Macromolecules 1994, *27*, 234–239

Solution Properties of a Diblock Copolymer in a Selective Solvent of Marginal Quality. 1. Phase Diagram and Rheological Behavior

D. F. Siqueira[†] **and S. P. Nunes***

Universidade Estadual de Campinas, Institute of Chemistry, 13081 Campinas-SP, Brazil

B. A. Wolf*

Johannes Gutenberg Universität, Institut für physikalische Chemie,
D-55099 Mainz, Germany

Received July 28, 1993; Revised Manuscript Received October 15, 1993[●]

ABSTRACT: A diblock copolymer of styrene and butyl methacrylate with narrow molecular weight distribution [P(S-*b*-BMA)] containing 1200 monomeric units of S and 1250 of BMA was studied in 2-propanol [2-POH], which is a nonsolvent for the S blocks and a Θ solvent (UCST) for the BMA blocks. The phase diagram of the present system is almost indistinguishable from that of 2-POH/PBMA if the molecular weight of the homopolymer is identical with that of the BMA block. The comparison of the intrinsic viscosities $[\eta]$ of P(S-*b*-BMA) and PBMA in 2-POH and of their variation with temperature demonstrates that $[\eta]_{\mathrm{P(S\text{-}b\text{-}BMA)}}$ reflects the presence of micelles rather than unimers. The rheological behavior of moderately concentrated solutions can be understood in terms of an overlap concentration c^* defined as $[\eta]^{-1}_{\mathrm{P(S\text{-}b\text{-}BMA)}}$. Below c^* the viscosity η changes with temperature as usual, and the liquids are Newtonian up to shear rates $\dot{\gamma}$ of several thousand inverse seconds. Above c^* the viscosity *increases* up to 1 order of magnitude as T is raised; shear thinning is observed within the entire $\dot{\gamma}$ range under investigation. All experimental findings can be consistently explained in terms of micelles in which the S blocks are effectively hidden in the cores and the PBMA blocks form the outer shell. The inverse temperature dependence of η stems from the expansion of the PBMA layers resulting from the improvement of thermodynamic quality of the solvent with rising distance from the miscibility gap of the system; the higher the temperature becomes, the more the coronae of the micelles penetrate each other and the more their relative movement is hindered.

Introduction

The properties of the solutions of block copolymer are in many respects quite different from those of homopolymers; this is particularly true for the rheological behavior which makes these substances very useful for some specific applications (e.g., as additives for automobile motor oil[1–3] and as gelification agents in the cosmetic industry[4,5]).

Block copolymers dissolve in nonselective solvents (good for both blocks) or in selective solvents (good for one block only). In the latter instance (where the liquid can be really good or marginal, i.e., a Θ solvent for the A blocks and a nonsolvent for the B blocks) micelles are normally formed with a core of B and a corona of A, which is swollen by the solvent.

Some rheological information on block copolymer solutions in selective solvents is available in the literature.[6–11] A transition upon the variation of composition was detected: above a characteristic concentration the viscosity increases more pronouncedly than below. This information stems from measurements of the zero shear viscosity as a function of concentration in the case of an ABA triblock copolymer in a mixed solvent[6] and of a styrene–2-vinylpyridine diblock copolymers in semidilute solution.[7] Hashimoto and co-workers[8,9] reported a critical concentration associated with an order-to-disorder transition which was detected in measurements of shear stresses at different shear rates for solutions of a polystyrene–polybutadiene diblock copolymer in *n*-tetradecane. Below this characteristic concentration the system is Newtonian; above it behaves shear thinning. At even higher concentrations, a further transition was detected above which a nonlinear plastic behavior predominates. Higgins and coworkers[10] showed that solutions of polystyrene-*block*-(ethylene-*co*-propylene) diblock copolymers in dodecane above a critical composition behave like "weak gels" with a pronounced frequency dependence of the dynamic viscosity.

In contrast to the results[2,3,6–11] discussed so far on solvents which are good for one block but precipitants for the other, there is almost no information on the miscibility and rheological behavior of systems under less favorable thermodynamic conditions, in which the solvent is marginal, i.e., a Θ **solvent**, for one block and a precipitant for the other. Solutions of poly(styrene)-*block*-poly(butyl methacrylate), P(S-*b*-BMA), in 2-propanol (2-POH) were therefore investigated up to concentrations of 8.5 wt % and in a temperature range from 15 to 40 °C; 2-propanol is a Θ solvent for the BMA blocks (Θ = 23.0 °C)[12–16] and a nonsolvent for the styrene blocks.

The present contribution deals with the phase diagram and the rheological behavior of 2-POH/P(S-*b*-BMA). The results of a study on the existence of micelles in dilute solution and their characterization by transmission electron microscopy, light scattering, and small-angle X-ray scattering will be reported in the next paper.[17]

Experimental Section

Materials. The linear copolymer poly(styrene)-*block*-poly(butyl methacrylate), P(S-*b*-BMA), was purchased from Polymer Standard Service, Mainz. It was obtained by anionic polymerization and consists (according to the characterization given by the supplier) of 1200 monomeric units of S and 1250 of BMA.

This starting material (F0) was fractionated in two steps according to a method developed by Sander,[18] and the different fractions were characterized by gel permeation chromatography (GPC); the results are shown in Figure 1. The first step of this procedure eliminates chains with low elution volume by a dropwise precipitation of the block copolymer from a concentrated solution in THF using a 7-fold surplus of methanol as precipitant. The segregated main fraction (F1) was redissolved in *n*-heptane at 65

[†] Performed some of the present work at the Johannes Gutenberg University of Mainz, within the project DAAD-Stifterverband/Brazil.

[●] Abstract published in *Advance ACS Abstracts*, December 1, 1993.

0024-9297/94/2227-0234$04.50/0

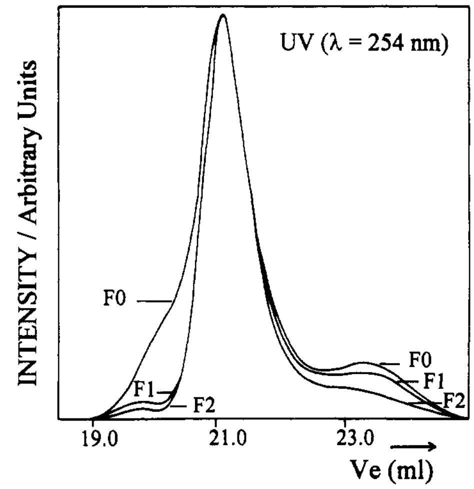

Figure 1. GPC diagrams of the original sample (F0) of the anionically prepared P(S-*b*-BMA), of the first (F1) and of the second fraction (F2).

°C, cooled to 54.5 °C, and kept at this temperature for 8 h. After that, the temperature was further decreased to the room temperature where a sol and a gel phase form. The gel contains the desired purified P(S-*b*-BMA); it was isolated from the gel by dissolution in THF and precipitation in methanol. This fraction (F2), which was used for the present study, has (according to GPC measurements in THF and evaluation by means of a universal calibration with PS) a molecular weight M_w of 280 kg/mol and a polydispersity index M_w/M_n of 1.17.

GPC Measurements. The GPC measurements were performed in a Waters U6K injection system, with a polystyrene gel column supplied by Polymer Standard Service (Mainz). A Knauer UV detector (254 nm) and a Showa-Denko differential refractometer were used as detectors. The eluent used was tetrahydrofuran (THF), the injection volume 50 μL, the sample concentration 2 mg/mL, and the measuring temperature 25 °C.

Phase Diagrams. The cloud points of the solutions of P(S-*b*-BMA) in 2-POH were determined (at nonshearing conditions) using an apparatus described by Horst.[19] It consists of a laser as radiation source and a photodiode as detector. The detector is connected to a microcomputer which controls the cooling rate and registers the light transmitted through the sample. Solutions were prepared within a concentration range between 0.4 and 9.8 wt % and measured in closed glass cells with an optical path of 1.2 mm. The turbidities were determined for cooling rates of 0.1 °C/min, with a minimum total reproducibility of the cloud point temperatures of 0.3 °C.

Coexisting Phases. To find out whether P(S-*b*-BMA) is fractioned during phase separation, the following experiment was performed. A 1.0 wt % copolymer solution was slowly (0.1 °C) cooled to 18.2 °C in a water bath. At this temperature, it takes 7 days to achieve equilibrium (as indicated by a constant position of the meniscus between the phases). The sol phase was then quantitatively withdrawn using a syringe, whereas the remaining gel was diluted with THF before its removal. The solvent was evaporated by a rotary evaporator, and the remaining phases were dried under vacuum at 50 °C for 3 days, weighted, and analyzed by GPC.

Capillary Viscometry. Flow times (>330 s) of dilute solutions of P(S-*b*-BMA) in 2-POH were determined in automatic Ubbelohde viscometers immersed in a water bath. The measurements were performed in the usual manner in a AVS automatic viscosity measuring instrument produced by Schott-Geräte (Mainz) with a reproducibility of ±0.1 s for pure 2-POH and for polymer concentrations ranging from 8.5 to 15 mg/mL (1.0 to 1.88 wt %) at 40 and 25 °C.

Rotational Viscometry. Rheological measurements were performed with the Haake rotational viscometer RV2 NV50/500, using a bell-shaped rotor, for shear rates $\dot{\gamma}$ from 5.4 to 5400 s^{-1}. Solutions of P(S-*b*-BMA) in 2-POH with compositions between 2.11 and 8.50 wt % were measured in two different ways. In one series, the temperature was kept constant (at 40, 35, 30, 25, 23, 22, 21, 20, 19, 18, and 17 °C), and $\dot{\gamma}$ was scanned. In a second set of experiments, the shear rate was kept constant at different values, and the system was cooled from 40 to 17 °C at a cooling rate of 0.1 °C/min.

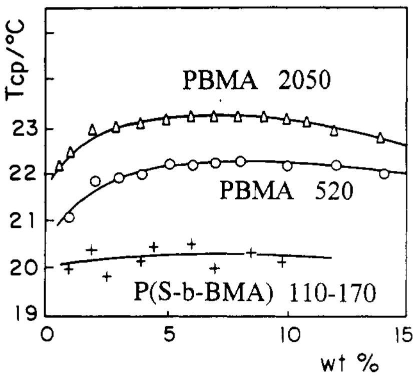

Figure 2. Cloud point curves of the system 2-POH/P(S-*b*-BMA) and of two samples[12,13] of PBMA in the same solvent.

Rheooptical Measurements. The phase separation of a 5.9 wt % P(S-*b*-BMA) solution in 2-POH was investigated in a rheooptical apparatus, developed by Horst.[19] It consists of the Haake rotational viscometer RV2 and a MK50/500 measuring head; the rotor (inner cylinder) and the stator bear windows that allow the detection of the light transmitted from a He–Ne laser across the sample. A photodiode, registering the results, is connected to a Hewlett-Packard computer, which also controls the experimental conditions. With this equipment it is possible to reach shear rates of 3000 s^{-1} and to measure turbidity and viscosity simultaneously, while the temperature is changed at a controlled rate. Typically, the experiments were performed choosing 26 °C as the starting and 20 °C as the end temperatures cooling with 0.1 °C/min at $\dot{\gamma}$ equal to 490, 980, and 1960 s^{-1}.

Results and Discussion

Phase Diagram. 2-POH is a selective solvent of marginal quality (Θ solvent) for the butyl methacrylate block of P(S-*b*-BMA), whereas it is a precipitant for the styrene block. In dilute solutions the polymer forms *inter*molecular aggregates (micelles) to avoid the highly unfavorable contacts between the S blocks and the solvent. The chemical potential of free chains of block copolymers in this selective solvent[20] is directly proportional to the (very large) interfacial tension between S blocks and the solvent. As will be demonstrated,[17] micelles are observed for this system even in very high dilution. The S cores are barely swollen by the solvent, and the properties of the solutions of P(S-*b*-BMA) resemble in some respects that of the PBMA homopolymer in the same solvent. This is particularly true for the phase separation behavior of the present system as can be seen from Figure 2.

This figure shows the cloud point curves for the system 2-POH/P(S-*b*-BMA) together with that of two samples of the homopolymer PBMA[12,13] in the same solvent. The data points scatter considerably more for the copolymer than for the homopolymer; this is so because of a remarkably large opalescence of the solutions of the block copolymers within the homogeneous region close to phase separation. The curves are shaped very similarly and can be superimposed to a high degree of accuracy if one compares the results for P(S-*b*-BMA) with that for a sample of PBMA with the same molecular weight as the BMA block of the copolymer. This observation indicates that the S domains are very effectively protected from any interaction with the solvent by the BMA coronae.

To test whether the molecular and/or chemical nonuniformity of the P(S-*b*-BMA) fraction F2 used for the rheological measurements can still be felt in the case of phase equilibria, it was investigated with a starting solution of 1.0 wt % copolymer (as described in the Experimental

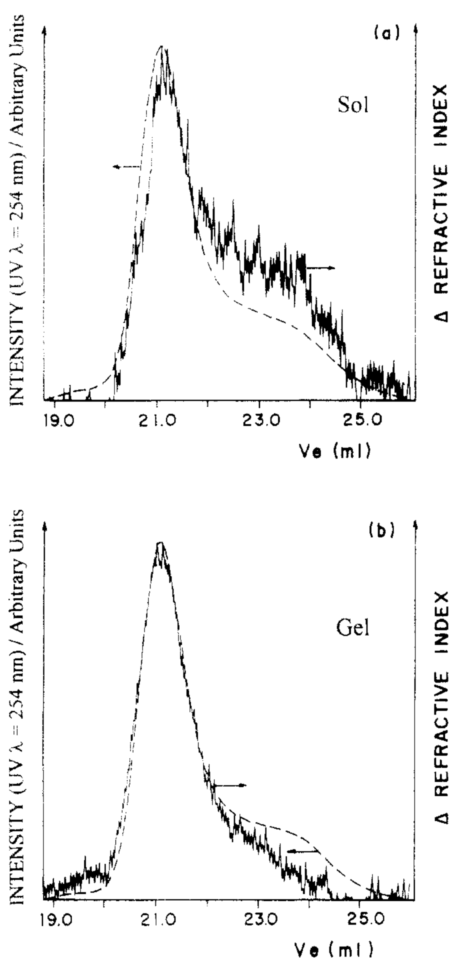

Figure 3. GPC analysis of the P(S-*b*-BMA) contained in the sol (a) and in the gel (b) phase that coexist at 18.2 °C for an overall polymer concentration of 1 wt %.

Section) to what extent the polymer is fractionated as the system demixes into a dilute (0.35 wt %) sol and concentrated (9.70 wt %) gel phase. The GPC diagrams of the polymer fractions shown in Figure 3 demonstrate that, although the maxima are practically identical, the sol contains more of the material with the larger elution volumes than the gel.

Intrinsic Viscosities. The normal evaluation[21] of the data with respect to the intrinsic viscosity $[\eta]$ turned out to be difficult for the solutions of P(S-*b*-BMA) in 2-POH because of nonlinear plots of the reduced specific viscosity η_{sp}/c_2 as a function of polymer concentration c_2. This behavior may be due either to micelle formation or to an intrachain phase separation, since 2-POH is a Θ solvent for the BMA block and a nonsolvent for the S blocks. Although the latter explanation via conformational anomalies in dilute solutions would be in accord with reports in the literature,[7,22] this effect is attributed to the formation of micelles,[17] and it is concluded that the hydrodynamic volume of isolated entities (chains or micelles) determined by extrapolation to infinite dilution corresponds to micelles rather than to unimers.

To overcome the above-mentioned difficulty in obtaining $[\eta]$ values in Huggins plots, the data stemming from capillary viscometry (filled symbols) were complemented by data for higher concentration obtained from rotational viscometry (open symbols). In this manner the intrinsic viscosities can at least be estimated to a high degree of reliability by the fact[23] that $\lim_{c_2 \to 0} (\partial \ln \eta / \partial c_2) = [\eta]$. From the initial slope of the polynomial regressions of $\ln \eta$ as a function of c_2 shown in Figure 4, one ends up with 14 ± 1 mL/g for 25 °C and 38.4 ± 0.8 mL/g for 40 °C.

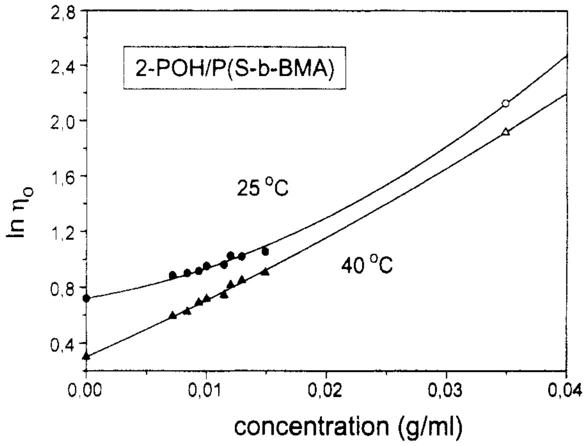

Figure 4. Plot of $\ln \eta_0$ as a function of concentration for 2-POH/P(S-*b*-BMA) at 25 and 40 °C. The filled symbols stand for capillary measurements and the open ones for rotational measurements.

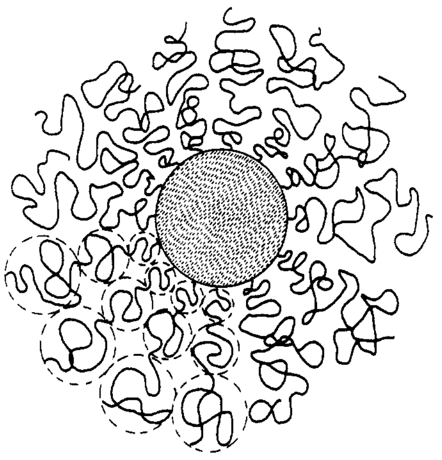

Figure 5. Scheme of the conformation of the BMA blocks of the corona of the micelles P(S-*b*-BMA); the core consists of the S blocks.

It is interesting to note that the intrinsic viscosity of the PBMA block alone is 16 mL/g at 25 °C as compared with the above 14 mL/g (ascribed to micelles) at the same temperature. In view of the observation[17] that the aggregates in 2-POH contain approximately 160 copolymer molecules, this observation is remarkable. Raising the temperature from 25 to 40 °C improves the quality of 2-POH considerably, expands the PBMA corona of the micelles, and almost triples their intrinsic viscosity. These data for the micelles have to be compared with that of the unimers of P(S-*b*-BMA) in cyclohexanone (a good solvent for both blocks) for which the intrinsic viscosity is approximately 7 times as large,[18] namely, 96 mL/g.

The above observations demonstrate that the styrene blocks are extremely contracted in the cores, avoiding any interaction with the solvent, even at higher temperatures. Since the BMA blocks are firmly attached to the S core, they assume a more contracted conformation than free molecules of the homopolymer PBMA with the same molecular weight under otherwise identical conditions. On the basis of a theoretical model reported in the literature,[20] one can draw the scheme presented in Figure 5.

This interpretation is also backed by the work of Yao et al.,[24] who showed by dielectric measurements for styrene–isoprene diblock copolymers in a selective solvent that the isoprene blocks of the corona are subjected to strong thermodynamic confinements as compared with the corresponding homopolymer.

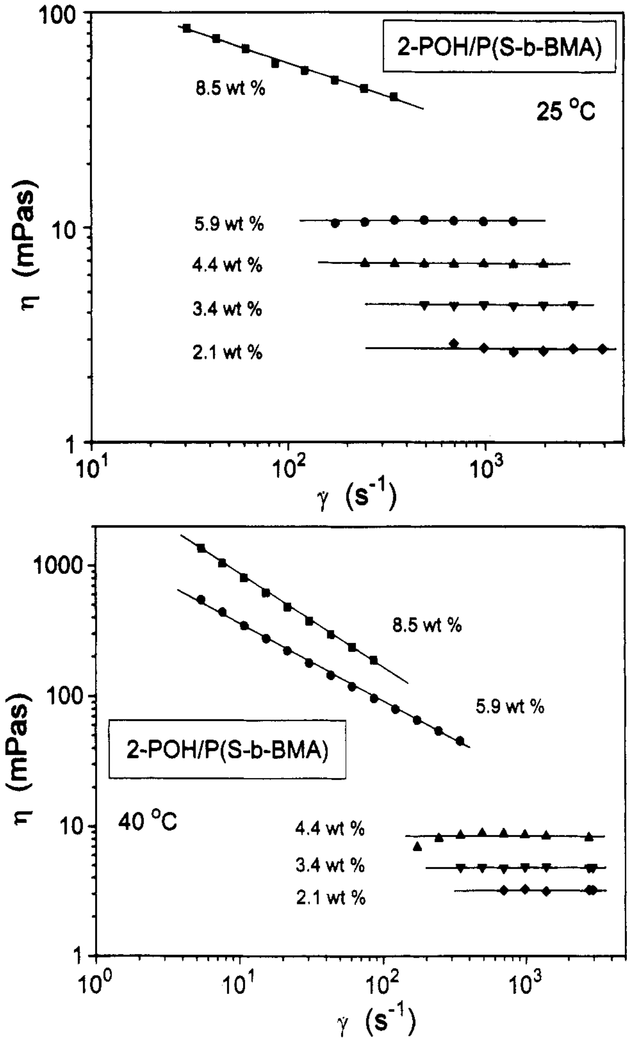

Figure 6. Flow curves for solutions of P(S-*b*-BMA) in 2-POH at 25 °C (a, top) and at 40 °C (b, bottom).

Viscosities as a Function of Shear Rate. The present investigation focuses on the rheological behavior as a function of composition (moderate polymer concentrations) and of the *T* distance from phase separation. Figure 6, a and b, shows steady-flow curves for 25 and 40 °C, respectively.

In the above temperature range the components are completely miscible. At 25 °C (Figure 6a) the solutions are Newtonian within the present range of shear rates up to 5.9 wt % (inclusive) of the polymer; at higher concentrations, above a certain characteristic concentration c^*, one observes shear thinning. As the temperature increases, c^* decreases (cf. Figure 6b, where the 5.9 wt % solution is already markedly non-Newtonian). The intuition that the above characteristic concentrations should correspond to the conditions at which the micelles begin to touch each other and the BMA blocks start to entangle to corroborated by the intrinsic viscosities and their *T* dependence. Equating the entanglement concentration, c^*, to the characteristic coil overlap concentration, which is the inverse[25] of $[\eta]$, leads to a fair agreement with the observations concerning shear thinning. The $[\eta]$ value for 25 °C leads to an entanglement concentration of 7.0 ± 0.5 wt %, and that for 40 °C results in 3.0 ± 0.1 wt %.

Keeping the polymer concentration constant at a comparatively large value, one can investigate how the non-Newtonian behavior varies with temperature. Figure 7 shows the results for the highest polymer content in terms of the power-law exponent defined as $d^* = \partial \ln \eta / \partial \ln \dot{\gamma}$.

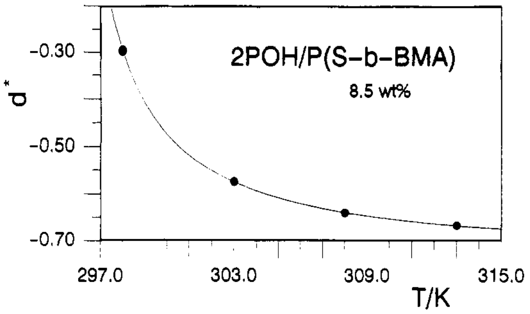

Figure 7. Temperature dependence of the power-law exponent d^* for an 8.5 wt % solution of P(S-*b*-BMA) in 2-POH.

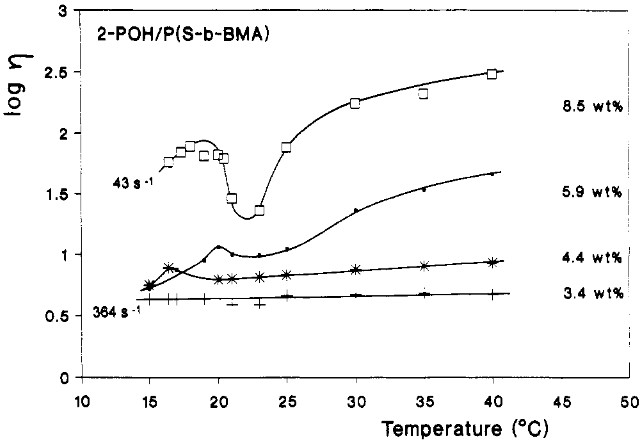

Figure 8. Temperature dependence of the viscosity for the system 2-POH/P(S-*b*-BMA) and shear rates of 43 and 346 s^{-1}, respectively.

According to these data, the extent of shear thinning is least close to phase separation and increases considerably as *T* is raised. This observation is in good agreement with the present molecular model: At low temperatures the PBMA blocks of the copolymer (from which the coronae of the micelle are made up) avoid the contact to the solvent so that the entanglement density remains low; as *T* is increased and the solvent becomes better, the degree of overlap of the shell of the micelles and consequently the number of entanglements between the PBMA strands rise. It is interesting to note that within the present *T* range the d^* value does not fall to −0.82, the value which is typical for solutions of homopolymers and which is found for PBMA.[12]

Viscosities as a Function of Temperature. The *T* dependence of the viscosity was measured in two different manners, as described before, with identical results (Figure 8). Dilute solutions of 2-POH/P(S-*b*-BMA) (2.11 < wt % < 3.37) show almost no dependence of viscosity on temperature up to $\dot{\gamma} = 4000\ s^{-1}$. For block copolymer concentrations higher than 4.4 wt %, when the micelles begin to entangle, one observes behavior which is contrary to that of homopolymer solutions.

The uncommon temperature dependence of η observed with higher polymer concentrations and temperatures above 25 °C is attributed to the expansion of the BMA blocks of the corona of the micelles due to the improving solvent quality discussed above; due to the increasing overlap, the freedom of the micelles to move in a comparatively independent manner is lost, and the viscosity rises. The maxima in $\eta(T)$ at the lower temperatures indicate the entrance into the two-phase region; this phenomenon[26] is not specific for the present solutions of block copolymers. The maximum in η results from the fact that the viscosity increases as one approaches the miscibility gap from the homogeneous state (due to

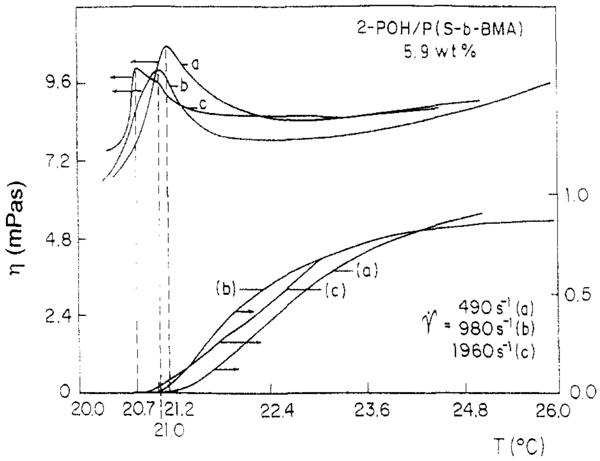

Figure 9. Viscosity η and transmittance I/I_0 of sheared 5.9 wt % solution of P(S-*b*-BMA) in 2-POH as a function of temperature for different indicated shear rates.

pronounced concentration fluctuations) until the demixing temperature is reached, where η falls rapidly. At this point a second phase is segregated, and the less viscous coexisting phase forms the matrix of a suspension and dominates the viscosity.

Phase Separation under Shear. The fact that the viscosity maxima in $\eta(T)$ coincide with the phase separation temperature can also be seen in the results of turbidimetry measurements in a rheooptical cell. Figure 9 shows how I/I_0, the fraction of light that passes the solution, and η (measured simultaneously in the same apparatus) depend on temperature for three different shear rates for solutions containing 5.9 wt % on the copolymer.

Within experimental error, no shear influence on phase separation was detected. The demixing temperatures obtained by turbidimetry under shearing (21.1 °C) and viscometry (20.7 °C) coincide with those for the system at rest (21.0 ± 0.31 °C) for the same concentration. There are many homopolymer systems described in the literature,[27,28] in which shear-induced demixing or dissolution is observed. Shear influences on phase separation have in these cases been explained in terms of the energy stored under flow,[27,28] which is primarily an entropic effect resulting from the stretching of parts of the molecules. The polymer chains tend to become locally extended under flow as compared to their random conformation at rest. In the case of solutions of block copolymers in a selective solvent, the equilibrium conformations are already highly constrained due to micelle formation, and changes under flow are obviously not large enough to cause an easily detectable shear effect on phase separation.

Conclusions

On the basis of the present thermodynamic and rheological information, one ends up with the following scheme for the dissolved state of P(S-*b*-BMA) in the Θ solvent 2-POH and its variation with temperature, which is shown for a mixture of supercritical polymer concentration.

For temperatures which are sufficiently larger than the Θ temperature (e.g., 40 °C), the BMA blocks are expanded due to the favorable interactions with 2-POH; a highly entangled matrix with high viscosity is formed (Figure 10, part a). As the temperature decreases, the viscosity of the solutions decreases, too (Figure 10, part b), in contrast to the normal behavior of 2-POH/homopolymer PBMA solutions.[12,13] The reason is that the interaction between 2-POH and the BMA blocks becomes worse, the PBMA blocks contract, the number of entanglements decreases, and the micelles can move more independently. Such an abnormal variation of η with T is sometimes very desirable, for instance in motor oil additives.

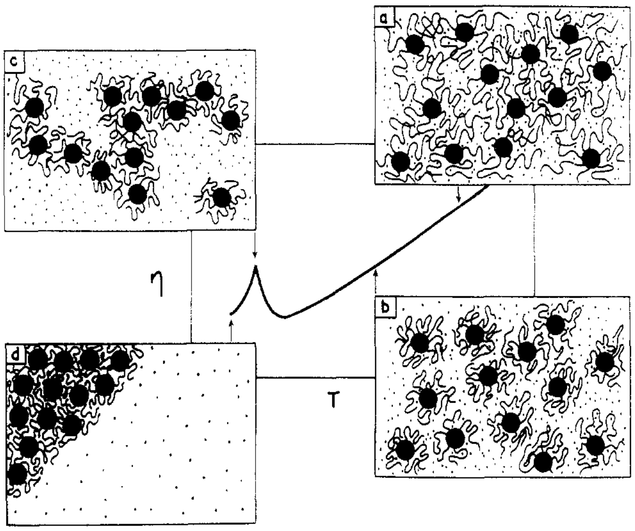

Figure 10. Scheme of the variations of the viscosity of solutions of P(S-*b*-BMA) in 2-POH (supercritical polymer concentrations) with temperature and of the corresponding states of the solute. The black parts indicate the cores of the micelles formed by the S blocks; the BMA blocks are represented by individual threads, and the dots stand for the solvent.

As the temperature reduction goes on and one approaches the critical temperature (Figure 10c), the curvature of the dependence of the Gibbs energy on composition becomes very minute.[29] The concentration fluctuates considerably, and the correlation length of the system becomes infinitely large.[30,31] In this temperature interval the precursors of the phases that coexist upon demixing are forming. The solutions can under such conditions in a simplified manner be considered to consist of large "fluctuates" (Figure 10, part c). This situation causes a considerable slowing down of molecular motion; moreover, since the thermodynamic conditions are becoming worse, contacts between BMA segments and 2-POH are replaced by intersegmental BMA contacts leading to an additional excess viscosity.

The system phase separates as T falls below the demixing temperature. The interfaces between the regions of different composition lose their diffuse character, and droplets of the more concentrated coexisting phase are now dispersed in a solvent-rich matrix phase (Figure 10, part d). The viscosity decreases and assumes values which become comparable to that of the pure solvent. It should be possible to describe the viscosity of such a mixture by analogy to the procedure used for emulsions on the basis of Einstein's equation.[32]

The results of the presented investigations can be expected to hold true for any block copolymer dissolved in a selective Θ solvent. Under these very poor thermodynamic conditions, the copolymer molecules aggregate to micelles even at extreme dilution. The micelle cores are practically inactive, and the phase diagram is almost identical with that of the homopolymer block.

The solutions are Newtonian only below a critical overlap concentration c^* of the micelles; above it, shear thinning is observed. Below the Θ temperature, the rheological behavior resembles that of the homopolymer. Above it, the viscosity *increases* with temperature since the entanglements between micelles are favored due to an expansion of BMA blocks under the improved thermodynamic conditions. Phase separation is not affected by shear.

Acknowledgment. The authors thank FAPESP, CNPq, and DAAD/Stifterverband for financial support.

References and Notes

(1) Barnes, H. A.; Hutton, F.; Walters, K. *An Introduction to Rheology*; Elsevier Science Publishers: Amsterdam, 1989.
(2) Maderek, E.; Wolf, B. A. *Angew. Makromol. Chem.* **1988**, *161*, 157.
(3) Price, C.; Hudd, A. L.; Stubberfield, R. B.; Wright, B. *Polym. Commun.* **1989**, *21*, 9.
(4) Riess, G.; Hurtrez, G.; Bahadur, P. *Encyclopedia of Polymer Science and Technology*; Interscience Publisher: New York, 1985; Vol. 2c.
(5) Bailey, F. E.; Koleske, J. K. *Poly(ethylene oxide)*, Academic Press: New York, 1976.
(6) Plestil, J.; Hlavata, D.; Houz, J.; Tuzar, Z. *Polymer* **1990**, *31*, 2112.
(7) Noda, I.; Yamaguchi, M.; Maeda, N.; Takahashi, Y.; Matsushita, Y. *Polym. J.* **1991**, *23* (3), 227.
(8) Hashimoto, T.; Shibayama, M.; Kawai, H.; Watanabe, H.; Kotaka, T. *Macromolecules* **1983**, *16*, 361.
(9) Watanabe, H.; Kotaka, T.; Hashimoto, T.; Shibayama, M.; Kawai, H. *J. Rheol.* **1982**, *26* (2), 153.
(10) Higgins, J. S.; Blake, S.; Tomlins, P. E.; Ross-Murphy, S. B.; Staples, E.; Penfold, J.; Dawkins, J. V. *Polymer* **1988**, *29*, 1968.
(11) Kotaka, T.; Watanabe, H. *Rheology and Polymer Processing, Multiphase System*; Hanser Publisher: New York, 1982, Chapter 5.2.
(12) Herold, F. Ph.D. Thesis, University of Mainz, 1982.
(13) Herold, F. K.; Schulz, G. V.; Wolf, B. A. *Polym. Commun.* **1986**, *27*, 59.
(14) Jelich, L. M.; Nunes, S. P.; Paul, E.; Wolf, B. A. *Macromolecules* **1987**, *20*, 1943.
(15) Nunes, S. P.; Wolf, B. A.; Jeberien, H. E. *Macromolecules* **1987**, *20*, 1948.
(16) Nunes, S. P.; Wolf, B. A. *Macromolecules* **1987**, *20*, 1952.
(17) Siqueira, D. F.; Nunes, S. P.; Wolf, B. A. Paper 2 *Macromolecules*, submitted for publication.
(18) Sander, U. Ph.D. Thesis, University of Mainz, 1989.
(19) Horst, R. Ph.D. Thesis, University of Mainz, 1992.
(20) Leibler, L.; Joanny, F. *Polym. Prepr.* (*Am. Chem. Soc. Div. Polym. Chem.*) **1988**, *29* (1) 418.
(21) Elias, H.-G. *Macromolecules*; Plenum Press: New York, 1984.
(22) Ogawa, E.; Sato, M.; Shima, M. *Eur. Polym. J.* **1981**, *17*, 497.
(23) Wolf, B. A.; Jend, R. *Macromolecules* **1979**, *12*, 732.
(24) Yao, M. L.; Watanabe, H.; Adachi, K.; Kotaka, T. *Macromolecules* **1991**, *24*, 6175.
(25) Simha, R.; Weissberg, S. G.; Rothmann, S. *J. Res. Natl. Bur. Stand.* **1949**, *42*, 409.
(26) Sezen, M. C.; Wolf, B. A. *Macromolecules* **1977**, *10*, 1010.
(27) Krämer-Lucas, H.; Schenck, H.; Wolf, B. A. *Makromol. Chem.* **1988**, *189*, 1613.
(28) Krämer-Lucas, H.; Schenck, H.; Wolf, B. A. *Makromol. Chem.* **1988**, *189*, 1627.
(29) Koningsveld, R.; Kleintjens, L. A.; Schoffeleers, H. M. *Pure Appl. Chem.* **1974**, *39*, 1.
(30) Leibler, L. *Encycl. Polym. Sci. Eng.* **1988**, *11*.
(31) Stanley, H. E. *Encycl. Polym. Sci. Eng.* **1988**, *4*.
(32) Nielsen, L. E. *Polymer Rheology*; Marcel Dekker: New York, 1977.