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A Rheological Evaluation of the Interactions in Water between a Cationic Cellulose Ether and Sodium Poly(2-acrylamido-2-methylpropanesulfonates)

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ABSTRACT: The rheology of solutions of a cationic cellulose ether (JR400) and either sodium poly(2-acrylamido-2-methylpropanesulfonate) (PAMPS) or a copolymer of sodium 2-acrylamido-2-methylpropanesulfonate and *N-n*-dodecylmethacrylamide (PAMPS-Dod) has been examined over a wide composition range in the semidilute regime (10 g L^{-1}) by steady shear and time-dependent steady shear measurements. Miscible combinations of pairs of oppositely charged polyelectrolytes form in two composition domains: (1) a polyanion-poor region which exhibits shear thinning characteristics and (2) a polyanion-rich region which presents Newtonian behavior at low shear rates and, as the shear rate is increased, passes through a shear-thickening region before exhibiting a sharp decrease in viscosity. The latter fluids exhibit significant thixotropy, which is shown to depend on the delay time between measurements and on the composition of the fluids. Models based on electrostatically driven interactions between two oppositely charged polyelectrolytes poorly matched in terms of size, rigidity, and charge density are proposed to account for the unusual rheological behavior of the polyelectrolyte complexes under study.

Introduction

Mixing oppositely charged polyelectrolytes results in the formation of interpolyelectrolyte complexes (PECs), a class of materials of considerable interest because of their potential use as polymeric reagents, membranes, actuators in biotechnology, and flocculants in various industrial and environmental processes.[1−4] These macromolecular assemblies are stabilized primarily by interpolymeric salt bonds, but other interactions, such as hydrogen bonding, hydrophobic interactions, charge transfer complexation, and van der Waals forces, can participate significantly in the formation of PECs and contribute to their stability.[5,6] Strongly ionized polyelectrolytes, such as poly(sodium styrenesulfonate) and poly(vinylbenzyltrimethylammonium chloride), even in dilute aqueous solutions, form water-insoluble complexes which contain equivalent quantities of ionizable groups of each type. This property, originally reported by Michaels and co-workers,[7] has led to the development of semipermeable membranes used in ultrafiltration and hemodialysis.[8]

A large number of oppositely charged polymers undergo complexation, but it can turn out to be challenging to form stoichiometric complexes. In fact, incorporation of a larger than stoichiometric proportion of one component often enhances the solubility of the complex and precipitation occurs only in a narrow composition domain near the equivalence point. Outside the immiscibility range, mixed oppositely charged polyelectrolytes form clear aqueous fluids imparted with unusual rheological properties,[9] taken to great advantage for developing “rheologically smart” fluids or carriers for the release of drugs.[10]

There has been a series of recent publications on the properties of polyelectrolyte complexes of natural polysaccharides, such as complexes of chitosan hydrochloride and dextran sulfate,[11] polygalacturonic acid,[12] or poly(acrylic acid).[13] Rodriguez et al. reported recently a rheological study of complexes of cationic cellulose ethers and Carbopol, a commercial poly(carboxylic acid).[14] They demonstrated that the rheology of cationic cellulose ethers can be modulated by addition of small amounts of an oppositely charged polymer, leading the way to the design of novel pH-sensitive fluids. Systems based on water-soluble cellulose derivatives present great commercial interest and are used in many industrial fluids. Because of their biocompatibility, they have found applications as thickeners in food and cosmetic products, where they are used in conjunction with other additives.[15]

Mixtures of cationic cellulose ether derivatives and oppositely charged surfactants have been investigated extensively, ever since Goddard reported that the addition of a surfactant, such as sodium dodecyl sulfate (SDS), to aqueous cationic cellulose ethers leads to a very large increase in solution viscosity or, in some cases, to phase separation.[16] Further studies have indicated that fluids containing cationic cellulose ethers and anionic surfactants systems are viscoelastic in given situations and exhibit shear thinning properties that depend in a subtle way on the molecular weight of the polymer and on the architecture of the surfactant.[17,18] The surfactant-triggered changes in viscosity of polyelectrolyte solutions have been attributed either to electrostatic interactions between the charged groups or to hydrophobic interactions between the nonpolar tails of the surfactant and hydrophobic patches along the polysaccharide backbone, or to interplay of both mechanisms.[19] Another factor that may contribute to the macroscopic rheology of mixed polymer/surfactant

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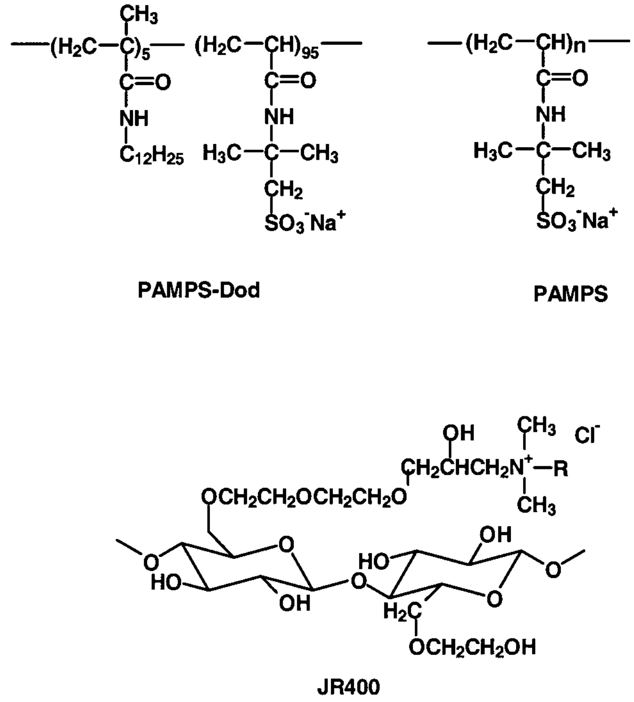

Figure 1. Structures of the polymers used in this study.

systems is related to the dynamic nature of surfactant micelles and of the surfactant clusters decorating the polymer backbone. The effect of the exchange of individual surfactant molecules between micelles and clusters, while difficult to assess, cannot be prevented, except by replacing the surfactant micelles by polymeric micelles.

Intrigued by the possibility of using polymeric micelles as surfactant substitutes in fluids containing cationic cellulose ethers, we undertook an investigation of a PEC system consisting of a cationic derivative of hydroxyethylcellulose ether, JR400, and a copolymer of sodium 2-acrylamido-2-methylpropanesulfonate and *N*-dodecylmethacrylamide (PAMPS-Dod), which carries ~5 mol % of *n*-dodecyl moieties randomly distributed along the chain (Figure 1). The hydrophobically modified polyanion, PAMPS-Dod, is known to associate in water, forming unimers ~6 nm in diameter as well as larger aggregates approximately 120 nm in diameter that consist of a small number of assembled chains.[20] Thus, conceptually, the JR400/PAMPS-Dod system presents similarities with a system consisting of JR400 and oppositely charged surfactant micelles.

The study was designed to probe the interactions between the two oppositely charged polymers in as broad a concentration spectrum as possible on the basis of steady shear experiments and time-dependent steady shear measurements. The total polymer concentration was the same in all samples, but the composition of the fluids varied from JR400-rich to PAMPS-Dod-rich mixtures. It turned out that, depending on the relative amounts of the two components, the fluids exhibited strikingly different rheological properties, displaying shear thinning behavior in the case of polyanion-poor mixtures but shear thickening characteristics in the case of polyanion-rich fluids. Control measurements were performed with mixtures of JR400 and the unmodified polyanion, sodium poly(2-acrylamido-2-methylpropanesulfonate) (PAMPS). The results of experiments carried out with JR400/PAMPS-Dod and JR400/PAMPS systems of varying compositions are presented here and compared in order to assess the relative importance of hydrophobic and electrostatic forces in controlling the rheology of these PEC-based fluids.

Experimental Section

Materials. Water was purified with a Millipore Milli-Q System. The polycation JR400 was obtained from Amerchol Corporation (Union Carbide) and was used as received. JR400 has a molecular weight of approximately 5×10^5 Da[21] and a positive charge content of 27 mol %, corresponding to 27 ammonium groups for every 100 glucose units.[22] The polyanions PAMPS and PAMPS-Dod were prepared as described earlier.[23,24] PAMPS-Dod has a *n*-dodecyl group content of 5 mol %. The molecular weights of PAMPS and PAMPS-Dod 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).

Fluids for Rheology Measurements. All solutions were prepared at ambient temperature. Stock solutions of each polymer, JR400, PAMPS, or PAMPS-Dod (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 stirred gently 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. Their ionic strength was not adjusted. They were stirred for 48 h. The stirring speed was adjusted for each sample to the highest setting possible without forming any bubbles. This speed varied, depending on the viscosity of the mixture. Finally, the mixtures were allowed to stand at ambient temperature for 24 h. Their appearance was recorded to construct a phase map. These 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 mixture (eq 1), where W_{p^-} and W_{p^+} are the weights of polyanion (PAMPS or PAMPS-Dod) and JR400 stock solutions, respectively. The ratio between the two components in each mixture is expressed also in terms of charge concentration ratios (c_-/c_+ or c_+/c_-), where c_- is the molal concentration of negative charges contributed by the polyanion and c_+ is the molal concentration of cationic charges contributed by JR400.

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

Rheological Measurements. Rheological measurements were performed with a ReoLogica StressTech controlled stress rheometer using a concentric cylindrical measurement system (bob and cup, 25 mm diameter). The temperature of the sample was set at 25.0 ± 0.1 °C. It was controlled with an external NESLAB water circulator. Samples were loaded into the cell with extreme care to prevent the formation of air bubbles. They were allowed to rest for 15 min before measurement. The rheometer was set automatically to determine the shear viscosity (η) with an applied shear rate ($\dot{\gamma}$) ranging between 0.01 and 785 s^{-1}. Scans were performed from low shear rate (0.01 s) to high shear rate values. Immediately after reaching the highest shear rate attainable for a given sample, the measurement was continued from high to low shear rate values. The time interval (Δt) between viscosity measurement at each shear rate was 10 s, unless otherwise stated.

Results and Discussion

Polymers and Their Miscibility. The polysaccharide JR400 (Figure 1) is a cationic water-soluble derivative of cellulose ether, obtained by reaction of (2,3-epoxypropyl)trimethylammonium chloride with poly[β-D-1,4-pyranoglucose-*g*-oxyethylene].[25] It is a rather rigid

Table 1. Physical and Structural Parameters of the Polymers Investigated

polymer	mol wt	mean contour length (nm)	critical overlap conc c^* (g L^{-1})	degree of modification	charge conc in a 10 g L^{-1} solution (mol L^{-1})
JR400	500 000[a]	~1000[a]	4.0	27 mol % (Me_3N^+-R)[a]	10×10^{-3}
PAMPS-Dod	53 000[b]	57		5 mol % (n-$C_{12}H_{25}$)[d]	41×10^{-3}
PAMPS	71 000[c]	77			44×10^{-3}

[a] From ref 23. [b] From GPC (see Experimental Section). [c] From ref 25. [d] From ^{1}H NMR spectrum; see ref 21.

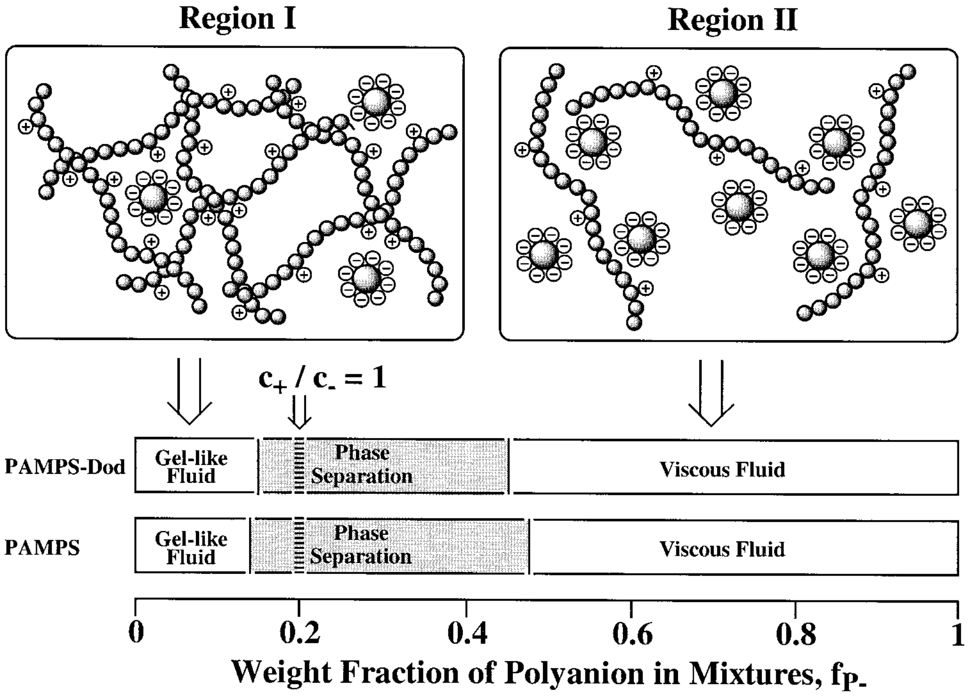

Figure 2. Phase maps of aqueous mixtures of JR400/PAMPS-Dod and JR400/PAMPS with a schematic representation of the microstructure of the clear homogeneous fluids in regions I and II. Widths of phase boundaries: $f_{P^-} \pm 0.05$ (region I) and $f_{P^-} \pm 0.025$ (region II).

polymer,[26] with a mean contour length of ~1000 nm.[22] It has on average 500 charges per chain with a mean intercharge distance of ~2 nm.[22] In contrast, PAMPS and PAMPS-Dod are flexible highly charged polyelectrolytes. In solution, in absence of shear, they adopt a coiled conformation, and, in the case of PAMPS-Dod, form micelles. Note that the fully extended PAMPS or PAMPS-Dod is much shorter than JR400, as judged in terms of contour length. The physical properties of the polymers and their aqueous solutions are listed in Table 1.

In all our measurements we kept the total polymer concentration constant. We chose a concentration of 10 g L^{-1}, a value higher than the critical concentration c^* of the individual components. Also, great care was taken to prepare all the solutions under identical conditions. They were obtained from well-equilibrated stock solutions of each polymer which were mixed and stirred at room temperature (see Experimental Section). Phase separation took place immediately upon mixing, but after prolonged gentle stirring, several mixed samples became clear and homogeneous fluids. After allowing sufficient time for equilibration, the physical appearance of the fluids was examined visually and recorded. Phase maps of the JR400/PAMPS and JR400/PAMPS-Dod systems are nearly identical (Figure 2). The miscible phases fall in two composition domains defined in terms of polyanion concentration as region I, a domain of polyanion-poor mixtures, and region II, a domain of polyanion-rich mixtures. Mixtures in the intermediate domain consisted of two distinct phases, a precipitate and a clear supernatant, with no indication of dissolution after stirring for over 1 week. Several mixtures of composition near the phase boundaries were turbid but stayed homogeneous even upon prolonged standing.

While fluids in regions I and II have similar appearance to the naked eye, their microstructures are expected to be very different, as represented pictorially in Figure 2. The major component in samples of region I is JR400. The polycation is present in concentrations well above c^*; therefore, the JR400 chains are entangled. The highly charged polyanions, PAMPS or PAMPS-Dod, primarily interact with the polycation chains via electrostatic forces. Because of the high charge density and low concentration of the polyanion, it is likely that each polyanion chain will associate with several polycations, acting as a cross-linker and reinforcing the entanglements of the JR400 chains. In region II, the situation is quite different, as shown schematically in Figure 2. The polyanion gradually becomes the major component as one moves toward the right-hand side of the solubility map, while the polycation concentration decreases to the point where its concentration is well below c^*. Electrostatic association between the two components will occur, possibly resulting in the formation of some loose network, as a consequence of the large difference in size and charge density of the two interacting partners.

Dynamic Viscosity. The viscosity of all mixed fluids was higher than the viscosity of single component solutions, as shown in Figure 3, which presents dynamic viscosity values measured at a frequency of 0.001 Hz

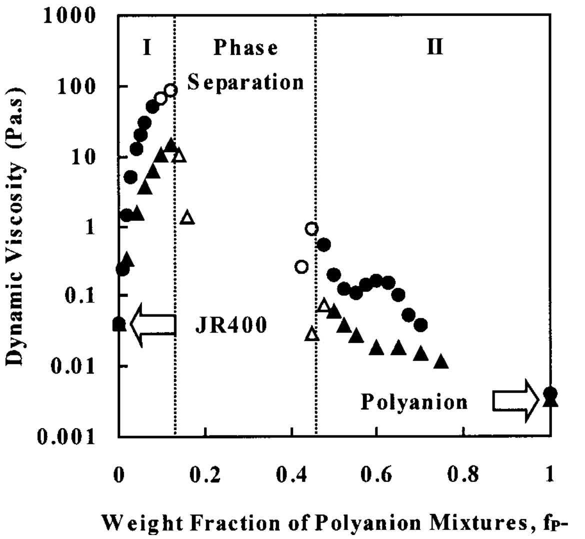

Figure 3. Plots of the dynamic viscosity η' measured at 0.001 Hz as a function of f_{P^-}, the weight fraction of PAMPS (triangle) or PAMPS-Dod (circle) in 10 g L^{-1} aqueous mixtures of JR400/PAMPS and JR400/PAMPS-Dod. The full symbols represent clear homogeneous mixtures, and the open symbols indicate turbid homogeneous mixtures.

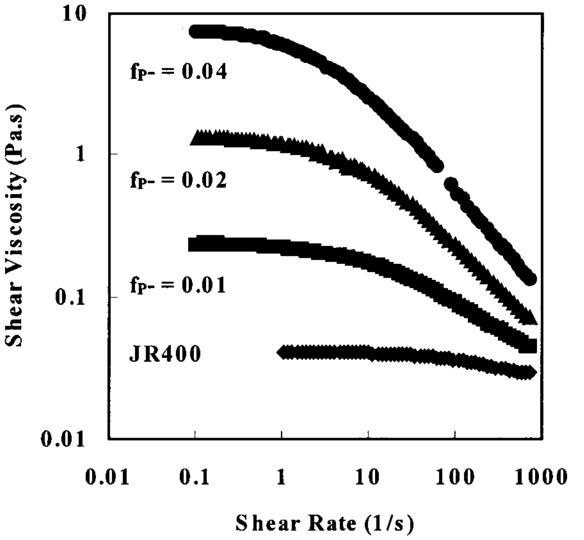

Figure 4. Steady shear viscosity as a function of shear rate for 10 g L^{-1} aqueous solutions of JR400/PAMPS-Dod mixtures with f_{P^-} 0.01, 0.02, and 0.04 and for a 10 g L^{-1} aqueous solution of JR400.

as a function of composition of JR400/PAMPS-Dod and JR400/PAMPS mixtures. The viscosity enhancement in mixed fluids was most pronounced for samples of region I. The viscosity increases from a value of 0.04 Pa·s recorded for JR400 (10 g L^{-1}) to nearly 87.8 Pa·s in JR400/PAMPS-Dod mixtures approaching phase separation. Note that, even though PAMPS does not carry any hydrophobic groups, it also acts as a viscosity enhancer when added in small amount to a JR400 solution. The magnitude of the mixed system viscosity is on the order of the viscosity of mixed aqueous solutions of JR400 and anionic surfactants.[16,18] For example, the viscosity of a 10 g L^{-1} JR400 solution containing sodium dodecyl sulfate (SDS) 1 mmol L^{-1} in concentration is of the order of 1 Pa·s.[18] In comparison, a solution JR30M, a cationic cellulose ether of higher molecular weight of identical concentration and surfactant content, has a viscosity of ~500 Pa·s.[18] The viscosity values of JR400/PAMPS-Dod and JR400/PAMPS fluids having a polyanion concentration of 1 mmol L^{-1} AMPS units (~0.2 g L^{-1} polymer) are 1.45 and 0.34 Pa·s, respectively. The qualitative agreement between viscosity values recorded with JR400/polyanions and JR400/anionic surfactant, but not with mixed solutions of anionic surfactants and the polymer polycation JR30M of higher molecular weight, may be coincidental. We prefer to take it as supporting evidence for the model depicted in Figure 2, which emphasizes the fact that the polyanions merely act as cross-linking points between cationic groups of JR400. The viscosity, which may be taken as a macroscopic reflection of the network structure, is controlled primarily by the concentration, charge, and molecular weight of the polyelectrolytes.

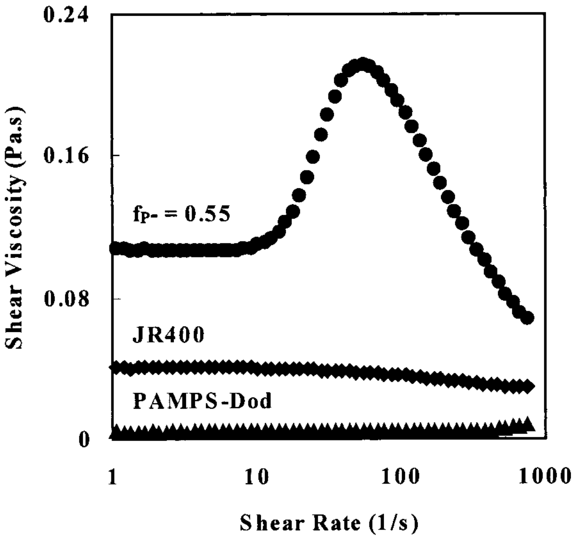

Figure 5. Steady shear viscosity as a function of shear rate for 10 g L^{-1} aqueous solutions of a JR400, PAMPS-Dod, and a JR400/PAMPS-Dod mixture with f_{P^-} 0.55.

Turning now to polyanion-rich homogeneous solutions of the JR400/PAMPS-Dod system (region II), the viscosity of all samples tested was enhanced by factors of 10−250, compared to that of PAMPS-Dod (0.004 Pa·s, 10 g L^{-1}). This modest viscosity enhancement may be taken as an indication that there exists a small number of connecting points between rigid polycation chains, presumably via polyanion chains adsorbed on JR400 via electrostatic bonds (Figure 2). The viscosity of JR400/PAMPS-Dod mixtures displayed a mild sensitivity to composition, decreasing with decreasing JR400 concentration. Mixed JR400/PAMPS systems also displayed a slight increase in viscosity, compared to the polyanion solution.

Shear-Dependent Viscosity Measurements. Region I: Shear Thinning Fluids. Shear rate-dependent viscosity profiles recorded with polyanion-poor fluids (region I) and a solution of JR400 are presented in Figure 4. As discussed previously (see Figure 3), the zero shear viscosity of mixed systems is enhanced by several orders of magnitude, compared to the viscosity of a JR400 solution, and the viscosity enhancement increases with increasing polyanion concentration. This pattern was taken as an indication of an increasingly higher level of polyanion cross-links between entangled polycation chains (Figure 2). The viscosity profiles of all polyanion-poor mixed systems display shear thinning characteristics with no evidence of shear thickening:

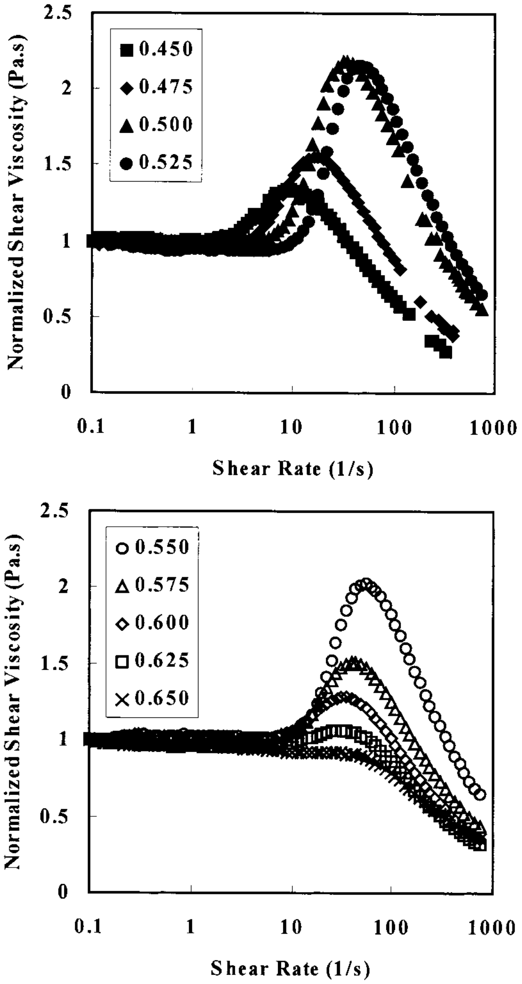

Figure 6. Normalized shear viscosity as a function of shear rate for 10 g L^{-1} aqueous solutions of JR400/PAMPS-Dod mixtures of various compositions.

below a critical shear rate (γ_{thin}), viscosity is independent of shear rate (Newtonian regime), and above γ_{thin}, it rapidly decreases with increasing shear rate. The value of γ_{thin} shows a marked dependence on the fluid composition, decreasing with increasing polyanion content. In all mixed systems, γ_{thin} is lower than the value recorded for a JR400 solution, which is weakly shear thinning but only under high shear rate. The data presented in Figure 4 have been fitted to the Carreau–Yasuda model,[27] which allows the determination of the relaxation time λ, equal to the inverse of the critical shear rate γ_{thin}. The relaxation times of the fluids increase with increasing polyanion concentration from 0.02 s ($f_{\mathrm{P}^-} = 0$) to 0.80 s ($f_{\mathrm{P}^-} = 0.08$), reflecting an increase in the size and/or number of cross-linking points between polymer chains as more polyanions are added to the system.[28]

Region II: Shear-Thickening Fluids. Turning to region II, Figure 5 shows a viscosity profile recorded for a JR400/PAMPS-Dod aqueous mixture with $f_{\mathrm{P}^-} = 0.550$. Three regimes can be identified in the shear response of the mixed fluid. Below a characteristic shear rate (γ_{crit}), the viscosity remains independent of shear rate (Newtonian regime). Above γ_{crit}, the viscosity increases with shear rate (shear thickening regime), until it reaches a maximum at another characteristic shear rate (γ_{cross}). Above γ_{cross}, the viscosity rapidly decreases with shear rate (shear thinning regime). Also presented in Figure 5 are the viscosity profiles of the single-component solutions. A 10 g L^{-1} solution of PAMPS-Dod exhibits a weakly shear thickening behavior under shear rates higher than ~500 s^{-1}, while a 10 g L^{-1} solution of JR400 is a weakly shear thinning fluid. The viscosity of a solution of PAMPS is independent of shear rate.

The viscosity profiles of fluids in region II show remarkable composition sensitivity. Shear thickening effects were observed only in the viscosity profiles of mixed JR400/PAMPS-Dod systems with a polyanion

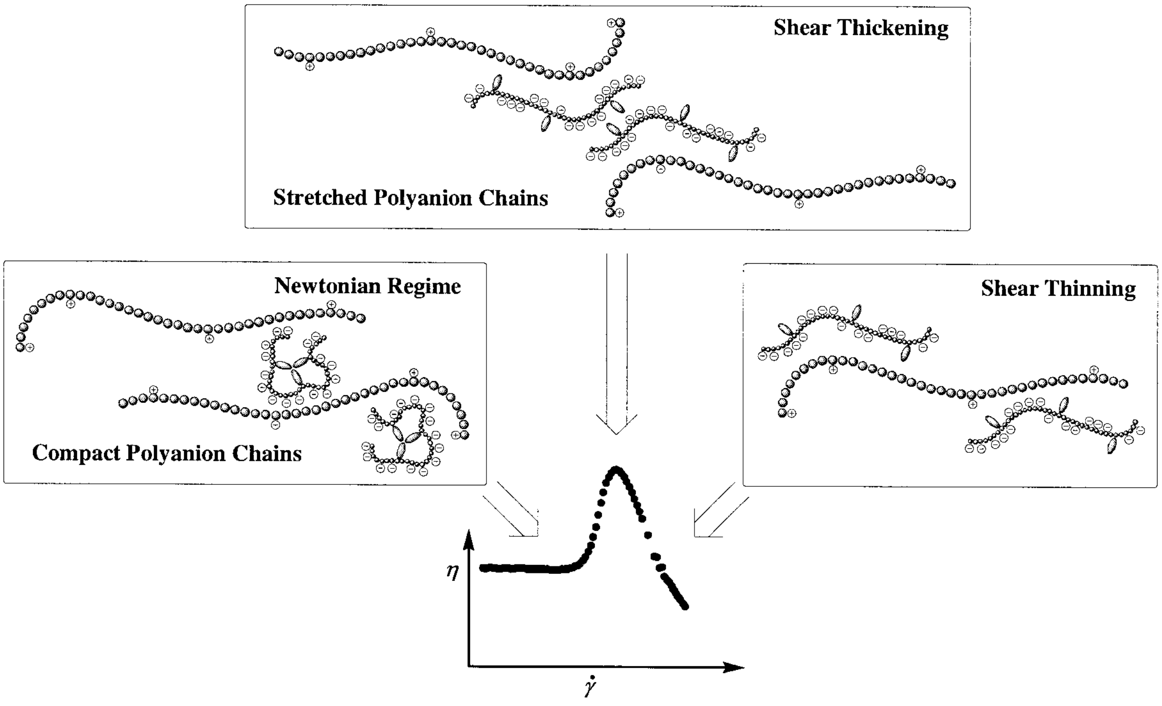

Figure 7. Conceptual model of the mechanisms of the shear thickening and shear thinning effects exhibited by region II fluids.

content ranging between $f_{p^-} \sim 0.450$, the miscibility limit, and 0.625. Samples of polyanion content 0.650 and higher exhibit typical Newtonian behavior up to shear rates of ~100 s^{-1} and display mild shear thinning properties when subjected to yet higher shear rates. Within the shear-thickening domain, as the polyanion content increases from $f_{p^-} = 0.450$ to $f_{p^-} = 0.525$, the relative magnitude of the shear thickening effect increases and the onsets of shear thickening and of shear thinning shift to higher shear rates (Figure 6). As the polyanion content further increases, the shear thickening effect decreases in magnitude, while the rate corresponding to the onset of shear thickening remains constant.

Shear-thickening effects are rarely observed in common polymer melts or solutions, but they are known to occur in complex fluids, such as dense suspensions,[29] wormlike micelles, and associating polymer solutions.[30-34] In all cases shear thickening behavior has been related to shear-induced changes of the fluid microstructure, such as shear-induced cross-linking,[35,36] shear-induced chain stretching, and network reorganization.[37,38] Recalling the hypothetical model depicted in Figure 2, in which rigid and extended polycation chains are loosely connected in a network via electrostatically linked polyanions, we propose the following model for the shear thickening behavior of region II fluids (Figure 7). Shearing the fluids causes the breaking and re-forming of cross-linking points, and at sufficiently high shear rate, it triggers a slight elongation of the polycations so that some junctions are broken and re-formed with aligned adjacent polycations, strengthening the network. Concomitant with the elongation of the polycation, unfolding of the PAMPS-Dod unimers may take place under shear, exposing hydrophobic groups, which can undergo interpolymeric association with adjacent PAMPS-Dod chains and thus contribute to the strengthening of the network. This type of shear-induced association has been invoked to explain the shear-thickening properties of solutions of hydrophobically modified polymers. Continued increase in shear rate results in further strengthening of the network until shear stresses become large enough to prevent further interchain junctions from forming. The network is no longer able to support higher stress, and beyond the shear rate corresponding to maximum viscosity, the network size decreases. Each subsequent jump in shear rate imposes increasing stress, the network unravels, and the viscosity of the fluid decreases. The fact that the shear thickening effect is strongest for mixtures containing approximately equal weight concentrations of each polymer (~5 g L^{-1} or $f_{p^-} \sim 0.5$, Figure 6) supports our interpretation, as under these conditions the number of interpolymeric junctions is expected to be the highest. We note that the shear rates required for shear thickening of mixed system are much lower than those required for a PAMPS-Dod solution (10 s^{-1} vs 500 s^{-1}). This provides further evidence that the unfolding of the polyanion in mixed solutions is promoted by electrostatic interactions between the oppositely charged polyelectrolytes.

Thixotropy. Further support for the proposed model was gathered from a study of the effect of shear history on the rheology of mixed fluids. Thus, we recorded shear viscosity profiles scanning first to high shear rate and then immediately back from high to low shear rates, keeping the time between viscosity measurements constant (10 s). Viscosity profiles recorded for three mixed fluids of region II and for a solution of PAMPS-Dod are presented in Figure 8. In this figure, the full symbols correspond to shear viscosity values obtained in the sweep to high shear rates, and the open symbols correspond to shear viscosity values measured in the sweep to low shear rates. The decreasing rate scan reasonably reproduces the viscosity measured in an increasing rate scan for a mixture of $f_{p^-} = 0.475$, but for shear thickening of mixtures $0.475 < f_{p^-} < 0.65$ it consistently resulted in lower viscosity maxima and higher critical shear rates for the maxima. The strongest thixotropy was observed in the case of a fluid with $f_p = 0.55$ (Figure 8c). The effect became progressively weaker as the polyanion content decreases, and it vanished in fluids of $f_{p^-} < 0.475$, a composition near the immiscibility boundary (Figure 8a,b). Solutions of PAMPS-Dod with no added JR400 exhibited weak thixotropic behavior (Figure 8d). It is important to point out that the viscosity value recorded at the end of a sweep to lower shear rates is the same as the initial viscosity of the system. Moreover, for all compositions the cycles were reproducible, confirming that equilibrium was attained

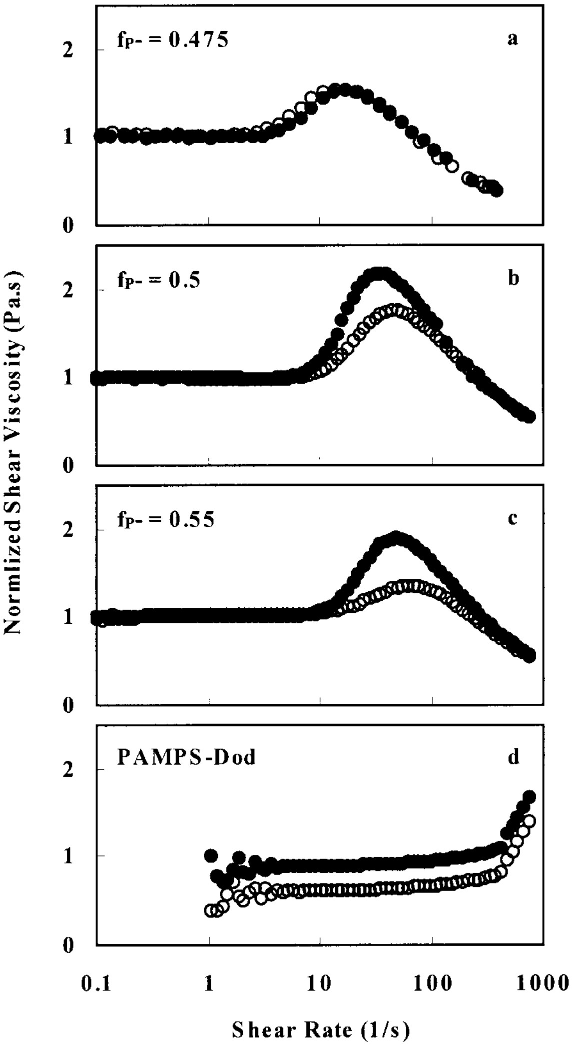

Figure 8. Normalized steady shear viscosity as a function of shear rate for 10 g L^{-1} aqueous solutions of JR400/PAMPS-Dod with f_{p^-} 0.475 (a), 0.500 (b), and 0.550 (c) and for a 10 g L^{-1} solution of PAMPS-Dod (d). The stress shear sweep experiments were performed from low shear rates to high shear rates (full symbols) and from high shear rates to low shear rates (open symbols).

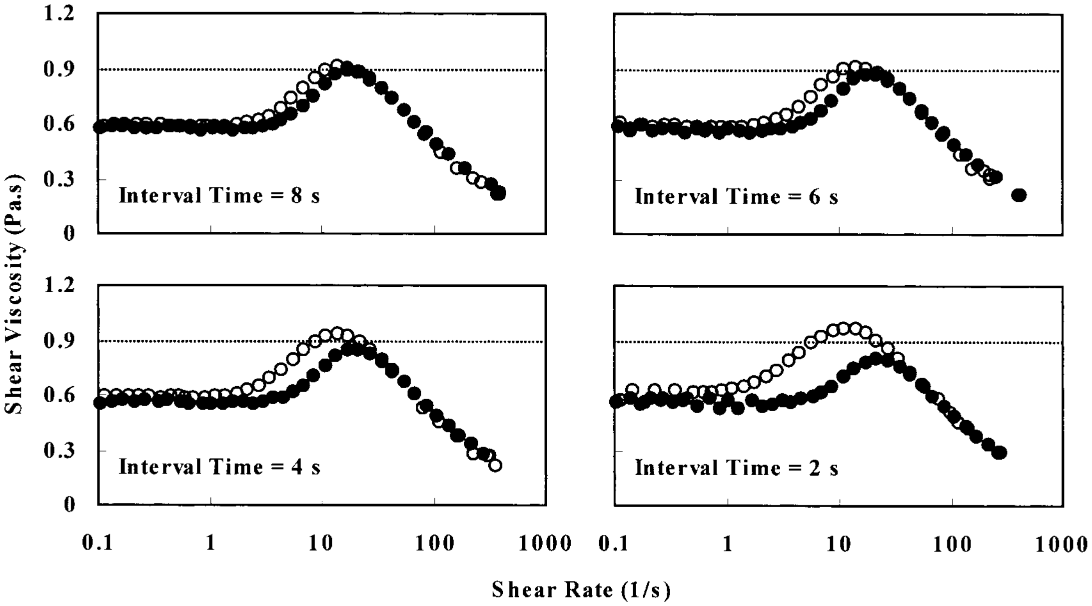

Figure 9. Steady shear viscosity as a function of shear rate for a 10 g L^{-1} aqueous solutions of JR400/PAMPS-Dod with f_{p^-} 0.475 for experiments carried out with interval times of 2, 4, 6, and 8 s between measurements. The stress shear sweep experiments were performed from low shear rates to high shear rates (full symbols) and from high shear rates to low shear rates (open symbols). The dotted lines correspond to the maximum viscosity reached with an interval time of 10 s.

throughout the measurements when the delay time was set at 10 s.

Effect of Delay Time. Viscosity profiles as a function of shear rates for a fluid with $f_{p^-} = 0.475$ employing four different delay times between measurements are shown in Figure 9, which presents sweep-up scans in full symbols and the corresponding sweep-down scans in open symbols. Recall that, in all experiments described previously, the delay time was set at 10 s, and under these conditions, the fluid with $f_{p^-} = 0.475$ displayed shear thickening and shear thinning properties, but no thixotropy (Figure 8d). Shortening the delay time between measurements carried out toward high shear rates had two effects. The magnitude of the shear thickening effect (η_{max}) decreased from 0.906 Pa•s ($t = 10$ s) to 0.729 Pa•s ($t = 2$ s), and the critical shear rate γ_{crit} shifted to higher shear rate. The trends were reversed when scans were performed from high shear rates to low shear rates. Under these conditions shortening the delay time resulted in an increase in η_{max}, from 0.904 Pa•s ($t = 10$ s) to 1.05 Pa•s ($t = 2$ s) and in a shift of both γ_{crit} and γ_{cross} to lower shear rates. Note that in all cases the changes in the magnitude of η_{max} are accompanied by corresponding changes in η_0, the viscosity at lowest shear rate, but to a lesser extent. Scan cycles repeated at a given delay time were always reproducible.

The hysteresis exhibited by the viscosity profiles and its dependence on the delay time between measurements is consistent with the existence of an interpolymeric network. In a sweep-up scan, shortening the delay time reduces the time of polyanion unfolding and consequently reduces the extent of disruption of the hydrophobic associations. When the highest shear rate is attained, the polyanion and the polycation are fully extended and aligned in the flow direction. Reducing the delay time in a subsequent sweep-down scan limits the time allowed for relaxation of the elongated chains, which retain their stretched conformation at lower shear rates. This alignment favors the formation of more interpolymeric cross-links; thus, viscosities are higher at lower shear rates than those obtained during a sweep-up scan.

It was important to determine whether the delay times also affect the data gathered from single-component samples. In the case of JR400, shortening of the delay time in a sweep-up scan resulted in a small increase in the viscosity with η_0 from 0.041 Pa•s ($t = 10$ s) to 0.051 Pa•s ($t = 1$ s). In addition, as the delay time decreased, the fluids became increasingly more thixotropic. Similar trends were observed in corresponding measurements carried out with solutions of PAMPS-Dod, except for very short delay times ($t < 5$ s) where it became impossible to obtain reliable sweep-down scans.

Conclusions

Concentrated mixtures of two oppositely charged polyelectrolytes, a stretched, rigid, lightly charged polycation and a flexible highly charged polyanion, form homogeneous fluids over wide composition domains. Electrostatic interactions promote the intermeshing of the two polyelectrolytes, resulting in the formation of networks with distinct microstructures, and consequently rheology, as a function of composition. Polyanion-poor fluids are shear thinning gels, while polyanion-rich fluids exhibit shear thickening properties. The shear thickening mixtures demonstrate significant thixotropic behavior, such that the observed apparent viscosity depends strongly on shearing history and on the delay time between measurements. Identical studies were performed on mixtures of one polycation but two different polyanions, either PAMPS or PAMPS-Dod, a strong polyanion carrying a small level of hydrophobic groups. A comparison of the rheology of the two mixed systems indicates that the microstructure of the fluids is controlled primarily by electrostatic forces. Hydrophobic forces may promote the formation of network, and thus, the magnitude of the shear thickening effect is enhanced in mixtures of JR400/PAMPS-Dod compared to that in mixtures of JR400/PAMPS. Current work in our laboratories indicates that the role played by hydrophobic forces becomes increasingly predominant with higher level of modification of either the polyanion or the polycation. The observations reported here may serve as a basis for the design of "rheologically smart" fluids controlled simply by the mixing ratio of two solutions of readily available polymers.

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