Composition-Dependent Rheology of Aqueous Systems of Amphiphilic Sodium Poly(2-acrylamido-2-methylpropanesulfonates) in the Presence of a Hydrophobically Modified Cationic Cellulose Ether

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ABSTRACT: The rheology of aqueous solutions of a hydrophobically modified cationic hydroxyethylcellulose ether (LM200) in the presence of hydrophobically modified poly(sodium 2-acrylamido-2-methylpropanesulfonates) (HM-PAMPS) was studied in the semidilute regime (10 g L^{-1}) by oscillatory shear and steady shear measurements. The polyanions were copolymers of sodium 2-acrylamido-2-methylpropanesulfonate and *N*-*n*-dodecylmethacrylamide (PA90Dod or PA80Dod) with dodecyl group content of 10 and 20 mol %, respectively. The LM200/polyanion mixtures underwent phase separation for compositions near charge neutralization but were homogeneous over wide composition ranges. Miscible fluids with excess polyanion with respect to the polycation content behaved as elastic gels, viscoelastic fluids, or viscous liquids, depending on the mixture composition and the level of hydrophobic modification of the polyanion. The viscous polyanion-rich fluids were Newtonian fluids at low shear rates; they increased in viscosity at moderate shear rates (shear thickening regime) and underwent shear thinning at high shear rates. In contrast, polyanion-poor mixtures were viscoelastic fluids and exhibited shear-thinning properties for all compositions and independently of the dodecyl content of the polyanion. The occurrence of two types of networks in LM200/HM-PAMPS mixed fluids is attributed to the disparity in the charge density, level of hydrophobic modification, and flexibility of the polycation and polyanions.

Introduction

The functions of many industrial and household fluids, such as paints, cosmetics, foodstuff, or solutions used in enhanced oil recovery, hinge critically on the fluid rheology either at rest or under applied stress. It is the task of many industrial scientists to design formulations of controlled flow properties under various conditions. While this area of science is considered by some as an “art”, a number of strategies have emerged from fundamental studies of the molecular interactions among the various components. A particularly successful approach for controlling the rheology of such fluids exploits the association characteristics of hydrophobically modified (HM) water-soluble polymers. HM-polymers, which contain hydrophilic and hydrophobic sections on a single chain, readily form networks in water via association of their hydrophobic sections.[1] In most practical applications HM-polymers are not used alone. Typical formulations include other additives such as salts, surfactants, or other polymers which may, or not, interact with the HM-polymer.[2] To unravel the complex mechanisms involved in multicomponent fluids, interactions taking place in two-component systems need to be understood first, not only empirically but also at the fundamental level. The solution properties of binary systems consisting of two different HM-polymers or of HM-polymers and either surfactants or polyelectrolytes have been investigated experimentally by several techniques, such as light scattering,[3] small-angle X-ray and neutron scattering,[4] NMR spectroscopy,[5] fluorescence spectroscopy,[6] and various rheological measurements.[7,8] Several models have been proposed to account for the properties of the mixed systems.[9]

The present work centers on binary mixtures containing Quatrisoft LM200 (LM200, Figure 1a), a commercial cationic HM-polysaccharide, employed extensively in cosmetics formulations.[10] It is a derivative of hydroxyethylcellulose ether substituted with a low level of cationic alkyl chains. The alkyl groups tend to assemble when LM200 is dissolved in water, creating intra- and interpolymeric hydrophobic microdomains. Goddard and Leung were the first to report that the addition of an anionic surfactant, sodium dodecyl sulfate (SDS), to aqueous solutions of LM200 severely affects their macroscopic properties and that “simple” binary mixtures of LM200 and SDS can be viscous homogeneous fluids, gels, or coacervates, depending on the relative amounts of the two components.[11,12] Guillemet and Picullel, probing the same system by viscometry and fluorescence probe measurements, shed further light on the molecular interactions at play in the mixed systems.[13,14] They demonstrated that the addition of anionic surfactants to aqueous solutions of LM200 disrupts the hydrophobic microdomains and that mixed micelles, consisting of surfactant molecules and entrapped polymer-linked hydrophobic groups, form readily, since both electrostatic and hydrophobic interactions acting in concert favor the interactions. This conclusion was confirmed by fluorescence measurements carried out with a pyrene-labeled LM200 sample.[15] The strength of the interactions was assessed recently by an evaluation of the dynamic properties of the LM200/SDS mixed micelles using a pressure jump method.[16] The

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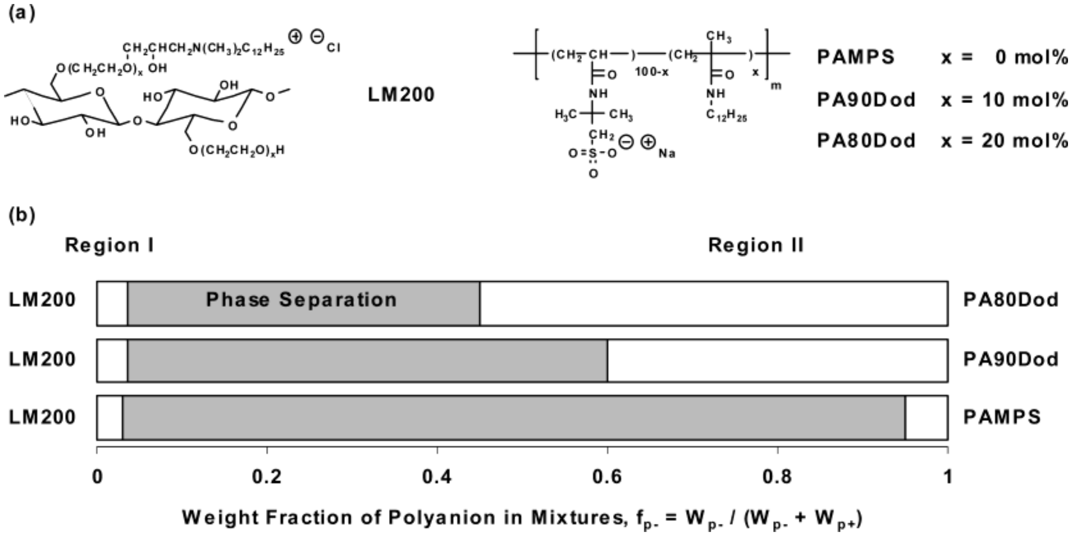

Figure 1. (a) Chemical structure of the polymers used in this study. (b) Phase diagrams for aqueous mixtures of LM200 and PAMPS or HM-PAMPS bearing different amount of *n*-dodecyl chains (PA90Dod or PA80Dod). Widths of phase boundaries: f_{P-} ± 0.005 (region I) and f_{P-} ± 0.025 (region II).

Table 1. Physical Characteristics and Structural Features of the Polymers Studied

	polymer	mol wt	mean contour length (nm)	*n*-dodecyl chain content (mol %)	charge content (mol %)	mean contour length between charges (nm)	charge concn in a 10 g L^{-1} solution (mM)	ref
polycation	LM200	100 000	200	5	5	10	2	15
polyanions	PA80Dod	33 000	36	20	80	0.25	35	23
	PA90Dod	37 000	40	10	90	0.25	39	23
	PAMPS	71 000	77		100	0.25	44	22

composition and dynamics of mixed micelles, which vary depending on the level of hydrophobic substitution of the polymer and the surfactant/polymer mixing ratio, determine to a large extent the macroscopic rheology of the mixed systems.[17] Thuresson et al.[18] assessed the phase behavior and rheology of mixtures of LM200 and a hydrophobically modified polyacrylate carrying a low level (~3 mol %) of dodecyl chains. The mixed fluids were shown to vary greatly in their appearance and rheology, depending on the molecular weight of the polyanion, the LM200 to polyanion ratio, and the presence of electrolytes.[19]

We report here a study of the rheology of mixed fluids containing LM200 and a class of HM-polyanions which, unlike HM-polyacrylates, are known to form unimolecular micelles (unimers) rather than multipolymeric micelles. The HM-polyanions selected are copolymers of sodium 2-acrylamido-2-methylpropanesulfonate (AMPS) and *N*-*n*-dodecylmethacrylamide incorporated at random along the polymer chain at the level of 10 and 20 mol % (PA90Dod and PA80Dod, Figure 1a). The reactivity ratios of AMPS and *N*-*n*-alkylacrylamides are nearly identical, ensuring random distribution of the two monomer units along the chain.[20] The topology of HM-PAMPS unimers in water resembles that of surfactant micelles, consisting of a hydrophobic core surrounded by negatively charged loops and having a diameter of ~12 nm.[21] However, unlike surfactant micelles which are in dynamic equilibrium, individual polymer-linked dodecyl groups cannot escape from the hydrophobic core of the unimers by virtue of their attachment to a macromolecule. The phase behavior, dynamic viscosity profile, and oscillatory shear response of the fluids were examined for three sets of samples, namely LM200/PA90Dod, LM200/PA80Dod, and LM200/PAMPS, of constant total polymer concentration. The experiments were designed to allow us to assess (1) the effect of the level of hydrophobic substitution of the polyanion on the properties of the fluids subjected to shear and (2) the paramount importance of the relative amounts of polyanion and polycation dissolved in the fluids.

Experimental Section

Materials. Water was purified with a Millipore Milli-Q System. The polycation Quatrisoft Polymer LM200 was obtained from Amerchol Corp. (Union Carbide Chemicals and Plastics Co. Inc.) and was used as received. It is the chloride salt of an *N*,*N*-dimethyl-*N*-*n*-dodecylammonium derivative of hydroxyethylcellulose ether with a degree of substitution of approximately 0.2 mmol of dodecyl chains per gram of polymer, corresponding, on average, to 1 dodecyl group per 19 glucose units. The molecular weight of LM200 is ca. 1×10^5 Da. The polyanion PAMPS was prepared as described earlier by free radical polymerization of sodium 2-acrylamido-2-methylpropanesulfonate (AMPS) in *N*,*N*-dimethylformamide (DMF) at 60 °C in the presence of 2,2′-azobis(isobutyronitrile) (AIBN).[22] PA90Dod and PA80Dod are copolymers of AMPS and *N*-*n*-dodecylmethacrylamide (DodMAm) with a dodecyl group content of 10 and 20 mol %, respectively, and were prepared under the same conditions.[23] The molecular weights of PAMPS, PA90Dod, and PA80Dod were determined by size exclusion chromatography (SEC) on a JASCO GPC-900 system equipped with Shodex Asahipak GF-7M HQ columns, eluted with a 0.2 M solution of $LiClO_4$ in methanol and calibrated with poly(ethylene glycol) standards (Scientific Polymer Products, Inc.). The physical and chemical characteristics of the polymers are given in Table 1.

Complex Fluid Preparation. All solutions were prepared at ambient temperature. Stock solutions of each polymer, LM200, PAMPS, PA90Dod, or PA80Dod (10 g L^{-1}), were prepared by dissolving each polymer in water over a period of 12 h to allow complete hydration and swelling. The stock solutions were then gently stirred for 24 h and allowed to equilibrate without stirring for another 24 h before use. Mixed solutions were prepared from weighed aliquots of stock solutions keeping constant the total polymer concentration (10 g L^{-1}), but varying the relative amounts of polyanion and polycation. The ionic strength of the mixed fluids was not adjusted. It varied depending on the ratio between the two components. Mixed solutions were stirred for 48 h, adjusting the stirring speed to the highest setting possible for each sample without forming foam or bubbles. This speed varied, depending on the viscosity of the mixed solutions. Finally, the samples were allowed to stand at room temperature in the dark for 24 h before analysis. Their appearance was recorded to construct a phase map. No attempt was made to determine the exact positions for the phase boundaries of the phase separation region, due to the prohibitively large number of samples that would be required for each LM200/polyanion system. The homogeneous mixtures were then subjected to rheological measurements.

The ratio between the two components is expressed as the weight fraction of polyanion (f_{P-}) in the sample (eq 1), where W_{P-} and W_{P+} are the weights of polyanion (PAMPS, PA90Dod, or PA80Dod) and LM200 stock solutions, respectively, used to prepare the mixed solution. The ratio between the two components is expressed also in terms of charge concentration ratios (c_-/c_+ or c_+/c_-), where c_- is the molar concentration of negative charges contributed by the polyanion and c_+ is the molar concentration of cationic charges contributed by LM200. Charges from the counterions of polymers (Cl$^-$ for LM200 and Na$^+$ for polyanions) are not considered. The charge concentration ratio c_-/c_+ is used ($0 \leq c_-/c_+ \leq 1$) to define mixtures where the polycation is the major component (polyanion-poor mixture, region I) while the charge concentration ratio c_+/c_- is used ($1 \geq c_+/c_- \geq 0$) to describe polyanion-rich mixtures (region II).

$$f_{P-} = \frac{W_{P-}}{W_{P-} + W_{P+}} \tag{1}$$

Rheological Measurements. Rheological measurements were performed at 25 °C with a ReoLogica Stress Tech controlled stress rheometer, equipped with a NESLAB water circulator to control the temperature within ±0.1 °C. A concentric cylindrical measurement system (bob and cup with a diameter of 25 mm) was used for all measurements. Each sample was loaded into the cell with extreme care to prevent the formation of air bubbles or foam and was allowed to rest for 15 min before measurement. The sample was covered to prevent slow evaporation of water over the long measurement period (ca. 6 h). The rheometer was programmed to determine the shear viscosity (η) with applied shear rate ($\dot{\gamma}$) ranging between 0.01 and 785 s^{-1}. Each scan started at low shear rate (0.01 s^{-1}) with the shear rate increasing steadily toward higher values. Immediately after reaching the highest attainable shear rate for each sample, the measurement was resumed with decreasing shear rates. The time interval between steady shear viscosity measurements at each shear rate was set at 10 s for all samples. Oscillation stress sweep measurements, at a shear stress range between 1.25×10^{-2} and 1.00 Pa, were performed at various frequencies (0.01−10 Hz) to determine a suitable stress amplitude. Oscillatory shear measurements for most of the samples were conducted within the linear viscoelastic region, where the dynamic storage modulus (G') and loss modulus (G'') are independent of a common applied stress (0.3 Pa). A delay time of 10 s and an integration time of 1 s were employed for all oscillatory shear measurements over a frequency range of 0.001−10 Hz. All measurements were carried out three consecutive times, and the results were reproducible for all samples. The magnitude of dynamic complex viscosity ($|\eta^*|$) is related to G' and G'' and to the frequency (f) (eq 2) and is given at a low frequency of 0.001 Hz. The dynamic moduli, G' and G'', are presented at 1 Hz.

$$|\eta^*| = \frac{(G'^2 + G''^2)^{1/2}}{2\pi f} \tag{2}$$

Results and Discussion

Polymers and Phase Diagram of Their Aqueous Mixtures. The polycation LM200 is a weakly charged hydrophobically modified polysaccharide (Figure 1a), in which the hydrophobic substituent, an *n*-dodecyl chain, is linked to the polymer backbone via a dimethylammonium chloride group. The level of hydrophobic substitution and, consequently, the charge of LM200 are low (ca. 5 mol %).[15] In aqueous solutions of LM200, hydrophobic microdomains form via intra- and/or interpolymeric association of the dodecyl chains, and this, even in solutions of low polymer concentrations. The polyanions PA80Dod and PA90Dod, which are copolymers of *N*-*n*-dodecylmethacrylamide (DodMAm) and sodium 2-acrylamido-2-methylpropanesulfonate (AMPS) (Figure 1a), are inherently flexible and highly charged. In water they form compact unimolecular micelles, approximately 10 nm in diameter, held together via intrapolymeric hydrophobic association of the *n*-dodecyl substituents.[21] Unimolecular micelle formation predominates up to polymer concentrations of 10 g L^{-1}. The characteristics of the polymers and their aqueous solutions are given in Table 1.

Mixtures of oppositely charged polyelectrolytes were prepared, and three sample sets, LM200/PAMPS, LM200/PA90Dod, and LM200/PA80Dod, were created, keeping the total polymer concentration constant (10 g L^{-1}), but varying f_{P-}, the polyanion-to-polycation ratio, expressed as the weight fraction of *polyanion* in each mixture (see Experimental Section). Immediate precipitation took place upon mixing well-equilibrated stock solutions of LM200 and the polyanion (PAMPS, PA90Dod, or PA80Dod). However, in a number of cases, phase-separated mixtures gradually became clear and homogeneous fluids after prolonged gentle stirring. Other mixtures, although homogeneous, remained turbid upon standing for over 1 week. In some mixtures two distinct phases, a precipitate and a clear supernatant, persisted after the mixtures had been stirred for 1 week or longer or heated to 80 °C for 2 days. Phase diagrams of the three mixed series were established by visual inspection of the mixtures equilibrated for 1 week (Figure 1b). Each diagram consists of three concentration domains: a phase-separated domain (shaded area) and two miscible fluid domains, region I and region II corresponding to the polyanion-poor mixtures and polyanion-rich mixtures, respectively. The breadth of the three domains is not the same in the three mixed systems. Mixtures of LM200 and PAMPS are immiscible over nearly the entire mixing range ($0.030 \leq f_{P-} \leq 0.950$).[24] The phase-separated domain narrows down significantly for the mixed systems of LM200/PA90Dod and LM200/PA80Dod, the latter presenting the widest miscibility range.

Dynamic Viscosity. The magnitude of dynamic complex viscosity of homogeneous mixed systems was measured at low frequency (0.001 Hz) and compared to that of single-component solutions. Turning our attention first to the polyanion-rich mixtures (region II), we observed that their viscosity is highly dependent on fluid composition and on the nature of the polyanion: the viscosity of LM200/PA80Dod mixtures increased from 2.42 mPa·s (PA80Dod) to 222.748 Pa·s ($f_{P-} = 0.425$), an enhancement of nearly 5 orders of magnitude, while in the case of LM200/PA90Dod, the viscosity increased from 2.85 mPa·s (PADod90) to 55.76 Pa·s ($f_{P-} = 0.625$),

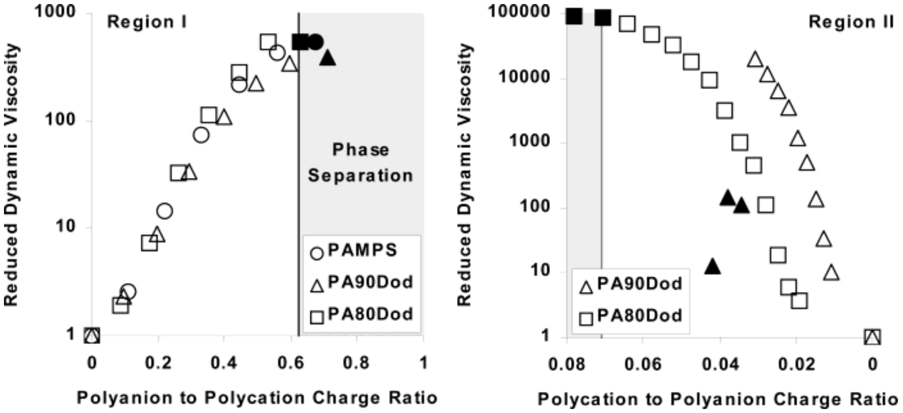

Figure 2. Variations of the magnitude of dynamic complex viscosity measured at 0.001 Hz relative to that of the single-component polymer solution (reduced dynamic complex viscosity) vs the ratio between the positive charge concentration (c_+), contributed from the polycation, and the negative charge concentration (c_-), contributed from the polyanion, for 10 g L^{-1} mixed systems of LM200/PAMPS (circle), LM200/PA90Dod (triangle), and LM200/PA80Dod (square). The open symbols represent clear homogeneous mixtures, and the full symbols represent turbid homogeneous mixtures.

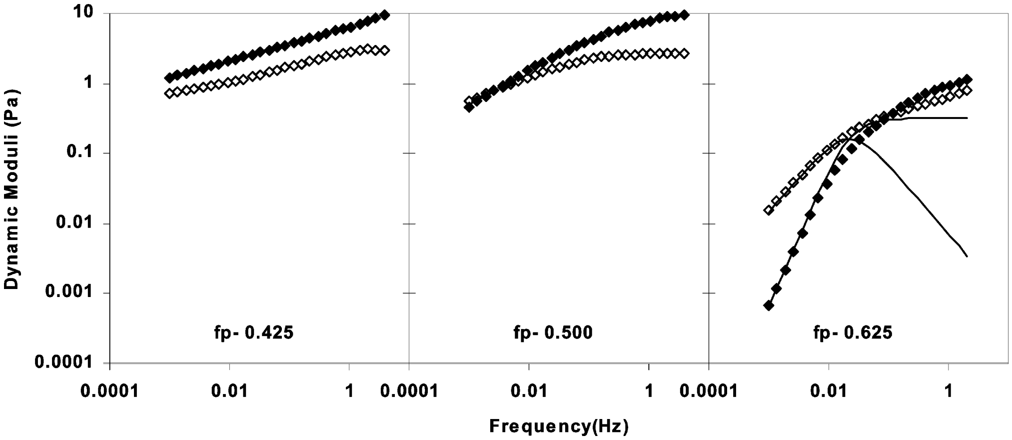

Figure 3. Effect of the mixture composition on the frequency dependence of the storage modulus (G', full symbols) and loss modulus (G'', open symbols) for 10 g L^{-1} aqueous LM200/PA80Dod mixtures with $f_{P-} = 0.425$, 0.500, and 0.625. The solid lines represent the best fit to the single mode Maxwell model.

or 4 orders of magnitude (Figure 2). A composition-dependent viscosity enhancement was also displayed by the polyanion-poor fluids (region I), but the effect was not as pronounced: the viscosity increased more than 500 times, compared to that of an aqueous LM200 solution (0.016 Pa•s), reaching values up to 8.61 Pa•s in the case of LM200/PA80Dod mixtures approaching phase separation ($f_{P-} = 0.035$) (Figure 2). The LM200/PA90Dod and LM200/PAMPS mixtures displayed similar trends.

The viscosity profiles of LM200/HM-PAMPS mixtures are similar to those reported by Kästner et al. in their study of the interactions of SDS and a hydrophobically modified cationic cellulose ether close in structure to the polymer LM200 investigated here.[17] They differ, however, from the profiles recorded for mixtures of HM-PAMPS and a cationic hydroxyethylcellulose ether, JR400, devoid of hydrophobic substituents. The JR400/HM-PAMPS fluids also exhibit a composition-dependent viscosity enhancement, but highly viscous fluids form in the *polyanion-poor* concentration domain (region I),[25] contrary to the fluids described here, which exhibit the highest viscosity in the *polyanion-rich* concentration domain (region II).

Properties of Mixed Systems under Oscillatory Shear. a. Polyanion-Rich Mixtures (Region II). The storage modulus (G') and the loss modulus (G'') of several homogeneous polyanion-rich samples were measured as a function of the frequency of applied oscillatory shear. The frequency dependence of G' and G'' of three mixed LM200/PA80Dod fluids subjected to shear are presented in Figure 3. The curves exhibit striking differences. The LM200/PA80Dod mixture of lowest polyanion content ($f_{P-} = 0.425$) presents features typical of physical gels:[26] (i) the storage modulus dominates the loss modulus over the entire frequency range (0.001–10 Hz), with no crossover within the frequency range studied; (ii) both G' and G'' follow a power law in frequency of nearly identical exponent ($G' \sim G'' \sim \omega^n$); (iii) the phase angle (δ) remained independent of frequency over the entire range. The gel characteristics of mixed systems fade as the polyanion content increases. For example, the LM200/PA80Dod of $f_{P-} = 0.50$ is viscoelastic, as indicated by the frequency profile (Figure 3, middle section) which displays a crossover of the G' and G'' profiles at low frequencies. The crossover frequency shifts to higher values as the polyanion content of the fluid increases, as shown in the profile recorded for a LM200/PA80Dod mixture of $f_{P-} = 0.625$ (Figure 3). In summary, polyanion-rich mixtures of LM200/PA80Dod behave as elastic gels for compositions of $0.425 \le f_{P-} \le 0.475$; they are viscoelastic fluids at moderate polyanion content $0.500 \le f_{P-} \le 0.650$ and viscous fluids when f_{P-} exceeds 0.675. We attempted

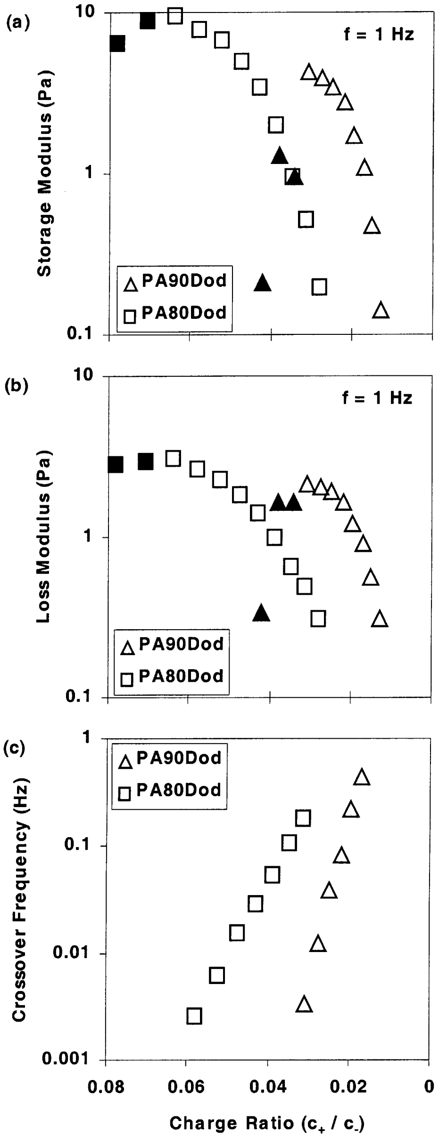

Figure 4. Mixture composition dependence of the dynamic moduli (G' and G''), measured at 1 Hz, and the crossover frequency of the G' and G'' curves, for 10 g L^{-1} mixed systems of LM200/PA90Dod (triangle) and LM200/PA80Dod (square). The open symbols represent clear homogeneous mixtures, and the full symbols represent turbid homogeneous mixtures.

to fit the frequency dependence of the dynamic moduli of the mixtures to the single mode Maxwell model,[27] but significant deviations between experimental and calculated values were detected for frequencies well below the crossover frequency (Figure 3). Moreover, the calculated and experimental crossover frequencies did not coincide, arguing against the existence of a single relaxation process. Measurements carried out with LM200/PA90Dod mixed samples revealed similar trends. Mixtures of high polyanion content were viscous fluids. Mixtures of $0.625 \leq f_{P-} \leq 0.750$ were viscoelastic. None of the examined fluids behave as gels, however.

To gain another view on the system, the values of G' and G'' measured at constant frequency (1 Hz) were recorded as a function of the charge ratio c_+/c_- for mixtures of LM200 with either PA80Dod or PA90Dod (Figure 4). Several trends became apparent. First, both $G'$and G'' decrease with increasing polyanion content (or decreasing c_+/c_- ratio). The drop in G' is much steeper than that of G'', indicating an increasingly dominant viscous response. Second, mixtures of identical charge ratio, but containing either PA90Dod or PA80Dod, have different dynamic moduli. Third, the maximum G'' values recorded for the two mixed systems are of the same order of magnitude, 2.13 and 3.08 Pa·s, respectively, but the maximum G' value is significantly smaller for the LM200/PA90Dod mixtures (4.24 Pa·s) compared to the LM200/PA80Dod mixtures (9.48 Pa·s). This result corroborates the fact that LM200/PA90Dod mixtures do not undergo physical gelation. Also shown in Figure 4 are the crossover frequency of the G' and G'' profiles obtained experimentally for the LM200/HM-PAMPS mixtures. In both sets of mixed systems, the crossover frequencies increase as the polyanion content increases at the expense of the polycation content. The decrease of the dynamic moduli, G' and G'', and the increase of the crossover frequency, with decreasing polycation content can be taken as an indication of the existence of a transient interpolyelectrolyte network in polyanion-rich mixtures and of its progressive breakdown as the mixtures are depleted of polycation. The interactions at play in the polyanion-rich fluids are represented pictorially in Figure 5. By analogy with polymer/surfactant systems, we propose that two types of “mixed micelles” are implied in the control of the fluid rheology, namely polyanion-mediated cross-linking points where a HM-PAMPS unimer entraps hydrophobic substituents from several polycation chains, and mixed micelles consisting of a HM-PAMPS chain capturing one or more hydrophobic substituent linked to a single polycation chain.

Physical gelation similar to that displayed by several mixed LM200/PA80Dod systems was observed by Hoffmann et al. in their rheological study of the interactions between anionic surfactants and a hydrophobically modified cationic polysaccharide of structure comparable to that of LM200, but of higher molecular weight (MW = 9.5×10^5 g mol^{-1}).[28] Such elastic behavior, however, was not detected in two apparently similar cases, namely mixtures of LM200 and either anionic surfactant micelles[12] or a hydrophobically modified polyacrylate with low hydrophobic substitution (3 mol %).[19] The latter fluids displayed properties similar to those of mixed LM200/PA90Dod, which carry fewer dodecyl chains than PA80Dod.

b. Polyanion-Poor Mixtures (Region I). The frequency dependence of G' and G'' of polyanion-poor mixtures was determined next, and several profiles are displayed in Figure 6 together with that of an aqueous LM200 solution. The LM200 solution showed typical Newtonian behavior, with $G' \sim \omega^2$, $G'' \sim \omega^1$, and $G'' > G'$ over the entire frequency domain studied (0.001−10 Hz). Mixed solutions, however, became non-Newtonian fluids when the polyanion content exceeded $f_{P-} = 0.015$. A crossover frequency was detected with mixtures of $f_{P-} \geq 0.02$, and as the polyanion content increased further, the crossover frequency shifted to lower values. It dropped to a value of ca. 0.1 Hz in the case of LM200/PA80Dod mixtures of $f_{P-} = 0.030$, a mixture that behaved as a viscous fluid ($G'' > G'$) at low frequencies, but became elastic ($G' > G''$) at frequencies higher than the crossover frequency ($G' = G''$). Similar trends were also recorded with LM200/PA90Dod and LM200/PAMPS mixtures.

Attempts were made to determine the time constant related to the relaxation process of the viscoelastic fluids

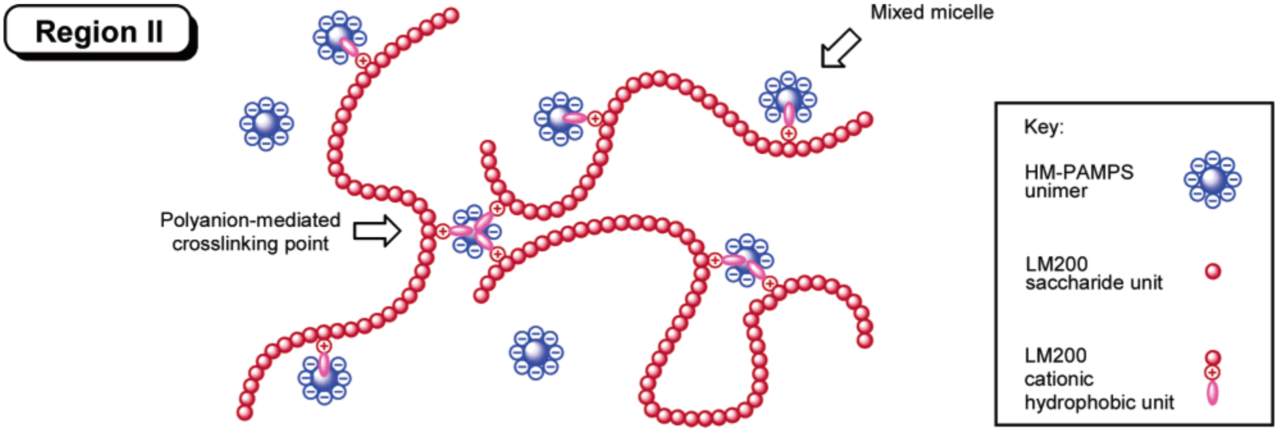

Figure 5. Conceptual model of the ordered structure formed by LM200 and HM-PAMPS in clear homogeneous fluids (region II). Anchoring of the alkyl chains of LM200 into the hydrophobic microdomains of HM-PAMPS via synergistic electrostatic and hydrophobic interactions creates polyanion-mediated cross-linking junctions.

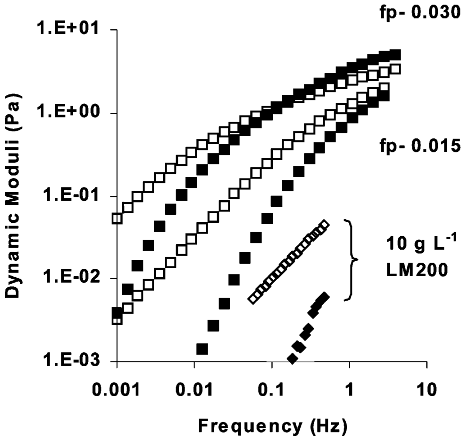

Figure 6. Storage modulus (G', full symbols) and loss modulus (G'', open symbols) as a function of frequency for a 10 g L^{-1} aqueous LM200 solution (diamonds) and for 10 g L^{-1} aqueous LM200/PA80Dod mixtures (squares) with $f_{P-} = 0.030$ and 0.015.

by fitting the profiles of G' and G'' to the single-mode Maxwell model. The viscoelastic fluids showed Maxwellian behavior at low frequencies ($G' \sim \omega^2$ and $G'' \sim \omega^1$). However, the crossover frequencies calculated from the Maxwell equations were consistently lower than the corresponding experimental values, an indication that several relaxation processes of broad relaxation times distribution take place in the mixed systems. The ineptness of Maxwell model to simulate the rheology of these fluids should not surprise, as it was observed also in previous related studies of associating polymer aqueous solutions,[29] aqueous mixtures of associating polymers,[30] associating polymer/surfactant aqueous mixtures,[31] and polycation/polyanion aqueous mixtures.

The data recorded with polyanion-poor mixtures were analyzed at a single frequency (1 Hz) as a function of composition, expressed in this case as the ratio c_-/c_+ of polyanion to polycation concentrations. The crossover frequency decreased gradually with increasing polyanion content (Figure 7, bottom), signaling the formation of a transient network between LM200 and polyanion chains. As the polyanion content increases, the cross-linking density grows and the interchain junctions have longer lifetimes. Supporting evidence for network formation was gathered from an examination of the G' and G'' dependence upon mixture composition at 1 Hz (Figure 7, top frames). Both moduli increased sharply

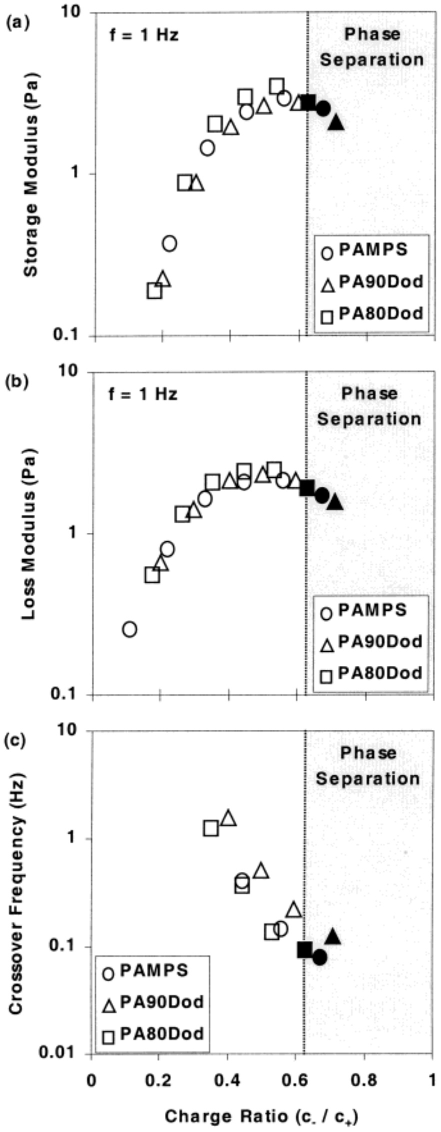

Figure 7. Mixture composition dependence of the dynamic moduli (G' and G''), measured at 1 Hz, and the crossover frequency of the G' and G'' curves, for 10 g L^{-1} mixed systems of LM200/PAMPS (circle), LM200/PA90Dod (triangle), and LM200/PA80Dod (square). The open symbols represent clear homogeneous mixtures, and the full symbols represent turbid homogeneous mixtures.

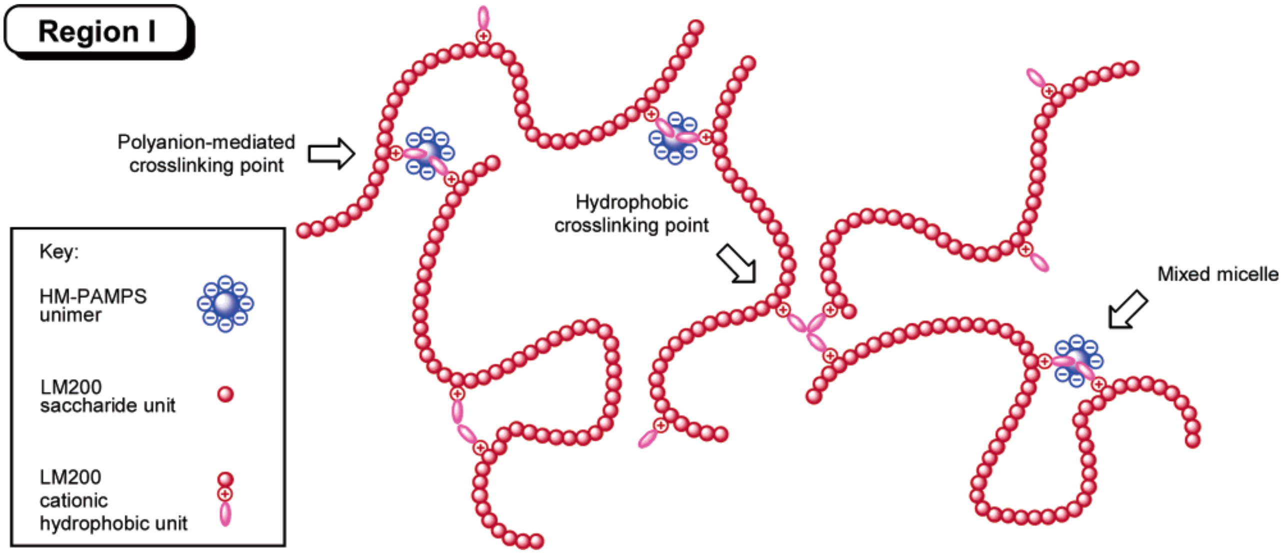

Figure 8. Conceptual model of the ordered structure formed by LM200 and HM-PAMPS in clear homogeneous fluids (region I). Anchoring of the alkyl chains of LM200 into the hydrophobic microdomains of HM-PAMPS via synergistic electrostatic and hydrophobic interactions creates polyanion-mediated cross-linking junctions.

with increasing polyanion content in the fluids. The value of G' increased faster than G'', passing through a maximum value for fluids of composition close to that corresponding to macroscopic phase separation. The parallel trends of the fluid composition dependence of G', G'', and the crossover frequency in the three series of mixed fluids is further evidence that the rheology of all polyanion-poor mixtures is driven by electrostatic interpolymeric interactions and that hydrophobic associations play only a minor part, in sharp contrast to the situation described above for polyanion-rich fluids. A conceptual representation of the network formed in polyanion-poor fluids is shown in Figure 8, where we depict both hydrophobic cross-linking points between two or more polycation chains and mixed micelles, where a HM-PAMPS unimer solubilizes several hydrophobic groups linked to the polycation. The latter assemblies may act as cross-linking points, if the entrapped hydrophobic groups are linked to separate polycation chains.

Properties of Mixed Systems under Steady Shear. a. Polyanion-Rich Mixtures (Region II). The viscosity profiles of several polyanion-rich viscous fluids under shear presented three regimes depending on the applied shear rate (Figure 9). At low shear rates, the viscosity was independent of shear rate (Newtonian regime). Beyond a critical shear rate ($\dot{\gamma}_{\rm crit}$), the viscosity increased sharply with shear rate (shear thickening regime). It reached a maximum value at a second critical shear rate ($\dot{\gamma}_{\rm cross}$) and dropped rapidly as higher shear rates were applied (shear thinning regime). All viscous fluids presented qualitatively the same three-regime viscosity profile, but the extent of shear thickening and the critical shear rate values depended on the mixture composition: increasing the polyanion content resulted in an increase of $\dot{\gamma}_{\rm crit}$ and $\dot{\gamma}_{\rm cross}$ and in a decrease of the shear thickening effect.

The elastic and viscoelastic polyanion-rich mixtures ($0.625 \leq f_{\rm P-} \leq 0.750$ for the LM200/PA90Dod mixtures and $0.425 \leq f_{\rm P-} \leq 0.650$ for the LM200/PA80Dod mixtures) exhibited only shear thinning: their viscosity gradually decreased over the entire shear rate range. This behavior is different from that of the single-component solutions (LM200, PA90Dod, or PA80Dod, 10 g L^{-1}) which are Newtonian fluids over a broad shear rate range (0.01−200 s^{-1}) and become weakly shear thickening under very high shear.

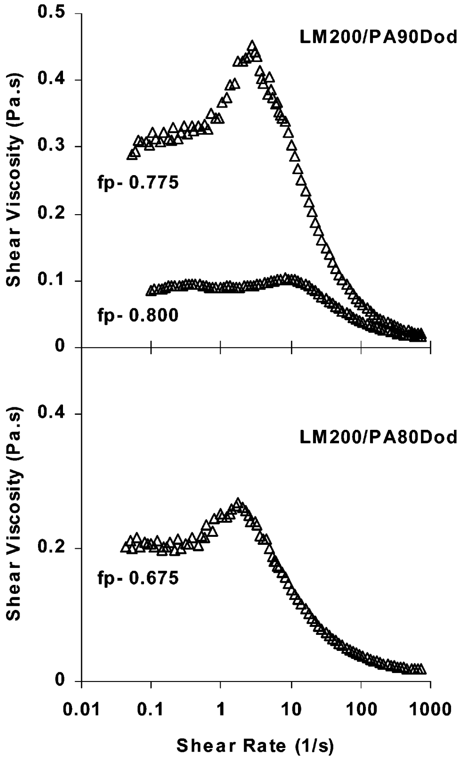

Figure 9. Steady shear viscosity vs shear rate for 10 g L^{-1} aqueous LM200/PA90Dod mixtures with $f_{\rm P-} = 0.775$ and 0.800 and for a 10 g L^{-1} aqueous LM200/PA80Dod mixture with $f_{\rm P-} = 0.675$.

We examined next the stress dependence at various frequencies of the storage and loss moduli, G' and G'', for mixtures that exhibit shear thickening behavior, such as the LM200/PA80Dod mixture of $f_{\rm P-} = 0.675$ (Figure 10). Both moduli were sensitive to the value of the applied stress: they remained constant at low stress (<0.10 Pa); they increased under higher stress, went through a maximum value, before decreasing under still higher stress. Assuming that interpolymeric associa-

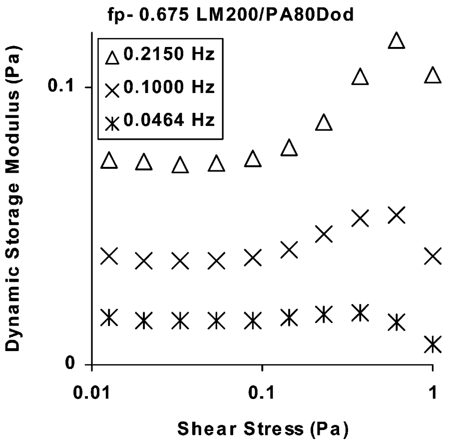

Figure 10. Shear stress dependence of the storage modulus (G') at various frequencies for a 10 g L^{-1} aqueous LM200/PA80Dod mixture with $f_{P-} = 0.675$.

tions depicted in Figure 5 take place within the polyanion-rich fluids at rest, the shear thickening effects signal, on a macroscopic scale, the shear-induced conversion from intrachain to interchain polymer associations,[32] leading to a transient cross-linked network of enhanced viscosity (Figure 11). Shear thickening behavior in aqueous solution has been reported for various associating polymers, such as telechelic polymers,[33] microblocky terpolymers,[34] and random copolymers.[35] It should be noted that mixed aqueous solutions of LM200 and a hydrophobically modified polyacrylate with low degree of substitution (3 mol %) did not undergo shear thickening but were detected in aqueous solutions of LM200 and anionic surfactant micelles.

b. Polyanion-Poor Mixtures (Region I). Polyanion-poor mixtures did not exhibit shear thickening. They all behaved as shear thinning fluids under steady shear conditions, and the onset of shear thinning shifted to lower shear rates with increasing polyanion content. The viscosity profiles of mixed solutions displayed a Newtonian regime at low shear rates (Figure 12). The dynamic viscosity profiles had the same overall shape as the shear viscosity profiles, but at high oscillatory frequencies η was higher than η^*. The invalidity of the Cox−Merz rule,[36] which states that η and η^* should coincide at identical values of shear rate and oscillatory frequency, suggests the existence of long-range interactions and confirms the presence of aggregates connected via a network, as reported in previous studies of polymer/surfactant,[37] cationic polymer/anionic surfactant,[38] or polycation/polyanion systems.

Conclusions

The interactions between a semiflexible hydrophobically modified polycation and amphiphilic polyanions forming unimolecular micelles have been monitored under conditions where the total polymer concentration is kept constant, but the relative amounts of polyanion and polycation are varied systematically. As the polyanion content gradually increases at the expense of the polycation, the system undergoes a sequence of states: homogeneous polycation solution → homogeneous viscoelastic and shear thinning polyanion-poor fluids → two-phase system → homogeneous polyanion-rich fluids which, depending on their compositions, may be either gels or viscous/viscoelastic fluids → homogeneous polyanion solution. The marked composition-dependent changes in macroscopic behavior reflect subtle changes in electrostatic and hydrophobic interactions between the polyanion and the polycation, which we have interpreted in terms of qualitative models depicted in Figures 5, 8, and 11. An interpolyelectrolyte network

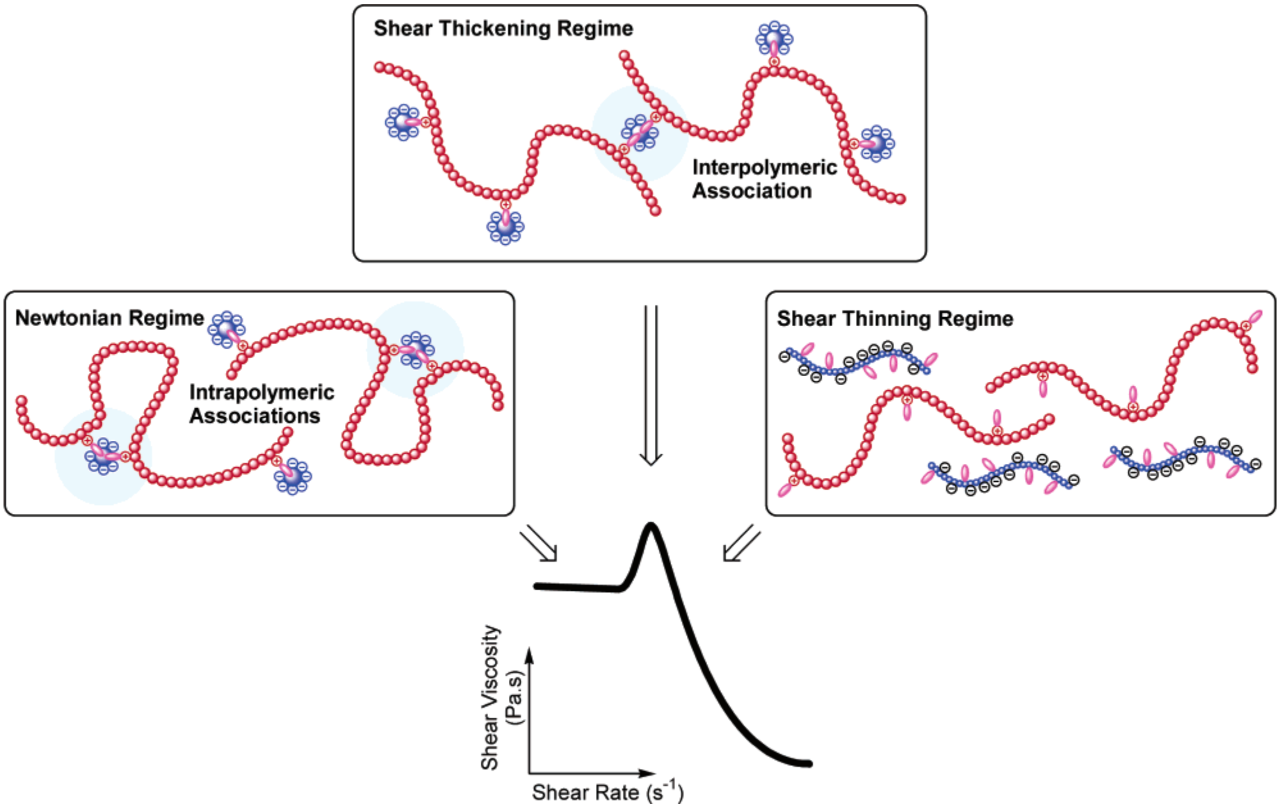

Figure 11. Schematic representation of the shear-induced reversible transformation between intrapolymeric and interpolymeric cross-linking junctions for the region II fluids displaying a three-regime shear viscosity profile.

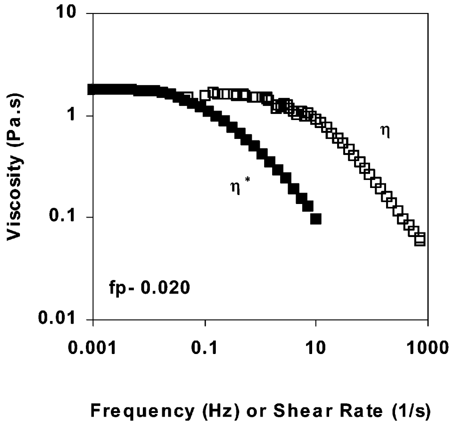

Figure 12. Steady shear viscosity (η) and dynamic complex viscosity (η^*) as a function of shear rate or frequency for 10 g L^{-1} aqueous LM200/PA80Dod mixture with $f_{P-} = 0.020$.

forms in all mixed fluids via the creation of mixed micelles consisting of polyanion unimers entrapping one or several dodecyl groups linked to the polycation. In polyanion-poor mixtures, the electrostatic forces prevail. Hydrophobic interactions are enhanced in polyanion-rich mixtures, which exhibit different rheological properties depending on the hydrophobicity of the polyanions. A current study by fluorescence spectroscopy of mixed systems consisting of LM200 and a dye-labeled HM-PAMPS, which confirms that the HM-PAMPS unimers are disrupted without intermingling of polyanion unimers, provides further support to the network model proposed.[39]

The complexation, phase separation, and redissolution phenomena exhibited by LM200/HM-PAMPS mixed fluids may serve as examples of polyelectrolyte/macroion systems recently studied by Skepö and Linse by means of Monte Carlo simulations,[9] with LM200 as semiflexible polyelectrolyte and HM-PAMPS unimers as macroions. From a practical perspective we anticipate that aqueous LM200/HM-PAMPS fluids may serve as smart rheology modifiers, providing a wide gamut of macroscopic properties by fine-tuning the fluid composition with no change of the individual components.

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