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Dielectric normal mode relaxation of undiluted poly(propylene glycol)s

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Abstract

Dielectric measurements were carried out for linear and star-shaped poly(propylene glycol)s (PPGs) of different molecular weights (M). A small loss peak due to the normal mode relaxation was observed on the low-frequency side of the main loss peak. Two peaks were resolved and the normal mode relaxation time τ_n, the distribution of relaxation times and relaxation strength were examined. The effect of OH groups attached at the chain ends on the normal mode relaxation was also investigated by using PPG samples whose end groups were substituted by acetyl groups. The results indicate that τ_n is proportional to M^2 in accordance with the Rouse theory. The mode distribution of star-shaped PPGs is slightly broader than that of linear PPGs. The effect of hydrogen bonding between the OH groups on the normal mode relaxation time is negligibly small. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Normal mode; Dielectric relaxation; Poly(propylene glycol)

1. Introduction

Polymers having the dipole moment aligned parallel to the chain contour exhibit a dielectric relaxation due to the fluctuation of the end-to-end vector of the chains [1–3]. Stockmayer [1] designated the parallel and perpendicular dipole components of the repeat units as type-A and -B dipoles, respectively. Dielectric relaxations associated with the type-A dipoles were called the *normal mode relaxation* [4] after the theory of normal modes proposed by Rouse [5] and Zimm [6]. The dielectric normal mode relaxation was first observed by Stockmayer and coworkers for linear and star-shaped poly(propylene glycol)s (PPGs) in the 1960s [7,8]. They reported that the relaxation time of a PPG agrees well with the theoretical relaxation time calculated with the zero shear viscosity of the PPG on the basis of the free draining model [5]. After their pioneering studies, the dielectric normal mode relaxation of undiluted polymers was not studied further until the 1980s, when *cis*-polyisoprene (*cis*-PI) was found to exhibit the dielectric normal mode relaxation [9]. The effects of entanglement on the normal mode relaxation of *cis*-PI were extensively studied over a wide range of molecular weight (M) [3,9–14]. Dielectric measurements on PPGs were reported by several authors [15–17], but they were mainly interested in the local motions of PPG.

Recently, Schonhals et al. [18–20] studied the dielectric relaxation of PPG, with an aim to clarify the relationship between the normal mode relaxation and local segmental motions. Schlosser and Schonhals [19] reported that the normal mode relaxation time of low molecular weight PPG is proportional to $M^{2.95}$. Since this behaviour was close to the prediction of the reptation model [21,22], they explained this M-dependence by an interesting model of *transient entanglement* proposed by Heinlich et al. [23], who assumed that PPG chains are connected at the ends by hydrogen bonds of the end OH groups. Alig et al. [24] carried out ^{13}C NMR measurements on the samples whose ends were substituted by trimethyl silyl groups and found evidence to support this model. These results contradict the dielectric data reported by Baur and Stockmayer [7]. They found that the dielectric normal mode relaxation of a PPG, whose ends are substituted by methoxy groups, was similar to those for non-end capped PPGs. In this paper, we reexamine the normal mode relaxation for well-characterized samples of linear and star-shaped PPGs. Our objective is to elucidate, in more detail, the dielectric behaviour, such as the M-dependence of the relaxation time and mode distribution. We also examine the dielectric normal mode relaxation of PPGs whose end groups are substituted by acetyl groups to test the transient entanglement model.

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Table 1
Sample characteristics

Code	M_w	M_n	M_w/M_n
PPGD-1	1060	980	1.1
PPGD-2	1950	1950	1.1
PPGD-3	2900	2600	1.1
PPGT-3	2990	2720	1.1
PPGT-6	5890	5360	1.1
PPGT-9	8790	7990	1.1
PPGT-14	14 000	12 000	1.2

2. Experimental

2.1. Materials

Linear PPG samples of the diol-type are coded as PPGD and the three-arm star-shaped PPGs (triol-type) are coded as PPGT. The code numbers indicate the molecular weight in kilograms per mole. The linear samples, PPGD-1, PPGD-2 and PPGD-3, were purchased from Mitsui Chemical Co. Ltd (Tokyo, Japan). The star-shaped samples, PPGT-3 and PPGT-14, were obtained from Takeda Co. Ltd (Osaka, Japan) and Asahi Glass Co. Ltd (Tokyo, Japan), respectively. PPGT-6 and PPGT-9 were purchased from Takeda Co. Ltd (Osaka, Japan).

Acetylation of PPGD-3 and PPGT-6 was carried out by adding 1.5 times excess acetylchloride (CH_3COCl) at 290 K and allowing the reaction to proceed for 24 h. Then the temperature was elevated to 320 K for 1 h to complete the reaction. The reaction products were washed with water and dried in vacuum at 370 K for 2 days. They are coded as PPGD-3Ac and PPGT-6Ac. Perfect substitution of the OH groups by acetyl groups was confirmed by ^{13}C NMR.

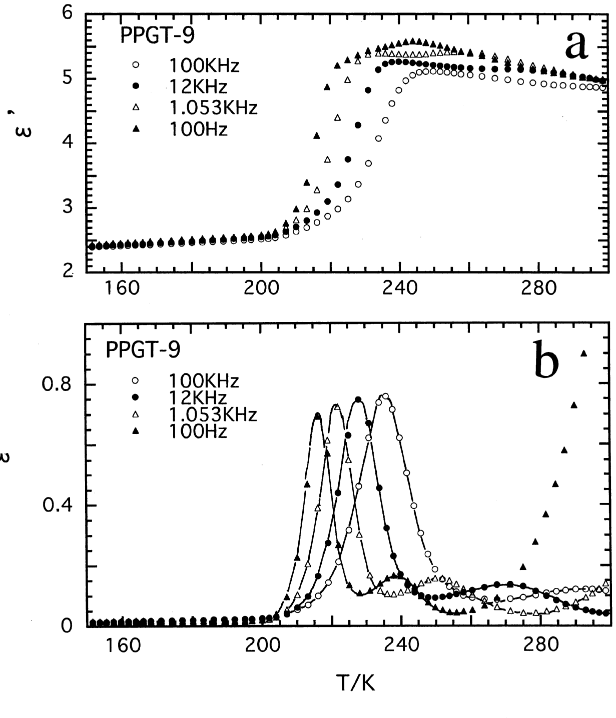

Fig. 1. Temperature dependence of: (a) dielectric constant ε' and (b) loss factor ε'' for PPGT-9 at 0.1, 1, 12, and 100 kHz.

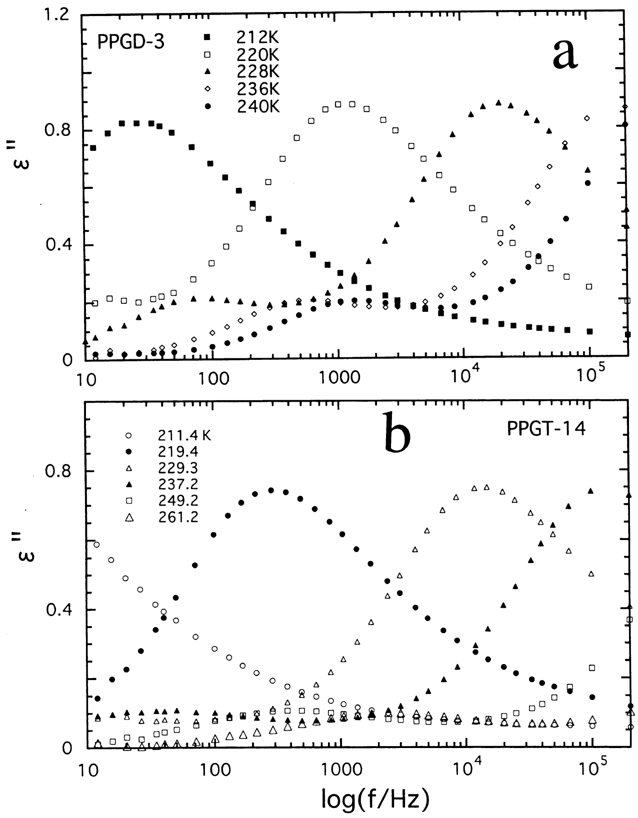

Fig. 2. Frequency dependence of dielectric loss factor ε'' at various temperatures for: (a) PPGD-3 and (b) PPGT-14. The main peak is due to the segmental mode and the small peak seen in the low-frequency side is due to the normal mode.

The number average molecular weights M_n of the samples were determined by ^{13}C NMR. The so-called end-group analyses were carried out, i.e. the intensities of the lines for the methylene and end C-OH groups were compared taking into account the effect of the spin–lattice relaxation time T_1. The polydispersity, the ratio of the weight and number average molecular weights M_w and M_n, was determined by gel permeation chromatography (Tosoh LS800, Tokyo, Japan). The characteristics of the samples are listed in Table 1.

2.2. Methods

Dielectric measurements were carried out on an RLC Digibridge (QuadTech 1693, Maynard, USA) in the frequency range of $10–10^5$ Hz. The data of capacitance, tan δ and temperature were accumulated in a personal computer (NEC 9800, Tokyo, Japan) through GP-IB (general purpose interface bus IEEE-488), and the dielectric constant ε' and the loss factor ε'' were calculated automatically. The dielectric cell used for the measurements on viscous liquids was reported previously [11]. Measurements

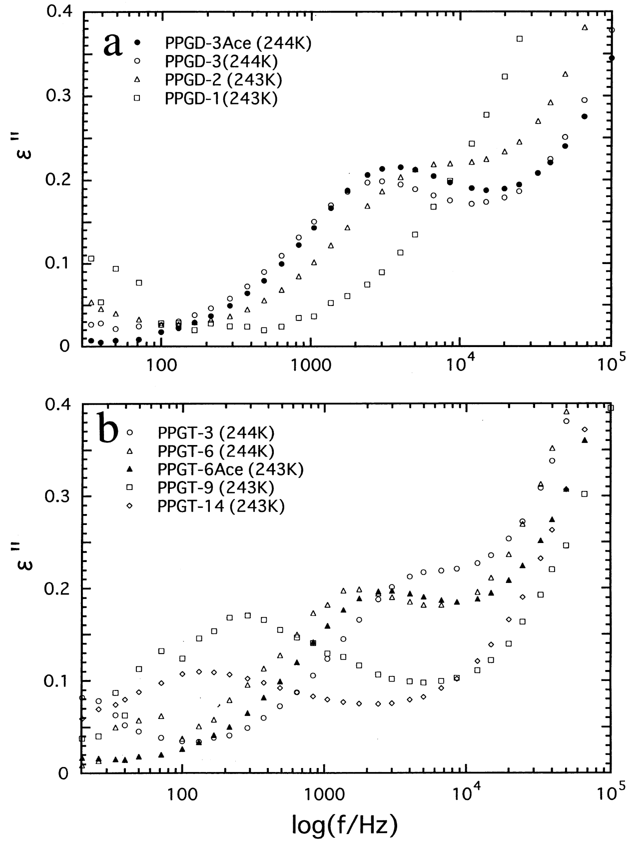

Fig. 3. Frequency dependence of dielectric loss factor ε'' at 243–244 K for: (a) PPGD and (b) PPGT samples. The loss peaks seen in these figures are due to the normal mode. The filled keys indicate the data for acetylated samples.

of ^{13}C NMR were made on a Varian UNITY + 600 spectrometer (California, USA). The glass transition temperature T_g was measured with a differential scanning calorimeter (DSC) (Seiko SSC580, Tokyo, Japan).

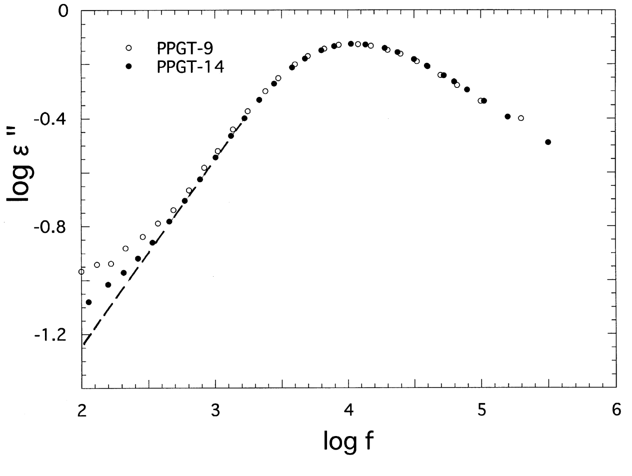

Fig. 4. Superposition of the log ε'' vs. log f curves of PPGT-9 and PPGT-14 at about 227 K. The contribution of the segmental mode in the low-frequency side was estimated by the linear extrapolation as indicated by the dashed line.

3. Results and discussion

3.1. Dielectric behaviour of PPGD and PPGT samples

Fig. 1 shows the representative temperature dependence curves of the dielectric constant ε' and the loss factor ε'' for PPGT-9. Similar curves were observed for the other samples. The glass transition temperature T_g was determined by DSC to be 200 ± 3 K for the PPGD and PPGT samples. As reported by Stockmayer et al. [7,8], the low- and high-temperature peaks can be assigned to the segmental mode and normal mode, respectively. The peak temperatures at a fixed frequency for the segmental mode were almost independent of molecular weight. On the other hand, the location of the normal mode shifted to higher temperature with increasing molecular weight. This is consistent with the assignment given above.

Fig. 2a and b shows the representative frequency dependence curves of ε'' of PPGD-3 and PPGT-14, respectively. Similar curves were observed for the other samples including PPGD-3Ac and PPGT-6Ac. The main ε'' peak and the small low-frequency peak correspond to the segmental and normal mode relaxations, respectively. Fig. 3 shows the ε'' curves at about 243 K, where the normal mode relaxation is seen. The ε'' curves shift to low frequency with increasing molecular weight. This is the typical behaviour of the normal mode relaxation. It is noted that the ε'' curves of the acetylated samples are very close to the non-acetylated samples of the same molecular weight. For the low molecular weight samples of PPGD-1, PPGD-2, and PPGT-3, the normal mode was observed only as a shoulder.

In order to analyse the normal mode relaxation, we attempted to resolve the loss curves into the contributions of the normal and segmental modes, assuming that the shape of the loss curve for the segmental mode is given by the Havriliak–Negami equation [25]. The log ε'' vs. log f curve of this equation conforms to a straight line in the regions far from the loss maximum, and the slopes on the low- and high-frequency sides of the peak are equal to α and $-\alpha\beta$, respectively. Here, α and β are the exponents of the inner and outer brackets of the Havriliak–Negami equation. For the present study, only the parameter α is important and we used the ε'' curves for high molecular weight PPGT to estimate the parameters of the Havriliak–Negami equation. Fig. 4 shows the log ε'' vs. log f curves for PPGT-9 and PPGT-14 at about 227 K. The ε'' curve of PPGT-14 was shifted slightly so that the best superposition is attained. Failure of superposition in the low-frequency region reflects the contribution of the normal mode, which depends on the molecular weight. The contribution of the segmental mode on the low-frequency side of the loss peak was estimated as shown by the dashed line with slope 0.68 and was expressed by $\log \varepsilon'' = 0.68 \log f + C$. The constant C depends on both the loss maximum frequency and the relaxation strength. We regarded C as an adjustable parameter. An

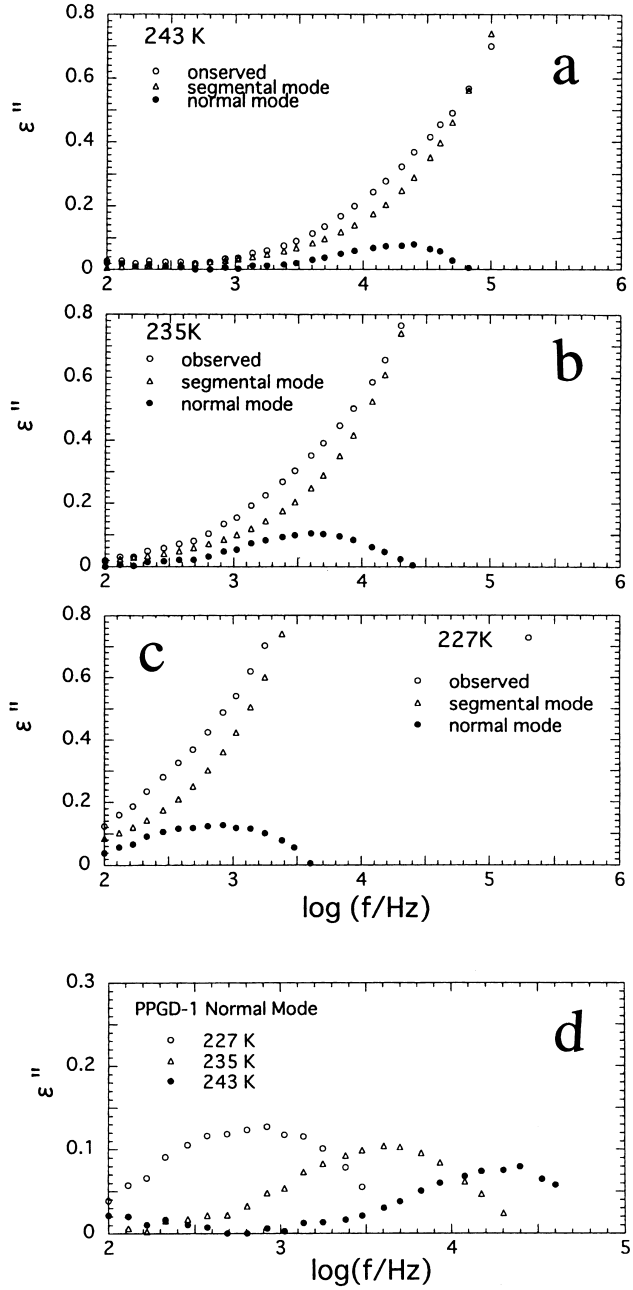

Fig. 5. Example of the ε'' curves of PPGD-1 resolved into the contributions of the segmental and normal modes at 243, 235, and 227 K (a, b, and c), (d) shows the ε'' curves for the normal modes thus resolved.

example of the resolution of the ε'' curves is shown in Fig. 5 for PPGD-1. Fig. 5a–c shows the contributions of the segmental mode and the normal mode at 243, 235, and 227 K, respectively, and Fig. 5d shows the ε'' curves for the normal mode at the three temperatures thus resolved. In this way the loss maximum frequencies f_{mn} of the normal mode for PPGD-1, PPGD-2 and PPGT-3 were determined. For the PPG samples with higher molecular weights, the ε'' curves were resolved as shown in Fig. 6. The dash–dot lines indicate the theoretical curves discussed later.

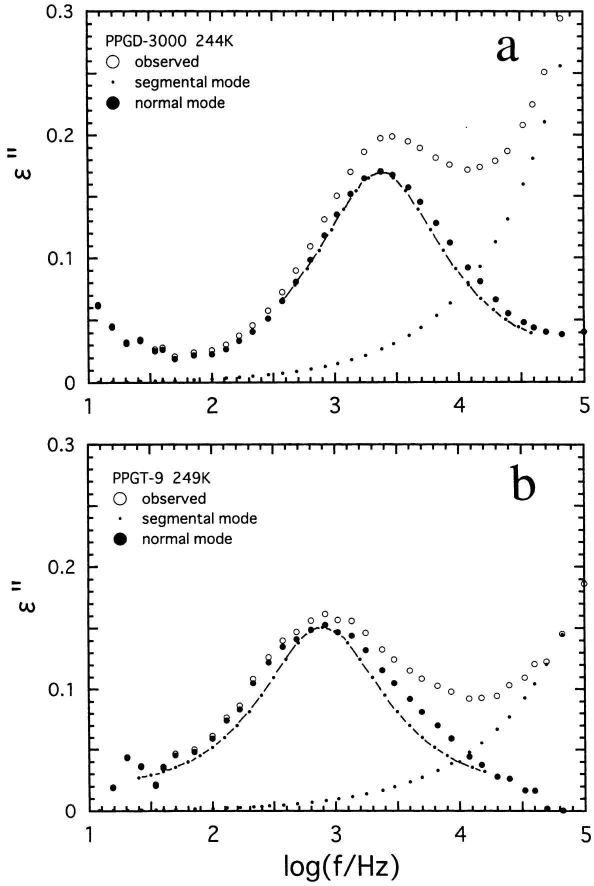

Fig. 6. Example of the ε'' curves resolved into the contributions of the segmental and normal modes for: (a) PPGD-3 and (b) PPGT-9. The dashed lines show theoretical ε'' curves calculated on the basis of the Rouse–Ham model (Eqs. (2) and (3)).

3.2. Molecular weight dependence of the normal mode relaxation time

The relaxation time τ_{n} for the normal mode is defined by

$$\tau_{\mathrm{n}} = \frac{1}{2\pi f_{\mathrm{mn}}}. \qquad (1)$$

In the present study dielectric measurements of the PPG samples with different molecular weights were made at various temperatures. To compare the relaxation times τ_{n} at a certain temperature, we used the Arrhenius plot of the loss maximum frequency f_{m} shown in Fig. 7. The slope of $\log f_{\mathrm{mn}}$ vs. $1/T$ around 243 K was determined and the values of τ_{n} were reduced to the values at 243.2 K.

Before analysing the M-dependence of τ_{n}, the alignment of the type-A dipoles in the present PPG samples should be considered. The manufacturers of the PPGD samples reported that the PPGDs were prepared by base-catalysed polymerization [26]. In this method, the initiator is bi-functional and hence the direction of the alignment of the type-A dipoles is inverted at the centre of the molecules. Such a chain can be regarded as a two-arm star-shaped polymer and is called a bifurcated chain. Obviously the arm molecular

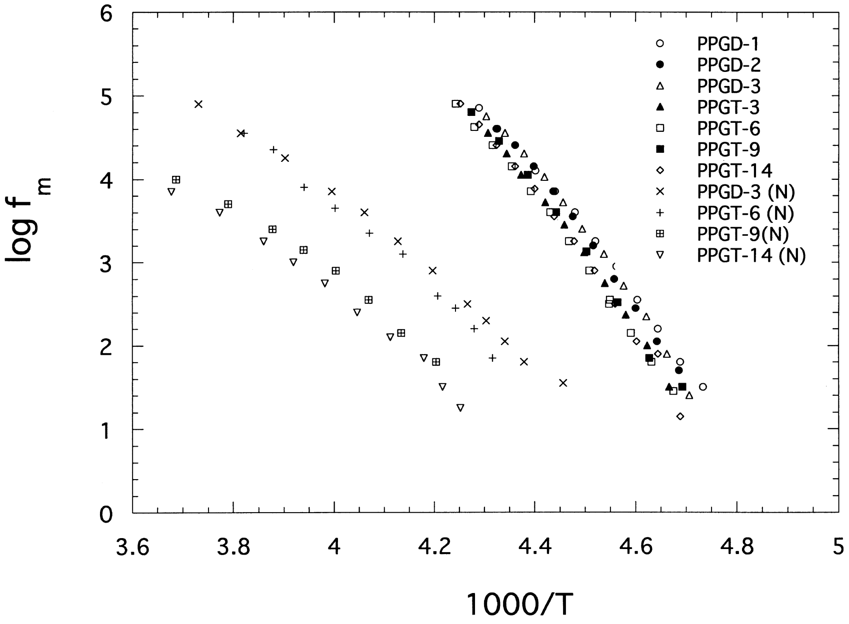

Fig. 7. Arrhenius plots for the segmental mode of all PPGD and PPGT samples and those for the normal mode (denoted as N) for relatively high molecular weight samples.

weight M_a of PPGD is $M/2$. On the other hand, the PPGT samples were prepared by a tri-functional initiator and the type-A dipoles are aligned in the direction from the centre to the chain end. Thus the arm molecular weight M_a of PPGT is equal to $M/3$.

For a bifurcated chain, the Rouse–Zimm theory [5,6] indicates that the normal modes with the even indices p become dielectrically active as pointed out by Baur and Stockmayer [7]. Therefore, the observed τ_n for a present linear PPG with molecular weight M ($=2M_a$) corresponds to the relaxation time for the second normal mode (τ_2) and is the same as τ_n of a PPG in which the type-A dipoles are aligned without inversion and whose molecular weight is M_a. The complex dielectric constant ε^* of a non-entangled bifurcated chain is given by

$$\varepsilon^* - \varepsilon_U = \frac{32\Delta\varepsilon}{\pi^2}\sum_{p=2}^{N}\frac{1}{p^2(1+i\omega\tau_p)} \qquad (2)$$

where ε_U is the unrelaxed dielectric constant, $\Delta\varepsilon$ the relaxation strength, p the mode number, and τ_p the relaxation time for the p-th normal mode. For bifurcated chains $p = 2k$ and k is the odd number ($k = 1, 3, 5, 7, \ldots$). According to the free-draining model [5], the relaxation time for the modes of $p = 2k$ is given by

$$\tau_p = \frac{\zeta N_a^2 b^2}{3k_B T k^2} \qquad (3)$$

where ζ, N_a, and b are the friction constant per bead, the number of beads in the arm, and the average distance between beads, respectively. Thus the Rouse theory predicts that the relaxation time of the PPGD samples is proportional to M_a^2.

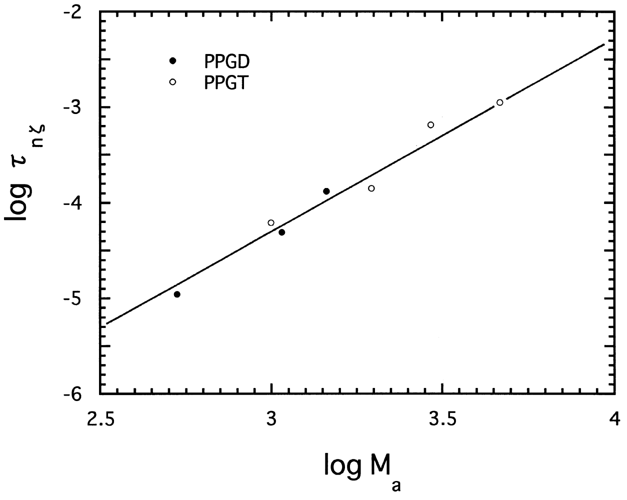

Fig. 8. Double logarithmic plot of the normal mode relaxation times reduced to the iso-friction state $\tau_{n\zeta}$ versus arm molecular weight M_a. The straight line is the best-fit curve with a slope of 2.0.

According to the Ham theory [27] on star-shaped polymers, τ_n of PPGT corresponds to the relaxation time of a linear PPG having uniaxially aligned type-A dipoles and having molecular weight $M_a = M/3$. Thus, the relaxation time of the PPGT samples is also given by Eq. (3). The theoretical considerations stated above indicate that the data of τ_n for the present samples of linear and star-shaped PPGs conform to a common curve if τ_n is plotted against the arm molecular weight.

Another important factor for analyses of the M-dependence of τ_n is the effect of the friction coefficient. Generally the relaxation time τ for large-scale motions of high

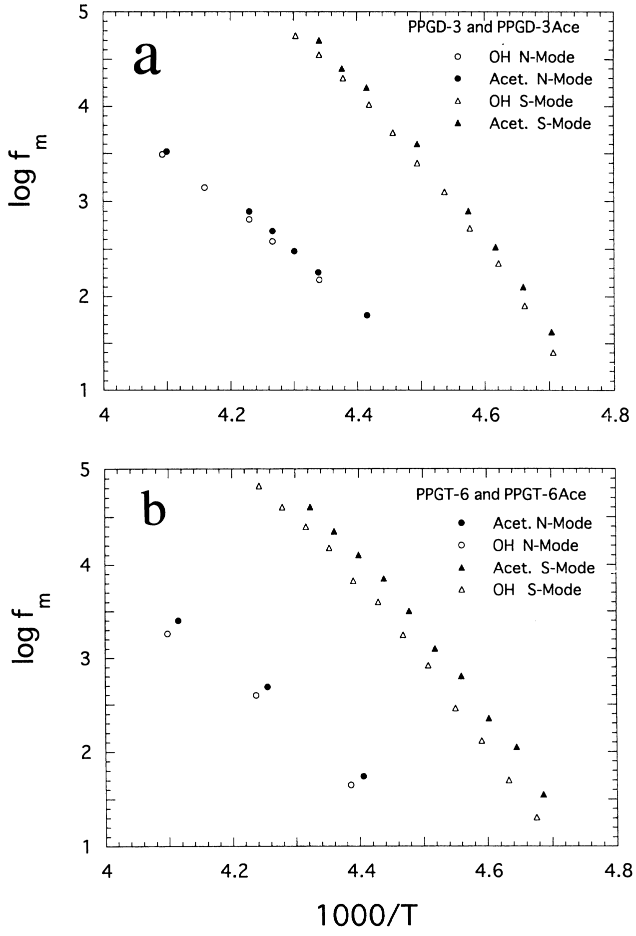

Fig. 9. (a) Comparison of the Arrhenius plots of the non-acetylated and acetylated samples of PPGD-3. (b) Similar comparison for PPGT-6.

molecular weight polymers can be written by the form [28]:

$$\tau = \zeta(T)F(M) \quad (4)$$

where $\zeta(T)$ and $F(M)$ are the friction factor and the structure factor, respectively. The friction factor is a function of temperature and is independent of the architecture of the polymer molecule. However, it is known that $\zeta(T)$ depends weakly on M for low molecular weight polymers such as the present PPG samples. For comparison of the M-dependence of τ_n with theories it is required to reduce the data into iso-friction state. As reported previously for *cis*-PI, the relaxation time for the segmental mode τ_s is proportional to $\zeta(T)$ [11], when temperature is higher than T_g + 30 K [11,29]. In Fig. 7 we note that the values of f_{ms} of PPGD samples are slightly higher than those of PPGT. Thus we converted τ_n of PPGD into the values ($\tau_{n\zeta}$) at the iso-friction state of the high molecular weight samples.

Fig. 8 shows the double logarithmic plot of $\tau_{n\zeta}$ vs. M_a. The solid line is the best-fit line with a slope of 2.0. It is seen that the data agree well with the Rouse–Ham theory. This result does not agree with the exponent of 2.95 reported by Schlosser and Schönhals [19], even though the range of molecular weight is similar. A possible origin for this discrepancy may be the error in the determination of the molecular weights of the samples used by Schlosser and Schönhals, who reported that the M of the samples were 1000, 2000, and 4000. They did not report details of the characterization.

We note that if the transient entanglement model is the case, τ_n does not obey the Rouse theory. The present result is not in accordance with the model of transient entangled chains proposed by Heinlich [23]. For PPGT-14, one might consider that this sample is in the entangled regime. Smith et al. [30] reported that the characteristic molecular weight M_c of PPG is 7000 from measurements of viscosity and diffusion coefficient. The arm molecular weight ($M_a = 4700$) of PPGT-14 is lower than M_c, but the span molecular weight ($= 2M_a$) is higher than M_c. Therefore this polymer is in the crossover region. However, in Fig. 8 we did not see the increase of τ_n due to entanglements.

3.3. Dielectric behaviour of acetylated PPG

In order to examine the effect of hydrogen bonding, we carried out dielectric measurements on acetylated PPGD-3 (PPGD-3Ac) and PPGT-6 (PPGT-6Ac). The ε'' curves of PPGD-3Ac and PPGT-6Ac were found to be very similar to the corresponding non-acetylated samples as shown in Fig. 3. Fig. 9 compares the effect of acetylation on the loss maximum frequencies f_{mn} for the normal modes. We see that f_{mn} of the acetylated samples is slightly higher than the non-acetylated PPG. In Fig. 9, it is seen that the loss maximum frequency for the segmental mode f_{ms} also shows the same behaviour as the normal mode. By substitution of the end OH groups by acetyl groups, both f_{mn} and f_{ms} increase slightly but the ratio f_{mn}/f_{ms} is approximately unchanged. This indicates that the OH groups at the chain ends do not affect the structure factor of Eq. (4), and hence the normal mode relaxation is almost independent of the OH group. The OH groups slightly increase the average internal viscosity. The reason for the absence of the influence of the OH groups may be ascribed to the relatively polar ether groups of the monomeric units. The interactions between the OH groups are similar to the interactions between the OH group and the ether groups of the repeat units and hence the hydrogen bonds of the OH groups are not effective. If the repeat units are non-polar, this effect becomes prominent as in ionomers.

3.4. Mode distribution

Distribution of the normal mode relaxation time is theoretically given by Eqs. (2) and (3). The dashed lines in Fig. 6 shows the theoretical curves. It is seen that the observed ε'' curve of PPGD-3 is slightly broader than the theoretical curve. The same behaviour was seen for low molecular weight *cis*-polyisoprene [11]. If the motions of the end groups of the PPGD molecules are impeded by hydrogen bonding, the mode distribution is no more described by Eqs. (2) and (3), and is described by models in which chains are

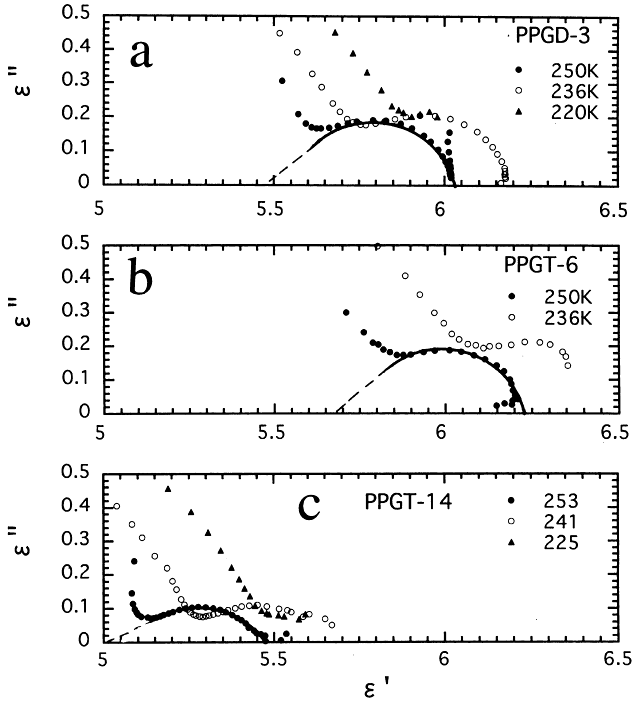

Fig. 10. Cole–Cole plots for the normal mode relaxation for: (a) PPGD-3, (b) PPGT-6, and (c) PPGT-14. The dashed line shows the estimated arc to determine the relaxed and unrelaxed dielectric constants.

composed of different kinds of bead [31–33]. Those models predict that the distribution of relaxation times becomes broader than the Rouse model. Thus it is concluded again that the data of the mode distribution are not in harmony with the transient entanglement model [23].

Comparing the behaviour of the normal mode relaxations of linear PPGD-3 and star-shaped PPGT-9, we see that the normal modes of PPGT-9 is broader than PPGD-3. Yoshida et al. [12] reported the dielectric normal mode relaxation of the six-arm star-shaped *cis*-PI. They found that the mode distribution of star-shaped *cis*-PIs is broader than linear *cis*-PI. The broadening of the normal mode in star-shaped polymers appears to be a general phenomenon.

3.5. Dipole moment

The dielectric relaxation strength $\Delta\varepsilon$ was determined by the Cole–Cole plots shown in Fig. 10. The average $\Delta\varepsilon$ value of PPGD-3, PPHT-6, and PPGT-9 was 0.52 ± 0.05. Theoretically $\Delta\varepsilon$ is given by [2,3]

$$\Delta\varepsilon = \frac{4\pi\rho N_A \mu^2 \langle r^2 \rangle}{3k_B TM} F \qquad (5)$$

where ρ is the density, N_A the Avogadro number, μ the type-A dipole moment per unit contour length, $\langle r^4 \rangle$ the mean square end-to-end distance, F the internal field factor, and M the molecular weight. For the normal mode relaxation F is found to be close to unity [3]. It is reported that $(\langle r^2 \rangle / M)^{1/2}$ of PPG in the unperturbed state is 7.50×10^{-11} cm [34]. From this value we determined μ to be 1.10×10^{-11} cgs cm with $F = 1$. If the length of the monomeric unit is taken to be 0.36 nm for the all-*trans* conformation, the parallel dipole moment per monomeric unit becomes 0.63 debye. This value is about three times larger than the value estimated by Baur and Stockmayer [7].

4. Conclusions

The dielectric loss curves of bifurcated linear poly(propylene glycol)s (PPGD) and tri-arm star-shaped poly(propylene glycol)s (PPGT) have resolved into the contributions of the normal and segmental modes, and the relaxation time, mode distribution, and relaxation strength for the normal mode have been determined. It is found that the molecular weight dependence of the normal mode relaxation time $\tau_{n\zeta}$ reduced to the iso-friction state where the friction is the same as that of high M samples is proportional to M^2. The distribution of normal mode relaxation times is close to that given by the free draining Rouse–Ham theory. The dielectric data for PPG samples whose OH groups are substituted by acetyl groups indicate that the normal mode relaxation time is slightly shorter than the non-substituted samples. However, if the data are reduced to the iso-friction state, no difference between the acetylated and non-acetylated samples is detected and hence the effect of the end OH groups on the normal mode relaxation is negligible. Thus, the present results are not in accordance with the transient entangle model proposed by Heinlich et al. The parallel component of the monomer dipole moment is determined to be 0.63 debye which is larger than the value reported by Baur and Stockmayer.

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