Controllable specific interactions and miscibility in polymer blends: 3. Non-radiative energy transfer fluorescence studies

Ming Jiang, Wenjie Chen and Tongyin Yu
Institute of Material Science, Fudan University, Shanghai 200433, People's Republic of China

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Polymer blends of poly(methyl acrylate) and modified polystyrene (PS(OH)) with introduced strong proton-donating hydroxyl groups have been studied by non-radiative energy transfer fluorescence. As the content of hydroxyl in PS(OH) increases from 0 to 1.6 mol%, the efficiency of energy transfer increases gradually. This modification corresponds to the morphological change observed by transmission electron microscopy (TEM) from the completely phase-separated state to the single-phase state. Blends with hydroxyl contents in PS(OH) > 7 mol% show much higher efficiency of energy transfer than miscible blends, indicating a certain structural change which cannot be detected by TEM. The effect of the formation rate of the toluene cast films on morphology and the effect of chromophore concentration on efficiency of energy transfer are also discussed.

(Keywords: polymer blends; hydrogen bonding; specific interaction; miscibility; fluorescence; non-radiative energy transfer)

INTRODUCTION

In previous papers in this series[1-3], we reported results of research into the effect on miscibility of introducing hydrogen bonding into immiscible blends. Styrene-based copolymers containing strong proton-donating units $(CF_3)_2(OH)C$–, denoted PS(OH), were produced by copolymerization. Various blends comprising PS(OH) and one of the polymers containing proton-acceptor groups, mainly polyacrylates such as poly(butyl acrylate) (PBA), poly(methyl methacrylate) (PMMA) and poly(butyl methacrylate) (PBMA), were studied by a combination of techniques. The outstanding strength of the hydrogen bonding between the hydroxyl linked with $-CF_3$ in PS(OH) and carbonyl in the polyacrylates was shown by a considerable frequency shift of the hydroxyl stretching in infrared (i.r.) spectra, as high as $\approx 200\ \mathrm{cm}^{-1}$. As a consequence of this strong interaction, the miscibility of the blends is greatly favoured, as explored by differential scanning calorimetry (d.s.c.) and transmission electron microscopy (TEM). Typically, ≈ 2 mol% of hydroxyl-containing units introduced into PS(OH) can make it completely miscible with PMMA. It is concluded that the morphological feature of this kind of blend is almost controllable since the structure and/or amount of the introduced groups forming hydrogen bonding can be readily adjusted in chemistry. This paper aims to investigate the state of mixing of the blends with a new and sophisticated technique, non-radiative energy transfer (NRET) fluorescence, with emphasis on a comparison with results obtained by electron microscopy.

The basic principle of NRET used in polymer–polymer miscibility studies can be described as follows[4]. In a system containing two kinds of fluorescing chromophores, if the emission spectrum of the first overlaps the absorption spectrum of the second, energy transfer through a non-radiative process from the first (donor, D) to the second (acceptor, A) may occur when the system is excited by irradiation which is selectively absorbed by the donor. The efficiency of energy transfer (E) characterized by I_D/I_A (where I_D and I_A are the emission intensities of the donor and acceptor, respectively) depends on the distance r between donor and acceptor according to the relation

$$E = R_0^6/(R_0^6 + r_0^6)$$

where R_0, the characteristic distance at which half of the excitation energy is transferred, is a constant for a given fluorescing pair in a given medium. Since E is sensitive to change in the distance r, particularly when the latter varies by an amount of the order of R_0, I_D/I_A can be used as a molecular probe of the proximity of donor and acceptor. Therefore, NRET can be used to explore polymer–polymer miscibility, provided the polymeric components in blends are labelled with fluorescing donor and acceptor, respectively. It is expected that the efficiency of energy transfer will decrease as the system goes from the intimate mixing state to the phase-separated state.

One of the great advantages of the NRET technique in miscibility studies is related to its scale of sensitivity, on which spatial heterogeneity can be detected, being of the order of 2 nm for most fluorescing pairs used. This makes the technique an important supplement to existing techniques since most of the common methods such as d.s.c. and dynamic mechanical analysis are only able to detect heterogeneity on a scale of ≈ 10 nm. However, the NRET technique can only provide information on the relative change of the degree of mixing of components

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in blends. Until now, no quantitative relationship has been established between the efficiency of energy transfer and parameters of the phase relationship.

EXPERIMENTAL

Monomers

p-(1,1,1,3,3,3-Hexafluoro-2-hydroxypropyl)-α-methylstyrene (HFMS) functioning as a proton donor in its copolymers with styrene was prepared as described in our previous paper[1]. 1-(9-Anthryl)ethyl methacrylate (9-AEMA) was prepared by esterification of methacryloyl chloride with 1-(9-anthryl)ethanol. The latter was produced by reduction of 9-acetylanthracene. Vinyl carbazole was obtained from the Aldrich Chemical Co.

Polymers

Copolymers of styrene and HFMS (PS(OH)) with different contents of hydroxyl-containing units were prepared by copolymerization in benzene at 60°C with AIBN as initiator. Dissolved gases in the monomers were removed before polymerization. The reaction proceeded until conversion of the monomers reached $\approx 10\%$, when the reaction mixture was poured into a large quantity of petroleum ether (b.p. 30–60°C). The products were purified by repeated dissolving and precipitation using a system of dichloromethane and methanol. Before use, the polymers were dried at 60°C under vacuum for 72 h.

PS(OH)-C, copolymers of styrene and HFMS labelled with carbazole, were prepared by terpolymerization of the corresponding monomers including vinyl carbazole by the same procedure as for PS(OH). The chromophore contents in the copolymers measured by ultraviolet (u.v.) spectroscopy were found to be close to the proportions of vinyl carbazole in the polymerization feeds.

PMMA and poly(ethyl methacrylate) (PEMA) were produced by polymerization of the purified monomers in benzene at 60°C with initiator AIBN for 4-5 h, followed by precipitation into methanol and repeat purification in dichloromethane/methanol.

PMMA-A and PBMA-A, the anthracene-labelled polymers, were prepared by copolymerization of the respective monomers and 9-AEMA by the same procedure as for the homopolymers, but the conversion of the monomers was kept $< 10\%$. Carbazole-labelled PMMA (PMMA-C) was produced by copolymerization of MMA and vinyl carbazole under the same conditions as for PMMA-A.

Characterization of polymers

The molecular weights of the homopolymers and copolymers were measured by gel permeation chromatography. The peak values of the elution curves were used to calculate the molecular weights based on polystyrene calibration.

The chromophore contents in the copolymers were determined by u.v. spectroscopy, by assuming that the extinction coefficients of the chromophores in the copolymers were the same as in the corresponding monomers.

The molar contents of hydroxyl-containing units in PS(OH) and PS(OH)-C were calculated from the results of fluorine content measurements. However, when the contents were < 1.5 mol%, the measurements yielded large errors and, therefore, in this region the molar contents were taken directly from the feeds of polymerization.

The resultant characterization data are listed in *Table 1*.

Fluorescence measurements

Solvent-cast films were used for fluorescence measurement. First, the polymers were dissolved in oxygen-free toluene to make a 5% solution and then the solution was spread on a small piece of Teflon plate. The solvent was allowed to evaporate at room temperature and the films were then dried under vacuum at room temperature for 2 days and at 90°C for 2 days successively. The solution preparation and solvent evaporation procedures were performed under a dry nitrogen atmosphere. The film thickness was in the range 10–15 μm, which was controlled by adjusting the quantity of solution cast onto a given plate surface. For PS(OH)-C with relatively high hydroxyl contents, the component polymers were dissolved separately in toluene followed by mixing with violent agitation to prevent gelation of the solution.

A SPEX 1212 spectrofluorometer was used for fluorescence measurements of the blend films. The films formed on Teflon plates were excited by radiation at 296 nm. The emission intensities at 350 and 415 nm were recorded as the emission of energy donor carbazole (I_C) and energy acceptor anthracene (I_A), respectively. The efficiency of energy transfer was characterized by the intensity ratio I_C/I_A.

Morphological observations

A Hitachi H500 transmission electron microscope (TEM) was used for morphological study. Two series of films cast at different rates of film formation were studied. The first series is the same as that for fluorescent measurement, with thickness of only 10–15 μm. Before microtoming, the thin films were immersed in epoxy resin precursor, followed by curing at 60°C for 48 h. Ultrathin sections were made by using a KLB-2088 microtome. The sections were stained with vapour of 1% solution of RuO_4 in water[1]. The films of the second series were relatively thick(≈ 1 mm) and formed over a much longer period. The films were prepared by allowing evaporation of toluene from solutions of the blend in loosely covered Teflon cells. The films formed in 5–6 days, followed by a complete drying process. The ultrathin sections were

Table 1 Characterization data of polymers

Polymer	Molecular weight $\times 10^{-4}$	Chromophore content (wt%)	Hydroxyl content (mol%)
PMMA-A	39	2.5	—
PMMA-C	35	0.7	—
PBMA-A	41	1.3	—
PS-C	2.3	0.3	—
PS(OH)-C-0.5	2.3	0.3	0.5
PS(OH)-C-1.0	3.6	0.3	1.0
PS(OH)-C-1.2	3.6	0.2	1.2
PS(OH)-C-1.4	4.3	0.2	1.4
PS(OH)-C-2	3.1	0.2	1.7
PS(OH)-C-3	2.4	0.2	3.3
PS(OH)-C-7	1.9	0.2	7.2
PS(OH)-C-18	1.2	0.3	17.6
PS(OH)-5	2.0	—	5.0
PS(OH)-8	1.9	—	7.6

made by microtoming the thick films directly without epoxy resin treatment. The staining procedure was the same as that used for the sections obtained from the thin films.

RESULTS AND DISCUSSION

Concentration dependence of the efficiency of energy transfer

NRET fluorescence has proved to be a powerful technique for monitoring the degrees of mixing of unlike polymer chains in a blend as functions of different structural parameters. For example, in the studies of Morawetz *et al.*[4], attention was paid to the effect of compositions of random copolymers, which were used as one-component polymers in the blends, on the efficiency of energy transfer. Obviously, in such studies, it is necessary to keep other factors which may affect the energy transfer as consistent as possible. Chromophore concentration is one of the important factors. However, as far as we know no data dealing with this effect have been published so far. Before discussing our main results, in which the density of hydrogen bonding is the main parameter, we first discuss results of the dependence of the efficiency of energy transfer on chromophore concentration. In this part of the study, the NRET of a series of blends comprising carbazole-labelled PMMA and anthracene-labelled PMMA, which can be regarded as typical miscible systems, were measured. In these blends, concentration variation of donor and acceptor was realized by changing the weight ratio of the labelled and unlabelled PMMA. The results shown in *Figure 1* clearly indicate the concentration dependence of I_A/I_C. As expected, I_A/I_C steadily increases with increasing concentration over the whole concentration range studied ([C] = [A], 0.002–0.01 M). Although the effect of concentration on energy transfer is not very great, e.g. at $[C] = [A] = 5 \times 10^{-3}$ M, a 10% variation of concentration leads to ≈ 10% change in I_A/I_C, it is not negligible. This shows the importance of keeping the concentration of chromophores consistent in miscibility studies by fluorimetry.

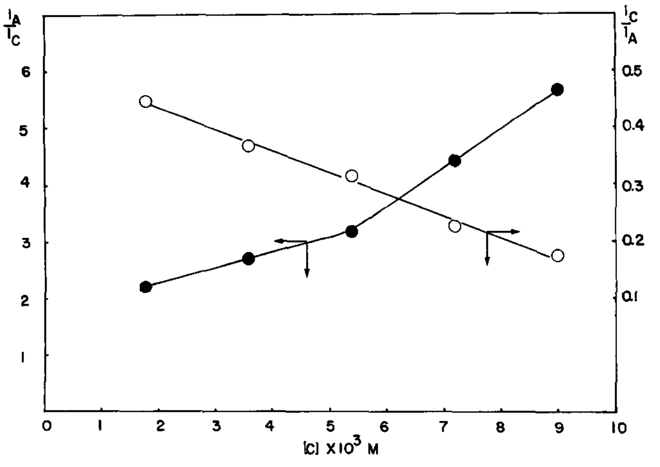

Figure 1 Dependence of the efficiency of energy transfer on concentration of chromophores ([C] = [A]) in blends of PMMA-A/PMMA-C (50/50 wt%), where C and A denote carbazole and anthracene, respectively

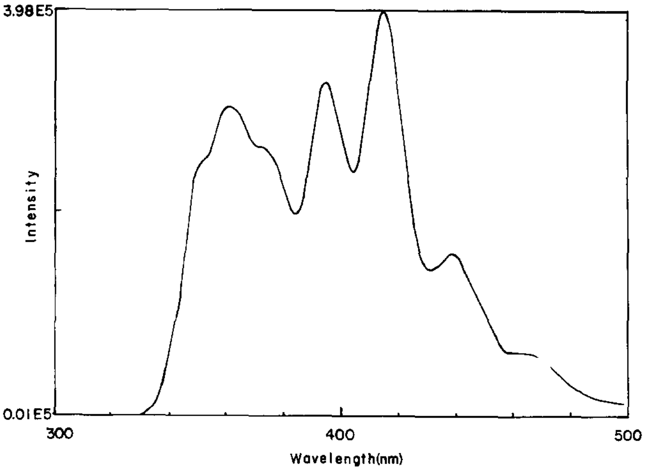

Figure 2 Fluorescence emission spectrum of PS(PH)-C/PMMA-A (50/50 wt%). Concentrations of anthracene (A) and carbazole (C) are both 5.17×10^{-3} M

Correlation of energy transfer efficiency and morphology

Since energy transfer measurements can only provide information on the relative variation of the degree of mixing in blends as a consequence of changes in some structural parameters, it would be instructive to compare data on energy transfer efficiency with results obtained by other techniques, in particular TEM, which usually gives the most intuitive, visual features of the spatial arrangement of component polymers. However, until now, no such comparison has appeared in the literature. In the papers of the groups of both Morawetz[4–6] and Teyssie[7,8], probably due to difficulties in gaining sufficient contrast between the components in the systems they studied for TEM observations, no morphological results have been reported. In the present investigation, efforts have been made to explore in parallel the variation of the energy transfer efficiency and morphology of a series of blends, PS(OH)-C/PMMA-A, as a function of hydroxyl content in PS(OH)-C. A typical emission spectrum of the blends is shown in *Figure 2*.

In this series of blends, the concentrations of carbazolyl and anthryl groups, which are attached to PS(OH) and PMMA, respectively, are kept constant (5.19×10^{-3} M) by mixing the labelled polymers with the corresponding unlabelled ones. The main results of the fluorimetry study and the corresponding micrographs of the blends are displayed in *Figure 3*. As increasing amounts of hydroxyl groups are introduced into the system, the ratio I_C/I_A first obviously and gradually decreases, implying an increase in energy transfer efficiency between donor and acceptor, and then levels off. The highest value of I_C/I_A for blend a, without intercomponent hydrogen bonding, corresponds to an immiscible phase feature: the phase size is of polydispersity with larger phase sizes ≈ 0.5–1 μm and the phase boundary is relatively distinct. A gradual increase in the introduced hydroxyl content causes a continuous increase in energy transfer efficiency accompanying the modification of the phase relationship: the phase size becomes smaller and smaller and the phase boundary becomes more and more indistinct with increasing connectivity. When the hydroxyl content in PS(OH)-C reaches 1.2 mol% (blend d), the two phases greatly interpenetrate and the size of some domains diminishes to only ≈ 20 nm. A further increment of

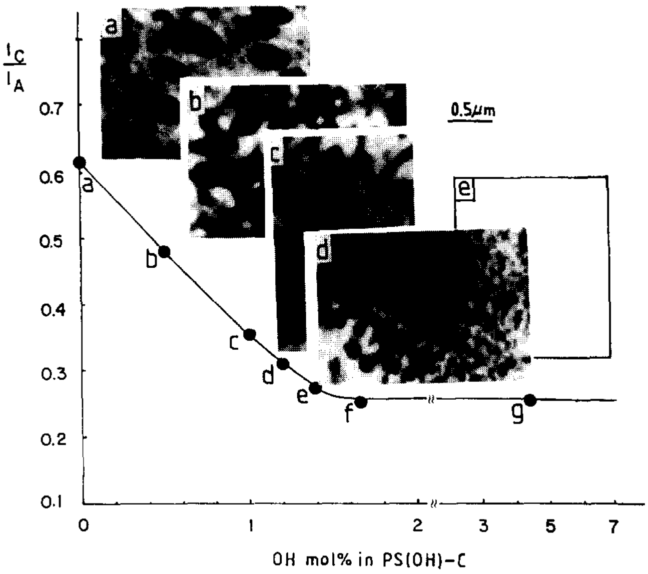

Figure 3 Variations of the energy transfer efficiency and morphologies of blends of PS(OH)-C/PMMA-A (50/50 wt%) as a function of hydroxyl content in PS(OH)-C. Concentrations of carbazole (donor) and anthracene (acceptor) are both 5.17×10^{-3} M

hydroxyl content, though very small (up to 1.4 mol%) leads to a substantial change in the morphology: blend e becomes transparent and no structure could be found under TEM. This comparison of morphological study and fluorescence measurements clearly shows that the variation of the efficiency of energy transfer of the blends as a function of the hydroxyl groups introduced does reflect the morphological variation of the blends from immiscibility to miscibility.

Note that although all the films e, f and g having hydroxyl group contents of 1.4, 1.7 and 3.3 mol%, respectively, are transparent, without phase structure being seen by routine TEM, the fluorescence measurements do indicate some difference in the degree of mixing. Among the films, I_C/I_A for blend e is slightly but clearly larger than those of the other films. However, for the donor–acceptor pair used in this study, the characteristic distance is 2.7–2.9 nm (Reference 4). Composition fluctuation on this scale in blends should be readily detected by routine TEM observations. The failure of TEM in examining the phase structure in blend e may, in our opinion, be an indication of the magnitude of the composition fluctuation being very small due to the presence of strong intercomponent interaction in the blend, leading to insufficient contrast under TEM observations.

The gradual transition of energy transfer efficiency with structural parameters, i.e. the density of hydrogen bonding in the present case and the composition of random copolymers in Morawetz's studies, is a common phenomenon. Morawetz *et al.*[4] proposed the following interpretations for the continuation of the variation: polydispersity of the component polymers; interpenetrating structure of blends; change of interfacial area; and composition fluctuation on a microscopic scale. Obviously, our results based on the simultaneous studies of fluorescence and TEM for the same series of blends have explored the essence of this gradual variation. What this modification of NRET reflects is the gradual variation of morphology from a completely phase-separated state to a state of sufficient mixing of unlike polymer chains as a consequence of progressive increase of the interaction between the components. Films a, b, c, d and probably e are all immiscible blends. However, they are different in morphological detail. Among the blends, the difference in the density of hydrogen bonding causes different driving forces for phase separation. Under certain conditions for making blends, the difference in the driving force will cause various extents of phase separation, i.e. different degrees of phase aggregation. Therefore, the gradual transition from immiscibility to miscibility rather than a sharp jump is almost a necessary consequence of the gradual change of the structural parameters. NRET studies prove to be able to reflect this gradual transition sensitively, but only qualitatively.

In the literature dealing with NRET miscibility studies, the ratio of emission intensities of donor and acceptor are compared with two reference emission intensity ratios associated, respectively, with maximum energy transfer for a miscible blend and the absence of energy transfer for an immiscible blend. The latter is often calculated by measuring the emission of the corresponding chromophores in solution, assuming that the extinction coefficients and relative quantum yields of the donor and acceptor are the same in solution and bulk blend. However, the reported experimental values of I_C/I_A for immiscible blends are much smaller than those calculated in References 4–8. Morawetz *et al.*[5,6] attributed this low experimental value in immiscible blends to the considerable contribution of energy transfer made by the pairs at interfaces. Recently, by measuring the efficiency of energy transfer of blend containing poly(vinyl chloride) in both solution and solid states, Zhao *et al.*[9] pointed out that the I_C/I_A value calculated from solution measurements is not adequate to be the reference without energy transfer since the assumptions on which the calculation was performed are not valid. For the chromophore pair of anthracene and carbazole, the reference value of I_C/I_A calculated from solution is 114 (Reference 6), two orders of magnitude higher than that obtained for bulk blend a, 0.62. Since the clear phase-separated feature of blend a has been shown by TEM, we are inclined to think that the reason given by Zhao *et al.*[9], namely the possible substantial differences in extinction coefficients and quantum efficiencies in solution and solid states, is responsible for the apparent discrepancy.

NRET of blends with higher hydroxyl contents

Although the results shown in *Figure 3* clearly demonstrate that blends giving the plateau value of I_C/I_A are miscible, single phase systems, the measurements have been extended to blends with higher hydroxyl content up to 17 mol% in PS(OH)-C. Two series of blends, PS(OH)-C/PMMA-A and PS(OH)-C/PBMA-A, were studied, covering a broad range of hydroxyl content. As shown in *Figure 4*, on a logarithmic scale, for two similar series, the efficiency of energy transfer shows almost parallel variation with increasing density of hydrogen bonding. This makes the data more convincing. The most remarkable feature of the results is the presence of two transitions and two plateaux.

As just discussed, the physical change reflected by the first transition is clarified by comparison with TEM observations. An additional measurement was made for a miscible reference blend composed of PMMA-A and

PMMA-C with the same concentration of fluorescing pairs as that in the series of blends. This reference blend gives an I_C/I_A value of 0.33, which is comparable with the plateau values (0.33 for PS(OH)-C/PBMA-A and 0.25 for PS(OH)-C/PMMA-A). This result provides further confirmation of the miscibility of the blends at the first plateau. Thus the appearance of the further increase in the efficiency of energy transfer as more hydroxyl is introduced is somehow unexpected. For both series, I_C/I_A drops to almost half the value at the first plateau as the hydroxyl content increases from 3 to ≈ 7 mol%. The origin of this substantial increase in efficiency of energy transfer is still questionable. We could not simply say that the blends corresponding to the second transition and plateau are even more miscible than those showing no phase structure under TEM observation and giving an efficiency of energy transfer as high as that of the miscible reference blend. Fortunately, some subsidiary experiments have provided leads in the search for the real cause. It was observed that blend solutions in toluene containing PMMA and PS(OH) with hydroxyl contents > 5 mol% in concentration of $\approx 5\%$ always became opaque on standing as a consequence of gel formation. In most cases the gel formed could not be dissolved by adding even a large amount of toluene, while it was readily destroyed and dissolved as a very small proportion of proton-acceptor solvent, say methyl ethyl ketone, was added.

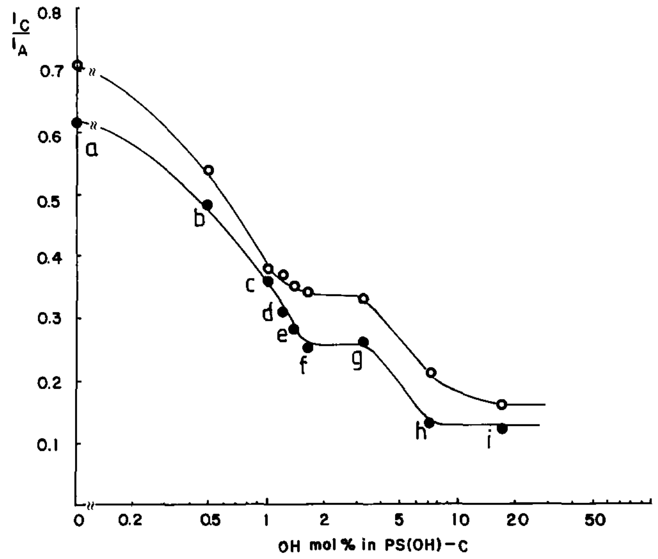

Figure 4 Variation of the efficiency of energy transfer in blends of PS(OH)-C/PMMA-A (50/50 wt%) (●) and PS(OH)-C/PBMA-A (○) as functions of hydroxyl content in PS(OH)-C. Concentrations of carbazole (donor) and anthracene (acceptor) are both 5.17×10^{-3} M

The result clearly demonstrates that the higher density of hydrogen bonding, which should be sensitive to the presence of small molecules of proton acceptor, is responsible for the crosslinking structure in the blends. Considering this result, we are inclined to attribute the unusually low values of I_C/I_A in blends h and i to the structural change associated with the high density of hydrogen bonding, i.e. when the latter reaches a certain level, accompanying the formation of physical crosslinking, segment pairing between unlike components may become more favoured than that between like components, leading to the unusually high efficiency of energy transfer. Of course, this preliminary explanation does not exclude other factors which may also contribute to the high energy transfer efficiency, e.g. lower molecular weight of PS(OH)-Cs with higher hydroxyl content than those with low hydroxyl content (*Table 1*) and the possible presence of non-random distribution of hydroxyl-containing units in PS(OH)-C chains with high hydroxyl units content.

Although the curves of both PS(OH)-C/PMMA-A and PS(OH)-C/PBMA-A systems show some distinct turning points, e.g. I_C/I_A reaches the first and second plateaux when the hydroxyl contents reach ≈ 1.6 and ≈ 7 mol%, respectively, we have no intention of emphasizing the values themselves as they are obviously affected by other factors. For example, decreasing the molecular weights of either PS(OH) or polyacrylates and increasing the evaporating rate of the solvent in the casting process will lead to shifts in the turning points to lower hydroxyl contents. What we are most interested in is how the efficiency of energy transfer varies with the density of hydrogen bonding, which is determined by the content of hydroxyl groups incorporated into PS(OH)-C.

The effect of rate of film formation

It has been realized that only non-equilibrium morphology can be obtained in any practical blend systems[10,11]. For immiscible blends prepared via the solvent casting procedure, phase separation is always incomplete and the extent to which segregation occurs could be varied by modifying the cast conditions. Therefore, the morphologies shown in *Figure 3* for films

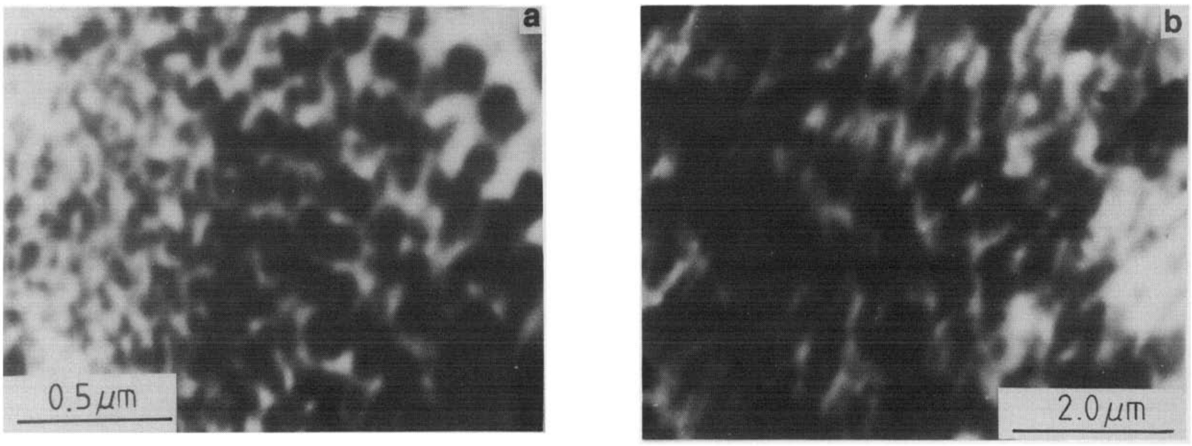

Figure 5 Micrographs of (a) thin and (b) thick films of PS(OH)-C-1.2/PMMA

formed in a rather short period with thicknesses of only 10–15 μm, which is required by the fluorescence measurements, must be far away from the equilibrium state. In fact, in the preparation of the thin blend films, the thickness of the starting solution spread on Teflon plates was only ≈ 1 mm, so films dry to the touch formed in only a few hours. This condition is quite different from the ordinary procedure for preparing solvent cast films[11,12].

To explore the effect of the rate of film-formation, the morphologies of a series of thick blend films of PS(OH)-C/PMMA-A, formed in loosely covered plates over a period of 5–6 days, were observed. The results show that although the morphological details are apparently different from the corresponding thin films, they indicate the same trend of morphological variation as the hydroxyl content increases from 0 to 1.6 mol%. As an example, micrographs of both thick and thin films composed of PS(OH)-C-1.2 and PMMA-A are shown in *Figure 5*. Due to the presence of 1.2 mol% hydroxyl, both blends show morphologies characteristic of indistinct phase boundary and great phase connectivity. Nevertheless, the phase size of the thick film is much larger than that of the thin one. Obviously, on the rather short time scale of the solvent casting process of making thin films, phase separation and segregation were probably frozen at a relatively early stage due to high viscosities encountered at high polymer concentrations. Fortunately, even under this condition the difference in driving force for phase separation due to the variation of the density of interaction between the components still causes a distinct variation in the degree of mixing.

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