ABC Heterotelechelic Associative Polyelectrolytes. Rheological Behavior in Aqueous Media

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ABSTRACT: A polystyrene–poly(sodium acrylate)–poly(*n*-butyl methacrylate) (PS–PANa–PnBMA) ABC triblock copolymer was synthesized by sequential anionic polymerization and modification of the poly-(*tert*-butyl acrylate) middle block by selective hydrolysis and neutralization to its ionic functions. Because of the fact that both outer hydrophobic blocks are very short comparable to the middle one, this polymer can be viewed as a "heterotelechelic" polyelectrolyte. The rheological behavior of the PS–PANa–PnBMA aqueous solutions was explored by steady state and oscillatory shear flow measurements. Dilute solutions ($c < 1$ wt %) exhibit very high viscosity, showing that these kinds of polymers can be used as effective thickeners. This behavior is attributed to the formation of a transient network constituted from PS and/or PnBMA physical cross-links interconnected by stretched polyelectrolyte chains. An unusual observation is that the viscosity of the system seems to be invariant over a wide temperature range. Finally, the differences between heterotelechelic and telehelic polyelectrolytes of the type PS–PANa–PS are also discussed.

Introduction

During the past decades block copolymers have been widely explored due to their ability to self-assemble into a wide variety of ordered structures. The observed morphologies are governed by several factors such as molecular weight interactions between the different chemically blocks, composition, and, finally, the macromolecular architecture. The simplest cases of the block copolymers are the AB and ABA types, and their phase behavior have been extensively studied both in solution and in the bulk.

More recently, a novel type of linear triblock copolymer, bearing three blocks of different nature (ABC type), exhibiting novel ordered structures and therefore new potential applications, has attracted the interest of several research groups.[1–22] In most cases the research efforts have been focused on the solid-state properties of linear ABC triblock copolymers, and only very few studies have been devoted to their solution properties.[23–29]

Different types of ABC amphiphilic block copolymers have been studied in aqueous solutions where micellization phenomena have been observed. The obtained micellar structures depend strongly on the nature, the position, and the mutual interactions between the different blocks. For instance, when the ABC is constituted from one hydrophobic (A) and two hydrophilic (B, C) blocks, the micelles exhibit a core–shell–shell structure with (A) core and two sequential (B), (C) coronas. On the other hand, when one hydrophilic (C) and two incompatible hydrophobic (A, B) blocks constitute the ABC copolymer, a core–shell structure was observed. In the latter case, the hydrophobic core is constituted from an inner (A) part and an outer (B) core layer, surrounded from the (C) corona.[28] Concerning the morphology of the micelles described above, they exhibit a spherical shape. Very recently, other types of morphologies such as rod and vesicular-like can be formed in water–organic solvent mixtures by hydrophobic–hydrophobic–hydrophilic ABC triblock copolymers, provided that the hydrophilic blocks are short.[29]

In the present paper preliminary results concerning the aqueous solution properties of an amphiphilic ABC triblock copolymer constituted from a central long polyelectrolyte (PANa) end-capped with two different incompatible short hydrophobic blocks (PS, PnBMA) will be reported. In fact, this polymer can be viewed as a hydrophobic end-capped telechelic polymer, with the novelty being that the hydrophobic ends are of different nature. To distinguish this type of polymers from the classical ones, they can be termed as "heterotelechelic". In aqueous media the hydrophobic end-blocks are anticipated to aggregate leading to the formation of an infinite transient network beyond a characteristic concentration denoted C_{gel}. Since the end-blocks PS and PnBMA are incompatible, this fact may have fundamental consequences on their aqueous properties (i.e., micelles, gels).

Very recently, the rheological behavior of a PS–PANa–PS (ABA) triblock copolymer (i.e., telechelic polyelectrolyte) in aqueous media has been reported for the first time.[30] This system exhibits some unique properties compared to those obtained from the classical associative aphiphilic telechelic polymers (e.g., end-capped poly(ethylene oxide)).[31–37] In dilute solutions (concentrations lower than 1 wt %) a transient network is formed, leading to the formation of a physical gel, characterized by low percolation concentration 0.2 wt %, yield stress, complex steady-shear viscosity profile, high plateau modulus, and long relaxation times. These characteristics are ascribed to the highly hydrophobic character of the PS junctions and the stretched conformation of the polyelectrolyte bridges of the network. A first attempt to compare the rheological behavior of the ABC with those of the corresponding ABA will also be presented.

Experimental Section

Materials. Tetrahydrofuran (THF) free from protonic impurities was obtained according to standard procedures. Styrene was distilled twice from sodium wire under vacuum. *tert*-Butyl acrylate (tBA) and *n*-butyl methacrylate (nBMA) were first vacuum-distilled from calcium hydride and accordingly were treated with triethylaluminum (10% solution in heptane). Once a faint yellow was obtained, the monomers were immediately vacuum-distilled into burets. *sec*-Butyllithium was prepared from 2-chlorobutane and Li metal pieces in benzene.

Synthesis. The PS−PtBA−PnBMA was synthesized by anionic polymerization in a glass reactor under inert atmosphere. The sequential addition of the monomers was the synthetic procedure. The polymerization of styrene was initiated first by using *sec*-butyllithium at −40 °C in THF. In the reaction medium a 6-fold LiCl to the active sites was present in order to provide "living" conditions for the polymerization of the second monomer (tBA). After the total consumption of styrene the medium was cooled to −70 °C, and tBA was added dropwise. A sudden color change showed a fast and quantitative initiation of tBA. Finally, the nBMA was introduced after 1 h the addition of tBA. Before the third addition, part of the solution was sampled out and the PS−PtBA precursor was isolated.
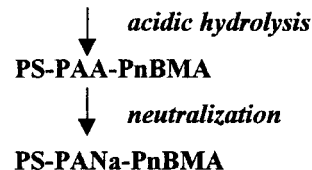
Hydrolysis of PS−PtBA−PnBMA. The PS−PtBA−PnBMA and its precursor PS−PtBA were subjected to acidic hydrolysis in 1,4-dioxane at 80 °C for more than 24 h. The degree of hydrolysis of the resulted polymers was measured by ^{1}H NMR in a mixture of deuterated MeOH:CHCl$_3$ (3:1) and were found to be 98 and 94%, respectively. It should be mentioned here that the protons of the styrene and the remaining tBA units are not visible when the polymer is dissolved in polar solvents like DMSO. The degree of hydrolysis was determined also by potentiometric titration. The solutions for the titration experiments were prepared by dissolving the copolymer in the acid form in a mixture of MeOH:H2O (1:2) 0.1 wt % concentration. Each system was titrated with 0.1N NaOH at least twice, and the acid content was determined 79 wt %.

Size Exclusion Chromatography. SEC was carried out using an apparatus equipped with RI detector (ERC-7515A, Rigas Labs). A set of three styragel columns (waters, HR2, HR3, and HR4) was used, and the calibration curve was obtained by PS standards. The mobile phase was tetrahydrofuran, and the flow rate was 1 cm^3 min^{-1}.

Static Light Scattering. The polymer samples for the SLS measurement were dissolved in tetrahydrofuran; the solutions were filtered through filters of 0.2 μm pore size. All the light scattering experiments were carried out using a thermally regulated (±0.1 °C) spectrogoniometer (model SEM RD, Sematech, France) equipped with a He−Ne laser (633 nm). The specific refractive index increment (dn/dc) required that the light scattering measurements were determined using the Chromatic KMX-16 differential refractometer at a wavelength of 633 nm.

Rheology. Rheological measurements were performed on two different rheometers. Time and frequency sweep tests were ran on a strain-controlled rheometer, Rheometrics RFS-II, equipped with a cone/plate geometry (diameter = 50 mm, angle = 2°, truncation = 45 μm). The steady-state rheological measurements of the solutions were conducted on a controlled stress rheometer (Rheometrics SR-200) equipped with automatic gap setting. A cone/plate geometry (diameter = 25 mm, angle = 2°, gap = 0.056 mm) for the more viscous samples and a couette geometry (cup diameter = 50 mm; cylinder with diameter = 48 mm and length = 25 mm) for the less concentrated samples were used. A rest period of 10 min was employed after loading the samples into the rheometer. This time was proved sufficient to prevent any shear history effect. The shear stress ramping rate used to collect the data were 0.3 and 0.5 Pa/s for the 0.6 and 0.8 wt % solutions, respectively. All the experiments were performed at 25 °C.

Scheme 1

s BuLi + S ⟶ PSLi

PSLi + tBA ⟶ PS-PtBALi

PS-PtBALi + nBuMA ⟶ PS-PtBA-PnBMA

↓ *acidic hydrolysis*

PS-PAA-PnBMA

↓ *neutralization*

PS-PANa-PnBMA

Sample Preparation. For the rheology measurements the solutions were directly prepared to 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 Milli-Q) to the final volume. The samples were stirred and heated for 48 h (this is the time which is required to attain equilibrium) at 100 °C. They were centrifuged several times for short periods during the heating procedure for better solution mixing. When equilibrium was attained, the samples were allowed to cool to room temperature and weighted. The concentrations were corrected to take into account possible loss of water (less than 1%) during the heating procedure. Good reproducibility in the rheological properties was found after that treatment.

Results and Discussion

Synthesis and Characterization. The heterotelechelic polyelectrolyte employed in the present study is in fact an ABC triblock copolymer with long B and short A, C blocks. The synthesis of the copolymer was performed according to Scheme 1. A polystyrene−poly-(*tert*-butyl acrylate)−poly(*n*-butyl methacrylate) (PS−PtBA−PnBMA) triblock copolymer was synthesized by anionic polymerization following the method of sequential addition of the monomers.

sBuLi was used as the initiator, and the polymerization of styrene was carried out at −40 °C. After the consumption of the monomer the reaction medium was cooled to −70 °C, and the *tert*-butyl acrylate was introduced dropwise. To avoid attack of the anionic sites to the carbonyl of the t-BA, a 6-fold LiCl per living ends was present in the medium.[38] Finally, the third monomer (n-BMA) was added after the consumption of the second monomer. The reaction medium was deactivated protonically, and the final product was precipitated in a MeOH/water (80:20) mixture, redissolved in benzene, and freeze-dried. The SEC chromatogram of the PS−PtBA−PnBMA triblock copolymer is illustrated in Figure 1. A well-defined ABC block copolymer with symmetrical monomodal peak and narrow molecular weight distribution can be observed. The copolymer was further characterized by static light scattering and ^{1}H NMR. The characterization data are collected in Table 1.

Subsequently, the triblock copolymer was subjected to acid-catalyzed hydrolysis in order to modify the ester groups of the PtBA middle block to its acid form. ^{1}H NMR spectra of the hydrolyzed copolymer showed that the 98% of the PtBA has been modified to poly(acrylic acid). Moreover, the hydrolysis is selective for the tBA groups and does not affect the nBMA groups as revealed by the remaining peak corresponding to the −O−CH$_2$−
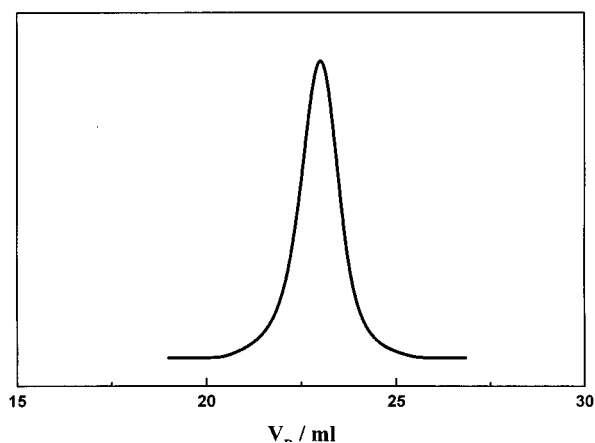
Figure 1. SEC chromatogram of the PS−PtBA−PnBMA triblock copolymer.

Table 1. Molecular Characteristics of PS−PANa−PnBMA

PS−PtBA−PnBMA (presursor)
M_w (LS): 113 000
M_w/M_n (GPC): $I = 1.16$
composition, wt % (NMR): 3.3% PS−95.6% PtBA−1,1% PnBMA
PS−PAA−PnBMA resulted from 98% hydrolysis of PtBA
M_w (calculated): 66 700
composition in monomer units
  PS$_{35}$−(PAA$_{827}$-co-PtBA$_{17}$)−PnBMA$_9$
PS−PANa−PnBMA resulted from 80% neutralization
M_w (calculated): 81 500

protons of the *n*-butyl ester group at 4 ppm in the ^{1}H NMR spectra. The degree of hydrolysis of the polymer was also determined by potentiometric titration with NaOH and was found to be 80%,which is significantly lower than that obtained by ^{1}H NMR. This discrepancy was also observed and discussed in the system PS−PAA−PS studied recently.[30]

Neutralization of the PAA middle block was carried out in solution by adding an equivalent amount of NaOH as determined from the potentiometric titration (i.e., degree of neutralization 80%). All the characterization data concerning the heterotelechelic polyelectrolyte are presented in Table 1.

Steady-State Shear Flow. Rheological characterization of the PS−PANa−PnBMA triblock copolymer in aqueous solutions was performed by steady-state shear flow measurements. In Figure 2 the steady-state shear viscosity, η, of a 0.3 wt % polymer solution is presented as a function of shear rate, $\dot{\gamma}$. In the same figure the shear rate dependence of η for the aqueous solution of PS−PANa diblock precursor of the same concentration is also depicted. The two polymers have the same molecular characteristics except that the PS−PANa−PnBMA bears nine nBMA hydrophobic units (1.5 wt % of the polymer) at the other end. This small difference on their molecular characteristics imposes dramatic differences on their rheological behavior. The PS−PANa solution behaves as a Newtonian liquid of very low viscosity whereas the PS−PANa−PnBMA solution exhibits a shear thinning effect over the entire shear rate region. The most significant effect is that the magnitude of the viscosity of the PS−PANa−PnBMA, at the lower $\dot{\gamma}$, reaches about 10^3 Pa·s, which is approximately 6 orders of magnitude higher than that of the PS−PANa precursor. The fact that such a value of η corresponds to an aqueous solution of very low concentration shows that this polymer exhibits a very powerful thickening efficiency.
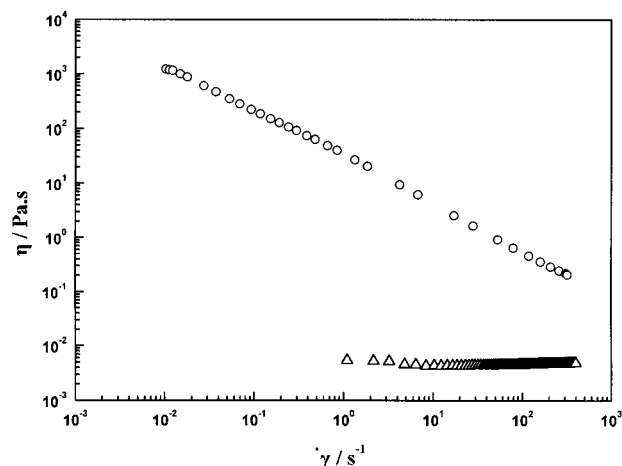

Figure 2. Steady-state shear viscosity η versus shear rate $\dot{\gamma}$ for 0.3 wt % aqueous solution of PS−PANa−PnBMA (○) and its PS−PANa precursor (△).
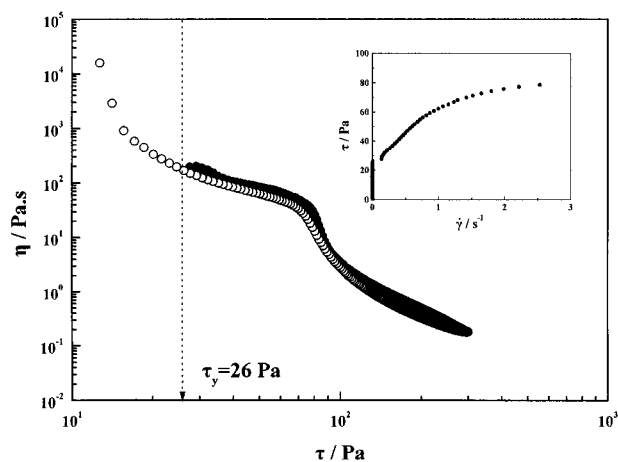

Figure 3. Steady-state shear viscosity η versus shear stress τ for 0.6 wt % aqueous solution of PS−PANa−PnBMA: closed symbols, increasing-τ curve; open symbols, decreasing-τ curve. In the inset, shear stress τ versus shear rate $\dot{\gamma}$ (magnification of the low shear rate region).

The rheological behavior of a more concentrated solution $c = 0.6$ wt % of PS−PANa−PnBMA was also examined. The viscosity profile of the solution can be illustrated better in a η versus shear stress plot (Figure 3). The system exhibits a yield stress at $\tau_y = 26$ Pa as can be observed from the shear stress versus $\dot{\gamma}$ plot in the inset of Figure 3. Once the yield stress is exceeded, the viscosity diminishes continuously along the entire shear rate region. Three shear thinning regions can mainly be distinguished. In the first region between 26 and 75 Pa the solution viscosity decreases smoothly. The second region is characterized by a discontinuity. Indeed, a sharp drop of the viscosity (1 order of magnitude lower) in a narrow shear stress range, i.e., $80 < \tau < 100$ Pa, can be observed. Finally in the third region, $\tau > 100$ Pa, the viscosity continues to decrease more sharply compared to that in the first region. This kind of behavior has been observed recently in PS end-capped poly(sodium acrylate) aqueous solutions and has been attributed to the formation of a transient network constituted from PS hydrophobic physical cross-links (aggregates) interconnected by PANa chains.[30]

A possible interpretation of the above observed flow behavior could be the following. Upon the application of a shear stress ($\tau > \tau_y$) the infinite network breaks
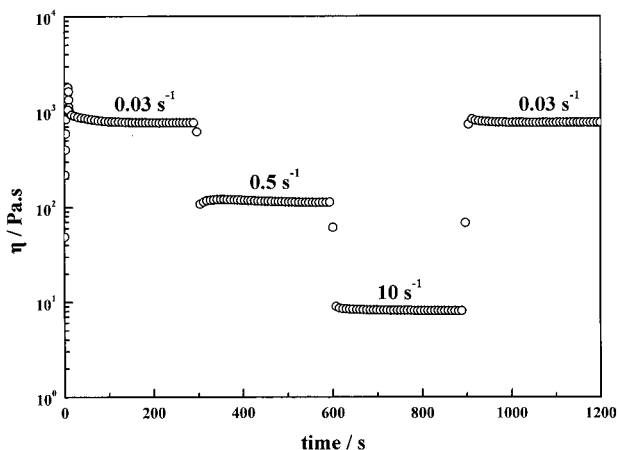
Figure 4. Steady-state shear viscosity η versus time at deferent shear rates for 0.6 wt % PS−PANa−PnBMA aqueous solution.

Figure 5. Storage modulus G' (circles) and loss modulus G'' (triangles) as a function of frequency for PS−PANa−PnBMA aqueous solutions at 0.6 wt % polymer concentration.

Figure 6. Steady-state shear viscosity η versus shear stress τ for 0.8 wt % aqueous solutions of PS−PANa−PnBMA (□) and PS−PANa−PS (○): closed symbols, increasing-τ curve; open symbols, decreasing-τ curve.

down to large finite clusters that can move past each other, allowing the solution to flow. A second dramatic event takes place at higher shear stress in the discontinuity region. At this point the large clusters are further disrupted to smaller fragments. In the present system and at this concentration these phenomena seem to be practically reversible as can be observed by comparing the increasing and decreasing shear stress curves (Figure 3). The reversibility is extended in the region of stresses higher that τ_y. An interesting phenomenon takes place for $\tau < \tau_y$. Upon decreasing τ, the viscosity continues to increase, reaching 1.5×10^4 Pa·s at $\tau = 13$ Pa, which is about 2 orders of magnitude higher than that attained at τ_y. The yield stress also has been shifted from 26 to 13 Pa.

A time sweep experiment was also performed at different constant shear rates for the 0.6 wt % polymer solution. As shown in Figure 4, the viscosity appears to be time independent at all shear rates examined. A viscosity overshoot observed just at the beginning of the first step is a typical behavior for structured fluids exhibiting a yield stress. An interesting and unusual effect observed in Figure 4 is the absence of thixotropy. In fact, after the disruption of the transient network upon shearing at 10 s^{-1}, which lies in the third shear thinning region (Figure 3), the system attains its initial superstructure instantaneously. This is in agreement with the shear rate sweep experiment illustrated in Figure 3. Furthermore, the viscosity values are in excellent agreement between the two experiments although they have been carried out with different experimental apparatus.

Oscillatory Shear Measurements. To confirm the existence of a strong physical network, oscillatory shear experiments were performed within the linear viscoelastic regime, by using a strain-controlled rheometer. The storage and the loss moduli as a function of frequency, ω, are plotted for 0.6 aqueous solutions in Figure 5. Over the entire frequency range studied, G' exceeds G'' by about 1 order of magnitude and is virtually independent of ω, indicating that the solution behaves like a highly elastic gel. Obviously, the frequency range examined in the present system is located in the plateau zone of the mechanical spectrum. The terminal zone cannot be explored since the network relaxation time, related to the detachment of a hydrophobe from a junction, is very high (>100 s). Stress relaxation experiments are needed for the determination
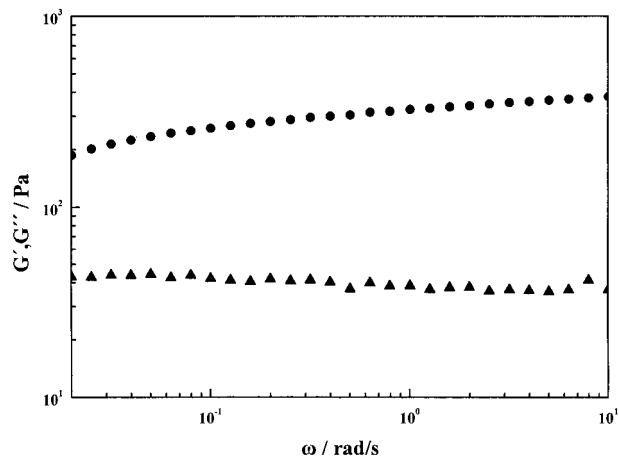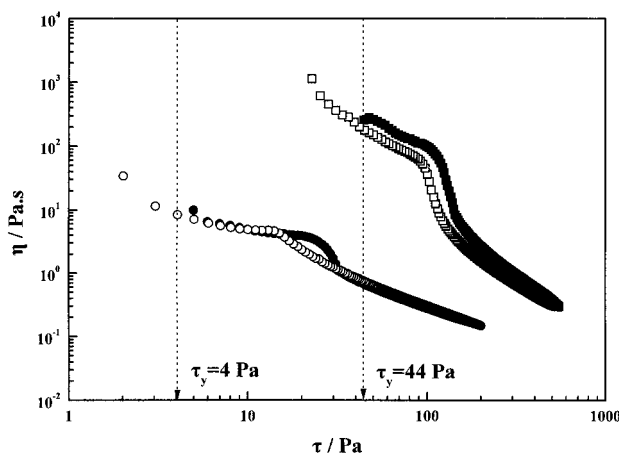
of the relaxation times and will be provided in a forthcoming paper.

Comparison between ABA and ABC Associative Polyelectrolytes. To elucidate the effect of the macromolecular architecture on the rheological phenomena of the aqueous solutions of the linear associative polyelectrolytes, we compare the steady-state flow behavior of the $PS_{23}-PANa_{1134}-PS_{23}$ with those of the $PS_{35}-PANa_{844}-PnBMA_9$. The viscosity profiles of 0.8 wt % solutions for both polymers are depicted in Figure 6.

The two systems although they exhibit similar viscosity profiles, i.e., three shear thinning regions with an intermediate discontinuity, they differ in various respects. The yield stress for the ABC has been shifted 1 order of magnitude to higher values. The magnitude of viscosity at a given stress, e.g. 44 Pa, is 300 times higher for the ABC. Finally, the recovery of the system upon decreasing τ also differs. The ABA exhibits only a hysteresis loop in the region of discontinuity while a thixotropic behavior in the entire shear thinning region can be observed for the ABC. We note here that this behavior depends on the concentration of the solution since it is not observed at $c = 0.6\%$. It seems that this hysteresis is attributed to the higher viscosity of the medium for the more concentrated solution and the difficulty of the system to attain the previous structure instantaneously. The two polymers are not strictly

comparable in terms of their molecular characteristics. The PS block is somewhat longer while the PANa middle block is shorter for the ABC triblock copolymer. However, the significant differences observed on their rheological behavior cannot be justified from these molecular dissimilarities and should be attributed to the different molecular architecture which imposes a different supramolecular structure.

Aggregation Mechanism. The telechelic polyelectrolytes are in fact amphiphilic triblock copolymers constituted from a hydrophilic long chain, end-capped at both ends with hydrophobic short blocks. These polymers undergo aggregation in aqueous solutions since water is a selective solvent for the middle block. The anticipated structure of the aggregates in the case of nonionic telechelics, at low concentrations, is the "flower"-type spherical micelles as have been observed for the poly(ethylene oxide) derivatives.[31] In the case where the middle block is ionic and especially fully charged, backfolding of the middle block is prevented from the coulomb repulsive interactions of the charges along the chains. On the other hand, the end hydrophobic groups (stickers) tend to associate by forming aggregates, which constitute reversible junctions between different polymer chains. If the attraction energy is much higher than the thermal one, the formation of finite size clusters of associating polyelectrolytes is quite possible in the dilute regime as predicted from recent theoretical considerations.[39] The system PS−PANa−PS seems to fulfill the above statement since the PS chains are highly hydrophobic.[40] At higher concentrations and beyond a percolation threshold, c_{gel}, an intercluster association will occur, and the formation of an infinite transient network is anticipated. This has also been observed with the PS end-capped polyelectrolytes.[30] The system of the present work should behave in principle in a similar manner. The only difference is that one of the PS hydrophobic ends has now been substituted with a somewhat less hydrophobic PnBMA block (smaller number of monomer units). The fact that these ends are incompatible may play an additional role. Two are the possible structures that may form with the heterotelechelic polyelectrolytes. The transient network is constituted from either mixed PS/PnBMA hydrophobic aggregates or two pure PS and PnBMA aggregates, which play the role of the physical cross-links. The latter seems to be more likely as the different block ends do not attract each other. However, more direct evidence is needed in order to elucidate the exact structure of the system, and to this direction further work is now in progress.

The rheological response of the system shows that at the concentrations examined an infinite transient network has been formed, and the gelation concentration is lower than $c = 0.3$ wt %. This is one of the advantages of the present system with respect to other nonionic telechelic water-soluble polymers.

Temperature Dependence. The effect of temperature on the steady-shear viscosity of an aqueous solution of 0.6 wt % was explored. The viscosity η as a function of shear rate at different temperatures is illustrated in Figure 7a. An unusual behavior can be observed. The viscosity profile seems to be temperature independent. This is clearly shown by plotting η at a fixed shear rate (0.1 s^{-1}) as a function of temperature (Figure 7b). As has been shown, the viscosity of the medium (water) has been increased about 6 orders of magnitude with
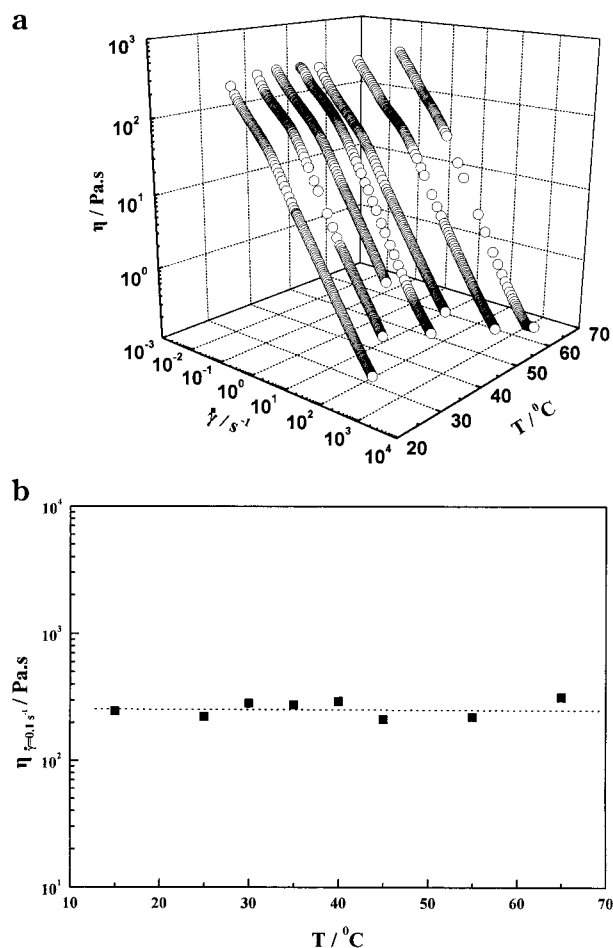

Figure 7. Steady-state shear viscosity η versus shear rate $\dot{\gamma}$ for 0.6 wt % PS−PANa−PnBMA aqueous solution at deferent temperatures (a) and η at $\dot{\gamma} = 0.1$ s^{-1} versus temperature (b).

the presence of a small amount of the polymer, and this has been attributed to the formation of an infinite physical network. Therefore, such high values of viscosity are due almost exclusively to the superstructure of the system. The fact that viscosity is nearly invariant with temperature should be ascribed to the stability of the structure over the temperature range examined, which is responsible for the viscometric behavior of the system. This unique property may be proved useful for specific applications.

Conclusions

In this work the aqueous solution behavior of an ABC triblock copolymer constituted from a long polyelectrolyte bearing at both ends hydrophobic short chains of different nature, named as heterotelechelic polyelectrolytes, is presented for the first time. This novel macromolecular architecture has fundamental consequences on the rheological properties of dilute aqueous polymer solutions.

The viscosity of a 0.3 wt % polymer solution is 6 orders of magnitude higher than that of water, suggesting that this kind of polymers can be used as effective thickeners. The steady shear viscosity profile reveals a complex rheological behavior, i.e., yield stress, several thinning regimes, reversibility at low concentrations. These properties were attributed to the formation of a transient network possibly constituted from two kinds of aggregates (PS and/or BMA) bridged by extended poly-

electrolyte chains. The critical concentration at which the infinite structure form is remarkably low, i.e., $c < 0.3$ wt %.

Comparing the rheological properties between the PS−PANa−PS and PS−PANa−PnBMA, we conclude that the latter exhibits more pronounced phenomena due to the different macromolecular architecture.

To the advantages of the present system we should add the fact that the ABC can be synthesized more easily than the ABA, using the sequential anionic "living" copolymerization technique. In this case, time-consuming procedures, e.g. fractionation, can be avoided.

Finally, it was observed that viscosity is nearly independent of temperature over a wide temperature range. This unusual rheological behavior of the present system may be proved useful for specific applications.

Further work is now in progress, the results of which will be reported in a forthcoming paper.

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