Intermacromolecular Complexation due to Specific Interactions. 2. Nonradiative Energy Transfer Fluorospectroscopy and Nuclear Magnetic Resonance Monitoring Miscibility−Complexation Transition

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ABSTRACT: The difference in chain arrangements between ordinary miscible blends and polymer complexes could be monitored by a nonradiative energy transfer (NRET), when part of one of the constituents, i.e., poly(methyl methacrylate) (PMMA), was labeled with fluorescence donor (c) and another part with acceptor (a). In blends composed of PMMA-a, PMMA-c, and modified polystyrene [PS(OH)] carrying hexafluoro-α-hydroxypropyl groups, a gradual decrease of the energy transfer efficiency was observed accompanying the transition from miscibility to the pairing of interacting polymer chains as the hydroxyl content in PS(OH) increases, from 2 to 10 mol %. Solid-state ^{1}H NMR relaxation measurements failed to reflect the transition. However, evidence of complexation between PMMA and PS(OH) with a high hydroxyl content was obtained by NMR NOE measurements in the blend solutions.

Introduction

In research on polymer blends, two areas have attracted interest in recent years. The first deals with miscibility enhancement of immiscible blends by introducing specific interactions,[1] e.g., ion−ion,[2] electron transfer,[3] and hydrogen bonding.[4−6] The second concerns intermacromolecular complexation due to inherent strong specific interactions between the blend components.[7] Except for stereocomplexes formed due to van der Walls interaction and spatial fitting of chain conformations of the components[8] as in mixtures of isotactic and syndiotactic PMMA, most intermacromolecular complexes are formed as a result of strong interactions, such as Coulombic and hydrogen bonding. Although both immiscibility−miscibility transition and complexation are caused by the same factor, complexation involves the pairing of the interacting chains, whereas mere miscibility is attained when the polymer-bound interacting groups associate at random with their opposite numbers on other chain molecules. The problem is then to distinguish the two cases.

In our preceding paper of this series,[9] we reported that in the systems composed of poly(alkyl acrylates) and PS(OH), a styrene copolymer with *p*-(hexafluoro-α-hydroxypropyl)-α-methylstyrene (HFMS), by increasing the HFMS content in PS(OH), both the transitions from immiscibility to miscibility and from miscibility to complexation can be realized. Thus, the polymer complex is produced by strengthening specific interaction in a miscible blend. The formation of the complex was evidenced by a clear increase of nonradiative energy transfer (NRET) efficiency in the miscible blends of fluorescence donor-labeled PMMA and acceptor-labeled PS(OH), as the hydroxyl content in PS(OH) extends to about 7−10 mol %. The same phenomenon is found in the system of poly(butyl acrylate) and PS(OH). This transition may be rather universal in the systems where interaction density or intensity can be adjusted. Therefore, exploring the molecular nature of the miscibility−complexation transition using more techniques capable of distinguishing polymer complexes from miscible blends becomes a challenging problem.

Both miscible blends and polymer complexes contain a single phase. Therefore, techniques sensitive to phase structure, such as differential scanning calorimetry (DSC), transmission electron microscopy (TEM), and dynamic mechanical analysis (DMA), will not distinguish a polymer complex blend from the corresponding miscible blend. However, in terms of molecular arrangements, i.e., chain spatial distributions at the molecular level, they are quite different. In ordinary miscible blends, different component chains are believed to be randomly mixed, while in polymer complexes, unlike chains are thought to be paired. However, this difference has not been convincingly detected by techniques other than NRET as mentioned above.[9]

There are several comparative studies of polymer complexes and "blends", the latter usually referring to miscibility. For example, Zhang et al.[10,11] have studied by NMR two kinds of blends, i.e., blends of poly(vinyl alcohol) (PVA) with poly(methacrylic acid) (PMAA) and blends of PVA with poly(acrylic acid) (PAA). The two systems showed quite different solubility behavior; i.e., PVA and PMAA precipitated in a 1:1 base ratio, characteristic of complex formation when their aqueous solutions were mixed. However, mixing PVA and PAA solutions did not result in precipitation; only transparent films were obtained after water evaporation. Therefore, PVA/PMAA and PVA/PAA were reported as a polymer complex and a miscible blend, respectively. It seemed disappointing that both systems presented quite similar NMR behavior including chemical shifts and relaxation time, etc. Quite recently, Maunu et al.[12] reported NMR results of blends of PAA/PEO, PAA/PVP, PMAA/PEO, and PMAA/PVP (PEO, poly(ethylene oxide); PVP, poly(vinylpyrrolidone)). The blends prepared by mutual precipitation from aqueous solutions and water-casting were referred to as complexes and blends, respectively. However, no clear differences between

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Table 1. Characterization Data of PS(OH) and Chromophore-Labeled PMMA

polymer PS	OH (mol %)	[η] (mL/g)
PS(OH)1	1.0	22.9
PS(OH)2	2.0	25.0
PS(OH)3	2.8	21.2
PS(OH)4	4.4	19.8
PS(OH)5	4.5	22.5
PS(OH)7	7.0	21.1
PS(OH)8	7.9	18.1
PS(OH)9	9.0	20.3
PS(OH)18	17.4	16.2
PS(OH)24	24	34.6

	$\bar{M}_w$	chromophore (mol %)
PMMA-a	98 000	0.25
PMMA-c	90 000	0.25

them in both ^{13}C peak chemical shifts and ^{1}H relaxation in the rotating frame, i.e., ^{1}H $T_{1\varrho}$, were detected. Thus, NMR is insensitive to differences between a complex and an ordinary miscible blend. Therefore, to distinguish a macromolecular complex from miscible blends, there is a need to develop techniques sensitive to molecular spatial distribution. Since we obtained preliminary and encouraging results from NRET fluorescence,[9] we make here a further effort to develop this technique. In recent years, high-resolution NMR has been proved very effective in studying specific interaction and miscibility in polymer blends. Various NMR parameters such as chemical shift, line width, relaxation times, spin diffusion, and nuclear Overhauser effect (NOE), etc., provided information about intermolecular interaction and the miscibility on different scales. Therefore, we try to use here NMR techniques to explore polymer–polymer complexation, as distinct from ordinary miscible blends.

Experimental Section

Monomers, Polymers, and Their Characterization. Hydroxyl-containing monomer *p*-(hexafluoro-α-hydroxypropyl)-α-methylstyrene (HFMS) was prepared as previously described.[5] Monomer 9-anthrylmethyl methacrylate (AMMA) was prepared by esterification.[9,13] PS(OH) with different contents of hydroxyl-containing units were prepared by copolymerization of styrene and HFMS as discussed previously.[5] The molar contents of HFMS in PS(OH) based on fluorine analysis and intrinsic viscosities of PS(OH) in toluene are listed in Table 1. PMMA-a, the AMMA-labeled PMMA, and PMMA-c, the carbozole-labeled PMMA, were produced by copolymerization of MMA with AMMA and vinylcarbazole, respectively.[13] The weight-average molecular weights of PMMA-a and PMMA-c were determined by size-exclusion chromatography (SEC) based on PS standards (Table 1).

In blend preparation, poly(styrene-*co*-acrylonitrile) (SAN) and polystyrene with narrow molecular weight distributions were used. A commercial SAN containing 22.6 wt % AN was fractionated. Three fractions with respective number-average molecular weights 5.3 × 10^{4}, and 15.6 × 10^{4}, and 21.2 × 10^{4} were employed. Commercial PS samples covering a broad molecular weight range prepared anionically with a dispersity index less than 1.05 were used as received.

NRET Fluorescence Measurements. The samples used in the fluorescence study were toluene-cast blend films of PS(OH)/PMMA-a/PMMA-c in a weight composition of 90/5/5. Polymer solutions were prepared in oxygen-free toluene. The solvent was allowed to evaporate at room temperature on a Teflon plate for 2 or 3 days followed by drying the film under vacuum at 60 °C for 3 days. Films with a thickness of 15 μm were used. Emission spectra were measured on a Hitachi 650–60 fluorescence spectrometer at room temperature. The excitation light at 294 nm was set perpendicular to the direction of emission. The energy transfer efficiency was characterized by the reciprocal of I_c/I_a, the ratio of emission intensity at 365 nm (I_c) to that at 416 nm (I_a), which are mainly contributed by energy-donor carbazole and energy-acceptor anthracene, respectively.

A series of parallel measurements were performed for blends of PS(OH)/PMMA-a/PMMA-c cast from tetrahydrofuran (THF) under the same conditions as mentioned above for the toluene-cast blends. In addition, blends of PS/PMMA-a/PMMA-c and SAN/PMMA-a/PMMA-c with different molecular weights of PS and SAN cast from oxygen-free toluene were prepared from the fluorescence measurements using the same procedure as is used for PS(OH)/PMMA-a/PMMA-c.

NMR Measurements. NMR studies include high-resolution ^{1}H spectra in solution, high-resolution ^{13}C spectra in solution, proton 1D nuclear Overhauser effect (NOE) spectra in solution, and CP/MAS solid-state ^{13}C NMR spectra. The experiments were conducted with a Bruker MSL-300 NMR spectrometer at 20 °C at frequencies of 300.13 and 75.47 MHz for ^{1}H and ^{13}C, respectively. The ^{1}H spectra were observed by the conventional single-pulse technique with a 90° pulse with a width of 6 μs and a repetition time of 5 s. Tetramethylsilane (TMS) was used as an internal chemical shift reference. In the ^{13}C spectra observations, a 90° single pulse with a 10 μs width was used. In the NOE measurements, the para and meta protons of the phenyl ring of PS(OH) were selectively irradiated with full presaturation. The NOE difference spectra were obtained by subtracting the normal proton resonance spectrum from the corresponding NOE spectrum. The solid-state ^{13}C spectrum measurements were performed by applying magic-angle sample spinning (MAS) and high-power spin decoupling. For improving the signal-to-noise ratio, the cross-polarization (CP) method was employed. The chemical shifts of ^{13}C spectra were obtained by taking the low-field carbon resonance of solid adamantane (37.6 ppm) as an external reference standard. Special attention was paid to the measurements of spin–lattice relaxation time ^{1}H T_1 and spin–lattice relaxation time in the rotating frame ^{1}H $T_{1\varrho}$ from CP/MAS ^{13}C NMR observations. By using suitable pulse sequences,[14] the relaxation information of an individual proton can be obtained from the individual carbon to which the proton is directly coupled.

The samples for solution NMR studies were prepared by dissolving PMMA and PS(OH), 50 mg for each, in 0.5 mL of deuterated chloroform at 50 °C. The solid-state blends were obtained as follows. First, 150 mg of PS(OH) and 150 mg of PMMA were dissolved in 3 mL of toluene followed by addition of 30 mL of methanol to precipitate the blend. The precipitate was dried under vacuum before the samples were used. A similar procedure was used for the blend preparation in trichloromethane/methanol.

Results and Discussion

A New Approach to NRET Fluorospectroscopy. Since NRET fluorescence was introduced for the study of polymer blends by Amrani et al.[15] about 15 years ago, this technique has proved to be an important supplement to the commonly used techniques such as DSC and TEM in studying the miscibility of polymer blends. Particularly, because NRET displays a resolution of about 2–4 nm, in the gap between routine techniques, this method has aroused increasing interest. In the conventional procedure of NRET, small portions of fluorescence energy donor and energy acceptor are attached to the component polymers. When the transition from immiscibility to miscibility of the blends occurs caused by the changing composition of the constituent random copolymer, the energy transfer between the donor and acceptor will dramatically increase since the average distance between them diminishes on a scale of 2–4 nm. In this laboratory, this technique has been successfully used in monitoring the miscibility enhancement caused by introducing hydrogen bonding as shown

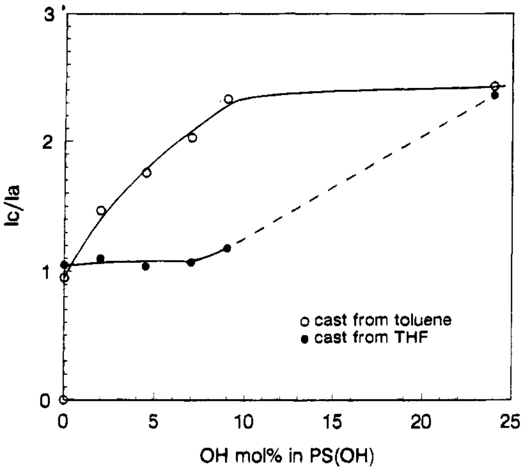


Figure 1. I_c/I_a of PMMA-a/PMMA-c/PS(OH) (5/5/90) blends, cast from toluene (○) and THF (●) as functions of the hydroxyl content in PS(OH).

in the systems of PMMA/PS(OH) and poly(butyl methacrylate)/PS(OH).[13] This gradual decrease of the reciprocal of energy transfer efficiency I_c/I_a from 1.6 to 0.4 accompanies the immiscibility–miscibility transition when the content of hydroxyl-containing units in PS(OH) reaches about 2 mol %. This amount of hydroxyl content has been confirmed to be sufficient to obtain miscible blends as judged by DSC and TEM. However, a further I_c/I_a decrease to 0.15 accompanies a further ascent of the hydroxyl content in PS(OH) to about 8–10 mol %. Combining the results of viscometry and NRET in solutions of the two component polymers in toluene, this energy transfer efficiency higher than that in the miscible blends could be rationalized by complexation between the constituents.[9] However, in comparison with the I_c/I_a change from immiscibility (1.6) to miscibility (0.4), the decrease corresponding to the probable transition from miscibility to complexation seemed to be small. We are trying, therefore, to find a better method for differentiating the molecular arrangement between an ordinary miscible blend and a polymer complex. For this purpose, a modified NRET approach has been used. Instead of attaching the donor and acceptor to the two components, part of the chains of one component is labeled with the donor and part with the acceptor. In blends composed of a donor-labeled polymer A, acceptor-labeled polymer A, and chromophore-free polymer B, an immiscible blend will give the largest energy transfer because polymer A chains with donor and acceptor labels are concentrated and randomly mixed in one of the phases. The efficiency is expected to decrease when the blend becomes miscible due to "dilution" of the labels by polymer B mixed with polymer A. A more pronounced variation is expected to accompany complexation. In the complex state, donor-labeled A and acceptor-labeled A are each paired with chains of polymer B. The donor and acceptor are to some extent "isolated" by the B chains, leading to a substantial decrease of the energy transfer efficiency. This efficiency change becomes even more substantial if polymer A constitutes the minor component, which is surrounded by the major component, i.e., chromophore-free polymer B. The experimental results are shown in Figure 1. For the blends of PMMA-a/PMMA-c/PS(OH) cast from toluene, the largest I_c/I_a (1.0) is associated with the immiscible blend without hydrogen bonding. This value increases to 1.4 as the OH content in PS(OH) ascends to 2.0 mol %, which is certainly miscible as evidenced by different techniques.[5,13] More pronounced variation of I_c/I_a occurs when the OH content increases further and finally levels off at a value of 2.4 after the OH content reaches 9 mol %. This much larger change of I_c/I_a occurring in the miscible blends caused by increasing hydrogen bonding density in comparison with that corresponding to the immiscibility–miscibility transition presents evidence of the difference in chain arrangements between the ordinary miscible blends and the polymer complex. It provides a criterion of complex formation. In the blends studied here the chromophore-labeled PMMA is a minor (10%) component, so that "complex blends" are in fact a homogeneous mixture of the complex with a probable composition of 1:1 base ratio[9] and excess PS(OH). Therefore, in these complex blends, PMMA-a/PS(OH) and PMMA-c/PS(OH) chain pairs are, to a great extent, isolated by the "free" PS(OH), presenting the least energy transfer efficiency. Our data show that, on increasing the amount of PMMA in the blends, the variation of I_c/I_a corresponding this miscibility–complexation transition gradually turns indistinct.

It was reported that miscibility[16] and complexation[9] in the blends due to hydrogen bonding were sensitive to the solvents used for blend preparation. Proton-accepting type solvents such as tetrahydrofuran (THF) and methyl ethyl ketone (MEK) destroy hydrogen bonding between the component polymers, retard miscibility, and prevent complexation. This is also confirmed by the I_c/I_a measurements of the PMMA-a/PMMA-c/PS(OH) blends cast from THF (Figure 1). Evidently, the toluene-cast blends and THF-cast blends show completely different I_c/I_a variations as functions of the hydroxyl content. In the THF-cast films the reciprocal of energy transfer efficiency is almost invariant with the value (1.05) of immiscible blends when the hydroxyl content varies from 0 to 7 mol %. A little increase of I_c/I_a is observed only when the hydroxyl content reaches 9 mol %, implying some enhancement of the miscibility. However, a considerable increase of I_c/I_a finally occurs reaching the value of 2.4, the same as that for toluene-cast complex blends, when the content in PS(OH) is as high as 24 mol %. This indicates that even in THF, which competes with PMMA as a hydrogen bond acceptor with hydroxyl in PS(OH), complexation is still finally possible provided the hydroxyl content in PS(OH) is high enough.

While the conventional NRET procedure is quite sensitive to the variation of phase structure, this modified approach is particularly susceptible to the subtle change of the chain interpenetration and chain arrangement in miscible blends. This is demonstrated by the following subsidiary experiments with two series of blends of PMMA-a/PMMA-c/PS and PMMA-a/PMMA-c/SAN, varying the molecular weights of PS or SAN. The former and the latter are typical immiscible[4,5] and miscible blends,[17] repsectively (Figure 2).

For the immiscible blends, I_c/I_a stays constant as the molecular weight of PS varies over a broad range from 2×10^3 to 3×10^5. This considerable variation of the PS molecular weight should give rise to an apparent change of phase structure of the immiscible blends such as phase shape, size, and interfacial area, etc. The data here prove the constancy of the modified NRET approach to the change in phase structure of immiscible blends. This is contrary to the conventional NRET procedure which has been reported to be sensitive to the change, but no quantitative relationship can be

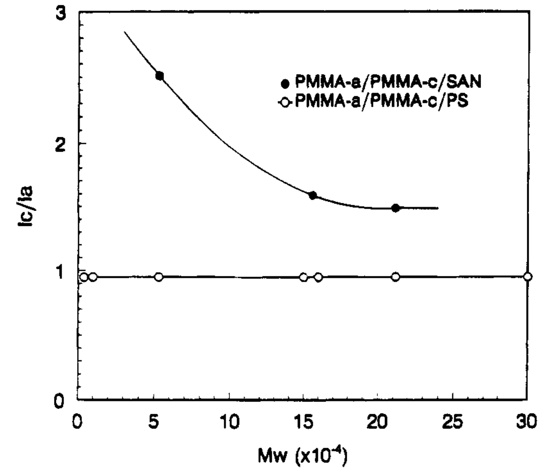


Figure 2. I_c/I_a of PMMA-a/PMMA-c/SAN (●) and PMMA-a/PMMA-c/PS (○) blends as functions of the molecular weights of SAN and PS.

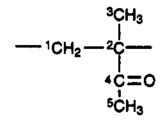
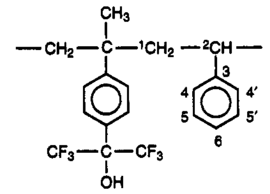
established.[13,15] For the miscible blends, using the modified procedure, an apparent increase of energy transfer efficiency in the blends is observed as the molecular weight of SAN increases from 5 × 10^4 to 21 × 10^4. This reflects the decrease of the degree of chain interpenetration or the extent of nonrandom mixing as the molecular weight of SAN increases. This kind of subtle variation in miscible blends was only monitored by excimer measurements as reported by Semerak and Frank.[18] However, in this method, one of the blend constituents must be an excimer-forming polymer and its content in the blends has to be kept at a level as low as about 0.01 wt %. Due to these limitations, the technique has not been widely used.

The procedure of labeling only one component was used by Zhao et al.[19] first for studying miscible PVC/PMMA blends, confirming the effect of molecular weight and tacticity of PMMA on the degree of chain interpenetration.

Solid-State ^{13}C NMR Studies. In this part of the study we take the advantage of accurate measurements of ^{1}H T_1 and $T_{1\varrho}$ for each type of protons based on ^{13}C CP/MAS techniques. Generally, this kind of study is able to provide information of how homogeneously the two component polymers mix, because, typically, ^{1}H $T_{1\varrho}$ presents information of homogeneity on a scale of 2–3 nm and ^{1}H T_1 on a scale of 20–30 nm.[20]

In this study, ^{13}C CP/MAS spectra of pure PMMA and PS(OH) with different OH contents and their blends (w/w, 1/1) prepared from a toluene/methanol system were measured. The assignments of the resonance peaks are shown in Table 2. For PS(OH), the content of hydroxyl-containing units is small and the chemical shifts are similar for styrene and HFMS; no separated peaks associated with the carbon atoms in the hydroxyl-containing units have been clearly detected.

Table 2. Assignments of ^{13}C CP/MAS Spectra of PS(OH) and PMMA

structure	chemical shift (ppm)	carbon assignment
	56.0	1
	44.0	2
	15.3	3
	176.6	4
	51.0	5
	39.4	1,2
	139.3	3
	128	4,4′,5,5′,6

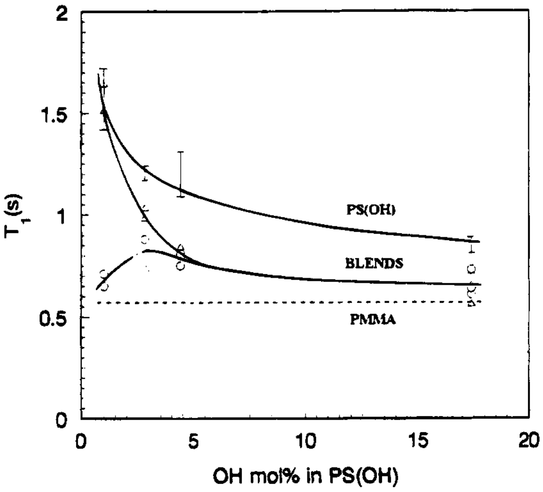


Figure 3. Spin–lattice relaxation time ^{1}H T_1 of PS(OH) and PS(OH)/PMMA blends as a function of the hydroxyl content in PS(OH). The bars show the value range of ^{1}H T_1 of the protons attached to different carbons in pure PS(OH). △ and ○ refer to ^{1}H T_1 of different protons of PS(OH) and PMMA in the blends, respectively. The mean value of ^{1}H T_1 of pure PMMA is shown as a dashed line for reference.

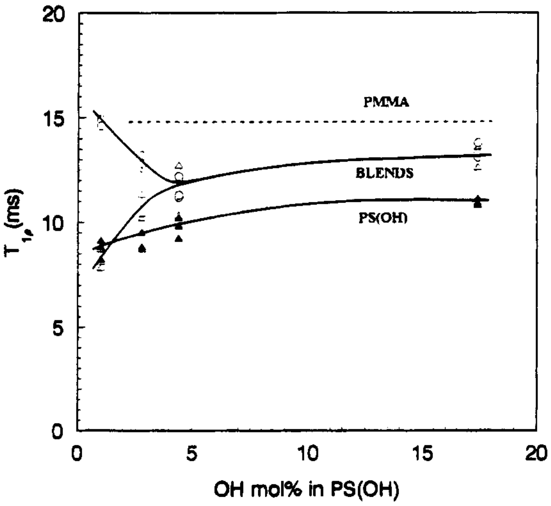


Figure 4. Relaxation time in a rotating frame ^{1}H $T_{1\varrho}$ of protons attached to different carbons in pure PS(OH) (▲), PS(OH) in the blends (△), and PMMA in the blends (○) as functions of the hydroxyl content in PS(OH). The mean value of ^{1}H $T_{1\varrho}$ of pure PMMA is shown as a dashed line for reference.

All carbon resonances of the pure polymer PMMA, PS(OH), and their blends show single-exponential decay in both ^{1}H T_1 and $T_{1\varrho}$ experiments. The corresponding ^{1}H T_1 and $T_{1\varrho}$ results for the main resonance lines are shown in Figures 3 and 4, respectively. For each pure polymer, i.e., PMMA and PS(OH) with different contents of hydroxyl, the protons attached to different carbons show similar relaxation times, indicating that the spin diffusion equalizes the relaxation rates of all protons. In addition, ^{1}H T_1 and ^{1}H $T_{1\varrho}$ values of PS(OH) show a gradual decrease and increase, respectively, as the hydroxyl content in PS(OH) is increased. Fortunately, the differences in both ^{1}H T_1 and $T_{1\varrho}$ between PMMA and PS(OH) are substantial; this makes it convenient to get information of the phase behavior of their blends by the relaxation time analysis. From Figure 3, it is clearly seen that for the blends PS(OH)1/PMMA and PS(OH)3/PMMA, T_1 values associated with PMMA and PS(OH) protons are apparently different but relatively close to those of the corresponding pure constituents. This indicates heterogeneity of the blends on a scale of 20–30 nm. However, the situation changes considerably when the hydroxyl content in PS(OH) increases; i.e., in PS(OH)4/PMMA and PS(OH)18/PMMA, all protons of the two components possess almost the same relaxation time ^{1}H T_1 within experimental error. This clearly indicates the homogeneity caused by increasing hydrogen-bonding density.

A similar situation can be found for the case of ^{1}H $T_{1\varrho}$ (Figure 4). For the blends with low hydrogen bonding density, i.e., PS(OH)1/PMMA and PS(OH)3/PMMA, different ^{1}H $T_{1\varrho}$ values for PS(OH) and PMMA are obtained. However, no substantial difference in ^{1}H $T_{1\varrho}$ between PS(OH) and PMMA components in the blends with higher hydroxyl contents, i.e., PS(OH)4/PMMA and PS(OH)18/PMMA, is observed. This means that the components are homogeneously mixed not only on a scale of 20–30 nm but also on a scale as low as 2–3 nm. This is evidence of the miscibility at a segmental level. Another series of ^{1}H T_1 and ^{1}H $T_{1\varrho}$ measurements carried out for blends precipitated from trichloromethane/methanol led to the same conclusions.

Generally, the general trend of miscibility enhancement of the blends PS(OH)/PMMA via introducing hydrogen bonding concluded from this NMR study is in good accordance with the results we have obtained for the blends based on IR, DSC, TEM, and NRET fluorospectroscopy.[5,6,13] The observations reported previously by a combination of the techniques have not shown an "intermediate range" of hydrogen content that causes blends to be homogeneous on large (20–30 nm) but not on small (2–3 nm) levels. NMR T_1 and $T_{1\varrho}$ measurements do not present any evidences for the presence of the range either.

On the basis of the NMR data, the least OH content in PS(OH) capable of making the blends miscible is between 2.8 and 4.4 mol %, which is apparently larger than the value of about 2 mol % on the basis of other techniques. This discrepancy can be attributed to the difference in blend preparations. The samples used in the previous experiments were toluene-cast films; a slow evaporation process favored establishing the intercomponent hydrogen bonding. However, the samples in this study were precipitates from toluene or trichloromethane by adding a large amount of methanol. Methanol, as a weak proton-donor solvent, is probably unfavorable for the hydrogen bonding between the polymer components and leads to a larger requirement of the hydroxyl content in PS(OH) for miscibility.

Although the NMR relaxation study has provided instructive information on miscibility and morphology, for the problem that concerns us most, i.e., to distinguish a polymer complex from an ordinary miscible blend, the relaxation studies seem powerless. Even for the blends with an OH content in PS(OH) as high as 18 mol %, in which complexation is believed to exist, the NMR results do not show any change. In terms of the "homogeneity scale", the complex behavior is the same as that of the ordinary miscible blends. Although in some NMR studies some blends were regarded as "complex",[10-12] this identification was mainly based on the stoichiometry of precipitation from solutions of polymer mixtures rather than its microstructural information.

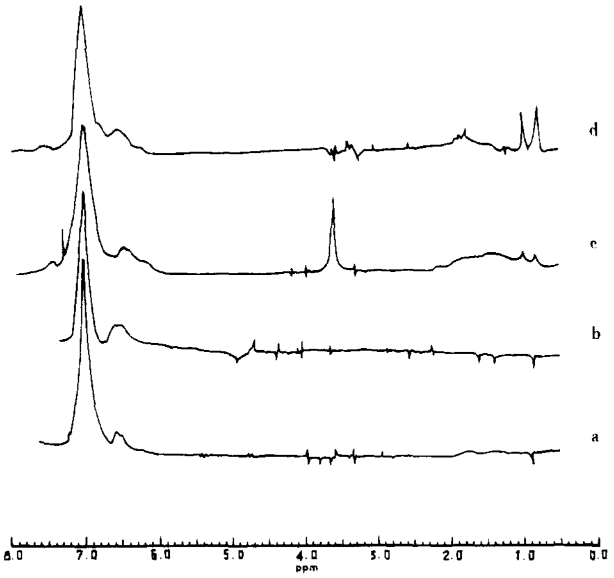


Figure 5. 1D NMR NOE spectra of blend solutions in $CDCl_3$ of PS(OH)1/PMMA (a), PS(OH)8/PMMA (b), PS(OH)18/PMMA (c), and PS(OH)18/PMMA after adding deuterated acetone (d).

Solution NMR Studies. In previous studies on the interaction and morphology of polymer blends of PMMA and PS(OH), it was found that complexation caused by hydrogen bonding in solvent-cast blends stemmed from intermacromolecular complexation in solution, even when the concentration is as low as 1×10^{-3} g·mL^{-1}.[9] This tight combination of component macromolecules in solution was evidenced by both viscometry and NRET fluorospectroscopy. High-resolution NMR of a blend solution, generally, may provide information of interaction and intimate molecular proximity and has been successfully used in many systems.[10,11,21-24] In this study, ^{1}H and ^{13}C spectra and ^{1}H NOE difference spectra of the blends in deuterated chloroform were measured. Usually, hydrogen bonding in solutions can be monitored through the characteristic downfield shifts of the resonances of protons and carbons in the H-bond-forming groups. Unfortunately, in the present case, the variation of the chemical shifts of the related resonances is not apparent enough to provide convincing information since the ^{1}H resonance peaks of hydroxyl (3.63 ppm) and methoxyl (3.6 ppm) are too close to each other to be resolved and OH-containing groups and carbonyl groups bonded in hydrogen bonds are always minor in the constituents.

NOE NMR has been a powerful tool for monitoring intermolecular interaction. According to theory,[25] NOE depends on the sixth power of the inverse of the interproton distance, the effective correlation time, and mixing time. Usually, an interproton distance larger than 4 Å results in no appreciable NOE. Therefore, NOE can be used as a probe of chain proximity on a scale as small as 4 Å. In recent years it has been successfully employed in systems with intercomponent ion–ion interaction[22,23] and hydrogen-bonding[21] and self-associating networks of graft copolymer.[24]

In this study, the main attention was paid to the effect of the hydroxyl content in PS(OH) on NOE of the solutions of PMMA and PS(OH) in deuterated chloroform. The related NOE spectra are shown in Figure 5. The phenyl-ring meta and para protons were selectively irradiated with presaturation. For the blend solution of PS(OH)1/PMMA, the only apparent signals observed in the difference spectrum are the presaturated phenyl-ring protons and the ortho protons. When the OH content increases to 8 mol %, although some fluctuation is observed, still no significant NOE is recorded. Both cases indicate that there is no intimate molecular proximity. However, for the case of a PS(OH)18/PMMA solution, in the NOE difference spectrum, a relatively sharp resonance of OCH_3 of PMMA around 3.6 ppm appears and a broad resonance peak covering a chemical shift from 0.6 to 2.0 ppm associated with $-CH-$ and $-CH_2-$ protons appears as well. This presents definite evidence of a proximity of less than 4 Å between phenyl-ring protons of PS(OH) and those of OCH_3 of PMMA, implying that PS(OH) chains are intimately associated with PMMA chains. Since the OCH_3 and the phenyl ring are on the outside of the PMMA and PS(OH) chains, they are more likely to come close to each other when the two polymer chains form a complex due to strong hydrogen bonding. Although complexation always accompanies entropy loss, it can be compansated by the favorable enthalpy of hydrogen bonding. That the driving force for complexation is hydrogen bonding has found further support from an additional experiment. As shown in curve d, the difference NOE curve of PS(OH)18/PMMA in $CDCl_3$ considerably changes when a small amount of deuterated acetone is added. The OCH_3 proton resonance peak almost disappears with fluctuation remaining and the resonance area from 0.6 to 2.0 ppm decomposes to some relatively well-resolved peaks. This presents evidence of dissociation of the component chains. Clearly, the proton-accepting ability of acetone added is responsible for this effect.

Generally, the NOE results in the $CDCl_3$ solution and those obtained from NRET fluorescence and viscometry for the blend solutions in toluene reported previously[9] supplement each other. They all show the dependence of the chain association on the hydroxyl content in PS(OH). However, the least values of OH contents in PS(OH) leading to complexation in the two cases are different. This becomes understandable if the difference of the solvents used is taken into account. Toluene is an inert solvent with no interference for hydrogen bonding between the components, while $CHCl_3$ competes with hydrogen bonding as reported by Qiu et al.[26] and Chen et al.[16]

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References and Notes

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