained by procedure A. There are many differences between this spectrum and the sum of spectra a–d in Figure 1. First, the aromatic proton signals of the 4VP units are shifted downfield, indicating the change from pyridine to pyridinium units. The shift is slightly smaller than in the case of pyridinium–methyl iodide; nonetheless, it clearly indicates ionization. From preliminary data,[25] this shift depends on the nature and length of the alkyl group bonded to the positively charged nitrogen; i.e., the longer the chain, the higher the shift downfield. This is consistent with the result presented here, i.e., that the hydrogen transferred from the SSA group shifts the aromatic signal less than the methyl from the methyl iodide. Second, except for all the signals of poly(S-*co*-SSA), the blend signals are shifted slightly upfield. This can be noticed on the α-methyl and both methoxy signals. The main methoxy peak seems split, with a small resonance at 3.56 ppm and a big one at 3.46 ppm. The shielded methoxy protons resonate at 3.0 ppm, as in poly(MMA-*co*-4VP), 0.1 ppm upfield from the ionic copolymer. The α-methyl protons resonate at 0.76 and 0.90 ppm, with the isotactic triad peak too close to the main-chain signal to be clearly identified.

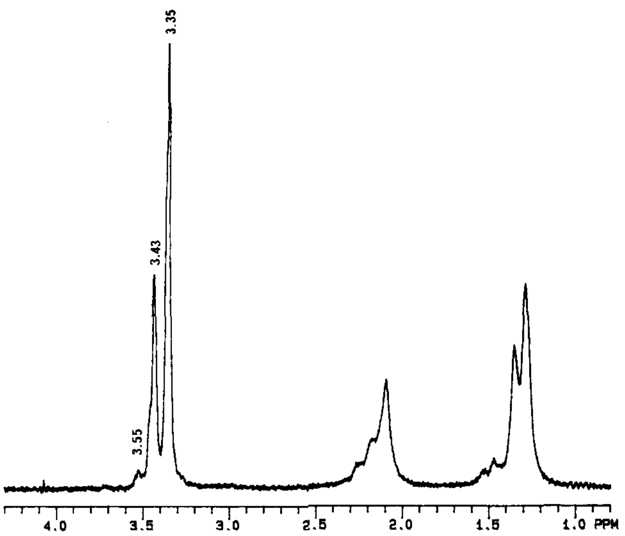


Figure 2. Spectrum of poly(MMA) in benzene-d_6.

The upfield shift of the methoxy protons, in particular, is of special interest. As mentioned before, the methoxy protons are very sensitive to the presence of a neighboring aromatic ring, and it is reasonable to believe that in the ionomer blend the two polymer chains come close together due to the presence of oppositely charged ions. A shielding factor, generated by the presence of the aromatic nuclei of poly(S-*co*-SSA), can be felt by the methoxy groups at distances of ca. 6 Å from the center of the benzene ring.[26] This shielding can be observed not only in the copolymers of MMA with aromatic monomers. The ^{1}H NMR spectrum of poly(MMA) in benzene, or in other aromatic solvents, presents a splitting of the methoxy signal according to the polymer tacticity. This splitting is rarely mentioned[27,28] and almost never used to determine the tacticity. Figure 2 presents the spectrum of poly(MMA) in benzene-d_6. The three methoxy peaks can be assigned to syndiotactic (3.35 ppm), heterotactic (3.43 ppm), and isotactic (3.55 ppm) triads. The highest shielding effect is experienced by the syndiotactic triad, where the methoxy protons are the most separated, allowing the molecules of benzene solvent to come closer. The difference between the two peaks is about 0.1 ppm, corresponding to an average distance of less than 6 Å between the methoxy protons and the solvent molecules.

It is worth mentioning that some other authors analyzed the spectrum of poly(MMA) in chlorobenzene and reported no splitting in the methoxy signal.[29] Their data were taken

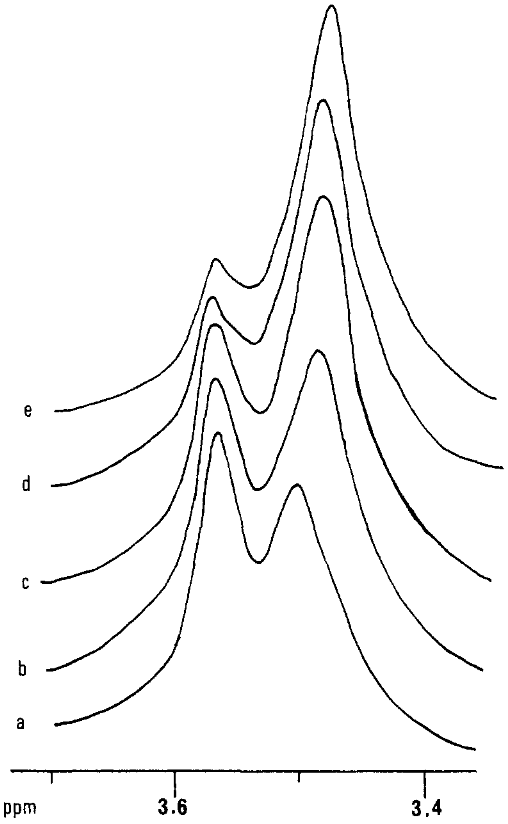


Figure 3. Methoxy signal of the mixture of poly(MMA-*co*-4VP) and poly(S-*co*-SSA) with 11 mol % 4VP and SSA, respectively. The mixture was prepared by procedure B: (a) 11, (b) 27, (c) 40, (d) 53, and (e) 67 min after setting the sample at 85 °C.

from an earlier paper, when the spectrometer resolution was probably rather poor and the splitting was not noticed. Their conclusion was that conformational calculation does not have to take into account the solvent factor, as this factor does not really affect the spectrum.

A more detailed analysis was performed on blends prepared by procedure B. The spectra, taken as a function of time, indicate an ongoing mixing process that starts probably when the two polymers start to dissolve and takes about 2 h at 85 °C. The proton transfer from the SSA groups to the 4VP groups is already finished in the first spectrum, taken at 11 min.

Figure 3 presents the main methoxy signal evolution in time. Initially, the signal at 3.56 ppm is the main one. It represents more than half of the methoxy protons after 11 min at 85 °C. In time, it diminishes, and most of the methoxy protons resonate at higher field (3.46 ppm). After about 2 h the initial unshielded signal is practically gone. Consequently, one can suppose that the proton transfer takes place immediately as the two polymers enter the solution. The proton is solvated by the Me_2SO and is freely transferred to the pyridine. The two kinds of oppositely charged ions are attracted to each other and have the tendency to form ion pairs. This is a slow process, dictated by the conformation of the two polymer chains. Eventually, at a given temperature and ionic group concentration, the system reaches an equilibrium. In the case presented here, the equilibrium is reached when most of the methoxy groups are situated in the neighborhood of the aromatic rings from poly(S-*co*-SSA), i.e., when most of the chains are aligned with each other. This high-field shift can be noticed on most signals of poly(MMA-*co*-4VP). Figure 4 presents this shift for the aromatic protons ortho to the nitrogen from the 4VP unit (a) and for the shielded methoxy signal (b). The same thing happens to the α-methyl signal (Figure 5). The initial signal at 0.84 ppm (syndiotactic) and 0.99 ppm (heterotactic) slowly disappears, and a more shielded signal at 0.76 ppm (syndio-

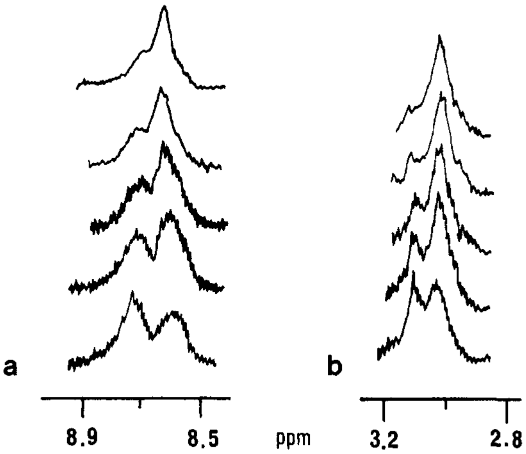


Figure 4. Aromatic protons ortho to the nitrogen (a) and the shielded methoxy signal (b) of the mixture presented in Figure 3 as a function of time. From bottom to top: 11, 27, 40, 53, and 67 min after the sample was set at 85 °C.

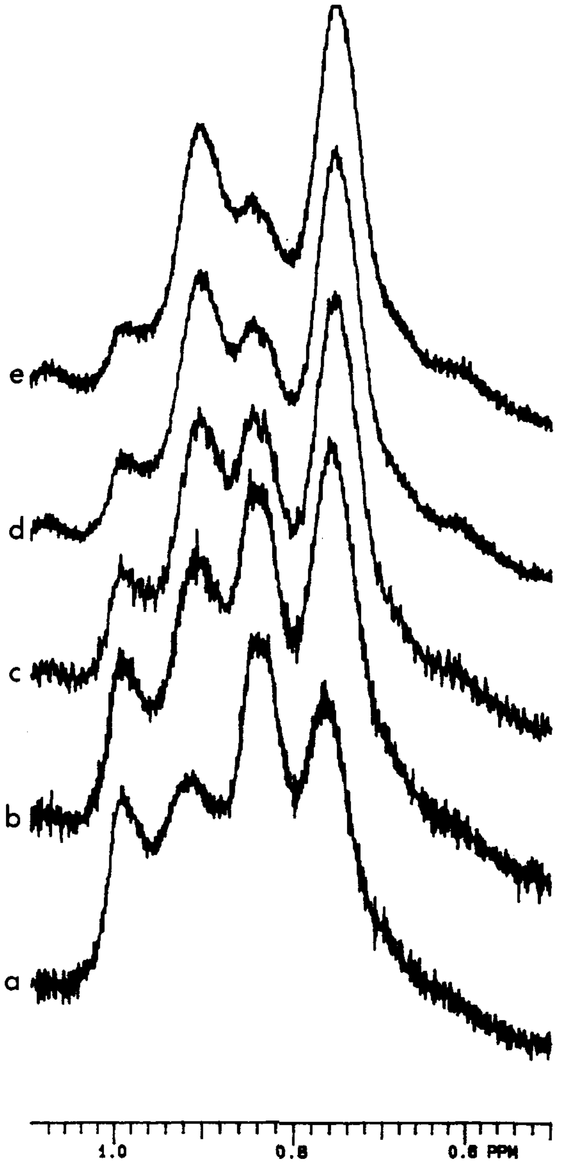


Figure 5. α-Methyl signal of the mixture presented in Figure 3 at (a) 11, (b) 27, (c) 40, (d) 53, and (e) 67 min.

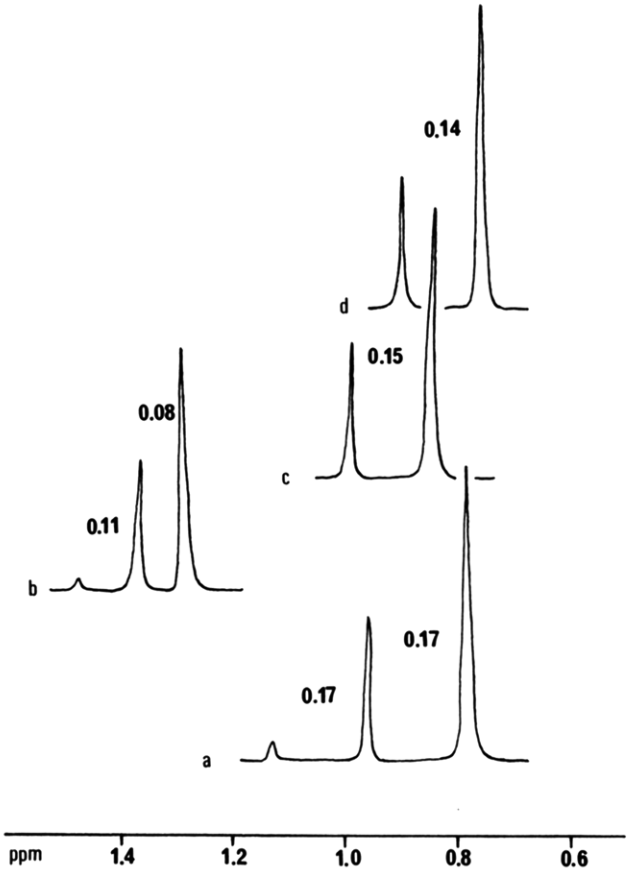


Figure 6. Simplified α-methyl signal of (a) poly(MMA-*co*-4VP) in Me_2SO-d_6, (b) poly(MMA-*co*-4VP) in C_6D_6, (c) the mixture presented in Figure 3 at the initial moment, and (d) the same mixture after ca. 2 h at 85 °C.

tactic) and 0.90 ppm (heterotactic) increases and remains the dominant signal toward the end of the process.

A schematic representation of the α-methyl signal is shown in Figure 6. For reasons of clarity, the signals that appear from MMA–4VP sequences are omitted and the lines are ideally narrow. In Me_2SO (a), the splitting of the α-methyl signal is the highest, and the signal as a whole appears at a higher field than in benzene (b). The splitting in triads is a result of the dipolar influence of the neighboring carboxy groups; hence the position of the signal and the distance between its parts are the result of a combination of conformational *and* solvent factors. For poly(MMA), it was demonstrated that conformational energy calculation using a truncation procedure in order to take into account the solvent influence gives different results depending on the cutoff distance.[30] However, the all-trans conformation is still the most favorable energetically. A picture of a syndiotactic poly(MMA) triad in the all-trans conformation is presented in Figure 7; it can be observed that the α-methyl protons form an "inner" core, less likely to be affected by the solvent or by another polymer than the methoxy protons. Consequently, the upfield shift generated by poly(S-*co*-SSA) in the immediate neighborhood of the poly(MMA-*co*-4VP) chain is similar to the effect of the benzene as solvent (the splitting, which is 0.17 ppm in Me_2SO, shrinks to 0.14 ppm in the mixture at equilibrium, but it is still much higher than in benzene as solvent (0.08 ppm)). However, the chemical shift of the α-methyl signal is very different from that of the pure poly(MMA-*co*-4VP) in benzene. It is not clear at this point why in the initial steps of the mixing process the α-methyl signal is slightly shifted downfield in comparison with that of pure poly(MMA-*co*-4VP) in Me_2SO.

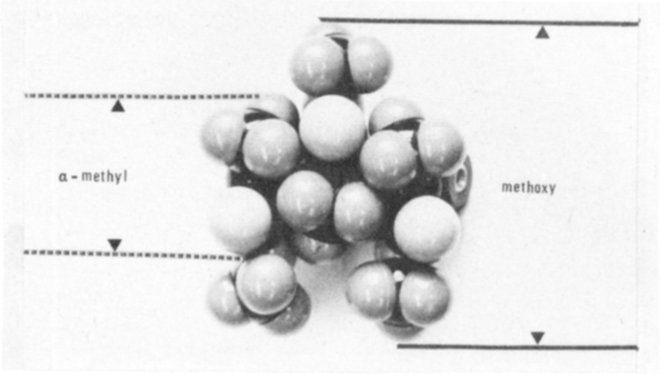


Figure 7. Model of a syndiotactic poly(MMA) triad.

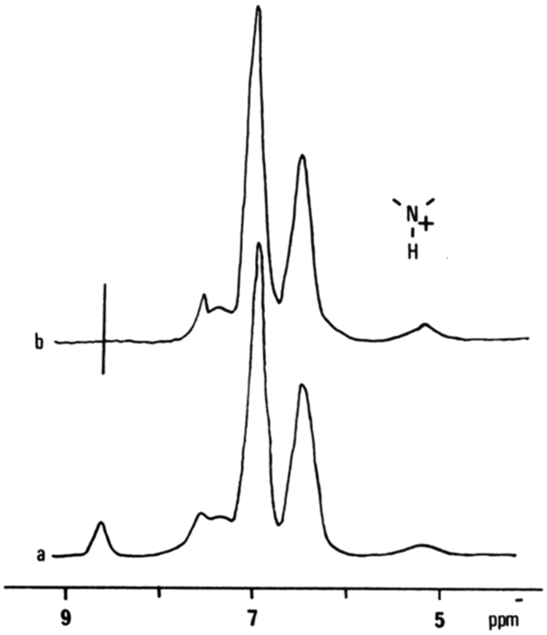


Figure 8. Aromatic part of the spectrum (Me_2SO-d_6, 85 °C) of the mixture presented in Figure 3 after 2 h at 85 °C: (a) without decoupling; (b) decoupling at 8.6 ppm.

A last observation in the spectra of the mixture is the signal of the hydrogen that was transferred from the SSA group to the 4VP. This is not always visible in the spectrum, depending on the quantity of water in the solvent. Being a quasi-labile proton, its position has to depend also on the pH of the solution. Other important factors are the scalar coupling to the CH aromatic protons of the pyridinium ion and the ionic charge on the nitrogen, both of them causing broadening of the signal to the extent that it can be lost in the noise. Figure 8 presents a spectrum of the mixture in equilibrium (after being heated for more than 2 h at 85 °C) without (a) and with (b) decoupling of the aromatic CH protons neighboring the nitrogen. The broad signal at ca. 5.1 ppm narrows when decoupling is applied. Therefore, this is the ^+NH signal.

Another possibility to prove the existence of intermolecular interactions between the two polymer chains is to measure the NOE-correlated two-dimensional spectra of the mixture. The NOESY sequence generates a two-dimensional spectrum that contains the one-dimensional spectrum on the diagonal and nondiagonal peaks that reflect through-space dipole–dipole coupling. If two protons are relatively close together, a cross peak will appear indicating the dipole–dipole interaction between them, even if they are not chemically bonded. As the NOE is proportional to the inverse sixth power of the internuclear distance, it is assumed that NOE-correlated cross peaks

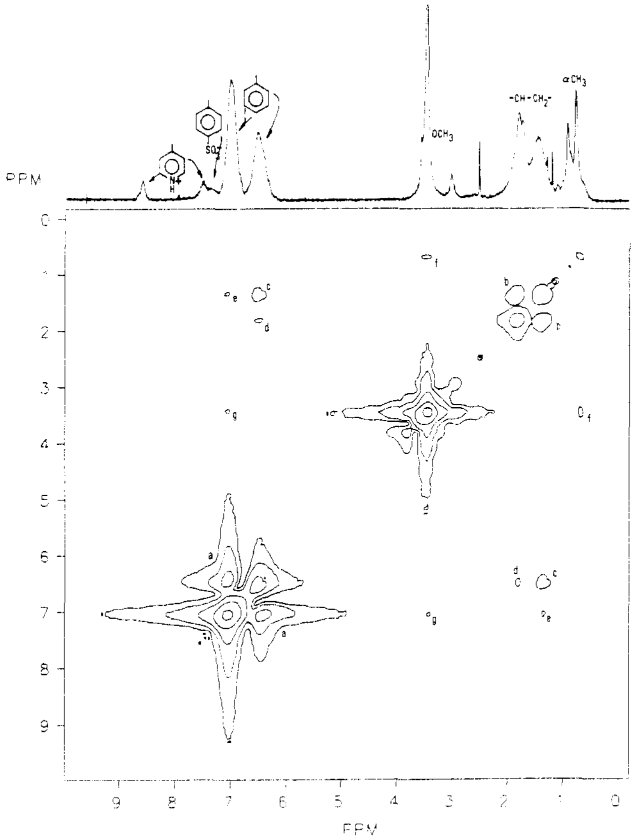


Figure 9. Two-dimensional NOESY spectrum of the mixture presented in Figure 3 taken after 2 h at 85 °C. Details of the procedure are given in the Experimental Section.

do not appear beyond a distance of about 4 Å between the participating protons.[28] The NOE2D sequence offered by Varian[19] claims to average out most of the scalar couplings. However, it is better to use both COSY (which gives only scalar coupling) and NOESY spectra and to concentrate on spectral differences. The COSY spectrum of the mixture prepared according to procedure A presents the expected scalar couplings and therefore will not be shown in this paper. When the spectrum vertical scale is increased in order to detect four-bond couplings,[28] too much noise comes out of the background, making a precise assignment impossible. This is due to the suppression of diagonal signals in the DQF pulse sequence. If a normal COSY pulse sequence is employed, some signals are too large compared to others (e.g., the aromatic protons of poly(S-*co*-SSA) as compared to the aromatic protons of 4VP), so some noise appears even before the regular ortho coupling peak of the 4VP aromatic protons.

The NOESY spectrum is presented in Figure 9. This procedure has no attenuation of diagonal signals; therefore some cross peaks are lost in the background noise. These peaks belong to all the aromatic 4VP protons, to the shielded methoxy protons, and to the heterotactic α-methyl protons. The main cross peaks visible in the spectrum appear from the ortho aromatic coupling (S protons) (a) and the CH–CH$_2$ coupling on the main chain (b). These protons are separated from each other by three chemical bonds and present scalar coupling. Their close vicinity generates the cross peaks in the NOESY spectrum. There are five other nondiagonal peaks. The most intense correlates the ortho aromatic protons of S and SSA units with the CH$_2$ chain protons belonging to the same or adjacent units (c). Two smaller cross peaks correlate the ortho aromatic protons of S and SSA units with the CH chain protons (d) and the meta and para aromatic protons of S units with the CH$_2$ chain protons (e), respectively. Another intramolecular cross peak correlates the syndiotactic α-methyl protons with the methoxy protons (f). All these correlations are very easy to explain by the spatial vicinity of the correlated protons.

Figure 10. NOE difference spectrum of the blend (normal spectrum presented in Figure 1c) arising from irradiation of the aromatic protons (7.00 ppm).

There is only one cross peak that correlates the two polymer chains, which appears between the nonshielded methoxy peak and the meta and para aromatic protons of the S units (g). One would expect cross peaks between all the signals that are shifted upfield during the mixing (Figures 3–5) and the aromatic S signal. However, it is important to remember that the aromatic shielding effect of ca. 0.1 ppm can appear at a distance of ca. 6 Å between the center of the aromatic ring and the shielded proton, whereas a NOESY cross peak is noticeable only when the direct distance between the two protons is equal to or less than ca. 4 Å. The only intermolecular cross peak that appears in Figure 9 belongs to the outer part of the poly(MMA) chain (see Figure 7) and to the external part of the poly(S) chain. Both of them have the highest probability to come close together in the mixing process, and both give relatively intense signals in the 1D NMR spectrum to afford the building of a cross peak. Using different mixing times, one can follow the buildup of this cross peak and find out more information about the proton–proton interaction. This kind of experiment will be performed in subsequent studies. However, different mixing times have been used in order to check the validity of this cross peak (an artifact can appear from the symmetrization procedure for intense peaks). The cross peak disappears when the mixing time is higher than 0.5 s, thus confirming the reality of the NOE correlation between the two types of protons.

An even better method to verify this correlation is by measuring one-dimensional NOEs. The procedure, with its advantages, is described in the literature.[22] Figure 10 presents the NOE difference spectrum of the blend (normal spectrum presented in Figure 1c and with the two-dimensional spectrum in Figure 9) arising from irradiation of the aromatic meta and para protons (7.00 ppm). All the NOE effects are negative, as expected for slowly tumbling macromolecules.[22] The most intense NOE effect is felt by the aromatic ortho protons, as expected. Smaller effects correlate these protons with the main-chain protons and with the aromatic protons ortho to the sulfonic acid group. There are two effects felt by the other polymer chain, and the main one is demonstrated by the methoxy protons. This confirms the result of the two-dimensional NOE-correlated spectra. A corresponding peak is noticeable in the NOE difference spectrum arising from irradiation of the methoxy protons, this time as a negative aromatic peak at 7.00 ppm. The other effect of irradiation at 7.00 ppm is felt by the aromatic protons of 4VP units in ortho position to the nitrogen. There seems to be no NOE effect on the α-methyl protons from the S aromatic ones. Quantitative measurements at different temperatures of the NOE effects in blends having different compositions, ionic group concentrations, solution concentrations, and molecular weights are in progress.

Conclusions

Poly(MMA) and poly(S) can be compatibilized by introducing groups that form ion pairs upon mixing. In Me_2SO solution at 85 °C, the proton transfer from an SSA group to a 4VP group is very rapid, but the subsequent forming of ion pairs and the alignment of the two chains is a slower process, which takes about 2 h for an 11% ionic group content. This process can be monitored by the upfield shift of most of the signals of poly(MMA-*co*-4VP). The signals shift upfield due to the screening effect of the neighboring aromatic S rings. A ca. 0.1 ppm shift suggests that most of the poly(MMA-*co*-4VP) chains are at a distance of maximum 6 Å from the poly(S-*co*-SSA) chains. One- and two-dimensional NOE-correlated spectra indicate that at least the methoxy protons of MMA are situated at a distance of ca. 4 Å from the aromatic protons of S units.

Studies of the kinetics of this coil overlap process and its dependence on temperature, ionic group concentration, and molecular weight are in progress.

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Registry No. (MMA)(4VP) (copolymer), 26100-41-4.

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Photophysics of Polystyrene. 2. Pariser–Parr–Pople Studies of Excimer Structure

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ABSTRACT: Calculations of the energies of the two lowest electronic transitions in various conformations of meso and racemic diads in polystyrene, based upon a modified Pariser–Parr–Pople method, have been performed. It is shown that the interactions between phenyl groups in the ground state do not result in dimer formation in polystyrene. In the case of electronic excitation, excimer formation is possible in a meso tt diad only.

Introduction

Excimer fluorescence, first observed by Förster and Kasper[1] in concentrated solutions of pyrene, was later studied both experimentally[2–5] and theoretically[2,4,6–11] for various organic and inorganic molecules. According to the mechanism of formation, excimers can be classified into inter- and intramolecular ones. In the case of small organic molecules in solution, excimer formation is a diffusion-controlled process.[4] On the other hand, intramolecular excimers are formed even in arbitrarily diluted solutions.[12] Studies of intramolecular excimers in dichromophore systems and vinyl macromolecules have been a subject of numerous experimental works.[13–18] It has been shown that for dichromophore systems, excimer formation depends

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