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Formation of molecular alloys by solid-state vitrification

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Abstract

Formation of a vitreous molecular alloy was observed when a mixture of deoxycholic acid (DCA) and tri-*O*-methyl-β-cyclodextrin (TMCD) crystals was subjected to mechanical milling at room temperature. Only a single glass transition temperature T_g, varying with the composition, was observed by DSC. This means that the vitreous state exhibits a single relaxation process as a whole by forming a molecular alloy. The T_g showed a maximum value at the equimolar composition, indicating a strong interaction between the two components. A study of the phase diagram clarified the existence of inter-molecular compounds between them. Thermal conductivity of the milled solid of equimolar mixture exhibited a temperature dependence characteristic of glassy materials. *p*-Terphenyl and tris(hydroxymethyl)aminomethane crystals could not be vitrified. When each of them was milled with DCA or TMCD, vitreous molecular alloys were obtained in a limited composition range. These alloys exhibited also a single T_g and underwent a phase separation on devitrification. Formation of molecular alloys was discussed based on the nature of disorder of the system. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Molecular alloy; Solid-state vitrification; Milling; DSC; Thermal conductivity

1. Introduction

Molecular crystals differ from other classes of solids in being composed of discrete molecules which are formed by strong covalent bonding among a few kind of atoms. These molecules are held together by weak inter-molecular forces such as the van der Waals and the hydrogen-bonding forces to form their crystalline lattices. It is this marked contrast between the intra- and inter-molecular interactive forces which introduces diversity to the physical properties of the molecular crystals [1]. A slight change in external variables can induce a transition from one to another phase possessing intriguing electric or magnetic property [2]. Altering the geometric and electronic structures of the molecules can vary the properties. The exploitation of these possibilities in development of new material is one of the rapidly growing fields in materials science.

In principle, molecular compounds can be obtained as crystalline as well as vitreous state [3]. The latter state has been produced traditionally by rapid cooling from the liquid phases. For molecular systems that undergo thermal decomposition on warming, vapor deposition on a cold substrate proved to be a useful alternative way to form the vitreous solids. Milling by the action of moving balls, that has been known as a technique for refining particles, turned out to produce metal alloys in vitreous states [4]. This solid-state vitrification method was applied successfully to some

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molecular crystals such as tri-*O*-methyl-β-cyclodextrin (TMCD) [5], salicin and others [6]. Contrary to metallic systems, the method has proved to be useful in the vitrification of single molecular systems. X-ray powder diffraction experiments showed that these mechanically milled samples exhibited halo patterns quite similar to those of liquid-cooled samples. The vitrified solid showed a glass transition, crystallization, and subsequent fusion on warming.

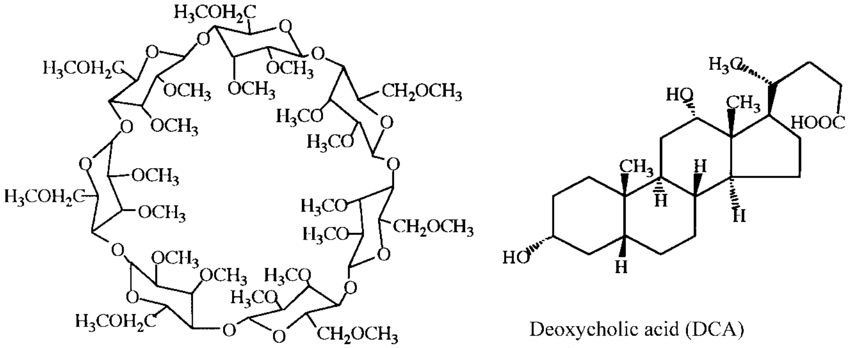
In a previous paper, we have reported briefly that a binary mixture of deoxycholic acid (DCA) and TMCD with $x_{\mathrm{DCA}} = 0.80$ exhibited only a single T_g, which is higher than those of the component systems [7]. In order to examine this effect in more detail, the composition was varied over the whole range. The existence of inter-molecular compounds between them was established by a study of the phase diagram for the devitrified samples. Furthermore, the formation of vitreous molecular alloys between two crystals, which are improbable to form any solid solution under thermal equilibrium conditions, is reported here.

2. Experimental

TMCD (permethylated-β-cyclodextrin) supplied by Toshin Chemicals and DCA by Merck were the same as those used in the previous study [7]. The molecular structure of each compound is drawn schematically in Fig. 1. Tris(hydroxymethyl)aminomethane (THAM) and *p*-terphenyl (*p*-TPH) crystals of analytical grade from Merck were used without further purification. The samples of DCA and THAM crystals were dried well at 378 K before use, since the T_g value depended strongly on the moisture content. Vitreous states of the binary systems were prepared by mixing gravimetrically two crystalline samples and subsequent milling of the mixture.

All the samples were milled by using a vibrating mill T1 100 (Heiko Manufacturing) in dry N_2 atmosphere at room temperature. A sectional view of the machine is drawn in Fig. 2. The machine was a cylindrical airtight stainless-steel vessel (pot) in which a cylindrical rod was placed. Both the rod and pot were covered by ceramics to avoid contamination of the sample by metal. The pot had 40 mm inner diameter and 50 mm length. The corresponding quantity of the rod was 27 and 40 mm, respectively. The pot was mechanically driven along horizontal direction backward and forward over a pre-determined period. The movement resulted in generation of compression and shear stresses to the crystalline sample placed between the rod and the pot. The sample space was about 10 cm^3.

X-ray diffraction pattern was obtained at room temperature on vitrified sample spread out on a glass sample holder. X-ray beam of Cu-Kα generated under a condition of 40 kV and 80 mA using a Rigaku RINT 2000 diffractometer was used as the source. The range of the diffraction angle 2θ was 6–70° and the scanning speed was $6^\circ\ \mathrm{min}^{-1}$.



Deoxycholic acid (DCA)
mp 451 K

Tri-O-methyl-β-cyclodextrin(TMCD)
mp 430 K

Fig. 1. Molecular structure of TMCD and DCA.

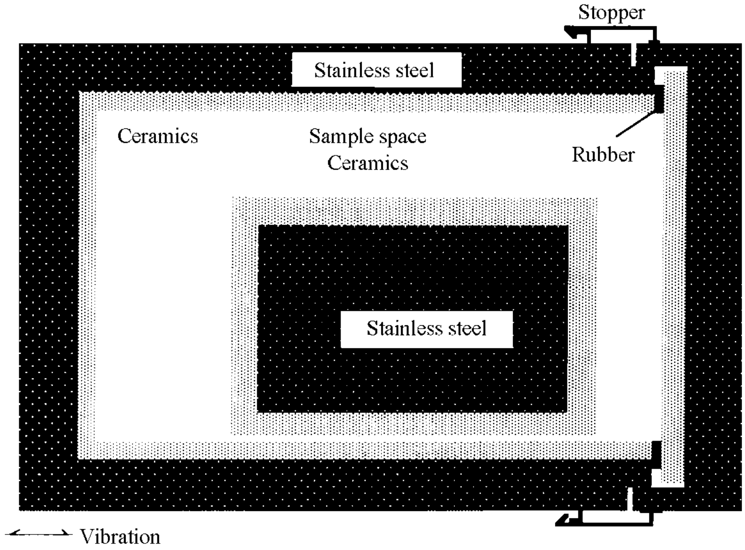


Fig. 2. Sectional view of milling machine.

Calorimetric measurements were carried out with a Rigaku 8240 differential scanning calorimeter (DSC), using a heating rate of 5 K min^{-1}. Anomalous heat effects due to glass transition, crystallization, and fusion characteristic of a vitrified solid were observed in general. The glass transition temperature T_g was determined to be an inflection point of the heat-capacity jump, while the temperatures of crystallization and fusion were to be the onset of each peak, respectively. The analysis was done with the Software TAS 300 system provided by Rigaku.

The transient hot-wire method [8] was used to measure the thermal conductivity λ of the vitreous equimolar mixture between TMCD and DCA. The hot-wire probe was made of Ni (0.1 mm in diameter) placed horizontally in a ring of constant radius within a Teflon cell. The wire, surrounded by the mixture of TMCD and DCA, was heated by a 1.4 s pulse of approximately constant power and the wire resistance was measured versus time. This enabled the temperature rise of the wire to be determined. A theoretical expression for the temperature rise was fitted to the data points, thereby yielding λ. The inaccuracy in the determination of λ was estimated to be ±2% [8].

The Teflon sample cell was mounted in a piston-cylinder type of pressure vessel with an internal diameter of 45 mm and a load was applied using a 5 MN hydraulic press. Temperature was varied by cooling or warming the whole pressure vessel and was measured using an internal chromel–alumel thermocouple, which had been calibrated against a commercially available (calibrated) silicon-diode thermometer. Pressure was determined from load/area with an empirical correction for friction, which had been established by comparison with directly measured pressure in a hydrostatic experiment. The inaccuracy in temperature was estimated as ±0.5 K and the inaccuracy in pressure as ±40 MPa at 1 GPa. Measurements were made along either isobars or isotherms. During the measurements along isobars, the heating rate was typically in the range 0.1–0.3 K min^{-1}.

3. Results and discussion

3.1. Totally miscible system

Both the TMCD and DCA crystals can be vitrified easily in their pure single systems, respectively. The X-ray results are summarized in Fig. 3, in which the relative scattering intensity I_{rel} is plotted against 2θ. The sharp Bragg peaks of the crystalline samples changed almost completely into a halo pattern after

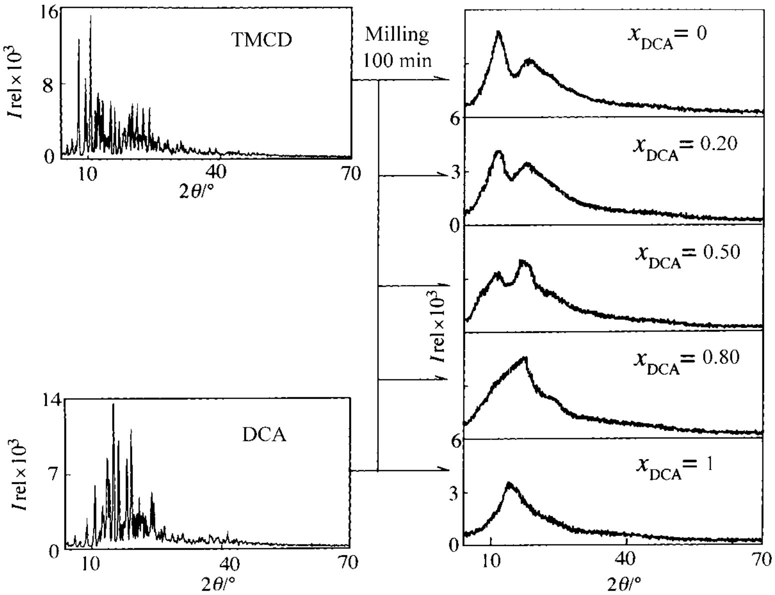


Fig. 3. X-ray diffraction patterns of TMCD+DCA binary system in crystalline and vitreous states.

milling for 100 min. The situation was the same for any mixture prepared from the two crystals. This is in sharp contrast to the metallic systems in which a long milling time extending over several thousand hours is necessary for the formation of a vitreous alloy. Vitrification of a pure metal has not been reported hitherto. At this stage, it is not clear whether the obtained solid for the present binary system is a simple mixture or a hybrid mixture of non-crystalline solids of each component.

The results of DSC experiments are shown in Fig. 4. Each of the curves exhibited anomalous effects arising from glass transition, crystallization and fusion, respectively. The observation of a single glass transition means that the vitrified binary solid forms a molecular alloy, in which two kinds of molecules were mixed on a microscopic level to the extent that the solid shows a single structural relaxation as a whole. The fusion occurred in a single step for the samples with $x = 0, 0.5$ and 1.0, whereas in double steps for $x = 0.2$ and 0.8. This indicated that the latter two solids underwent a phase separation on the devitrification.

The glass transition temperature T_g is plotted against mole fraction x in Fig. 5. In many binary systems, T_g changes almost linearly with the composition. Gordon et al. [9] succeeded to reproduce the observed variation of T_g with x in most cases based on the regular solution model.

$$T_g(x) = \frac{xT_{g,1} + K(1-x)T_{g,2}}{x + K(1-x)} \quad (1)$$

where $T_{g,1}, T_{g,2}$ are the glass transition temperatures of the first and second component and K is a fitting parameter. A large deviation from the linear behavior (dotted line in Fig. 5) was observed when the two components interact strongly with each other. Typical examples are 1,2-propanediamine+glycerol, and 1,2-propanediamine+1,3-propanediol, in which the maximum deviation reaches about 30 K [10]. A similar positive deviation of $T_g(x)$ was observed also for some systems composed of alcohols and secondary amines [11]. Formation of excess hydrogen bonds between hydrogen atoms and lone pairs of hydroxyl groups in the solution was suggested. Such extra structural formation will hinder the molecular motion in the solution. Takeda et al. [12] proposed a thermodynamic model by taking into account the excess mixing entropy S^E between the two components and determined the value S^E by fitting the model curve to the experimental data. The quantity S^E, amounting to -20 J K^{-1} mol^{-1} for the above diamine systems, is

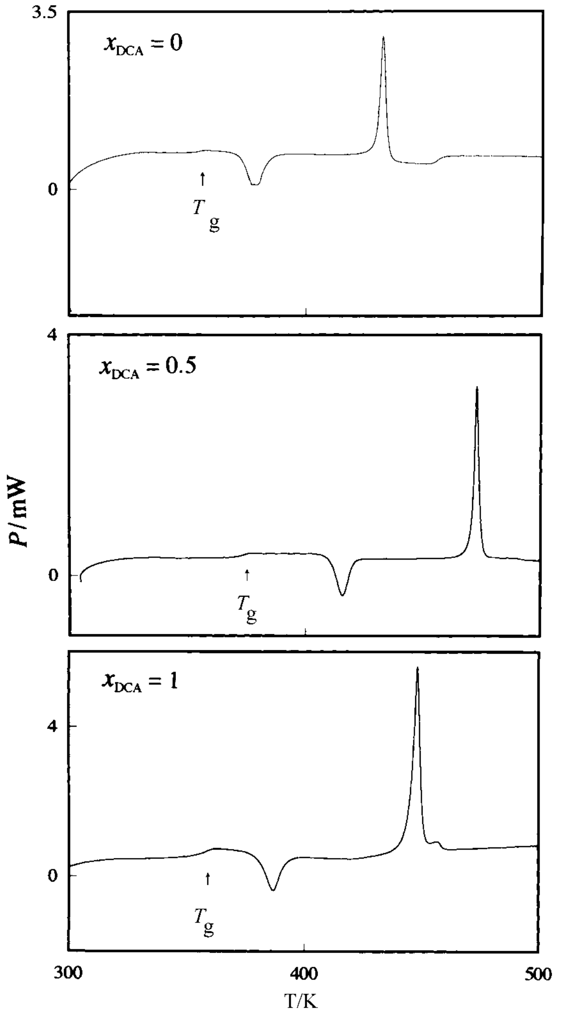


Fig. 4. DSC curves of TMCD+DCA binary system.

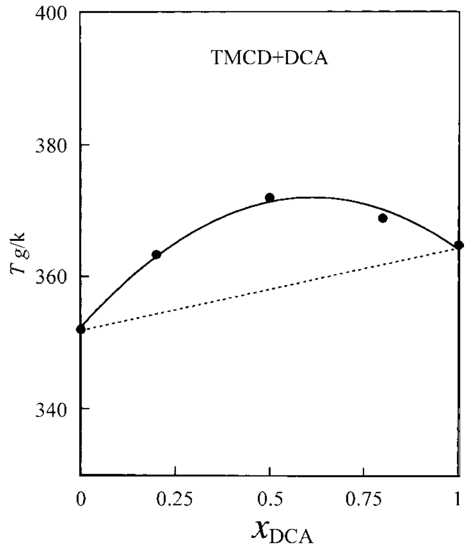


Fig. 5. Variation of T_g with composition for TMCD+DCA binary system.

the origin of the large deviation of T_g from a linear behavior for which S^E is almost zero. A negative value of S^E is in accord with the formation of a local structure in the solution. Strong interactive forces between the two kinds of molecules reduce the mobility of each molecule, resulting in higher T_g at nearly equimolar composition.

In order to confirm the possible interaction between TMCD and DCA molecules, the phase diagram was studied by observing the melting behavior of the devitrified samples. The results are given in Fig. 6. It is evident from the figure that 1:1 and 1:4 intermolecular compounds are formed in the system. The former melted congruently at 470 K, while the latter incongruently at 427 K. The two components would be partially miscible in the crystalline phase, because there was no clear indication of the eutectic peaks for the samples in the very vicinity to $x = 0$ and 1. Owing

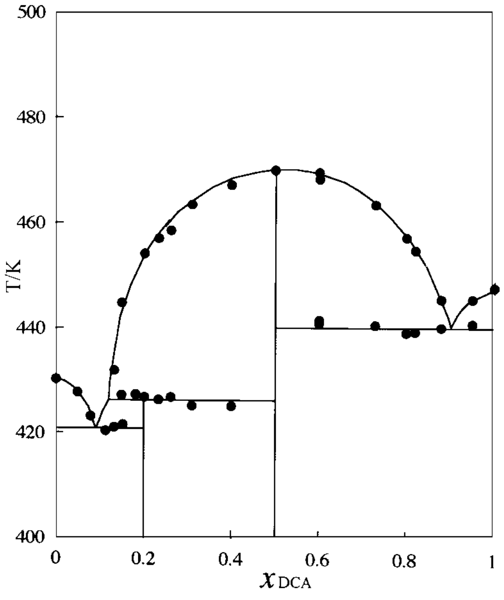


Fig. 6. Phase diagram of TMCD+DCA binary system.

to the scatter in the data for the composition range $x_{\mathrm{DCA}} < 0.3$, the proposed composition 1:4 is not absolutely definitive. However, the existence of the 1:1 compound is clearly conclusive. The fusion temperature of the 1:1 compound was higher by 40 K than TMCD and by 22 K than DCA. It is this strong interactive force which suppresses the molecular motion and increases T_g about 15 K for the vitreous solid with $x_{\mathrm{DCA}} = 0.50$. No structural information for the two kinds of inter-molecular compounds is available. Incidentally, both substances have an ability to form inclusion compounds. TMCD is known to enclathrate several organic molecules such as benzoic acid [13]. DCA is a steroidal compound classified as a bile acid and has long been known to form multi-molecular inclusion compounds [14]. Structural determination of the present inter-molecular compounds will surely contribute to the development of supramolecular chemistry.

The thermal conductivity λ for the vitreous 1:1 compound of TMCD and DCA was investigated under pressure. Figs. 7 and 8 show isobaric and isothermal data for λ, respectively, and the data agree within experimental inaccuracy. The most important result, which can be inferred from the measurements of λ, is that this new glassy state exhibits the same characteristics as other glassy states. Almost a fingerprint of glassy states is found in the behavior of $\lambda(T)$. All topological glasses exhibit a $\lambda(T)$, i.e. increasing with increasing temperature above the well-known plateau in λ, which occurs at low temperatures. The behavior is contrary to that of crystalline substances that exhibit opposite temperature dependence above the Debye temperature, besides a few exceptions, due to the increase in phonon–phonon scattering. This universal behavior of increasing λ with increasing temperature can be attributed to the additional heat carried by high-frequency vibrations. The strong frequency-dependent phonon scattering due to structural disorder limits the mean free path of these phonons to the order of the interatomic spacing, and therefore the phonon–phonon scattering is not significant. As a consequence of the frequency-dependent scattering, there is a mobility edge frequency above which the vibrations become localized. In one model [15], localized vibrations associated with the boson peak can carry heat through hopping to yield the observed increase in $\lambda(T)$. In another model [16], the phonons just below the mobility edge are responsible for the rise in $\lambda(T)$ and the character of the heat transport is diffusive.

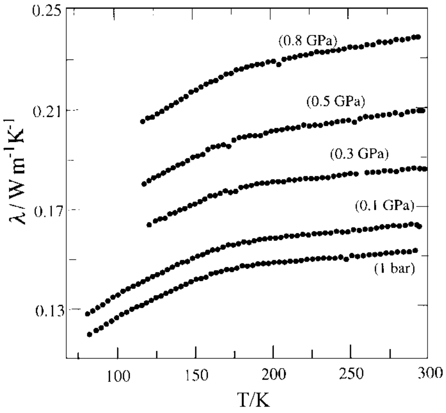


Fig. 7. Isobaric thermal conductivity for vitreous 1:1 compound of TMCD and DCA at pressures given in parentheses. The atmospheric pressure results have been calculated by a linear extrapolation of data at 0.1 GPa.

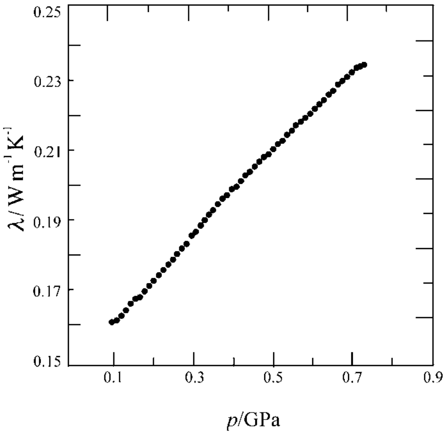


Fig. 8. Isothermal thermal conductivity for vitreous 1:1 compound of TMCD and DCA at 295 K.

As shown in Fig. 7, the vitreous 1:1 compound exhibits a glassy behavior in $\lambda(T)$ at all pressures. The magnitude of λ is also similar to that of comparable glassy states, e.g. polymer glasses. Near room temperature, the magnitude of λ for molecular glasses is typically of the order of 10^{-1} W m^{-1} K^{-1}, while λ of network glasses such as SiO_2 is an order of magnitude larger. Another common feature of λ for glasses is found in the density dependence of λ, which is described by the Bridgman parameter $g = (\partial \ln \lambda / \partial \ln \rho)_T$, where ρ is the density. Generally, amorphous states exhibit a Bridgman parameter which is close to $3(\pm 1)$ at room temperature [17,18]. Since there are no *pVT* data available for the vitreous 1:1 compound, the value of *g* cannot be calculated. If one assumes $g = 3$ and uses the values for $\lambda(p)$ at 300 K (Fig. 8), then a rough value of 5 GPa for the bulk modulus is obtained.

It is not easy to speculate about the mechanism by which two kinds of molecules mix microscopically so rapidly during the formation of a molecular alloy. The early investigator [19] assumed that the pulverized particles fused because of the high rate of plastic deformation in the milling process, and the consequent rise in powder temperature. Rapid cooling of the melt by heat conduction into the less deformed interior regions of the particles might then be responsible for the vitrification. However, energy calculations and temperature measurements indicated that the temperature rise was not high enough for the powder to fuse. Many researchers nowadays believe that destabilization of the crystalline phase occurs first by the accumulation of various lattice defects.

One strong evidence against the fusion mechanism is provided by α-D-glucose, whose fusion temperature is about 428 K. This substance cannot be vitrified by mechanical milling. The X-ray diffraction peaks remained unchanged at all even after milling for 300 h. Glucose has long been known to be a good glass-former by liquid cooling. It turned out that glucose molecules isomerize on fusion to yield an equimolar mixture of α- and β-pyranose [20]. A mixture has generally less crystallization tendency than a pure substance. Thus, the vitreous glucose realized by melt-cooling does not contain any of the original molecules. These observations clearly deny the possibility of the proposed melt-quench mechanism for the solid-state vitrification by milling process.

Despite the variety of the solid-state vitrification techniques such as particle irradiation, ion implantation, and mechanical milling, Koike [21] has noticed a number of common observations showing a large lattice strain and softening of shear elastic constants. Based on the experimental results, he proposed a vitrification mechanism by introducing static displacement of atoms that causes lattice strain. The model calculation showed that a crystalline structure becomes unstable at a critical strain value. The critical strain is expressed in terms of the elastic constants of the crystal. Various lattice defects produced by the destruction of the three-dimensional periodicity will also play important roles in the alloying process [22]. These theoretical considerations explain why molecular crystals can be vitrified by mechanical milling much more easily than the metallic system. The different behavior is entirely due to smaller elastic constants for the molecular crystals. As an example, the elastic constants c_{ij} of Fe and benzene crystals [23,24] in units of 10^8 N m^{-2} are

$$\text{Fe (cubic)}: \quad c_{11} = 2430, c_{12} = 1380, c_{44} = 1219$$

$$\text{C}_6\text{H}_6 \text{ (orthorhombic)}:$$

$$c_{11} = 61.4, c_{13} = 40.1, c_{22} = 65.6, c_{23} = 39.0,$$
$$c_{33} = 58.3, c_{44} = 19.7, c_{55} = 37.8, c_{66} = 15.3$$

Thus, molecular crystals destabilize easier than metals under the same external stresses.

Molecules located nearby lattice defects are in energetic states, which are much higher than those for molecules on regular sites. These molecules are, therefore, believed to have a higher mobility than the regular molecules. The existence of molecules with extremely high mobility has been confirmed experimentally for ice when the crystalline sample was finely powdered to an average particle size less than 150 μm. NMR spectra of the pulverized ice samples showed a very narrow line superimposed on the normal broad line [25,26]. The narrow component appeared even at 170 K, being 100 K below the fusion temperature. NMR spin-lattice relaxation time of the narrow component ice showed that the relevant water molecules move from one site to another site at a rate several orders of magnitude faster than in bulk ice. As the temperature rises the number of mobile water molecules increases substantially, long before there is any evidence of structural melting.

Although the authors ascribed the quasi-liquid-like behavior only to molecules located on the surface of the crystal, we can reasonably extend the responsible entity to molecules associated with lattice defects. Lattice points on a surface are kind of lattice defects in the sense that the surface molecules suffer from interactive forces which are quite different from those of the interior molecules due to a smaller number of neighbors. A pulverization process must introduce various kinds of lattice defects into the crystal in addition to the increase in the surface area. These experiments on ice were originally intended for obtaining a possible explanation of the "regelation" phenomenon in ice, but it turned out that the existence of highly mobile molecules at the solid surface is of quite general occurrence in solids. Nowadays, the phenomenon is called surface melting, which is considered to take place at temperatures $T > \frac{2}{3}T_{\mathrm{fus}}$, where T_{fus} is the fusion temperature of the bulk crystal [27,28]. In this way, the old proposal of melt-quench mechanism for the solid-state vitrification has revived now in a contemporary outfit. Destruction of the three-dimensional periodicity (fusion) occurs actually in the crystal by compression and shear stresses, but not by heat. The process results in the formation of highly mobile molecules and allows for mutual mixing in their neighborhood.

3.2. Partially miscible system

Neither pure THAM nor pure *p*-TPH crystals can be vitrified. However, these crystals can form molecular alloys with TMCD or DCA over a limited composition range when they are mixed and subjected to mechanical milling. Fig. 9 shows a series of X-ray diffraction patterns for the binary system of TMCD+*p*-TPH milled for 200 min, respectively. For the samples $0.50 < x_{\mathrm{TMCD}} < 1$, each solid exhibited only a halo pattern. A tiny amount of a crystalline component was observed in the $x_{\mathrm{TMCD}} = 0.50$ sample. For the samples $x_{\mathrm{TMCD}} < 0.40$, many Bragg peaks arising from *p*-TPH crystals were superposed on the halo pattern, showing coexistence of *p*-TPH crystals and a vitreous alloy. The situation was essentially the same for the binary system of DCA+THAM in which coexistence of crystalline THAM and the molecular alloy occurred at compositions $x_{\mathrm{DCA}} < 0.75$.

The glass transition temperature T_g of both systems is plotted in Fig. 10 as a function of composition x. The T_g value of TMCD and DCA decreases gradually with increasing amount of *p*-TPH and THAM, respectively. As described above, the formation of the molecular alloys is possible only in a limited composition range in the two cases. For the system TMCD+*p*-TPH, the limiting value of the composition $x_{\mathrm{TMCD}} = 0.5$ for the formation of the molecular alloy will indicate that each *p*-TPH molecule is enclathrated inside the cavity of the TMCD host molecule, as in the case of benzoic acid.

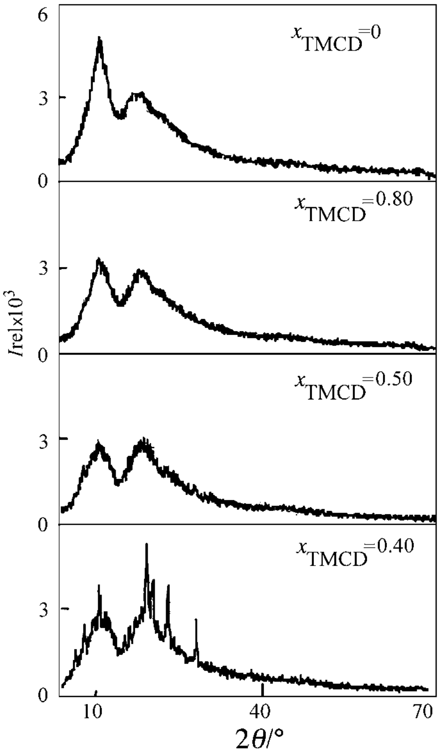


Fig. 9. X-ray diffraction patterns of TMCD+*p*-TPH binary system in crystalline and vitreous states.

Another binary system TMCD+*o*-TPH provides us a necessary condition for the solid-state vitrification to be successful by milling at room temperature. *o*-TPH has been well known as a good glass-former [29]. Thus, the system is strongly expected to be totally miscible over the whole composition range. For the composition $0.4 < x_{\mathrm{TMCD}} < 1$, each crystalline mixture produces a vitreous solid exhibiting a single T_g. The dependence of T_g on the mole fraction x_{TMCD} is drawn in Fig. 11. The extrapolated value of T_g to $x_{\mathrm{TMCD}} = 0$, 245 K, agrees well with the literature value, 240 K, determined by adiabatic calorimetry [29]. However, the milled samples for $x_{\mathrm{TMCD}} < 0.25$ gave halo pattern contaminated by many strong Bragg peaks. For a sample, say $x_{\mathrm{TMCD}} = 0.25$, the hypothetical T_g of 290 K indicates that the milling temperature is just in the so-called

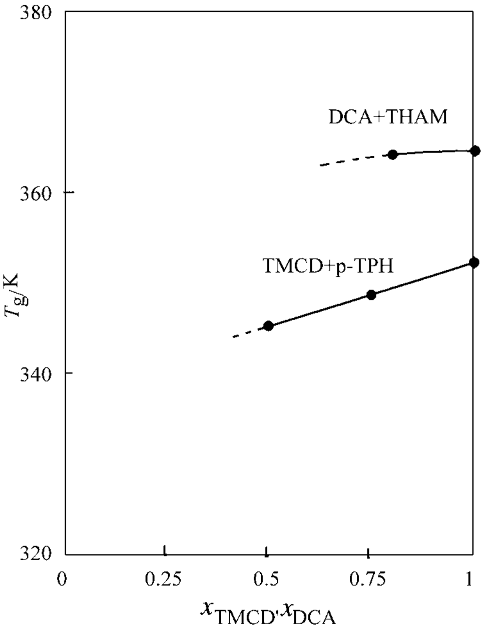


Fig. 10. Variation of T_g with composition for TMCD+*p*-TPH and DCA+THAM binary systems.

"crystallization-dangerous" region. The sample would be in vitreous state during an initial stage of the process, but the continued mechanical stimulation must induce a partial crystallization in the vitrified solid. The formation of molecular alloys is possible only in a frozen-in disordered state. Thus, the solid-state vitrification by mechanical milling should be applied to the system whose hypothetical T_g must be sufficiently higher than the milling temperature. A milling machine with a built-in cooling device will widen the class of crystals that can be vitrified.

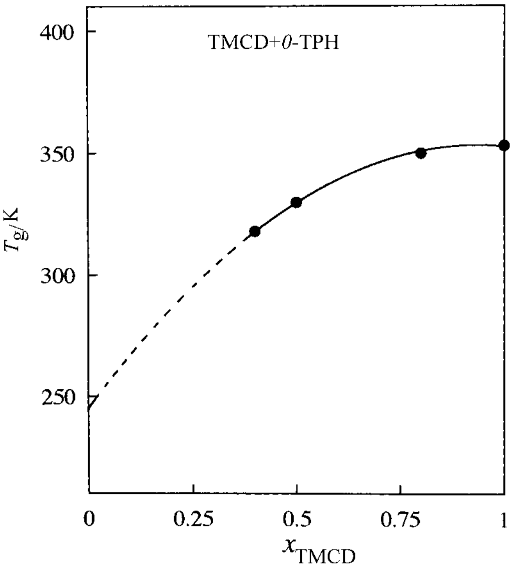


Fig. 11. Variation of T_g with composition for TMCD+*o*-TPH binary system.

Mutual miscibility of binary molecular system depends strongly on the disorder of the phase in which the mixing process takes place. In a gaseous phase for which the entropy is the largest among the three states of aggregation of molecules at low and moderate pressures, any two substances are miscible homogeneously. Since interactive forces among the constituent molecules are weak, the entropy of mixing is the main driving force for the uniform mixing to take place. In a liquid phase for which the entropy is intermediate in magnitude between that of a gas and a crystal, any two liquids are mostly mutually miscible. Some liquids of different nature, such as water and oils, are immiscible and exhibit phase separation. The mutual solubility of two liquids changes with temperature and pressure. Energetic as well as entropic factors must be taken into account in considering the mutual miscibility. In the crystalline phase for which the entropy is the smallest, formation of a solid solution between two molecular crystals is highly limited. The crystal structure of each system is another important factor in addition to the thermodynamic variables. Thus, the space group should be the same for the two crystals. Similar size of the unit cells and similar shapes of the two molecules are also required [30].

Plastic crystals (PCs), in which the constituent molecules are orientationally disordered but positionally ordered, provide an intriguing example with respect to the mutual miscibility in the solid state. The PC phase appears between ordered crystalline and isotropic liquid phases, and the entropy is rather similar in magnitude to that of the liquid phase. Most of the molecules in the PC phase form a face-centered cubic lattice by virtue of enhanced orientational degree of freedom. Owing to the great deal of orientational disorder, many binary systems are mutually miscible in this meso phase. D- and L-camphor belong to this category [31]. The miscibility property was stated by Timmermans [32] as one feature of the PC. A uniform solid solution of the PCs can be obtained either by liquid cooling and annealing or by a mechanical milling [33]. When the solid solution is cooled to undergo a phase transition into an ordered phase, the corresponding components exhibit a phase separation. When the ordering transition occurs at low temperatures at which the mutual diffusion constants of the molecules are small compared to the experimental time, positional disorder remains down to the lowest temperature. The failure to maintain the thermal equilibrium results in a definite amount of unremoval entropy or residual entropy in the system [34,35].

Vitreous solids have liquid-like structure, and therefore large amount of the entropy. Vitreous solids can be regarded as a kind of liquid with extremely high viscosity. Thus, two kinds of vitreous solids can have good mutual miscibility apart from the kinetic effect. From these points of view, the formation of totally miscible molecular alloys is regarded as a kind of mixing process occurring at the surface of each solid when mutual molecules are in close contact under the compression and shear stresses. The formation of partially miscible molecular alloys is a dissolution process of a crystal into a vitreous solid. Compared to the metallic system, studies of solid solutions of molecular systems have been delayed owing to the serious limitations for the formation. Now it has been shown that the formation of many molecular alloys was possible under non-equilibrium conditions. Development of new vitreous molecular materials with novel properties generated by hybridization of two functional molecules is highly desiderated.

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