Complexation of Acrylic Acid Copolymers with Polybases: Importance of Cooperative Effects

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ABSTRACT: The formation of polymer complexes stabilized through hydrogen bonds was studied in the case of homopolymer/copolymer couples. We used two homopolymers, poly(ethylene oxide) (PEO) and poly(*N*-vinylpyrrolidone) (PVP), as hydrogen-bond acceptors and several copolymers of acrylic acid (AA) with vinylsulfonic acid (VS) or with 2-acrylamido-2-methylpropanesulfonic acid (AMPS) as hydrogen-bond donors. Under acidic conditions (e.g., pH $\simeq$ 3), the strong-acid groups (VS or AMPS) are dissociated and uncomplexable, while the carboxylic groups (COOH) can be complexed by the polybase (PEO or PVP). Potentiometric and viscometric studies were performed and it was found that the properties and the structure of the complexes formed depend on the experimental parameters: molar content of sulfonated monomers, concentration of polyacid and polybase, molecular weight of polymers, and nature of polybase. There is a dramatic influence of the content of uncomplexable groups on the complexation reaction. In some cases, the presence of even a low content of sulfonate groups in the polyacid chain prevents complex formation: for instance, a polyacid containing more than 10% of sulfonate groups cannot be complexed by PEO. Upon experimental conditions, the structure of the complex ranges from a compact form, implying a low viscosity and occasionally precipitation, to a highly branched gellike form, leading to an important increase in viscosity. The results obtained with the above polybase/copolyacid systems seem to be similar to experimental results concerning the complexation of polybases with partially neutralized poly(acrylic acid), and they are in good agreement with predictions of a theoretical model previously reported.

Introduction

Many biological macromolecules may give aggregates or gels in aqueous solution. This phenomenon is due to the existence of several types of interactions between the polymer chains: electrostatic attractions, hydrogen bonds, hydrophobic interactions, double- or triple-helix formation, etc. Unfortunately, most of these systems are complex and it is difficult to estimate the contribution of each type of interaction to the rheological behavior of their aqueous solutions.

On the other hand, systems containing water-soluble synthetic polymers may offer an attractive simple model in which only one type of interaction is predominant. In fact, several authors attempted to point out the importance of a specific type of interaction on the solution behavior of water-soluble polymers.[1-9] A great number of studies have been devoted to polymer complexes,[10,11] which are mixtures of two polymers dissolved in a common solvent interacting mainly by one type of interaction, for instance, electrostatic attractions between anionic and cationic polyelectrolytes or hydrogen bonding between a polyacid (H-bond donor) and a polybase (H-bond acceptor). Most of these studies concern homopolymer pairs[12-41] and rarely homopolymer/copolymer systems.[41-52] However, in systems containing a copolymer, it is easy to adjust the interactive forces by changing the copolymer composition.

In our previous papers,[53-56] we studied the influence of the copolymer structure on the complexation between a polybase (PEO, PVP, or poly(vinyl methyl ether)) and poly(acrylic acid) (PAA). Poly(acrylic acid) can be partially neutralized by addition of a strong-base solution (NaOH), and thus it can be considered as a copolymer bearing acrylate (COO^-) and undissociated carboxylic groups (COOH). The carboxylic groups can form H bonds with the hydrogen-bonding acceptor groups of the polybase, whereas acrylate groups cannot interact with the polybase and behave as "structure defects" (inactive groups). Our experimental results showed that the complexation reaction and the structure of the complex depend on parameters such as degree of neutralization of PAA, nature of the polybase, and concentration and molecular weight of the polymers. These results were interpreted in terms of a theoretical model,[56] based on three important assumptions: (1) the acrylate groups are randomly distributed in the PAA chain; (2) only acid sequences whose lengths are longer than a critical chain length are complexable; (3) the state and the behavior of complexable acid sequences along a PAA chain are independent of each other. However, this very simple system, PAA/polybase, presents an important drawback. Because of the electrostatic repulsions, the uncomplexable acrylate groups do not necessarily have a random distribution along the PAA chain. Furthermore, their position in the PAA chain is not fixed and can change during the complexation of the polyacid by the polybase.

On the other hand, Wang and Morawetz[51] and Yang et al.[52] published new results relating to the complexation in homopolymer/copolymer systems. They found that the presence of inactive groups in the copolymer chain has a relatively moderate influence on the complex formation. Consequently, the validity of the concepts of critical chain length and of uninterrupted complexed sequences could be questionable.

To obtain further information about the importance of the copolymer structure on the complexation between polyacids and polybases, we give in the present investigation some new results concerning complexation through H bonding between a homopolymer (polybase) and several synthetic copolymers (polyacid). Polyacids were prepared by radical copolymerization of acrylic acid and vinylsulfonic acid or 2-acrylamido-2-methylpropanesulfonic acid. Under appropriate pH conditions, these copolymers have undissociated carboxylic groups (complexable by the polybase) and dissociated sulfonate groups (uncomplexable). The distribution of sulfonate groups in the polymer chain

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Table I
Commercial Homopolymers Used in This Work

sample	ref	sample	ref
PAA-670	54	PEO-750	55
PEO-20	54	PVP-55	54
PEO-100	54	PVP-900	55

depends on the reactivity ratio of each monomer in the copolymerization reaction and remains unchanged during the complexation of the polyacid by the polybase. The above systems were studied by viscometry and potentiometry, and the results were compared with the predictions of our theoretical model[56] and with the experimental results of previous studies related to PAA/polybase couples. Finally, the concept of critical chain length and its impact on the quantitative interpretation of the results are discussed.

Experimental Section

Materials. The origin, method of purification, and molecular weight of the commercially available homopolymers used in this work (Table I) were reported earlier.[54,55] Their weight-average molecular weight ($\bar{M}_w$) is 1000 times the numerical index used for sample designation.

Copolymers of acrylic acid with vinylsulfonic acid or with 2-acrylamido-2-methylpropanesulfonic acid were prepared by radical copolymerization in aqueous solution. Acrylic acid (Fluka, synthetic grade), 2-acrylamido-2-methylpropanesulfonic acid (Merck-Schuchardt, synthetic grade), and vinylsulfonic acid sodium salt (30% in water, Fluka, technical grade) were used as monomers. The other reagents were of synthetic grade. Water was purified by a Milli-Q system (Millipore).

In a typical example, PAAMPS-770-10 was prepared by dissolving 25.92 g (0.36 mol) of acrylic acid, 8.28 g (0.04 mol) of AMPS, and 32 mL of 10 M NaOH (0.32 mol) in the required quantity of water in order to obtain a total volume of 180 mL. In this way, 80% of the acid monomers were neutralized (pH = 4.8 ± 0.2), and the total monomer concentration was 2 mol·L^{-1}. The reaction was conducted at 20 °C in a reactor equipped with a mechanical stirrer, condenser, nitrogen inlet tube, and thermometer. The solution was bubbled with nitrogen for 20 min, and then the initiator couple, 0.332 g (1.46×10^{-3} mol) of ammonium persulfate and 0.553 g (2.91×10^{-3} mol) of sodium metabisulfite each dissolved in 10 mL of water, was added to the reactor. After 3 h of stirring, the polymer was precipitated by addition of the reaction solution to a large excess of methanol. The precipitated solid was kept in methanol for 24 h and then dried under vacuum at 50 °C to a constant weight. The copolymer was further purified and transformed into the acid form by ultrafiltration in a Pellicon-Cassette system (Millipore) using IRIS-3026 (Rhône-Poulenc) ultrafiltration membranes of 10 000 nominal molecular weight cutoff. All copolymers were ultrafiltered first with a large excess of aqueous HCl solution (pH $\simeq$ 1.6) and then with pure water (until no detection of Cl$^-$) and finally freeze-dried.

More details about the polymerization reaction, copolymer composition, and molecular weight are given in Table II. PAVS and PAAMPS designate the copolymers of acrylic acid respectively with vinylsulfonic acid and with 2-acrylamido-2-methylpropanesulfonic acid. The first numerical index following the sample designation corresponds to the weight-average molecular weight (×1000) of the copolymer and the second to the molar percentage of sulfonated monomer units in the copolymer. For example, the molecular weight $\bar{M}_w$ of PAAMPS-770-10 is 770 000 and it contains 10 mol % of AMPS.

Table II
Copolymers Prepared by Radical Copolymerization in Aqueous Solution[a]

sample	sulfonated monomer in feed, mol %	sulfonated monomer in copolymer,[b] mol %	$\bar{M}_w \times 10^{-3}$ [c]	$\bar{M}_w/\bar{M}_n$ [c]
PAVS-1000-4[d]	25	3.8	>1000	
PAVS-70-3.5[d]	10	3.4	70	1.9
PAVS-160-9[d]	25	8.9	160	3.4
PAVS-230-11	50	11.2	230	4
PAVS-480-5	25	4.8	480	6
PAVS-660-2	10	2.1	660	9
PAAMPS-940-5	5	5.1	940	30
PAAMPS-770-10	10	10.0	770	24
PAAMPS-660-16	15	16.0	660	5.6
PAAMPS-105-20	20	19.6	105	2.0
PAAMPS-115-25	25	25.6	115	1.9
PAAMPS-1000-3	2.5	2.8	>1000	

[a] Total monomer concentration: 2 mol·L^{-1}. pH = 4.8 ± 0.2. Initiators: $[(NH_4)_2S_2O_8] = 1.46 \times 10^{-3}$ mol·L^{-1}, $[Na_2S_2O_5] = 2.91 \times 10^{-3}$ mol·L^{-1}. Temperature: 20 °C. [b] Derived from elemental analysis data. [c] Size-exclusion chromatography data. PAVS-1000-4 and PAAMPS-1000-3 were partially excluded by the column set. [d] For these polymerizations an $(NH_4)_2S_2O_8$/tetramethylethylenediamine (TMEDA) couple was used as initiator. The concentration of monomers was 1 mol·L^{-1}, and the temperature was 5 °C. For PAVS-1000-4: $[(NH_4)_2S_2O_8] = 2.91 \times 10^{-3}$ mol·L^{-1}, [TMEDA] = 5.83×10^{-3} mol·L^{-1}, solvent = H_2O. For PAVS-70-3.5: $[(NH_4)_2S_2O_8] = 8.73 \times 10^{-3}$ mol·L^{-1}, [TMEDA] = 1.75×10^{-2} mol·L^{-1}, solvent = 80% H_2O/20% EtOH. For PAVS-160-9: $[(NH_4)_2S_2O_8] = 8.73 \times 10^{-3}$ mol·L^{-1}, [TMEDA] = 1.75×10^{-2} mol·L^{-1}, solvent = 90% H_2O/10% EtOH.

Apparatus. A size-exclusion chromatography apparatus (Waters 201) equipped with a differential refractometer (Waters R401) and a continuous viscometer detector[57] was used for polymer molecular weight determination. The column set consisted of four Shodex OHpak columns (B-803/S, B-804/S, B-805/S, B-806/S). An aqueous solution of 0.5 M $LiNO_3$ and 6×10^{-3} M NaN_3 was used as elution solvent. Pullulan standards (Shodex) were used for universal calibration. The columns and detectors were thermostatically controlled at 40 ± 0.1 °C. Two of the samples (PAVS-1000-4 and PAAMPS-1000-3) were partially excluded by the column set; their weight-average molecular weight is greater than 10^6.

Elemental analyses for the copolymers were conducted by the Central Service of Microanalyses of CNRS (France). The molar content of sulfonated monomer in the copolymers was calculated by the ratio of sulfur to carbon (S/C).

For copolymers with relatively high content of AMPS monomer (>15%), ^{13}C NMR spectra were accumulated at 62.9 MHz using a Bruker WP 250 spectrometer with a flip angle of about 15° and a 1.5-s relaxation delay. A solution, 10% by weight, of each sample in a 25/75 D_2O/H_2O mixture was used. The AMPS content was estimated by comparing C=O peaks corresponding to acrylic and 2-acrylamido-2-methylpropanesulfonic acids.

Potentiometric measurements were carried out with an Orion EA 920 pH meter and a Ross combination pH electrode (Orion, ref 81-03 SC). The neutralization curve for the copolymer PAAMPS-115-25 was obtained with an automatic titration apparatus (TAT-5, Tacussel) using a glass–calomel unitubular electrode (TCBC 11/HS, Tacussel). Measurements were performed under slow stirring and a N_2 atmosphere in a thermostatically controlled cell at 30 ± 0.1 °C.

Both an Ubbelohde type viscometer and a Low-Shear 30 apparatus (Contraves) were used to obtain viscosity values in the Newtonian plateau. Temperature was controlled to 30 ± 0.1 °C.

Preparation of the Mixtures. First, stock solutions of polyacid and polybase were prepared (0.06 or 0.6 mol·L^{-1} in monomer units). Partial neutralization of polyacids was achieved by preliminary addition of the required quantity of a NaOH solution (Titrisol, Merck). Mixtures of the desired composition were prepared by mixing the appropriate stock solutions and, if necessary, further dilution with water. All measurements were made 1 day after the preparation of the samples; thus complexation equilibrium was completely established.[19,55]

For each series of experiments, the polyacid concentration was kept constant (0.01, 0.02, 0.1 mol·L^{-1} in monomer units), and the polybase concentration was adjusted to obtain the desired concentration ratio, τ = [polybase]/[polyacid].

Results and Discussion

Copolymers. Choice of the Copolymer. The copolymer must bear at the same time active and inactive groups.

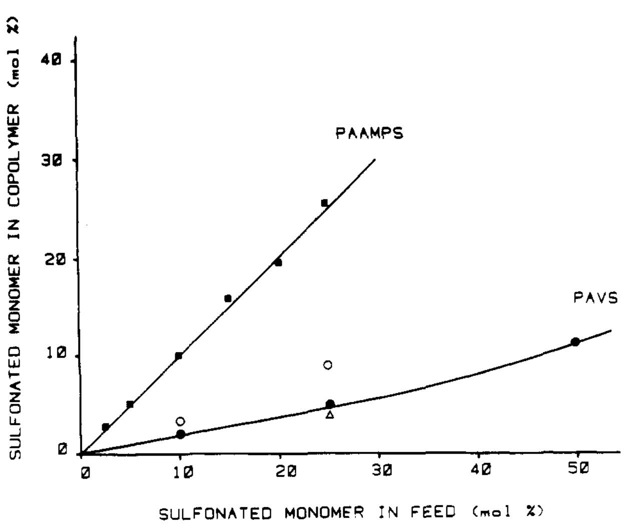


Figure 1. Sulfonated monomer content in the copolymer versus monomer composition in the feed. (■) PAAMPS copolymers. (●, ○, △) PAVS copolymers: for (○) a $H_2O/EtOH$ mixture was used as solvent; for (○) and (△) the couple $(NH_4)_2S_2O_8$/TMEDA was used as initiator. More details are given in Table II.

Inactive units must be inert toward their own and the homopolymer chains. Moreover, these groups must not be hydrophobic since this feature may alter the physicochemical characteristics of the copolymer and contribute to a complementary stabilization of the complex. Finally, copolymers of various compositions and fixed polymerization degree are preferred, but in most cases, both these requirements are difficult to satisfy. Further problems related to the copolymerization reaction can also arise.

Copolymerization. Two series of acrylic acid copolymers were prepared. In the first, vinylsulfonic acid and, in the second, 2-acrylamido-2-methylpropanesulfonic acid were used as strong-acid comonomers. The vinylsulfonate group has a volume not very different from that of the acrylate group, contrary to 2-acrylamido-2-methylpropanesulfonate, which is a very bulky group. Unfortunately, because of the great difference in the reactivity ratio, $r_1 = 5.8$, $r_2 \simeq 0$,[58] it was difficult to copolymerize vinylsulfonic and acrylic acid monomers. The obtained PAVS copolymers bear only a few vinylsulfonic units, and their distribution is not random.

In Figure 1, the copolymer composition is plotted against the feed composition. The deviation from ideality is very important and seems to be dependent on the solvent composition. The deviation from ideal copolymerization decreases if an 80/20 (or 90/10) water/ethanol mixture is used as solvent. Our results are comparable to those reported by Breslow and Kutner.[58]

To minimize the drift in the copolymer composition, we stopped the copolymerizations at conversions between 30 and 50%. Moreover, the PAVS copolymers used in this study have only a low content of sulfonated units (<11%); thus in a rough approximation we will assume that their distribution is not too far from the random one.

The second sulfonated monomer, AMPS, is much more bulky than acrylic acid but copolymerizes very easily. The copolymerizations were stopped at conversions between 50 and 70%, and Figure 1 shows the copolymer composition as a function of the AMPS in the feed. It is obvious that this copolymerization can be assumed to be ideal. According to our findings, the reactivity ratios r_1 and r_2 (Figure 1) seem to be very close to 1. No literature data were found for comparison. Consequently, the PAAMPS copolymers are considered as perfectly random.

Characterization. The sulfonated monomer content in the copolymer or copolymerization degree

$$\kappa = \frac{[SO_3H]}{[SO_3H] + [COOH]} \times 100$$

was estimated by elemental analysis using the ratio of sulfur to carbon. The relative error in determination of κ does not exceed 7%. The κ values are summarized in Table II.

To check the results of elemental analysis, we estimated the sulfonated monomer content by ^{13}C NMR spectroscopy. This can be easily achieved for PAAMPS copolymers with a relatively high content in AMPS (>15%) by comparison of the carbonyl peaks corresponding to AA (179.3 ppm) and to AMPS (176.1 ppm). The following values of κ were obtained: $\kappa = 15.9\%$ for PAAMPS-660-16; $\kappa = 19.4\%$ for PAAMPS-105-20; $\kappa = 26.8\%$ for PAAMPS-115-25. There is a very good agreement with the values of κ obtained by elemental analysis.

Average molecular weights and polydispersity of the copolymers were obtained by size-exclusion chromatography. The results, reported in Table II, show that the molecular weight and polydispersity of the copolymers vary regularly with the copolymerization degree. For PAAMPS copolymers, the weight-average molecular weight and polydispersity decrease when κ increases. The variation of $\bar{M}$ with κ can cause some drawbacks in part of our work. They will be discussed in the following sections.

Partial Neutralization of the Copolymers. The above-described copolymers are used either in their acid form or in their partially neutralized form. In aqueous solution, two dissociation equilibria occur:

$$SO_3H \overset{K_{d,1}}{\rightleftharpoons} SO_3^- + H^+ \quad (1)$$

and

$$COOH \overset{K_{d,2}}{\rightleftharpoons} COO^- + H^+ \quad (2)$$

with $K_{d,1} \gg K_{d,2}$.

In pure water, the dissociation of sulfonic groups will be complete, especially for copolymers with a low content of sulfonated monomers (for instance, $\kappa < 15\%$). Such dissociated groups will be uncomplexable and they have a fixed position in the macromolecular chain. The presence of sulfonic groups increases the concentration of free H^+ in the solution and the electrical potential around the polymer chain.[59] Under these conditions, equilibrium 2 is displaced toward the acid form (COOH). The degree of self-dissociation of COOH groups

$$\delta = [COO^-]_{self\text{-}dissoc}/[polyacid]$$

is very close to zero and thus $\kappa \gg \delta$. Consequently, there is a negligible amount of acrylates in the copolymer chain, and therefore only the sulfonate units having a fixed position will influence the complexation reaction.

Progressive neutralization of our copolymers by a strong base, for instance, NaOH, leads first to neutralization of the sulfonic groups (SO_3H) and then the acrylic groups (COOH). This is due to the difference in the acid strength of the two monomers. Acrylic acid is a weak acid with a relatively high value of $pK_a = 4.25$,[60] while sulfonic monomers are very strong acids. The difference in their behavior during neutralization is clearly illustrated by the neutralization curves of PVS[61] and PAA.[59] Such a situation is also observed in the neutralization curve of our copolymers. See, for instance, the neutralization curve of the copolymer PAAMPS-115-25 in Figure 2. Two well-defined

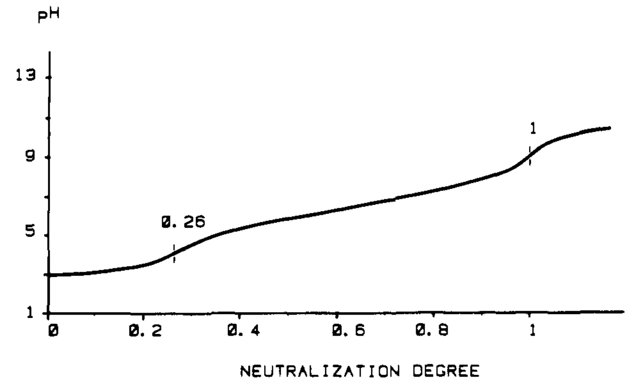


Figure 2. Neutralization curve for PAAMPS-115-25.

and well-separated end points were obtained; the first corresponds to the total neutralization of the sulfonic groups and the second to the acrylic groups. The degree of copolymerization calculated from this curve is $\kappa = 26.3\%$, in very good agreement with results of elemental analysis and ^{13}C NMR.

In the following, we assume that if the degree of neutralization is equal to the copolymerization degree ($\alpha = \kappa$) only the sulfonic units will be neutralized ($SO_3^-Na^+$). Similarly to the unneutralized copolymers ($\alpha = 0$), only a very small fraction of COOH self-dissociates: $\delta \ll \kappa$, reaction 2. As in the previous case (when $\alpha = 0$), the complexation reaction will be influenced only by the presence of sulfonated groups.

On the other hand, the self-dissociation of the acrylic groups, even in a low extent, allows the potentiometric study of the complexation and the estimation of the complexation degree (see potentiometry section).

Viscometry. Dilute Solutions. Figure 3 shows plots of the specific viscosity, η_{sp}, of the polyacid/polybase mixtures against the concentration ratio τ = [PB]/[PA]; [PB] and [PA] are the concentrations in unit mol·L^{-1} of the polybase and the polyacid, respectively. The polyacid concentration is kept constant, [PA] = 0.01 unit mol·L^{-1}, and consequently τ is proportional to the polybase concentration. In the same figure are plotted the viscosity curves for each of the two polybases alone (PEO and PVP) at the same concentrations as used in the mixtures.

When $\tau < 1$, addition of PEO or PVP in the solution of PAVS-70-3.5 results in a decrease in viscosity. Further addition of polybase, $\tau > 1$, results in a steady increase in η_{sp}. This behavior is typical of systems forming polymer complexes.[13,20] The decrease in viscosity for $\tau < 1$ was always ascribed to the compact structure of the complex: the total hydrodynamic volume of complexed chains is smaller than the hydrodynamic volume of the free chains. The increase in viscosity obtained for higher concentrations in polybase ($\tau > 1$) was ascribed to the presence of free polybase chains.[13,20] The slope of the viscosity curve, especially for $\tau > 2$, is very similar to the viscosity increase observed in pure polybase solution (Figure 3).

The difference in the behavior of the two polybases is striking. The addition of PVP in the polyacid solution results in a more pronounced viscosity decrease than the addition of PEO. Undoubtedly, this difference is due to the higher proton-accepting power of PVP. In fact, it has been well proved that PVP forms more stable complexes with polyacids than PEO.[19,23,26,54,55] By increasing the copolypolymerization degree of the polyacid from 3.5% to 9% (PAVS-160-9), one can practically prevent its complexation with PEO; no decrease in viscosity is observed. On the other hand, addition of PVP leads to a decrease in viscosity almost as important as in the case of the PAVS-70-3.5/PVP couple. These results are very similar to those obtained when a partially neutralized poly(acrylic acid) is used as polyacid. The complexation of PAA with PEO was prevented for neutralization degrees, α, higher than 12%, while PVP was complexed even for α = 20%.[54,55]

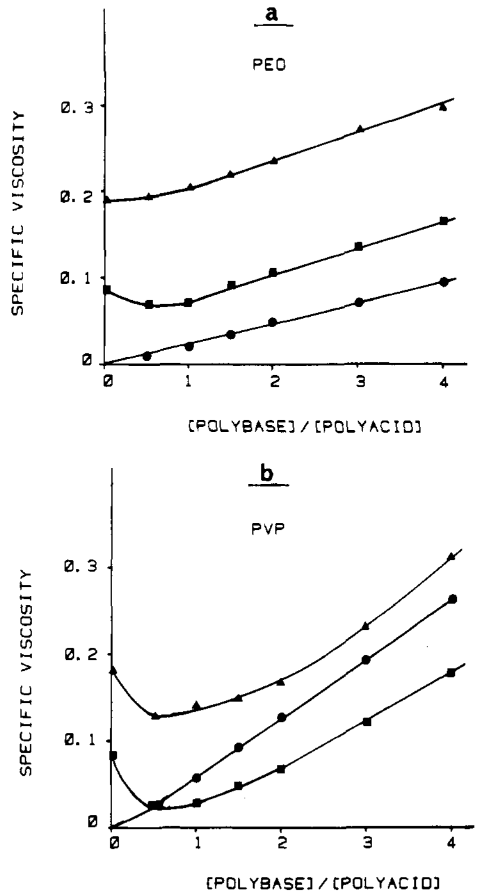


Figure 3. Specific viscosity versus concentration ratio for polybase/polyacid systems in dilute solution. [Polyacid] = 0.01 unit mol·L^{-1} Polybase: (a) PEO-20; (b) PVP-55. (●) Polybase alone; (■) polybase/PAVS-70-3.5; (▲) polybase/PAVS-160-9.

Concentrated Solutions. If the concentration and the molecular weight of the polymers are sufficiently high, the complexation between a polyacid and a polybase may lead to mixtures of very high viscosity.[55] We performed viscosity measurements with PAVS and PAAMPS copolymers of high molecular weight (typically $\bar{M}_w > 660\,000$) at constant polyacid concentration, [PA] = 0.1 unit mol·L^{-1}. These polyacids were partially neutralized in order to have all the sulfonated monomers in the neutralized form ($\alpha = \kappa$). Under these experimental conditions and when the copolymerization degree is low enough (lower than about 3% for PEO and 8% for PVP), phase separation occurs and bulk solid particles appear and precipitate. Hence, no viscosity measurement is possible. For copolymerization degrees higher than these values, no precipitation occurs, and mixtures of very high viscosity are obtained (Figure 4). Unfortunately, our copolymers do not have a constant molecular weight, and thus the curves of Figure 4 are not directly comparable with each other. The values of the viscosity and the shape of the curves obtained are nevertheless in very good agreement with our previous results concerning PAA/polybase systems.[55] Similar results were obtained by using the copolymers in their acid form ($\alpha = 0$).

This important increase in viscosity can be ascribed to the structure of the complex. In fact, because of the

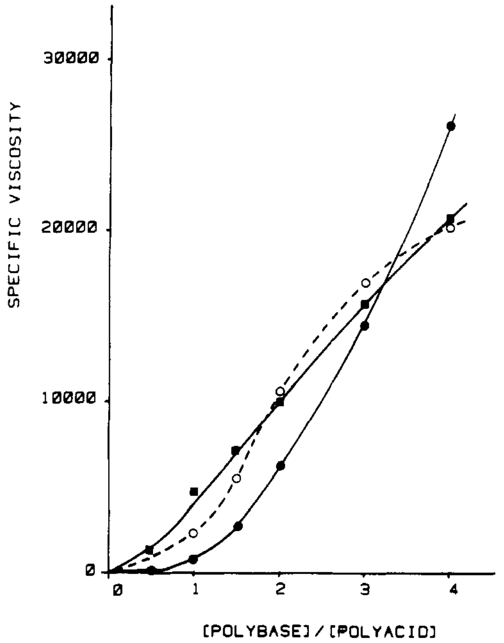


Figure 4. Specific viscosity versus concentration ratio for polybase/polyacid systems in concentrated solution. [Polyacid] = 0.1 unit mol·L^{-1}. (●) PEO-750/PAVS-1000-4; (○) PVP-900/PAAMPS-770-10; (■) PVP-900/PAAMPS-660-16.

presence of the sulfonated groups, the polyacid chain is divided into acrylic acid sequences of various lengths. Furthermore, the formation of hydrogen bonds is governed by a cooperative effect, and thus it is reasonable to assume that only acid sequences longer than a critical chain length, l_c, can be complexed. When the degree of copolymerization, κ, is very low, close to zero, only a few very long acid sequences are present in the copolymer chain. They are much longer than l_c, and so the polyacid chain is almost entirely complexable. The formed complex is very compact, leading to a low viscosity of the mixture and possibly to precipitation. When κ is higher than a limit value, κ_{lim}, characteristic of the polybase/polyacid couple, all the acrylic acid sequences are shorter than l_c and complexation is prevented. Finally, for values of κ between 0 and κ_{lim}, especially when $\kappa \simeq \kappa_{\text{lim}}/2$, the number of complexable acrylic acid sequences ($l > l_c$) per chain may be relatively high. Under these conditions and if the molecular weight and the concentration of both polyacid and polybase are high enough, multichain association occurs. Each polyacid chain is complexed by several chains of polybase and vice versa. The system turns into a network-like structure similar to a physical gel having a very high viscosity.

The comparison between the curves reported in Figure 4 and the data relating to the PAA/polybase systems[53,55] may be easier if we use as a parameter the "gain in viscosity", defined by

$$g = \frac{(\eta_{\text{sp}})_{\text{mixture}}}{(\eta_{\text{sp}})_{\text{polybase}} + (\eta_{\text{sp}})_{\text{polyacid}}}$$

The gain in viscosity for the mixtures PVP-900/PAAMPS-770-10 and PVP-900/PAAMPS-660-16 is of the same order of magnitude as for the mixtures PVP-900/PAA-800 (α = 10 and 15%);[55] the molecular weights of the three polyacids are similar. When PEO-750 is used as polybase and PAVS-1000-4 as polyacid, the gain in viscosity is much higher than for the PEO-750/PAA-800 couple (α = 4%).[53] This difference is especially due to the very high molecular weight of PAVS-1000-4 ($\bar{M}_w > 10^6$; see Table II).

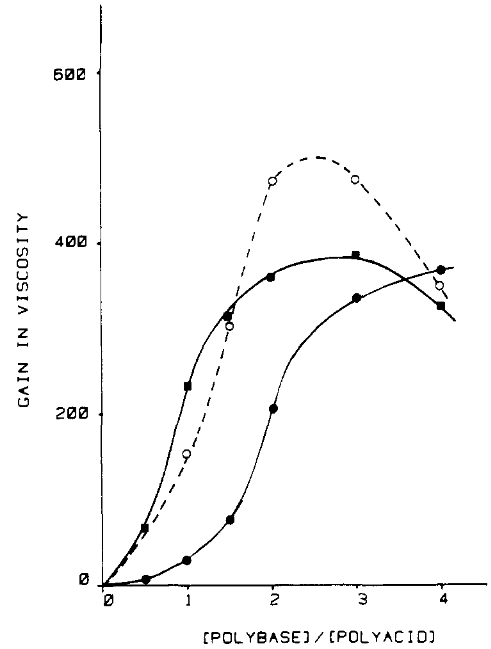


Figure 5. Gain in viscosity versus concentration ratio. Conditions and symbols as in Figure 4.

In summary, the viscometry results obtained with copolyacid/polybase systems in both dilute and concentrated solutions are quite comparable to those relating to polybase/partially neutralized PAA couples.

Potentiometry. This method is widely used for the study of polymer complexes stabilized through hydrogen bonds.[13,20,21,30,37,44-48,54,62] When a polybase (proton acceptor) is added to a polyacid solution (proton donor), the following complexation equilibrium takes place:

$$\text{COOH} + \text{O} \overset{K_c}{\rightleftharpoons} \text{COOH}\cdots\text{O} \qquad (3)$$

where K_c is the apparent constant of complexation between a COOH and a proton-accepting group. At the same time, the dissociation equilibrium of the polyacid occurs; see eq 2. Because of the complexation (eq 3), the concentration of free COOH decreases, and consequently, the concentration of H$^+$ also decreases (eq 2) and the pH of the solution increases. The variations of pH are readily measurable if PAA is used as polyacid.[53,54] Unfortunately, in the case of our copolymers, it is difficult to follow the complexation potentiometrically if the degree of neutralization is lower than the sulfonated monomer content. In fact, the shift in the H$^+$ concentration due to the complexation is negligible versus the actual H$^+$ concentration due to the dissociation of the strong-acid groups (SO$_3$H). However, this problem disappears when the degree of neutralization is equal to or higher than the sulfonated monomer content ($\alpha \geq \kappa$). In such a case, only equilibria 2 and 3 have to be taken into account.

Thus in this study potentiometric measurements were performed by using partially neutralized PAAMPS and PAVS copolymers in order to have $\alpha = \kappa$. The polyacid concentration was kept constant, [PA] = 0.02 unit mol·L^{-1}, and the polybase concentration varied in order to obtain concentration ratios, τ = [PB]/[PA], between 0 and 2. Measurements of pH as a function of τ were performed for several polybase/polyacid couples. Some typical curves are plotted in Figures 6 and 7.

Figure 6 shows plots of the pH against the concentration ratio for three PEO/polyacid couples. As expected, the increase in pH is important for the copolymer with a low content in sulfonated monomer (PAVS-660-2, $\alpha = \kappa =$

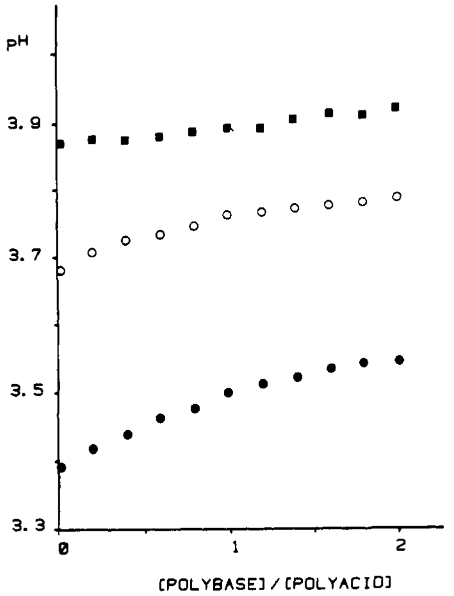


Figure 6. Change in pH of a polyacid solution upon complexation by PEO-100. Polyacids: (●) PAVS-660-2; (○) PAVS-70-3.5; (■) PAAMPS-940-5. Polyacid concentration = 0.02 unit mol·L^{-1}.

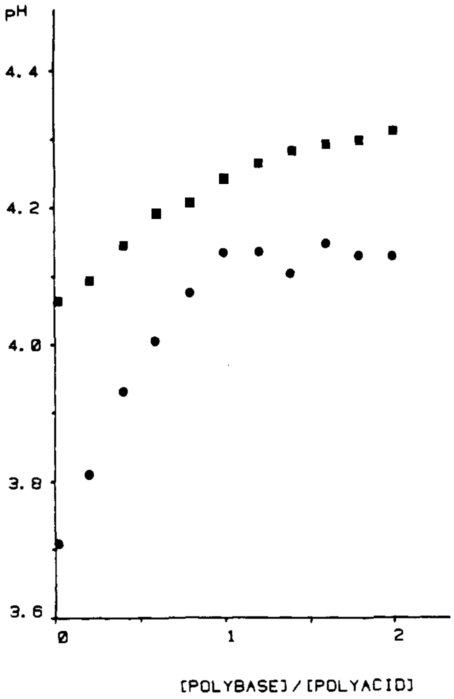


Figure 7. Change in pH of a polyacid solution upon complexation by PVP-55. Polyacids: (●) PAVS-480-5; (■) PAAMPS-770-10. Polyacid concentration = 0.02 unit mol·L^{-1}.

2.1%) and very smooth for the copolymer with the highest content in sulfonated groups (PAAMPS-940-5, $\alpha = \kappa =$ 5.1%). It must be noted that no variation in pH occurs for systems containing a polyacid with a copolymerization degree of 9 or 10% (PAVS-160-9 and PAAMPS-770-10). This fact implies that the limit value of the copolymerization degree ($\kappa_{\rm lim}$), beyond which no complexation occurs, is smaller than 9%, i.e., lower than the limit value of the neutralization degree ($\alpha_{\rm lim} \simeq 12\%$) obtained when partially neutralized poly(acrylic acid) had been used.[54]

Similar results are obtained if PVP is used as polybase (Figure 7). With this polybase, the increase in pH as a function of τ is sharper than in the case of PEO. Even polyacids containing more than 10% of sulfonated groups can be complexed by PVP. This difference is due to the strong proton-accepting character of PVP and it is in good agreement with our previous results.[54]

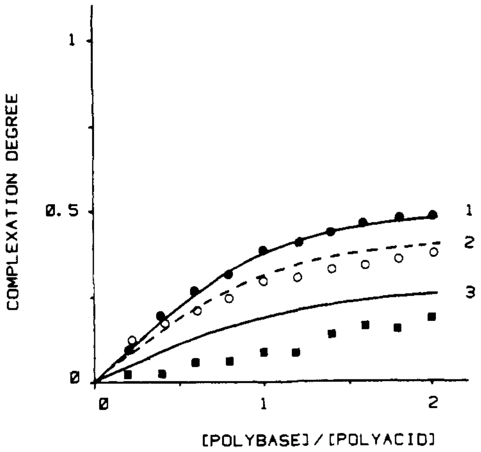


Figure 8. Variation of the complexation degree with the concentration ratio for the system PEO/polyacid. The points were derived from the pH results reported in Figure 6. Theoretical curves were obtained with $K_s = 5 \times 10^4$ mol^{-1}·L, $l_c = 40$, degree of polymerization = 1000, and polyacid concentration = 0.02 unit mol·L^{-1}. Curve 1 and (●) for PAVS-660-2; curve 2 and (○) for PAVS-70-3.5; curve 3 and (■) for PAAMPS-940-5.

From potentiometry results, one can readily calculate the degree of complexation θ, which is the ratio of the concentration of complexed carboxylic groups to the total concentration of the polyacid:[13,21,30,53,54,62]

$$\theta = \frac{[\mathrm{COOH}\cdots\mathrm{O}]}{[\mathrm{PA}]} = \frac{[\mathrm{complex}]}{[\mathrm{PA}]} \tag{4}$$

To calculate θ, we assume that the dissociation constant of the carboxylic groups

$$K_{\rm d} = [\mathrm{COO^-}][\mathrm{H^+}]/[\mathrm{COOH}] \tag{5}$$

(written $K_{\rm d,2}$ in eq 2) remains unchanged when the polybase is added. This implies that, during the complexation, the constant $K_{\rm d}$, which is an apparent dissociation constant of a polyacid, is not much influenced by small variations in the pH. Furthermore, it is supposed that the local dielectric constant around a free COOH does not change; i.e., there is not any effect due to the complexation of the neighboring COOH groups.

The relation for calculation of θ is slightly different from that used for the partially neutralized PAA[54] (see Appendix):

$$\theta = (1 - \alpha - \delta') - \left\{(1 - \alpha - \delta)\frac{(\alpha - \kappa + \delta')\delta'}{(\alpha - \kappa + \delta)\delta}\right\} \tag{6}$$

with α the neutralization degree, κ the sulfonated monomer content, and δ and δ' the fraction of acrylate groups due to the self-ionization of the COOH respectively in the absence and in the presence of polybase.

From the experimental results of Figures 6 and 7 and by using eq 6, the degree of complexation is calculated and plotted against the concentration ratio (points in Figures 8 and 9). The curves given in the same figures were obtained according to a theoretical model and will be discussed in the next section.

Comparison with a Theoretical Model. In a previous paper, we had attempted to predict theoretically the behavior of systems interacting through H bonds. We proposed a theoretical model especially adapted for macromolecular association through weak and reversible interactions. Our model predicts the variation of the

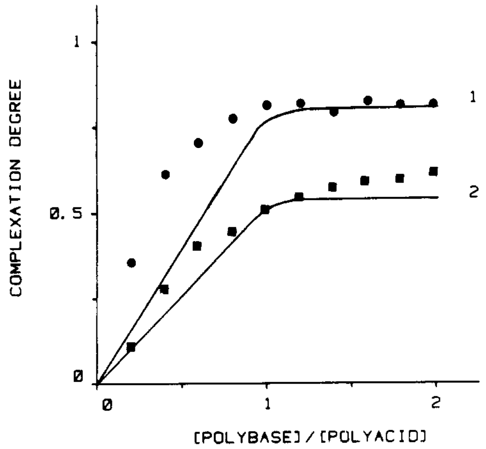


Figure 9. Variation of the complexation degree with the concentration ratio for the system PVP/polyacid. The points were derived from the pH results reported in Figure 7. Theoretical curves were obtained with $K_S = 10^6$ mol^{-1}·L, $l_c = 13$, degree of polymerization = 1000, and polyacid concentration = 0.02 unit mol·L^{-1}. Curve 1 and (●) for PAVS-480-5; curve 2 and (■) for PAAMPS-770-10.

degree of complexation as a function of experimental parameters such as the concentration and molecular weight of the polymers and the degree of neutralization or copolymerization of the polyacid. This model also gives a qualitative picture of the viscometric behavior of our systems.[56]

Taking into account the complexity of such systems, the theoretical approach must be based on some simplifying assumptions. In our case, the following assumptions were made.

(1) There is a random distribution of uncomplexable groups (acrylates or sulfonates) on the polyacid chain. This implies that carboxylic sequences are also randomly distributed on the polyacid chain.

(2) The complexation between a polyacid and a polybase is characterized by the cooperative formation of H bonds.[10–14,16,19–21] In other words, oligomers of the polybase (polyacid) cannot be complexed with a long chain of polyacid (polybase) if the oligomer is not long enough (i.e., if their polymerization degree is smaller than a critical chain length, l_c). For a partially neutralized PAA only carboxylic sequences with a length equal to or larger than l_c are considered as complexable. Therefore, the polyacid chain can be illustrated by an alternation of complexable carboxylic sequences of length $\geq l_c$ and of uncomplexable sequences containing sulfonated (and/or acrylate) groups and short acid sequences of length $< l_c$ (see Scheme 2 in ref 56).

(3) The behavior of a complexable sequence is independent of the state of complexation of other complexable sequences of the same polymer chain. For two complexable sequences along a given chain of polyacid, the actual complexation of the first sequence does not influence the complexation of the second one, even in the case where the two complexable sequences are close to each other.

(4) The system can be viewed as a complexation equilibrium between complexable sequences of polyacid and polybase:

$$\begin{Bmatrix}\text{free complexable}\\ \text{sequences of PA}\end{Bmatrix} + \begin{Bmatrix}\text{free complexable}\\ \text{sequences of PB}\end{Bmatrix} \underset{}{\overset{K_s}{\rightleftharpoons}} \begin{Bmatrix}\text{complexed}\\ \text{sequences}\end{Bmatrix} \qquad (7)$$

with K_s the complexation constant between sequences. To simplify numerical calculations, we take the length of all complexable sequences as equal to an average length, L, given by

$$L = \frac{\text{no. of COOH in acid sequences of length} \geq l_c}{\text{no. of acid sequences of length} \geq l_c} \qquad (8)$$

On the basis of the above-mentioned assumptions, the degree of complexation θ can be expressed as a function of K_s, l_c, N, C_A, p, and τ,[56] where N is the polymerization degree of the polyacid, C_A its concentration, and p the ratio of inactive groups:

$$p = ([SO_3^-] + [COO^-])/[\text{polyacid}] \qquad (9)$$

If $\alpha = \kappa$, the presence of COO$^-$ is due to the self-ionization of carboxylic groups (see Appendix).

Theoretical values of θ can be plotted against concentration ratio, τ, for known experimental parameters N, C_A, and p. The values of K_s and l_c are chosen so as to obtain the best fit between experimental points and theoretical curves (see Figure 1 in ref 56). K_s and l_c are characteristic and unique for each polyacid/polybase couple. Since the nature of complexable sequences (acrylic acid) is the same in the PAVS and PAAMPS copolymers and in the partially neutralized PAA, we will use the values of K_s and l_c used for the partially neutralized PAA/polybase systems[56] (Table III).

Table III
K_S and l_c Values for Fitting θ as a Function of τ[a]

polybase	K_S/(mol^{-1}·L)	l_c
PEO	5×10^4	40
PVP	10^6	13

[a] Reference 56.

Figures 8 and 9 show theoretical curves of θ as a function of τ corresponding to experimental results (points) plotted in the same figures. The values of p used to plot each theoretical curve correspond to the known experimental value of p obtained at $\tau = 1$. Generally, there is a good agreement between the theoretical curves and the points derived from experimental results. Still a disagreement is observed in two cases. The first is the system PEO/PAAMPS-940-5; the experimental points (lower set of points in Figure 8) are situated under the theoretical curve. This discrepancy must be correlated with the difference in the limit values $\kappa_{\lim}$ and $\alpha_{\lim}$ (as we have seen, $\kappa_{\lim} < \alpha_{\lim}$). The second is the system PVP/PAVS-480-5; for values of $\tau < 1$, the experimental points are located above the theoretical curve. This phenomenon may be attributed to the strong proton-accepting power of PVP, which results, under suitable conditions ($\kappa < 10\%$ and $\tau < 1$), in a local stoichiometry between acid and base groups higher than 1:1.[54]

A more general comparison between experimental results obtained with copolymers (PAVS, PAAMPS) or with partially neutralized poly(acrylic acid) and predictions of the theoretical model is given in Figure 10. In this figure, the negative logarithm of the complexation degree ($-\ln \theta$) is plotted against the ratio of inactive groups, p, for a fixed concentration ratio (τ = [PA]/[PB] = 1). The points correspond to the experimental results of this study (for PAVS and PAAMPS) and of a previous study[63] (for PAA). The curves are predicted by our theoretical model. A very good agreement between experiment and theory is observed, giving evidence for the validity of our assumptions. Furthermore, it is obvious that the polybase/acidic copolymer systems behave similarly to the polybase/partially neutralized PAA systems.

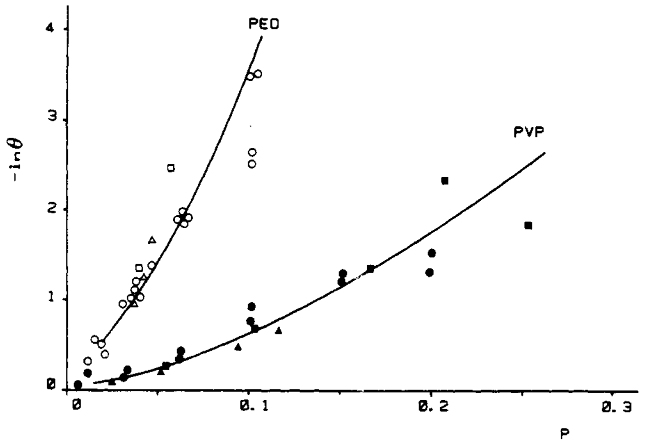


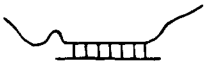
Figure 10. Variation of $-\ln\theta$ with the ratio of inactive groups $p = ([SO_3^-] + [COO^-])/[\text{polyacid}]$. The points were derived from pH measurements. Open symbols were obtained with PEO as polybase and full symbols with PVP. The polyacids used were (●, ○) partially neutralized PAA, (■, □) PAAMPS copolymers, and (▲, △) PAVS copolymers. [Polyacid] = [polybase] = 0.02 unit mol·L^{-1}. Theoretical curves were obtained with the values of K_S and l_c given in Table III and for a polymerization degree = 1000.

The general agreement between experimental results obtained with the two kinds of systems (copolymers or PAA) proves that the random distribution of inactive groups along the polyacid chain is an assumption that can be used for the three kinds of polyacids (PAA, PAVS, and PAAMPS). The fact that the acrylate groups do not have a fixed position on the PAA chain does not seem to alter greatly the behavior of its complexes. The small differences observed when PEO is used as polybase ($\kappa_{\text{lim}} < \alpha_{\text{lim}}$; see also Figure 8) are probably due to the weak-proton-accepting character of PEO. This implies that even a minor change in the chemical nature of the polyacid (VS or AMPS groups instead of acrylates) may influence the complexation reaction. On the other hand, with PVP (a very strong proton acceptor) such differences are unimportant (see Figure 10).

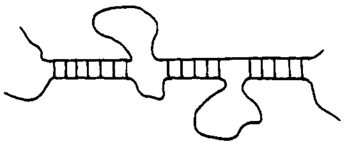
Local Structure of Complexed Sequences. The most important assumption of our model is the existence of a critical chain length. In fact, this concept was introduced long ago by groups working in the polymer complex field. It was related to the cooperativeness of reactions between polymer chains.[10-13,19-21,24,30,62]

As defined in the previous section, only oligomers with a degree of polymerization equal to or higher than the critical chain length can be complexed with long chains of the complementary polymer. From a thermodynamic point of view, the formation of one noncovalent bond (H bond, electrostatic) between two macromolecular species in solution is quite improbable, while the formation of a large number of such bonds leads to a thermodynamically stable complex.[11]

For this reason, many authors have proposed a zipping mechanism for the complexation between complementary macromolecules and a ladder structure for the resulting complex.[11,12,17,19-21,24,62,64-67] This structure can be represented by the following scheme:



Obviously, if the two complementary chains are very long, such an uninterrupted ladder structure is rather improbable. Moreover, experimental results showed that even in the case of homopolymer couples, the complexation is not perfect—a fraction of the interactive monomers is not involved in the complex. The structure proposed for such complexes is shown in the following scheme:[17,66,67]



The formation of this structure is governed by steric and kinetic factors.[45,66] As far as we know, among the experimental methods used until now, there is none that can give a direct proof of the existence of such uninterrupted sequences.

In this study, we primarily used the critical chain length concept for the qualitative interpretation of our experimental results and for the development of our theoretical model. This theoretical model is especially adapted for polymer systems interacting through weak interactions, for instance, H bonds. Furthermore, it was supposed that there is no neighboring effect. In practice, when two complexable sequences are very close to each other, the actual complexation of the first one must favor the complexation of the second one (a kind of secondary cooperative effect).

Recently, Wang and Morawetz[51] and Yang et al.[52] published results relating to the complexation of homopolymer/copolymer couples, and they questioned the requirement of long sequences of uninterrupted H bonds as a prerequisite for complexation. The copolymers they used complex the homopolymer despite the high number of inactive groups they contain (up to ~40%). Taking into account the very low probability of having long complexable sequences in such copolymers as well as steric factors, they conclude that the concept of complexed sequences of uninterrupted H bonds is unrealistic. Yang et al.[52] studied their complexes mainly in the solid state or in organic solvents, and so comparison with our systems is difficult. On the other hand, the results of Wang and Morawetz[51] were obtained in dilute aqueous solution, and consequently it is interesting to discuss their arguments and conclusions.

Wang and Morawetz studied the complexation of a dansyl-labeled poly(acrylic acid) (PAA*) with copolymers of *N,N*-dimethylacrylamide (DAAm) and acrylamide (AAm). The dansyl content of PAA* was 1.3 mol %. When complexation occurs, the fluorescence emission of the dansyl label increases because the polymer association reduces the exposure of the dansyl groups to water molecules. The increase in fluorescence depends on the extent of complexation. They assumed that under suitable pH conditions (pH = 4), only the strong-proton-accepting groups (DAAm) can be complexed by the polyacid, while the weak-proton-accepting groups (AAm) remain uncomplexable. At pH = 4, they found that even the copolymer containing 34% of AAm groups gives a weak complexation. They note that such a copolymer bears only short complexable sequences. In fact, this conclusion is in rather good agreement with our results. The critical chain length depends on the affinity between the two complementary groups and decreases as the interaction strength increases. *N,N*-Dimethylacrylamide is a disubstituted amide and as a proton acceptor can be compared to *N*-vinylpyrrolidone. Consequently, the critical chain length of PDAAm must be small enough, similar to l_c of PVP (about 13). The probability of finding sequences of 13 DAAm units in the above copolymer is low but not negligible.

A second argument put forward by Wang and Morawetz concerns the complexation between a homopolymer and an alternating copolymer in which one of the comonomers cannot participate in the hydrogen bonding.[44,46] Nevertheless, the formation of such complexes does not call into question the critical chain length concept. The structure of alternating copolymers is very regular and only the distance between active (complexable) groups is higher than in the corresponding homopolymer, resulting in a decrease in the affinity of the copolymer toward the complementary homopolymer. The effective monomer unit of the copolymer can be considered to be constituted by an active and a nonactive group. In these polymer complexes a stoichiometry different from 1:1 was found.[10] Presumably they contain a large number of small loops.

A nice proof of the importance of structure regularity to interpolymer association has been given for pairs of polymers containing electron-accepting and electron-donating groups.[68] These systems present exciplex formation, a short-range and directional interacting force similar to the hydrogen-bonding force. It was clearly shown that polymers containing interactive groups at regular and relatively long distances give a more efficient interchain association than polymers with a higher content of randomly distributed interactive groups. The authors conclude that asociation occurs via a zipping process.[68]

The third argument of Wang and Morawetz is related to the local structure of the complexed chains. They claim that uninterrupted hydrogen bonding between PEO and PAA residues is improbable because of the formation of consecutive 11-membered rings. In fact, this argument must be valid mainly because of the steric constraints occurring upon the pairing of PAA and PEO chains. Possibly inside a complexed sequence there is rather a rapid rearrangement of the hydrogen bonds which allows the instantaneous breaking of some H bonds and leads to the dynamic stabilization of the system. In this case all the COOH groups inside the complexed sequence are involved in the complex but the static representation of such a sequence as an alignment of contiguous H-bonded groups becomes unsuitable. Whatever the actual local structure of the complexed sequence, the picture of the copolymer as an alternating chain of complexable and uncomplexable sequences remains a valid assumption for our model.

To get a rough idea about the possible formation of such uninterrupted H bonds, we used molecular space-filling models (CPK atomic models, Harvard). Sequences of 20 repeating units of PAA and PEO were constructed. The formation of contiguous H bonds seems to be dependent on the tacticity of the PAA sequence. When the PAA sequence is atactic (e.g., 30% isotactic, 50% heterotactic, 20% syndiotactic), uninterrupted hydrogen bonding may occur. Of course, pairing induces more or less important strains in some parts of the complexed sequence. The breaking of one or two H bonds cancels out a great part of the strains and increases the flexibility of the complexed sequence. On the other hand, in the case of a stereoregular PAA sequence, it is impossible to form uninterrupted H bonds. An excess of PEG is needed in order to complex all the acrylic acid units. A stoichiometry (EO:AA) between 3:2 and 2:1 was found. Similar stereoregularity effects were reported by Kim et al. for polymer complexes of poly(methacrylic acid) with PEO.[69]

The last and most interesting argument concerns the derivation of the degree of complexation from potentiometry measurements. We assumed that the local dielectric constant around a free COOH is not influenced by the complexation of the neighboring COOH groups. This assumption must be quite valid if the complex is not very compact. In this case, the complex is well swelled by the solvent, and the microenvironment of COOH will be mainly water molecules. On the other hand, in the case of a compact complex, the local dielectric constant is probably modified; the COOH groups are less exposed to the aqueous environment. Consequently, if the degree of copolymerization (or neutralization) of the polyacid is close to zero and the resulting polymer complex is very compact, an overestimation of the values of θ is plausible. However, in general, we find a good agreement between values of θ estimated from experimental results and theoretical predictions, and this irrespective of the degree of copolymerization (Figures 8–10) or of the degree of neutralization (see Figure 1 in ref 56) of the polyacid. This agreement tends to prove the validity of our assumption. Only in the case of PVP complexes and for values of κ (or α) < 10% were very compact structures obtained (at high concentrations precipitation occurred). This probably leads to a change in the local dielectric constant and to an overestimation of θ. This would be another explanation for the high values of θ obtained with the polyacid/PVP couples at $\alpha < 10\%$ and $\tau < 1$ (see Figure 9 and ref 54).

It is interesting to note that recently a new theoretical approach to the association mechanism between macromolecules was proposed. This approach is based on thermodynamic considerations and assumes that the structure defects decrease the free energy of the association reaction and thus lead to a decrease in the affinity of one polymer for the other.[70]

Conclusion

There is a dramatic influence of the inactive group content, κ, on the complexation reaction between a homopolymer (polybase) and a copolymer (polyacid). In dilute solution and for low values of κ, the complex exhibits a compact structure, leading to a sharp decrease in the viscosity. On the other hand, in concentrated solutions of high molecular weight polymers and if the values of κ are high enough (about 4–5% for PEO and 10–15% for PVP), mixtures of very high viscosity are obtained. There is formation of a network-like structure.

The complexation behavior of these copolymers toward PEO and PVP is very similar to the behavior of partially neutralized poly(acrylic acid) toward the same polybases. There is also good agreement between experimental results and the predictions of a theoretical model based on the concept of critical chain length. This concept seems to be very useful for the description of polymer systems associated through weak interactions.

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Appendix

The dissociation reaction gives

$$K_d = [COO^-][H^+]/[COOH] \qquad (5)$$

Because of the condition $\alpha \geq \kappa$, we have

$$\alpha - \kappa = [COO^-]_{neut}/[PA]$$

Self-ionization of the polyacid implies

$$[COO^-]_{self\text{-}ioniz} = [H^+] = \delta[PA]$$

Taking into account the above relations, we have

$$[\mathrm{COO^-}] = [\mathrm{PA}](\alpha - \kappa + \delta)$$

$$[\mathrm{H^+}] = [\mathrm{PA}]\delta$$

$$[\mathrm{COOH}] = [\mathrm{PA}](1 - \alpha - \delta)$$

and from eq 4

$$[\mathrm{complex}] = [\mathrm{PA}]\theta$$

Before addition of the polybase, substitution in eq 5 gives

$$K_\mathrm{d} = \frac{(\alpha - \kappa + \delta)\delta}{1 - \alpha - \delta}[\mathrm{PA}] \qquad (5')$$

After addition of the polybase, eq 5 becomes

$$K_\mathrm{d}' = \frac{(\alpha - \kappa + \delta')\delta'}{(1 - \alpha - \delta') - \theta}[\mathrm{PA}] \qquad (5'')$$

Because of our assumption that $K_\mathrm{d} = K_\mathrm{d}'$, eqs 5′ and 5″ give

$$\frac{(\alpha - \kappa + \delta)\delta}{1 - \alpha - \delta} = \frac{(\alpha - \kappa + \delta')\delta'}{(1 - \alpha - \delta') - \theta}$$

and finally

$$\theta = (1 - \alpha - \delta') - \left\{(1 - \alpha - \delta)\frac{(\alpha - \kappa + \delta')\delta'}{(\alpha - \kappa + \delta)\delta}\right\} \qquad (6)$$

Supplementary Material Available: Five prints of molecular models depicting the complexed sequence of 20 repeating units (3 pages). Ordering information is given on any current masthead page.

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Registry No. PVP·PAVS, 132492-05-8; PEO·PAVS, 132492-08-1; PVP·PAAMPS, 132492-06-9; PEO·PAAMPS, 132492-07-0; PEO (SRU), 25322-68-3; PVP (homopolymer), 9003-39-8; PAVS (copolymer), 25053-28-5; PAAMPS (copolymer), 40623-75-4.