Complexation between Poly(styrene-*co*-4-vinylphenol) and Poly(styrene-*co*-4-vinylpyridine) in Solution

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ABSTRACT: Complexation between poly(styrene-*co*-4-vinylphenol) (STVPh) and poly(styrene-*co*-4-vinylpyridine) (STVPy) in solution has been studied by a combination of static and dynamic laser light scattering. It was found that the complexation was strongly influenced by the phenol and pyridyl contents and the solvent used. In a stronger proton-acceptor solvent, the complexation only happens when the phenol and pyridyl contents are higher than a certain value, indicating a competition between the formation of the polymer−polymer and polymer−solvent hydrogen bonding. The addition of water, a strong hydrogen-bonding solvent, can completely destroy the complexation, clearly showing that it is the hydrogen bonding that induces the complexation. When the molar ratio of the monomer units of STVPh to STVPy is ∼1:1, the scattering intensity reaches a maximum, indicating that the complexation has a 1:1 stoichiometry. On the other hand, when STVPy was in excess in the solution mixture, each STVPh chain is complexed with a certain number of the STVPy chains over a wide range of composition and vice versa, suggesting the complexation is sterically governed.

Introduction

Complexation between complementary polymers has attracted great attention because it is important toward the understanding of higher-order structures of biological materials.[1−3] For example, a double-helix DNA is a ladder-like structure bridged by many hydrogen bondings. Recently, the complexation has also been used in such areas as chemical engines, actuators, biosensors, separations, drug delivery.[4] At the present stage of research, a deeper understanding of both the formation and structures of the complexes remains a challenge. Various techniques including laser light scattering (LLS), such as viscometry, conductimetry, turbidity, UV, IR, NMR, and the nonradiative energy transfer (NRET) fluorescence, have been used to study the complexation between different pairs of polymers.[1−11] Among them, LLS is one of the most sensitive methods for the study of the formation of large supermolecular structures and complexation because the scattered light intensity is proportional to the square of the molar masses.

Most of the previous LLS studies on the polymer complexation were the characterizations of nonstoichiometry complexation in aqueous solutions consisting of at least one type of high molar mass polyelectrolytes.[11] Djadoun[12] used small-angle light scattering to investigate the association between cationic polystyrene and anionic poly(methyl methacrylate) (PMMA) ionomer chains in ethyl benzoate (an isorefractive solvent of PMMA). Tsuchida *et al.*[13,14] studied the influence of the polymer concentration, pH, and temperature on the complexation between poly(methacrylic acid) (PMAA) and poly(ethylene oxide). Hara and Nakajima[15] studied the composition and ionic strength dependence of the complexation between heparin and partially aminoacetalized poly(vinyl alcohol). They concluded that the shape of the complexes are spherical after a comparison of their experimental scattering curves with the theoretical predictions for monodisperse spheres, coils, and rods. Dautzenberg *et al.*[16,17] used an improved LLS data analysis algorithm to study the structural detail of large complexes. Further, Dubin *et al.*[18−20] used a combination of static and dynamic LLS to reveal the architecture of the complexes between poly(dimethyldiallylammonium chloride) and a mixture of the anionic and nonionic micelles.

On the other hand, introducing specific interactions has attracted much attention in material research and development because it can improve the miscibility between otherwise immiscible polymers.[5] In the blend of PMMA and poly[styrene-*co*-*p*-(1,1,1,3,3,3-hexafluoro-2-hydroxypropyl)-α-methylstyrene] [PS(OH), a modified polystyrene], the transitions from immiscibility to miscibility and then from miscibility to complexation can be induced simply by increasing the hydroxyl content of PS(OH).[5−7] Recent studies concluded that the complexation takes place not only in bulk but also in solution, even in dilute solutions. Our previous LLS results of the complexation between poly(styrene-*co*-4-vinylphenol) (STVPh) and poly(ethyl methacrylate) (PEMA) in toluene were not only consistent with but also gave more quantitative results than the NRET and viscosity results.[21] We found that when STVPh was in excess, each PEMA chain is able to complex with a certain number of the STVPh chains, suggesting a “nucleation” in the initial stage of the blending. In this study, we extend our LLS investigation to the complexation between STVPh and poly(styrene-*co*-4-vinylpyridine) (STVPy). The advantage of this system is that the structures of the two polymer chains are similar and the strength of the interaction between the two polymer chains can be continuously adjusted by varying the phenol and pyridyl contents.

Experimental Section

Sample Preparation. Poly(styrene-*co*-4-vinylphenol) (STVPh) samples with different phenol contents were prepared by copolymerization of styrene and 4-methoxylstyrene, followed by a demethylation procedure.[22] Poly(styrene-*co*-4-vinylpyridine) samples were made by copolymerization of styrene and 4-vinylpyridine at 60 °C using 2,2′-azobisisobutyronitrile (AIBN) as the initiator. The molar content of

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Table 1. LLS Results of STVPh and STVPy in Toluene or THF at 25 °C

sample	phenol (mol %)	pyridyl (mol %)	M_w (10 g/mol)	A_2 (mol^{-4} mL·mol/g^2)	$\langle R_g\rangle$ (nm)	$\langle R_h\rangle$ (nm)	$\langle R_g\rangle/\langle R_h\rangle$	dn/dC (mL/g)
STVPh0	0		3.1					0.110
STVPh3	3		1.0	4.9	~12	9	1.4	
STVPh6	6		3.7	1.0	40	26	1.5	
STVPh9	9		4.0	3.4	42	27	1.6	0.115
STVPh12	12		2.9	1.3	39	26	1.5	
STVPh15	15		3.9	0.6	36	23	1.5	0.111
STVPh50[a]	50		4.0	2.4	49	38	1.3	0.195
STVPy14[a]		14	0.8	3.3	20	11	1.8	
STVPy25[a]		25	1.2	2.8	24	14	1.7	0.201
STVPy50[a]		50	1.6	2.4	22	15	1.5	0.197

[a] Measured in THF.

phenol or pyridyl of the copolymers are governed by the feeding composition. Table 1 summarizes the respective LLS results of STVPh and STVPy in toluene and THF at 25 °C before the mixing of the solutions. In Table 1, the number following STVPh or STVPy represents the molar percent of 4-vinylphenol (VPh) or 4-vinylpyridine (VPy) in the copolymer.

All solutions were clarified with a 0.2 μm Whatman PTFE filter. The mixtures with different compositions were prepared by adding dropwise a proper amount of the dust-free STVPh solution to ~1 mL of previously clarified STVPy solution with vigorous mixing or vice versa. The weight of 1 drop of the solution is ~0.01 g and the adding rate is about 1 drop/s. The final composition of the solution mixture was determined by weighing. The initial concentrations of the STVPh and STVPy solutions were 1.00×10^{-4} g/mL, except when specified otherwise. When one of the two components is in excess, the solution mixtures are stable even after standing for 2 months. Nevertheless, fresh solution mixtures were used in LLS.

The complex dispersions with different water contents were prepared by adding dropwise a proper amount of dust-free deionized water to ~2 mL of the initial solution mixture. The scattering intensity and $\langle R_h\rangle$ were measured after the solution mixture had reached its equilibrium.

Laser Light Scattering (LLS). A modified commercial LLS spectrometer (ALV/SP-125) equipped with a multi-τ digital time correlator (ALV-5000) and a solid-state laser (ADLAS DPY 425 II, output power ≅ 400 mW at $\lambda_0 = 532$ nm) was used. The incident beam was vertically polarized with respect to the scattering plane. All LLS measurements were done at 25.0 ± 0.1 °C. The specific refractive index increment (dn/dC) was determined by a novel and precise differential refractometer.[23]

In static LLS, for each solution mixture, the angular dependence of the excess absolute time-averaged scattered intensity, known as the excess Rayleigh ratio $R_{vv}(q)$, of a set of dilute copolymer solutions were measured. $R_{vv}(q)$ is related to the weight average molar mass M_w, the second virial coefficient A_2, and the z-average root mean square radius of gyration $\langle R_g^2\rangle_z^{1/2}$ (or simply as $\langle R_g\rangle$) as[24]

$$\frac{KC}{R_{vv}(q)} \cong \frac{1}{M_w}\left(1 + \frac{1}{3}\langle R_g^{\,2}\rangle_z q^2\right) + 2A_2C \tag{1}$$

where $K = 4\pi^2n^2(\mathrm{d}n/\mathrm{d}C)^2/(N_A\lambda_0^4)$ with N_A, n, and λ_0 being Avogadro's constant, the solvent refractive index, and the wavelength of light in vacuum, respectively. $q = (4\pi n/\lambda_0)\sin(\theta/2)$ with θ being the scattering angle. The polymer concentration (C) is in the unit of g/mL. It should be noted that eq 1 is valid only for a homopolymer solution. However, in this study, the values of dn/dC of STVPh and STVPy are nearly identical, so that we can still use eq 1 for all static LLS calculations.

In dynamic LLS, the intensity–intensity time correlation function $G^{(2)}(t,q)$ in the self-beating mode was measured. $G^{(2)}(t,q)$ can be related to the normalized first-order electric field time correlation function $|g^{(1)}(t,q)|$ as[25,26]

$$G^{(2)}(t,q) = \langle I(0,q)\, I(t,q)\rangle = A[1 + \beta|g^{(1)}(t,q)|^2] \tag{2}$$

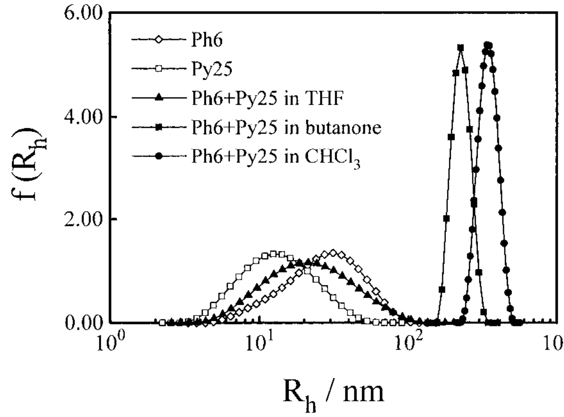

Figure 1. Comparison of hydrodynamic radius distributions [$f(R_h)$] of STVPh6, STVPy25, and the equimolar STVPh6 + STVPy25 solution mixtures respectively in CHCl$_3$, butanone, and THF, where $\theta = 15°$.

where A is a measured base line, β a parameter depending on the coherence of the detection, and t the delay time. For a polydisperse sample, $|g^{(1)}(t,q)|$ is related to the line-width distribution $G(\Gamma)$ as

$$|g^{(1)}(t,q)| = \langle E(0,q)\, E^*(t,q)\rangle = \int_0^\infty G(\Gamma)e^{-\Gamma t}\, \mathrm{d}\Gamma \tag{3}$$

$G(\Gamma)$ can be calculated from the Laplace inversion of $G^{(2)}(t,q)$ on the basis of eqs 2 and 3. In this study, the constrained regularization CONTIN program developed by Provencher[27] was used. For a diffusive relaxation, Γ is a function of both C and q,[28,29] namely $\Gamma/q^2 = Df(C,q)$, where D is the translational diffusion coefficient at $C \to 0$ and $q \to 0$ and $f(C,q) \to 1$ at $C \to 0$ and $q \to 0$. Therefore, for a dilute solution at a small scattering angle, $\Gamma/q^2 \approx D$. Further, D can be converted to the hydrodynamic radius (R_h) using the Stokes–Einstein equation: $R_h = k_BT/6\pi\eta D$, where η is the solvent viscosity, k_B the Boltzmann constant, and T the absolute temperature.

Results and Discussion

Effects of Solvent on the Complexation. Figure 1 shows the hydrodynamic radius distributions of STVPh6, STVPy25, and the STVPh6 + STVPy25 solution mixtures in CHCl$_3$, butanone, and THF, respectively, where the molar fraction (X_{STVPy}) of the monomer unit STVPy is 0.5 and is defined as

$$X_{\mathrm{STVPy}} = \{[\text{monomer unit}]_{\mathrm{styrene}} + [\text{monomer unit}]_{\mathrm{vinylpyridine}}\}_{\mathrm{STVPy}} / \{[\text{monomer unit}]_{\mathrm{styrene}}\}_{\mathrm{STVPy+STVPh}} + [\text{monomer unit}]_{\mathrm{vinylpyridine}} + [\text{monomer unit}]_{\mathrm{vinylphenol}} \tag{4}$$

There is no obvious change of $f(R_h)$ in THF after mixing STVPh6 and STVPy25, while in both CHCl$_3$ and bu-

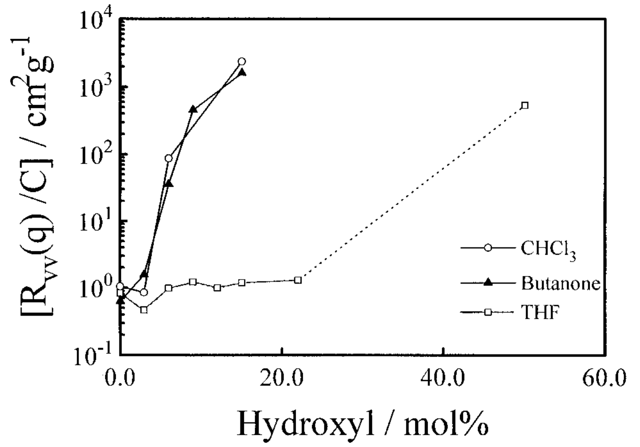

Figure 2. Phenol content dependence of the reduced Rayleigh ratio $[R_{vv}(q)/C]$ of the equimolar STVPy25 + STVPh solution mixtures in CHCl$_3$, butanone, and THF, where $\theta = 15°$.

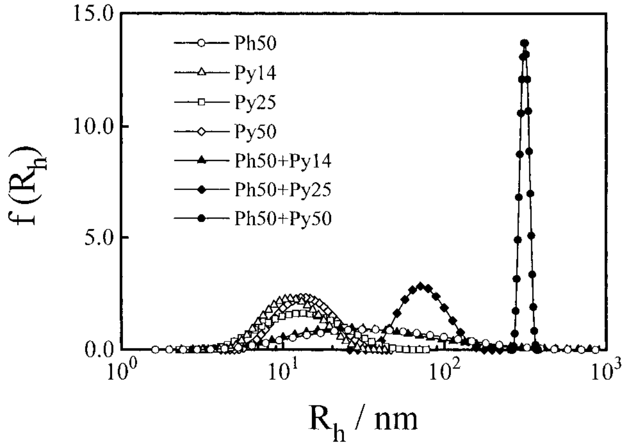

Figure 3. Pyridyl content dependence of the hydrodynamic radius distributions $[f(R_h)]$ of STVPh50, STVPy, and the equimolar STVPh50 + STVPy complexes, where the pyridyl content of STVPy ranges from 14 to 50 mol % and $\theta = 15°$.

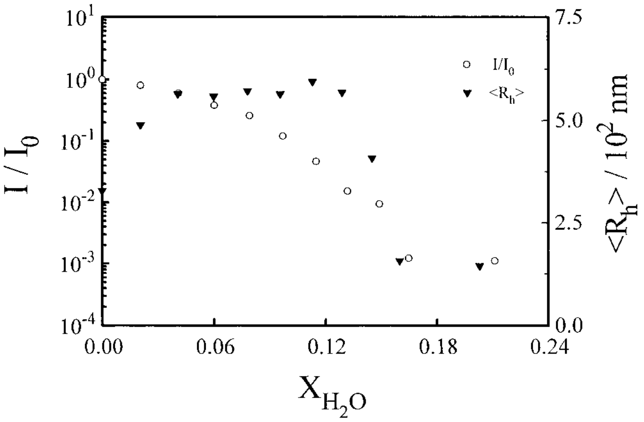

Figure 4. Water content dependence of the relative scattering intensity (I/I_0) and average hydrodynamic radius $[\langle R_h \rangle]$ of the equimolar STVPh50 + STVPy50 complexes in THF.

tanone, $f(R_h)$ shifts to higher R_h after mixing. It was known that two polymer chains with two complementary functional groups can interwind to form large aggregates in the solution mixture. These large intermolecular aggregates were evidenced not only by a dramatic increase of the scattering intensity but also by an increase of the energy-transfer efficiency in NRET.[30,31] In comparison with the interchain interaction in solid form, the complexation of two complementary polymer chains in solution is a result of the competition between STVPh−STVPy interaction and STVPh− or STVPy−solvent interaction. In CHCl$_3$ a stronger complexation between STVPh6 and STVPy25 is expected because CHCl$_3$ is nearly inert to the hydrogen bonding, while THF is very able to form the hydrogen bonding with a hydroxyl in STVPh, so that there is no obvious complexation between STVPh6 and STVPy25. This explains that butanone as a relative weak proton-accepting solvent leads to smaller STVPh6 + STVPy25 complex clusters. This cooperative interaction has long been recognized in the complexation between poly(ethylene glycol) (PEG) and PMAA in aqueous solution, wherein the cooperative interaction between PEG and PMAA is so strong that the hydrogen bonding between PEG or PMAA and water is overcome as long as the molar mass of the PEG or PMAA chains reaches a critical value.[1−3] The complexation can also be viewed in the terms of the scattered light intensity.

Figure 2, respectively shows the phenol content dependence of the reduced Rayleigh ratio $R_{vv}(q)/C$ of the STVPh/STVPy25 mixtures in CHCl$_3$, butanone, and THF. A combination of static and dynamic LLS results showed that STVPy25 can complex with STVPh in THF, CHCl$_3$, and butanone as long as the phenol contents are respectively higher than ~50, ~6, and ~6 mol %, which follows the order of the ability to form the hydrogen bonding, i.e., THF > Butanone ~ CHCl$_3$. The cooperative character of the complexation can also be revealed by varying the pyridyl content of STVPy.

Figure 3 shows that, for a given phenol content of 50 mol %, the pyridyl content of STVPy can greatly affect the complexation between STVPh and STVPy. The minimum pyridyl content to initiate the complexation between STVPh50 and STVPy in THF is ~25 mol %. The shifting of $f(R_h)$ toward a larger size clearly indicates the complexation between STVPh and STVPy. The narrow width of $f(R_h)$ suggests that as the strength of the interaction between STVPh and STVPy increases, the complexation leads to the collapse of the polymer chains. The competition between the polymer−polymer and polymer−solvent hydrogen bonding can be better demonstrated by adding some strong proton-accepting solvents, such as DMF and water, into the solution mixture containing the complexes.

Figure 4 shows the water content dependence of the relative scattering intensity I/I_0 and the average hydrodynamic radius $\langle R_h \rangle$ of the STVPh50 + STVPy50 complexes in THF, where X_{H_2O} is the molar fraction of water added in THF, I_0 is the scattering intensity before adding water into the solution mixture, the molar ratio of the monomer units of STVPh50 to STVPy50 is 1:1, and the total polymer concentration of the solution mixture is 1.00×10^{-4} g/mL. On the basis of eq 1, the scattering intensity is proportional to the square of molar mass. The third-order decrease of I/I_0 clearly indicates the dissociation of the STVPh50 + STVPy50 complexes after the addition of water, because water can form a stronger hydrogen bonding than THF, so that the hydrogen bonding between STVPh and STVPy is destroyed. A comparison of I/I_0 and $\langle R_h \rangle$ in Figure 4 indicates that the initial increase of $\langle R_h \rangle$ indicates the swelling of the STVPh50 + STVPy50 complexes prior to their dissociation. Figure 5 shows the corresponding NRET fluorescence results. It reveals the swelling of the complexes after the addition of water in terms of the decrease of the energy transferring efficiency between the two complementary polymers.[31] The fact that water as a nonsolvent can partially destroy the STVPh50

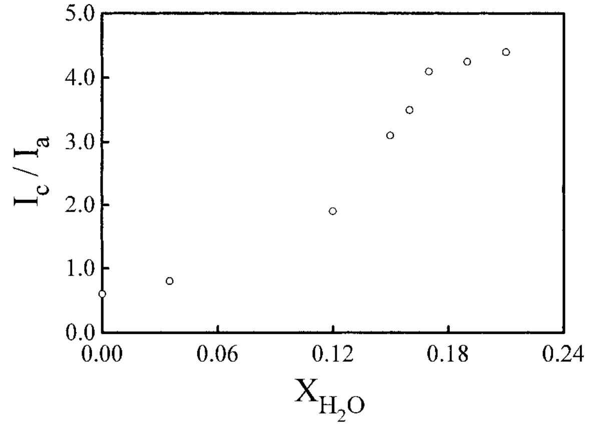

Figure 5. I_c/I_a of blends of STVPh50 and STVPy50 in THF as a function of the amount of added water.

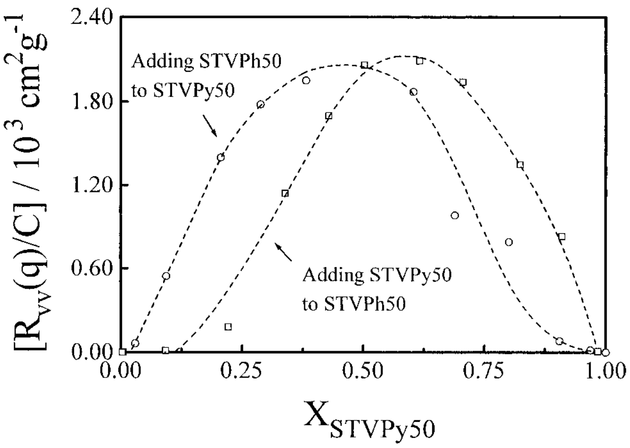

Figure 6. Composition dependence of the reduced Rayleigh ratio $[R_{vv}(q)/C]$ of the STVPh50 + STVPy50 solution mixture, where $\theta = 15°$ and the solvent is THF.

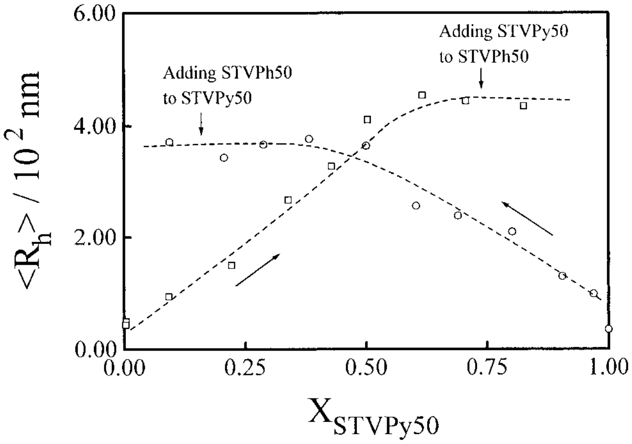

Figure 7. Composition dependence of the average hydrodynamic radius $[\langle R_h \rangle]$ of the equimolar STVPh50 + STVPy50 solution mixture, where $\theta = 15°$ and the solvent is THF.

+ STVPy50 complexes strongly supports that the complexation is through the hydrogen bondings between STVPh and STVPy.

Structure of the STVPh + STVPy Complexes. Figures 6 and 7 respectively show the composition dependence of the reduced Rayleigh ratio $[R_{vv}(q)/C]$ and average hydrodynamic radius ($\langle R_h \rangle$) of the solution mixture. When one component is in excess, the average size of the STVPh50 + STVPy50 complexes is small and $R_{vv}(q)/C$ is low, indicating that most of the polymer chains exist as individual chains in the solution mixture.

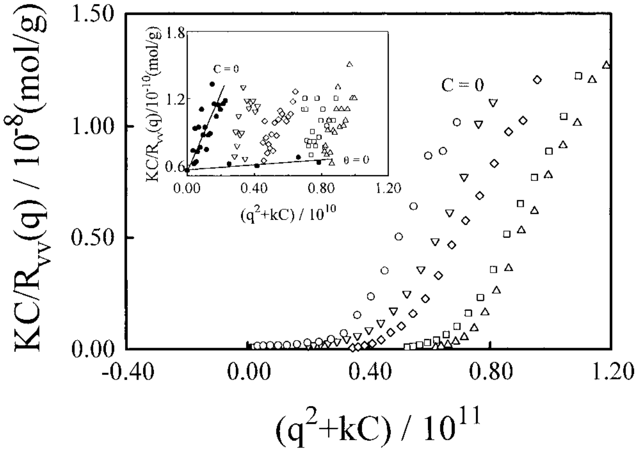

Figure 8. Typical Zimm plot of an equimolar STVPh50 + STVPy50 solution mixture, where the total polymer concentrations are ∇, 2.76×10^{-6} and 5.21×10^{-6} g/mL; $\square$, 8.25×10^{-6} g/mL; and Δ, 9.79×10^{-6} g/mL and the solvent is THF. The insert shows a Zimm plot at low scattering angle range.

Figure 6 shows a maximum of $R_{vv}(q)/C$ when the molar fraction of the monomer unit STVPy (X_{STVPy}) ~ 0.5. It should be noted that when $X_{STVPy} \sim 0.5$, the viscosity of the solution mixture reaches a minimum as long as the phenol and pyridyl content are higher than a certain value.[30,31] This composition at which the viscosity reaches a minimum is generally regarded as the fixed mean stoichiometry of the complexation. In contrast, there is no distinct maximum of $\langle R_h \rangle$ in Figure 6. $\langle R_h \rangle$ strongly depends on the order of blending STVPh and STVPy. It is interesting to note that $\langle R_h \rangle$ reaches a plateau when $X_{STVPy} \geq 0.5$. If the order of mixing STVPh and STVPy is reversed, the plateau changes to another direction, indicating that the complexation is dependent on the blending process. A combination of Figures 6 and 7 shows that the complexation between STVPh and STVPy reaches the highest degree when the monomer units of STVPh and STVPy are equimolar, i.e., the stoichiometry of STVPh50 and STVPy50 is 1.1 in terms of the monomer units ratio.

Figure 8 shows a typical Zimm plot of an equimolar mixture of STVPh50 and STVPy50 in solution, where the total polymer concentration ranges from 2.76×10^{-6} to 9.79×10^{-6} g/mL. The insert shows the Zimm plot at low-angle range. The dn/dC values of STVPh50 and STVPy50 at 25 °C and wavelength of 532 nm are 0.195 and 0.197 mL/g, respectively. Nearly parallel curves in Figure 8 indicate that the dilution of the solution mixture has no effect on the conformation of the STVPh50 + STVPy50 complexes. A curvature of $R_{vv}(q)/C$ versus q^2 is expected because the size of the complexes is relatively larger. On the basis of eq 1, the extrapolation of $q \rightarrow 0$ was actually conducted in the low-angle range of 6° − 20° to ensure that $R_g q < 1$. In Figure 7, the values of M_w. R_g, and A_2 are 1.7×10^{10} g/mol, 316 nm, and ~0, respectively. It should be stated that the plot of $\log[KC/R_{vv}(\theta)]$ versus $\log(q)$ leads to a very rough estimate of $KC/R_{vv}(q) \sim q^{-4}$, indicating the complexes have a compact spherical conformation.

If there is no free individual polymer chains in the solution mixture and the average composition of the complexes is equimolar, the estimate of the average number of the STVPh50 and STVPy50 chains per complex particle will be $\sim 2.2 \times 10^4$ and $\sim 5.4 \times 10^{-4}$, respectively. Further, if the complexes are spherical with an average radius of $\langle R_h \rangle = 344$ nm, the estimate of the chain density of the complexes is ~0.21 g/mL, very similar to the chain density of PEG + PMAA complexes determined using the viscometry method[32] and close to the chain density of a collapsed linear polymer chain,[33] suggesting the complexation-induced collapse of the STVPh and STVPy chains. The value of $A_2 \sim 0$ has been observed from various kinds of polymer aggregates in solution. For example,[21] a scaling relation of $\langle R_g \rangle \sim M_w^{0.5}$ was observed for the solution mixture of STVPh and PEMA, suggesting that the complexation leads to solution into a θ state.

In our previous study of the complexation between STVPh and PEMA in toluene,[21] we have shown that when one polymer component of the solution mixture is in excess, the composition of the complexes can be estimated from static LLS results. The principle is as follows: for a very dilute A + B blend solution at a small scattering angle, the terms of $2A_2M_wC$ and $^1/_3\langle R_g^2\rangle_z q^2$ in eq 1 are so small that eq 1 can be rewritten as

$$R_{vv}\,(q \to 0, C \to 0) = KM_wC = K(M_CC_C + M_AC_A) \quad (6)$$

Assuming that A is in excess and the solution mixture contains only the A + B complexes and individual A chains, so that $M_wC = M_CC_C + M_AC_A$, where M_C and M_A are the average molar mass of the complexes and individual A chains and C_C and C_A are the concentrations of the complexes and individual A chains, respectively. When A is in excess, it is reasonable to expect that each B chain is complexed by a number (N) of A chains or, in other words, each B chain acts as a "nucleus", so that the molar number (N_C) of the complexes per unit volume should equal the molar number (N_B) of B chains per unit volume, i.e., $N_C = N_B = C_B/M_B$, where C_B and M_B are the concentration and molar mass of individual B chains, respectively. Therefore, $M_C = NM_A + M_B$, $C_C = (NM_A + M_B)N_C$, and $C_A = C - NM_AN_C$. Equation 6 can be rewritten as

$$KM_wC = K[(NM_A + M_B)^2N_C + (C - NM_AN_C)M_A] \quad (7)$$

or

$$\frac{C_B}{C} = \frac{M_B(M_W - M_A)}{(NM_A + M_B)^2 - NM_A^2} \quad (8)$$

where M_A, M_B, C_B, and C are known in the solution mixture. Therefore, N can be estimated from M_w measured in static LLS on the basis of eq 8. Knowing N, we can further estimate the weight fraction (X_C) and radius of gyration of the complexes in the solution mixture because $X_C = C_C/C = (NM_A + M_B)N_C/C$ and $\langle R_g^2\rangle M_w = X_C\langle R_g^2\rangle_C M_C + (1 - X_C)\langle R_g^2\rangle_A M_A$, where $\langle R_g\rangle_C$ and $\langle R_g\rangle_A$ are the radius of gyration of the A + B complex and polymer A, respectively. Table 2 summarizes the values of N, X_C, and $\langle R_g^2\rangle_C$.

N varies in a small range of 50–80 and 6–9 respectively for two different orders of mixing STVPh50 to STVPy50 over a wide range of the mixture composition, suggesting that the complexation between STVPh50 and STVPy50 has a nearly fixed ratio when one polymer component is in excess. The small variation of $\langle R_g\rangle_C$ shown in Table 2 also supports that the complexation between STVPh50 and STVPy50 has a nearly fixed composition, which is understandable because each STVPh50 chain can only attract a certain number of the STVPy50 chains and so does each STVPy50 chain. The higher value of N in the case of adding STVPh50 to STVPy50 can be attributed to the length difference between the STVPh50 and STVPy50 chains; namely one longer STVPh50 chain can complex with many shorter STVPy50 chains, but one shorter STVPy50 chain can only accommodate a few STVPh50 chains.

Table 2. Static LLS Results of the STVPh50 + STVPy50 Complexes in THF at 25 °C

$C_{STVPh50}$ (g/mL)	$C_{STVPy50}$ (g/mL)	M_w (g/mol)	N	X_C	$\langle R_g\rangle_C$ (nm)
		When STVPy50 is in excess			
0.00	1.00×10^{-4}	1.6×10^5	1	0.000	22
1.03×10^{-7}	1.00×10^{-4}	4.2×10^5	63	0.027	51
1.75×10^{-7}	1.00×10^{-4}	3.9×10^5	45	0.035	53
3.12×10^{-7}	1.00×10^{-4}	7.9×10^6	63	0.097	48
4.00×10^{-7}	1.00×10^{-4}	1.3×10^6	51	0.088	54
5.80×10^{-7}	1.00×10^{-4}	1.9×10^6	65	0.16	51
7.37×10^{-7}	1.00×10^{-4}	5.4×10^6	63	0.20	47
9.07×10^{-7}	1.00×10^{-4}	6.4×10^6	94	0.36	53
1.38×10^{-6}	1.00×10^{-4}	8.6×10^6	76	0.45	55
1.66×10^{-6}	1.00×10^{-4}	2.8×10^7	160		
3.25×10^{-6}	1.00×10^{-4}	2.0×10^8	303		
		When STVPh50 is in excess			
1.00×10^{-4}	0.00	3.9×10^5	1.0	0.000	49
1.00×10^{-4}	7.90×10^{-7}	4.2×10^5	7.1	0.014	58
1.00×10^{-4}	1.02×10^{-6}	4.2×10^5	6.5	0.017	48
1.00×10^{-4}	1.48×10^{-6}	4.9×10^5	8.6	0.033	53
1.00×10^{-4}	3.06×10^{-6}	5.0×10^5	6.5	0.052	44
1.00×10^{-4}	3.77×10^{-6}	7.5×10^5	9.5	0.091	42

On the basis of our results, the complexation can be described as follows: at the initial stage of adding dropwise the A component to the solution containing excess complementary B, each A chain added immediately attracts a number of the complementary B chains, so that there is little chance for two complexes to stick together to form a larger complex. As the concentration of A increases, two or more complex particles surrounded by the B chains can be "connected" by one or more A chains. As a result, the B chains are gradually surrounded by A chains. In the case that the molar ratio of the total monomer units of A and B is 1:1, the size of the A + B complexes will reach a maximum, similar to a polycondensation.

Conclusions

The complexation between STVPh and STVPy is a cooperative process, which requires a certain strength of the interaction between the two complementary chains, i.e., a certain content of the phenol and pyridyl groups to induce the complexation. The addition of a strong proton-accepting solvent, such as water, can destroy the complexation, clearly showing the complexation is through the hydrogen bonding. Therefore, in a stronger proton-accepting solvent, such as THF, the complexation requires higher phenol and pyridyl contents. Our results indicate that at the initial stage of adding dropwise one polymer component to another complementary polymer solution, each polymer chain added is complexed with a certain number of the complementary polymer chains, like a "nucleation". The complexation reaches the highest degree when the composition of the solution mixture is equimolar. The estimated chain density of the STVPh50 + STVPy50 complexes is ~0.21 g/mL, very close to that of a collapsed linear polymer, indicating the collapse of the STVPh and STVPy chains induced by the complexation between the phenol and pyridyl groups on the two complementary chains.

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