Intermacromolecular Complexation Due to Specific Interactions. 5. The Hydrogen-Bonding Complex of Poly(styrene-*co*-4-vinylphenol) and Poly(ethyl methacrylate)

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ABSTRACT: The complexation between poly(styrene-*co*-4-vinylphenol) (STVPh) and poly(ethyl methacrylate) (PEMA) due to hydrogen bonding in nonaqueous media was investigated by viscometry, laser light scattering (LLS), and nonradiative energy-transfer (NRET) fluorospectroscopy. The formation of STVPh/PEMA complexes in solutions strongly depends on the hydroxyl content in STVPh and the solvent used. The minimum OH content in STVPh required to form interpolymer complex aggregates is 9 mol % in toluene and 22 mol % in 1-nitropropane. Such a large difference can be attributed to the two solvents having different abilities of accepting protons. Complete decomplexation of the STVPh/PEMA complexes in toluene can be realized by adding a small amount of tetrahydrofuran. LLS experiments reveal that the size of the complex aggregates depends on the blend composition and is a maximum at 1:1 base ratio. In addition, a new modified NRET procedure to monitor the interpolymer complexation is proposed in this paper.

Introduction

Interpolymer complexation has long attracted the interests of the scientific community over the past decades. Except for stereocomplexes[1] formed by van der Waals interaction, most interpolymer complexes reported in the literature are based on water-soluble homopolymer pairs in aqueous media[2−5] due to strong interactions, e.g., Coulombic, hydrogen bonding, etc.

Based on our long-term study on miscibility enhancement via introducing specific interactions, such as hydrogen bonding, it is found that by progressively increasing the OH groups introduced into an otherwise immiscible blend (for example, polystyrene/poly(methyl methacrylate)), not only miscibility[6] but also interpolymer complexation[7−9] can be realized in the bulk. Such complexation behavior in both the bulk and solution has been explored by viscometry, NRET fluorospectroscopy,[7,8] NMR NOE,[9] etc. Although the driving force for miscibility and complexation is the same, namely, hydrogen bonding, the density of the hydrogen bonding required is different. Accordingly, we are particularly interested in studying the dependence of complexation both in solution and in the bulk on the functional group content in the component polymers.

Frechet and de Meftahi[10] and Goh *et al.*[11] reported that mixing solutions of poly(4-vinylphenol) (PVPh) and poly(styrene-*co*-vinylpyridine) (STVPy) in tetrahydrofuran (THF) resulted in a precipitate, which was regarded as the complex. Goh *et al.*[12] also reported that poly(styrene-*co*-allyl alcohol) can form precipitates with poly(*N*,*N*-dimethylacrylamide) and poly(*N*-methyl-*N*-vinylacetamide) in methyl ethyl ketone but not in *N*,*N*-dimethylformamide solution. Kwei *et al.*[13] reported that PVPh can form complexes with poly(*N*,*N*-dimethylacrylamide) or poly(ethyloxazoline) in dioxane. Kwei *et al.*[14] also reported that phenol−formaldehyde resin can form complexes with poly(*N*,*N*-dimethylacrylamide) in dioxane solution even when 40% of the hydroxyl groups in the former polymer is reduced through methylation. Although these papers reported the formation of complexes, little attention was paid to the dependence of the complexation on the structural parameters, especially the content of the interaction sites and the consequent hydrogen-bonding density. In our previous paper,[15] viscometry, NRET fluorospectroscopy, and LLS methods confirmed that poly(styrene-*co*-4-vinylphenol) (STVPh) and STVPy can form complex aggregates in THF if the contents of hydroxyl and pyridyl in the copolymers are sufficiently high.

In this contribution, we focus on the complexation between STVPh and poly(ethyl methacrylate) (PEMA) in nonaqueous solutions. Here, it should be noted that the hydrogen-bond-forming behavior of the phenol hydroxyl in STVPh is different from the hydroxyl in PS-(OH), namely, poly(styrene-*co*-*p*-(hexafluoro-α-(hydroxypropyl))-α-methylstyrene), reported previously.[7,8] The former has quite a strong self-association in an inert solvent, while the latter has a weak self-association due to the existence of a steric bulky trifluoromethyl group.[16] The copolymer STVPh can change its interaction site content, while PEMA has its interaction site localized in each monomer unit. This enables us to explore the functional group content dependence of complexation more easily. The present investigation was motivated with the following objectives: (1) to reveal the OH content dependence of complexation between STVPh and PEMA by a combination of techniques; (2) to show the effect of solvent used on complexation; (3) to find a new approach of detecting interpolymer complexation by NRET fluorescence; (4) to observe complex aggregates in solutions directly by LLS.

Experimental Section

Monomers, Polymers, and Characterization. Vinylcarbazole was purchased from Aldrich and used as received. The energy-acceptor-containing monomer, 9-anthrylmethyl methacrylate, was synthesized as previously described.[17]

STVPh, a copolymer of styrene and 4-vinylphenol with or without fluorescent-label carbazole, was prepared as previously described.[18] Anthracene-labeled PEMA was a copolymer of ethyl methacrylate and 9-anthrylmethyl methacrylate. The

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Table 1. Characteristics of the STVPh Copolymers

polymer[a]	OH content, mol %	$10^{-3}M_n$, g/mol	M_w/M_n	chromophore,[b] mol %
STVPh1	1.1	103	1.48	0.09
STVPh3	3.1	103	1.47	0.09
STVPh6	6.0	157	2.03	0.11
STVPh9	9.1	132	2.17	0.12
STVPh12	11.8	157	2.01	0.12
STVPh17	17.2	135	2.18	0.13
STVPh22	22.4	130	2.44	0.13
STVPh1[c]	1.0	53.7	1.48	
STVPh6[c]	6.1	92.6	3.15	
STVPh12[c]	12.4	87.6	2.68	
STVPh15[c]	15.1	94.1	3.08	
STVPh31[c]	30.6	104	2.74	

[a] The number following STVPh represents the approximate integer value of the molar content of 4-vinylphenol in the copolymer. [b] Vinyl carbazole unit. [c] Unlabeled polymer.

Table 2. Characteristics of PEMA

polymer	$10^{-3}M_n$, g/mol	$10^{-3}M_w$, g/mol	M_w/M_n	chromophore,[a] mol %
PEMA	118	211	1.79	0.30
PEMA[b]	27.7	46.3	1.67	

[a] 9-Anthrylmethyl methacrylate unit. [b] Unlabeled polymer.

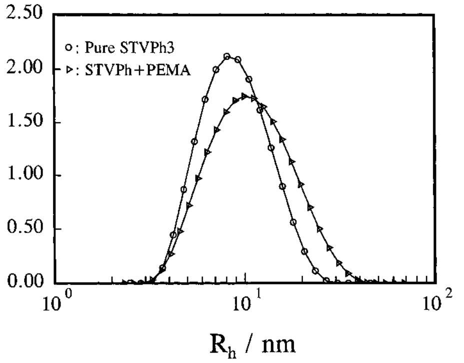

Figure 1. Hydrodynamic radius distribution f(R_h) of STVPh3 and of the STVPh3/PEMA blend (50/50 wt/wt) in toluene. The total polymer concentration is 1.0×10^{-4} g/mL. Scattering angle is 15°.

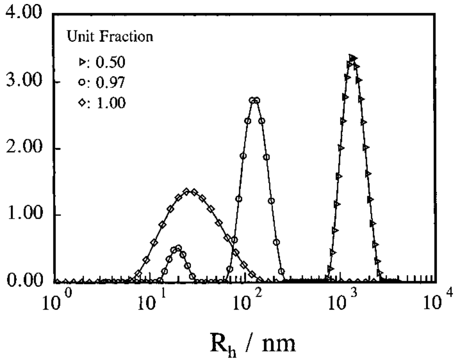

Figure 2. Hydrodynamic radius distributions f(R_h) of STVPh9 and of the STVPh9/PEMA blends with various blend compositions in toluene. Same measuring condition as in Figure 1.

unlabeled and labeled PEMAs were prepared in benzene at 60 °C using azoisobutyronitrile as the initiator. The total conversion of the monomers was kept at less than 10%.

The chromophore contents in the copolymers were determined by UV spectroscopy, assuming the extinction coefficients of the chromophores in the copolymers to be the same as those of the corresponding monomers. The characterization data for STVPh and PEMA are listed in Table 1 and Table 2, respectively. The number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of these polymers were determined by size-exclusion chromatography, based on a calibration with polystyrene standards.

Laser Light Scattering (LLS). LLS measurements were made using a modified commercial LLS spectrometer (ALV/SP-125) equipped with a multi-τ digital time correlator (ALV-5000). A solid-state laser (ADLAS DPY425 II, output power ca. 400 mW at $\lambda_0 = 532$ nm) was used as the light source. The incident light was vertically polarized with respect to the scattering plane. In the present study, the temperature was controlled at 25.0 ± 0.1 °C. The specific refractive index increment (dn/dC) was determined by a novel and precise differential refractometer.[19]

Solutions of the two-component polymers were prepared by dissolving each in a proper amount of the solvent (toluene or 1-nitropropane) and then diluting into 1.0×10^{-4} g/mL solutions. The solutions were made dust-free by filtration through a 0.2-μm Whatman PTFE filter. The component polymer solutions were mixed directly in the scattering cell as previously described.[15] It is worth pointing out that gentle agitation is necessary to avoid precipitation during the mixing of two-component solutions, especially when toluene was used as the solvent. The measurement started just after the mixing.

In dynamic LLS, the intensity−intensity time correlation function was measured in the self-beating mode. The constrained regularization CONTIN program developed by Provencher[20] was used to obtain the line-width distribution $G(\Gamma)$. For a diffusive relaxation, the translational diffusion coefficient D can be calculated from Γ.[21] The hydrodynamic radius (R_h) can be obtained from D by using the Stokes−Einstein equation; i.e., $R_h = k_BT/6\pi\eta D$, where η is the solvent viscosity; k_B, the Boltzmann constant; and T, the absolute temperature. Details of the analysis can be found elsewhere.[22]

Fluorescence Measurements. Fluorescence emission spectra of the polymer solutions were recorded on a HITACHI 650-60 fluorescence spectrometer at 25 °C. The wavelength of the excitation light was set at 294 nm, and detection of emission was at a direction perpendicular to the direction of the excitation light. The energy-transfer efficiency was characterized by I_c/I_a, the ratio of the emission intensities at 365 nm (I_c) to that at 416 nm (I_a), contributed mainly by the energy donor carbazole and the energy acceptor anthracene, respectively. The component polymer solutions of 1.0×10^{-3} g/mL were prepared with an oxygen-free solvent. The blend mixtures of STVPh/PEMA were prepared by mixing the corresponding component solutions in a quartz cell directly with stirring and then purging with nitrogen for at least 1 min before each recording. The concentration of carbazole in the blend solution was kept at 0.52×10^{-5} M. When the OH content in STVPh was higher than 9 mol %, violent agitation was necessary to avoid any large precipitate forming during the initial blending of the two polymer solutions.

Viscosity Measurements. The reduced viscosities η_{sp}/C of the polymer blend solutions were measured as a function of composition using an Ubbelohde viscometer at 30.00 ± 0.05 °C. The original concentrations of the component polymers were kept at 1.5×10^{-3} g/mL. All the measurements were done 10 min after the mixing or to allow thermal equilibrium to be reached. When 1-nitropropane ($PrNO_2$) was used as the solvent, the blend solution was clear if the OH content was below 15 mol % and was turbid and stable when over 22 mol %. For the solutions in toluene, the measurements could only be performed properly for STVPh3/PEMA because mixing the solutions of STVPh with higher hydroxyl contents with PEMA resulted in precipitation.

Results and Discussion

Direct View of Complex Aggregates through LLS. LLS has been applied in studying interpolymer complexation in both aqueous[23] and nonaqueous[15,22] solutions. The technique has proved to be very useful in the investigation of the aggregation process, especially in very dilute solutions, where the conventional viscometry is not sensitive. In our previous work,[22] efforts were made to study the structure and composi-

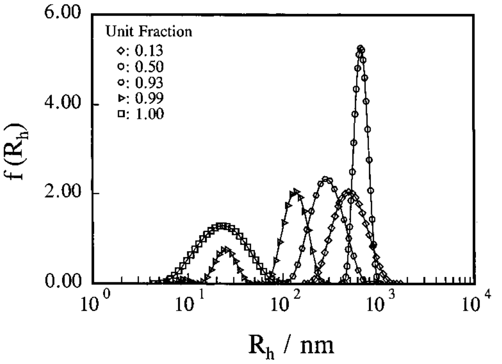

Figure 3. Hydrodynamic radius distributions f(R_h) of STVPh15 and of the STVPh15/PEMA blends with various blend compositions in toluene. Same measuring condition as in Figure 1.

tion of the complex aggregates between STVPh and PEMA in toluene, with particular emphasis on the case where STVPh is in excess. In this study using LLS, attention is focused on the solvent effect on complexation and on a comparison between the results of LLS and viscometry.

Figures 1, 2, and 3 depict the apparent hydrodynamic radius distributions f(R_h) of STVPh3, STVPh9, and STVPh15 and of their blends with PEMA in toluene. Here, the STVPh unit fraction Fr is defined as the ratio of moles of styrene and vinylphenol monomer units of STVPh to those of PEMA plus STVPh. We may note at the outset that the refractive index increment (dn/dC) of STVPh with different OH contents ranges from 0.110 to 0.115 mL/g in toluene, while for PEMA it is only about 0.006 mL/g.[22] Therefore, PEMA cannot be "seen" in this LLS study, and it is the STVPh that makes the dominant contribution to the intensity of scattered light of the blend solutions. As shown in Figure 1, f(R_h) of the STVPh3/PEMA (50/50 wt/wt) blend is very similar to that of component STVPh3 by itself; i.e., the presence of PEMA does not show any significant effect on the R_h distribution of STVPh3. Pure STVPh9 solution has a rather broad distribution f(R_h) extending to 100 nm (Figure 2), which should be attributed to the existence of self-association between the hydroxyl in STVPh in toluene. In contrast, in the case of STVPh9/PEMA blends, the R_h distribution is completely changed. The addition of only 3 wt % PEMA here changes it to a bimodal form. The peak at small value (ca. 20 nm) can obviously be assigned to the free STVPh9 in solution, while the other peak located at as high as 100 nm unambiguously belongs to the STVPh9/PEMA complex aggregates. Because LLS is more sensitive to high molar mass particles, although the peak at 100 nm has a greater area than does the one at 20 nm, the weight fraction of complex aggregates in the blend mixture is still much smaller than that of individual STVPh chains. Further addition of PEMA causes the small R_h peak of the individual STVPh9 to gradually disappear and the large R_h peak of the complex aggregates to move to an even larger R_h value. Finally, only one R_h peak at the range of ca. 1000 nm can be detected for the STVPh9/PEMA blend solution reaching a 1:1 base ratio.

Formation of the complex aggregates becomes more obvious when the OH content is 15 mol % (Figure 3). Even when the added PEMA is as little as 1 wt %, it causes a significant change in the R_h distribution. The f(R_h) of the blend solution has two peaks, a large one in the same range as pure STVPh15 and a small one at a much large size (100 nm), corresponding to the complex aggregates. When the amount of PEMA added reaches 7 wt %, there exists only a single peak in the R_h distribution; i.e., most of STVPh15 may have formed aggregates with the PEMA. When Fr of STVPh approaches 0.5, the apparent R_h of the aggregates becomes even larger, while the R_h distribution becomes narrower. Also, we should point out that complexation between STVPh and PEMA takes place and becomes detectable even at such a low concentration as 1.0×10^{-4} g/mL, $^1/_{15}$th of the concentration used in the viscosity measurements, which will be discussed below.

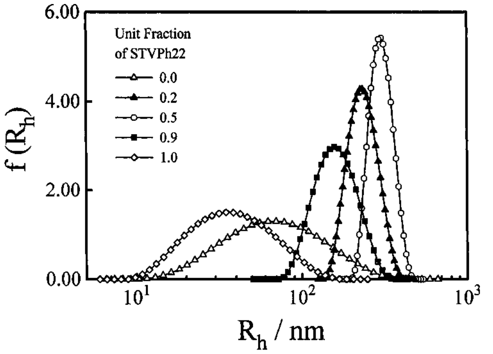

Figure 4. Hydrodynamic radius distributions f(R_h) of STVPh22, PEMA, and their blends with various blend compositions in 1-nitropropane. Same measuring condition as in Figure 1.

All the above results are obtained in the blend solutions in toluene. However, it is not possible to extend the study to STVPh with still higher hydroxyl contents because the copolymers with OH contents higher than 17 mol % are insoluble in toluene. It was found that 1-nitropropane can dissolve STVPh with OH content up to 31 mol %. This allows us to study the complexation for STVPh with higher OH content as well as the influence of the solvent on the complexation. Here, unlike the case with toluene, both component polymers contribute to the scattered light since, for both, dn/dC is non-zero. Our LLS data reveal that no aggregates were formed in the STVPh15/PEMA blend in $PrNO_2$. Figure 4 shows the f(R_h) of STVPh22, PEMA, and their blends with various compositions in $PrNO_2$. It can be seen that both component polymers have single broad R_h distributions with the peak at a few tens of nanometers. The STVPh/PEMA blend solutions at Fr = 0.2, 0.5, and 0.9 in $PrNO_2$ look clear and have single R_h distributions at much larger values, i.e., a few hundred nanometers, and are undetectable below 60 nm. Meanwhile, the width for these R_h curves is narrower than for either component alone. Therefore, we conclude that the component polymers form the interpolymer complex aggregates when the OH content in STVPh reaches 22 mol %. The composition dependence of the average hydrodynamic radius $\langle R_h \rangle$ of the STVPh22/PEMA blend in $PrNO_2$ is shown in Figure 5. It is found that a maximum appears at a STVPh22 unit fraction of 0.5, i.e., at a 1:1 STVPh22/PEMA base ratio. This means that the unlike polymers with 1:1 base ratio have the strongest tendency to form complex aggregates.

NRET Fluorescence Monitoring Complexation. The principle of the technique is that the efficiency of the energy transfer between a fluorescence energy donor and acceptor depends strongly on their proximity over a scale of ~2−4 nm. Therefore, the energy-transfer efficiency is expected to reflect the distance and degree of interpenetration between a pair of polymers provided the components are labeled with energy donor and energy acceptor, respectively. Figure 6 gives the OH

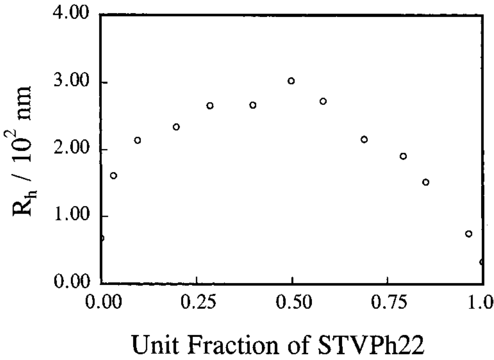

Figure 5. Blend composition dependence of the average hydrodynamic radius $\langle R_h \rangle$ for STVPh22/PEMA blends in 1-nitropropane. Same measuring condition as in Figure 1.

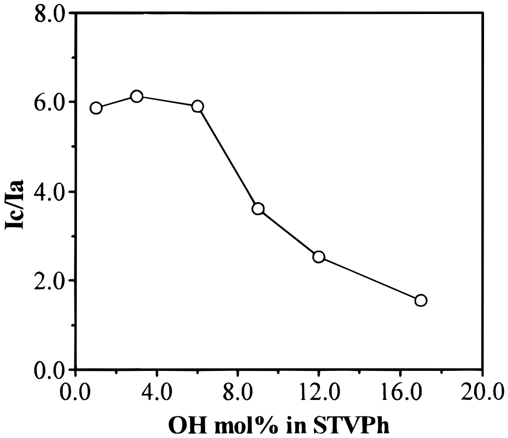

Figure 6. I_c/I_a of STVPh/PEMA blends (50/50 wt/wt) in toluene as a function of the OH content in STVPh. Concentrations of carbazole [C] and anthracene [A] are 0.52×10^{-5} and 1.31×10^{-5} M, respectively. The total concentration of polymers is 1.0×10^{-3} g/mL.

content dependence of the I_c/I_a values of the blends composed of STVPh (labeled with carbazole) and PEMA (labeled with anthracene) in toluene. At low OH content (1−6 mol %), the energy-transfer efficiency remains at a low level, obviously due to the independence of the component polymers; at high OH content (9−17 mol %), together with the appearance of turbid dispersion, the I_c/I_a value considerably decreases with the OH content; i.e., the energy-transfer efficiency obviously increases, caused by increasing interpenetration between STVPh and PEMA chains. This result is in good agreement with the above LLS results.

Figure 7 depicts the I_c/I_a values of STVPh/PEMA (50/50 wt/wt) blends in toluene as a function of the amount of added THF. Three different types of behavior, similar to those reported previously,[7,15] can be observed. (1) In the case of very low OH contents (1−3 mol %), as expected, the I_c/I_a value remains at a high level as more and more THF is added. This confirms that both component chains are originally well separated and remain so with addition of THF. (2) When the OH content in STVPh reaches 6 mol %, a slight increase in the I_c/I_a value is seen with the initial addition of THF. This may be attributed to the dissociation of hydrogen bonding between the component polymers. (3) When the OH content is further increased to 9 mol % or more, an increase in I_c/I_a with the addition of THF is apparent, together with a clearing of the originally turbid mixture. This indicates that interpenetration between unlike chains due to the formation of hydrogen bonding is being gradually disrupted. Finally, as more THF is added, all the blends reach almost the same high I_c/I_a value, showing that complexation between STVPh and PEMA is actually destroyed. In addition, Figure 7 also clearly shows that the higher the OH content is, the more THF is required to destroy complexation.

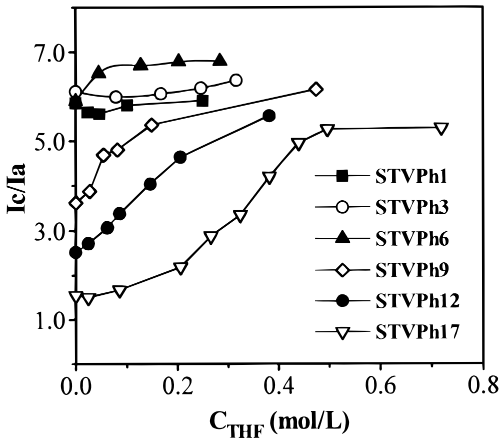

Figure 7. I_c/I_a of STVPh/PEMA blends (50/50 wt/wt) in toluene as a function of the amount of added THF, for different OH contents in STVPh. Same [C] and [A] as in Figure 6. The total concentration of polymers is 1.0×10^{-3} g/mL.

A New NRET Procedure for Detecting Complexation. In order to detect complexation more efficiently, a modified NRET procedure is designed. The basic idea is as follows. In a series of blend solutions with constant energy-donor and -acceptor concentrations but different compositions, which can be adjusted by mixing with unlabeled components, we may expect I_c/I_a to show a significant dependence on complexation. In practice, the blend solution STVPh/PEMA with a 50/50 wt/wt composition is composed of carbazole-labeled STVPh and anthracene-labeled PEMA only. In the case of asymmetric compositions, the unlabeled polymer should be dissolved in the corresponding labeled polymer solution first and then mixed with the solution of another labeled polymer. If there exists no interpenetration between the unlike chains, the existence of the unlabeled component polymer will not cause any change of I_c/I_a. If complexation takes place in the system, the unlabeled polymer will also join the complexes, thereby causing an increase in the I_c/I_a value. Here, we should point out that, in the experiments, the total concentration of polymer must vary with the blend composition in order to keep the concentrations of the energy donor and acceptor constant.

Figure 8 displays the blend composition dependence of I_c/I_a of STVPh/PEMA in toluene for various OH contents in STVPh. It can be seen that at the STVPh weight fraction of 0.5, the STVPh1/PEMA and STVPh6/PEMA blend solutions have high I_c/I_a values, while for the STVPh12/PEMA, a much lower value. This variation of I_c/I_a with the OH content is indicative of complex formation as stated above (Figure 6). Now let us examine the variation of I_c/I_a with the blend composition. For the case of a 1 mol % OH content, I_c/I_a does not change with the blend composition. This means that the excess of unlabeled polymers does not alter the distribution of the unlike labeled polymers. As the OH content reaches 6 mol %, the excess of unlabeled PEMA (STVPh6 weight fractions of 0.2 and 0.33) does not cause significant changes in the I_c/I_a value, while unlabeled STVPh6 leads to a slight increase (STVPh6 weight fractions of 0.67 and 0.8). In these two cases, there is

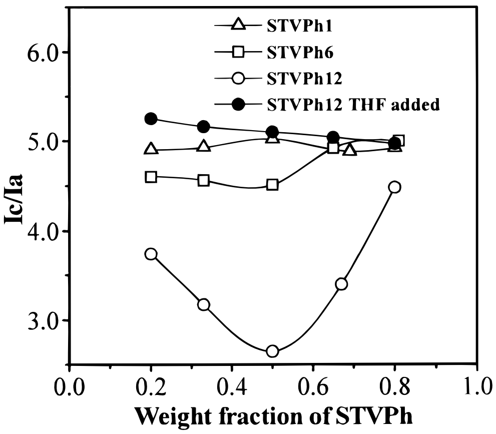

Figure 8. I_c/I_a of STVPh/PEMA blends in toluene as a function of the weight fraction of STVPh, showing the effect of the OH content in STVPh. Same [C] and [A] as in Figure 6. The total concentration of polymers is 1.0×10^{-3} g/mL.

no significant interpenetration between unlike polymers.

However, when the OH content is further increased to 12 mol %, either the unlabeled STVPh or PEMA results in a considerable increase in the I_c/I_a value, together with the appearance of turbidity. This behavior is understandable since the energy donor and acceptor are to some extent "separated" by the unlabeled polymer chains that have joined the complex aggregates. Such a significant change in I_c/I_a with the blend composition can be regarded as an indication of complexation. It also can be seen in Figure 8 that by the addition of 1% THF (v/v), the I_c/I_a of the STVPh12/PEMA blend solution is increased to the same level as for the STVPh1/PEMA blends, independent of composition. This is evidence of complete destruction by THF of the hydrogen-bonding complex aggregates between the component chains.

The above discussion clearly indicates the new NRET procedure as an efficient means for monitoring interpolymer complexation in solution.

Complementary Evidence of Complexation from Viscometry. Viscometry has been used as an effective means for elucidating complexation based on the fact that interpolymer complexation in solution is always accompanied by a contraction or collapse of the component polymer coils, resulting in a decrease in viscosity.[7,8,15,24] In practice, in a plot of reduced viscosity of blend solutions vs concentration, the data following the additivity of the component viscosity means no significant chain interpenetrating, while negative deviation from the additivity indicates intermacromolecular complexation. In the systems we studied before,[7-9,15] complexation and its dependence on the content of hydrogen-bond-forming groups found by viscometry are, in general, in good agreement with those from other techniques such as NRET fluorescence and LLS. However, in the use of viscometry to judge complexation, precipitation of polymers due to the low solubility of the complex in solution often seriously disturbs the viscosity measurements. In the present study, toluene and $PrNO_2$ were used as solvents, showing different results. In toluene, which was an typical inert solvent with no effect on hydrogen bonding between STVPh and PEMA, complexation was often accompanied by precipitation. This made quantitative examination of the viscosity impossible. In $PrNO_2$, which is a weakly polar solvent showing influence on hydrogen bonding between STVPh and PEMA, probably due to its good solvating power for the complex aggregates, stable dispersion of the complex rather than precipitates is formed.

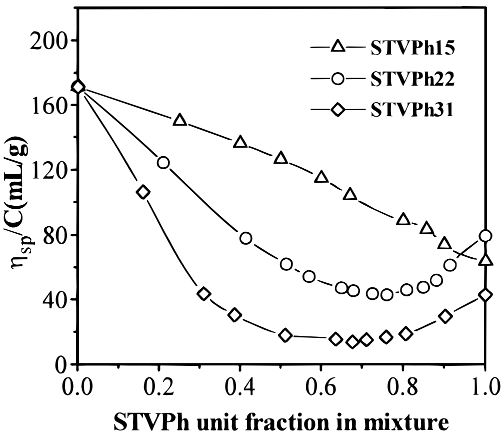

Figure 9. Reduced viscosity of STVPh/PEMA blends in 1-nitropropane as a function of the unit fraction of STVPh, showing the effect of the OH content in STVPh. The total concentration of polymers is 1.5×10^{-3} g/mL.

Figure 9 shows the OH content dependence and the blend composition dependence of the reduced viscosities of STVPh/PEMA blend solutions in $PrNO_2$. It can be seen that the blend solutions show two types of viscosity−composition relationship depending on the OH content in STVPh. For a 15 mol % OH content, the reduced viscosities of the mixtures vary rather smoothly with the composition, and the values are very close to that obtained from the additivity rule, whereas for OH contents of 22 and 31 mol %, a minimum appears in the curves.

According to the scaling theory,[25] there exists a fundamental distinction between dilute solutions where the coils are separated and semidilute solutions where the coils overlap. At the overlap threshold ($C = C^*$), the coils begin to touch one another. For the present case, the value of C^*, as estimated from $C^* = 1/[\eta]$, is greater than 5×10^{-3} g/mL since the intrinsic viscosity $[\eta]$ for either component is less than the maximum reduced viscosity, 180 mL/g. The concentration of our solutions was 1.5×10^{-3} g/mL, well below C^*. Therefore, the "smooth" variation of the viscosity with the composition at an OH content of 15 mol % just means no interpenetration between the unlike chains and the polymer coils behave independently. And in the case of large OH contents, i.e., 22 and 31 mol %, the large negative deviation from the additivity rule can be obviously attributed to intermolecular complexation rather than coil overlap. This viscosity result shows that the OH content in STVPh and the consequent hydrogen-bonding density are dominant factors governing the complexation between STVPh and PEMA. This conclusion is in good agreement with those obtained from LLS and NRET fluorospectroscopy, although the total concentration of the polymers in the viscometry experiments (1.5×10^{-3} g/mL) is much higher than in the LLS experiments (1.0×10^{-4} g/mL).

In toluene, the blend solutions with 3 mol % OH content display viscosity values in accordance with additivity. However, when the OH content increases to 9 mol %, the solution viscosity dramatically decreases, and especially, for the blend solutions with compositions ranging from 40 to 80 unit fractions of STVPh, precipitation occurred. After filtration, the viscosity dropped to very low values, which indicated that most of the polymer chains joined the complex aggregates. The blend solutions of STVPh 15/PEMA showed the same results.

A comparison of the results in toluene and $PrNO_2$ demonstrates that although the complex can form in both solvents, the minimum OH contents required to form interpolymer complexes are different: 9 mol % is enough for toluene, while 22 mol % is needed in $PrNO_2$. Such a large difference can be interpreted by the consideration that $PrNO_2$, being a polar molecule in the present system, can compete with PEMA to form a hydrogen bond with STVPh in solution. A similar effect of solvent on complexation was found in the STVPh/STVPy system.[15] It is therefore understandable that competition between polymer−polymer interaction and polymer−solvent interaction is probably the decisive factor governing complexation in solution.

Conclusions

(1) The complexation of STVPh and PEMA strongly depends on the OH content in STVPh. For example, in toluene, 9 mol % or a higher OH content is required to induce the complexation between STVPh and PEMA. (2) The complexation between STVPh and PEMA also depends on the nature of the solvent, particularly on its proton-accepting ability. The STVPh/PEMA blend could also form the interpolymer complex in 1-nitropropane, but 22 mol % or a higher OH content in STVPh would be required. Adding small amount of THF can even destroy the STVPh/PEMA complexes formed in toluene or 1-nitropropane. The higher the OH content in STVPh, the more THF is needed to destroy the STVPh/PEMA complexes. (3) A modified NRET procedure that measures I_c/I_a as a function of the composition of blends has proved to be effective in monitoring complexation. (4) The LLS results reveal the dependence of the size of the complex aggregates on both hydroxyl content in STVPh and blend composition. The peak size of the aggregates substantially increases from about 10^2 nm for the blends with large excess of STVPh up to about 10^3 nm for the blend having a 1:1 base ratio.

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