Dielectric relaxation of model network polymers

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Model network polymers derived from narrow distribution α,ω-dihydroxypoly(propylene oxide) and a triisocyanate, tris(4-isocyanatophenyl)thiophosphate, were used. Dielectric relaxation measurements were carried out on these networks with different molecular weights between crosslink points. Two relaxation processes were identified and the complex permittivity was assumed to be the sum of two Havriliak–Negami contributions to obtain relaxation parameters. The relaxation strength of the higher frequency process was found to be proportional to the estimated concentration of the ether oxygen group, on the other hand, the relaxation strength of the lower frequency process was found to be proportional to that of the urethane group. From this result, it is reasonable to consider that the higher frequency process is due to motions involving the ether oxygen group and the lower frequency process is due to motions involving the urethane group.

(Keywords: networks; dielectric relaxation; urethane; crosslink mobility; chain mobility)

INTRODUCTION

In recent years, model network polymers derived from poly(propylene oxide) (PPO) with multifunctional isocyanates have been used to investigate relationships between the structure and properties of crosslinked systems[1–8]. The networks, which are obtained by polymerization of narrow molecular distribution α,ω-dihydroxypoly(propylene oxide) with tris(4-isocyanatophenyl)thiophosphate are amorphous[4,6,8], and it has been shown that different relaxation processes exist in them on the basis of high resolution solid state n.m.r. and dielectric measurements[4,5]. In particular, two relaxation processes have been found in the dielectric spectra. However, the underlying molecular motions responsible for them have not yet been clarified.

The dielectric properties of polar polymers such as oxide polymers and polyurethanes have been widely investigated[9,10]. PPOs, prepared by a non-stereospecific base-catalysed reaction, are amorphous liquids, and have narrow molecular weight distributions[4,11]. They exhibit two different dielectric relaxation processes both in the diluted and undiluted states[12–14]. The lower frequency process, which is molecular weight dependent, is explained by the normal mode theory, and the higher frequency process, which is independent of molecular weight, is attributed to local segmental motions. In the case of networks, the normal mode type of motion should not occur because the molecular weight is considered to be infinite.

It has been reported that the dielectric relaxation of polyetherurethane segmented copolymers in the audiofrequency region (kHz) is dominated by the motion of ether segments, and Maxwell–Wagner polarization due to the heterogeneous nature of the structure occurs in the low audio to sub-audiofrequency region[10,15,16]. These polymers have been shown to be microphase separated on the basis of various techniques[17–21].

In this study, model network polymers derived from PPO with different molecular weights end linked with trifunctional isocyanate were used and dielectric measurements were carried out in the frequency range of 66 Hz to 100 kHz at various temperatures. D.s.c. measurements and wide-angle X-ray diffraction (WAXD) studies were also employed to confirm the amorphous single phase nature of the network polymers.

EXPERIMENTAL

Materials

The networks are similar to those described previously[1–5]. α,ω-Dihydroxypoly(propylene oxide)s of nominal molecular weights 1000 (PPO1000), 2000 (PPO2000), 3000 (PPO3000) and 4000 (PPO4000) were obtained from Aldrich Chemical Co. The PPO was dried azeotropically in benzene and stored under dry argon. Hydroxyl group functionality was determined by titration (ASTM D4274). Tris(4-isocyanatophenyl)thiophosphate, supplied by Mobay Chemical Co., was recrystallized twice from dry toluene solution and stored under dry argon in a refrigerator.

Networks were prepared by dissolving under dry argon 0.33 mol of crosslinker with 0.50 mol of PPO using dry tetrahydrofuran (THF, Aldrich) as a solvent. Solutions were evaporated *in vacuo* to remove THF and poured into a Teflon-lined aluminium mould and then heated to 90°C *in vacuo* for 3 days. After the reaction, the network film was extracted with dry THF and dried *in vacuo* for 2–7 days at room temperature.

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Films for dielectric measurements with uniform thickness in the range of 0.4 mm were cut into discs of 20 mm diameter, and gold electrodes were coated onto both surfaces of the discs. Films for d.s.c. and WAXD measurements were used without gold electrodes. Network samples prepared from PPO1000, PPO2000, PPO3000 and PPO4000 are designated as N1000, N2000, N3000 and N4000, respectively.

Methods

Dielectric measurements were carried out using a DETA mk-II (Polymer Laboratories Ltd) in the frequency range of 66 Hz to 100 kHz at various temperatures. WAXD patterns were obtained using a Siemens two-dimensional area detector with CuKα radiation, and air scattering in the diffraction angles up to 18° was subtracted.

RESULTS

The frequency dependences of the dielectric constant, ε', for N4000 at various temperatures are shown in *Figure 1*. Frequency dependences of dielectric constants normalized to the lower frequency peak height and position, ε'', are shown in *Figure 2*. As is seen in both figures, but most clearly in *Figure 2*, two relaxation processes exist in these networks. It is clear that the relative intensity of the higher frequency process decreases with decreasing molecular weight between crosslink points.

For a quantitative treatment, the complex permittivity was assumed to be the sum of two Havriliak–Negami contributions[22]:

$$\varepsilon^*(\omega)=\varepsilon_\infty+\sum_{j=\mathrm{h,l}}\Delta\varepsilon_j/[1+(\mathrm{i}\omega\tau_{ij})^{1-\alpha_j}]^{\beta_j} \qquad (1)$$

where ε^* is the complex dielectric constant, $\Delta\varepsilon_j=\varepsilon_{j0}-\varepsilon_{j\infty}$, where ε_{j0} and $\varepsilon_{j\infty}$ are the low- and high-frequency limits

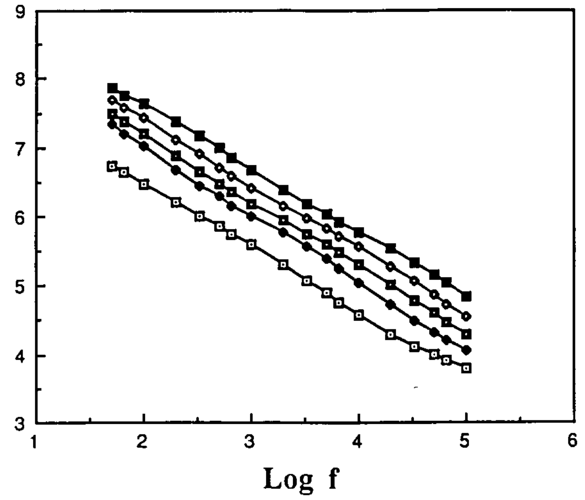

Figure 1 Dielectric constant ε' of N4000 as a function of frequency at various temperatures: (□) −60°C; (◆) −55°C; (□) −50°C; (◇) −45°C; (■) −40°C

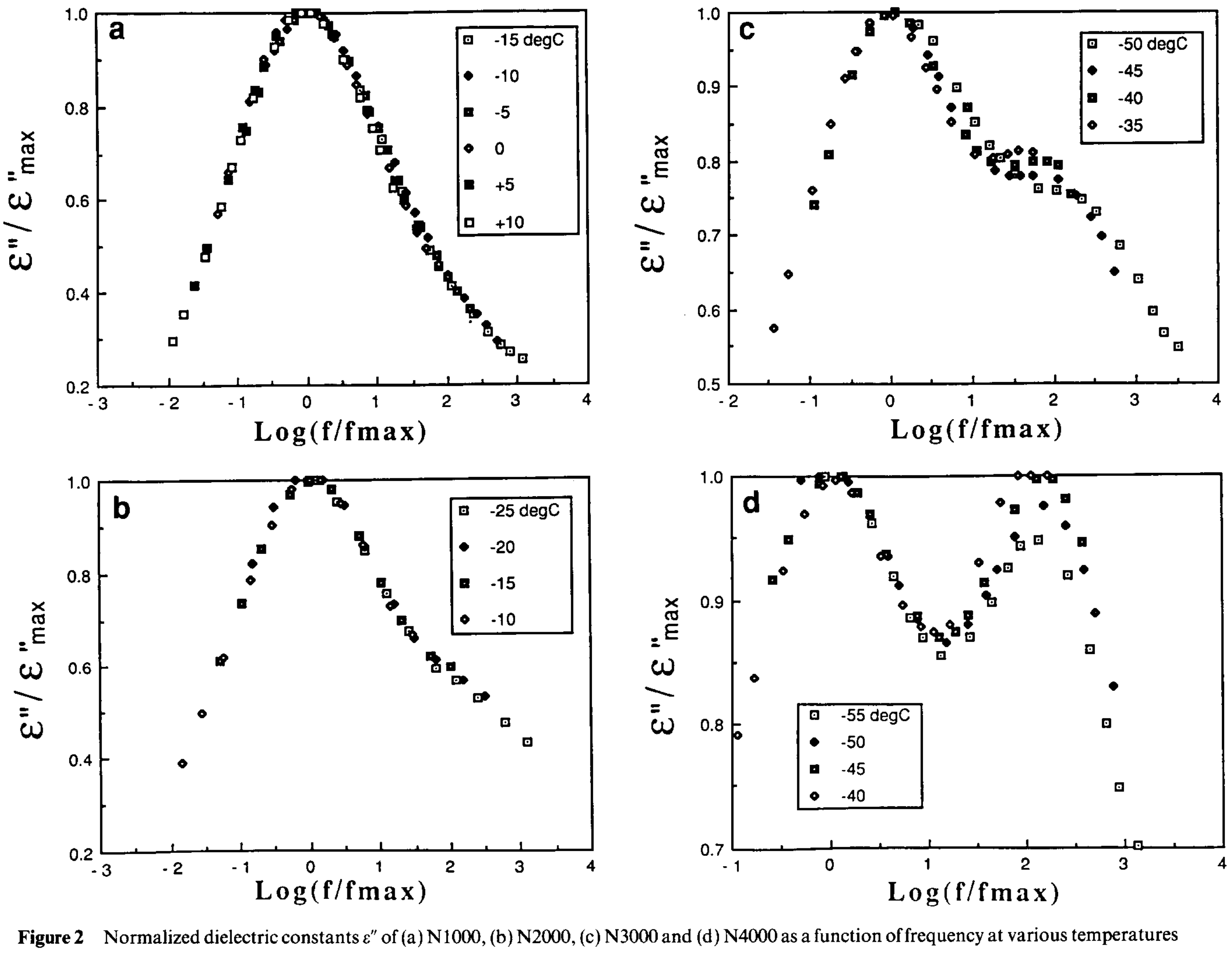

Figure 2 Normalized dielectric constants ε'' of (a) N1000, (b) N2000, (c) N3000 and (d) N4000 as a function of frequency at various temperatures

of the dielectric constants, respectively, ω is the angular frequency, τ_0 is the relaxation time, α and β are parameters characterizing the shape of the dielectric relaxation curves, and l and h denote the lower and higher frequency relaxation, respectively. The real and imaginary parts are given in the following equations:

$$\varepsilon'(\omega)=\varepsilon_\infty+r^{-\beta/2}\Delta\varepsilon\cos(\beta\theta) \tag{2}$$

$$\varepsilon''(\omega)=r^{-\beta/2}\Delta\varepsilon\sin(\beta\theta) \tag{3}$$

$$r=[1+(\omega_0\tau_0)^{1-\alpha}\sin(\alpha\pi/2)]^2+[(\omega\tau_0)^{1-\alpha}\cos(\alpha\pi/2)]^2 \tag{4}$$

$$\theta=\arctan\frac{(\omega\tau_0)^{1-\alpha}\cos(\alpha\pi/2)}{1+(\omega\tau_0)^{1-\alpha}\sin(\alpha\pi/2)} \tag{5}$$

Equations (2) and (3) contain α, β, $\Delta\varepsilon$ and τ_0. In other words, if equation (2) is used as the model equation for the frequency-dependent data, then four of the five parameters can be determined. These can be used to calculate $\varepsilon'(\omega)-\varepsilon_\infty$ from equation (2). The best fitted results were obtained to minimize the standard deviation, SD, given by equation (6):

$$\mathrm{SD}=[(\varepsilon''_{\mathrm{obs.}}-\varepsilon''_{\mathrm{calc.}})/n]^{1/2} \tag{6}$$

where n denotes the number of data points. The SD of ε' was obtained with the parameters which minimize the SD of ε'' in the present analysis.

The observed data were found to be fit assuming two relaxation processes typically shown in the case of N4000 in *Figure 3*. However, the results for the N1000 case might be criticized because the relaxation strength of the higher frequency process in N1000 is ~5% that of the lower frequency process. This will be discussed later. The dielectric parameters and the SDs obtained in this analysis are listed in *Tables 1* and *2*, respectively.

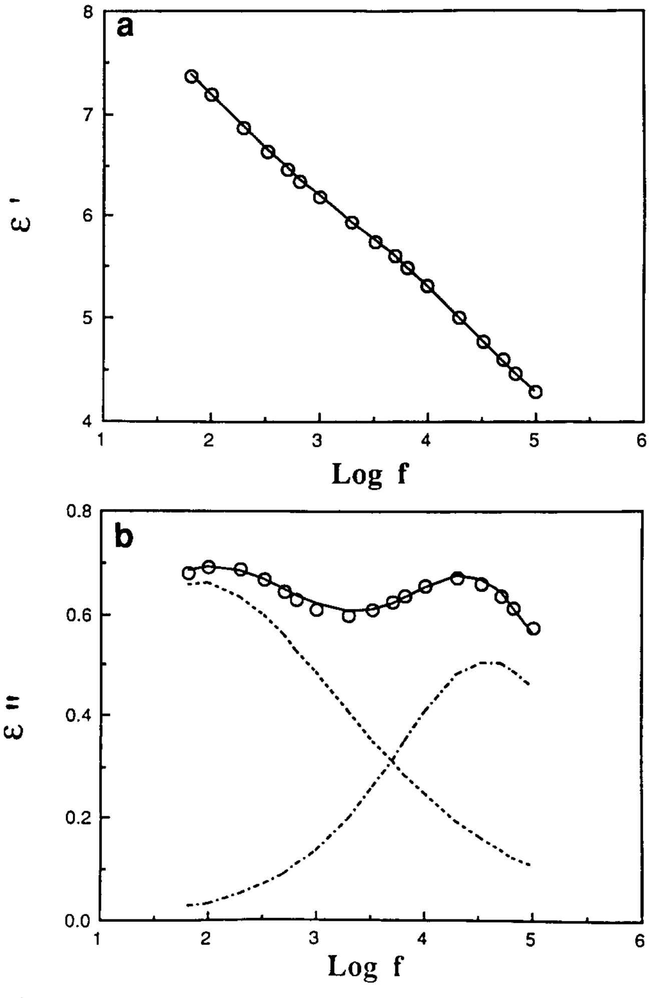

Figure 3 Frequency dependences of (a) ε' and (b) ε'' for N4000 at −50°C. Solid and broken lines are those calculated from equation (1)

Table 1 Havriliak–Negami parameters of dielectric relaxation of network polymers at various temperatures

	T (°C)		α	β	$\Delta\varepsilon$	ε_0	$\log\tau_0$
N1000	−15.2	h[a]	0.265	0.806	0.407	3.43	−5.45
		l[a]	0.540	0.847	8.49		−2.51
	−10.2	h	0.196	0.882	0.265	3.45	−5.84
		l	0.501	0.732	8.08		−2.84
	−5.2	h	0.198	0.853	0.462	3.39	−6.22
		l	0.499	0.814	7.54		−3.37
N2000	−30.2	h	0.367	0.832	0.991	2.79	−4.97
		l	0.561	0.894	5.58		−1.91
	−25.0	h	0.367	0.832	1.07	2.72	−5-45
		l	0.561	0.894	5.44		−2.47
	−19.5	h	0.193	0.800	0.713	2.93	−5.72
		l	0.551	0.873	5.19		−3.13
N3000	−50.2	h	0.423	0.789	1.85	2.95	−4.92
		l	0.528	0.836	4.20		−2.21
	−45.2	h	0.276	0.753	1.42	3.19	−5.28
		l	0.497	0.802	4.05		−2.80
	−40.2	h	0.230	0.787	1.22	3.34	−5.66
		l	0.499	0.826	3.92		−3.36
	−35.2	h	0.197	0.814	1.07	3.36	−6.01
		l	0.502	0.814	3.88		−3.78
N4000	−60.3	h	0.421	0.750	2.27	3.31	−4.41
		l	0.519	0.771	3.95		−1.48
	−55.2	h	0.343	0.762	1.92	3.47	−4.96
		l	0.529	0.800	3.79		−2.23
	−50.3	h	0.350	0.820	1.95	3.45	−5.27
		l	0.530	0.842	3.62		−2.58
	−45.2	h	0.297	0.814	1.76	3.54	−5.52
		l	0.524	0.813	3.58		−2.93
	−40.2	h	0.290	0.838	1.70	3.54	−5.79
		l	0.530	0.858	3.45		−3.29

[a] h, higher frequency relaxation; l, lower frequency relaxation

Relaxation strengths for all samples are plotted against temperature in *Figure 4*. From this figure, it seems to be reasonable to assume a linear temperature dependence of the relaxation strength in this temperature region to obtain the estimated value of the relaxation strength at a given temperature. In any case, the temperature dependences of the relaxation strengths are not large.

The logarithm of the frequency of the maximum dielectric loss listed in *Table 1* is plotted against reciprocal absolute temperature in *Figure 5*. The apparent activation energy listed in *Table 3* was obtained from the slope of this plot assuming a linear Arrhenius dependence. The higher frequency process has a slightly smaller activation energy than the lower frequency process.

It is not likely that the two relaxation processes could be Maxwell–Wagner polarization processes because the structure of the networks is single phase and amorphous from WAXD results. It has been reported for model polyurethane networks that two large relaxation processes are observed in dynamic mechanical spectra, and that one of these processes is probably due to the relaxation of dangling chains which have free ends but are connected to the network[7]. PPO3000-based polymers used in this study contain ~5% monofunctional chains[1] and these could lead to dangling chains in the network. Thus, it might be assumed that one of the relaxation processes is due to the relaxation of such chains. However, the results for N3000 in *Table 1* indicate such an assignment is unlikely because the relaxation strength

Table 2 Standard deviations for ε' and ε'' (in parentheses)

N1000		N2000		N3000		N4000	
T (°C)	SD	T (°C)	SD	T (°C)	SD	T (°C)	SD
−15.2	0.061 (0.0072)	−30.2	0.020 (0.0097)	−50.2	0.058 (0.007)	−60.3	0.017 (0.0051)
−10.2	0.057 (0.0051)	−25.0	0.058 (0.0053)	−45.2	0.033 (0.0059)	−55.2	0.044 (0.0073)
−5.2	0.070 (0.0074)	−19.5	0.072 (0.0038)	−40.2	0.032 (0.0052)	−50.3	0.012 (0.0045)
				−35.2	0.045 (0.0010)	−45.2	0.024 (0.0040)
						−40.2	0.041 (0.0069)

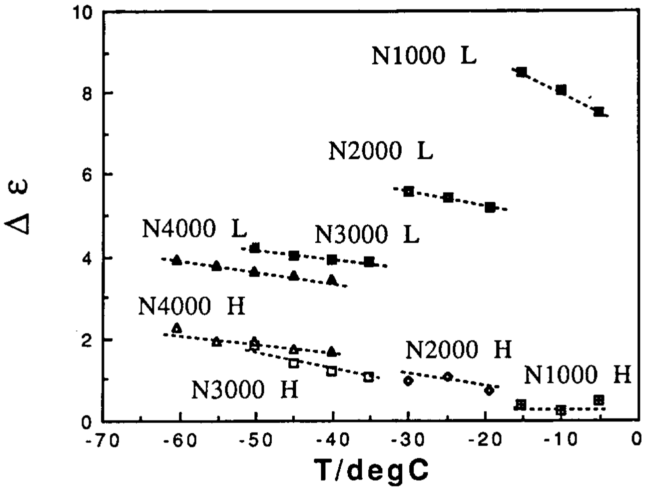

Figure 4 Temperature dependences of the relaxation strengths: (L) lower frequency process; (H) higher frequency process

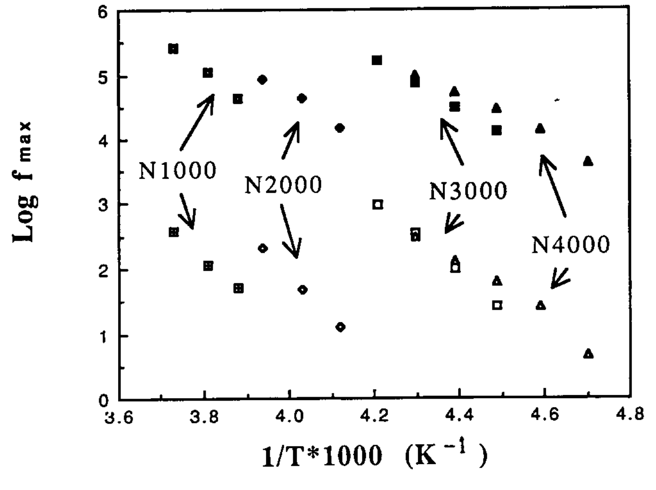

Figure 5 Arrhenius plots of the peak frequency ($\log f_{\text{max}}$) against the reciprocal of the absolute temperature

ratio of the higher frequency process to the lower frequency process is >30%.

The networks have at least two different dipole moments associated with the ether oxygen group and the urethane group and both concentrations change with the molecular weight between crosslink points. Dickinson *et al.*[5] reported that the crosslink point motion, which is detected by the ^{31}P n.m.r. relaxation, begins at a much higher temperature than the segmental glass transition temperature, T_g. This strongly suggests that the dipolar species located near the crosslink point reorients as a result of motions of the crosslink and this occurs at the lower frequency and that the dipolar species in the backbone chain reorients as a result of the segmental motions accompanying T_g and this occurs at the higher frequency.

Table 3 Apparent activation energies of dielectric relaxation processes

	ΔE_a (kcal mol^{-1})	
	Lower frequency	Higher frequency
N1000	26.3	23.4
N2000	31.0	19.0
N3000	25.8	18.0
N4000	19.8	15.1

In order to verify the hypothesis described above, the relaxation strength of each process was compared with the concentration of each dipolar group. The relaxation strength was obtained at the temperature T_0 which gives the frequency of the maximum loss equal to 100 kHz for the higher frequency process and 100 Hz for the lower frequency process. The concentrations of the ether oxygen group and the urethane group were estimated by assuming the structure of the networks to be ideal under the stoichiometric condition employed and by assuming the densities of samples are equal to those obtained before[3]. *Figure 6* shows the dependence of the relaxation strength on the dipole moment concentration, and an almost linear dependence is shown. From this result, it is reasonable to consider that the lower frequency process is due to motions involving the urethane group and the higher frequency process is due to motions involving the ether oxygen group.

The change in shape of the dielectric relaxation spectra is shown in *Figure 7* where the Havriliak–Negami parameters α and β are plotted against the logarithm of the relaxation time. It is clearly seen that the two relaxation processes depend differently on the relaxation time in this temperature range. It should be mentioned that the parameters α and β are very nearly linear functions of $\log \tau_0$, and that β is almost constant for both processes.

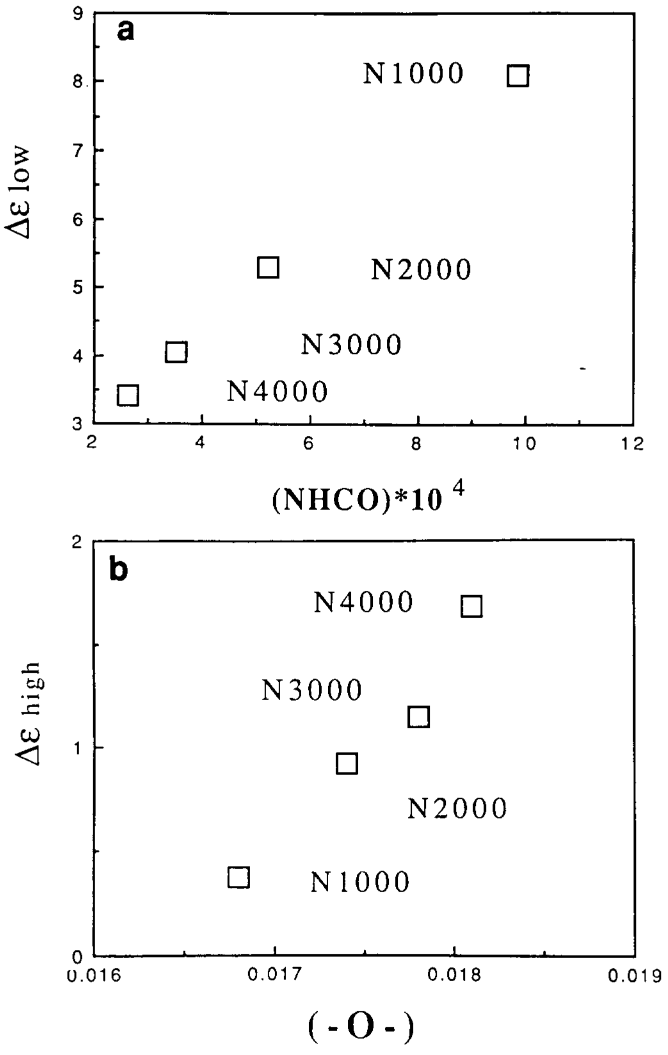

Figure 6 Dependences of the relaxation strengths on the concentrations of the dipolar groups: (a) $\Delta\varepsilon_{low}$; (b) $\Delta\varepsilon_{high}$

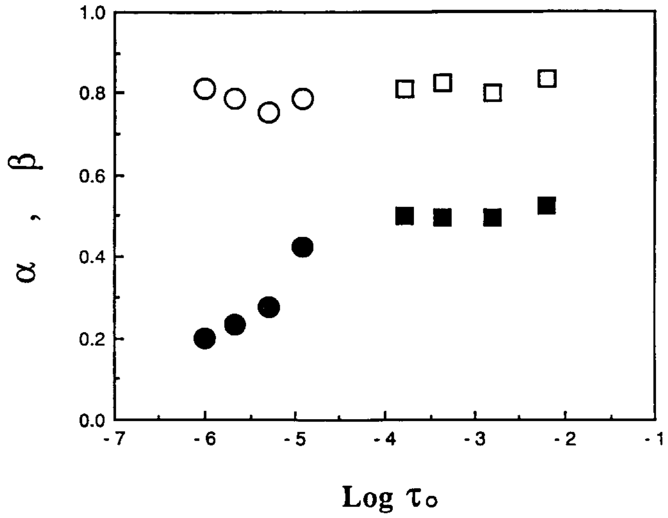

Figure 7 Plots of α and β against $\log\tau_0$ of N3000: (■) α and (□) β of the lower frequency process; (●) α and (○) β of the higher frequency process

DISCUSSION

It is suggested that the higher frequency process is due to the relaxation of the ether group and the lower frequency process is due to the relaxation of the urethane group. In order to confirm this assignment, the normalized absorption curves of the higher frequency process calculated by equation (1) are compared with those of pure PPO liquids. It is well known that in pure PPO liquids the main dispersion occurs at the same frequency for all molecular weights at a given temperature[12], and the shape of the dispersion is independent of temperature and pressure[23]. In *Figure 8*, the normalized absorption curves of the higher frequency process for N4000 are shown together with those observed for PPO4000. It is clearly seen that the dispersion in N4000 approaches that of PPO4000 as the temperature increases. In the case of pure PPO liquids, it is well known that at lower frequencies there exists a small secondary relaxation which depends strongly on the molecular weight[12]. In the present study, the two relaxations are modelled with the Havriliak–Negami equation, and the parameters describing the main dispersion in PPO4000 were found to be $\alpha = 0.30$ and $\beta = 0.77$ in the temperature range from −55 to −45°C.

The relaxation strength is a measure of the number and the orientation correlations of dipole moments along the polymer chains. The Frohlich–Kirkwood g factor given in equation (7) indicates the extent of the correlation of the dipolar motions involved in the relaxation process[9,24]:

$$\varepsilon_0-\varepsilon_\infty=\left(\frac{3\varepsilon_0}{2\varepsilon_0+\varepsilon_\infty}\right)\left(\frac{4\pi N}{3kT}\right)\left(\frac{\varepsilon_\infty+2}{2}\right)g\mu_0^2 \qquad (7)$$

where N is the number of dipoles per unit volume, μ_0 is the effective moment of one molecule surrounded by vacuum, k is the Boltzmann constant and T is the temperature. In this study, values of 3.6 D (ref. 25) and 1.2 D (ref. 24) for μ_0 were employed for the urethane group and the ether unit, respectively. The g values obtained were 0.1–0.2 for the higher frequency process and 1.9–2.7 for the lower frequency process, respectively. There was no significant dependence of the g value on the molecular weight between crosslinks in the observed temperature region. Mashimo *et al.* studied the dielectric relaxation behaviour of PPO chains in the diluted state

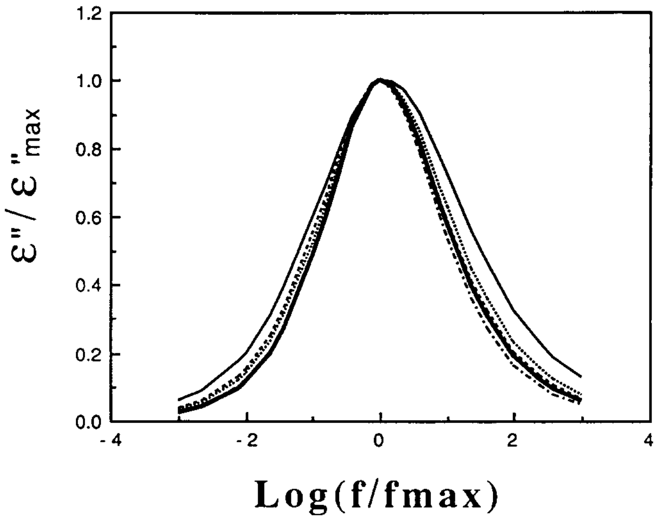

Figure 8 Comparison of the normalized calculated spectra of the N4000 higher frequency process with that of the PPO4000 main dispersion: (▬) PPO4000; (—) N4000 at −60°C; (···) N4000 at −55°C; (- - -) N4000 at −50°C; (—·) N4000 at −40°C

and reported that the value of g is 0.48 for the higher frequency process of PPO4000 at 25°C[14]. The g value would increase with increasing temperature because the correlation of dipole moments could become less significant with increasing temperature. The results in the present study for the higher frequency process seem to be reasonable on this basis. For the lower frequency process, g is nearly 2, suggesting a strong interaction between urethane groups. Few studies on g values of polymers such as polyurethanes have been made. This interaction might be due to the hydrogen bonding present in the system. One other possibility would be a contribution from the ether oxygen of the crosslinker. The crosslinker used in the present study has a dipole moment in the ether oxygen and this could contribute to the lower frequency process of the networks. In this case the g value of the lower frequency process could be smaller than that obtained above and the relaxation process would be more complicated because this ether group seems to have different frequencies of rotational reorientation from those in the chain.

Apparent activation energies for the higher frequency process are 15–23 kcal mol^{-1} and seem to depend on the molecular weight between crosslinks. The potential barrier height[23] is thought to be 2–3 kcal mol^{-1}. However, the value of the activation energy is generally largely determined by intermolecular (viscous) effects. On this basis the results suggest that the local viscosity decreases with increasing molecular weight between crosslinks.

Yoshihara and Work reported on the dielectric relaxation of undiluted poly(4-chlorostyrene) and suggested that the β parameter may characterize effects of chain connectivity[26]. As is seen in *Figure 7*, the β parameter is almost constant for both processes, and this result suggests that the chain connectivity of the backbone chains is similar for the networks. Previous studies[4] of the same networks using ^{13}C n.m.r. showed that the decay of the backbone carbon magnetization is biphasic for N1000 and N2000, and that the slow component is associated with remote backbone carbon atoms. The fraction of the slow component amounts to $\sim$20% of the repeat units at -30°C. From this point of view, it is estimated that the motions of two to four propylene units in the backbone chain could be influenced by the presence of one urethane group. Studies on the co-operative motion of copolymers indicate that the third or fourth nearest neighbouring dipole along the chain is the most remote dipole which correlates with the central dipole[27]. This estimation is consistent with the present result. Therefore, it is reasonable to consider that the lower frequency process is due to motions involving the urethane group and the higher frequency process is due to motions involving the ether oxygen group.

Finally, we would like to comment on the method of data analysis. In the present study, the dielectric data have been analysed as a single data set at constant temperature assuming the presence of two relaxation processes. As is mentioned above for N1000, the relaxation strength of the higher frequency process at -5 to -15°C is $\sim$5% that of the lower frequency process. It may therefore be possible that an equally good fit could be obtained assuming only one relaxation process for this case. In order to evaluate this possibility, a statistical method which is capable of analysing the pooled data sets containing all the observed data should be employed.

CONCLUSIONS

Two dielectric relaxation processes are observed in the network polymers studied and these are assigned to molecular processes by comparison with the estimated concentrations of two dipolar groups. Relaxation parameters are discussed concerning the molecular motions of the network system. It is concluded that the two relaxation processes have different mobilities even though both dipole moments are attached to the same molecular chain and no phase separation occurs.

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