

Dielectric γ Relaxation in Polyethylene at Low Temperature

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Synopsis

Dielectric γ relaxation in polyethylene with various degrees of branching and/or with various heat treatments has been measured in the ranges of frequency 10 – 10^4 Hz and temperature -90 to -130°C . The difference between the dispersion maps obtained from the frequency dependence of the dielectric loss and from the temperature dependence suggests that the temperature dependence of the relaxation intensity in polyethylene is not negligible. With an increase in crystallinity owing to the decrease in branching, the relaxation time shifts to longer time or higher temperature side and the activation energy increases steeply, whereas the quite opposite tendency was observed for the heat treated polyethylene with different crystallinity. The distribution of relaxation times becomes narrower with increasing temperature. At higher temperatures, the distribution in the specimens with various degrees of branching becomes narrower with the increase in the crystallinity, whereas in the specimens with various heat treatments, the dependence of the distribution on crystallinity tends to cease. Defects in the crystalline phase increase with an increase in branching and in crystallinity through heat treatments, and the dielectric γ relaxation in polyethylene differs depending on the branching and/or heat treatments.

INTRODUCTION

A dielectric relaxation process in polyethylene at room temperature in the microwave region is observed in the vicinity of 1 GHz and referred to as γ relaxation. The author has proposed a quantitative relation between the absorption intensity of the relaxation process and several factors affecting the relaxation process.¹ He has also reported on the crystallinity dependence of the absorption intensity in polyethylene.²

Although the relaxation process is assumed to be multiple,^{3–8} and consists of three components ascribed to motions of polar groups in (1) the amorphous phase, (2) defects in the crystalline phase, and (3) the cilia attached to the chain-folded surfaces of crystallites in polyethylene, it is difficult to separate it into each component because of very close existence. The γ process may be regarded as a single relaxation process attributed to polar groups with somewhat of a wide distribution of relaxation times. This concept depicts an outline of the relaxation behavior of polyethylene.

In this article, dielectric γ relaxation behavior of polyethylene with various degrees of branching and/or with various heat treatments is investigated at low temperature.

EXPERIMENTAL

Specimens

Polyethylene is often oxidized for ease of measurement of dielectric loss; the structure of polyethylene is liable to change when an excess of oxygen atoms is introduced into the molecular chains of polyethylene during oxidation. Also, antioxidants and residual catalysts in polyethylene affect the loss. The effects of antioxidant (less than 0.1 wt % of Ionox 330 or Antage BHT and less than 200 ppm of residual catalyst in medium-pressure process polyethylenes) on the loss were negligible in preliminary experiments. The polyethylenes with antioxidant and residual catalyst not affecting the loss were used as specimens. The greatest degree of branching in the specimens was 41 per 1000 carbon atoms of the main chain, and the least almost zero. The degree of branching was estimated from the number of methyl groups which were calculated from 1378 cm^{-1} of characteristic absorptions for methyl groups.¹ The polyethylene specimens with various degrees of branching were prepared by pressing at 170°C for 1 min after degassing for 1 min, then cooling under a water press. The specimens with various heat treatments were prepared by cooling from 145 to 115°C at a uniform cooling rate after melting of polyethylene at 170°C , then cooling from 115°C to room temperature without control at pressures below 2×10^{-5} torr. The shape of the specimens was a disk 7 cm in diameter and 1 mm thick. Two pieces of aluminum foil were attached to both faces of the disk to form a pair of electrodes.

Methods

The densities of the specimens were measured at 23°C with a density-gradient tube filled with an isopropyl alcohol-water mixture.

The degrees of crystallinity, χ_w , were estimated from the densities as 1.014 g/cm^3 for the crystalline phase of polyethylene and 0.850 g/cm^3 for the amorphous phase.

The dielectric losses were measured with a capacitance bridge (type 1621, made by General Radio) in the range of 10 – 10^4 Hz in frequency and -95 to -130°C in temperature, in some cases -77 to -190°C .

RESULTS

The frequency dependences of the loss expressed in terms of $\tan \delta$ for polyethylene with 41 branches per 1000 carbon atoms of the main chain at various temperatures are shown in Figure 1. With a decrease in temperature, the peak frequency (f_{\max}), at which $\tan \delta$ becomes a maximum on a $\tan \delta$ -vs.- $\log f$ plot (where f is frequency), shifts toward lower frequency, and the intensity of the relaxation becomes weaker. This tendency does not change with the degree of branching. The temperature dependences of the loss with the data given in Figure 1 are shown in Figure 2. With a decrease in frequency, the peak temperature (T_{\max}), at which $\tan \delta$ becomes a maximum on a $\tan \delta$ -versus-temperature plot, shifts toward lower temperature, and the intensity of the relaxation becomes weaker. This tendency does not change with the degree of branching,

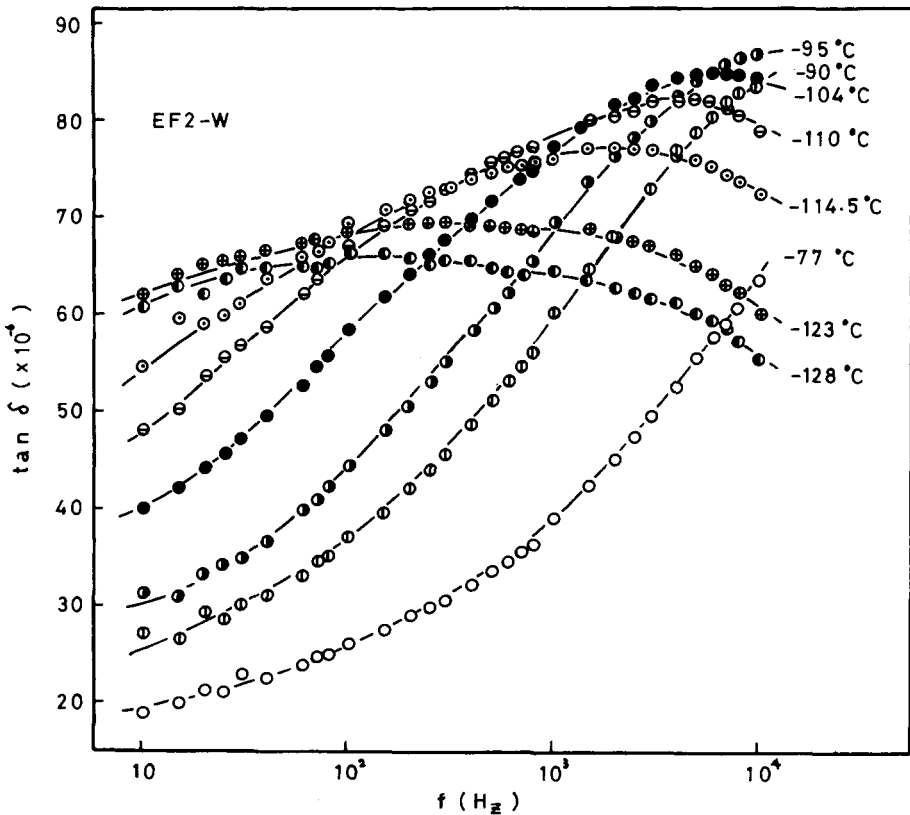


Fig. 1. Frequency dependence of dielectric loss ($\tan \delta$) at various temperatures for polyethylene.

as in the case of the frequency dependence of the loss. However, there is a difference between the dispersion maps obtained from the frequency dependence of the loss and those from the temperature dependence. The two kinds of dispersion maps in polyethylene with 41 branches are shown in Figure 3. The dispersion map from the temperature dependence is present on the side of lower frequency or higher temperature in comparison with that from the frequency dependence. The magnitude of the discrepancy between the two maps becomes larger with decreasing temperature. This tendency does not change with the degree of branching.

The dispersion maps from the frequency dependences of the losses at various temperatures in polyethylenes with various degrees of branching are shown in Figure 4. With increase in the degree of branching, f_{\max} tends to shift toward higher frequency or lower temperature, and the slope of the f_{\max} -vs.- $1/T$ plot tends to become gentle.

The activation energies for orientation of dipoles in polyethylenes with different densities ascribed to change in the degree of branching are calculated from Figure 4 and are shown in Table I. The activation energy increases rapidly with a decrease in the degree of branching.

Figure 5 shows the dispersion maps from the frequency dependences of the losses at various temperatures for the polyethylenes crystallized by various heat

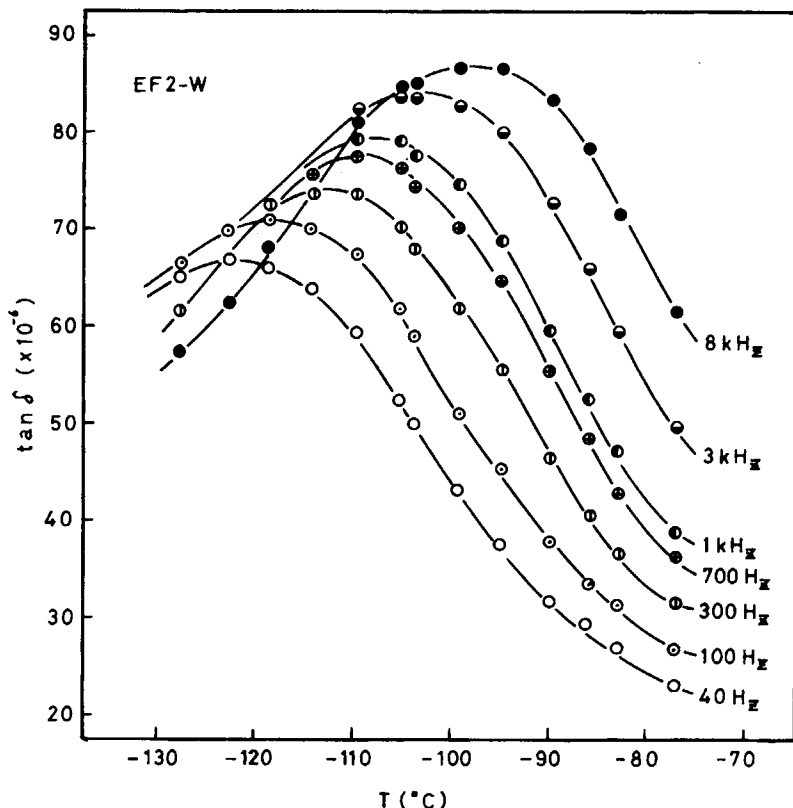


Fig. 2. Temperature dependence of dielectric loss at various frequencies for polyethylene.

TABLE I
Activation Energies and Densities for Polyethylene with Various Degrees of Branching

Sample	ρ , g/cm ³	Degree of crystallinity, ^a χ_w	Degree of branching, ^b CH ₃ /1000C	ΔH^* , kcal/mole
E39	0.947	0.635	0.00	12.1
E29	0.948	0.638	0.07	9.8
E6	0.940	0.592	4	8.0
E22	0.930	0.532	12	6.9
EG3	0.927	0.510	17	6.2
EG2	0.925	0.498	24	5.9
EF2	0.920	0.467	41	5.3

^a Weight fraction of crystal parts.

^b Number of branching per 1000 carbon atoms.

treatments. With increase in the crystallinity, f_{\max} shifts toward high frequency or lower temperature, and the slope of the f_{\max} -vs.- $1/T$ plot becomes gentle. The activation energies in polyethylenes with various heat treatments decrease linearly with increasing density (Table II).

On application of the Cole-Cole empirical relationship, the loss factor (ϵ'') is expressed as follows:

$$\epsilon'' = \frac{1}{2} (\epsilon_0 - \epsilon_\infty) \frac{\sin(\beta\pi/2)}{\cosh \beta x + \cos(\beta\pi/2)} \quad (1)$$

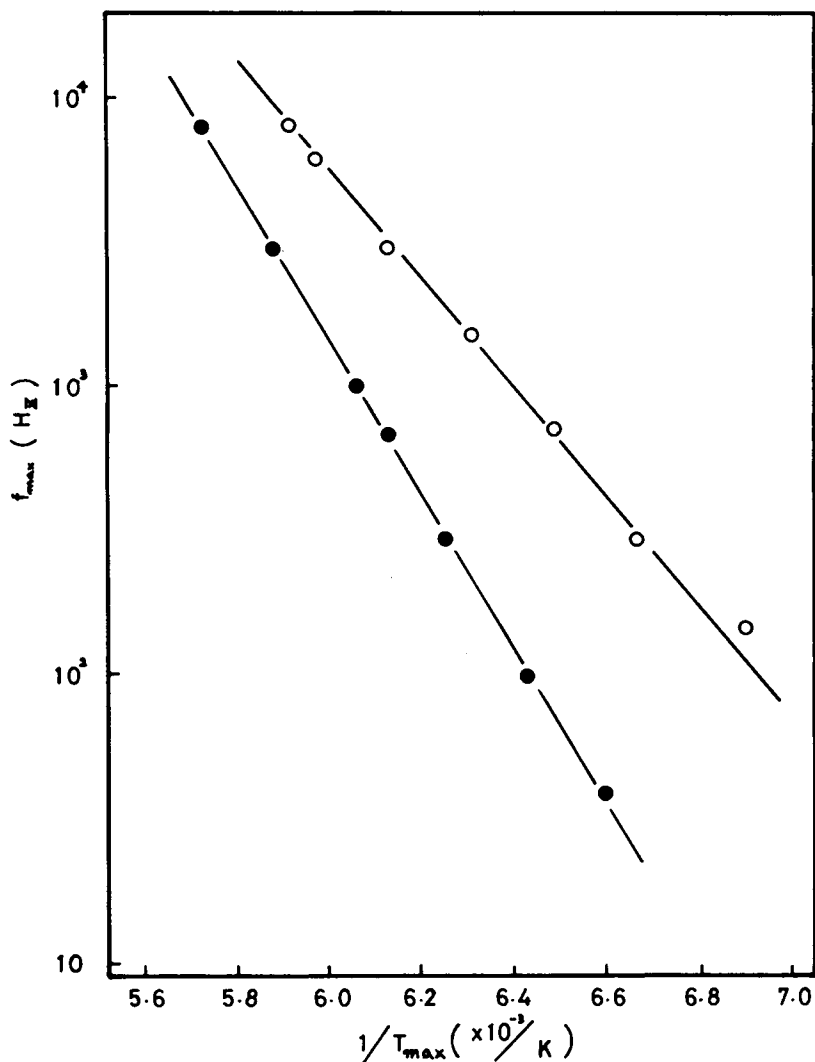


Fig. 3. Dielectric dispersion maps estimated from frequency dependence and temperature dependence for polyethylene: (O) from frequency dependence; (●) from temperature dependence (PE:EF2-W).

TABLE II
Activation Energies and Densities for Polyethylene with Various Heat Treatments

Sample	ρ , g/cm ³	χ_w	ΔH^* , kcal/mole
E39-1	0.947	0.635	12.1
E39-2	0.958	0.697	10.1
E39-3	0.968	0.753	8.6

where x is given by $x = \ln(\omega\tau)$, ω is angular frequency, ϵ_0 is the dielectric constant at $\omega = 0$, ϵ_∞ is the constant at $\omega = \infty$, τ is relaxation time, and β is Cole-Cole's parameter. Since the equation of $\epsilon''/\epsilon''_{\max} \approx \tan \delta/\tan \delta_{\max}$ holds for low-loss

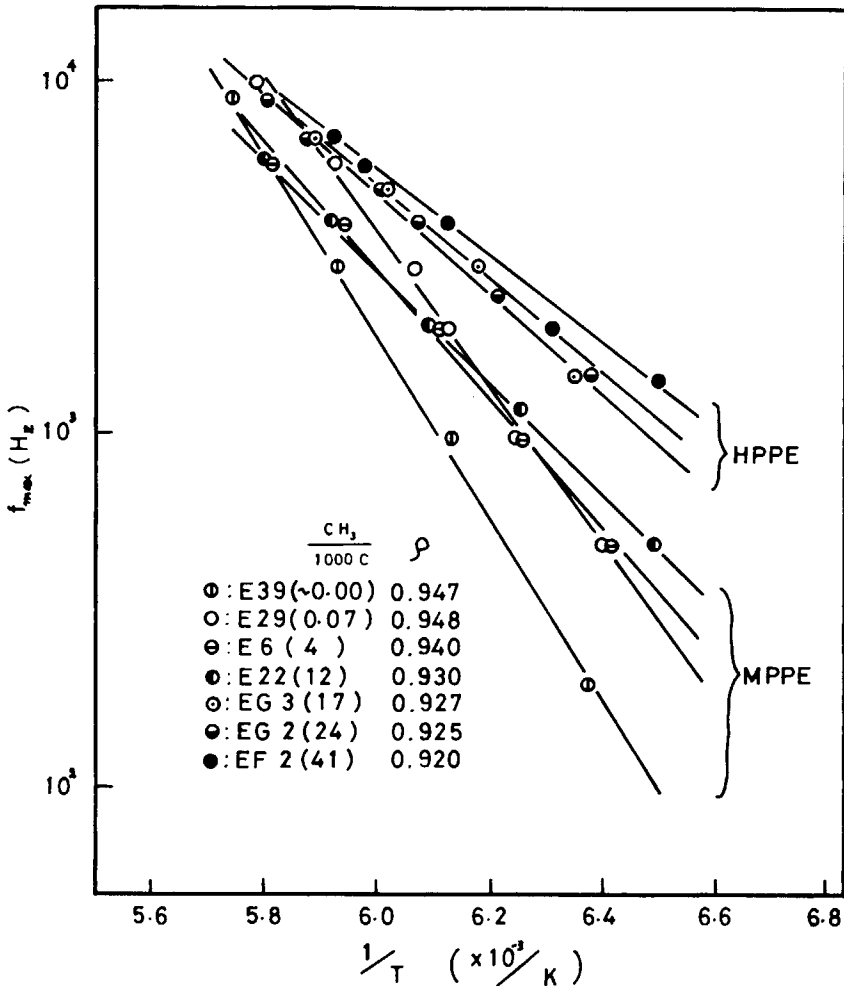


Fig. 4. Dielectric dispersion maps for polyethylene with various degrees of branching. HPPE: high-pressure process polyethylene; MPPE: medium-pressure process polyethylene.

polyethylenes by use of the maximum of dielectric loss factor (ϵ''_{\max}) and that of the loss tangent ($\tan \delta_{\max}$), the following relationship exists between $\tan \delta / \tan \delta_{\max}$ and f/f_{\max} :

$$\frac{\tan \delta}{\tan \delta_{\max}} = \frac{1 + \cos(\beta\pi/2)}{\cosh[\beta \ln(f/f_{\max})] + \cos(\beta\pi/2)} \quad (2)$$

Accordingly, parameter β can be estimated as follows: First, the ratios of $\tan \delta / \tan \delta_{\max}$ calculated from the observed values and those from the calculated ones with eq. (2) for various values of β are plotted against $\ln(f/f_{\max})$. Second, the graph for the observed values overlap the calculated, and the value of β for the curve from the calculated value which agrees with one from the observed is regarded as the value of β for the specimen. The observed values for β are in agreement (Fig. 6) with the calculated value from eq. (2).

The dependence of β on the degree of branching and temperature is shown in Figure 7. The value of β increases with increasing temperature. The de-

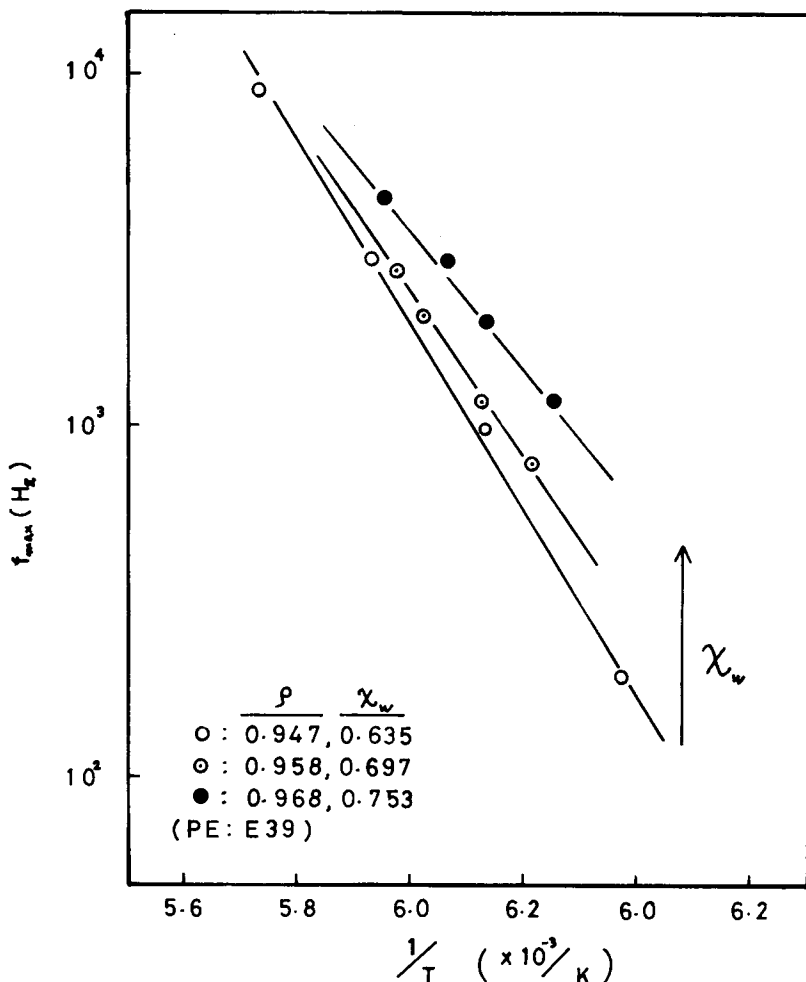


Fig. 5. Dielectric dispersion maps for polyethylene crystallized by various heat treatments.

pendence of β on the degree of branching becomes pronounced with increasing temperature, and the value of β decreases with increase in the degree of branching. The changes in β for specimens with various degrees of crystallinity depending on heat treatments are shown in Figure 8. With increasing temperature, β increases in a manner similar to that for the branching dependence of β (Fig. 7), while the dependence of β on crystallinity diminishes.

DISCUSSION

The relaxation intensity of the γ relaxation process in polyethylene below -90°C changes appreciably with temperature. On application of Onsager's theory⁹ to the γ relaxation process ascribed to polar groups in polyethylene, the intensity of the dispersion ($\epsilon_0 - \epsilon_\infty$) is expressed as follows:

$$\epsilon_0 - \epsilon_\infty = \frac{4\pi}{3kT} \frac{3\epsilon_0}{2\epsilon_0 + \epsilon_\infty} \left(\frac{\epsilon_0 + 2}{3} \right)^2 N\mu_0^2 \quad (3)$$

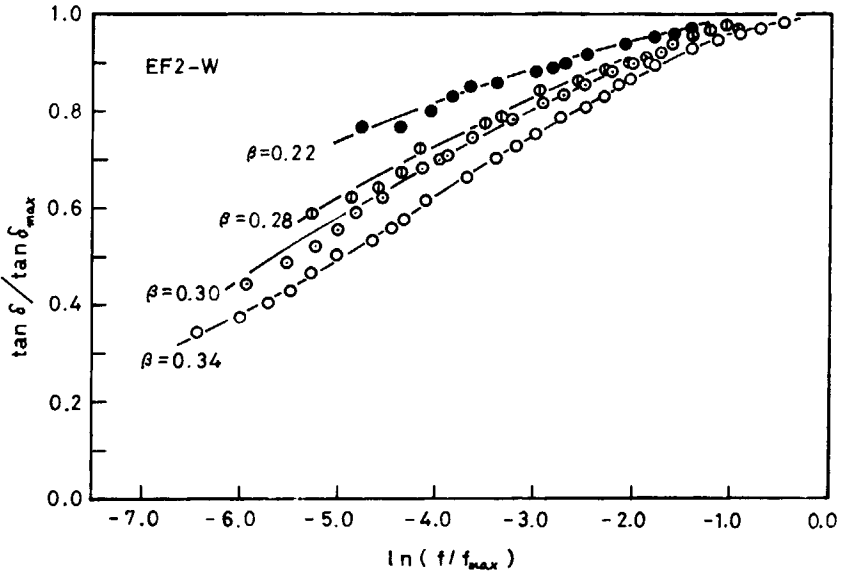


Fig. 6. Normalized frequency dependence of dielectric loss at various temperatures for polyethylene: (O) -100.5°C ; (\odot) -104.0°C ; (\otimes) -108.5°C ; (\bullet) -122.5°C ; (—) calculated from eq. (2).

where k is Boltzmann's constant, T is absolute temperature, N is the number of polar groups per unit volume, and μ_0^2 is the mean-square value of the permanent dipole moment of a polar group. The intensity of the dispersion is proportional to the reciprocal of the absolute temperature, as seen from eq. (3). In the case of negligibly low temperature dependence of the relaxation intensity, the relaxation time τ_a is often expressed as follows:

$$\tau_a = \tau_0 \exp(\Delta H^*/RT) \quad (4)$$

where ΔH^* is the activation energy for orientation of the dipoles, R is the gas constant, and τ_0 is relaxation time at very high temperature. The relaxation time and the activation energy can be estimated from the change in f_{\max} on the absorption curves against temperatures.¹⁰⁻¹⁴ When the complex dielectric constant is expressed in terms of the Cole-Cole relationship,¹⁵ the dielectric constant ϵ' and the loss factor ϵ'' are expressed as follows:

$$\epsilon' = \epsilon_{\infty} + \frac{1}{2} (\epsilon_0 - \epsilon_{\infty}) \left(1 - \frac{\sinh \beta x}{\cosh \beta x + \cos(\beta\pi/2)} \right) \quad (5)$$

$$\epsilon'' = \frac{1}{2} (\epsilon_0 - \epsilon_{\infty}) \frac{\sin(\beta\pi/2)}{\cosh \beta x + \cos(\beta\pi/2)} \quad (6)$$

The relaxation time of a single relaxation (Debye relaxation), τ_D , is calculated from $\partial \epsilon'' / \partial f = 0$ at $\beta = 1$:

$$\tau_D = 1/2\pi f_{\max} \quad (7)$$

where f_{\max} is the frequency at the loss maximum in an ϵ'' -vs.- f plot. The relaxation time at the loss maximum in a $\tan \delta$ -vs.- f plot, τ_f , is calculated from $\partial \tan \delta / \partial f = 0$; the following relation is obtained between τ_f and τ_D :

$$\tau_f = \left(\frac{\epsilon_{\infty}}{\epsilon_0} \right)^{1/2\beta} \tau_D \quad (8)$$

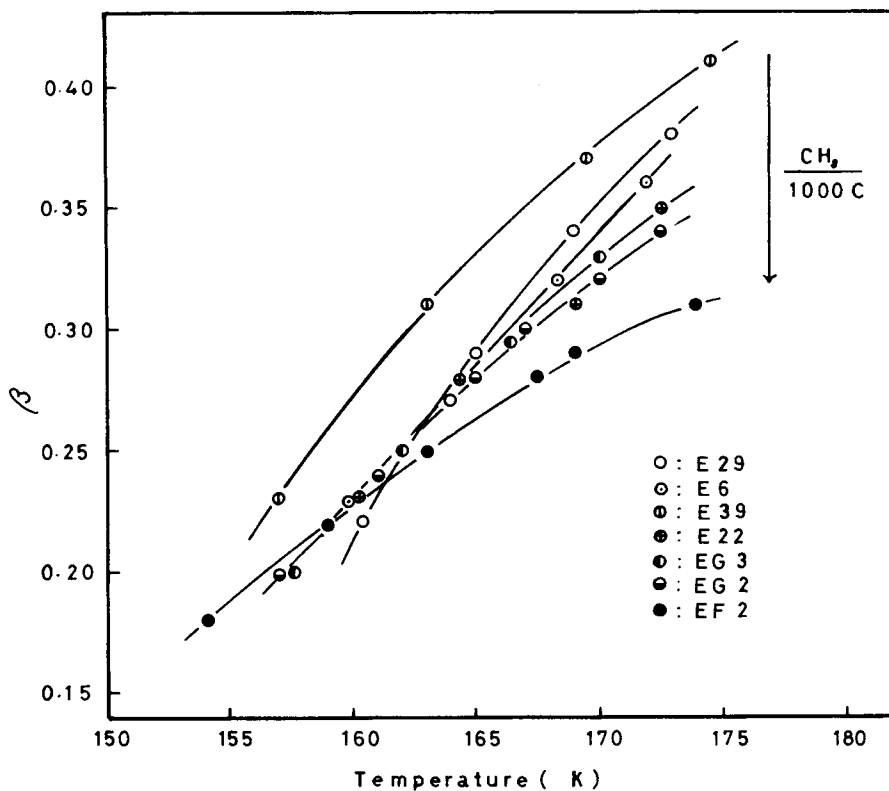


Fig. 7. Temperature dependence of β for polyethylene with various degrees of branching.

On the other hand, the relaxation time can be estimated from the temperature dependence of $\tan \delta$. However, the relaxation time at the loss maximum in a $\tan \delta$ -vs.-temperature plot, τ_t , is not in agreement with τ_f except for the case of $\partial(\epsilon_0 - \epsilon_\infty)/\partial T \approx 0$. The dispersion map estimated from the temperature dependence differs from the one estimated from the frequency dependence in polyethylene at low temperature. The activation energy (Fig. 3) estimated from the frequency dependence of $\tan \delta$ is 8.3 kcal/mole (Fig. 3); that from the temperature dependence is 11.9 kcal/mole. The discrepancy between activation energies is nearly 4 kcal/mole.

The temperature dependence of the relaxation intensity in polyethylene is not negligible, and it may be unsuitable to discuss the relaxation times, the distributions of relaxation times, and the activation energies on the basis of the temperature dependence of the absorption intensity in polyethylene at low temperature.

The fact that the activation energy increases with a decrease in the degree of branching (Table I) indicates that molecular chains in polyethylene become difficult to move with a decrease in the branching. Such experimental results have been reported by Kline.¹⁶ According to Illers⁵ and Wada,¹⁷ the γ relaxation process with f_{\max} on the high-frequency side is assigned to a relaxation process arising from defects in the crystalline phase and that on the low-frequency side is assigned to that arising from local mode relaxation in the amorphous phase. Both relaxation processes become similar with increasing temperature. Each

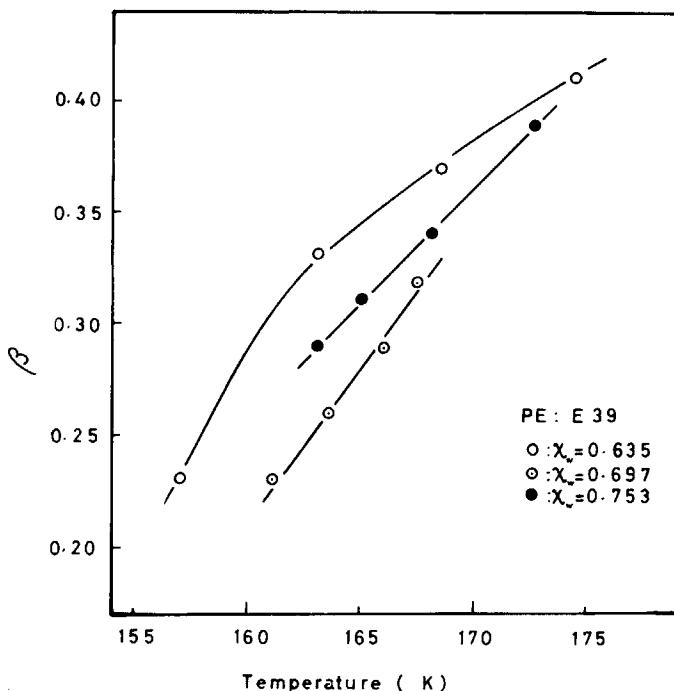


Fig. 8. Temperature dependence of β for polyethylene crystallized by various heat treatments.

frequency dependence curve for $\tan \delta$ corresponding to the plots in Figures 4 and 5 has a maximum. The peak frequency f_{\max} shifts with degree of branching or heat treatment; it is difficult to distinguish between the relaxation process due to the defects and that due to the local mode. Therefore, if the relaxation process is regarded as a relaxation process consisting of two components, due to defects and local mode, it may be regarded as follows: With increase in the degree of branching, the component due to defects tends to increase more than an increase in that one due to the local mode, and the activation energy decreases.

The influence of the crystallinity in polyethylene on the relaxation behavior is not so simple. The relaxation times and activation energies in melt-crystallized polyethylenes with various degrees of branching increase with increasing crystallinity due to a decrease in the degree of branching (Table I), while those in polyethylenes with various heat treatments decrease with increasing crystallinity (Table II). The crystallinity dependence in polyethylenes with various heat treatments is shown in Figure 5. Although different density ranges are involved (Figs. 4 and 5), the relaxation mode changes gradually from the local mode to the mode because of the defects with increasing crystallinity, according to Illers. This suggests that heat treatments lead to an increase in the defects with thickening of the lamellas. Such a change in the relaxation behavior has been observed by Sinnott,¹⁸ who investigated relaxations in the single crystals of polyethylene. From the results above, the crystallinity dependences of the relaxation behavior in polyethylene below -90°C differ considerably depending on the degree of branching and/or the heat history of the polyethylene specimens.

The differences of the logarithms of the relaxation times due to the degrees

of branching or the heat treatments, though not explicit from Figures 4 and 5, decrease with increasing temperature. The temperature at which the relaxation times of specimens with various degrees of branching and heat treatments become similar is a temperature between about -80 and 90°C (Figs. 4 and 5). This temperature corresponds to a glass transition temperature reported by Tobolsky¹⁹ and Boyer²⁰ ($T_g = 81^\circ\text{C}$). If their value is accepted as the glass transition temperature, the fact that polyethylenes with various degrees of branching and heat treatments have a similar relaxation time may be interpreted as follows: The molecular segments, consisting of the order of several monomer units and causing the relaxation process in polyethylene, can easily move at temperatures above T_g where segmental molecular chains of several tens in monomer unit start to move. At such a temperature, the interaction between the molecular chains containing polar groups in the defects and the chains adjacent to the defects becomes weak, and their restraint potentials in the amorphous phase and in the defects in the crystalline phase would become similar. The most frequent relaxation times for both relaxation processes due to the defects and the local mode become similar; and in addition, the difference between the relaxation times for specimens with various degrees of branching and those with various heat treatments may become small. The activation energy in that case is estimated at about 5 kcal/mole. Although the distributions of the relaxation times become narrower with increasing temperature, they have a certain distribution corresponding to the degrees of branching (Fig. 7). The temperature where the relaxation time estimated from the frequency dependence of $\tan \delta$ becomes almost the same as the one estimated from the temperature dependence on Figure 3 is about -85°C and is approximately consistent with the temperature where the difference disappears between the relaxation times of specimens with various degrees of branching and those with various heat treatments. These facts suggest that the temperature dependence of the relaxation intensity in polyethylene becomes negligible at temperatures above T_g because the discrepancy between τ_f and τ_T arises from the temperature dependence of the intensity.

The temperature dependences of the distribution of relaxation times in polyethylenes with various degrees of branching are shown in Figure 7. The value of β decreases with increase in the degree of branching, and the difference of β depending on the degree of branching becomes explicit with increasing temperature, in spite of the fact that the two most frequent relaxation times corresponding to the local mode and the mode due to the defects converge with increasing temperature (Fig. 4). On the other hand, the difference of β depending on heat treatment decreases with increasing temperature (Fig. 8). This temperature dependence of β is completely contrary to that with various degrees of branching. Although interpretations may be drawn, from Figures 4 and 7, that the segmental molecular chains in defects in crystalline phase have more various relaxation times in comparison with the chains in amorphous phase and also the sizes and/or shapes of the defects become inhomogeneous with increase in the degree of branching, and, from Figure 8, that the sizes of the defects become large and the heights of the potential barrier, restraining the segmental motion of the molecular chains, become low and homogeneous with increasing temperature, corroborative data have not been obtained. In either case, β increases and the distribution of the relaxation times become narrower with increasing temperature. This is caused by the fact that the thermal motion of the segmental

molecular chains becomes active with increasing temperature and the differences between the relaxation times due to the sizes and/or amounts of the defects in the crystalline phase become small.

CONCLUSIONS

The discrepancy between both dispersion maps estimated from the frequency dependence of $\tan \delta$ and from the temperature dependence of $\tan \delta$ in polyethylene increases with decrease in temperature. The distribution of relaxation times depends on temperature. According to Muller²¹ and Ishida,²² the data at different temperatures cannot be superimposed in the case where the shapes of the absorption curves change with temperature. The time-temperature reducibility is not applied to the relaxation process in polyethylene at temperatures below -80 to -90°C .

The γ relaxation behavior of polyethylenes may differ considerably depending on the degree of branching and heat treatments, even if they have the same densities. Up to the present time, the relaxation behavior of polyethylene with the same density has been often treated as the same; however, it is necessary to bear in mind the degree of branching and the heat history of the specimens in the discussing the relaxation behavior at low temperature.

In this article, the discussion of the relationships between the molecular chains in the amorphous phase or in defects in the crystalline phase and the restraint potential around the chains has not been beyond speculation. Although there are several studies^{3,23,24} on the relation between a restraint potential and motions of molecular chains in defects in crystallites, the general relationship is not yet clear. A method of neutron small-angle scattering²⁵ may become useful for detection of sizes and/or shapes of defects in the crystalline phase; the dielectric γ relaxation behavior of polyethylene will become clearer when the relationship is elucidated.

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