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High-pressure and molecular weight variation of electrical relaxation in poly(ethylene oxide)

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Vacuum audio frequency complex admittance measurements have been performed on poly(ethylene oxide) using a fully automated dielectric spectrometer. Measurements have been made over the temperature range 5.5–320 K for molecular weights from 1.85×10^4 to 4×10^6 . The γ relaxation is essentially unchanged over the range of molecular weights studied. This represents evidence against assigning the γ relaxation to the motion of end groups. Next, previously reported data for the γ relaxation are reanalyzed using a reduced plot. The activation volume is found to be 3–4 cm³/mol in good agreement with the previous work and the small value implies that the relaxation is associated with the motion of very small segments of the polymer chain. Next, the relaxation associated with the glass transition α_a is only observed in temperature for some samples but is observed in both frequency and temperature for others. The strength of α_a decreases monotonically as molecular weight decreases. Finally, α_a was studied up to pressures of about 0.2 GPa for 5×10^6 molecular weight material. The results for the shift of α_a with pressure are in qualitative agreement with recent theories.

I. INTRODUCTION

Poly(ethylene oxide) (PEO) is of current interest as the prototype polymeric solid electrolyte.^{1–3} As a consequence, the basic properties of this material, and particularly the electrical properties, are being extensively studied. As a result, there is a considerable amount of literature relating to this material. Much of the early work has been reviewed by McCrum *et al.*⁴ and Hedvig.⁵ References to some of the more recent work can be found in the papers by Porter and Boyd,⁶ and Se *et al.*⁷ More recently, the authors have presented^{8–11} the results of audio frequency electrical relaxation (DR) measurements on PEO and PEO complexed with a variety of alkali metal and alkaline earth salts. In addition, the effect of high pressure on the electrical conductivity in some of those materials has been presented.¹² In PEO to date, it appears that only the γ relaxation has been studied at high pressures.¹³ In the present paper, the effect of pressure on the glass transition relaxation α_a is reported. In addition, the previously reported data for the effect of pressure on the γ relaxation¹³ are reanalyzed in terms of a reduced plot. Finally, in order to gain further information concerning γ and α_a different molecular weights have been studied.

II. EXPERIMENT

The PEO was obtained from Polysciences, with a molecular weight (MW) of 1.85×10^4 – 5×10^6 . All but the 1.85×10^4 samples were melt pressed at about 100 °C using a Buehler Simplimet II press. The melt-pressed samples were about 25 mm in diameter and 1.5 mm thick. Aluminum electrodes were evaporated onto the surfaces in a three-terminal configuration. For the vacuum measurements, the guarded electrode was about 14 mm in diameter while for the high-pressure measurements (MW 5×10^6) it was 9 mm in diameter. The remainder of the guarded side of the sample was the guard ring and the full face of the opposite side of the sample

was evaporated as the high electrode. The guard gap was on the order of 0.1 mm wide.

Measurements of the capacitance and conductance divided by the angular frequency were performed in vacuum over the temperature range 5.5–320 K as described elsewhere.⁹ In the present case, a new bridge constructed by one of the authors (C.G.A.) was used to perform the measurements. The new, fully automated bridge operates at 17 frequencies over the range 10–10⁵ Hz.

The data were transformed to the complex dielectric constant, $\epsilon^* = \epsilon' - j\epsilon''$ using procedures described in detail elsewhere.⁹ Once again no thermal expansion correction was included in the data reduction. The results of room-temperature geometrical measurements and the capacitance data at 5.5 K yielded $\epsilon' = 2.87, 3.01, 2.89$, and 2.95 for MW $4 \times 10^6, 6 \times 10^5, 3 \times 10^5$, and 1×10^5 , respectively. These values agree to within the experimental uncertainty in that the precision is estimated to be about 3%. The values are, however, not accurate to 3% as thermal expansion of the samples was neglected in the data analysis.

The MW 1.85×10^4 samples were not melt pressed as they were received as platelets. They were also evaporated in a three-terminal configuration with a 9-mm-diam guarded electrode. The thickness was about 0.5 mm and the guard ring was about 5 mm wide. However, a geometrical measurement was not used. The low-temperature value of ϵ' was set equal to the average of the values quoted above for the higher molecular weight materials.

The high-pressure measurements were carried out in the vessel described elsewhere.¹⁴ The pressure fluid was a mixture of pentane and Spinesstic 22 and the temperatures were achieved using a mechanically refrigerated ethylene glycol bath. Some of the high-pressure audio frequency complex impedance measurements were performed using a different, fully automated bridge constructed by one of the authors (C.G.A.) which operates with a more restricted frequency range.

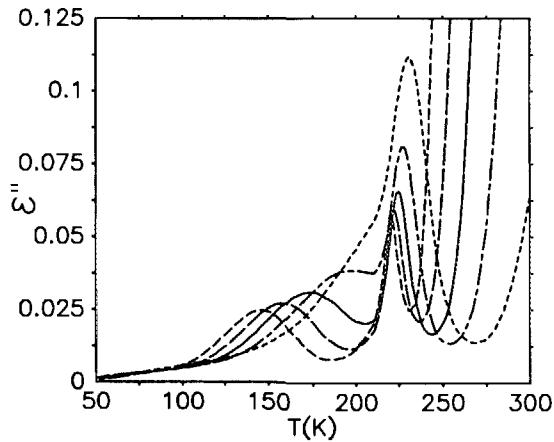


FIG. 1. ϵ'' vs T (K) for PEO with molecular weight 4×10^6 . The curves (from left to right) are medium dash—10 Hz; long dash— 10^2 Hz; solid— 10^3 Hz; chain link— 10^4 Hz; short dash— 10^5 Hz. Straight line segments connect the datum points which are not shown.

III. RESULTS AND DISCUSSION

Figure 1 shows typical vacuum electrical relaxation spectra at five frequencies between 10^2 and 10^5 Hz for PEO, in this case for a sample of molecular weight 4×10^6 . Figure 2 shows the data at 10^3 Hz for five molecular weights between 1.85×10^4 and 4×10^6 . The relaxation spectra at five frequencies for the 1.85×10^4 molecular weight material are shown in Fig. 3. Two strong features are observed, the γ relaxation with peaks from about 140–200 K and the α_a relaxation. It is interesting to note that at the highest frequency, the α_a and γ relaxations merge as predicted by Porter and Boyd.⁶ In addition, there is a weak relaxation region in all of the samples from 60–100 K. The latter relaxation will not be discussed further in this paper. As no features were observed below 50 K, that region is not shown in the plots.

The first result of interest is that it is clear from Fig. 2 that the γ relaxation does not vary much with molecular weight. If anything, there is a slight decrease in the strength as the molecular weight decreases. This argues against as-

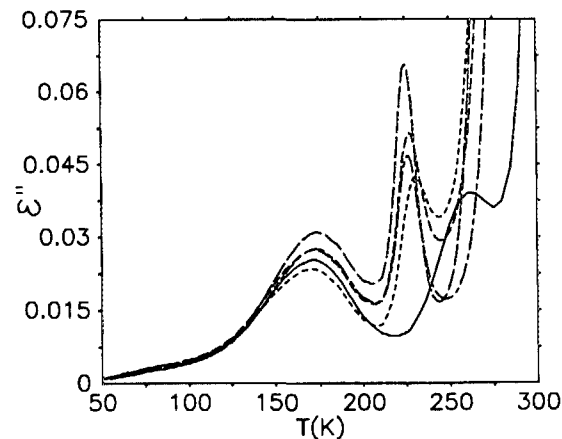


FIG. 2. ϵ'' vs T (K) for PEO at 1000 Hz with various molecular weights: long dash— 4×10^6 ; medium dash— 6×10^5 ; chain link— 3×10^5 ; short dash— 1×10^5 ; solid— 1.85×10^4 . Straight line segments connect the datum points which are not shown.

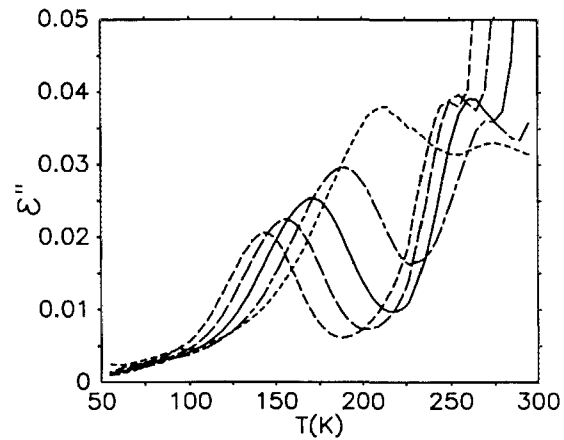


FIG. 3. ϵ'' vs T (K) for PEO with molecular weight 1.85×10^4 . The curves (from left to right) are medium dash—10 Hz; long dash— 10^2 Hz; solid— 10^3 Hz; chain link— 10^4 Hz; short dash— 10^5 Hz. Straight line segments connect the datum points which are not shown.

signing it to chain end hydroxyl groups.⁵ A similar result and conclusion was obtained by Se *et al.*⁷

In order to gain further information concerning the γ relaxation, high-pressure measurements were performed and have been reported previously.¹³ In that paper, the data were analyzed using the “standard” technique of fitting a Cole–Cole expression to individual data sets. The relaxation time for each pressure and temperature was then determined from the peak position. In the present paper the data are reanalyzed in terms of a “reduced plot.” The plot is shown in Fig. 4. All of the data for 17 frequencies, three temperatures, and seven pressures have been “normalized” to a common curve using least-square-fitting computer techniques described elsewhere.¹³ In Ref. 13, this type of fitting procedure was applied to vacuum data using a Havriliak–Negami expression. In the present case, the empirical expression of Jonscher¹⁵ has been used:

$$\epsilon'' = \frac{\epsilon_s - \epsilon_\infty}{[(\omega/\omega_p)^{-m} + (\omega/\omega_p)^{(1-n)}]} \quad (1)$$

The significant best-fit parameters are $n = 0.84$ and

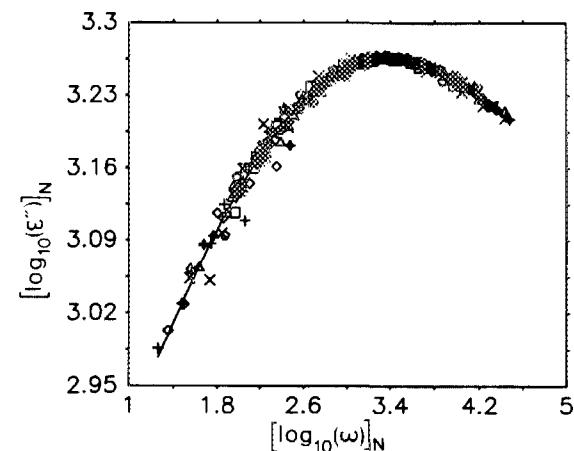


FIG. 4. “Reduced plot” for the γ relaxation in PEO (MW 5×10^6). The best fit Jonscher curve and data points for 17 frequencies, three temperatures, and seven pressures are shown. The peak position and strength are arbitrary.

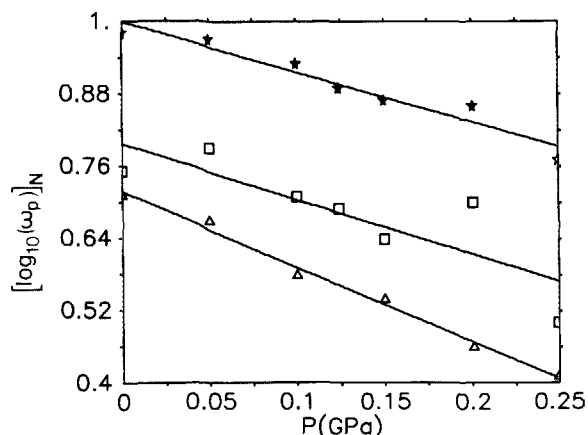


FIG. 5. Peak shift vs pressure at three temperatures, 185, 182, and 179 K from top to bottom, for the results shown in Figure 4. Also shown are the best fit straight lines.

$m = 0.33$. The strength and peak position are arbitrary, however, further information can be gained from the amount of shift in $\log_{10}(\omega_p)$ necessary to reach the master curve. The results for these logarithmic frequency shifts of the data to the master curve for both pressure and temperature are shown in Fig. 5. The resultant slopes for the pressure data are given in Table I. These were then used to calculate the activation volume via:

$$\Delta V^* = -kT \frac{d \ln \omega_p}{dP}. \quad (2)$$

The resultant activation volumes are also listed in Table I along with the results from the previous paper. The agreement is quite good considering the widely differing techniques used to arrive at the results. The activation volume, 3–4 cm^3/mol , is very small which supports assigning the relaxation to either chain end hydroxyl groups or very small segments of the polymer chain. However, considering the above results of the molecular weight studies, the latter mechanism is to be preferred.

Finally, the variation of the glass transition with molecular weight is of interest. Since the strength of α_a decreases with decreasing molecular weight, it is apparent that the degree of crystallinity increases with decreasing molecular weight over the range of molecular weights used in the present study. This is a well-known phenomenon in PEO. Also, the work of Faucher *et al.*¹⁶ indicates that there is a maximum in the glass transition temperature at a molecular weight of about 6000. This increase in T_g with decreasing

TABLE I. Pressure derivative of the relaxation time and activation volume for the gamma relaxation at various temperatures for pure PEO.

T (K)	$\frac{d \ln \omega_p}{dP}$ (GPa) ⁻¹	ΔV^* (cm ³ /mol)	ΔV^* (cm ³ /mol)*
Sample No. 2 (Cast film)			
179	2.9	4.3	4.3
182	2.1	3.2	...
185	1.9	2.9	4.7

* Reference 13.

molecular weight is evident in Fig. 2, although the shift in peak positions between the 1×10^5 and the 1.85×10^4 molecular weight samples is enhanced by the change in the frequency dependence of the peak position which can be observed by comparison of this effect in Figs. 1 and 3.

The results for the high molecular weight material are particularly interesting in that a peak for α_a was never observed in frequency at any single temperature over the frequency range 10 – 10^5 Hz, although it is observed in the temperature sweeps. For the 18 500 MW material, however, the material exhibited more normal behavior with the peak being observed in frequency as is apparent in Fig. 3. However, as mentioned above, this is the only material which was not melt-pressed and thus the result may not solely be a consequence of the molecular weight. Experiments to determine the origin of this phenomenon are currently being undertaken.

As the effect of pressure on the glass transition in PEO does not appear to have been reported previously, those measurements were carried out for the high molecular weight material. Some of the data at 1000 Hz are shown in Fig. 6. For this peak, very strong shifts with pressure are observed as is expected for a glass transition. The shift of the peak position T_a with pressure is shown for two frequencies in Fig. 7 together with the best fit of the following equation to the data:

$$T_a = T_a^0 + BP + CP^2. \quad (3)$$

The best fit parameters for these two frequencies and those for a lower correlation fit at a third frequency are listed in Table II. The curvature which is apparent in the plots is consistent with the predictions of theoretical treatments involving cooperative relaxation phenomena¹⁷ and with pressure results for other polymers.¹⁸

Since the peaks were not observed in frequency, a complete treatment in terms of the WLF equation cannot be carried out. However, both the frequency dependence of the effect of pressure on T_a and the magnitude of dT_a/dP agree qualitatively with the predictions of Questad and Oskooie-Tabrizi¹⁸ who show that

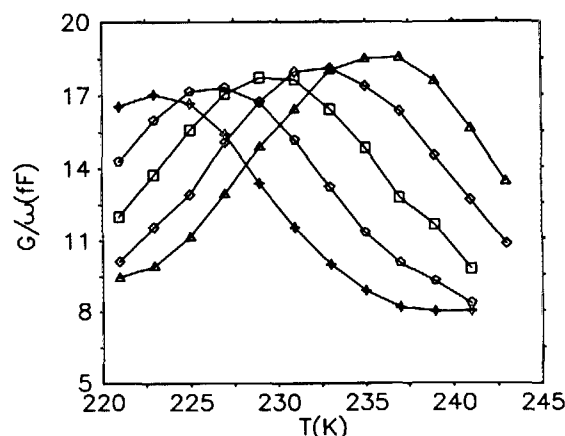


FIG. 6. G/ω (pF) vs T (K) at several pressures at 1000 Hz in the region of the glass transition for PEO (MW 5×10^6). The curves from left to right are 0.0001 (1 atm), 0.04, 0.08, 0.12, and 0.16 GPa. For clarity, straight line segments connect the datum points and data at other pressures have been omitted.

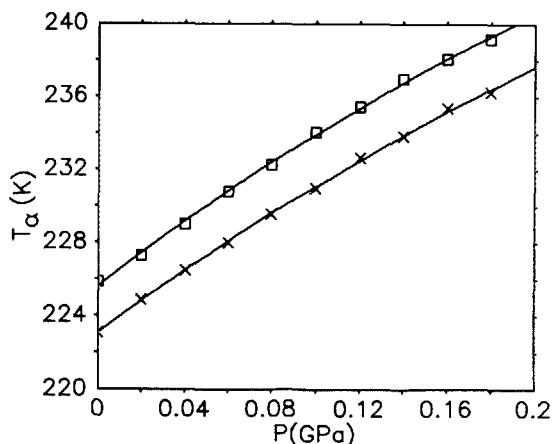


FIG. 7. Peak position vs P (GPa) at two frequencies, 1000 Hz (crosses) and 10 000 Hz (squares), for the α_a relaxation in PEO (MW 5×10^6). Also shown are the best fit quadratic curves.

$$\frac{dT_\alpha}{dP} = \frac{\Delta V^*}{\Delta E^*} (T_\alpha^0 - T_r), \quad (4)$$

where T_α^0 represents the zero pressure peak position, ΔE^* and ΔV^* are the activation enthalpy and volume, respectively, and T_r is the minimum temperature at which the activated process is still possible. It is clear from the results that dT_α/dP and T_α^0 are larger for larger frequencies. This proportional dependence on frequency for both quantities is consistent with Eq. (4). Further, the values of T_α^0 and dT_α/dP for PEO would fit well on the plot in Fig. 5 of Questad and Oskooie-Tabrizi¹⁸ and thus PEO can be grouped with poly (vinyl acetate) (PVAc), acrylonitrile-butadiene-styrene (ABS), polyurethane elastomers (PU), and polyvinylidene fluoride (PVDF), in that it follows Eq. (4).

IV. SUMMARY

In summary, then, vacuum audio frequency complex admittance measurements have been carried out on PEO at low temperatures for a variety of molecular weights. The γ relaxation varies very little over the range of molecular weights studied. This represents evidence against assigning the γ relaxation to motion of end groups. Next, previously reported data for the γ relaxation are reanalyzed using a reduced plot. The activation volume obtained is in good agreement with the previous work and the fact that a very small value is found implies that the relaxation is associated with small segments of the polymer chain. It is found that the relaxation associated with the glass transition is only observed in temperature for some samples but is observed in

TABLE II. Best fit parameters in Eq. (3) for peak position versus pressure for the α_a relaxation in pure PEO.

f (Hz)	T_α^0 (K)	B (K/GPa ⁻¹)	C (K/GPa ⁻²)	rms deviation
10^3	223.1	87.8	- 75.3	0.11
$10^{3.5}$	224.3	87.9	- 56.4	0.21
10^4	225.6	91.8	- 86.7	0.15

both frequency and temperature for others. Finally, the relaxation associated with the glass transition was studied up to pressures of about 0.2 GPa for the high molecular weight material. The results are in qualitative agreement with recent theories.

ACKNOWLEDGMENT

This work was supported in part by the Office of Naval Research.

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