A Novel Change of Light Transmission in Supercooled Liquid State of Ethylbenzene

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By the continuous elevation of temperature, ethylbenzene in the supercooled liquid state first turns opaque and then becomes transparent again before it finally crystallizes. These observations are possibly related to the appearance of the second amorphous state with a correlated structure that has recently been reported for triphenyl phosphite.

Supercooled liquid states of simple organic compounds have been studied extensively in relation to the so-called "fragility" of glass-forming materials.[1,2] Most of organic glasses turn into supercooled liquids at the glass transition, and then crystallize by the further temperature elevation. It has been reported however that the supercooled liquid of triphenyl phosphite (hereafter TPP) shows a structural change into a novel state that has a correlated structure but is apparently amorphous.[3–6] This state has been considered to be an intermediate state between the supercooled liquid and crystal as the ordinary glass is, and was called the "glacial" state.[3] Although the nature of the glacial state has not yet been clarified well, the above findings have indicated that supercooled liquids of organic compounds are closely on the verge of the development of correlated structures. For the further study of the glacial state, it has been desired to find similar phenomena for compounds other than TPP.

In this letter, we report that ethylbenzene (hereafter EB), whose amorphous state has been known to undergo a glass transition,[7] shows a temporary loss of transparency in the supercooled liquid state when the temperature is raised continuously. This seems to indicate that there is a new state located between the supercooled liquid and crystal, and its behavior resembles that observed for TPP. Thus we consider that EB might be a new example for the study of the glacial state.

The amorphous state of EB is usually prepared by the rapid cooling of the liquid with liquid nitrogen, but in the present study, we employed the method of vacuum deposition of the vapor on to cold gold substrates at 78 K. The main purpose of this was originally to study the light interference in the amorphous films.[8] The samples thus prepared were films with the thickness of about 11 μm. Light transmission through the samples was monitored using an Ar^+ ion laser and a photodiode by raising the temperature with a constant rate. The laser light was introduced with the incidence angle of 60°. For the study of the structure of the newly found state of EB, X-ray diffraction and Raman scattering were measured using the apparatus employed in the previous studies.[9]

Figure 1 shows the temperature evolution of the light intensity transmitted through an EB film prepared as described above. The temperature was raised with the rate indicated in the figure caption. A similar result for a toluene film is shown for comparison. These amorphous films showed first a gradual decrease in the light transmission when the temperature was raised from 78 K to about 95 K. This is due to the change in the interference condition of the transparent amorphous films, and is related to the structural relaxation in these films.[10] Both the EB and toluene films showed then an abrupt increase of the light transmission in the region around 115 K. This is also considered due to the change in the interference condition of the films, but in this case, it accompanied the glass transition of the samples.[7] After the glass transition, the EB and toluene films are considered to have changed into the supercooled liquids, and these supercooled liquids eventually crystallized when the temperature was raised to the region around 130 K. The crystallization of the samples was confirmed by the appearance of the Bragg peaks in their X-ray diffraction patterns as it will be described later.

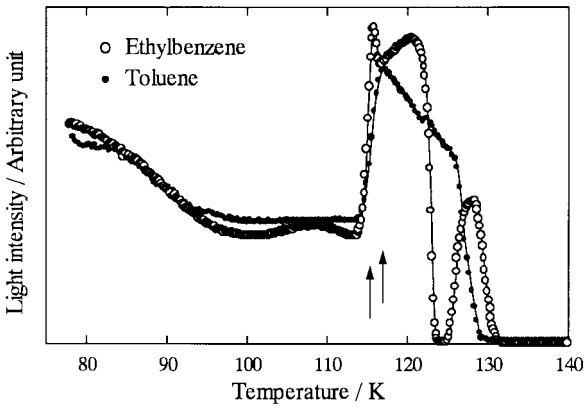

Figure 1. Change of laser light intensity transmitted through the sample films of ethylbenzene and toluene during the temperature elevation with constant rates (0.36 K/min for ethylbenzene and 0.35 K/min for toluene). Ethylbenzene shows an extra decrease of light transmission at about 124 K at this rate of the temperature elevation. Arrows indicate the glass-transition temperatures of ethylbenzene (115 K) and toluene (117 K) (ref 7).

The difference between the behaviors of EB and toluene was seen when the temperature was raised to about 125 K. While the toluene film was almost transparent until the final crystallization started around 126 K, the EB film showed an abrupt decrease in the light transmission around 124 K and recovered the transparency a little before it finally crystallized around 130 K. By the inspection of the sample, we noticed that the temporary decrease in the light transmission around 124 K was due to the occurrence of light scattering in the film. Thus, we consider that there appeared between 123 and 130 K a new state whose refractive index was different from that of the supercooled liquid state. The above behavior of EB films was reproduced even if the rate of the temperature elevation was changed in the range from 0.1 to 1 K/min. The temperatures, at which every change described above occurred, were slightly dependent on the rate of the temperature elevation.

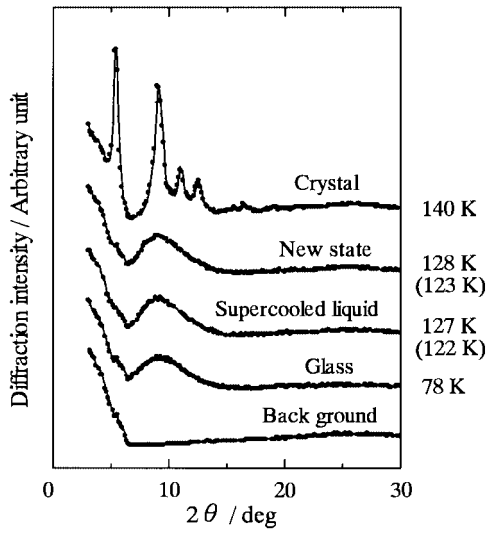

Figure 2. Evolution of X-ray diffraction pattern of an ethylbenzene film due to the temperature elevation. The temperatures in parentheses are those at which the measurement was performed after the sample was annealed at the temperature indicated above them.

Figure 2 shows the evolution of the X-ray diffraction of an EB film. A molybdenum X-ray source was used in this measurement. Since the X-ray diffraction was measured by raising the temperature stepwise and keeping it constant during each run, the temperatures at which different states of EB appeared did not coincide necessarily with the above description of the light transmission. In the glass state below the glass-transition temperature T_g around 115 K, the diffraction pattern comprised a broad peak around $2\theta = 9°$. Such a pattern was almost unchanged in the supercooled liquid state above T_g, and was unchanged even after the sample temporarily lost the transparency (this particular sample kept the transparency until 127 K, and temporarily lost it at 128 K). The structureless pattern indicates that the new state has a liquid-like or amorphous structure. After the eventual loss of the transparency above about 133 K, Bragg peaks appeared as shown in the diffraction pattern of the crystal at 140 K.

Similarly, we measured Raman spectra of EB films in the small-wavenumber region below 200 cm^{-1}. The glass and supercooled liquid showed a broad band peaking around 100 cm^{-1} in the spectra corrected for the thermal excitation of vibrational modes. These features are almost the same as that toluene shows in the low temperature region.[11] We did not observe any appreciable change of the broad-band shape in the temperature region of the new state. Since some new structures weakly appeared in the region of the broad band after the eventual loss of the sample transparency, the broad band is considered to be related to lattice vibrations of the crystal. So far from the X-ray and Raman measurements, we have not yet obtained any indication that the new state of EB is an amorphous state with a correlated structure as was reported for TPP.[5]

In summary, we have found that EB shows a novel change of optical transmission in its supercooled liquid state, and this behavior resembles that of TPP. Although we have not yet obtained any indication that this is due to the appearance of a state with a correlated structure, the new state has a high possibility to be related to the glacial state of TPP. One thing that prevents detailed studies of the new state is the fact that it crystallizes easier than the glacial state of TPP. Namely, if we keep the temperature constant as long as an hour in the region of the new state, the sample starts to crystallize. We therefore had to lower the temperature a little below the region of the new state when we measured the X-ray diffraction or Raman scattering. It should be noted that the optical transmission did not recover by this lowering of the temperature, indicating that the appearance of the new state was irreversible. Thus it is considered that we were observing the X-ray diffraction and Raman scattering of the new state, although the temperature was lowered to the region of the ordinary supercooled liquid. The above situation encountered for EB may arise from the small and simple molecular structure of EB compared with that of TPP. We are trying to see the behavior of TPP with the same experimental method as employed in the present study. However, we have not yet succeeded to prepare a vapor-deposited glass film of TPP because of its small vapor pressure.

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