Radiation-Induced Solid-State Polymerization in Binary Systems. III. Physical Properties of the Glassy Phase in Polymeric Systems

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SUMMARY

In order to obtain fundamental information for polymerization of some acrylic monomers in the glassy state, glass formation and the characteristics of multicomponent systems containing acrylic monomers were investigated. Glassy states were obtained by selecting the proper balance of three conditions: supercooling tendency of the mixtures, second-order transition temperatures, and cooling rate. Systems that form glasses at -78°C were classified into Type I (monomer as part of glass-forming matrix) and Type II (monomers dissolved in glass-forming matrix). All multicomponent systems containing acrylamide or acrylic acids form a glassy state at liquid nitrogen temperature. The phase diagrams of glassy systems of Type I show the formation of a molecular complex in the range of the glass-forming composition. Second-order transition temperatures were determined dilatometrically. Finally, the formation and structures of the supercooled state were identified by studying their infrared spectra.

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INTRODUCTION

The mechanism of glass formation and the properties of the glassy state were investigated in order to obtain fundamental knowledge for the polymerization of some acrylic monomers in the glassy state.

Radiation-induced solid-state polymerization of eutectic mixtures of some acrylic monomers with organic substances has recently been investigated [1].

It was found that a glassy phase is formed in some binary systems if the components interact strongly with each other, as is the case with mixtures of organic acids and amides.

In bulk polymerization (without diluent) crystallization of monomer occurs readily, and in solution polymerization low monomer concentration must be retained to avoid the crystallization of monomer. Both factors are detrimental to the rate of polymerization. When polymerization is initiated in a glass-forming system, high viscosities of the supercooled system at high monomer concentration are maintained throughout the polymerization. Polymerization takes place easily even at very low temperature and the mechanism can be studied over a wide temperature range.

EXPERIMENTAL

Purified components were mixed in the melt. Glasses were formed by cooling the mixtures in Dry Ice ($-78°C$) or liquid nitrogen ($-196°C$) baths or in baths of various cryostatic mixtures. Transition temperatures were estimated by dilatometric methods. Phase equilibrium diagrams were obtained by differential thermal analysis.

RESULTS AND DISCUSSION

Mechanism of Glass Formation

In a previous paper [1] we showed that molecular interaction affects the crystallization process. The deviation of the liquidous of the phase diagrams from ideal solutions decreases with the increase of mutual molecular interaction in binary systems containing acrylamide or acrylic acid.

$$\Delta X = X_{ideal} - X_{obs} = \exp\frac{-H_A(T_A^\circ - T)}{RT_A^\circ T} - \exp\frac{-(H_A + H_m)(T_A^\circ - T)}{RT_A^\circ T}$$

$$= X_{ideal}\left[1 - \exp\frac{-H_m(T_A^\circ - T)}{RT_A^\circ T}\right] \qquad (1)$$

where X_{obs} = mole fraction of component A (monomer) in real system; X_{ideal} = mole fraction of component A (monomer) in ideal system. T_A° = melting point of component A (monomer); T = temperature; H_A = heat of fusion of component A (monomer); H_m = heat of mixing of the two components.

It was found that in systems with large $|\Delta X|$, the supercooling tendency to form a stable glassy state is very high; for example, acrylamide-itaconic acid, $\Delta X = -0.28$, acrylic acid-acetamide, $\Delta X = -0.34$. The crystallization process consists of the nucleation and crystal growth. It is expressed as follows [2, 3]:

$$\Delta G_c \propto \frac{16\pi\gamma^3\nu^2}{3(kT\ln\alpha)^2} \qquad (2)$$

where ΔG_c = difference of the free energy between the new phase and the old phase at the critical state of nucleus formation; γ = surface tension of the liquid; ν = molar volume of the liquid; T = temperature; α = degree of supersaturation ($\alpha = [X]/[X_0]$ where $[X]$ is the concentration and $[X_0]$ is the saturation concentration).

$$V_N = A\exp\frac{-\Delta G_c}{kT} = A\exp\frac{-16\pi\gamma^3\nu^2}{3k^3T^3(\ln\alpha)^2} \qquad (3)$$

where V_N = rate of nucleation; A = preexponential constant.

$$V_L = C\exp-\frac{1}{kT}\left\{\Delta\mu + \frac{\gamma^2T_m}{4T(T_m - T)}\right\} = CD\exp\frac{-\gamma^2T_m}{4kT^2(T_m - T)} \qquad (4)$$

where V_L = rate of crystal growth; $\Delta\mu$ = activation energy of diffusion; D = diffusion rate; T_m = melting temperature; $T_m - T$ = degree of supercooling; C = preexponential constant.

In α can be rewritten as Eq. (5) using the relation between the concentration (X_{obs}) and the temperature (T) in Eq. (1):

$$\ln \alpha = \ln X/X_0 = \ln X - \ln X_0$$

$$= \frac{-(H_A + H_m)(T_A^\circ - T_1)}{kT_A^\circ T_1} - \frac{-(H_A + H_m)(T_A^\circ - T_2)}{kT_A^\circ T_2}$$

$$= \frac{(H_A + H_m)(T_1 - T_2)}{kT_1 T_2} = \frac{(H_A + H_m)(T_m - T)}{kT_m T} \tag{5}$$

where T_1 = temperature at concentration X; T_2 = temperature at concentration X_0; $T_1 - T_2 = T_m - T$ = degree of supercooling.

Equation (3) can be rewritten as Eq. (6) using Eq. (5):

$$V_N = A \exp \frac{-16\pi\gamma^3 \nu^2 T_m^2}{3 (H_A + H_m)^2 (T_m - T)^2} \tag{6}$$

According to Eq. (6), V_N decreases with decreasing H_m and with increasing molecular interaction.

Equation (4) includes the diffusion term. The rate of crystal growth decreases with the decrease of diffusion of the component molecules. Viscosity of the binary systems is expressed as follows [4]:

$$\eta = X_A W_A (d/d_A)\eta_A + X_B W_B (d/d_B)\eta_B + 2(X_A X_B W_A W_B d^2 /d_A d_B)\eta_{AB} \tag{7}$$

where X_A, X_B = mole fraction of component A, B; W_A, W_B = weight fraction of component A, B; d, d_A, d_B = specific gravity of binary system, component A, and B; η_A, η_B = viscosity coefficient of component A, B.

η_{AB} is the parameter of molecular interaction between the two components (mutual coefficient of viscosity). Its contribution to the viscosity of the system greatly increases with increasing molecular interaction. The mixture becomes very viscous when the components form a highly associated system [1].

Molecular interaction is directly responsible for the glass formation and stabilization of the glassy state, because the rate of crystallization is zero or negligibly small in the glassy system. Figures 1 and 2 give the experimental curves of the induction time for crystallization in various systems. Induction time for crystallization is the time required for the formation of a stable nucleus which can grow rather than dissociate. ΔG_c in Eq. (2)
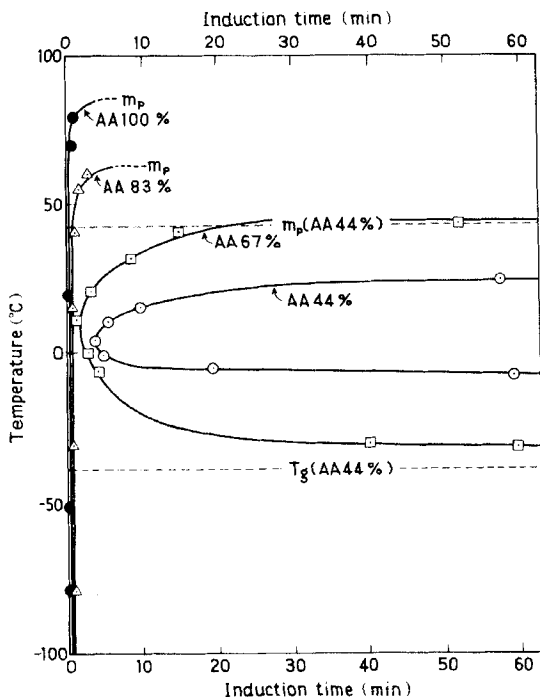
Fig. 1.   Relationship between induction time and cooling temperature in the
system acrylamide (AA)-itaconic acid. Mixing temperature, 90°C.

is the free-energy difference of stable nucleus formation, and induction time
relates directly to ΔG_c and V_N.

Figures 1 and 2 show that there are two types of induction curves. In
curves of the first type (for example, AA 100% curve in Fig. 1), the in-
duction times are relatively short for all temperatures and decrease with
decreasing temperatures. In curves of the second type (for example,
AA 44% curve in Fig. 1), the induction times become infinitely large
below a critical temperature, which is very important for glass formation.
In systems with large molecular interaction, such a critical temperature is
relatively high and glass is formed over a wide temperature range.

The curve becomes parabola-shaped in the second type at relatively high tem-
peratures, with the induction time decreasing with decreasing temperature be-
cause of supercooling [term $T - T_m$ in Eqs. (6) or (4)] but increasing at lower
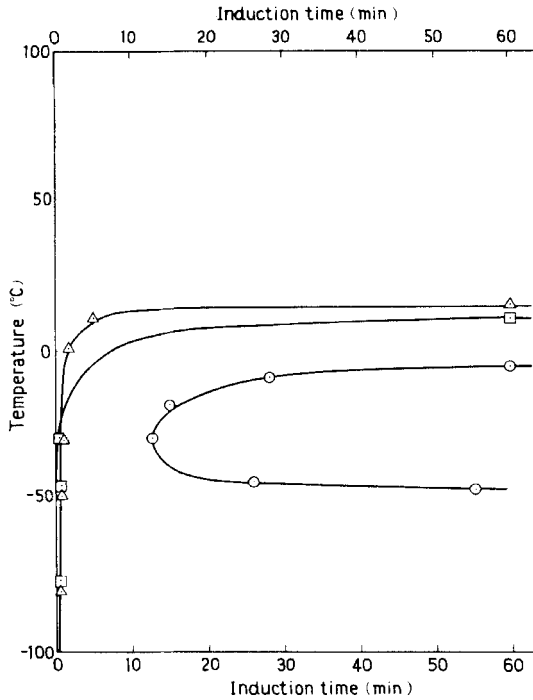temperatures because molecules interact more strongly [diffusion term in

Fig. 2. Relationship between induction time and cooling temperature in the system acrylamide-propionic acid-acetamide. ○ (1:0.5:1) forms glass at −78°C; □ (1:1:0.5) no glass formation; △ (1:0.5:0.5) no glass formation.

Eq. (6)]. The reason for this is the sharp increase in the viscosity of the mixture near the glass transition temperature.

In almost all organic and inorganic glass-forming systems, the viscosity increases from 10^4 to 10^{13} P between $T_g + 50°C$ and T_g [5].

Crystal growth is almost completely inhibited at T_g because the molecules can no longer diffuse. Thus, in systems of relatively higher T_g, the parabola shape of the induction curve is narrower.

The value of T_g is very important for the glass formation. The following relationship was found between viscosity and glass transition temperature; it is valid for the temperature range between T_g and $T_g + 100°C$ [6]:

$$\log \frac{\eta}{\eta_{T_g}} = \frac{-17.4(T - T_g)}{56.6 + (T - T_g)} \qquad (8)$$

where η_T = viscosity of system at temperature T (between T_g and $T_g + 100°C$); η_{T_g} = viscosity at T_g.

Assuming the viscosity is about 10^{13} P at T_g, we can rewrite Eq. (8) as Eq. (9):

$$T_g = T + \frac{56.6}{\dfrac{17.4}{\log \eta_T - 13} + 1} \qquad (9)$$

A system with high T_g is more viscous at a given temperature. The T_g would also be higher in a system with strong association.

In other words, glass formation is determined by three factors: (1) super-cooling tendency (induction time), (2) the value of T_g, and (3) cooling condition (cooling-bath temperature or cooling rate). Systems with strong association have large $|\Delta X|$ and they fill conditions (1) and (2) for glass formation.

It should be mentioned that the induction time of crystallization is shorter for pure components as compared with eutectic mixtures. Pure components form glasses very poorly, even when the compounds are rapidly quenched to liquid nitrogen temperature, because they crystallize too readily.

It is often desirable to increase the number of components in order to facilitate glass formation.

Classification of Glass-Forming Systems

A number of systems that exist in the glassy state at $-78°C$ are listed in Table 1. These systems are divided into two types. Type I consists of mixtures with substantial molecular interaction between monomer and nonpolymerizable organic substances. In Type II the monomers are dissolved in nonpolymerizable mixtures capable of glass formation.

Type I was divided into two subgroups. The first includes binary systems consisting of acrylamide-organic acid and acrylic acid-organic amide mixtures; the acid-amide combination was found to be especially effective in glass formation. The other Type I subgroup is a three-component system containing acrylamide and succinic acid. In this subgroup, two compounds do not interact sufficiently to form a glass and it is necessary to add a third component.

Type II was also divided into two subgroups. In one (binary systems), the monomers are dissolved in organic liquids, such as glycerol, ethylene

Table 1. Classification of Glass-Forming Systems

Type	Subgroup	Components
Ia	Two-component systems	Acrylamide-itaconic acid, Acrylamide-malonic acid, Acrylamide-acrylic acid, Acrylamide-phenol, Acrylamide-pyrogarol,	Acrylic acid-formamide, Acrylic acid-acetamide, Acrylic acid-propionamide, Methacrylic acid-formamide, Methacrylic acid-acetamide, Methacrylic acid-propionamide, etc.
	Three-component systems	Acrylamide-succinic acid-urea, Acrylamide-succinic acid-thiourea, Acrylamide-succinic acid-crotonic acid,	Acrylamide-succinic acid-tartaric acid, Acrylamide-succinic acid-sorbic acid, Acrylamide-succinic acid-hydroquinone, etc.

IIb

Two-component systems

Monomer-gylcerol,
Monomer-ethylene glycol,
Monomer-diethylene glycol,
Monomer-triethylene glycol,
Monomer-propylene glycol,

Monomer-triethanolamine,
Monomer-triacetin,
Monomer-2-ethyl-1.3-hexandiol,
Monomer-n-propanol,
Monomer-iso-propanol, etc.

Three-component systems

Monomer-itaconic acid-formamide,
Monomer-itaconic acid-acetamide,
Monomer-itaconic acid-propionamide,
Monomer-succinic acid-formamide,
Monomer-succinic acid-acetamide,
Monomer-succinic acid-propionamide,
Monomer-malonic acid-formamide,
Monomer-malonic acid-acetamide,

Monomer-malonic acid-propionamide,
Monomer-formic acid-formamide,
Monomer-formic acid-acetamide,
Monomer-formic acid-propionamide,
Monomer-propionic acid-formamide,
Monomer-propionic acid-acetamide,
Monomer-propionic acid-propionamide, etc.

aType I: Glass-forming system with molecular interaction of components. At least one component is a polymerizable monomer.
bType II: Glass-forming system where monomer is added to a glass-forming mixture.

Table 2. Some Phase Equilibria of Type I

| Systems A - B	Eutectic point formed by molecular complex and component A		Eutectic point formed by molecular complex and component B		Molecular complex	
	Temperature, °C	Composition, mole fraction of monomer	Temperature, °C	Composition, mole fraction of monomer	Melting point, °C	Composition, mole fraction of monomer
Acrylamide-malonic acid	24	0.65	30	0.42	45	0.59
Acrylamide-phenol	-18	0.65	-32	0.27	18	0.45
Acrylic acid-formamide	-48	0.53	-60	0.15	-8	0.36
Acrylic acid-acetamide	-35	0.63	-22	0.35	5	0.46
Acrylic acid-propionamide	-36	0.76	-24	0.40	15	0.50
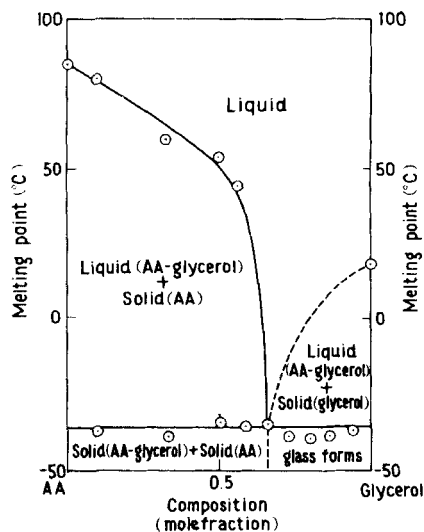
Fig. 3. Phase diagram of the system acrylamide (AA)-glycerol.

Transition Temperature of Glass-Forming Systems

Change in temperature does not cause a change in the transparent appearance of glassy systems. The glass transition temperature can be used to describe the change from liquid to glass. This temperature can be measured dilatometrically (volume change as a function of the temperature). Our results are shown in Table 3.

When the temperature is lowered to $T_g + 50°C$ (T_S, W.L.F. temperature [6]), the viscosity of the sample begins to increase nonlinearly; near T_g the viscosity increases rapidly, and a hard gel is obtained below this temperature. Many fine cracks may also be observed in some samples.

Our glassy systems should be considered as amorphous solids below T_g and as supercooled liquids above T_g.

DTA showed no transition temperature, but crystallization peaks are sometimes observed when mixtures are warmed up between T_S and T_g.

Measurement of Infrared Spectrum

The infrared spectrum of acrylamide-acrylic acid mixtures was measured at low temperatures in order to determine the structure of the mixture in the glassy state. The liquid sample was placed between two pieces of

Table 3. Transition Temperatures of Glass-Forming Systems

Systems	Composition	Glass transition temperature, °C	Eutectic temperature, °C
Acrylamide-itaconic acid	1:0.8	–39	+42
Acrylamide-malonic acid	1:1	–60	+30
Acrylamide-succinic acid-acetamide	1:0.5:1	–74	—
Acrylamide-acrylic acid	1:1	–100	–10
Acrylamide-propionic acid-acetamide	1:1:0.5	–100 ∿ –105	—
Acrylamide-propionic acid-formamide	1:1:0.5	–110	—
Acrylamide-propionic acid-formamide	1:1:1	–115 ∿ –120	—
Acrylic acid-acetamide	1:0.5	–110 ∿ –115	–35
Acrylic acid-formamide	1:1 (in volume)	–135 ∿ –145	–50

KRS-5 disk, and the sample holder was cooled in a copper block to about –100°C before pumping to the vacuum. The temperature was measured at the copper block using a copper-constantin thermocouple. With liquid nitrogen as coolant, the temperature was about –165°C. When cooling was stopped and the system was allowed to warm, the rate of temperature increase was about 1°C/min. The measurement of spectrum was made in the region of 400-4000 cm^{-1} with a Beckman IR-9 grating infrared spectrometer. The results of an equal molar mixture of acrylamide and acrylic acid are shown in Figs. 5(a) and 5(b). (A) is the spectrum at room temperature before cooling, and (B) is the spectrum after cooling to –165°C (in 20 min). (C) is the spectrum at –70°C after warming up from (B) (a large spectral change was observed near –80°C). Spectrum (D) was obtained by rapid cooling of state (C) to –165°C. When (D) was warmed slowly, the system came back to the initial state (A) near 0°C, passing through state (C). Spectra (A) and (B) are similar in spite of the large temperature difference, though three weak bands at 540 (doublet), 675, and 1400 cm^{-1} were observed in (B).
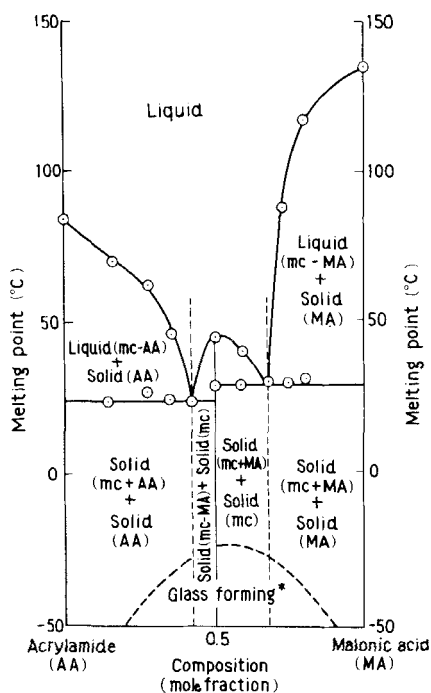
Fig. 4. Phase diagram of the system acrylamide-malonic acid. mc: molecular complex. *Glass forms easily in this range.

(C) shows the characteristics of the crystalline state (narrow band width and band splitting). (D) shows sharp bands with many bands split. Furthermore, (C) changes reversibly to (D) but (B) changes irreversibly to (C); this shows that the supercooled (B) has a very similar structure to that of the liquid state (A), and both (C) and (D) correspond to the crystalline state. There is a crystalline transition between (C) and (D), since the spectral difference is significant.

For example, the intensity of the 937.5 cm^{-1} absorption band, which is found only in states (C) and (D), changes with temperature. A continuous recording of the intensity of the 937.5 cm^{-1} absorption band is shown in Fig. 6.

A phase transition between (B) and (C) can be recognized near -80°C, and a transition between (C) and (A) appears near -30°C. The former corresponds to the glass-crystal transition and the latter to the melting of crystal.
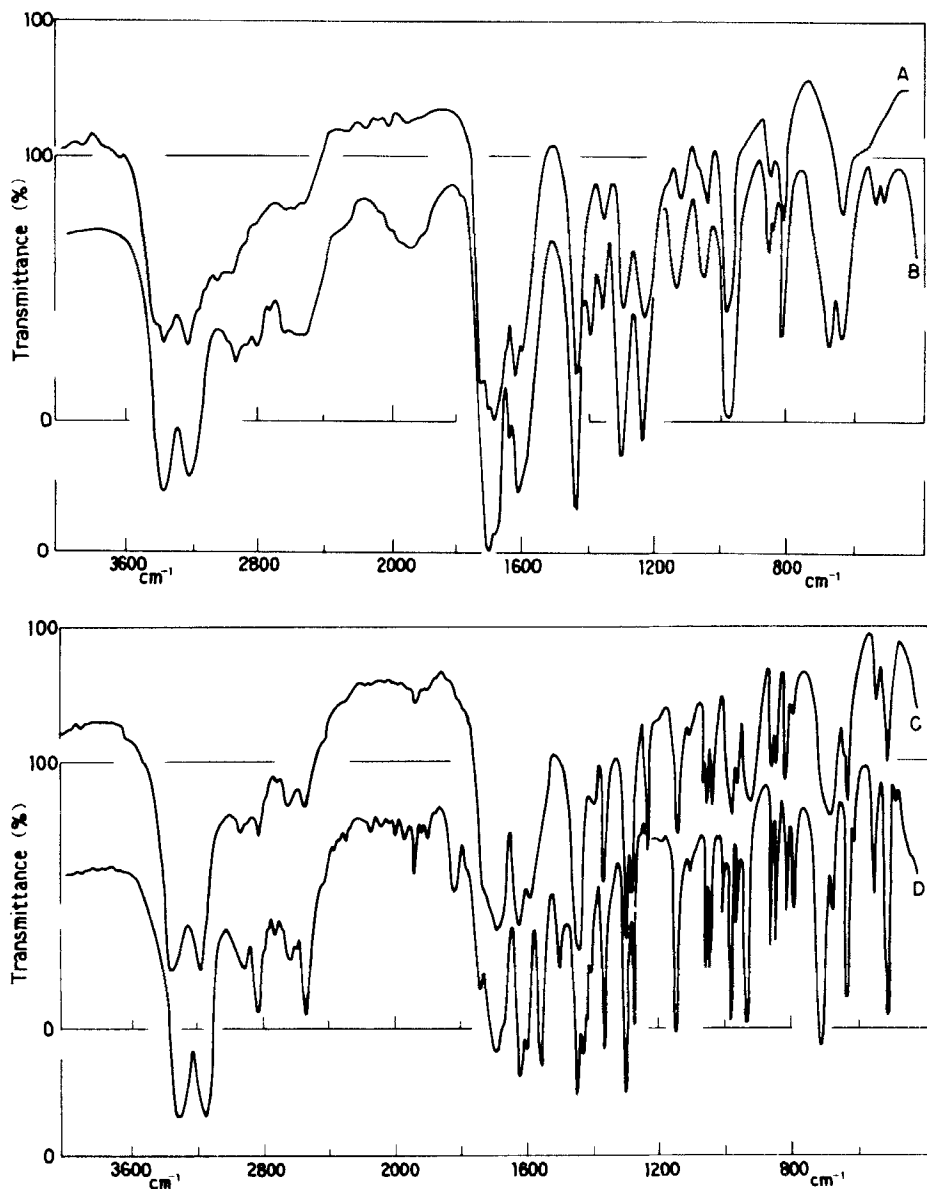
Fig. 5. (a). Infrared spectra of the binary mixture of acrylamide and acrylic
acid (1:1). Upper curve (A) measured at room temperature; lower curve
(B) measured at –165°C after rapid quenching from liquid state at 70°C.
(b). Upper curve (C) measured at –70°C, annealed from (B); lower curve
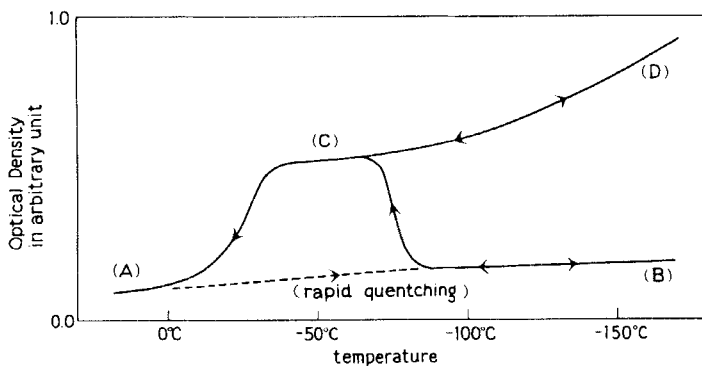   (D) measured at –165°C after (C) was cooled again to –165°C.

Fig. 6. Intensity change of the 937.5 cm^{-1} band at various temperatures.

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