Factors Affecting the Size of Aqueous Poly(vinylphenol-*co*-potassium styrenesulfonate)/Poly(ethylene oxide) Complexes

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ABSTRACT: The diffusion properties of complexes formed between poly(ethylene oxide) (PEO) and poly(vinylphenol-*co*-styrenesulfonate) (PKS) in aqueous medium were investigated by diffusion ordered NMR (DOSY), fluorescence photobleaching recovery (FPR), and viscosity measurements. All three techniques showed that PEO/PKS complexes range from single PEO coils with bound PKS molecules to large complex species containing many PEO chains. For a given PKS structure, there are two important transitional PEO molecular weights. The lowest one, ~8000 Da, corresponds to the onset of PEO/PKS complex formation. The second transitional PEO molecular weight is between 10^5 and 10^6 Da and corresponds to the onset of multi-PEO chain complex species which are important for flocculation. PKS functions as a physical cross-linking agent for PEO. If there is too little PKS, multiple PEO chains are not bound together. Similarly, high concentrations of PKS give small complexes because there are few opportunities for connecting multiple PEO chains together, since all the PEO chains are saturated with bound PKS.

Introduction

Mixtures of high molecular weight poly(ethylene oxide), PEO, and water soluble phenolic polymers are used as flocculants (retention aids) in the papermaking process.[1,2] The active flocculating agent is a water soluble complex formed between the nonionic PEO and anionic phenolic polymers. These are unusual flocculants because they depend on electrostatic attraction to the target colloids, which makes them effective in dirty systems. All the commercial phenolic polymers used in papermaking retention are poorly defined condensation polymers. In an effort to understand mechanisms, our laboratory has investigated PEO/phenolic polymer complexes based on well defined, linear poly(vinylphenol-*co*-potassium styrenesulfonate) (PKS)[3] and tyrosine rich polypeptides.[4] Since typical phenolic polymers have molecular weights between 10^4 and 10^5 Da and the PEO molecular weight is usually greater than 2×10^6 Da, the complexes are large. Our attempts to understand the structure and function of the PEO/phenolic polymer complexes have focused on two distance scales. Our previous papers described NMR characterization of the complexes at the level of segmental interactions−both hydrogen bonding and hydrophobic interactions between the aromatic rings and the PEO ethylene groups occurred.[3,5] Described in this paper are the results of a systematic investigation of the sizes of PEO/PKS complexes determined by viscosity, fluorescence photobleaching recovery (FPR), and diffusion ordered NMR spectroscopy (DOSY) measurements.

The literature describes the use of dynamic light scattering (DLS) to characterize the size of both PEO and PEO/phenolic polymer species in aqueous solution. Results for simple PEO solutions show the presence of very large species which must involve multiple PEO chains. The explanations have been controversial. Polverari and van de Ven summarize this literature and make the case for cluster formation.[6] Others have argued the observations reflect the presence of impurities in the PEO.[7−9] This controversy emphasizes the importance of careful control of the PEO dissolution process.[10]

DLS measurements of PEO/phenolic polymer complexes have shown two extreme behaviors. Complexes formed with relatively hydrophobic phenolic polymer shrink[11] and often show phase separation. By contrast, more hydrophilic phenolic polymers cause the PEO chain to expand.[12] It is difficult to develop general mechanisms from the existing studies because the commercial phenolic polymers employed were poorly characterized as a result of their complexity. In this work we report the first application of fluorescence photobleaching recovery (FPR) to the characterization of PEO/phenolic polymer complexes.

A FPR measurement is simple in concept:[13,14] the molecule of interest is labeled by covalent attachment of a fluorescent molecule; thus, only the fluorescently tagged species is observed. Measurements begin when a bright laser flash dye erases (bleaches) the dye from regions of the sample chamber not covered with a mask. With time, unbleached molecules from neighboring masked regions diffuse into the unmasked regions, giving an increase in fluorescent emission. The rate of recovery of the fluorescence signal can be used to obtain the self-diffusion coefficient. A comparison of dynamic light scattering and FPR techniques has appeared.[15]

Diffusion ordered NMR spectroscopy (DOSY) is another option for the measurement of PEO/phenolic polymer diffusion properties. DOSY is based on pulsed field gradient NMR that encodes the information about the translational motion into NMR data.[16] It combines the selectivity of high-resolution NMR with the hydrodynamic information provided by pulsed field gradient NMR. Information about chemical shift is present in one dimension, and the self-diffusion coefficient, in the second dimension of DOSY spectra. The most distinguishable feature of DOSY is the fact that NMR active impurities are detected but do not interfere with mea-

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Table 1. Properties of Poly(vinylphenol-*co*-styrenesulfonate) Potassium Salt[a]

sample name	phenolic content (molar fraction)	M_w (Da)	polydispersity
PKS.34	0.34	141 000 ± 8000	1.4 ± 0.1
PKS.48	0.48	158 000 ± 5000	1.6 ± 0.1
PKS.67	0.67	210 000 ± 7000	1.6 ± 0.1
PKS.74	0.74	41 000 ± 1000	1.9 ± 0.1
PKS.82	0.82	127 000 ± 3000	1.9 ± 0.1

[a] The phenolic content was measured by ^{1}H NMR in d_6-DMSO, and the molecular weight distribution was determined by GPC-LS. The standard deviation was calculated by three to five repeat measurements.

surements. Therefore, there has been increasing interest in using DOSY to study polymer mixtures.[17−20]

This paper describes results from a systematic study of the influence of phenolic content of PKS copolymers, PKS/PEO mixing ratio, ionic strength, temperature, and molecular weight of PEO on complex formation. DOSY and FPR, together with viscosity measurements, were used to characterize the diffusion properties of the complexes.

Experimental Section

Materials. 5-(4,6-Dichlorotriazinyl)aminofluorescein (5-DTAF) was purchased from Molecular Probes. Poly(ethylene oxide) (PEO) samples (Polyox N-12K, $M_w = 1 \times 10^6$ Da; Polyox N-3000, $M_w = 4 \times 10^5$ Da; Polyox N-750, $M_w = 3 \times 10^5$ Da; Polyox -10, $M_w = 1 \times 10^5$ Da) were gifts from Union Carbide (Danbury, CT). Poly(ethylene glycol) (PEG with $M_w = 8 \times 10^3$ Da) was purchased from Amresco, Ohio. All chemicals were used without further purification.

Synthesis of Poly(vinylphenol-*co*-potassium styrenesulfonate) (PKS). PKS was synthesized by free radical polymerization of 4-acetoxystyrene with sodium 4-styrenesulfonate, followed by extensive hydrolysis in 1 M KOH solution. The detailed procedure for purification and characterization was reported previously.[3] PKS.48 was designated as PKS with a phenolic mole fraction of 0.48. The properties of five PKS copolymers are summarized in Table 1.

Viscosity Measurements. Viscosity was measured with an ATS Rheosystems Rheometer (Stresstech HR) at 298 K and a shear rate of 37.32 s^{-1}. PEO or PKS stock solutions (1 g/L) were prepared 48 h before the experiments. The stock solutions were diluted to the desired concentration 2 h before the experiments. PEO and PKS solutions were well mixed 30 min before viscosity measurements and then kept at room temperature to allow the mixture to reach steady-state behavior.

Fluorescence Photobleaching Recovery. PKS.48 was labeled with 5-(4,6-dichlorotriazinyl)aminofluorescein (5-DTAF) by standard methods.[21] In a typical experiment, 1.00 g of PKS was dissolved in 100 mL of nanopure water. The pH of the PKS solution was adjusted from pH 6 to pH 10−11 by adding 1.38 g of solid K_2CO_3. 5-DTAF (17 mg) was dissolved in 10 mL of acetone with stirring. The two solutions were mixed together at room temperature, giving a feed ratio of phenolic groups in PKS.48/DTAF of 100:1 (mole/mole). Soon after mixing, a clear bright yellow solution was obtained, indicating the start of the labeling reaction. The mixture was gradually heated to 308 K for 5 min and then kept in the dark at room temperature for 26 h to allow the labeling reaction to complete.

The mixture was poured directly into 1 L of 2-propanol and then heated to 313 K for 3 min. Yellow PKS was precipitated out from 2-propanol. The labeled PKS was purified three times by dissolving in water followed by precipitation in 2-propanol, yielding a colorless 2-propanol supernatant. The product was air-dried, followed by vacuum-drying for over 24 h at 313 K.

Fluorescence photobleaching recovery (FPR) was used to evaluate the purification efficiency. The self-diffusion coefficient (D) of 5-DTAF at 298 K was measured to be (4.8 ± 0.2) × 10^{-10} m^2/s, which is close to the self-diffusion coefficient of fluorescein, which is 5.5 × 10^{-10} m^2/s.[22] After covalent bonding with DTAF, the apparent diffusion coefficient of labeled PKS.48 was about 10^{-12} m^2/s, suggesting no free dye was in the labeled PKS.48 solutions.

Detailed information about the instrument was described previously.[23] In this technique a striped pattern was created by illuminating a coarse diffraction grating (Ronchi ruling) held in the rear focal plane of a standard epifluorescence microscope with an intense, brief laser flash. With the laser intensity greatly reduced, an electromechanical modulation detector system monitored the subsequent disappearance of the pattern due to exchange of molecules that were bleached (i.e. in the bright regions during the flash) and those that were not (i.e., molecules that were not illuminated during the flash). The ac amplitude from the modulation detector decayed exponentially as described by the following equation:

$$ac(t) = \exp(-K^2 D_{app} t) \quad (1)$$

where the spatial frequency of the grating is $K = 2\pi/L$, where L is the distance between stripes in the Rochi ruling, and D_{app} is the apparent self-diffusion coefficient of the labeled PKS.48. For most of the samples, two different K values were employed to ensure the absence of nondiffusive signal recovery.

(a) Data Analysis. Due to the broad distribution of PKS molecular weights, a one-exponential model did not fit the data well. Thus, a two-exponential mode was used in FPR data analysis. The apparent diffusion coefficient D_{app} of the DTAF-bonded PKS was expressed as a number averaged value.

(b) Sample Preparation. PEO and PKS.48 were dissolved separately in Nanopure water at least 48 h before FPR experiments. The two solutions were mixed at a specified ratio with shaking and stored at room temperature for 3 h with occasional shaking to obtain steady-state behavior. The sample was loaded into a rectangular glass cell (VitroCom Corp.), having a path length of 100 μm, which was then frame sealed. The temperature of the FPR sample deck was controlled by a NESLAB RTE-111 circulating water bath with a temperature control accuracy of ±0.02 K. A 15-min incubation time was employed after every change in temperature to achieve thermal equilibrium. For the complex formation at different ionic strengths, KCl powder was added directly to the premixed PKS.48/PEO solution.

DOSY Experiments and Data Procession. DOSY experiments were performed on a Bruker DPX250 spectrometer. The strength of the gradient field G was measured directly according to the Bruker menu with a Bruker phantom sample. The self-diffusion coefficient for residual HDO in D_2O was found to be 1.9 × 10^{-9} m^2/s at 298 K, which was consistent with the reported data.[24] The probe temperature was maintained at 298 ± 0.5 K. A stimulated echo (STE) pulse sequence was employed. Typical parameters of DOSY experiments were as follows: diffusion time (Δ), 600 ms; gradient pulse (δ), 10 ms; number of scans, 8−32; number of dummy scans, 120; number of sampled points in the gradient strength dimension, 8; number of sampled points in the spectral dimention, 16K (frequency resolution was not a critical factor); relaxation delay, 3 s; 90° pulse (^{1}H), 8 μs. Upon formation of complexes with PKS, the ^{1}H chemical shift of PEO shifted to the high frequency.[3] The apparent self-diffusion coefficient D_{app} was determined by fitting the decay of the echo amplitude for the complexed PEO signal only. The standard derivation for fitting was about 5%.

Fluorescence Spectroscopy and Dynamic Light Scattering. Fluorescence emission spectra were recorded with a Perkin-Elmer luminescence spectrophotometer LIS 50B. A high-quality quartz cuvette with a 10 mm path length was used.

Dynamic light scattering measurements were performed with a 632.8 nm laser and an ALV 5000 correlator. The samples were maintained at 298 K, and measurements were recorded at scattering angles of 30°, 45°, 60°, 70°, and 90°. The data were analyzed with a third-order cumulant approach. The

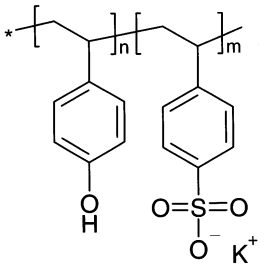

Figure 1. Structure of poly(vinylphenol-*co*-styrenesulfonate potassium salt) (PKS). The phenolic content is $n/(n + m)$.

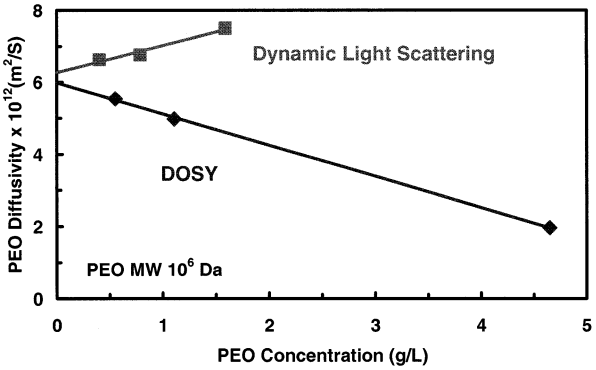

Figure 2. Diffusion coefficient values for PEO measured by DLS and DOSY as functions of polymer concentration at 298 K.

apparent mutual diffusion coefficient was extracted from a linear relationship between Γ versus q^2, where Γ is the decay rate and q is the magnitude of the scattering vector. The sample cell and Millipore filters were exhaustively cleaned with nanopure water. They were tested for the absence of dust by visual observation with 100× magnification at a scattering angle of 30°; dust particles smaller than 0.2 μm were readily observed when present.

PEO (1.587 g/L, molecular weight 1×10^6 Da) was prepared with occasional shaking 72 h before DLS experiments. The PEO solution was filtered into a clean DLS cell with a 0.45 μm filter, followed by a 0.2 μm Millipore filter. More dilute solutions were obtained by direct dilution with water.

Results

Effect of PKS Phenolic Content on Size of PEO/PKS Complexes. It is generally proposed that when PEO/phenolic polymer complexes form, the phenolic groups are the main interaction site with PEO through hydrogen bonding between the phenolic hydroxyl group and the ether oxygen of PEO.[1,2,25] Our recent NMR studies demonstrated that both the phenolic and the styrenesulfonate rings in PKS (see Figure 1 for structure) interacted with PEO,[3] although the interaction between the phenolic group and PEO was stronger.[5] However, none of the previous studies gave information about the size of the PEO/phenolic polymer complexes.

DOSY and viscosity measurements were used to probe the influence of the phenolic composition in PKS on complex size. To verify our DOSY measurements, both the self-diffusion coefficient and the mutual diffusion coefficient from DOSY and DLS were measured and are shown in Figure 2 for PEO, 10^6 Da. Extrapolation to infinite dilution gave the absolute diffusion coefficient (D_0) as $(6.1 \pm 0.2) \times 10^{-12}$ m^2/s at 298 K, which is within 2% of the literature value,[7] thus confirming the validity of our DOSY experiments. Self-diffusion and mutual diffusion have different responses to the change in concentration. For neutral polymer solutions, the slopes of the two curves are generally opposite.[26]

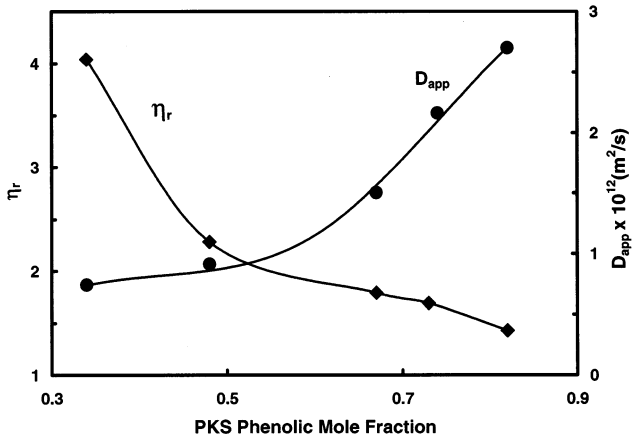

Figure 3. Relative viscosity (η_r) and apparent self-diffusion coefficient (D_{app}) of a PEO/PKS complex as a function of the mole fraction of phenolic groups in the PKS (see Figure 1 for structure). Relative viscosity is the solution viscosity divided by the viscosity of water. Experimental conditions: [PEO] for viscosity, 24 mg/L; [PEO] for DOSY, 1 g/L; PEO M_w, 1 MDa; PKS/PEO (w/w), 2; shear rate, 37 s^{-1}.

DOSY results for PEO/PKS complexes are shown as a function of the PKS phenolic molar content in Figure 3. The smallest D_{app} of 1 g/L PEO (M_w 1 MDa) in the presence of PKS was 9.0×10^{-13} m^2/s, which is substantially lower than the D_{app} value with free PEO. This suggests that the biggest complex species consists of multiple PEO chains. On the other hand, there was no systematic trend relating the complex diffusion coefficient to the PKS molecular weight (i.e. compare the results in Figure 3 with the molecular weight data in Table 1).

The relative viscosity (η_r) of 24 mg/L PEO (M_w 1 MDa) mixtures with 50 mg/L PKS at low shear (37.32 s^{-1}) is shown in Figure 3 as a function of PKS phenolic content. The viscosity readings were independent of time,[27] and the highest phenolic content PKS mixtures gave the lowest viscosity readings, which is in agreement with the diffusion behavior also shown in Figure 3.

Effect of PEO/PKS Mixing Ratio. The apparent diffusion coefficient (D_{app}) of labeled PKS.48 was measured by FPR as a function of the ratio of PEO to labeled PKS.48 in the solution. The results are shown in Figure 4, where PEO/PKS.48 concentrations are expressed as moles of ethylene groups in PEO per aromatic group in PKS. The D_{app} decreased with PEO addition to reach a minimum value when the ratio of ethylene groups to aromatic rings was between 1.8 and 2.9. Note that FPR measurement with random labeling gives D_{app} as the number averaged self-diffusion coefficients of both free and complexed PKS. The results on the left-hand side of Figure 4 reflect the case where PKS was in excess so that uncomplexed PKS dominated the average D_{app}.

Effect of temperature. It is known from ^{1}H NMR measurements that aqueous PEO/PKS complex formation is enhanced by elevating the temperature.[3,5] FPR measurements were made as a function of temperature to determine whether the temperature sensitivity was reflected in the size of the PEO/PKS complexes. Figure 5 shows the D_{app} values for PEO/PKS.48 complexes as a function of the reciprocal of temperature. Also shown in Figure 5 is the functionality predicted by the Arrhenius equation. The slope of the Arrhenius dependence

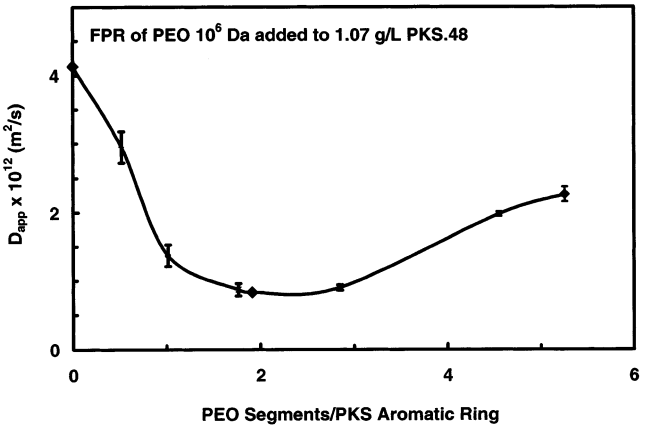

Figure 4. Effect of the PEO dose on the apparent diffusion coefficient (D_{app}) of labeled PKS.48 at 298 K measured by FPR. The error bars reflect the range of three measurements.

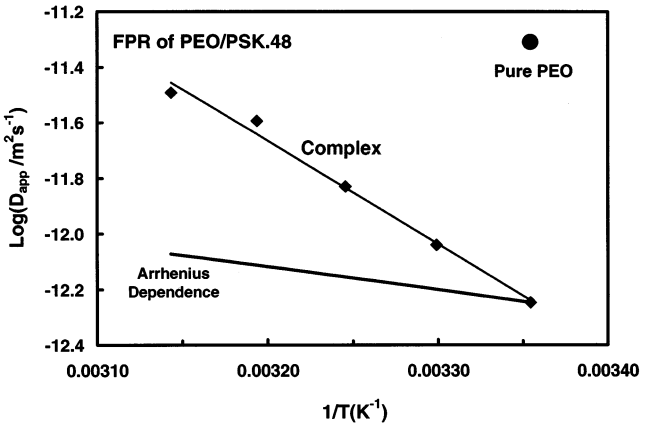

Figure 5. FPR measurements of the apparent self-diffusion coefficient of a PKS.48/PEO mixture at different temperature: PKS.48 concentration, 1.06 g/L; PKS.48/PEO (w/w) = 1; PEO M_w, 1 MDa.

corresponds to the hydrogen bonding energy of a water molecule.[22] The temperature sensitivity of PEO/PKS.48 was greater than that predicted by the Arrhenius equation This indicates that elevating the temperature produced larger diffusion coefficients, which in turn indicate smaller complexes. PEO/PKS.48 complexes were heated to 323 K and then cooled to 300 K. No hysteresis in the D_{app} values was observed, which is consistent with previous NMR measurements of the fraction of PEO segments in contact with PKS.[3]

Ionic Strength Effect on the Size of the Complexes. The influence of KCl on the size of PEO/PKS complexes was probed by both viscosity and FPR measurements, and the results are summarized in Figure 6. KCl addition caused the complex to shrink and ultimately to phase separate. D_{app} was more than 2 times higher in 15 mM KCl than in 2 mM KCl. The complexes phase separated in 50 mM KCl at 298 K, whereas PEO alone must be heated to 370 K to observe a cloud point. Salt addition screened the electrostatic repulsion between charged styrenesulfonate groups, enabling the complexes to collapse because of the hydrophobic interactions between aromatic rings and PEO. The salting out of PKS/PEO complexes suggests that the local hydrophobicity of PKS/PEO complexes was higher than that of either pure PEO or pure PKS. However, PKS was not surface active and surface tension measurements showed no significant surface tension lowering upon complex formation.

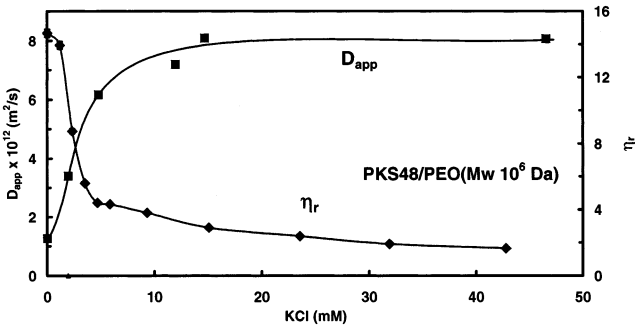

Figure 6. Effect of ionic strength on the apparent diffusion coefficient and viscosity of PKS.48/PEO mixtures: PKS.48 concentration, 1.06 ± 0.01 g/L; PKS.48/PEO (w/w) = 1.17 ± 0.04; PEO M_w, 1 MDa; 298.00 ± 0.02 K; shear rate, 37.32 s^{-1}.

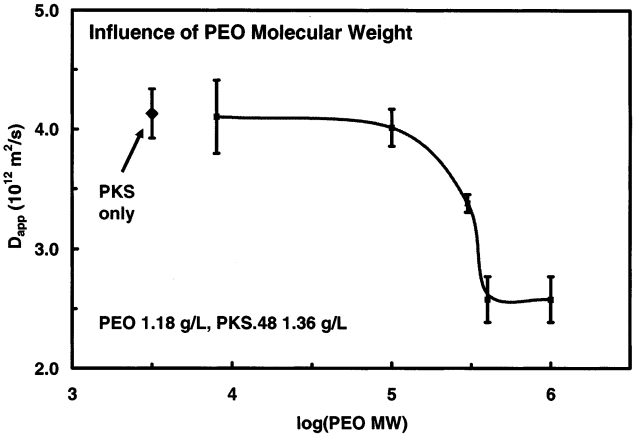

Figure 7. Effect of PEO molecular weight on the apparent diffusion coefficient (D_{app}) of PKS.48/PEO mixtures at 298 K.

The viscosity results, also shown in Figure 6, were consistent with the FPR data. That is, the relative viscosity η_r decreased with increasing KCl concentration (C_s). Plotting $\ln(\eta_r)$ versus C_s yielded a straight line with a slope of -0.57 ± 0.03, which is very close to 0.6 for synthetic polyelectrolytes as proposed by Cox.[28]

Effect of PEO Molecular Weight. It was known from the early days of flocculation work with PEO/phenolic polymer complexes that very high molecular weight PEO was required for effective flocculation.[1] In this work we employed FPR diffusion coefficient measurements to explore molecular weight sensitivity. Figure 7 shows that, up to 1×10^5 Da, there was no obvious change in D_{app}, suggesting that the labeled PKS.48 was not bound to larger aggregates. By contrast, higher PEO molecular weights gave large PEO/PKS.48 complexes.

Initial experiments with mixtures of high molecular weight PEO and fluorescent PKS revealed that the presence of PEO increased the fluorescent intensity. We concluded that, for unknown reasons, the complexed PKS was responsible for the increased intensity. In view of the FPR results in the last paragraph, it was of interest to determine whether low molecular weight PEO complexed with PKS. Figure 7 shows the relative emission intensity of labeled PKS.48 at 498 nm as a function of the concentration of 8000 Da PEO, where the relative intensity is the emission intensity of labeled PKS.48 in the presence of PEO divided by the emission intensity of PKS.48 in the absence of PEO. The presence of the low molecular weight PEO greatly enhanced the

relative emission intensity of PKS, which we believe is an indication of PEO/PKS complex formation.

Discussion

In this work we have considered the influence of the PEO molecular weight, PKS composition, and the ratio of PEO to PKS on the apparent diffusion coefficient of PKS. The diffusion behaviors reflect the size and shape of the complexes, so it is of interest to extract from the diffusion coefficients the corresponding floc size and composition.

It is clear from the diffusion characteristics that the complexes can be larger than the PEO coils in aqueous solution. The PKS cofactor is charged; thus, we anticipate some expansion of PEO chains upon PKS binding. However, the very low complex diffusion coefficients must correspond to multiple PEO chains per complex. Indeed, at high concentration, the PEO/PKS complexes form macroscopic gels.

Xia et al. employed the following mass balance to calculate the weight average molecular weight (M_x) of a complex:[29]

$$M_x = \alpha M_w(1 + \beta) \tag{2}$$

where M_w is the weight averaged molecular weight of PEO, β represents the mass ratio of bound PKS to PEO, and α is the number of PEO chains per complex. For the PEO/PKS system, both flocculation measurements and diffusion coefficient measurements (Figure 4) suggest that $\beta \sim 2$ gives the maximum floc size.

To determine α from eq 2, it is necessary to estimate the molecular weight of the complex, M_x, from the diffusion coefficients. On the basis of DLS in the dilute regime, Devanand and Selser derived the following equation to link PEO molecular weight to its diffusion coefficient in water, where λ is a constant.[7]

$$D = \frac{\lambda}{\bar{M}_w^{0.571}} \tag{3}$$

It is assumed that eq 3 also predicts the properties of the PEO/PKS complex. Taking the ratio of the diffusion coefficient for PEO (4.9×10^{-12} m^2/s, from DOSY measurements in 1 g/L PEO) to that of the complex (9.0×10^{-13} m^2/s for 1 g/L PEO + 2 g/L PKS measured with FPR and DOSY) and applying eq 3 gives a molecular weight $\bar{M}_x = 1.9 \times 10^7$ Da for the complex. Application of this value to eq 2 yields an α value of 6. Under the assumption of eq 3, the largest complexes consisted of about six PEO chains bound together with twice their mass of PKS chains (~38 PKS chains with M_w 158 000 Da).

The size of the PEO/PKS complex is sensitive to the ratio of the two species in the mixture. When the PEO dose was small (left-hand portion of Figure 4), the PEO is present as individual chains saturated with bound PKS—this is illustrated in Figure 9A. At very low PEO doses, most of the PKS is free and has the diffusion characteristics of unbound PKS. On the other hand, when the PEO is present in excess (right-hand portion of Figure 4), all the PKS is bound to sparsely coated individual PEO chains and the diffusion coefficient is approaching the value of PEO coils with a single bound PKS molecule (see Figure 9C). Only at intermediate ratios of PEO to PKS can the PKS bind together multiple PEO chains. This is illustrated in Figure 9B.

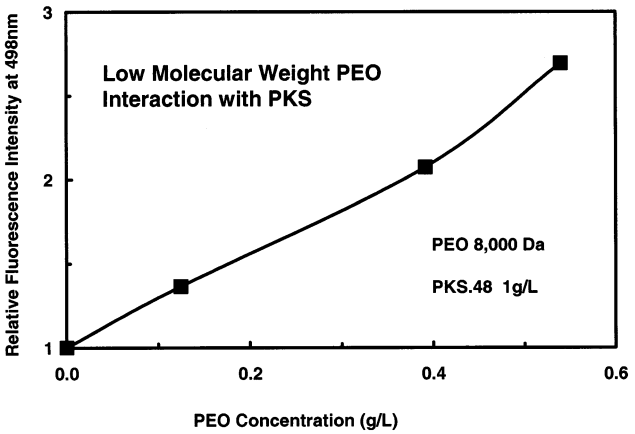

Figure 8. Effect of PEO (M_w 8000 Da) on the emission intensity of labeled PKS.48 at 498 nm. [PKS.48] = 1.0 g/L.

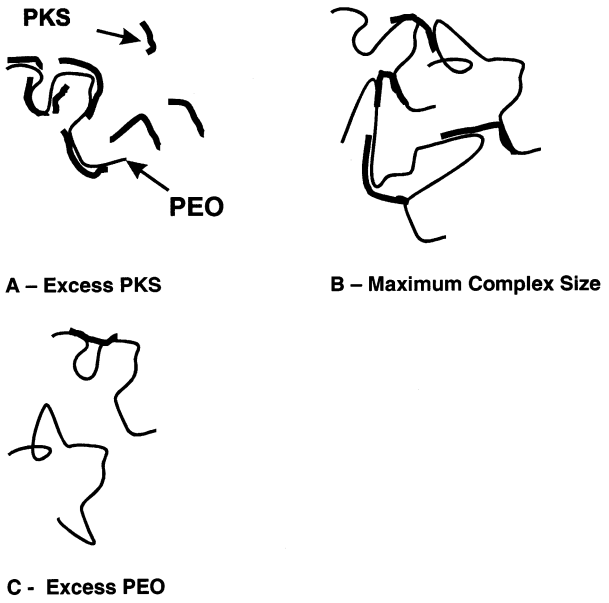

Figure 9. Schematic illustrations of the proposed complex structures.

PEO/phenolic polymer complex formation shows interesting molecular weight effects. The fluorescent intensity measurements (Figure 8), and isothermal titration calorimetric measurements with polypeptide,[4] showed that PEO with a molecular weight as low as 8000 Da will form complexes with a phenolic polymer. Similarly, phenolic polymers larger than ~1000 Da bind to high molecular weight PEO.[4,25] On the other hand, complexes formed with low molecular weight PEO are not large and are not effective flocculants.[1] Therefore, it is of interest to understand the factor leading to large PEO/phenolic polymer complexes.

The fundamental requirement for the formation of large polymeric networks is that the number of phenolic polymer molecules per PEO chain connecting two PEO coils together must exceed two. In the case of PKS.48, which has a M_w of 158 000 Da, PEO's of 100 000 Da or smaller do not form multiple PEO chain aggregates (see Figure 7). A possible explanation is that when PEO and PKS molecules have comparable chain lengths, there is little opportunity for binding multiple PKS chains to a single PEO.

Finally, the detailed composition of PKS is also important. Figure 3 shows that the largest complexes correspond to PKS with the lowest phenolic content.

This could be due to two effects. First, the lower the phenolic content, the higher the sulfonate content, giving more electrostatic expansion of the complex. Second, the actual configuration of PKS in the complex is sensitive to phenolic content. If, as we believe, the phenolic groups have the highest interaction energy with PEO, PKS with high phenolic content will have more segments in direct contact with PEO than will PKS with low phenolic content. This is analogous to polymers adsorbing on a surface—PKS's with high phenolic content have a flat configuration and little opportunity to reach out and collect a second PEO chain. In other words, phenolic polymers with high phenolic content are relatively poor coupling agents between different PEO chains because their interactions are so strong with the first PEO which they encounter.

Conclusions

The main conclusions of this paper are as follows:

(i) DOSY, FPR measurements with fluorescent labeled phenolic polymer (PKS), and viscosity measurements all show that PEO/PKS complexes range from single PEO coils with bound PKS molecules to large complex species containing multiple PEO chains.

(ii) A transitional PEO molecular weight between 10^5 and 10^6 Da corresponds to the onset of multi-PEO chain complex species which are important for flocculation.

(iii) PKS functions as a physical cross-linking agent for PEO. If there is too little PKS, multiple PEO chains are not bound together. High concentrations of PKS give small complexes, since there are few opportunities for connecting multiple PEO chains together because all the PEO chains are saturated with bound PKS.

(iv) The decrease in PEO/PKS complex size with increasing temperature or salt addition is reminiscent of the behavior of PEO—surfactant complexes. However, there is no evidence of the PKS lowering surface tension with or without PEO.

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