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Liquid–Liquid Relaxation in the Supercooled Liquid State of Ethylbenzene: Thermal Studies Using a Prototype DTA Sensor for the Study of Vapor-deposited Samples

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A prototype sensor for differential thermal analysis (DTA) was developed for in situ studies of the thermal behavior of molecular films vapor-deposited onto a cold substrate in a vacuum. The system was applied to the study of ethylbenzene (EB). By raising the temperature at a constant rate, we observed in the supercooled liquid (SCL) state a small exothermic peak simultaneously with the characteristic light scattering reported previously. These observations and additional optical experiments on the irreversibility of the phenomena indicated that a structural relaxation occurred from a less stable SCL to a more stable SCL.

The behavior of vapor-deposited molecular glasses has attracted growing attention in recent years.[1–6] We observed indications of liquid–liquid structural transformation in the SCL states of EB and related compounds for samples obtained through the glass transition of vapor-deposited glasses.[3] These indications were determined through study of light scattering in the samples. The results of the light-scattering study, however, did not provide conclusive proof of the structural change in the bulk of the samples.[7] We thus planned to make in situ thermal measurement on vapor-deposited samples while simultaneously monitoring the scattering of laser light.

Sample films were vapor-deposited on cold metal substrates with a thickness of approximately ten micrometers. In our earlier studies on EB, we found a curious intensity depression of the laser light reflected from the sample in the SCL state when we raised the temperature continuously.[8] This result was due to temporal light scattering. We recently found that EB and related compounds form glasses with different densities depending on the temperature of the vapor deposition (T_d).[2,3] Glasses, deposited at a T_d much lower than the glass-transition temperature (T_g) of the compound, had densities less than those estimated for the SCL at the corresponding temperature, whereas glasses deposited at a T_d only slightly lower than the T_g had densities larger than the SCL. We abbreviate hereafter the low-density glasses as LDG and the high-density glasses as HDG.

Interestingly, the samples originally made as LDG exhibited the above-described reflected light depression when the temperature was raised to the region of the SCL state. However, the samples obtained from HDG did not show such a behavior. Figure 1 compares the typical intensity evolutions of the laser light reflected from EB samples originally prepared as LDG and HDG, respectively.[3] The rate of temperature elevation was 0.28 K min^{-1}. The patterns of the light intensity evolution were analyzed using our previously reported method,[9] and we determined the temperature region where each sample existed as a SCL as indicated in the figure. Note that the sample originally made as LDG exhibited a strong intensity depression (see the arrow) in the SCL state, while the sample originally made as HDG showed no such depression. We have recently come to consider that the depression is caused by light scattering due to the refractive index inhomogeneity accompanying the structural change in the SCL state of the sample originally made as LDG.[3] The two kinds of SCL did crystallize, however, at almost the same temperature (see the decreases of the light intensity at about 129 K) into the same crystalline state as revealed by X-ray analysis,[10] which suggests that the structures of the two kinds of SCL were the same just before the crystallization.

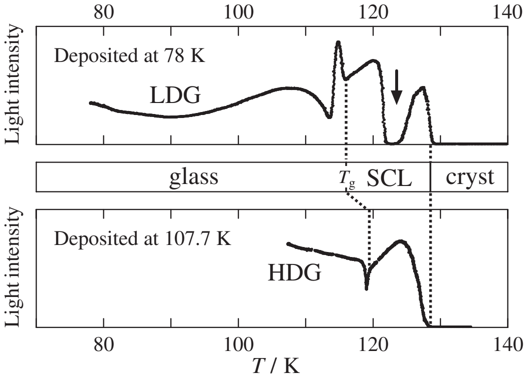

Figure 1. Comparison of the reflected-light intensity data for two types of vapor-deposited EB samples, and the temperature regions distinguished with the sample states.

To explore further the cause of the characteristic depression of the reflected-light intensity observed for some of the vapor-deposited samples, we fabricated a DTA sensor that worked as the substrate for the vapor deposition. A schematic cross section is displayed in the graphical abstract. The central part of the sensor was made of a constantan disk (0.2 mm thick and 18.5 mm in diameter) and two copper leads crimp-contacted to the disk that worked as a thermocouple. The constantan disk was silver-soldered to a caved copper block that was mounted on a cold finger cooled with cold He gas. A laterally U-shaped copper piece was attached to the copper block and made a shadow on one half of the constantan disk during the vapor deposition. The bottom face of the U-shaped piece was plated with gold and worked as the substrate for the vapor deposition and also for monitoring the reflected-light intensity. A laser beam (532 nm) was introduced from the bottom of the vacuum chamber, and the reflected intensity was monitored with a silicon photocell. The small cave made in the copper block was filled with He gas during vapor deposition to diminish the temperature rise of the constantan disk and was then evacuated during the DTA measurement to improve the sensitivity.

Figure 2 shows the evolutions of the DTA signal and the simultaneous change of the reflected-light intensity during the temperature elevation of EB samples deposited at 78 and 105 K,

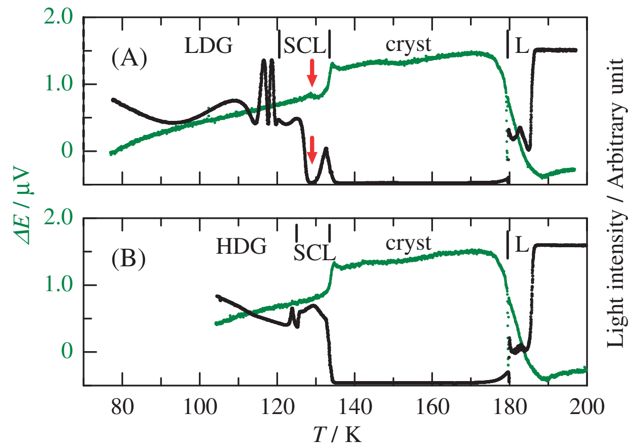

Figure 2. DTA signal (green) and reflected-light intensity (black) during the temperature elevation of EB samples. The deposition temperature and sample thickness were (A) 78 K and 11.1 μm and (B) 105 K and 10.8 μm.

respectively. The rate of the temperature elevation was 0.88 K min^{-1} in these experiments. The abscissa represents the temperature of the copper block, and the ordinate represents the output of the thermocouple (green) in μV and that of the silicon photocell (black) in an arbitrary unit.

The evolution of the reflected-light intensity in Figure 2 nearly reproduced the results observed previously for the samples prepared under similar conditions,[3] although the characteristic temperatures indicating the changes in the sample state were slightly higher than those in Figure 1. These differences were mainly due to the poor thermal conductivity of the constantan disk and also due to the rate of the temperature elevation faster than that in previous studies. One may also notice that the shapes of the change in the reflected-light intensity in Figure 2 are different a little from those in Figure 1. This is due to the difference in the interference condition which was caused by the difference in the wavelength and incidence angle of the laser light. The analysis[9] of the light-intensity change indicated that the change of the sample state occurred in the following sequence: glass (LDG or HDG), supercooled liquid (SCL), crystal (cryst), and liquid (L) states as indicated by the symbols inserted in Figure 2.

The gradual upward shift of the DTA signal observed in the wide temperature range in Figure 2 was caused by insufficient radiation shielding in the prototype experimental system. Note that both of the samples deposited at 78 and 105 K showed similar anomalies in the DTA signal and light intensity at about 134 K (due to crystallization) and at about 180 K (due to fusion). On the other hand, the sample deposited at 78 K showed a small exothermic peak of the DTA signal and a deep depression of the light intensity at about 129 K (red arrows), whereas the sample deposited at 105 K showed no anomaly in this temperature region.

The anomaly of the DTA signal at crystallization comprised a small exothermic peak and a remarkable stepwise increase. The former is due to the release of heat accompanying crystallization of SCL. The integrated areas of these peaks shown by the two samples which were originally prepared with similar thicknesses were almost the same in harmony with our postulate that the SCL states of these samples were the same just before the crystallization. However, the cause of the stepwise increase of the DTA signal at crystallization is not clear at present. One possibility is that the effect of the thermal radiation coming from the room-temperature vacuum chamber became larger when the sample turned from a transparent liquid to an opaque polycrystalline state. We are now preparing a new radiation shield to diminish this effect.

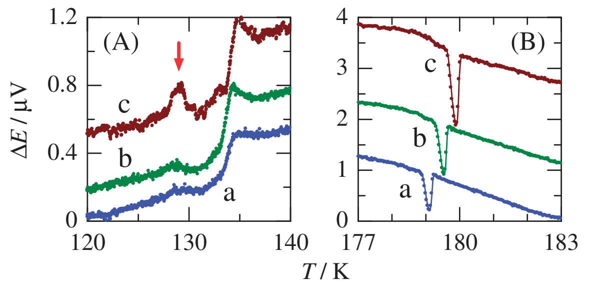

Figure 3. Comparison of the DTA signals observed for three samples prepared at 78 K with different thicknesses: a, 8.4; b, 11.1; and c, 15.7 μm. (A) The region of the exothermic peak due to liquid–liquid relaxation. (B) The region of endothermic peak due to fusion. Plots in (A) and (B) are arbitrarily shifted along the ordinates.

The anomaly of the DTA signal at around the sample fusion comprises a rather gradual but prominent downward change and a very sharp depression at about 179 K which was almost the same as the melting point of EB (178.2 K).[11] The former change was due to the sample evaporation which was also indicated by the change in the reflected-light intensity. It is noted that the evaporation slowly started at temperature about 5 K lower than the melting point and terminated at about 187 K.

To confirm the appearance of the exothermic peak accompanying the depression of the reflected-light intensity in the SCL state, we compared results for three samples similarly prepared at 78 K with different thicknesses. Figure 3 displays the results for these samples; (A) the region of the exothermic peak in question and (B) the region of the endothermic peak due to sample fusion. The endothermic peak shifted slightly to the high-temperature side for thicker samples, which was attributed to the delay in the temperature rise in the sample.

The areas of exo- and endothermic peaks observed in Figure 3 showed correlations with the sample thickness as shown in Figure 4. Here, we made a correction for the sample evaporation in estimating the area of the endothermic peak due to fusion. For this, we graphically estimated the sample amount remaining at fusion on the basis of the magnitude of downward changes of the DTA signal before and after the fusion. It is noted that the corrected data of the area of the endothermic peak (Figure 4B) has a good correlation with the sample thickness, indicating that our DTA sensor worked reasonably. We then estimated the enthalpy change causing the exothermic peak observed in the SCL state to be about 3 kJ mol^{-1} on the basis of the enthalpy of fusion of EB (9.18 kJ mol^{-1}).[11]

Since first observing the intensity depression of the reflected light in the SCL state of EB,[8] we have searched for its cause.[3] At one point we considered that some undulations at the sample surface might be formed due to the difference between the expansion coefficient of the metal substrate and the molecular liquid.[7] The enthalpy change observed in the present study,

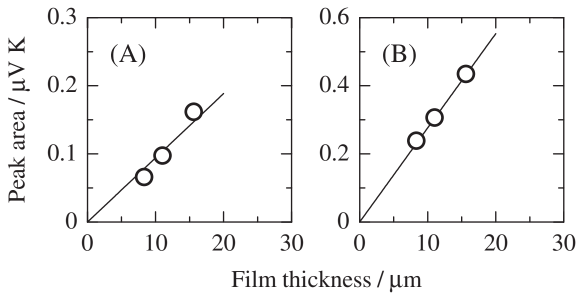

Figure 4. Comparison of the apparent peak area of DTA signals displayed in Figure 3; (A) exothermic peaks due to liquid–liquid relaxation and (B) endothermic peaks due to fusion. The data for fusion were corrected for the partial evaporation of the sample preceding the fusion.

however, correlates with the sample thickness and is of the same order as the enthalpy of fusion. These results indicate that the observed anomaly is not due to a change at the sample surface but due to a bulk structure change which induces inhomogeneity in refractive index causing light scattering. To explore the nature of this structural change, we further examined the reversibility of the intensity depression of the reflected light.[10] Thus, we first raised the temperature of a sample deposited at 78 K up to the temperature where the light-intensity depression almost terminated and cooled the sample down to about 90 K where it was considered to turned into glassy state. We then raised the temperature again with the same rate as in the first trial. We found no depression of the light intensity this time. The results indicated that the anomalous phenomenon related to the depression of the reflected-light intensity was irreversible. Therefore, the structural change in the SCL state was not a change accompanying a phase transition but a change due to a structural relaxation in the SCL state.

It is recalled now that the above relaxation phenomenon was not observed for SCL appearing from HDG but only for SCL appearing from LDG, whereas both types of SCL exhibited almost the same crystallization phenomena at about 129 K (Figure 1). These facts indicate that the SCL appearing from LDG was less stable and relaxed into a more stable SCL state, while HDG turned directly into the more stable SCL and did not exhibit the relaxation. These behaviors of the samples are in harmony with our previous postulate on this relaxation phenomenon.[3]

From a chemical viewpoint, one may ask what is the difference in the liquid structure before and after the structural relaxation in the SCL state. The T_d dependence of the initial density of vapor-deposited glasses[2,3] implies that molecules deposited on the top surface of the sample are frozen rapidly in highly disordered intermolecular conformations when the substrate temperature is sufficiently low, whereas they may have a short but definite time for migrating on the sample surface to some extent when the substrate temperature is close to T_g. In the latter case, the deposited molecules may find local minima of intermolecular conformation making the resultant average density of the sample to be comparable to or sometime larger than SCL. The fact that the samples originally deposited as HDG do not show anomaly in the SCL state implies that the content of such locally stable conformations decreases gradually as the sample temperature is continuously raised in the SCL state. On the other hand, the samples originally made as LDG are considered to maintain highly disordered structures even after the structural relaxation in the glassy state and find themselves unstable after undergoing glass transition. This may be the cause of the relaxation phenomena observed in the SCL state. We are now searching for stable intermolecular conformations of EB and related compounds by using molecular orbital calculations and have found that the interaction between the quadrupole moment of the phenyl ring and alkyl group is important for making stable intermolecular conformations.[10]

In conclusion, we found that it is possible for the structure of the SCL appearing through the glass transition to depend on the structure of the original glass, and relaxation phenomena from one SCL to another SCL are sometimes observed for compounds which can form locally stable intermolecular conformation. Such observations suggest the concept of "polyliquidism" in analogy with "polyamorphism" which came to be common after the discovery of the low- and high-density amorphous states of water.[12,13] Phenomena related to polyliquidism have already reported for liquid phosphorus at high temperatures and high pressures[14] and for the supercooled liquid of triphenyl phosphite (TPP) at low temperatures.[15] The latter is a case discovered for the supercooled state of a molecular compound as in our observations on EB, and detailed studies should be made on the similarity and difference between these two cases.

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