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Rheological Properties of Physical Gel Formed by Triblock Polyampholyte in Salt-Free Aqueous Solutions

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ABSTRACT: Linear and nonlinear viscoelastic properties of an asymmetric triblock copolymer poly(acrylic acid)−poly(2-vinylpyridine)−poly(acrylic acid) (PAA−P2VP−PAA) in salt-free aqueous solutions have been investigated. At pH 3.4, long-range electrostatic interactions prevail, due to protonated P2VP units and negative PAA end groups. Above a critical C_g = 2.5% w/w, a transient network is formed through intermolecular electrostatic interactions between negatively charged groups located at the end PAA blocks and positively charged protonated pyridine groups located at the middle long P2VP block. The so-formed network exhibits some atypical rheological behavior characterized by a strain hardening of storage modulus in intermediate strain amplitudes and a pronounced shear thickening in moderated shear stresses. The shear-induced changes in the structure of the network have been attributed to enhancement of the number of elastically active bridges through association of free dangling ends and a transition from intra- to intermolecular association.

Introduction

Associative water-soluble polymers are polymers that self-assemble through temporary junctions of functional groups. Through this generic description, different varieties of associative thickeners can be distinguished. Traditional associative polymers consist of neutral polymers containing hydrophobic associative groups. In this category, telechelic polymers (chains end-capped by hydrophobic groups) are often considered as a model of hydrophobic associative polymers. Extensive investigations of telechelic solutions (mostly PEO polymer derivatives) using light scattering and rheometric techniques have been carried on during this past decade. Above a critical association concentration, polymer chains self-associate in flowerlike micelles constituted by a hydrophobic core, surrounded by a corona of hydrophilic polymer loops.[1] With increasing concentration, a second association process occurs between flower micelles, corresponding to the formation of bridges.[2−4] The interconnections of flowerlike micelles leads generally to a sol−gel transition which produces a sharp increase of the viscosity. The nonlinear behavior of telechelic associative polymers exhibits a local shear thickening proceeding a pronounce shear thinning. In the linear viscoelastic range a Maxwell model, corresponding to a single relaxation time and an elastic plateau modulus, generally describes dynamic moduli.

Charged polymers display also an associative character and can be classified in two typical groups according to their architecture: hydrophobically associative polyelectrolytes and polyampholytes. In the former group, telechelic polyelectrolyte like its neutral parents is end-capped by hydrophobic groups, but the ionic character of the main backbone induces additional interactions such as Coulomb repulsive forces between

monomers (intramolecular) and also between chains (intermolecular) and interactions with counterions. In dilute solution, polymer chains can be aggregated in finite size clusters, resulting from equilibrium between the energy of attraction of hydrophobic stickers and the contribution of the additional electrostatic forces.[5,6] A direct consequence of the intramolecular repulsions is an expected stretched conformation of the polyelectrolyte into the cluster. Above a percolation concentration, clusters are connected by stretched polymer chains in a transient three-dimensional network. Such particular microstructure is responsible for the unusual rheological behavior characterized by an apparent yield stress, low gelation concentration, short linear viscoelastic range close to 1%, and high plateau modulus.[7,8]

Instead of being localized at the ends, hydrophobic groups can be distributed along the backbone. Hydrophobically modified alkali-swellable emulsion polymers (HASE) can be classified in this group. While the polymers are in the emulsion state at low pH, they become water-soluble above pH 7 by ionization of polymer chains. Above a critical concentration, a transient network is formed through intermolecular association of the hydrophobic groups. The rheological behavior of HASE physical gel is somehow comparable to that of nonionic telechelic polymers, showing a more or less pronounced shear thickening at moderate shear rate and a sharp increase of the Newtonian viscosity and the plateau storage modulus with increasing concentration. However, HASE systems present an unusual viscoelastic behavior characterized by a local increase of both G' and G'' moduli at intermediate strain amplitudes.[10−13] Such a strain dependence of G' and G'' moduli seems to be typical of HASE systems.

Polyampholytes are another category of charged water-soluble associative polymers in which opposite charges coexist along the macromolecular chain. In this case electrostatic interactions between oppositely charged units are responsible for their behavior in aqueous media.[14,15] Recently, a rich phase behavior was observed

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by a weak polyampholyte of a block copolymer architecture, i.e., poly(acrylic acid)-*b*-poly(vinylpyridine)-*b*-poly(acrylic acid) (PAA_{134}–$P2VP_{628}$–PAA_{134}).[16] Depending on pH of the solution three distinct regions can be distinguished. In the high-pH region compact micelles with P2VP hydrophobic cores and PAA charged chains in the corona were formed. In the intermediate-pH region and around the isoelectric point the polymer precipitates. Finally, in the low-pH region and low concentrations the polymer is molecularly dissolved. The net charge of the polyampholyte is positive since the majority of the P2VP units are protonated, exhibiting a polyelectrolyte character.

A novel behavior was observed at pH 3.4 (close to the phase separation limit) and at elevated concentrations. Despite the lack of hydrophobic blocks (which play the role of stickers in physical gelation phenomena), this polymer is self-assembled to a three-dimensional transient network through electrostatic interactions. In the present article the rheological properties of this novel physical gel will be demonstrated and compared with those of other hydrophobically associated water-soluble polymers. It should be mentioned here that although much work has been reported concerning polyampholyte chemical gels,[17] this is the first work dealing with a polyampholyte physical gel.

Experimental Section

Material and Solution Preparation. The polymer studied is a poly(2-vinylpyridine), P2VP, end-capped by two poly-(acrylic acid), PAA, chains. The desired PAA–P2VP–PAA has been obtained by acid-catalyzed hydrolysis of poly(*tert*-butyl acrylate)–poly(2-vinylpyridine)–poly(*tert*-butyl acrylate), PtBA–P2VP–PtBA, in dioxane.[16] The M_w of the copolymer is 8.5×10^4 g/mol, corresponding to a degree of polymerization of 628 for the central P2VP block and 135 for each PAA end-blocks. These ionizable blocks are respectively weak acid and weak basic moieties. The copolymer is water-soluble, and its aqueous solutions give a pH close to 3.5 All polymer solutions were obtained by dissolving the appropriate amount of polymer in pure water. Shaking ensured the homogenization of the solutions. For the more concentrated solutions, this shake was assured by a series of brief centrifugations of the samples. Between each centrifugation, the position of the samples rotates. The measurements were performed at least 24 h after preparation. During this lap of time, the samples were let at rest at room temperature. All the prepared polymer solutions were clear, showing that no macroscopic aggregation was present in the solutions.

Rheometry. The linear and nonlinear rheological properties of the polymer solutions were studied using a stress-controlled Rheometric Scientific SR 200, equipped with either a cone and plate geometry (diameter = 25 mm, cone angle = 5.7°, truncation = 56 μm) or a Couette geometry (gap = 1.1 mm) depending on the viscosity of the solutions. After loading, each sample is let at rest for 5 min before measurements to remove the mechanical history. Viscosity measurements were taken in an "equilibrium" state of the samples under shear, based on the condition that the time evolution of the shear rate was smaller than 1%/s. If this condition was not respected, a limited time of 100 s was chosen to avoid too long measurement. The temperature is fixed at 25 ± 0.1 °C, and the samples were enclosed in a small volume to prevent them from prospective water evaporation.

Results

Nonlinear Behavior. Viscosity measurements have been carried out in a concentration range from 0.16 to 6 wt %. Figure 1 shows the apparent viscosity vs shear stress for some polymer solutions studied in this con-
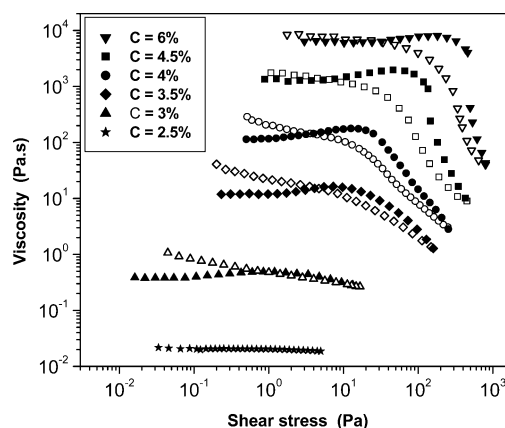

Figure 1. Apparent viscosity as a function of shear stress for 2.5, 3, 3.5, 4, 4.5, and 6 wt % polymer solution in water. Full symbols correspond to data obtained by increasing stress and open symbols to that obtained by decreasing stress.
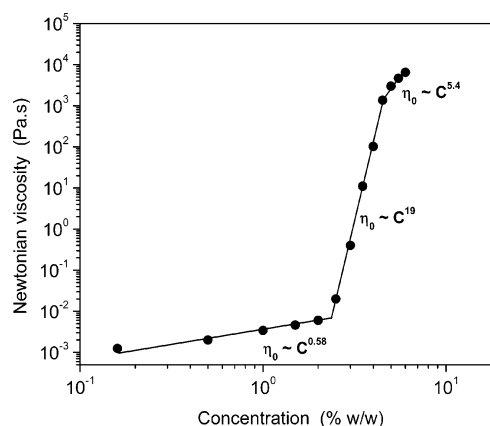

Figure 2. Zero-shear viscosity as a function of polymer concentration.

centration range. For each concentration, a cycle of increasing shear stress (full symbols) and decreasing shear stress (open symbols) has been applied. Three concentration regimes can be defined according to viscous behavior observed. Below a concentration C_g of 2.5 wt %, corresponding to the semidilute regime, polymer solutions exhibit a Newtonian response in the shear stress range studied. Above C_g, the steady shear viscosity profile depends on the way the shear stress is applied and also on the concentration range. With an increasing shear stress, first a Newtonian plateau is observed, followed by a shear thickening effect, and then the viscosity decreases at elevated shear stress. The shear thinning effect is very pronounced above C = 4.5 wt %. This concentration C' marks the beginning of a third concentration regime. The change in the flow behavior around C' is more obvious when the applied shear stress decreases. In fact, the viscosity increases continuously for a concentration below this critical concentration and overtakes the initial value at low shear stress while the viscosity reaches the initial Newtonian value at low shear stress for concentrations above C'.

Newtonian viscosities obtained from Figure 1 by increasing the shear stress are plotted in Figure 2 as a function of polymer concentration. The three concentration regimes discussed previously are clearly identifiable in this representation. A semidilute regime, an intermediate regime, and a more concentrated regime are described by a power law dependence of the Newtonian
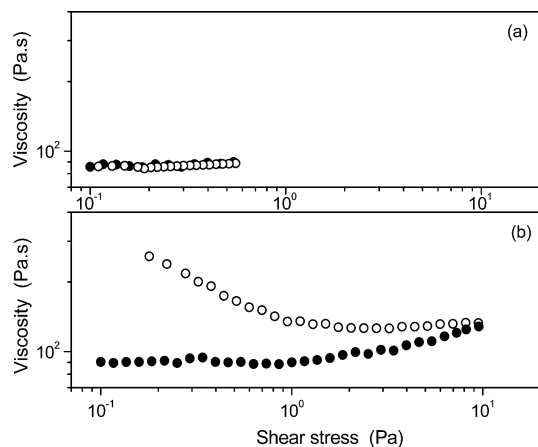
Figure 3. Viscosity as a function of shear stress for a 4 wt % polymer solution. Cycle of increasing and decreasing shear stress in the Newtonian region (a) and up to the shear thickenig region (b). The cycle has been described using the notation of Figure 1.
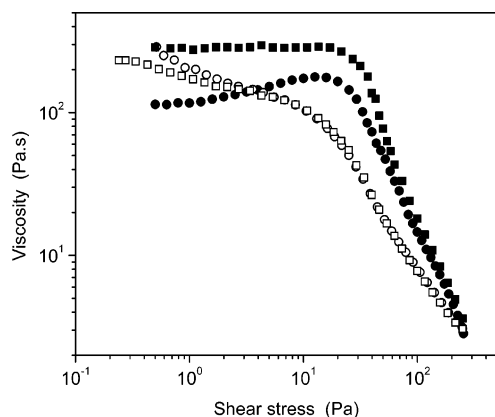

Figure 4. Thixotropic flow curve of 4 wt % polymer solution. Square symbols and circle symbols correspond respectively to the first and the second flow cycle. The cycle has been described using the notation of Figure 1.

viscosity with an exponent of about 0.58, 19, and 5.4, respectively. Only the exponent of 0.58, observed in the semidilute regime, is in good agreement with the scaling theory of semidilute unentangled polyelectrolyte solutions.[18] However, from a qualitative point of view, a similar dependence of Newtonian viscosity with concentration has been observed for hydrophobically associative polymer solutions forming micellar gel.[19-21]

To have some physical insight into the microstructure in the intermediate regime, a complementary study has been carried out at C_p = 4 wt %. Figure 3 shows an increasing/decreasing stress sweep test in the linear regime (a) corresponding to the Newtonian behavior and up to the shear thickening regime (b). This figure clearly shows that the enhancement of viscosity with decreasing stress is only in the nonlinear regime. Two consecutive cycles of increasing and decreasing shear stress have been applied in an extended shear stress range. Figure 4 shows the viscosity of the solution as a function of the shear stress. After the first cycle, the viscosity at low stress is 3 times higher than that at the initial state. Preshearing has modified irreversibly the initial structure. In the second cycle, the shear thickening effect has been vanished, and the viscosity profile obtained by increasing the shear stress is simply characterized by an expanded Newtonian plateau followed by a shear-thinning effect. When the applied shear stress de-
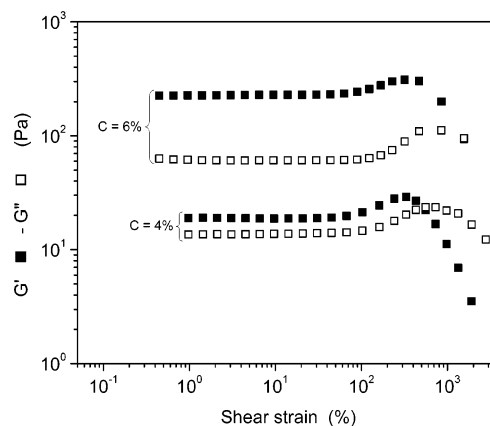

Figure 5. Storage modulus G' and loss modulus G'' as a function of shear strain for 4 and 6 wt % polymer solutions.

creases, the flow curve is similar to that observed during the first cycle. These original results show that the thickening effect depends on the mechanical history imposed on the structure.

Linear Behavior. The strain dependence of the storage modulus and the loss modulus has been first measured in order to determine the linear viscoelastic regime. Figure 5 represents the storage modulus and the loss modulus as a function of strain for 4 and 6 wt % polymer solutions measured at the frequency of 0.5 Hz. As the strain increases, both moduli exhibit a plateau value G'_0 and G''_0 until a critical strain γ_c of about 50%, above of which moduli increase, reach a maximum value, and decrease. It has to be noted that the strain hardening of the storage modulus appears at a lower strain than that of the loss modulus. While such a peak in the loss modulus profile has been observed for associative polymer solutions,[8,9] a peak in the storage modulus is in great contrast to those generally observed, characterized by a pronounced decrease of G' with increasing strain beyond the linear viscoelastic regime. According to our knowledge, only HASE solutions present a similar strain dependence of G' and G'' moduli, which however do not exhibit a shear thickening effect in the shear viscosity profile.[10-13] For these systems, the strain hardening increases with increasing the length of the hydrophobic groups, i.e., the strength of the associative junction. Moreover, these peaks are only observed at high frequency for which the polymer network does not have sufficient time to relax within the time of one oscillation cycle. Dynamic measurements have been extended in the concentration range from 3.5 to 6 wt %.

Our interest focuses on the unusual strain dependence of the G' modulus. Figure 6 represents the storage modulus as a function of strain at different polymer concentrations. All the polymer solutions studied in this concentration range exhibit a peak in the storage modulus. Let us try to compare the shear thickening effect (shear-induced viscosity enhancement) and the strain hardening of the G' modulus. At a concentration of 4 wt %, the shear thickening effect arises at a shear rate of about 0.2 s^{-1}. In dynamic measurements, the product $\gamma_c f$ is the shear rate reached at the critical shear strain amplitude, with f the frequency. This shear rate, of about 0.25 s^{-1}, is in the same order of magnitude than that obtained in steady shear flow. So, from a phenomenological point of view, the peak in the storage modulus has some similarity with the shear-thickening behavior
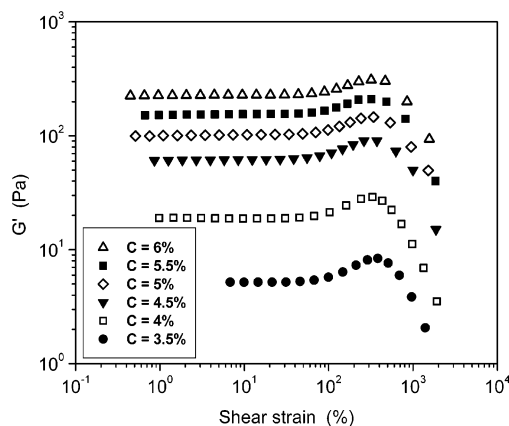
Figure 6. Storage modulus G' as a function of shear strain for 3.5, 4, 4.5, 5, 5.5, and 6 wt % polymer solutions.
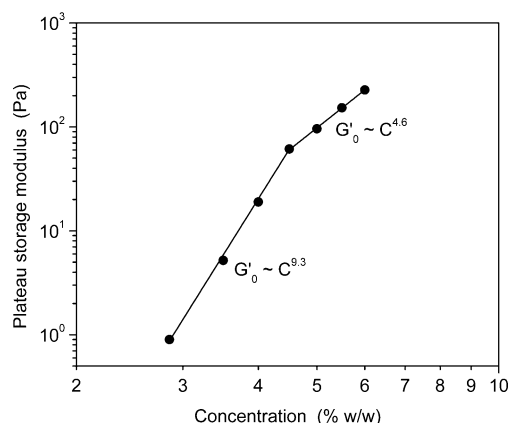

Figure 7. Plateau values of the storage modulus G'_0 as a function of polymer concentration.

Figure 8. Reduced storage modulus G'/G'_0 as a function of shear strain for 3.5 (●), 4 (□), 4.5 (▼), 5 (◇), 5.5 (■), and 6 (△) wt % polymer solutions. Inset: intensity of the reduced storage modulus G'_{max}/G'_0 as a function of polymer concentration.

Figure 9. Storage modulus G' and loss modulus G'' as a function of frequency for 3.5, 4.5, and 6 wt % polymer solutions.

observed in the weakly nonlinear part of the flow curve. Besides, it occurs that both viscoelastic moduli are significantly enhanced by polymer addition.

This concentration dependence is illustrated in Figure 7, showing the plateau storage modulus as a function of polymer concentration. It is noted that the term "plateau" is used in this work to qualify the linear viscoelastic modulus obtained at a fixed frequency (0.5 Hz). The concentration dependence of the plateau storage modulus has been described using a power law with an exponent of 9.3 below C and 4.6 above C. The Newtonian viscosity and the storage moduli are material properties, which exhibit the same qualitative dependence as a function of concentration. In the third regime, these material properties increase more slowly than in the intermediate regime. It should be noted that the exponents of the power laws in both material properties beyond the percolation threshold are much higher than those observed in other water-soluble polymeric thickeners, approaching the theoretical predictions of Semenov et al.[20]

Let us now look at the qualitative behavior of the storage modulus. Figure 8 shows the reduced storage modulus as a function of shear strain for concentration between 3.5 and 6 wt %. The arising of the strain hardening appears at the strain amplitude of about 50% for the storage modulus and does not depend on polymer concentration. This figure points out a significative dependence of the peak intensity of the reduced storage modulus, noted G'_{max}/G'_0, with polymer concentration. The inset shows the peak intensity of the reduced storage modulus as a function of polymer concentration.
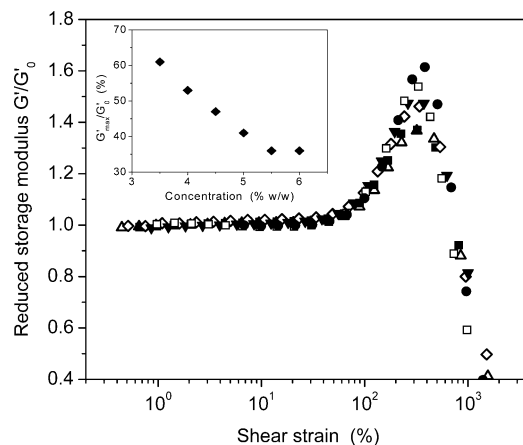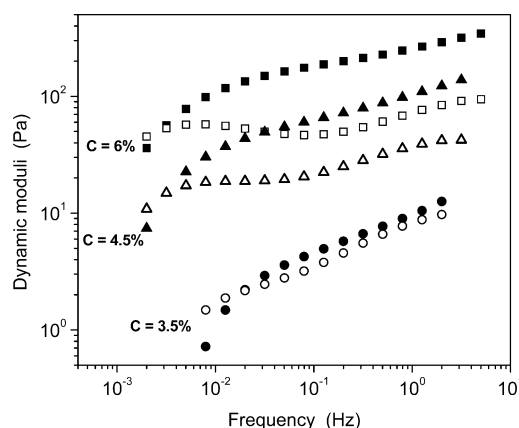
The peak intensity of the storage modulus decreases significantly with increasing concentration up to about 5 wt % and then levels off.

The variation of dynamic moduli with frequency has been measured in the linear viscoelastic range. Figure 9 shows the dynamic moduli as a function of frequency for 3.5, 4.5, and 6 wt % polymer concentrations. Two viscoelastic behaviors can be distinguished in accordance with concentration regimes: in the intermediate regime both modules depend on frequency, showing that the solutions behave like a viscoelastic liquid. On the contrary, in the third regime dynamic moduli are practically independent of frequency, at least in the range of frequency studied, showing that concentrated solutions behave like an elastic gel.

In all concentrations studied it was not possible to observe the terminal zone of the relaxation spectrum. Therefore, we were not able to apply any model to determine the relaxation behavior of the system. However, a rough estimation of the longest relaxation time, τ, could be given by the intersection of the storage and loss modulus curves. In the third concentration regime τ is of the order of 300 s, and it seems to be independent of polymer concentration.

Discussion

In the dilute regime ($C < C_g = 2.5$ wt %), the polyampholyte is expected to form aggregates due to the electrostatic interactions between oppositely charged

blocks. The elucidation of the microstructure of the associated macromolecules below C_g will be the subject of a forthcoming publication. Although the structure of these aggregates has not been yet investigated, we could assume two possible mode of association.

Negatively charged PAA units at both ends of the polymer form polyelectrolyte complexes with the neighboring positively charged P2VP units within a single copolymer molecule. Because of the hydrophobic nature of these polyelectrolyte complexes, the polymer is transformed to a hydrophobically end-capped polyelectrolyte, which could form "flowerlike" micelles with loops of extra P2VP charged chains in the corona. By increasing concentration, a network of bridging micelles should be formed.[22] This scenario requires the existence of high negative charge density in the PAA end-blocks, which it is not favored at pH 3.4. Moreover, the rheological behavior of such a system should resemble to that of telechelic polyelectrolytes,[7,8] whereas it differs in many respects.

Another more plausible association mechanism could be suggested. Some negative charges on PAA blocks interact with the positive charges located along the major P2VP protonated middle chain imposing intra and/or intermolecular associations (Figure 10a). This leads to the formation of open loose aggregates without discernible hydrophobic domains since the polyelectrolyte complexes are short due to the limiting number of negative charges in the PAA blocks. Above C_g, a percolation process due to electrostatic associations between oppositely charged groups leads to the formation of a loose network (Figure 10b). Beyond C_g, the rheological properties of this network are highly enhanced by polymer addition while they increase to a lesser extend above C'. Let us discuss now the nature of this network. The value of γ_c, close to 50%, is rather important in comparison to that measured for telechelic polyelectrolyte solutions ($\gamma_c \sim 1\%$).[8] The short value of the linear viscoelastic range has been attributed to a stretched conformation of the polyelectrolyte arising from intramolecular electrostatic repulsions. The high value of γ_c obtained with $PAA_{135}-P2VP_{628}-PAA_{135}$ tends to prove that the polyampholyte is not fully stretched. This result is in good agreement with recent AFM observations of P2VP polymer at pH 3.4.[23] A second point to be mentioned is some similarities observed in the rheological behavior of HASE, i.e., strain hardening at the upper limit of the linear viscoelastic range, local shear thickening followed by a shear thinning beyond a critical shear stress, and a sharp concentration dependence of the Newtonian viscosity.

We present a possible microstructural interpretation of the rheological behavior. The character of the polymer under investigation is hydrophilic (lack of hydrophobic stickers), and this is a fundamental difference from the amphiphilic character of the associative polymers studied so far. The transient network is mainly composed of elastically active chains arisen from intermolecular electrostatic interactions between negatively charged groups located in the end PAA blocks and positively charged protonated pyridine groups located in the middle long P2VP block.[16] Intramolecular associations are likely to occur since at pH 3.4 the long P2VP chains do not adopt exclusively a stretched conformation as we mentioned above. Moreover, a number of PAA block ends may stay unassociated (dangling ends) as they are water-soluble, contrary to what occurs in hydrophobi-
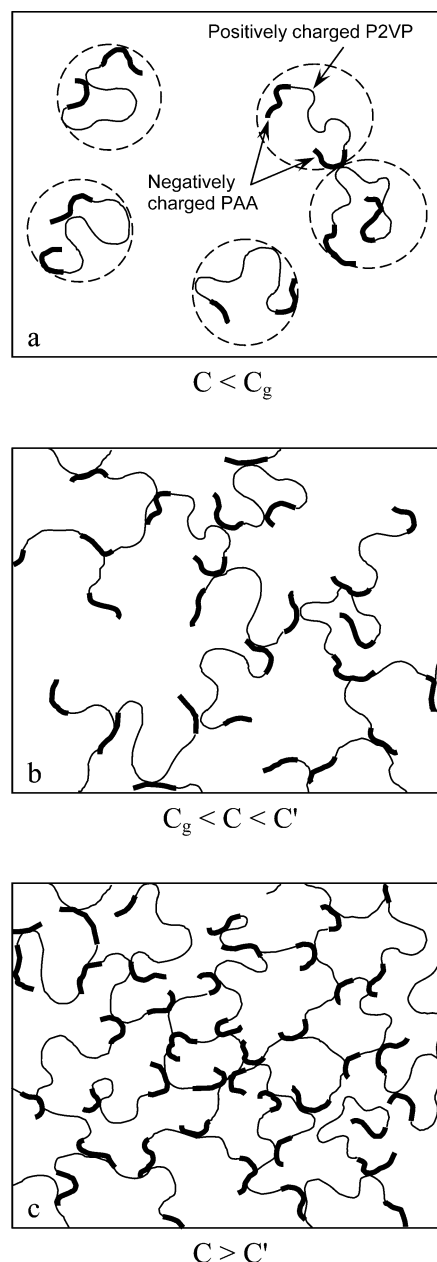

Figure 10. Schematic representation of the possible molecular microstructure at rest in (a) the dilute regime, (b) the intermediate regime, and (c) the more concentrated regime.

cally associative polymers. The last two cases lead to a number of elastically inactive chains (dead branches for the network) that nevertheless can be considered as potentially active in the rheological behavior of the solutions (Figure 10b). It is admitted that the storage modulus reflects the number density of the elastically active chains. As the strain amplitude increases beyond γ_c, the dangling ends are forced to form new electrostatic junctions. Moreover, competition between dissociations and associations promotes extra intermolecular associations due to an intra- to intermolecular transition. Both processes lead to an increase of G' modulus and shear viscosity. The proposed microstructural analysis is corroborated by the concentration dependence of the peak intensity of the reduced dynamic moduli: by increasing polymer concentration, the decrease of the peak intensity of the storage modulus may be attributed to the progressive reduction of the number of extra intramolecular associations. Finally, as the strain am-

plitude increases further, the dissociation rate is more important than the association rate; the network collapses leading to a drop in the dynamic moduli.

Using the microstructural organization proposed here, the influence of the mechanical history on the viscous behavior could be interpreted as follows: At the intermediate shear stress corresponding to the shear-thickening effect, the shear flow forces both intramolecular associated and "dangling" ends to form new elastically active intermolecular bridges which harden the transient network. At high shear stress, the gradually fragmentation of the network leads to a decrease of the viscosity. As the shear stress decreases from high stresses, intermolecular junctions are gradually created leading, at low stress, to a new transient network characterized by a higher number of bridges than in the initial structure. The relaxation time, i.e., the time needed to achieve this more structured organization, of about 300 s, is rather long in comparison to the experiment time and could explain the lower viscosity observed in this rebuilding procedure. When this new structure is submitted to an increasing stress, there is only a competition between association and dissociation of efficient associative junctions from the network. The shear flow does not increase the number of elastically active bridges, and therefore no shear-thickening effect is observed.

In summary, the rheological results suggest that below C' a loose network is formed, allowing pronounced thickening effects by concentration enhancement and/or shearing, while above C', a complete 3-dimensional network almost free from "dangling ends" is achieved as is illustrated in Figure 10.

Concluding Remarks

The rheological properties of a physical gel formed by an asymmetric triblock polyampholyte of the type $PAA_{135}-P2VP_{628}-PAA_{135}$ in salt-free aqueous solutions have been presented. To the best of our knowledge, it is shown for the first time that a weak polyampholyte with asymmetric triblock copolymer architecture can form an infinite three-dimensional reversible network in a certain pH. It is also the first example of a double hydrophilic block copolymer (lack of hydrophobic stickers) that behaves as a strong thickener (6 orders of magnitude higher viscosity at 4 wt % polymer concentration).

Particular attention has been paid to the association mechanism and the structure of the transient network formed above $C_g = 2.5$ wt %. The molecular dynamics of the network exhibits some particular behavior that differs from other associative polymer solutions (peak in both G' and G'' moduli in intermediate strain amplitude, prolonged shear thickening in moderated shear stress). The whole set of rheological data support the coexistence in the network of elastically active and inactive polymer chains named "dead branches" attributed to dangling ends and intramolecular association. Shear induces structural rearrangements by promoting the intra- to intermolecular associations and forcing the dangling ends to join the mechanically active network. The rheological properties of the system are strongly concentration dependent. Two concentration regimes can be identified above the percolation concentration C_g with characteristic flow behavior. The transition concentration C' between these regimes has been interpreted in term of mechanically efficient connectivity of the network.

(i) For concentrations below C', the network contains many dangling ends and intramolecular associations (elastically inactive branches). The rheological properties are strongly improved by polymer addition, which enhances the network connectivity. The exponents of η_0 and G_0 power laws are the highest ever observed in associative polymers.

(ii) Above C', a complete 3-dimensional network is achieved for which polymer addition improves to a lesser extent its rheological properties.

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