Dielectric loss of an oligomeric poly(propylene oxide) in the liquid region above T_g

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Dynamic dielectric studies of oligomeric poly(propylene oxide) (PPO) of $\overline{M}_n$=3034, between −10° and 40°C at 0.1, 1, and 10 KHz, reveal a glass transition and a $T>T_g$ liquid–liquid transition. Analysis of $d\epsilon'/dT$ in the liquid region of PPO also indicates the presence of T_{11}. The activation enthalpies for the T_g and T_{11} transitions have been calculated to be 39 and 18 kCal mol^{-1}, respectively. The T_{11} transition in poly(propylene oxide) has been assigned to the motion of the entire polymer molecule.

Keywords Electrical properties; poly(propylene oxide); transition temperatures; dielectric; frequency dependence; activation energy

INTRODUCTION

This note is concerned with dielectric loss as a function of temperature, for poly(propylene oxide) (PPO) of nominal molecular weight 4000. While this and related oligomers have been studied before by both dielectric loss[1,2] and dynamic mechanical loss[3−5], the data have always been presented as a function of frequency or reduced frequency. The dielectric data of Baur and Stockmayer[1] on several PPO oligomers show a double dispersion in both ε' and ε''. The high frequency process corresponds to segmental motion and is invariant with molecular weight. The low frequency process corresponds to motion of the entire polymer molecule, shifting to lower frequency and becoming more diffuse as molecular weight increases. Yano, Rahalakar, Hunter, Wang and Boyd[6] reported dielectric loss as a function of temperature for PPO, but they covered only the $\alpha=T_g$ loss peak and not the $T>T_g$ peak which is of particular interest to us.

Based on these results, we anticipated that ε'' as a function of temperature would exhibit a low temperature loss process corresponding to T_g and a $T>T_g$ process corresponding to a liquid–liquid or T_{ll} process. This expectation was based on mechanical loss data of PIB ($\bar{M}_v = 1.35\times10^6$) as a function of temperature in which T_g and $T>T_g$ loss processes were observed[7]; and the same data plotted against reduced frequency which showed these two processes as a fast and a slow loss peaks respectively[8]. Similar mechanical loss peaks were reported for *cis-trans*-vinyl poly(butadiene) (molecular weights of 10 000 to 100 000) first as a function of temperature[9] and later as a function of frequency[10]. We are not aware of dielectric data on oligomeric PPO which would permit a similar comparison of $\varepsilon''-T$ and $\varepsilon''-\log f$. McCammon and Work[11] reported dielectric data as a function of temperature for PPO but internal evidence, including their reference[3], indicates that this is a high molecular weight, partially crystalline specimen in no way comparable with PPO used in our studies (P4000).

EXPERIMENTAL PROCEDURE

Barlow and Erginsav[12] reported a number average molecular weight of 3034 by osmometry for poly(propylene oxide) P4000, used in our studies.

The capacitance and dissipation factor (tan δ) of poly(propylene oxide) P4000 were determined in a two terminal liquid type dielectric cell with hollow cylindrical electrodes, using a Hewlett-Packard 4262A LCR meter. The HP-4262A bridge has a capability of measuring capacitance from 10.00 pF to 10.00 mF and dissipation factor from 0.001 to 19.9. The frequencies of measurements were 0.1, 1 and 10 KHz. The measurements of capacitance and dissipation factors were carried out at 5°C intervals between −100° and 40°C. Between −40°C and +40°C the temperature was controlled to ±0.1°C. Temperature between −100°C and −40°C are accurate to within ±0.5°C. The ratio between the capacitance of PPO and capacitance of air gives the real part of dielectric constant, ε', whereas ε'', the imaginary part of the dielectric constant, is obtained from ε' and tan δ ($=\varepsilon''/\varepsilon'$).

The first order derivative of ε' with respect to temperature was obtained using a Hewlett-Packard Model HP-1000 computer and plotted on a Hewlett-Packard Model HP-98725 plotter. The derivative curve was smoothed over by a three point fit.

RESULTS AND DISCUSSION

The variation of dielectric constant ε' with temperature at 0.1, 1 and 10 KHz, given in *Figure 1*, shows the presence of two transitions; at given frequency ε' increases in two steps with increasing temperature; the first jump corresponds to a prominent transition as the value of ε' increases quite significantly. The second jump is less prominent and it occurs on the high temperature side of the major transition. The two transitions occur at higher temperatures at higher frequencies. The frequency dependence of the less intense transition with respect to the temperature at which it occurs is greater than that of the major transition. At temperatures higher than the second transition temperature, ε' decreases with increase

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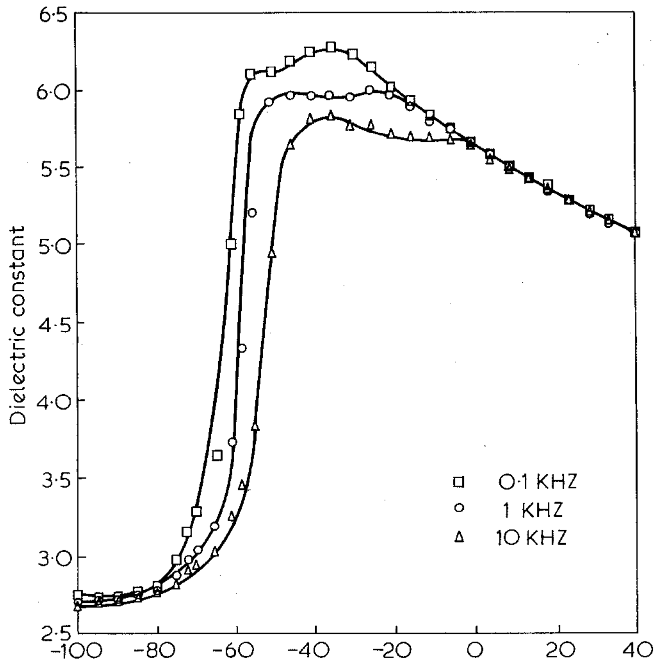

Figure 1 Dielectric constant, ϵ', as a function of temperature at 0.1, 1 and 10 KHz for oligomeric poly(propylene oxide) ($\bar{M}_n = 3034$). The two step jump in ϵ' indicates T_g and T_{ll} for PPO

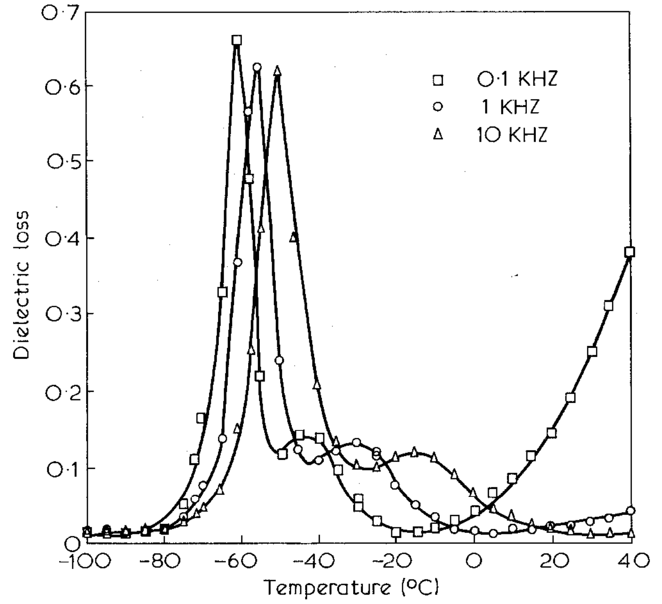

Figure 2 Dielectric loss, ϵ'', *versus* temperature at 0.1, 1 and 10 KHz for poly(propylene oxide) ($\bar{M}_n = 3034$). T_g and T_{ll} peaks can be seen in these data also

in temperature. This is due to (1) thermal expansion of PPO which reduces the concentration of dipoles contributing to the dielectric constant and (2) increase in thermal fluctuations of dipoles. Comparison of our ε' data with the dielectric data of Baur and Stockmayer[1] and Alper and coworkers[2] show that the prominent transition in *Figure 1* corresponds to the glass transition; the transition above T_g corresponds to the molecular weight dependent 'secondary relaxation process' of Baur and Stockmayer and Alper and coworkers. Dielectric loss as a function of temperature at 0.1, 1 and 10 KHz for PPO, given in *Figure 2*, also shows these two transitions: (1) the main glass transition and (2) a $T > T_g$ liquid–liquid transition. ε' and ε'' data of Baur and Stockmayer[1] and Alper *et al.*[2] are represented in the frequency domain; our representation is in the temperature domain. Their high frequency transition corresponds to our low temperature process and their 'slow process' corresponds to our $T > T_g$ liquid–liquid transition. The low frequency dielectric data for pure PPO by Yano *et al.*[6], given in their *Figures 1* and *2*, have an apparent $T > T_g$ transition which has not been interpreted by the authors of ref. 6 as they were mainly concerned with the $\alpha = T_g$ transition in their studies.

The transition temperatures and the corresponding $\varepsilon''_{\max}$ for the glass transition and the liquid–liquid transition and the T_{ll}/T_g ratios at 0.1, 1 and 10 KHz frequencies are tabulated in *Table 1*. The authors of ref. 6 report T_g values over a broad frequency range for PPO 4000. Their results appear in *Figure 3* showing curvature of the broad frequency range which they employed. Alper *et al.*[2] provide dielectric loss data for P4000 as a function of frequency, but their *Figure 4* plots dielectric relaxation times for both the α and β processes so that we can compare our results with theirs as shown in *Figure 3*. Data of Alper and coworkers also show curvature over the broad frequency range used in their experiments. The glass transition temperatures and the $T > T_g$ temperatures reported by Alper *et al.* for the frequencies used in our experiments, can be seen to compare very well with our data. Thus, the dielectric parameters from our experiments, listed in *Table 1*, are in general agreement

Table 1 Dielectric transition parameters for poly(propylene oxide)

Frequency (KHz)	Glass transition T_g (K)	Glass transition $\epsilon''_{\max}$	Liquid–liquid transition T_{ll} (K)	Liquid–liquid transition $\epsilon''_{\max}$	T_{ll}/T_g
0.1	212	0.657	228	0.136	1.08
1	218	0.625	243	0.129	1.11
10	223	0.619	258	0.114	1.16

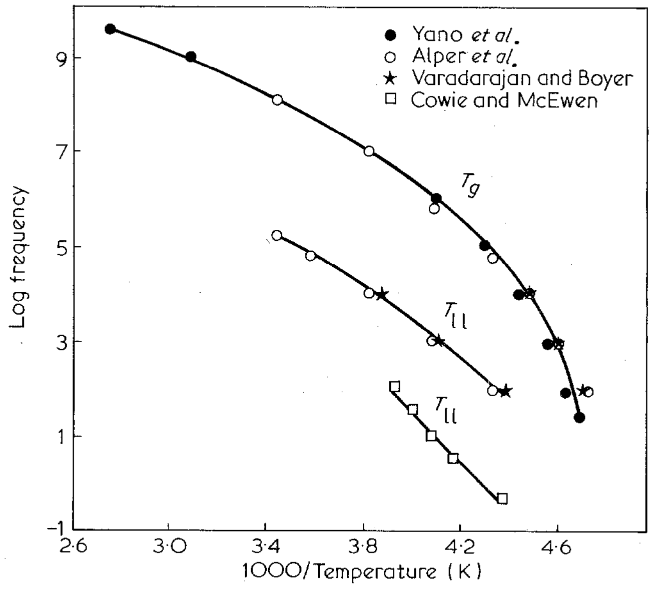

Figure 3 Arrhenius plots for T_g and T_{ll} for PPO. Dielectric data from Alper *et al.*[2], Yano *et al.*[6] and the present study have been used for T_g. For T_{ll} dielectric data from ref. 2 and this study and dynamic mechanical results from Cowie and McEwen[3] and Cowie[4] have been compared

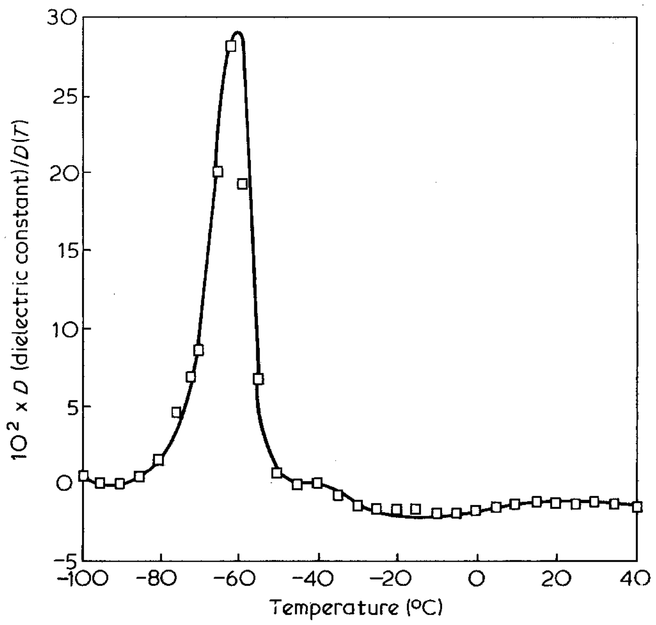

Figure 4 $d\varepsilon'/dT$ as a function of temperature at 0.1 KHz for poly (propylene oxide) ($\bar{M}_n$ = 3034). The derivative was smoothed over three points

with literature data for PPO of comparable molecular weight, given in refs. 1, 2 and 6. Linear least square analysis of the transition temperature–frequency data from our studies resulted in activation enthalpies of 39 and 18 kcal mol^{-1} for T_g and T_{ll}, respectively. Analysis of data by Alper and coworkers in the frequency range of our study gives activation enthalpies of 34 and 18 kcal mol^{-1} for T_g and $T > T_g$ peaks, again confirming the excellent agreement of our results with results reported in the literature. Cowie and McEwen[3], using a limited frequency variation in their dynamic mechanical studies, have found that the activation enthalpy for T_{ll} is about 1/2 of that of T_g, in essential agreement with our observation for PPO. Comparison of the variation of T_g and T_{ll} with frequency over a much broader frequency range, as is evident from *Figure 3*, reveals that the ratio of the activation energies varies between 1 and 2.5, mainly due to the deviation of the glass transition from Arrhenius behaviour.

Alper *et al.*[2] note that for P4000, the mechanical correlation time, τ, for the α peak is twenty times greater than the electrical correlation time, τ. *Figure 3* suggests that the corresponding ratio of τ(mechanical)/τ(dielectric) for the T_{ll} peak is approximately 100 and somewhat frequency dependent. Moreover, the apparent activation energies at lower frequencies (~10–100 Hz) are 27 KCal (113 KJoules) per mol for mechanical *versus* 17 KCal (72 KJoules) per mol for dielectric. This large spread in relaxation times between electrical and mechanical loss for the T_{ll} peak may arise as follows: As noted by Baur and Stockmayer[1], a component of the electrical dipole is additive in the direction of the chain length. We suggest that the mechanical dipole (a term used, for example, by Gisolf[13]) involves $\geq$CH–CH$_3$ and its sterically hindered motion about the chain backbone. The longer mechanical relaxation times presumably result from such steric hindrance.

Stratta *et al.*[14] have observed a $T > T_g$ mechanical loss peak in low molecular weight poly(oxetane), 2-methyl $-\!\!(CH_2–CH_2–CH(CH_3)–O)\!\!-$ and 3-methyl $-\!\!(CH_2–CH(CH_3)–CH_2–O)\!\!-$ which possess mechanical dipoles. They used the blotting paper technique with a torsion pendulum at 3–7 Hz.

The low T_{ll}/T_g ratios of 1.08, 1.11 and 1.16 at 0.1, 1 and 10 KHz, respectively, can be explained by the low molecular weight of P4000. Baur and Stockmayer[1] showed merged α–β peaks for PPO 1000, some separation for PPO 2000, and complete separation for PPO 4000. This merging was also noted by Alper *et al.*[2]. Cowie and McEwen[3] found separated loss peaks at all three molecular weights and all four frequencies. The ratio of T_{ll}/T_g decreased from 1.07 to 1.05 to 1.04 as molecular weight decreased. T_{ll}/T_g ratio has been shown[15] to decrease with decreasing molecular weight for other polymers like polystyrene as well.

In the liquid region, at high enough temperatures, the presence of ionic impurities results in conduction loss and this d.c. conductivity dominates in contributing to ε'' at low frequencies[16]. In *Figure 2* for example above −15°C ε'' increases with temperature at 0.1 KHz. This d.c. conductivity in most cases would mask any transition in the $T > T_g$ region. The T_{ll}/T_g ratio of PPO of $\bar{M}_n = 3034$ is low enough to separate the T_{ll} peak from the d.c. conduction loss; hence T_{ll} can be seen in ε''-temperature plots. In general this is not the case. Therefore, to reduce the d.c. conductivity effect, $d\varepsilon'/dT$ can be analysed for any underlying transitions in the liquid region above T_g[17]. *Figure 4* shows the variation of $d\varepsilon'/dT$ with temperature at 0.1 KHz. The T_g maximum and the $T > T_g$ maximum can be observed in these data. Analysis of $d\varepsilon'/dT$ at 1 and 10 KHz showed that T_g and T_{ll} increase with frequency; the T_{ll} is more frequency dependent than T_g as in the case of ε''-temperature data.

In a companion paper, the dielectric loss of poly(0.6 4-chloro styrene-co-0.4 2-chloro styrene) was observed as a function of temperature[18]. T_g and $T > T_g$ or T_{ll} loss peaks were observed on this high molecular weight polymer. As expected from *Figure 4*, T_{ll} is substantially above T_g and occurs at temperatures where conduction losses are significant. Hence the use of $d\varepsilon'/dT$ to locate T_{ll} was essential.

CONCLUSIONS

In summary, poly(propylene oxide) of $\bar{M}_n = 3034$ exhibits a T_g and a T_{ll} transitions in dielectric studies. The frequency dependences of these two transition temperatures are different as indicated by the activation enthalpy of T_{ll} being approximately 1/2 of that of T_g. This results in better resolution of T_g and T_{ll} peaks at higher frequencies. Based on literature data and our data, the $T > T_g$ peak observed for poly(propylene oxide) in dielectric and dynamic mechanical studies can be assigned to the motion of poly(propylene oxide) molecule as a whole.

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