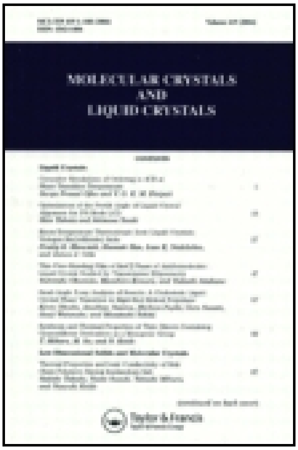

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Enthalpy Relaxation of Glassy State of Cholesteryl 4-A-n-Alkoxy-3-methoxybenzoates

K. Kasuga [a] , H. Hatakeyama [a] & T. Hatakeyama [b]

[a] Industrial Products Research Institute, 1-1-4, Higashi, Tsukuba, Ibaraki, 305, Japan

[b] Research Institute for Polymers and Textiles, 1-1-4, Higashi, Tsukuba, Ibaraki, 305, Japan

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Enthalpy Relaxation of Glassy State of Cholesteryl 4-*n*-Alkoxy-3-methoxybenzoates

K. KASUGA and H. HATAKEYAMA
Industrial Products Research Institute, 1-1-4, Higashi, Tsukuba, Ibaraki 305, Japan

and

T. HATAKEYAMA
Research Institute for Polymers and Textiles, 1-1-4, Higashi, Tsukuba, Ibaraki 305, Japan

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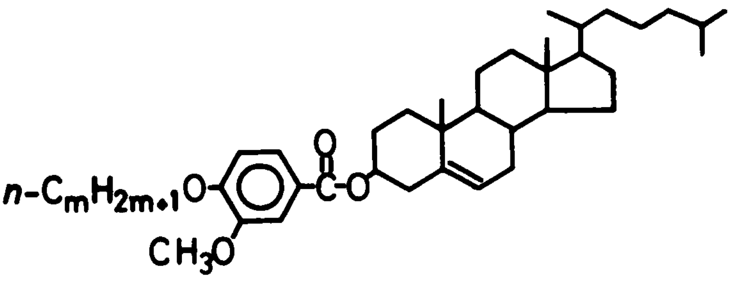
The enthalpy relaxation process of the glassy state of the new liquid crystalline compound, cholesteryl 4-*n*-alkoxy-3-methoxybenzoate (I), was studied by differential scanning calorimetry (DSC). The excess enthalpy was calculated from DSC curves of the annealed samples. Assuming the total excess enthalpy, ΔH_o of quenched sample could be calculated by the equation, $\Delta H_o = \Delta C_p(T_g - T_a)$, where ΔC_p is the heat capacity difference between the liquid state and the glassy state at the glass transition temperature (T_g) and T_a is the annealing temperature. From the change of the excess enthalpy with the annealing time, the relaxation time was obtained. The relaxation times of three homologues were calculated in order to compare the relaxation rate. The effect of the structure of the compounds on the relaxation process was found, *i.e.*, the relaxation time increases with the increase of the chain length of the *n*-alkoxyl group.

Keywords: liquid crystal, cholesteryl benzoate, enthalpy relaxation, glassy state, differential scanning calorimetry, heat capacity

INTRODUCTION

In a previous paper, we described the synthesis and thermal properties of a homologous series of cholesteryl 4-*n*-alkoxy-3-methoxybenzoates (I).[1] Eighteen homologues were synthesized from vanillin by changing the 4-*n*-alkoxyl group, and their mesomorphic properties were studied by differential scanning calorimetry (DSC) and polarizing microscopy. It was found that all of those homologues showed liquid crystalline properties. The homologues from cholesteryl 3,4-dimethoxybenzoate ($m = 1$) to cholesteryl 4-*n*-hexyloxy-3-methoxybenzoate ($m = 6$) showed a cholesteric phase (Ch). The other higher homologues (from $m = 7$ to $m = 18$) indicated smectic A (S_A) and Ch phases. At the same time, it was found that those esters changed into the glassy state when they were quenched from either mesophases and/or the isotropic liquid phase. Although the formation of the glassy state has



(I) m = 1, 2,-----, 18

been observed in several liquid crystalline compounds already,[2,3] it still seems a rare phenomenon among liquid crystalline compounds.

It is known that an enthalpy relaxation takes place, when the glassy sample is annealed isothermally below the glass transition temperature (T_g).[4] We observed this phenomenon in our glassy cholesteryl esters. In order to analyze such an enthalpy relaxation process, it is convenient to evaluate the enthalpy change by annealing in the glassy state.[5] And such enthalpy change can be expressed as variations in the enthalpy displacement from the equilibrium glassy state, *i.e.*, excess enthalpy. There are several methods of estimating the excess enthalpy.[6-9] Recently, Yoshida *et al.* reported a new method of estimating it by using a differential scanning calorimeter.[10] They calculated the values of the excess enthalpy from two DSC curves for the annealed and quenched samples. And from the relationship between excess enthalpy and enthalpy relaxation time, the relaxation rate and the activation energy were obtained. They applied this method to the analysis of the enthalpy relaxation process of polymer glasses and the effects of the structure of the polymers on the relaxation process were evaluated quantitatively.[10-13]

This report details our attempts to apply this method to the analysis of the enthalpy relaxation process of glassy cholesteryl esters.

EXPERIMENTAL

Sample preparation

The samples, cholesteryl 4-*n*-alkoxy-3-methoxybenzoates, were prepared by the same method as reported previously.[1] At first 4-*n*-alkoxy-3-methoxybenzoic acids were synthesized from vanillin. The acids obtained were converted to corresponding acid chlorides. The reaction of the acid chlorides with cholesterol yielded the desired esters, which were purified by recrystallization from hexane and dried under high vacuum at 60°C for 24 hr prior to use.

Differential scanning calorimetry

Thermal analysis was carried out using a differential scanning calorimeter (DSC), Perkin-Elmer Model II, equipped with a low temperature cell. The sample weight was about 4 mg. The scanning rate was 10K/min. The temperature was varied from 240 to 430K. The transition temperatures and enthalpies measured with DSC were calibrated using indium as the standard.

Measurement of glass transition temperature

There are several methods of evaluating the glass transition temperature in DSC measurements. In this case, the glass transition temperature was defined as the point where the extrapolated baseline in the glassy state and the extrapolated slope line in glass transition cross each other.

Estimation of excess enthalpy

Excess enthalpies were calculated from DSC curves according to the method reported by Yoshida *et al.*[10]

Figure 1 shows the change of the specific heat capacity, which was obtained by DSC measurement, for quenched (solid line) and for annealed (chain line) samples. In the figure, T_a represents the annealing temperature and T_g represents the glass transition temperature.

The excess enthalpy, ΔH_o of quenched glass can be expressed as equation 1

$$\Delta H_o = \Delta C_P(T_g - T_a) \tag{1}$$

where ΔC_P represents a difference in specific heat capacities of the liquid state and the glassy state at T_g. On the other hand, the decreased enthalpy during annealing, *i.e.*, relaxation enthalpy, ΔH_d also can be expressed as follows

$$\Delta H_d = \int_{T_a}^{T_f} (C_{Pa})\mathrm{d}T - \int_{T_a}^{T_f} (C_{Po})dT \tag{2}$$

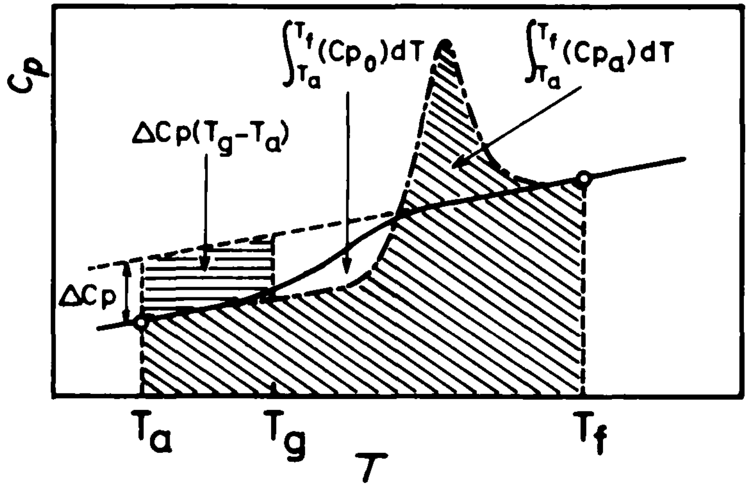


FIGURE 1 Schematic diagram of specific heat capacity change for quenched (solid line) and annealed (chain line) glasses.

where Cp_a and Cp_o represent the specific heat capacities of the annealed and the quenched glasses respectively. Therefore, the value of ΔH_d can be obtained by integrating two DSC curves for the annealed and the quenched glasses in Figure 1 over the temperature range from T_a to T_f. Finally, excess enthalpy, ΔH_t of the sample, which was annealed at T_a for time t, was defined as follows.

$$\Delta H_t = \Delta H_o - \Delta H_d \tag{3}$$

In this way, the value of the excess enthalpy was calculated from DSC curves.

RESULTS AND DISCUSSION

Figure 2 shows DSC curves of cholesteryl 4-*n*-octyloxy-3-methoxybenzoate ($m = 8$) over a temperature range from 240K to 450K. On heating, the DSC curve of a solution-grown sample exhibited three endothermic transitions (Run 1). The pattern of the curve suggested the existence of two kinds of mesophases. By microscopic observation, it was found that the sample showed two kinds of mesophases, *i.e.*, smectic A (S_A) and cholesteric (Ch) phases. Therefore, three endothermic peaks in Run 1 are attributed to the crystalline–S_A, S_A–Ch, Ch-Isotropic liquid transitions respectively from the lower temperature side. Run 2 in Figure 2 is the heating DSC curve of the sample which was cooled rapidly from the isotropic liquid to 240K. At around 280K, an endothermic jump was observed. This anomaly was thought to be caused by glass transition, since the following experiment supported this. Figure 3 shows DSC curves of the sample which was annealed at the temperature of 5K lower than 279.5K, which was assumed to be the glass transition temperature. The number on each curve shows the annealing time in min. In each of the curves, a peak as well as the endothermic jump, was observed. As the annealing time becomes longer, the peak area increases and the glass transition

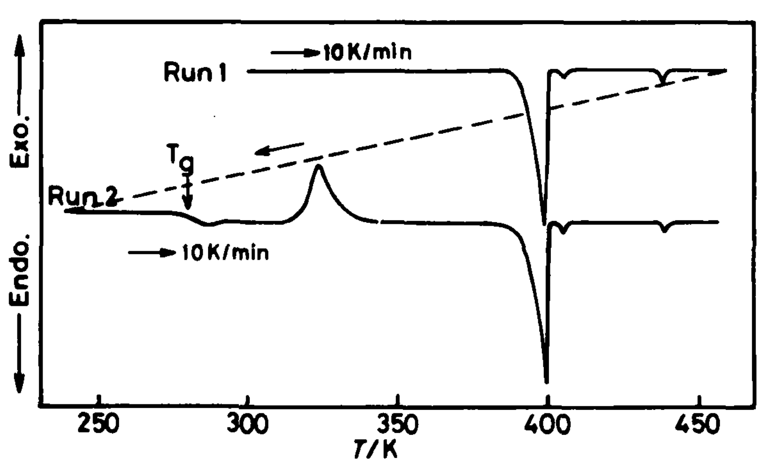


FIGURE 2 DSC curves of cholesteryl 4-*n*-octyloxy-3-methoxybenzoates.

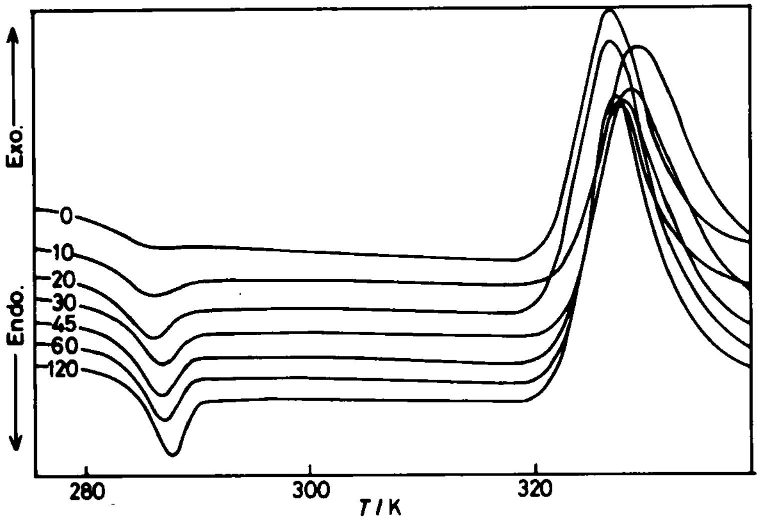


FIGURE 3 DSC curves of annealed samples. Numbers show annealing time in min.

temperature shifts to a higher side. From those DSC curves, values of the excess enthalpy (ΔH_t) were calculated according to the method which was previously described. The same experiment was also carried out under different annealing temperatures.

Figure 4 shows the relationship between the excess enthalpy and the annealing time. Numbers (5, 10, 15) in the figure represent the temperature differences (K) between the glass transition temperature (T_g) and the annealing temperature (T_a). The following equation was used in order to compare the relaxation times of polymer glasses[10]

$$\Delta H_t = \Delta H_o \exp(-t/\tau) \tag{4}$$

where τ is the relaxation time and ΔH_o and ΔH_t represent the excess enthalpies of the glass before annealing and after annealing for t hrs. Equation 4 can be rewritten as follows:

$$\ln(\Delta H_t/\Delta H_o) = -t/\tau + \text{const.} \tag{5}$$

Figure 5 shows the relationship between the logarithmic relative decrease of enthalpy, $\ln(\Delta H_t/\Delta H_o)$ and the annealing time. As can be seen from the figure, the relationship between $\ln(\Delta H_t/\Delta H_o)$ and the annealing time is not linear as in the case of polymer glasses.[10] When the annealing time increases or the annealing temperature decreases, the change of $\ln(\Delta H_t/\Delta H_o)$ becomes smaller, *i.e.*, the relaxation takes place more slowly.

From equation 5, the relaxation time, τ was obtained as follows:

$$\tau^{-1} = -\mathrm{d}[\ln(\Delta H_t/\Delta H_o)]/\mathrm{d}t \tag{6}$$

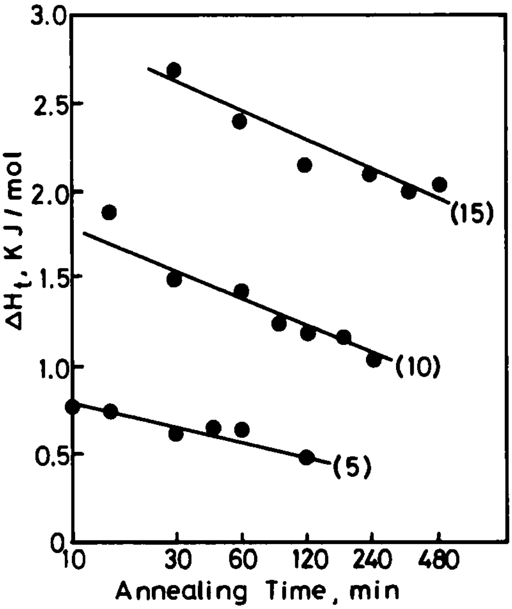


FIGURE 4 Relationship between excess enthalpy, ΔH_t and the annealing time. Numbers in parentheses show temperature difference between glass transition temperature and annealing temperature.

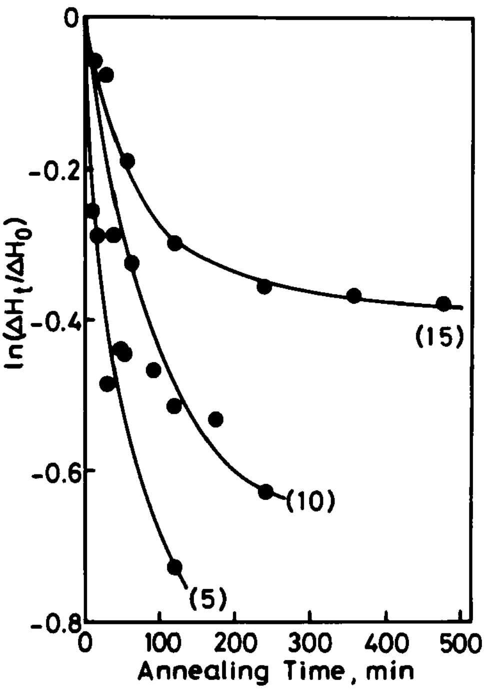


FIGURE 5 Relationship between logarithmic relative decrease of enthalpy, ln($\Delta H_t/\Delta H_o$) and annealing time. Numbers in parentheses show temperature difference between glass transition temperature and annealing temperature.

Therefore, from the gradient of the curves in Figure 5, the value of the relaxation time can be calculated. Figure 6 shows the relationship between the logarithmic relaxation time, which was calculated by equation 6, and the excess enthalpy, ΔH_t. These lines indicate a linear relationship. The open circle on each line in Figure 6 represents the relaxation time at a point when the enthalpy is reduced to one-half of the initial excess enthalpy, $\tau_{(1/2)}$. Figure 7 shows the relationship between $\tau_{(1/2)}$ and the reciprocal of the annealing temperature. The relaxation time ($\tau_{(1/2)}$) shows an Arrhenius temperature dependence, expressed in equation 7

$$\tau^{-1} = A \exp(-Ea^*/RT) \tag{7}$$

where Ea^* is the apparent activation energy of enthalpy relaxation. The value of Ea^*, which was calculated from $\tau_{(1/2)}$, was ca. 350 kJ/mol.

In order to estimate the effect of the *n*-alkoxyl group on the relaxation process, the same experiment as mentioned above was carried out on the *n*-butyloxy and *n*-hexyloxy homologues. Figure 8 shows the relationship between $\ln(\Delta H_t/\Delta H_0)$ and the annealing time on three homologues ($m = 4, 6, 8$). In this case, the temperature difference between T_a and T_g is 5 K. It can be seen clearly from the figure that relaxation takes place more rapidly on the sample, which has a shorter *n*-alkoxyl group. Table I lists the calculated value of the $\tau_{(1/2)}$, T_g and T_a of three homologues. The relaxation time increases with the increase of the chain length of the *n*-alkoxyl

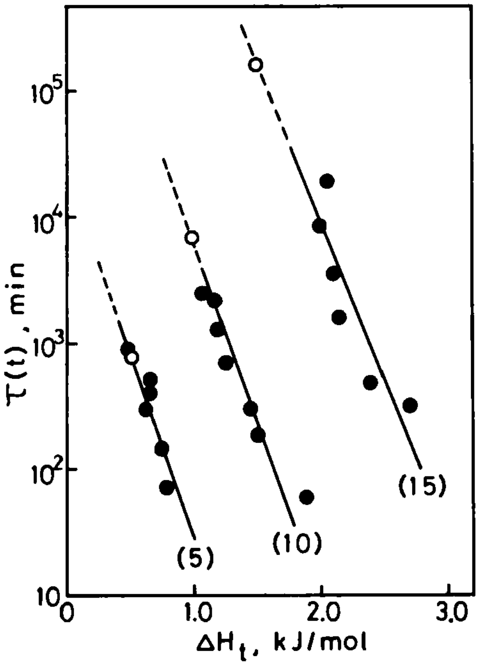


FIGURE 6 Relationship between logarithmic relaxation time and excess enthalpy. Numbers in parentheses show temperature difference between glass transition temperature and annealing temperature.

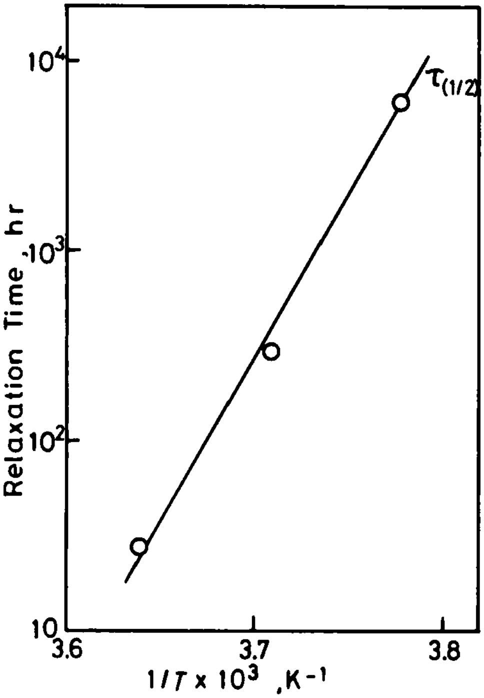


FIGURE 7 Relationship between $\tau_{(1/2)}$ and reciprocal of annealing temperature.

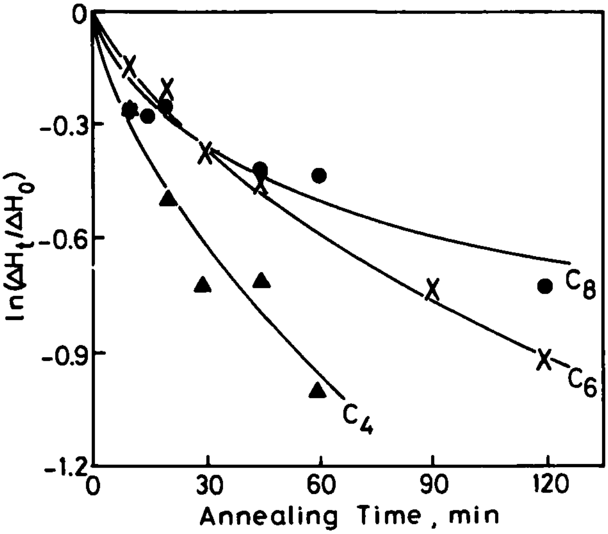


FIGURE 8 Relationship between $\ln(\Delta H_t/\Delta H_o)$ and annealing time on three homologues.

TABLE I

Calculated value of $\tau_{(1/2)}$ of three homologues

sample	T_g(K)	T_a	$T_g - T_a$	$\tau_{(1/2)}$(min)
n-butoxy(4)	288	283	5	70
n-hexyloxy(6)	280.5	275.5	5	180
n-octyloxy(8)	279.5	274.5	5	770

T_g: glass transition temperature.
T_a: annealing temperature.

group. Similarly in the case of polymer glasses,[10] the relaxation time increases with the increase of the mass of the side chains of the polymers. From our results, it was found that, in compounds with small molecular weights, the rate of enthalpy relaxation was also affected significantly by a slight change in the structure of the compound.

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