Dielectric relaxation of amorphous poly(propylene oxide)s at gigahertz frequencies

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(Received 1 April 1993; revised 5 August 1993)

Dielectric relaxation properties of amorphous poly(propylene oxide)s with nominal molecular weights of 1000 and 2000 have been studied as a function of temperature at gigahertz frequencies using a time-domain reflectometry method. Two relaxation processes were observed in the dielectric spectra. The dielectric relaxation parameters were quantitatively estimated by the Havriliak–Negami equation. At the lower frequency side of the main dispersion, a normal-mode relaxation was seen and the relaxation times obtained from the spectra were found to be approximately one decade longer than the values calculated assuming the Rouse–Zimm theory. The hydrogen-bonded structures in the system are discussed. The relaxation strength is also discussed in terms of chain conformation. The relaxation times of the higher frequency process were found to be independent of the molecular weight. The shortest possible relaxation times estimated by the Vogel–Fucher–Tamman equation were in good agreement with those reported before.

(Keywords: dielectric relaxation; poly(propylene oxide); time-domain reflectometry)

INTRODUCTION

Molecular motions of amorphous liquid poly(propylene oxide)s (PPOs) have been widely investigated by different techniques such as dielectric[1–10], mechanical[11–14], n.m.r.[15], and light-scattering methods[16–20]. Atactic PPOs are amorphous[21] and the α, α′, β, and γ relaxations are known to be active[10,22]. It has been shown from studies in the audio frequency region that the relaxation time of the principal α dispersion resulting from chain segmental motions is independent of the molecular weight. However, the secondary α′ process, for which the relaxation time is longer than that of the main dispersion, depends strongly on the molecular weight. Stockmayer[2] has pointed out that this slow-mode relaxation (normal-mode motion) could be explained quantitatively by a Rouse–Zimm-type motion of whole chains. Since the dipole moment situated on each propylene oxide unit does not bisect the C–O–C bond angle, a cumulative dipole along the chain exists and this dipole moment could be responsible for the dielectric activity of the normal-mode motion. Mashimo *et al.*[9] have studied the dielectric properties of PPO in dilute solutions and have shown that the α′ normal-mode process could be explained by the Rouse–Zimm theory. This normal-mode motion in the undiluted PPO was also seen in the viscoelastic spectra[11–14]. Recently, Imanishi *et al.* have found the dielectric normal-mode motions of *cis*-polyisoprene in dilute[23], semidilute[24], and concentrated solutions[25], as well as in the bulk state[26,27].

Light-scattering studies show the relaxation behaviour in the gigahertz region[16–20]. Wang and Huang[16,17] have recognized the structural relaxation of PPO in light-scattering spectra and Patterson *et al.*[18] have found two different relaxation processes for PPO (nominal molecular weight 4000) from Brillouin spectroscopy. The tan δ values obtained were found to show two maxima, one at 50°C and one at 100°C. The former peak is considered to correspond to the β relaxation and the latter to the α relaxation. Borjesson *et al.*[19] have suggested that the single relaxation time theory could not be applicable to these processes.

Many models for the molecular motions of polymer chains have been proposed[22,28]. Since each technique has its own experimental limitations, the results give information on only a part of the total phenomenon. In the present paper, the α′ normal-mode process above room temperature, i.e. the relaxation at gigahertz frequency, is of particular interest. Yano *et al.*[5] reported the dielectric results in the frequency range 30 Hz to 8 GHz only on the segmental motion of PPO. The α′

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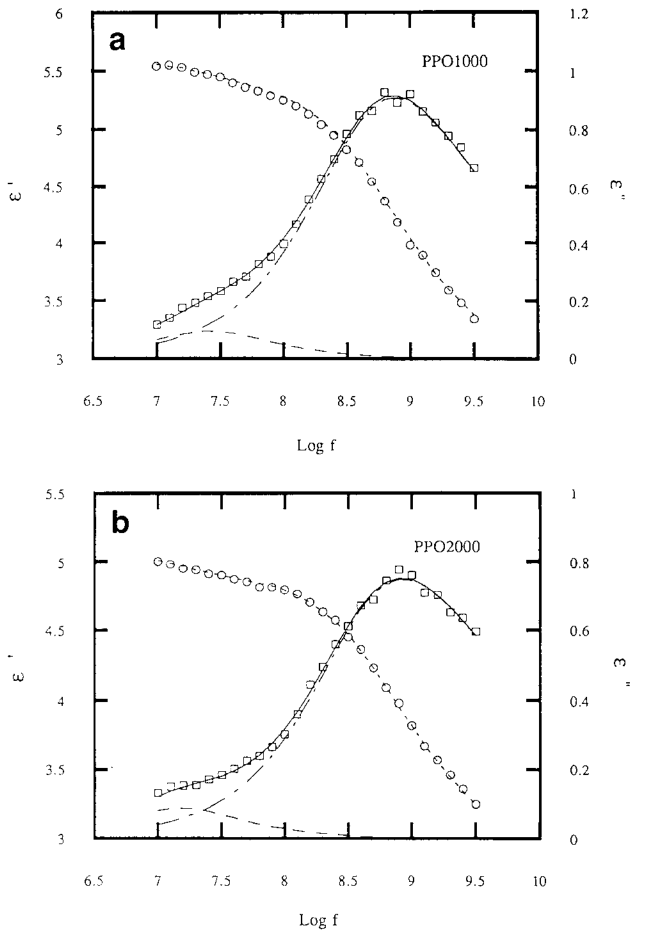

Figure 1 Dielectric dispersion spectra for (a) PPO1000 and (b) PPO2000 observed at 55°C. The broken lines are for the data calculated from equation (3). (○) ε'; (□) ε''

normal-mode process in undiluted PPO liquids above room temperature has still not been investigated. Time-domain reflectometry (TDR) is a powerful technique for the measurement of the complex permittivities of materials over a wide frequency range[29–31]. The advantage of the TDR technique is that the complex permittivity can be obtained over a wide frequency range (100 kHz to 10 GHz) with a single measurement. Since the relaxation behaviour of PPO at gigahertz frequencies is of particular interest, the TDR method was employed for the investigation.

EXPERIMENTAL

Two PPO samples were studied in the present work and the details of these samples are reported elsewhere[32,33]. PPO samples with nominal molecular weights of 1000 and 2000 (Aldrich) were azeotropically dried in benzene solutions and stored under dry nitrogen. The number average molecular weights (polydispersities) by vapour pressure osmometry (gel permeation chromatography) have been reported to be 965 (1.01) and 2020 (1.01), respectively[32].

TDR measurements were carried out in the frequency range 10 MHz to 3.2 GHz at 25–55°C. A detailed description of the system has been reported already[29,30]. A step-like voltage pulse generated by a step-recovery diode was propagated through the coaxial line and applied to the sample cell located at the end of the coaxial line. The reflected voltage pulse from the sample cell was also propagated through the same line and accumulated at the sampling head. An HP5412A and an HP54120A were used for the generator and the digitizing oscilloscope mainframe, respectively.

In the present study, a bilinear coefficient method was employed to obtain the complex permittivity[34]. Using the Fourier transform $V_x(\omega)$ of the signal reflected from the dielectric cell with the sample placed at the end of the coaxial line, and using $V_0(\omega)$ for the empty cell, the complex permittivity of the sample $\varepsilon^*(\omega)$ is given in a bilinear form

$$\varepsilon^* = (1 - A^*)\Omega/(1 + B^*\Omega) \qquad (1)$$

$$\Omega = (c/j\omega d)(V_0 - Z_x)/(V_0 + V_x) \qquad (2)$$

where c is the speed of light, ω is the angular frequency and d is the effective electrical length of the cell. The complex coefficients A^* and B^* are determined by measuring standard samples with known permittivities. Acetone, benzene, and chlorobenzene were used in the present work.

The densities of the PPO samples were measured using a DMA-602 oscillating densitometer (Anton Parr) and the viscosities were measured using a cone–plate-type viscometer (Tokyou Seimithu Co. Ltd). A temperature controller with an accuracy of +0.01°C was used for the present measurements.

RESULTS

Typical dielectric dispersion spectra for PPO1000 and PPO2000 at 45°C are shown in *Figure 1*. The main dispersion is considered to be due to local segmental motions. The shoulder appearing at the lower frequency side of the main dispersion in the loss curves seems to be due to the normal-mode motions of whole chains. In order to discuss the relaxation parameters quantitatively, the complex permittivity was assumed to be the sum of two Havriliak–Negami[35] contributions

$$\varepsilon^* = \varepsilon_\infty + \Delta\varepsilon_h/[1 + (j\omega\tau)_h^{\beta_h}]^{\alpha_h} + \Delta\varepsilon_l/[1 + (j\omega\tau)_l^{\beta_l}]^{\alpha_l} \qquad (3)$$

where ε^* is the complex permittivity, $\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$, where ε_0 and ε_∞ are the lower and upper limits of the dielectric constants, respectively, ω is the angular frequency and τ is the relaxation time. The parameters α and β characterize the shape of the dielectric relaxation curve, and h and l denote the higher and lower frequency process, respectively. Appropriate values for the parameters in equation (3) were chosen to give curves best fitted to the observed spectra. The details of the analysis have been reported elsewhere[33]. The results obtained in the present analysis are shown in *Figure 1* and the observed data are found to be well represented by assuming two relaxation processes. The values of the parameters are listed in *Table 1*, and the deviations of the calculated data from the observed data for both ε' and ε'' were within experimental error. The shape parameters for the normal-mode process (lower frequency process) were assumed to be equal or close to unity. Mashimo *et al.*[9] have also analysed the dielectric spectra of PPOs in dilute solutions using a TDR method and best-fit results were obtained assuming the Havriliak–Negami parameters α and β to be equal to unity for the normal-mode process. The normalized loss curves for the main dispersion are shown in *Figure 2*.

Table 1 Havriliak–Negami parameters for the dielectric relaxation of PPO1000 and PPO2000 at various temperatures

M	Temperature (°C)	$\log\tau$	α	β	$\Delta\varepsilon$	ε_∞	g
		Higher frequency process					
1000	25.0	−8.85	0.49	0.87	3.67	2.42	0.8
	35.0	−9.14	0.55	0.89	3.15	2.58	0.7
	45.0	−9.28	0.55	0.89	3.03	2.57	0.7
	55.0	−9.44	0.56	0.90	2.80	2.60	0.6
2000	25.0	−8.78	0.41	0.91	2.92	2.32	0.7
	35.0	−9.07	0.46	0.89	2.75	2.36	0.7
	45.0	−9.26	0.48	0.90	2.56	2.41	0.7
	55.0	−9.43	0.48	0.90	2.50	2.39	0.6
		Lower frequency process					
1000	25.0	−7.91	0.97	1.00	0.21		
	35.0	−8.13	1.00	1.00	0.27		
	45.0	−8.00	1.00	1.00	0.22		
	55.0	−8.21	1.00	0.98	0.19		
2000	25.0	−7.82	0.96	1.00	0.12		
	35.0	−7.89	0.92	1.00	0.16		
	45.0	−7.90	0.96	1.00	0.15		
	55.0	−7.97	0.96	1.00	0.18		

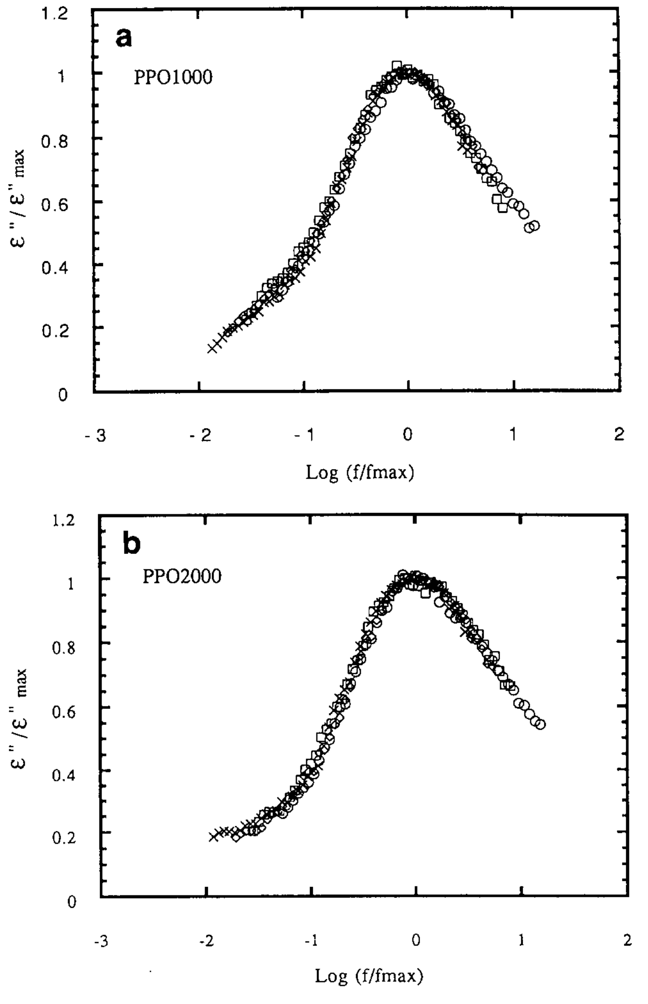

Figure 2 Normalized dielectric constants ($\varepsilon''/\varepsilon''_{max}$) for (a) PPO1000 and (b) PPO2000 as a function of frequency at various temperatures: (○) 25°C; (□) 35°C; (◇) 45°C; (×) 55°C

The shape of the curves seems to be independent of the temperature and this assumption is consistent with the results reported by Williams[3]. The shape of the curves also seems to be independent of the molecular weight.

The relaxation times calculated from the apparent peak frequencies for the main dispersion (lower frequency process) were plotted against the reciprocal of the temperature (*Figure 3*). It appears to be reasonable to consider that the dependence of the relaxation times in the present study is given by the following Vogel–Fucher–Tamman equation

$$f_m = f_0 \exp[-B/(T-T_0)] \qquad (4)$$

where f_m is the apparent peak frequency of the loss curve, and f_0, B, and T_0 are adjustable parameters. A least-squares method was employed and the values for f_0, B, and T_0 were found to be 480 GHz, 538 K, and 207 K, respectively. The solid line in *Figure 3* represents the results obtained assuming equation (4) to be valid, and the values of the parameters are discussed in the following section.

DISCUSSION

Lower frequency dispersion

In the present study, it is clearly shown that the normal-mode process can be observed in the gigahertz frequency range. The relaxation times observed for the normal-mode loss curves of PPO1000 and PPO2000 are plotted in *Figure 3*. Bauer and Stockmayer[1,2] found the normal-mode relaxation for liquid PPO and demonstrated a satisfactory explanation of the relaxation time assuming the Rouse–Zimm theory

$$\tau = 0.304 M\eta/RT\rho \qquad \text{(free draining)} \qquad (5)$$

where η/ρ is the kinetic viscosity of the polymer. The viscosities and densities of the polymers were measured and the relaxation times of the normal-mode process (lower frequency) were calculated using equation (5). The results are also shown in *Figure 3* and it can be seen that the observed relaxation times (lower frequency process) are approximately one decade longer than the values calculated. Johari[10] has reported the results of the dielectric study of PPO4000 (nominal molecular weight 4000) and the relaxation times of the normal-mode

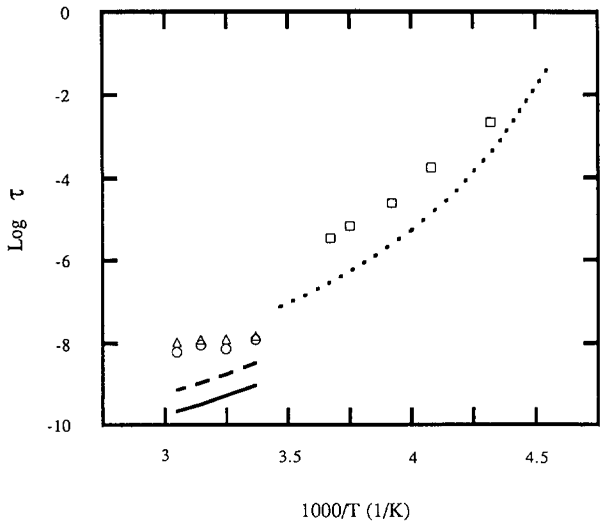

Figure 3 Relaxation times of the normal-mode motions plotted against reciprocal temperature: (○, △) observed normal-mode processes for PPO1000 and PPO2000: (——, – – –) calculated relaxation times for PPO1000 and PPO2000 normal-mode processes; (□) normal-mode process for PPO4000 (ref. 10); (···) calculated relaxation times for PPO4020 (ref. 14)

process measured by him are plotted in *Figure 3*. Cochrane *et al.*[14] reported the temperature dependence of the viscosity and the density for PPOs with different molecular weights. The relaxation times for PPO with a molecular weight of 4020 were calculated from Cochrane's data using equation (5) and are also plotted in *Figure 3*. Although the molecular weight of the PPO used in Johari's investigation is only approximate, comparing his data with our results and those of Cochrane we find that the temperature dependence of the normal-mode relaxation (lower frequency process) of PPO4000 is found to be significantly different and the relaxation times deviate from those predicted by the Rouse–Zimm theory.

The conformations of the various PPOs could differ if the hydroxy end groups form hydrogen-bonded structures in the system. It seems likely that such structures should affect the dielectric relaxation properties of the whole chains. The viscosity could be less sensitive to the presence of hydrogen-bonded structures if the hydrogen bonds between the hydroxy groups are weak. The presence of hydrogen-bonded structures in PPO has been inferred from the results of thermodynamic[36] and spectroscopic[20] investigations. A small amount of water present as an impurity is also deemed to be responsible for hydrogen bonding. Cochrane *et al.*[14] have pointed out from viscoelastic investigations of undiluted dry and water-contaminated PPOs that the limiting long-term recoverable compliance increases with the presence of a small amount of water without an accompanying measurable change in the steady-state viscosity.

In order to confirm that the lower frequency process is the normal-mode process, the relaxation strength should be discussed. The dielectric relaxation strength is given by

$$\Delta\varepsilon/\rho = 4\pi N_A \mu^2 \langle r^2 \rangle / 3k_B T M \qquad (6)$$

where $\langle r^2 \rangle$ is the mean-square end-to-end distance and the other symbols have the usual meanings. Some theoretical and experimental investigations have been reported for *cis*-polyisoprene systems[23–27]. Using the observed values in the present study, the mean-square end-to-end distance was estimated. The $\langle r^2 \rangle$ values of PPO2000 are found to be 1.13 to 1.39 times larger than those of PPO1000 in the present study. Mashimo *et al.*[9] have reported the relaxation strengths of this process (lower frequency) in PPO in solution and the $\langle r^2 \rangle$ can be estimated from their data to be an increasing factor of the molecular weight. Therefore the lower frequency process may reasonably be considered to be the normal-mode motion. However, since the dielectric normal-mode processes of PPOs at gigahertz frequencies (far above the glass transition temperature) have not been reported in the literature, further investigations are needed to clarify the molecular dynamics of this particular system.

Higher frequency dispersion

It is obvious that the observed higher frequency relaxation is due to the segmental motion (α relaxation) of PPO chains and the temperature dependence of the peak frequency should be given by equation (4). The adjustable parameters have been obtained by different methods and the values of $\log\langle\tau_0\rangle = \log(1/2\pi f_0)$ can be considered as the shortest possible relaxation times for these polymers. For instance, Johari[10] has obtained $\log\langle\tau_0\rangle = -11.1$ for PPO4000 from dielectric measurements and Borjesson *et al.*[19] have obtained $\log\langle\tau_0\rangle = -13.5$ for PPO10 000 from Brillouin scattering measurements. In the present study the value obtained as −11.7 and this is close to the value (−12.8) obtained by Yano *et al.*[5] from dielectric measurements at gigahertz frequencies for PPO2025 and PPO4000. The present result clearly shows that the shortest possible relaxation time is independent of the molecular weight. This could be evidence for the local segmental motion of the chains.

Mashimo *et al.*[9] have reported that the apparent activation energy is 2.7 kcal mol^{-1} (1 cal = 4.2 J) for the segmental motion (higher frequency process) in dilute PPO solutions at gigahertz frequencies. This value suggests that the activation energy corresponds to the barrier height for segmental local-mode motions (higher frequency process). It could be reasonable to assume an Arrhenius dependence for the peak frequencies in the present case, giving an apparent activation energy of approximately 9.0 kcal mol^{-1}, which suggests viscous effects.

The relaxation strength is a measure of the number and orientation correlations of dipole moments along the polymer chains. The Fröhlich–Kirkwood g factor indicates the extent of the correlation of the dipolar motions involved in the relaxation process[22]. In this calculation a value of 1.20 D was used for the perpendicular component of the ether oxygen dipole moment[9]. The g values obtained were 0.6 to 0.8 for PPO1000 and PPO2000. These values indicate an antiparallel arrangement in the dipole moments of the ether oxygen groups.

CONCLUSIONS

The dielectric properties of neat PPO liquids with nominal molecular weights of 1000 and 2000 were investigated using time-domain reflectometry at gigahertz frequencies. The results can be summarized as follows.

1. The dielectric normal-mode motion (lower frequency process) was observed at the lower frequency side of the main segmental dispersions (higher frequency process) at gigahertz frequencies.
2. The observed relaxation times of the normal-mode motion (lower frequency process) were found to deviate from the values predicted by the Rouse–Zimm theory, and the presence of hydrogen-bonded structures was discussed as a possible reason for this deviation.
3. The relaxation parameters for the segmental motions (higher frequency process) were discussed in terms of the Vogel–Fucher–Tamman equation.

ACKNOWLEDGEMENT

K. I. thanks the Fuji Photo Film Co. Ltd for his sabbatical leave.

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