polymer communications

Hydrogen-bonded polymer complexes

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Hydrogen-bonded polymer complexes formed from poly(4-hydroxystyrene) and poly(*N*,*N*-dimethylacrylamide) were studied by cross-polarization/magic angle spinning ^{13}C nuclear magnetic resonance spectroscopy. Evidence for specific interaction was provided by a shift of ~3 ppm in the phenolic carbon resonance peak. The proton spin-lattice relaxation times are shorter than the values predicted by a linear model. On the other hand, the rotating frame spin lattice relaxation times, $T_{1\rho}$, of the complexes agree with the predictions. The scale of homogeneity is estimated from the $T_{1\rho}$ data to be ~2.5 nm.

(Keywords: hydrogen bonding; polymer complexes)

Introduction

In a previous publication[1] interpolymer complexation between poly(4-hydroxystyrene) (PHOST) and poly(*N*,*N*-dimethylacrylamide) (PDMA) via hydrogen bonding interaction was reported to yield mutual precipitates from acetone, dioxane or methanol solutions. The precipitates had high glass transition temperatures (T_gs) and in many cases low heat capacities. These observations suggest a strong influence of the interaction on the segmental mobility of the complexes. In this study, solid state nuclear magnetic resonance (n.m.r.) spectroscopy was used to obtain information about the homogeneity of the complexes and the changes in mobility brought about by the hydrogen bonding interaction. Our study was stimulated by the work of Natansohn and Simmons[2,3] who also used n.m.r. to investigate charge-transfer interaction in blends or copolymers.

Experimental

Poly(4-hydroxystyrene) was purchased from Polyscience Inc. After purification by reprecipitating from methyl ethyl ketone solution into excess hexane, the polymer was dried in vacuum at 90°C for 7 days. The number and weight average molecular weights of the sample were determined by gel permeation chromatography to be 0.55 and 4.06×10^4 (polystyrene equivalent), respectively. Poly(*N*,*N*-dimethylacrylamide) was synthesized from distilled monomer by free radical polymerization at 70°C. The resulting polymer was purified by dialysis in water before freeze drying. The molecular weight of the polymer was determined by viscometry, in water at 25°C, to be 25 800.

Mutual precipitates formed upon mixing methanol or acetone solutions (5×10^{-3} g ml^{-1}) of the component polymers were isolated by centrifugation and dried in vacuum at 90°C for 7 days. The compositions of the precipitates were determined by elemental analysis of nitrogen. For the purpose of comparison, blend samples were prepared by casting films from *N*,*N*-dimethylformamide (DMF) solutions (2% by weight). The films were dried under the same condition for 14 days.

The T_gs of the polymers were determined using a differential scanning calorimeter (DuPont, 9900). The beginning, midpoint and end of the specific heat change were recorded. The midpoint was taken as T_g while the temperature span from the beginning to the end is referred to as the width of the transition. The samples were conditioned at 150°C for 1 h prior to measurement.

^{13}C solid state n.m.r. measurements were carried out using a General Electric GN-300 spectrometer equipped with a cross-polarization/magic angle spinning (CP/MAS) probe from Chemagnetics Corporation. The spectrometer operated at a proton frequency of 300.5 MHz and a carbon frequency of 75.5 MHz. All samples were spun at speeds of ~4400 Hz. The proton spin-lattice relaxation time, T_1, was measured by the inversion recovery method and the relaxation time in the rotating frame, $T_{1\rho}$, by using a 90° pulse followed by a phase shifted proton locking pulse and proton–carbon Hartman–Hahn contact[4–6].

Results and discussion

The two solvents used for the complexation study, methanol and acetone, differ in their powers as competitors for hydrogen bonding. Methanol is a much weaker donor than phenol and is not expected to compete, to any significant extent, with PHOST in hydrogen bonding with PDMA. While acetone is a weaker acceptor than a dimethyl substituted amide group the difference is not as large as that between methanol and phenol, as judged from the enthalpy–frequency shift relationship[7,8]. Therefore, some degree of competition between acetone and PDMA for bonding with PHOST cannot be ruled out. The difference in the hydrogen bonding affinities of the two solvents is partially reflected in the compositions of the precipitates (*Figure 1*); the precipitates from methanol tend to contain smaller amounts of PDMA. On the other hand, there are two common aspects. First, the compositions of both the

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methanol and acetone precipitates vary only over a narrow range when the feed compositions are changed from 10 to 90%. Second, there appears to be an 'azeotrope' composition at ~50–55% PDMA in each case. These results confirm earlier findings[1].

The methanol precipitates have high T_gs (*Figure 2*) which exceed the calculated weight average values of the component polymers by as much as 50°C. The T_gs of the acetone precipitates are comparable to the values for the cast films; they are lower than the values for the methanol precipitates but are still significantly higher than the calculated weight averages. Again these results confirm earlier reports. We also note that the acetone precipitates tend to have broad transitions with an average transition width of 30°C while the corresponding values for the methanol precipitates and cast films are 17 and 22°C, respectively. A large transition width in a blend implies a broad spectrum of segment mobilities due to local compositional heterogeneities caused, in this case, by locally different degrees of hydrogen bonding.

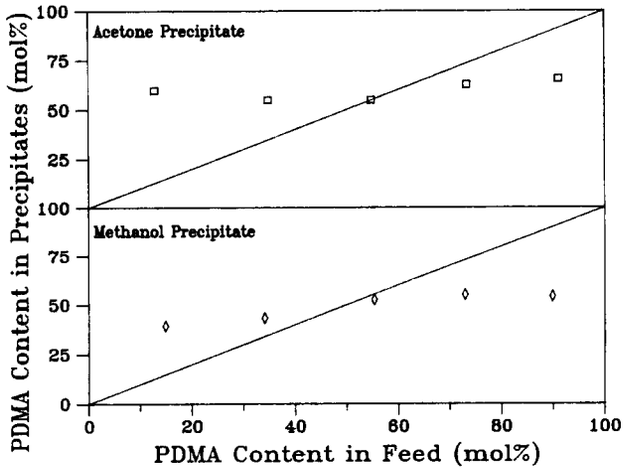

Figure 1 Compositions of the PHOST–PDMA mutual precipitates

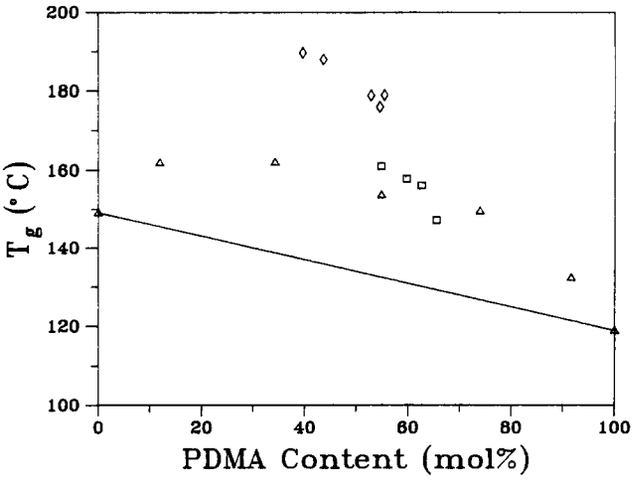

Figure 2 Glass transition temperatures of precipitates and cast films: (◇) methanol precipitate; (□) acetone precipitate; (△) films cast from DMF

The T_g data of the cast films fit the following equation[9]:

$$T_g = W_1 T_{g_1} + W_2 T_{g_2} + q W_1 W_2 \qquad (1)$$

with a q value of 100. In equation (1), W_1 and W_2 are the weight fractions of the component polymers. The mutual precipitates are limited in the range of compositions and therefore the data are inadequate for testing the applicability of equation (1); but if it is assumed that the equation is also applicable, then the q values are 110 for the acetone precipitates and 200 for the methanol precipitates. Large positive deviations of T_g values from the calculated weight averages now appear to be a common occurrence in strongly interacting blends[2,3,9–12].

The CP/MAS ^{13}C n.m.r. spectra of PHOST, PDMA and their mixtures are shown in *Figure 3*. Of particular interest is the peak at 152 ppm due to the phenolic carbon which is shifted to 155 ppm as a result of interaction with PDMA. A shift of 2–3 ppm has been reported earlier by Qin *et al.* in related systems[13,14]. However, the resonance at 174 ppm due to the carbonyl carbon remains essentially unchanged.

A single exponential decay of the n.m.r. signal was observed for each mixture in the relaxation experiments. This is indicative of interaction, via spin diffusion, between the two component polymers. The T_1 and $T_{1\rho}$ relaxation times are listed in *Table 1*. The relaxation times from different peaks are essentially identical and the experimental deviation is <5% in three consecutive measurements. These results can be viewed as strong evidence of extensive mixing of the two types of segments. The average values of T_1 and $T_{1\rho}$ for each specimen are plotted in *Figure 4* as a function of PDMA content. Note that the T_1 values for the mixtures are smaller than the value for either component.

A linear model has been used successfully in the

Table 1 T_1 and $T_{1\rho}$ relaxation times from CP/MAS ^{13}C n.m.r.

Sample	PDMA (mol%)	Peak (ppm) 36 T_1 (s)	36 $T_{1\rho}$ (ms)	115 T_1 (s)	115 $T_{1\rho}$ (ms)	155 T_1 (s)	155 $T_{1\rho}$ (ms)	174 T_1 (s)	174 $T_{1\rho}$ (ms)
PDMA	(100)	2.21	24.1	–	–	–	–	2.19	23.9
PHOST	(0.00)	1.51	6.1	1.49	5.9	1.50 (@152 ppm)	–	–	–
Blend	(34.2)	1.28	10.3	1.29	10.7	1.29	9.1	1.35	10.8
	(54.8)	1.52	12.9	1.49	13.3	1.51	12.9	1.51	12.4
	(73.9)	1.54	16.2	1.55	16.6	1.54	16.7	1.60	16.0
Methanol precipitate	(55.4)	1.41	8.7	1.40	8.7	1.37	8.6	1.39	8.6
Acetone precipitate	(54.7)	1.49	10.8	1.47	10.7	1.50	10.5	1.49	10.6

Measured at 22.5 ± 0.5°C

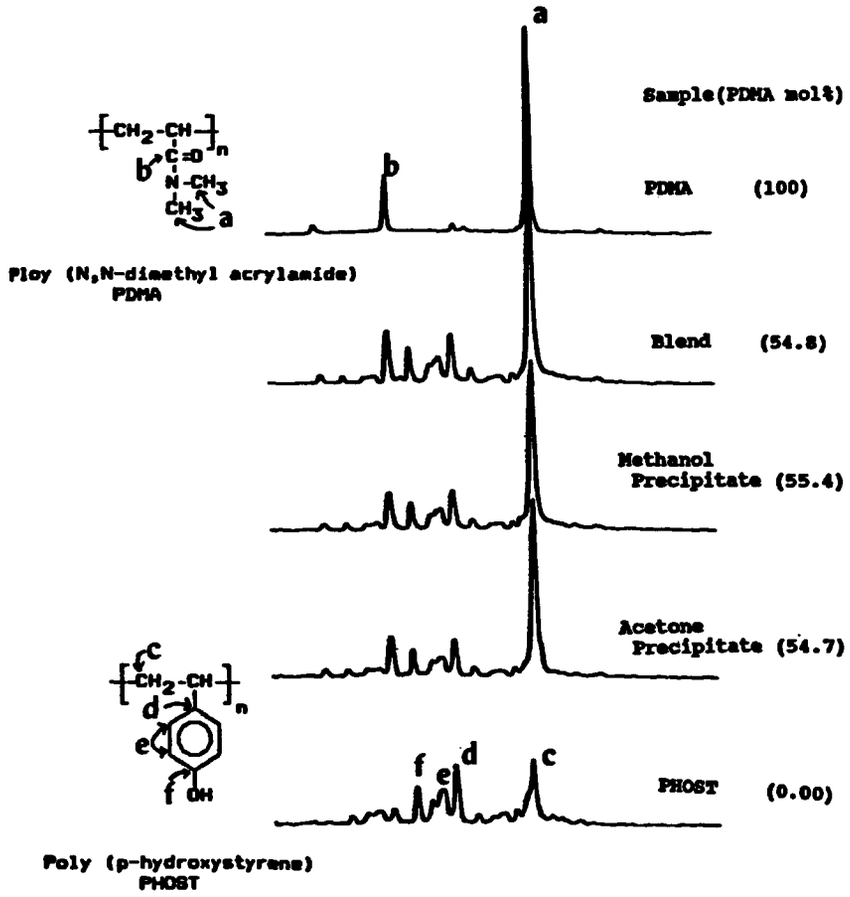

Figure 3 CP/MAS ^{13}C n.m.r. spectra

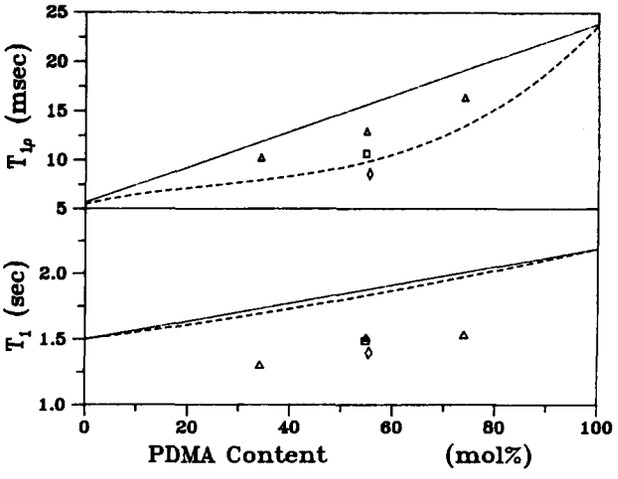

Figure 4 T_1 and $T_{1\rho}$ relaxation times

analysis of the relaxation rate of a mixture[6,15]:

$$k_1 M_1 + k_2 M_2 = \mathrm{d}M_T/\mathrm{d}t \qquad (2)$$

where k_1 and k_2, respectively, denote the intrinsic relaxation rate (T_1^{-1} or $T_{1\rho}^{-1}$) of components 1 and 2 and M_1 and M_2 are the magnetizations associated with the respective protons. The total magnetization is denoted by M_T. On the assumption of a common spin temperature the above equation may be stated for the corresponding number of protons present:

$$k_1 \frac{N_1}{N_T} + k_2 \frac{N_2}{N_T} = k \qquad (3)$$

where N represents the number of protons. The derivation of equation (3) is based on the assumption that spin diffusion allows all the material to relax totally through the two relaxation sinks, but is not a rate-determining step. Clearly, our T_1 data do not meet the predictions of equation (3) which is indicated by the broken line in *Figure 4*. Thus, the strong interaction between PHOST and PDMA changes the nature of the correlation times of motion (on a time scale of ~ 1 s). Similar departures from equation (3) have been reported by Natansohn and Simmons[2,3] for $T_{1\rho}$ in charge-transfer complexes.

The $T_{1\rho}$ results of the cast films are somewhat larger than the predicted values. The data for the two precipitates, however, are close to the calculated values from equation (3). An estimate of the maximum diffusive path length L can be derived from the approximated formula

$$L = (6DT)^{1/2} \qquad (4)$$

For $T_{1\rho}$ of 10 ms and a spin diffusion coefficient, D, of 10^{-12} cm^2 S^{-1}, $L \simeq 2.5$ nm. Therefore if heterogeneities are present in the precipitates their linear dimensions are < 2.5 nm.

Conclusions

Hydrogen bonding interaction in PHOST–PDMA complexes is manifested in n.m.r. spectra by a shift of ~ 3 ppm in the phenolic carbon resonance. As a result of the interaction, the complexes have T_gs much higher than the calculated weight average values. In particular, the T_g values of the methanol precipitates are higher than

those of the component polymers. The T_1 values are shorter than the values predicted by a linear model. However, the $T_{1\rho}$ values of the precipitates agree with the predictions. The scale of homogeneity is estimated from the $T_{1\rho}$ data to be ~ 2.5 nm.

Acknowledgement

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