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Intermacromolecular Complexation due to Specific Interactions
4. The Hydrogen-Bonding Complex of Vinylphenol-Containing Copolymer and Vinylpyridine-Containing Copolymer

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ABSTRACT: The complexation of poly(styrene-*co*-vinylphenol) (STVPh) and poly(styrene-*co*-vinylpyridine) (STVPy) in nonaqueous solution was investigated with emphasis on the effect of the hydroxyl and pyridyl contents in the component polymers. Viscometry, nonradiative energy transfer fluorospectroscopy, and dynamic laser light scattering have led to the same conclusion, i.e., STVPh and STVPy blend can form an interpolymer complex due to hydrogen bonding in tetrahydrofuran, butanone, and chloroform, provided the contents of the hydroxyl and pyridyl reach certain respective levels. The size distribution of the complex aggregates is relatively narrow with a peak size 1 order of magnitude larger than those of the component polymer coils. The minimum content of the interaction groups required for complexation strongly depends on the solvent used. Chloroform and butanone are almost inert for hydrogen bonding between the polymers, tetrahydrofuran has a substantial influence on complexation, and addition of *N*,*N*-dimethylformamide into the dispersion of complex aggregates in THF even causes decomplexation.

Introduction

Polymer−polymer complexation has attracted extensive attention in the past 2 decades. Except for stereocomplexes[1] formed due to the van der Waals force and spatial fitting of chain conformations of the components, interpolymer complexes can be formed by intermolecular secondary binding forces, such as Coulombic interaction and hydrogen bonding, etc.[2] Tsuchida et al.[2,3] reviewed the formation, structure, and properties of the intermacromolecular complexes, especially the polyelectrolyte complexes.

Most of the hydrogen bonding complexes reported in the literature are composed of water-soluble polymers in aqueous media,[2−7] while only a few studies on complexation in nonaqueous media have been reported. Kwei et al.[8] found that poly(4-vinylphenol) (PVPh) can form complexes with poly(*N*,*N*-dimethylacrylamide) or poly(ethyloxazoline) in dioxane. Goh et al.[9] reported that poly(styrene-*co*-allylalcohol) can form a complex with poly(*N*,*N*-dimethylacrylamide) and poly(*N*-methyl-*N*-vinylacetamide) in methyl ethyl ketone but not *N*,*N*-dimethylformamide (DMF) solution. Recently, Frechet et al.[10] and Goh et al.[11] reported that mixing solutions of PVPh and poly(styrene-*co*-vinylpyridine) (STVPy) in THF led to a precipitate, which was regarded as the complex.

In our laboratory, it is of particular interest to study interpolymer complexes via hydrogen bonding as an extension of our long-term studies on miscibility enhancement by introducing hydrogen bonding into polymer blends. Our previous work[12] reported that miscibility can be realized in otherwise immiscible blends of polystyrene(PS)/poly(alkyl (meth)acrylate) by introducing hydroxyl into PS to form PS(OH), i.e., a copolymer of styrene and *p*-(1,1,1,3,3,3-hexafluoro-2-hydroxypropyl)-α-methylstyrene, even when the OH content in PS(OH) is ca. 2 mol%. Furthermore, complexation between PS(OH) and poly(methyl methacrylate)[13] or poly(butyl methacrylate)[14] can be realized by further strengthening the hydrogen bonding in the system. This kind of complexation in solution was clearly explored and confirmed by the viscometry, nonradiative energy transfer (NRET) fluorospectroscopy,[13,14] and NMR NOE[15] methods.

In the literature, much attention has been paid on the miscibility of blends comprising vinylphenol homopolymer or its copolymer (e.g. STVPh) since phenol hydroxy, as a proton-donating group, is effective in forming hydrogen bonding with a variety of proton-accepting polymers. Although there is successful theoretical prediction[16] and substantial experimental accumulation when dealing with the miscibility in the systems, not much attention has been paid on the complex formation in the blends.[8,10,11]

In this paper, our study focuses on complexation between STVPh and STVPy in solutions with emphasis on the effect of the density of interaction sites. Differing from most of the intermolecular complexes reported in the literature, in which each repeat unit of one or both component polymers possesses its own complementary binding site, here, the hydrogen-bonding density is controllable by adjusting either hydroxyl or vinylpyridine contents in the corresponding copolymers. This makes the study of the hydrogen-bonding density dependence on complexation realistic. The complexation is judged by variation of viscosity with blend composition in solution and nonradiative energy transfer efficiency between the component polymers labeled with fluorescent chromophores. In particular, dynamic light scattering is employed to "see" the complex aggregates in solution directly. Obviously, this study on complexation of STVPh and STVPy in solution is very instructive in exploring the miscibility and complexation of the blends in bulk, which will be reported in our forthcoming papers.

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Table 1. Characteristics of the STVPh Copolymers

polymer[a]	OH content (mol %)	$M_n \times 10^{-3}$ (g/mol)	M_w/M_n	chromophore content (mol %)
STVPh3	3.1	102.5	1.47	0.09
STVPh6	6.0	156.5	2.03	0.11
STVPh9	9.1	131.9	2.17	0.12
STVPh12	11.8	156.8	2.01	0.12
STVPh17	17.2	135.4	2.18	0.13
STVPh22	22.4	129.8	2.44	0.13
STVPh50	49.8	134.8	1.92	0.13
STVPh15	15.1	94.1	3.08	
STVPH30	29.6	115.8	2.54	
STVPh70	69.7			
PVPh	100			

[a] The number following STVPh represents the approximate integer value of the molar content of 4-vinylphenol in the copolymer.

Table 2. Characteristics of the STVPy Copolymers

polymer[a]	VPy content (mol %)	$M_n \times 10^{-3}$ (g/mol)	M_w/M_n	chromophore content (mol %)
STVPy25	25.2	29.2	1.44	0.37
STVPy50	49.6	25.3	1.43	0.25
STVPy75	74.9	19.8	1.58	0.16
STVPy14	13.7	35.4	1.51	

[a] The number following STVPy represents the approximate integer value of the molar content of 4-vinylpyridine in the copolymer.

Experimental Section

Monomers, Polymers, and Characterization. Styrene, 4-methoxystyrene, and 4-vinylpyridine (VPy) were vacuum distilled in the presence of calcium hydride just before use. The energy-donor monomer, vinylcarbazole, purchased from Aldrich, was used as received without further purification. The energy-acceptor monomer, 9-anthrylmethyl methacrylate, was synthesized as previously described.[13,17]

A series of STVPh copolymers with or without fluorescent label carbazole, was prepared through ether cleavage of the corresponding parent copolymer of styrene and 4-methoxystyrene with or without carbazole as previously described.[18] Anthracene-labeled STVPy was produced through copolymerization of styrene, VPy, and 9-anthrylmethyl methacrylate at 60 °C using azoisobutyronitrile as initiator, and the total conversion of the monomers was kept at less than 10%.

The chromophore contents in the copolymers were determined by UV spectroscopy, assuming that the extinction coefficients of the chromophores in the copolymers are the same as those of the corresponding monomers. The molar contents of VPy in the STVPy were obtained from nitrogen measurements, while the molar contents of OH in STVPh were calculated from the ^{1}H-NMR analysis of the methoxy contents in the parent copolymers since the ether cleavage reaction was proved to be complete.[18] The characterization data for STVPh and STVPy copolymers are listed in Table 1 and Table 2, respectively. The number-average molecular weight (M_n) and polydispersity index of those copolymers were determined by size exclusion chromatography, based on a universal calibration with PS standards.

Viscosity Measurements. Measurements of the reduced viscosities η_{sp}/C of the polymer blend solutions were conducted as a function of composition using an Ubbelohde viscometer at 30 ± 0.05 °C. The original concentrations of the component polymers were kept at 1.5×10^{-3} g/mL. STVPy samples with VPy contents at three levels, i.e., 25, 50, and 75 mol %, were used. When THF was used as the solvent, the appearance of the blend mixtures could be classified into two cases: the solution remains clear when the OH content is relatively low; the solution turns a stable dispersion, and the viscosity still can be measured when the OH content is high. The reduced viscosities were measured 10 min after mixing the STVPh and STVPy solutions in the viscometer in order to reach thermal equilibrium. When chloroform was used as the solvent, depending on the hydroxyl content in STVPh, the mixed solutions may remain clear or become turbid due to precipitation. For the late case, the viscosity was measured after filtrating of the precipitates.

Fluorescence Measurements. Emission spectra of the polymer solutions were recorded on a HITACHI 650−60 fluorescence spectrometer at room temperature (ca. 25 °C). The component polymer solutions were prepared with oxygen-free solvents. The STVPh/STVPy blend solutions were prepared by mixing the corresponding polymer solutions in a quartz cell with stirring, and purged with nitrogen for at least 1 min before each recording. Since the concentrations of both polymer solutions before mixing were low (1.0×10^{-3} g/mL), the concentration of carbazole [C] in solution was kept at 0.5×10^{-5} mol/L. For each series of blends comprising the same STVPy, the ratio of concentration of carbazole to that of anthracene [C]/[A] was kept at a constant value. The wavelength of the excitation light was set at 294 nm, and the direction of the excitation light was perpendicular to that of the emission detected. The energy transfer was characterized by I_c/I_a, the ratio of the emission intensity at 365 nm (I_c) to that at 416 nm (I_a), which were mainly due to the contributions of the energy-donor carbazole and the energy-acceptor anthracene, respectively. In terms of the phase behavior, the solutions in THF for NRET measurement are similar with those for viscometry mentioned above.

Dynamic Laser Light Scattering (LLS). LLS measurements were performed on a modified commercial LLS spectrometer (ALV/SP-125) equipped with a multi-τ digital time correlator (ALV-5000). As light source, a solid-state laser (ADLAS DPY425 II) was used. The output power was ca. 400 mw at $\lambda_0 = 532$ nm. 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 solutions of two component polymers were prepared by dissolving the polymers in a proper amount of solvent (THF, butanone), followed by diluting to 1.0×10^{-4} g/mL solutions, respectively. The dust-free polymer solutions were made by filtration through a 0.2-μ Whatman PTFE filter. Mixing of the component polymer solutions was carried out directly in a scattering cell. One dust-free component solution with calculated volume was added into the scattering cell, and then the other dust-free component solution was added in drops under gentle agitation. The solution mixture was further agitated 1 min more to allow the complete mixing of the two polymer solutions. Since the solution concentrations used here were very low, all the mixed solutions looked clear.

In dynamic LLS, the intensity-intensity time correlation function $G^{(2)}(q,t)$ was measured in the self-beating mode, and $G^{(2)}(q,t)$ had the following relationship to the normalized first-order electric field time correlation function $|g^{(1)}(q,t)|$.[19]

$$G^{(2)}(q,t) = A(1 + \beta|g^{(1)}(q,t)|^2) \qquad (1)$$

where A is a measured baseline, β is an instrument parameter depending upon the coherence of the detection, t is the delay time, and q is scattering vector.

$$q = (4\pi n/\lambda_0)\sin(\theta/2) \qquad (2)$$

where n is the solvent refractive index and θ is the scattering angle. For a polymer system, i.e., a polydisperse system, $|g^{(1)}(q,t)|$ is further related to the line-width distribution $G(\Gamma)$ by an integral equation

$$|g^{(1)}(q,t)| = \int_0^\infty G(\Gamma)e^{-\Gamma t}\,d\Gamma \qquad (3)$$

The constrained regularization CONTIN program developed by Provencher[20] was used to obtain $G(\Gamma)$ based on eqs 1 and 3. For a diffusive relaxation, Γ is a function of both c and q, i.e.[21]

$$\Gamma/q^2 = D(1 + K_dC)(1 + f\langle R_g^{\,2}\rangle q^2) \qquad (4)$$

where D is the translational diffusion coefficient at $c \rightarrow 0$ and $q \rightarrow 0$, f is a dimensionless constant, and K_d is the diffusion second virial coefficient.

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 solvent viscosity, k_B the Boltzman constant, and T the absolute temperature.

Results and Discussion

Viscometry and the Dependence of Complexation on Interaction Density. As reported in our previous papers,[13,14] interpolymer complexation in solution always accompanies a contraction or collapse of the component polymer chains, resulting in a viscosity decrease, turbidity or even precipitation. Viscometry has been proved and widely used as an effective method for monitoring complexation.[2,13,14] It is worthwhile noting that in this kind of study, polymer aggregates may form when complexation occurs so the measured viscosities are apparent values, different from those in real solutions. However, there exist many factors, such as the nature of the solvent, composition, molecular weight, etc., affecting the formation of interpolymer complexation. Besides these factors, we are particularly interested in the effect of the functional group contents in one or both of the component polymers on the complexation. For this purpose, it is desirable to measure the viscosities of the blend solutions in an inert solvent, such as toluene, which does not affect the formation of hydrogen bonding between the component polymers. Unfortunately, in this study, toluene is not able to dissolve both STVPh and STVPy with the high content of interaction units. So, THF was used as the common solvent. Although THF influences the formation of hydrogen bonding between the polymers, we are still able to get the general tendency of the dependence of complexation on hydrogen bonding density.

Figure 1 shows the variation of the apparent reduced viscosities of STVPh/STVPy25 solutions in THF as a function of the unit fraction of STVPh, i.e., the ratio of the moles of styrene and vinylphenol monomer units of STVPh to those of STVPh plus STVPy25. Here, the VPy content in STVPy is fixed at 25 mol %. Clearly, depending on the hydroxyl content in STVPh, there exist two kinds of viscosity-unit fraction behavior. In the case of OH content being 22 mol %, the reduced viscosities of STVPh/STVPy25 mixtures change smoothly with the unit fraction of the STVPh, and the values are very close to the corresponding values calculated by the additivity rule. In the other case, when the OH content in STVPh reaches 30 mol %, the blend solutions show a small negative deviation from the additivity with a minimum in the viscosity profile; meanwhile, the blend solutions turn turbid. This negative deviation of the reduced viscosities of the blend solutions becomes more substantial when the OH content in STVPh increases to 50 mol % or more.

It is well known that a fundamental distinction exists between dilute solutions where the coils are separate and semidilute solutions where the coils overlap.[22] At this overlap threshold ($C = C^*$), the coils begin to touch one another. In the present study, the maximum reduced viscosity of the copolymers is only 160 mL/g; therefore, the C^* of all the polymers in THF is higher than 6×10^{-3} g/mL as estimated by $C^* = 1/[\eta]$, where $[\eta]$ is the intrinsic viscosity of the copolymer. In our viscosity experiment, the total concentration of polymers in blend solution is ca. 1.5×10^{-3} g/mL, obviously less than C^*. This means that the coils of the two component polymers would be well separated if strong interaction between the polymers did not exist. Clearly, the "smooth" variation of the viscosity just mentioned reflects the case of no apparent association of the polymer coils in solution and the polymer coils behaving independently. In contrast, it is understandable that polymer chains make much larger contribution to viscosity in swollen coils than in the collapsed aggregates. The dramatic decrease of the apparent viscosities of the blend solutions can be attributed to the formation of complex aggregates caused by an increase in the hydrogen bonding density.

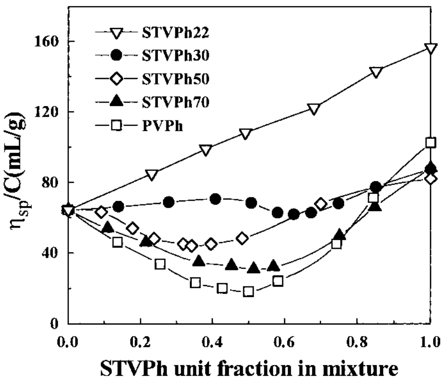

Figure 1. Reduced viscosity of STVPh/STVPy25 solutions in THF as a function of the unit fraction of STVPh, showing the effect of the hydroxyl content in STVPh.

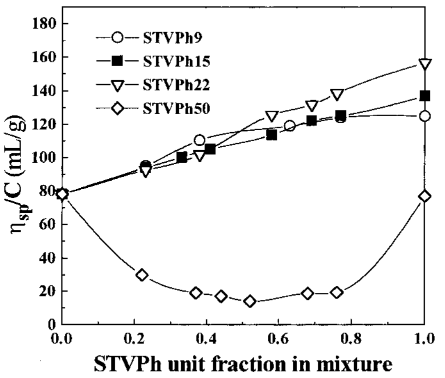

Figure 2. Reduced viscosity of STVPh/STVPy50 solutions in THF as a function of the unit fraction of STVPh, showing the effect of the hydroxyl content in STVPh.

It is widely accepted that the composition corresponding to the viscosity minimum can be regarded as the fixed mean stoichiometry (FMS) of the complex.[6a] It can be clearly seen from Figure 1 that FMS of the STVPh/STVPy25 blends varies with the content of hydroxyl in STVPh and gradually approaches to equal the base ratio (1:1) as the hydroxy content reaches 50 mol % or more. This kind of variation was observed for the blends of PS(OH) and poly(methyl methacrylate) in the inert solvent toluene as reported previously.[13] The explanation was that the complex aggregates may form a loose structure with many "free" styrene units when the OH content is low while the complex aggregates form a 1:1 dense structure when the OH content is high enough. The results of this research for STVPh/STVPy are in general accordance with the above picture.

In the present case, we enjoy the advantage of being able to change conveniently the functional group contents in both copolymers. Figures 2 and 3 depict the variation of the reduced viscosities of STVPh/STVPy50

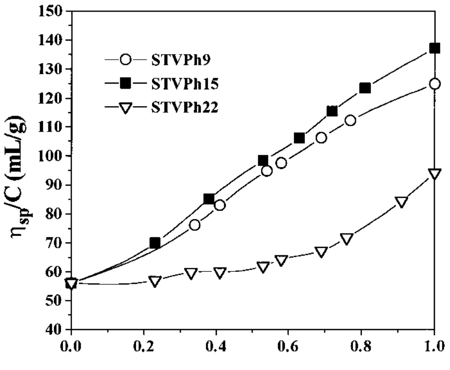

Figure 3. Reduced viscosity of STVPh/STVPy75 solutions in THF as a function of the unit fraction of STVPh, showing the effect of the hydroxyl content in STVPh.

and STVPh/STVPy75 in THF as a function of the unit fraction of STVPh. Here, it is necessary to point out that it is not possible to measure the viscosity of the mixture solutions of STVPh50/STVPy75 since the precipitate particles formed in the solutions tended to adhere on the capillary wall of the viscometer even in a very dilute solution (e.g. 5 × 10^{-4} g/mL). Also, at each level of VPy, there are two kinds of viscosity-unit fraction profiles depending on the OH content in STVPh. It is interesting to note that only 22 mol % OH content in STVPh is enough to form complexes with STVPy75 in THF, which is supported by NRET data, while STVPh22 can not form complexes with STVPy50 as reported later. If this is combined with the result of Figure 1, it can be concluded that the greater VPy content in STVPy is, the smaller OH content in STVPh is needed to form interpolymer complex aggregates in THF. Clearly, it is the hydrogen-bonding density in the blend system that determines whether or not the interpolymer complexation takes place.

Although the viscosity measurements of the blend solutions in THF provide a clear indication of the complexation dependence on the interaction site density, the smallest contents of the functional groups needed for complexation are believed to be greater than the minimum values required for complexation in bulk or in an inert solvent because THF was found to influence the hydrogen bonding, such as between PS(OH) and poly(alkyl methacrylate).[13,14] Therefore, efforts were made to find solvents which have a lower ability to form hydrogen bonds than THF. In this purpose, the results of the blend solutions of the STVPh/STVPy50 in chloroform, which can dissolve STVPh with a relatively low OH content and STVPy, are shown in Figure 4. Similar to the viscosity behavior in THF, there also exist two types of viscosity-unit fraction relationship. It can be seen that no interpolymer complexation occurs when the OH content in STVPh is less than 3 mol %, and the blend solutions remain clear. However, the apparent viscosities are significantly lower than the values calculated by the additivity rule when the OH content in STVPh reaches 6 mol %. Compared with Figure 2, it is clear that the least OH content (6 mol %) in STVPh required to form complexes with STVPy50 in chloroform is a great deal less than that required in THF (>22 mol %). This obvious difference can be undoubtedly attributed to the quite different nature of the solvents, since chloroform is almost inert to strong hydrogen bonding while THF, as a proton-acceptor type solvent, has a certain ability to form hydrogen bonds with hydroxyl units in STVPh.

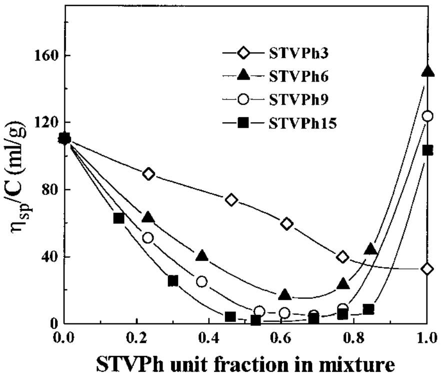

Figure 4. Reduced viscosity of STVPh/STVPy50 solutions in chloroform as a function of the unit fraction of STVPh, showing the effect of the hydroxyl content in STVPh.

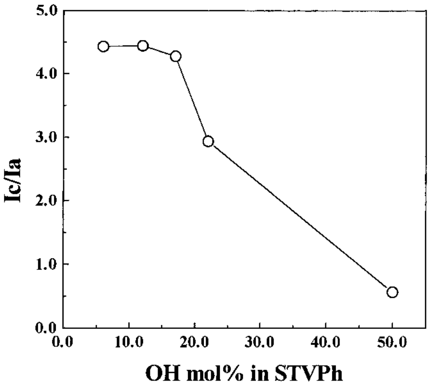

Figure 5. I_c/I_a of STVPh/STVPy75 (50/50 wt/wt) solutions in THF as a function of the hydroxyl content in STVPh. ([C] = 0.5 × 10^{-5} mol/L, [C]/[A] = 0.68, and [C] and [A] are the concentrations of carbazole and anthracene, respectively.)

NRET Fluorospectroscopy Monitoring Complexation. Our previous studies[13,14] on intermacromolecular complexation showed that NRET fluorospectroscopy is a sensitive technique for monitoring complexation and variation in the microstructure of the polymer coils in solution. The principle of this technique is that this efficiency of the energy transfer between a fluorescence energy donor and energy acceptor depends strongly on their proximity over a scale of ~2−4 nm. Since the sensitive scale is much smaller than the diameter of ordinary polymer coils in solution, the NRET technique is expected to be an effective way to reflect the distance and the degree of interpenetration between the two component polymers with labels of energy donor and acceptor respectively. Figure 5 shows the I_c/I_a ratio of the STVPh/STVPy75 blend solutions in THF as a function of the OH content in STVPh. Here the energy donor (carbazole, c) and energy acceptor (anthracene, a) are attached to STVPh and STVPy, respectively. Note the energy transfer efficiency is inversely proportional to I_c/I_a. Clearly, the low energy transfer level is associated with the blend solutions in which the OH content in STVPh is relatively low (≤17 mol %), and I_c/I_a does not change over this OH content range. This implies that the coils of the two component polymers are well separated in the solution, and there is no obvious interpenetration between the unlike chains. However, when the OH content in STVPh reaches 22 mol % or more, the solutions show much higher energy transfer efficiencies accompanying the appearance of turbidity and decrease of viscosity as shown in Figure 3. In particular, when the OH content increases to 50 mol %, the I_c/I_a value of the blend solution drops to 0.6, very

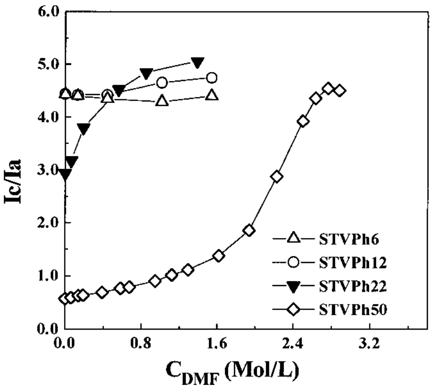

Figure 6. I_c/I_a of blends of STVPy75 and STVPh with different OH content (50/50 wt/wt) in THF as a function of the amount of added DMF. ([C] and [A] are the same as in Figure 5).

different from the value for the low OH content (by a factor of 7). Such high energy transfer efficiency indicates the intimate proximity and high interpenetration of the unlike polymers as a result of complex formation. Obviously, this result is in good agreement with the viscosity results and they complement each other.

A more powerful proton-acceptor type solvent DMF was used here to study the effect of solvent on the complexation. Figure 6 illustrates the dependence of I_c/I_a of STVPh/STVPy75 solutions in THF on the amount of added DMF. Depending on the OH content in STVPh, there exist two different types of behavior. When the OH content in STVPh is relatively low (6 and 12 mol %), the I_c/I_a value changes very little with the addition of DMF. This indicates that addition of DMF does not disturb the spatial distribution of the chains, because the unlike chains are orginally well-separated without interpenetration before adding DMF. However, for the blends with the OH content in STVPh of 22 mol % or more, adding DMF causes the I_c/I_a value to gradually increase first and then level off. This variation accompanied the complete clearing of the turbid solutions. This implies that the interpolymer complex aggregates originally formed in THF can be completely destroyed by adding sufficient amounts of DMF. Incidentally, this result provides additional evidence that the driving force of complexation is hydrogen bonding between the components.

In the other two series of blends of STVPh/STVPy25 or STVPh/STVPy50, addition of DMF causes qualitatively similar variations of I_c/I_a. As examples, three curves for the blend solutions of STVPh50 with the respective counterparts of STVPy25, STVPy50, and STVPy75 are shown in Figure 7. It is found that the variation from the complex aggregates to separated coils caused by addition of DMF can be realized in all the three cases. These curves show that the least concentrations of DMF required for completely destroying the complex aggregates for the cases of STVPy25, STVPy50, and STVPy75 are 0.45, 1.5, and 2.8 mol/L, respectively. It simply indicates that the higher the content of the interaction site, the higher the concentration of DMF is needed for decomplexation. This is understandable because DMF, being a strong proton-accepting solvent, plays a role of destroying the hydrogen-bonding between hydroxyl and pyridyl groups.

Direct View of Complex Aggregates by LLS. Laser light scattering has been widely used to investigate polymer–polymer–solvent ternary systems, including polymer pairs without specific interactions in nonaqueous media,[23] and polyelectrolyte pairs in water or in polar solvent.[2] However, to our knowledge, LLS study on interpolymer complexation in nonpolar solvent has not been reported up to now.

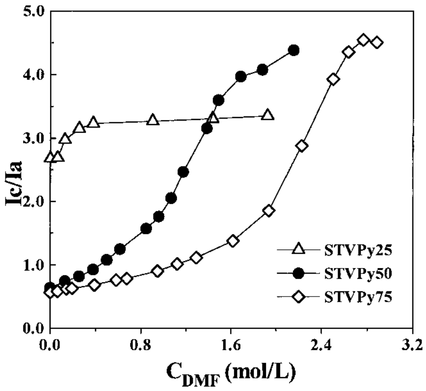

Figure 7. I_c/I_a of blends of STVPh50 and STVPy with different VPy contents (50/50 wt/wt) in THF as a function of the amount of added DMF. [C] = 0.5 × 10^{-5} mol/L.

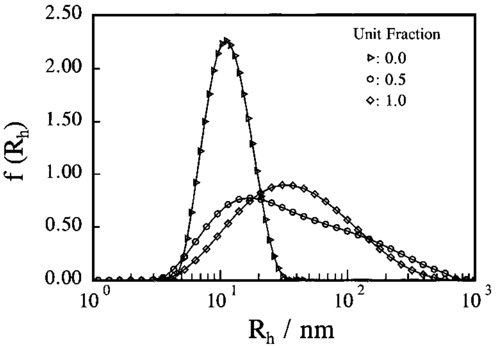

Figure 8. Hydrodynamic radius distributions $f(R_h)$ of STVPh50, STVPy14, and their blend (50/50 wt/wt) in THF. The total concentration of polymers is 1.0 × 10^{-4} g/mL; the scattering angle is 15°.

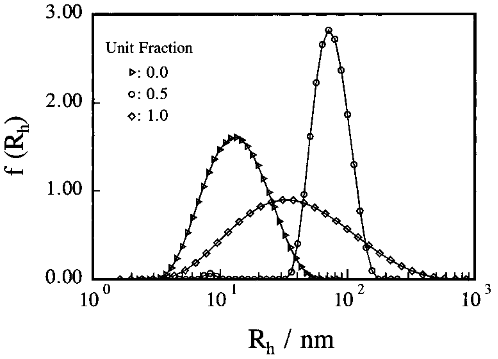

Figure 9. Hydrodynamic radius distributions $f(R_h)$ of STVPh50, STVPy25, and their blend (50/50 wt/wt) in THF. Measuring conditions are the same as in Figure 8.

Interpenetration or aggregation between unlike chains should accompany a variation of the particle sizes and the hydrodynamic radius. Therefore, LLS is believed to be effective to monitor this variation. In this paper, attention is paid on the effect of VPy content in STVPy on complexation, while the OH content in STVPh is fixed at 50 mol %. Figures 8–10 show the apparent hydrodynamic radius distributions $f(R_h)$ of STVPh50, STVPy moieties with various VPy content, and their blends (50/50 wt/wt) in THF. It can be seen that the various STVPy moieties have a relatively narrower R_h distribution, while STVPh50 has a rather broad one extending to the 10^2 nm range. This unusual broad

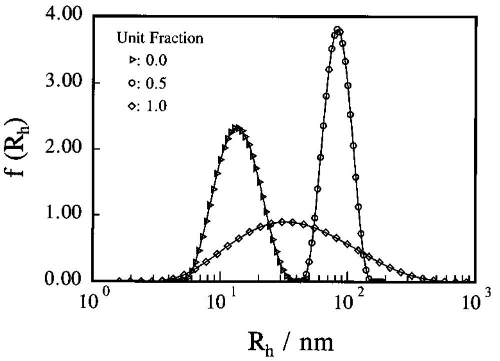

Figure 10. Hydrodynamic radius distributions $f(R_h)$ of STVPh50, STVPy50, and their blend (50/50 wt/wt) in THF. Measuring conditions are the same as in Figure 8.

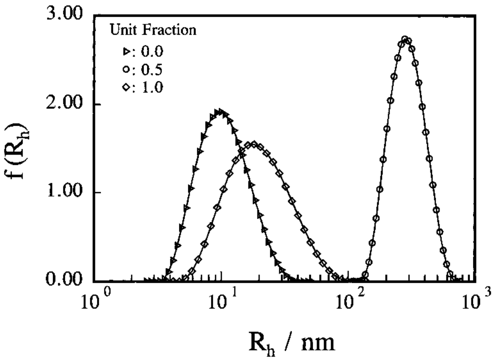

Figure 11. Hydrodynamic radius distributions $f(R_h)$ of STVPh6, STVPy25, and their blend (50/50 wt/wt) in butanone. Measuring conditions are the same as in Figure 8.

distribution, in our opinion, reflects the presence of both intramolecular and intermolecular associations of STVPh due to hydrogen bonding between vinylphenols even in THF. It is noted that depending on the VPy content in STVPy, STVPh50/STVPy blends show completely different R_h distributions. In Figure 8, when VPy content is only 14 mol %, the R_h distribution of STVPh50/STVPy14 blend is very similar to that of pure STVPh50, and the peak position of the blend is quite close to that of pure STVPh50 at about 25 nm. This implies that there is no apparent aggregation or interpenetration between the component polymers. However, this situation is completely changed when the VPy content in STVPy reaches 25 mol % (Figure 9). The most remarkable feature of the R_h distribution of STVPh50/STVPy25 blend solution is that the peak position moves to ca. 80 nm, significantly larger than the peak position of either component. It is interesting to note that the distribution of this blend is bimodal with a small peak located at about 9 nm, which can obviously be attributed to the remaining individual polymers in solution. This result clearly shows that, even at very low concentration (1×10^{-4} g/mL) in THF, STVPh50 and STVPy25 chains form complex aggregate with a size increase by a factor of 3 in comparison with the pure component.

A similar R_h distribution, shown in Figure 10, is observed for the blend solutions of STVPh50/STVPy50. The only difference is that there is no signal detected around the size range of the pure component. This fact means that all of the polymer chains may have joined in the complex aggregates. Besides, in comparison with STVPh50/STVPy25 blend, the R_h distribution of STVPh50/STVPy50 blend is apparently narrower. It is worth noting that although the total concentration of polymers here is very low (1.0×10^{-4} g/mL), which is only $^{1}/_{15}$th of the polymer concentration used in viscosity measurements and well below the overlap threshold C^*, the complexation and its dependence on the content of interaction site in the component polymers are clearly revealed. More importantly, LLS and viscometry and NRET fluorospectroscopy have led to the same conclusion.

As mentioned above, THF, being a proton-acceptor type solvent, can compete with STVPy to form a hydrogen bond with STVPh. For studying the effect of solvent on complexation, butanone was also chosen for comparing with THF in addition to chloroform, which was almost inert for hydrogen bonding but with limited solubility for STVPh with high OH content. Butanone has the following advantages. The STVPh/STVPy blend in butanone usually forms a stable dispersion while in chloroform it forms large aggregates causing precipitation. Butanone possesses a rather weak proton-accepting ability and causes very little effect on the polymer complexation in the present case. However, butanone can not dissolve STVPy with high VPy content. Therefore, the STVPh/STVPy25 blend in butanone was selected to be studied.

Figure 11 shows the apparent hydrodynamic radius distributions $f(R_h)$ of STVPh6, STVPy25, and their blend (50/50 wt/wt) in butanone. The peak position of STVPy25 is at about 12 nm. The R_h distribution of STVPh6 is relatively broad due to the presence of self-association between phenol hydroxy with a peak at about 25 nm. Mixing the component polymers in the 1:1 ratio leads to a visually clear solution, showing a narrow R_h distribution with the peak at about 300 nm. Obviously, this fact confirms the formation of interpolymer complex aggregates between STVPh6 and STVPy25 in butanone, which is in good agreement with the viscosity data (Figure 4) for the blend solutions in chloroform. Although it was reported that butanone could destroy the hydrogen bonding between PS(OH) and poly(ethyl methacrylate) in toluene,[12b] it appears to be almost ineffective for the hydrogen bonding between the hydroxyl in STVPh and pyridyl in STVPy because the pyridyl has a much higher hydrogen-accepting ability than butanone. In addition, our LLS data also show that the STVPh6/STVPy25 solution in THF has almost the same $f(R_h)$ as that of STVPh6, indicating no complexation. This result is in good agreement with the result based on the viscosity and fluorescence data that STVPy25 could not form interpolymer complex with STVPh containing hydroxy less than 22 mol % in THF. Clearly, such different complexation behavior of STVPh6/STVPy25 blend in two solvents could unambiguously be attributed to the fact that THF has a much stronger proton-accepting ability than butanone.

Conclusions

A combination of techniques, i.e., viscometry, NRET fluorospectroscopy, and dynamic laser light scattering, has shown that STVPh/STVPy blend systems can form interpolymer complex aggregates in suitable solvents provided the OH and VPy contents in the corresponding component polymers are high enough. The size of the complex aggregates is usually 1 order of magnitude larger than the individual polymer coils and possesses a relatively narrow distribution. The least functional group content in the copolymers needed to form complex aggregates depends largely upon the proton-accepting ability of the solvent. For example, for STVPy25 in butanone, which has little effect on complexation, 6 mol % of hydroxy in STVPh leads to complexation while a much higher value of 30 mol % is required in THF. Furthermore, addition of sufficient DMF into the complex dispersion results in complete decomplexation.

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