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Effect of DMF on the Rheological Properties of Telechelic Polyelectrolyte Hydrogels

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ABSTRACT: The influence of addition of dimethylformamide (DMF) on the linear and nonlinear rheological properties of a reversible hydrogel composed of triblock copolymers of ionized poly(acrylic acid) (PAA) end-capped with short polystyrene (PS) blocks is reported. Steady state, oscillatory shear, and stress relaxation experiments were carried out to characterize the rheological behavior of a 0.6 wt % PS−PAA−PS physical gel in water−DMF binary solvent mixtures. The rheological properties of the hydrogel were shown to depend significantly on DMF content. The main effect of addition of DMF is the overall rearrangement of the structure from a concentrated suspension of (percolating or closely packed) swollen finite polyelectrolyte clusters (microgels) to a more homogeneous, kinetically, controlled 3D transient network. The structural rearrangement is induced mainly by changes in the PS mobility and exchange dynamics as well as by PAA conformational changes.

Introduction

Among the numerous hydrophobically modified water-soluble polymers, telechelic polymers composed of a linear hydrophilic backbone end-capped by short hydrophobic (e.g., alkyl or perfluoroalkyl) groups have attracted special attention in the last 2 decades thanks to their well-defined and controllable macromolecular architecture. This particular interest mainly comes from the richness of the tunable rheological properties of these polymers in aqueous media, which make them useful as rheology modifiers in various aqueous formulations: latex paint formulations, drilling fluid formulations, injectable hydrogels, etc. More precisely, the associative telechelic polymers in aqueous solutions exhibit interesting linear rheological properties (thickening effect), but also interesting nonlinear rheological behavior (strong shear-thinning, shear-thickening), above a given polymer concentration. These rheological properties originate from the ability of these polymeric systems to form flower-like micelles at low concentrations, which can further associate above a threshold concentration to form a three-dimensional transient network.[1,2] Among telechelic associative polymers, attention was focused mainly on nonionic polymers derived from poly(ethylene oxide), belonging to the class of hydrophobically modified ethylene oxide urethane (HEUR) block copolymers.[3−7]

Recently, associative telechelic polyelectrolytes, which are composed of a charged hydrophilic central chain, were designed and their rheological properties were studied in aqueous media.[8−11] The main feature that makes telechelic polyelectrolytes different from the conventional telechelics (i.e., with a nonionic hydrophilic part) is that the chain conformation of the bridging chains of the resulted transient network depends on its degree of neutralization and can be tuned by external stimulus such as pH and ionic strength. At a certain pH (depending on the polyelectrolyte nature) and under free salt conditions, the central chain adopts a stretched conformation, which affects the association mechanism and the rheological properties. For instance, gelation appears at remarkably low concentrations (on the order of 1 wt %), the strain amplitude defining the limit of the linear viscoelastic regime, γ_{LVR}, is very low (on the order of 1%) while the magnitude of the plateau modulus is very high for concentrations in the unentangled regime, making these hydrogels "fragile" but strongly elastic materials.[8b]

Very recently, associative 4-armed star block copolymers of the same nature (PAA-*b*-PS)$_4$ were shown to form physical gels in relatively low concentrated polymer aqueous solutions. More importantly, the copolymer topology (e.g., star versus linear) and the length of the PS hydrophobic stickers were shown to significantly influence the hydrogel rheological properties, which has to be taken into account in the associative polymer design.[12]

The main interest of these charged associative polymeric systems comes from the sensitivity of their rheological properties to pH and ionic strength, two parameters which significantly influence not only the conformation of the chains but also the structure and topology of the network they can form.[10,13]

Such amphiphilic triblock copolymers (i.e., PMMA−PDEAEMA−PMMA, PMMA−PMAA−PMMA, PS−P2VP−PS) [where PMMA is poly(methyl methacrylate), PDEAEMA is poly((diethylamino)ethyl methacrylate), PMAA is poly(methacrylic acid), P2VP is poly(2-vinylpyridine)] have been used to design pH-driven actuators.[14] Dynamic pH experiments have shown that immersed in water nanostructured films, constituted of spherical hydrophobic glassy microdomains in a polyelectrolyte matrix, exhibited autonomous volume periodic transitions, responding to pH with the aid of a chemical oscillator. The nanostructured hydrogel deformed affinely upon pH-oscillations resulted in a robust working soft material, capable of exerting an external force.[14]

Instead of varying the pH or the ionic strength of the medium, another way to tune the rheological properties of associative

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polyelectrolytes or polyampholytes is to play with the dielectric permittivity of the medium, through the addition of an organic solvent.[15,16] In the present paper, we aim at discussing the effects of addition of dimethylformamide (DMF) on the rheological properties of a hydrogel formed by polystyrene-*b*-poly(acrylic acid)-*b*-polystyrene (PS−PAA−PS) associative polyelectrolyte. The results were discussed in terms of PAA conformation changes, network rearrangement and PS mobility changes induced by varying both the dielectric permittivity of the medium and the solubility of the polymeric blocks in water/DMF binary solvent mixtures.

Experimental Part

Materials. The polymer used in this study is a PS−PAA−PS triblock copolymer prepared by acidic hydrolysis of the corresponding PS−Poly(*tert*-butyl acrylate)−PS precursor which was synthesized by anionic polymerization. The degree of hydrolysis of the middle block was determined by ^{1}H NMR to be 98%. The molecular characteristics of the precursor are $M_w/M_n = 1.16$, $N_{PS} = 23$, and $N_{PtBA} = 1134$. The M_w of the neutralized PS−PAA−PS was calculated to be 107400 Da. Details of the synthesis and characterization procedure are reported elsewhere.[8a]

Rheology. Rheological measurements were performed on two different rheometers. Dynamic mechanical tests were carried out with a strain controlled rheometer, Rheometric RFS-II, equipped with a cone/plate geometry (diameter = 50 mm, angle = 2°, truncation = 45 μm).The flow properties of the solutions were studied with a stress controlled rheometer, Haake Rheostress RS-150, with cone/plate geometry (diameter = 35 mm, angle = 2°, truncation = 103 μm). For all experiments, the temperature was fixed at 25 °C, and a solvent trap was used to prevent solvent evaporation.

Sample Preparation. The solutions were directly prepared at the final desired concentration. A proper amount of polymer (acid form) was weighted in a screw-capped vial. First an equivalent amount of 0.1 N NaOH was added to neutralize the PAA units and then water (Millipore)/DMF solvent mixture was added to the final weight. The samples were stirred for 24 h at room temperature and then heated for 24 h at about 100 °C. They were shaken several times for short periods during the heating procedure. Finally, they were allowed to cool down to room temperature. Good reproducibility in the rheological properties was found after that treatment. Hereafter the polymer concentration, C_P, is given in wt % of the acid form.

Transmission Electron Microscopy. The morphologies were observed using a CEM902 Zeiss transmission electron microscope operating at 80 kV. Samples were deposited onto carbon-coated grids (400 mesh, Neyco) using a one-drop method: 10 μL of the polyelectrolyte solution was applied onto the grids, allowed to stand for 1 min, and then removed by capillary forces using filter paper.

Results and Discussion

Oscillatory Shear. Linear viscoelastic moduli G' and G'' have been plotted as a function of frequency for a 0.6 wt % PS−PAA−PS hydrogel with 5 and 30 wt % DMF, in Figure 1. Both moduli are weakly dependent on frequency (at least in the range investigated), and $G' \gg G''$, underlining the solid-like character of the hydrogels due to the formation of a structured fluid. This behavior is observed for all DMF concentrations up to 30 wt %. Thus, addition of DMF affects the magnitude of moduli and not the overall viscoelastic behavior of the hydrogels which remains predominantly elastic.

More interesting effects were observed in the strain dependence of the viscoelastic response. The storage modulus G' has been plotted as a function of shear strain amplitude, for different DMF concentrations, at a fixed frequency of 1 Hz, in Figure 2.

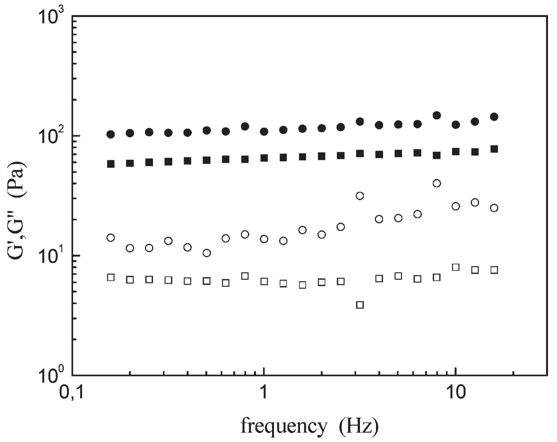

Figure 1. Storage modulus G' (full symbols) and loss modulus G'' (open symbols) as a function of frequency at a fixed strain amplitude of 0.3%, of a 0.6 wt % PS−PAA−PS hydrogel, with 10 wt % (●, ○) and 30 wt % (■, □) DMF.

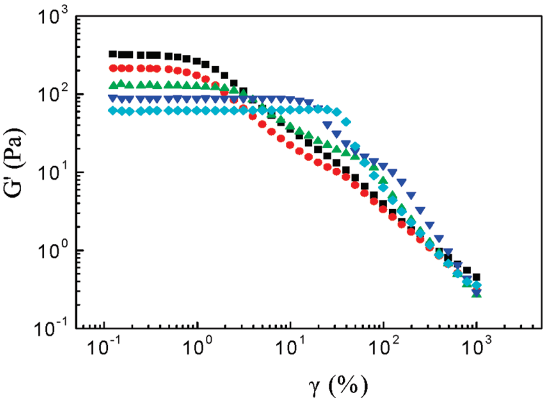

Figure 2. Storage modulus G' as a function of shear strain amplitude, at a fixed frequency of 1 Hz, of a 0.6 wt % PS−PAA−PS hydrogel, with 0 (■), 5 (●), 10 (▲), 20 (▼), 30 (◊) wt % DMF.

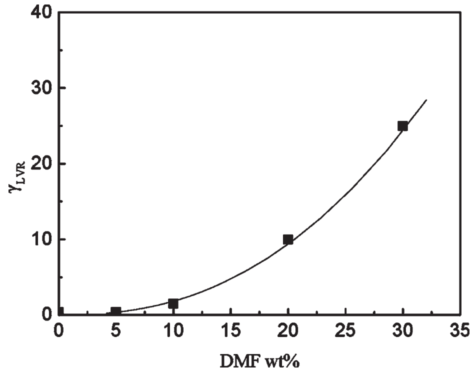

Figure 3. Linear viscoelastic regime: critical strain amplitude as a function of DMF concentration for a 0.6 wt % PS−PAA−PS hydrogel.

In order to investigate more precisely the strain dependency of the viscoelastic response, the critical shear strain amplitude γ_{LVR}, defining the limit of the linear viscoelastic regime, was plotted as a function of DMF content in Figure 3. It should be noticed that the loss modulus G'' (not plotted in Figure 2) exhibited the same extent of the linear viscoelastic regime as G'.

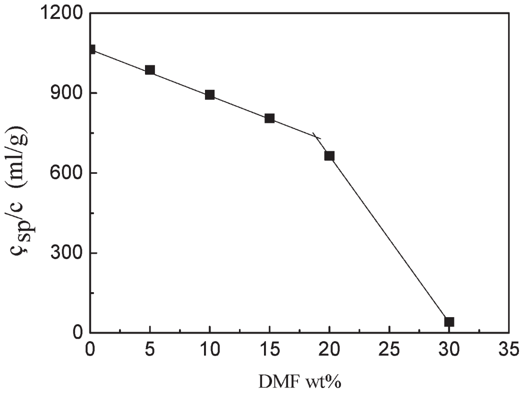

Figure 4. Reduced viscosity of 0.05 wt % PAA aqueous solutions as a function of DMF content.

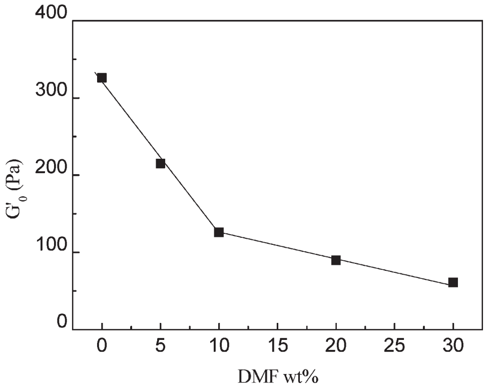

Figure 5. Plateau storage modulus G'_0 of a 0.6 wt % PS−PAA−PS hydrogel as a function of DMF concentration.

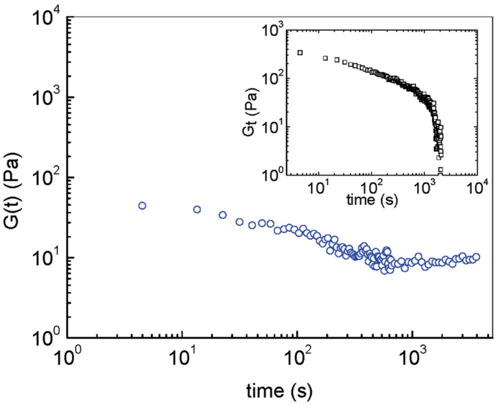

Figure 6. Stress relaxation modulus as a function of time, at a fixed strain of 1% for a 0.6 wt % PS−PAA−PS hydrogel with 30 wt % DMF, and without DMF (inset).

The amount of DMF strongly influences the extent of the linear viscoelastic regime, as the critical shear strain amplitude increases significantly with increasing DMF content. This effect could be attributed to the greater flexibility of the PAA elastically active chains, since their degree of ionization is expected to decrease when the dielectric permittivity of the medium is lowering, thus favoring unstretched macromolecular conformation. The influence of DMF addition on the PAA conformation is evidenced when plotting the reduced viscosity of neutralized PAA homopolymer in dilute solution as a function of DMF content (Figure 4). Addition of DMF leads to a decrease of the reduced viscosity of the solution which can be attributed to a decreasing stretching of the PAA chains upon decreasing the dielectric permittivity of the solvent; this effect is even more marked above 20 wt % DMF. Moreover comparing the behavior of our system in pure water (PS$_{23}$−PAA$_{1134}$−PS$_{23}$) with that of PS$_{27}$−PAA$_{139}$−PS$_{27}$[12] we observe that much shorter central PAA block leads to significant linear regime expansion, which is consistent with the decreasing stretching of the PAA chains (shorter end to end distance) upon DMF addition.

The effect observed in Figure 3 has also been reported in 4-armed star block copolymers, (PAA−PS)$_4$ of the same nature as the triblock copolymer studied here, just by decreasing the PS length.[12] The addition of a good solvent for PS blocks (our case) decreases the hydrophobic interactions which is equivalent to shortening the PS block. Therefore, it seems that both effects, induced by DMF addition (PAA stretchability and PS solubility/hydrophobicity) influence the extent of the linear viscoelastic regime. Figure 4 suggests that the effect of dielectric constant on the central polyelectrolyte block probably dominates at high DMF content (above ~15 wt %), whereas at low DMF concentrations (i.e., inferior to ~15 wt %), the properties and behavior of PS groups prevail.

Another manifestation of DMF induced structure rearrangement can be seen in Figure 5, where the plateau storage modulus G'_0 of a 0.6 wt % PS−PAA−PS hydrogel has been plotted as a function of DMF content.

The results show that the elastic modulus, which characterizes the elastic energy stored in the hydrogel, decreases significantly when the amount of DMF increases. This decrease is even more pronounced at low contents of DMF (up to 10%).

At high DMF content (above ~15 wt %), where the effect of dielectric permittivity of the medium prevails, PAA chains adopt more flexible conformations (Figure 4) favoring conformational transitions of PAA chains from bridging to looping. Assuming the existence of a physically cross-linked network, such conformational transitions would decrease the number of elastically active chains of the network, which decreases the elastic modulus, as predicted by the Green−Tobolsky model.[17]

However at low DMF concentration (below ~15 wt %), where the effect of the dielectric constant is negligible, the abrupt G'_0 decrease shown in Figure 5 cannot be attributed to the same mechanism. In this DMF concentration domain, the influence of DMF on the PS junctions predominate, and the abrupt G'_0 decrease could be explained by structure rearrangements coming from the DMF induced mobility enhancement of the hydrophobic PS stickers in the physical cross-links.

Stress Relaxation. Figure 6 shows the stress relaxation modulus $G(t)$ versus time, in the linear regime, for a 0.6 wt % PS−PAA−PS hydrogel, with 30 wt % DMF. The PS−PAA−PS hydrogel without DMF (inset of Figure 6) exhibited a linear viscoelastic response dominated by a long relaxation time, on the order of 1000s, whereas the addition of 30 wt % DMF leads to much longer terminal relaxation times, which could not be determined within the time of experiment (~5000 s).

Such results cannot be understood within the classical framework of transient network models, where the relaxation time is attributed to the average associative junction lifetime, related to the association strength. Indeed, DMF should increase the mobility of the PS stickers in the hydrophobic domains (possibly due to preferential adsorption of DMF to the PS domains) and decrease the interfacial tension between the hydrophobic junctions and the medium, thus

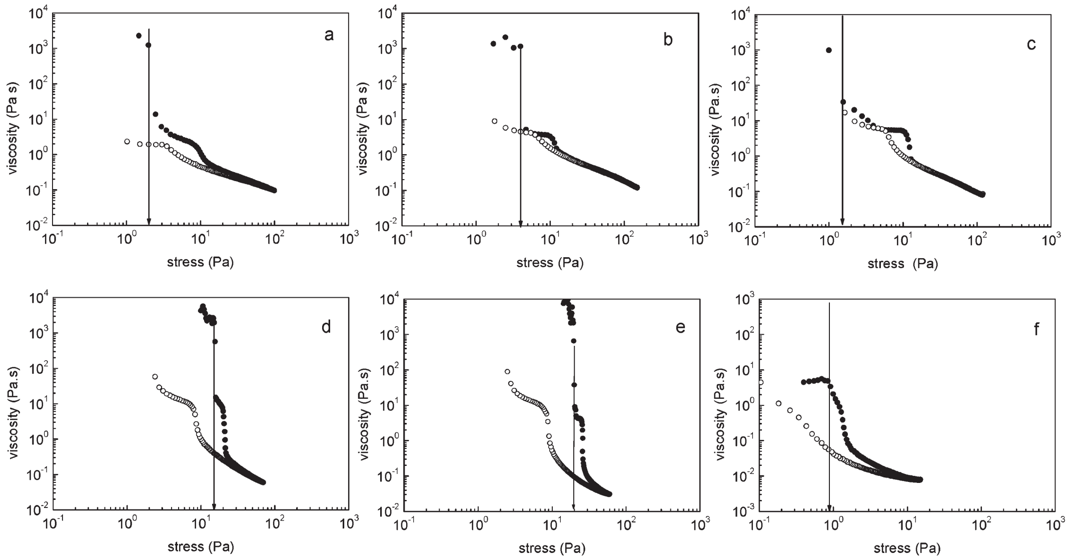

Figure 7. Apparent viscosity as a function of increasing (filled symbols) and decreasing (open symbols) shear stress of a 0.6 wt % PS−PAA−PS hydrogel, with (a) 0, (b) 5, (c) 10 (d) 20, (e) 30, and (f) 40 wt % DMF.

favoring the detachment of the chain-end stickers from the junctions, leading to a decrease of the relaxation time. Therefore, we suggest that the existence of a very long terminal relaxation time scale at high DMF concentration requires significant changes in the structure and system dynamics, as discussed below.

Steady Shear Flow. The up and down (increasing and decreasing stress) steady state shear flow curves of a 0.6 wt % PS−PAA−PS hydrogel, for different DMF concentrations, are plotted in Figure 7. All graphs clearly exhibit the existence of an apparent yield stress, corresponding to the divergence of the apparent viscosity. Figure 7a shows that, without DMF, three regions can be distinguished: once the apparent yield stress is exceeded, a first strong shear-thinning region, then an intermediate region characterized by a tendency to plateau, and finally a smoother shear-thinning region.

Adding DMF first modifies the apparent yield stress, as can be seen in Figure 8: the apparent yield stress increases with increasing DMF concentration from 10 to 30 wt %, then decreases sharply with further DMF addition. The increase of the apparent yield stress with increasing DMF content up to 30 wt % can be related to the increase of the critical strain amplitude defining the extent of the linear viscoelastic regime.

The drastic decrease of the apparent yield stress followed by a dramatic drop of the low-shear viscosity, more than 3 orders of magnitude, from 30 to 40 wt % DMF content, is indicative of a gel-to-sol transition. Above 30 wt %, a dramatic effect appears due to a synergistic action, i.e., the significant enhancement of PS mobility (increasing further the sticker exchange) and the enhancement of PAA flexibility (decrease of PAA end-to-end distance shifting the percolation threshold at higher concentrations). Both effects weaken the network connectivity, leading eventually to a gel-to-sol transition.

It is worth mentioning that the maximum low-shear Newtonian viscosity was observed at 30 wt % DMF although the storage modulus was about 1 order of magnitude lower than that in pure water. This could be related with the huge increase of the terminal relaxation time observed in the stress relaxation experiments.

Finally, comparing increasing and decreasing stress flow curves in Figure 7, hysteresis phenomena can be observed, which are particularly marked at high DMF concentrations. This particularly interesting feature might be indicative of significant differences in the structure at low and high DMF concentrations. The very pronounced hysteresis phenomenon observed at high DMF concentrations means that once destroyed, the structure takes time to recover. The very slow structural dynamics revealed by hysteresis is in agreement with the stress relaxation results, characterized by the absence of measurable relaxation time within the experimental time window.

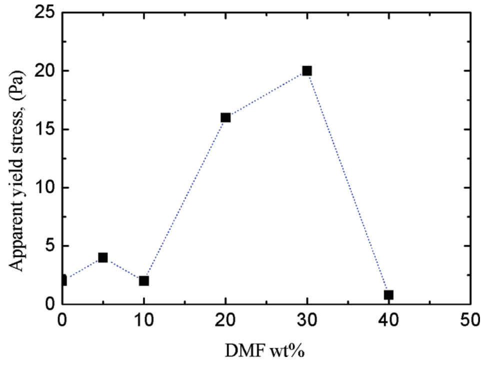

Figure 8. Apparent yield stress of a 0.6 wt % PS−PAA−PS hydrogel as a function of DMF weight concentration.

Transmission Electron Microscopy. Transmission electron microscopy (TEM) was used to gain further information about the structural states at different DMF contents. Low concentration solutions (1 mg/mL) were prepared and heated above 100 °C in closed vials (same conditions as for gel preparation) for several days and left at room temperature overnight. TEM micrographs obtained by solvent casting on carbon grids are depicted in Figure 9 for different DMF percentages. In Figure 9 (left), corresponding to pure aqueous solutions, irregular large aggregates (see also Figure S1b in the Supporting Information), which have been formed at concentrations lower than the gelation threshold, can clearly be seen. In the magnified image (Figure 9, left lower and Figure S1a in the Supporting Information), one could recognize also individual nanoparticles of variable sizes (20−200 nm) which probably correspond to frozen flower like micellar-type aggregates. The dark spherical

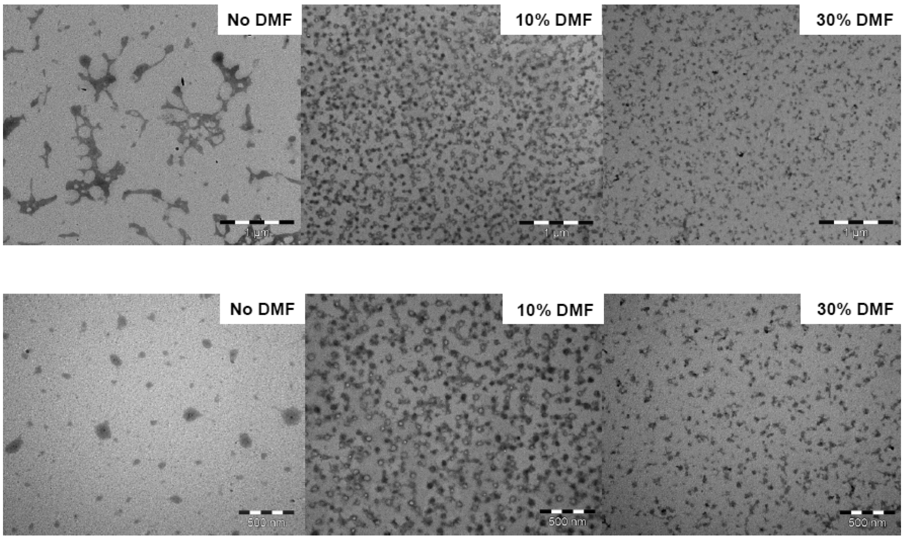

Figure 9. TEM micrographs of PS−PAA−PS embedded on carbon grid from 1 mg/mL solution, (left) in pure water, (middle) 10 wt % DMF, and (right) 30 wt % DMF, at two magnifications. Scale = 1 μm (upper part); 500 nm (lower part).

domains in the center should be attributed to the PS cores. Core−shell micellar structures have also been imaged by TEM without staining in PS−PAA[19] and PnBA−PAA[20] diblock copolymers.

It is reasonable to assume that above the gelation point, the system would resemble a concentrated suspension of (percolating or densely packed) weakly interacting swollen finite polyelectrolyte clusters (microgels).[18] This could explain why the hydrogels studied in this work are so "fragile" in water (low linear viscoelastic limit), still exhibiting significant elasticity (large G' values). This could also explain why the apparent yield stress is low and the viscosity is recovered upon decreasing shearing without significant hysteresis. These results are reminiscent of those published in a previous paper,[8b] where similar rheological properties were hypothesized to be attributed to the existence of a percolation network of finite clusters (swollen microgels), somewhat analogous to the structure of colloidal gels.[21] We should note here that the rheological properties (i.e., short linear regime, long relaxation times, elastic behavior, easy structure recovery) in our case are quite similar to those observed with aqueous suspensions of 1 wt % PAA chemical microgels (Carbopol) (Supporting Information).

To explore the influence of the presence of DMF on the structure of the aggregates, TEM observations of samples for 10 and 30 wt % DMF aqueous solutions were performed (Figure 9, middle and right).

The structure of the aggregates is significantly different, even in the presence of only 10 wt % DMF. The main information gained from this picture is that smaller, less polydispersed in size and more homogeneously distributed aggregates were formed as compared to pure water, which should result in a more homogeneous 3D structure at concentrations above the gelation threshold. At this DMF concentration small spherical aggregates can be seen on the TEM micrograph of about 60 nm in diameter, which seem interconnected to form larger multiaggregate clusters (see also Figure S2 in the Supporting Information). The light gray parts between the spherical aggregates may correspond to PAA bridges (several chains). Smaller in size and homogeneously distributed aggregates are also observed at 30% DMF which however look less interconnected than in 10% DMF. Because of low contrast it is not easy to characterize clearly the morphology of these aggregates. Although qualitative, the information gained by TEM, contributes to the better understanding of the rheological behavior of our system.

The physical gels in pure water have been prepared at high temperatures (100 °C) where the exchange of the PS_{23} stickers from the hydrophobic junctions, even very slow, allows the formation of a structure of concentrated (perhaps weakly associated) swollen finite polyelectrolyte clusters (microgels). These clusters are "frozen" at room temperature due to the high T_g and high hydrophobicity of the PS blocks. It should be mentioned that at room temperature the polymer does not swell spontaneously to form a gel. Upon adding DMF (good solvent of PS) the rate of sticker exchange increases[22] and the PAA chains become more flexible. This induces rearrangements in the structure of the aggregates, as revealed by TEM in dilute solution, affecting therefore the global structure and the dynamics of the network. Stress relaxation showed very long relaxation times in the presence of DMF, which is consistent with the formation of a more homogeneous 3D network with non "frozen" but kinetically controlled PS junctions and more flexible PAA elastic chains. This physical picture could also explain why the network is less "fragile" (significant extended linear viscoelastic regime) than in pure water but also why the hysteresis in the flow curve is more pronounced at high DMF concentrations (Figure 7).

To sum up, it seems that the main effect of the addition of DMF on the hydrogel rheological properties is the overall rearrangement of the structure from a concentrated suspension of (percolating or closely packed) swollen finite polyelectrolyte clusters (microgels) to a more homogeneous, kinetically controlled, 3D transient network. It is very likely that these structure rearrangements are mainly governed by variations in the exchange of the PS stickers between the hydrophobic junctions which become possible but still extremely slow in the presence of DMF. In the absence of DMF no exchange of the PS stickers is possible. The observed relaxation (Figure 6) is attributed to the movement of the densely packed microgel-like clusters (several micrometers in size).

Conclusion

This study demonstrates the effects of addition of DMF on the rheological properties of a physical hydrogel constituted of a

0.6 wt % charged PAA chains end-capped with short PS blocks (stickers). Adding DMF was shown to influence significantly the linear and nonlinear rheological properties of the hydrogel. The addition of DMF exerts a double effect. First, it decreases the dielectric permittivity of the medium, which lowers the charge density of the ionized PAA blocks of the triblock copolymer, and therefore the repulsive electrostatic interactions, leading to a greater flexibility of the elastically active chains of the network. Second, as a good solvent of PS, it affects the mobility of PS stickers in the hydrophobic junctions, and also the PS exchange dynamics.

The whole set of experiments, including TEM observations, tends to show that the significant rheological changes of the hydrogel upon DMF addition are mainly due to changes in the hydrophobic interactions that affect the network junctions (aggregation number and dynamics), and thus the overall network structure. Because of the increase of the PS exchange rate induced by DMF addition, the percolating network (or closely packed suspension) of frozen microgels rearranges toward a kinetically controlled three-dimensional transient network.

At high DMF content (above 30 wt %) a dramatic effect appears due to a synergistic action, i.e., the significant enhancement of PS mobility (increasing further the sticker exchange) and the enhancement of PAA flexibility (decrease of the effective PAA end-to-end distance shifting the gel point at higher concentrations). Both effects weaken the network connectivity, leading eventually to a gel-to-sol transition.

The findings of the present work enable a better understanding of the behavior of the PS−PAA−PS telechelic polyelectrolyte hydrogels. It is obvious that the exchange dynamics of the hydrophobic chain-ends (stickers) is critical, affecting significantly the structure formed upon association of the copolymer in aqueous media.

Finally we would like to mention that, during the preparation of the manuscript, we became acquainted with the very recent paper by Nicolai et al.,[23] which stimulated the discussion of our results.

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Supporting Information Available: Figures showing more TEM micrographs and rheological properties concerning PAA chemical microgles (Carbopol) in aqueous solution. This material is available free of charge via the Internet at http://pubs.acs.org.

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