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Intermacromolecular complexation due to specific interactions: 3. Miscibility and complexation of PBMA and PS(OH)

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The structural changes as a function of OH concentration in the blend system of poly(n-butyl methacrylate) (PBMA) and hydroxyl-modified polystyrene (PS(OH)) are investigated by a non-radiative energy transfer technique and viscometry. It is shown that, for blends cast from toluene, only 1 mol% OH concentration in PS(OH) is capable of rendering PS(OH) miscible with PBMA. When the OH concentration in PS(OH) increases to 18 mol%, complexation is able to take place between PS(OH) and PBMA. This indicates that by progressively increasing the hydrogen bonding interaction, PS(OH)/PBMA blends can achieve immiscibility–miscibility–complexation transitions successively. For blends cast from tetrahydrofuran (THF), miscibility is achieved when OH concentration increases to 2.8 mol%, and no complexation occurs even at OH concentration as high as 24 mol%. In addition, the glass transition temperatures for THF-cast blends are lower than those of the corresponding blends cast from toluene. The high glass transition temperatures for blends cast from toluene can be attributed to an extensive degree of interpolymer hydrogen bond formation.

(Keywords: miscibility; complexation; hydrogen bonding)

Introduction

In our previous papers of this series[1,2], the miscibility and complexation of hydroxyl-modified polystyrene (PS(OH)) and poly(methyl methacrylate) (PMMA) have been investigated by nuclear magnetic resonance (n.m.r.), viscometry and non-radiative energy transfer (n.r.e.t.) techniques. PS(OH)s are the copolymers of styrene and *p*-(hexafluoro-2-hydroxyisopropyl)-α-methylstyrene (HFMS). It was demonstrated that, by progressively strengthening the intercomponent interactions (hydrogen bond), the PS(OH)/PMMA blend can achieve immiscibility–miscibility–complexation transitions successively, which, in terms of molecular arrangements, correspond to changes of the unlike polymer chains from the separated state to the randomly mixed state and, furthermore, to the paired state. Immiscibility–miscibility transitions can routinely be distinguished by their morphological change from the separated phase to the single phase[3]. However, for the miscibility–complexation transition, the miscible blend and the complex blend possess identical morphology (single phase) and cannot be distinguished by commonly used techniques such as differential scanning calorimetry (d.s.c.) and transmission electron microscopy (TEM). In this case, more sensitive techniques such as n.r.e.t. and n.m.r. should be used[4].

In the area of miscibility enhancement by the introduction of hydrogen bonding, concerted effort has been placed on clarifying the necessary favourable interpolymer interactions required to achieve miscibility[5–7], and little attention has been paid to the structural changes related to miscibility and complexation[8–10]. In order to gain a more explicit understanding of the structural changes as a function of strengthening the interpolymer interactions at a molecular level, we have extended the experiment to the system PS(OH)/poly(n-butyl methacrylate) (PBMA), with OH concentration in PS(OH) up to 24 mol%. The n.r.e.t. technique and viscometry were employed in solution and in bulk[11,12]. The main interest of the n.r.e.t. technique lies in its ability to monitor changes in blend miscibility at a scale of *c.* 3 nm, which is well below the scale of d.s.c.[13,14]

Experimental

Monomers, polymers and characterization. Hydroxyl-containing monomer HFMS and energy-acceptor-containing monomer 9-anthryl methyl methacrylate (AMMA) were prepared as previously described[1,3].

PS(OH) is a copolymer of styrene, HFMS and vinyl carbazole. PBMA is a copolymer of n-butyl methacrylate and AMMA. Copolymerization was conducted in benzene at 60°C using azobisisobutyronitrile as initiator. The total conversion of the monomers was kept at less than 10%. The molar contents of HFMS in PS(OH) were calculated from fluorine measurements. The chromophore contents in copolymer are determined by u.v. spectroscopy, assuming that the extinction coefficient of the chromophores in the copolymers is the same as in the corresponding monomers. Characterization data of polymers are listed in *Table 1*.

Fluorescence measurements. Steady-state fluorescence spectroscopy was conducted on a Hitachi 650-60

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Table 1 Characterization of fluorophore-labelled polymers

Polymers	$[\eta]$ (ml g^{-1})	Hydroxyl (mol%)	Chromophore (mol%)
PS	23.2	0	0.25
PS(OH)-1	22.4	1.0	0.25
PS(OH)-2	21.8	2.3	0.25
PS(OH)-3	21.2	2.8	0.30
PS(OH)-5	19.8	4.5	0.25
PS(OH)-10	17.4	9.5	0.24
PS(OH)-18	16.2	17.4	0.26
PS(OH)-24	34.6	24.0	–
PBMA-1	52.2	–	1.0
PBMA-2	55.7	–	0.25

fluorescence spectroscope at 25°C. An excitation wavelength of 294 nm was used. The energy transfer efficiency was characterized by 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 carbazole and anthracene, respectively. Samples of polymer solution (1 mol%) were prepared with carbazole-labelled PS(OH) and anthryl-labelled PBMA-1. Before measurement, the individual solutions of PS(OH) and PBMA-1 were mixed in equal molar ratio in a quartz cell (1 × 1 cm) and degassed with nitrogen for 1 min. The excitation was set in the direction perpendicular to the detection of emission. The samples of blend films used in the fluorescence measurement were solvent-cast films of PS(OH)/PBMA-2 in 50/50 weight composition. The films were prepared from 5 wt% polymer solutions (THF, toluene); the solvent was allowed to evaporate at room temperature on a Teflon plate for 2 or 3 days, after which the films were dried under vacuum at 60°C for 3 days. Films of 15 μm thickness were used. The incident excitation beam was oriented at 60° and the axis of observation was oriented at 30° with respect to the sample surface. Each value of I_c/I_a is the average value of three samples.

Viscosity measurements. Viscosities of solutions were measured at 30 ± 0.05°C with an Ubbelohde-type viscometer. A Huggins' plot was used to estimate the intrinsic viscosities $[\eta]$. The kinetic energy correction was always neglected.

Glass transition measurements. The glass transition (T_g) values of polymer films were determined with a Dupont 1090B thermal analyser. The polymer sample and an empty reference pan were heated at a rate of 10°C min^{-1} up to 140°C for 5 min. The sample was then rapidly quenched in liquid nitrogen and the thermal behaviour was recorded from −10 to 120°C.

Results and discussion

Hydroxyl concentration dependence of complexation. For hydrogen bonding interpolymer complexes, interpolymer complexation in solution always accompanies a contraction of the component polymer chains, resulting in a viscosity decrease[15]. Viscometry has been proven to be an effective method for the characterization of complexation and macrostructure of the complex[16]. *Figure 1* shows the reduced viscosity of the PS(OH)/PBMA mixture as a function of solution composition (the molar ratio of PS(OH)/PBMA) in toluene. For mixtures of PS(OH)/PBMA with OH concentration less than 18 mol%, the viscosity changes monotonically with the mixture composition; the reduced viscosity of mixed solution at each composition equals the weight average viscosity value of the two component polymers, indicating that no complex is formed in these solutions[15]. When OH concentration in PS(OH) reaches 18 mol%, the progressive addition of PS(OH) into the PBMA solution induces a pronounced decrease in solution viscosity, showing evidence of complex formation. In this plot, the viscosity minimum is observed at a molar base ratio of PS(OH)/PBMA of 2.5 : 1, which is regarded as the fixed mean stoichiometry (FMS) of the complex[16]. When OH concentration in PS(OH) increases to 24 mol%, PS(OH) is able to form a stoichiometric complex with PBMA at a base ratio of 1 : 1. This implies that, for PS(OH)-24/PBMA complex, the hydrogen bonding density in PS(OH) is strong enough to prevent the remaining inert segments from possessing their own PBMA counterpart, leading to a paired structure[1]. In comparison with the PS(OH)/PMMA complex, the critical OH concentration to achieve complexation for PS(OH)/PBMA (18 mol%) is much higher than that for PS(OH)/PMMA (8 mol%). It seems that the butyl groups in PBMA exert a considerable steric hindrance to complex formation.

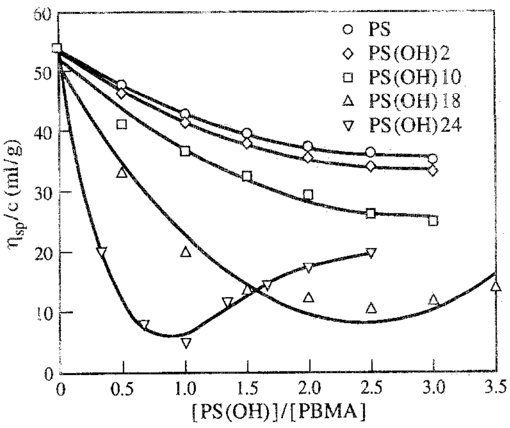

Figure 1 Plots of reduced viscosity as a function of molar composition for PS(OH)/PBMA mixtures in toluene solution

It is worth noting that mean stoichiometry variation with hydrogen bonding density has been reported in several complex systems[15,17]. Generally, the FMS value of a complex depends on both the interaction densities and the molecular weights of the component polymers. In the laboratory, interpolymer complexes are commonly prepared by mutual precipitation. It was demonstrated previously that, when two polymers are mixed at a certain composition, the complex precipitate thus obtained always has a composition in between the feed composition and its FMS[1].

Plots of viscosity *versus* composition for PS(OH)/PBMA mixture in THF are depicted in *Figure 2*. All of the mixtures show a homogeneous variation of viscosity *versus* composition, indicating that no complex can be formed in THF solution even at an OH concentration as high as 24 mol%. This is because THF is also a proton acceptor and can compete with PBMA to form hydrogen bonds with PS(OH). This property can be confirmed with n.r.e.t. spectroscopy by adding a small amount of

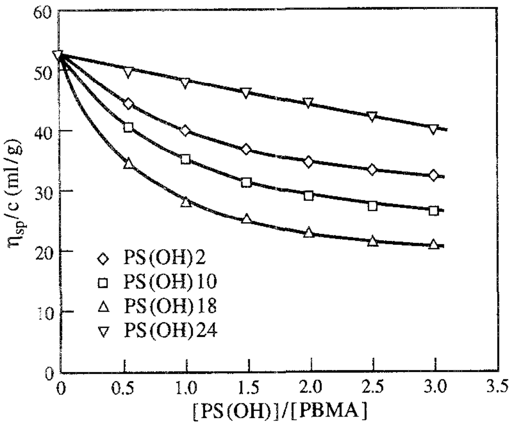

Figure 2 Plots of reduced viscosity as a function of molar composition for PS(OH)/PBMA mixtures in THF solution

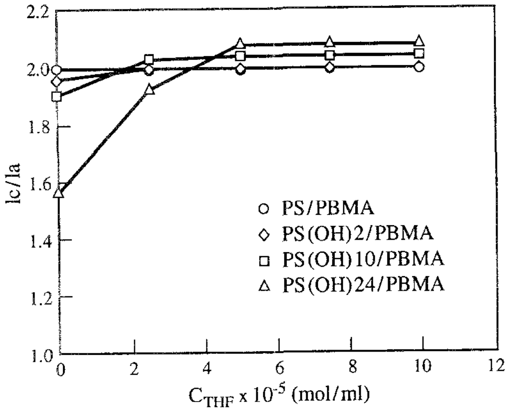

Figure 3 Ratio of donor and acceptor fluorescence of PS(OH)/PBMA (1 : 1) in toluene as a function of THF concentration

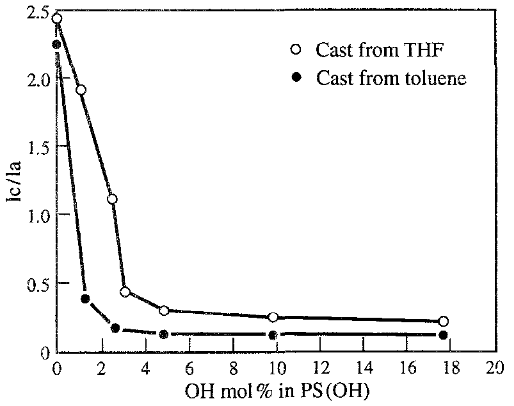

Figure 4 Ratio of donor and acceptor fluorescence of PS(OH)/PBMA blends as a function of OH content

THF into the PS(OH)/PBMA (1 : 1 molar ratio) toluene solution. As shown in *Figure 3*, in the absence of THF, i.e. the points intersecting the vertical axis, a much lower I_c/I_a value is exhibited by the PS(OH)-18/PBMA mixture, while the others remain close together at a rather higher value. The lower I_c/I_a value is obviously an indication of enhanced mutual approach between PS(OH) and PBMA due to complexation[18]. With the addition of THF, the I_c/I_a value of the PS/PBMA solution remains constant, as expected. But for the complexed mixture of PS(OH)-18/PBMA solution, the addition of THF causes the initial I_c/I_a value to increase dramatically up to the same level as the PS/PBMA solution, suggesting that the PS(OH)-18/PBMA complex is broken down to an isolated state. Close inspection reveals that a small change of I_c/I_a—an increase with OH concentration in PS(OH)—is also shown by other PS(OH)/PBMA mixtures, which may be related to a kind of weak association between PS(OH) and PBMA chains.

Complexation effect on blends. In probing the miscibility of polymer blend with the n.r.e.t. technique, it is desirable to keep the concentration of the labelled chromophore between 10^{-3} and 10^{-2} mol l^{-1} to avoid interference from radiative energy transfer and energy migration[13,14]. Therefore, in the present study, the concentration of chromophores was controlled at 2.5×10^{-3} mol l^{-1}, almost the lowest concentration ever used in a miscibility study. At this concentration, the n.r.e.t. technique is expected to show a higher sensitivity to the change in the miscibility region. The I_c/I_a value as a function of OH concentration for PS(OH)/PBMA blends cast from toluene and THF is illustrated in *Figure 4*. It is shown that about 1 mol% of OH units (HFMS) in PS(OH) are capable of rendering PS miscible with PBMA for blends cast from toluene, and a higher OH concentration (*c.* 2.8 mol%) is required when the blend is cast from THF. The critical OH concentration to achieve miscibility (cast from toluene) is in agreement with the previous d.s.c. measurement reported by Pearce *et al.*[5]. Interestingly, the OH concentration required to achieve miscibility for the PS(OH)/PBMA blend (1 mol%) is smaller than that for the PS(OH)/PMMA blend (2 mol%), which is in contrast to the complexation behaviour of both systems. In addition, the I_c/I_a values for the critical miscible blend in both solvents are about 0.40, similar to the value (0.45) of the model blend PMMA-a/PMMA-c (50/50) with the same labelling concentration[1]. This suggests that, in this state, the affinity between the unlike polymer chains and the like polymer chains is nearly the same. The chains of the two polymers in the blends can be considered to be in a randomly distributed state. In the plateau region of the miscibility blends (*Figure 4*), the change of I_c/I_a decreases continuously, although at a progressively decreasing rate, with OH concentration. This means that the affinity between unlike polymer chains is further enhanced by the increase of hydrogen bonds. The more efficient energy transfer can be attributed to a higher proportion of close proximity between PS(OH) and PBMA[14].

It is well known that the miscibility of hydrogen bonding blends depends profoundly on the casting solvent[11]. The proton donor (or acceptor) solvent can suppress the miscibility of the blend by forming polymer–solvent hydrogen bonding. This phenomenon is clearly observed in the PS(OH)/PBMA system. As mentioned above, for THF-cast blends, more OH concentration is required for PS(OH) to achieve miscibility with PBMA than for toluene-cast blends. The casting solvent effect is still observable in the area of miscibility. As shown in *Figure 4*, in the OH range of 2.8–18 mol%,

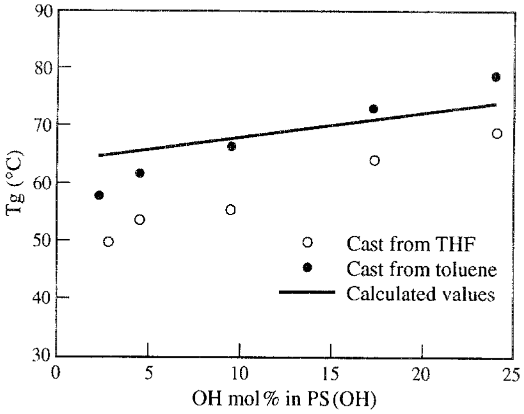

Figure 5 Effect of hydrogen bonding density on T_g for PS(OH)/PBMA blends

the I_c/I_a values of THF-cast blends are always lower than those of the corresponding toluene-cast blends. Among them, the complex blend of PS(OH)-18/PBMA exhibits the most efficient energy transfer. This gives further evidence that the interpenetration of unlike chains in the blend is enhanced by hydrogen bonding.

The d.s.c. result for PS(OH)/PBMA miscible blends is shown in *Figure 5*. The calculated weight-average T_g values of the component polymers are also shown in this plot as an oblique line, where the slight slope is caused by the increasing T_g values of PS(OH) incorporated with higher concentration of OH units. From this plot, the following observations should be addressed.

(1) For blends cast from both solvents, the miscibility ranges determined by d.s.c. are in agreement with the n.r.e.t. measurement.
(2) Owing to the solvent casting effect, the T_g values for blends cast from THF are systematically lower than those of the corresponding blends cast from toluene, showing a correlation with the result of *Figure 4*. The higher T_g values for toluene-cast blends can be attributed to an extensive degree of interpolymer hydrogen bond formation[4].
(3) For the complex blends PS(OH)-18/PBMA and PS(OH)-24/PBMA, the T_g values exceed the weight-average values of the component T_gs, while for the ordinary miscible blend, the T_g is lower than the calculated T_g value. In addition, the T_gs from THF- and toluene-cast blends fall in two parallel lines with greater slope than the calculated T_gs, indicating that the T_g increment rates for PS(OH)/PBMA blends cast from both solvents are higher than the calculated values. The extra increase of T_g also results from the gradual increase in hydrogen bond formation.

Conclusion

The structural changes as a function of OH concentration in the system PS(OH)/PBMA were investigated by n.r.e.t. technique, viscometry and d.s.c. Results show that the affinity between PS(OH) and PBMA can be greatly enhanced by hydrogen bonding interaction. For blends cast from toluene, an OH concentration of only 1 mol% is capable of rendering PS(OH) miscible with PBMA. When the OH concentration is PS(OH) increases to 18 mol%, PS(OH) is able to form complexes with PBMA. The stoichiometric complex with 1 : 1 base ratio is achieved for PS(OH)/PBMA with 24 mol% OH concentration. This indicates that, in the OH range under investigation, PS(OH)/PBMA blends can achieve immiscibility–miscibility–complexation transitions successively, which, in terms of chain arrangements, correspond to the changes of unlike chains from the separated state to the randomly mixed and to the close proximity state. For blends cast from THF, the hydrogen bonding between PS(OH) and PBMA is weakened by the competing binding of THF molecules. As a result, the immiscibility–miscibility transition is achieved at a higher OH concentration of about 2.8 mol%, and no complexation can be achieved even at OH concentration as high as 24 mol%. In addition, in the miscibility region, the T_g values for blends cast from THF are consistently lower than those of the corresponding blends cast from toluene. The high T_g values in toluene can be attributed to an extensive degree of interpolymer hydrogen bond formation[4].

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