Dynamical heterogeneity in glassy *n*-butanol

S. Yu. Grebenkin and V. M. Syutkin*

Institute of Chemical Kinetics and Combustion, Novosibirsk 630090, Russia

(Received 16 January 2007; revised manuscript received 24 May 2007; published 6 August 2007)

The light-induced *cis-trans* isomerization of azo dye molecules (1-naphthyl-*p*-azomethoxybenzene) is used as a probe process for dynamical heterogeneity in glassy *n*-butanol (T_g=114 K). The characteristic lifetime of heterogeneity is found to vary with temperature according to the Arrhenius law from 3×10^4 s at 100 K to 4×10^3 s at 110 K with the activation energy of 17 ± 5 kJ/mole.

PACS number(s): 61.43.Fs

I. INTRODUCTION

At present it is known that the dynamics of molecules in supercooled molecular liquids becomes spatially heterogeneous as the glass transition temperature, T_g, is approached from above (for a detailed discussion of this subject, see Refs. [1–3]). Thus, for example, the rotation rate of molecules in some regions of the sample can be an order of magnitude higher than in other regions. A characteristic size of these regions is roughly estimated at 2 to 3 nm.[4,5] The dynamical properties of the regions fluctuate with time. As a result, a slow molecule after a time becomes a fast one and vice versa. This process is often spoken of as the exchange of dynamical environments.[1]

At temperatures above T_g+10 K, the time of exchange coincides with the time of the large-scale molecular rearrangements that manifest themselves as the α-relaxation.[6] As the temperature decreases and the liquid becomes extremely viscous, the exchange time can significantly exceed the *average* time of the large-scale rearrangements.[7–10] It is possible that the exchange process adds a new time scale to the molecular dynamics in liquids near T_g. The structural origin of these long lived heterogeneities is not clear at present.

The dynamics of molecules in glasses is less understood. It is well-known that at temperatures not far below T_g, molecular rearrangements do not freeze and provide structural relaxation.[11] As a glass relaxes, its configurational state continuously changes towards the equilibrium state. The relaxation times dramatically depend on the depth of previous annealing.[11–13] In addition to the structural relaxation, other kinds of relaxation processes are observed in glasses. An example is thermally activated reorientational motions of molecules observed as the β-peak in a spectrum of dielectric loss.[14,15] These motions are preserved up to very low temperatures.

Rotational and translational dynamics of a variety of probes in several polymeric glass formers have been reported by Torkelson and co-workers.[16–18] The rotational reorientation of sufficiently large probes is coupled to the polymer α-relaxation both above and below T_g.[18] Above T_g, the temperature dependence of the average reorientation time, $\langle \tau \rangle$, follows a Williams-Landel-Ferry (WLF) equation.[19] Below T_g, the temperature dependence of $\langle \tau \rangle$ deviates from the WLF fit to the data above T_g, yielding a much lower temperature dependence which can be described approximately by an Arrhenius equation. An Arrhenius-like behavior is observed also for the α-relaxation in amorphous polymers below T_g, where the sample is out of equilibrium.[12] Recently, a similar temperature dependence of the rotational reorientation time of guest molecules was reported for *o*-terphenyl.[20]

Isomerization reaction merocyanine$\rightarrow$spiropyran[21,22] and racemization of bridged paddled binaphthyls[23] in polymer matrices exhibit a temperature dependence of the width of the rate distribution reflecting the reorganization of local environments with temperature. However, temporal fluctuations of rates were not observed on the time scale of the experiment.[22]

What will happen to the exchange process if a liquid is cooled to the glassy state? Based on a sharp increase in exchange time near the glass transition temperature[8] one can expect only static heterogeneity within the time window of conventional experiments. On the other hand, for a large system of interacting particles, the potential energy surface contains a great many minima for configurations which the molecules can attain with respect to their orientations and/or positions (the concept of the potential energy landscape[24] is reviewed in Ref. [25]). The manner in which a system walks on its landscape sets the dynamics of molecules. We believe that a large number of minima are thermally available even in the equilibrium state. The reversible transitions between such minima (molecular rearrangements) can provide the fluctuating change of environment of probe molecules. Note that in thin polyvinylacetate films not far below T_g the lifetime of heterogeneities is comparable to the α-relaxation time.[26]

In the present work we demonstrate with *n*-butanol that dynamical heterogeneity can be observed in low molecular weight glass formers. The light-induced *cis-trans* isomerization of azo dye molecules has been used as a probe process for dynamical heterogeneity. Such a process has been studied extensively in amorphous polymers.[27–30]

The quantum yield of photoisomerization of azo dye molecules in disordered solids depends on their location.[30] The isomerization kinetics is nonexponential. If the molecule environments are fluctuating with time, the kinetics of photoisomerization can depend on exposure, i.e., on the product of light intensity and irradiation time. Indeed, because the molecules with a higher quantum yield isomerize more rapidly, the distribution of molecules over quantum yields is altered upon isomerization. In turn, the exchange of environments leads to the recovery of the initial distribution. As a result, the lower the light intensity, the closer the kinetic curve of photoisomerization is to the exponent.
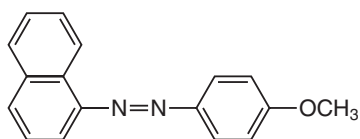
054202-1

FIG. 1. The chemical structure of NAMB.

II. EXPERIMENT

To remove water, n-butanol of 98% purity (Reachim) was boiled for 2 h with calcium oxide and then subjected to fractional distillation. The fraction with a boiling temperature of 390.7 K was used. T_g of n-butanol measured by the calorimetric method is 114 K.[31] Azo dye 1-naphthyl-p-azomethoxybenzene (NAMB) was synthesized in our laboratory in accordance with Becker *et al.*[32] and used after thin-layer chromatography purification. Its chemical structure is depicted in Fig. 1.

The samples were prepared as follows. A cell with the solution of NAMB in n-butanol (a concentration from 10^{-4} to 3×10^{-4} mol/l) was placed in a quartz thermostat located in a spectrophotometer (SPECORD UV VIS, Carl Zeiss, Jena). Thermostat temperature was maintained to within 0.1 K with a gaseous nitrogen flow using a temperature controller (Polikon 613, Thermex, Saint-Petersburg). The temperature was known to within 0.5 K absolute accuracy. Thereafter the sample was irradiated with light of wavelength 405 nm for 1 min at 273 K to convert about 75% of NAMB molecules into the *cis*-form. Then the sample was cooled with a rate of about 10 K/min to the experimental temperature (100–110 K) and annealed for 2 h. At temperatures 10 K below T_g, the low molecular weight glass formers achieve equilibrium after several hundred hours of aging.[13] So, the samples annealed during 2 h are most likely to be out of equilibrium. At the same time, the strongest decrease in the oxygen diffusion in n-butanol at 100 K is observed during the first 2 hours of isothermal aging.[33]

We found no difference in the kinetic curves obtained after 2 and after 10 h of the aging at 100 K. As the duration of kinetic experiments did not exceed 8 h, we can conclude that the structural relaxation does not affect the isomerization kinetics for the samples annealed for 2 h.

The kinetics of *cis-trans* isomerization induced by the 546 nm light was monitored. The photoequilibrium fraction of *cis*-molecules is less than 1%. The amount of light that a sample absorbs at a wavelength of 546 nm was less than 1%. Therefore the light intensity was considered constant throughout the sample.

A 500 W high-pressure mercury arc lamp (DRSh-500-2M) powered with direct current was used as a light source to induce isomerization. A monochromatic light was isolated using glass filters immersed into a water bath. The photon flux at 546 nm measured by the rate of azobenzene photoisomerization in isooctane[34] was about $(7.5 \pm 1) \times 10^{16}$ photon/(s cm^2). This light intensity was taken as 1 arbitrary unit (a.u.).

Two experimental setups represented schematically in Fig. 2 were used. In setup I, the sample (plastic cell with a horizontal cross section of 4×10 mm^2 and a height of
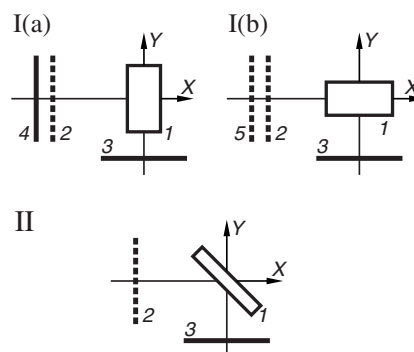

FIG. 2. Schematic representation of the experimental setups, view from above. The irradiation and probe beams are propagated along the X and Y axes, respectively; the intensity of irradiation light is set by neutral glass filter *2*; polarizer *3*, depending on its orientation, transmits light polarized either in the vertical (along axis Z) or horizontal (along axis X) direction. In setup I, depending on the orientation of plastic cell *1*, polarizer *4* or neutral filter *5* is used. In setup II, Pyrex cell *1* is oriented at an angle of 45° to axes X and Y.

15 mm) was irradiated isotropically in the following way. First, the sample was exposed to the horizontally polarized light [setup I(a)], then it was rotated around the vertical axis through 90° and irradiated through a neutral filter with nonpolarized light [setup I(b)]. In both cases the irradiation time was the same. The transmittance of the neutral filter is equal to the doubled transmittance of the polarizer.

In setup II, in addition to the plastic cell, the Pyrex cell with a horizontal cross section of 1×8 mm^2 and a height of 15 mm was used. The side 8×15 was positioned at an angle of 45° both to the irradiation and probe beams. The plastic cell was oriented along the X axis [as in the case of setup I(b)]. The sample was irradiated with nonpolarized light.

Since the probe light falls not normally to the surface of the Pyrex cell, the value of light reflection from the sample depends on light polarization. We have found that distortions of the kinetic curves are negligible.

The kinetics of isomerization was monitored by measuring a sample absorbance at a wavelength of absorption maximum of *trans*-isomer (379 nm). Note that the extinction of *cis*-isomer at this wavelength is about five times as low as that of *trans*-isomer. Figure 3 shows the absorption spectra of NAMB before (dotted line) and after (solid line) the isomerization.
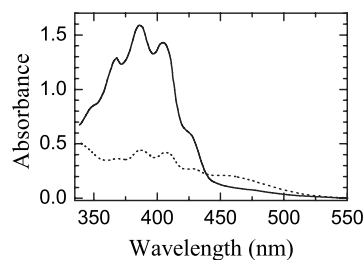

FIG. 3. UV-Vis absorption spectra of NAMB in n-butanol at 110 K: after 1 min of irradiation with light of wavelength 405 nm at 273 K (dotted line); and after subsequent 30 min irradiation with light of wavelength 546 nm at 110 K (solid line).
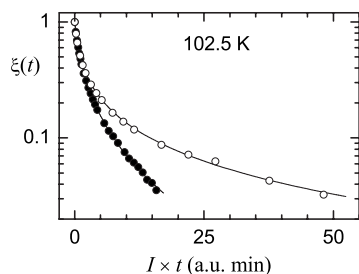
FIG. 4. *Cis-trans* isomerization kinetics of NAMB at light intensity 0.53 a.u. (open circles) and 0.022 a.u. (closed circles). Experimental setup I was used. The lines are guides for the eye.

The photoisomerization of NAMB molecules is accompanied by its orientation.[35] In order to get the time dependence of isomeric composition, we have recorded the absorption of both the vertically and horizontally polarized light, $A_\parallel$ and $A_\perp$, respectively. The combination of these values as

$$A(t) = \frac{2A_\parallel(t) + A_\perp(t)}{3}$$

is determined by the composition of isomers independently of molecule orientations. In the present work we use the value of $A(t)$ as absorbance.

Denote $[A(t) - A(\infty)]/[A(0) - A(\infty)]$ by the Greek letter ξ. The value of $A(\infty)$ was determined when the absorbance of the sample shows no further change with time. In the present work, all the kinetic curves are plotted in the coordinates

$$\xi(t) \text{ vs } I \times t,$$

where I is the light intensity, and t is the time. The value of $\xi(t)$ varies from 1 to 0.

III. RESULTS

A. Kinetics of NAMB isomerization

Figure 4 shows the kinetic curves for *cis-trans* photoisomerization of NAMB at two different light intensities. One can see that the isomerization kinetics is nonexponential. The samples were irradiated isotropically, therefore all orientations of the NAMB molecules are kinetically equivalent. In this case, only the glass heterogeneity can be a reason for the nonexponential kinetics. In other words, the quantum yield of photoisomerization of NAMB molecules depends on their location.

The abscissa in Fig. 4 plots the exposure, i.e., the product of light intensity and irradiation time. In case the quantum yield of isomerization does not vary with time, the data at different light intensities must fit the same curve. As follows from Fig. 4, at short times the kinetic curves for both samples coincide and diverge with increasing time. The kinetic curve obtained at low light intensity is noticeably closer to exponent than that obtained at high light intensity.

Figure 5 shows the kinetic curve for *cis-trans* photoisomerization of NAMB obtained under noncontinuous irradiation with light of intensity 1 a.u. (open circles). The irradiation periods of τ were followed by dark periods of 7τ.
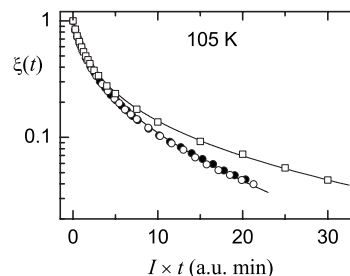

FIG. 5. *Cis-trans* isomerization kinetics of NAMB obtained using different irradiation procedures: irradiation with the light of 1 a.u. intensity during the periods τ, followed by dark periods 7τ (open circles); continuous irradiation with the light of 1/8 a.u. intensity (closed circles); and continuous irradiation with light of intensity 1 a.u. (open squares). The lines are guides for the eye. Experimental setup II with a Pyrex cell was used.

As a result, the average intensity of the light was 1/8 a.u. For comparison, the same figure depicts the kinetics of isomerization under continuous irradiation with light of intensity 1/8 a.u. (closed circles). One can see that the kinetic curves coincide. When the sample is irradiated continuously with the light of intensity 1 a.u., the photoisomerization is more retarded. Hence a change in the kinetic law of isomerization with varying light intensity is due to some dark precesses only.

The reported data can be explained under the assumption of the environment exchange, resulting in change of the isomerization quantum yield with time. Indeed, at low light intensity the lifetime of "slow" *cis*-molecules is longer than the exchange time. Environments of such molecules change prior to their isomerization resulting in recovery of the initial distribution over quantum yields. As a result, the lower the light intensity is, the closer the kinetic curve of photoisomerization is to the exponent.

B. Lifetime of heterogeneity

To estimate the exchange time, we have simulated the kinetics of the $cis \rightarrow trans$ photoreaction using Monte Carlo techniques (we ignore the reverse process $trans \rightarrow cis$ as its ensemble average rate constant is less than that of the forward process by a factor of 100; this follows from the fact that the photoequilibrium fraction of *cis*-molecules is less than 1%). Define the specific rate constant, k, as the product of the extinction coefficient of the *cis* particles and the quantum yield of photoreaction. A distribution function over values of $\ln k$ was set in the form

$$G(\ln k) = \begin{cases} G_0 \exp\left(-\dfrac{(\ln k - \mu)^2}{2\sigma^2}\right) & \text{if } 0 < k \leq k_{max}, \\ 0 & \text{otherwise}. \end{cases}$$

Here G_0 is the normalized factor, and μ, σ, and k_{max} are the fitting parameters. The k_{max} parameter sets the asymmetry of the $G(\ln k)$ function. The asymmetric distribution function is used because at low temperatures (see Fig. 4) almost half of the particles (most fast ones) have close k values whereas for the second half, k values differ greatly.
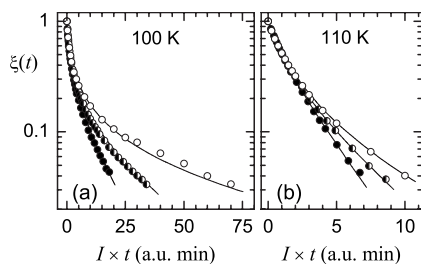
FIG. 6. Fitting results for the isomerization kinetics of NAMB (solid lines) obtained in the model of heterogeneous medium with the exchange of environments. Light intensity 1 a.u. (open circles), 0.127 a.u. (half-filled circles), and 0.042 a.u. (closed circles). Experimental setup II with a Pyrex cell was used.

The calculation procedure was as follows. At first, a random number k from the G-distribution was assigned to each of 10^6 *cis* particles as the initial value of the specific rate constant. This value varies at the rate of q. A random number from the G-distribution was taken as a new k value. The same approach was proposed in Refs. 21 and 36.

A standard Metropolis algorithm was used.[37] In each elementary step of simulation, a *cis* particle is randomly chosen. With the probability $Ik/(Ik_{max}+q)$ it is transformed into *trans* and with the probability $q/(Ik_{max}+q)$ its quantum yield is changed. After each step, the time is increased to $1/N(t)(Ik_{max}+q)$ where $N(t)$ is the number of *cis* particles at this time. $N(t)/N(0)$ corresponds to the experimental value $\xi(t)$. We fitted both the distribution function parameters (μ, σ, and k_{max}) and the exchange rate to satisfactorily describe experimental data for all light intensities at every temperature.

The fitting results are shown in Fig. 6 by solid lines. It is seen that the experimental data are well-described by the suggested model. When the temperature is lowered, the distribution broadens due to an increase in the fraction of "slow" molecules. Figure 6 shows that the lower the temperature is, the stronger is the nonexponentiality of the kinetic curves.

Figure 7 shows the Arrhenius plot for the exchange time which we define as $\tau_{ex}=1/q$. Least-squares fitting of the data gives the activation energy of 17±5 kJ/mole. Note that this value coincides with the activation energy of β-relaxa-
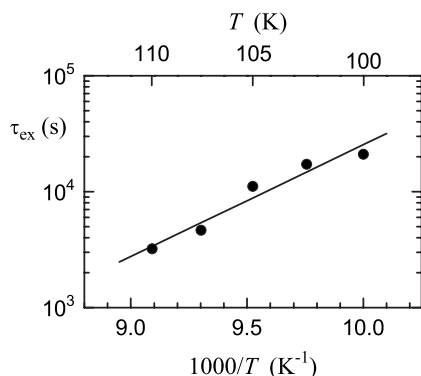

FIG. 7. Arrhenius plot for exchange time, τ_{ex}. The straight line has a slope corresponding to an activation energy of 17 kJ/mole.
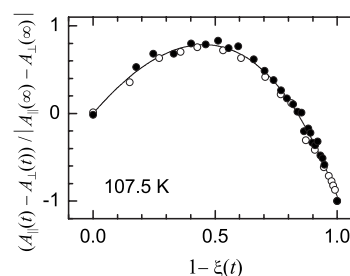

FIG. 8. Absorption anisotropy normalized to the absolute value of the stationary anisotropy during isomerization of NAMB molecules in setup II with a plastic cell. Light intensity 1 a.u. (open circles) and 0.042 a.u. (closed circles). The line is a guide for the eye.

tion.[15,31] At the same time, the τ_{ex} value and the characteristic time of β-relaxation, τ_β, are quite different. For example, at 105 K, $\tau_{ex} \approx 10^4$ s whereas $\tau_\beta = 4 \times 10^{-4}$ s.[15] The extrapolation of the Arrhenius plot to T_g gives the exchange time of the order of 10^3 s.

Note that at high light intensity the isomerization rate is much larger than the rate of exchange. Therefore the values of μ, σ, and k_{max} are determined by the kinetic curve obtained at high light intensity. The exchange rate q is determined by the kinetic curves obtained at low light intensities.

The exchange times and the structural relaxation times[33] are of the same order. It seems plausible that both of these processes are due to the same molecular rearrangements.

C. Rotation of NAMB molecules

Rearrangements of host molecules are not the only possible reason responsible for an environment change of probe molecules. Rotation and diffusion of a probe molecule also lead to a change in its environment and for this reason to a change of reactivity.

To ascertain whether the molecules rotate or not we have analyzed the results of measurements carried out using the setup II. In this case, the photons polarizations lie only in the YZ plane (see Fig. 2). For this reason, the light absorption anisotropy arises upon photoisomerization.[38] Figure 8 shows the dependence of anisotropy on isomeric composition of NAMB molecules at two different light intensities. The value of $1-\xi(t)$ increases with time proportionally to the fraction of *trans* molecules. When the photoequilibrium is reached, it is equal to 1.

An increase in anisotropy in the beginning of irradiation can be explained under the following conditions:[38] (i) the probability of a *cis*-molecule to absorb a photon is proportional to $\cos^2\theta$ where θ is the angle between the direction of photon polarization and the transition dipole;[39] (ii) the direction of transition dipole of the NAMB molecule does not change essentially upon isomerization. In this case, the *trans*-isomers with a dipole moment lying in the YZ plane are generated faster than those the dipole moment of which is directed along the X axis. An increase in the $A_\parallel$ value exceeds an increase in the $A_\perp$ value and hence $A_\parallel > A_\perp$.

The initial angle distribution of *cis*-molecules is isotropic. In the absence of molecule photoorientation and rotation, the

angle distribution of *trans*-molecules should be isotropic and absorption anisotropy should be equal to zero when all the *cis*-molecules convert to *trans*. However, as shown in Fig. 8, at long times the absorption anisotropy passes through zero and becomes negative. This fact witnesses to the NAMB photoorientation process which is observed for these molecules also in glassy o-terphenyl.[35]

We have established that the anisotropy induced by long irradiation of the samples does not decrease in the dark during the maximum experiment time. Keeping in the mind that after long irradiation the portion of *trans*-isomer exceeds 99% we can conclude that *trans*-molecules do not rotate in the dark.

Rotation of molecules alters their angle distribution and hence leads to the dependence of absorption anisotropy on light intensity. Indeed, at low light intensity the molecules have more time to change their orientation. As evident from Fig. 8, the absorption anisotropy does not depend on light intensity. Based upon that, we conclude that the *cis*-molecules of NAMB also do not rotate.

It is unlikely that in an isotropic medium particles can diffuse without turns. Therefore we believe that NAMB molecules do not change their location upon isomerization. Thus we exclude rotation and diffusion of NAMB molecules as a reason of environmental change.

IV. CONCLUSIONS

We have studied the *cis-trans* photoisomerization kinetics of 1-naphthyl-*p*-azomethoxybenzene molecules in glassy *n*-butanol at temperatures from 100 to 110 K and established that the quantum yield of isomerization fluctuates with space and time. The characteristic lifetime of heterogeneity changes with temperature according to the Arrhenius law from 3×10^4 s at 100 K to 4×10^3 s at 110 K. The activation energy of the exchange process is equal to 17 ± 5 kJ/mole.

*Corresponding author. syutkin@ns.kinetics.nsc.ru

[1] M. D. Ediger, Annu. Rev. Phys. Chem. **51**, 99 (2000).

[2] R. Richert, J. Phys.: Condens. Matter **14**, R703 (2002).

[3] H. Sillescu, R. Böhmer, G. Diezemann, and G. Hinze, J. Non-Cryst. Solids **307-310**, 16 (2002).

[4] U. Tracht, M. Wilhelm, A. Heuer, H. Feng, K. Schmidt-Rohr, and H. W. Spiess, Phys. Rev. Lett. **81**, 2727 (1998); U. Tracht, M. Wilhelm, A. Heuer, and H. W. Spiess, J. Magn. Reson. **140**, 460 (1999).

[5] S. A. Reinsberg, X. H. Qiu, M. Wilhelm, H. W. Spiess, and M. D. Ediger, J. Chem. Phys. **114**, 7299 (2001); S. A. Reinsberg, A. Heuer, B. Doliwa, H. Zimmermann, and H. W. Spiess, J. Non-Cryst. Solids **307-310**, 208 (2002); X. Qiu and M. D. Ediger, J. Phys. Chem. B **107**, 459 (2003).

[6] R. Böhmer, G. Hinze, G. Diezemann, B. Geil, and H. Sillescu, Europhys. Lett. **36**, 55 (1996); S. C. Kuebler, A. Heuer, and H. W. Spiess, Phys. Rev. E **56**, 741 (1997); U. Tracht, A. Heuer, S. A. Reinsberg, and H. W. Spiess, Appl. Magn. Reson. **17**, 227 (1999).

[7] M. T. Cicerone and M. D. Ediger, J. Chem. Phys. **103**, 5684 (1995).

[8] C.-Y. Wang and M. D. Ediger, J. Phys. Chem. B **103**, 4177 (1999); J. Chem. Phys. **112**, 6933 (2000).

[9] H. Wendt and R. Richert, Phys. Rev. E **61**, 1722 (2000).

[10] L. A. Deschenes and D. A. Vanden Bout, J. Phys. Chem. B **106**, 11438 (2002).

[11] C. A. Angell, K. L. Ngai, G. B. McKenna, P. F. McMillan, and S. W. Martin, J. Appl. Phys. **88**, 3113 (2000).

[12] A. Alegria, E. Guerrica-Echevarria, I. Telleria, and J. Colmenero, Phys. Rev. B **47**, 14857 (1993); A. Alegria, L. Goitiandia, I. Telleria, and J. Colmenero, Macromolecules **30**, 3881 (1997).

[13] P. Lunkenheimer, R. Wehn, and A. Loidl, J. Non-Cryst. Solids **352**, 4941 (2006); P. Lunkenheimer, R. Wehn, U. Schneider, and A. Loidl, Phys. Rev. Lett. **95**, 055702 (2005).

[14] G. P. Johari and M. Goldstein, J. Chem. Phys. **53**, 2372 (1970).

[15] G. P. Johari and M. Goldstein, J. Chem. Phys. **55**, 4245 (1971).

[16] D. B. Hall, D. D. Deppe, K. E. Hamilton, A. Dhinojwala, and J. M. Torkelson, J. Non-Cryst. Solids **235-237**, 48 (1998).

[17] J. S. Royal and J. M. Torkelson, Macromolecules **23**, 3536 (1990); **25**, 1705 (1992); **26**, 5331 (1993).

[18] A. Dhinojwala, G. K. Wong, and J. M. Torkelson, Macromolecules **25**, 7395 (1992); **26**, 5943 (1993); J. Chem. Phys. **100**, 6046 (1994); A. Dhinojwala, J. C. Hooker, and J. M. Torkelson, J. Non-Cryst. Solids **172-174**, 286 (1994).

[19] M. L. Williams, P. F. Landel, and J. D. Ferry, J. Am. Chem. Soc. **77**, 3701 (1955).

[20] S. Yu. Grebenkin and B. V. Bol'shakov, J. Phys. Chem. B **110**, 8582 (2006).

[21] R. Richert, Chem. Phys. **122**, 455 (1988).

[22] R. Richert, Macromolecules **21**, 923 (1988).

[23] J.-W. Park, M. D. Ediger, and M. M. Green, J. Am. Chem. Soc. **123**, 49 (2001).

[24] M. Goldstein, J. Chem. Phys. **51**, 3728 (1969).

[25] P. G. Debenedetti and F. H. Stillinger, Nature (London) **410**, 259 (2001).

[26] E. Vidal Russell and N. E. Israeloff, Nature (London) **408**, 695 (2000).

[27] W. J. Priest and M. M. Sifain, J. Polym. Sci., Part A-1 **9**, 3161 (1971).

[28] K. Horie and I. Mita, Adv. Polym. Sci. **88**, 79 (1984).

[29] J. G. Victor and J. M. Torkelson, Macromolecules **20**, 2241 (1987).

[30] I. Mita, K. Horie, and K. Hirao, Macromolecules **22**, 558 (1989).

[31] S. S. N. Murthy and S. K. Nayak, J. Chem. Phys. **99**, 5362

(1993).

[32] H. Becker, W. Berger, G. Domschke, E. Fanghanel, J. Faust, M. Fischer, F. Gentz, K. Gewald, R. Gluch, R. Mayer, K. Muller, D. Pavel, H. Schmidt, K. Schollberg, K. Schwetlick, E. Seiler, and G. Zeppenfeld, *Organicum*, 15th ed. (VEB Deutscher Verlag der Wissenschaften, Berlin, 1976).

[33] V. M. Syutkin, B. V. Bol'shakov, and A. G. Dzhonson, Chem. Phys. **324**, 307 (2006).

[34] G. Zimmerman, L. Chow, and U. Paik, J. Am. Chem. Soc. **80**, 3528 (1958).

[35] S. Yu. Grebenkin and B. V. Bol'shakov, J. Photochem. Photobiol., A **184**, 155 (2006).

[36] R. Richert and A. Heuer, Macromolecules **30**, 4038 (1997).

[37] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. N. Teller, and E. Teller, J. Chem. Phys. **21**, 1087 (1953).

[38] *Photoreactive Organic Thin Films*, edited by Z. Sekkat and W. Knoll (Academic Press, San Diego, 2002).

[39] Libration of molecules modulates the θ value and substantially diminishes their orientational nonequivalence.