Macromolecules **1994**, *27*, 427–431

Interpolymer Association between Acrylic Acid Copolymers and Poly(ethylene glycol): Effects of the Copolymer Nature

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Received August 3, 1993; Revised Manuscript Received November 1, 1993[●]

ABSTRACT: The interpolymer association between acrylic acid (AA) copolymers and poly(ethylene glycol) (PEG) was investigated through viscometric and potentiometric measurements. The AA copolymers used contained carboxylate (COO^-), sulfonate (SO_3^-), or isopropylamide ($CONHCH(CH_3)_2$) groups introduced by neutralization, copolymerization, or condensation reactions, respectively. The experiments were performed under a low and constant ionic strength, $I \cong 1.0 \times 10^{-3}$ M, and constant pH conditions, following the known isoionic dilution method. The poly(acrylic acid) association with PEG, due to interpolymer hydrogen bonding, results in the formation of compact aggregates. When the percentage molar degree of substitution (DS) in carboxylate or sulfonate groups is higher than 10%, the interpolymer association is prevented, while this still exists for DS = 30% in isopropylamide groups. The obtained results show a significant differentiation in the association between the AA copolymers containing charged groups, COO^- or SO_3^-, and neutral groups, $CONHCH(CH_3)_2$. The presence of these neutral groups in a first stage till DS = 10%, probably due to synergistic hydrophobic forces, favors the interpolymer association. This association is weakened later and finally prevented for DS > 30% because of a corresponding decrease of the hydrogen bonding, which is mainly responsible for this interpolymer association.

Introduction

The interpolymer association between a polyacid (e.g., poly(acrylic acid) (PAA)) and a polybase, i.e., a proton-acceptor polymer (e.g., poly(ethylene glycol (PEG)), in water solution has been extensively studied during the past decades.[1-13] This association has been generally attributed to hydrogen bonding. Usually in the literature such an interpolymer association is referred to as "interpolymer complexation", and the resulting aggregates are referred to as "polymer complexes". In this work we use the term "interpolymer association", which has a more general meaning than the terms "complexation" or "polymer complex formation". Two of the most used experimental procedures for this investigation are viscometry[3,4,6,8,11] and potentiometry,[4,6,7,11,13] while fluorescence methods have also recently found a wide application.[8-10,12,13] The cooperative character of this interpolymer interaction[1,2,4,5,11] and, as a consequence, the existence of a minimum chain length[5,6] for the associating polymers are generally accepted. Nevertheless the prerequisite of long sequences for complexation has recently been questioned[9,14] on the basis of steric factors[9] and experimental findings on a similar system.[14]

In this work we have studied the above-mentioned ternary system (PEG/PAA/H_2O) by measuring the intrinsic viscosity ($[\eta]$) of the polymer mixture at constant pH and ionic strength following a recent refinement[15] of the known isoionic dilution method.[16,17] We have also used the potentiometric method to calculate the degree of association (θ) and the apparent association constant (K_{app}), expressing the equilibrium between associated and nonassociated groups. To study the influence of the presence of inactive groups in the PAA chain on the interpolymer association, we have used partially neutralized PAA samples, copolymers of acrylic acid (AA) with sulfonated monomers, and copolymers of AA with isopropylacrylamide (IPA).

Experimental Section

The PAA sample used was a 25% aqueous solution obtained from Polysciences. It was diluted to a 5% solution with 0.1 M HCl and then purified by ultrafiltration and freeze-dried. Its molecular mass was determined viscometrically in 0.5 M NaBr after 100% neutralization[19] and was found to be equal to 1.3×10^5. The partially neutralized PAA samples were prepared by neutralization with 0.0100 M NaOH solution. The copolymers of AA with vinylsulfonic acid (PAVS-70-3.5 and PAVS-160-9) and with 2-acrylamido-2-methylpropanesulfonic acid (PAAMPS-105-20) have been described elsewhere.[11] The numbers 70, 160, and 105 represent the molecular mass of each copolymer in thousands, while the numbers 3.5, 9, and 20 represent the percentage molar degree of substitution (DS) in sulfonic groups of each copolymer. The copolymers of AA with IPA were prepared from the above-mentioned PAA sample through a condensation reaction with isopropylamine in solution in *N*-methyl-2-pyrrolidone (NMP) in the presence of a carbodiimide.[18] For instance, a copolymer with DS = 10% in IPA groups is prepared as follows: 5 g of PAA is added to 80 mL of NMP, and the mixture is slightly heated under stirring. After complete dissolution the solution is cooled to 10 °C and 0.41 g of IPA dissolved in 10 mL of NMP is added dropwise under vigorous stirring. The mixture is stirred at room temperature overnight for complete dissolution. Then a solution of 1.43 g of dicyclohexylcarbodiimide in 10 mL of NMP is added to the reaction solution. The reaction solution is stirred overnight and becomes turbid because of the produced dicyclohexylurea. Then the mixture is added to 1 L of water, and dicyclohexylurea is completely precipitated. The mixture is filtered and the filtrate is ultrafiltrated after addition of 100 mL of 0.1 M HCl. Finally, the copolymer is recovered by freeze-drying. The content of the obtained copolymers in IPA was determined by ^1H NMR spectroscopy and elemental analysis. ^1H NMR spectra were recorded on a Bruker WP 250 spectrometer (250 MHz) with a flip angle of about 75° and an acquisition time ranging from 3 to 4 s. Elemental analyses were conducted by the Central Service of Microanalyses of CNRS (France). We have

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[●] Abstract published in *Advance ACS Abstracts*, December 15, 1993.

0024-9297/94/2227-0427$04.50/0

Table 1. Characteristics of the Polymers Used

sample	$M_w \times 10^{-3}$	DS, mol %
PAA	130	
PAVS-70-3.5	70	3.5
PAVS-160-9	160	9
PAAMPS-105-20	105	20
PAAIPA-10	137[a]	10
PAAIPA-17.5	143[a]	17.5
PAAIPA-29	151[a]	29
PEG	42.5	

[a] The molecular masses of these three copolymers have been calculated from the corresponding DS and the degree of polymerization, $DP_w = 1.8 \times 10^3$, of the initial PAA sample.

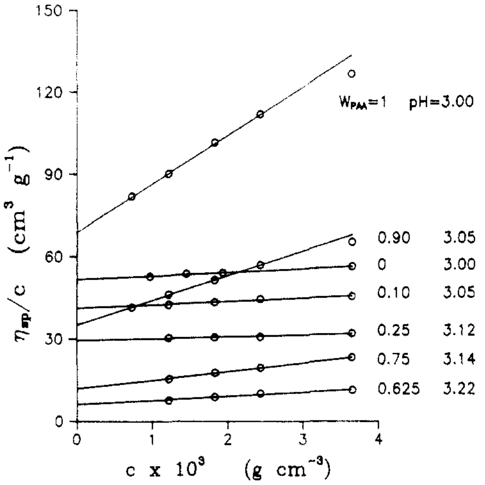

Figure 1. η_{sp}/c versus c for the PEG/PAA/H_2O ternary system at various weight fractions, w_{PAA}, at constant pH, using the isoionic dilution process. The corresponding pH values are also indicated.

prepared three copolymers of this type (Table 1). The PEG sample used was a product of Fluka, purified by precipitation with hexane from chloroform solution. Its molar mass has been determined viscometrically in water[20] and has been found to be equal to 4.25×10^4. The information about the polymers used is summarized in Table 1. Water was purified by a Milli-Q system (Millipore) in the French laboratory and by a Seralpur Pro 90 C system in the Greek laboratory.

Viscosity measurements were carried out at 30 °C with an automated viscosity measuring system (Schott-Geräte AVS 300) equipped with an Ubbelohde type viscometer. Kinetic energy corrections were taken into account.

Potentiometric measurements were carried out at 30 °C with a WTW 525 pH meter equipped with a pH precision electrode assembly (Metrohm).

Results and Discussion

Viscometry. Figure 1 presents the reduced viscosity, η_{sp}/c, versus concentration, c, for the polymer mixture PEG/PAA in water at various compositions, expressed as the weight fraction of PAA, w_{PAA}. The pH of the initially used PAA solution was set at 3.00 by choosing the appropriate polyacid concentration. The same pH value was also adjusted for the PEG solution by using HCl. The solvent used for the dilutions of each mixture was a HCl solution of the same pH as that of each polymer mixture. Therefore, the pH of the solvent was 3.00 for the solutions of the two pure constituents but somewhat greater for the solutions of their mixtures, because of the polyacid–polybase interaction through hydrogen bonding (see Figure 1). The pH variations in the mixtures are discussed in detail later in the potentiometry section. As can be seen, the obtained results agree with a Huggins law behavior

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c \tag{1}$$

giving by extrapolation to zero concentration the value of $[\eta]$ and from the slope of the straight line the Huggins constant, k', characterizing the polymer/solvent interactions. These results are attributed to the fact that during this isoionic dilution procedure the pH of each polymer (or polymer mixture) solution is kept constant so that the dissociation degree, α, of the polyacid and the ionic strength of the solutions do not change during dilution. In fact, α is given by the formula

$$\alpha = \frac{[COO^-]}{[COOH]_0} = \frac{K_d}{[H^+]} \tag{2}$$

where $[COOH]_0$ is the total molar concentration of the carboxylic and carboxylate groups, $[COO^-]$ is the concentration of the carboxylate group, K_d is the apparent equilibrium dissociation constant of PAA, and $[H^+]$ is the hydrogen ion concentration. Under constant pH and ionic strength conditions, K_d is also constant (see eq 9).

To make the comparison between the several systems easier, we present the intrinsic viscosity ratio $[\eta]_r = [\eta]/[\eta]_{id}$ for each polymer mixture as a function of the mole fraction in carboxylic groups, $N_{COOH} = n_{COOH}/(n_{COOH} + n_{PEG})$, where n_{COOH} and n_{PEG} are the unit moles of the poly(carboxylic acid) and the poly(ethylene glycol), respectively. $[\eta]_{id}$ is the ideal intrinsic viscosity of the polymer mixture, i.e., the weight average of the intrinsic viscosities $[\eta]_1$ and $[\eta]_2$ of the two pure components, according to the formula

$$[\eta]_{id} = w_1[\eta]_1 + w_2[\eta]_2 \tag{3}$$

where w_1 and w_2 are their weight fractions. $[\eta]$ is the experimentally determined value.

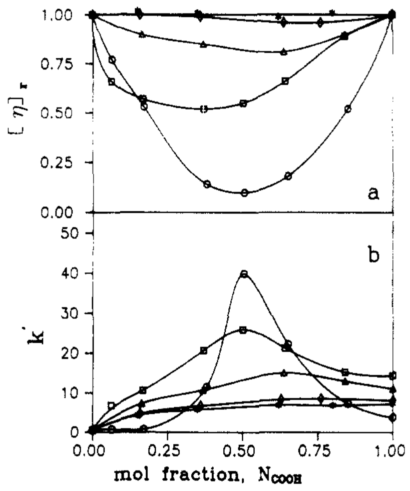

Figure 2. (a) Intrinsic viscosity ratio, $[\eta]_r$, versus the mole fraction, N_{COOH}, for the PEG/PAA/H_2O ternary system at various DS: 0 (○), 2.75 (□), 4.7 (△), 8.0 (◇), 12.0% (*). $I = 1.0 \times 10^{-3}$ M. (b) Huggins constant, k', versus N_{COOH} for the same systems as in a.

Figure 2a presents the ratio $[\eta]_r$ versus N_{COOH} for five PAA/PEG systems in which COOH groups have been partially substituted by COO^- through neutralization, so that DS extends from 0 to 12%. The experiments were performed at constant ionic strength $I = 1.0 \times 10^{-3}$ M by using NaCl for the partially neutralized samples.[15] We observe a strong interaction between PAA and PEG for the unneutralized sample, DS = 0%. This interaction gradually weakens as DS increases and it disappears for DS = 12%, where $[\eta]_r$ is equal to unity over the entire composition range. From the shape of the curves it is obvious that the aggregates (or the complexes) formed have a compact structure and the compactness decreases as DS increases. Moreover, for DS = 0% a clear minimum

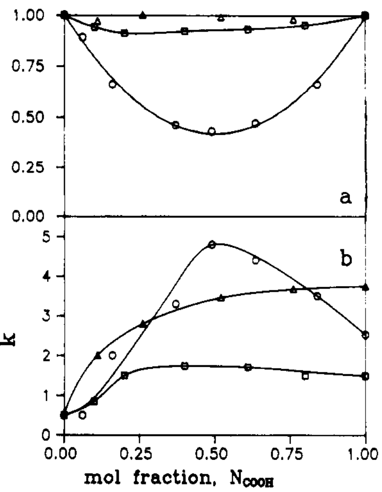

Figure 3. (a) $[\eta]_r$ versus N_{COOH} for the PEG/PAVS-70-3.5/H_2O (○), PEG/PAVS-160-9/H_2O (□), and PEG/PAAMPS-105-20/H_2O (△) ternary systems at pH = 3.00. (b) k' versus N_{COOH} for the same systems as in a.

appears at a molar ratio of 1:1, expressing a tendency for the formation of a hydrogen bond between one carboxylic unit of the PAA and one ether oxygen of the PEG. Figure 2b presents the corresponding variation of the Huggins constant, k'. Although the physical meaning of k' is not very clear, we observe that k' dramatically increases as the association occurs. This increase in k' is probably related to increased interpolymer interactions between PAA and PEG chains as compared to the binary PAA (or PEG)/solvent systems. The high increase in k' with increasing interpolymer interaction has been well established in systems where strong hydrophobic interactions between the polymer segments occur.[21,22]

Figure 3 shows $[\eta]_r$ vs N_{COOH} (Figure 3a) and k' vs N_{COOH} (Figure 3b) for the sulfonated samples at pH = 3.00. As in the case of the unneutralized homopolymer, PAA (Figure 1), the pH of the polyacid solutions was set at 3.00 by adjustment of their concentrations. As shown in Figure 3a, the presence of 3.5% of sulfonated units in the PAVS-70-3.5 copolymer does not prevent the formation of a compact interpolymer complex exhibiting a viscosity minimum at a 1:1 proton donor–proton acceptor ratio. On the contrary, the PAVS-160-9 and PAAMPS-105-20 copolymers, with 9 and 20% sulfonated groups, respectively, show either a slight or the absence of interpolymer interaction with PEG. The same conclusions can be drawn from Figure 3b, where k' presents a maximum at N_{COOH} = 0.5 for the PAVS-70-3.5/PEG/H_2O system. The variation of k' for the two other systems seems to agree with the absence of interpolymer association.

Figure 4 shows the viscometric behavior of the homopolymer PAA and the PAAIPA copolymers with PEG at pH = 3.00. Here again we have adjusted the pH of the polyacid solutions by using the appropriate polymer concentrations. We observe that the $[\eta]_r$ curve (Figure 4a) is displaced gradually to higher values as the DS in IPA groups of the polymer chain increases. The variation of k' is shown in Figure 4b. We also observe a displacement of the minimum of $[\eta]_r$ and maximum of k' to the right as the content of the polyacid in IPA groups increases. This displacement can, nevertheless, be corrected if we assume that intramolecular hydrogen bonding occurs between the amide and the carboxylic groups, which inactivates one carboxylic group for each amide group (see Figure 5). The obtained results, after the new calculation of the mole fraction, N_{COOH}, of the free active carboxylic groups, are depicted in Figure 4 by the dashed lines and exhibit their minimum or maximum values correspondingly at N_{COOH} = 0.5. In this new calculation of N_{COOH} we consider that all the amide groups are able to form intramolecular hydrogen bonds. In fact, if such hydrogen bonding occurs only between adjacent acid and amide units, we have to account for the fraction of amide units centered in amide–amide–amide triads. This fraction is lower than 10% for random copolymers. A random distribution of the amide units in this type of copolymers has been reported.[23] Furthermore, some intramolecular hydrogen bonding could occur between nonadjacent acid and amide units after the folding up of the chain. At this point we have to note that the solutions used for the viscometric study of the systems presented in Figure 4 showed a slight turbidity, especially around the N_{COOH} = 0.5 composition. This turbidity was gradually weakened as the DS was increased. Nevertheless it did not really inhibit the viscosity measurements as for all systems and compositions studied we did not observe any kind of precipitate while the flow time for all solutions was stable.

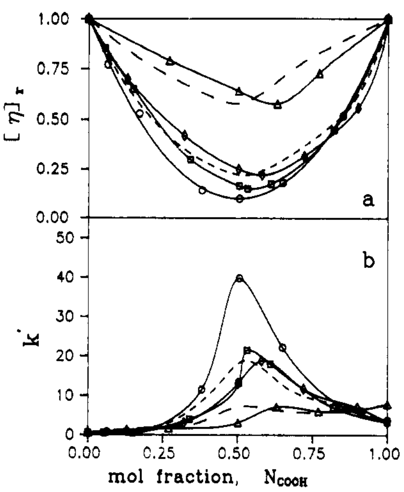

Figure 4. (a) $[\eta]_r$ versus N_{COOH} for the ternary systems PEG/PAA/H_2O (○), PEG/PAAIPA-10/H_2O (□), PEG/PAAIPA-17.5/H_2O (◇), and PEG/PAAIPA-29/H_2O (△) at pH = 3.00. The dashed lines represent a new calculation of N_{COOH} for the last two systems after the assumption that each amide group of the copolymer inactivates one carboxylic group. (b) k' versus N_{COOH} for the same systems as in a.

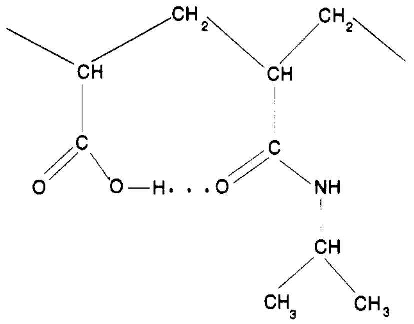

Figure 5. Schematic representation of the intrachain hydrogen bonding in the PAAIPA chain.

The interpolymer association in the systems of Figure 4 was also studied at a slightly higher pH, i.e., 3.40. This pH was reached after a slight neutralization, approximately 1%, of the initial copolymer solution having a concentration about 2 g L^{-1}. The results of the relative intrinsic viscosity, $[\eta]_r$, at N_{COOH} = 0.5 are plotted as a function of DS in Figure 6. Similar curves were obtained for the other systems (Figures 2–4) and reported in the same figure. From Figure 6 we see that as the number of carboxylate or sulfonate units increases, the value of $[\eta]_r$ increases sharply to reach the ideal behavior, $[\eta]_r$ = 1, indicating

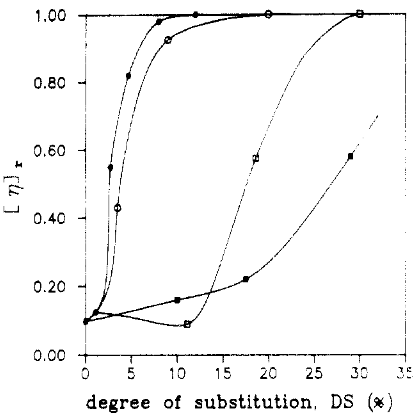

Figure 6. $[\eta]_r$ versus DS at $N_{COOH} = 0.5$ for the ternary systems PEG/PAA partially neutralized/H_2O (●), PEG/PAA sulfonated/H_2O (○), PEG/PAAIPA/H_2O at pH = 3.00 (■) and PEG/PAAIPA/H_2O at pH = 3.40 (□).

the absence of any interpolymer interaction for DS > 10%. The obtained results for the interpolymer association of the partially neutralized PAA or its sulfonated copolymers with PEG agree with recent findings.[10,11] Nevertheless when the inactive group is the IPA group, this transition to the ideal behavior is more gradual and only at pH = 3.40 is DS = 30% sufficient to inhibit the association. This behavior could be explained as follows: The presence of COO^- or SO_3^- groups in the PAA chain increases its rigidity because of electrostatic intrachain repulsions and makes difficult the hydrogen-bonding formation between the carboxylic groups of the polyacid and the ether oxygens of PEG. The presence of neutral IPA units, on the contrary, does not influence the flexibility of the chain. In fact, the intrinsic viscosities of PAA and PAAIPA-10 are very similar (69 and 61, respectively, at pH = 3.00) while the intrinsic viscosity increases dramatically when PAA is neutralized at 10% ($[\eta] = 410$). Moreover, the IPA groups are more hydrophobic than COO^- or SO_3^-, contributing to an increased hydrophobicity of the copolymer chain and subsequently to the stabilization of the formed interpolymer aggregate by a synergistic hydrophobic effect. This hydrophobic action is also evidenced by the gradual decrease in $[\eta]$ of the PAAIPA copolymers as the content in IPA units increases (unpublished results). It is noteworthy that the PAAIPA-10 copolymer gives at pH = 3.40 relatively more compact aggregates than it does at pH = 3.00 (Figure 6). This behavior is not at present explained but it is presumably due to a combination of hydrophobic and electrostatic effects.

Potentiometry. This method is widely used for the study of polymer complexes stabilized through hydrogen bonding.[4,5,11,24-27] The interpolymer association between a polyacid, such as PAA and its copolymers, and a polybase, such as PEG, takes place through an association equilibrium

$$\mathrm{COOH} + \mathrm{O}< \overset{K_{app}}{\rightleftharpoons} \mathrm{COOH{\cdots}O}< \qquad (4)$$

where K_{app} is the apparent constant of the interpolymer association given by

$$K_{app} = \frac{[\mathrm{COOH{\cdots}O}<]}{[\mathrm{COOH}][\mathrm{O}<]} \qquad (5)$$

where [COOH···O<] is the concentration of the associated carboxylic units and [COOH] and [O<] are the concentrations of the free carboxylic and ether oxygen units, respectively. This association induces a displacement of the PAA dissociation equilibrium

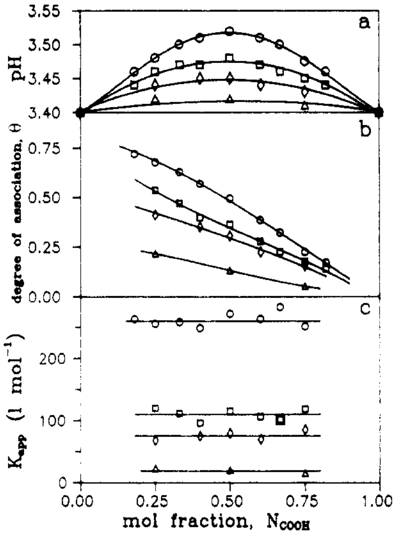

Figure 7. (a) pH versus N_{COOH} for the ternary systems PEG/PAA/H_2O (○), PEG/PAAIPA-10/H_2O (□), PEG/PAAIPA-17.5/H_2O (◇), and PEG/PAAIPA-29/H_2O (△). The pH of the pure constituents was 3.40, while their ionic strength had been adjusted at $I = 1.0 \times 10^{-3}$ M with a dilute NaCl solution. (b) Degree of association, θ, versus N_{COOH} for the same systems as in a. (c) Apparent association constant, K_{app}, versus N_{COOH} for the same systems as in a.

$$\mathrm{COOH} \rightleftharpoons \mathrm{COO^-} + \mathrm{H^+} \qquad (6)$$

to the undissociated form, resulting in an increase of the pH of the polyacid/polybase mixture as compared to the pH of the pure PAA and PEG solutions. To avoid the appearance of any turbidity in our polymer mixtures, the pH of the PAA and PAAIPA solutions was adjusted to 3.40 by using the appropriate polyacid concentration, $[\mathrm{COOH}] \cong 1.5 \times 10^{-2}$ M. The pH of the PEG solution was also adjusted to the same value by addition of HCl. The ionic strength of the initial polymer solutions was set at $I = 1.0 \times 10^{-3}$ M by using NaCl.

The obtained potentiometric results are shown in Figure 7a, in which the variation of pH as a function of N_{COOH} is presented for the systems PAA/PEG, PAAIPA-10/PEG, PAAIPA-17.5/PEG, and PAAIPA-29/PEG. From these results we can see that the interpolymer association is gradually weakened as DS increases according to the less pronounced pH increase in the polymer mixtures. For the PAA/PEG and PAAIPA-10/PEG systems a maximum in pH appears at $N_{COOH} = 0.5$, in accordance with the minimum found in the intrinsic viscosity variation (Figure 4a). Concerning the PAAIPA-29/PEG system, we point out that the observed pH increase (0.05–0.02 pH unit) is of the order of the experimental error, which is estimated to be ±0.01 pH unit.

Figure 7b presents the variation of the degree of association, θ, which is the ratio of the concentration of associated carboxylic groups, [COOH···O<], to their total concentration, $[\mathrm{COOH}]_0$,[4,6,8,9] versus N_{COOH}:

$$\theta = \frac{[\mathrm{COOH{\cdots}O}<]}{[\mathrm{COOH}]_0} = \frac{[\mathrm{COOH}]_0 - [\mathrm{COOH}] - [\mathrm{COO^-}]}{[\mathrm{COOH}]_0} \qquad (7)$$

For the calculation of θ we took into account the change of the dissociation constant of the carboxylic groups

$$K_d = [\mathrm{COO^-}][\mathrm{H^+}]/[\mathrm{COOH}] \qquad (8)$$

following the Kern empirical equation[28]

$$pK_d = -\log_{10} K_d = a + b\,pH \tag{9}$$

Taking into account the fact that our experiments have been made under conditions of constant ionic strength, by the use of NaCl, and of the same pH of the pure components, by the use of HCl in the case of the PEG solution, we have also used the equation

$$[COO^-] = [H^+] + [Na^+] - [Cl^-] \tag{10}$$

resulting from the electroneutrality of the solutions. Then we calculated θ

$$\theta = \frac{[COOH]_0 - [COOH] - [H^+] - [Na^+] + [Cl^-]}{[COOH]_0} \tag{11}$$

by combining eqs 7 and 10. The [COOH] was found through pH measurements of the mixtures by using eqs 8 and 9. We observe a gradual decrease of θ as the degree of substitution increases. It is interesting to compare this finding to the viscometric results obtained under the same conditions of pH and ionic strength (empty squares in Figure 6). From the viscosity results it could be concluded that the PAAIPA-10 copolymer interacts more strongly with PEG at $N_{COOH} = 0.5$ than PAA does because of its lower value in $[\eta]_r$. In fact, viscosity measures the hydrodynamic volume and thus the compactness of the complex, which is improved by the hydrophobic nature of IPA units. On the other hand, pH measures the extent of hydrogen bonding between the polyacid and PEG, which obviously decreases by introducing IPA units in the polyacid chain. It is clear that in polyacid–polybase association where hydrogen bonding is combined with hydrophobic interactions the use of both viscometry and potentiometry is needed.

Finally, we have calculated the apparent interpolymer association constant, K_{app}, given by eq 5. The obtained results are shown in Figure 7c. We observe that K_{app} remains constant in a broad composition region, $0.2 < N_{COOH} < 0.8$, indicating that this apparent constant of complexation is independent of the composition mixture and of the degree of association, θ. We also observe that K_{app} is dramatically decreased from the value of 260 L mol^{-1} for the complex formation between PAA and PEG to the much lower value of 105 L mol^{-1} for the PAAIPA-10/PEG complex. Then it decreases more slowly to 75 L mol^{-1} for the PAAIPA-17.5/PEG aggregate to reach the very low value of 20 L mol^{-1} for the PAIPA-29/PEG system, which, as we have seen from viscosity measurements (Figure 6), is an interpolymer association limit for this system.

Conclusions

We have presented a viscometric and potentiometric study of interpolymer association between PEG and acrylic acid copolymers under constant pH and constant ionic strengh conditions. The ionic strength was in all experiments low, $I = 1.0 \times 10^{-3}$ M. We have shown the importance of the nature of inactive groups in the polyacid chain, either charged (COO^- or SO_3^-) or neutral hydrophobic groups ($CONHCH(CH_3)_2$), on the complex stability. When DS in ionic groups in the polyacid chain exceeds 10%, the interpolymer association is prevented. On the other hand, when nonionic and relatively hydrophobic groups are introduced into the polyacid chain, its affinity toward PEG is decreased much less than in the case of ionic groups and association occurs even if DS reached 30%, provided that the pH is still low (pH = 3.00). When the pH is increased to 3.40, corresponding to the introduction of 1% COO^- groups in the copolymer, the sample containing 29% IPA units is no longer associated with PEG.

This large difference in the behavior of the two kinds of acrylic acid copolymers can be explained by the assumption that the inactive charged groups not only interrupt the associating COOH sequences but also increase the rigidity of the polymer chain because of intrachain electrostatic repulsions. As a consequence, the resulting chain does not have the necessary flexibility to find the PEG chain at the proper conditions for interpolymer association. On the contrary, the presence of nonassociating neutral groups in the PAA chain does not considerably influence the flexibility of the chain and strengthens the interpolymer association by hydrophobic interactions, which are counterbalanced only when DS is increased very much and the necessary hydrogen bonding cannot take place.

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