Rheological Properties of Poly(ethylene oxide) Aqueous Solutions

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ABSTRACT: This article describes the rheological properties of certain poly(ethylene oxide)s dissolved in water-based solvents. The experimental results show that the rheological properties in aqueous solutions are significantly affected by the solvent properties, which have been changed by the use of ethanol–water mixtures and electrolyte solutions and by the variation of the ambient pressure and temperature. The variation of the temperature and pressure is seen to change the polymer chain configuration and also the interactions of polymer segments with the solvent molecules. This gives rise to distinctive and apparently unusual rheological properties for these systems with the variation of the ambient temperature and pressure. The study generally illustrates that the rheology of these systems are, to a large degree, influenced by the hydrogen bonding in the solvent and between the solvent as well as the polymer. At a first-order level, the increase of the pressure and the temperature and also the addition of electrolytes, and the inclusion of an aqueous diluent, produce comparable effects. In essence, these changes seem to disrupt the hydrogen bonding structure in the solutions and, hence, the solvent quality in a comparable fashion. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 419–429, 1998

Keywords: rheology; PEO; temperature; pressure; solvent quality

INTRODUCTION

The study of the flow behavior of polymeric fluids has recently attracted increasing attention because of their inherent complexity and the increasing number of applications that involve such polymer-based fluids. It is recognized that the rheological properties of polymer solutions are determined by the bulk polymer properties (such as the chemical formulation, the molecular weight, and its distribution), the solvent properties, the polymer concentration, and external variables such as the temperature and the pressure.[1–5] For many polymer solutions, the rheology is also strongly shear rate or time dependent.[6,7]

The "solvent quality," which is the mutual affinity of the solvent and polymer molecules, significantly influences the rheological properties of polymer solutions because the interaction between the solvent and the polymer species dramatically changes with the variation of the solvent quality. This causes changes in the polymer chain configuration and the dimensions of the polymer chains within the solvent. Previous studies on this topic have been often carried out by investigating the rheological properties for a given polymer in different solvents, such as the so-called poor, theta, and good solvents;[8,9] "poor" and "good" denote weak and strong polymer/solvent interactions, while the theta condition is where the interactions in solution are comparable to those that exist in the solid polymer. The value of these studies is frequently limited because of problems associated with obtaining a wide range

of solvents with thermodynamically different interaction qualities for a given polymer. In the present work the rheological properties of poly-(ethylene oxide) (PEO) aqueous solutions have been varied by adding electrolytes or ethanol to water, and also by the variation of the temperature and the pressure. The solvent quality of water for PEO is significantly altered by these variables. The main focus of this study has been to probe the influence of the pressure upon the rheological properties. The results are described and discussed in terms of the interaction between the solvent and the PEO chains.

EXPERIMENTAL SECTION

Materials

Three PEO polymers with approximate weight average molecular weights of 35,000, 100,000, and 1 million (Aldrich Chemical Co., UK) were used as received. All the inorganic salts and the ethanol were analytical grade materials and were used without further purification. PEO solutions with a polymer molecular weight of 1 million were used throughout the study, except where specifically indicated.

Aqueous solutions of PEO were prepared by dispersing the solid polymeric powder into deionized water under mild mixing conditions. In the cases of the addition of salts or ethanol to the water, the polymer solutions were prepared by dispersing the polymer powder into preprepared electrolyte or ethanol aqueous solutions. The polymer concentrations were prepared as dry (as received) weight percentages and all the solutions were stored for at least 1 week at ca. 5°C before the rheological measurements were undertaken.

Measurement Techniques

A Bohlin VOR viscometer (Bohlin Rologi, Sweden), and a high temperature and high pressure Haake Searle-type rotational viscometer (Haake Mess-Technik GmbH u. Co, Germany) were used. All of the measurements were carried out, either in a shear rate sweep, or in a constant shear rate mode, as a function of the temperature and pressure. A thin layer of silicone oil was deposited to the upper free surface of the samples to prevent the evaporation of the solvents when the measurements were undertaken at high temperatures with the Bohlin VOR viscometer. The experimental results to be described were obtained using the Bohlin VOR system except where indicated.

High-pressure viscometry measurements were performed with a modified commercial Haake Searle-type high-temperature and high-pressure viscometer equipped for variable rotational speeds. The equipment consisted of a high pressure vessel capable of maintaining a pressure of up to 1000 bar, which was situated inside an electrically heated metal block, incorporating a basic Haake Searle-type viscometer unit, RV 100. In this viscometer, the mechanical junction between the driving motor and the rotor, located inside the pressure vessel, is established by means of permanent magnets. The measurable shear stress range, which is limited by the magnetic couple strength, was 2.5 to 60 Pa. The temperature was varied from room temperature (20°C) to 150°C and the shear rates of up to 1130 s^{-1} could be applied. The rotor inside the pressure vessel is supported by a hard steel spindle positioned on the rotor's bottom, which is embedded with a polycrystalline diamond bearing. On the top of the rotor, a rotor location pin is used to guide the rotor. The geometry of the rotor is 16 mm in radius and 125 mm in height, and the gap between the rotor and the wall is 0.8 mm. The rotor, after being positioned, has an axial play of about 0.07 mm. The essential requirement in operating this viscometer is to maintain smooth and stable rotation of the rotor with a low and steady friction that arises from the two mechanical contact surfaces between the rotor and the supporting spindle. In the present work, this friction force is calibrated regularly and deducted from the measurement data. Because of structural features that provide the special high-pressure capability of the viscometer, the reproducibility of the results tended to be poor at low shear rates (below 40 s^{-1}) and for the lower viscosity samples (less than 20 mPa s) because the measured shear stresses are small compared to the stresses arising from the mechanical friction. A detailed description of the structure and performance of this viscometer may be found in ref. 10.

EXPERIMENTAL RESULTS AND DISCUSSION

Thermal Effects

The rheological experiment probes the mobility of fluids under the influence of an imposed stress, at a given temperature, it thus senses the stress-induced thermal mobility of the constituent mol-
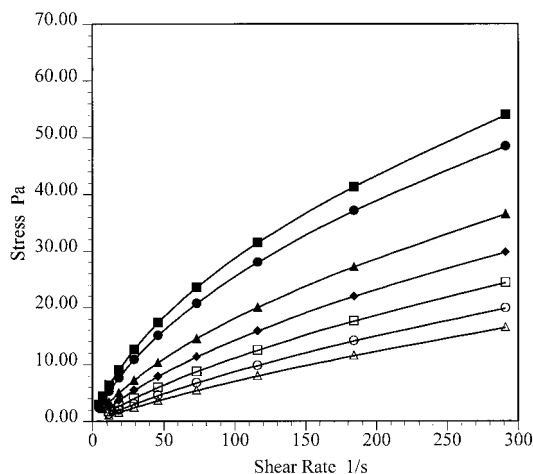
Figure 1 Temperature effects upon shear stress and shear rate relationships for 2% PEO ($M_w = 1$ million) in aqeous solution: (■) 20°C; (●) 25°C; (▲) 40°C; (◆) 50°C; (□) 60°C; (○) 70°C; (△) 80°C.

ecules and is, therefore, a sensitive probe for monitoring polymer–polymer and polymer–solvent interactions. Normally, an increase of the temperature endows the molecules with a higher thermal energy and thus induces a decrease in the viscosity.

Figure 1 shows the experimental rheograms for a 2% PEO aqueous solution obtained at different temperatures. The data in Figure 1 were accurately fitted by the power law equation: $\tau = k\dot{\gamma}^n$, where τ is the applied shear stress, $\dot{\gamma}$ is the shear rate, k is a constant, and n is the power law index.

It is noticed that the flow behavior approaches that of Newtonian fluids at high temperature, and that the power law index, n, increases with the increasing of the ambient temperature. The power law indices obtained from the data for these PEO aqueous solutions, with different concentrations at different temperatures, are shown in Figure 2. The power law index, n, for all of the four solutions increases in a way that is nearly linear with increasing temperature. For the solutions with high solute concentrations, the value of n shows a stronger temperature dependence. It is believed that the rheological changes induced by the temperature increase arise from two effects whose consequences are reflected in the value of the power law index. One effect is caused by the fact that the solubility of PEO in water decreases with increasing temperature; the polymer chains "shrink" at high temperatures and adopt more compact conformations that reduce their common intermolecular entanglements. The other is that increasing the temperature gives rise to a more

highly energized, and less highly organized flow unit, and as a result, causes an increase in the free volume of the system.

It has been shown that, for many Newtonian fluids, the viscosity and temperature interrelationship may be accurately represented by an Arrhenius-type equation. For non-Newtonian fluids, it is also possible to accurately express the temperature dependence of the viscous flow in terms of the Arrhenius-type equation, but now involving an activation energy at a constant shear rate for a given solution concentration:[1,4]

$$\eta_{\dot{\gamma}} = A \exp\left(\frac{E_{\dot{\gamma}}}{RT}\right) \tag{1}$$

where $\eta_{\dot{\gamma}}$ and $E_{\dot{\gamma}}$ are the apparent viscosity and the activation energy, respectively, at a given shear rate. A is a constant, R is the gas constant, and T is the absolute temperature. Taking the partial derivative of eq. (1) we obtain:

$$\left\{\frac{\partial(\ln \eta_{\dot{\gamma}})}{\partial\left(\frac{1}{T}\right)}\right\}_{p,c,\dot{\gamma}} = \frac{E_{\dot{\gamma}}}{\rho} \tag{2}$$

Thus, the activation energy, $E_{\dot{\gamma}}$, at a given shear rate, may be obtained directly from plots of $\ln \eta_{\dot{\gamma}}$ against $1/T$. Figure 3 shows such a series of plots for 2% PEO aqueous solutions at different shear rates. The calculated activation energies, at the different shear rates for the various PEO solutions, are shown in Figure 4; the computed ac-
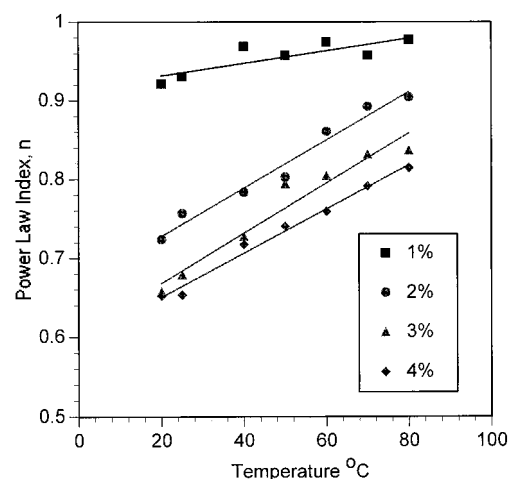

Figure 2 Temperature effect upon the power law index for PEO ($M_w = 1$ million) aqeous solutions in different concentrations: (■) 1%; (●) 2%; (▲) 3%; (◆) 4%.
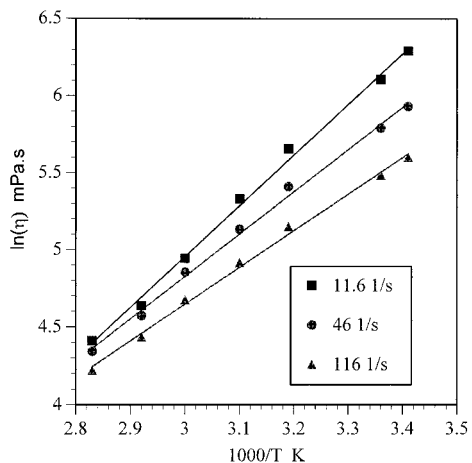
Figure 3 Plots of $\ln\eta$ against $1000/T$ for a 2% PEO (M_w = 1 million) in aqueous solution at various shear rates.

tivation energies decrease with increasing of the shear rate, and for a given shear rate with the increasing of the polymer concentration.

According to certain established molecular theories for viscous flow, the activation energy may be taken as a measure of the "height" of a potential energy barrier that is associated with the energy required to create "holes," or to move the molecules or parts of molecules from one "hole" to the next in the liquid.[1,11] However, in the case of polymeric fluids, the macromolecules that have large volumes move in "units" of a fixed size, which is rather independent of the total length or size of the molecules. In practice, the viscosity also often depends upon the actual size of the molecules, because there has to be a cooperative movement between the segments so that the molecules as a whole may progress in the shear field.[11] The size, or length, of the mobile chain segments, is believed to be determined by the flexibility of polymer chains and the environment close to the polymer chains; that is, the solvent properties and the interactions between the polymer segments themselves and with the solvents. Under the action of a shear stress, the alignment, orientation, and disentanglement of the polymer chains occurs, and this enables the polymer molecules to move more easily. This, in turn, causes a corresponding decrease of the activation energies with the increase of the shear rate. The data given in Figure 4 are consistent with these simple ideas.

However, an anomaly seems to occur in the comparison of the activation energies for the different solution concentrations at the same shear rate; that is, the activation energies are lower in the high concentration solutions compared to those in the low concentration solutions (also see Fig. 4). Previous studies regarding the thermodynamic properties of PEO in aqueous solutions have revealed that the enthalpy and entropy of the systems are reduced in the dissolution and the dilution processes as the dilution level increases.[12,13] A negative dissolution enthalpy indicates that energetically favourable interactions are formed during the dissolution as a result of the formation of hydrogen bonding between the PEO chains and the water molecules. When the solution is dilute, more water molecules can access the polymer chains and, thus, more hydrogen bonds are created between the chains and water molecules; this is the origin of the negative enthalpy dilution. The negative entropy of both the dissolution and dilution processes infer that, during the dissolution of the polymer, an ordered structure is created in the solution. The presence of this ordered structure is suggested to be the result of the arrangement of water molecules along the polymer chains through the action of hydrogen bonding.[12,14,15] A structure has been proposed by Kjellander et al. for PEO in water, corresponding to two or three water molecules associated with each ether oxygen of the ethylene oxide main chain.[15] With the decreasing of the PEO concentration, more water molecules are able to arrange along the polymer chains, hence, increasing the regularity of the structure. This effect causes a reduction of the system entropy of dilution. With more order, that is, with more water molecules associated with the PEO chains, it is expected that a higher activation energy for
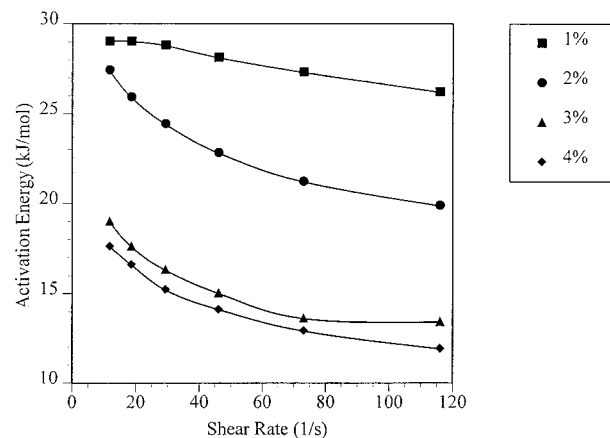

Figure 4 Shear rate and polymer concentration influences upon the activation energy for PEO in aqeous solutions.
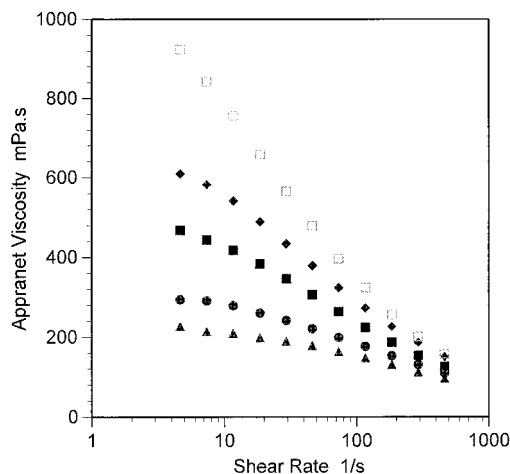
Figure 5 Apparent viscosity and shear rate relationship for 2% PEO (M_w = 1 million) in aqueous saline solutions and ethanol–water mixtures at 25°C: (■) water; (●) 0.2M K$_2$SO$_4$; (▲) 0.3M K$_2$SO$_4$; (◆) 25% ethanol–water; (□) 50% ethanol–water.

viscous flow is necessary. By adopting the above analysis, we may further rationalize the trends in the activation energies of the PEO aqueous solutions shown in Figure 4.

Effects of Solvent Properties

There are many reports about the influence of inorganic salts on the deterioration of the solvent properties for aqueous PEO solutions.[16–18] The presence of these salts, or rather their ions, in solution disrupts the hydrogen bonding and, hence, the ordered water structure along the PEO chains, although the details are still not well understood. Bailey et al. have reported that the intrinsic viscosity of PEO in salt solutions is lower than that in pure water solution under comparable conditions, which suggests that the polymer chains are more contracted in the electrolyte solutions.[19] Figure 5 shows the apparent viscosity and the shear rate interrelationship for a 2% PEO in different aqueous solvents. The addition of potassium sulphate into the solution decreases the viscosity greatly and the effects become more pronounced with increasing salt concentration. The flow curves of the two doped aqueous solutions show a more Newtonian fluid type behavior compared to that of the pure water, and also the power law index increases with increasing temperature. This behavior is similar to that observed in pure water solutions (see Fig. 6). These results are in contrast to those reported in a recent study on the effects of dissolved salts upon

the rheological properties for aqueous PEO solutions where the addition of up to 0.5M sodium chloride in the solutions did not apparently change the steady shear and dynamic properties of the solutions.[20] These authors, therefore, concluded that for inert nonionic polymers such as PEO, their rheological properties are not affected by the change in the solvent environment induced by ionic species. Obviously, this conclusion is too simplistic and provides an incomplete description of what occurs. In our experiments, we have observed that the presence of dissolved potassium sulphate, sodium carbonate, and potassium chloride significantly changes the rheological properties of aqueous PEO solutions.

To further study the solvency effects upon the rheological properties, 25% (w/w) and 50% ethanol–water mixed solvents were used for preparing 2% PEO solutions. From a comparison of the solubility parameters and the relative strengths of the hydrogen bonding, it is clear that ethanol is a significantly poorer solvent for PEO than water. A microcalorimetric study of PEO in water and in ethanol–water mixed solvents has revealed that the intermediate heats of dilution in water and ethanol–water mixed solvents are exothermic, and that the values in water are higher than those in ethanol–water solvents.[10] It can, therefore, be concluded that the solvency is decreased by adding ethanol into water for PEO. The flow curves for the 2% PEO, in these two solutions, are also illustrated in Figure 5, and power law index and temperature relationships are shown in Figure 6. Compared with the curves of the pure wa-
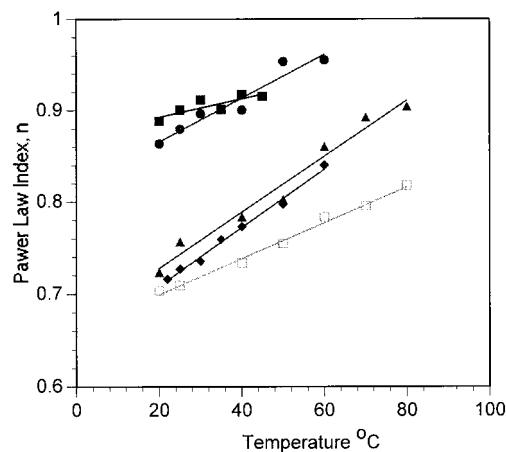

Figure 6 Temperature effects upon the power law index for PEO (M_w = 1 million) in aqueous saline solutions and ethanol–water mixtures: (■) 0.3M K$_2$SO$_4$; (●) 0.2M K$_2$SO$_4$; (▲) water; (◆) 25% ethanol–water; (□) 50% ethanol–water.

ter and the aqueous electrolyte solutions, a difference between the electrolyte solutions and mixed ethanol–water solvent is noted. Under similar conditions (reduction of the solvency), the flow curves for the ethanol–water mixed solutions move upwards from the curve for the pure water solution, instead of moving downwards, as is the case of the salt-doped solutions. Furthermore, the ethanol–water mixed solutions exhibit a more pronounced shear thinning behavior, or a smaller power law index (see Figs. 5 and 6), implying the presence of stronger interaction units between the polymer chains. There are many reports claiming that the viscosity of moderately concentrated polymer solutions increases as the solvent quality decreases. This is in contrast to the situation at high dilution.[9,21] The explanation offered for this observation is in terms of a so-called "pull-along" effect resulting from the preference of intersegment contacts over solvent/segment contacts in a "bad" solvent. The higher number of contact sites between segments renders their movement less independent; they pull the neighboring segments to some extent with them as they flow, and consequently, raises the effective size of the flow unit. The results from the ethanol–water mixed solutions might be interpreted with the above arguments. However, for the electrolyte solutions the effects observed are obviously due to different causes.

Pressure Effects

The general behavior, as was revealed by previous work concerning polymer solutions, is that under the action of a hydrostatic pressure, the compression of polymer solutions leads to a decrease of the free volume and an increase of the density of the solution as well as the volume fraction of the solute. Thus, the viscosity of polymer solutions is gradually increased with increasing pressure, although the amount of the increase of the viscosity with the pressure varies between polymer species as well as the polymer concentration, the solvent quality, and the temperature.[2–5, 8,9,21,22]

In the present experiments we have found that the flow curves of the shear stress and shear rate at different pressures, up to 1000 bar, do not change significantly. For the purpose of distinguishing trends, we only present experimental data at a constant shear rate. To obtain reproducible and accurate results, we also choose data from high shear rates, although the absolute value of the shear rate may vary somewhat be-
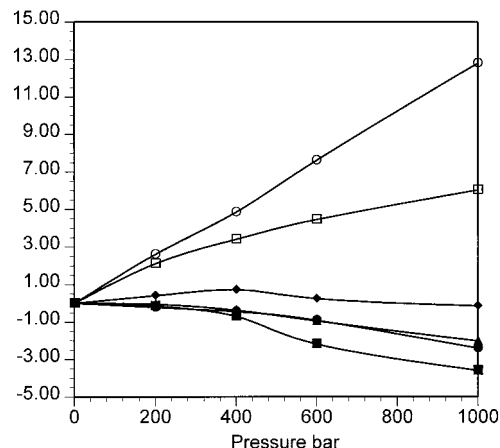

Figure 7 Pressure effect upon the relative viscosity difference, η^*, for 2% PEO (M_w = 1 million) aqueous solution at different temperatures; data are measured by Haake viscometer at a shear rate of 226 s^{-1}: (■) 17°C; (●) 20°C; (▲) 25°C; (◆) 35°C; (□) 60°C; (○) 80°C.

tween one sample and another. Figure 7 shows the pressure effect upon the relative viscosity difference:

$$\eta^* = \frac{\eta_p - \eta_1}{\eta_1} \times 100\%$$

where η_p and η_1 are the apparent viscosity at a pressure of P and 1 bar, respectively, at different temperatures for a 2% PEO aqueous solution. From Figure 7, it is seen that the relative viscosity difference decreases with increasing pressure at temperatures below 35°C, and that the lower the temperature, the more is the reduction of the * value. However, above 35 C, an increase of the * value with increasing pressure is observed, and this increase becomes more pronounced at higher temperatures. Figure 8 shows the pressure effect upon the * parameter for different molecular weight aqueous PEO solutions with different concentrations at 25°C. Except for the 2% PEO solution with a 1M molecular weight, the values for a 15% PEO solution with a molecular weight of 35,000 and 100,000 show an increase with increasing pressure at 25°C, and the same trend was also evident at 17°C.

For economy of presentation in the following, we consider the parameter:

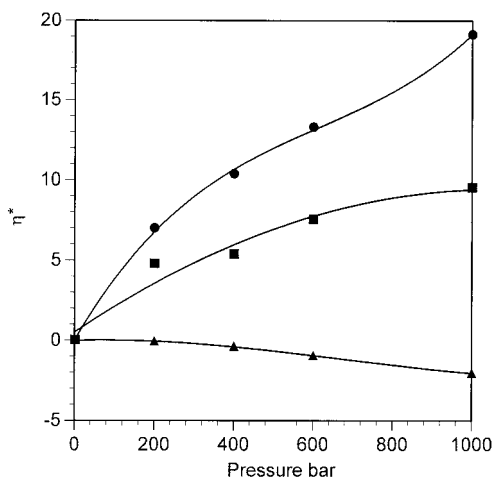$$\eta_{1000}^* = \frac{\eta_{1000} - \eta_1}{\eta_1} \times 100\%$$

Figure 8 Pressure effect upon the relative apparent viscosity difference, η^*, for PEO aqueous solution with different molecular weights and different concentrations at 25°C; data are measured by Haake viscometer at a shear rate of 226 s^{-1}: (■) 35,000, 15%; (●) 100,000, 15%; (▲) 10^6, 2%

Figure 10 Concentration effects upon η_{1000}^* for PEO with molecular weight of 10^6 in aqueous solution at different temperatures; data are measured by a Haake viscometer.

where η_{1000} and η_1 are the apparent viscosities at 1000 bar and 1 bar, respectively, as a representative parameter in discussing the pressure effects. Figure 9 shows the interrelationship between and temperature for PEO with a 100,000 molecular weight in 0.2M potassium sulphate solution, at different concentrations. Figure 10 shows the same relationship for PEO with a 10^6 molecular
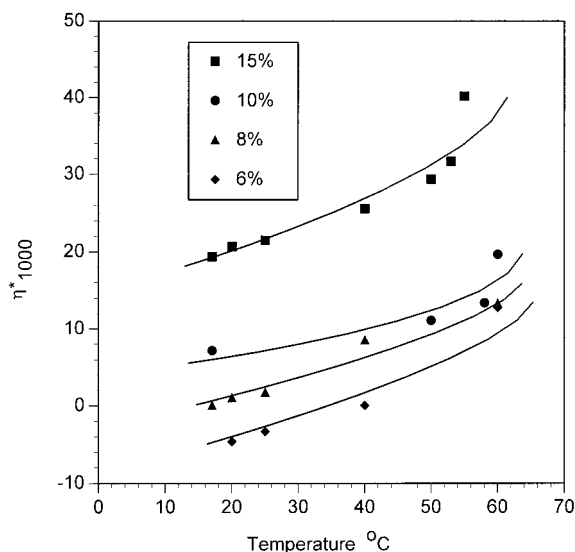
weight in aqueous solution. Figures 11 and 12 provide the relationships between and temperature for 2% PEO in aqueous saline solutions and in ethanol–water solutions, respectively. From the above figures, the major features to be noticed are that (1) η_{1000}^* for all the solutions increases with increasing temperature; (2) η_{1000}^* increases with increasing polymer concentrations; (3) η_{1000}^* increases with increasing polymer molecular weight at the same concentration; (4) η_{1000}^* increases with the addition of ethanol in the aqueous solutions; (5) η_{1000}^* shows a stronger temperature dependence for PEO in aqueous electrolytes

Figure 9 Concentration effects upon η_{1000}^* for PEO with a molecular weight of 100,000 in 0.2M potassium sulphate aqeous solution at different temperatures; data are measured by a Haake viscometer.
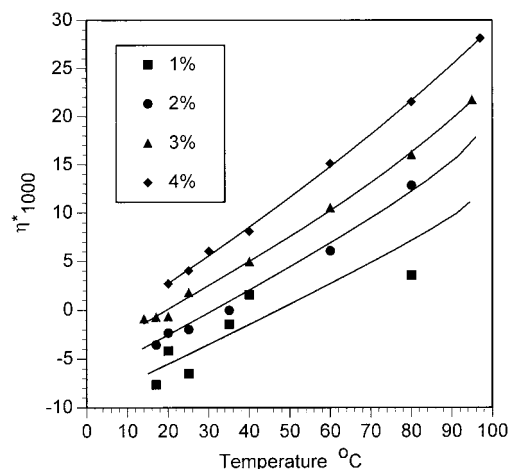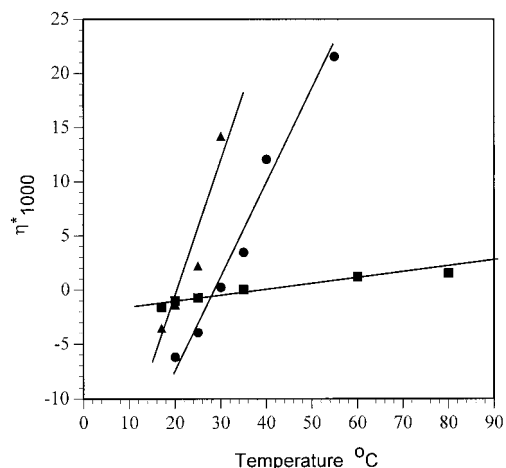

Figure 11 η_{1000}^* and temperature relationships for PEO (M_w = 1 million) in aqueous electrolyte solutions; data are measured by a Haake viscometer: (■) water (●) 0.2M K$_2$SO; (▲) 0.3M K$_2$SO$_4$.

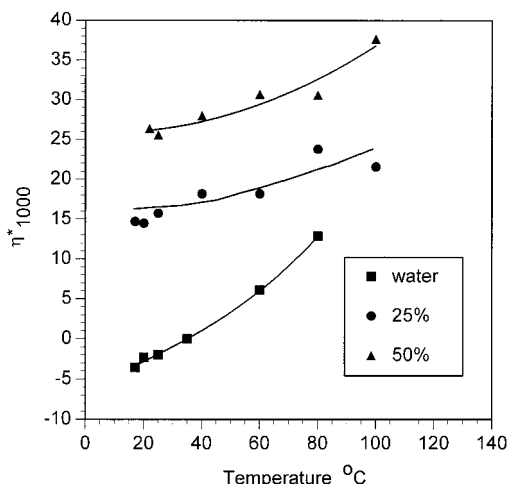**Figure 12** $\eta_{1000}{}^*$ and temperature relationships for PEO ($M_w = 1$ million) in ethanol–water mixed solvents; data are measured by a Haake viscometer.

solutions than that in pure water; and (6) the negative $\eta_{1000}{}^*$ values occur at low temperatures and at low polymer concentrations, except for the solutions composed of ethanol–water mixed solvents, and the lower the temperature, the more is the reduction of the viscosity with the increasing of the pressure.

Wolf et al. have studied the pressure effects upon the viscosity and the solvency for different polymer solutions.[9,21,22] They reported that the pressure effect becomes more significant in changing the viscosity when the solvent quality is decreased. Cook et al. also claimed that the pressure effect is less pronounced in "good" solvents than in solvents due to the expansion of the polymer chain dimension.[23]. Because the solvent qualities of aqueous PEO solutions become worse when the temperature increases, the pressure effects increase with increasing temperature; in addition, the compressibility of the liquids also increases with increasing temperature. The increases of the values of $\eta_{1000}{}^*$, compared with the values in pure water solutions with the addition of salts and ethanol into the solutions, may also be ascribed to the deterioration of the solvent quality.

The reduction of the viscosity, negative h* or $\eta_{1000}{}^*$ value, caused by the application of pressure at low temperatures for PEO in aqueous and electrolyte solutions, are unusual. Currently, the only pure liquid that is known to exhibit a similar behavior is water.[24] For pure water at temperatures below 30°C, the initial application of pressure, up to 2000 bar, causes the viscosity to de-

crease. As greater pressures are applied, the viscosity passes through a minimum and then increases. Above 30°C, the minimum disappears, and only the increase of the viscosity is observed with the progressive application of pressure. The accepted explanation for this result is that the application of pressure breaks down the hydrogen bonding between the water molecules and, thus, reduces the extent of the water cluster structure, which is less dense than that of "free water." The initial compression of the water results in the disruption of the water structure and, hence, a lower viscosity. On the other hand, the compression increases the water density as it reduces its free volume. This factor leads to the rising of the viscosity. With a further increasing of the pressure, the effect of densification becomes dominant, and an increase of the viscosity with pressure occurs. Because of the thermal disruption of the hydrogen bonding and, hence, the cluster structure of water, the pressure induced disruption of the hydrogen bonds is now less significant, and meanwhile, the densification is more pronounced, when the temperature is increased. In this circumstance above ca 30°C, only the rise of viscosity, with increasing of the pressure, is observed.

For the present PEO solutions, we may suppose that a similar interpretation for the pressure dependence of the viscosity can be adopted, and as a result, a better understanding of the pressure effects may be obtained. At 17°C the apparent viscosity of the 2% PEO aqueous solution decreases by about 7 mPa s at the pressure difference of 1000 bar. Under the same conditions, the pure water viscosity decreases by less than 0.2 mPa s. Thus, it is evident that the application of the pressure breaks hydrogen bonds not only within the water molecules but also between the PEO chains and the water molecules. At high temperatures, the apparent viscosity increases with increasing the pressure due to the reduction of hydrogen bonds by the thermal energy and the increase of the compressibility of the solution. The experimental results show that pressure influence upon the apparent viscosity of the PEO solution is similar to that of water, although the minimum value of the viscosity does not appear in the data of the 2% PEO aqueous solution at the available pressure range. The effect of the polymer concentration upon the $\eta_{1000}{}^*$ value, at lower temperatures, shows that the $\eta_{1000}{}^*$ value becomes less negative with increasing concentration, which means that either the effect of pressure upon disrupting hydrogen bond is less sig-
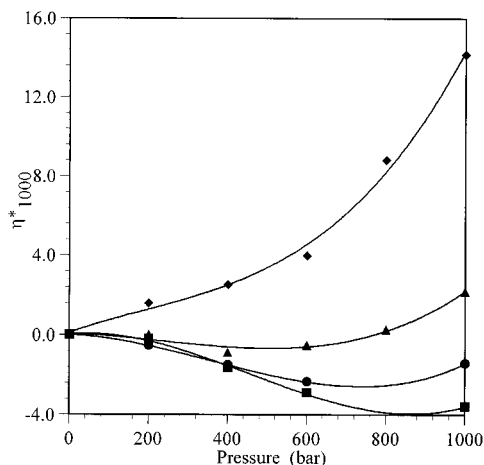
Figure 13 Pressure effect upon the relative viscosity difference, η^*, for 2% PEO (M_w = 1 million) in $0.3M$ K_2SO_4 aqueous solution at different temperatures; data are measured by Haake viscometer at a shear rate of 226 s^{-1}: (■) 17°C; (●) 20°C; (▲) 25°C; (◆) 30°C.

nificant or that the densification effect is more dominant for the concentrated solutions. From the previous discussion, we recall that the dilution of PEO solutions brings about a reduction of the enthalpy and entropy of mixing, which results from the formation of hydrogen bonds between the polymer chains and the water molecules and the arrangement of these molecules. This result implies that a higher percentage of the PEO segments are associated with the water molecules in dilute solutions than in concentrated solutions. Thus, the η_{1000}^* values for dilute solutions are more negative than those for the concentrated solutions at lower temperatures. On the other hand, the increase of the concentration reduces the free volume of the solutions, which leads to a more significant increase of the viscosity induced by the compression, and consequently, trends towards a reduction of the effect upon the viscosity due to the disruption of hydrogen bonds. This factor also plays an important role in the temperature variation of the η_{1000}^* values for concentrated solutions at high temperatures.

For PEO in electrolyte solutions, a reduction of the viscosity with the application of the pressure was also observed. The negative values at low temperatures indicates that the hydrogen bonding is not completely suppressed by the salts in the current concentration range. We note here that Sawamura et al. have estimated, from studies of the viscosity of aqueous sodium chloride solutions at high pressure, that the hydrogen bonding in water is not entirely destroyed until

the salt concentration is above $4M$.[25] Figure 13 shows the pressure effects upon the relative viscosity difference for 2% PEO in $0.3M$ K_2SO_4 aqueous solution at different temperatures. The differences between Figure 7 and Figure 13 are that a minimum viscosity and the absence of the reduction of * value above 25°C are observed with the increase of the pressure in Figure 13; meanwhile, no minimum viscosity and the absence of the reduction of * above 35°C are observed in Figure 7. These results indicate that the presence of K_2SO_4 in the PEO solution reduces the extent of the hydrogen bonding, and thus naturally decreases the pressure influence upon the disruption of the hydrogen bonding. As a consequence, the increase of the viscosity resulting from the compression of the system becomes more pronounced. With the increase of the temperature, the extent of hydrogen bonding also reduces, and the compression effect becomes more significant than that noted at low temperatures. The above analysis illustrates that the increase of temperature, pressure, and also the addition of the salts, have similar effects upon the hydrogen bonding; namely, in disrupting the hydrogen bonding between the water molecules and the PEO chains.

It should be mentioned that a phase separation is observed, which is induced by the increase of the pressure for PEO in aqueous salt solutions at elevated temperatures.[26] For this reason, in this article, the results for PEO in aqueous salt solutions are restricted to low temperatures; for example, the data below 30°C are presented for PEO in $0.3M$ K_2SO_4 aqueous solution, where the phase separation does not occur in the current pressure range. The detailed data regarding the phase behavior of PEO aqueous solutions at different pressures will be published in another article.

When ethanol–water mixed solvents are used, there are several different factors that determine the effect of pressure upon the η_{1000}^* parameter. First, the compressibility of ethanol is about two times greater than that of water, and thus, we can infer that the compressibility of the mixed solvent is higher than that of water.[27] Second, unlike water or aqueous electrolyte solutions, the viscosity of the mixed solvent does not show any reduction with increasing pressure at any temperature, which implies a stronger densification and less extensive hydrogen bonding in the mixed solvents.[28] The third and crucial factor is that the volume of the mixed solvents (in the concentration range between 25 and 50%) is about 5% lower than that of the ideal mixed solution; this volume

contraction can be regarded as a reduction of the free volume of ca 5% of the total solvent volume.[27] This decrease of the free volume for the mixed solvents may be the main reason for the exclusive increase of the viscosity and the η_{1000}* values for PEO in the mixed solvents compared with those for PEO in a pure water solvent or in aqueous electrolyte solutions.

The activation energies, at constant shear rates, for the PEO solutions at different pressures are shown in Tables I and II. The data from Table I show that the activation energies for these aqueous PEO solutions are decreased by the increasing of the pressure. The pressure influence upon the activation energy for pure water shows a similar trend.[24,29] The activation energy for PEO in 0.2M potassium sulphate shows the highest pressure dependence, while it has less effect in pure water and has the smallest effect in ethanol–water mixed solutions (see Table II). This decrease of the activation energy can be attributed to the disruption of the hydrogen bonding and the ordered structure induced by the pressure in PEO solutions, which is consistent with the results for the concentration influence upon the activation energy (see Fig. 4). Obviously, in electrolyte solutions, the application of pressure and the presence of salts have equivalent effects in breaking down the hydrogen bonding. This produces a co-ordinated effect in decreasing the activation energy and, hence, causes a stronger pressure dependence than that observed in pure water. Similar pressure effects upon the activation energy of water containing electrolytes have been also reported previously.[25,30] For PEO in ethanol–water mixed solvents, as the amount of hydrogen bonding between polymer chains and solvent molecules is less and its strength is weaker due to the presence of the ethanol, the activation energy exhibits very small changes with the variation of pressure.

Table I   Activation Energies for 2% PEO Solutions at Different Pressures

Pressure Bar	Water	0.2M K$_2$SO$_4$
1	18.3	17.9
200	17.9	17.1
400	17.5	16.4
600	17.0	15.6
1000	16.3	13.3

Unit: kJ mol^{-1}; M_w = 1 million; shear rate: 226 s^{-1}.

Table II   Activation Energies for 2% PEO Solutions at Different Pressures

Pressure Bar	Water	25% Ethanol	50% Ethanol
1	18.7	15.9	14.6
200	18.4	15.7	14.5
400	18.0	15.5	14.1
600	17.7	15.3	14.0
1000	16.9	15.0	13.7

Unit: kJ mol^{-1}; M_w = 1 million; shear rate: 226 s^{-1}.

CONCLUSIONS

The experimental results provided show that aqueous PEO solutions, with high molecular weight, exhibit pronounced shear thinning behavior. The apparent viscosity and the shear thinning effects are decreased with the increase of the temperature and the addition of electrolytes in water, but are increased by addition of a poor solvent, ethanol, in water. The activation energy for viscous flow is decreased with the increase of the shear rates and the polymer concentrations.

The pressure effects vary with the polymer molecular weight, the polymer concentration, the solvent quality, and the temperature. The decrease of the apparent viscosity, at low temperature, with application of pressure is contrary to the normal phenomenon induced by pressure, although similar results have been observed for pure water. The experimental results show that the increase of temperature or pressure and the addition of electrolytes in PEO aqueous solutions create an equivalent effect in disrupting the hydrogen bonding not only between the water molecules,[31,32] but also between PEO chains and the water molecules. This reduces the solvent quality and the interactions between the PEO chains and the solvents.

The experimental results reported in this work suggest that the rheological method offer an effective mean to probe the properties of polymer solutions, such as the chain structure and the interactions between polymer chains and solvent molecules. The results also provide a better understanding of the nature and extent of the hydrogen bonding present in the solutions. It is notable that the influence of temperature, pressure, dissolved ions, and changes in solvent quality may be traced to changes in the hydrogen bonding in the solutions. To a first order, these influences produce comparable, and apparently additive, effects upon the rheology of PEO solutions.

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