Glass transition of associated solvents studied by fluorescence measurement of doped chromophores

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The fluorescence lifetime of a triphenylmethane dye, malachite green, doped in three glass-forming associated solvents, 1-propanol, propylene glycol, and glycerol, was measured in a wide temperature range. For each sample three temperature regimes were found in the temperature dependence of the nonradiative relaxation time of malachite green. The lower crossover temperature corresponds to the calorimetric glass transition temperature, and the higher one, 30–50 K above the lower one, is attributed to the critical temperature that is predicted by mode-coupling theory.

I. INTRODUCTION

Despite the importance and the long history of the study of the glass transition, there are still a lot of open questions to be addressed. In order to clarify the mechanism of the glass transition, much effort has been devoted in recent years to the study of the dynamics of glass-forming systems. One important theoretical consideration is provided by mode-coupling theory (MCT),\textsuperscript{1,2} which predicts a dynamical glass transition from ergodicity to nonergodicity at a critical, or crossover, temperature well above the calorimetric glass transition temperature $T_g$. Stimulated by the progress of theoretical work, experimental studies on the dynamics of monomer and polymer glass formers have been performed intensively. Especially, typical fragile glass formers with rigid molecular structures have been studied by many researchers by means of neutron scattering,\textsuperscript{3–6} light scattering,\textsuperscript{4,6} and viscosity measurements.\textsuperscript{2} Crossover of the temperature dependence of viscosity from the Vogel-Tammann-Fulcher (VTF) law or an Arrhenius behavior at low temperatures to a power law has been reported for several glass formers,\textsuperscript{2} although the crossover is smooth and ambiguity remains in the precise positioning of the critical temperature. The temperature dependence of dynamical spectra of fragile glass formers has been obtained in a wide frequency range, and crossover phenomena at the critical temperature have been found by light scattering and neutron scattering measurements.\textsuperscript{3–6}

On the other hand, studies on the glass transition of associated glass formers such as alcoholic glasses, which can, in general, form glass very easily and are much more important in application, do not seem to be so successful thus far. The results of light scattering of glycerol, for example, deviate from the prediction of MCT, and the critical temperature obtained scatters from 225 to 310 K.\textsuperscript{7–9} The reason for the deviation from the MCT results is attributed to the contribution of intramolecular and intermolecular vibrational modes. It shows that in associated solvents with flexible molecular structure, the crossover phenomena can be masked by highly temperature-dependent motions of many other freedoms that are not relevant to the glass transition in conventional microscopic measurements. However, the basic mechanism of the glass transition of associated solvents is expected to be essentially the same as that for nonassociated molecules, and crossover phenomena above $T_g$ are also expected to exist.\textsuperscript{10}

In the present paper we studied the dynamics of the glass transition of several associated solvents by using a microscopic approach with a molecular probe, and crossover phenomena above $T_g$ were clearly observed.

A triphenylmethane (TPM) dye, malachite green (MG), the molecular probe used in this study, was doped in three associated solvents, 1-propanol (PR), propylene glycol (PG), and glycerol (GL). The excited-state dynamics of TPM dyes is known to be influenced strongly by the microscopic viscosity of the environment.\textsuperscript{11–13} In nonviscous solvents, the nonradiative relaxation process of TPM dyes occurs very rapidly, typically in a few picoseconds. In viscous solvents, on the other hand, the fluorescence lifetime becomes very long. At low temperatures, it is only limited by the radiative lifetime, and the fluorescence yield can be nearly unity. The viscosity-dependent nonradiative process is thought to be due to diffusive rotational motion of the three phenyl rings of the TPM dyes around their axes.\textsuperscript{11} The internal potential for the rotational motion of the phenyl rings of these molecules has been shown to be barrierless and flat.\textsuperscript{11,13} Thus MG molecules can serve as a sensitive probe of the fluctuational motion of the host medium on a microscopic scale, i.e., on the order of several angstroms. Furthermore, the nonradiative relaxation time of MG changes with temperature just in the mesoscopic time range, i.e., $10^{-11}–10^{-8}$ s, which is predicted to be the relevant dynamical window for the observation of the transition from a viscous liquid to a glassy solid by MCT.\textsuperscript{2} Hence observation of crossover phenomena above $T_g$ can be expected in the present study.

II. EXPERIMENTAL DETAILS

The fluorescence lifetime of MG doped in PR, PG, and GL was measured in a wide temperature range from the glassy to the liquid state. The three glass-forming solvents were purified by vacuum distillation. The calorimetric glass
transition temperatures of PR, PG, and GL are reported to be 100, 172, and 193 K, respectively. The concentrations of the three MG solutions were all about $1.3 \times 10^{-5}$ mol/l. Each solution was sealed in a 1-mm glass cell. The sample, mounted in a cryostat, was at first cooled down from room temperature to 10 K at a rate of 2 K/min; then the fluorescence lifetime was measured from the lowest to the highest temperature step by step. The cw mode-locked pulses from a yttrium aluminum garnet (YAG) laser (Coherent, Antares) were frequency doubled and then used to synchronously pump a mode-locked dye laser (Coherent, Satori) at a repetition rate of 76 MHz. The output pulses from the dye laser with a 0.3-ps pulse width at a 642-nm wavelength were attenuated to a few milliwatts and focused on the sample. The emitted fluorescence was wavelength resolved by a spectrometer and the output spectrum was time resolved by a synchroscan streak camera (Hamamatsu Photonics, model M1955). The resolution time of the whole apparatus is about 25 ps. No wavelength dependence of the fluorescence decay was found in our experiment, and then the observing wavelength window was selected to be from 674 to 692 nm. As an example, the fluorescence decay curves of MG in GL taken by this system are shown in Fig. 1(a). In the measurement of the slow decay at low temperatures a different experimental system was employed. A cw argon-ion laser (Spectra-Physics, model 2030) served as a pump source for a synchronously pumped dye laser (Spectra-Physics, model 375B) cavity dumped at a repetition rate of 4 MHz. The output pulses irradiated in the sample kept in the cryostat. The emitted fluorescence was detected with a spectrometer (Chromex, 2501S) attached to a photon-counting streak scope (Hamamatsu, C4334). The fluorescence decay curves of MG in GL taken with this system are shown in Fig. 1(b). The change of the laser power by several times did not give any significant change in the fluorescence lifetime. Therefore we can neglect the effect of heating of the sample by laser pulses.

III. RESULTS AND DISCUSSION

In the temperature range of more than about 30 K above $T_g$ of each sample, the decay curve was found to be biexponential. The decay time constant of the fast component is in the range of 100–600 ps and increases when the temperature is lowered. The amplitude gradually decreases with decreasing temperature. In the low-temperature range, the fluorescence decay curve of MG is expressed well by a single-exponential function. Biexponential relaxation of MG has also been observed in other liquids and in solid polymers. The origin of the fast component in the present experiments is not fully understood yet, and we will not discuss it further in this paper. We will focus on the slow component since it is shown that the nonradiative decay time of the slow component of MG serves as a measure of the mobility of the surrounding solvent matrices.

Figure 2 shows the temperature dependence of the fluorescence lifetime of the slow component $\tau_s$ of MG in PR, PG, and GL. The relative errors of the time constants are estimated to be about 1.5%. The fluorescence lifetime becomes longer with decreasing temperature. Extrapolation of the value of the fluorescence lifetime to 0 K gives the value of the radiative lifetime $\tau_r$, 4.49, 4.42, and 4.20 ns for MG in PR, PG, and GL, respectively. The nonradiative relaxation rate $\tau_{nr}^{-1}$ of MG was obtained by subtracting the radiative relaxation rate from the fluorescence rate. The Arrhenius plots of the nonradiative lifetime are shown in Fig. 3 with the error bars. One may notice that the error bars are enlarged, especially in the low-temperature range where the difference between $\tau_s^{-1}$ and $\tau_r^{-1}$ is small. This is due to the subtraction procedure used to obtain $\tau_{nr}$. In this temperature region, however, scattering of the data is very small. This shows that errors in $\tau_s$ and $\tau_r$ are correlated and the true errors in $\tau_{nr}$...
are much smaller than the error bars shown in the figures. In each curve three temperature regimes are clearly recognized. The lower crossover temperature is located close to the calorimetric glass transition temperature $T_g$, and the higher crossover temperature $T_c$ is about 30–50 K above $T_g$. In the temperature dependence of the macroscopic viscosity of these solvents, no kink above $T_g$ could be observed. Since $T_c$ is just in the temperature range where the critical phenomena is expected to appear by MCT, it is reasonable to attribute it to the critical temperature which is predicted by MCT or experimentally observed in fragile glass formers.

The reason why the crossover phenomenon has been clearly seen in our experiment can be attributed to the special nature of our molecular probe, MG. The nonradiative relaxation time measured in our experiment represents the time required by the phenyl rings of MG to reach the position of a sink to the ground state by the diffusive rotational motion, which is initiated by the laser-pulse excitation to the excited state. The finding that the lifetime changes with temperature appreciably even more than 50 K below $T_g$ shows that the friction to the rotational motion of phenyl rings caused by the surrounding medium is very weak. It has been attributed partly to the propeller structure of the three phenyl rings of MG, which prevents solvent molecules from coming into close contact and partly to the smallness of the rotational angle required for the nonradiative process. Furthermore, concerted motion of the three phenyl rings may require a very small sweep volume. Thus the dynamics of the solvents in the supercooled state can be probed in the mesoscopic time window of $10^{-11} - 10^{-8}$ s and in a length scale of several angstroms. This feature is quite different from most of other molecular probes, and just because of this fact, it is easy to understand that although the dynamics of molecular probes in glass-forming media, associated or nonassociated, have been reported by many researchers, no crossover at $T_c$ is found in most of their results.

In the light scattering experiments the relevant spatial scale is of the order of the wavelength of the excitation light, which is about three orders of magnitude larger than that in our experiment. Moreover, the relevant spatial scale of dielectric measurements is even larger. It implies that the motions of the host media probed in our experiment are not the same as in the light scattering or dielectric experiments. The relevant spatial and temporal scales of our measurement are rather similar to those of the neutron scattering experiments. We think, therefore, that the measurement using MG as a probe might provide another useful approach to the study of the microscopic dynamics of the glass transition.

**FIG. 2.** Fluorescence lifetime of the slow decay component of MG in PR (square), PG (triangle), and GL (circle) is plotted as a function of temperature. The relative errors of the time constants are estimated to be about 1.5%.

**FIG. 3.** Arrhenius plot of the nonradiative relaxation time of MG. The solid line represents the fitting curve obtained with the fitting function, Eq. (1). The positions of $T_c$ and $T_g$ are indicated by arrows. The error bars indicate the fitting errors. The three curves correspond to MG in (a) PR, (b) PG, and (c) GL, respectively.
Along with the experimental data \( \tau_{\text{nr}} \) (open circles) for the MG-GL sample. The positions of \( T_c \) and \( T_g \) are indicated by arrows.

Being limited to the study on the observation of \( T_c \) in associated solvents, we noticed a few reports. The temperature dependence of the Debye-Waller factor in several organic glasses measured by Mössbauer scattering\(^{20}\) has a kink 30–50 K above \( T_g \). The rotational correlation time of chlorine dioxide in 2-methyl-1-propanol and in 1-propanol obtained by electron-spin-resonance (ESR) measurements\(^{21}\) seems to show crossover about 40 K above \( T_g \). These examples, along with the present study, suggest that in associated solvents, the crossover phenomena at \( T_c \) can probably be observed only by a very small probe which is sensitive to the density fluctuation on a small scale and less coupled to the thermally activated hopping process, which plays an important role in determining the properties of the material on a comparably large scale.

In order to argue this point further, we compare the obtained temperature dependence of \( \tau_{\text{nr}} \) with the macroscopic viscosity. In a model system of MG where a particle moves diffusively on a flat excited-state potential and relaxes to the ground state at a point sink, the nonradiative relaxation time \( \tau_{\text{nr}} \) can be related to the microscopic viscosity as

\[
\tau_{\text{nr}} = C \eta/T.
\]

Here \( C \) is a proportionality constant, \( \eta \) is the microscopic viscosity experienced by the relevant particle, and \( T \) is the temperature. In our previous study of the fluorescence decay of MG in polymers, this relation was shown to be valid in a wide temperature range.\(^{12,13}\) The calculated nonradiative relaxation time \( \tau_{\text{cal}}^{\text{nr}} \) using this relation and the macroscopic viscosity of GL (Ref. 15) is shown in Fig. 4, along with the nonradiative relaxation time obtained from the experiment. The proportionality constant is assumed to be \( C = 10^{-8} \text{ K s/P} \). Similar behavior is found also in the MG-PG and MG-PR systems. One can see that the difference between \( \tau_{\text{cal}}^{\text{nr}} \) and \( \tau_{\text{nr}} \) increases with decreasing temperature. Even in the temperature region above \( T_c \), the lifetime calculated from the macroscopic viscosity has a stronger dependence on the temperature than the observed one. It shows that the rotational motion of the phenyl rings of MG molecules is not fully coupled to the macroscopic viscosity of the host media. The separation of the macroscopic motion of the host and the microscopic motion of MG molecules is more enhanced in the lower-temperature regions. This separation, we believe, enables MG molecules to probe fluctuational motions of the hosts in the appropriate spatial and temporal windows for the observation of crossover phenomena at \( T_c \), which is obscured in macroscopic measurements.

The fact that the temperature dependence of \( \tau_{\text{nr}} \) consists of three regimes shows that the dominant dynamical mode of the surrounding solvent molecules which affects the rotational motion of phenyl rings of MG is different in each temperature region. The temperature dependence of the nonradiative relaxation rate was fitted to the summation of three rates \( \tau_L^{-1}, \tau_M^{-1}, \) and \( \tau_H^{-1} \), relevant to the lowest, the middle, and the highest temperature regions, respectively.

\[
\tau_{\text{nr}}^{-1} = \tau_L^{-1} + \tau_M^{-1} + \tau_H^{-1},
\]

with

\[
\tau_L = \tau_L^0 \exp\left[ E_a /k_B T \right],
\]

\[
\tau_M = \tau_M^0 \exp\left[ B/(T - T_0) \right] \quad \text{for } T > T_0,
\]

\[
\tau_H = \tau_H^0 \left[ T_c /((T - T_c)) \right] \gamma \quad \text{for } T > T_c.
\]

The fitting curves are plotted in Fig. 3, and the parameters obtained by the fitting are summarized in Table I. The temperature dependence of \( \tau_{\text{nr}} \) for each solvent shows a small bump around \( T_g \), where deviation from the fitting curve is seen. This is probably due to the annealing effect by keeping the sample around \( T_g \) for a long time, since it took about 10 min to take data at each temperature.

The lowest-temperature region exhibits an Arrhenius dependence. This is consistent with other studies on the molecular mobility in solid polymers,\(^{12,13,17,19}\) where Arrhenius behavior of the microscopic viscosity or of the diffusion constant is reported below the glass transition temperature. In the present study, not the microviscosity, but the nonradiative relaxation time has an Arrhenius temperature dependence. It is not contradictory since the difference between the two is small in a narrow temperature range. Below \( T_g \), the thermally activated hopping stops and the position of molecules are almost frozen in a hydrogen-bonding network. However, a conformation change of hydrocarbon groups of the molecules, which do not participate in the network, may still occur and affect the diffusive rotational motion of phenyl rings of MG. Therefore, below \( T_g \), it is reasonable that the microscopic friction for the rotational motion of phenyl rings has a definite activation energy for each solvent. The activation energy obtained increases in the order of MG-PR, MG-PG, and MG-GL systems, which agrees with the order of the strength of the hydrogen bonding or the stiffness of the network.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( E_a ) (kJ/mol)</th>
<th>( B ) (K)</th>
<th>( T_0 ) (K)</th>
<th>( \gamma )</th>
<th>( T_c ) (K)</th>
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<tr>
<td>1-propanol</td>
<td>1.92</td>
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<td>98.1</td>
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<td>126.6</td>
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<tr>
<td>Propylene glycol</td>
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<td>34.0</td>
<td>177.9</td>
<td>1.89</td>
<td>211.3</td>
</tr>
<tr>
<td>Glycerol</td>
<td>5.23</td>
<td>44.0</td>
<td>198.9</td>
<td>2.28</td>
<td>247.4</td>
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</table>

FIG. 4. Calculated nonradiative relaxation times \( \tau_{\text{cal}}^{\text{nr}} \) (solid circles) by using the macroscopic viscosity (see text) is plotted along with the experimental data \( \tau_{\text{nr}} \) (open circles) for the MG-GL sample. The positions of \( T_c \) and \( T_g \) are indicated by arrows.

The host and the microscopic motion of MG molecules is more enhanced in the lower-temperature regions. This separation, we believe, enables MG molecules to probe fluctuational motions of the hosts in the appropriate spatial and temporal windows for the observation of crossover phenomena at \( T_c \), which is obscured in macroscopic measurements.
In the middle and highest regions, where the Arrhenius plots are curved, we used the VTF form, Eq. (3), and the power law, Eq. (4), respectively, although our data quality is not good enough to determine the specific functional form. The VTF form is a conventionally used form for viscosities above $T_g$. A power law as in Eq. (4) is predicted by MCT above the critical temperature and shown to be valid also experimentally for many glass-forming solvents.

The obtained characteristic temperature $T_0$ of the VTF relation coincides with the literature value of the glass transition temperature $T_g$ within 6 K. The values of $T_g$ are 30–50 K higher than $T_c$. MCT predicts the position of the crossover temperature to be in this temperature region. Values of $T_g$ for PG and GL have been reported by other studies. A scaling study of the dielectric $\alpha$ relaxation by Schönhals et al. reported 251.3 and 248.8 K for PG and GL, respectively. Light scattering studies from two groups reported very different values of the crossover temperature of GL, i.e., $225 \pm 5$ K (Ref. 8) and 310 K. Then one can see that the reported values are very much scattered, while the values obtained in this study for the three solvents are consistent with each other and consistent with each value of $T_g$. The observation of the crossover point is straightforward, and both $T_g$ and $T_c$ are observed simultaneously in the present study.

IV. CONCLUSIONS

In conclusion, the present result suggests that crossover phenomena, as predicted by MCT, actually exist above $T_g$ even in associated solvents and play an important role in the glass transition of them. This study shows that the measurement using MG, or other molecular probes with weak coupling to large-scale fluctuation of the host, may provide a method to investigate the glass transition in the mesoscopic temporal and spatial windows, which is relevant to the essential mechanism of the glass transition.

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