Dielectric relaxations in the liquid and glassy states of poly(propylene oxide) 4000

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The dielectric permittivity and loss of poly(propylene oxide) of molecular weight 4000, PPO(4000), have been measured in the temperature range 77 K–305 K and frequency range $10^{-2}-2\times10^{5}$ Hz. Two relaxation regions are observed above the glass transition temperature, T_g (= 200 K), and two below T_g. The rate of the highest temperature, or lowest frequency, α' relaxation processes has a temperature dependence which indicates its approach below T_g towards that of the lower-temperature higher frequency, α, process. The rates of both processes can be described by the Vogel–Fulcher–Tamman equation with nearly the same value of T_0. The rate of β-relaxation shows an Arrhenius dependence on temperature with an activation energy of 19.4 kJ mol^{-1}, and may merge with the α-relaxation at $T>250$ K. The relaxations in PPO(4000) are remarkably similar to those observed in molecular liquids and glasses.

(Keywords: dielectric relaxation; poly(propylene oxide) 4000; liquid state; glassy state; glass transition temperature)

INTRODUCTION

Molecular motions in amorphous poly(propylene oxide) have been studied by dielectric[1–7], viscoelastic[8], light scattering[5,9,10] and mechanical[11–14] methods and by n.m.r. spectroscopy[15]. Some of these show that in a certain range of molecular weight, two dielectric relaxation processes occur in PPO above T_g. The rate of the first, relatively small magnitude, low-frequency and high-temperature process, depends upon the molecular weight of PPO and its magnitude is directly related to the cumulative dipole moment along the contour of the polymer chain. Bauer and Stockmayer[2] suggested that this process arises from the Bueche[16]–Rouse[17]–Zimm[18] type of modes of motion of whole chains. The rate of the second, large-amplitude, high-frequency and low-temperature process, whose freezing-out on a time scale of 10^4 s causes the glass transition, is relatively less sensitive to variation in molecular weight. This process is thought to be due to the local orientations of the individual dipole moments of the C–O–C angle, as most of the macroscopic polarization is associated with this orientation.

The mobility of a polymer chain in the rigid glassy state of low molecular weight PPO has not been studied. Dielectric measurements of PPO samples[3] which were rubbery solids at room temperature, and therefore of high molecular weight, have shown a secondary, or β-relaxation process. Arrhenius plots of its rate could not be made mainly because of the extremely broad peaks observed in the isochronal measurements. Mechanical relaxation studies[13,14] have also indicated the presence of a β-relaxation process at $70<T<120$ K in high molecular weight PPO. It is suggested that the process is associated with the cooperative motion of possibly three or four units of the chain accompanying the methyl group reorientation in the amorphous polymer. In addition, Crissman, Sauer and Woodward[14] have observed two further relaxations, namely γ and δ at 90 K and 20 K, respectively, in the isochronal mechanical measurements at 10^4 Hz. They suggested that the γ-process is due to the reorientation of the methyl group and this is confirmed by the n.m.r. studies of PPO containing CD_3 groups[15]. We describe a detailed study of molecular relaxation of poly(propylene oxide) of molecular weight 4000, PPO(4000), in both the supercooled liquid and the glassy states using dielectric measurements over a wide frequency range.

EXPERIMENTAL

The measurement assembly, the thermostat and the dielectric cell have been described in a previous publication[19] and only a brief account is needed here. The capacitance, conductance and the dielectric loss tangent, $\tan\delta$, were measured from 50 Hz to 200 kHz with a GR.1615 A ratio arms bridge, a Hewlett-Packard oscillator and a Rohde and Schwarz tunable amplifier, and below 50 Hz with a low-frequency bridge built after the design by Cole and Berberian[20]. The dielectric cell was a three terminal type, constructed of stainless steel electrodes contained in a glass jacket which in turn contained the liquid under study. The temperature was measured by means of a thermocouple kept inside a hole drilled into one of the electrodes and was controlled to within 0.1 K from 77 K to 305 K. The measured capacitance and $\tan\delta$ were accurate to within 0.1% and 1% respectively.

The sample of PPO(4000) was obtained from PolySciences, Inc. Its molecular weight was nominally 4000 and was a left-over sample from a previous study by Patterson *et al.*[9] The glass transition temperature, T_g, was measured by differential calorimetry.

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RESULTS

The dielectric loss tangent, tan δ, of the polymer at 1 kHz is plotted against temperature in *Figure 1*, where the glass transition temperature T_g (= 200 K) is indicated. It clearly shows three relaxation regions, two as peaks above T_g at 245 K and 215 K in the supercooled polymer liquid and one as peak at 165 K in the glassy polymer. The possibility of a fourth region is indicated by a decrease in ∂ logtan $\delta/\partial T$), with temperature near 115 K in *Figure 1*. (On cooling from ~140 K, the (∂ logtan $\delta/\partial T$) first increases and then shows a decrease at ~115 K. In the absence of a further relaxation region, the (∂ logtan $\delta/\partial T$) would increase monotonically with decreasing temperature.) The two relaxation regions above T_g are identified as α'- and α-processes, which correspond to the 'secondary B' and 'primary A' processes, respectively, of several earlier studies[2,4,6,7] of the polymer. The β-relaxation below T_g is identified as in the literature. The α'- and α-relaxation regions are more clearly discerned in the dielectric loss, ε'', spectrum of PPO(4000) shown in *Figure 2*, where only a few isothermal spectra are given in order to avoid crowding. The frequency locations of the α'- and α-processes are similar to those observed by others[2,4,6,7], but the contribution to ε'' from a large d.c. conduction at the low-frequency side of the α'-peak is relatively less in our measurement. This is also apparent in *Figure 1*, where the d.c. conduction begins to dominate the value of tan δ at $T > 270$ K. Thus the sample of PPO(4000) studied here had less ionic impurities than those samples previously studied[2-4,6,7].

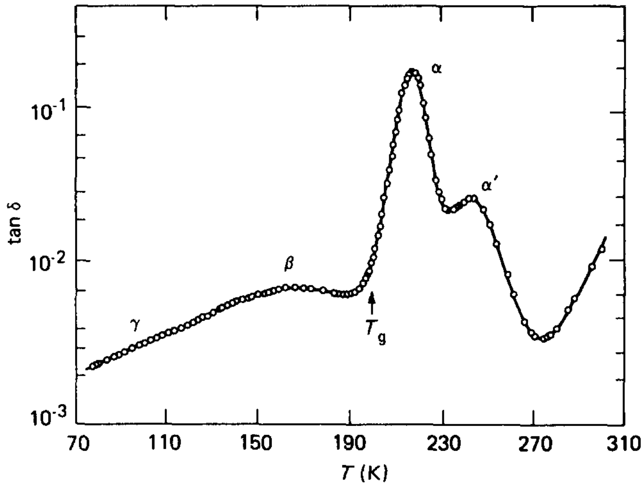

Figure 1 Dielectric loss tangent, tan δ, of PPO(4000) at 1 kHz plotted against temperature

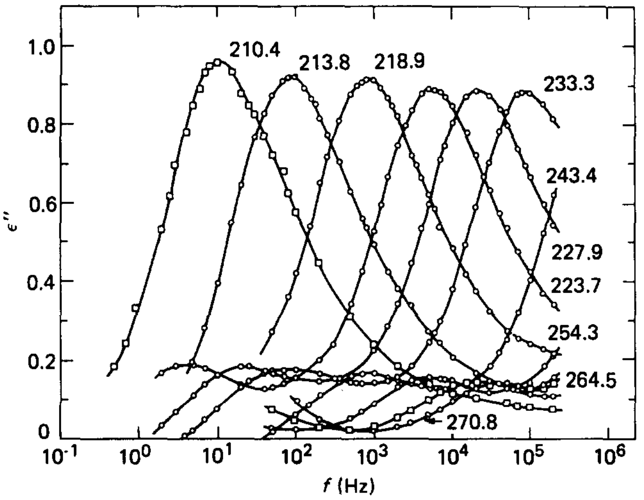

Figure 2 Dielectric loss, ε'', spectra of α'- and α-processes in PPO(4000). Only a few spectra are shown to avoid crowding in the Figure. Temperature (K) is indicated along the curves

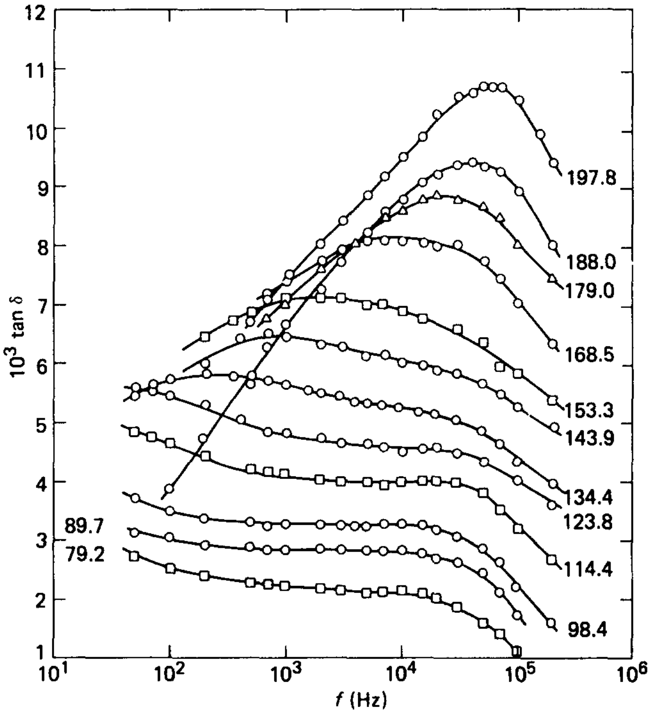

Figure 3 Dielectric loss tangent, tan δ, spectra of the β- and γ-relaxation processes in PPO(4000). Temperature (K) is indicated along the curves

The isothermal spectra of tan δ in the glassy region of the polymer are given at several temperatures in *Figure 3*. There is clear evidence that the broad relaxation observed at 197.8 K broadens further and gives indication of two components, β and γ, as the temperature is decreased. The two components, β and γ, become evident at 123.8 K, which results from a combined ($\beta+\gamma$) processes being transformed continuously as T is decreased to give β and γ as partly resolved processes. A peak of δ-relaxation does not appear at $T > 77$ K, and the frequency region of the shoulder associated with the relaxation process remains unaffected by a change in temperature.

The frequency of maximum loss, f_m, obtained from *Figures 2* and *3*, is plotted against the reciprocal temperature in *Figure 4*. The values of f_m for the α- and α'-processes in the literature have been compared several times[4-8], despite the fact that the mean average molecular weight, and its distribution, of the PPO(4000) used in different studies are not identical. A comparison of the literature data with ours, therefore, seems unnecessary. There is little doubt that the values of f_m for the α-relaxation process are much less affected by the change in molecular weight than those for the α'-process and we also find that the difference in the f_m of the α-process reported here from the literature values is insignificant.

Both the α'- and α-relaxation processes occur with a rate, the temperature dependence of which is given by the Vogel–Fucher–Tamman equation, $f_m = A\exp[-B/(T-T_0)]$. For the α'-relaxation,

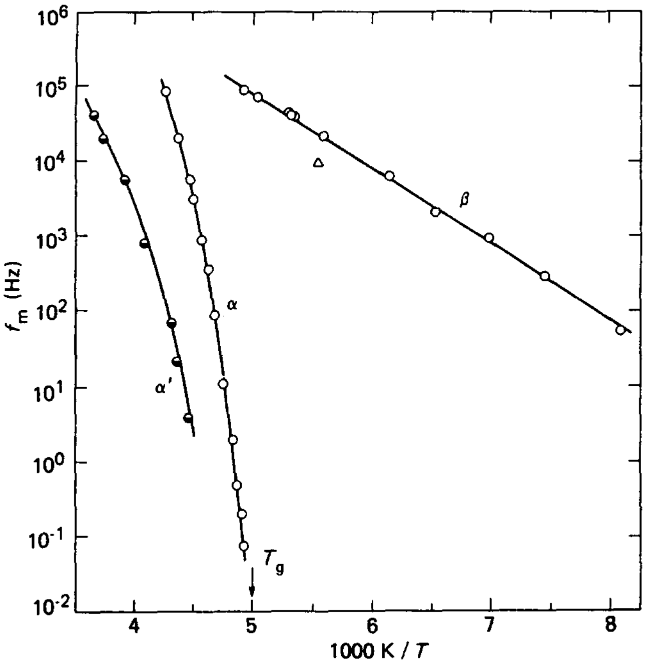

Figure 4 Frequency of maximum loss of the α'-, α- and β-relaxation processes in PPO(4000) plotted against reciprocal temperature. (△) is datum for mechanical relaxation[14]

$A = 181$ MHz, $B = 790.6$ K and $T_0 = 178$ K and for α-relaxation, $A = 18.9$ GHz, $B = 716.4$ K and $T_0 = 176$ K. These values indicate, as is also apparent in *Figure 4*, that the α'- and α-relaxation peaks would overlap increasingly as the temperature is decreased below T_g. The rate of β-relaxation changes with temperature according to the equation, $f_m = f_0 \exp(-E/RT)$, where $f_0 = 8.9$ GHz and the Arrhenius energy $E = 19.4\ \mathrm{kJ\ mol^{-1}}$. The β- and α-relaxations may merge at high temperatures while the α'-relaxation continues to diverge from the extrapolated plot of both the β-relaxation and the α-relaxation.

In order to observe both the α- and β-relaxation peaks at a temperature above T_g, the entire spectrum of dielectric loss was measured at 202.8 K. This is shown in *Figure 5*, where the two relaxation peaks can be clearly discerned. It is important to note that at 202.8 K, the α-relaxation peak in *Figure 5* represents a sum of the contributions from both the α'- and α-processes because of the proximity of the two relaxations at this temperature. Measurements at frequencies less than 10^{-2} Hz would more clearly resolve a spectrum in which all the three relaxations are present.

DISCUSSION

Relaxations above T_g

The half-width (frequency width at half-height) of the spectrum of α-relaxation at 210.4 K in *Figure 2* is 2.0 decades of frequency and remains constant with changing temperature. The spectrum is asymmetric and its shape can be satisfactorily fitted both to the Cole–Davidson[21] skewed arc function with $\beta = 0.39$, and Williams–Watts[22] function with $\beta = 0.52$. Such satisfactory fit of the shape to the two functions has also been shown by Alper *et al.*[4] However, the data could not be fitted to either of the two functions in the lowest and highest extremes of frequency, for the reason that at low frequencies contributions from the α'-process and at high frequencies contributions from the β-process begin to dominate the shape of the spectrum. The Williams–Watts[22] function often fits less satisfactorily at the high frequency end of the spectrum[23], mainly because of the contribution to ε'' and tan δ from the β-relaxation process.

The half-width of the α'-relaxation could not be accurately determined, but by an approximate estimate from the low-frequency side, after deducing contributions from α-relaxation at the high frequency side, the half-width of the peak is ~1.6 decades at temperatures between 227.9 K and 243.4 K. This means that the reorientation process of the dipole component along the length of the chain is closer to a single relaxation time (half-width ~1.14 decades) than that of the component perpendicular to the length of the chain. This may be confirmed from studies of other similar polymers. The shape of the α'-relaxation can also be fitted to the Cole–Davidson[21] and Williams–Watts[22] functions but such a fit is less satisfactory because of the contributions from the α-relaxation at the high-frequency end.

From the pressure dependence of the rates of α-, and β-relaxations, Williams[24] has deduced that in polymers with dipoles rigidly attached to the main chain, the α- and β-processes may coexist at $T > T_g$ although no direct evidence for the existence of the two relaxation processes at $T > T_g$ was known. *Figure 5* makes it clear that both α- and β-relaxations exist at ~3 K above T_g in PPO(4000) and that their relative amplitudes of ε'' are in the ratio of 22:1.

The glass transition temperature of PPO is relatively independent of the molecular weight of the polymer and is within a few degrees of 200 K. Apparently, the same physical process of segmental motion of the polymer chain near T_g is involved in the different polymers and

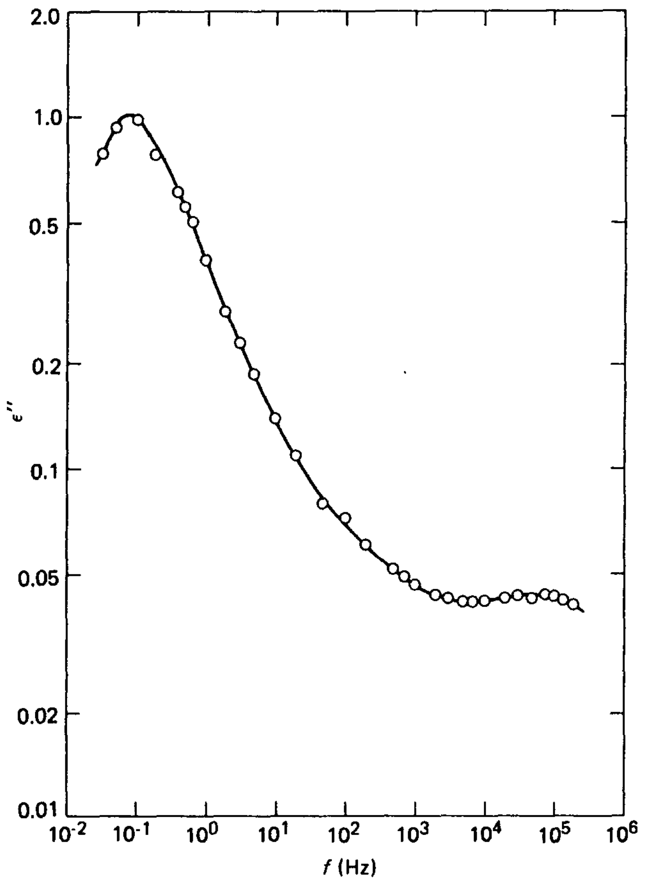

Figure 5 Isothermal loss spectrum of PPO(4000) at 202.8 K, showing both the α- and β-processes at $T > T_g$

Alper *et al.*[4] have shown that the relaxation rate of the α-process for a polymer of molecular weight 400 is about the same as that of PPO(4000) despite the ten-fold increased number of repeat units in the latter. Therefore, the segmental motions must involve very few bonds, so that the end effects of a polymer chain may be negligible.

Relaxations below T_g

Figure 3 shows that the height of the β-relaxation peak rapidly increased with temperature—by about 50% from 143.9 K to 197.8 K. Clearly, either the number of chain segments involved in the relaxation increased with temperature or the total dipolar reorientation associated with a given segment increased but the number of such segments remained unchanged with increasing temperature. The former assumes the structure of a glassy polymer as consisting of statistically distributed regions of high volume and high entropy—such regions represent density fluctuations in a liquid above T_g, which become frozen-in below T_g. The latter assumes a dense random packed structure with each segment capable of moving by a small angle. Both may reflect the predominance of intermolecular barriers, as the effect of physical ageing on β-relaxation in PPO(4000)[19] seems to suggest so. When PPO(4000) is densified by either slow cooling or by isothermal annealing, the strength of its β-relaxation is decreased[19]. The effect of densification on the strength of β-relaxation is an indication of the greater role of intermolecular barriers in determining the localized motions in a polymer glass.

The γ relaxation observed at $T<143.9$ K in *Figure 3* may be attributed to the reorientation of $-CH_3$ group as suggested by Crissman *et al.*[14] and confirmed by Conner *et al.*[15]

The features of small scale motions associated with the β-relaxation process are not easily rationalized in terms of phenomenological theories based upon our concepts of free volume[25,26], or configurational entropy[27], although the change in the rate of α-relaxations, or of viscous flow, can be explained by them. Therefore, the presence of such relaxations in amorphous polymers is explained by *ad hoc* hypotheses, often in terms of the rotation of a side group attached to the main polymer chain, and it is asserted that the relaxation involves an intramolecular barrier and not a set of intermolecular barriers. The lack of a side group in PPO(4000) and the observations of β-relaxation in rigid molecular glasses[28] are clearly in conflict with the suggestion that only intramolecular barriers play a role in determining the features of the β-relaxation process. One may consider that highly localized motions of the $HC(CH_3)-O-CH_2-$ group, confined only to a few repeat units and determined by the local amorphous packing, appear as β-relaxation and that the number of such groups and/or regions, where correlated motions of such groups occur, grow in size as the temperature is raised. This would rationalize the observation of the increase in the height of the β-relaxation peak with temperature without resorting to special mechanisms of polymer chain movement. Thus the observed β-relaxation in PPO(4000) is made possible by the statistical distribution of low-density regions, or defects, in the structurally non-uniform packing in its glass. The occurrence of a β-relaxation in PPO(4000) without a dipolar side group is an interesting example which raises the possibility of the β-relaxation as a precursor of the glass transition mechanism.

The relaxation rates

The rates of α′ and α relaxations plotted in *Figure 4* indicate that the two processes would approach the same value of f_m near T_g. The slope, i.e. $\partial \log f_m/\partial(T^{-1})=BT^2/(T-T_0)^2$ of the α′ process at 233 K is 14071 K and that of the α-process at the same temperature is 11876 K, which indicates that the α′-process has a higher 'activation energy' and involves a higher degree of cooperativity of segmental motions, than the α-process. This seems consistent with the suggestion of Baur and Stockmayer[2] that the α′-process represents the overall motion of the polymer chain. However it must, in our view, result from the elementary processes involved with the glass transition in such a way that it becomes indistinguishable from the α-process at temperatures where the relaxation becomes very slow. The rates of the α′- and α-processes progressively diverge with increasing temperature. We suggest that at $T>T_g$, the loss spectrum would show the two processes more separated in the frequency of these peaks than is observed in this study.

It is clear that the rate of β-relaxation approaches the rate of α-relaxation at $T>250$ K. This is remarkably similar to the behaviour observed for chlorobenzene–decalin mixture[28], where the reorientation of individual molecules involves intermolecular barriers. In view of this and other similarities noted in glasses of different types[28], we suggest that the motions of a segment of a polymer chain is merely a special case when the interactions acquire a highly directional character of tetrahedral bonding and of a fixed distance between the CH_2 groups, while in a molecular glass where the interactions are relatively weak, molecules can occupy all possible sites around each other whilst constrained in the distance and interaction energy by a suitable intermolecular potential. In this sense the mechanism of relaxation in a polymer, such as PPO(4000), is not fundamentally different from that in molecular liquids and glasses. Therefore, these relaxations are best interpreted in a general way that transcends the details of molecular structure and does not require specific models for motions.

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