Dielectric Relaxation and Molecular Motion
of Poly(tert-Butyl Crotonate)

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Dielectric properties of poly (tert-butylcrotonate) (PTBC) and poly (tert-butyl methacrylate) (PTBM) were studied in a wide temperature range from −195 to 200°C at several frequencies between 30Hz and 1MHz. In PTBM, the α and β relaxations were observed near 120 and 59°C at 30Hz, respectively, which are due to a micro-brownian molecular motion of main chain and local molecular motion of ester group, respectively. In PTBC, the β relaxation is observed near −58°C at 30Hz, but the α relaxation was not found up to 200°C. By examining molecular motion through the relaxations, it was concluded that the backbone chain of PTBC is stiffer than that of PTBM.

KEY WORD: Poly (tert-butyl crotonate)/ Poly (tert-butyl methacrylate)/
Dielectric Relaxation/ Flexibility of Backbone Chain/

I. INTRODUCTION

Generally, poly(α-substituted carboxylate) is flexible in the backbone chain. For example, the backbone chains of poly (alkyl methacrylate) are flexible and the flexibility is comparable with that of poly (alkyl acrylate). Recently, Nagasawa and his colleagues, however, found that the backbone chain of poly (tert-butyl crotonate) (PTBC) is much stiffer, compared with that of poly (tert-butyl methacrylate) (PTBM), from light scattering,[1] intrinsic viscosity[2] and small angle X-ray scattering measurements[3] in rather dilute solution. They also indicated that the enhanced stiffness of PTBC is caused by the steric hindrance between the β-methyl group and the tert-butyl group.[3] These stiff chains of PTBC should be sensitively reflected to molecular motion in its solid state, but no paper has been published, to our knowledge. On the other hand, molecular motions of poly (alkyl methacrylate) have been studied from dielectric and mechanical measurments by several workers.[4-8] Starting at the highest temperature, the α, β and γ relaxations are usually observed, which are attributed to micro-brownian molecular motion of main chains, local molecular motion of ester group and rotational molecular motion of alkyl group, respectively. The glass transition temperatures, T_g, lay in the temperature range of −65 (n-dodecyl ester) to 105°C (methyl ester), depending somewhat on the length and bulkiness of the ester group. T_g of PTBM is reported to be about 78°C[7].

The purpose of this work is to study dielectric relaxations of PTBC and PTBM and to clarify variation of flexibility of polymer chains by substituted position of methyl group.

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TABLE I Physical Properties of Samples.

Polymer	Tacticity	$T_g(K)$	M_v
PTBC-1	~atactic[a]	>470	3.42×10^4
PTBC-2	~atactic[a]	>470	1.82×10^5
PTBM	~atactic[b]	358	1.67×10^6

a) The tacticity estimated from carbon-13 NMR spectrum is
   (mM) $\simeq 0.70$ and (rR) + (mR) $\simeq 0.30$.[3,10]
b) Isotactic triad content is ca. 50%.[3]

II. EXPERIMENTAL

PTBM and PTBC were supplied from Nagasawa laboratory of Nagoya University.[9] Characteristic data of samples are listed in Tab. I. Molecular weights, M_v, were determined by viscosity measurements in toluene solution for PTBC[2] and in n-butyl acetate solution for PTBM.[11] The glass transition temperatures, T_g, were determined by differential scanning calorimetry (DSC) (Perkin Elmer, DSC-II). T_g for PTBC was not found up to 200°C. The film samples were prepared by casting from benzene solution. The films for dielectric measurements were annealed for two hours at 100°C for PTBM and at 140°C for PTBC. The film thickness is about 0.3 mm.

Dielectric measurements were carried out with a transformer bridge in the temperature range from −195 to 200°C and at several frequencies between 30Hz and 1MHz. The details of the electrode system are described previously.[12]
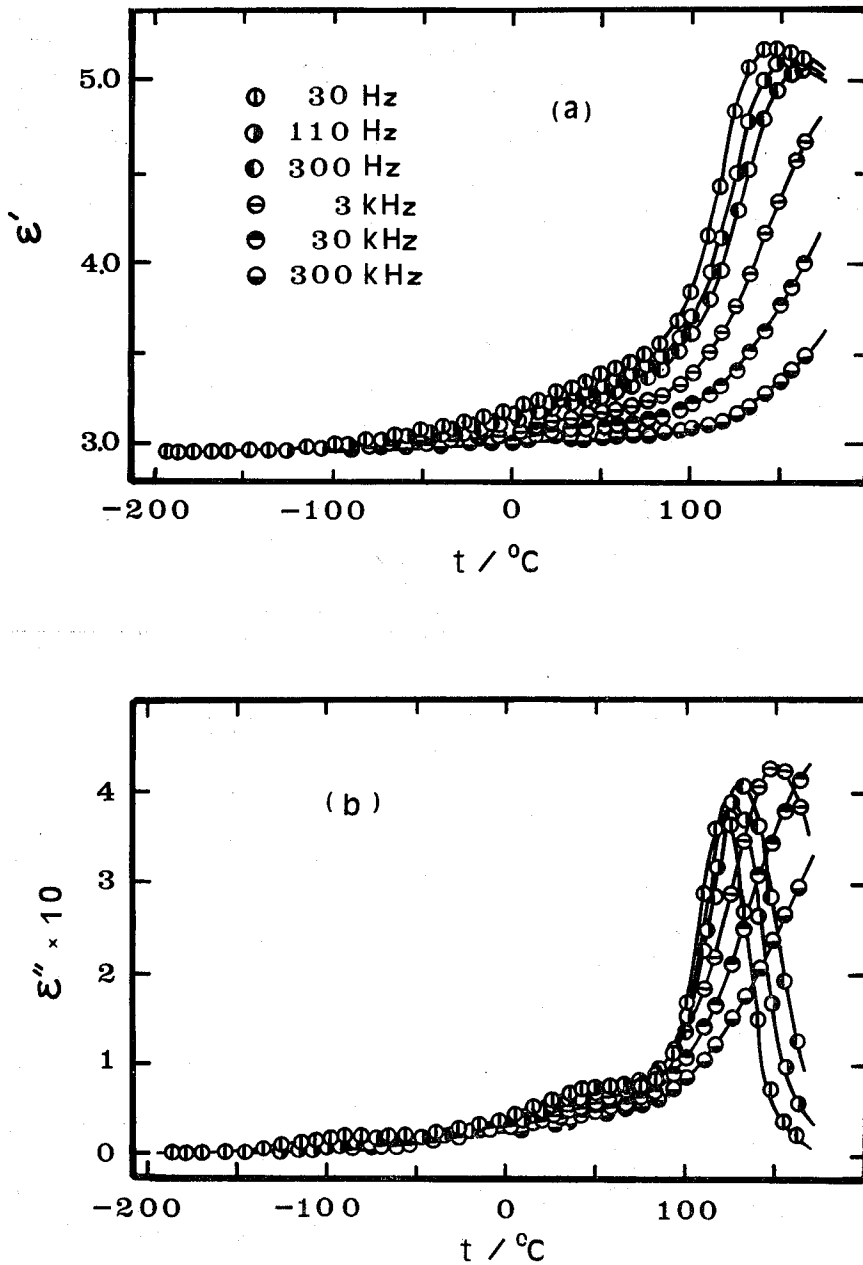
III. RESULTS AND DISCUSSION

The dielectric and mechanical relaxations of PTBM have been studied by a few workers.[4−8] From dielectric measurements in the temperature range of −80 to 170°C, Mikhailov, Burstein and Krasner,[6] and Heijboer[5] found α and β relaxations, which are attributable to micro-brownian molecular motion of main chains and local molecular motion of the ester groups. On the other hand, Hoff, Robinson and Willbourn,[4] and Shen and Strong[7] indicated that the γ relaxation is not seen, since tert-butyl group is symmetrical. Our dielectric data for PTBM in the wide teperature range of −195 to 180°C are shown in Fig. 1. The α and β relaxations are observed near 120 and 59°C at 30Hz, respectively, being fairly well consistent with the other worker's data.[5,6] One very small peak near −90°C might be due to a very small amount of water in the polymer matrix[13].
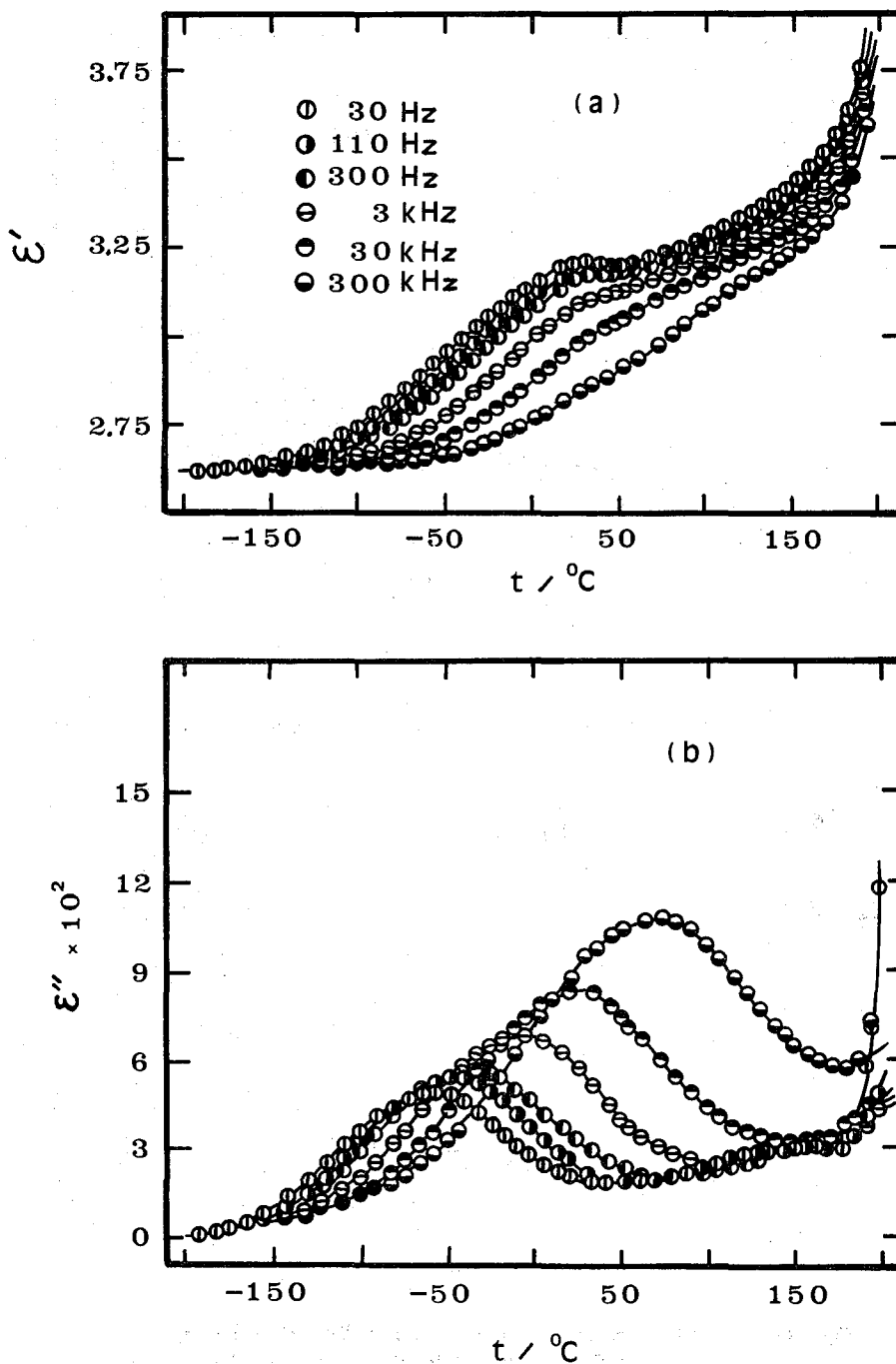
Figures 2(a) and (b) show temperature dependences of dielectric constant, ε', (a) and the loss, ε'', (b) at several frequencies for PTBC ($M_v=3.4 \times 10^4$), respectively— these dielectric data were almost same to those for PTBC of ($M_v=1.8 \times 10^5$), which shows no dependence of molecular weight. There is observed one dielectric relaxation near −58°C which is ascribed to β relaxation. Since PTBC was pyrolyzed up to 200°C, we could not obtain the dielectric data at higher temperatures above 200°C. The α relaxation is not observed up to 200°C, and this suggests that the α relaxation would exist above 200°C.

Arrhenius plots for the relaxations in PTBM and PTBC are shown in Fig. 3. The

Figs. 1(a) and (b)   Temperature dependences of dielectric constant, ε', (a) and the loss, ε'', (b) in PTBM at several frequencies.

Figs. 2(a) and (b) Temperature dependences of dielectric constant, ε', (a) and the loss, ε'', (b) in PTBC at several frequencies.

Dielectric Property of Poly(Tert-Butyl Crotonate)
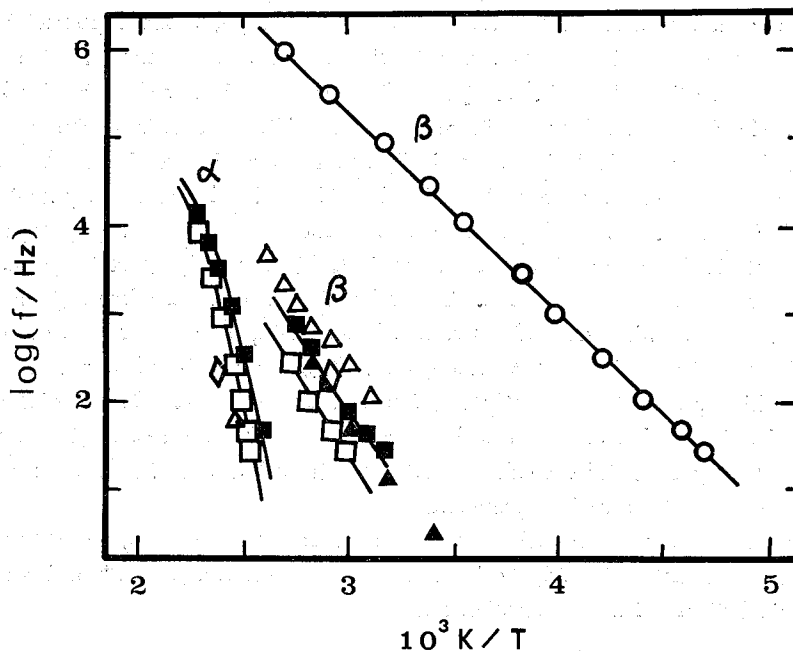
Fig. 3. Arrhenius plots for α and β relaxations in PTBM and PTBC.
    ○ : the present data for PTBC,
    □ : the present data for PTBM,
    ■ : plots of logarithm of relaxation frequency, $\log f_m$, versus
        $1/T$ in PTBM.
    △ : dielectric data for PTBM by Heijboer[5] (This is the plots
        of $\log f_m$ versus $1/T$)
    ▲ : mechanical data for PTBM by Heijboer[5]
    ◇ : dielectric data for PTBM by Mikhailov[6]

TABLE II Relaxation Parameters for Several Samples.

Polymer.	Repeating unit	ΔH(kJ/mol)		T_{max} for β relaxation at 30Hz (K)	T_g(K)	Ref.
		α	β			
PTBC	CH$_3$ CH$_3$ CH$_3$ (structure) COOR COOR (R=tert-Butyl)		43	215	>470	present work
PTBM	CH$_3$ CH$_3$ (structure) COOR COOR (R=tert-Butyl)	WLF	75	332	358	present work
PTBM		188.4	71	310*	351	5, 7, 17
PTBA	(structure) COOR COOR (R=tert-Butyl)				316	8
PMA	(R=Methyl)	WLF	40	153*	280	8, 17, 18

* These values were estimated by extrapolating the Arrhenius plots to 30Hz.

plots for the α relaxation of PTBM show so-called WLF type, which supports that the α relaxation is due to a micro-brownian molecular motion of main chains. The relaxation parameters are listed in Tab. II. T_g for PTBC is much higher than that for PTBM, and this is clearly caused by the difference in the stiffness of their backbone chains. The β-methyl group in PTBC hinders sterically rotational motion of C(COOR) $-$C(Me) bond more than the α-methyl group in PTBM. This steric hindrance may lead to the enhanced T_g in PTBC. Of course, replacement of the methyl group by hydrogen atom reduces the steric hindrance further. Therefore, T_g for poly (tert-butyl acrylate) (PTBA) is lower than that for PTBM. The relaxation temperature for the β relaxation, T_{max}, is not connected with the stiffness of backbone chain, since the β relaxation is due to the local molecular motion of the ester group. T_{max} for PTBC is lower than that for PTBM and higher than that for poly (methyl acrylate) (PMA). This indicates that the local molecular motion of the ester is more hindered by the α-methyl group than by the β-methyl group. The smaller value of ΔH in PTBC than in PTBM for the β relaxation supports the above interpretation.

Figures 4 and 5 show Cole-Cole plots for the α and β relaxations, respectively. Those for the β relaxation is fairly well fitted to the Cole-Cole equation[14] which assumes the symmetrical distribution of relaxation time,

$$\varepsilon^* = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty) \frac{1}{1 + (i\omega\tau_0)^\beta}$$

but the α relaxation obeys Williams-Watts equation[15] for the non-symmetrical distribution,

$$\varepsilon^* = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty) \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{(\omega\tau_0)^{n\beta}} \cdot \frac{\Gamma(n\beta+1)}{\Gamma(n+1)} \left(\cos\frac{\pi n\beta}{2} - i\sin\frac{\pi n\beta}{2}\right)$$

Where, ε^*, ε_∞, ε_0, τ_0 and β are complex dielectric constant, limiting high frequency dielectric constant, limiting low frequency dielectric constant, relaxation time and distribution parameter of relaxation time. Williams et al.[16] indicated that the α relaxation shows generally non-symmetrical distribution of relaxation time and is well fitted to Williams-Watts equation. The above results on PTBM and PTBC support their conclu-
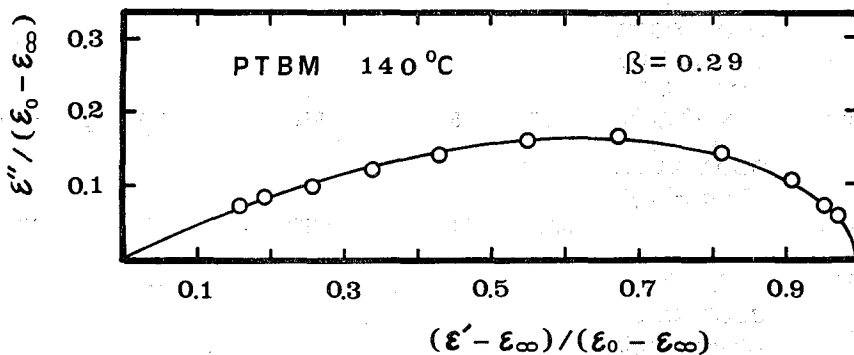

Fig. 4. Cole-Cole plots for α relaxation in PTBM. The solid line is obtained from Williams-Watts equation.
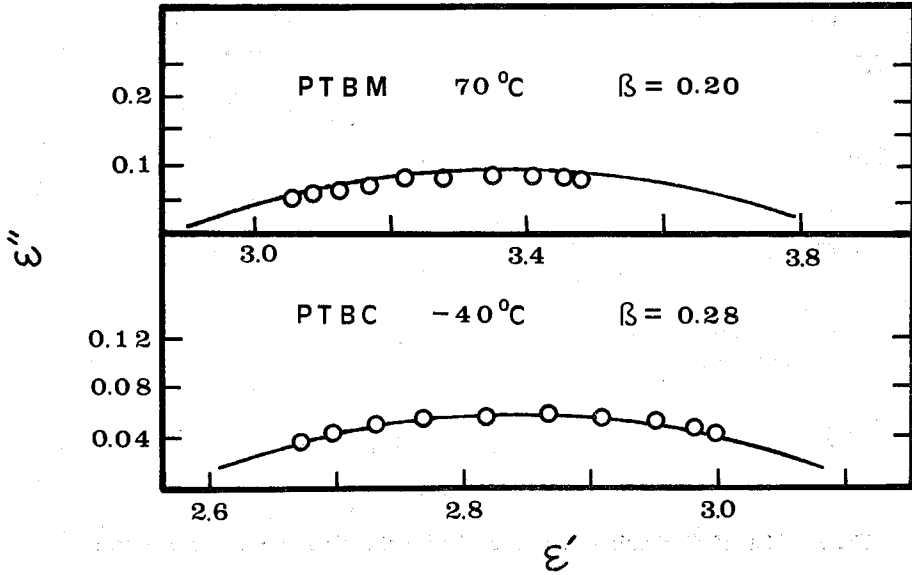
Fiy. 5. Cole-Cole plots for β relaxation. The solid line is obtained from
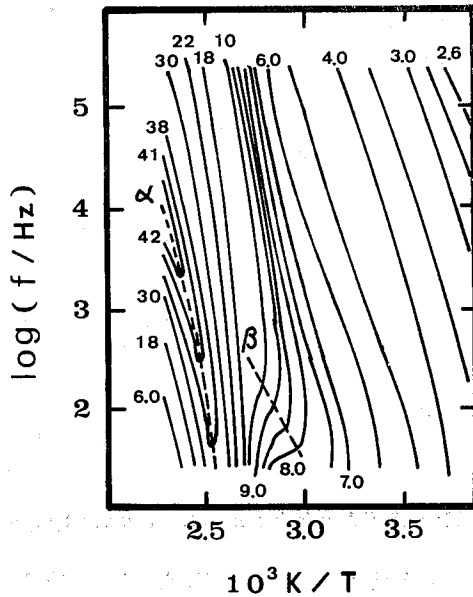Cole-Cole⸮equation.

Fig. 6. Contour map of ε'' against log f and $1/T$ in PTBM.
The figures on contour lines are the values of ε'' in
order of 10^{-2}.

sion. We think that the distribution of relaxation time in polymeric system can be qua-
litatively understood from contour map of ε''–frequency–temperature. Figure 6 shows
contour map of ε'' against logarithm of frequency, log f, and reciprocal of temperature,
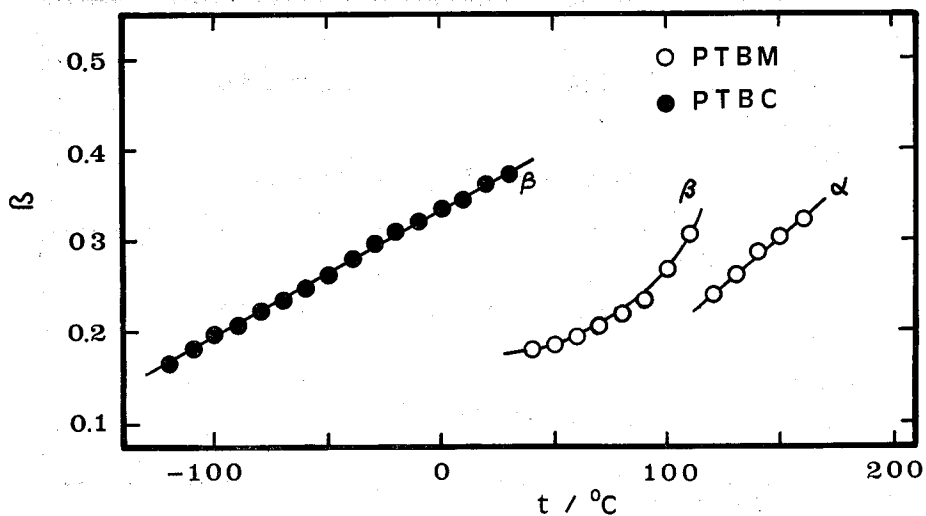
(213)

Fig. 7. Plots of distribution parameter of relaxation time, β, versus temperature.
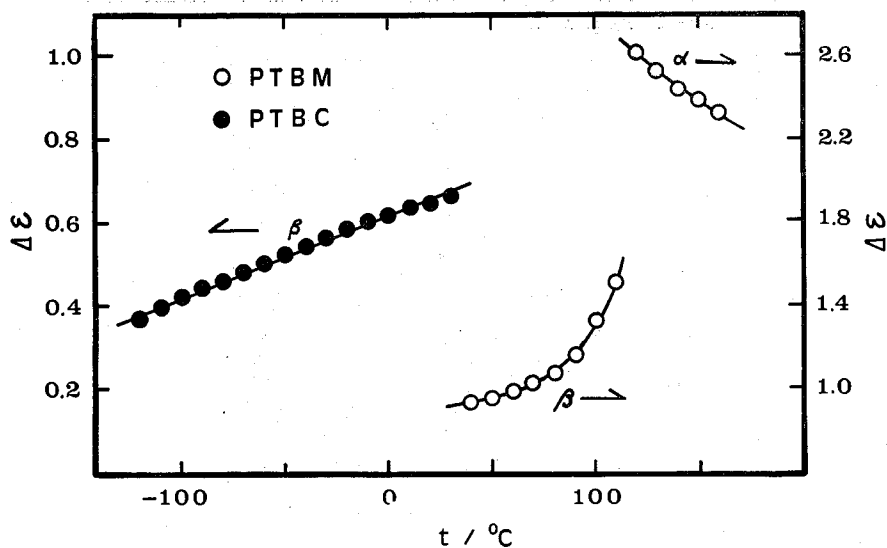

Fig. 8. Plots of dielectric increment, $\Delta\varepsilon$, versus temperature.

$1/T$, for PTBM. The theoretical base for the distribution of relaxation time is only on ε''–log f plots. Since the Arrhenius plots of the α relaxation are non–linear and obey the WLF equation, it seems to be resonable that the α relaxation is non–symmetrical. This situation may indicate a new way on discussing the dielectric mechanisms of polymer.

Distribution parameter, β, and dielectric increment, $\Delta\varepsilon$, for the relaxations are shown as a function of temperature in Figs. 7 and 8, respectively. Distributions of relaxation times are considerably broad for both α and β relaxations. The difference of chemical

structure between PTBM and PTBC are only in the substituted position of methyl group and the dipole moment of both polymers comes mainly from the ester group. Actually, the values of $\Delta\varepsilon$ for the β relaxation show little difference between PTBC and PTBM. As temperature is increased, the values of $\Delta\varepsilon$ increase in the β relaxation and vice versa in the α relaxation. This variation suggests that the local molecular motion of the ester group locked in the polymer matrix is gradually released with increasing temperature to T_g, and that above T_g, the orientation of the polar segments responsible for the α relaxation towards the applied electric field is disturbed by thermal fluctuation with increasing temperature.

In conclusion, this work indicates that the backbone chain of PTBC is much stiffer in the solid state, compared with that of PTBM, which is caused by the steric hindrance between β-methyl group and tert-butyl group. This conclusion supports Nagasawa et al's results in the dilute solution.

ACKNOWLEDGEMENT

REFERENCES

(1) I. Nada, T. Imai, T. Kitano and M. Nagasawa, *Macromolecules*, **14**, 1303 (1981).
(2) I. Noda, Y. Yamamoto, T. Kitano and M. Nagasawa, *Macromolecules*, **14**, 1306 (1981).
(3) Y. Muroga, I. Sakuragi, I. Noda and M. Nagasawa, *Macromolecules*, **17**, 1844 (1984).
(4) E. A. W. Hoff, D. W. Robinson and A. H. Willboun, *J. Polym. Sci.*, **18**, 161 (1955).
(5) J. Heijboer, *Makromol. Chem.*, **35A**, 86 (1960).
(6) G. P. Mikhailov, L. L. Burshtein and L. V. Krasner, *Vysokomolekul. Soedin.*, **7**, 870 (1965).
(7) M. C. Shen and J. D. Strong, *J. Macromol. Sci. (Phys.)*, **B1(1)**, 15 (1967).
(8) N. G. McCrum, B. E. Read and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids*, Wiley, New York, 1967, Chap. 8.
(9) T. Kitano, T. Fujimoto and M. Nagasawa, *Macromolecules*, **7**, 719 (1974).
(10) Y. Muroga, I. Noda and M. Nagasawa, *Macromolecules*, **13**, 1981 (1980).
(11) M. Kozhokaryu, V. S. Sakazka and K. G. Berdnikova, *Vysokomolekul. Soedin.*, **8**, 1063 (1967).
(12) N. Koizumi and S. Yano, *Bull. Inst. Chem. Res., Kyoto Univ.*, **47**, 320 (1969).
(13) T. Suzuki, K. Adachi and T. Kotaka, *Polymer J.*, **13**, No. 4, 385 (1981).
(14) K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1941).
(15) G. Williams and D. C. Watts, *Trans. Faraday Soc.*, **66**, 80, (1970).
(16) G. Williams, D. C. Watts, S. B. Dev and A. M. North, *Trans. Faraday Soc.*, **67**, 1323 (1971).
(17) G. P. Mikhailov, *Physics of non-Crystalline Solids*, North Holland, Amsterdam, p. 270 (1965).
(18) G. P. Mikhailov, A. M. Lobanov and H. A. Shevelev, *High Mol. Wt. Compds.*, **3**, 794 (1961).