

Interchain Hydrogen-Bonding-Induced Association of Poly(acrylic acid)-graft-poly(ethylene oxide) in Water

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ABSTRACT: Poly(acrylic acid)-graft-poly(ethylene oxide) (PAA-g-PEO) in aqueous solutions shows one fast and one slow relaxation mode in dynamic light scattering (DLS), but the mixture of PAA and PEO (PAA/PEO) in aqueous solution only has a single fast mode. The effects of pH, polymer concentration, and salt concentration on these two modes have been investigated using laser light scattering (LLS), viscometry, and rheological measurements. Our results showed that the hydrogen bonding between carboxylic group and ether oxygen led to the formation of large complexes among PAA-g-PEO chains, which were absent between PAA and PEO chains in PAA/PEO aqueous solutions. The addition of formamide can break these interchain complexes because the hydrogen bonding between formamide and PAA segment is stronger than that between PEO and PAA segment. Thermodynamically speaking, the formation of hydrogen bonds among PAA-g-PEO chains leads to a less entropy loss than that between PAA and PEO chains in PAA/PEO aqueous solution, because in the former case PEO is already chemically connected to PAA backbone. Therefore, the same enthalpy gain is sufficient to compensate the entropy loss in PAA-g-PEO aqueous solution relative to that in PAA/PEO aqueous solution, resulting in large interchain PAA-g-PEO complexes.

Introduction

Polymer–polymer complexes, which are resulted from non-covalent associations between groups of different polymer chains, have been studied extensively during recent years due to their potential industrial and biomedical applications.^{1–8} When two dissimilar polymers are mixed in a common solvent, certain interchain interactions may take place between them.⁹ And if interpolymer interaction outweighs polymer–solvent interaction, the mobility of polymer chains could be confined to a certain extent, thus resulting in the formation of supramolecular structures or aggregates.¹⁰ On the basis of the types of the dominating interaction force, interpolymer complex can be divided into several classes: polyelectrolyte complex, formed due to Coulombic force; hydrogen-bonding complex, which is stabilized through hydrogen bonds; charge-transfer complex; and stereocomplex, etc.^{11–18} Because the utilization of these interactions to prepare new polymer materials can sometimes greatly improve their performances, lots of attention have been drawn in this field recently.

A certain number of studies have been focused on the structure and properties of the polymer complexes in solution,^{10,19} since the polymer complexation can be used to control the properties of polymer solution, especially to enhance the solution viscosity, or to prepare drug delivery systems to achieve the controlled release.^{10,20–22} Among the various interpolymer complexes, the hydrogen-bonding complex has attracted the most attention.^{10,15,19,20,23–25} Extensive studies on the complex formation between poly(acrylic acid) (PAA) or poly(methacrylic acid) (PMAA) and poly(ethylene oxide) (PEO) or poly(ethylene

glycol) (PEG)^{20–23,26,27} have been carried out by using viscometry,^{10,20,23} potentiometry,²³ turbidimetry,²³ infrared spectroscopy,^{12,28,29} fluorescence spectroscopy,^{19,30} solid-state ¹³C nuclear magnetic resonance (NMR),^{17,31} and electron spin resonance (ESR).^{32,33} It was suggested that the driving force for the formation of a hydrogen bond between ether and carboxylic acid in aqueous solution is very weak. Therefore, the stable PAA–PEO complex can be formed only by the cooperative interactions between many such groups.^{23,25,34–36} Thus, to form complexes, the molecular weight of the interaction polymers should exceed a critical value in order to have a critical number of interaction sites per polymer chain. For the PAA/PEO mixture system, the complex can only exist when the molecular weight of PEO is larger than about $8.8 \times 10^3 \text{ g mol}^{-1}$.^{23,34} Frank et al.³⁴ found that PAA can still form complexes with PEO when the molecular weight of PAA as low as $1.9 \times 10^3 \text{ g mol}^{-1}$. Bailey et al.²⁰ studied the influences of pH values and composition on the interpolymer association by viscometry, and they pointed out that low pH value and high polymer concentration are favorable for the formation of interpolymer complex. The results of ¹³C CP/MAS NMR (cross-polarization/magic angle sample spinning nuclear magnetic resonance) study by Miyoshi et al.³¹ showed that, in PAA/PEO blends (solid), there exist three kinds of hydrogen bonding for the carboxylic group of PAA, namely, (1) the complex form, interpolymer hydrogen bonding with PEO molecules; (2) the dimeric form, intrapolymer hydrogen bonding within PAA molecules; and (3) the free form, no particular form of hydrogen bonding. Khutoryanskiy et al.³⁷ studied the pH effect on the complex formation between PAA and PEO by fluorescent methods; their results showed that insoluble interpolymer complexes come up below a certain critical pH values of complexation ($\text{pH}_{\text{crit},1}$); and the formation of hydrophilic

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interpolymer associates is possible above $\text{pH}_{\text{crit},1}$ and below a certain $\text{pH}_{\text{crit},2}$. Studies were also taken on the conformation changes of PAA or PMAA gels in the PEO solutions,^{5,38,39} and the results showed that the contraction of the gel took place as a result of the formation of an intermolecular polymer complex on the basis of hydrogen bonding, which was influenced by the concentration and molecular weight of PEO. Compared to the studies on PAA/PEO mixtures, only a few were concerned with the complexation of PAA–PEO copolymers.^{40,41} These copolymers could be PAA-*b*-PEO and PAA-*g*-PEO prepared by the copolymerization of AA and methacryloyl-capped PEO.

However, only a few of those studies have explained the complexation from the thermodynamic point of view.³⁶ The formation of hydrogen-bonding complex is controlled by the competition between the enthalpy gain of hydrogen-bonding energy and the entropy loss of motion freedom. In this study, we compared the complexation in PAA-*g*-PEO and PAA/PEO mixture in aqueous solution by LLS and viscometry and demonstrated that it is totally different in these two cases even when both the molecular weight and composition of the two components are the same. The reason why the formation of PAA-*g*-PEO intermolecular hydrogen-bonding complex is easier originates from the facts that the copolymer has a less entropy loss in the complexation process. To achieve better insight into the complexation of PAA-*g*-PEO, the effects of pH, concentration of polymer, and concentration of salt have been investigated.

Experimental Section

Materials. Potassium bis(trimethylsilyl)amide (0.5 mol L^{-1} solution in toluene) and poly(acrylic acid) (PAA) aqueous solution (weight fraction 35%, $M_w = 2.5 \times 10^5 \text{ g mol}^{-1}$) from Sigma-Aldrich, *N*-(3-(dimethylamino)propyl)-*N*-ethylcarbodiimide hydrochloride (EDC) and 1-hydroxybenzotriazole (HOBt) from Shanghai Medpep Co., Ltd., and ethyl ether, acetic acid, and sodium hydroxide from Beijing Chemical Works were used without further purification. Ethylene oxide (EO) from Beijing Chemical Reagents Co. was purified by distillation with CaH_2 and KOH and stored in the atmosphere of Ar at $-18 \text{ }^\circ\text{C}$. Tetrahydrofuran (THF) from Beijing Chemical Works was purified by distillation with Na and stored in the atmosphere of Ar. *N,N*-Dimethylformamide (DMF) from Beijing Chemical Works was purified by distillation with CaH_2 under reduced pressure. Water used in this study was purified with a Milli-Q system from Millipore. Dialysis bag (regenerated cellulose, cutoff molecular weight = $1.4 \times 10^4 \text{ g mol}^{-1}$) from Beijing Jingkehongda Biotechnology Co., Ltd., was pretreated by successively boiling in ethanol/water (1:1 v/v), 0.01 M NaHCO_3 , and 0.001 M 2-[2-(bis(carboxymethyl)amino)ethyl(carboxymethyl)amino]acetic acid (EDTA) aqueous solution.

Synthesis of Amine-Terminated PEO. PEO with a primary amine group was synthesized using potassium bis(trimethylsilyl)amide ($[(\text{CH}_3)_3\text{Si}]_2\text{NK}$) as the initiator of EO polymerization through the route reported in ref 42, and the M_w of PEO is $2.0 \times 10^3 \text{ g mol}^{-1}$, determined by $^1\text{H NMR}$ measurement and GPC.

Synthesis of PAA-*g*-PEO. PAA-*g*-PEO was prepared according to the classical reaction of amino with carboxylic groups in the presence of EDC and HOBt.^{43–45} Typically, the reaction was carried out according to the procedure as followed. Lyophilized PAA (20 g) was dissolved in DMF (900 mL) over 24 h at room temperature, and triethylamine (31 mL) was added. The obtained solution was bubbled with Ar for 1 h. Then, HOBt (0.34 g), EDC (0.95 g), and PEO (5.0 g) were added subsequently. The mixture was kept stirring at room temperature for 5 days. Precipitate of PAA-*g*-PEO with amide graft linkage was obtained by the addition of NaOH aqueous solution (10 g NaOH in 20 mL of water), then redissolved in water, and reprecipitated in THF twice. After the crude product was

Table 1. Details of Preparation and Characteristics of PAA-*g*-PEO

	PEO:PAA (g:g in reactant)	graft yield of PEO (%)	PEO (wt %)	no. of PEO grafts in each copolymer
PAA- <i>g</i> -PEO-0.08	0.2:20	8.0	0.08	0.10
PAA- <i>g</i> -PEO-0.12	1:20	2.4	0.12	0.15
PAA- <i>g</i> -PEO-7	5:20	30.1	6.98	9.40
PAA- <i>g</i> -PEO-13	7.5:20	39.6	12.93	18.50
PAA- <i>g</i> -PEO-27	10:20	75.0	27.27	46.80

dissolved in water, it was dialyzed against water for 4 days and then lyophilized. The composition of the copolymer was determined by $^1\text{H NMR}$.⁴⁴ Five PAA-*g*-PEO samples with different PEO contents were obtained, and the weight percent of PEO was 0.08%, 0.12%, 6.98%, 12.93% and 27.27%. They were named as PAA-*g*-PEO-0.08, PAA-*g*-PEO-0.12, PAA-*g*-PEO-7, PAA-*g*-PEO-13, and PAA-*g*-PEO-27, respectively. The details are listed in Table 1.

Viscometry and Rheological Measurements. Viscosities of polymer aqueous solution at different concentrations were measured at $20 \text{ }^\circ\text{C}$ with a Ubbelohde viscometer. Steady-shear viscosities of polymer aqueous solution at varying shear rates were measured on TA Instruments AR2000ex rheometer at $20 \text{ }^\circ\text{C}$. Double concentric cylinder geometry with inner radius of 28 mm and outer radius of 30 mm was used for the measurement.

Laser Light Scattering. A commercial LLS spectrometer (ALV/DLS/SLS-5022F) equipped with a multi- τ digital time correlator (ALV5000) and a cylindrical 22 mW UNIPHASE He–Ne laser ($\lambda_0 = 632.8 \text{ nm}$) was used. The spectrometer has a high coherence factor of $\beta \sim 0.95$ because of a novel single-mode fiber optical coupled with an efficient avalanche photodiode. The LLS cell is held in a thermostat index matching vat filled with purified and dust-free toluene, with the temperature controlled to within $0.1 \text{ }^\circ\text{C}$. The details of LLS instrumentation and theory can be found elsewhere.^{46–48} In static LLS (SLS), the angular dependence of the excess absolute time-averaged scattered intensity, i.e., the Rayleigh ratio $R_{\text{v}}(q)$, where q is the scattering vector ($q = (4\pi/\lambda_0) \sin(\theta/2)$), of a very dilute dispersion can lead to the weight-averaged molar mass M_w and the z -averaged root-mean-square radius of gyration, $\langle R_g^2 \rangle_z^{1/2}$ (or written as $\langle R_g \rangle$), of scattering objects.⁴⁹ In dynamic LLS (DLS), the intensity–intensity time correlation function $g^{(2)}(t, q)$ in the self-beating mode was measured, where t is the decay time. $g^{(2)}(t, q)$ can be related to the normalized first-order electric field time correlation function $|g^{(1)}(t, q)|$ via the Siegert relation as

$$g^{(2)}(t, q) = A[1 + \beta |g^{(1)}(t, q)|^2] \quad (1)$$

where $A (\equiv \langle I(0) \rangle^2)$ is the measured baseline. For the broadly distributed relaxation spectrum, $|g^{(1)}(t, q)|$ is related to a characteristic relaxation time distribution $G(\tau)$ as

$$\begin{aligned} g^{(1)}(t, q) &\equiv \langle E(0, q)E^*(t, q) \rangle / \langle E(0, q)E^*(0, q) \rangle \\ &= \int_0^\infty G(\tau) e^{-t/\tau} d\tau \end{aligned} \quad (2)$$

$G(\tau)$ can be calculated from the Laplace inversion of the measured $g^{(2)}(t, q)$ on the basis of eqs 1 and 2.⁵⁰ In this study, the CONTIN program supplied with the correlator was used. $G(\tau)$ can be inverted to a line-width distribution, $G(\Gamma)$, for a pure diffusive relaxation, and Γ is related to the translational diffusion coefficient D by $(\Gamma/q^2)_{q \rightarrow 0, C \rightarrow 0} = D$, so that $G(\Gamma)$ can be converted to a translational diffusion coefficient distribution $G(D)$ or further to a hydrodynamic radius distribution $f(R_h)$ via the Stokes–Einstein equation, $R_h = k_B T / 6\pi\eta_0 D$, where k_B , T , and η_0 are the Boltzmann constant, the absolute temperature, and the solvent viscosity, respectively.

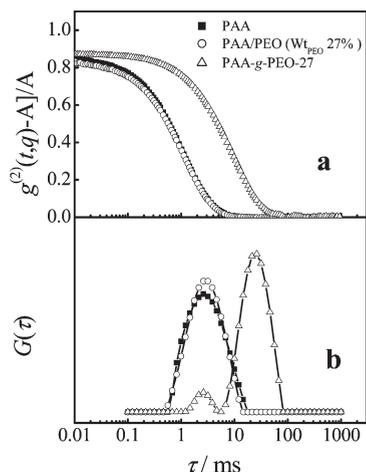


Figure 1. Intensity–intensity time correlation functions [$g^{(2)}(t,q) - A/A$] (a) and (b) their corresponding characteristic relaxation time distribution function $G(\tau)$ of PAA, PAA/PEO, and PAA-g-PEO-27 aqueous solution at 20 °C. The concentration of polymer was 10^{-3} g mL $^{-1}$, and the concentration of NaCl was 1 M, pH = 7.0.

Results and Discussion

Comparison of PAA-g-PEO to PAA/PEO Aqueous Solutions. *LLS Study.* The complexes formed between PAA and PEO through hydrogen bonding have been studied widely; many researchers observed that complexes could not be formed unless the molecular weight of PEO is larger than a critical value, around 8.8×10^5 g mol $^{-1}$ when the molecular weight of its counterpart, PAA, is high enough.²³ The molecular weight of PEO used in our study is 2.0×10^3 g mol $^{-1}$, much lower than the critical value. From the DLS data as shown in Figure 1 which were measured at pH 7.0, there is no difference between the intensity–intensity time correlation function (Figure 1a) of pure PAA aqueous solution and the mixture of PAA and PEO aqueous solution (27 wt % of PEO) and also in the corresponding plots of characteristic relaxation time distribution (Figure 1b) analyzed by the CONTIN method. Moreover, no difference is found in weight-average molecule weight from SLS. Since the M_w of PEO is much smaller than PAA (2.5×10^5 g mol $^{-1}$), if there is no significant interaction between PAA and PEO, the PEO chain can be neglected in the DLS and SLS measurements. Actually, our data clearly indicated that the existence of PEO can hardly influence the measured results of PAA in its aqueous solution. Therefore, we can conclude that there is no obvious interaction between PAA and PEO, or at least the interaction is not strong enough to form a stable complex. Mixtures of PAA and PEO with different PEO contents were measured, and the same results were obtained.

However, also seen in Figure 1, there exists obvious difference in intensity–intensity time correlation functions of PAA-g-PEO aqueous solution, from PAA or PAA/PEO solution. The appearance of a slow mode indicated that interaction between PAA and PEO segments is strong enough to form a complex or aggregate in PAA-g-PEO aqueous solution.^{40,41}

The characteristic relaxation time distributions of graft polymer PAA-g-PEO with different PEO content are shown in Figure 2. When PEO content of PAA-g-PEO is very low, such as 0.08%, there is no significant difference in the characteristic relaxation time distribution of PAA-g-PEO solution from pure PAA solution (Figure 1b); i.e., the interaction of PEO and PAA chain is inconspicuous. When

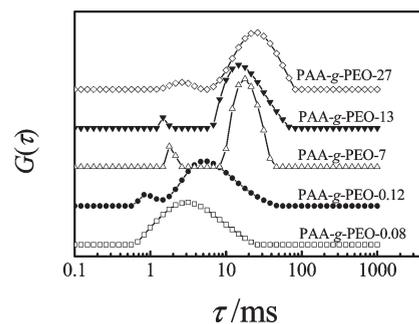


Figure 2. Characteristic relaxation time distribution function $G(\tau)$ of PAA-g-PEO with different PEO contents at 20 °C. The concentration of copolymer was 10^{-3} g mL $^{-1}$, and the concentration of NaCl was 1 M, pH = 6.6.

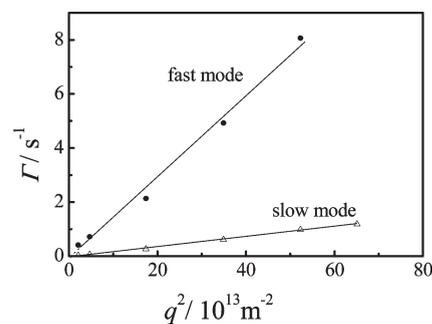


Figure 3. Scattering vector (q) dependence of average characteristic relaxation rate (Γ) of fast and slow relaxation modes in PAA-g-PEO-13 aqueous solution at 20 °C. The concentration of polymer was 10^{-3} g mL $^{-1}$, and the concentration of NaCl was 1 M, pH = 6.6.

PEO content in graft polymer increased to 0.12%, the relaxation time distribution becomes different from that of PAA solution due to the increasing interaction between PEO and PAA chains. The relaxation time becomes longer, which suggests the formation of larger structure. When PEO content further increases to 6.98%, 12.93%, and 27.27%, the intramolecular and intermolecular hydrogen bonding between carboxylic groups in PAA segments and ether oxygen in PEO segments increase significantly, resulting in the association of PAA-g-PEO chains in aqueous solution. As shown in Figure 2, two relaxation modes can be found; the slow mode is about 1 order of magnitude slower than the fast mode. In the following part, we focused on graft polymer with three higher PEO contents: PAA-g-PEO-7, PAA-g-PEO-13, and PAA-g-PEO-27.

The average characteristic relaxation rate ($\langle \Gamma \rangle$) is obtained from $\langle \Gamma \rangle = 1/\langle \tau \rangle$. As shown in Figure 3, the plots of the average characteristic relaxation rate of fast mode and slow mode of PAA-g-PEO-13 vs q^2 are both straight lines, and the extrapolation at $q \rightarrow 0$ passes through the origin. It clearly reveals the diffusive character of the two modes. Each slope leads to a $\langle D \rangle_0$ and further to a $\langle R_h \rangle$. The corresponding $\langle R_h \rangle$ (in the following part, R_h are used for simplicity) of the slow mode is about 200 nm, which can be attributed to the formation of complexes through the intermolecular hydrogen bonding, while the fast mode is attributed to a single molecule with association formed through the intramolecular hydrogen bonding between the grafted PEO chain and the backbone PAA chain.^{40,41} The apparent molecular weight measured by SLS is around 3.8×10^6 g mol $^{-1}$ (a weight-average molecular weight neglecting the dn/dc difference between PAA and PEO segments) which is about 10 times larger than a single copolymer chain.

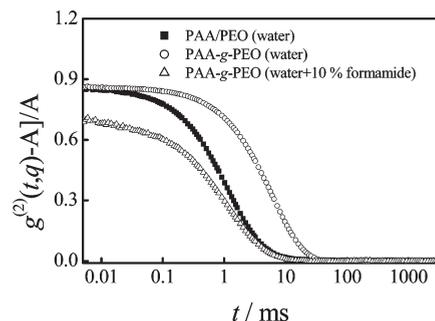


Figure 4. Intensity–intensity time correlation function [$g^{(2)}(t, q) - A$]/ A of PAA/PEO, PAA-g-PEO in aqueous solution ($C_{\text{NaCl}} = 1 \text{ M}$), and PAA-g-PEO in formamide–water solution (formamide: 10 wt %, salt free) at 20 °C. The concentration of polymer was $10^{-3} \text{ g mL}^{-1}$, the content of PEO for all samples was 7.0 wt %, and the pH for the aqueous solutions was set at 4.0.

In order to identify that it is the hydrogen bonding which led to complexation in PAA-g-PEO aqueous solution, formamide was introduced as a competitive agent for hydrogen bonds.⁵¹ Figure 4 shows the intensity–intensity time correlation function of PAA-g-PEO-7 in a formamide–water mixture (formamide: 10 wt %) with comparison to PAA-g-PEO-7 and PAA/PEO in aqueous solution. The slow mode in PAA-g-PEO aqueous solution disappears after the addition of 10 wt % formamide, and the decay time is almost the same as PAA/PEO aqueous solution. The variation of correlation functions of PAA-g-PEO in water/formamide and PAA/PEO aqueous solution is originated from the solvent difference in these two systems, which led to the scattering contrast difference. So we can conclude that interactions between PAA and formamide dominate those between PAA and PEO segments, and almost all PAA–PEO hydrogen bonds are replaced by PAA–formamide hydrogen bonds, which results in the breakage of PAA–PEO intermolecular complexes structure.

Viscosity and Rheological Measurements. To further confirm the intermolecular association of PAA-g-PEO in aqueous solution and identify the difference between PAA-g-PEO and PAA/PEO solutions, viscosity measurements were performed since intermolecular association can enhance the viscosity of polymer solution. Figure 5 shows the relative viscosity of PAA, PAA/PEO (PEO content is 7.0 wt %) mixture, PAA-g-PEO-7, and PAA-g-PEO-27 aqueous solutions, with polymer concentration from dilute to concentrated. The viscosity of PAA/PEO aqueous solution is almost the same as that of PAA solution, but the viscosity of PAA-g-PEO-7 solution is much higher than that of PAA or PAA/PEO solution in the studied concentration range. The PAA-g-PEO-27 solution is more viscous than PAA-g-PEO-7 at the concentrations higher than $5 \times 10^{-4} \text{ g mL}^{-1}$.

The viscosity of polymer solution depends on several factors such as polymer concentration, polymer molecular weight, polymer conformation, interpolymer interaction, and interaction between polymer and solvent. When polymer concentration and polymer molecular weight are fixed, interpolymer interaction becomes the main factor affecting polymer solution viscosity. It is the interpolymer interactions that lead to association of polymer chains and consequently with enhancement in the solution viscosity.¹⁰ The above results of viscosity measurement further confirmed the formation of complex of PAA-g-PEO chains in aqueous solution, whereas it is absent in PAA/PEO aqueous solution. The variation of the viscosity changes with concentration for PAA-g-PEO-7 and PAA-g-PEO-27 originated from PEO

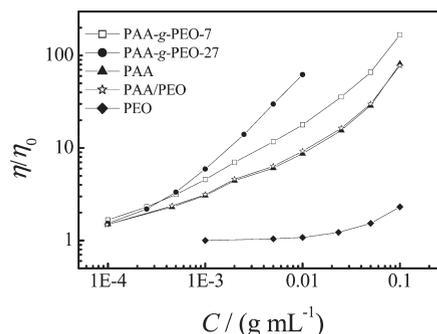


Figure 5. Concentration dependence of the relative viscosity of PAA, PAA/PEO, PAA-g-PEO-7, and PAA-g-PEO-27 at 20 °C at pH 6.0, without salt and weight fraction of PEO in PAA/PEO is the same as in PAA-g-PEO-7. η_0 is the viscosity of water.

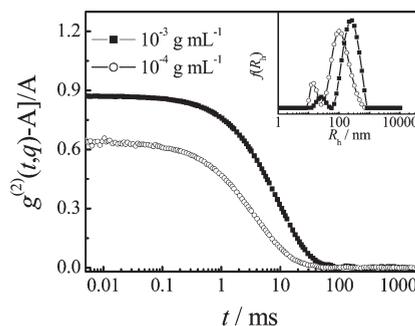


Figure 6. Intensity–intensity time correlation function [$g^{(2)}(t, q) - A$]/ A of PAA-g-PEO-27 in aqueous solution at 20 °C at pH 6.0. The concentrations of polymer was 10^{-3} and $10^{-4} \text{ g mL}^{-1}$, the concentration of NaCl is 1 and 0.1 M, respectively ($C_{\text{polymer}}/C_{\text{NaCl}}$ are the same for two samples), and the inset is the corresponding R_h distribution.

content difference, which induces intermolecular association variation. Compared with PAA-g-PEO-7, the PEO content is much higher in PAA-g-PEO-27, and more and larger intermolecular associates maybe formed at high concentrations, resulting in a higher viscosity. This conclusion can also be obtained from Figure 2; the R_h corresponding to slow mode for PAA-g-PEO-27 is larger than that of PAA-g-PEO-7, and so does the amplitude of slow mode. Additionally, the viscosity change trend with concentration is very steep for PAA-g-PEO-27. Figure 6 shows the intensity–intensity time correlation function of PAA-g-PEO-27 with the concentration of 10^{-3} and $10^{-4} \text{ g mL}^{-1}$; the inset is the corresponding R_h distribution. It can be clearly seen that the R_h of both fast mode and slow mode at the concentration of $10^{-3} \text{ g mL}^{-1}$ is larger than that at $10^{-4} \text{ g mL}^{-1}$, and so does the amplitude of slow mode. These results indicate that at higher concentration, PAA-g-PEO-27, tends to form more and larger intermolecular associations, leading to a steep increase of viscosity with concentration.

Figure 7 illustrates the shear rate dependences of η of PAA-g-PEO-7 and PAA-g-PEO-27 aqueous solution at concentrations of 10^{-3} and $10^{-2} \text{ g mL}^{-1}$. As is clearly shown, PAA-g-PEO-7 solutions exhibit a slightly shear thinning at these two concentrations. Meanwhile, in the case of PAA-g-PEO-27, it exhibits obvious shear thinning, and the viscosity decreases by about 2 orders of magnitude as the shear rate increased from 0.01 to 100 s^{-1} . In aqueous solution of PAA-g-PEO, the intermolecular and intramolecular hydrogen bonding make polymer chains associate together, and the dynamic hydrogen bonding can act as shear reversible cross-links between the chains. The abruptly decrease in viscosity

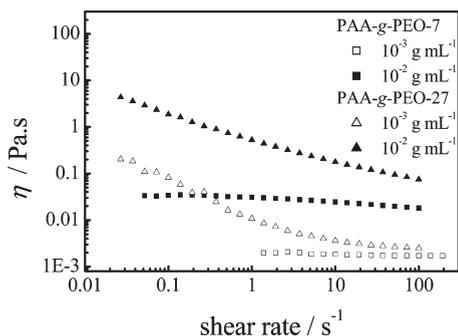


Figure 7. Shear rate dependence of η of PAA-g-PEO-7 and PAA-g-PEO-27 salt-free solution at two concentrations (10^{-3} and 10^{-2} g mL^{-1}) at 20°C , $\text{pH} = 6.0$.

with the increase of shear rate is ascribed to the breakdown of the network junctions; that is, the rate of network disruption exceeds the rate at which associations are re-formed.^{44,52,53}

Property Discussion of PAA-g-PEO and PAA/PEO in Aqueous Solution. When the PEO content is similar in both PAA-g-PEO and PAA/PEO system, and the PEO molecular weight is much lower than the critical value, the complex formed only in the PAA-g-PEO aqueous solution. It seems that the hydrogen bonding between PAA and PEO segments are much more stable and effective in the PAA-g-PEO than that in PAA/PEO. According to the study of Terao et al.¹⁷ and Somasundaran et al.,²⁵ the strength of hydrogen bonding between polymer chains depends on two factors: one is the strength of a single hydrogen bond, and the other is cooperative interaction among the hydrogen bonds. As the strength of a single hydrogen bond of PAA-PEO is very weak, the complex can be formed only through the cooperative interaction among many such groups. The stability of the complex will depend on the predominance of hydrogen-bond (H-bond) over thermal or Brownian motion.²⁵ So high PEO molecular weight is needed to form a complex with PAA; the longer the PEO chain, the more interaction sites a PEO molecule have which increases the possibilities of including this PEO molecule into an aggregate.

From the point of view of thermodynamics: in the PAA/PEO system, the H-bonds formed between PAA and PEO are enthalpically favorable but entropically unfavorable. A stable complex can form through many H-bonds only when the enthalpy gain can more than compensate for the entropy loss, i.e., the entire $\Delta G < 0$. In PAA/PEO aqueous solution with low PEO molecular weight, in order to form a stable complex, more translational entropy will be sacrificed in bringing these PEO chains together compared with the PAA/PEO system having longer PEO chains. Thus, a relatively long PEO chain is favored for the formation of stable complex.

In our case of PAA-g-PEO, the entropy loss resulting from bringing polymers together during the formation of hydrogen-bonding complex is much less than that in PAA/PEO case, since the PEO segment is already adjoined to PAA backbone by a chemical bond. So the enthalpy gain could more easily compensate for entropy loss, resulting in the formation of a complex due to hydrogen bonding in PAA-g-PEO thermodynamically more favorable.

Influence of pH Value. The pH-dependent association of PAA-g-PEO-7 and PAA-g-PEO-13 in aqueous solutions was also studied, as shown in Figure 8a,b. The complexes are formed at all pH values, from acidic to basic conditions, but they are different in the various pH ranges. As shown in Figure 8a, for PAA-g-PEO-7, when $\text{pH} < 4.4$, the R_h of the complexes decreases with pH; in the pH range of 4.4–6.6,

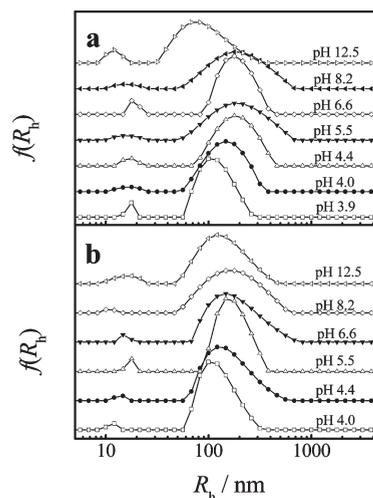


Figure 8. The pH dependence of the hydrodynamic radius of PAA-g-PEO-7 (a) and PAA-g-PEO-13 (b) in aqueous solution at 20°C . The concentration of polymer was 10^{-3} g mL^{-1} , and the concentration of NaCl was 1 M.

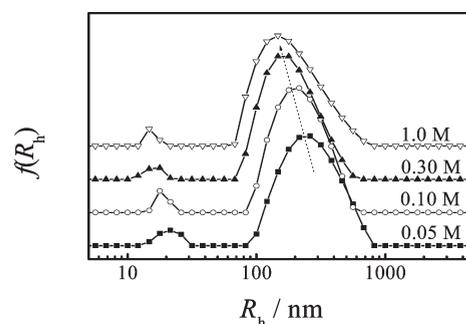


Figure 9. Salt concentration dependence of PAA-g-PEO-13 in aqueous solution at 20°C , and the concentration of polymer was 10^{-3} g mL^{-1} , $\text{pH} = 6.6$.

there is little change of R_h ; when $\text{pH} > 8.2$, R_h and the apparent molecular weight decreases as pH increase. At low pH values, the carboxylic group in PAA backbone is protonated, and stronger cooperative hydrogen bonding can be achieved. Thus, the complex was more hydrophobic and more collapsed. With pH increases, the ionization of carboxylic group was enhanced, leading to weaker cooperative hydrogen bonding between PEO and PAA chains. When $\text{pH} > 8.2$, PAA segments are almost completely ionized. However, there are still large structures in the solution, although they are much smaller, which can be ascribed to the ion-dipole interaction according to the researches before.^{20,27,40}

The situation is similar for PAA-g-PEO-13: when $\text{pH} < 4.4$, R_h decreases as pH decreases; in the pH range of 5.5–8.2, there is little change of R_h with pH; when $\text{pH} > 8.2$, R_h decreases as pH increases. The study of the PAA/PEO mixtures from other researchers^{23,37} showed that PAA/PEO form complexes at low pH, but the complexes deform at neutral condition, suggesting that the cooperative interaction of hydrogen bonding decrease as the amount of hydrogen bonds decrease. In other words, the enthalpy gain decreases and cannot compensate for the entropy loss, and the complexes become unstable. It is interesting that, in our study, the complexes are still stable in neutral and weak basic solution. This phenomenon further confirmed our thermodynamic-based explanation above.

Influence of NaCl Concentration. Figure 9 shows the influence of NaCl concentration on the chain association in PAA-g-PEO-13 aqueous solution, at the polymer concentration of 10^{-3} g mL $^{-1}$ and pH 6.6. Under the low NaCl concentrations, i.e., below 0.05 M, it is very difficult for polymer solution to pass through the syringe filter during the preparation of LLS samples, which makes our LLS study only possible above 0.05 M salts.

In the whole studied range of salt concentration, stable complex can always formed and the complex size changes with salt concentration. With the increases of salt concentration from 0.05 to 0.30 M, R_h of the complex decreases from 259 to 184 nm. In the salt range of 0.30–1.0 M, R_h changes little. As pH of aqueous solution was 6.6, part of carboxylic groups of PAA backbone tended to be deprotonated and existed as $-\text{COO}^-$. Under low salt concentrations (0.05–0.30 M), charged $-\text{COO}^-$ electrostatically repelled each other. However, with the increase of NaCl concentration, more Na^+ around $-\text{COO}^-$ shielded the electrostatic repulsion between $-\text{COO}^-$ of PAA backbones, so R_h of the complex decreases. As salt concentration further increase to the range from 0.30 to 1.0 M, the electrostatic interaction of $-\text{COO}^-$ had been fully screened, allowing little change in R_h of the complex. In conclusion, as the NaCl concentration increases, the hydrogen-bonding complexes are getting more compact, which is consistent with the results reported by Khutoryanskiy et al.⁵⁴

Conclusion

The current study of hydrophilic poly(acrylic acid) (PAA) grafted with different amounts of hydrophilic poly(ethylene oxide) (PEO), i.e., PAA-g-PEO, in aqueous solutions shows that they can form large interchain complexes, which were reflected in the appearance of a slow mode in the line-width distribution measured in dynamic laser light scattering. On average, these interchain complexes have a finite hydrodynamic radius of ~ 200 nm and an aggregation number of ~ 10 . From a rheological point of view, the PAA-g-PEO aqueous solution shows a shear-thinning behavior and is much viscous than the PAA solution or the PAA and PEO mixture solution under identical experimental conditions. The interchain complexes are formed via the hydrogen bonding between the carboxylic group on PAA segments and the ether oxygen on PEO segments because the addition of formamide can dissolve them. The effects of pH and salt concentration on the interchain complexes further confirmed the hydrogen-bonding assumption. In contrast, there is no interchain complexation in the solution mixture of PAA and short PEO chains, which indicates that here the enthalpy gain is not sufficient to compensate the translational entropy loss. Therefore, the relatively less loss of the translational entropy plays an important role in the formation of stable interchain PAA-g-PEO complexes. The PAA-g-PEO copolymer developed in the current study has some potential applications in encapsulating and delivering cationic or hydrogen-accepting agrochemicals or drugs.

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References and Notes

(1) Chatterjee, S. K.; Ghosh, S.; Chatterjee, N. *Angew. Macromol. Chem.* **1991**, *184*, 99.

- (2) Kawamura, A.; Yoshioka, Y.; Harada, A.; Kono, K. *Biomacromolecules* **2005**, *6*, 627.
- (3) Kawamura, A.; Kojima, C.; Iijima, M.; Harada, A.; Kono, K. *J. Polym. Sci., Part A* **2008**, *46*, 3842.
- (4) Serra, L.; Doménech, J.; Peppas, N. A. *Eur. J. Pharm. Biopharm.* **2006**, *63*, 11.
- (5) Kim, I. S.; Kim, S. H.; Cho, C. S. *Arch. Pharm. Res.* **1996**, *19*, 18.
- (6) Zhang, Y. B.; Wu, C.; Fang, Q.; Zhang, Y. X. *Macromolecules* **1996**, *29*, 2494.
- (7) Wang, X. H.; Goh, S. H.; Lu, Z. H.; Lee, S. Y.; Wu, C. *Macromolecules* **1999**, *32*, 2786.
- (8) Li, M.; Jiang, M.; Wu, C. *J. Polym. Sci., Part B* **1997**, *35*, 1593.
- (9) Tsuchida, E.; Abe, K. *Adv. Polym. Sci.* **1982**, *45*, 1.
- (10) Dan, Y.; Chen, S. Y.; Zhang, Y. F.; Xiang, F. R. *J. Polym. Sci., Part B* **2000**, *38*, 1069.
- (11) Wang, Y. P.; Zhou, L.; Sun, G. M.; Xue, J.; Jia, Z. F.; Zhu, X. Y.; Yan, D. Y. *J. Polym. Sci., Part B* **2008**, *46*, 1114.
- (12) Song, T.; Goh, S. H.; Lee, S. Y. *Macromolecules* **2002**, *35*, 4133.
- (13) Huang, X. D.; Goh, S. H. *Macromolecules* **2000**, *33*, 8894.
- (14) Wang, Y.; Goethals, E. J.; Du Prez, F. E. *Macromol. Chem. Phys.* **2004**, *205*, 1774.
- (15) Matsukawa, S.; Ando, I. *Macromolecules* **1997**, *30*, 8310.
- (16) Lu, X. Y.; Weiss, R. A. *Macromolecules* **1995**, *28*, 3022.
- (17) Miyoshi, T.; Takegoshi, K.; Terao, T. *Macromolecules* **1999**, *32*, 8914.
- (18) Kaczmarek, H.; Szalla, A.; Chaberska, H.; Kowalonek, J. *Surf. Sci.* **2004**, *566–568*, 560.
- (19) Koussathana, M.; Lianos, P.; Staikos, G. *Macromolecules* **1997**, *30*, 7798.
- (20) Bailey, F. E.; Callard, R. W.; Lundberg, R. D. *J. Polym. Sci., Part A* **1964**, *2*, 845.
- (21) Hayashi, Y.; Harris, J. M.; Hoffman, A. S. *React. Funct. Polym.* **2007**, *67*, 1330.
- (22) Lele, B. S.; Hoffman, A. S. *J. Controlled Release* **2000**, *69*, 237.
- (23) Ikawa, T.; Abe, K.; Honda, K.; Tsuchida, E. *J. Polym. Sci., Part A* **1975**, *13*, 1505.
- (24) Saravanan, S.; Reena, J. A.; Rao, J. R.; Murugesan, T.; Nair, B. U. *J. Chem. Eng. Data* **2006**, *51*, 1246.
- (25) Pradip; Maltesh, C.; Somasundaran, P.; Kulkarni, R. A.; Gundiah, S. *Langmuir* **1991**, *7*, 2108.
- (26) Baranovsky, V.; Shenkov, S.; Rashkov, I.; Borisov, G. *Eur. Polym. J.* **1992**, *28*, 475.
- (27) Liu, Q.; DuWijn, J. R.; VanBlitterswijk, C. A. *Eur. Polym. J.* **1997**, *33*, 1041.
- (28) Choi, H. K.; Kim, O. J.; Chung, C. K.; Cho, C. S. *J. Appl. Polym. Sci.* **1999**, *73*, 2749.
- (29) Chun, M. K.; Choi, H. K.; Kang, D. W.; Kim, O. J.; Cho, C. S. *J. Appl. Polym. Sci.* **2002**, *83*, 1904.
- (30) Natarajan, P.; Raja, C. *Eur. Polym. J.* **2004**, *40*, 2291.
- (31) Miyoshi, T.; Takegoshi, K.; Hikichi, K. *Polymer* **1997**, *38*, 2315.
- (32) Tan, L.; Chen, S. M.; Ping, Z. H.; Shen, Y. M. *Magn. Reson. Chem.* **2003**, *41*, 481.
- (33) Tan, L.; Lu, G. Q.; Chen, S. M.; Ping, Z. H.; Shen, Y. M. *Magn. Reson. Chem.* **2003**, *41*, 939.
- (34) Oyama, H. T.; Tang, W. T.; Frank, C. W. *Macromolecules* **1987**, *20*, 474.
- (35) Oyama, H. T.; Tang, W. T.; Frank, C. W. *Macromolecules* **1987**, *20*, 1839.
- (36) Osada, Y. *J. Polym. Sci., Part A* **1979**, *17*, 3485.
- (37) Khutoryanskiy, V. V.; Dubolazov, A. V.; Nurkeeva, Z. S.; Mun, G. A. *Langmuir* **2004**, *20*, 3785.
- (38) Cao, Y. P.; Liu, G. Q.; Liu, X. Y.; Ding, X. B.; Peng, Y. X.; Chan, A. S. C. *New J. Chem.* **2003**, *27*, 1065.
- (39) Yu, X. H.; Tanaka, A.; Tanaka, K.; Tanaka, T. *J. Chem. Phys.* **1992**, *97*, 7805.
- (40) Khoussakoun, E.; Gohy, J. F.; Jérôme, R. *Polymer* **2004**, *45*, 8303.
- (41) Holappa, S.; Karesoja, M.; Shan, J.; Tenhu, H. *Macromolecules* **2002**, *35*, 4733.
- (42) Yokoyama, M.; Okano, T.; Sakurai, Y.; Kikuchi, A.; Ohsako, N.; Nagasaki, Y.; Kataoka, K. *Bioconjugate Chem.* **1992**, *3*, 275.
- (43) Nakajima, N.; Ikada, Y. *Bioconjugate Chem.* **1995**, *6*, 123.
- (44) Hourdet, D.; L'Alloret, F.; Audebert, R. *Polymer* **1994**, *35*, 2624.
- (45) Gaucher, A.; Wakselman, M.; Mazaleyrat, J. P.; Crisma, M.; Formaggio, F.; Toniolo, C. *Tetrahedron* **2000**, *56*, 1715.

- (46) Chu, B. *Laser Light Scattering*; Academic Press: New York, 1974.
- (47) Berne, B. J.; Pecora, R. *Dynamic Light Scattering*; Plenum Press: New York, 1976.
- (48) Wu, C.; Zhou, S. Q. *J. Polym. Sci., Part B* **1996**, *34*, 1597.
- (49) Zimm, B. H. *J. Chem. Phys.* **1948**, *16*, 1099.
- (50) Yuan, G. C.; Wang, X. H.; Han, C. C.; Wu, C. *Macromolecules* **2006**, *39*, 3642.
- (51) Wu, C. *J. Polym. Sci., Part B* **1994**, *32*, 803.
- (52) Angelopoulos, S. A.; Tsitsilianis, C. *Macromol. Chem. Phys.* **2006**, *207*, 2188.
- (53) Strandman, S.; Hietala, S.; Aseyev, V.; Koli, B.; Butcher, S. J.; Tenhu, H. *Polymer* **2006**, *47*, 6524.
- (54) Khutoryanskiy, V. V.; Mun, G. A.; Nurkeeva1, Z. S.; Dubolazov, A. V. *Polym. Int.* **2004**, *53*, 1382.