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Light-Scattering Studies of Short- and Long-Range Density and Anisotropy Fluctuations in a Bulk Polysiloxane

T. Kanaya,[†] A. Patkowski,*,[‡] E. W. Fischer, J. Seils, H. Gläser, and K. Kaji[†]

Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128, Mainz, FRG

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ABSTRACT: The effect of long-range density fluctuations on the primary (α-) relaxation in poly(methyl-*p*-tolylsiloxane) (PMpTS) was studied by means of light scattering. It is shown that the long-range density fluctuations (clusters) contribute only to the polarized (VV) and not to the depolarized (VH) correlation functions and make the system apparently nonergodic in the time scale of the α-process. Samples with different amounts of clusters were obtained by annealing at 55 °C for different time intervals in temperature jump experiments: +120 → +55 → −2.6 °C. The mean relaxation times and their distribution of the α-process obtained from the VH correlation functions (sample with clusters) and both VV and VH correlation functions (cluster-free sample) were equal and did not depend on the amount of clusters, indicating no coupling between the long-range density fluctuations and the primary α-relaxation.

Introduction

In this work, we have studied the effects of the long-range density fluctuations on the primary α-process of poly(methyl-*p*-tolylsiloxane) (PMpTS) near the glass transition temperature ($T_g = -17$ °C). For this purpose, we have prepared PMpTS with various degrees of clusters.

The primary α-relaxation process is directly connected to the glass transition in low molecular weight glass-forming materials, as well as amorphous polymers, and is dominated by cooperative motions of glass-forming molecules or segments in amorphous polymers near the glass transition temperature T_g. This process is characterized by a wide distribution of relaxation times, and the mean relaxation time τ increases rapidly with approaching T_g to diverge at a critical temperature T_0, the so-called Vogel−Fulcher temperature, which is usually about 50 K below T_g. The non-Arrhenius temperature dependence is well described by the Vogel−Fulcher equation. The dynamical properties of the α-process have been extensively studied by many techniques such as mechanical relaxation,[1] dielectric relaxation,[2−4] dynamic light scattering,[2,3,5] and quasielastic neutron scattering.[6−9] Motions probed by each technique are in principle different although excellent agreements between mechanical and dielectric relaxations of poly(vinylethylene),[10] between dielectric relaxation and photon correlation spectroscopy of poly(methylphenylsiloxane),[2] and among dielectric, mechanical, nuclear magnetic resonance, and neutron scattering of poly(vinyl methyl ether)[8] have been reported near T_g. Dramatic slowing down of the α-relaxation on approaching T_g is explained in some theoretical models by the increasing cooperativity of the process.[11,12] This cooperativity is characterized by the correlation length of cooperatively rearranging domains (CRD) (or regions, CRR) which constitute the smallest domain in which the α-relaxation process can take place. So far there is no direct experimental evidence for the existence of these CRD's. The fluctuation theory by Donth[13] predicts that the characteristic length of the cooperative domain ξ_α increases with decreasing temperature according to $\xi_\alpha \sim (T - T_0)^{-\nu}$ ($\nu = {}^2/_3$ for 3-dimensional system) and that ξ_α is about 10−20 Å near T_g. Fischer et al.[14] have confirmed this relation for *o*-terphenyl on the basis of the results of depolarized dynamic light-scattering and viscosity experiments.

In addition to the α-relaxation both low molecular weight and polymeric glass-forming liquids exhibit unusual features in a light-scattering experiment: (i) excess isotropic Rayleigh intensity, which is q dependent, (ii) an additional ultraslow component in the polarized photon correlation function, and (iii) a high Landau−Placzek ratio, though no theoretical predictions have been reported. These unusual features can be explained by long-range density fluctuations, so-called clusters. The correlation length of the long-range density fluctuations at quasi-equilibrium increases with decreasing temperature and is typically several hundred to several thousand angstroms, which is about 2 orders of magnitude larger than the characteristic length of the cooperative domains.

Although both the primary α-process and the long-range density fluctuations are typical features of glass-forming materials, the relation between them has not yet been investigated so far.

Experimental Section

Materials. The light-scattering experiments were performed on poly(methyl-*p*-tolylsiloxane) (PMpTS) of molecular weight $M_w = 1.5 \times 10^4$, which is below the entanglement molecular weight for this system. The molecular weight distribution M_w/M_n measured by GPC amounted to 1.09. The procedures of synthesis and purification of PMpTS are described elsewhere.[21] The glass transition temperature determined by DSC measurement is −17 °C. The refractive index of PMpTS at $\lambda = 647$ nm (n) is 1.5473 at 20 °C and its temperature dependence is well described by $n = 1.5551 - 0.00039298T$. The light-scattering sample was prepared by filtering PMpTS directly through a 0.22 μm Millipore filter in a dust-free cylindrical Pyrex cell with an inner diameter of 10 mm. The whole filtering apparatus was kept at 120 °C during the filtration.

Light-Scattering Measurements. The static light scattering (SLS), i.e., the measurements of the angular dependence of the polarized and depolarized scattering intensities, was performed using experimental systems described previously.[17,19,22] The incident beam from a krypton-ion laser (λ = 647 nm) was polarized vertically to the scattering plane.

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* To whom correspondence should be addressed.

[†] Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu 611, Japan.

[‡] Also at the Institute of Physics, A. Mickiewicz University, Poznan, Poland.

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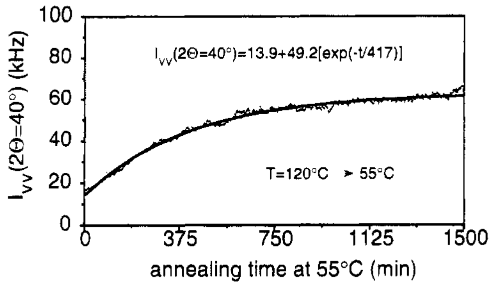

Figure 1. Time evolution of the polarized (VV) scattering intensity of PMpTS measured at a scattering angle of $2\theta = 40°$ after a temperature jump from 120 to 55 °C. The solid line is a fitting curve: $I(2\theta = 90°) = 13.9 + 49.2\,[1 - \exp(-t/417)]$.

Vertical (polarized, VV) and horizontal (depolarized, VH) components of the scattered light were measured at scattering angles 2θ from 25 to 140°. The corresponding scattering vector length $q = (4\pi n/\lambda) \sin \theta$ amounted to 0.0063–0.027 nm^{-1}. In order to diminish the effects of the nonergodicity of the sample, the sample cell was rotated at frequencies from 0.5 to 5.5 rpm. The cell housing was made of glass-ceramics (Macor) and contained a double glass cylindrical window. The space between the glass cylinders was evacuated in order to increase the thermal insulation of the interior of the cell. The intensity of scattered light was measured using a photon-counting system. The absolute Rayleigh ratio was calculated using toluene as a standard, with $R_{\text{tol}} = 9.6 \times 10^{-6}$ cm^{-1} at $\lambda = 647$ nm, $T = 20$ °C.

The dynamic light-scattering measurements, i.e., photon correlation spectroscopy (PCS) measurements, were performed using the same optical setup as for the SLS. The correlation functions for vertical polarized and horizontal depolarized components of the scattered light were measured using a digital correlator (ALV-5000, Langen, FRG).

Results and Discussion

Preparation and Characterization of PMpTS with and without Clusters. In the previous paper[20] we found a temperature of about 90 °C, above which no more clusters are formed, as indicated by the q dependence of the static intensity. The cluster growth kinetics can be characterized by the equilibration time τ_{eq}, which has been determined by monitoring the polarized (VV) scattered intensity after a temperature jump from 120 °C to a given temperature below 90 °C. Figure 1 shows a time evolution of the VV scattered intensity at a 40° scattering angle after a temperature jump from 120 to 55 °C. The time evolution is well described by

$$I(q,t) = I_{\text{int}}(q) + \Delta I[1 - \exp(-t/\tau_{\text{eq}})] \qquad (1)$$

where $I_{\text{int}}(q)$ and ΔI are initial intensity just after quenching and intensity increment after equilibration. The determined equilibration time of the clusters τ_{eq} is very long, e.g., 35 h at 30 °C. In order to prepare the so-called "cluster-free" PMpTS samples, we therefore quenched the sample from 120 to −2.6 °C after keeping it for more than 2 h at 120 °C. The cluster growth rate at −2.6 °C is very slow, probably more than 20 days, so that it would be impossible to detect cluster growth within the experiments. In Figure 2a the curve denoted "0 h" was measured for such a cluster-free state and shows no q dependence. In addition to PMpTS without clusters, PMpTS with various degrees of clusters was also prepared by two-step quenching. We first kept PMpTS at 120 °C for 2 h, and then quenched to 55 °C to keep for a given annealing time: 1, 2, 3, 5, and 18 h in this work. During this period, clusters were formed according to eq 1 and then frozen by quenching to −2.6 °C. The long-range density fluctuations were controlled in this way and characterized by (i) static light scattering, i.e., q dependent scattered intensity, and (ii) time dependent fluctuation of the scattered intensity.

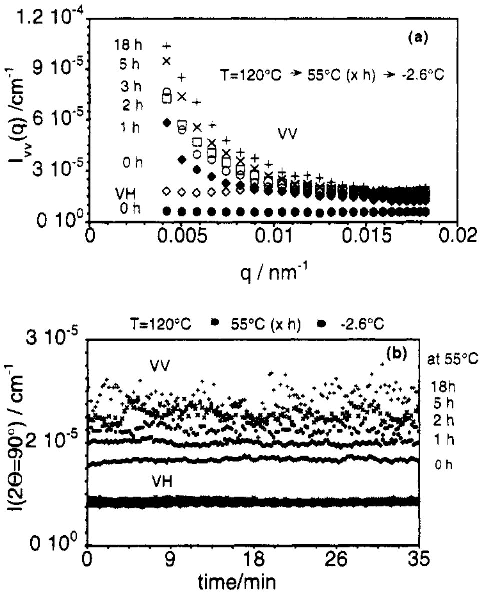

Figure 2. (a) Polarized (VV) scattering intensity $I_{\text{VV}}(q)$ of PMpTS: (◇) 0 h, (◆) 1 h, (○) 2 h, (□) 3 h, (×) 5 h, (+) 18 h, and (●) VH. (b) Time dependent fluctuations of $I_{\text{VV}}(q)$ and $I_{\text{VH}}(q)$ at scattering angle $2\theta = 90°$ for various annealing times at 55 °C. The measurements were made after the second quench to −2.6 °C.

Figure 2a shows the q dependence of the polarized (VV) scattered intensity $I_{\text{VV}}(q)$ as a function of annealing time (as indicated in the figure) at 55 °C. The scattered intensity increases with annealing time in the low q range and the correlation length ξ_{OZ} evaluated from the isotropic scattered intensity $I_{\text{iso}}(q)$ $[=I_{\text{VV}}(q) - (4/3)I_{\text{VH}}(q)]$ using the Ornstein–Zernike formula:

$$I_{\text{iso}}(q) = \frac{I_{\text{iso}}(0)}{1 + \xi_{\text{OZ}}^{2} q^{2}} \qquad (2)$$

also increases, indicating growth of clusters. On the other hand, such excess intensity at low q is not observed in the depolarized (VH) scattered intensity $I_{\text{VH}}(q)$ (Figure 2a). The lack of the excess $I_{\text{VH}}(q)$ is commonly observed in both low molecular weight and polymeric glass-forming materials.[15–20] Note that no changes were observed in these spectra after photon correlation measurements below 5 °C, suggesting no growth of clusters.

Figure 2b shows time dependent fluctuations of the scattered intensities at −2.6 °C for the polarized (VV) and depolarized (VH) components, showing that these fluctuations are not frozen at −2.6 °C. It is clear that the intensity fluctuation of the VV component becomes larger with annealing time, indicating that the inhomogeneity of the system becomes larger with annealing time. On the other hand, the fluctuation of the VH component is independent of annealing time at 55 °C. The increase of the excess intensity corresponds to growth of clusters in this system. It is noted that the sample annealed at 55 °C for 18 h is almost in a quasi-equilibrium state; i.e., no cluster growth is observed for longer annealing times.

$g^{(2)}(t)$ of PMpTS and Apparent Nonergodicity. The depolarized (VH) and polarized (VV) intensity correlation functions $g^{(2)}(t)$ for the α-process measured

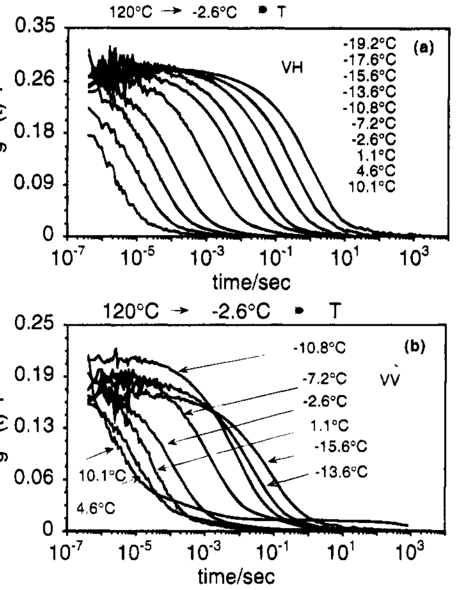

Figure 3. (a) Depolarized (VH) scattering intensity correlation functions $g^{(2)}(t)$ and (b) polarized (VV) ones of cluster-free PMpTS as a function of temperature. The correlation functions were measured at a scattering angle 2θ of 90°.

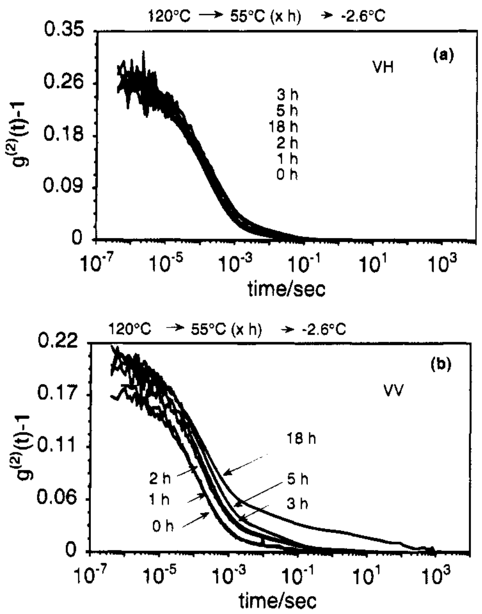

Figure 4. (a) Depolarized (VH) scattering intensity correlation functions $g^{(2)}(t)$ and (b) polarized (VV) ones of PMpTS with clusters as a function of annealing time at 55 °C. The measurements were made at a temperature −2.6 °C and at scattering angle $2\theta = 90°$.

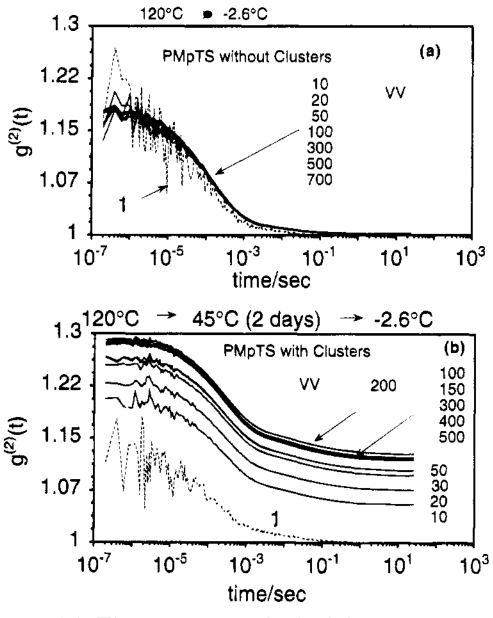

Figure 5. (a) Time-average (dashed line) and ensemble-average (solid line) $g^{(2)}(t)$'s of the polarized (VV) scattering intensity from PMpTS without clusters. The accumulation time of the time-average $g^{(2)}(t)$ is 100 s. The numbers in the figure correspond to numbers of ensembles averaged. The measurements were made at a temperature −2.6 °C and a scattering angle of $2\theta = 90°$. (b) The same as (a) for PMpTS with clusters. The sample was prepared by annealing at 45 °C for 2 days.

at a scattering angle of $2\theta = 90°$ are shown in Figure 3a,b for the "cluster-free" PMpTS at various temperatures near T_g. In cluster-free PMpTS the ultraslow process due to the clusters does not exist so that the α-process is the slowest one. The correlation functions $g^{(2)}(t)$ decay to the base line (=1) in this temperature range, except for that of the VV component at 10.1 °C, suggesting that the ultraslow process appears out of the time window of the correlator during the measurement of $g^{(2)}(t)$ at 10.1 °C. In fact we found that the VV static component shows excess scattered intensity after the correlation function measurement, confirming that the cluster's growth is not negligible above ca. 10 °C. The data above 10 °C may include effects of the clusters while $g^{(2)}(t)$ of the VH component is apparently not affected by the clusters because the ultraslow process is not detectable in the VH components.

The VH and VV intensity correlation functions $g^{(2)}(t)$ measured at $T = -2.6$ °C and $2\theta = 90°$ are shown in Figure 4a,b, respectively, for PMpTS with various degrees of clusters, i.e., as a function of the annealing time at 55 °C. $g^{(2)}(t)$ of the VV component strongly depends on the annealing time, while $g^{(2)}(t)$ for the VH component is almost independent of the annealing time. As shown before, the polarized intensity is increasing with annealing time at 55 °C (Figure 1) and the ultraslow process appears in $g^{(2)}(t)$ of the VV component, though it does not relax completely in the time window of our correlator. This leads to an apparent nonergodicity of the system[23] within this time range.

In order to confirm the apparent nonergodicity of the system, we have measured both ensemble-average and time-average $g^{(2)}(t)$ for the VV scattered intensity of PMpTS with and without clusters. PMpTS with clusters annealed at 45 °C for 2 days was used for the measurements. The results are shown in Figure 5a,b for PMpTS with and without clusters, respectively. The dashed line in Figure 5a is the time-average $g^{(2)}(t)$ for PMpTS without clusters, which decays to the base line (=1). The data points are scattered due to the short accumulation time (100 s), so that quantitative analysis was not made. The ensemble-average $g^{(2)}(t)$'s are also shown in Figure 5a. It is very clear that the ensemble-average $g^{(2)}(t)$ is identical with the time-average one for PMpTS without clusters, confirming that the system is ergodic. On the other hand, in the case of PMpTS with clusters, nondecaying components are not observed in the time-average $g^{(2)}(t)$, while the ensemble-average $g^{(2)}(t)$ shows a nondecaying plateau, which may arise from the ultraslow process. This is a typical behavior of nonergodic systems,[23] confirming that PMpTS with clusters is a nonergodic system in the time scale of the experiment. However, it has been shown for other glass-forming liquids with long-range density fluctua-

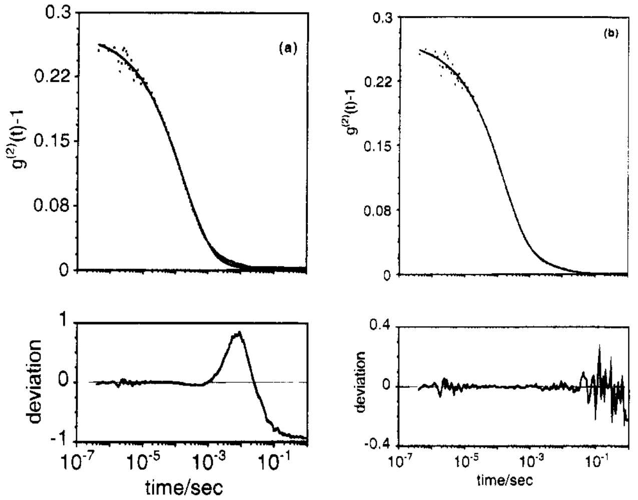

Figure 6. Results of fits to the depolarized (VH) intensity correlation function $g^{(2)}(t)$ of PMpTS without clusters at −2.6 °C using single (a) and double (b) KWW functions, respectively (eqs 4 and 7).

tions that the KWW parameters of the α-relaxation obtained from the time-averaged VH-correlation functions and the ensemble-averaged VV-correlation function are practically identical.[24]

Analysis of $g^{(2)}(t)$. The intensity correlation function $g^{(2)}(t)$ is related to the correlation function of the scattered electric field $g^{(1)}(t)$ through the Siegert relation:

$$g^{(2)}(q,t) = A(1 + c|g^{(1)}(q,t)|^2) \tag{3}$$

where c is the coherence factor. In eq 3, $g^{(2)}(t)$ is the ensemble-average correlation function which for ergodic systems can be replaced by the time-average correlation function.

Due to the appearance of the ultraslow mode, which close to T_g does not relax within the time window of the correlator, the VV correlation functions for glass-forming liquids with long-range density fluctuations should be analyzed using the procedures established for nonergodic media.[23] As mentioned above, it is possible to use directly the time-averaged VH correlation function of samples with clusters to obtain the Kohlrausch–Williams–Watts (KWW) parameters of the α-process.

For the analysis of $g^{(2)}(t)$, we first employed the KWW function (eq 4) for $g^{(1)}(q,t)$, which has been widely accepted for the analysis of density and optical anisotropy fluctuations of glass-forming materials.

$$g^{(1)}(q,t) = A \exp\left[-\left(\frac{t}{\tau_{\mathrm{KWW}}}\right)^{\beta_{\mathrm{KWW}}}\right] \tag{4}$$

Here, the exponent β_{KWW} ($0 < \beta_{\mathrm{KWW}} \leq 1$) is a measure of the width of the relaxation time τ_{KWW} distribution and the mean relaxation time $\langle\tau_{\mathrm{KWW}}\rangle$ is given by

$$\langle\tau_{\mathrm{KWW}}\rangle = \frac{\tau_{\mathrm{KWW}}}{\beta_{\mathrm{KWW}}}\Gamma\left(\frac{1}{\beta_{\mathrm{KWW}}}\right) \tag{5}$$

where Γ is the gamma function. An example of the results of the fits is shown in Figure 6a. The agreement between the observed and calculated correlation functions is not very good, and the deviation is evident especially in the long time region, suggesting that there exists an additional process slower than the α-process and faster than the ultraslow process.

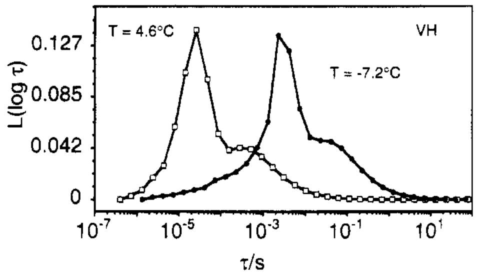

Figure 7. Results of the inverse Laplace transformation on the depolarized (VH) correlation functions of PMpTS without clusters at −7.2 °C (●) and 4.6 °C (□).

The distribution of the relaxation times $L(\ln \tau)$ can be obtained using CONTIN.[25] In this procedure the experimental $g^{(1)}(t)$ can be described by the Laplace transformation of a distribution of relaxation times $L(\ln \tau)$.

$$g^{(1)}(t) = \int \exp(-t/\tau)\, L(\ln \tau)\, \mathrm{d} \ln \tau \tag{6}$$

Typical examples of the CONTIN fit are shown in Figure 7, clearly showing a bimodal distribution of the relaxation times. Because one of the modes corresponds to the α-process, which is usually described using the KWW correlation function, we have used a double KWW function to describe both processes

$$g^{(1)}(q,t) = A_1 \exp\left[-\left(\frac{t}{\tau_1}\right)^{\beta_1}\right] + A_2 \exp\left[-\left(\frac{t}{\tau_2}\right)^{\beta_2}\right] \tag{7}$$

in order to be able to compare the parameters of the α-process. As seen in Figure 6b, the agreement is very good and the mean relaxation times obtained from the double KWW and CONTIN fits are in good agreement.

The slower process, termed the α′-process, has been observed in other polymers by means of dielectric relaxation[26,27] and dynamic light scattering.[2] In the case of poly(methylphenylsiloxane) (PMPS),[2] which has a structure similar to that of PMpTS, the α′-process has been assigned to the normal mode because its mean relaxation time ⟨τ⟩ is proportional to molecular weight squared M^2, as predicted by the Rouse theory.[28] However, this problem is beyond the aim of this paper. We will not discuss the origin of the α′-process here, but we will merely present the experimental results to show the effects of the clusters on the α′-process.

α-Process of PMpTS without Clusters. An activation plot of the inverse of the relaxation times $1/\tau_{\mathrm{KWW}}$ for the α- and α′-processes of cluster-free PMpTS is shown in Figure 8a, where both the relaxation times evaluated from the polarized (VV) and depolarized (VH) components are included. τ_{KWW} obtained from the VV component are rather scattered, especially for the α′-process, because a small amount of clusters formed during the quenching process makes the system slightly nonergodic. Values of τ_{KWW} obtained from the VV components are, however, essentially the same as those from the VH components within experimental error for both the α-process and the α′-process. The same results have been reported in some glass-forming materials.[2,29,30] The VH component is governed by orientational motions while the VV component is dominated by both orientation and density fluctuations. The fact that relaxation times τ_{KWW} evaluated from the VV and VH components are identical suggests that both the motions are strongly coupled in this system near T_g probably because of the strong cooperativity.

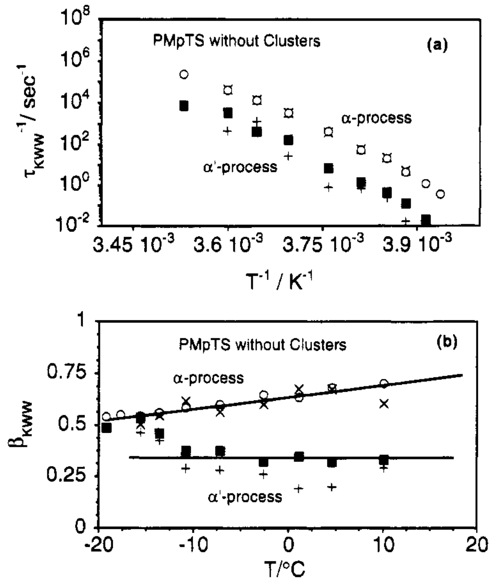

Figure 8. Temperature dependencies of KWW parameters (a) $1/\tau_{\mathrm{KWW}}$ and (b) β_{KWW} for the α- and α'-processes of PMpTS without clusters: (○, ■) estimated from $g^{(2)}(t)$ of the depolarized (VH) component; (×, +) estimated from $g^{(2)}(t)$ of the polarized (VV) component.

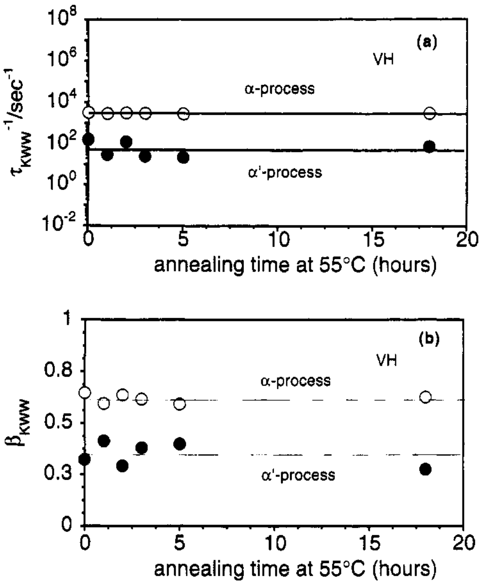

Figure 9. Annealing-time dependencies of KWW parameters (a) $1/\tau_{\mathrm{KWW}}$ and (b) β_{KWW} for the α- and α'-processes. Annealing temperature is 55 °C. The parameters were estimated from $g^{(2)}(t)$ of the depolarized (VH) component.

The exponent β_{KWW} for cluster-free PMpTS was also evaluated from the VV and VH components and plotted against T in Figure 8b, showing that both β_{KWW}'s are the same within the experimental error. The value of β_{KWW} of the α-process is 0.55 at T_g (=−17 °C) and increases with temperature to be 0.7 at 10.1 °C, indicating that distribution of the relaxation time becomes wider upon cooling. The temperature dependence of β_{KWW} also means that the temperature−time (or temperature−frequency) superposition of $g^{(2)}(t)$ is not fulfilled for the α-process. On the other hand, β_{KWW} of the α'-process is almost independent of temperature while it seems to increase near T_g.

The dependence of the KWW parameters τ_{KWW} and β_{KWW} on q was also examined by measuring $g^{(2)}(t)$ as a function of scattering angle from 30 to 120 °C to find that both τ_{KWW} and β_{KWW} are independent of scattering angle or q. The same results have been always observed for density fluctuations of glass-forming materials.[2,29,30]

Effects of Clusters on the α-Process. As shown above, PMpTS with clusters exhibits an ultraslow mode which, close to T_g does not relax within the time window of the experiment and makes the system apparently nonergodic. We therefore analyzed only the VH intensity autocorrelation functions which do not contain any contribution of this ultraslow mode. In order to study possible effects of the long-range density fluctuations on the α-relaxation we analyzed these VH correlation functions as a function of the annealing time at 55 °C.

The KWW parameters $1/\tau_{\mathrm{KWW}}$ and β_{KWW} are plotted against the annealing time at 55 °C in Figure 9a,b, respectively, showing that they both are independent of the annealing time for the α-process and the α'-process though the data points are rather scattered due to the contamination of the VV component. It is directly concluded from this figure that the α- and α'-processes of PMpTS observed in the depolarized (VH) component (the orientational motions) are not affected by the clusters or the long-range density fluctuations, at least in the examined temperature range, within experimental error. As shown for PMpTS without clusters, the orientational motions are strongly coupled to the density fluctuations near T_g. In principle the long-range density fluctuations could couple to the short-range density fluctuations (α-process). In this case the correlation functions measured in the time range of the α-process for the samples with and without clusters would be different. Since in our experiments we do not see such a difference, we can conclude that the effect of long-range density fluctuations on the α-process is negligible.

In order to see the possible relations between the clusters and the α-process we briefly discuss the spatial scales of both processes. As shown in the previous paper,[20] the correlation length of the clusters is of the order of several hundred angstroms. The temperature dependence of the characteristic length ξ_α of the α-process (the cooperative region), has been predicted by the fluctuation theory[11,13] as

$$\xi_\alpha = A_\alpha (T - T_0)^{-\nu} \tag{8}$$

where $\nu = 2/d$ ($= {}^2/_3$ in $d = 3$ dimensions) and T_0 is the Vogel temperature. This relation has been confirmed by Fischer et al.[14] using the results of depolarized dynamic light-scattering and viscoelastic experiments on *o*-terphenyl. On the basis of the theory, the values of ξ_α at T_g have been estimated from the calorimetric data to be 7−22 Å for various kinds of glass-forming materials.[12] We do not know the characteristic length ξ_α of PMpTS, but we expect that it is not very different from those of other glass-forming materials.

The temperature dependence of the α- and α'-processes can be described by the Vogel−Fulcher−Tammann (VFT) equation:

$$\log \tau = \log \tau_0 + \frac{B}{T - T_0} \tag{9}$$

The parameters B and T_0 within the limited temperature range are the same for the α- and α'-processes and amount to B = 680 K and T_0 = 214 K.

The correlation length ξ_c of the clusters[20] is at least 1 order of magnitude larger than the characteristic length ξ_α of the α-process in the examined temperature

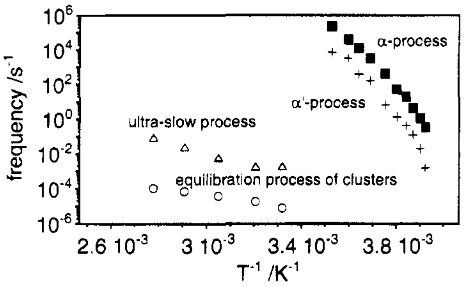

Figure 10. Temperature dependencies of the mean relaxation time $\langle \tau_{KWW} \rangle$ (eq 5 in text) of the α- (■) and α'-processes (+) of PMpTS without clusters. The relaxation time of the ultraslow process (△) measured at a scattering angle of 40° and the equilibration time of the clusters[20] (○) are also included for comparison.

range. Furthermore, the relaxation time of the ultraslow process is much longer than that of the α-process, e.g., about 10 decades at 30 °C, as shown in Figure 10, where relaxation times of all processes are included for comparison.

Conclusions

In this work, we have prepared PMpTS with and without clusters or long-range density fluctuations. PMpTS with clusters shows a typical nonergodic behavior in the polarized intensity correlation function $g^{(2)}(t)$. The analysis in terms of the double KWW function elucidated that the α'-process slower than the α-process exists in PMpTS. The α-processes observed in the polarized (VV) and depolarized (VH) intensity correlation functions $g^{(2)}(t)$ are identical, indicating that the orientational motions are strongly coupled to the density fluctuations near T_g. It was also found that the α-process observed in the depolarized (VH) intensity correlation function is not affected by the clusters, at least in the examined temperature range. However, detailed analysis of $g^{(2)}(t)$ of the polarized (VV) intensity is a further problem.

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