Change of the amorphous state by heat treatment below the glass transition temperature

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This study was undertaken to elucidate the state of a polymer in the amorphous state through a change of motion of the molecular chain caused by heat treatment below the glass transition temperature. From dielectric measurements of amorphous poly(ethylene terephthalate) heat-treated below T_g, it was found that the average relaxation time, the distribution of relaxation time and the dielectric strength increase with increase of heat treatment. From these results, it was concluded that the amorphous state becomes more random by heat treatment.

Keywords Amorphous; local mode; relaxation; dielectric; heat-treatment; poly(ethylene terephthalate)

INTRODUCTION

In the study of the structure of the amorphous state, most attention hitherto has been paid to the elucidation of the state of aggregation. However, as it has been revealed in recent years that the nature of materials in the amorphous state is considerably different from that of crystals, a number of studies on the control of material properties through control of the amorphous structure are being undertaken at present. Some models have been proposed regarding the structure of polymers in the amorphous region. They are (1) a one-phase model (random coil model[1-10]) in which the amorphous region is regarded as homogeneous; (2) a two-phase model[11-14] in which the amorphous region is considered to retain local order; and (3) other models[15-17]. However, it is still not known which model can explain the amorphous structure of polymers[18].

In our previous papers[19,20], we described measurements of i.r., density and rate of crystallization of poly(ethylene terephthalate) (PET) treated with heat below the glass transition temperature (T_g) and discussed, through the results, the state of amorphous PET. The present study was undertaken to elucidate the state of a polymer in the amorphous region through a change of motion of the molecular chain caused by heat treatment below T_g.

Two kinds of motion are known regarding the molecular motion of the main chain of a polymer. One is micro-Brownian motion above T_g and the other is local mode motion below T_g[21,22]. The latter is torsional vibration about the main chain and takes a locally semi-stable conformation. This motion is excited by heat to fairly large amplitude, which causes a large interaction among neighbouring molecular chains, and thus the motion is considerably damped. The range of propagation of the torsional vibration depends on the length of the main chain that retains order. According to Hayakawa and Wada[23], the length of the molecular chain retaining order affected the relaxation strength of local mode relaxation. The theory suggested that it seems reasonable to assume that the local mode relaxation reflects the state of the amorphous region. Therefore a change of the amorphous state caused by volume relaxation, which is a result of heat treatment below T_g, would alter the average relaxation time, the distribution of relaxation time and the relaxation strength of local mode motion, and consequently a change of the amorphous state may be found by observation of these factors.

EXPERIMENTAL

Sample preparation

Poly(ethylene terephthalate) (PET) film, 50 μm thick and supplied by Teijin Co., was used for the experiments. Examination by an Abbe refractometer revealed that the film was entirely isotropic. No crystals were observed in the film by X-ray analysis. An abnormal endothermic peak at T_g was not recognized in differential scanning calorimetry. The density and the area of abnormal endothermic peak at T_g of the sample simply increases with an increase in the treating time. This indicates that volume relaxation took place during the treatment. A piece of the PET film was placed in a sealed aluminium envelope, heated at 59°C (below T_g) for 123 h, 890 h or 3770 h and submitted to the measurement.

Dielectric measurement

Dielectric measurement for the frequency range between 20 and 10^5 Hz was carried out with a General Radio type 1620-A bridge, and an Ando Electric ultra low-

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frequency bridge TR-4 was employed for the measurement of the range between 20 and 10^{-1} Hz. The temperature range in the measurements was between zero and $-70°C$. The observed dielectric dispersion of PET in the temperature range was considered to be due to the damped motion of the molecular chain[24].

RESULTS AND DISCUSSION

Figures 1 and *2* show the frequency dependence of ε' and ε'' at various temperatures for the 3770 h heat-treated sample: ε' and ε'' are the real and imaginary components of the complex dielectric constant, respectively. *Table 1* shows the temperature dependence of $\varepsilon''_{\max}$ for various samples. Three significant figures on measurements of ε' and ε'' can be obtained under these experimental conditions. The curves of ε'' as a function of frequency are so broad and asymmetric (as shown in *Figure 2*) that they do not fit the Debye and Cole–Cole equations, these being symmetric curves.

It is said that the local mode process contains at least two superimposed loss processes[25,26], since this process of PET is broad and asymmetric as shown in *Figure 2*. But there is not enough evidence to support this contention. The mechanism of this process is considered to be one process due to the damped motion of the molecular chain[24]. We will publish a report of multiplicity on local mode relaxation of PET in the future.

Davidson–Cole's equation is used in the method of analysis for an asymmetric and one-process dispersion. *Figure 3* shows the frequency dependence of ε'' calculated by Davidson–Cole's equation at various β, which is constant in this equation. The values of ε'' are normalized as follows:

$$\Delta\varepsilon = 1 = \int_{\infty}^{\infty} \varepsilon'' \mathrm{d}(\omega\tau)$$

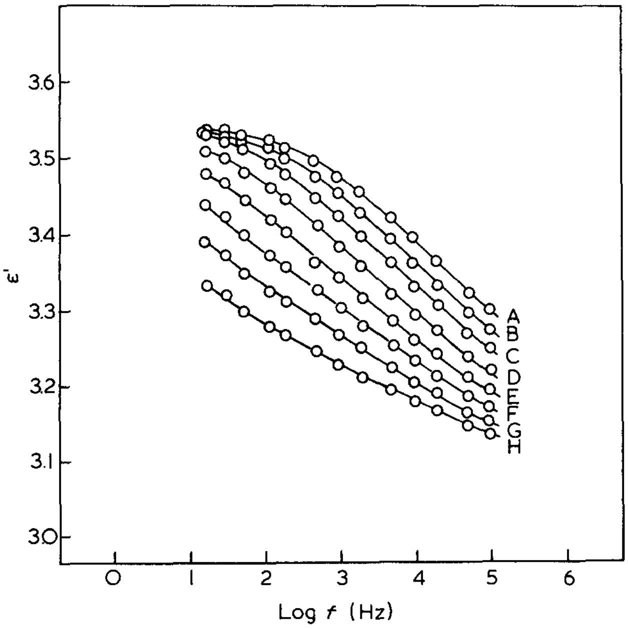

Figure 1 Frequency dependence of ε' at various temperatures for 3770 h heat-treated sample: curve A, 0°C; B, −10°C; C, −20°C; D, −30°C; E, −40°C; F, −50°C; G, −60°C; H, −70°C

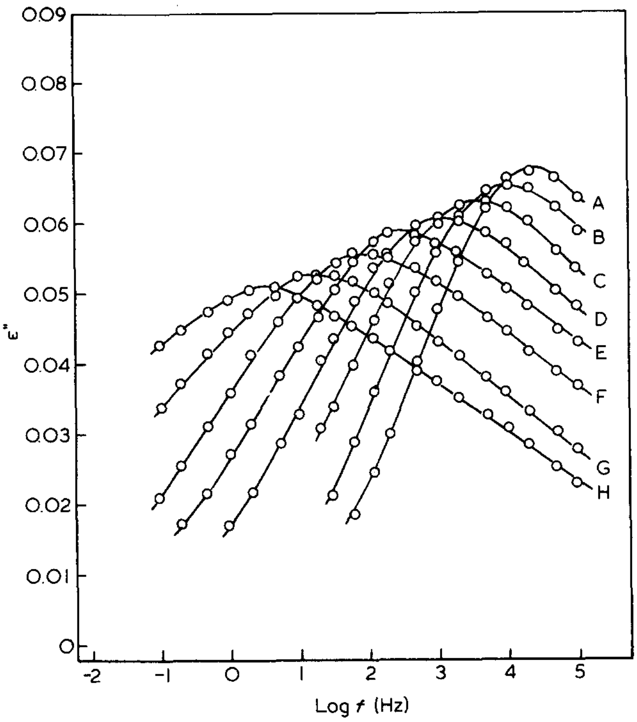

Figure 2 Frequency dependence of ε'' at various temperatures for 3770 h heat-treated sample: for symbols see *Figure 1*

Table 1 Temperature dependence of dielectric loss at absorption maximum ($\epsilon''_{\max}$)

Temperature (°C)	$\epsilon''_{\max}$			
	untreated	123 h	890 h	3770 h
0	0.0709	0.0698	0.0685	0.0675
−10	0.0686	0.0674	0.0664	0.0653
−20	0.0663	0.0645	0.0640	0.0630
−30	0.0635	0.0620	0.0616	0.0605
−40	0.0607	0.0600	0.0595	0.0580
−50	0.0580	0.0574	0.0575	0.0554
−60	0.0563	0.0547	0.0541	0.0530

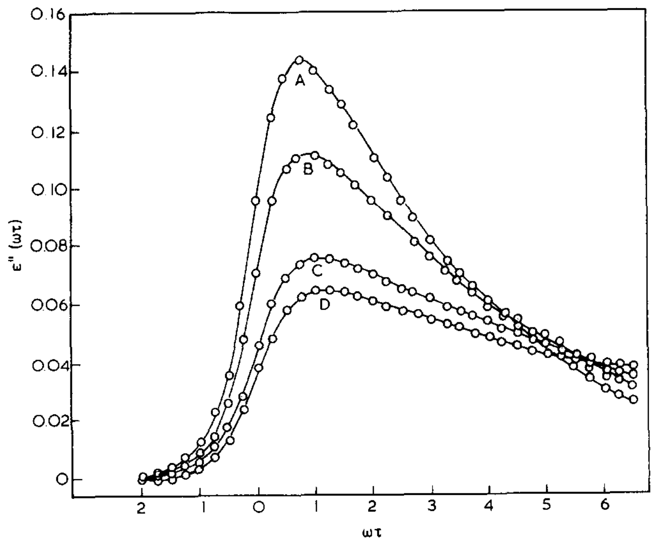

Figure 3 Frequency dependence of ε'' calculated by the Davidson–Cole equation at various β: curve A, 0.11; B, 0.95; C, 0.06; D, 0.05

where $\Delta\varepsilon$ is dielectric strength, ω is frequency and τ is relaxation time.

Comparing *Figure 2* with *Figure 3*, the high-frequency portions of these curves were fitted to Davidson–Cole's equation at adequately small β, but the low-frequency portions of these were not. The curves of Davidson–Cole's equation are steeper in the low-frequency region than the curves obtained. There is also Havriliak–Negami's equation[27] to represent the data. This equation is a general representation of the three known equations, i.e. Debye, Cole–Cole ($\varepsilon^* - \varepsilon_\infty = (\varepsilon_0 - \varepsilon_\infty)/(1 + (j\omega\tau)^\beta)$) and Davidson–Cole ($\varepsilon^* - \varepsilon_\infty = (\varepsilon_0 - \varepsilon_\infty)/(1 + j\omega\tau)^\beta$), and is described as follows[27]:

$$\varepsilon^* - \varepsilon_\infty = (\varepsilon_0 - \varepsilon_\infty)/[1 + (j\omega\tau)^{1-\alpha}]^\beta \qquad (1)$$

where ε^* = complex dielectric constant, ε_0 = the limiting low-frequency dielectric constant, ε_∞ = the limiting high-frequency dielectric constant, ω = frequency, τ = relaxation time, and $1-\alpha$ and β are constants which take a value between 0 and 1.

The complex plane plot of ε^* ($= \varepsilon' + j\varepsilon''$) is linear at small ε' and is an arc at large ε'. *Figure 4a* shows the result obtained at 10°C and the complex plot is an arc. The complex plane plot at low temperature is linear as shown in *Figure 4c*, namely, it is linear at small ε'. Havriliak–Negami's equation is in very good agreement with the observed dispersion. Limits ε_0 and ε_∞ can be obtained as crossover points of the real axis and the extrapolated lines towards the high- and low-frequency sides respectively. Relaxation strength $\Delta\varepsilon$ ($\varepsilon_0 - \varepsilon_\infty$) is given by calculation. *Figure 5* shows the relationship between measurement temperature and $\Delta\varepsilon$ in untreated and heat-treated samples, and *Figure 6* shows the change of $\Delta\varepsilon$ at −40°C

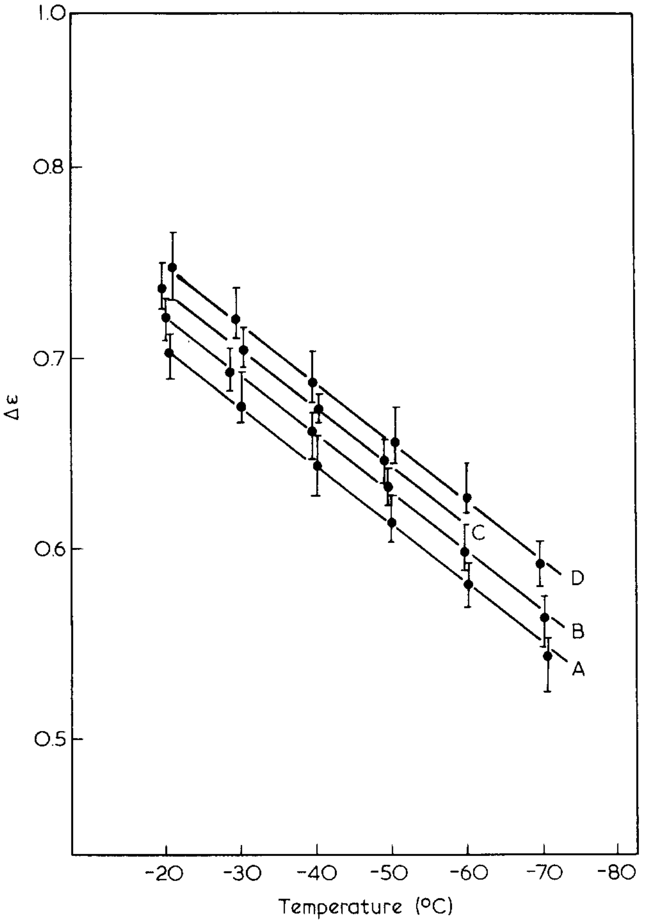

Figure 5 Temperature dependence of dielectric strength ($\Delta\varepsilon$). Heat-treated time: curve A, untreated; B, 123 h; C, 890 h; D, 3770 h

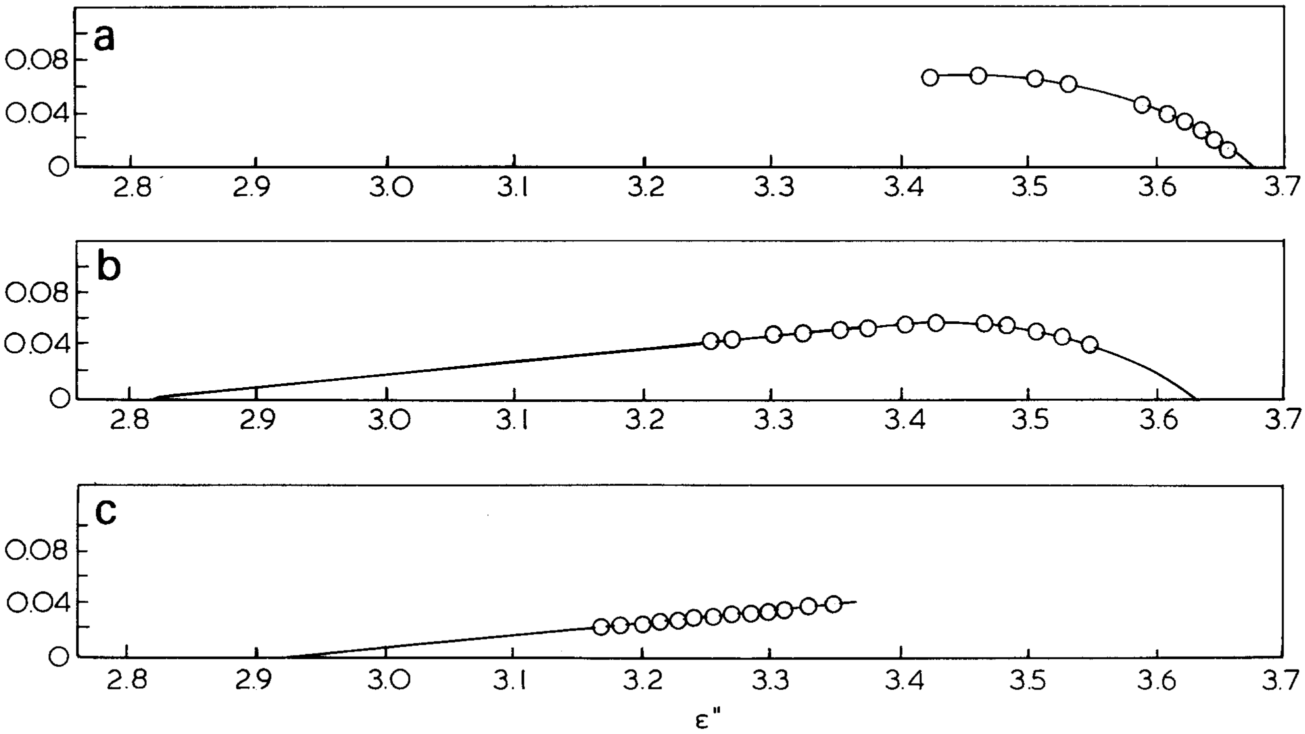

Figure 4 Loci in the complex plane of the skewed arc function for 3770 h heat-treated sample. (a) The complex plane plot is an arc at measured temperature 10°C. It cannot be obtained for lack of ε_∞. (b) The plot shows that ε_0 and ε_∞ can be obtained as crossover points of the real axis at adequate measured temperature (for example, at −40°C). (c) The complex plane plot is linear at measured temperature −80°C. It cannot be obtained for lack of ε_0

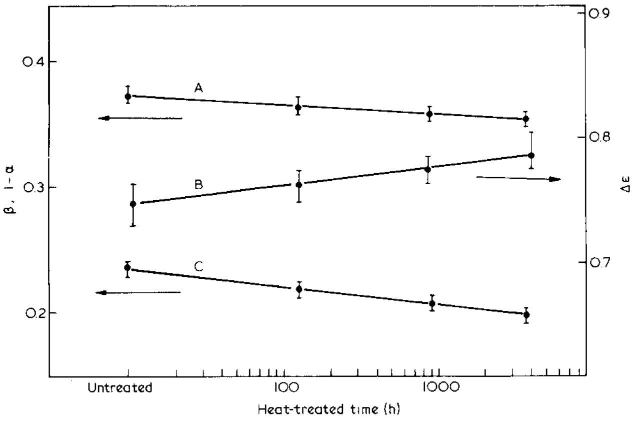

Figure 6 Change of dielectric strength ($\Delta\varepsilon$) and parameters of the Havriliak–Negami equation ($1-\alpha$ and β) at −40°C with heat-treated time: curve A, $1-\alpha$; B, $\Delta\varepsilon$; C, β

against the treating time. It can be seen from *Figures 5* and *6* that $\Delta\varepsilon$ decreases with decrease in measurement temperature and that $\Delta\varepsilon$ increases with increase in heat treatment time at constant temperature. Hayakawa and Wada reported that an increase in the number of atoms, which correlatively move in the main chain, intensifies the relaxation strength[23,24]. On the basis of the reports, we may reasonably assume that intensification of relaxation strength by heat treatment indicates an increase in the number of atoms correlatively moving in the main chain. In other words, the heat treatment below T_g resulted in volume relaxation and removal of distortion in the molecular chain in the frozen state, and thus the number of correlatively moving atoms increases.

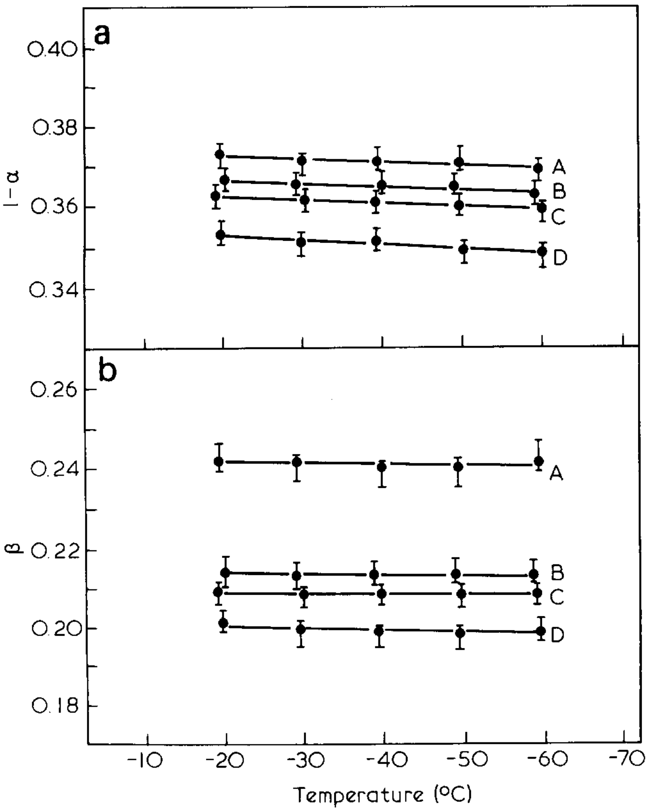

Figure 7 Temperature dependence of (a) $1-\alpha$ and (b) β: for symbols see *Figure 5*

Change of the parameters, $1-\alpha$ and β, in the Havriliak–Negami equation against the heat treatment time is shown in *Figure 6*. Both parameters decrease with elongation of the treatment time. *Figure 7* shows the temperature dependence of the parameters $1-\alpha$ and β of the heat-treated samples. Although the parameter $1-\alpha$ decreases slightly with decreasing temperature, its temperature dependence is small. The other parameter β is less dependent upon temperature than is $1-\alpha$. It almost does not change with temperature. As the parameter $1-\alpha$ represents the width of dispersion (distribution of relaxation time of local mode motion), equation (1) indicates that according as the parameter $1-\alpha$ approaches zero, the width of dispersion becomes wider, deviating from the simple dispersion. The width of dispersion can also be expressed, in a rough approximation, by reduced loss curve (plot $\varepsilon'/\varepsilon'_{max}$ against $\log f/f_{max}$)[28]. The reduced loss curves at 0°C of the untreated sample and the sample treated under the above-mentioned condition for 3770 h are shown in *Figure 8*. As seen in *Figure 8*, the heat treatment yielded a decrease in the component having the longer relaxation time. Incidentally, the reduced loss curves of the samples treated for 123 and 890 h are drawn between the curves shown in *Figure 8*. Since the width of the curves on the high-frequency side at 0°C is unknown, the reduced loss curves at −60°C are shown in *Figure 9*. As seen in *Figure 9*, since the width of the curve of the heat-treated sample becomes narrow on the low-frequency side

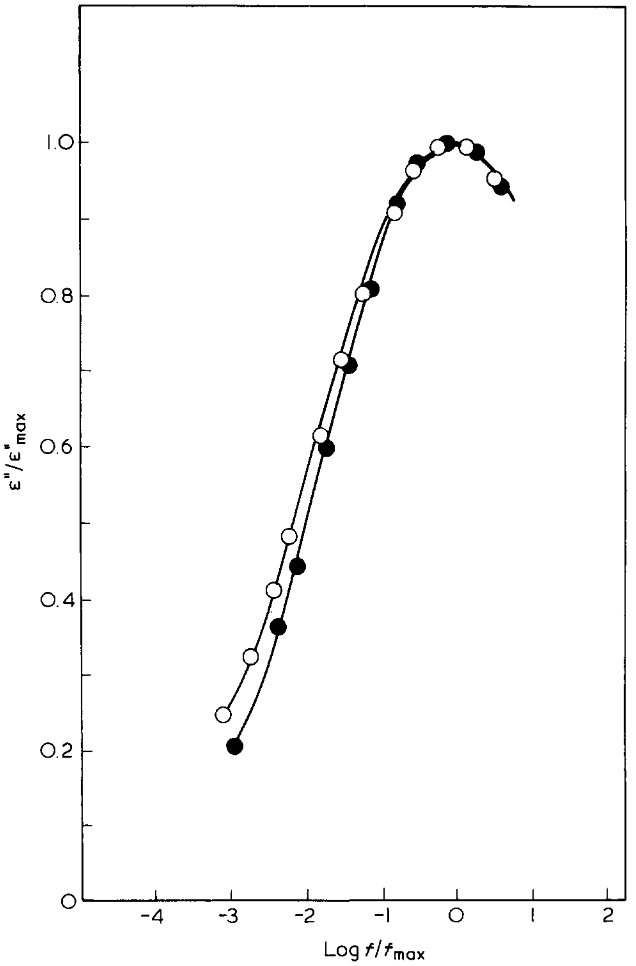

Figure 8 Reduced loss curves of untreated and 3770 h heat-treated samples at 0°C: ○, untreated; ●, 3770 h

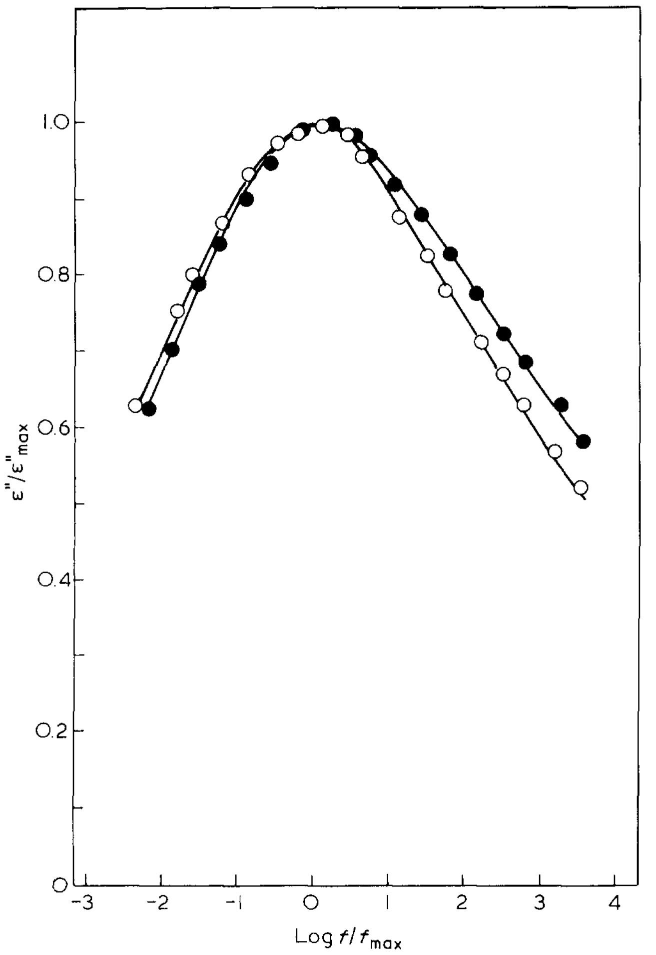

Figure 9 Reduced loss curves of untreated and 3770 h heat-treated samples at −60°C: for symbols see *Figure 8*

and broadens on the high-frequency side, the half-width value of the curve increases. In other words, *Figure 9* indicates that distribution of relaxation time is broadened by heat treatment, and this fact is in agreement with the results shown in *Figures 6* and *7*. As we reported in previous papers[19,20], heat treatment of PET below T_g gives rise to an increase in its density. The density increase reflects the fact that the molecular chain was packed compactly by the treatment. The compact packing results in an increase in interactions within the molecular chain, and thus the distribution of relaxation time is broadened. On the basis of this fact, it is assumed that the state of PET in the amorphous region gets closer to a more random liquid state when subjected to the treatment.

The temperature dependence of frequency at maximum absorption (f_{max}) of untreated and heat-treated samples is shown in *Figure 10*. The average relaxation time can be calculated using f^{max}. Also the temperature dependence of frequency (f) at the point $\omega\tau = 1$ on the complex plane plot, which was obtained according to Havriliak–Negami's method, is seen in *Figure 11*. If the local mode process of PET has a single relaxation time, f_{max} agrees with f ($\omega\tau = 1$). The activation energy obtained from *Figures 10* and *11* is about 13 kcal mol^{-1} and about 15 kcal mol^{-1} for untreated and 3770 h treated samples respectively. Accordingly f_{max} and f in the high-temperature region scarcely depend on the period of the heat treatment but, according to whether the observation

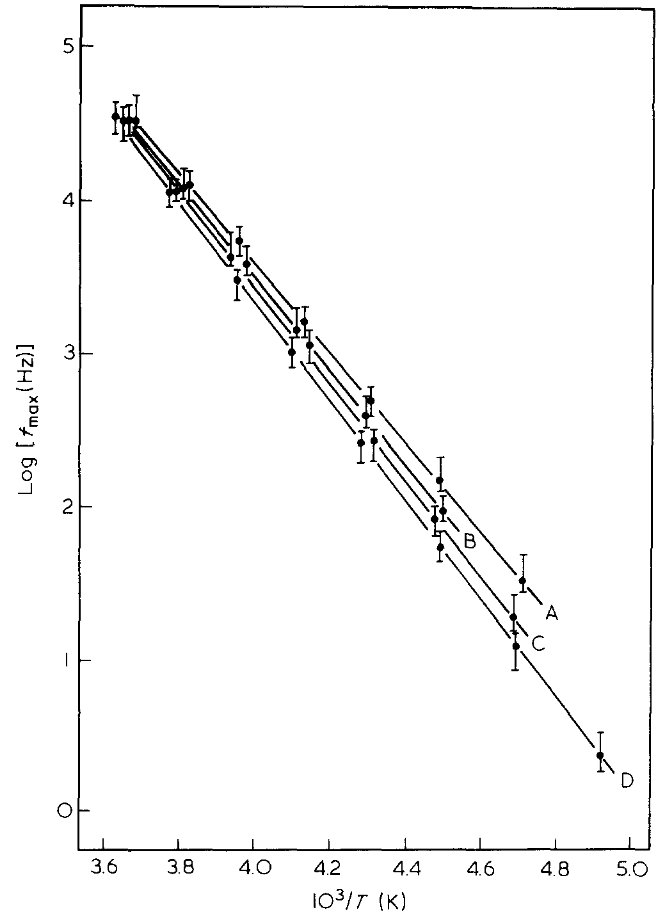

Figure 10 Temperature dependence of frequency at maximum absorption (f_{max}): for symbols see *Figure 5*

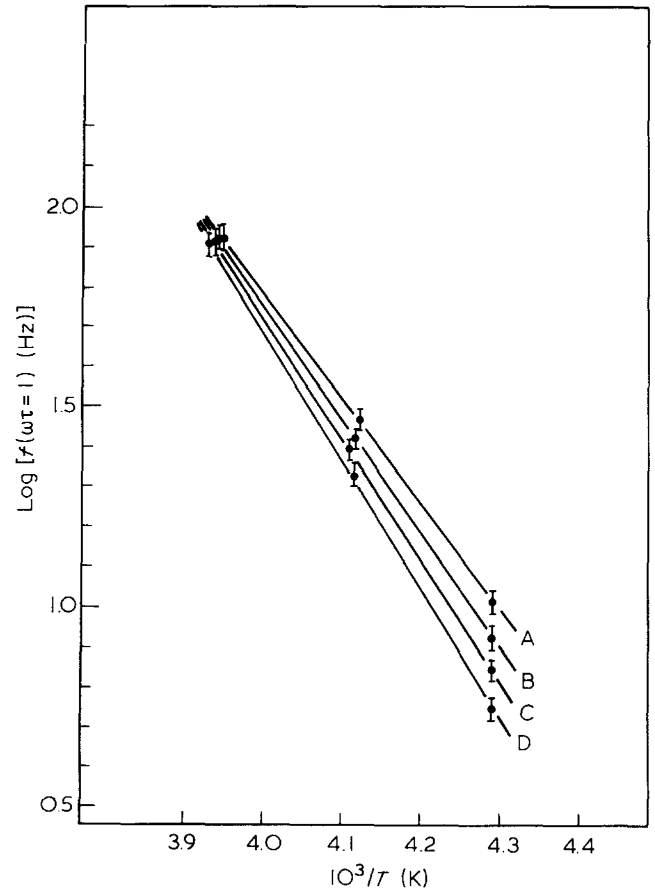

Figure 11 Temperature dependence of frequency (f) at $\omega\tau = 1$: for symbols see *Figure 5*

temperature is lowered, a change of f_{max} and f due to a difference of the treatment period can be observed. *Figure 12* shows change of f_{max} and $f(\omega\tau=1)$ at -40°C against the treatment time. In this case, f is rather smaller than f_{max} but both are shifted towards the low-frequency side at extension of the treatment time. Since the relaxation time is inversely proportional to the frequency ($\tau=2\pi/f$), the heat treatment causes increases in relaxation time and average relaxation time, which are obtained from f and f_{max} respectively. The increase in the relaxation time by heat treatment seems to be attributed to the compact packing of the molecular chain, a decrease in free volume and an elongation of the molecular chain relating to local mode motion.

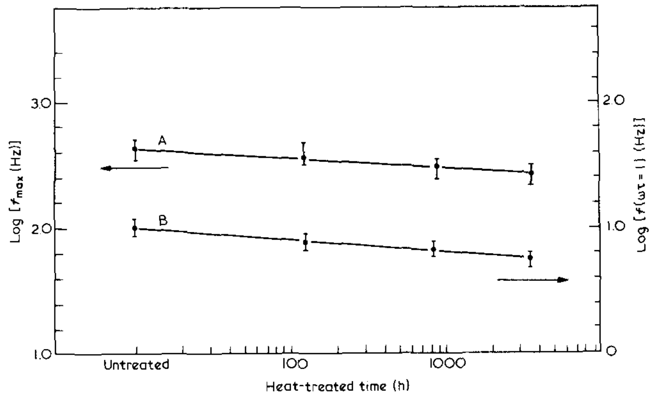

Figure 12 Change of f_{max} and f ($\omega\tau=1$) at -40°C with heat-treated time: curve A, f_{max}; B, f ($\omega\tau=1$)

CONCLUSION

From consideration of the above-mentioned results, the following conclusions are drawn: (1) the heat treatment removes the distribution of molecular chain in the frozen state and the number of correlatively moving atoms in the molecular chain increases; (2) the length of the molecular chain relates to local mode motion and is elongated by heat treatment to increase the amplitude and extension of relaxation time; and (3) the amorphous state becomes more random by heat treatment.

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