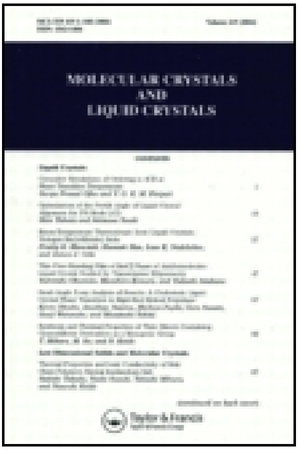

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Enthalpy Relaxation Behavior of Liquid-Crystalline Glasses of an Esterified Cholesterol Derivative and its Complex Salts with Aliphatic Amines

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Enthalpy Relaxation Behavior of Liquid-Crystalline Glasses of an Esterified Cholesterol Derivative and its Complex Salts with Aliphatic Amines

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A cholesteryl hydrogen phthalate (CHP) and its complex salts with normal aliphatic amines (C_n-amines) are capable of forming a glassy liquid-crystalline phase, where an anisotropic organization of their fluid mesophase is frozen in an uncrystallized solid state. Differential scanning calorimetry (DSC) measurements were conducted for these glassy materials to examine an enthalpy relxation phenomenon, occurring when they were annealed adequately at temperatures lower than the glass transition temperature. The enthalpy relaxation behavior, monitored as evolution of a DSC endothermic peak, was analyzed in terms of a Kohlrausch-Williams-Watts type of stretched exponential equation, and the overall relaxation time τ and a parameter β chracterizing the distribution of the relaxation mode were evaluated. It turned out that the τ values obtained for CHP/C_n-amine salts were rather smaller than those for CHP *per se*, and β became close to unity when CHP was complexed with the C_n-amines through ionic interaction, the latter component employed having 12, 16, and 18 carbons. The activation energy for the relaxation process of the CHP/C_n-amine samples was considerably small, compared with that in the case of CHP alone, and tended to decrease with an increase in the carbon number of the amine component. An attempt was also made to estimate the fragility of these samples as glass.

Keywords: Cholesterol derivative; Aliphatic amine; Complex salt; Liquid-crystalline glass; Enthalpy relaxation

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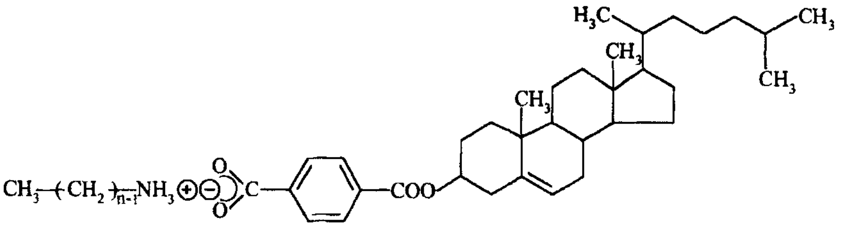
1. INTRODUCTION

The physical aging in glassy solids, ocurruring during annealing below the glass transition temperature T_g, is interpreted as a non-equilibrium phenomenon. Execess thermodynamic quantities such as volume and enthalpy, usually frozen in solids vitrified by rapid cooling below T_g, decrease toward the respective equilibrium values with an elapse of time of the aging. This relaxation behavior toward an equilibrium state is commonly referred to as volume relaxation or enthalpy relaxation,[1,2] which often gives rise to serious changes in the macroscopic properties of materials, such as mechanical and viscoelastic properties.[3–6] Thus there have been a lot of studies on the physical aging of glass-forming materials, from both theoretical and practical standpoints. The great majority of the works have been concerned with organic materials represented by amorphous polymer solids. However, the relaxation phenomena in the polymer amorphous regions have not yet been elucidated sufficiently. The molecular weight distribution of polymers and other possible factors originating from the condensed phase consisting of flexible chain molecules entangled mutually, would be responsible for the difficulty of the definite characterization.

The glassy materials selected for the present study of enthalpy relaxation may be classified into a specific kind, distinguishable from both amorphous polymer glasses and isotropic liquid glasses. They have a relatively low molecular weight of less than 1000 and possess a long-range order of orientation found in a liquid-crystalline mesophase. In a number of phase studies for mesogenic compounds, such a "liquid-crystalline glass"[7] is already recognized as an anisotropic solid phase without crystallinity, appearing occasionally in a thermal transition scheme, or as a state in which a birefringent architecture is immobilized via chemical crosslinking reactions or rapid quenching of a fluid mesophase. So far, however, little attention has been paid to the physical aging and structural relaxation behavior for the liquid-crystalline glasses.

In a preceding paper,[8] one of the authors (YN) reported the complex formation and phase behavior of the binary mixtures of cholesterol derivative compounds having a carboxyl group at their terminal end with a series of normal aliphatic amines, $C_nH_{2n+1}NH_2$ (abbreviated as C_n-amines). For example, cholesteryl hydrogen phthalate (CHP) provided a stoichiometric 1:1 complex with C_n-amines (n=12 to 18) through ionic interaction between carboxylic acid and amino groups, as formulated below:

All the complex salts examined there exhibited an enantiotropic type of thermotropic liquid crystallinity. At room temperature (~20°C) or lower temperatures, however, they assumed a glassy state with the original mesomorphic order preserved therein, as was also the case for CHP *per se*. The transition behavior is



CHP/C_n-amine (n = 12 - 18)

thus in contrast with that of most liquid crystals which prefer to crystallize upon cooling below the melting point.

In the present paper, we describe the enthalpy relaxation in the liquid-crystalline glasses of CHP and CHP/C_n-amine salts, through differential scanning calorimetry (DSC) measurements for the aged samples. A particular interest may be focused on the effect of the amino-alkyl chains, possibly serving as a flexible spacer for the mesogenic steroid core, on the enthalpy relaxation in the ordered molecular assemblies.

2. EXPERIMENTAL SECTION

2.1. Original Materials and Preparation of Salts

CHP was purchased from Tokyo Kasei Kogyo Co. and purified by recrystallization from an ethanol solution. C_n-amines of n=12, 16, and 18, all guaranteed reagent-grade, were also obtained from Tokyo Kasei Kogyo Co. and employed without further purification.

Preparation of complex salts of CHP with C_n-amines was carried out in almost the same manner as that reported previously.[8] Each component was dissolved in ethanol at 1 wt% at room temperature (~20°C) with continuous stirring, and then two solutions were mixed with each other in an equimolar proportion. CHP/C_n-amine complex salts were obtained as a laminate product on a glass tray, each cast from the corresponding mixed solution by solvent evaporation at 25°C.

2.2. Instrumentation

DSC measurements were performed with a Seiko DSC 6200. The instrument was calibrated with an indium standard. A weighed amount of respective samples

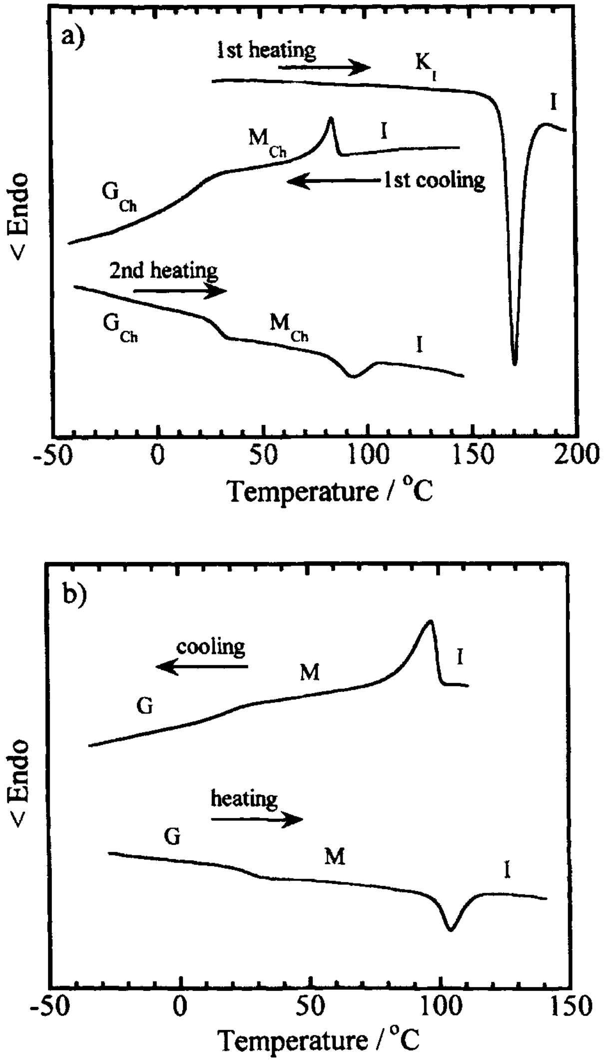


FIGURE 1 DSC thermograms of (a) CHP and (b) CHP/C_{18}-amine complex salt

(4.5–5.5 mg) was sealed in an aluminum pan. Thermograms were recorded at a scanning rate of 10°C min^{-1} (for heating) or 20°C min^{-1} (for cooling), unless otherwise specified.

Annealing treatment for aging of liquid-crystalline glasses was carried out in the DSC cell, when the time period of annealing, i.e., the aging time (t_a), was shorter than 3 hr. In the case where a long term exceeding 3 hr was required for the annealing, samples were aged in a thermo-regulated incubator, Torrey Pines Scientific Model IN30.

Fourier transform infra-red (FT-IR) spectra were measured with a Jasco spectrophotometer FT/IR-550 equipped with a diffuse reflectance instrument (DR-81).

Polarized optical microscopy was conducted with an Olympus BX60 microscope equipped with a Mettler FP82 hot-stage. Samples were usually sandwiched between a slide and cover glass.

2.3 Aging Procedure and Enthalpy Relaxation Measurements

Mesomorphic ordered glasses of CHP and CHP/C_n-amine salts used for the present relaxation study were prepared directly in the DSC apparatus, by supercooling from the respective liquid-crystalline state appearing in their phase transition schemes (see the next section). The liquid-crystalline glasses were aged at a selected temeprature T_a lower than T_g for a certain period, and then subjected to the measurements of enthalpy relaxation. Caution was exercised so that all the samples had almost the same thermal history. A sequence of procedure of the aging and measurements is summarized below:

1) Cooling the original samples at 20°C min^{-1} to an aging temperature T_a from a mesomorphic state at a temperature T_M higher than T_g by ca. 50°C, after they were once melted;

2) Aging the galssy samples at T_a in the DSC cell or thermo-regulated incubator over a time period of t_a;

3) Quenching the aged samples to −50°C from T_a at a cooling rate of 40°C min^{-1};

4) Heating the frozen samples from −50°C again to $T_M \fallingdotseq T_g$+50°C at a rate of 10°C min^{-1}, whereupon the enthalpy relaxation was monitored as an endothermic peak emerging just after the onset of the glass transition in the DSC thermograms.

3. RESULTS AND DISCUSSION

3.1. Basic Scheme of Thermal Transition Behavior

Figure 1a depicts DSC thermograms of CHP, obtained in usual scanning cycles. On heating the original CHP (K^I) crystallized from ethanol solution, it melts at 167°C to transform solely into an isotropic liquid (I). On cooling the CHP melt, the isotropic liquid phase changes into a cholesteric type of liquid crystal (M_{Ch}) at ~87°C. In observation of the corresponding cooling process with a polarizing microscope, the development of a Grandjean-planar texture was noted at ca. 90°C, following the transient appearance of a focal conic texture. Upon continued cooling of the mesomorphic CHP, it is vitrified at ca. 30°C without crystallizing or losing its anisotropic texture. A glassy solid (G_{Ch}) retaining a cholesteric structure is thus obtained. In the second heating scan, the ordered glass changes again into the cholesteric fluid mesophase around 30°C and eventually into the isotropic liquid at 91.4°C. In additional cooling and heating cycles, CHP shows the same enantiotropic phase behavior, $I \Leftrightarrow M_{Ch} \Leftrightarrow G_{Ch}$.

In similar repeated DSC cycles, CHP/C_n-amine complex salts also present an enantiotropic scheme, $I \Leftrightarrow M \Leftrightarrow G$, without showing any transition signal associated with crystal fusion of the two contituent species. A typical example of DSC thermograms is given in Figure 1b. The data were obtained for a CHP/C_{18}-amine system after preheating to 130°C. A single glass transition and a mesophse (M) – isotropic liquid (I) phase transition are clearly observed in both cooling and heating scans. Polarized microscope observations revealed that all the salts examined preferred a molecular arrangement to orient perpendicular rather than parallel to the surface plane of a slide glass in the liquid-crystalline state. The homeotropic character was confirmed from a conoscopic image obtained by insertion of condenser and Bertrand lenses in the microscope; i.e., the interference figure demonstrated explicitly that the liquid-crystalline molecular assembly has a uniaxial orientation distribution of positive optical anisotropy. This result indicates that a smectic-like layer structure tends to develop in the liquid-crytalline complex systems, or there may be considerably poor periodicity if a cholesteric twisted structure is still possible, but with the helical axis parallel to the surface plane of the sample.

In conventional DSC measurements, the glass transition temperature T_g of a glassy material is evaluated from the onset point (or midpoint) of a base-line shift appearing in a thermogram due to the discontinuity in specific heat that is caused by passing through the transition of the material on heating. However, this evaluation is often affected seriously by some kinetic effects, i.e., the value of T_g is variable depending on the scanning rate and the conditions of pretreatment of the sample.[9,10] To minimize the contribution of such factors and determine a more accurate T_g value for the liquid-crystalline glasses prepared in this study, we adopted a method proposed by Richardson *et al.*[10] For this purpose, the DSC output data of heat flow was converted into the corresponding relative enthalpy *H* and a plot of *H* against temperature was constructed. Following that, two tangential lines were drawn on both sides of the glass transition region in the *H* versus tempertaure curve and a value of temperature at the point of intersection was read off as T_g. As a result of the regression analysis, the T_gs of unaged CHP and

CHP/C_n-amine salts of n=12, 16, and 18 were estimated to be, respectively, 25.8, 10.5, 19.0, and 20.0°C. In preparation of their aged samples for examining the enthalpy relaxation behavior, the annealing temperature T_a was selected as $T_a=T_g-\Delta T$, where AT ranged from 2.8°C to 25.5°C (see Table I).

TABLE I Enthalpy relaxation data for the liquid-crystalline glasses of CHP and CHP/C_n-amine complex salts

Sample	$T_g/°C$	$T_a/°C$	T_g-$T_a/°C$	*ln* τ/s	β	$Ea/kJ\ mol^{-1}$	*m*
CHP	25.8	7.0	18.8	12.4	0.69	154	27
		15.0	10.8	10.4	0.74		
		20.0	5.8	9.22	0.78		
		23.0	2.8	8.97	0.70		
CHP/C_{12}-amine	10.5	0.0	10.5	7.20	0.78	58	11
		2.0	8.5	6.67	0.71		
		5.0	5.5	6.33	0.62		
		7.7	2.8	6.72	0.61		
CHP/C_{16}-amine	19.0	0.0	19.0	7.32	0.98	52	9
		5.0	14.0	6.86	0.92		
		9.0	10.0	6.61	0.90		
		12.0	7.0	6.33	0.84		
CHP/C_{18}-amine	20.0	−5.5	25.5	7.77	1.00	47	8
		−0.3	20.3	7.19	0.98		
		4.5	15.5	6.95	0.91		
		7.0	13.0	6.80	0.84		

3.2. Analysis of Enthalpy Relaxation of Aged Liquid-Crystalline Glasses

The enthalpy relaxation of glassy materials is observable usually as an endothermic peak in their DSC thermograms just after the onset of the glass transition when the aged samples are reheated. Figure 2 exemplifies DSC thermograms of liquid-crystallline CHP glasses aged for different periods of time at 20.0°C. The enthalpy Δ*H* can be evaluated from the endothermic peak area shaded in each data. The area increases with aging time, accompanied by a systematic shift in the peak position to the side of higher temperature.

The time evolution of the enthalpy of CHP's annealed at various temperatures lower than T_g is illustrated in Figure 3. This result demonstrates clearly that the physical aging of the liquid-crystalline glasses is attended by relaxation of their enthalpy, which continues until the respective sample is equilibrated at the given

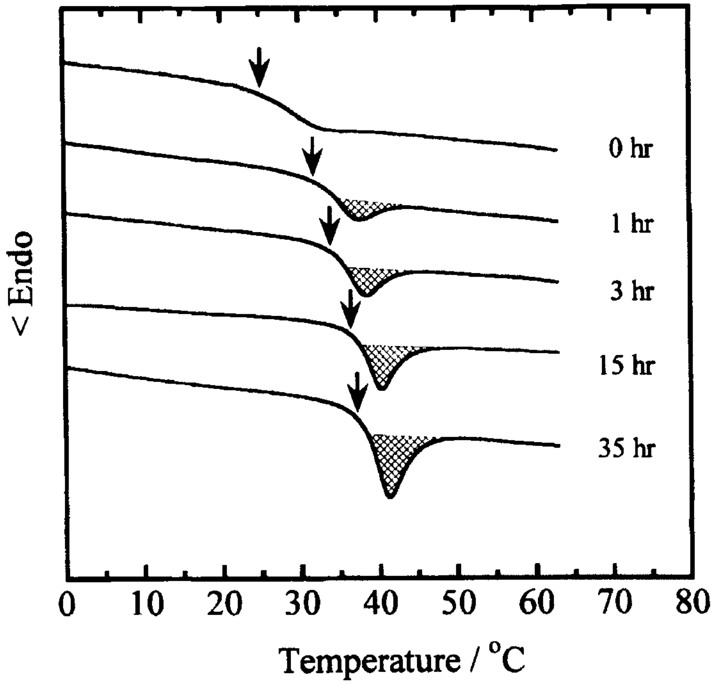


FIGURE 2 DSC thermograms of glassy CHP samples aged for different periods of time at 20.0°C. Arrows indicate the onset point of a base-line shift in heat flow caused by passing through the glass transition on heating

temperature. In the figure, the enthalpy goes up rapidly with time in a relatively early stage of the aging and eventually levels off to converge at an equilibrium value ΔH_∞. As the aging temperature is lowered, the ΔH_∞ becomes larger and the enthalpy relaxes slower. Similar observations in tendency of the dependence of ΔH on aging time and temperature were noted for liquid-crystalline glasses of CHP/C_n-amine salts.

To describe more quantitatively the kinetics of the enthalpy relaxation during isothermal annealing of the glassy materials, it is useful to employ the following Kohlrausch-Williams-Watts (KWW) type of equation with a stretched exponential term: [11]

$$\Delta H = \Delta H_\infty[1 - \Phi(\mathrm{t})] \tag{1}$$

$$\text{with} \quad \Phi(\mathrm{t}) = \exp[-(\mathrm{t_a}/\tau)^\beta] \tag{2}$$

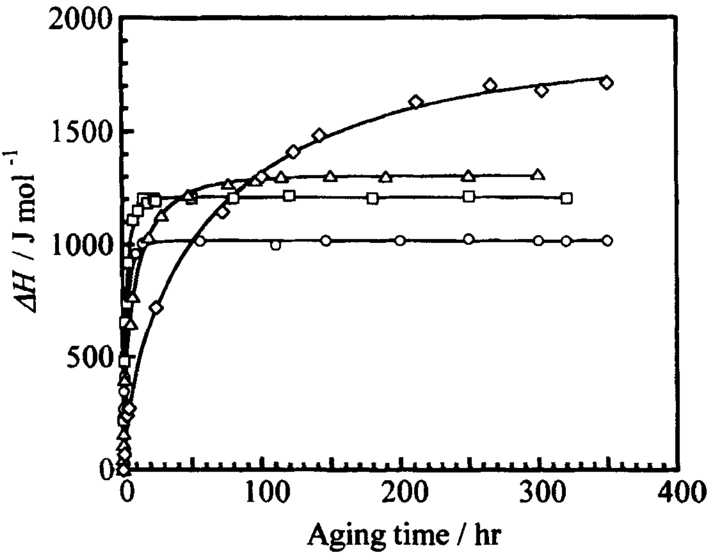


FIGURE 3 Time evolution of the relaxation enthalpy calculated from a DSC endothermic peak area (see Fig. 2), for liquid-crystalline glasses of CHP that were aged at different temperatures: ○, 23.0°C; □, 20.0°C; △, 15.0°C; ◊, 7.0°C

where Φ(t) is the stretched exponential function containing the relaxation time τ and a non-exponential parameter β ($0<\beta\leq1$). The parameter β is a measure indicating the degree of distribution of the relaxation time; viz., a value of $\beta=1$ means that there occurrs just a single relaxation mode, while, in contrast, when the width of the distribution is rather broad due to coexistence of plural relaxation modes in the aging process, the parameter assumes a much smaller value to approach zero. The β and τ can be obtained by fitting a ΔH vs. t_a curve calculated in terms of eqs. 1 and 2 with suitable values of the parameters to the experimental data. The time evolution curves of relaxation enthalpy for CHP, illustrated in Figure 3, were actually drawn according to the fitting procedure. Similar fitting by using the KWW stretched exponential equation was applied to the corresponding data for the cholesteryl salts with C_n-amines, and the overall β and τ were determined. The result of the quantification is tabulated in Table I.

Figure 4 shows plots of the parameter β against the reciprocal of aging temperature, constructed for the respective liquid-crystalline glasses of CHP and CHP/C_n-amine complex salts. As can be seen from the figure and Table I, the β values for the liquid-crystalline glasses examined here are considerably larger than those (roughly 0.5–0.55)[12] reported for many amorphous polymers. Espe-

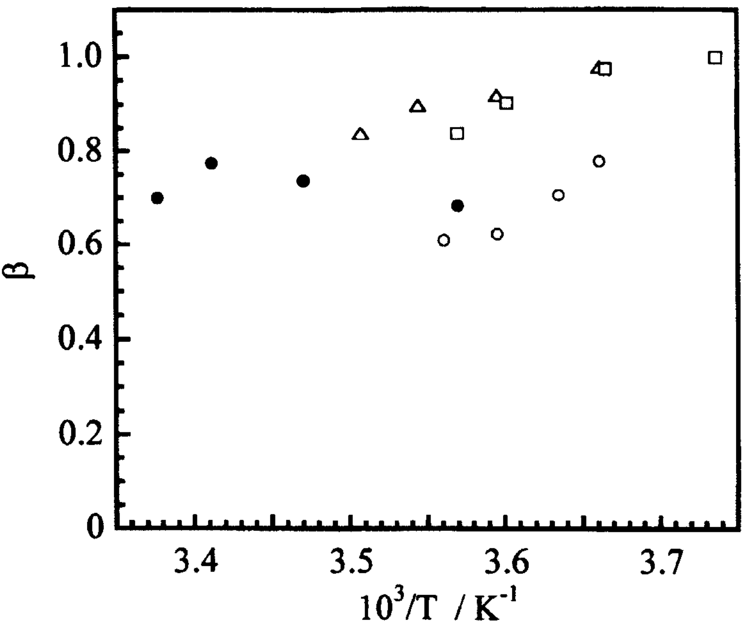


FIGURE 4 Plots of the parameter β against the reciprocal of aging temperature for four series of liquid-crystalline glassy samples: ●, CHP; ○, CHP/C_{12}-amine; △, CHP/C_{16}-amine; □, CHP/C_{18}-amine

cially, it is of great interest to find that when CHP is complexed with the C_n-amines of n≥16 through ionic interaction, the β becomes close to unity so that the enthalpy relaxation proceeds preferably according to a Debye type of single exponential function. Thus it may be deduced that the presence of a higher molecular ordering in the organic glasses results in a narrower distribution of the enthalpy relaxation mode. In comparison between the complex salts, the β value tends to increase with an increase in the carbon number of the amine component at almost the same aging temperature. Concerning the temperature dependence of the parameter, it decreases gradually with increasing aging temperature, except for the case of CHP alone providing an approximately constant β of 0.7–0.75. It follows that the degree of distribution of the relaxation time is smaller in the case where CHP is complexed with C_n-amines having a much longer carbon chain and the resulting salts are aged at comparatively lower temperatures below T_g.

Figure 5 shows the logarithmic plots of τ versus the reciprocal of absolute temperature for the CHP and CHP/C_n-amine samples, making clear the dependence of the enthalpy relaxation time on the aging temperature. It is evident here that the relaxation times observed for the CHP/C_n-amine salts are rather shorter than those

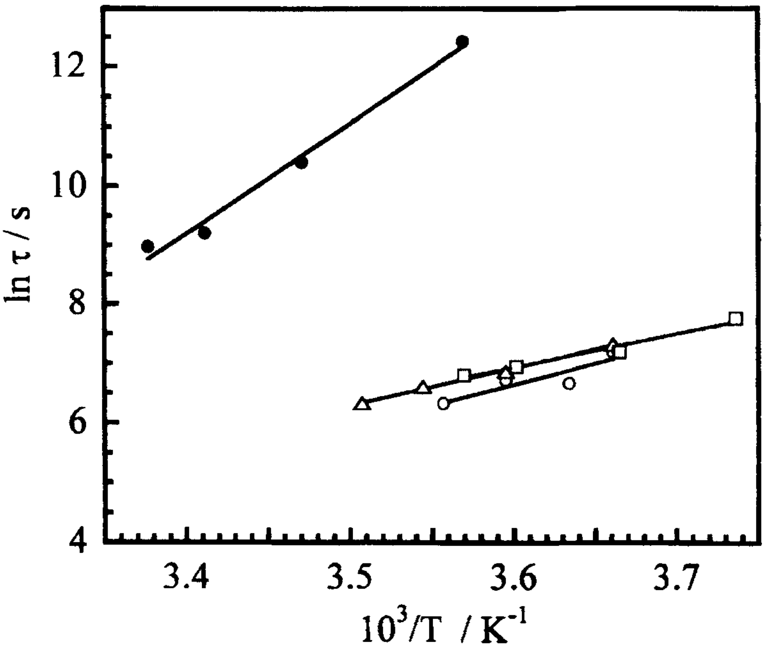


FIGURE 5 Logarithmic plots of the enthalpy relaxation time τ against the reciprocal of aging temperature for liquid-crystalline glasses of CHP and CHP/C_n-amine salts. Symbols are the same as those used in Figure 4

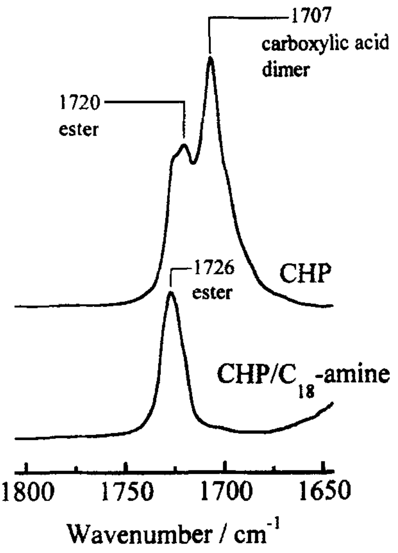
for CHP *per se*. Furthermore, the temperature dependence is found to be represented by the Arrhenius equation for all the series of the glassy samples, as follows:

$$\tau^{-1} = \tau_0^{-1} \exp[-\mathrm{Ea}/(\mathrm{RT})] \qquad (3)$$

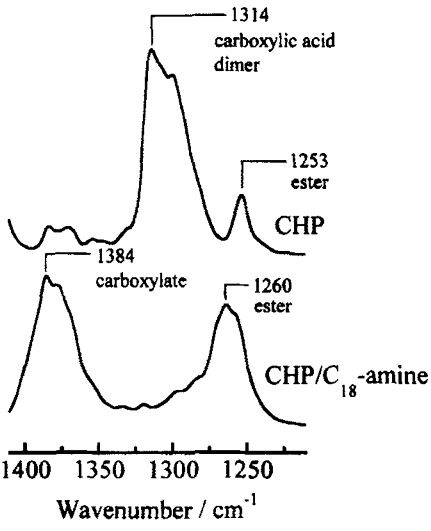
where Ea is the activation energy for the enthalpy relaxation process in the glassy state, and τ_0^{-1} and R are the pre-exponential factor and the gas constant, respectively.

The activation energy Ea can be calculated from the slope of each straight line drawn according to eq. 3 in Figure 5. The result of the evaluation is also listed in Table I. Obviously, the activation energy required for the relaxation in the CHP/C_n-amine glasses is much smaller, roughly one third, compared with that in the case of CHP alone, and there occurs a slight decrease in the Ea value with an increase in the carbon number of the amine component.

Figure 6 displays FT-IR spectra of CHP and CHP/C_{18}-amine glassy samples, depicted on an enlarged scale for two frequency regions: C=O stretching region



(a) C=O stretching frequency region



(b) C-O stretching frequency region

FIGURE 6 FT-IR spectra obtained for liquid-crystalline glassy samples of CHP and CHP/C_{18}-amine

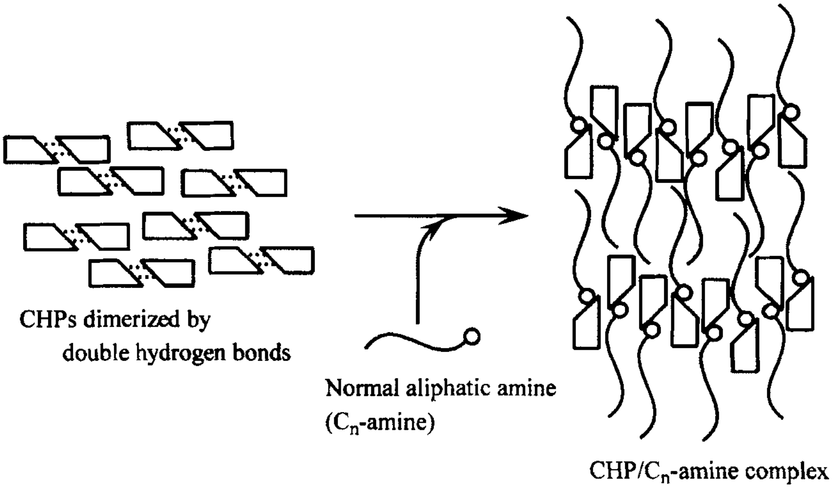


FIGURE 7 Schematic representation of a model for interpreting the molecular assembly of liquid-crystalline CHP and the structural change following its complexation with C$_n$-amine

(Fig. 6a) and C-O stretching region (Fig. 6b). Judging from the data given in the top of the figures, CHP molecules are possibly dimerized in the liquid-crystalline glassy state, to form a long conjugated system through dual intermolecular hydrogen bonding between the carboxyl groups at their terminal ends. On the other hand, the equimolar mixture of CHP and C$_{18}$-amine yields a complete salt via ionic interaction between carboxyl and amino groups, as evidenced by the emergence of a carboxylate signal at 1384 cm^{-1} as well as by the disappearance of C=O and C-O stretching bands at 1707 cm^{-1} and 1314 cm^{-1}, respectively, indicating the absence of the acid carboxyl group (see the bottom of the figures). The complexation was also ascertained by the disappearance of an N-H stretching band at 3333 cm^{-1}, i.e., by the absence of isolated amine. On the basis of this spectroscopic result and the microscopic observations mentioned already, it is possible to depict a model scheme for interpreting the molecular assmbly of CHP and the structural change following its complexation with C$_n$-amine, as shown diagrammatically in Figure 7. In the liquid-crystalline system of uncomplexed CHP, the constituent dimer has mutually conjugated twin hydroxyterephthaloyl groups with a bulky steroid mesogen attached to both sides. It is thus reasonable to presume that the dimer units form a considerable rigid matrix and, accordingly, the molecular motions should be rather restricted due to steric hindrance of neighboring dimers and the orientation fluctuation should also be samll. In contrast, the structural unit in the CHP/C$_n$-amine system is a cholesteryl salt with an amino-alkyl chain serving as a flexible tail for the mesogenic steroid core. It is therefore plausible that the tadpole-shaped constituent has comparatively higher molecular mobility and the local orientation fluctuation is also greater even though a smectic ordering rather than nematic one prevails in the complex system. This model scheme may be suitable for explanation of the result of the comparative study of enthalpy relaxation behavior: the values of the relaxation time and activation energy obtained for CHP/C_n-amine salts were appreciably smaller than those for CHP *per se*. The significance and usefulness of such a concept of the mesogenic complex formation through specific intermolecular interactions (e.g., hydrogen bonding[13] and ionic interaction[14]) have recently been demonstrated by Kato *et al.* for a variety of pairs of organic compounds with complementary functional groups.[15]

According to Angell,[16] glassy materials as well as viscous liquids can be classified for convenience into two categories: i) strong glasses and ii) fragile ones. In the former case, a relation of the relaxation time τ versus T_g/T can be expressed by the Arrhenius form, where T_g/T is the inverse of a reduced aging temperature. In contrast to this, the fragile glasses show the corresponding relation deviated from the Arrhenius type of equation. It is suggested that such strong liquids and glasses form a kind of network architecture with developing chemical bonds or interactions as junctions or entanglements and the structure is usually less sensitive to temperature variation. On the other hand, fragile liquids and glasses are solely made up via the van der Waals force and their local sturcuture is much affected by changing temperature. The fragility, m, of glassy materials is generally defined in the following fashion; a larger m denoting higher fragility.

$$\mathrm{m} = \mathrm{d}\log\tau/\mathrm{d}(\mathrm{T_g}/\mathrm{T})|_{\mathrm{T}=\mathrm{T_g}} \qquad (4)$$

An attempt was made to estimate this parameter representing the fragility as glass for liquid-crystalline CHP and CHP/C_n-amine salts. Tg-based temperature dependence of the enthalpy relaxation time for the liquid-crystalline glasses is shown in Figure 8, compiling the so-called Angell plots with ordinary logarithm of τ as ordinate. All the samples give a linear relation and therefore fall under the category of strong glasses defined above. Values of the fragility parameter estimated from the slope of each Angell plot are listed in Table I. As demonstrated here explicitly, the salt formation of the cholesteryl ester CHP gives rise to appreciable lowering of the fragility. It can therefore be reasonably presumed that the normal aliphatic amines serving as a long tail for the individual mesogenic steroid core act as a diluent solvent for the system of molecular assemly to enhance the cooperative micro-Brownian motions at temepratures near the glass transition region. This would allow the glassy materials to be less fragile.

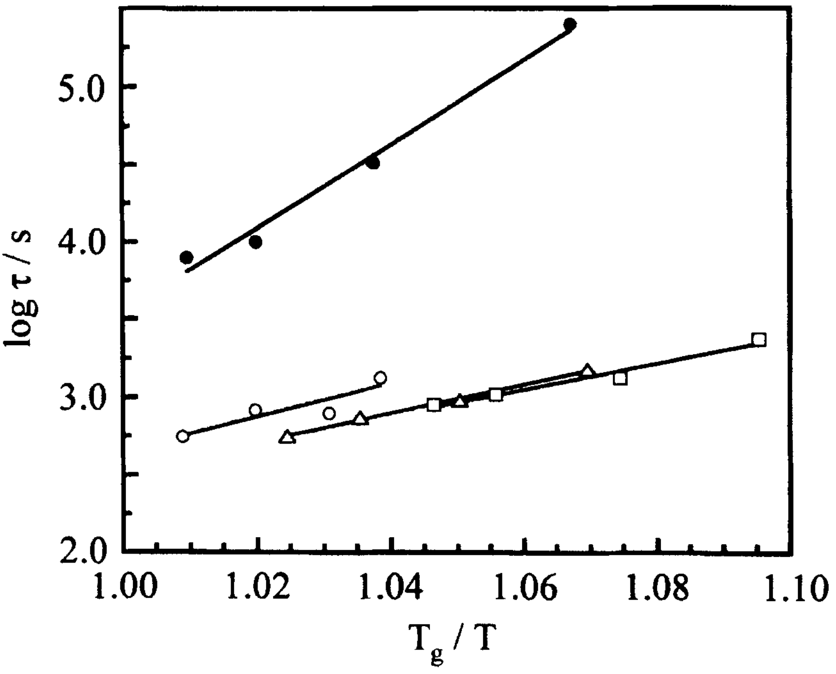


FIGURE 8 Plots of log τ against the inverse of T_g-reduced aging temperature (a ratio in the absolute unit K), constructed for four series of liquid-crystalline glassy samples: ●, CHP; ○, CHP/C_{12}-amine; △, CHP/C_{16}-amine; □, CHP/C_{18}-amine. The slope of each line, obtained by the least square fitting, gives a fragility parameter, m

As is already described, the distribution of the relaxation time in the glassy CHP is wider than that in the CHP/C_n-amine salts. The above observation of a comparatively higher fragility for the uncomplexed CHP is in accordance with a general trend suggested by Böhmer:[17] the distribution in the relaxation process is wider as the relevant material becomes more fragile. This suggestion was, however, made for the enthalpy relaxation phenomena of amorphous glasses.

4. CONCLUSION

A comparative study of enthalpy relaxation phenomena was accomplished for the liquid-crystalline glasses obtained for an ionic cholesteryl derivative CHP and its complex salts with normal aliphatic amines (C_n-amines). The relaxation behavior could be analyzed satisfactorily in terms of a KWW type of stretched exponential function. The results are summarized in Table I. Of particular significance are the following points: 1) The parameter β characterizing the distribution of the relaxation mode became close to unity when CHP was complexed with C_n-amines through ionic interaction; however, even the β values obtained for the uncomplexed CHP glasses were larger than those for conventional amorphous polymer materials; 2) The values of relaxation time (τ) and activation energy (Ea) obtained for CHP/C_n-amine salts were rather smaller than those for CHP *per se*; 3) The parameter m representing the degree of fragility of glassy materials was comparatively smaller in the complex salt system, and the value tended to decrease with an increase in the carbon number of the amine component.

FT-IR measurements revealed that, when CHP was incorporated with C_n-amine in an equimolar proportion, a change in intermolecular interaction took place, from the hydrogen-bonding dimerization of carboxylic acid groups to the ionic complexation between carboxyl and amino groups. At the same time, this interaction change would be attended by transformation of the molecular arrangement in the liquid-crystalline phase, as was modeled in Figure 7. In the complexed CHP/C_n-amine system, the normal amino-alkyl chains attached as a flexible tail to the mesogenic steroid core can be assumed to fill the role of diluent solvent for the whole system of molecular assembly. This results in the prevalence of higher molecular mobility and greater orientational fluctuation, in spite of the development of a higher mesomorphic ordering, compared with the case in the system of CHP alone, which would be responsible for the observations of the difference in enthalpy relaxation behavior between the two systems.

References

1. A. Weitz and B. Wunderlich, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 2473 (1974).
2. J.M.G. Cowie and R. Ferguson, *Macromolecules*, **22**, 2307 (1989).
3. R.M. Mininni, R.S. Moore, J.R. Flik, and S.E.B. Petrie, *J. Macromol. Sci. -Phys.*, **B8**, 343 (1973).
4. J.Y. Cavaille, S. Etienne, J. Peres, L. Monnerie, and G.P. Johart, *Polymer*, **27**, 686 (1986).
5. C. Banwens-Crowet and J.C. Banwens, *Polymer*, **27**, 709 (1986).
6. L.C.E. Struik, "Physical Aging in Amorphous Polymers and Other Materials", Elsevier, Amsterdam, 1978.
7. G.P. Johari and J.W. Goodby, *J. Chem Phys.*, **77**, 5165 (1982).
8. N. Kimura, N. Takeshima, Y. Nishio, and H. Suzuki, *Mol. Cryst. Liq. Cryst.*, **286**, 35 (1996).
9. N. Kimura, K. Aizawa, Y. Nishio, and H. Suzuki, *Kobunshi Ronbunshu*, **53**, 866 (1996).
10. M.J. Richardson and N.G. Savill, *Polymer*, **16**, 753 (1975).
11. G. Williams and D.C. Watts, *Trans. Faraday Soc.*, **66**, 80 (1970).
12. H. Yoshida, *Kobunshi Ronbunshu*, **53**, 874 (1996).
13. T. Kato, J.M.J. Fréchet, P.G. Wilson, T. Saito, T. Uryu, A. Fujishima, C. Jin, and F. Kaneuchi, *Chem. Mater.*, **5**, 1094 (1993).
14. S. Ujiie and K. Iimura, *Chem. Lett.*, **1994**, 17.
15. T. Kato, *Ekisho*, **4**, 4 (2000).
16. C.A. Angell, *J. Non-Cryst. Solids*, **131–133**, 13 (1991).
17. R. Böhmer, *J. Non-Cryst. Solids*, **172–174**, 628 (1994).