Enthalpy Relaxation of Liquid Crystalline Polymer with Cyanobiphenyl Group in the Side Chain: Activation Energy Spectrum Analysis

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ABSTRACT: In the enthalpy relaxation of poly(cyanobiphenyl hexylacrylate) (PCBA6), the decrease in enthalpy was measured as a function of ageing time and ageing temperature in order to analyse it using activation energy spectrum (AES) model. In AES model the decrease in enthalpy is considered to be controlled by molecular processes whose energies are distributed over a continuous spectrum. The relaxation functions were derived from the enthalpy data for four PCBA6 samples of different molecular weights(M_w), then they were verified to obey stretched exponential forms. The relaxation times showed Arrhenius type temperature dependences to give E_{app}, apparent activation energies, which became plateau around 200 kJ/mol as the rise in M_w. A plot of reduced ageing times was constructed after the manner of time–temperature reducibility. The fraction of free volume and the thermal expansion coefficient of glass transition were calculated by the method of WLF plot. Then, it was found that these values were relatively large, which is attributable to a property of a side-chain type polymer. AES showed bell-shaped curves; the beginning and the end of the peak were considered to coincide with the lower and the upper limits of activation energies of the relaxation processes, respectively. AES results, such as the area, the height of the peak, the upper and the lower limits, were discussed in terms of the molecular weight and the ageing temperature.   [doi:10.1295/polymj.PJ2007054]

KEY WORDS   Liquid Crystalline Polymer / Cyanobiphenyl Group / DSC / Glass Transition / Enthalpy Relaxation / Activation Energy Spectrum /

Polymer glasses are essentially thermodynamic non-equilibrium states. Structure and properties change with thermal ageing 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 (PCBA6) 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] A better understanding of the enthalpy relaxation is expected. Specifically, a relationship should be clarified between relaxation phenomena and the properties relevant to molecular mechanism. A quantitative characterisation of this relationship is preferable. For this purpose, this study applies the activation energy spectrum model (AES model) to the enthalpy relaxation.

Currently a lot of research works are being carried out for enthalpy relaxation of polymer; for example, the study with respect to potential possibilities for improving the piezoelectric properties of polyamide,[3] that to relate it to the transition of domain morphology of polyurethane with hard-segment domain,[4] that with respect to improving thermal and mechanical properties of blends.[5] It may be said physical ageing and enthalpy relaxation are presently interesting subjects in physical properties of polymer.

AES 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.[6] However, it is applicable to any amorphous material and gives information about thermally activated processes which are available to contribute to observed changes in the properties upon relaxation. By "processes", is meant any thermally activated rearrangement of single atoms or atom groups. In glassy polymers, the rearrangement corresponds to the structural changes of the polymer chains, which often cause the optical texture to vary in liquid crystalline polymer. The variation is also observed for PCBA6 as shown in Figure 1. The photographs in Figure 1 were taken by a polarising optical microscope for the same sample of PCBA6 before and after the thermal ageing. They clearly show the change of the size of the nematic domain.

It is well-known that the macroscopic property change, for example volume, the refractive index etc. upon the physical ageing is closely related to the structural relaxation toward equilibrium in the glassy state. The structural state can be considered by introducing a fictive temperature, T_f, which is the

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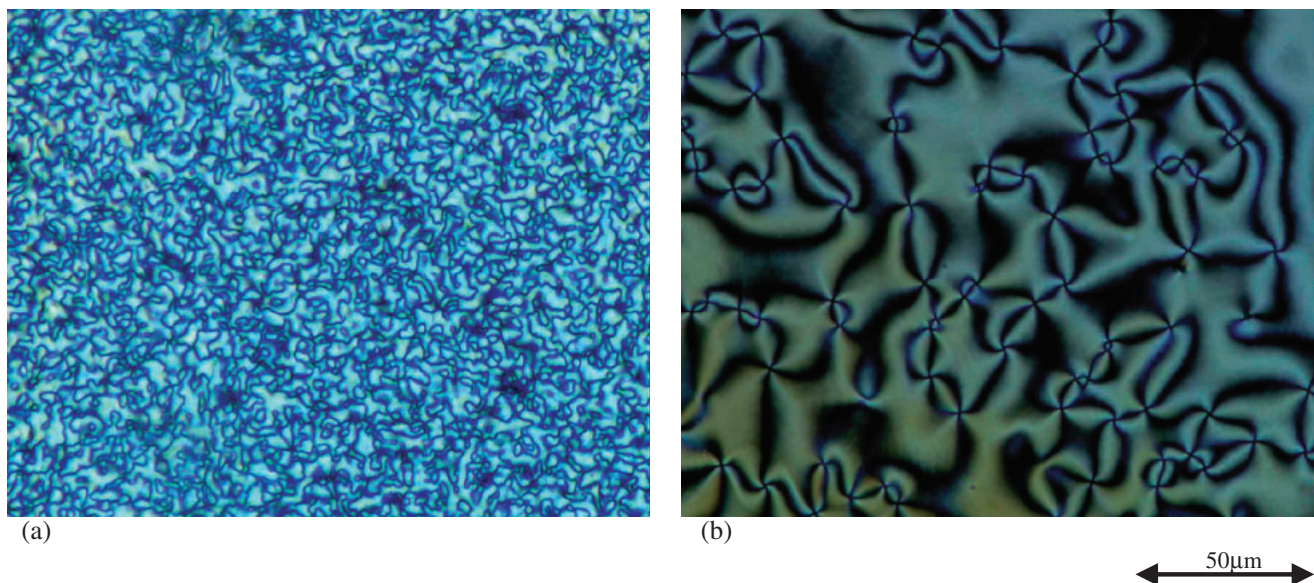
Figure 1. Polarising optical microscopy images taken at 298 K for poly(6-(4′-cyanobiphenyl-4-yloxy) hexylacrylate before (a) and after (b) the thermal ageing.

temperature at which the measured value of a property would be its equilibrium value. With incorporating fictive temperature, it has been attempted to analyse the relaxation, particularly in terms of nonlinearities of the kinetics of ageing.[7–11] The nonlinearity of the kinetic is referred to in the sense that the decay function of the kinetic, the formula definition will be given in experimental section, depends on the extent of departure from equilibrium. The models shown in these attempts to describe relaxation time of the decay function were firstly developed on the ageing process of inorganic glasses. Therefore, insufficiency is also pointed out in applying them to polymers owing to topological constraints of the polymer chains.[12] An approach to overcome these constraints and difficulties of analysis is to develop the configurational entropy model, which describes the evolution equation after a thermal perturbation.[13,14] With the configurational entropy model, the enthalpy relaxation was studied to reproduce experimental traces of DSC for side-chain type liquid crystalline polymer.[15] Although it is very interesting that the calculation curve agrees well with the experimental data, the paper also reports that some values of parameters in the model were not unambiguously determined.

As can be seen above, many models are proposed for enthalpy relaxation. However, an analysis of the relaxation using AES model is limited except for the work of Lorenzo et al.,[16] and hence, further information will be able to be deduced from it. In fact, it was not until AES was considered in this study that some new aspects were found; for example, the relation between the areas of spectra and total numbers of processes, and so on. It is also of interest the parameters obtained from the derived AES.

Generally speaking, the glass transition temperature and the behaviour 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 behaviour comes from molecular mechanisms where the motion of the chains dominates the relaxation. Only parts of the chain have the motion to influence this behaviour 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. Although a generality has almost been obtained as mentioned above concerning the relation between glass transition temperature and molecular weight, the investigation of enthalpy relaxation with polymers of different molecular weights seems to be limited except for a work done by Alvaretz et al.; which is concerned with the relaxation and fragility for comb-like polymer of cyanobiphenyl groups.[17] With these backgrounds this study deals with the enthalpy relaxation of PCBA6 with different molecular weights.

EXPERIMENTAL

Materials and Methods

The monomer 6-(4′-cyanobiphenyl-4-yloxy) hexylacrylate was synthesized by the method reported by Sibaev et al.[18] PCBA6 was prepared by radical polymerisation in an absealed ampoule for 30 h at 333 K. A mixture of toluene and dimethyl sulfoxide was used as the polymerisation solvent. α, α-azobisisobutyronitrile was used as a radical initiator. PCBA6 was pu-

Table I. Molecular Weight, Specific Heat Increment, and sub-Glass Transition Temperature of PCBA6

Sample code	M_w	M_w/M_n	$\Delta C_p/\mathrm{J\,g^{-1}\,K^{-1}}$	T_{g1}^*/K
B	2×10^5	1.8	0.32	312
C	6.5×10^4	1.3	0.31	312
D	3.1×10^4	1.4	0.31	312
E	1.2×10^4	1.2	0.31	309

*Determination was described in the text.

rified 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 was summarised in Table I, 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. Fraction E showed a slightly lower T_{g1} in comparison with T_{g1} values of other fractions, which is roughly expected because a larger length of the polymer backbone hinders the motions of the chain segments giving rise to a higher glass transition temperature. The phase behaviour was observed under a polarising optical microscope equipped with a hot stage and confirmed to be the same as that reported previously.[19] Polystyrene was used for reference to discuss temperature dependence of relaxation time. The molecular weight of polystyrene used was; $M_w = 7.9 \times 10^4$, $M_w/M_n = 1.39$.

The change in enthalpy was measured using DSC (SEIKO DSC120). The temperature scale was calibrated with the melting transition of the following four substances. Those are tin(505.1 K) and indium(429.8 K) as a high temperature references, biphenyl(341.6 K) and water(273.2 K) as a low temperature references. The energy input was calibrated with the heat of fusion of indium(3.3 kJ/mol). In order to achieve the highest precision possible, the calibrations were checked repeatedly during the series of measurements.

Measurement of Enthalpy

In order to obtain comparable results, the thermal program imposed on PCBA6 was always the following: starting from a temperature of 433 K, well above the clearing temperature, the sample was cooled to a specified ageing temperature, T_A, then the ageing was carried out. After a given ageing time, t_A, the DSC heating curve was obtained at a rate of 5 K min^{-1}, for the temperature region from 253 to 433 K in order to determine the enthalpy loss,

$\Delta H(t_A, T_A)$. The ageing temperature was chosen below the sub-glass transition temperature determined by the method written later.

Determination of glass transition temperature is required to find the asymptotic value of $\Delta H(t_A, T_A)$ using the following relation.[20]

$$\Delta H(\infty, T_A) = \Delta C_P(T_g - T_A) \qquad (1)$$

Eq. (1) implies that $\Delta H(\infty, T_A)$ increases as the ageing temperature decreases, which is the expected behaviour because the enthalpy loss during the equilibration process is larger when the glass is far from the metastable equilibrium state.

The enthalpy loss during isothermal ageing can be written as;

$$\Delta H(t_A, T_A) = \Delta H(\infty, T_A) \times (1 - \phi) \qquad (2)$$

where ϕ is the relaxation function. The following expression was taken into account as a relaxation function.

$$\phi = \exp\left[-\left(\frac{t_A}{\tau}\right)^\beta \right] \qquad (3)$$

Eq. (3) is in the form of a stretched exponential function and is regarded as a phenomenological description of the relaxation during isothermal ageing of glassy materials.[21] The relaxation time, τ, and the shape parameter, β, characterise this function. Eq. (3) 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.[22,23]

In this study, a nonlinear fitting analysis was carried out to determine the asymptotic value, $\Delta H(\infty, T_A)$ in addition to the method of eq. (1).[24] It analyses the measured data of t_A and $\Delta H(t_A, T_A)$ in connection with eqs. (2) and (3) to find the values of τ, β and $\Delta H(\infty, T_A)$.

On the other hand, the use of eq. (1) to determine $\Delta H(\infty, T_A)$ is based on the assumption that the relation of H vs. T for PCBA6 is linear for $T < T_g$. It should be noted that, in practice, it is more likely not to be linear in H vs. T relation. However, it seems to be unabe to verify the linearity experimentally because it is impossible to measure H vs. T curve of liquid for $T < T_g$.

Under these circumstances, $\Delta H(\infty, T_A)$ were determined by both methods of eq. (1) and a nonlinear fitting analysis and compared with each other. It was found that there were almost no differences. Therefore, the method of eq. (1) was used in this study with the sub-glass transition temperature determined as follows.

Several definitions for the locations of the glass transition temperatures on DSC curves are currently
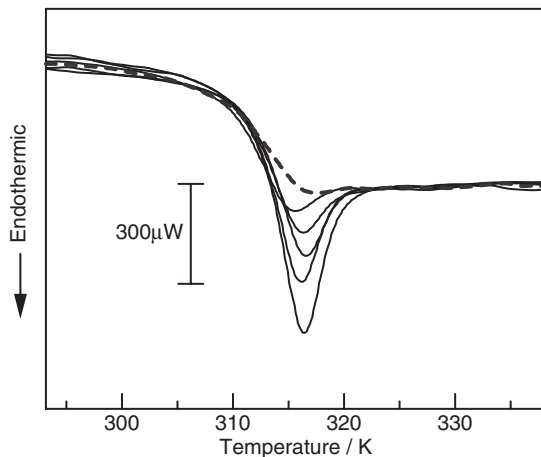
Figure 2. Heating DSC curves of PCBA6-B with the ageing of $T_A = 306$ K(solid lines), and without the ageing(dashed line). The ageing times were; $t_A = 10$, 20, 50, 110 and 6000, in the order of decreasing intensity. The heating rate was 5 K/min.

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 in DSC scans.[25] Figure 2 shows the heating DSC curves for the fraction B of PCBA6, which is to be written as PCB6A-B. The curves were those of samples with ageing $(T_A = 306$ K), and without ageing. When method (b) was used, $T_g = 310$ K was observed, which closely agrees with the reported value.[19] The well-known behaviour of an annealed sample to superheat to endothermic peak is apparent in Figure 2. The equivalence between the energy absorbed during heating through the glass transition and the enthalpy loss associated with the isothermal ageing process is well established.[26,27] Then, $\Delta H(t_A, T_A)$, was evaluated from the area bounded by the DSC curves with and without ageing. As shown in Figure the temperature of the endothermic peak shifted higher with the ageing time. Because the temperature of the peak corresponds to the process of recovery of enthalpy during the heating of the aged sample, the increase of this temperature is due to the decrease of the molecular mobility of the chain segments (required for the recovery of the enthalpy to take place) as a consequence of the decrease in the free volume.[17]

On the other hand, Cowie and Ferguson adopted method (c) simply for convenience.[12] 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.[28] Below this temperature, the quasi-static process of a decrease in excess enthalpy takes place upon isothermal ageing. Above this temperature, there

is not any excess enthalpy.

In fact, H *vs. T* curve of PCBA6-B was constructed after obtaining the C_p *vs. T* curve; which was calculated from the data without ageing shown in Figure 2 with reference to temperature dependence of C_p of Indium.[29] It was tried to find the cross point using the two extrapolation lines for the enthalpic T_g as the point of intersection of H *vs. T* curves for the glassy and liquid states of PCBA6-B.[20,26] However, it was difficult to draw the extrapolation lines; that is, the temperature regions of linear approximations could not be made clearly. In contrast to this extrapolation method, the appearance of enthalpy loss was clear. That is, it was tested whether or not $\Delta H(t_A, T_A)$ appeared for PCB6A-B by ageing at several temperatures. $\Delta H(t_A, T_A)$ appeared at temperatures lower than 312 K. This temperature, coming from the observation of enthalpy loss, was regarded as the sub-glass transition temperature, T_{g1}, and emphasised in this study. T_{g1} was then used to evaluate the asymptotic value of the enthalpy loss by substituting in T_g of eq. (1).

## RESULTS AND DISCUSSION

Relaxation Function

$\Delta H(t_A, T_A)$ of PCBA6 of respective fractions were measured for various ageing times at various ageing temperatures. $\Delta H(\infty, T_A) - \Delta H(t_A, T_A)$, which is called as the excess enthalpy, was calculated and plotted against t_A for PCBA6-B in Figure 3. The value of $\Delta H(\infty, T_A) - \Delta H(t_A, T_A)$ decreased with the progress of ageing, showing that the enthalpy of PCB6A-B approached to the equilibrium state.
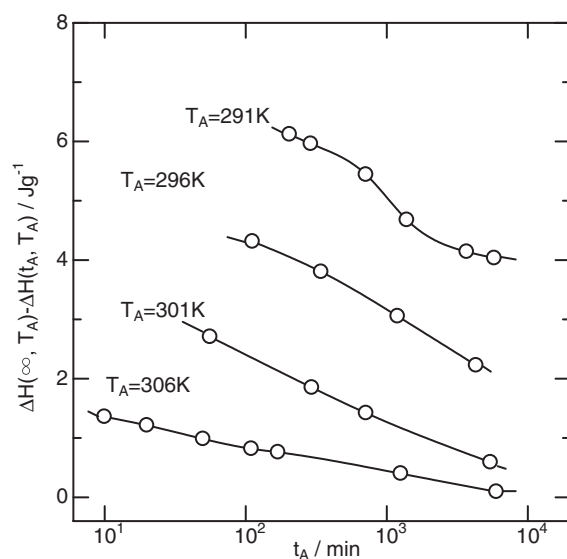
Figure 3. $\Delta H(\infty, T_A) - \Delta H(t_A, T_A)$ as a function of the ageing time, t_A and ageing temperature T_A for PCBA6-B ($M_w = 2.0 \times 10^5$).
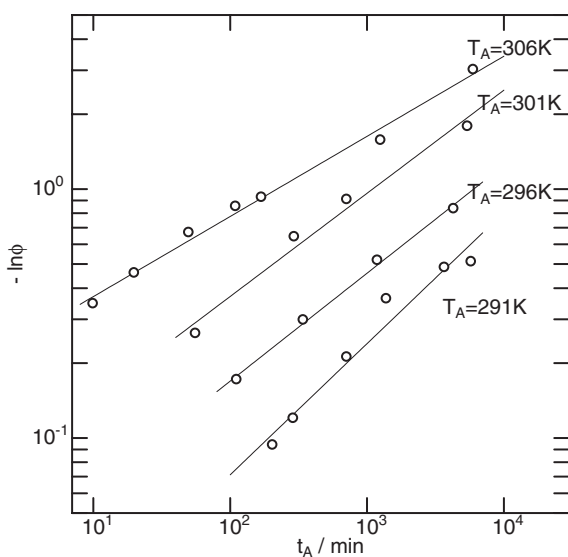
Figure 4. Double logarithmic plots of $-\ln\phi$ vs. t_A for PCBA6-B. The ageing temperature, T_A was shown in the figure.
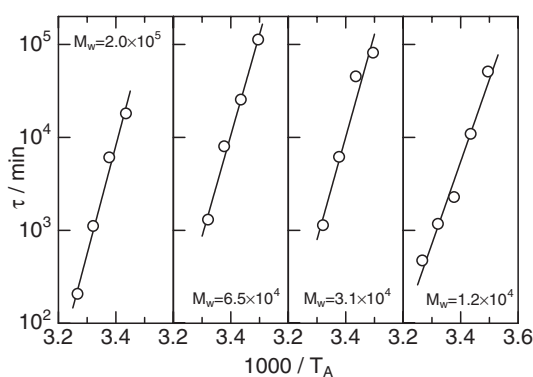
Figure 5. The relations of τ and $1000/T_A$ in semi-logarithmic plots. M_w for respective fractions are displayed in the figure.

The slopes of the plots decreased as the rise in T_A. ϕ was, then, calculated by eq. (2) using the measured value. Then, it was verified whether eq. (3) can be applied to the obtained data by making double logarithmic plots of $-\ln\phi$ vs. t_A. As a result, the relation between $-\ln\phi$ and t_A was double logarithmically linear as shown in Figure 4. In addition, as the ageing temperatures increased the value of $-\ln\phi$ increased. The same tendency was observed for the enthalpy measurements for PCBA6 of other fractions.

The parameters β and τ were determined from the plots of Figure 4. Then, semi-logarithmic plots of τ vs. $1000/T_A$ were constructed. (see Figure 5.) The results of the plots for the respective fractions were found to be Arrhenius type temperature dependences. They were interpreted in terms of the equation shown below;

$$\tau = \tau_0 \exp(E_{app}/kT_A) \qquad (4)$$

where E_{app} is the apparent activation energy and k is Boltzmann's constant.

Concerning the temperature dependence of τ, a generalised version of the Arrhenius type has already been proposed.[7] It can be rewritten as;

$$\tau = A \exp\left(\frac{x\Delta h}{RT} + \frac{(1-x)\Delta h}{RT_f}\right) \qquad (5)$$

where x $(0 < x \leq 1)$ is the nonlinearity parameter, which defines the thermodynamic and structural contribution to the relaxation time.[8] Δh is an activation enthalpy, A pre-exponential factor, R gas constant, T_f fictive temperature. Δh may be found from the relationship between DSC scan rate and T_g. A different approach to analyse the temperature dependence of τ has also been developed by Hodge, with introducing Kauzmann temperature.[10] These two are generalised version of Arrhenius' equation and imply that the relaxation time depends on both temperature and the structural state developed by the system during the ageing process; that is $\tau = \tau(T_f, T)$. Many investigations to interpret τ of enthalpy relaxation using these equations can be seen including the enthalpy relaxation of side-chain type liquid crystalline polymers.[15,30] Therefore, it is necessary to analyse the relation between τ and T_A of PCBA6 taking account of the nonlinearity parameter, x. This is currently under investigation and will be the subject of a separate work. To incorporate x into the relation of τ and T_A has significance also in accounting for pre-exponential factor, which was described in the section of AES.

E_{app} for the respective fractionated samples were calculated and plotted in Figure 6 as a function of weight-average molecular weight which were determined by GPC calibrated by polystyrene. It should be remarked that E_{app} derived here is considered to be different from the activation energy shown in the AES analysis. While E_{app} of PCBA6 of $M_w = 1.2 \times 10^4$ was relatively lower, E_{app} of other PCBA6 fractions showed almost constant values. In Figure 6 a dashed line was drawn in the lower M_w region to
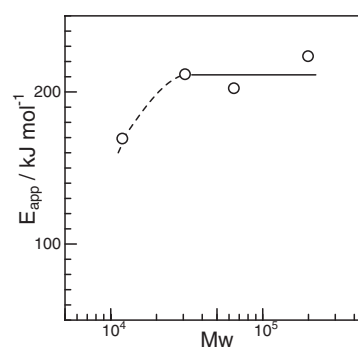
Figure 6. Apparent activation energies calculated from temperature dependences of τ were plotted against M_w.

show a tentative tendency. Because the M_w region of PCBA6 used in this study is limited, it cannot readily be concluded that E_{app} of the lower M_w region will increase with the increase in M_w, in addition, E_{app} *vs.* M_w has a critical point to separate the M_w dependence. However, it is often seen as the references were shown below, that thermal properties such as activation energy, T_g etc., approach to plateau in high M_w region.[20] Also for PCBA6, E_{app} is considered to approach to plateau as shown by a solid line in Figure 6.

Because τ characterises the rate of decrease in $(\Delta H(\infty, T_A) - \Delta H(t_A, T_A))$ during the isothermal ageing, E_{app} corresponds with the energy required to change the rate by raising the ageing temperature, taking account of the result that the slope of $(\Delta H(\infty, T_A) - \Delta H(t_A, T_A))$ decreased with the rise in T_A. It can easily be understood from this meaning of E_{app} that the plateau value appeared. The same behaviour as seen in Figure 6 can be seen in some literatures, although properties measured and hence the ways to determine E are somewhat different from those used in this study. Those are, for example, flow activation energies of polyvinylchlorides,[31] poly-butadienes,[32] and self-diffusion of cis-1,4 polyiso-prenes.[33,34]

In order to lay more confidence on E_{app} value obtained here, the same manner was applied to polystyrene of $M_w = 7.9 \times 10^4$ to compare it with a value found in literature. As a result, E_{app} was measured to be 1070 kJ/mol. This value is considered to be appropriate, although it was slightly smaller than $E_H = 1192$ kJ/mol.[12,20] They calculated E_H through τ data obtained using differential coefficients of plots of $(\Delta H(\infty, T_A) - \Delta H(t_A, T_A))$ *vs.* t_A which also appear in this study. Cowie *et al.* made an argument concerning E_{app} found for poly(vinyl methyl ether) to be much lower than that of polystyrene, that the energy barrier for main-chain segmental motion influences E_H value. However, it can be said that other factors like free volumes of comb-like chains must be considered taking account of the result that PCBA6 which has larger side chains showed E_{app} values much lower than that of PS.

Next, the reduced ageing time was discussed in order to confirm the meaning of τ described above. As the parameter to reduce the ageing time, an average relaxation time $\langle \tau \rangle$ shown in eq. (6) was tested in addition to τ itself.

$$\langle \tau \rangle = \frac{\tau}{\beta} \Gamma(1/\beta) \qquad (6)$$

This expression was derived to average relaxation times distributed over the stretched exponential function.[35] The reduced plot of ϕ *vs.* $\log(t_A/\tau)$ and $\log(t_A/\langle \tau \rangle)$ for PCBA6-B were shown in Figures 7
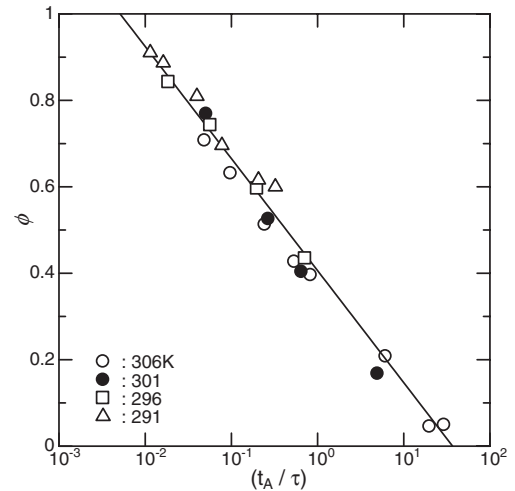

Figure 7. The relations of ϕ and t_A/τ obtained for PCBA6-B at $T_A = 291$, 296, 301 and 306 K.
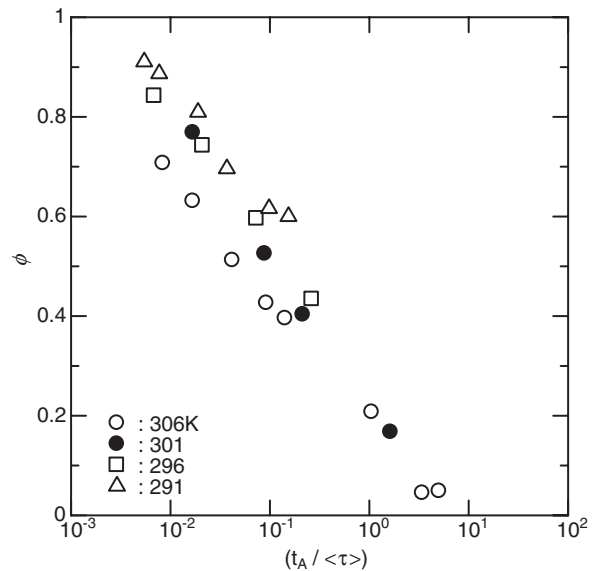
Figure 8. The relations of ϕ and $t_A/\langle \tau \rangle$ obtained for PCBA6-B at $T_A = 291$, 296, 301 and 306 K. $\langle \tau \rangle$ were calculated from equation (6).

and 8 respectively. As a result of the plots, it was found that the reduced data using (t_A/τ) lie on approximately the same curve, while the data of $(t_A/\langle \tau \rangle)$ didn't. It can be said τ itself is favoured as a parameter to reduce in spite of the fact that ϕ data measured fitted well to the stretched exponential function. The plot of Figure 7 showed a better linear relation than the data of enthalpy relaxation for poly(vinyl methyl ether).[12] The range of t_A taken in this experiment might have been narrower than that used for poly-(vinyl methyl ether), and hence the relaxation of both the initial and terminal stages were not observed in this experiment. Also, the variable of $\log \tau$ can be interpreted as a shift factor in the time domain.
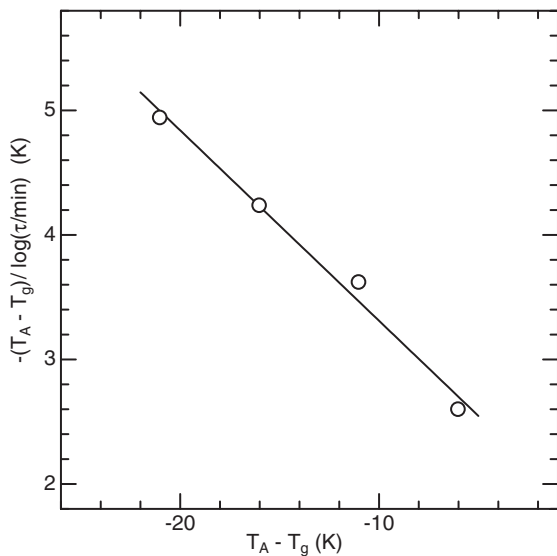
Figure 9. WLF plot constructed for temperature dependence of τ of PCBA6-B.

Because it is well-known that the shift factor can generally be described by WLF type equation, the following equation was applied.

$$\log(\tau) = -\frac{C_1(T_A - T_g)}{C_2 + (T_A - T_g)} \qquad (7)$$

A plot of $-(T_A - T_g)/\log(\tau)$ *vs.* $(T_A - T_g)$ for PCB6A-B was shown in Figure 9. It clearly shows a linear relation. $C_1 = 6.54$ and $C_2 = 11.66$ were obtained here. If the free volume theory could be applied to this result, $f_g = 0.066$ and $\alpha_f = 56 \times 10^4/\text{deg}$ are obtained as parameters concerning glass transition.[36] f_g is the fractional free volume at glass transition temperature, α_f the difference between the thermal expansion coefficients above and below the glass transition temperature. As regards these parameters, it is said that $f_g = 0.025 \pm 0.003$ for various polymers, and $\alpha_f = 4.8 \times 10^4/\text{deg}$ as to be the "universal" value.[37] Precisely, the parameters of both f_g and α_f derived from WLF type equation are considered for the thermal expansions in which the contribution mainly comes from the skeletal chain. Although a simple comparison may be difficult, f_g and α_f of PCBA6 are fairly large. PCBA6 has large free volume and also expands well at T_g. These properties come from the mesogenic side chains and their cooperative mobility respectively. This result is consistent with the fact that E_{app} values of PCBA6 shown in Figure 6 were relatively lower than such conventional polymers as PS and PET.[20,38]

Activation Energy Spectrum

The decrease in enthalpy caused by thermal ageing shown in Figure 3 is related to the approach of

PCBA6 to its corresponding equilibrium state at T_A and is controlled by molecular processes whose activation energies, E, are distributed over a continuous spectrum according to the AES model.[6] This model predicts that $\Delta H(t_A, T_A)$ can be obtained by the integral,

$$\Delta H(t_A, T_A) = \int_0^{kT_A \ln(\nu_0 t_A)} P(E)\mathrm{d}E \qquad (8)$$

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

$$P(E) = c(E) \times q_t(E). \qquad (9)$$

$q_t(E)$ is the number density of processes having E. The processes contribute to the decrease in enthalpy after time t_A. $c(E)$ is the measured enthalpy change if only one process having E is thermally activated per unit volume of material. In practice, more than one type of single atom or multi-atom process may have the same value of activation energy; the value of $c(E)$ 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 $c(E)$.[6] ν_0 is the frequency factor for single atom processes. The value of ν_0 is on the order of $10^{12}/\text{sec}$ 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. From eqs. (2) and (8), the following equation can be derived, thus, the activation energy spectrum, the relationship between $P(E)$ and E, can be calculated.

$$P(E) = -\frac{\Delta H(\infty, T_A)}{kT_A} \cdot \frac{d\phi}{d \ln t_A}\bigg|_{t_A = \frac{1}{\nu_0}\exp\frac{E}{kT_A}} \qquad (10)$$

In the AES shown in this study, $P(E)$ was shown as the enthalpy change by the processes per mole, and E is the energy per mole. The spectrum gives information about the processes controlling the relaxation. A similar treatment to derive AES can be found for the enthalpy relaxation of inorganic glasses[39] and liquid crystalline polymer.[16]

Figure 10 shows the AES for the enthalpy relaxation of PCBA6 of different M_w at various ageing temperature T_A. As can be seen easily from the Figure, AES obtained had the bell-shaped curve. The energies of the processes to contribute to the enthalpy change have both the lower and upper limits. In other words, enthalpy change does not take place when the energy lower than the limit is applied. Also, any higher energy than the upper limit is not required to cause the enthalpy change. Further, the maximum values of the peaks, which are written as peak heights, decreased monotonously as T_A increased.
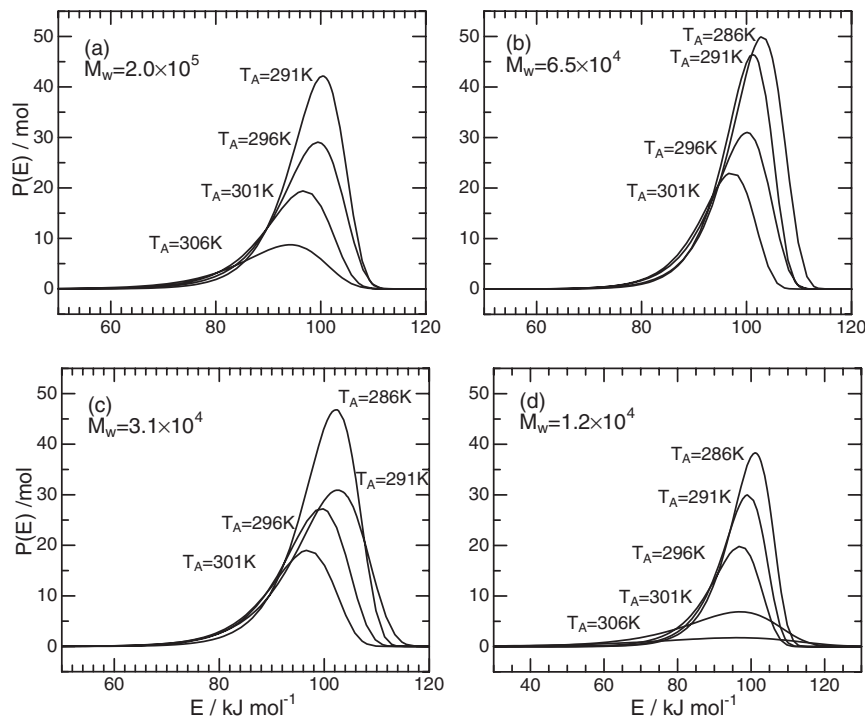
Figure 10. Activation energy spectra for the enthalpy relaxations of PCBA6 of several fractions. M_w and T_A were displayed in the figure.

Before going into details of AES results, the bell shaped curve must be explained here; that is, the calculation result using eqs. (3) and (10) necessarily gives a bell shape. As long as the relaxation function is expressed by an exponential function, no matter whether it is stretched or not, the $P(E)$ *vs.* E curve becomes bell shaped, and hence both the lower and upper limits of energy appear. In addition, the energy at which the peak takes the maximum, which is denoted by E_{top}, is exclusively influence by τ. E_{top} shifts to a higher value as τ increases, which means the rate of decrease in enthalpy is low. Further, β value has an influence on both the peak height and the spectrum width. As β increases, the peak height decreases, simultaneously the spectrum becomes broader.

As can be seen in Figure 10, E_{top} was inconsistent with the E_{app} value obtained from the plot of $\log(\tau)$ *vs.* $1000/T_A$. It is clear from eqs. (4) and (10) that the maximum should be located at the energy being correspondent with τ. Although this inconsistency seems curious at first glance, it is not wrong. If $v_0 = (1/\tau_0)$ had been assumed, E_{top} would have nearly been equal to E_{app}. E_{top}, however, did not become equivalent but became about half the value of E_{app} in this study, because this assumption was not made.

More precisely, it is necessary to discuss AES calculation done with a single average value of v_0 all through the process towards equilibrium state. If eq. (5) is taken into consideration, the pre-exponential factor is not a single average value. Presumably, the

relaxation time as well as v_0, both may be considered to vary because the structural state really varies while the process toward the equilibrium state. Considering these circumstances, AES derived from eq. (10) shows an energy distribution which occurs when a sample was located at T_A right after the rapid change of thermal condition which is experimentally the cooling process.

As a first of AES results, E_{top} shifted to lower values with the increase in T_A, which can easily be interpreted qualitatively taking account of the relation between temperature and the molecular mobility. The energies required to activate relaxation processes in high temperature are lower than those in low temperature. A comparison of E_{top} was tried here with that in literature. Although the reports on the activation energies for polymers with cyanobiphenyl group in the side chain were limited, as an analogue, viscosity was reported for polymers with cyanophenyl benzoate groups. The activation energy was reported to be, $E_{visc} = 108\,kJ/mol$, which was slightly higher than E_{top} of approximate value found in Figure 10.[40]

Next, the areas under the spectra decreased as T_A increased. According to AES model, the area is proportional to the total number of processes included in the material. Therefore, the processes considered in eq. (8) were to have a temperature dependence in their numbers. The number is large in low temperature ageing, then decreases with the rise in temperature and becomes zero above T_g. Although there might

be loss of generality, it becomes easier to realize by putting an idea that there are more processes than PCBA6 molecules, and the number of processes included in one molecule vary with temperature. As a speculation, the processes might express a difference in conformation of a molecule between the unannealed glass state and the equilibrium glass state. Regardless of this speculation, the total number of processes corresponds with $\Delta H(\infty, T_A)$.

Next, there were differences in the curvatures of the peaks between at their beginnings and at the ends. T_A apparently don't effect on the curvatures at the beginnings of the peaks which correspond with the lower limits. It is tried to estimate approximately the lower limits of the activation energy from the AES curves for samples of respective fractions. They are; 65, 70, 65 and 40 kJ/mol for $M_w = 2.0 \times 10^5$, 6.5×10^4, 3.1×10^4 and 1.2×10^4 respectively; showing a plateau value appeared around 65 kJ/mol as the rise in M_w.

Under the experimental temperatures, the peak heights at $T_A = 301$ K also had a result of a plateau value. That is, the peak heights at $T_A = 301$ K are 19.0, 22.9, 19.7 and 6.8/mol for $M_w = 2 \times 10^5$, 6.5×10^4, 3.1×10^4 and 1.2×10^4 respectively; showing a plateau value against M_w. AESs of $M_w = 1.2 \times 10^4$ at $T_A = 301$ and 306 K showed particularly lower peak heights, as well as broader spectral widths; which implies the activation energies of the process have wide distribution. On the other hand, such plateau values as seen on the peak heights were not observed at the ageing temperatures of $T_A = 296$, 291 and 286 K. When the ageing temperature is high, which means it locates near T_g, the distribution of the activation energy becomes different from that with the aging temperature located away from T_g.

CONCLUDING REMARKS

Analysis of the enthalpy relaxation was carried out using AES model for PCBA6. The relaxation functions obeyed stretched exponential forms. The apparent activation energies were calculated from Arrhenius type temperature dependences of the relaxation times, which were much lower than those reported previously. The relaxation time could also be interpreted as a shift factor in the time domain. Then, parameters of free volume concerning glass transition were evaluated and compared with those values of other polymers. The thermal expansion coefficient was relatively high, which was considered to come from a property of a side-chain type polymer. In the AES analysis, attentions were directed to the energy at the maximum of the peak, the peak height, the area bounded by AES, the upper and the lower limits of the energy. The behaviour of these properties were discussed in terms of T_A and M_w. Some properties showed plateau values as the rise in M_w. The AES analysis shown here helps to clarify the relationship between the relaxation phenomenon and property.

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