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<p>Photon correlation spectroscopic (PCS) and holographic grating relaxation (HGR) techniques are used to measure the dynamics of density fluctuations in liquid orthoterphenyl, salol and poly(propylene glycol) oligomers in both the normal and supercooled liquid regimes down to their glass transition temperatures. In the PCS study a strongly temperature dependent nonhydrodynamic mode due to structural relaxation is observed in each of the above mentioned glass forming liquid. The shape of the nonhydrodynamic mode is nonexponential and can be fit to a stretch exponential function for each liquid. The nonhydrodynamic mode measured in PCS is shown to be the dynamic longitudinal compliance of the liquid. The tracer diffusion coefficients of camphorquinone in the above glass forming liquids do not obey the Stokes-Einstein equation. The slowness of the structural relaxation of the host liquid and the finite size of the tracer are identified to be the cause for the departure from the Stokes Einstein equation.</p>					
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**Holographic Grating Relaxation and Photon Correlation  
Spectroscopic Studies of Viscoelastic Liquids  
Above the Glass Transition  
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**Introduction**

The viscoelastic properties of polymeric and low molecular weight glass-forming liquids are greatly influenced by the onset of the glass transition process. In addition the dynamics of density fluctuations is closely associated with the viscoelastic response of the liquid and thus it is strongly affected by the glass transition.

The dynamics of density fluctuations of the viscoelastic liquid above the glass transition temperature ( $T_g$ ) can be probed by the techniques of dynamic light scattering. In particular, density fluctuations can be investigated by the photon correlation spectroscopic (PCS) technique in the dynamic range of  $10^{-6}$ - $10^2$ s.

The time correlation function of the density fluctuations  $C(t)$ , above  $T_g$  is characterized by a highly nonexponential shape. This nonexponential shape is associated with the  $\alpha$ -relaxation process in the glass-forming liquid. The  $\alpha$ -process gradually freezes out as the temperature of the liquid is slowly lowered toward  $T_g$  and consequently the time correlation function  $C(t)$  reflects the freezing of the  $\alpha$ -process.

With very few exceptions, the normalized time correlation function  $C(t)$  for one long system can be represented by the Kahlrausch-Williams-Watts (KWW) stretched exponential function

$$C(t) = \exp[-(t/\tau_0)^\beta] \quad (1)$$

where  $\beta$  ( $0 < \beta \leq 1$ ) is the measure of the deviation from the single exponential function. If the nonexponential correlation function is due to the distribution of relaxation times, then a smaller  $\beta$  value indicates of a wider relaxation time distribution. The mean relaxation time  $\bar{\tau}$  is given by the area of  $C(t)$  and is related to the intrinsic relaxation time  $\tau_0$  and  $\beta$ ,

$$\bar{\tau} = \int_0^\infty dt \exp\{-(t/\tau_0)^\beta\} = \frac{\tau_0}{\beta} \Gamma(\beta^{-1}) \quad (2)$$

In recent years, the laser-induced holographic grating relaxation (HGR) technique has also been introduced to investigate the tracer (or self) diffusion process of the photochromous dye molecule in various amorphous polymer hosts, above and below  $T_g$ .<sup>2</sup> The HGR tracer diffusion studies of the photochromous dye molecule in low molecular weight glass-forming liquids have also been carried out.<sup>3</sup> Free volume theory has so far been used to interpret the HGR data. Recent efforts to correlate the tracer diffusion coefficient with the Stokes-Einstein (SE) equation have not been successful.<sup>3</sup>

In this communication, we provide both PCS and HGR data for ortho-terphenyl, a glass forming molecular liquid, and poly (propylene glycol). We show that the tracer diffusion coefficient of the photochromic dye molecule is closely related to the density fluctuation of the glass-forming host liquid. The dynamics of the glass transition can thus be probed by either using the PCS or the HGR technique. As shown here for the first time, the PCS technique provides more detailed information in that it now gives the density-density correlation function, whereas the HGR technique gives only the area of the correlation function.

## Experimental

Orthoterphenyl (OTP) was purchased from Matheson, Coleman and Bell Manufacture Co. The sample was purified by repeated recrystallization. Poly(propylene glycol) (PPG) polymer with molecular weight 4000 was purchased from Merck. Camphorquinone (CQ) and methyl red (MR) photochromic dyes were purchased from Aldrich and purified by recrystallization. The PCS experiments were carried out using similar optical setups as described previously.<sup>4</sup>

For the HGR experiment less than 0.5 wt % of CQ or MR was dissolved directly in the glass forming liquid. The sample was filtered into a thin glass-cell. The sample cell was first put in a cryostat (Oxford Instrument Inc.) through a special holder. The temperature readings of the cryostat was calibrated to within 0.2°K. The experimental setup for the HGR experiment was similar to that used in our previous studies,<sup>2</sup> with the exception of using a third He-Ne laser beam as the probing beam and employing a computer controlled electronic shutter and a chopper. With this modification, the set-up can be used to measure a wide dynamic range covering 10 orders of magnitude of diffusion coefficient from  $10^{-5}$  to  $10^{-15}$  cm<sup>2</sup>/s.

## Results and Discussion

Upon interacting with the Ar<sup>+</sup> laser radiation at 514.5 nm, MR undergoes a trans to cis isomerization. Thus, the relaxation time is associated with the HGR curve is related to the lifetime of the cis isomer  $\tau_L$  and the relaxation time due to diffusion  $\tau_D$  according to

$$\tau^{-1} = \tau_D^{-1} + \tau_L^{-1} \quad (3)$$

where  $\tau_D$  is related to the tracer diffusion coefficient  $D$  according to  $D = \frac{\lambda^2}{16 \pi \tau \sin^2 \theta/2}$ .

Here  $\theta$  is the crossing angle of the coherent writing laser beams and  $\lambda$  is the wavelength of the writing beams. By carrying out the HGR experiment at different crossing angle  $\theta$ , we have separated  $\tau_L$  and  $\tau_D$  from the measured  $\tau$  values. The experiment was repeated at different temperatures. The tracer diffusion coefficient and lifetime of MR in OTP plotted with respect to the reciprocal of the temperature are shown in Figs. 1 and 2, respectively. One notes that by lowering the temperature about 100 K from 357 to 255 K, the tracer diffusion coefficient of methyl red decreases more than 10 order of magnitude from  $5.2 \times 10^{-6}$  to  $9.2 \times 10^{-16}$  cm<sup>2</sup>/s. The variation of the lifetime  $\tau_L$  is not as spectacular; it increases from 2.2 s at room temperature (298 K) to about 60s at 255 K.

While the lifetime variation with temperature for MR in OTP is Arrhenius, with activation energy approximately equal to  $12.87 \pm 0.3$  kcal/mol, the temperature variation of  $D$  is not Arrhenius. Over the temperature range study, the diffusion data can be fit to the Williams-Landel-Ferry (WLF) equation

$$\log D(T) = \log D(T_g) + \frac{C_1^D (T - T_g)}{C_2^D + T - T_g} \quad (4)$$

where  $D(T)$  is the tracer diffusion coefficient at temperature  $T$  (in K). The value of  $D$  at  $T_g$  is the extrapolated value, which is equal to  $7 \times 10^{-18}$  cm<sup>2</sup>/s. The WLF coefficient  $C_1^D$  and  $C_2^D$  are equal to 24.2 and 54.3 K, respectively.

The tracer diffusion data for CQ in PPG are given in Table 1 for the temperature varying from 286.0 to 233.2 K. The temperature dependence of  $D$  is not Arrhenius. The WLF equation fit to the diffusion data give  $C_1^D = 13.5$  and  $C_2^D = 35$  K. However, the value of  $C_1^D$  strongly correlates with the extrapolated value of the tracer diffusion

coefficient at  $T_g$ , which can not be measured.

The WLF equation is derived from free volume theory by assuming that  $D$  (neglecting the linear temperature factor) is given by<sup>5</sup>

$$D = D_{\infty} \exp(-B_D/f) \quad (5)$$

where  $f$  is the fractional free volume and  $B_D$  is a temperature independent parameter.  $D_{\infty}$  is the diffusion coefficient at high temperature when fractional free volume is large. Similarly, the shear viscosity  $\eta$  is expressed in terms free volume theory by<sup>6</sup>

$$\eta = \eta_{\infty} \exp(B/f) \quad (6)$$

where  $\eta_{\infty}$  is the viscosity at high temperature. The temperature independent constant  $\beta$  is in general larger than  $B_0$ . The difference is argued as due to the fact that rearrangement of the liquid structure is needed to provide enough free volume for the diffusant to jump into the available space.<sup>6</sup>

It follows from Eqs. (5) and (6) that

$$D\eta^{\gamma} = \text{constant} \quad (7)$$

where  $\gamma = B_D/B$  is in general less than 1. If  $\gamma = 1$ , then  $D$  follows the temperature dependence of  $\eta$ . For systems with  $D$  following the Stokes Einstein (SE) equation, one has  $\gamma = 1$ . For systems in which the viscoelastic effect prevails  $\gamma$  will in general be less than 1.

Using the viscosity data provided in ref. 1, we have found that  $\gamma = 0.75$  for the tracer diffusion data for CQ in PPG. For MR in OTP, we find by using the viscosity data of Laughlin et al.<sup>8</sup> that  $\gamma = 0.80$  for temperature below 260 K. Above 300 K, we obtain  $\gamma = 1$ . The crossover from  $\gamma = 0.80$  to  $\gamma = 1$  occurs in the vicinity of 273 K. The  $\gamma = 0.80$  value for MR in OTP compares quite well with the result of  $\gamma = 0.79$  for the Aberchrome 540 (ACR) dye in OTP investigated by Lohfink et al.<sup>3</sup>

The tracer diffusion coefficient  $D$  is related to the friction coefficient  $\zeta$  due to the solvent molecules by

$$D = \frac{kT}{\zeta} \quad \text{and the surrounding} \quad (8)$$

If the intermolecular interaction potential between the tracer

solvent molecules is given by  $\sum_j u(|\underline{r} - \underline{r}_j|)$ , where  $\underline{r}$  and  $\underline{r}_j$  are the position of the tracer and

solvent molecule  $j$ , respectively. By taking the Fourier transform of the intermolecular potential and neglecting the interaction between tracer molecules (valid in very dilute tracer concentration), one can show that the tracer diffusion coefficient  $D$  is related to the time correlation function of the density fluctuation  $C(t)$  by<sup>9</sup>

$$D = kT / \left[ |F_q|^2 \int_0^{\infty} dt C(t) \right] \quad (9)$$

when  $F_q$  is the intermolecular force averaged over the distance of  $q^{-1}$ ,  $q$  is the amplitude of the scattering vector. For dense fluids,  $F_q$  is expected to be independent of  $q$  as the averaged inter-molecular force should be uniform. The time integral over the correlation function  $C(t)$  is the mean relaxation time  $\bar{\tau}$ , given in Eq. (2). Thus, Eq. (9) indicates that  $D$  is proportional to  $T/\bar{\tau}$ . This prediction is clearly born out in the CQ in PPG as shown in Table I. Other glass forming liquids also yield similar results. The mean relaxation times  $\bar{\tau}$  for OTP and PPG were obtained from PCS experiments.

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**Table I**

$\bar{\tau}$  tracer diffusion data of CQ in PPG (MW = 4000) at various temperatures.

T(K)	$\bar{\tau}$ (s)	D (cm <sup>2</sup> /s)	$\bar{\tau}$ D (cm <sup>2</sup> )
286.0	---	2.3 x 10 <sup>-9</sup>	---
273.5	---	9.1 x 10 <sup>-10</sup>	---
259.6	---	2.9 x 10 <sup>-10</sup>	---
248.7	---	8.9 x 10 <sup>-11</sup>	---
240.3	---	2.4 x 10 <sup>-11</sup>	---
233.2	---	7.0 x 10 <sup>-12</sup>	---
225.1	9.5 x 10 <sup>-5</sup>	5.3 x 10 <sup>-12</sup>	5.0 x 10 <sup>-16</sup>
220.0	1.0 x 10 <sup>-3</sup>	6.0 x 10 <sup>-13</sup>	6.0 x 10 <sup>-16</sup>
215.4	6.0 x 10 <sup>-3</sup>	1.1 x 10 <sup>-13</sup>	6.6 x 10 <sup>-16</sup>
210.2	1.5 x 10 <sup>-1</sup>	4.0 x 10 <sup>-15</sup>	6.0 x 10 <sup>-16</sup>

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Figure 1: Temperature dependence of the tracer diffusion coefficient of MR in OTR.

Figure 2: Temperature dependence of the lifetime of MR in OTR.