Macromolecules **2003,** *36,* 1349−1354

Soluble Hydrogen-Bonding Interpolymer Complexes and pH-controlled Thickening Phenomena in Water

M. Sotiropoulou,[†] G. Bokias,[‡] and G. Staikos*,[†]

Department of Chemical Engineering, University of Patras and Institute of Chemical Engineering and High-Temperature Chemical Processes, ICE/HT-FORTH, PO Box 1414, GR-26504 Patras, Greece, and Department of Chemistry, University of Patras, GR-26504 Patras, Greece

Received August 2, 2002; Revised Manuscript Received October 14, 2002

ABSTRACT: The hydrogen-bonding interpolymer association between poly(acrylic acid) (PAA) and the poly(*N*,*N*-dimethylacrylamide) (PDMAM) side chains of a negatively charged graft copolymer was studied in aqueous solutions. The graft copolymers, P(AA-*co*-AMPSA)-*g*-PDMAM, contain 50 wt % PDMAM, while their backbone comprises acrylic acid (AA) and mostly 2-acrylamido-2-methylpropane sulfonic acid (AMPSA) units. The formation, at low pH, of compact and soluble hydrogen-bonding interpolymer complexes between PAA and the side PDMAM chains, is suggested by combining turbidimetry and dilute solution viscosity measurements. Moreover, in semidilute solutions, the pH-controlled association−dissociation of these water-soluble hydrogen-bonding interpolymer complexes results in a spectacular pH-controlled thickening behavior.

Introduction

The formation of hydrogen-bonding interpolymer complexes between proton donor and proton acceptor polymers in aqueous solution has been widely studied during the past four decades.[1−4] The proton donors are usually weak polycarboxylic acids, for instance poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAA), whereas the proton acceptors are nonionic polybases, for instance poly(ethylene oxide), poly(meth)acrylamides, poly(*N*-vinylpyrrolidone), etc. In general, in aqueous solutions of mixtures of such complementary polymers, hydrogen-bonding association between the carboxylic groups of the polyacid and the nonionic polybase occurs, leading to the formation of compact hydrogen-bonding interpolymer complexes. An important limitation of these interpolymer complexes is that they are usually soluble only within a narrow pH window.[5−8] At pH values higher than 4−5, dissociation of these hydrogen-bonding interpolymer complexes occurs, due to the increase of the ionized sites (carboxylate groups) in the polyacid chain. These noncomplexable, negatively charged, groups are structural defects, not allowing to the polyacid chain to adopt the appropriate conformation in order to associate with the nonionic polybase chain.[9−12] On the other hand, at pH values lower than 3−3.5, the hydrogen-bonding interpolymer complex formed precipitates, because the fraction of the carboxylate anions in the polyacid chain, mainly responsible for the solubility of the complex, decreases considerably.[13−18] In summary, when pH is higher than 4−5 hydrogen-bonding interpolymer complexation is not possible, while at pH lower than 3−3.5 associative phase separation takes place.

Extension of the solubility of the hydrogen-bonding interpolymer complexes in the low pH region is of importance, as this would allow original properties to be observed and could enlarge the spectrum of the potential applications of such complexes. In this study we present a synthetic method to achieve this goal by the covalent binding of the nonionic polybase onto a hydrophilic negatively charged backbone (Scheme 1). The backbone consists of acrylic acid (AA) and 2-acrylamido-2-methylpropane sulfonic acid (AMPSA) monomer units, while poly(*N*,*N*-dimethylacrylamide) (PDMAM) is used as the nonionic polybase. The synthesis of these graft copolymers involves three steps: (i) synthesis of the backbone through free-radical copolymerization of AA with AMPSA in water; (ii) synthesis of the end-functionalized PDMAM chains through telomerization, using an NH_2-containing transfer agent; and (iii) grafting of the amine-terminated PDMAM chains to the copolymer backbone through amide formation in water, by means of a water-soluble coupling agent.

PDMAM is a water-soluble polymer with important proton acceptor properties and forming hydrogen-bonding interpolymer complexes with PAA,[19−27] precipitating out from water even at pH values as high as 3.7.[24,26] When the above-described graft copolymers are mixed with PAA in aqueous solution in the low pH region, hydrogen−bonding interpolymer complexes between the PDMAM side chains and PAA are also formed. Nevertheless, the large fraction of the negatively charged AMPSA units introduced into the graft copolymer backbone provides the interpolymer complexes formed with sufficient hydrophilicity, so that in dilute solution their solubility is assured even at low pH,[28] while in semidilute solution a thickening phenomenon is observed by decreasing pH.

Experimental Section

Materials. The two samples of PAA used, PAA90 (Polysciences) and PAA500 (Aldrich) with nominal molecular masses 90 000 and 500 000 Da, respectively, were dissolved in a 0.01 N HCl solution, dialyzed against water through a cellulose membrane with a molecular weight cutoff 12 kDa (Sigma) and finally obtained by freeze-drying.

The monomers acrylic acid (AA) and 2-acrylamido-2-methylpropane sulfonic acid (AMPSA) were purchased from Polysciences, while the monomer *N*,*N*-dimethylacrylamide (DMAM) was a product of Aldrich. Ammonium persulfate (APS, Serva),

---

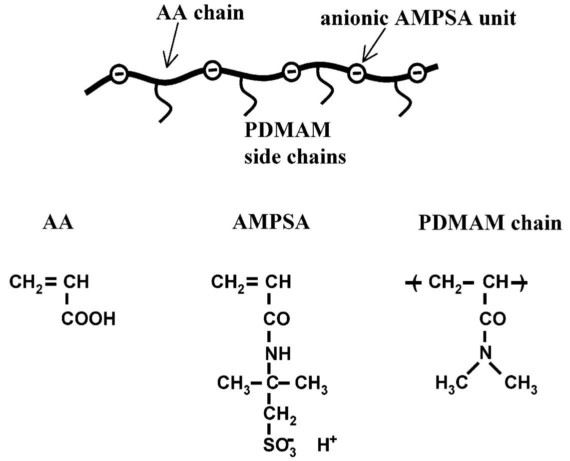
* To whom correspondence should be addressed. E-mail: staikos@chemeng.upatras.gr.

[†] Department of Chemical Engineering.

[‡] Department of Chemistry.

10.1021/ma021256n CCC: $25.00

Scheme 1. A Schematic Depiction of the Graft Copolymers Prepared to Form Hydrogen-Bonding Interpolymer Complexes with PAA Soluble at Low pH[a]



[a] The chemical structure of the monomers comprising the graft copolymers is also presented.

potassium metabisulfite (KBS, Aldrich), 2-aminoethanothiol hydrochloride (AET, Aldrich), and 1-(3-(dimethylamino)propyl)-3-ethyl-carbodiimide hydrochloride (EDC, Aldrich) were used for the synthesis of the graft copolymers.

For the preparation of the buffer solutions NaCl, citric acid (CA), and Na_2HPO_4 from Merck were used.

Water was purified by means of a Seralpur Pro 90C apparatus combined with a USF Elga laboratory unit.

Polymer Synthesis. Amine-terminated PDMAM was synthesized by free radical polymerization of DMAM in water at 30 °C for 6 h using the redox couple APS and AET as initiator and chain transfer agent, respectively. The polymer was purified by dialysis against water through a membrane and freeze-dried.

Two copolymers of AA and AMPSA, P(AA-*co*-AMPSA36) and P(AA-*co*-AMPSA70), containing 36 mol % and 70 mol % AMPSA units respectively, were prepared by free radical copolymerization of the two monomers in water, after partial neutralization (80−85% mol) with NaOH at pH ∼ 6−7, at 30 °C for 6 h using the redox couple APS/KBS. The products obtained were then fully neutralized (pH = 11) with NaOH, purified by dialysis and freeze-dried. Their composition was determined by acid−base titration and by elemental analysis-(Carlo-Erba CHNS-O elemental analyzer EA 1108).

The graft copolymers, P(AA-*co*-AMPSA36)-*g*-PDMAM and P(AA-*co*-AMPSA70)-*g*-PDMAM, were synthesized by a coupling reaction between P(AA-*co*-AMPSA36) or P(AA-*co*-AMPSA70) and amine-terminated PDMAM. The two polymers were dissolved in water at a 1:1 weight ratio. Then, an excess of the coupling agent, EDC, was added and the solution was let under stirring for 6 h at room temperature. Addition of EDC was repeated for a second time. The products were purified with a Pellicon system equipped with a tangential flow filter membrane (Millipore, cut off = 100 kDa) and freeze-dried.

Characterization. The chemical composition of the copolymers has been assessed by elemental analysis and acid−base titration. The molecular weights of the polymers synthesized were determined by light scattering in NaCl 1 M. The characterization results are reported in Table 1.

Size exclusion chromatography (Waters 501 HPLC pump equipped with two Shodex OH-pak columns, B804 and B805) was used to confirm the completion of the grafting reaction.

Turbidimetry. The change in absorbance at 490 nm of aqueous polymer mixtures was monitored as a function of pH at room temperature by means of a Hitachi spectrophotometer model U 2001, equipped with a circulating water bath.

Rheology. Reduced viscosity studies and intrinsic viscosity determination were carried out with an automated viscosity measuring system (Scott-Geräte AVS 300, Germany) equipped with an Ubbelohde-type viscometer, at 25 ± 0.02 °C.

Steady-state shear viscosity measurements of semidilute aqueous polymer mixtures were performed on a Rheometrics SR-200 controlled-stress rheometer, using a cone-plate geometry (diameter = 25 mm, angle = 2°).

Sample Preparation. For the physicochemical studies in dilute solution, pH adjustment was achieved by appropriately mixing 0.05 M CA with 0.05 M Na_2HPO_4 solutions. Both solutions were containing NaCl at a concentration of 0.1 M for the adjustment of the ionic strength.

For the rheological studies in semidilute solution, pH adjustment was achieved by appropriately mixing 0.15 M CA with 0.15 M Na_2HPO_4 solutions.

Results and Discussion

Dilute Solutions. All the physicochemical studies in dilute aqueous solution were performed using the lower molecular weight PAA sample, PAA90.

The turbidity behavior of aqueous PDMAM/PAA90, P(AA-*co*-AMPSA36)-*g*-PDMAM/PAA90 and P(AA-*co*-AMPSA70)-*g*-PDMAM/PAA90 mixtures is presented in Figure 1 as a function of pH. The concentration of PAA90 and PDMAM is 2×10^{-3} g/mL, while the concentration of the two graft products is 4×10^{-3} g/mL. Thus, the quantity of the PDMAM chains (graft or not) is the same in all mixtures.

The PDMAM/PAA90/water system turns strongly cloudy as pH decreases at values lower than 3.75, whereas the solution is clear for higher pH values. This is in good agreement with literature results[24,26] and reflects the strong proton-acceptor ability of PDMAM. When pH is higher than 3.75, the hydrogen-bonding interpolymer complex is soluble and dissociates as pH increases, due to the increased ionization of the weak polyacid PAA90. On the contrary, when pH decreases to values lower than 3.75, associative phase separation is observed as the hydrogen-bonding interpolymer complex formed is now precipitating.

When the homopolymer PDMAM is replaced by the graft copolymers in its aqueous mixtures with PAA90, the observed turbidity is substantially decreased. Indeed, the P(AA-*co*-AMPSA36)-*g*-PDMAM/PAA90/water system is clearly less turbid than the corresponding PDMAM/PAA90/water system in the low pH region, whereas the turbidity is practically negligible in the case of the P(AA-*co*-AMPSA70)-*g*-PDMAM/PAA90/water system, even at pH values as low as 2.5. These results suggest that either interpolymer complexation is less favorable (or not allowed) when the PDMAM chains are covalently bound onto a charged backbone or that the interpolymer complexes formed are more hydrophilic and soluble in water.

We obtain additional convincing evidence, that such hydrogen-bonding interpolymer complexes are formed in these mixtures, from the viscometric study in dilute solution. In Figure 2a we have plotted the dependence of the reduced viscosity of P(AA-*co*-AMPSA70)-*g*-PDMAM/PAA90 mixtures versus the PAA90 weight fraction W_{PAA90} for several pH values. The experiments were performed at constant total polymer concentration, 2.5×10^{-3} g/mL. As, due to the ionic strength of the buffer solutions used, no polyelectrolyte effect is observed in such mixtures, the weight-average reduced viscosity of the two components (dotted lines) is a good approximation of the ideal behavior expected in the absence of any interaction between the two polymer components.[29] Thus, any deviation from linearity reveals interaction between the two polymers and the formation of hydrogen-

Table 1. Characterization of the Polymer Backbones and the Graft Copolymers Used in the Present Study

	chemical characterization							
	feed composition		mol % in AMPSA units		weight % in PDMAM		mean composition	
polymer	mol % in AMPSA units	(weight % in PDMAM)	acid−base titration	elemental analysis	acid−base titration	elemental analysis	mol % in AMPSA units	wt % in PDMAM
P(AA-*co*-AMPSA36)	35		39	33			36	
P(AA-*co*-AMPSA70)	65		70	70			70	
P(AA-*co*-AMPSA36)-*g*-PDMAM		50			50	49		50
P(AA-*co*-AMPSA70)-*g*-PDMAM		50			53	50		52

	physicochemical characterization				
	static light-scattering measurements			intrinsic viscosity measurements	
polymer	refractive index increment	second osmotic virial coefficient mol cm^3/g^2)	$M_w \times 10^5$	intrinsic viscosity	Huggins coefficient
PDMAM	0.155	6.1	0.42	22.6[a]	0.52
P(AA-*co*-AMPSA36)	0.147	1.4	5.0	120[b]	0.49
P(AA-*co*-AMPSA70)	0.132	1.6	2.0	46[b]	0.90
P(AA-*co*-AMPSA36)-*g*-PDMAM	0.151	1.8	9.5	152[b]	0.48
P(AA-*co*-AMPSA70)-*g*-PDMAM	0.143	2.4	4.5	69[b]	0.72

[a] In methanol at 25 °C. [b] In NaCl 1 M at 25 °C.

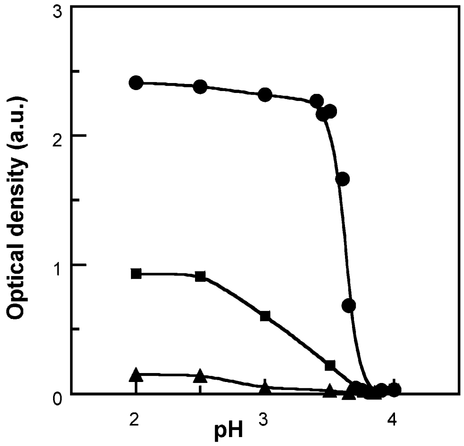


Figure 1. Turbidimetric curves of the mixtures (●) PDMAM/PAA90, (■) P(AA-*co*-AMPSA36)-*g*-PDMAM/PAA90, and (▲) P(AA-*co*-AMPSA70)-*g*-PDMAM/PAA90 in buffer solutions versus pH, at 25 °C. The concentration of PAA90 and PDMAM is 2.0×10^{-3} g cm^{-3}, while the concentration of the graft copolymers is 4.0×10^{-3} g cm^{-3}.

bonding interpolymer complexes. As it is seen in Figure 2a, the reduced viscosity of the mixtures is lower than the corresponding average value for pH = 2.5 or pH = 3.5, while it is close to the corresponding average value for higher pH values (pH = 3.75 or pH = 4).

As the reduced viscosity of PAA90 increases with increasing pH, due to the corresponding increase of the ionization degree of the polyacid, the comparison of the reduced viscosity behavior of the mixtures at various pH values is not straightforward. To obtain a more clear representation of the reduced viscosity behavior of the system we are using the reduced viscosity ratio $r_{\eta_{\rm red}}$ defined as

$$r_{\eta_{\rm red}} = \frac{\eta_{\rm red}}{w_1(\eta_{\rm red})_1 + w_2(\eta_{\rm red})_2} \qquad (1)$$

where $\eta_{\rm red}$ is the reduced viscosity of the mixture, w_1 and w_2 are the weight fractions of the two polymer components in the mixture and $(\eta_{\rm red})_1$ and $(\eta_{\rm red})_2$ are the corresponding reduced viscosities of the two pure components. By using the ratio $r_{\eta_{\rm red}}$, the reduced viscosity of the mixture is compared with the additive value of the reduced viscosities of the two pure polymer components. Thus, any deviation of $r_{\eta\rm red}$ from unity offers a strong evidence of interpolymer association.

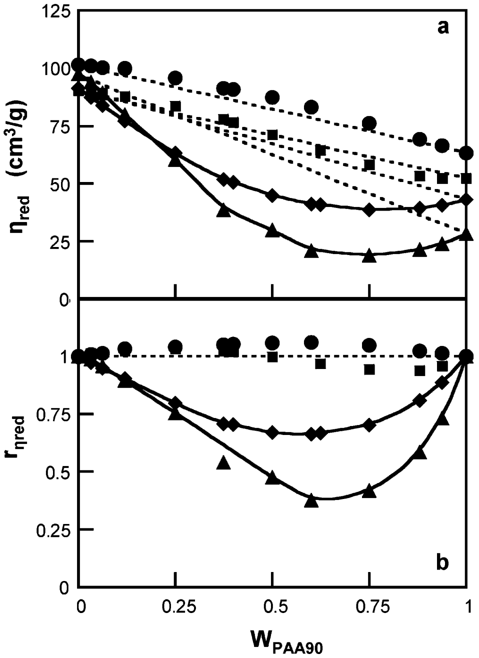


Figure 2. (a) Variation of the reduced viscosity, $\eta_{\rm red}$, of P(AA-*co*-AMPSA70)-*g*-PDMAM/PAA90 polymer mixtures in buffer solutions as a function of their weight composition in PAA90 $W_{\rm PAA90}$ at (●) pH = 4, (■) pH = 3.75, (◆) pH = 3.5, and (▲) pH = 2.5 at 25 °C. The total polymer concentration is 2.5×10^{-3} g cm^{-3}. (b) Variation of the reduced viscosity ratio $r_{\eta_{\rm red}}$ versus $W_{\rm PAA90}$ for the same mixtures.

As we see in Figure 2b, the ratio $r_{\eta\rm red}$ is around unity for the P(AA-*co*-AMPSA70)-*g*-PDMAM/PAA90/water system at pH = 3.75 and pH = 4, while it is lower than unity at lower pH values. Moreover, the curve for pH = 2.5 is systematically below the corresponding curve for pH = 3.5. These observations suggest that hydrogen-bonding interpolymer complexes of compact structure are formed between the two polymers, as pH decreases

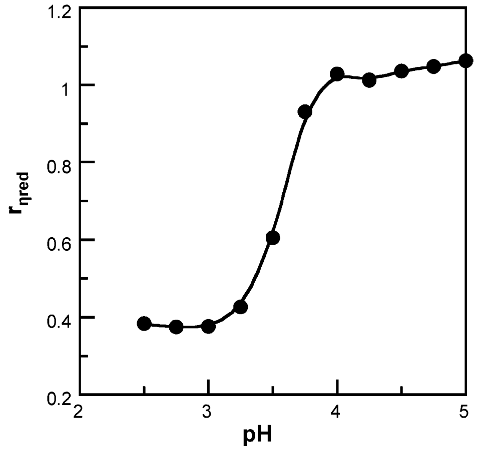


Figure 3. Variation of the reduced viscosity ratio $r_{\eta_{\text{red}}}$ versus pH for an aqueous P(AA-*co*-AMPSA70)-*g*-PDMAM/PAA90 mixture with a PAA weight composition, $W_{\text{PAA90}} = 0.6$ at 25 °C. The total polymer concentration is 2.5×10^{-3} g cm^{-3}.

to values lower than 3.75. Furthermore, decreasing pH favors the compactness of these complexes, as it is usually observed for hydrogen-bonding interpolymer complexes.[12,30−32] The position of the minimum should be indicative of the unit mole apparent stoichiometry of the complex formed between PAA and the PDMAM side chains of the copolymer. At pH = 2.5 this minimum occurs at $W_{\text{PAA90}} = 0.6$ indicating that four carboxylic groups correspond to each PDMAM monomer unit.

The pH-controlled formation-dissociation of the hydrogen-bonding interpolymer complex is revealed by studying the variation of the ratio $r_{\eta_{\text{red}}}$ versus pH. In Figure 3 this variation is presented for the P(AA-*co*-AMPSA70)-*g*-PDMAM/PAA90 mixture with a composition $W_{\text{PAA90}} = 0.6$, i.e., the composition where the minimum was observed in Figure 2b. The ratio $r_{\eta_{\text{red}}}$ decreases from around 1 at pH higher than 4 to about 0.4 as pH decreases to 3 and then it remains constant at this value. This behavior induces that at pH > 4 interpolymer association does not occur and an almost ideal behavior is observed. As pH decreases at values lower than 4 a hydrogen-bonding interpolymer complex is formed between PAA and the PDMAM chains grafted to the P(AA-*co*-AMPSA70) backbone. The stability of the reduced viscosity ratio at pH lower than 3 should be related with the fact that in this pH region the hydrogen-bonding interpolymer complex formed has achieved its final conformation and a further shrinkage in its hydrodynamic volume should not be possible. We should remind that the formation of the corresponding hydrogen-bonding interpolymer complex between the two homopolymers, PAA90 and PDMAM, in this pH region cannot be followed in a similar way, because associative phase separation takes place already at pH = 3.75.

Semidilute Solutions. The observed hydrogen-bonding interpolymer association between the negatively charged graft copolymer of PDMAM with PAA is expected to influence considerably the rheological behavior of such mixtures in semidilute aqueous solutions. To study these effects, we have used the high molecular weight PAA sample, PAA500.

In Figure 4, the viscosity of P(AA-*co*-AMPSA70)-*g*-PDMAM/PAA500 mixtures in semidilute aqueous solutions at pH = 3 is plotted as a function of the shear rate. The experiments were performed at constant P(AA-*co*-AMPSA70)-*g*-PDMAM concentration ($c = 3 \times 10^{-2}$ g/mL) and different PAA500 concentrations, between 0 and 6×10^{-2} g/mL. For the sake of comparison we have also plotted the corresponding curve of the pure PAA500 aqueous solution at the highest studied concentration (6×10^{-2} g/mL) and at the same pH. The viscosity of the two pure polymer solutions is rather low (on the order of 10^{-2} Pa s) and its behavior versus share rate is Newtonian. In contrast, the viscosity of their mixtures increases significantly by increasing the PAA500 concentration, while its profile changes completely. At low shear rate the solution is still Newtonian, whereas for higher shear rates an important shear thinning behavior is observed. If shearing is stopped, the solutions recover their initial viscosity values and we obtain the same viscosity profiles when we repeat the experiments. Such a behavior is usual in associating polymer systems forming reversible networks through noncovalent cross links, as it happens with the hydrophobically modified polymers.[33−35]

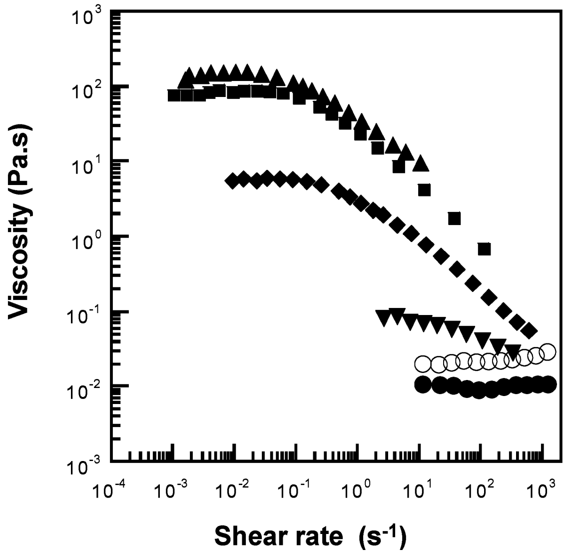


Figure 4. Shear rate dependence of the viscosity of P(AA-*co*-AMPSA70)-*g*-PDMAM/PAA500 polymer mixtures in semidilute aqueous solutions at pH = 3 and T = 25 °C at different PAA500 concentrations, C_{PAA500}. (▼) $C_{\text{PAA500}} = 5 \times 10^{-3}$ g cm^{-3}. (◆) $C_{\text{PAA500}} = 1 \times 10^{-2}$ g cm^{-3}. (■) $C_{\text{PAA500}} = 3 \times 10^{-2}$ g cm^{-3}. (▲) $C_{\text{PAA500}} = 6 \times 10^{-2}$ g cm^{-3}. The curves for the two pure components are also given: (●) pure P(AA-*co*-AMPSA70)-*g*-PDMAM at concentration $C = 3 \times 10^{-2}$ g cm^{-3}, that is, the same with its concentration in all the mixtures and (○) pure PAA500 at C = 6×10^{-2} g cm^{-3}.

The viscosity at the Newtonian plateau of P(AA-*co*-AMPSA70)-*g*-PDMAM/PAA500 aqueous mixtures at pH = 3 and pH = 4 is plotted in Figure 5 as a function of the PAA500 concentration. At pH = 4, the viscosity of the mixtures is rather low and it increases slightly upon addition of PAA500. In fact, the viscosity of the mixtures, more or less, corresponds to the additive value of the viscosities of the two pure components at this pH value. As it was shown in the dilute solution study, at pH = 4 no hydrogen-bonding complexation occurs between the polyacid and the PDMAM side chains of the graft copolymer, explaining the above-described behavior of the semidilute solutions. On the contrary, at pH = 3, the viscosity of the mixture increases considerably as the concentration of PAA500 increases (up to 3−4 orders of magnitude) and tends to reach a plateau value. This behavior is explained by the formation of a strong hydrogen-bonding interpolymer complex between the PDMAM side chains and PAA500 at pH = 3. The plateau observed is probably related with a

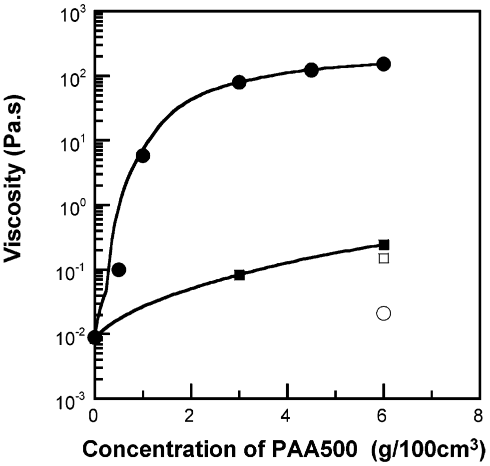


Figure 5. Variation of the Newtonean plateau viscosity of P(AA-*co*-AMPSA70)-*g*-PDMAM/PAA500 polymer mixtures in semidilute aqueous solutions versus the PAA500 concentration at (●) pH = 3 and (■) pH = 4 , at 25 °C. The concentration of the graft copolymer, P(AA-*co*-AMPSA70)-*g*-PDMAM, is always 3×10^{-2} g cm^{-3}. The viscosity values of pure PAA500 solutions at (○) pH = 3 and (□) pH = 4 are also indicated.

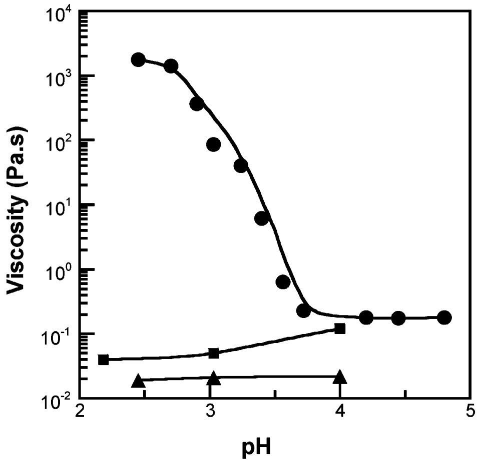
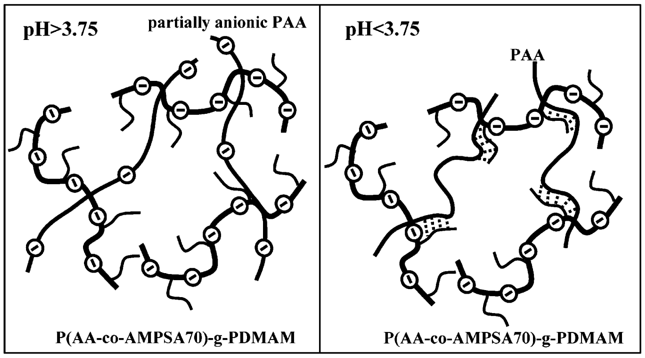


Figure 6. pH variation of the Newtonean plateau viscosity, in semidilute aqueous solutions, of a 1:1 (w:w) (●) P(AA-*co*-AMPSA70)-*g*-PDMAM/PAA500 polymer mixture, and the two pure components, (▲) P(AA-*co*-AMPSA70)-*g*-PDMAM and (■) PAA500, at C = 6×10^{-2} g cm^{-3} and T = 25 °C.

saturation of the PDMAM side chains with the PAA500 chains, expected to occur at a mixture composition corresponding to the stoichiometry of the complex. It is noteworthy that significant thickening properties through hydrogen-bonding interpolymer complexation are very rare and they have been observed only in mixtures of high molecular weight polybases with charged copolymers of acrylic acid.[6,11,36,37]

Scheme 2. A Schematic Explanation of the pH-Controlled Thickening Behavior of the P(AA-*co*-AMPSA 70)-*g*-PDMAM/PAA500 Mixtures in Semidilute Aqueous Solution through Reversible Hydrogen-Bonding Association



The pH-controlled thickening behavior of the P(AA-*co*-AMPSA70)-*g*-PDMAM/PAA500 aqueous mixtures is nicely demonstrated in Figure 6. In this Figure, the pH dependence of the Newtonian plateau viscosity of a 1:1 (w/w) P(AA-*co*-AMPSA70)-*g*-PDMAM/PAA500 mixture in semidilute solution in water is presented and compared with the viscosity of the two polymer components. As expected, the viscosity of the two pure polymer components is relatively low, on the order of $10^{-2}-10^{-1}$ Pa s. The viscosity of the graft copolymer does not essentially depend on the pH of the solution due to its highly charged backbone. The viscosity of PAA500 increases as pH increases as a result of the gradual ionization of the carboxylic groups and the charge density increase of the macromolecular chain. However, this increase is smooth and the viscosity remains low. On the contrary, the mixture of the two polymers exhibits a characteristic pH-controlled thickening behavior. For pH values higher than 3.75 the viscosity is constant at about 10^{-1} P s, that is, more or less, the additive value of the viscosities of the two pure polymer components in this pH range. As pH decreases from 3.75 to 2.5, a dramatic viscosity enhancement of about 4 orders of magnitude is observed. To our knowledge, such a behavior, i.e., viscosity increase with pH decrease, has not been reported before. It is due to the graft copolymer architecture combining the proton acceptor ability of the PDMAM side chains with the strongly hydrophilic character of its negatively charged backbone.

A more detailed explanation of the aforementioned pH-controlled thickening behavior is schematically presented in Scheme 2. At pH > 3.75 no hydrogen-bonding interpolymer complexation occurs between PAA and the PDMAM side chains of the graft copolymer, due to the existence of a considerable fraction of anionic COO$^-$ groups on the PAA chains. In this case, the viscosity of the solution is the expected for entangled polyelectrolyte chains in the semidilute regime. On the contrary, as pH decreases at values lower than 3.75, the fraction of the anionic COO$^-$ groups on the PAA chains becomes very low and hydrogen-bonding association between PAA and the PDMAM side chains of the graft copolymer is taking place. This hydrogen-bonding interpolymer complexation, in this low pH region, would lead to phase separation, if we used the PDMAM homopolymer (Figure 1). In our case, a macroscopic phase separation is inhibited because the PDMAM chains are grafted to a negatively charged, strongly hydrophilic, polymer backbone. In dilute solutions a significant decrease of the reduced viscosity is observed at low pH (Figures 2 and 3) due to the compact structure of the hydrogen-bonding interpolymer complexes formed. In semidilute solutions a spectacular viscosity increase is observed (Figures 4−6). The interpolymer entanglement allows now to each polyacid chain to associate with PDMAM chains originated from different graft copolymer chains so that a physical network is formed.

Conclusion

The graft copolymers P(AA-*co*-AMPSAx)-*g*-PDMAM, where x is the mol fraction in AMPSA units of the polymer backbone, presented in this work, combine nicely two distinct characteristics, i.e., the ability of

PDMAM to form strong hydrogen-bonding interpolymer complexes with weak polyacids and the strong hydrophilic character of their backbone, due to its high content in negatively charged AMPSA units. Thus, when these products are mixed in aqueous solution with PAA at pH lower than 3.75, compact hydrogen-bonding interpolymer complexes are formed between the PDMAM side chains and the PAA chains, as revealed by the decrease of the reduced viscosity of their mixtures in dilute solutions. These interpolymer complexes are soluble in water, even at much lower pH depending on x. For instance, for $x = 70$ the complexes with PAA are soluble even at pH = 2. In contrast, the corresponding hydrogen-bonding interpolymer complexes formed between the two homopolymers, PDMAM and PAA, are not soluble in water at pH lower than 3.75.

This solubility in the low pH region of the above hydrogen-bonding interpolymer complexes prompts for a further investigation and observation of new original properties. In the present study, we have explored just one case, revealed in semidilute aqueous solutions: in the low pH region, the aforementioned polymer mixtures exhibit a striking pH-controlled thickening behavior by forming a hydrogen-bonding reversible network. Here, we have presented a first rheological characterization of the hydrogen-bonding network under shear. A detailed study of the reversibility of the network formation and mainly of its viscoelastic nature is under way.

In this work we have presented a basic concept for the formation of hydrogen-bonding interpolymer complexes, soluble in the low pH region, by using mixtures of negatively charged graft copolymers containing PDMAM side chains, with PAA. Other side chains, such as polyacrylamide, poly(ethylene glycol) or poly(*N*-isopropylacrylamide) and other weak polyacids, such as PMAA could also be used to modulate the solution behavior and other special characteristics, such as the thermal sensitivity, of these polymer mixtures in water.

Controlling the rheology of aqueous formulations is just one possible application of these systems. As it is known, polymers and systems displaying a physicochemical response to stimuli, such as pH, have been proposed as potential drug delivery systems.[38-41] In a respective manner, the pH-controlled hydrogen-bonding interpolymer complex formation presented in the present work could possibly find applications in oral drug delivery systems, where the active substance should be protected from degradation in the low pH gastric environment and released later in the higher pH intestine environment.

Acknowledgment. M. Sotiropoulou acknowledges financial support by the Operational Program for Education and Initial Vocational Training on "Polymer Science and Technology" 3.2a, 33H6, administered through the Ministry of Education in Greece.

References and Notes

(1) Bekturov, E. A.; Bimendina L. A. *Adv. Polym. Sci.* **1980**, *43*, 100.
(2) Tsuchida, E.; Abe, K. *Adv. Polym. Sci.* **1982**, *45*, 1.
(3) Jiang, M.; Li, M.; Xiang, M.; Zhou, H. *Adv. Polym. Sci.* **1999**, *146*, 121.
(4) Bokias, G.; Staikos, G. *Recent Res. Dev. Macromol. Res.* **1999**, *4*, 247.
(5) Antipina, A. D.; Baranovskii, V. Yu.; Papisov I. M.; Kabanov V. A. *Vysokomol. Soyedin.* **1972**, *A14*, 941.
(6) Iliopoulos, I.; Audebert, R. *Polym. Bull.* **1985**, *13*, 171.
(7) Sivadasan, K.; Somasundaran, P.; Turo, N. J. *Colloid Polym. Sci.* **1991**, *269*, 131.
(8) Petrova, T.; Rashkov, I.; Baranovsky, V.; Borisov, G. *Eur. Polym. J.* **1991**, *27*, 189.
(9) Iliopoulos, I.; Audebert, R. *Eur. Polym. J.* **1988**, *24*, 171.
(10) Oyama, H. T.; Hemker, D. J.; Frank, C. W. *Macromolecules* **1989**, *22*, 1255.
(11) Iliopoulos, I.; Audebert, R. *Macromolecules* **1991**, *24*, 2566.
(12) Bokias, G.; Staikos, G.; Iliopoulos, I.; Audebert, R. *Macromolecules* **1994**, *27*, 427.
(13) Baily, F. E., Jr.; Lundberg, R. D.; Callard, R. W. *J. Polym. Sci.: Part A* **1964**, *2*, 845.
(14) Ikawa, T.; Abe, K.; Honda, K.; Tsuchida, E. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 1505.
(15) Klenina, O. V.; Fain, E. G. *Polym. Sci. U.S.S.R.* **1981**, *23*, 1439.
(16) Ohno, H.; Matsuda, H.; Tsuchida, E. *Makromol. Chem.* **1981**, *182*, 2267.
(17) Eustace, D. J.; Siano, D. B.; Drake, E. N. *J. Appl. Polym. Sci.* **1988**, *35*, 707.
(18) Usaitis, A.; Maunu, S. L.; Tenhu, H. *Eur. Polym. J.* **1997**, *33*, 219.
(19) Yang, T. P.; Pearce, E. M.; Kwei, T. K.; Yang, N. L. *Macromolecules* **1989**, *22*, 1813.
(20) Wang, Y.; Morawetz, H. *Macromolecules* **1989**, *22*, 164.
(21) Wang, L. F.; Pearce, E. M.; Kwei, T. K. *J. Polym. Sci.: Part B* **1991**, *29*, 619.
(22) Aoki, T.; Kawashima, M.; Katono, H.; Sanui, K.; Ogata, N.; Okano, T.; Sakurai, Y. *Macromolecules* **1994**, *27*, 947.
(23) Meaurio, E.; Velad, J. L.; Cesteros, L. C.; Katime, I. *Macromolecules* **1996**, *29*, 4598.
(24) Soutar, I.; Swanson, L.; Thorpe, F. G.; Zhu, C. *Macromolecules* **1996**, *29*, 918.
(25) Aoki, T.; Sanui, K.; Ogata, N.; Maruyama, N.; Ohshima, H.; Kikuchi, A.; Sakurai, Y.; Okano, T. *Kobunshi Ronbunshu* **1998**, *55*, 225.
(26) Shibanuma, T.; Aoki, T.; Sanui, K.; Ogata, N.; Kikuchi, A.; Sakurai, Y.; Okano, T. *Macromolecules* **2000**, *33*, 444.
(27) Annaka, M.; Noda, H.; Motokawa, R.; Nakahira, T. *Polymer* **2001**, *42*, 9887.
(28) Dautzenberg, H.; Jaeger, W.; Kotz, J.; Philipp, B.; Sheidel, C.; Stcherbina, D. *Polyelectrolytes: Formation, Characterization and Application*; Hanser, 1994.
(29) Williamson, G. R.; Wright, B. *J. Polym Sci.: Part A* **1965**, *3*, 3885.
(30) Ohno, H.; Abe, K.; Tsuchida, E. *Makrokol. Chem.* **1978**, *179*, 755.
(31) Baranovsky, V.; Shenkov, S.; Rashkov, I.; Borisov, G. *Eur. Polym. J.* **1992**, *28*, 475.
(32) Staikos, G.; Karayanni, K.; Mylonas, Y. *Macromol. Chem. Phys.* **1997**, *198*, 2905.
(33) McCormick, C. L.; Bock, J.; Schulz, D. N. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley-Interscience: New York, 1989; Vol. 17, p 730.
(34) Schulz, D. N.; Glass, J. E. *Polymers as Rheology Modifiers*; ACS Symposium Series 462; American Chemical Society: Washington, DC, 1991.
(35) Potemkin, I. I.; Khokhlov, A. R. In *Polymer Gels and Networks*; Osada, Y., Khokhlov, A. R., Eds.; Marcel Dekker: New York, 2001; p 47.
(36) Iliopoulos, I.; Audebert, R.; Quivoron, C. In *Reversible Polymeric Gels and Related Systems*; Russo, P. S., Ed.; ACS Symposium Series 350; American Chemical Society: Washington, DC, 1987; p 72.
(37) Iliopoulos, I.; Halary, J. L.; Audebert, R. *J. Polym. Sci. Polym. Chem.* **1988**, *26*, 275.
(38) Langer, R. *Science* **1990**, *249*, 1527.
(39) Chen, G.; Hoffman, A. S. *Nature* **1995**, *373*, 49.
(40) Thomas J. L.; You, H.; Tirrel, D. A. *J. Am. Chem. Soc.* **1995**, *117*, 2949.
(41) Bae, Y. H. US Patent 5,484,610, 1996.

MA021256N