Intermacromolecular complexation due to specific interactions: 1. The hydrogen-bonding complex between poly(methyl methacrylate) and modified polystyrene

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Intermacromolecular complexation between poly(methyl methacrylate) and modified polystyrene (PS(OH)) with the introduction of strong proton-donating hydroxyl groups has been studied by means of viscometry and non-radiative energy transfer (NRET) spectrofluorimetry. By increasing the hydroxyl content in PS(OH), both the transitions from immiscibility to miscibility and then from miscibility to complexation in the toluene-cast blends can be realized. A stoichiometric complex (1:1 base ratio) forms when the hydroxyl content reaches a high ($\sim$24 mol%) value. The NRET studies present evidence that in the complex, the polymer chains prefer to form unlike segment pairs rather than like ones. An apparent solvent effect on complexation is also observed for both solution and solvent-cast films

(Keywords: intermacromolecular complex; polymer blends; hydrogen bonding)

INTRODUCTION

Based on the type of interactions which lead to complexation, macromolecular complexes can be divided into four classes, i.e. hydrogen-bonding complexes, polyelectrolyte complexes, stereocomplexes and charge-transfer complexes. In the first publication in this series, we shall deal only with hydrogen-bonding complexes. Although many complex-forming polymer pairs in which the component polymers possess proton-donor and proton-acceptor properties have been extensively studied, most of these are water soluble polymers and the complexation occurs in water or in strongly polar solvents[1]. In early work, interest was focused on the formation and composition of the complexed states. Recently, much attention has been paid to the microstructure of the complexes, and in particular the degree of chain interpenetration in the complexes. In this respect, cross-polarization/magic angle spinning (CP/MAS) ^{13}C n.m.r. is of great advantage, as has been reported by Suzuki *et al.*[2] for poly(4-hydroxystyrene)/poly(*N*,*N*-dimethylacrylamide) and Zhang *et al.*[3] for poly(vinyl alcohol)/poly(acrylic acid).

The study of hydrogen-bonding complexation in our laboratory is actually an extension of our long-term research on the introduction of hydrogen bonding in order to enhance miscibility in polymer blends. In our previous papers[4–6], it was reported that the introduction of a hydroxy-containing unit, i.e. *p*-(1,1,1,3,3,3-hexafluoro-2-hydroxy-propyl)-α-methylstyrene (HFMS) into polystyrene, to give a material which we shall refer to as PS(OH), can greatly improve its miscibility with poly(acrylic ester)s. For example, less than 2 mol% of HFMS in PS can render it completely miscible with poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), poly(butyl methacrylate) (PBMA) or poly(butyl acrylate) (PBA), as judged by differential scanning calorimetry (d.s.c.), transmission electron microscopy (TEM) and non-radiative energy transfer (NRET) spectrofluorimetry. For the latter technique, of course, energy-donor and energy-acceptor labels were attached to PS(OH) and PMMA, respectively. This miscibility enhancement, which occurs as a result of intercomponent hydrogen bonding, is theoretically supported by the work of Yang *et al.*[7].

The most outstanding results to be obtained from the NRET study of this system relate to the blends with a high hydrogen-bond density[6], i.e. when the hydroxyl content in PS(OH) reaches $\sim$7–10 mol%, the blends show unusually high energy-transfer efficiency, which is double that of the corresponding miscible blends. Meanwhile, it was reported[6,8] that precipitation occurred when mixing solutions of higher-hydroxyl-content PS(OH) and poly(acrylic ester)s. Both these results provide clear indications of complex formation between the components with high hydrogen-bonding densities. In this paper, viscometry and NRET spectrofluorimetry are used as the main techniques for studying the process of complexation between PS(OH) and PMMA, with an emphasis on the conditions for formation of the complex, chain interpenetration in the complex and the effect of solvent on the complexation.

Differing from all of the intermolecular complexes previously reported in the literature, in which the repeat units of both component polymers possess their own complementary binding sites, in this present system, since

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the hydroxyl content can be varied by simply changing the HFMS content in the polymerization feed, the hydrogen-bonding intensity is therefore controllable. This presents the great advantage of realizing transitions from immiscibility to miscibility, and then to complexation, in the same blend system. Therefore, in this study we are able to concentrate on the relationship between the hydrogen-bonding density and complexation, which has not so far been studied for any complex systems with synthetic polymers.

EXPERIMENTAL

Materials

p-(1,1,1,3,3,3-Hexafluoro-2-hydroxypropyl)-α-methylstyrene (HFMS) was synthesized as previously described[4]. 9-Anthryl methyl methacrylate (AMMA, m.p. 85–87°C) was prepared by esterification of methacryloyl chloride with 9-anthrylmethanol according to the procedure of Stolka[9]. Vinyl carbazole (VC) was purchased from Aldrich.

Polymers

Carbazole-labelled PS(OH), i.e. copolymers of styrene, HFMS and VC, were prepared by terpolymerization of the corresponding monomers. Anthracene-labelled polymers (PMMA-A), were produced by polymerizing methyl methacrylate and AMMA. Polymerization was allowed to proceed to a low conversion of ~10% at 60°C in benzene using azoisobutyronitrile (AIBN) as the initiator. The precipitation of fractions of PMMA, to give samples PMMA-1,2,3,4, was conducted in chloroform using methanol as the precipitant.

Characterization of polymers

The compositions, and values obtained for the intrinsic viscosity $[\eta]$ and the Huggins constant k' in toluene of the PS(OH) copolymers are listed in *Table 1*: the chromophore contents were determined from u.v. spectroscopic measurements, assuming that the extinction coefficients of the chromophores in the copolymers were the same as those in the corresponding monomers. The molar content of HFMS in the various PS(OH) copolymers was calculated from fluorine measurements; these values were found to be slightly lower than the feed compositions. The characterization data for the PMMA polymers are listed in *Table 2*. The weight-average molecular weight M_w, the number-average molecular weight M_n and the molecular weight distribution index M_w/M_n were determined by gel permeation chromatography, based on a universal calibration with PS standards[10].

Table 1 Characteristics of the PS(OH) copolymers

Polymer	VC content (mol%)	OH content (mol%)	$[\eta]$ (ml g^{-1})	k'
PS	0.25	0	23.2	0.37
PS(OH)-1	0.25	1	22.9	0.49
PS(OH)-2	0.25	2.3	21.8	0.51
PS(OH)-3	0.30	2.8	21.2	0.58
PS(OH)-5	0.25	4.4	19.8	0.72
PS(OH)-8	0.50	7.9	18.1	0.57
PS(OH)-10	0.24	9.5	17.4	0.55
PS(OH)-18	0.26	17.4	16.2	0.44
PS(OH)-24	–	24.0	34.6	0.51

Table 2 Characteristics of the PMMA samples[a]

Polymer	M_w ($\times 10^{-4}$)	M_n ($\times 10^{-4}$)	M_w/M_n	Chromophore (mol%)
PMMA-A1	9.0	6.82	1.32	0.25
PMMA-A2	13.8	11.5	1.20	0.50
PMMA-C	14.6	10.6	1.38	0.25
PMMA-1	37.2	26.8	1.39	–
PMMA-2	28.2	22.6	1.25	–
PMMA-3	20.4	16.6	1.23	–
PMMA-4	8.4	7.25	1.16	–

[a] PMMA-A, PMMA-C denote anthracene-labelled and carbazole-labelled PMMA, respectively

Viscosity measurements

The viscosities of the polymer solutions were measured with an Ubbelohde viscometer (at 30±0.05°C). Huggins' plots were used to estimate the intrinsic viscosities, with the kinetic energy calibration being neglected. Measurements of the reduced viscosities η_{sp}/c of PMMA-A1/PS(OH) mixtures were conducted as a function of the composition, with the original concentrations of the individual polymers being kept at $\sim 1.5 \times 10^{-3}$ g ml^{-1}. Mixing of toluene solutions of PMMA and PS(OH) resulted in three different systems, i.e. a solution which remained clear, when the OH content in PS(OH) was less than ~5 mol%, solutions which turned turbid but were still stable on standing, when the OH content was in the intermediate range (8–18 mol%) and the occurrence of precipitation, when the OH content reached 24 mol%. For the first two cases, the viscosities were measured 10 min after mixing the PMMA-A1 and PS(OH) solutions in the viscometer, while for the last case, the measurements were performed after the precipitate was separated.

Fluorescence measurements

Emission spectra of the polymer solutions were recorded on a HITACHI 650-60 fluorescence spectrophotometer at an ambient temperature of ~25°C. Polymer solutions were prepared with oxygen-free solvents. A mixed solution of PMMA-A2 and PS(OH), contained in a quartz cell, was purged with nitrogen for at least 1 min before each recording; the PMMA-A2 concentration in this solution was 1×10^{-3} g ml^{-1} so as to keep the anthracene label at a low concentration of 5×10^{-5} M. The concentration of carbazole in the mixture solution was maintained at 2.5×10^{-5} M. The excitation light, at a wavelength of 294 nm, was set at a direction which was perpendicular to that in which the emission was detected. The energy transfer was characterized by I_c/I_a, i.e. the ratio of the emission intensity at 365 nm (I_c) to that at 416 nm (I_a), which was mainly associated with the energy-donor, carbazole and the energy-acceptor, anthracene, respectively. The solvent-cast blend films were prepared on a Teflon plate from 5 wt% solutions in toluene or tetrahydrofuran (THF), containing equal molar amounts of PS(OH) and PMMA-A2. The solvent was allowed to evaporate at room temperature for 2–3 days, and the films were then dried under vacuum at 60°C for 3 further days. The film thickness was ~15 μm. For the system with the highest OH content (24 mol%), violent agitation was necessary in order to prevent any precipitation occurring during the initial mixing of the toluene solutions of the two polymers.

Complex composition analysis

Mutual precipitation experiments were carried out in toluene for the PMMA-3/PS(OH) system. The precipitate which formed upon mixing the individual solutions (each 1 wt%) of PMMA-3 and PS(OH) was separated from the solution by filtration, washed twice with toluene and then dried to constant weight under vacuum at 60°C. The PS(OH) content of the precipitate was obtained by u.v. spectroscopic analysis in THF, using a calibration curve which was obtained with a PMMA/PS(OH) mixture of equimolar composition.

RESULTS AND DISCUSSION

Hydroxyl content dependence of complexation

Since polymer–polymer complexation in solution always accompanies a contraction or collapse of the component polymer coils, resulting in a viscosity decrease, turbidity or even precipitation, viscometry has proved to be a useful technique for the elucidation of complexation, and measurement of the viscosity variation with composition has been commonly used as a basis for the estimation of the complex composition[1]. Here, in addition to such factors as composition, nature of the solvent, molecular weight, etc., which are commonly studied in polymer–polymer complexation, particular attention was also paid to the effect of the hydroxyl content and the consequent hydrogen-bond density on complexation. *Figure 1* shows the variation of the reduced viscosity (η_{sp}/c) of the PS(OH)/PMMA solutions in toluene as a function of the molar ratio, i.e. the ratio of the total number of moles of styrene and HFMS monomer units of the PS(OH) to that of PMMA. In these solutions, the PS(OH) components have different OH contents covering a range from 0–24 mol%. It can be seen that depending on the OH content in the PS(OH), the solutions show two kinds of viscosity–composition relationship. For mixtures with an OH content which is lower than 4.4 mol%, the reduced viscosity values of the two polymer mixtures vary rather homogeneously with the composition, with the values being close to the weight-average viscosity of both components. However, for the mixtures with OH contents higher than 8 mol%, a dramatic viscosity decrease appears with the initial addition of the PS(OH) to the PMMA solution, and then reaches a minimum, which is much smaller than that of the viscosities of either of the pure components at the same concentration. This quite different viscosity behaviour as a function of composition, which is mainly dependent on the hydroxyl content, can, in our opinion, be attributed to the difference in interaction behaviour between the components. For the first case, with a lower hydrogen-bonding density, the 'smooth' variation of the viscosity (closely following the additive rule) indicates no apparent association of the polymer coils in solution, while for the latter cases, the dramatic decrease of the viscosity implies collapse of the coils and aggregation caused by the formation of the intermolecular complex[1]. The composition of the mixture which corresponds to the minimum in the curve of η_{sp}/c against composition is usually regarded as the fixed mean stoichiometry (*FMS*) of the complex[11]. Actually, at this point, the solution exhibits the largest turbidity and the maximum amount of precipitate. When the base ratio of PS(OH)/PMMA in the mixed solution is higher than its *FMS* value, the viscosity shows a gradual increase with further increases in the PS(OH) content. This is believed to be caused by the increase in the concentration of uncomplexed PS(OH) molecules[11].

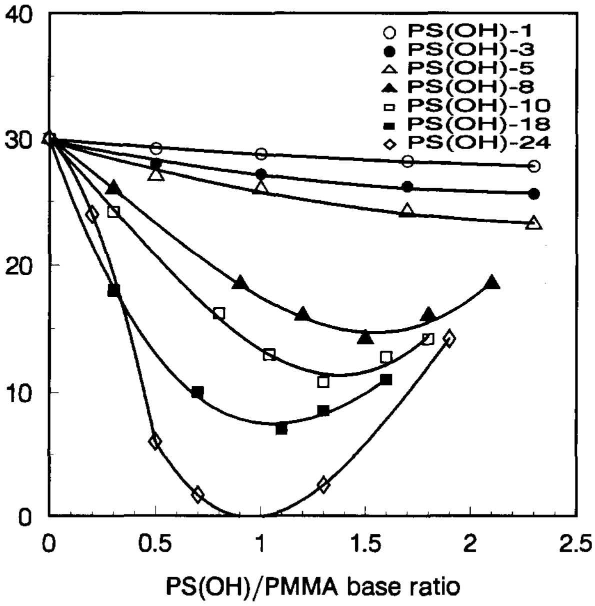

Figure 1 Reduced viscosities of the solutions of PS(OH)/PMMA-A1 in toluene as a function of the PS(OH)/PMMA-A1 base ratio showing the effect of the hydroxyl content of PS(OH)

Differing from most systems that are capable of forming macromolecular complexes in solution via hydrogen bonding, in this present case the hydrogen bonding between the components is controllable, so this provides the possibility of investigating the effect of hydrogen-bond density on the *FMS* values. For the mixture with the highest OH content, i.e. PS(OH)-24/PMMA, the minimum value of η_{sp}/c approaches zero at an exactly equal base molar composition, indicating that both polymer chains are completely precipitated out from the solution by forming a complex with a 1:1 base molar ratio. As the OH content in PS(OH) and the hydrogen-bond density decreases, the minimum value of η_{sp}/c is increased and progressively shifts towards higher values of the PS(OH)/PMMA base ratio, which suggests that the interpolymer complex gradually becomes less compact and more PS(OH) segments are incorporated in the complex[12]. This behaviour becomes understandable if we take into account the fundamental fact that, in our system, for PS(OH) only the units containing hydroxyl groups are capable of forming strong interactions with PMMA, while each unit in PMMA has its carbonyl group available to form hydrogen bonds. Therefore, it is only when the OH content reaches a certain value, i.e. ~8 mol% in this present case, that complexation becomes possible. However, in this case, due to the fact that the greater part (92%) of the units are 'inert', the complex may form a loose structure with many PS units being 'free', without their PMMA counterpart units (*Figure 2a*). However, when the number of interaction sites reaches a high value (24 mol%), i.e. about a quarter of the units in PS(OH) being capable of forming hydrogen bonds, this relatively high density of hydrogen bonding may be able to restrict the remaining inert units from assuming positions possessing their own PMMA counterpart units, leading to a 1:1 dense complex, which is completely insoluble in toluene (*Figure 2b*). Generally,

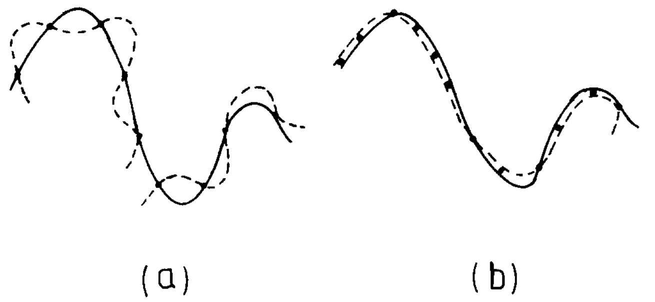

Figure 2 Schematic representations of models for (a) loose structure and (b) compact structure of PMMA/PS(OH) complexes with low and high hydroxyl contents of PS(OH), respectively: (——) PMMA chain; (- - -) PS(OH) chain; (●) hydrogen bond

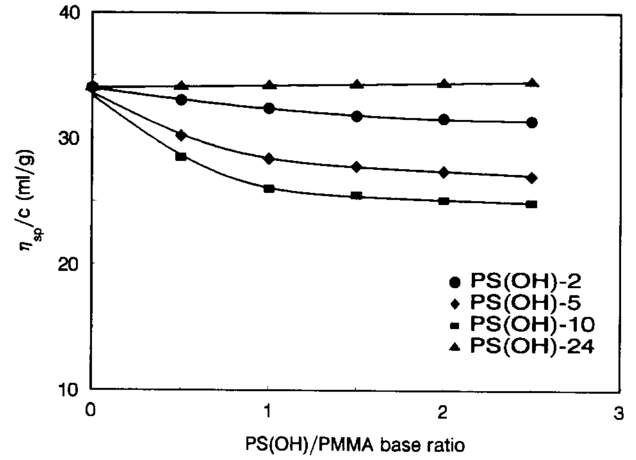

Figure 3 Variation of reduced viscosities of solutions of PS(OH)/PMMA-A1 in THF as a function of the PS(OH)/PMMA-A1 base ratio

the *FMS* value depends on both of the interaction force magnitude and the molecular weights of the component polymers[1]. In our system, for the three blend series with OH contents of 24, 18, and 8 mol%, the *FMS* values are 1.0, 1.1 and 1.5, respectively. Because the molecular weights of the PS(OH) used in the experiments are of the same order of magnitude, it is therefore reasonable to assign this *FMS* change to the difference in interaction magnitude. There are only a few reports in the literature dealing with the mean stoichiometry varying with the change of interaction, e.g. for poly(acrylic acid)/poly(acrylamide)[13] and poly(acrylic acid)/poly(vinyl pyrrolidone)[14]. The results suggest that the complexes formed have a fixed mean stoichiometry which depends only on the pH when the system is equilibrated.

In a previous paper from this laboratory[5], it was reported that the complex of PS(OH)-18/PEMA formed in toluene can be destroyed by the addition of a small amount of a proton-donor-type solvent, such as methyl ethyl ketone, and this was considered to be the result of competition of the solvent molecules for hydrogen bonding. This effect of solvent on the complexation can be further studied in more detail by using a proton-acceptor solvent, such as THF. *Figure 3* depicts the dependence of η_{sp}/c on the PS(OH)/PMMA molar ratio in THF. The results are quite different from those obtained in toluene, i.e. in spite of the OH content of the PS(OH), all of the blend solutions are completely transparent and show a homogeneous variation of η_{sp}/c with composition, presenting only a small difference from the weight-average η_{sp}/c values. This result clearly indicates that no complex is formed in THF solutions, even when the OH content is as high as 24 mol%. Obviously, this can be attributed to the proton-accepting ability of THF, which supplants most of the hydrogen-bonded carbonyl groups of PMMA. This solvent effect can be more clearly seen in *Figure 4*, in which the reduced viscosity difference, $\Delta\eta_{sp}/c$, between the experimental and the weight-average values for solutions of PS(OH)/PMMA with equal base ratios is plotted against the hydroxyl content in PS(OH). This difference with THF is almost always negligible over the whole hydroxyl content range, and is similar to that found for blend solutions with low hydroxyl contents (<8 mol%) in toluene, which also show no complexation. However, in toluene, an apparent viscosity drop appears over the OH content range from 8 to 24 mol%, indicating the formation of an intermacromolecular complex. Finally, it should be mentioned that in some non-complexation cases, a slight downward curvature in the viscosity–composition curves can still often be observed at the initial mixing stage of the polymer solutions. This is due to the large viscosity difference between the two components; a linear relationship is only exhibited for mixtures of components with similar viscosity values[1].

Composition of the complex precipitate

As mentioned above, each PS(OH)/PMMA pair with a different OH content exhibits a definite but OH-content-dependent *FMS* value, which has commonly been considered as representing the complex composition. However, it does not mean that we will always get a complex precipitate having this definite composition by mixing together the component solutions. In a recent report[8] on poly(4-hydroxystyrene)/poly(*N*,*N*-dimethylacrylamide), the compositions of the hydrogen-bonding complex precipitates are found to be strongly influenced by the feed composition of the initial solution. However, for the stereocomplex of poly(D-lactic acid)/poly(L-lactic acid)[15], the precipitate composition was found to be independent of the solution feed. In this work, mutual precipitation and analysis of the precipitate compositions was carried out for toluene solutions with different feed compositions of PS(OH)-8/PMMA, PS(OH)-18/PMMA

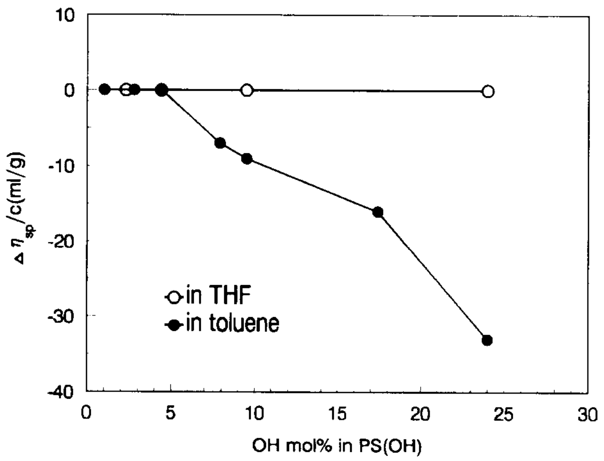

Figure 4 The difference between the measured and the calculated weight-average reduced viscosities, $\Delta\eta_{sp}/c$, of the PS(OH)/PMMA-A1 solutions (base ratio 1:1) as a function of the hydroxyl content of PS(OH), showing the effect of solvent on the viscosity behaviour: (○) THF; (●) toluene

Table 3 The compositions and *FMS* values of PS(OH)/PMMA-3 complexes

	Complex precipitate		
PS(OH)/PMMA ratio in feed	PS(OH)-8/PMMA	PS(OH)-18/PMMA	PS(OH)-24/PMMA
5:1	1.98	1.79	1.56
1:1	1.15	1.05	1.0
1:5	0.90	0.82	0.6
FMS	1.5	1.1	1.0

and PS(OH)-24/PMMA. The compositions and yields of the complex precipitates are compiled in *Table 3*. The *FMS* values are also listed for comparison.

From *Table 3* it is clear that the composition of each of the complex precipitates always lies in between its *FMS* value and that of the initial feed composition. In analogy with the behaviour of the *FMS* value changing with the OH content, the values of the complex composition in terms of the PS(OH)/PMMA base ratio decrease as the OH content in the PS(OH) copolymers increases. On these grounds, however, it seems that the composition of the complex precipitate only fluctuates around its *FMS* values, i.e., in other words, the variation in the precipitate composition is much less than that of the feed composition. It is particularly interesting to note that, when PMMA and each of the PS(OH) species are mixed in an equal base ratio, complex precipitates of equimolar composition are preferentially formed, irrespective of the differences in the *FMS* values.

The yields of the complex precipitates from PS(OH)/PMMA (1:1 base ratio) toluene solutions as a function of the PMMA molecular weight at different levels of PS(OH) hydroxyl content are depicted in *Figure 5*. This figure shows that generally the precipitate yields increase with increases in both the molar content of OH in the PS(OH) and the molecular weight of the PMMA. This means that both a high molecular weight and a high OH content favour stabilization of the PS(OH)/PMMA complexes. It is interesting to note that when the OH content and the molecular weight of the PMMA reach 24 mol% and 2×10^5, respectively, all (i.e. 100%) of the polymer components precipitate to form the 1:1 complex. In fact, all of the results mentioned above dealing with the precipitate composition and yield may lead to the same conclusion, i.e. that PMMA and PS(OH) have a strong tendency to form a molecular complex, of equimolar composition, provided the OH active sites content in the PS(OH) is sufficient and the feed composition is close to the equimolar ratio.

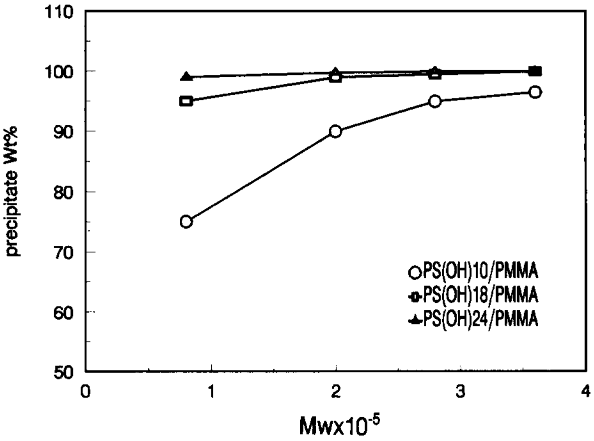

Figure 5 Yield of complex precipitate from PMMA/PS(OH) toluene solutions (1:1 base ratio) as a function of the molecular weight of PMMA

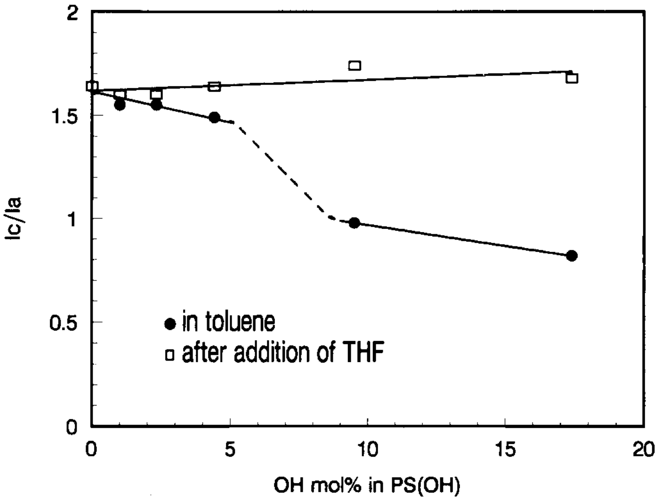

Figure 6 I_c/I_a of PS(OH)/PMMA-A2 solutions in toluene and THF as a function of the OH content of PS(OH)

Fluorescence study of the blend solution

In order to obtain a more detailed understanding of the complexation, particularly in terms of the variation of the microstructure of the polymer coils in solution, a more sensitive technique, i.e. non-radiative energy transfer (NRET) fluorescence spectroscopy was employed. The basic principle of the method used here is that the efficiency of the energy transfer between a fluorescence donor and acceptor depends strongly upon the proximity of these two species over the scale from ~2–4 nm. Since this sensitive scale is smaller than the diameter of ordinary polymer coils in solution, a NRET measurement is expected to be a sufficiently powerful way to detect the intermolecular interpenetration of the polymer chains in solution. Recently, this method has been successfully used for the characterization of complexation and association in aqueous solution[16,17]. In this present case, an energy donor (carbazole) and an energy acceptor (anthracene) are incorporated into PS(OH) and PMMA, respectively. The variation of the energy-transfer efficiency, which is proportional to I_a/I_c, of the blend solution in toluene as a function of the OH content in the PS(OH) has been studied. The results are shown in *Figure 6*, where the reciprocal values, i.e. I_c/I_a, are used. Clearly, the data can be classified into two levels. The low-energy-transfer level, associated with the rather well separated coils of the component polymers, is given by the blend solutions with low (0–5 mol%) hydroxyl content in the PS(OH),

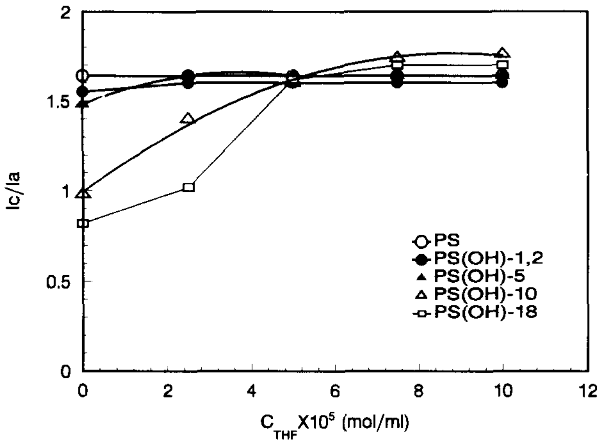

Figure 7 I_c/I_a of PS(OH)/PMMA-A2 solutions in toluene as a function of the amount of added THF, shown for different hydroxyl contents of PS(OH)

while the high-energy-transfer level, caused by a high interpenetration between the PMMA and PS(OH) chains, is presented by the blend solutions with high OH content. Apparently, this explicit result is in good agreement with the viscosity results, and they thus supplement each other. The fluorescence results visualize the structural variation of the polymer chains in solution during the course of complexation.

Since in the viscosity study the effect of a proton-acceptor type of solvent, i.e. THF, on complexation has been clearly observed, it is obviously worthwhile exploring the solvent effect on the chain interpenetration behaviour by the fluorescence technique. *Figure 7* shows the results obtained by NRET fluorescence spectroscopy for solutions of PS(OH)/PMMA in toluene as a function of the amount of added THF. Three different types of behaviour were observed:

(1) In the absence of any OH content, i.e. a PS/PMMA mixture, the I_c/I_a value remains almost constant with the addition of THF, as expected. This indicates that both polymer chains remain unperturbed by the THF molecules.

(2) For PS(OH) with OH contents from 1–5 mol%, the corresponding blend films were found to vary from immiscible to completely miscible over this region but no complex formation was observed; a slight increase in I_c/I_a occurred with the initial addition of THF. The variation can obviously be attributed to the dissociation of the hydrogen bonding in the solutions.

(3) Finally, for the blend solutions of PS(OH)-10/PMMA and PS(OH)-18/PMMA, an apparent transitional change of I_c/I_a is observed, which accompanies the originally turbid mixed solutions becoming clear. This means that the intimate interpenetration between the PS(OH) and PMMA chains, as a result of the strong hydrogen bonding, is disrupted. When the THF concentration increases to 10^{-4} mol ml^{-1}, which is about the same as the molar concentration of the PMMA chains in the solution, all values of I_c/I_a reach the same level as that given by the PS/PMMA system (without any hydrogen bonds), irrespective of the OH content difference in the PS(OH) copolymers. This indicates that the complexation of PS(OH) and PMMA is now almost completely destroyed.

Fluorescence study of the blend films

In a previous paper from this laboratory[4], the NRET fluorescence technique was successfully used for blend films of PS(OH)/PMMA and PS(OH)/PBMA. A remarkable feature of the related results obtained was the existence of two plateaux in the curves of I_c/I_a against the OH content. The first plateau, located at an OH content from ~1.6 to 4 mol%, was confirmed as being associated with complete miscibility. However, the nature of the second plateau, located at a higher OH content (>7 mol%), and showing a much higher energy transfer than that of the miscible blends, was not fully understood. Now, with this new data obtained from viscosity and fluorescence studies of the blend solutions, in which the PS(OH) used covers a much broader range of hydroxyl contents, we are able to understand the solid-state behaviour of PS(OH)/PMMA blends with high OH contents more clearly. In this work, the energy-transfer efficiency measurements of PS(OH)/PMMA blends cast from toluene were repeated with reduced chromophore concentrations in both polymers in order to achieve greater precision. The results are shown in *Figure 8*. The I_c/I_a value of a blend composed of an anthracene-labelled PMMA, and a carbazole-labelled PMMA which is regarded as a miscible blend reference, having the same concentration of the label as that in the PS(OH)/PMMA blends, was also measured and the result is depicted as a dashed line in *Figure 8*. As expected, the I_c/I_a values of PS(OH)/PMMA gradually decrease with increasing OH content of the PS(OH). When the OH contents exceed 2.3 mol%, the rate of decrease of I_c/I_a becomes more moderate, indicating blend miscibility[18]. At this stage, the I_c/I_a values drop to levels which are below the reference value of the PS(OH)/PMMA blend. As reported previously[6], a further substantial increase of the energy transfer efficiency, i.e. an apparent decrease of I_c/I_a, is observed when the OH content increases further; the highest efficient energy transfer, which is about twice as much as that of the miscible blends, is attained when the hydroxyl content

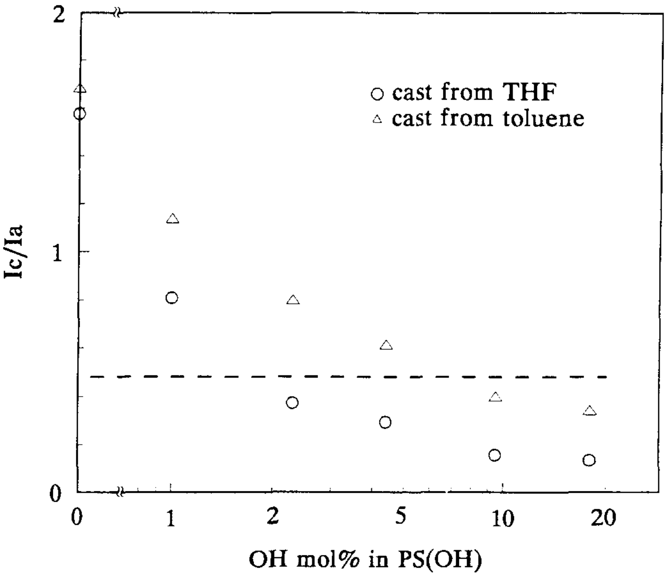

Figure 8 I_c/I_a of PS(OH)/PMMA-A2 films cast from toluene (○) and THF (△), as a function of the hydroxyl content of PS(OH)

reaches ~10 mol%. Combining the results of the viscosity and the NRET fluorescence spectroscopic studies for these blend solutions, it is quite reasonable to attribute this unusually high energy-transfer efficiency to complexation between PS(OH) and PMMA in the solid state. The I_c/I_a values for the miscible blends are ~0.35–0.45, while the complex gives values which are as low as 0.15–0.18. This clearly indicates that the fluorescent donor and acceptor, which are incorporated into the PS(OH) and PMMA, respectively, have more opportunity to be in close proximity than in the miscible blends. Since for a blend miscible at the molecular scale, the two kinds of component chains are believed to be randomly distributed, the NRET fluorescence results present here convincing evidence for the unusual arrangement of the polymer chains in the complex, i.e. the PMMA chains actually prefer to form unlike segment pairs with the PS(OH) units rather than like pairs.

All of the results mentioned above have been obtained for PS(OH)/PMMA blends cast from toluene, which is believed to be an inert solvent in respect of hydrogen bonding between the component polymers. We shall now discuss the case of using a proton-acceptor type of casting solvent (THF). The related fluorescence results are also shown in *Figure 8*. In comparison with the data obtained for toluene-cast films, the following conclusion can be drawn:

(1) The energy-transfer efficiency of THF-cast films is always lower than that of the corresponding toluene-cast films, regardless of the OH content of the PS(OH). This means that THF, as a proton acceptor, shows its ability to prevent hydrogen bonding between PS(OH) and PMMA, not only in dilute solution, as discussed earlier, but also in the final blend films.

(2) Although the results of the fluorescence measurements for the dilute blend solutions in THF demonstrate that hydrogen bonding between PS(OH) and PMMA is almost completely destroyed (*Figure 7*), for the blend films with high OH contents cast from THF, miscibility can still be realized, as evidenced by the optical transparency and low value of I_c/I_a (0.40) when compared with the reference blend of PMMA-A/PMMA-C (0.45). Actually, the solvent-cast films are produced from the solutions as a result of progressive evaporation of the solvent and at the latter stage, the solution becomes very concentrated and the THF has almost completely evaporated, so it is reasonable to believe that the proton acceptor, i.e. the carbonyl group on the PMMA, and the strong proton donor, $-C(CF_3)_2-OH$, still have the opportunity to form hydrogen bonds. However, we notice that for the THF-cast films, much more OH content (> 10 mol%) is needed to achieve miscibility than that required (less than 2 mol%) for the toluene blends.

(3) Differing from the toluene-cast films, the lowest I_c/I_a value for the THF-cast films is only comparable with the miscible reference blend and the second drop in I_c/I_a does not occur, even when the OH content reaches 18 mol%.

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