Viscoelastic Character of Poly(ethylene Oxide) in Aqueous Solutions: Effect of Shear Rate, Concentration, Salt, and Anionic Surfactant

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Synopsis

A technique useful for estimating the viscoelastic properties of dilute solution poly(ethylene oxide) was developed. With this technique, the effects of concentration, shear rate, presence of salt and/or anionic surfactant, and molecular weight on the viscoelastic properties in dilute solution were determined. Differences in the viscoelastic properties of commercial grade materials were observed. An explanation for the differences in salt and surfactant solutions based on formation of a weak ionic network is presented.

INTRODUCTION

High-molecular-weight poly(ethylene oxide) (PEO) is widely used as a thickening, flocculating, or suspending agent. One of the advantages of this use is that only very low aqueous solution concentrations are required in order to achieve dramatic effects.[1] The rheology of dilute aqueous solutions of PEO has been studied, but we are aware of no description of the viscoelastic properties of commercial PEO solutions, particularly in combinations with solutes of the type discussed in this paper. Other workers have studied the effect of electrolytes[2] or concentration,[3] but only a limited number of materials were tested and the experiments were limited to Newtonian viscosity measurements.

The present work was undertaken to develope a new technique that could be used to characterize the diltute solution viscoelastic properties of a variety of commercial PEO. The technique was also applied to evaluate the effects of molecular weight, concentration, electrolyte, and surfactant on the viscoelastic response. An extension of this work would be to correlate these properties with viscoelastic character, which could then be used to experimentally control or predict the viscoelastic behavior of new combinations of the variables. Additionally, this information will be of importance to other workers in the elucidation of molecular models of the dilute solution viscoelasticity and in explaining the large friction reduction observed for dilute aqueous solutions of high-molecular-weight PEO.

EXPERIMENTAL

Stress relaxation after cessation of steady-state flow was used to investigate the viscoelastic properties of PEO in aqueous solution. The stress

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relaxation method was chosen because it could be easily and inexpensively applied using a Wells-Brookfield cone-and-plate viscometer. Patton[4] describes a similar use of this viscometer for investigations of paints.

A solution of 1–5% of a specific PEO (Union Carbide Polyox) was made in distilled water or in a known aqueous solution of salt or surfactant. A 2-ml portion was placed on the plate, and a 3° cone was placed into position for all experiments. The sample assembly was equilibrated at 30°C. A low shear rate for the instrument $(1, 2, 5 \ s^{-1})$ was then used to place the solution into a steady-state flow. After the dial reading had stabilized, the motor was turned off and the change in dial reading was recorded as a function of time. This procedure was repeated a minimum of two times to obtain the average dial reading decay versus time. This experimental configuration measures the rate of return of a calibrated spring attached to the cone spindle. The spring was extended during rotation by resistance of the solution to flow. The dial reading is then a measure of the stress generated at a given shear rate. Plotting the logarithm of the dial reading versus time shows the stress relaxation characteristics of that solution. In treating the data, we focused on the initial apparent viscosity (η_a, y-axis intercept) at a given shear rate and the curvature of the stress relaxation line. A purely viscous fluid (newtonian) would show instanteous loss of stress, whereas a fluid with a simple first-order relaxation would appear as a straight line in this analysis.

For these studies, the molecular weight of the PEO was taken from the manufacturer's specification(s) and ranged from 60,000 to 25,000,000. The use of different lots of a grade tested the variability of the viscoelasticity within a grade designation. Sample codes and supplied molecular weights are shown in Table I.

RESULTS AND DISCUSSION

Stress Relaxation of PEO Materials in Water

In Figure 1 are shown a series of stress relaxation curves for seven different PEO materials in water measured with the Wells-Brookfield cone-and-plate viscometer. These materials represent different grades of PEO as defined by Union Carbide and different lots of the same grade. Figures 2 and 3 show similar results but for materials that had to be measured at lower concentrations because of instrument limitations.

It is apparent that a wide variety of viscoelastic response is exhibited by these materials, even in the most dilute solutions, with time scales of hundreds of seconds in some cases. The memory functions for relaxation of stress do not bear any simple correlation with molecular weight average or breadth as may be seen by comparing the A and B samples. The variability from lot to lot (e.g., A2, A3, and A4) exceeded the trends seen between types. In addition to the figures, the curves can be quantitatively represented using Tobolsky's procedure X.[6] The equations and coefficients representing the curves are available on request.

TABLE I
List of PEO and Supplier's Molecular Weights

PEO[a]	Molecular Weight[b] ($\times 10^{-3}$)
B1	900 (broad)
A1	600 (broad)
C	1000 (narrow)
B2	900 (broad)
A2	600 (broad)
B3	900 (broad)
D2	4000 (very broad)
A3	600 (broad)
B4	900 (broad)
D1	4000 (very broad)
E1	5000 (very broad)

[a] Union Carbide Polyox Series.
[b] Approximate weight-average molecular weight derived from rheological measurements by Union Carbide and reported molecular weight distribution.[5]
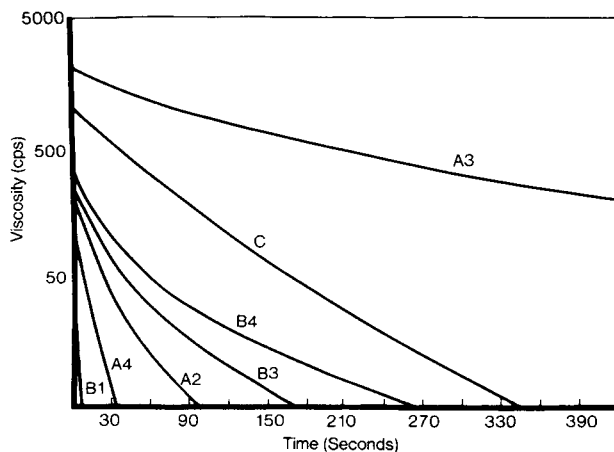
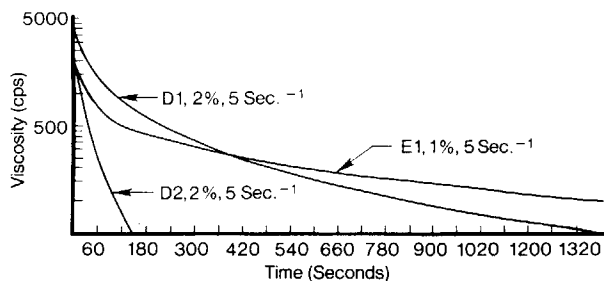Fig. 1.   Relaxation of apparent viscosity, 5% PEO in H_2O, shear rate 5 s^{-1}, 30°C samples as indicated.

Fig. 2. Relaxation of apparent viscosity, PEO in H_2O, 30°C samples indicated, shear rate 5 s^{-1}.

Effect of Shear Rate and PEO Concentration

The effect of changing shear rate prior to the stress relaxation experiments for a given concentration of a PEO material is shown if Figure 4. This same behavior was found for other PEO materials at different concentrations. The shear rate in this range does not have a significant effect on the stress relaxation curve. The relaxation processes of the solution are only slightly affected at very short times. This suggests that the stress relaxation curves of different PEO materials measured under low and only slightly differing shear rates can be directly compared.

The PEO concentration has an important effect on the stress relaxation curve, as shown in Figure 5. There appears to be a systematic variation toward simple single relaxation time behavior as concentration decreases.

Effect of Salt and Surfactant on the Stress Relaxation

The effect of salt on the stress relaxation of a PEO solution is shown in Figure 6 for different concentrations and types of salts. Figures 7 and 8 show the effect of an anionic surfactant at different concentrations and for a mixed surfactant-salt system.

Salts exhibit an increasing effect on the rate of stress relaxation as the anionic charge and the concentration of the salt increases. A change in the cation had little or no effect. This is analogous to the results of Bailey and
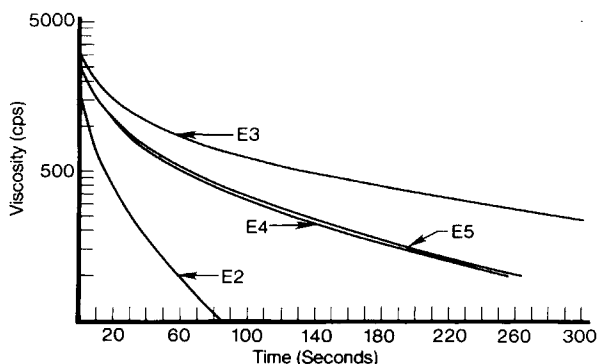

Fig. 3. Relaxation of apparent viscosity, 1.5% PEO in H_2O, shear rate 5 s^{-1}, 30°C, different lots of sample E.
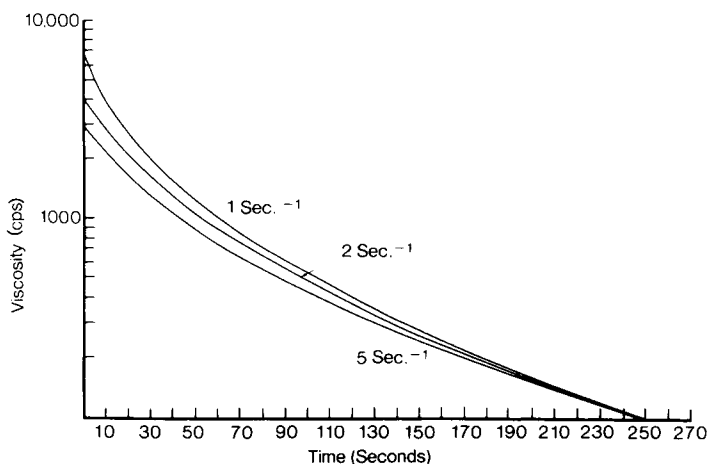
Fig. 4. Effect of shear rate on stress relaxation, 5% B4 in H_2O, 30°C. Full scale viscosity = 25,000 cps, 1 s^{-1}; 12,250 cps, 2 s^{-1}; 5000 cps, 5 s^{-1}.

Callard[2] for the precipitation of PEO from solution by salts and the effect of salts on the intrinsic viscosity of PEO solutions. Observations can be made generalizing the salt effect. First, the viscosity (which is proportional to the y-axis intercept) of the PEO salt solution is slightly decreased from that of the PEO alone. Second, the time for detectable residual stress of the solution (x-axis intercept) is decreased. Third, the relative curvature of the stress relaxation data is reduced. These changes occur because the solution relaxation processes are altered by the addition of salt. This change shifts the solution to a more Newtonian response. This increase in the viscous versus elastic properties implies that the polymer's solution conformation has changed. This experimental result is understandable if the effect of salt is to contract the polymer and render it in a less extended state. This observation is expected, as salt competes with the polymer for the water of hydration. The breaking of intermolecular hydrogen bonds as presented by Güner and Güven[3] probably is also responsible, in part, for the changes observed.
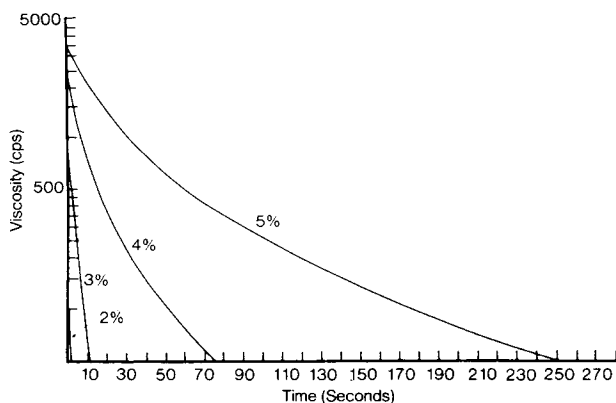

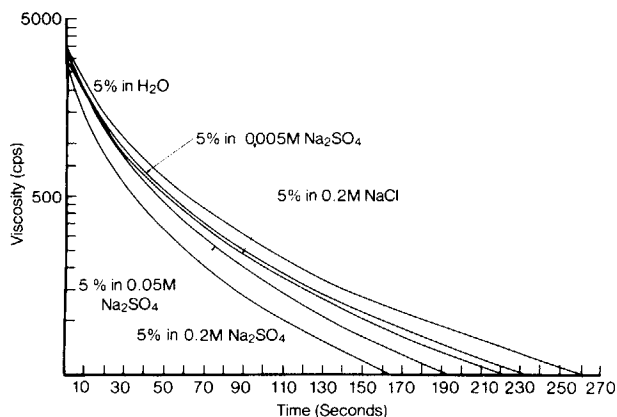Fig. 5. Effect of PEO concentration on stress relaxation, B4, shear rate 5 s^{-1}, 30°C.

Fig. 6.   Effect of salt on stress relaxation, 5% B4, shear rate 5 s^{-1}, 30°C.

The anionic surfactant decreases the stress relaxation in one case (Fig. 7) and increases it in the other (Fig. 8). This mixed effect is attributed to the difference in molecular weight distribution for these two materials. Without a further characterization of the molecular weight distributions, it can only be hypothesized that the effect observed is dependent on the number-average molecular weight (M_n). M_n for B4 would be substantially lower than the reported M_w due to the breadth of the distribution, however, M_n for C is expected to be close to the reported M_w value because of its reported narrow distribution.

The effect of salt and surfactant together is not additive. A consideration of the entire solution structure must be used to suggest possible explanations. At the concentration of surfactant present, the critical micelle concentration was exceeded. If, in these solutions, the PEO can interact with the micelles by long-range mobile ion bridges, the solution will effectively acquire a more extended structure that may border on a weak gel.[7] The mobile ion bridges between micelles and solvated PEO are present due to the high salt concentration. In a surfactant-only solution, the micelles are
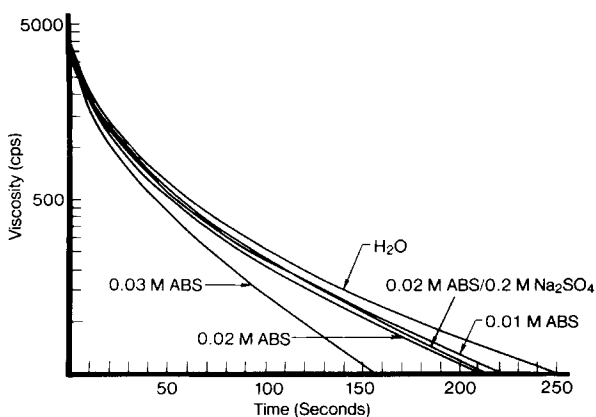

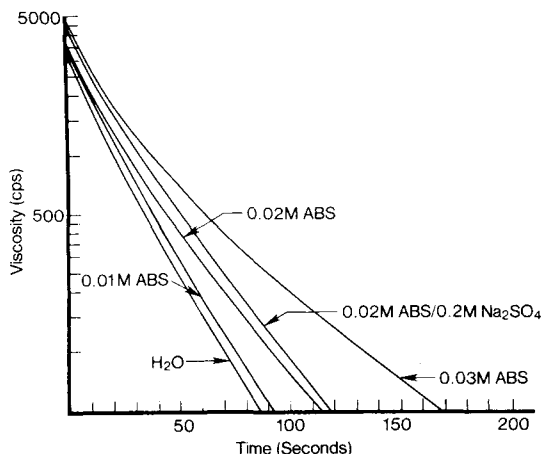Fig. 7.   Effect of Na$_2$SO$_4$ and alkylbenzene sulfonate (ABS) on stress relaxation, 5% B4, shear rate 5 s^{-1}, 30°C.

Fig. 8. Effect of Na_2SO_4 and alkylbenzene sulfonate (ABS) on stress relaxation, 4% C, shear rate 5 s^{-1}, 30°C.

present, but without the salt an extensive ionic network is not formed. The increase in the gelation for the salt-surfactant system is evident from examination of the two examples given (Figs. 7 and 8). It is for this reason that intermolecular hydrogen bond breaking cannot account for the total effect due to salt and/or surfactant.

The entire interactive system with salts, surfactant, and PEO is probably a complex structure, highly shear dependent and variable with temperature and concentration. Anomalous results coming from viscosity measurements on such systems are the rule rather than the exception.[7]

CONCLUSIONS

The stress relaxation measurement developed is an accurate predictor of a PEO material's viscoelastic character relative to other PEO polymers, under identical measurement conditions. The technique can be readily extended to other viscoelastic solutions and is expected to be valuable for general correlation of solution properties with viscoelastic character. This will be particularly true for samples for which a more accurate determination of the molecular weight is possible.

This measurement is valuable, because the manufacturer's specification does not define a unique material. This would be important for those cases in which the viscoelastic character has a major impact on the application. The measurement is easily applied and can be corrected for shear rate and PEO concentration effects. This then allows an extension of the comparison of viscoelastic character between PEO materials measured under different conditions.

The effect of salt and surfactant in aqueous PEO solutions producing a weak gelling phenomenon was also highlighted by the technique. This suggests that other viscoelastic solutions, when measured under standard conditions, may be found to exhibit similar unexpected behavior. With this measurement technique this type of phenomenon can now be investigated routinely.

References

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