

Nuclear Overhauser Effect Study on Intermolecular Interaction and Miscibility of Polymer Blends in the Solution State

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Received June 26, 1991; Revised Manuscript Received April 23, 1992

ABSTRACT: In order to study the intermolecular interaction responsible for the miscibility of poly(4-vinylphenol)/poly(methyl acrylate) (PVPh/PMA) and poly(4-vinylphenol)/poly(methyl methacrylate) (PVPh/PMMA) blends, the ¹H high-resolution NMR spectra are observed in tetrahydrofuran (THF) solution. The nuclear Overhauser enhancement effects (NOE) which give information about the proximity are measured by means of NOE difference spectroscopy and two-dimensional NOE spectroscopy. The results indicate that PVPh can be close to PMA or PMMA at distances less than 4 Å in THF solution. The intermolecular hydrogen-bonding interaction between the phenolic OH of PVPh and the C=O of PMA or PMMA is responsible for the miscibility of these blends.

Introduction

In recent years, several researchers have studied the intermolecular interaction and the miscibility of polymer blends in the solution state by observing the nuclear Overhauser enhancement effect (NOE).¹⁻⁵ Although the solid-state morphology is lost in solution, the specific interaction responsible for mixing two different polymers in the solid state will be retained. Since a number of miscible blends are prepared from solution, the study in the solution state is of fundamental importance. Because of the inverse sixth-power dependence on the interproton distance, NOE appears only for a pair of protons separated by less than approximately 4 Å.⁶ NOE is, hence, a sensitive tool for studying the proximity.

Recently, we studied poly(4-vinylphenol)/poly(methyl acrylate) (PVPh/PMA) and poly(4-vinylphenol)/poly(methyl methacrylate) (PVPh/PMMA) blend solids prepared by cast from tetrahydrofuran (THF) solution. We suggested that the intermolecular hydrogen-bonding interaction is responsible for intimate mixing of the PVPh/PMA blend.⁷ As for the PVPh/PMMA blend, the mixture of the two polymers in THF solution is clear and completely miscible at lower polymer concentrations. However, as the concentration gradually increases in the course of casting, the phase separation occurs. The PVPh/PMMA blend obtained is immiscible and assumes the domain structure; the domain size is larger than 200–300 Å.

In the course of casting, solutions of PVPh/PMA and PVPh/PMMA blends encounter several different mixing states, i.e., the homogeneously miscible solution state, the phase-separated solution state in which two phases of different polymer compositions coexist, and the liquid-solid separated state. It is of interest to examine the characteristics of intermolecular interaction in each state.

In this paper, we report the results of high-resolution ¹H NMR studies of PVPh/PMA and PVPh/PMMA blends in deuterated tetrahydrofuran (THF-*d*₈) solution including two-dimensional (2D) NMR measurements. We study the effects of polymer concentration and temperature on the intermolecular interaction and the miscibility of the blends.

Experimental Section

PVPh of the molecular weight of 1500–7000 was obtained from Polysciences Inc. PMA and PMMA were obtained from Aldrich

Chemical Co. Inc. Informed number and weight average molecular weights, respectively, were 10 600 and 30 700 for PMA and 46 400 and 93 300 for PMMA. PVPh was mixed with PMA (or PMMA) in a molar ratio of 1 to 1 in THF-*d*₈ (99%) at 45 °C by stirring for more than 10 h. The polymer concentrations were 2, 10, 20, 30, and 40 wt %.

The NMR experiments were performed at 270 MHz on a JEOL JNM-GX270 spectrometer. The ¹H spectra were observed by the conventional single-pulse method with a 90° pulse width of 19 μs and repetition time of 4 s. Tetramethylsilane (TMS) was used as an internal chemical shift reference. The experiments were carried out at 25 °C and 45 °C, and the temperature was controlled within 1 °C using a JEOL temperature controller.

The NOE difference spectra were obtained by subtracting the normal spectrum from the spectrum irradiated selectively at the OCH₃ proton resonance of PMA or PMMA. The radio-frequency field strength of the selective irradiation was about 15 Hz. We also obtained the NOE difference spectra by another method: the selectively irradiated spectrum was subtracted from the spectrum irradiated at a position 5 kHz higher than TMS (out of spectral region). The two methods were found to give the same results. We, hence, report here only the difference spectra obtained by the first method. All observed NOEs were negative. The NOE value was obtained from the difference spectra: we calculated the area ratio between a particular resonance and the selectively irradiated one corrected by the proton number. It is expressed in percent.

The 2D-NOE spectra were obtained by the (90°-*t*₁-90°-*t*_m-90°-*t*₂)_n pulse sequence at seven different NOE mixing times *t*_m's of 5, 20, 60, 100, 160, 200, and 500 ms. The 2D experiments were taken with 2048 data points along *t*₂ and with 128 *t*₁ increments.

Results and Discussion

Phase Separation in the Solution State. The red color of the THF solution is an indicator of PVPh. Solutions of PVPh/PMA = 1/1 at 45 °C are clear and orange at all polymer concentrations. After standing for 2 days at 25 °C, the solutions at concentrations higher than 20 wt % undergo phase separation into two phases, orange and yellow; both phases are clear. We consider that the orange and yellow phases are PVPh-rich and PMA-rich phases, respectively.

PVPh/PMMA solutions at concentrations lower than 10 wt % are homogeneous and yellow at 25 °C. When the polymer concentration is higher than 20 wt %, white aggregates of PMMA precipitate out from the orange solution at 25 °C as well as 45 °C. At polymer concentrations higher than 40 wt %, even if the PVPh/PMMA mixture is stirred in THF for 1 day at 45 °C, white small

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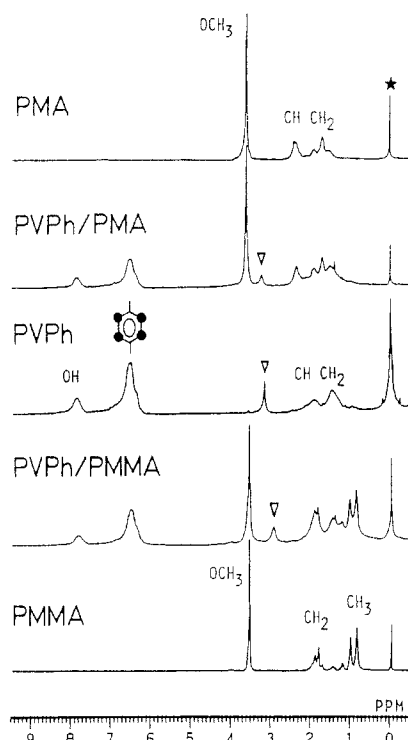


Figure 1. ^1H spectra of PMA, PVPh/PMA = 1/1 blend, PVPh, PVPh/PMMA = 1/1 blend, and PMMA at a concentration of 10 wt % at 45 °C. ∇ and \star peaks are the resonances of H_2O and TMS.

flakes of PMMA remain undissolved. The orange soluble part is very viscous.

We studied three different mixture systems: (i) the miscible solution system, i.e., the PVPh/PMA = 1/1 blend at 45 °C and the PVPh/PMMA = 1/1 blend at concentrations lower than 10 wt %, (ii) the phase-separated system, i.e., the PVPh/PMA = 1/1 blend at 25 °C at concentrations higher than 20 wt %; (iii) the solid-liquid-separated system in which PMMA partly precipitates out from the solution, i.e., the PVPh/PMMA = 1/1 blend at concentrations higher than 20 wt %.

Figure 1 shows the ^1H spectra of PMA, the PVPh/PMA = 1/1 blend, PVPh, the PVPh/PMMA = 1/1 blend, and PMMA in THF solution at 10 wt % and at 45 °C. Peaks of PVPh at about 1.5, 1.9, and 6.5 ppm are assigned to the main-chain CH_2 protons, the main-chain CH protons, and the phenolic ring protons, respectively. The phenolic OH proton of PVPh resonates at 7.9 ppm in THF solution. Assignments of the spectra of PMA and PMMA are referred to previous reports.⁸⁻¹⁰

NOE of PVPh/PMA Blends. Figure 2 shows the 2D-NOE spectra of the PVPh/PMA = 1/1 blend at 40 wt % (system i) and at 45 °C obtained with an NOE mixing time t_m of 500 ms.¹¹ We can see several positive cross peaks (i.e., negative NOE). There appear intramolecular NOE cross peaks between the OH and the phenolic ring protons of PVPh and between the side-chain and the main-chain protons of both polymers. Intermolecular NOE cross peaks also appear between the OCH_3 protons of PMA and the OH proton as well as the phenolic ring protons of PVPh; these cross peaks are enclosed by rectangles in the figure. The results obtained here imply that PVPh and PMA are intimately mixed in THF solution at 45 °C at interproton distances less than 4 Å. As for the resonances of the main-chain protons of both polymers, we cannot distinguish the intramolecular NOE cross peak from the intermolecular one because of spectral overlap.

We observed 2D-NOE spectra as a function of NOE mixing time t_m for the PVPh/PMA = 1/1 blend at 40 wt

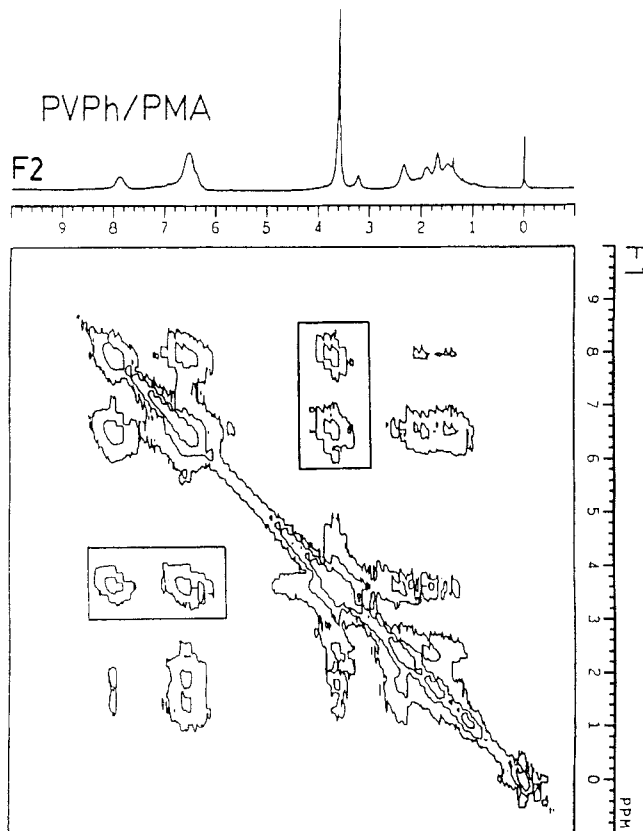


Figure 2. 2D-NOE spectrum of the PVPh/PMA = 1/1 blend at a polymer concentration of 40 wt % at 45 °C observed at an NOE mixing time of 500 ms. Intermolecular negative NOE cross peaks are enclosed by boxes. In the upper part the normal 1D spectrum is shown.

% at 45 °C (system i). Even at a short mixing time of 5 ms, there appeared not only intramolecular NOE cross peaks but also intermolecular ones between the OH proton of PVPh and the OCH_3 protons of PMA. The intermolecular NOE cross peak between the phenolic ring proton of PVPh and the OCH_3 protons of PMA appeared only at mixing times longer than 100 ms. These results suggest that the interproton distance between the OCH_3 protons of PMA and the OH proton of PVPh is as small as the intramolecular distance between the OH proton and the phenolic ring protons of PVPh: a distance capable of making a hydrogen bond. The distance between the OCH_3 protons of PMA and the phenolic ring protons of PVPh is larger than that. These results indicate that the intermolecular hydrogen bond between the phenolic OH proton of PVPh and the $\text{C}=\text{O}$ oxygen of PMA is formed in solution; the hydrogen-bonding interaction is responsible for the miscibility of the PVPh/PMA blend.

We observed 2D-NOE spectra for the phase-separated system of PVPh/PMA blends at concentrations of 20 and 30 wt % and at 25 °C (system ii); there coexist PVPh-rich and PMA-rich phases. The results are similar to those of the 40 wt % sample at 45 °C (system i). This indicates that the two polymers in each phase are intimately mixed at smaller distances less than 4 Å.

Figure 3 shows the NOE difference spectra of the PVPh/PMA = 1/1 blend at 20 wt % measured at 45 °C (system i) (bottom) and 25 °C (system ii) (top). In all cases the OCH_3 proton resonance of PMA indicated by the triangle was fully saturated. The spectra show an intermolecular negative NOE, i.e., positive peaks, at the OH proton position (7.9 ppm) and the phenolic ring proton position (6.5 ppm) of PVPh; these are indicated by circles. The main-chain CH_2 and CH protons of both polymers show

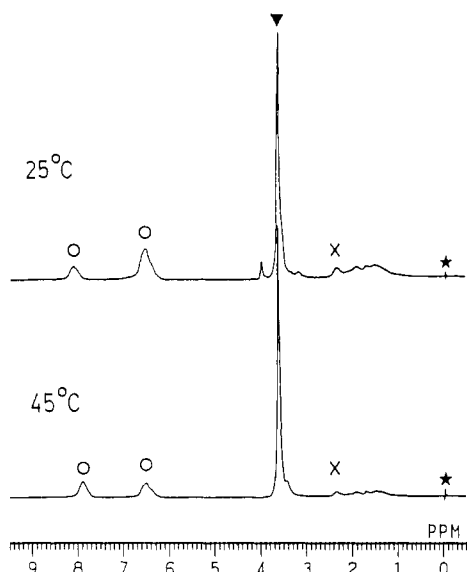


Figure 3. 1D-NOE difference spectra of PVPh/PMA = 1/1 blend of 20 wt % at 25 and 45 °C. Marks "x" and "o" represent intramolecular and intermolecular negative NOEs, respectively. The OCH₃ resonance of PMA (▼) was fully saturated.

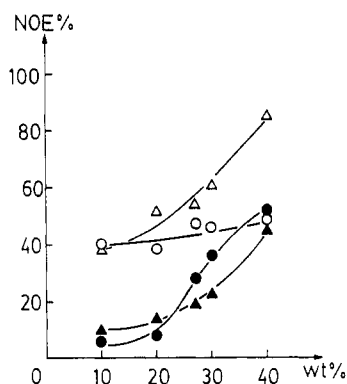


Figure 4. Concentration dependence of the negative NOE value for the PVPh/PMA = 1/1 blend: OH resonance at 25 °C (○) and 45 °C (Δ); phenolic ring resonance of PVPh at 25 °C (●) and 45 °C (▲).

a negative NOE at 2.4–1.5 ppm. An intramolecular NOE can be identified for the CH proton of PMA at 2.4 ppm as indicated by the cross. These results are in agreement with those obtained from the 2D-NOE experiments.

Figure 4 shows the concentration dependence of the NOE value of PVPh/PMA = 1/1 blends at 25 and 45 °C deduced from the NOE difference spectra. The OH proton of PVPh shows remarkable negative NOE at both temperatures even at low concentrations, but the NOE of the phenolic ring protons is not so significant. At 25 °C, the negative NOE of the phenolic ring protons increases remarkably with increasing concentration, while the increase is not remarkable for the OH proton. At a concentration of 40 wt %, the NOE of the phenolic ring protons is approximately the same as that of the OH proton. The NOEs of both resonances show a remarkable increase with increasing concentration at 45 °C.

The intermolecular NOE of the OH proton of PVPh provides evidence for the association of the two polymers; the association is probably brought about by hydrogen bonding. At 45 °C, the increase of polymer concentration further enhances the hydrogen-bonding association between the two polymers. At 25 °C, the increase in polymer concentration gives rise to phase separation, the PMA-rich and PVPh-rich phases. Since most of the OH protons of PVPh in the PMA-rich phase are associated with the

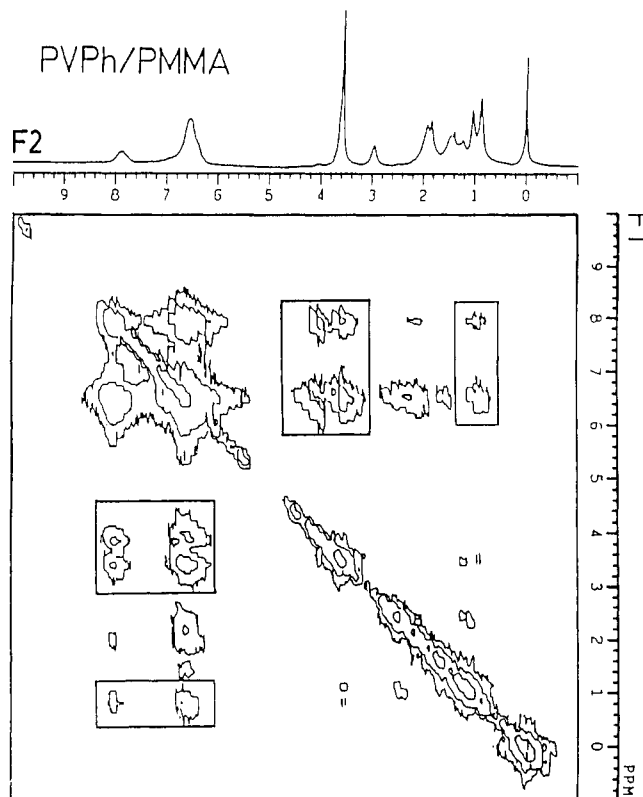


Figure 5. 2D-NOE spectrum of the PVPh/PMMA = 1/1 blend at a polymer concentration of 40 wt % at 45 °C observed at an NOE mixing time of 500 ms. Intermolecular negative NOE cross peaks are enclosed by boxes. In the upper part the normal 1D spectrum is shown.

C=O oxygen of PMA, further increase in concentration does not enhance the hydrogen-bonding interaction, resulting in a less significant increase in NOE.

The intermolecular NOE of the phenolic ring protons is observable only at higher concentrations. The increase in polymer concentration reduces nonspecifically the average interproton distance between the two polymers. This is probably a reason for the increase of the intermolecular NOE between the side chain of PMA and the phenolic proton of PVPh.

NOE of PVPh/PMMA Blends. Figure 5 shows the 2D-NOE spectra of the PVPh/PMMA = 1/1 blend at 40 wt % (system iii) observed at 45 °C with an NOE mixing time t_m of 500 ms. Intermolecular NOE cross peaks appear as shown in the boxes, suggesting that the interproton distance between PVPh and PMMA in THF can be shorter than 4 Å. The NOE mixing time dependence of the 2D-NOE experiments (not shown here) indicates that the intermolecular NOE cross peaks between the OH proton of PVPh and the OCH₃ protons of PMMA appear even at a short mixing time of 5 ms; the cross peaks between the phenolic ring protons of PVPh and the OCH₃ protons of PMMA appear at mixing times longer than 100 ms. The NOE cross peaks between the OH proton as well as the phenolic ring protons of PVPh and the α -CH₃ protons of PMMA also appear at a mixing time of 500 ms. These results suggest that PMMA dissolved in solution can intimately associate with PVPh through the intermolecular hydrogen bond, though the solubility of PMMA in THF is low; the interproton distance between the two polymers can be less than 4 Å. The distance between the side-chain protons of PVPh and those of PMMA is shorter than that between the side-chain protons of PVPh and the α -CH₃ protons of PMMA.

Figure 6 shows the NOE difference spectra of the PVPh/

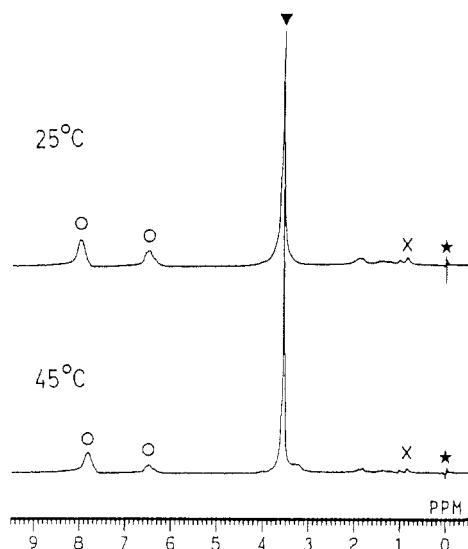


Figure 6. 1D-NOE difference spectra of the PVPh/PMMA = 1/1 blend of 20 wt% at 25 and 45 °C. Marks "X" and "O" represent intramolecular and intermolecular negative NOEs, respectively. The OCH₃ resonance of PMMA (▼) was fully saturated.

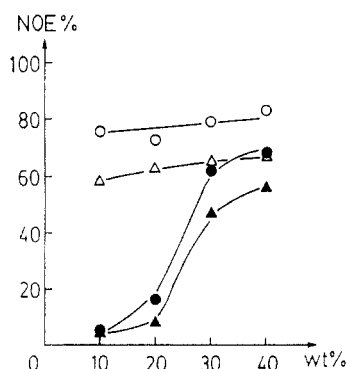


Figure 7. Concentration dependence of the negative NOE value for the PVPh/PMMA = 1/1 blend: OH resonance at 25 °C (○) and 45 °C (△); phenolic ring resonance of PVPh at 25 °C (●) and 45 °C (▲).

PMMA blend at 25 and 45 °C. The OCH₃ resonance of PMMA was fully saturated. We can see negative intermolecular NOEs between the OH and ring protons of PVPh and the OCH₃ protons of PMMA as indicated by circles.

Figure 7 shows the concentration dependence of the NOE value of the PVPh/PMMA blend at 25 and 45 °C. The concentration dependence of the NOE for PVPh/PMMA is almost similar to those of the PVPh/PMA blend at 25 °C. These results indicate that the intermolecular interaction of PVPh/PMMA is similar to that of the PVPh/PMA blend at 25 °C.

Intermolecular Hydrogen Bonding. The NOE results indicate that the intermolecular hydrogen-bonding interaction operates between PVPh and PMA or PMMA in the solution state. Such a short-range interaction may give rise to a change in chemical shift of the OH proton of PVPh which directly participates in hydrogen bonding.

Figure 8 shows the concentration dependence of the chemical shift of the phenolic OH proton of PVPh at 25 and 45 °C for pure the PVPh sample and PVPh/PMA = 1/1. The concentration dependence for the PVPh/PMMA = 1/1 blend is also shown in Figure 9.

With increasing concentration, the OH resonance shifts downfield in all cases, while the other resonances remain unchanged (data not shown). The OH resonance appears at lower fields at 25 °C than at 45 °C. These results are indicative of hydrogen bonding. The OH resonance of the blends appears at 0.05–0.15 ppm higher field than in

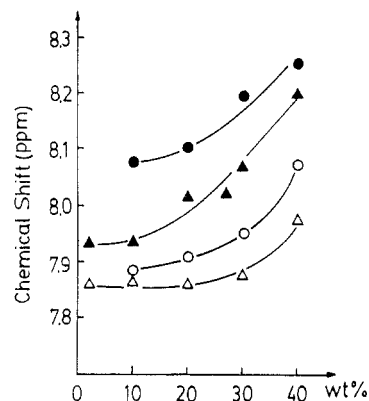


Figure 8. Concentration dependence of the chemical shift of the phenolic OH resonance of pure PVPh at 25 °C (●) and 45 °C (○) and of the PVPh/PMA = 1/1 blend at 25 °C (▲) and 45 °C (△).

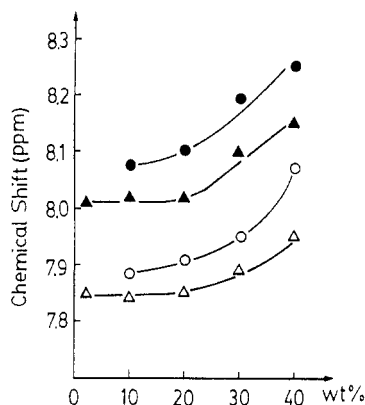


Figure 9. Concentration dependence of the chemical shift of the phenolic OH resonance of pure PVPh at 25 °C (●) and 45 °C (○) and of the PVPh/PMMA = 1/1 blend at 25 °C (▲) and 45 °C (△).

the pure PVPh, suggesting that the hydrogen-bonding interaction in the blends is different from that in pure PVPh.

General Remarks. The miscibility of polymer blends in the solid state depends on various factors. In addition to the specific intermolecular interaction between two polymers, the sample preparation conditions also affect the miscibility.

The mixing of two polymers on a molecular scale is achieved by the solution cast method. The homogeneous mixing in solution, however, does not always guarantee a homogeneous blend in the solid state. In the PVPh/PMA blends, the two polymers are well dissolved in THF at 45 °C in the whole concentration range. The two polymers are closely associated through the specific intermolecular interaction. We can obtain a miscible blend when we evaporate the solvent at 45 °C. At 25 °C, the phase separation occurs at higher concentrations. In practice, the phase-separation process is slower (about 2 days) than the solvent evaporation process. In 1 day, about 95% of THF solvent evaporates and polymer chains are fixed in the solid state. We can obtain a miscible blend of PVPh/PMA before the phase separation occurs.

On the other hand, for the PVPh/PMMA blend, the homogeneous solution is achieved only at lower concentrations. As the solvent evaporates, because of the different solubility of PVPh and PMMA in THF, PMMA partly precipitates out from the solution, while PVPh still remains soluble. The evaporation of solvent causes the dissociation of intermolecular interaction and the phase separation. We obtain an immiscible blend when the solvent evaporates. THF is not a good solvent for making

PVPh/PMMA blends. In fact, it has been reported recently that intimately miscible blends of PVPh and PMMA can be obtained using methyl isobutyl ketone as a casting solvent.¹²

Finally, it should be noted that the present NOE study only indicates whether a miscible phase exists, but not whether the whole system is miscible.

Acknowledgment. This work was supported by Grants-in-Aid from the Ministry of Education, Science, and Culture of Japan (Nos. 02554014 and 02750623). We are grateful to Mr. S. Tsuda for his kind help in the 2D-NMR experiment.

References and Notes

- (1) Natansohn, A.; Eisenberg, A. *Macromolecules* **1987**, *20*, 323.
- (2) Crowther, M. W.; Cabasso, I.; Levy, G. C. *Macromolecules* **1988**, *21*, 2924.

- (3) Mirau, P. A.; Tanaka, H.; Bovey, F. A. *Macromolecules* **1988**, *21*, 2929.
- (4) Mirau, P. A.; Bovey, F. A. *Macromolecules* **1990**, *23*, 4548.
- (5) Zhang, X.; Takegoshi, K.; Hikichi, K. *Polym. J.* **1991**, *23*, 79.
- (6) Noggle, J. H.; Schirmer, R. E. *The Nuclear Overhauser Effect*; Academic Press: New York and London, 1971.
- (7) Zhang, X.; Takegoshi, K.; Hikichi, K. *Macromolecules* **1991**, *24*, 5756.
- (8) Chang, C.; Muccio, D. D.; Pierre, T. St. *Macromolecules* **1985**, *18*, 2154.
- (9) Schilling, F. C.; Bovey, F. A.; Bruch, M. D.; Kozlowski, S. A. *Macromolecules* **1985**, *18*, 1418.
- (10) Chûjô, R.; Hatada, K.; Kitamura, R.; Kitayama, T.; Sato, H.; Tanaka, Y. *Polym. J.* **1987**, *19*, 413.
- (11) Ernst, R. R.; Bodenhausen, G.; Wokun, A. *Principles of Nuclear Magnetic Resonances in One and Two Dimensions*; Oxford University Press: Oxford, U.K., 1987.
- (12) Serman, C. J.; Painter, P. C.; Coleman, M. M. *Polymer* **1991**, *32*, 1049.

Registry No. PVPh, 59269-51-1; PMA, 9003-21-8; PMMA, 9011-14-7.