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Behavior of Glass and Supercooled Liquid Alkylbenzenes Vapor-Deposited on Cold Substrates: Toward the Understanding of the Curious Light Scattering Observed in Some Supercooled Liquid States

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Ethylbenzene (EB) films prepared on cold metal substrates by vapor deposition in vacuum show a curious light scattering in the supercooled liquid (SCL) state when the temperature is raised at a constant rate. To investigate the cause of this phenomenon, we examined the behavior of similarly prepared samples of a series of alkylbenzenes. We found that the vapor-deposited glass of propylbenzene (PB) and isopropylbenzene (IPB) showed a deposition-temperature (T_d) dependence of the initial molar volume (V_m) on deposition similar to EB glass. Interestingly, the samples of the three compounds, which were formed initially as glasses with V_m much larger than that of SCL at the same temperature, exhibited the curious light scattering when they transformed to SCL states after the temperature elevation to above their glass-transition temperature, while the corresponding samples with initial V_m smaller than that of SCL did not exhibit this light scattering. On the basis of these observations, a hypothesis on the cause of the light scattering in the SCL state is proposed in relation to structural transformation between different SCL states. A microscopic mechanism of the formation of a high-density glass with V_m smaller than that of SCL is briefly discussed by referring to the observations of toluene samples which showed a slightly different T_d dependence of V_m and did not show the curious light scattering in the SCL state.

We have studied the structure and relaxation behavior of amorphous molecular systems prepared by vapor deposition on cold metal substrates.[1–6] The samples were films with a thickness of about 10 µm. Such amorphous samples usually tend to crystallize when they are annealed with temperature elevation.[1–6] However, vapor-deposited amorphous samples of certain compounds undergo a glass transition and transform into supercooled liquid (SCL) states by temperature elevation without experiencing crystalline states.[7–10] Similar phenomena have been known for a variety of bulk amorphous materials prepared by liquid quenching.[11–13] Such special amorphous states are called glasses by analogy with conventional glass. A common structural feature of these glass-forming molecular compounds is their flexibility which permits various intra- and intermolecular conformations and hinders crystallization.

We found that glass samples of ethylbenzene (EB) and related alkylbenzenes could be prepared by vapor-deposition with good reproducibility. We studied the properties of these materials using laser light interference in film samples.[14,15] One of the remarkable observations during these studies was that the density and relaxation behavior of the glass state systematically depended upon the vapor-deposition temperature (T_d).[15] Glass samples deposited at a T_d much lower than the glass-transition temperature (T_g) had a lower density than that estimated for the SCL state at the same temperature. In this paper, we call such a glass "low-density glass" (LDG). In contrast, glass samples deposited at a T_d close to T_g sometimes had a higher density than that estimated for the SCL state at the same temperature. We call these glasses "high-density glass (HDG)."

We recently confirmed that the above LDG samples sometimes show a curious light scattering at a temperature above T_g after they were transformed into SCL state by temperature elevation, while HDG samples did not show this light scattering in the SCL state. Thus we believe that the curious light scattering first observed for the SCL state of EB years ago[16] has an important relationship with the structure of the original glass state of the sample. We examined the similar behavior of related alkylbenzenes to clarify the mechanism of this curious light scattering effect.

In this paper, we first summarize the features of the intensity evolution of laser light reflected from samples of toluene (TL), EB, propylbenzene (PB), and isopropylbenzene (IPB) vapor-deposited at different T_d. We next describe the molar volume V_m of the deposited sample as estimated by analysis of the evolution of reflected light intensity, and compare the behavior of V_m evolution after annealing samples deposited at different T_d. In the second half of this paper, we return to the intensity evolution of laser light reflected from samples of the four compounds, and discuss the differing conditions under which the curious light scattering occurred in SCL states. We observed that TL did not show the formation of HDG with a good reproducibility, nor did it show the curious light scattering effect. On the basis of these observations, we propose a hypothesis regarding the appearance of the different types of SCL from LDG and HDG, and describe a possible cause for the curious light scattering effect in the SCL state.

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Table 1. Principal Data in the Analysis of the Results Obtained for Samples Deposited at 78 K and the Glass-Transition Temperature Reported for Bulk Samples

	n[a)]	ρ/g cm^{-3} [b)]	T_g/K[c)]	n_0[d)]	ρ_0/g cm^{-3} [d)]	Δn	T_g(bulk)/K
Toluene	1.505	0.866	116.3	1.624	1.031	−0.049	113,[e)] 115,[f)] 117[g)]
Ethylbenzene	1.503	0.867	116.2	1.615	1.023	−0.048	111,[e)] 113,[f)] 115[g)]
Propylbenzene	1.499	0.862	125.7	1.598	1.002	−0.047	122[e)]
Isopropylbenzene	1.498	0.862	129.4	1.595	1.000	−0.044	125,[e)] 126[h),i)]

a) Refractive indices at 514.5 nm estimated from the data at 293 K in Ref. 17. b) Density data at 293 K from Ref. 19. c) T_g observed for samples deposited at 78 K. d) Estimated values at T_g. e) Ref. 20. f) Ref. 11. g) Ref. 21. h) Ref. 22. i) Ref. 23.

Experimental

The apparatus and experimental procedure were very similar to those previously described.[14] Reagent-grade liquids of TL (Wako Pure Chemical), and of EB, PB, and IPB (Tokyo Chemical Industry) were purified by distillation over molecular sieves and fractional crystallization prior to use. The glass samples were prepared by deposition of a room-temperature vapor onto a gold-plated copper substrate. The substrate was cooled using a cold flow of helium gas, and was maintained at a constant temperature during the vapor deposition. The base pressure of the vacuum chamber was about 10^{-7} Pa. The sample was deposited at a rate of about 0.2 µm min^{-1} to a final thickness of about 10 µm. The sample thickness was estimated by monitoring the interference fringe of reflected laser light (514.5 nm light of an Ar$^+$ laser) during vapor deposition. The intensity of the reflected laser light was measured using a silicon photocell. The incident angle of the laser light was 60 degrees from normal to the substrate. After deposition, the sample temperature was elevated at a constant rate of 0.28 K min^{-1}.

Raman spectra of the samples were monitored using the above laser light during deposition and the subsequent temperature elevation. This was important to confirm the purity of the deposited material and its final crystallization at an elevated temperature, although the obtained spectra are not presented in this paper. A Triax 550 monochromator (Jobin Yvon-Spex) equipped with a CCD detector cooled by liquid nitrogen was used for the measurement. The scale of the Raman shift was calibrated using atomic emissions from a neon lamp.

Results and Discussion

Interference Fringe of Reflected Light during Vapor Deposition at a Constant Temperature and Its Evolution due to Temperature Elevation. As has been described in our previous papers,[4,14,15,17] laser light reflected from the sample on a metal substrate showed a periodic change in intensity as sample thickness increased via constant-rate vapor deposition. This was due to changing conditions of the light interference in the sample. We call the pattern of this intensity change the fringe, although we do not present an example here. When we closed the valve of the vapor inlet, the fringe immediately stopped changing at a certain phase. The approximate final thickness of the sample was calculated by eq 3 which is presented in the following section. In the calculation, we used a refractive index estimated from the room-temperature refractive index[18] and temperature dependence of the density[19] of the liquid of each compound, assuming a constant molar refraction R_m represented by eq 1 below. The data of the four compounds used in the calculation are listed in Table 1, along with other data used in subsequent analysis. The thickness of the samples was thus determined to be about 10 µm.

Since the supply of the material was interrupted when we closed the valve, and since the vapor pressures of the four compounds were considered to be small enough in most of the part of the temperature region studied, further changes in the reflected light intensity were mainly attributed to a change in the sample state. Figures 1a–1d show the evolution of reflected light intensity observed for samples of the four compounds deposited at 78 K during the temperature elevation. Figures 1e–1h show similar evolutions of reflected light intensity, but in these cases, T_d for each compound was chosen close to T_g of each compound as indicated in the figure. The meaning of the symbols G, L, and C in Figure 1 will be explained later.

Analysis of the Evolution of the Fringe due to Temperature Elevation. Our method of analysis was described in detail elsewhere.[14,15] Here, we briefly explain several important points regarding the analysis. We first assumed a constant molar refraction R_m, represented by eq 1[24] (the so-called Lorentz–Lorenz equation) for the compounds studied.

$$R_m = \frac{n^2 - 1}{n^2 + 2} V_m \tag{1}$$

where n is the refractivity of the sample and V_m is the molar volume. This was a rough assumption for compounds with anisotropic molecular structures, but may be applicable to a disordered molecular system such as a glass or liquid.[25]

We also assumed uniaxial thermal expansion of the sample deposited on the metal substrate. This was reasonable for thin films of soft materials deposited on metal substrates. Thus, we can relate a small change ΔV_m in V_m to a small change Δd in the sample thickness d as

$$\Delta V_m / V_m = \Delta d / d \tag{2}$$

Turning back to the light interference in the sample, the repetition number N of the fringe during vapor deposition at a constant temperature is expressed by

$$N = \frac{2d}{\lambda} \sqrt{n^2 - \sin^2 \theta} \tag{3}$$

where λ and θ are the wavelength and incident angle of the light, respectively.[4] In the annealing process after vapor deposition, both n and d were considered to be variable. If we consider small changes in N, d, and n from an arbitrary reference point on the fringe where these three quantities have the values N_0, d_0, and n_0, N can be rewritten using eqs 1 and 2 as a function including n as the only variable. Since this is a

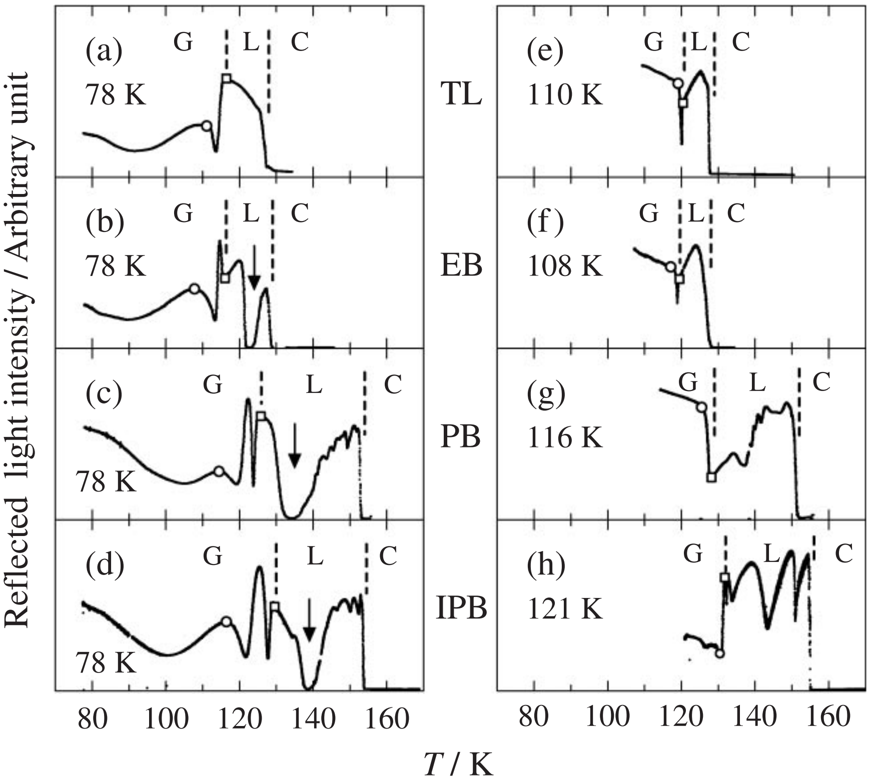

Figure 1. Intensity evolution of light reflected from samples deposited on a cold gold substrate during temperature elevation. Data (a)–(d) are for samples of TL, EB, PB, and IPB, respectively, deposited at 78 K. Data (e)–(h) are for corresponding samples deposited at the indicated temperature, which was 0.92–0.95 times the T_g of each compound. Open circle and open square indicate T_r and T_g, respectively, of each sample. See the text for the meaning of the characteristic temperature T_r. The symbols G, L, and C indicate glass, SCL, and crystal, respectively, and the dashed lines between symbols indicate the temperature where the structural change between the two states occurred.

complicated function, we expanded it as a polynomial of the small change in n.

In the actual analysis, we conventionally estimated Δn which caused a unit increase in N after solving the quadratic equation of Δn. Using the values of R_m of each compound under investigation, and of n_0 at a certain reference point on the fringe, we estimated Δn for each sample. As the reference point for the analysis, we chose a point on the fringe slightly above T_g, which was empirically found to be the temperature at which the change in the reflected-light intensity showed an anomaly. In other words, we determined T_g for each sample by examining the evolution of the fringe, locating the temperature where the sample began to show a normal thermal expansion after a rapid change in volume due to the structural relaxation just below T_g. Then, n during the temperature elevation of the glass sample was calculated by ascending the fringe back to the start point of the temperature elevation using the phase difference from the reference point. Finally, V_m at each point upstream from the reference point was calculated by eq 1. Several constants used in the analysis are listed in Table 1.

We could not estimate V_m at points significantly downstream from the reference point on the fringe, because the reflected light intensity in such a region was affected by light scattering in the sample. All samples of the four compounds crystallized once the temperature was raised past a certain value. This caused serious light scattering due to the appearance of crystal grains. In the case of EB, PB, and IPB, an additional, curious light scattering effect was observed in the SCL states of samples deposited at a T_d much lower than T_g, as indicated by the arrows in Figures 1b–1d. This curious light scattering is the main focus of this paper, and will be discussed further in the later section.

T_d-Dependence of the Initial V_m of the Glass on Vapor Deposition. The evolution of V_m was derived from the analysis of the interference fringe which was similar to those in Figure 1. The results are summarized in Figure 2 for almost all samples of the four compounds. Most of the results for EB were the same as those reported in Ref. 15, and the results for TL and PB at T_d around 78 K reproduced well the corresponding data reported in our previous paper.[14]

We plotted in Figure 3 the initial V_m values of all samples as a function of T_d. The initial V_m of the glasses of the four compounds on deposition was much larger than that estimated for SCL at the same temperature (dashed lines in Figures 2 and 3) if T_d was much lower than T_g, and the initial V_m tended to be smaller as T_d was higher. We call these glasses LDG, as mentioned in the introduction. However, in the cases of EB, PB, and IPB, the initial V_m showed a minimum at a T_d of about 0.9 times T_g. Interestingly, the initial V_m of these three compounds was smaller than the corresponding value of SCL at the same temperature when T_d was close to T_g. We call these glasses HDG, as mentioned in the introduction.

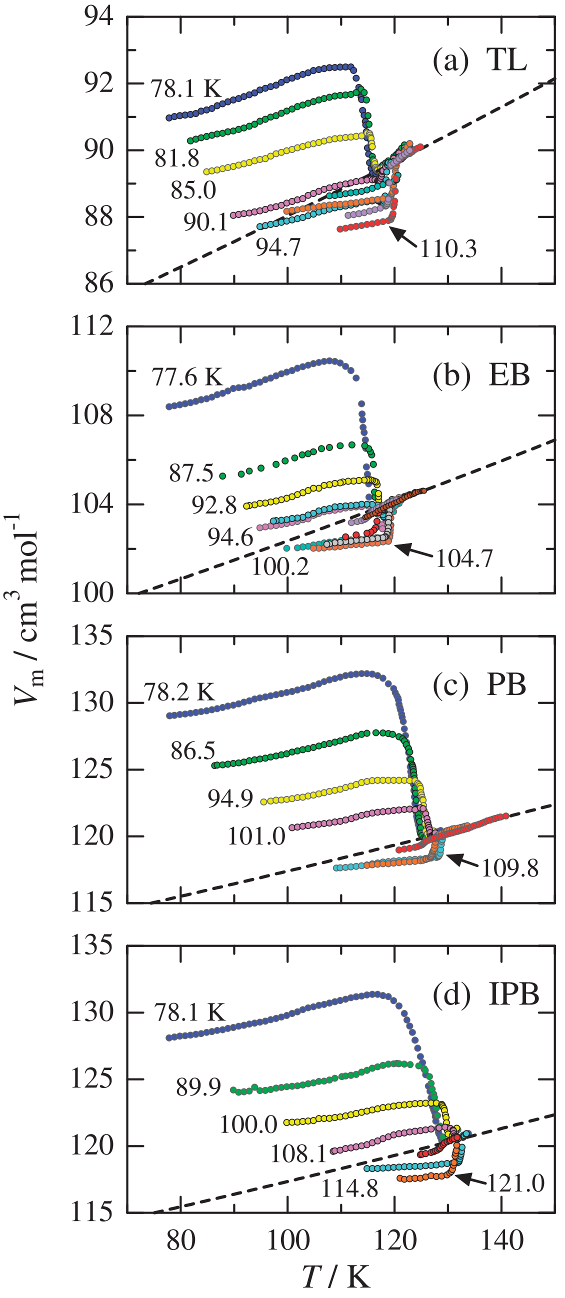

Figure 2. V_m evolution of the samples due to temperature elevation of four compounds deposited at T_d which is indicated in the figures. Dashed lines indicate the V_m evolution of SCL estimated by extrapolation of the density data (Ref. 19) of the liquid state of each compound. We performed so many experiments in the vicinity of T_g of each compound that T_d values are indicated for only several representative plots.

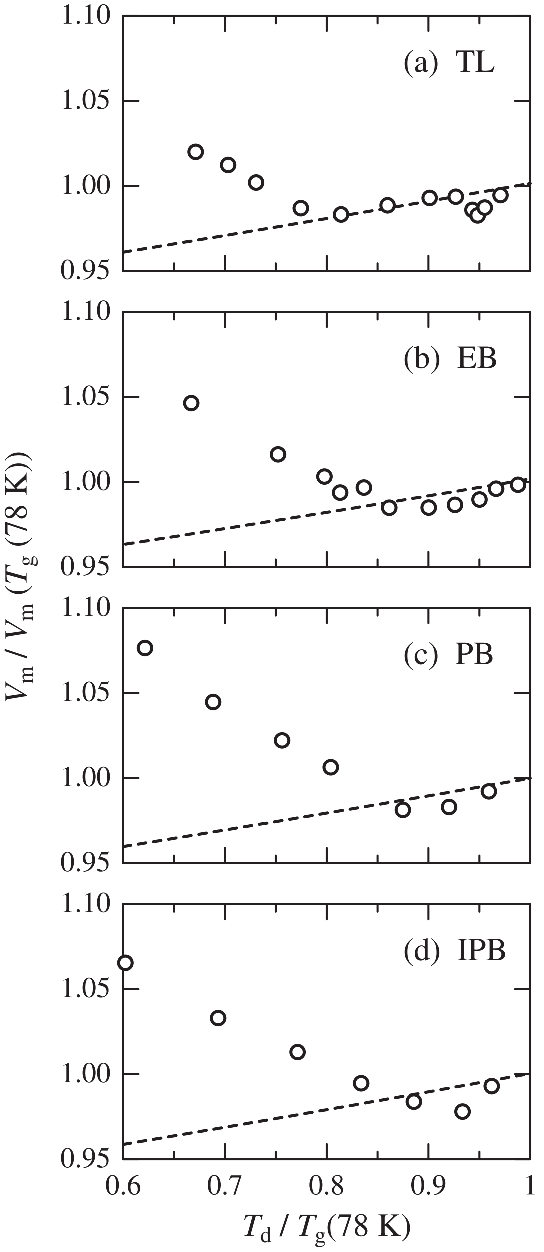

Figure 3. T_d dependence of the initial V_m on deposition of the four compounds. The abscissa represents T_d normalized with the T_g of each compound observed for the sample deposited at 78 K. The ordinate represents V_m normalized with the value of the sample (deposited at 78 K) at its T_g. Dashed lines indicate the V_m of SCL estimated by extrapolation of the density data (Ref. 19) of the liquid state of each compound.

As to the cause of the large initial V_m of LDG deposited at lower temperatures, the excess volume or voids formed among molecules due to the rapid freezing in the deposition process are considered. On the other hand, the small initial V_m of HDG deposited at temperatures near T_g is attributed to the formation of locally stable intermolecular conformations due to the deposition of the room-temperature vapor onto a substrate kept at rather high temperatures. We believe that, in this process, molecules deposited on the substrate have some respite time before frozen and are favored for the formation of locally stable molecular aggregates.

In contrast to the cases of EB, PB, and IPB, the initial V_m of TL showed a minimum at around 95 K which was about 0.8 times T_g, and increased along the line of V_m of SCL (dashed line) above this temperature. This implies that TL molecules assumed intermolecular conformations on deposition similar to those of the SCL state at the same temperature, but then behaved like glass when the temperature was subsequently raised for annealing. Curiously, the initial V_m of TL had values smaller than SCL in a narrow temperature range around 111 K (about 0.95 times T_g). We are not presently confident about the reproducibility of these results, but they could imply that TL might show an initial V_m smaller than SCL when certain conditions are fulfilled during the vapor deposition. This critical behavior of TL will be discussed again in the final section.

T_d-Dependence of the Manner of V_m Evolution below the T_g Region. As to the evolution of V_m during the temperature evolution for annealing, two distinct features are seen in Figure 2. One is the increase in V_m (thermal expansion) in the initial period, followed by a rapid decrease in V_m before merging with the SCL line. This feature was observed for LDG deposited at T_d's much lower than T_g. The other feature is that, after weak thermal expansion in the initial period, V_m showed a rapid increase before merging with the SCL line. This feature was seen for HDG deposited at T_d's close to T_g.

The initial thermal expansions were considered to be those of the glassy solid which was formed by the rapid freezing of the molecules deposited on the substrate. The significant difference between the two features of the V_m evolution was the rapid volume change following the initial expansion. The volume decrease observed for LDG just below T_g can be understood as a shrinkage due to structural relaxation taking place in the glass which includes fairly a large excess volume or voids among the molecules.

On the other hand, the relaxation accompanied by a volume increase observed for HDG was unexpected if we adhered to the ordinary concept that glass tends to include an excess volume. However, such an increase in volume may occur when a system frozen in a non-equilibrium disordered state with an anomalously dense structure is warmed to its T_g. As described in the preceding section, the unexpected formation of HDG may be possible if the deposited molecule retains the room-temperature kinetic energy for some time and the environment around the molecule is favorable for the formation of locally stable molecular aggregates.

As we have already mentioned, we determined T_g of each sample by carefully seeking the point on the fringe at which the light-intensity evolution accompanying a rapid volume change transformed into a different evolution accompanying the normal thermal expansion of SCL. As a result, all plots representing V_m evolution in Figure 2 merged with the SCL line. The overall appearance of the V_m evolutions plotted in Figure 2 indicates that our analysis of the fringe was essentially correct, as long as the estimation of the refractive index n_0 at the reference point from the extrapolation of the liquid lines was correct. It should be noted however that the SCL line with which V_m of the glass merged might be different between the cases of LDG and HDG as it will be discussed in the later sections.

It should be also noted that the T_g value determined by our method was sometimes higher than that determined by other methods, such as adiabatic calorimetry (Table 1). The reason for this may be that we raised the sample temperature at a constant rate.

Stability of the Glass against the Thermal Motion of Molecules. The rates of initial thermal expansion observed for LDG in Figure 2 (see the initial inclination of the evolution of V_m) are comparable with that of SCL, while those of HDG were smaller than for SCL. The close molecular packing in HDG may be the cause of the small thermal expansion.

In our previous paper,[17] we defined the temperature T_r at which the V_m evolution changes from normal thermal expansion to an evolution accompanying a rapid structural relaxation. We marked this point on each fringe in Figure 1 with an open circle. Naturally, the difference between T_r and T_g was small for HDG prepared at a T_d close to T_g, while the corresponding difference for LDG was rather large.

Interestingly, T_g of LDG seemed slightly lower as its T_d was lower, and T_g of HDG was apparently higher than that of LDG (Figure 2). The former implies that the molecular attraction was slightly weaker in LDG at a lower density, and molecular motions of large amplitude were allowed at a lower temperature in the lower-density LDG. On the other hand, in the HDG of each compound studied here the denser ones tended to show a higher T_g. Thus, we believe that the close molecular packing in these glasses hinders large-amplitude thermal motions of the molecules. These results stand in contrast to the ordinary concept that T_g of a compound has one specific value. However, the present results are acceptable if we acknowledge that the manner of molecular aggregation in vapor-deposited glass depends on T_d.

One might think that the spontaneous thermal effects accompanying the structural relaxation just below the glass transition could affect the observed T_g. However, the thickness of the film was as thin as about 10 µm. As a result, the temperature difference between the substrate and top surface of the sample was as small as a few degrees Kelvin at most even in the deposition process of the room-temperature vapor of dichloroethane by using the trans–gauche thermal equilibrium.[6] We thus consider that the thermal effect accompanying the structural relaxation, which was estimated to bring about much less enthalpy change than vapor deposition from the magnitude of the accompanying volume change, do not shift T_g appreciably.

In Figure 4, we plotted T_r and T_g of a glass sample of each of the four compounds as a function of T_d. These quantities were normalized with T_g of a sample of the same compound deposited at 78 K. Both T_r and T_g showed obvious maxima at $T_d/T_g(78\,\mathrm{K})$ of around 0.9, indicating again the stability of the dense glass against the thermal motion of the molecules. The difference between T_g and T_r of a compound tends to increase as the alkyl chain becomes longer. This reflects the fact that a compound with a more complex molecular structure undergoes a more complex relaxation process. Note that T_g for the LDG of all compounds converged to a single value as T_d was lowered into the very-low-temperature region. This implies that the glass frozen at very-low temperatures relaxed toward the same valley in the energy landscape after heated beyond T_r.

Light Scattering Observed for SCL States Appearing from LDG of EB, PB, and IPB. Returning to Figure 1, the open square on the fringe of the reflection intensity in each part of the figure indicates the glass-transition point. We confirmed the accuracy of these assignments with the results from the V_m

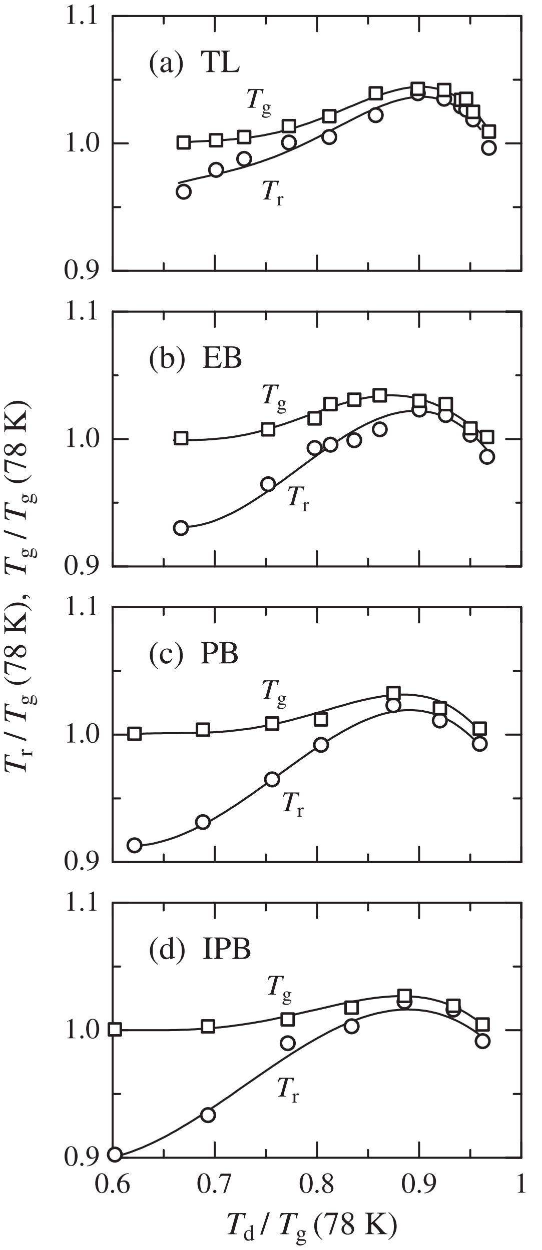

Figure 4. T_d dependence of T_r (open circles) and T_g (open squares) of the four compounds. The abscissa represents T_d normalized with the T_g of each compound observed for the sample deposited at 78 K. The ordinate represents T_r or T_g; both quantities normalized with the T_g of each compound observed for the sample deposited at 78 K.

evolution shown in Figure 2. Thus, the state change of each sample displaying an evolution of light intensity can be separated into glass and SCL regions at the dashed line indicating T_g. On the other hand, as already mentioned in the above section, the SCLs of the four compounds were found to crystallize when the temperature was raised into a certain region characteristic to each compound. This change was confirmed by the appearance of Bragg peaks in the X-ray diffraction patterns[16,17,26] and changes in Raman spectra,[17,26] and was also visually detected by an abrupt increase in laser-light scattering. Thus, the temperature boundary between SCL and crystalline regions was determined for all samples, as shown with another dashed line in each part of Figure 1. The symbols G, L, and C in Figure 1 indicate the glass, SCL, and crystalline states, respectively, of each sample.

Figures 1a–1d show the light-intensity data recorded for the samples that were formed initially as an LDG of each of the four compounds. The samples of EB, PB, and IPB (Figures 1b–1d) showed a temporary strong decrease in the light intensity in the SCL state (see the deep depressions of the fringes of the three compounds indicated with arrows). For these three compounds, a similar depression was observed for almost all samples that were initially prepared as LDG by vapor deposition. Note that LDG of TL showed no such depression (Figure 1a). This will be discussed in the last section.

We found a similar curious depression of reflected-light intensity from a vapor-deposited EB sample years ago,[16] and investigated the cause of this phenomenon.[27] We confirmed that the appearance of the depression was caused by light scattering, and that its behavior depended on the incident wavelength and temperature. Once, we considered on the basis of these observations that the light scattering could have taken place at the surface of the SCL film on the substrate. Surface undulations could appear with temperature elevation, due to the difference in the thermal expansion coefficient between the organic liquid and the metal substrate, thus causing light scattering.[27]

In contrast to the above-mentioned SCL states which appeared from the LDG states of EB, PB, and IPB and caused curious depressions in the reflected-light intensity, the SCL states appearing from the HDG states of these compounds showed no such conspicuous depression, as Figures 1f–1h show.[28] Despite these observations, the final crystallization was found to take place at almost the same temperature characteristic to each compound irrespective of the type of original glass state. This implies that the state of each compound immediately prior to crystallization was the same, irrespective of the appearance of the deep depression, and made us renounce the hypothesis that the sample surface was the cause of the light scattering.

A New Hypothesis on the Cause of the Light Scattering in SCL States. After the recent finding of the HDG states of EB,[15] we have come to believe that the manner of molecular packing must be different between LDG and HDG. Thus, the SCL state appearing from LDG may contain a small amount of locally stable intermolecular conformations and have a lower density. We hereafter call such an SCL a low-density liquid (LDL). On the other hand, the SCL state appearing from HDG may contain a large amount of locally-stable intermolecular conformations and have a higher density. We hereafter call such an SCL a high-density liquid (HDL). Since SCL may have a high viscosity in the temperature region close to T_g, LDL and HDL are not considered to easily undergo mutual structural transformation. If this is the case, and if the SCL states immediately prior to crystallization are the same, irrespective of the appearance of the deep depression of the fringe of light interference, it may be reasonable to consider that a structural transformation of the sample occurred in the temperature region of the deep depression. In other words, LDL and HDL may have coexisted in the temperature region of the depression, and

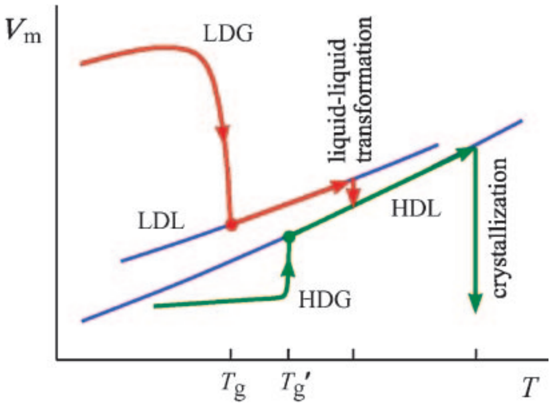

Figure 5. Schematic diagram explaining the hypothesized cause of the curious light scattering observed in the SCL state of EB, PB, and IPB. LDG turns into LDL at T_g, and HDG turns into HDL at T_g'. The light scattering is believed to be observed when LDL relaxes to HDL. See the text for the abbreviations and also for the relation of the two blue curves representing V_m of SCL to the dashed lines in Figures 2 and 3.

the light scattering may have occurred due to the resulting inhomogeneity of the refractive index in the sample.

To visualize the above revised hypothesis, we depict schematically in Figure 5 the temperature dependence of V_m for molecular systems undergoing the glass transition. The new feature of this figure is the two blue solid curves representing V_m of the SCL states. The smaller V_m curve represents HDL and corresponds to the curve obtained by extrapolating the temperature dependence of the room temperature liquid. As we mentioned above, we believe that LDG vapor-deposited at low-temperatures turns into LDL through the glass transition, while HDG deposited at temperatures close to T_g turns into HDL. We also believe that LDL is unstable compared with HDL in the temperature region of the supercooled liquid, and that LDL turns into HDL via a relaxation process when the temperature is raised to a point where the viscosity become small enough to allow the structural transformation. The short vertical arrow in Figure 5 connecting the two SCL curves schematically represents the structural transformation from LDL to HDL. If this hypothesis is correct, we must modify Figures 2 and 3 by separating the dashed line which indicates the temperature dependence of the molar volume of SCL state into two lines. Unfortunately, we have not yet found direct evidence for the liquid–liquid structural transformation in the temperature region of the depression of reflected light intensity, nor obtained the estimation of the difference in molar volume of these two kinds of SCL.

The new hypothesis described so far is closely related to the recent topic of the state transformation between different liquid states.[29–33] We have already obtained X-ray diffraction and Raman scattering evidences in support of our hypothesis: The EB crystals appearing from the SCL states are the same, irrespective of the type of the original glass (LDG or HDG), and these EB crystals include a tight molecular packing different from that of the crystal usually obtained by cooling the room-temperature EB liquid.[26] The latter observation supports the assumption that the source of the crystal was a dense SCL, formed from HDG through the glass transition after relaxation accompanied by an abrupt volume expansion.

Special Behavior of TL among the Alkylbenzenes Studied. As we have mentioned in previous sections, TL shows behavior different from the other three compounds, EB, PB, and IPB, in several ways. It does not form HDG with a good reproducibility. Nor does it exhibit the curious light scattering in the SCL state observed for samples appearing from the LDG of the other three compounds. These characteristics may be related to the fact that the methyl group is the shortest in length of the alkyl groups and seems not to help the formation of the dimer.[26] Thus, the content of locally-stable intermolecular conformations in the vapor-deposited glass of TL may be small and not depend significantly on T_d. This may allow the structure of the SCL states appearing from the LDG of TL to immediately relax to the structure of the equilibrium SCL state expected at each temperature. As a result of this quick relaxation, TL may not show a structural transformation between two SCL states which might otherwise have appeared from the LDG and HDG states, and thus not show the curious light scattering in the SCL state.

Conclusion

To study the cause of a curious light scattering observed for the SCL state of EB samples prepared by vapor deposition on cold metal substrates, we examined the behavior of similarly prepared samples of a series of alkylbenzenes. We found that the vapor-deposited glass of PB and IPB showed the T_d dependence of the initial V_m on deposition, similar to the case of EB, and that the initial V_m could be smaller than the V_m of SCL at the same temperature when T_d was as high as 0.9 times T_g. We called such a HDG in contrast with the LDG prepared by vapor-deposition at a T_d much lower than T_g. We found that many SCL samples appearing from the LDG of PB and IPB showed curious light scattering similar to the case of EB, but the corresponding samples of TL did not show this light scattering. We believe that, in the cases of EB, PB, and IPB, two types of SCL states (LDL and HDL) appeared from LDG and HDG, respectively, above their T_g. In other words, LDL and HDL may have contained different concentrations of locally-stable molecular conformations. In the formation of stable molecular conformations, ethyl or propyl substituents may play an important role. As a result of these considerations, we proposed a hypothesis that LDL appearing from LDG was less stable, and relaxed to the more stable HDL in a certain temperature region. The coexistence of these two SCL states in the sample during the structural transformation may have caused the curious light scattering, which we have been studying for years. However, several issues remain unsolved. What is the mechanism of the formation of HDG? Is there any evidence of the existence of two types of SCL? Is there any direct evidence of the structural transformation between them? What are the dynamics of the structural transformation? We are now trying to find the evidence to support the above hypothesis. Preliminary X-ray and Raman observations of the crystalline state appearing from SCL indirectly help us to understand the nature of the SCL appearing from the HDG of alkylbenzenes. Molecular orbital calculations also seem helpful in elucidating the structure of the locally-stable molecular conformations.

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