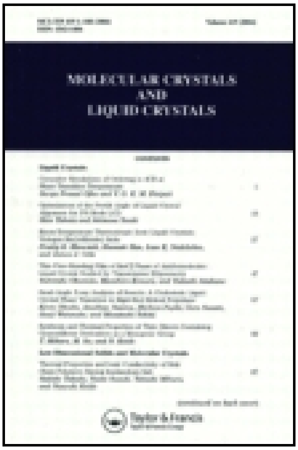

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Enthalpy Relaxation as a Function of Aging Temperature for Poly-Cyanobiphenyl Hexylacrylate Analyzed by Activation-Energy-Spectrum Model

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Excess enthalpy was measured during thermal aging for poly(6-(4′-cyanobiphenyl-4-yloxy) hexylacrylate) at various temperatures. The relaxation behavior was analyzed on the basis of the activation-energy spectrum (AES) model. The relaxation time was evaluated and its dependence on the aging temperature was explained using an Arrhenius-type equation. The apparent activation enthalpy was 220 kJ/mol, lower than those values reported for other polymers. The AES obtained showed a maximum value. The measurement was also carried out with different molecular weights, and the systematic variations could be observed for the AES.

Keywords: activation-energy spectrum; cyanobiphenyl group; DSC; enthalpy relaxation; glass transition; liquid-crystalline polymer

INTRODUCTION

Polymer glasses are essentially thermodynamic nonequilibrium states. Structure and properties change with thermal aging in the state below the glass transition temperature after a rapid change in thermodynamic conditions.

The physical properties of a liquid-crystalline polymer with cyanobiphenyl groups in the side chain (PCBA) have previously been studied with respect to the effects of molecular weight and spacer length, and it was shown that enthalpy-relaxation phenomena can be observed with good reproducibility [1,2]. The author has been seeking a better understanding of the enthalpy relaxation of this polymer.

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Specifically, a relationship has been sought between relaxation phenomena and molecular motion, and a quantitative characterization of this relationship. To achieve that goal, this study applies the activation energy spectrum (AES) model to the enthalpy relaxation.

The AES model was first applied to a liquid-crystalline polymer by Lorenzo et al., who examined the phenomenology of enthalpy relaxation of a liquid-crystalline polymer [3]. This model was originally developed for relaxation in metallic or oxide glasses; the relaxation phenomena are those such as Curie temperature, Young's modulus, and resistivity [4]. However, it is applicable to any amorphous material and gives information about thermally activated processes that are available to contribute to observed changes in the properties upon relaxation. By "processes" any thermally activated rearrangement of single atoms or atom groups is meant. In glassy polymers, the rearrangement corresponds to the motion of the polymer chains, which leads to the enthalpy relaxation.

Generally speaking, the glass transition temperature and the behavior of the enthalpy of relaxation are independent of the molecular weight when it is high, and they show molecular weight dependence when it is low. This behavior comes from molecular mechanisms where the motion of the chains dominates the relaxation. Only parts of the chain have the motion to influence this behavior in the glass state (which is called the "segmental motion"). The length of the part participating in the motion will not change in high-molecular-weight compounds even if the total length of the chain changes. However, it is yet unclear whether PCBA shows molecular-weight dependence of the relaxational behavior. It is interesting to clarify this. This study was begun with the expectation of obtaining information about relaxation behavior, molecular weight, and spacer length. The information must include the energy characterizing the rearrangement, which contributes to the enthalpy of relaxation. As a first step in the study, the relaxation behavior of poly(6-(4′-cyanobiphenyl-4-yloxy) hexylacrylate) (PCBA6) was investigated.

EXPERIMENTAL

Materials and Methods

The monomer 6-(4′-cyanobiphenyl-4-yloxy) hexylacrylate was synthesized by the method reported by Sibaev et al. [5]. PCBA6 was prepared by radical polymerization in an absealed ampoule for 30 h at 60°C. A mixture of toluene and dimethyl sulfoxide was used as the polymerization solvent to prepare a high-molecular-weight polymer.

TABLE 1 Molecular Weight, Specific Heat Increment, and Subglass Transition Temperature

Sample code	M_w	M_w/M_n	DP	$\Delta Cp/J\ g^{-1}K^{-1}$	$T_{g1}/°C$
B	2.0×10^5	1.8	580	0.32	39
D	6.5×10^4	1.3	180	0.31	39
E	1.2×10^4	1.2	40	0.31	36

M_w: The weight-average molecular weight.

M_n: The number-average molecular weight.

DP: Degree of polymerization was calculated by dividing M_w by molecular weight of the monomer.

T_{g1}: Determination was described in the text.

α,α-Azobisisobutyronitrile was used as a radical initiator. PCBA6 was purified by repeated precipitation from a tetrahydrofuran solution added to methanol. The polymer was fractionated by GPC. The weight-average molecular weight (M_w) of each fractionated polymer was determined by GPC calibrated with polystyrene standards. The molecular weight and the index of distribution, M_w/M_n, of the fractionated PCBA6 is summarized in Table 1, together with the sub-glass transition temperature, T_{g1} (a detailed description is given in the next section), and ΔC_p, the specific heat increment between the liquid-crystalline states and the glass states. The phase behavior was observed under a polarizing microscope equipped with a hot stage and confirmed to be the same as that reported previously [6]. Schlieren textures characteristic of the nematic liquid-crystalline phase were observed.

The change in enthalpy was measured using DSC (SEIKO DSC120). The temperature scale was calibrated with the melting transition of the following four substances: tin (231.9°C) and indium (156.6°C) as high-temperature references, biphenyl (68.4°C) and water (0°C) as low-temperature references. The energy input was calibrated with the heat of fusion of indium (3.3 kJ/mol). To achieve the highest precision possible, the calibrations were checked repeatedly during the series of measurements.

Measurement of Enthalpy

To obtain comparable results, the thermal program imposed on PCBA6 was always the following: starting from a temperature of 160°C, well above the clearing temperature, the sample was cooled to a specified aging temperature, T_A, and then the aging was carried out. The cooling rate observed was 12°C min^{-1}. After a given aging time, t_A, the DSC heating curve was obtained at a rate of 5°C min^{-1}, for the temperature region from -20 to 160°C. The aging temperature was chosen below the sub-glass transition temperature determined by the following method.

Several definitions for the location of the glass transition temperature on DSC curves are currently in use for different situations. The three most commonly used are (a) the extrapolated onset T_g, (b) the midpoint T_g, and (c) the enthalpic T_g. Among these, method (b) seems to be used most frequently [7]. When this method was used, $T_g = 37$°C as shown in Fig. 1, which closely agrees with the result reported previously [6]. Figure 1 shows the heating DSC curves of PCBA6-B with aging ($t_A = 343$ min) and without aging. The well-known behavior of an annealed sample to superheat to endothermic peak is apparent in Fig. 1. The excess enthalpy, $\Delta H(t_A, T_A)$, was evaluated from the area bounded by the DSC curves with and without aging.

In contrast, Cowie and Furgeson adopted method (c) simply for convenience [8]. This method, however, has significance to relaxation phenomenon beyond mere convenience. That is, T_g determined by method (c) shows not only a glass transition temperature, but also a temperature region in which relaxation takes place [9]. Below this

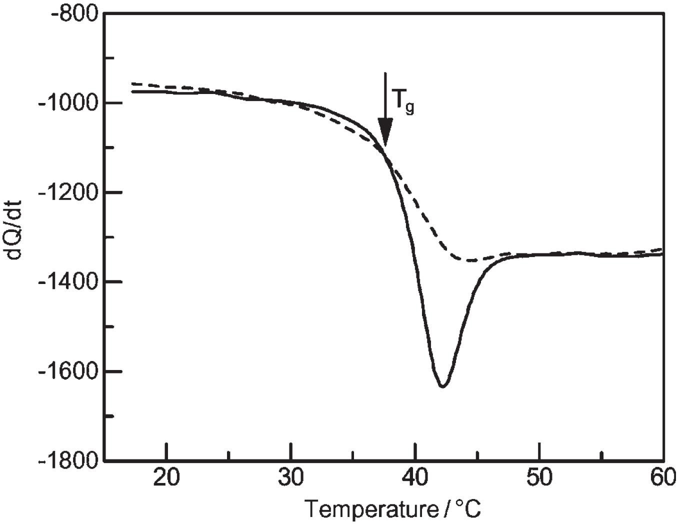

FIGURE 1 Heating DSC curves of PCBA6-B with the aging of $t_A = 343$ min, $T_A = 296$ K (solid line), and without the aging (dashed line). dQ/dt is the heat flow in the unit of mW. T_g in the figure means the glass transition temperature determined by the method (b) described in the text.

temperature, the quasi-static process of a decrease in excess enthalpy takes place upon isothermal aging. Above this temperature, there is not any excess enthalpy.

In fact, it was tested whether the excess enthalpy appears for PCBA6-B by aging at several temperatures. It appeared at temperatures lower than 39°C. As for T_g determined by method (c), it was 39.2°C as shown in Fig. 2. Figure 2 shows the temperature dependence of enthalpy for PCBA6-B without aging, which was obtained from the DSC curve shown in Fig. 1 through C_p data [10]. It can be seen in some literatures that the linear approximations have been made to obtain the cross point in the enthalpy curves [11–13]. It is necessary to avoid drawing the line deliberately when making the linear approximation over the wide temperature range including the transition region. Therefore, the approximation of the least squares method was made in Fig. 2 by placing the priorities on a broader approximation region and a lower value for the sum of squares ($|r^2|$) in the residue.

The two temperatures were nearly equivalent. This temperature, coming from the observation of excess enthalpy, was regarded as the

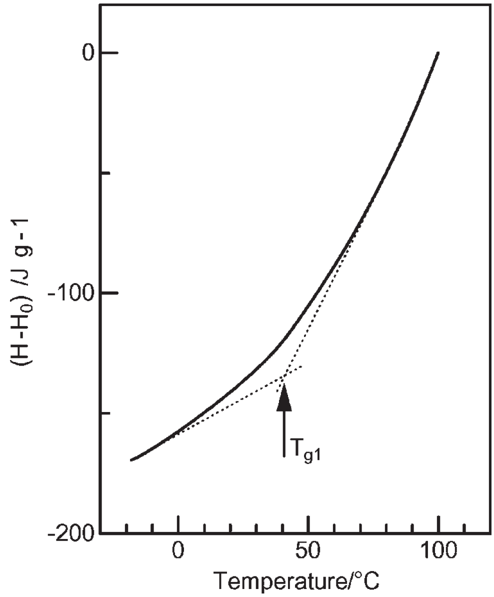

FIGURE 2 Relation between enthalpy and temperature for PCBA6-B without aging. The enthalpy shown in this figure is relative value. The reference, H_0, was taken as the enthalpy at 100°C. The dashed lines are the extrapolation lines. The cross point corresponds with T_g determined by (c).

sub-glass transition temperature, T_{g1}, and emphasized in this study. T_{g1} was then used to evaluate the asymptotic value of the excess enthalpy in Eq. (2) instead of using T_g in method (b).

THEORETICAL

The activation energy spectrum for PCBA6 was evaluated following the description of Lorenzo et al. The decrease in enthalpy that occurs in PCBA6 upon isothermal aging below T_{g1} can be represented in terms of the expression

$$\Delta H(t_A, T_A) = \Delta H(\infty, T_A) \times (1 - \phi) \tag{1}$$

where $\Delta H(\infty, T_A)$ is the asymptotic value of $\Delta H(t_A, T_A)$ and ϕ is the relaxation function. $\Delta H(\infty, T_A)$ can be calculated with the equation [11]

$$\Delta H(\infty, T_A) = \Delta C_p(T_{g1} - T_A). \tag{2}$$

These enthalpy changes are related to the approach of PCBA6 to its corresponding equilibrium state at T_A and are controlled by molecular processes whose activation energies, E, are distributed over a continuous spectrum according to the AES model. This model predicts that $\Delta H(t_A, T_A)$ can be obtained by the integral

$$\Delta H(t_A, T_A) = \int_0^{kT_A \ln(\nu_0 t_A)} P_0(E) \mathrm{d}E \tag{3}$$

where $P_0(E)$ is the enthalpy change related to the relaxation process with activation energies in the range $E+\mathrm{d}E$, and is expressed by

$$P_0(E) = \mathrm{c}(E) \times \mathrm{r_t}(E).$$

$\mathrm{r_t}(E)$ is the number density of processes of activation energy E. The processes contribute to the enthalpy of relaxation after time t_A. $\mathrm{c}(E)$ is the measured enthalpy change if only one process that has activation energy E is thermally activated per unit volume of material. In practice, more than one type of single atom or multiatom process may have the same value of activation energy; the value of $\mathrm{c}(E)$ will then depend on the type of process occurring with the energy value E. One may usually, without loss of generality, regard the processes as being all of one type with a single average value of $\mathrm{c}(E)$ [4]. k is Boltzmann's constant and ν_0 is the frequency factor for single-atom processes. The value of ν_0 is on the order of 10^{12}/s, which is derived from the frequency of the Debye temperature, $\theta_D = (h\ \nu_D)/k$; h and ν_D are Planck's constant and the Debye frequency, respectively.

A description of the ν_0 value is also given. The activation-energy spectrum, the relationship between $P_0(E)$ and E, can be calculated by the following equation, which is derived from Eq. (3):

$$P_0(E) = -\frac{\Delta H(\infty, T_A)}{kT_A} \cdot \frac{d\phi}{d \ln t_A}\bigg|_{t_A = \frac{1}{\nu_0}\exp\frac{E}{kT_A}}. \tag{4}$$

Therefore, it is possible to obtain the AES given that $\Delta H(\infty, T_A)$ and ϕ are known. The spectrum gives information about the processes controlling the relaxation.

RESULTS AND DISCUSSION

Relaxation Function

It is necessary to determine a relaxation function from the experimental results to evaluate the AES. The following two expressions were taken into account as possible relaxation functions:

$$\phi = -a \times \log(t_{\mathrm{A}}) + b \tag{5}$$

$$\phi = \exp\left[-\left(\frac{t_A}{\tau}\right)^{\beta}\right] \tag{6}$$

The meaning of Eq. (5) is the same as $\Delta H(t_{\mathrm{A}}, T_{\mathrm{A}}) = (\mathrm{const}) \times \log(t_{\mathrm{A}})$. The AES model states, concerning the relaxation phenomenon amenable to this equation, that the total available enthalpy change is independent of its activation energy after all the processes associated with this activation energy have contributed to the relaxation during the irrespective aging times. Because $\Delta H(t_{\mathrm{A}}, T_{\mathrm{A}})$ is a direct expression for the enthalpy measurement in comparison to ϕ, used in Eq. (5), $\Delta H(t_{\mathrm{A}}, T_{\mathrm{A}})$ was plotted against the logarithm of aging time. The result for PCBA6-B is shown in Fig. 3. There seems to be a linear relation between $\Delta H(t_{\mathrm{A}}, T_{\mathrm{A}})$ and $\log(t_{\mathrm{A}})$. Equation (5), however, was not chosen as the relaxation function for the reason described as follows.

Equation (6) is in the form of a stretched exponential function and is regarded as a phenomenological description of the relaxation during isothermal aging of glassy materials [14]. The relaxation time, τ, and the shape parameter, β, characterize this function. Equation (6) is also referred to as the Kohlrausch–Williams–Watts equation, and the shape parameter is said to be related to the distribution of the relaxation time, whether τ distributes narrowly or widely [15,16]. The meaning of β is discussed later. A log–log plot of $-\ln\phi$ and t_{A} was made in Fig. 4 to verify whether the experimental results fit into stretched

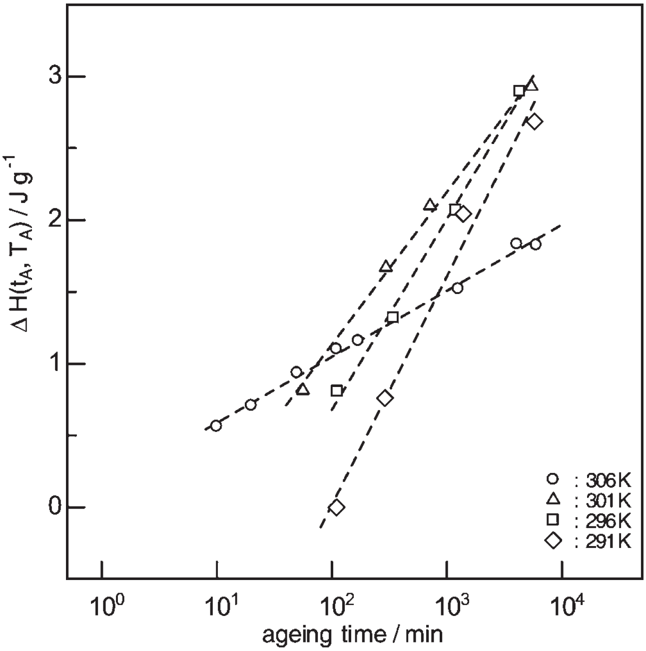

FIGURE 3 $\Delta H(t_A, T_A)$ plotted as a function of aging time for PCBA6-B. The aging temperature, T_A, was shown in the figure. The dashed lines in the figure can be drawn on the assumption of a linear relation between $\Delta H(t_A, T_A)$ and log (t_A), whereas this assumption was not made in this study.

exponential functions. Overall, there exists a linear relationship between $-\ln\phi$ and t_A on a log–log plot.

The same tendency was observed for the results of the enthalpy measurements of PCBA6-D and PCBA6-E; that is, linear relationships seemed to apply to both a $\Delta H(t_A, T_A)$ vs. $\log(t_A)$ plot and the log–log plot of $-\ln\phi$ and t_A. It was difficult to judge which was the better equation, (5) or (6), to fit with the experimental results [17]. When $-\ln\phi$ and t_A show a completely linear relationship in a log−log plot, the relationship between $\Delta H(t_A, T_A)$ and $\log(t_A)$ becomes a sigmoidal curve on a linear plot. This sigmoidal curve moves closer to a straight line with varying values of β and τ. Therefore, it was difficult to judge which was the better equation. See Ref. [17].

Equation (5) holds with respect to the change in enthalpy, which is subject to the assumption that $P_0(E)$ is constant. Gibbs et al. [4] point out that this assumption is likely to be ineffective in developing the AES model. Lorenzo et al. [3] also remark that the assumption is

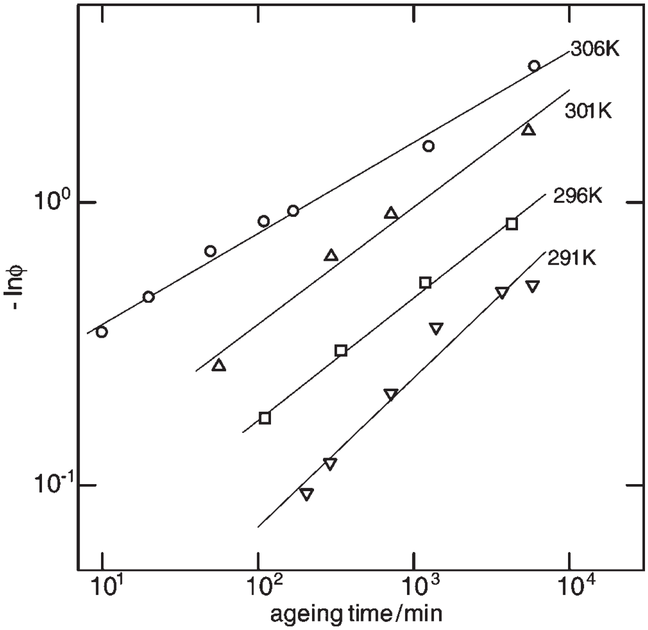

FIGURE 4 The plot of $-\ln\phi$ as a function of aging time for PCBA6-B. The aging temperature, T_A was shown in the figure.

not severe. Taking into account the fact that the stretched exponential function is well accepted to express a relaxational phenomenon, Eq. (6) was chosen in this study as a relaxation function to express the change in enthalpy of PCBA6.

AES from Stretched Exponential Function

The parameters β and τ can be determined for respective aging temperatures by applying Eq. (6) to the experimental data. Because there were some reports concerning the T_A dependence of the τ value for other polymers, a plot of $\log(\tau)$ vs. $1000/T_A$ was constructed according to the literature [3,12,18]. The result of the plot for PCBA6-B is displayed in Fig. 5. This result can be explained in terms of an Arrhenius-type equation:

$$\tau = \tau_0 \exp(E_{app}/kT_A) \tag{7}$$

where E_{app} is the apparent activation enthalpy. This result gives $E_{app} = 220\,\mathrm{kJ/mol}$ (equivalent to 2.3 eV). This calculated value was

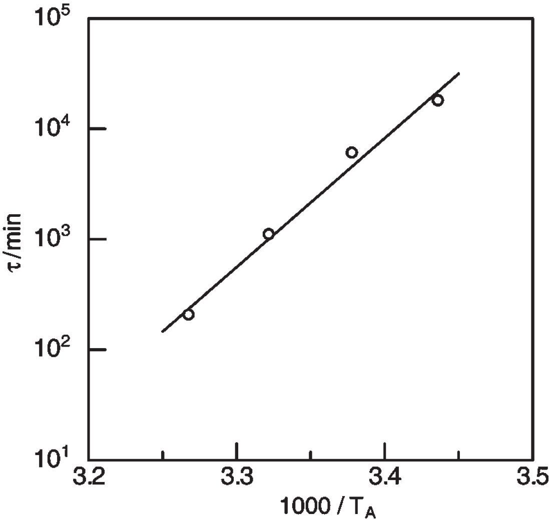

FIGURE 5 The relation of τ and $1000/T_A$ displayed for PCBA6-B. The apparent activation enthalpy calculated was 220 kJ/mol.

lower than those reported for other amorphous polymers [12,18]. Conversely, it was higher than the apparent activation enthalpy of a main chain-type liquid-crystalline polymer [3]. It can be presumed that whether the mesogenic group exists and whether a side chain exists may influence the enthalpy controlling the temperature variation of the relaxation time. Lorenzo et al. [3] have pointed out that the liquid-crystalline nature will lead to a low value of E_{app}.

Before explaining the AES results, it is important to remark upon the determination of the ν_0 value. Lorenzo et al. [3] assumed that τ_0, the preexponential factor of Eq. (7), is equivalent to $(1/\nu_0)$, and then gave the ν_0 value from the τ_0 obtained from the plot of log(τ) vs. $1000/T_A$ in the calculation of AES. This assumption, however, is poorly justified. Because the value of ν_0 is originally comparable to that of the Debye frequency in theory, $\nu_0 = 10^{12}$/s was used here. It is currently ambiguous which is valid, $\nu_0 = (1/\tau_0)$ or $\nu_0 = 10^{12}$/s. The ν_0 value can be higher by more than a few orders than the Debye frequency considering the presence of high-frequency intramolecular vibration. Although Gibbs et al. [4] pointed out that the value of ν_0 is not sensitive to the AES calculated, in practice, this problem is considered to influence the results of the analysis, in particular, the relationship between relaxation processes and the activation energy. Therefore in the future, it is necessary to investigate it in detail.

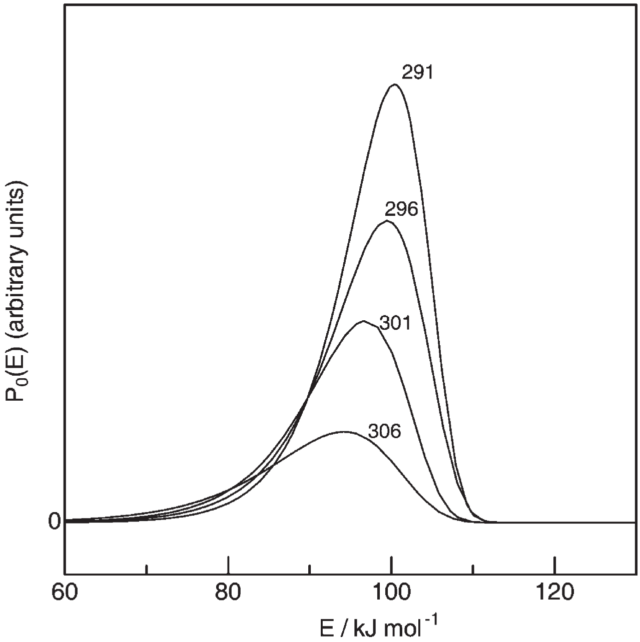

FIGURE 6 Activation energy, E, spectra for the enthalpy relaxation of PCBA6-B. The number in the figure indicates the aging temperature in K.

Figure 6 shows the AES for the enthalpy relaxation of PCBA6-B at different T_A. The spectra obtained began to increase at around 80 kJ/mol and pass through a maximum, then decrease to a zero value at around 110 kJ/mol. This means that the activation energies of almost all the processes are within this range in spite of the variation of the aging temperature. The peak top shifted to the lower energy value and the width of the spectra broadened with the increase in T_A, showing that lower energy can bring about the evolution of relaxation when the aging temperature is higher. This result is acceptable, taking account of the increase in molecular motion caused by the rise in temperature.

When we see a maximum in the AES, let the energy of the maximum be E_{max}. It was inconsistent with the E_{app} value obtained from the plot of log(τ) vs. $1000/T_A$. It is clear from Eqs. (4) and (6) that the maximum is located at the energy value t $= \tau$ [19]. Although this inconsistency seems curious at first glance, it is not wrong. If $\nu_0 = (1/\tau_0)$ had been assumed, E_{max} would have nearly been equal to E_{app}. E_{max}, however, did not become equivalent to E_{app}, but became about half the value of E_{app} in this study, because this assumption was not made. This is because there is no theoretical reason for the equivalence between them on the basis of their physical meaning. In fact, an example of the AES analysis showing that E_{max} and E_{app} are two times different can also be seen in the literature that concerns itself with the relaxation responses of amorphous selenium [19]. The results of analysis shown here should, therefore, be understood not quantitatively but qualitatively.

The half-widths of the spectra were plotted against the reciprocals of β after the manner displayed by Lorenzo et al. [3]. There was a linear relationship between the half-width and $1/\beta$. Therefore, β, a parameter characterizing the relaxation function, has some meaning related to the distribution of the relaxation process.

Figure 7 shows the dependence of the AES on the molecular weight for the enthalpy of relaxation upon aging at 306 K. The peak height decreased with the decrease in molecular weight, showing a decrease in the area beneath the spectrum. The area represents the total number of available relaxation processes during thermal aging. This result can be interpreted to some extent with the following idea. The longer a chain, the more diverse is the mode of its motion during relaxation.

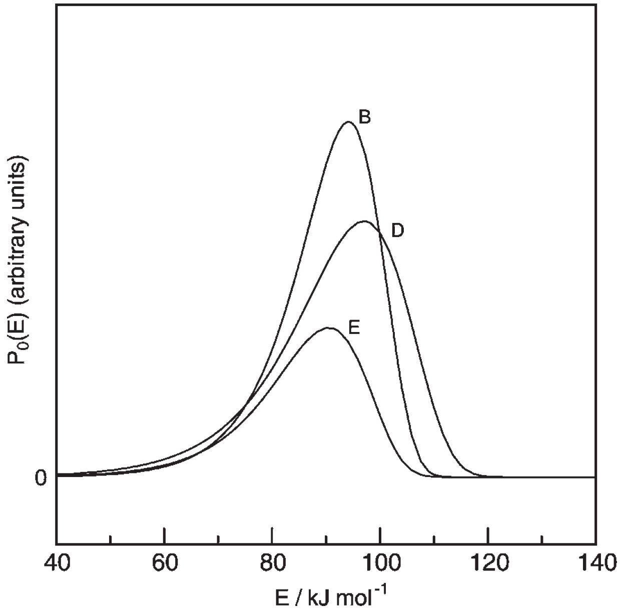

FIGURE 7 Activation energy, E, spectra for the enthalpy relaxation of PCBA6 of different molecular weights. The aging temperature was 306 K. The sample code was indicated in the figure.

The diverse mode of the motion subsequently leads to an increase in the number of processes. However, this idea is insufficient because the relationship between the range of molecular weights studied here and the molecular motion is unclear. At present, a comprehensive interpretation of these results has not been obtained. A molecular mechanism must be added in a future study.

CONCLUDING REMARKS

The phenomenology of the enthalpy of relaxation of PCBA6 was analyzed using an AES model with several aging temperatures. The relaxation function was determined to be a stretched exponential function by fitting the experimental results. The spectra obtained show a bell-shaped curve, showing that the activation energies of all the relaxation processes lie within a certain range. The dependence of AES on the molecular weight was observed. The peak height decreased with a decrease in the molecular weight. The reason for this result is currently unclear and will be the subject of a future investigation.

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