Viscoelastic Properties of Physical Gels Formed by Associative Telechelic Polyelectrolytes in Aqueous Media

Constantinos Tsitsilianis*

Department of Chemical Engineering, University of Patras, and Institute of Chemical Engineering and High-Temperature Chemical Processes, ICEHT-FORTH, P.O. Box 1414, 26500 Patras, Greece

Ilias Iliopoulos

Matière Molle et Chimie, UMR-167, ESPCI-CNRS-ATOFINA, 10 rue Vauquelin, F-75231 Paris, Cedex 05, France

ABSTRACT: We report on the viscoelastic response of a physical gel formed in aqueous solutions of poly-(sodium acrylate) end-capped with short polystyrene (PS) blocks. Above a percolation threshold (c_{gel} = 0.2 wt %) a transient network is formed constituted of PS hydrophobic domains (cross-links) interconnected via fully charged polyelctrolyte chains. Oscillatory shear and step-strain experiments were employed to study the viscoelastic properties. The stretched conformation of the charged middle blocks (bridges) and the high hydrophobicity of the PS ends have fundamental consequences on the various viscoelastic parameters: (1) The linear viscoelastic behavior is only observed at very small strains, indicating that the telechelic polyelectolytes form weak gels. (2) The magnitude of the plateau modulus, in the unentangled regime, is very high due to the stretched conformation of the polyelectrolyte chains that limits the formation of elastically inactive loops. (3) The lifetimes of the physical cross-links are influenced by the high hydrophobicity of the PS ends, compensated largely by the stretching of the polyelectrolyte chains which increases the disengagement probability. The final result is that slow mode relaxation phenomena predominate (relaxation times of the order of 10^2−10^3 s).

Introduction

Associative water-soluble polymers (AP) are amphiphilic substances with very interesting solution properties since they form reversible aggregates through intramolecular and/or intermolecular interactions. Their unique properties in aqueous systems make them very useful materials as rheology modifiers, suspension stabilizers, and drug carriers in pharmaceutical applications.[1,2]

Depending on the architecture, two types of AP's can be distinguished: graft copolymers where the hydrophobic moieties are side groups distributed, more or less randomly, along the hydrophilic backbone, and telechelic polymers where the hydrophilic chain is end-capped by hydrophobic short blocks.

In the past decade a considerable amount of work has been reported on associative graft copolymers,[3] ionic or nonionic, referred to also as hydrophobically modified (HM) water-soluble polymers,[3a] as well as on nonionic telechelic polymers represented mainly by poly(ethylene oxide) derivatives.[4] Recently, we focused our attention on a novel type of AP, namely "telechelic polyelectrolyte". It consists of a long poly(sodium acrylate) backbone, end-capped with short polystyrene blocks (PS−PANa−PS).[5]

The PS−PANa−PS/H_2O system exhibits some unique solution and rheological properties. At concentrations above a critical value (cac), but still in the dilute regime, association phenomena occur, leading to the formation of finite size clusters. The stabilization of optimum size clusters arises from the interplay between the energy of attraction of hydrophobic ends (stickers) on one hand and chain repulsion due to the nonscreened Coulomb interactions of the charged groups, and the contribution from the translational entropy of counterions, on the other hand.[6]

At concentrations beyond a percolation threshold, a three-dimensional transient network form by PS hydrophobic domains (physical cross-links) interconnected via stretched polyelctrolyte chains. The so-formed physical gel exhibits a remarkably different rheological behavior than the nonionic end-capped associative polymers. Steady-state shear experiments showed low gelation threshold, i.e., c_{gel} = 0.2 wt %, a yield stress, and an unusual shear viscosity profile. Preliminary dynamic measurements revealed that the physical gel exhibits a behavior similar to that of chemically cross-linked gels. This is ascribed to the fact that the attraction energy, ϵ, of the PS hydrophobic blocks is much higher than the thermal energy ($\epsilon \gg kT$).[7]

In this work, oscillatory shear and stress relaxation experiments were employed to study the viscoelastic properties of gels formed by PS−PANa−PS in aqueous media. As will be demonstrated, the viscoelastic properties of these gels are strongly influenced by the stretched conformation of the PANa strands. Since the conformation of the bridged chains depends on their degree of ionization, the gel properties can be controlled by the pH of the solution.

Experimental Part

Materials. The polymer used in this study is a polystyrene−poly(acrylic acid)−polystyrene (PS−PAA−PS) triblock copolymer prepared by acidic hydrolysis of its 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 and potentiometric titration and was found to be 98% and 80%, respectively. 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 107 400 Da. Details of the synthesis and characterization procedure are reported elsewhere.[5]
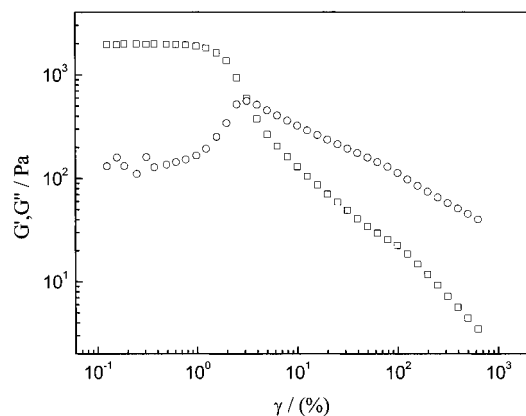
Figure 1. Storage modulus G' (□) and loss modulus G'' (○) as a function of deformation γ at 1 Hz for PS−PANa−PS in water (c_p = 1 wt %) at 25 °C.

Rheology. Rheological measurements were performed on a strain-controlled rheometer, Rheometric RFS-II, equipped with a cone/plate geometry (diameter = 50 mm, angle = 2°, truncation = 45 μm).

Sample Preparation. For the rheological measurements, the solutions were directly prepared to the final desired concentration. The 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) was added to the final volume. The samples were stirred for 24 h at room temperature and then heated for 24 h at 95−100 °C. They were shaken several times for short periods during the heating procedure. Finally, they were allowed to cool to room temperature, and the vials were weighted. The concentration was corrected to take into account the loss of water (less than 1%) during the heating procedure. 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.

Results and Discussion

Oscillatory Shear Flow. Dynamic strain sweeps were conducted first, at different concentrations and frequencies, to establish the linear viscoelastic regime. In Figure 1, representative plots of the storage (G') and loss (G'') modulus are depicted as a function of strain, γ, at 1 Hz, for a 1 wt % polymer. The linear viscoelastic regime (LVR) is defined as the regime below the critical value $\gamma_{LVR} \approx 1\%$ where G' remains invariant with respect to strain. This low γ_{LVR} value classifies this gel to the category of the so-called "weak" physical gels that, in fact, are structured fluids behaving as liquids at relatively large deformations. However, the magnitude of the elastic modulus in the LVR is high (more than 10^3 Pa for $c_p \sim 1$ wt %), which is rather unexpected for a weak gel. These results differ remarkably from those observed for nonionic telechelics, where γ_{LVR} is much higher and G_0 is much lower (e.g., for fluorinated end-capped PEO (F−PEO−F) at c_p = 4 wt %, γ_{LVR} = 40%, and G_0 = 50 Pa).[8] The low value of γ_{LVR} should be attributed to the already stretched conformation of the polyelectrolyte (PANa) strands that connect the hydrophobic (PS) aggregates.[5] In this case, chain elongation by shearing cannot any more occur, and this leads to fast gel softening. We note here that all the examined concentrations are above the c_{gel} = 0.2 wt %, established by steady-state viscosity measurements,[5] and exhibit the same profile for the G', G'' vs γ curves. Furthermore, the γ_{LVR} is independent of frequency and does not practically vary with concentration, in accordance with the state of the stretched conformation of the bridged chains.
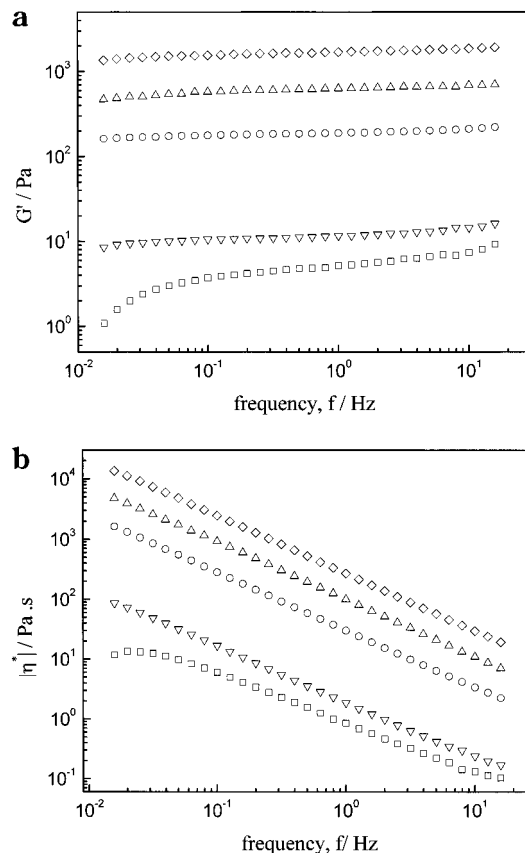

Figure 2. Storage modulus G' (a) and complex viscosity $|\eta^*|$ (b) as a function of frequency for various polymer concentrations: 1% (◇), 0.8% (△), 0.6% (○), 0.4% (▽) 0.3% (□).

Accordingly, frequency sweep experiments were performed in the linear viscoelastic regime. The storage modulus (G'), the loss modulus G'', and the complex viscosity $|\eta^*|$ were monitored as a function of frequency (f). Where the magnitude of complex viscosity is given as

$$|\eta^*| = (\eta'^{\,2} + \eta''^{\,2})^{1/2} \qquad (1)$$

where η' and η'' are the equivalent dynamic viscosities. In all concentrations examined and in the entire frequency range swept G' and G'' are parallel (with $G' > G''$) and almost frequency independent. This is a characteristic behavior of an elastic gel (with either permanent or long-lived cross-links). The G' values, for several polymer concentrations, are shown in Figure 2a. Only at the lowest polymer concentration (0.3 wt %) a significant decrease in G' is observed at low frequencies. This behavior is unique as compared with other associative polymeric systems, either telechelic or of graft type, which in general exhibit a frequency-dependent viscoelastic response (i.e., $G'' > G'$ at low frequencies and $G' > G''$ at higher frequencies[3,4]). This significant differentiation should be attributed to the long lifetime of the hydrophobic junctions and to a short strand relaxation time in the present system.

The value of the complex viscosity decreases monotonically and linearly (on a log−log plot) with increasing frequency, and only at c_p = 0.3 wt % a Newtonian plateau (although very small) is observed at very low frequencies (Figure 2b). It is of interest here to try to compare the dynamic complex viscosity $|\eta^*|(\omega)$ with the steady shear viscosity $\eta(\dot{\gamma})$ values.
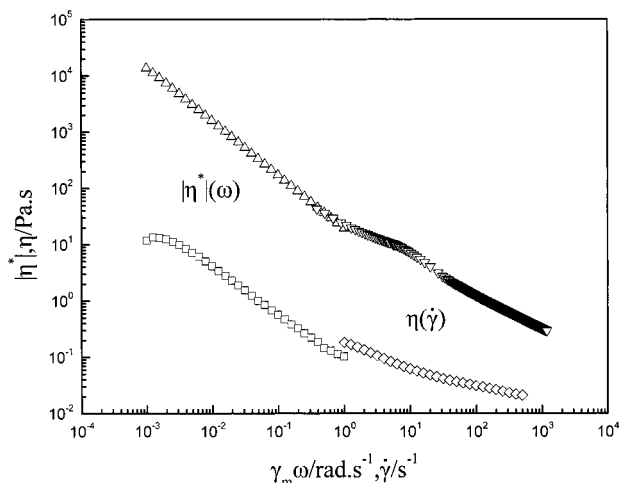
Figure 3. Complex and steady-state viscosity, $|\eta^*|(\omega)$ ($\triangle$, $\square$) and $\eta(\dot{\gamma})$ ($\triangledown$, $\diamond$), as a function of $\gamma_m\omega$ and $\dot{\gamma}$, respectively. Polymer concentration: 1 wt % (upper curves) and 0.3 wt % (lower curves).

Since the present system exhibits a yield stress, a nonlinear rheological model combining elastic, viscous, and yielding phenomena was used to correlate $|\eta^*|(\omega)$ and $\eta(\dot{\gamma})$ values.[9] According to this model, at low frequencies the $|\eta^*|(\omega)$ is dependent on frequency and strain through the parameter $\gamma_m\omega$ (i.e., the maximum imposed shear rate), where γ_m is the amplitude of the oscillation. If $|\eta^*|$ is plotted against $\gamma_m\omega$, the plots for all strain values would superimpose with a slope of -1 at low frequencies which corresponds to a yield stress behavior. Hence, if the steady shear viscosity η is plotted against $\dot{\gamma}$ and the complex viscosity $|\eta^*|$ against $\gamma_m\omega$, the curves will superimpose at the same numerical values of $\gamma_m\omega$ and $\dot{\gamma}$. The equivalence of the functional dependence of $|\eta^*|(\gamma_m\omega)$ and $\eta(\dot{\gamma})$ provides an analogy to the empirical Cox–Merz rule.[10] In Figure 3, complex viscosity and steady shear viscosity data have been plotted as a function of $\gamma_m\omega$ and $\dot{\gamma}$, respectively, for 1 wt % polymer solution. In the region ($0.1-1$ rad s^{-1}) where the $\eta(\dot{\gamma})$ and $|\eta^*|(\gamma_m\omega)$ can be compared, it is seen that the curves superimpose and satisfy the modified Cox–Merz rule. Moreover, the slope of the $|\eta^*|$ vs $\gamma_m\omega$ curve was calculated to be -0.96, in excellent agreement with the value -1 predicted by the model. A slight deviation from the modified Cox–Merz rule can be observed for the solution with the lowest polymer concentration ($c_p = 0.3$ wt %). This is probably due to the fact that at such a low concentration the network structure is weak, and yielding phenomena seem to be absent.

In Figure 2b, a strong concentration dependence of the complex viscosity $|\eta^*|$ is evidenced. Since there exist no Newtonian plateau, $|\eta^*|$ values were obtained at the same lowest frequency (0.016 Hz) and have been plotted as a function of concentration in a log–log plot (Figure 4). The complex viscosity increases with a power law of 5.9, which is very high, compared to the expectations for a polyelectrolyte in the unentangled semidilute regime (a power law with exponent 0.5 is predicted theoretically[11,12] and found experimentally for a non-associative poly(sodium acrylate) of comparable molecular weight with the polymer under investigation.[5]

It should be noted here that the scaling exponent determined by steady shear viscosity measurements is 4.2,[5] and this is accounted for by the fact that the $|\eta^*|$-(ω) and $\eta(\dot{\gamma})$ values have been obtained at different
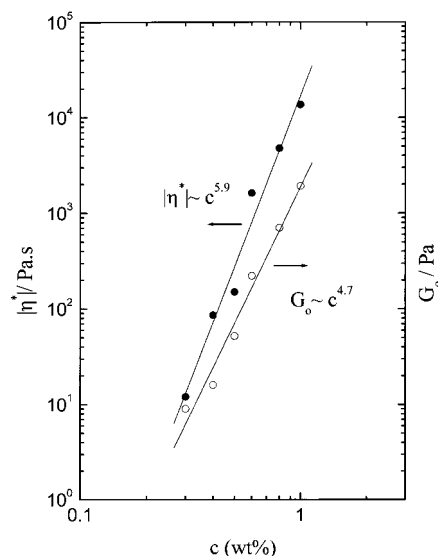

Figure 4. Double-logarithmic plot of the $|\eta^*|$ (at 0.016 Hz) and plateau modulus G_0 (at 10 Hz) as a function of polymer concentration.

effective shear rates, i.e., $\sim 10^{-3}$ rad s^{-1} and 1 s^{-1}, respectively, and by the fact that $|\eta^*|$ includes the effects of the elastic contribution (Figure 3).

Obviously, the high exponents observed for the concentration dependence of the viscosity of the telechelic polyelectrolytes in the unentangled regime are caused by the hydrophobic end groups (PS blocks), which are responsible for the formation of a three-dimensional transient network giving rise to the elastic response of these dilute solutions. High exponents have theoretically been predicted and experimentally observed also for nonionic associative telechelics for concentrations above the gelation concentration.[4c,h,13,14]

An analogous scaling behavior is exhibited for the plateau modulus, G_0. As is implied from the profile of the dynamic storage modulus (Figure 2a), essentially only the plateau zone of the dynamic spectrum is visible, for all concentrations examined. G_0 values (taken at 10 Hz) are plotted vs concentration in Figure 4. It is seen that G_0 scales with concentration with a power law of 4.7, which is again much higher than the theoretically predicted exponent for polyelectrolytes in this concentration regime (i.e., 1).[12,15]

The elastic behavior of nonionic telechelic polymers is often discussed in terms of a transient network of elastic chains. In such a case the plateau modulus is given by[16]

$$G_0 = gnkT \qquad (2)$$

where g is a correction factor usually taken as unity for systems with a large junction functionality,[4a] n the number density of elastically active chains, k the Boltzmann constant, and T the absolute temperature. For unentangled networks (as in the present system) and taken as n the number density of all the macromolecular chains in the solution, the quantity G_0/nkT (also called the reduced modulus) denotes the fraction of elastically active chains.

As reported recently by Pham et al.,[18] for end-capped PEO telechelics the plot of G_0/nkT vs concentration (expressed as the hydrodynamic volume fraction of micelles) identifies two regimes. A low concentration regime where the reduced modulus varies linearly with
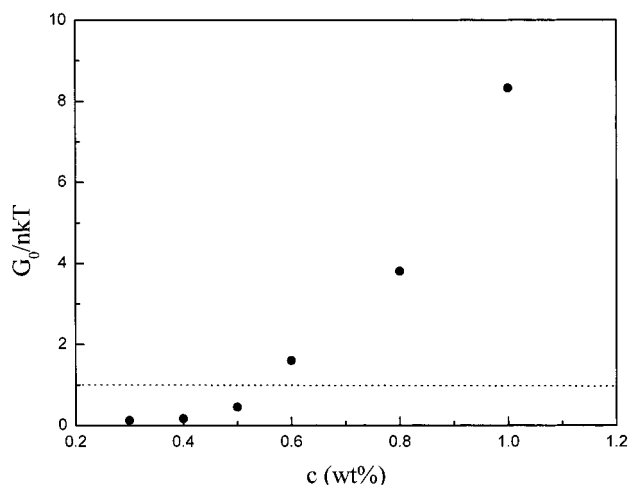
Figure 5. Reduced plateau modulus, G_0/nkT, as a function of polymer concentration.

concentration and a higher concentration regime where the reduced modulus tends to level off. The value of the asymptote depends on the size of the end hydrophobes. For the polymer with octadecyl end groups the reduced modulus exceeds the value of 1 (approaching the value of 1.4), and this was attributed to the extra contributions of the excluded-volume interactions of the micellar structure (flowerlike micelles).[14,18] Asymptotic values lower than unity were observed by Annable et al.,[4b] and even lower values have been reported for a F−PEO−F polymer.[13a] In these cases, the low proportion of chains contributing to the modulus is due to the existence of looped chains (both ends are located in the same hydrophobic aggregate), which are elastically inactive. In the case of strong polyelectrolytes (such as in the present study) looping is not favored since repulsive interactions along the chain prevent back-folding. This is one of the fundamental differences between the nonionic and ionic telechelic AP's. A direct consequence is that eq 1 does not apply to our system. The reduced modulus, G_0/nkT, exceeds unity by far for concentrations above 0.5% (Figure 5). This may be attributed to the stretched conformation of the polyelectrolyte strands arising from the presence of negative charges along the chain. As has recently been demonstrated by Serero et al., the network elasticity increases dramatically at large strains due to the enhancement of chain stiffness of the elastically active chains[8] in the stretched conformation. Preliminary results have verified the significant effect of charge density of the polymer chain on G_0. In Figure 6 dynamic sweep experiments demonstrate that G_0 decreases significantly, by almost a factor of 5, when changing the degree of ionization, α, from 1 to 0.6, for a polymer concentration 0.8 wt % (G_0/nkT decreases to 0.86). However, at $\alpha = 0.6$ there are enough charges along the chain, and the degree of chain stretching should remain still very high. Therefore, the chain stiffness may not be the only factor contributing to the observed high values of G_0. We should note here that the details of the mechanism behind the behavior of telechelic associative polyelectrolytes remain not fully clear. In a recent theoretical work, Potemkin et al.[6] have reported on the formation of multichain clusters in the dilute solution of such systems. Such clusters may be viewed as colloidal particles with some sticky character since some of the hydrophobic ends are close to the cluster surface. It is reasonable to assume that, by increasing polymer concentration, the clusters percolate
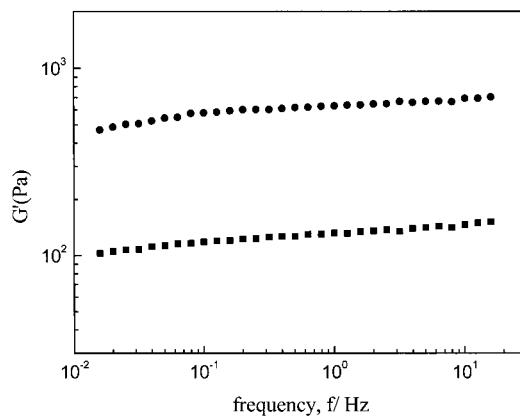

Figure 6. Storage modulus G' as a function of frequency for two different degrees of ionization, α, for a 0.8% polymer concentration: $\alpha = 1$ (●), $\alpha = 0.6$ (■).
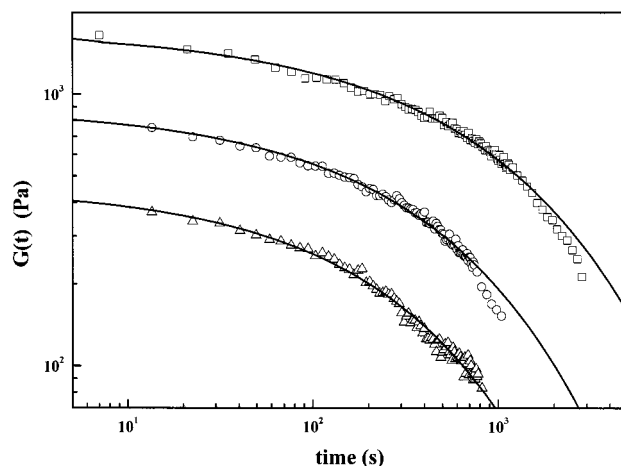

Figure 7. Stress relaxation function $G(t)$ obtained in step-strain experiments as a function of time for c_p: 1 wt % (□), 0.8 wt % (○), and 0.6 wt % (△) at 25 °C.

and form a *cluster network*, somewhat analogous to the *fractal colloidal gels*.[19] The elasticity of such a colloidal gel is governed by the intrinsic stiffness of the colloidal aggregate network: G' is almost independent of the frequency and strongly increases with particle volume fraction according to a power law $G' \sim \phi^\nu$ (with ν in the range 3.2−4.5). Such a power law has been observed also in the present system. It would be of interest to perform further studies to explore the resemblance of the behavior of our telechelic associative polyelectrolyte with the behavior of colloidal gels.

Stress Relaxation. As mentioned above, the dynamic frequency sweep experiments do not show the terminal zone for the solutions with concentrations higher than c_{gel}. Therefore, step-strain experiments were performed in an attempt to probe the relaxation process of these physical gels: a shear deformation is applied to the sample (the strain amplitude γ_0 lies in the linear viscoelastic regime), and the response is recorded as a function of time. The stress relaxation modulus $G(t) = \sigma(t)/\gamma_0$ ($\sigma(t)$ is the shear stress remaining in the system after time t has elapsed), for a number of polymer solutions, is presented as a function of time in a log−log plot in Figure 7.

For some nonionic telechelic APs,[4b] a Maxwellian behavior (a single relaxation time) has been observed, in agreement with the simple theory of rubber elasticity.[16] From the data of Figure 7, it is obvious that our

**Table 1. Viscoelastic Parameters of the PS−PANa−PS/
H₂O System from Stress Relaxation Experiments**

c_p (wt %)	G_0 (Pa)	τ (s)	α	T (°C)
1.0	1714	827	0.48	25
0.8	894	427	0.51	25
0.6	455	293	0.52	15
0.6	662	350	0.59	20
0.6	627	309	0.50	25
0.6	439	261	0.67	30
0.6	338	120	0.70	50

system does not follow such a behavior. The $G(t)$ vs t curve can be fitted by a stretched exponential function as also reported for F−PEO−F[8,13,19] and Monte Carlo simulations.[20]

$$G(t) = G_0 \exp\left[-\left(\frac{t}{\tau}\right)^\alpha\right] \quad (3)$$

where $G(t)$ is the relaxation function, τ the mean relaxation time, and α $(0 < \alpha < 1)$ the stretched exponent which contains information about the shape of the relaxation time distribution. The curves through the data demonstrate rather good fits to eq 3 with small deviations at long t. The calculated values of G_0, τ, and α are listed in Table 1. The G_0 values increase with concentration, and their magnitudes are in good agreement with the results of oscillatory measurements. Similarly, the relaxation times increase with increasing c_p, in agreement with the results of nonionic telechelic APs (F−PEO−F). However, there is a big difference in the τ values with respect to F−PEO−F.[13] For the same concentration (e.g., 1 wt %) the mean value of the relaxation times is about 2 orders of magnitude higher for the present telechelic polyelectrolyte. Another difference is that the distribution of τ is broader for the present system as α take values close to 0.5 (for F−PEO−F, $\alpha = 0.8$).[8,13]

The observed relaxation times are related to the lifetime of the physical junctions. The high hydrophobicity of the PS end blocks (23 monomer units each block) speaks for long τ. On the other hand, the chain stretching (due to charge repulsions along the chain) should decrease τ since the probability of the junction breakage is now enhanced.[21,22] Indeed, as reported by Séréro et al., the elastic modulus enhancement at large strains is accompanied by a significant reduction of the relaxation time (τ decreases by a factor of ~10).[8] As a result of this balance, the observed relaxation in the present system is still rather slow.

The temperature dependence of ln τ for a 0.6 wt % polymer concentration was finally examined. In Figure 8, τ is plotted as a function of inverse temperature. As can be seen, the network relaxation time decreases with temperature, exhibiting an Arrhenius behavior. The activation energy was estimated to be 24 kJ/mol (~10 kT), showing a weak temperature dependence of τ in the temperature range investigated. This activation energy is surprisingly low as compared to the reported values for telechelic nonionic polymers. That should be attributed to the strong stretching of the chains that substantially increases the disengagement probability of the hydrophobic end cap from the hydrophobic aggregate.[8,22,23]

To explore the viscoelastic response of the system at elevated temperatures, a frequency sweep experiment was performed at 50 °C for a 1 wt % solution. As can be observed in Figure 9, the system still responds as an
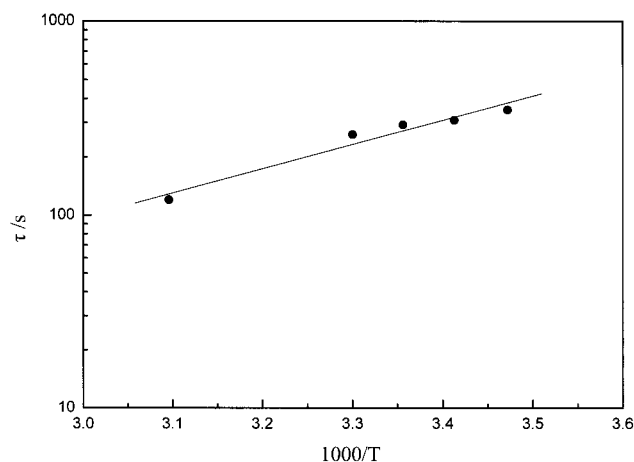
Figure 8. Arrhenius plot of the mean relaxation times τ for $c_p = 0.6$ wt %.
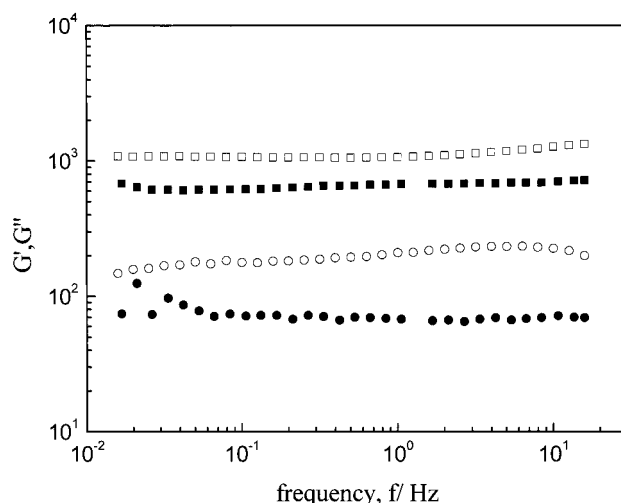
Figure 9. Storage modulus G' (squares) and loss modulus G'' (circles) as a function of frequency for $c_p = 1$ wt % at 25 (open symbols) and 50 °C (closed symbols).

elastic gel, since G' and G'' are parallel and virtually independent of frequency over the entire frequency range. A rough estimation of the activation energy for the plateau modulus was 31 kJ/mol. Provided that $\eta(\gamma) = \tau G_0$, the activation energy based on the viscosity should be equal to the sum of the contributions from the relaxation time and the modulus (i.e., 31 + 24 = 56 kJ/mol). The activation energy for the steady-shear viscosity at the same temperature range was determined to be 61 kJ/mol, showing good agreement between the values obtained from different rheological techniques.

Conclusions

The viscoelastic response of a physical gel formed by charged poly(acrylic acid) end-capped with PS short blocks was examined through oscillatory shear and stress relaxation measurements. The physical gel is made up of PS junctions bridged by stretched PAA long chains. The ionic nature of the bridges and the high hydrophobicity of the chain end blocks are responsible for a remarkably different viscoelastic behavior of the present system with respect to the conventional nonionic telechelic APs. The stretched conformation of the charged middle blocks (bridges) has fundamental consequences on the various viscoelastic parameters (i.e., γ_{LVR}, G_0,

τ): (1) γ_{LVR} is very low, demonstrating that the telechelic polyelectrolytes form weak gels. (2) The magnitude of the plateau modulus is very high for concentrations in the unentangled regime. Back-folding of the chains is not favored, and therefore the number of active chains is expected to be considerably higher than the number observed for nonionic telechelics where many chains form loops (flowerlike micelles) that are inactive. Furthermore, the plateau modulus is considerably higher than the values calculated with the assumption that all chains in the system are flexible and active. This is mainly due to the stretched conformation of the elastic chains. (3) The lifetimes of the physical cross-links are influenced from the high hydrophobicity of the PS junctions on one hand, compensated largely from the stretching of the polyelectrolyte chains that increase the disengagement probability. The final result is about 2 orders of magnitude longer relaxation times for the present system as compared to those of the fluorinated PEO telechelics.

A unique property of these gels is the possibility to control their viscoelasticity by changing the conformation of the elastic chains through the pH of the solution. Further work is in progress to explore in more detail the influence of the degree of ionization on the viscoelastic behavior of these physical gels.

References and Notes

(1) Winnik, M. A.; Yekta, A. *Curr. Opin. Colloid Interface Sci.* **1997**, *2*, 424.

(2) Goethals, E. J. *Telechelic Polymers: Synthesis and Applications;* CRC Press: Boca Raton, FL, 1989.

(3) Wang, T. K.; Iliopoulos, I.; Audebert, R. In *Water-Soluble Polymers. Synthesis Solutions Properties and Applications;* Shalaby, S. W., McCormick, C. L., Butler, G. B., Eds.; ACS Symposium Series 467; American Chemical Society: Washington, DC, 1991; p 218. (b) Aubry, T.; Moan, M. *J. Rheol.* **1994**, *38*, 1681. (c) Tirtaatmadja, V.; Tam, K. C.; Jenkins, R. D. *Macromolecules* **1997**, *30*, 1426. (d) English, R. J.; Culati, H. S.; Jenkins, R. D.; Khan, S. A. *J. Rheol.* **1997**, *41*, 427. (e) Xu, B.; Yekta, A.; Winnik, M. A.; Sadeghy-Dalivand, K.; James, D. F.; Jenkins, R.; Bassett, D. *Langmuir* **1997**, *13*, 6903. (f) Thuresson, K.; Lindman, B.; Nyström, B. *J. Phys. Chem. B* **1997**, *101*, 6450. (g) Vittadello, S. T.; Biggs, S. *Macromolecules* **1998**, *31*, 7691. (h) Ragalado, E. J.; Selb, J.; Candau, F. *Macromolecules* **1999**, *32*, 8580. (i) Smith, G. L.; McCormick, C. L. *Macromolecules* **2001**, *34*, 918.

(4) Jenkins, R. D.; Silebi, C. A.; El-Aasser, M. S. *Polym. Mater. Sci. Eng.* **1989**, *61*, 629. (b) Annable, T.; Buscall, R.; Ettelaier, R.; Whittlestone, D. *J. Rheol.* **1993**, *37*, 695. (c) Alami, E.; Almgren, M.; Brawn, W.; François, J. *Macromolecules* **1996**, *29*, 2229. (d) Kaczmarski, J. P.; Glass, J. E. *Macromolecules* **1993**, *26*, 5149. (e) Xu, B.; Li, L.; Yekta, A.; Masoumi, Z.; Kanagalingam, S.; Winnik, M. A.; Zhang, K.; Macdonald, P. M.; Menchen, S. *Langmuir* **1997**, *13*, 2447. (f) Tam, K. C.; Farmer, M. L.; Jenkins, R. D.; Bassett, D. R. *J. Phys. Chem.* **1993**, *97*, 8336. (g) Thuresson, K.; Nilsson, S.; Kjonjksen, A.-L.; Walderhang, H.; Lindman, B.; Nyström, B. *J. Phys. Chem. B* **1999**, *103*, 1425. (h) Chassenieux, C.; Nicolai, T.; Durand, D. *Macromolecules* **1997**, *30*, 4952.

(5) Tsitsilianis, C.; Iliopoulos, I.; Ducouret, G. *Macromolecules* **2000**, *33*, 2936.

(6) Potemkin, I. I.; Vasilevskaya, V. V.; Khokhlov, A. R. *J. Chem. Phys.* **1999**, *111*, 2809.

(7) Vasilevskaya, V. V.; Potemkin, I. I.; Khokhlow, A. R. *Langmuir* **1999**, *15*, 7918.

(8) Sévéro, Y.; Jacobsen, V.; Berret, J.-F. *Macromolecules* **2000**, *33*, 1841.

(9) Doraiswamy, D.; Mujumdar, A. N.; Tsao, I.; Beris, A. N.; Danforth, S. C.; Metzner, A. B. *J. Rheol.* **1991**, *35*, 647.

(10) Cox, W. P.; Merz, E. H. *J. Polym. Sci.* **1958**, *28*, 619.

(11) Fuoss, R. M. *Discuss. Faraday Soc.* **1951**, *11*, 125.

(12) Dobrynin, A. V.; Rubinstein, M. *Macromolecules* **1999**, *32*, 915.

(13) Cathébras, N.; Collet, A.; Viguier, M.; Berret, J.-F. *Macromolecules* **1998**, *31*, 1305. (b) Sévéro, Y.; Aznar, R.; Porte, G.; Berret, J. F.; Calvet, A.; Collet, A.; Viguier, M. *Phys. Rev. Lett.* **1998**, *81*, 5584.

(14) Semenov, A. N.; Joanny, J.-F.; Khokhlov, A. R. *Macromolecules* **1995**, *28*, 1066.

(15) Dobrynin, A. V.; Colby, R. H.; Rubinstein, M. *Macromolecules* **1995**, *28*, 1859.

(16) Green, M. S.; Tobolsky, A. V. *J. Chem. Phys.* **1946**, *14*, 80.

(17) Tanaka, F.; Ishida, M. *Macromolecules* **1996**, *29*, 7571.

(18) Pham, Q. T.; Pussel, W. B.; Thibeault, J. C.; Lau, W. *Macromolecules* **1999**, *32*, 5139.

(19) Gisler, T.; Ball, R. C.; Weitz, D. A. *Phys. Rev. Lett.* **1999**, *82*, 1064. (b) Buscall, R.; Mills, P. D. A.; Goodwin, J. W.; Lawson, D. W. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 4249.

(20) Nguyen-Misra, M.; Mattice, W. L. *Macromolecules* **1995**, *28*, 6976.

(21) Ng, W. K.; Tam, K. C.; Jenkins, R. D. *J. Rheol.* **2000**, *44*, 137.

(22) Tanaka, F.; Edwards, S. F. *Macromolecules* **1992**, *25*, 1516. (b) Tanaka, F.; Edwards, S. F. *J. Non-Newtonian Fluid Mech.* **1992**, *43*, 247.

(23) Marrucci, G.; Bhargava, S.; Cooper, S. L. *Macromolecules* **1993**, *26*, 6483.