The effect of water on dielectric relaxations in the glassy states of poly(propylene oxide) and propylene glycol

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The dielectric permittivity and loss of poly(propylene oxide), $M_w = 425$ and propylene glycol (PG) and their mixtures with water were measured in the temperature range 77–320 K and frequency range 12–5 $\times 10^5$ Hz. PPO-425 has two relaxation processes which appear as β- and α-peaks, but the β-peak in PG is masked by a large contribution to the loss from the α-process. Addition of water up to 1.25 wt % changes the temperature or the rate of the α-process in both PPO-425 and PG, and increases the half-width of the α-relaxation in PG. Water decreases both the rate and the strength of the β-process in PPO-425. The strength of the β-process increases with increase in the molecular weight of PPO. Therefore, the β-process is related to the increasingly less efficient packing of a high molecular weight polymer chain. The increase in permittivity on cooling the liquids is more than that anticipated from the temperature effect alone. This increase is due to the enhanced short-range orientational correlation of the dipoles which may also involve H-bonding through the water molecules.

(Keywords: dielectric relaxation; poly(propylene oxide); propylene glycol)

INTRODUCTION

Hydrogen bonding of water to the terminal OH groups of a polymer chain affects its relaxation behaviour substantially differently than that of the non-polymeric materials with similar OH groups. This effect is particularly interesting since the relaxation characteristics of the two types of materials are found to be qualitatively similar[1]. From an earlier study, we reported that water antiplasticized polypropylene oxide ($M_w = 4000$) and caused its β-relaxation peak to shift to a higher temperature[2], but plasticized anhydrous glucose[3] and caused its β-peak to shift to a lower temperature, despite the fact that H-bonding was the predominant interaction in both cases. It therefore seemed important to study the effect of water on the relaxations in the non-polymeric and polymeric forms of the same substance.

For molecular weights greater than 425, the glass transition temperature (T_g) of the polypropylene oxide polymers (PPO) does not significantly change with the molecular weight, and remains within a few degrees of 200 K[4]. The lower molecular weight polymer PPO-425 has been studied at $T > T_g$ by both the dielectric and dynamic mechanical methods with the main intention of investigating the normal modes of motions of the polymer chain[5]. These modes appear as a low-strength dielectric relaxation peak[4,5] at $T \gg T_g$ in PPO-4000 but do not in PPO-425. We recently reported[6] that PPO-4000 also exhibits a β-relaxation at $T \geqslant T_g$ which is associated with the localized motions of its chain segments and contributes to the short-time dielectric and dynamic-mechanical properties of the polymer at $T \leqslant T_g$. We then suggested that these local motions may be the precursor of the long-range motions of a polymer chain. Therefore, it seemed useful to study whether or not β-relaxation occurs in PPO-425 and in its monomer propylene glycol (PG), and whether the relaxation strength depends upon the molecular weight.

This study has three purposes, namely: (1) to determine how the addition of water affects the dielectric behaviour of both liquid and the glassy states of PPO-425 and of PG, (2) to investigate for the existence of β-relaxation in the two substances and its connection with the long-range motion of polymer chain and the monomer, and (3) to determine whether H-bonding of the terminal OH groups by water in a polymer affects its relaxations similarly to that in the corresponding monomer.

EXPERIMENTAL

The capacitance, conductance and the loss factor of the melt and glass samples were measured over the frequency range 12–5 $\times 10^5$ Hz by the combined use of a General Radio 1689 impedance bridge and a General Radio 1615A capacitance bridge. The latter assembly has been described earlier[6].

The three-terminal dielectric cell was constructed of stainless steel. Micalex discs were used to separate the low and high electrodes from the ground shields. In all respects the cell was similar to the one described earlier[6]. The capacitance of the cell in air was nominally 11 pF.

The thermostat assembly was constructed of a cylindrical aluminium block which had a heater wire wound around it and whose temperature could be controlled to within ± 0.5 K. The dielectric cell, contained in a hermetically sealed glass tube, was snugly fitted inside a ~ 27 mm diameter concentric cavity in the
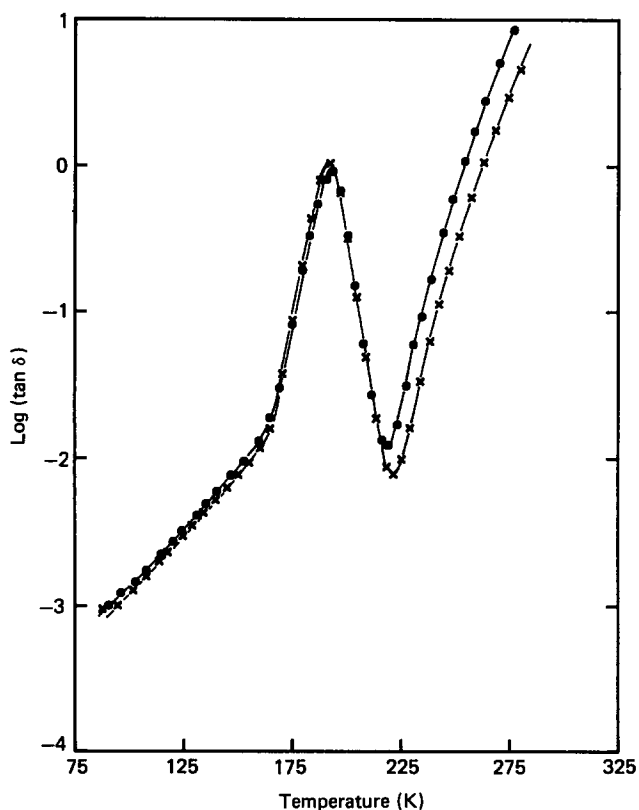
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Figure 1 The dielectric loss tangent, tan δ at 1 kHz plotted against temperature: ●, pure propylene glycol; and ×, 1.2 wt% water propylene glycol mixture

block. The entire assembly was kept in a dewar containing liquid nitrogen.

Polypropylene oxide -425 and propylene glycol (PG) were obtained from Aldrich Chemical Company. The mixtures with distilled deionized water were prepared by weighing.

RESULTS

Pure propylene glycol (PG) and PPO-425 have been studied by several workers before[1,5]. Since our samples may differ from theirs, in both their constitution and molecular weight distribution, it was necessary to measure the dielectric behaviour of the pure samples again so that a justifiable comparison with the water mixtures could be made. This was done and the results are included here.

Plots of the dielectric loss factor, tan δ, measured at 1 kHz in the temperature range 77–280 K for PG, and its 1.2 wt% H_2O mixture are shown in *Figure 1*. Only one relaxation, namely the α-peak, is observed in PG, whose height increased by $\sim 10\%$ on the addition of 1.2 wt% H_2O, and whose temperature remained almost unchanged. The minimum at $T \approx 225$ K became deeper and shifted to a higher temperature by ~ 4 K. At $T \approx 275$ K, the tan δ increased by a factor of ~ 3 and further increased with temperature.

Plots of tan δ measured at 1 kHz for PPO-425 and its 0.48 wt%-, and 1.25 wt%-water mixtures against temperature are shown in *Figure 2*. PPO-425 shows two relaxation peaks, one, the β-peak at $T \sim 163$ K in the glassy state and the second, the α-peak at 213 K in the liquid region followed by a minimum at 240 K. Addition

of 0.48 wt% water shifts the β-peak to ~ 175 K and the α-peak to ~ 215 K. For 1.25 wt% water mixture, the β-relaxation peak becomes a low-temperature shoulder to the α-peak and the height and the position of the α-relaxation peak do not significantly change. The height of the β-peak is lower in the water mixture than in PPO-425, the minimum near 240 K remains unchanged in its position but becomes shallower for the 0.48 wt% water mixture and deeper for the 1.25 wt% water mixture than in PPO-425.

The dielectric loss spectra of the α-relaxation region of PG and its water mixture are shown in *Figure 3*. It is seen that, for the same temperature, the height of the α-relaxation peak is increased by $\sim 10\%$, and its frequency only slightly. The half-width of the spectrum of PG in *Figure 3* is 1.37 decades, which is increased to 1.41 ± 0.07 decades on the addition of 1.2 wt% water. The spectrum can be fitted to Kohlrausch–Williams–Watts relation[7] with the value of β of 0.82 ± 0.02 for PG and 0.80 ± 0.05 for its 1.2 wt% water mixture. These values are given in *Table 1*.

The corresponding spectra of the α-relaxation region of PPO-425 and its water mixtures are shown in *Figure 4*. It is evident that, for a given temperature, the height of the α-peak is increased by $\sim 15\%$, but its frequency only slightly on the addition of water. The half-width of the spectrum for PPO-425 is 1.80 decades, which is the same as for the 0.48 wt% water mixture. The value of β for both PPO-425 and its mixture is 0.61. These values along with those[2] for PPO-4000 are listed in *Table 1*.

The isothermal spectrum of tan δ for the β-relaxation in
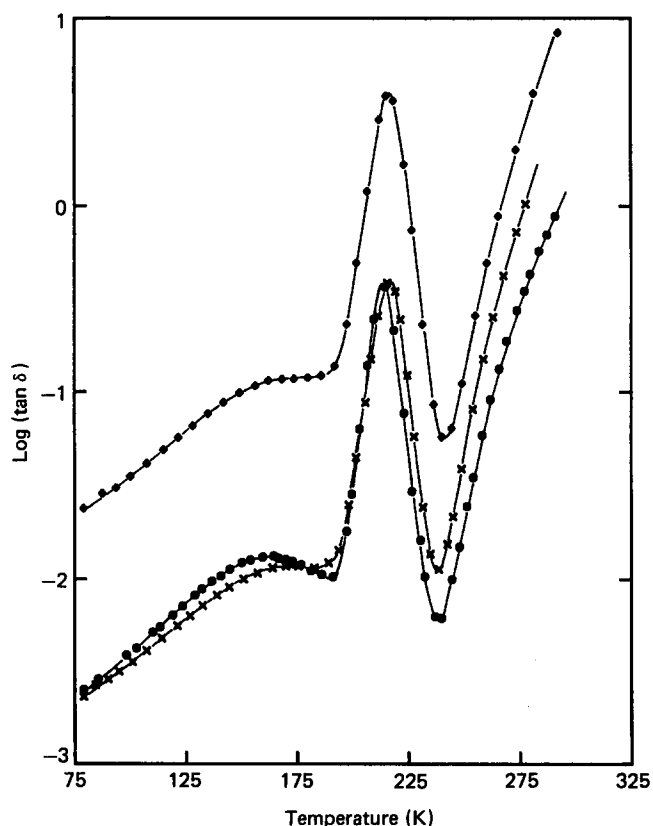

Figure 2 The dielectric loss tan δ, at 1 kHz plotted against temperature: ●, pure PPO-425; ×, 0.48 wt% water mixture of PPO-425; and ◆, 1.25 wt% water mixture of PPO-425 (plot shifted upwards by one logarithmic scale)
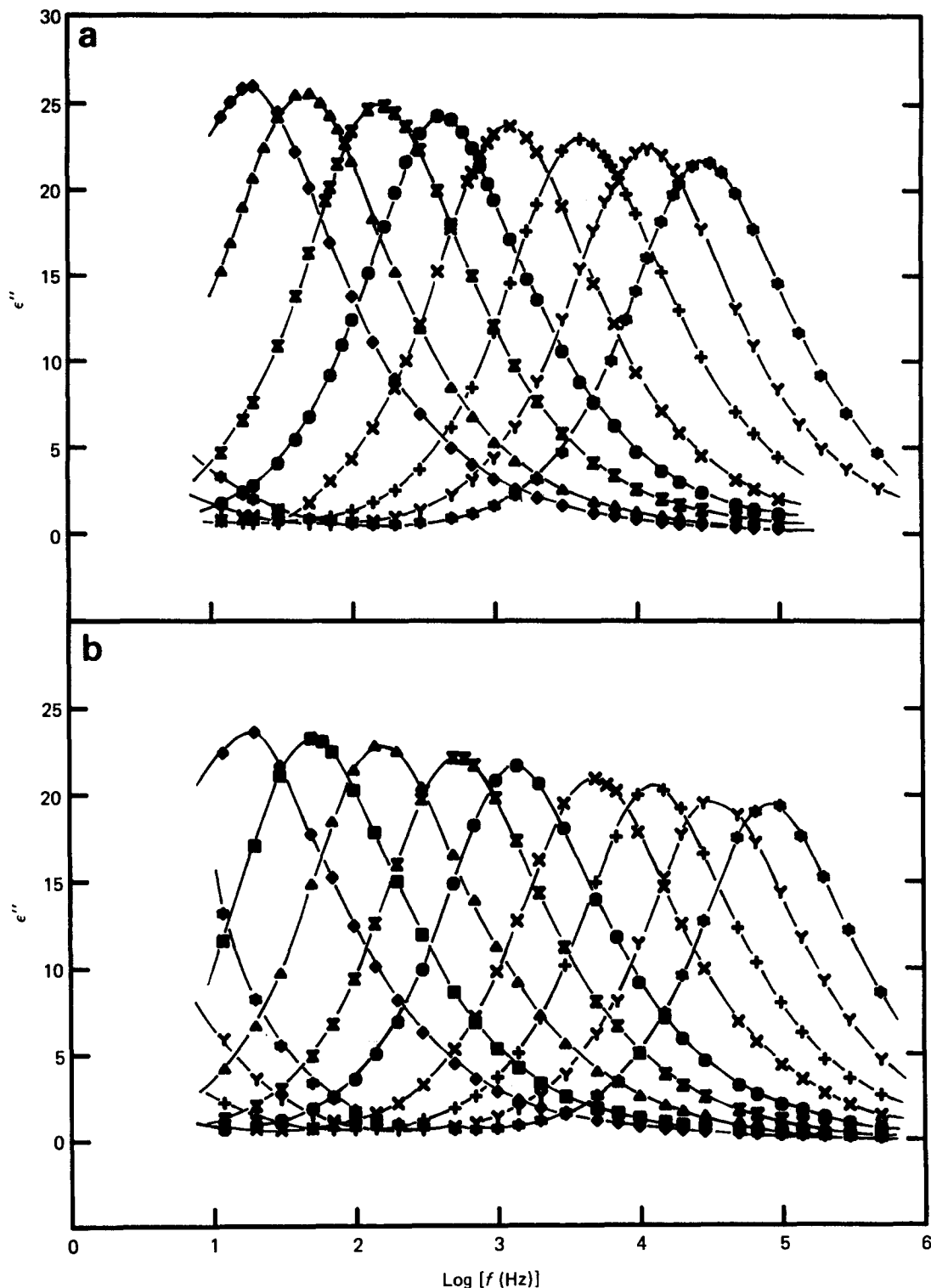
Figure 3 The isothermal spectrum of ε'' in the α-relaxation region of (a) 1.2 wt % H_2O–PG mixture and (b) pure PG. For pure PG, the temperatures are: ◆, 186.3; ■, 188.6; ▲, 191.9; ✱, 195.5; ●, 198.9; X, 203.5; +, 207.4; Y, 211.0; ★, 216.4 K. For 1.2 wt % H_2O–PG mixture, the temperatures are: ◆, 185.8; ▲, 188.0; ✱, 191.6; ●, 194.8; X, 198.5; +, 202.9; Y, 207.2; ★, 211.2 K

PPO-425 and in its water mixture are shown in *Figure 5*. The addition of water lowers the height of the tan δ peak. Because of the overlap of a high-frequency, γ-process in these spectra, it is not certain whether or not the half-width of the spectrum is altered on the addition of water. The frequency of maximum loss, f_m, for the β-peak in PPO-425, plotted against the reciprocal temperature, in *Figure 6*, is described by the Arrhenius equation

$f_m = f_0 \exp(-E/RT)$ with $f_0 = 6.31\,THz$ and $E = 28.7\,kJ\,mol^{-1}$. Because of a substantial overlap of a high-frequency process in the 0.48 wt % water mixture, its f_m for the β-process could not be accurately determined.

The rate of the α-process represented by the peak frequency in *Figures 3* and *4* is plotted against the reciprocal temperature in *Figure 6*. The data were fitted to Vogel–Fulcher–Tamman equation,

Table 1 The various parameters of the α-relaxation process and of the contribution to dielectric permittivity from orientation polarization for pure PG and PPOs and their water mixtures

Materials	$\nu_{1/2}$	β	T_0 (K)	A (Hz)	B (K)	$\Delta\varepsilon$ (219.5 K)
Propylene glycol (PG)	1.37	0.82	100	5470	2866	45.0
PG+1.2 wt% H_2O	1.41	0.80	95	9600	3067	49.1
PPO-425	1.8	0.61	152	25.45	1603	10.4
PPO-425+0.48 wt% H_2O	1.8	0.61	160	1.98	1272	11.7
PPO-4000*	2.0	0.51	178	18.8	640	3.35
PPO-4000+1.23 wt% H_2O*	2.0	0.51	168	840	1051	4.90

*Data from reference 2
Vogel–Fulcher–Tamman equation: $f_m = A \exp[-B/(T - T_0)]$

$f_m = A \exp[-B/(T - T_0)]$, and the values of the parameters obtained are given in *Table 1*. These values are useful only for obtaining the data in the frequency range 12–200000 Hz. The results in the α-relaxation region for pure PG agree reasonably well with those obtained by several other workers[1] and those of PPO-425 with the results of Alper *et al.*[5] Thus the interpretation of these results is the same as already given by them. Our concern is mainly with the effect of (1) water on the relaxations in the liquid and glassy states of PPO-425 and PG and (2) molecular weight on the relaxations in the glassy state of PPOs.

DISCUSSION

The effect of water on relaxations

We earlier reported[2] that water antiplasticized PPO-4000, in that its addition caused the relaxation rate of the α-process to decrease. These data, which are included in *Figure 6*, show that the rate of the α-process in PPO-4000–1.23 wt% water mixture is nearly the same as of PPO-425 and of PPO-425–0.48 wt% water mixture. *Figure 6* also shows that the f_m of the α-process in PPO-425 changs only slightly on the addition of up to 0.48 wt% water, and that the same is true for PG up to 1.2 wt% water.

We calculate that a weight fraction of 8.5% water in PPO-425 is needed to achieve a linear combination of its polymer chains into one long chain, if the bonding occurred via H-bonds at the chain terminating hydroxyl groups. The 0.48 wt% and 1.23 wt% water, added to the polymer is clearly insufficient to achieve this. The 1.2 wt% water in PG is also much less than necessary to link the PG molecules to form a long chain. In both cases, the effect of water on the α-relaxation rate is small and we conclude that the calorimetric T_g of PPO-425 and PG would remain nearly unchanged on the addition of small amounts of water. Since the change in the relaxation rates represents the effect on the friction coefficient of segmental motions, this implies that small amounts of H-bonded water does not affect these coefficients, but considerably affects the corresponding coefficients of the β-process, for its rate is decreased or its temperature is increased in the isochrones of *Figures 1* and *2*.

The spectrum of β-relaxation in PPO-425 is more clearly resolved than in its water mixture, as is seen in *Figure 5*. The height of the β-peak decreases with decreasing temperature and at temperatures below 162.8 K, the broad relaxation further broadens and gives indication of two components, β and γ. As the spectrum broadens rapidly, the two components (β and γ) seem to

become more separated but cannot be seen as distinct peaks, or a shoulder, at temperatures as low as 77 K.

The addition of water to PPO-425 causes its spectrum to become more clearly evident as a combination of β- and γ-processes at $T < 164.8$ K. With decrease in temperature, there is a continuous transformation of the (β and γ) process, although neither is clearly resolved in our temperature range in *Figure 5*. The height of the (β and γ) spectrum is 0.0119 in PPO-425 at 158.4 K, and 0.0105 in its 0.48 wt% water mixture at 157.8 K. The decrease in the height suggests that the presence of water causes a decrease in the number of localized orientational degrees of molecular freedom in a glassy matrix of PPO-425. This is likely to be the case if H-bonding of water prevents the restricted rotation of the dipolar chain segments of PPO-425 at $T < T_g$ while the large dipole moment of water makes no contribution to the β-process, but a substantial contribution to the α-process. In most other H-bonded polymers, e.g. nylon 66, the addition of water increases both the rate and the height of the β-peak[8], an observation reported also for several non-H-bonded polymers[9], and glucose–water mixtures[3]. The behaviour of PPO-425 and PPO-4000 (reported earlier[2]) contrasts with that of other polymers and this, we suggest, is a reflection of the special types of local segmental motion in a polymer which has no side group or a side chain and in which packing of the chain is significantly affected by H-bonding with water.

Hydrogen bonding with water increases the total polarization or the strength of dielectric relaxation in PPOs and PG, as seen in *Figure 7*, and almost all of this increase appears in the α-process. This is partly due to the much higher dipole moment of H_2O and partly due to any dipolar correlations introduced by the H-bonding. The plots of $\Delta\varepsilon$ ($= \varepsilon_0 - \varepsilon_\infty$) against temperature of both the PPO-425 and PG and their respective water mixtures are given in *Figure 7*, and the values of $\Delta\varepsilon$ at 219.5 K for PPO-4000[2,6], PPO-425 and PG and their water mixtures are given in *Table 1*. The plots in *Figure 7* and the data in *Table 1* show that $\Delta\varepsilon$ increases on the addition of water and that this increase per unit wt% of water is lower the higher the molecular weight of the polymer PPO. These values are 3.4, 2.7 and 1.3 per unit wt% of water in PG, PPO-425 and PPO-4000, respectively.

As seen in *Table 1*, the Kohlrausch–Williams–Watts parameter[7], β, for the α-process in PG is decreased on the addition of water. For PPOs, this parameter remains unchanged on the addition of water, but decreases with the increase of molecular weight of the PPO. Thus the effect of water on the properties of PG in this sense is similar to the increase in the molecular weight of PPO.
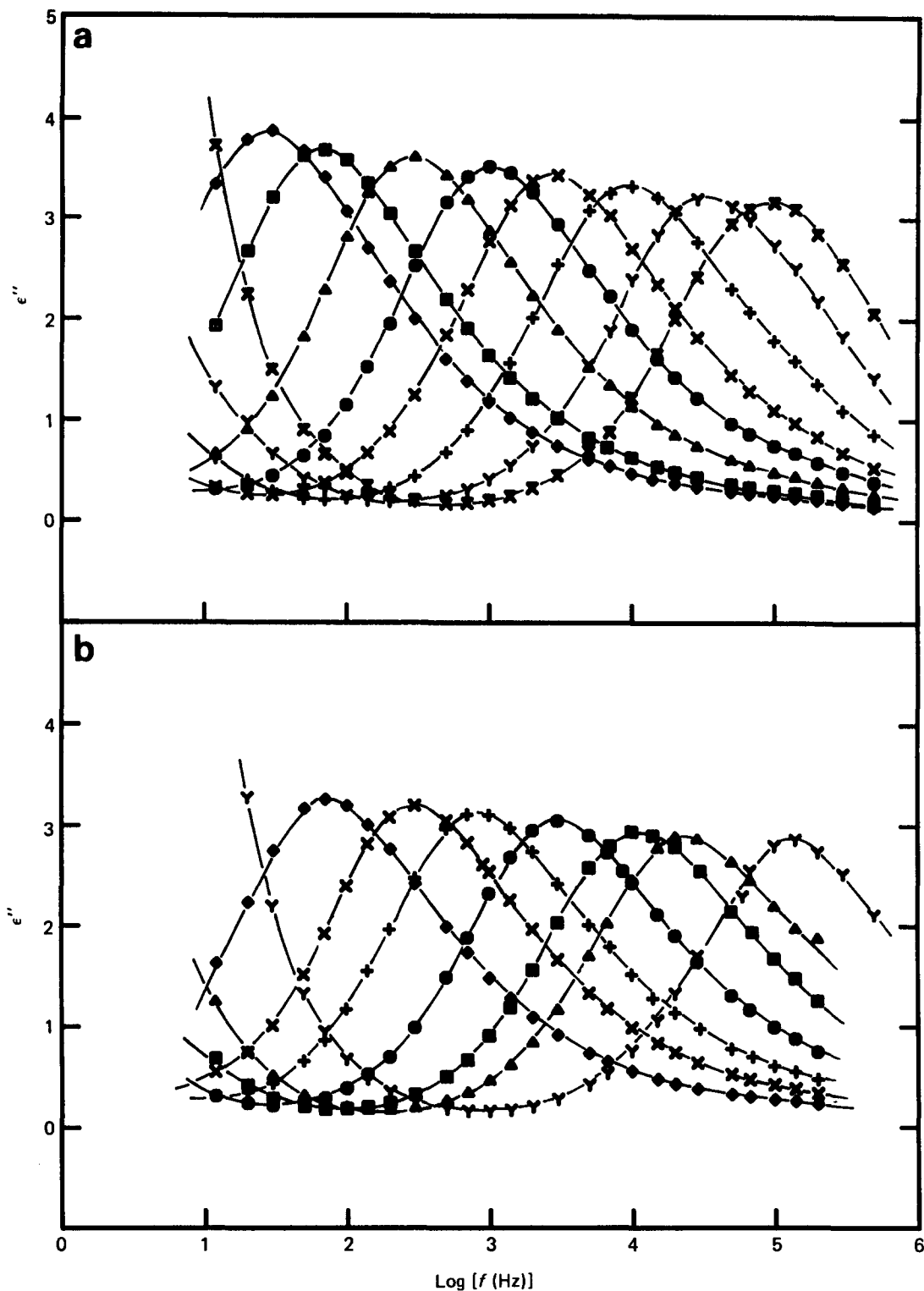
Figure 4 The isothermal spectrum of ε'' in the α-relaxation region of (a) 0.48 wt % H_2O-PPO-425 mixture and (b) pure PPO-425. For pure PPO-425, the temperatures are: ◆, 212.8; ×, 216.1; +, 218.7; ●, 222.4; ■, 226.6; ▲, 229.6; Y, 236.7 K. For 0.48 wt % H_2O-PPO-425 mixture, the temperatures are: ◆, 211.0; ■, 212.8; ▲, 216.3; ●, 219.6; X, 222.5; Y, 231.1; ▼, 235.3 K

This further suggests that water H-bonds with the terminal OH groups of PG to form short polymer chains which are more stable than the chains formed by the H-bonds between the PG molecules themselves.

β-process and the molecular weight

A β-relaxation peak is not resolved either in the isochrone of *Figure 1* or in the isothermal spectrum (not

included here) of PG. Nevertheless, as shown earlier[10,11], when a plot of the difference between the tan δ at 1 kHz and at 10 kHz is made against temperature, a peak is observed at $T < T_g$ (ref. 11). This indicates the presence of a β-process with a low peak which is therefore masked by the large contribution to tan δ from the α-process, and/or whose position in the temperature and frequency planes is too close to the tan δ peak of the α-process, and, therefore,
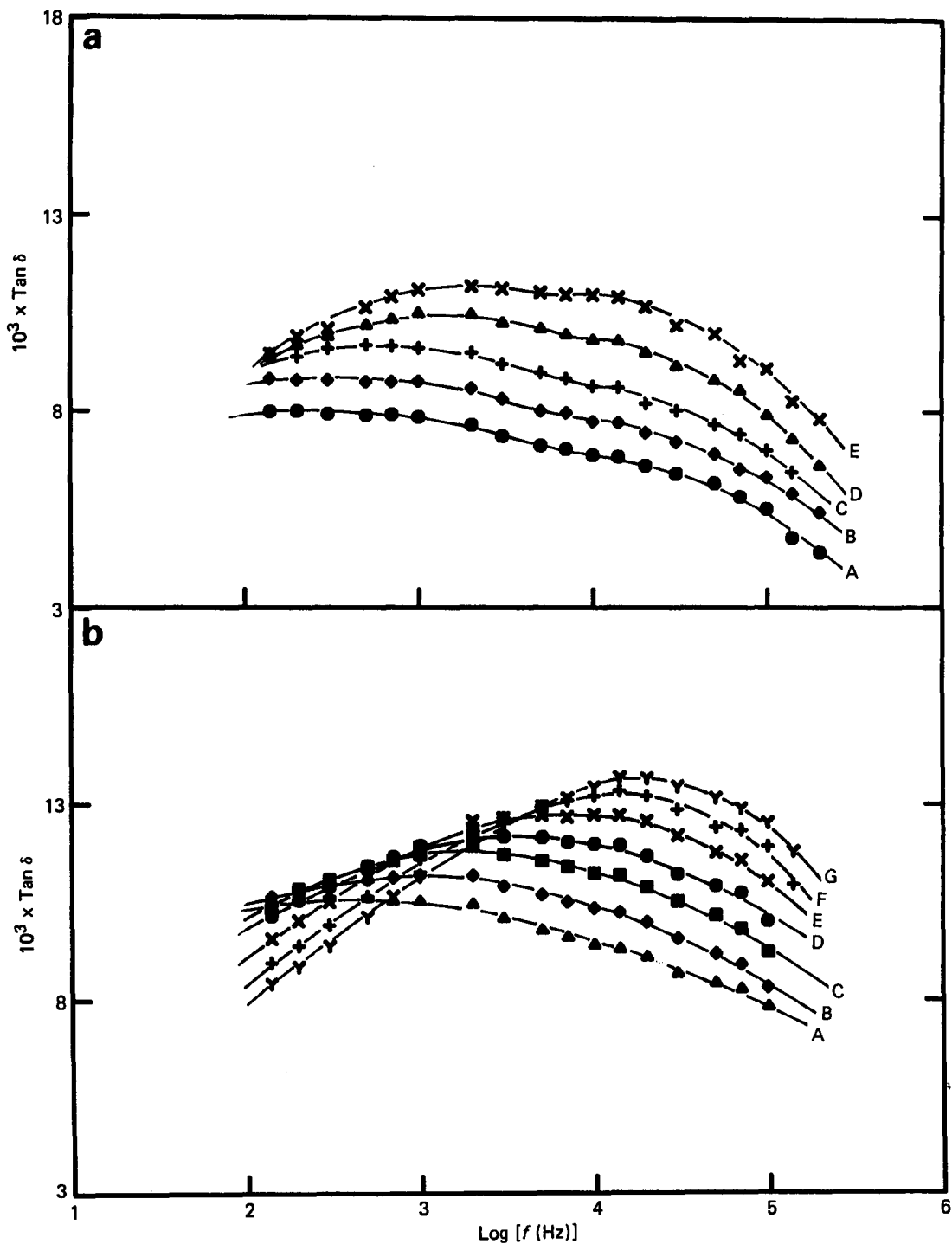
Figure 5 Plots of tan δ against the logarithm of frequency for the β and the γ-processes. (a) PPO-425–0.48 wt % water. The temperatures are: A, 139.1; B, 145.1; C, 150.9; D, 157.8; E, 164.8 K. (b) Pure PPO-425. The temperatures are: A, 148.4; B, 153.2; C, 158.4; D, 162.8; E, 168.3; F, 173.1; G, 177.3 K

is not observed in the isochrones and the isothermal spectrum. In either case, β-process occurs in PG at $T < T_g$ and its strength is much less than in the PPO's.

The ratio between the heights of the tan δ peaks of the β- and α-processes is 1:31 in PPO-425, 1:28.6 in PPO-4000[2,6] and 1:10.3 in a high molecular weight PPO[12], which had the same T_g as PPO-4000 but which was solid at 298 K. Therefore, it seems that the strength of the β-process relative to the α-process increases as the molecular weight of the PPO is increased, and that this strength is unmeasurable in PG, but is $\sim 1/10$ of the α-process in an unspecified high-molecular weight[12] PPO.

Since the contribution to permittivity due to the orientation polarization, given in *Table 1*, is 13 times greater in PG than in PPO-4000, it follows that the mechanism of β-process involves a relatively greater number of dipoles and/or a larger angle of dipolar orientation in the polymeric than in the molecular PG. This is remarkable, as it suggests that the strength of the β-process in a polymer without a side chain, or a side group, is related with its molecular weight, or alternatively, with the configurational restrictions of a polymer chain. It also implies that the packing of a polymer chain in its glassy state allows greater freedom
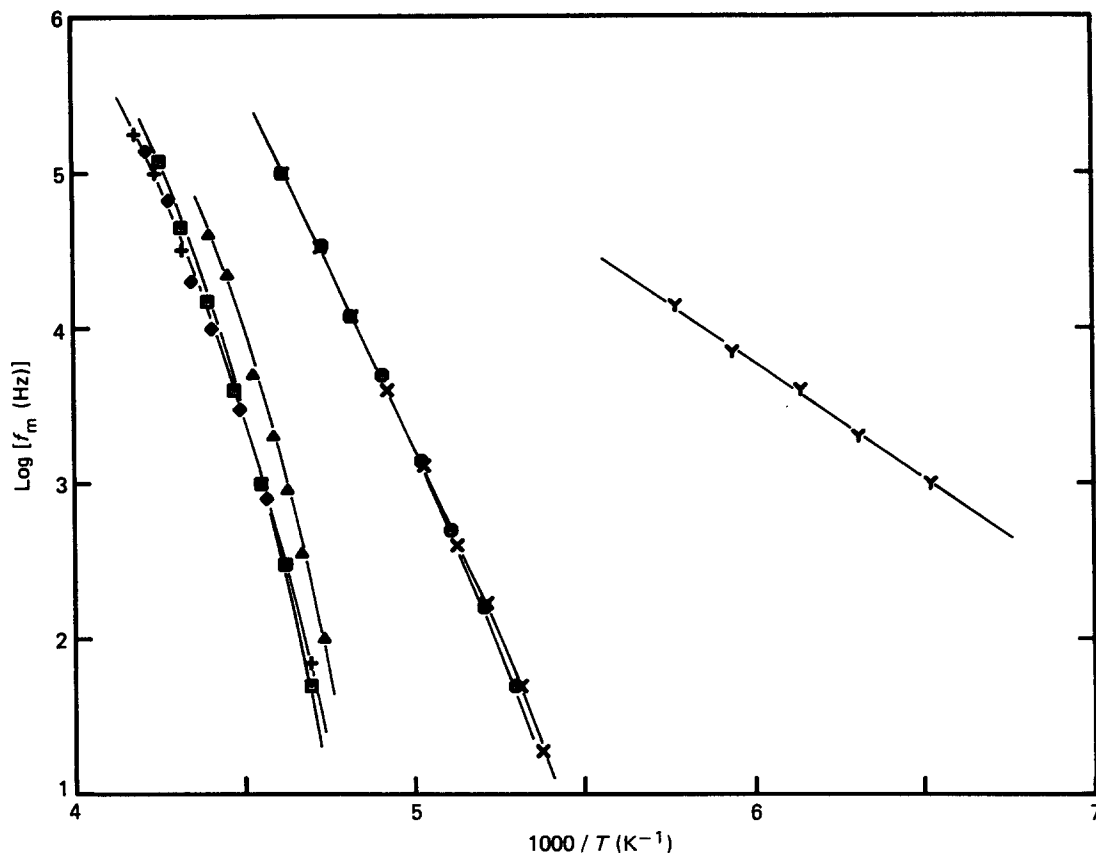
Figure 6 The frequency of maximum loss in the α-relaxation region for: ○, PG; ×, 1.2 wt% H_2O–PG mixture; ◆, PPO-425; +, 0.48 wt% H_2O–PPO-425 mixture; ▲, PPO-4000; □, 1.23 wt% H_2O–PPO4000 mixture. The data for PPO-4000 are taken from literature[2]. Also plotted is the f_m for the β-process in PPO-425, represented by Y
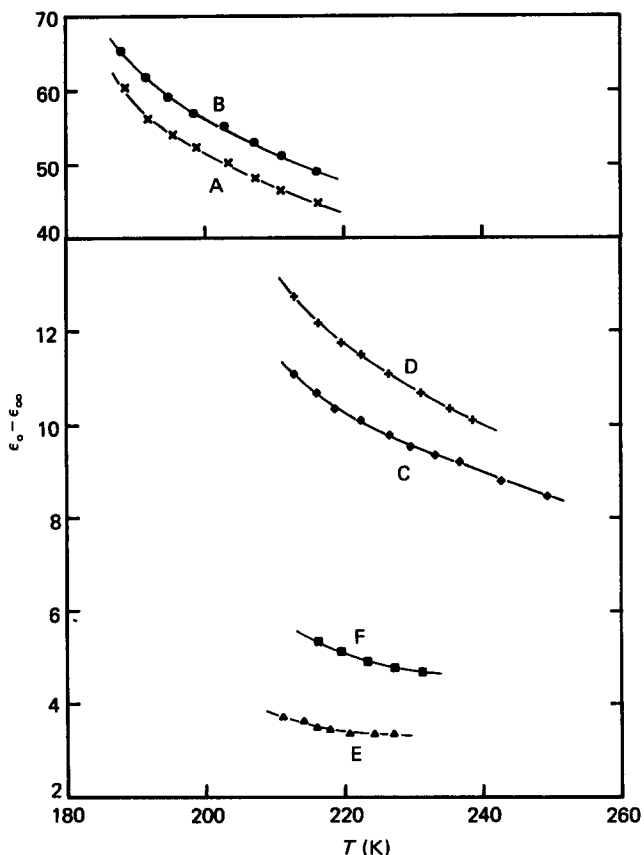

Figure 7 $(\varepsilon_0 - \varepsilon_\infty)$ plotted against temperature for: A, PG; B, 1.2 wt% H_2O–PG mixture; C, PPO-425; D, 0.48 wt% H_2O–PPO-425 mixture; E, PPO-4000; F, 1.23 wt% H_2O–PPO-4000 mixture

for localized motions of chain segments than in the corresponding state of its monomer form. We intend to pursue similar comparative studies of other polymers as a function of their molecular weight in order to further elucidate the mechanism of β-process. We also note that the presence of 0.48 wt% water in PPO-425, as seen in *Figure 2*, reduces the height of the β-peak by ~10%. This may partly be due to the decrease in the number of dipoles capable of reorientation in the more efficiently packed glassy matrix, in which H-bonding has occurred.

The dielectric permittivity

The contribution to dielectric permittivity from orientation polarization, $\Delta\varepsilon$, of PPO-425, PG and its water mixtures, plotted against temperature in *Figure 7*, shows that the values increase more rapidly in the PPO-425–0.48 wt% water mixture than for PPO-425. Since $\Delta\varepsilon \propto N_d g\mu^2/kT$ (where N_d is the number of dipoles per unit volume, g is the dipolar orientational correlation factor, μ is the dipole moment and k the Boltzmann constant), $T\Delta\varepsilon$ should increase by as much as N_d increases. The coefficient of thermal expansion of PPO-425 and PG is likely to be of the order of 10^{-4} K^{-1}, which suggests that for an 80 K change of temperature, N_d changes by ~8%. Since the change observed in $T\Delta\varepsilon$ over the same temperature range in *Figure 7* is ~40%, we conclude that the dipolar orientational correlation factor, g, increases with decreasing temperature and that this increase is greater in the water mixtures than in the PPO-425 or PG. Thus the high value of permittivity of the polymers at low temperatures is attributable to the

orientational correlation of the dipoles within the chain segments.

CONCLUSIONS

(1) The addition of up to 1.25 wt % water to PPO-425 and PG has a marginal effect on the relaxation rate of the α-process, but increases its strength. It broadens the α-relaxation spectrum of PG, but has no effect on that of PPO-425.

(2) Water decreases both the rate and the strength of the β-process in PPO-425, an effect that contrasts with the observations on other polymers.

(3) The strength of the β-process is lowest in PG and increases with increase in the molecular weight of the polymer. Its rate at a given temperature in PPO-425 is the same as in PPO-4000. Therefore, the degree of localized dipolar reorientation in the glassy matrix increases with the molecular weight of PPO. It seems that the origin of the β-process is connected with the less efficient packing of a polymer chain of high molecular weight.

(4) The increase in permittivity per unit wt % of water is highest for PG and decreases with increasing molecular weight of PPO. The temperature dependence of the permittivity is more than anticipated from the density and temperature effects alone. This is due to the enhanced short-range orientational correlation of dipoles within the chain, or between the chains, the latter resulting from H-bonding through an intervening water molecule.

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