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CRYSTALLIZATION AND GLASS TRANSITION OF CHLOROBENZENE/TOLUENE BINARY AMORPHOUS SYSTEMS

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Abstract

Crystallization and glass-transition phenomena were studied for amorphous chlorobenzene (CB)/toluene (TL) binary systems as the function of composition. Samples were prepared by vapor-deposition onto cold substrates, and their structural changes due to temperature elevation were monitored with Raman scattering and light transmission. It was found that the crystallization temperature (T_c) of CB-rich amorphous samples increases as the TL concentration is increased. This is similar to the linear dependence of glass-transition temperatures (T_g) of many organic compounds on the concentration of additive. Also found was that T_c of TL-rich supercooled-liquids decrease as the CB concentration is increased. Issues related to the two kinds of T_c are discussed briefly.

Keywords: amorphous, crystallization, glass, glass transition, supercooled liquids

Introduction

Amorphous systems made with simple organic molecules undergo structural relaxation and finally crystallize when the temperature is raised. This process takes place in two types of the manner. One is the process in which the material undergoes the direct crystallization from the amorphous state [1]. Although this is a kinetic process that depends on the thermal history of the sample, it has been found that there is a fairly defined crystallization temperature (T_c) for the amorphous state of each compound. In the other process, the material undergoes first the well-known glass transition [2], and finally crystallizes through the supercooled-liquid state [3]. The direct crystallization is usually seen for compounds with rigid molecular structures, and the process through the glass transition tends to be seen for those with flexible molecular structures. As for binary organic molecular systems, the glass-transition temperature (T_g) sometimes shows a linear dependence on the composition. This relation has been employed to estimate the fictive T_g of some compounds for which the neat material does not show the glass transition [4].

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We have recently studied the effect of toluene (hereafter TL) doping on T_c of amorphous benzene prepared by vapor deposition onto cold substrates, and found that T_c increases by as much as 20 K by the addition of 0.07 mole fraction of TL [5]. In this paper, we report the results of a similar study of the effect of TL-doping on T_c of amorphous chlorobenzene (hereafter CB), and report also the structural changes from CB-doped TL-rich glasses. As for the TL-rich samples, we found, in addition to the dependence of T_g on the CB concentration, that T_c of supercooled-liquids decreases almost linearly as the CB concentration is increased. These T_g and T_c seem to be merged into each other by the increase of the CB mole fraction to the level as large as 0.3. Some issues are discussed briefly in relation to the two types of T_c, that is, of the direct crystallization from amorphous state and of the crystallization from the supercooled-liquid state.

Experimental

Amorphous films of CB/TL mixtures were prepared by the vapor deposition onto cold substrates in vacuum chambers with the base pressure below 10^{-7} Pa. The substrates were gold-plated copper blocks, and were cooled at 78 K with coolant-flow-type cold fingers. Thickness of all the samples was made to be about 10 μm by monitoring the interference of the transmitted laser light. It should be noted that the composition of a vapor-deposited binary amorphous sample is not the same as that of the source solution prepared in advance at room temperature, since vapor pressures of the components are different. The composition of each amorphous sample in this work was determined from the intensity ratio of the 701 cm^{-1} band of CB and the 785 cm^{-1} band of TL in the Raman spectrum, taking the data for the room-temperature solutions with known compositions as the reference.

Structural changes in the films were monitored with Raman scattering and light transmission during the temperature elevation with a constant rate of 0.28 K min^{-1}. Raman spectra were measured with a Triax 550 monochromator (Jobin Yvon-Spex) equipped with a CCD detector, using a He-Ne laser operating at 633 nm as the excitation source. The laser power at the sample was estimated to be about 10 mW. The same laser was also used for the light-transmission measurement and the sample-thickness monitoring. We estimated the width and integral intensity of Raman bands by fitting with a Gaussian function. The spectral slit width of the monochromator was set to be 1.5 cm^{-1}.

Results and discussion

Figure 1 shows the Raman-spectral evolution of a sample with the composition $CB_{0.12}TL_{0.88}$ during the continuous temperature elevation. It took 100 s to record one spectrum. Thus the temperature indicated beside each spectrum represents an approximate temperature for each measurement. The band around 1000 cm^{-1} includes the modes assigned mainly to the skeletal vibration of the phenyl ring of both CB and TL

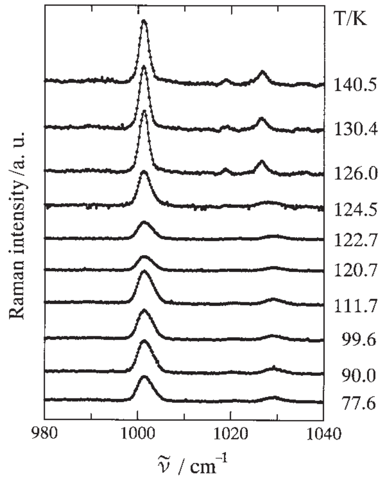

Fig. 1 An example of Raman spectral evolution during the temperature elevation (sample: $CB_{0.12}TL_{0.88}$). Base line of each spectrum is arbitrarily shifted

molecules. The initial amorphous sample showed a broad bandwidth, and at about 124.5 K, the bandwidth began to narrow. This change is ascribed to the crystallization of the sample, and is considered to arise from the difference in the molecular-conformation ordering between amorphous and crystalline states [1]. We chose the 1000 cm^{-1} band in the following analyses, since it was more sensitive against the structural change of the sample than other Raman bands.

Samples of neat CB and TL similarly show abrupt changes in the width of the 1000 cm^{-1} band. The results are plotted in Fig. 2 along with those for $CB_{0.12}TL_{0.88}$. For all the samples, the bandwidth was large for the initial amorphous state, and it changed in a narrow temperature region to a small constant value. Thus CB is considered to crystallize around 110 K, and TL crystallizes around 130 K. The mixed sam-

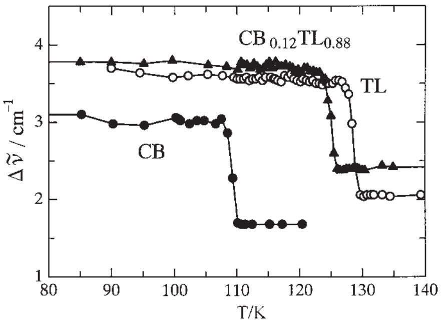

Fig. 2 Width change of the Raman band around 1000 cm^{-1} of neat CB, neat TL, and $CB_{0.12}TL_{0.88}$ samples

ples showed T_c that falls between these two temperatures. T_c estimated by such a method naturally depends on the rate of temperature elevation. However, it has been found that the obtained T_c is reproducible within a few degrees even if the rate had been changed by an order of magnitude. The result for CB is in harmony with that of our previous study [6]. It is noteworthy that no appreciable spectral change was observed for TL around 117 K where the glass transition is expected to occur [7]. This is the same as our previous study on the glass transition of butanenitrile [8].

Figure 3 shows the intensity change of the laser light transmitted through three samples identical respectively to those in Fig. 2. The light intensity for CB started to decrease around 106 K, and reached to a constant value around 109 K. After this, the sample film showed serious light scattering and seemed opaque. Thus CB is said to have crystallized around 109 K from the result of the light transmission. This value of T_c is slightly lower than that obtained from the result of Raman measurements. This is considered to arise from the difference in the amount of crystalline part in the sample that indicates the occurrence of crystallization. Namely, the transmission-light intensity is affected by the light scattering due to rather a small amount of the crystalline particles in the sample, while the Raman-band width depends on the substantial ratio of crystalline and amorphous parts in the sample. Thus the light transmission method tends to give a slightly lower value of T_c.

In contrast to the result for CB, the transmission-light intensity for TL showed a small change around 115 K before it finally exhibited an abrupt decrease. This small change is ascribed to the structural relaxation in advance of the glass transition [9], although the shape of the anomaly is not the same as the previously reported data [10, 11]. From the present result, we estimated T_g of neat TL to be 117 K where the anomaly seems to come to an end. This agrees well with the literature data [7]. Thus the light intensity transmitted through thin amorphous films indicates the occurrence of glass transition more sensitively than Raman spectra.

For the mixtures of CB and TL, the light transmission and Raman spectrum were monitored similarly during the temperature elevation (see the data for $CB_{0.12}TL_{0.88}$ in Figs 2 and 3 for example). Figure 4 summarizes the observed phenomena as the func-

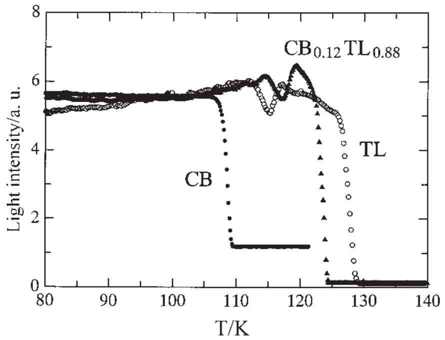

Fig. 3 Change in transmission-light intensity for neat CB, neat TL, and $CB_{0.12}TL_{0.88}$ samples which are identical respectively to those in Fig. 2

tion of the mole fraction of TL, x_{TL}. In this figure, T_c estimated from the mid point of Raman-bandwidth change is plotted with closed circles for the direct crystallizations. On the other hand, T_g estimated from the light transmission for TL-rich samples is plotted with open squares. In addition, T_c succeedingly observed for the super-cooled-liquid states of the TL-rich samples is plotted with open circles; the T_c values being again estimated from the Raman bandwidth.

As it is seen in Fig. 4, T_g of TL-rich glassy samples increases almost linearly as the CB concentration is increased. This behavior corresponds to that observed for many organic glasses [4]. Interestingly, the extrapolation of the line implied by these plots of T_g roughly points to the expected T_g of neat CB (128 K, the closed square in Fig. 4) estimated by the thermal studies of ethylbenzene/CB bulk mixtures [4]. Thus the simple linear dependence of T_g on the composition of binary organic mixtures is approximately confirmed also for the present binary system. Qualitative thermodynamical explanations of the linear dependence of T_g have been given [4], although the glass transition is essentially of kinetic nature.

In contrast to the behavior of T_g of binary mixtures, so far as we know, very few have been reported for the composition dependence of T_c of amorphous or super-cooled-liquid binary molecular systems [12]. We would like to discuss here two features seen in Fig. 4. The first is that T_c of CB-rich samples (direct crystallization) increases as x_{TL} is increased. This is interpreted with the increase of the potential-barrier height *vs.* the structural relaxation in amorphous states. Although the present results are similar to that of amorphous benzene doped with TL [5], the concentration dependence is much smaller. This is considered to arise from the difference in the compatibility of the dopant molecule to the lattice of the host compound. Namely, the mo-

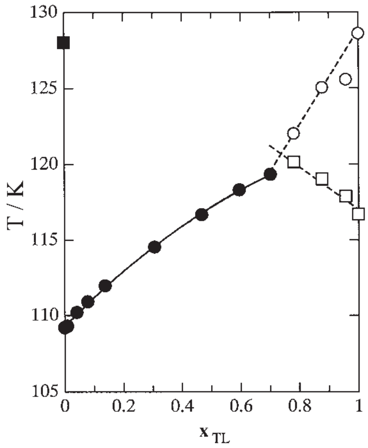

Fig. 4 Plots of T_c and T_g for binary systems of CB and TL as the function of TL mole fraction x_{TL}. ● – T_c of direct crystallization of amorphous samples , □ – T_g of TL-rich samples, open circles – T_c of crystallization from TL-rich super-cooled-liquids, a ■ – literature data of fictive T_g of neat CB estimated from T_g measurements on ethylbenzene/CB binary systems. Solid and dashed lines are guides to the eye

lecular shape of TL resembles that of CB while it is much different from the shape of the benzene molecule. The fact that the direct crystallization is observed even for samples in which TL concentration is larger than CB concentration implies that TL and CB molecules make mixed crystals by the direct crystallization.

The second feature is that T_c of the supercooled-liquid states of TL-rich samples decreases as the CB concentration is increased. The rate of crystal growth from liquids generally depends on both the molecular diffusion and nucleation [3]. As to the composition dependence of T_c observed for the present binary system, it is plausible that the addition of CB in supercooled-liquid TL makes the nucleation easier, since the clustering of each component may occur in the solution. However, detailed experimental and theoretical studies are needed to discuss this further. There is an open issue whether CB molecules are incorporated in TL crystals growing from the solution.

Interestingly, T_c of the supercooled-liquid state of a TL-rich sample approaches T_g of the same sample as the CB concentration is increased, and they are merged into each other around x_{TL}=0.75. On the other hand, we observed clear direct crystallizations even for the sample of $CB_{0.30}TL_{0.70}$. Thus the plots of two types of T_c (closed circles and open circles in Fig. 4) come across each other as if there is some connection between these two types of crystallizations.

Hikima *et al*. [13] have proposed a mechanism for the crystal growth occurring in the low-temperature region around or below T_g. Their mechanism is discriminated from that for the ordinary crystal growth in liquids, and encourages us to study the mechanism of the direct crystallizations of the CB-rich samples. However, such an attempt arouses another issue whether a crossover of different crystallization mechanisms takes place for CB/TL binary systems in a narrow concentration region around x_{TL}=0.75.

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