Length scale of heterogeneities in glassy propylene carbonate probed by oxygen diffusion

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A new method using the quenching of guest molecule phosphorescence by molecular oxygen is proposed for determination of heterogeneity size in glassy matrixes. The method is based on the high sensitivity of the diffusion of oxygen molecules to spatial density fluctuations. Phenanthrene phosphorescence decay was monitored at different concentrations of molecular oxygen in propylene carbonate below T_g. An unusual dependence of the phosphorescence decay on oxygen concentration was observed: an increase in the concentration leads to anomalously large increase in the quenching rate at short times. This dependence is considered to be caused by matrix heterogeneity. To describe the phosphorescence decay, we use a model of glass as a heterogeneous medium where oxygen jump rates are spatially correlated. The length of spatial correlation for the jump rates is taken as heterogeneity size. Using the model, the value of 1.5 ± 0.5 nm was obtained for the size of structural heterogeneities in glassy propylene carbonate. The dispersion of barriers for oxygen jumps is estimated to be 4 ± 1 kJ/mole and the average barrier energy is found to be 50 kJ/mole. © 2010 American Institute of Physics. [doi:10.1063/1.3469775]

I. INTRODUCTION

At present, the dynamics in deeply supercooled liquids and polymeric melts is considered to be spatially heterogeneous.[1–3] The characteristic times of molecular motions in different regions of a matrix can differ by several orders of magnitude. The results of NMR measurements show that the typical size of the regions of different mobility, ξ_{het}, falls in the range from 1 to 3.5 nm for various glass formers, just above T_g.[4–8] With time, the "fast" regions can convert into the "slow" ones and vice versa.[9–16]

Below T_g, the lifetime of the regions of different mobility becomes very long. It is reasonable to assume that these regions can manifest themselves as static (structural) heterogeneities. Few literature data are available on the size of structural heterogeneities in glasses.

Leheny *et al.*[17] performed structural studies of propylene glycol through its glass transition using neutron diffraction experiments. They have failed to find any evidence for static heterogeneities of nanometer size. On the other hand, the density fluctuations quenched in from the liquid state are detected in silica and other oxide glass formers.[18–21] The length scale of density fluctuations has been determined to be 2 nm.[18,19]

Vogel *et al.*[22] studied the diffusion of silver ions in glass $(AgI)_{0.43}-(Ag_4P_2O_7)_{0.57}$ using NMR four-time correlation function. They reported that the "fast and slow ionic jumps are intimately mixed rather than grouped into extended domains." At the same time, Wang and Ediger[23] studied the translational motion of tetracene in polystyrene using the ho-lographic fluorescence recovery technique. They concluded that the van Hove function is non-Gaussian below T_g due to the matrix heterogeneities of 2 nm size, roughly.

The excess (compared with the Debye law) of vibrational density of states in the terahertz frequency range is commonly observed in glasses.[24,25] It is often related to strong scattering of vibrations caused by fluctuations of elastic constants and/or density in disordered structures.[26–30] Meanwhile, an explanation not based on spatial heterogeneity was also proposed.[31,32]

In organic glasses, nanoscale density fluctuations are not observed via optical, neutron, and x-ray scattering.[17,33–35] At the same time, the structural heterogeneity can manifest itself in the dynamic glass properties.[36–38] In the present work, a new method is proposed to measure the size of heterogeneities in glassy matrixes. It is based on high sensitivity of the diffusion of oxygen molecules to matrix heterogeneities. Oxygen is known to be an effective quencher of triplet states.[39] The presence of mobile oxygen molecules in organic glass containing small concentration of phenanthrene causes a substantial decrease in the intensity of phenanthrene phosphorescence.[40–42] We demonstrate that the phosphorescence quenching kinetics can be used to determine the spatial correlation length of the oxygen diffusion rate. This length is considered as the size of structural heterogeneities.

The structure of the paper is as follows. In Sec. III, we give the physical insight into the kinetics of phosphorescence quenching in heterogeneous medium. Then, in Sec. IV, we describe the model of glassy matrix. Finally, in Sec. V, the results are demonstrated and discussed. The calculation procedure is described in the Appendix.

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II. EXPERIMENTAL

A. Materials

Propylene carbonate (PC, Fluka, >99.0%) and phenanthrene (Aldrich, ≥99.5%) were used as received. The glass transition temperature of PC is 158 K based on differential scanning calorimetry at a 10 K/min heating rate after quenching from the liquid state.[34]

B. Sample preparation

The samples were prepared from phenanthrene solution in PC with a concentration of 0.01 mol/l in quartz ampoules (3 mm inside diameter and the height of 20 cm). The obtained solution is ideal as the intrinsic lifetime of the triplet state of phenanthrene does not depend on its concentration in organic molecular glasses in the range from 0.001 to 0.05 mol/l.[42,43] The solution was saturated with oxygen at room temperature.

At a saturation pressure of 0.5–1.5 MPa, specially designed ampoules were used to saturate PC with gas.[44] A solution was poured into the flask welded to the ampoule and connected to a gas cylinder with compressed oxygen. The liquid in the flask was degassed and stirred under oxygen for 45 min. Then the oxygen-saturated solution was poured out into the ampoule, frozen, and the ampoule was detached from the gas cylinder.

To saturate PC with oxygen at a pressure of 3.3 MPa, the ampoule with a solution (without the flask) was connected to the vacuum line and immersed in liquid nitrogen. The air over the frozen solution was pumped out. Then the ampoule was connected to the vessel with oxygen. Once the necessary amount of oxygen was condensed on the cold walls of the ampoule (determined by pressure drop), the ampoule was sealed and the sample was unfrozen. Saturation of the solution was carried out for 10 days with repeated shaking. In both cases, the sample height was 6 cm.

The oxygen-saturated solution was frozen in two steps. First, the lower part of the ampoule, 3 cm high, was immersed in liquid nitrogen. The remaining part of the sample was frozen 40 s later. The upper liquid part of the sample (3 cm) served as a plug to prevent oxygen exchange between the lower part of the sample and the gas phase. The sample cooling rate was about 200 K/min through the glass transition. The glass appeared to be transparent with a small number of cracks.

Oxygen solubility in PC was measured at room temperature. It obeys the Henry law with the constant equal to $(1.74 \pm 0.03) \times 10^{19}$ m^{-3} Pa^{-1}. The oxygen concentration in glass was calculated, taking into account the thermal expansion of PC. The samples with oxygen concentration of 9.6×10^{18}, 2.88×10^{19}, and 6.34×10^{19} cm^{-3} were prepared (the saturation pressure was 0.5, 1.5, and 3.3 MPa, respectively). The average distance between the oxygen molecules in oxygen-saturated samples varies from 2.5 at high to 4.7 nm at low oxygen concentration.

C. Deoxygenation of sample

To measure phosphorescence decay time of phenanthrene in the absence of oxygen, the sample was prepared as follows. The ampoule with a solution was connected to the vacuum line and the air in the liquid was removed by repeated "freeze-pump-thaw" procedure until the gas pressure above liquid became 0.7 Pa. Then the sample was frozen in liquid nitrogen. The oxygen concentration in this sample is estimated to be less than 2×10^{16} cm^{-3}. The ampoule was filled with pure nitrogen up to a pressure of 13 kPa and sealed. Nitrogen filled up the cracks and provided heat exchange between the walls of the ampoule and the sample.

D. Phosphorescence measurement

Phenanthrene was excited by the light of a pulsed nitrogen laser (337 nm, 15 ns, average energy per pulse of 30 μJ). The height of illuminated sample area was about 5 mm; this area was 1 cm above the ampoule bottom. The laser pulse excites about 0.01% of phenanthrene molecules. Phenanthrene phosphorescence decay was measured using the photomultiplier FEU-119 and the digital oscilloscope ISA BUS CompuScope (Gage Applied Science, Inc.) at a wavelength of 500 nm with a 20 ms delay after a laser pulse.

The samples were preannealed at 152 K ($T_g - 6$) for 2 $\times 10^5$ s to reach the equilibrium state of the matrix.[45] The phenanthrene phosphorescence was measured at temperatures from 140 to 152 K in glasses with the structure corresponding to the equilibrium at 152 K. To preserve glass structure, the annealed samples were cooled to $T < 152$ K at the rate of about 3 K/s. The sample temperature was kept to within 0.1 K using gaseous nitrogen flow. The temperature measuring accuracy was ± 0.5 K.

Keeping the prepared samples at experimental temperature for 2 days does not cause the change in phosphorescence kinetics. Based on that, we believe that the oxygen concentration remains constant during the experiment.

III. KINETICS OF PHOSPHORESCENCE QUENCHING IN HETEROGENEOUS MEDIUM: A THEORETICAL OUTLINE

A. Model of quenching sphere

The probability of phenanthrene deactivation by a quencher in a unit of time is given by the equation

$$K(r) = K_0 \exp[-2(r - R_0)/L], \tag{1}$$

where r is the distance between phenanthrene and oxygen molecules, R_0 is the minimal distance between these molecules, K_0 is the probability of quenching in a unit of time at $r = R_0$, and L is the exchange interaction length.

In organic low-molecular-weight and polymeric glasses, the phenanthrene phosphorescence quenching is well described by the following set of parameters: $R_0 = 0.65$ nm, $K_0 = 2 \times 10^7$ s^{-1}, and $L = 0.055$ nm.[40,41,47,48] The phosphorescence quenching in glass matrix is determined by only the parameter L and the combination $K_0 \exp(2R_0/L)$. The accuracy of their values was claimed to be $\pm 10\%$.
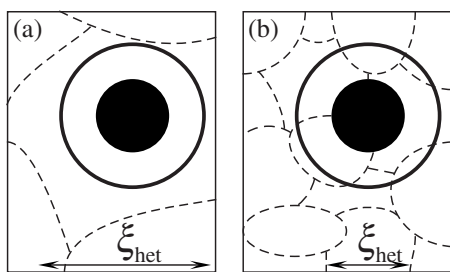
FIG. 1. Schematic illustration of heterogeneous media for (a) large and (b) small heterogeneity sizes. Phenanthrene molecule is indicated by the solid circle, its quenching sphere is denoted as the circumference. The dashed lines separate the regions of different oxygen mobility. The arrows denote the typical size of heterogeneity.

The probability of phenanthrene deactivation by oxygen increases sharply with decreasing the distance between the particles and reaches a very high value at R_0. Therefore, quenching can be considered as an instant contact reaction occurring at some quenching radius, $\rho > R_0$.[49]

In PC matrix at 152 K, the oxygen diffusion coefficient is about $D \approx 3 \times 10^{-14}$ cm^2/s (see Sec. V) and, therefore, the inequality $D \ll K_0 L^2$ is valid; in this case, the ρ value can be expressed by the equation[50,51]

$$\rho \approx R_0 + \frac{L}{2}\left(\ln\frac{K_0 L^2}{D} - 0.232\right), \qquad (2)$$

whence it follows that $\rho = 0.9 \pm 0.1$ nm.

The quenching probability of a phenanthrene molecule per unit of time, K_Q, is equal to the rate of collisions between the phenanthrene quenching sphere and oxygen molecules.[52]

B. Influence of heterogeneity size on phosphorescence quenching kinetics

In supercooled liquids and glasses, the free volume is distributed in the form of cavities of atomic length scale.[53,54] At the temperature several degrees below T_g, the changes in matrix structure are very slow, therefore one can consider that the cavities are fixed in space. However, small molecules, such as oxygen, preserve high translational mobility in organic low molecular weight[40,42,55–57] and polymeric[41,58] glasses. The molecules move due to thermoactivated jumps over potential barriers from one cavity to another.[59–61] In different regions, the rates of the jumps can vary by several orders of magnitude.[60]

The essence of the proposed method is based on the sensitivity of the phosphorescence quenching kinetics to the heterogeneity size, ξ_{het}. To explain this sensitivity, consider two cases: (i) ξ_{het} is much more and (ii) ξ_{het} is much less than the quenching radius ρ. In the first case, the quenching spheres of almost all phenanthrene molecules are located completely in single regions, as it is shown in Fig. 1(a). Then the distribution of phenanthrene molecules over quenching probability (K_Q-distribution) just reflects the distribution of the regions over oxygen jump rates.[62]

If $\rho > \xi_{het}$, the quenching sphere of each phenanthrene molecule crosses a number of regions [see Fig. 1(b)]. As a result, the averaging of heterogeneities over the surface of quenching sphere occurs and the K_Q-distribution becomes more narrow than the distribution over jump rates. Thus, the more the ratio ρ/ξ_{het}, the narrower the distribution of phenanthrene molecules over quenching rates. In the limiting case $\rho \gg \xi_{het}$, the quenching rate of all phenanthrene molecules is given by averaging over the whole heterogeneity distribution. This is the case of homogeneous quenching.

The distribution of phenanthrene molecules over quenching rates depends not only on ξ_{het}, but also on the distribution of the regions over oxygen jump rates. The wider the distribution over jump rates, the wider the distribution of phenanthrene molecules on quenching rates. It turned out that for any ξ_{het} we can find such a jump rate distribution that gives preassigned quenching kinetics (some examples are given below, see Sec. V). Hence, we cannot determine the ξ_{het} value unambiguously using a single quenching curve.

C. Influence of oxygen concentration on phosphorescence quenching kinetics

To find the size of heterogeneity *and* the distribution of oxygen molecules over jump rates we need more than one quenching curve. The additional curves can be obtained by merely varying oxygen concentration. The only condition is that these curves must depend on ξ_{het} differently. To meet this condition, the oxygen concentration should be changed from such a high value that any region neighboring to phenanthrene contains a molecule of oxygen to the concentration about an order of magnitude less.

At such a high and such a low oxygen concentration, quenching occurs in different ways. Indeed, at high concentration, a noticeable portion of phenanthrene molecules have oxygen in their vicinity at a moment of excitation. A part of these molecules is separated from the oxygen molecules by fast regions only. These molecules are quenched first, providing the high initial quenching rate which is reflected by the *steep* (accelerated) initial part of the quenching curve. Then the rest of the molecules are quenched, at a lower rate, by oxygen having arrived from a distance or located in neighboring slow regions.

At low oxygen concentration, all the phenanthrene molecules are quenched mainly by the oxygen molecules arriving from a distance. During traveling, oxygen molecules pass through a quantity of the regions. As a consequence, the diffusivity of oxygen is averaged over the set of regions to some value. This is why the quenching curve does not contain an accelerated initial part at low oxygen concentration.

Thus, in a heterogeneous medium, at high oxygen concentration, too strong decrease in quenching rate is observed at short times of the process. The wider the distribution over jump rates is, the stronger the decrease in quenching rate is. A simultaneous successful fitting of the quenching curves obtained at high and low oxygen concentrations gives the heterogeneity size and the parameters of distribution over jump rates unambiguously.

Under our experimental conditions, we found that the oxygen concentration of 6.34×10^{19} cm^{-3} can be used as a *high* concentration, and the concentration only six times less can be used as a *low* one.
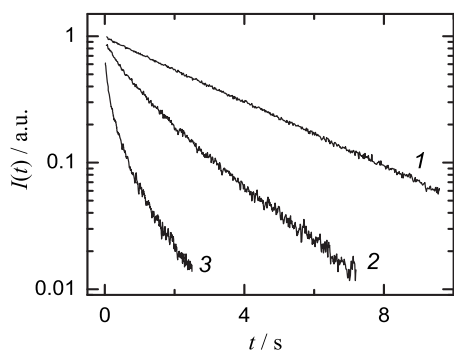
FIG. 2. The time profile of phenanthrene phosphorescence intensity at oxygen concentrations: (1) $<2\times10^{16}$ (degassed sample), (2) 9.6×10^{18}, and (3) 6.34×10^{19} cm^{-3}, $T=152$ K.

FIG. 3. The kinetics of phenanthrene deactivation at oxygen concentrations of 9.6×10^{18} (circles), 2.88×10^{19} (triangles), and 6.34×10^{19} cm^{-3} (squares), $T=152$ K. The lines are the curves simulated with the proposed model using the parameter values listed in the second row of Table I (marked by bold). Simulation of the kinetics of phosphorescence quenching at low oxygen concentration using any parameter set (listed in the table) gives identical curves.

IV. MODEL OF HETEROGENEOUS GLASS

A heterogeneous medium was modeled by a simple cubic lattice with energy barriers of different heights between the sites.[63] The barrier heights are Gaussian-distributed values with zero mean. The matrix heterogeneity is introduced by means of the spatial correlation of neighbor barriers heights. The correlation function was chosen to decay with distance r as

$$C(r) = \exp(-2r^2/\xi_{het}^2).$$

The size of heterogeneities ξ_{het} is defined as the distance at which the spatial correlation function amounts to 13.5%. The lattice constant λ (jump length) was varied from 0.3 to 0.5 nm (a mean distance between PC molecules in the glassy state is 0.5 nm).

Oxygen molecules can occupy only the lattice sites and can jump only into one of six nearest sites. The probability of an oxygen molecule transition from the site i to the site j in a unit of time is defined by the equation

$$P_{ij} = P_0 \exp\left(-\frac{\varepsilon_{ij}}{RT}\right),$$

where ε_{ij} is the energy barrier between the sites, P_0 is the pre-exponential factor, R is the universal gas constant, and T is temperature.

The free parameters of the model are (i) the size of heterogeneities ξ_{het}, (ii) the dispersion of barrier energy, $\sigma = \sqrt{\langle\varepsilon_{ij}^2\rangle}$, and (iii) the pre-exponential factor P_0. The pre-exponential factor affects the time scale of oxygen diffusion only. The calculation procedure is described in detail in the Appendix.

V. RESULTS AND DISCUSSION

A. The kinetics of phenanthrene phosphorescence quenching

Figure 2 shows the phenanthrene phosphorescence decay in glassy PC at various oxygen concentrations. In the absence of oxygen, the phosphorescence decay is described by the exponential law with time constant $\tau_0=3.48\pm0.01$ s. The increase in temperature from 96 to 152 K leads to the decrease in the phosphorescence lifetime from 3.59 to 3.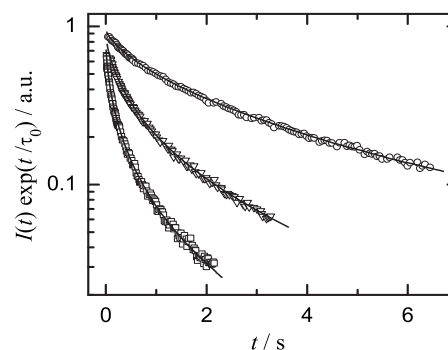48 s. Based on such a weak temperature dependence, we considered the value 3.48 s to be the lifetime of phenanthrene triplet state.[64] Oxygen accelerates the phosphorescence decay due to the deactivation of phenanthrene.

Hereinafter, to isolate quenching caused by oxygen from the phosphorescence time profile, the data are plotted as $I(t)\exp(t/\tau_0)$ versus t, where t is the time and $I(t)$ is the phosphorescence intensity. Figure 3 demonstrates the phosphorescence decay caused by oxygen only. The deactivation kinetics does not obey the exponential law due to the matrix heterogeneity. The lines represent the result of best fitting of experimental curves with the proposed model at a lattice constant of 0.5 nm. One can see that the suggested model well describes the experimental data. The fitting parameter values are $\xi_{het}=1.5$ nm, $\sigma=4$ kJ/mole, and $P_0=2.6$ s^{-1}.

The modeling curves are very sensitive to the change of the fitting parameters. Even small change in ξ_{het} at fixed σ and P_0 causes strong change of simulated curves. At the same time, this change can be essentially compensated by corresponding variations of σ and P_0. To estimate the error in determination of ξ_{het} we fitted the quenching curves with other parameter values. At first, we fixed a new value of ξ_{het} and found the values of σ and P_0 which provide best fitting of the quenching curve at low oxygen concentration. Then we simulated the quenching curves at high oxygen concentration using the obtained parameters.

Two examples of the simulation curve are shown in Fig. 4 together with the experimental quenching curve. For clarity, we demonstrate the curves simulated using ξ_{het} values of 1.0 and 2.8 nm. All the values of fitting parameters are listed in Table I. The figure demonstrates a distinct difference between the curves simulated at ξ_{het} equal to 1.0 and 2.8 nm, and the experimental curve. At short times, the simulations using ξ_{het} equal to 1 and 2.8 nm yield the larger and smaller quenching rates than it is observed in experiment. At the same time, the fitting of the quenching curve at low oxygen concentration using the same parameter sets is good (see Fig. 3, top curve).

The simulation of quenching curves at ξ_{het} values ranging from 1 to 2.8 nm in 0.1 nm steps gives the error estimation for the heterogeneity size of ±0.4 nm. Inaccuracy in the
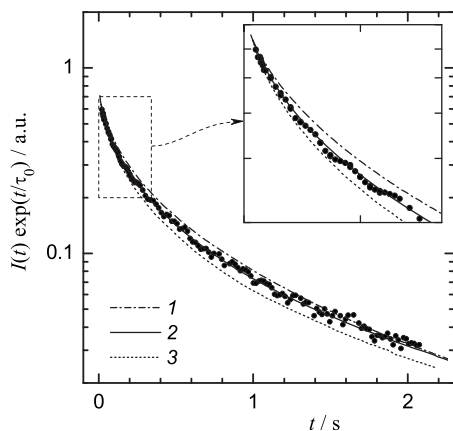
FIG. 4. The kinetics of phenanthrene phosphorescence quenching at oxygen concentration of 6.34×10^{19} cm^{-3} (high concentration), $T = 152$ K. The lines were simulated with the proposed model using the parameter values listed in Table I: ξ_{het} is equal to (1) 2.8, (2) 1.5, and (3) 1.0 nm. The values of σ and P_0 are listed in Table I.

parameters of Eq. (1) increases the error of ξ_{het} by 0.1 nm. The dispersion for activation energy of oxygen jumps is found to be 4 ± 1 kJ/mole.

B. Independence of the determined heterogeneity size on lattice constant

The simulated results reflected in Figs. 3 and 4 were obtained using the lattice constant of 0.5 nm. To determine whether the obtained value of heterogeneity size depends on lattice constant, additional simulations were done. The phosphorescence quenching curves (for all oxygen concentrations) were simulated at different lattice constant, viz., 0.3, 0.4, and 0.5 nm. We found no dependence of ξ_{het} and σ on λ. The pre-exponential factor P_0 depends on lattice constant in such a way that the diffusion coefficient $D \sim \lambda^2 P_0$ remains constant, as it must be.

C. Estimation of average barrier energy

The average barrier energy was estimated and compared with the calculated value for dispersion of barrier heights. To do this, the quenching curves of phenanthrene deactivation were obtained at different temperatures in the range from 140 to 152 K. The obtained curves were fitted with the proposed model. Satisfactory agreement between the model and the experiment is observed for all temperatures and all oxygen concentrations if the parameters ξ_{het} and σ determined at

TABLE I. Fitting parameters obtained for PC at 152 K using the proposed model of phosphorescence quenching in heterogeneous media at a lattice constant of 0.5 nm. All the parameter sets give a good fit to the quenching curve obtained at low oxygen concentration (9.6×10^{18} cm^{-3}). Only the parameters marked by bold give a good fit to the quenching curves at all the concentrations.

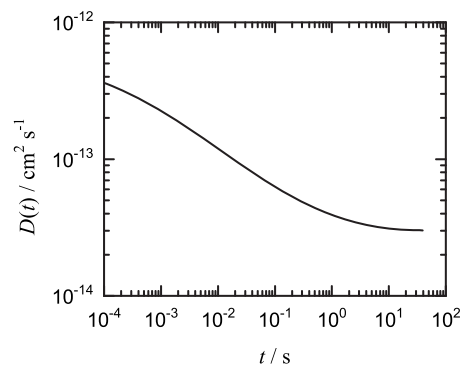| ξ_{het} (nm)	σ (kJ mole^{-1})	P_0 (s^{-1})
1.0	7.6	0.25
1.5	**4.0**	**2.6**
2.8	2.1	9.1

FIG. 5. The effective diffusivity of oxygen in the lattice with a heterogeneity size of 1.5 nm at $T = 152$ K. The values of σ and P_0 are listed in Table I.

152 K are used (marked by bold in Table I). We found that the temperature dependence of pre-exponential factor $P_0(T)$ is described by the Arrhenius equation with the activation energy $\varepsilon_c \approx 45$ kJ/mole.

In a heterogeneous medium, the real diffusion pathways pass over low barriers. The temperature dependence of $P_0(T)$ is determined by the highest barrier which is overpassed by particles while they are walking through the sample.[66] Its height is approximately equal to the experimentally determined value of ε_c. On the other hand, this height (that is the percolation level) in the three-dimensional random Gaussian potential is equal to $\langle \varepsilon \rangle - 0.95\sigma$.[67] Hence, $\varepsilon_c \approx \langle \varepsilon \rangle - 0.95\sigma$ and the average barrier energy is determined to be about 50 kJ/mole.

As the values ξ_{het} and σ do not depend on temperature we can conclude that the matrix structure is invariable in the measured temperature range. In contrast, the oxygen diffusion strongly depends on temperature. Hence, the diffusion of oxygen in glassy PC is decoupled from the rearrangement of the matrix.

D. Effective diffusivity of oxygen

The mean square displacement of oxygen molecules $\langle r^2(t) \rangle$ in lattice without phenanthrene was calculated as a function of time using the parameters determined above (marked by bold in Table I). We present the results averaged over 100 lattices with 50 000 random starting positions of oxygen molecule for each lattice. The effective diffusivity of oxygen was calculated as[68]

$$D(t) = \frac{\langle r^2(t) \rangle}{6t}. \tag{3}$$

Figure 5 shows the dependence of $D(t)$ on time. The anomalous transport[69–71] of oxygen is observed at short times. It follows from Fig. 5 that at $t > 1$ s the mean square displacement of oxygen grows almost linearly with time, which means that the diffusion becomes Fickian. The Fickian diffusion coefficient of oxygen was determined to be $\approx 3 \times 10^{-14}$ cm^2/s.

Note that the decrease in diffusivity and the decrease in quenching rate with time are of the same origin. Both phenomena are caused by the matrix heterogeneity.

VI. CONCLUSIONS

The concept of glassy PC as a heterogeneous medium with a typical size of heterogeneity of 1.5 ± 0.5 nm provides a good description of the phenanthrene phosphorescence quenching by oxygen at all oxygen concentrations. The dispersion of barriers for oxygen jumps in PC matrix in the range of 140–152 K is estimated to be 4 ± 1 kJ/mole.

It is established that the size of heterogeneity in glassy PC is close to the size of dynamic heterogeneities usually observed above T_g in molecular supercooled liquids. Therefore, we suppose that, in liquids, the heterogeneous dynamics originates from the structural heterogeneity which, in its turn, is caused by the difference in free volume in different regions. Actually, the issue of the origin of the spatially heterogeneous dynamics remains open for discussion.[2,72] Recently, Tanaka *et al.*[73] on the basis of numerical simulations came to the conclusion that "the heterogeneous dynamics is a result of critical-like fluctuations of static structural order."

Quenching of phenanthrene phosphorescence by molecular oxygen can be used as the method for determination of heterogeneity size in glassy matrices. The heterogeneity size which is comparable with the diameter of quenching sphere can be measured. If the heterogeneity size is much larger than the diameter of quenching sphere, then the quenching probability of a phenanthrene molecule depends mainly on the diffusivity of its region. In this case the method cannot be used. We estimate the upper limit of measurable heterogeneity size to be about 5 nm.

Quenching of phenanthrene phosphorescence can be used also as the method to determine oxygen diffusivity in organic glasses.

ACKNOWLEDGMENTS

APPENDIX: COMPUTATIONAL PROCEDURES

The Monte Carlo simulations were performed on a simple cubic lattice of size $100 \times 100 \times 100$ sites with periodic boundary conditions. Each site corresponds to a cavity where an oxygen molecule can reside. The lattice constant λ (jump length) was varied from 0.3 to 0.5 nm. Phenanthrene molecules are "embedded" randomly in the centers of lattice interstitial sites. The distance between phenanthrene molecules always exceeds 3.5 nm (the probable quenching of two phenanthrene molecules by the same oxygen molecule being negligibly low). The minimal distance between the centers of phenanthrene and oxygen molecules R_0 is larger than the distance between phenanthrene and its nearest sites. Therefore, these sites are inaccessible for oxygen molecules. Oxygen molecules are distributed randomly over the remaining lattice sites. Spatially correlated barrier energies ε_{ij} are assigned to each bond between the nearest sites i and j.

1. Modeling of spatial heterogeneity in the lattice

The lattice with spatially correlated energy barriers between the sites was emulated as follows. First, the uncorrelated random numbers u_{nm}, taken from the Gaussian distribution with zero mean and unit variance, were assigned to all bonds connecting the nearest sites n and m. Then a random number v_{ij} for the bond between the sites i and j was calculated from the equation

$$v_{ij} = \sum_{nm} g(r_{ij,nm}) u_{nm} / \sum_{nm} g(r_{ij,nm})$$

using

$$g(r_{ij,nm}) = \exp(-r_{ij,nm}^2 / 2r_0^2),$$

where $r_{ij,nm}$ is the distance from the middle of the bond $i-j$ to the middle of the bond $n-m$ and r_0 is the parameter that sets the correlation length. The summation is performed over all the bonds. We have established that at $r_0 \geq \lambda/2$ the distribution function of numbers v_{ij} can be satisfactorily described by the Gaussian function with zero mean ($\langle v_{ij} \rangle = 0$) and dispersion

$$\sigma_v(r_0) = \sqrt{\langle v_{ij}^2 \rangle} = 0.0875(r_0/\lambda)^{-1.52 \pm 0.02}.$$

The spatial correlation function of v_{ij} values,

$$C(r_{ij,nm}) = \langle v_{ij} v_{nm} \rangle / \sigma_v^2,$$

is well described by the function

$$C(r) = \exp(-r^2 / 2r_c^2),$$

with $r_c = (1.405 \pm 0.01) r_0$. Here, the brackets $\langle \cdots \rangle$ mean averaging over all the pairs of lattice bonds. The correlation function decreases sharply with distance at $r > 2r_c$. Therefore, the value $\xi_{het} = 2r_c$ is used as the characteristic size of heterogeneities.

The barrier energies ε_{ij} were calculated as

$$\varepsilon_{ij} = v_{ij} \sigma / \sigma_v.$$

The fitting parameter σ is equal to the dispersion of ε_{ij}-distribution.

2. Oxygen walking in the lattice

The probability of mutual collisions of oxygen molecules is low (the fraction of sites occupied by oxygen is below 0.01), therefore, we considered oxygen molecules to diffuse independently. The probability of oxygen transition from site i to site j in a unit of time is set by the equation

$$P_{ij} = P_0 \exp\left(-\frac{\varepsilon_{ij}}{RT}\right),$$

where P_0 is the pre-exponential factor, R is the universal gas constant, and T is temperature. $P_{ij} = 0$ if the site j is inaccessible for oxygen molecules. The probability of oxygen molecule to escape from the ith site in a unit of time is given by the equation

$$P_i = \sum_{j=1}^{6} P_{ij},$$

where summation is performed over the sites nearest to the site i.

The instant of time of the nth jump of the molecule located at the ith site after the $(n-1)$th jump obeys the equation[74]

$$t_n = t_{n-1} - \ln \zeta / P_i, \quad n = 1, 2, \ldots,$$

with ζ randomly uniformly distributed in the interval $(0,1]$ and $t_0 = 0$. If a molecule leaves the site i then it arrives to a neighboring site j with the probability P_{ij}/P_i.

3. Phenanthrene phosphorescence quenching by oxygen molecules

At the initial moment, 64 excited phenanthrene molecules were placed randomly in the lattice. The quenching probability of the mth phenanthrene molecule in a unit of time at a moment t is set by the equation

$$k_m(t) = 1/\tau_0 + \sum_i \delta_i(t) K(r_{im}),$$

where τ_0 is the lifetime of the excited state in the absence of oxygen, $\delta_i(t)$ is the number of oxygen molecules in the ith site, and r_{im} is the distance from the ith site to the mth phenanthrene molecule. $K(r)$ is set by Eq. (1).

Just after the laser pulse, the moment of quenching of the mth phenanthrene molecule t_m is determined by the positions of oxygen molecules at $t=0$,

$$t_m = -\ln \zeta / k_m(0).$$

If at time $t_n < t_m$, a jump of an oxygen molecule causes a change in the k_m value by more than 10^{-10} s^{-1} (that holds if the distance between this oxygen molecule and the mth phenanthrene molecule is less than 1.55 nm), then the new value of t_m is set by the equation

$$t_m = t_n - \ln \zeta / k_m(t_n).$$

If up to time t_m, the k_m value remains unchanged, the mth phenanthrene molecule is deactivated. The phenanthrene phosphorescence intensity $I(t)$ is proportional to the number of the excited phenanthrene molecules.

The presented quenching curves are averages over 100 curves calculated for different lattices with different phenanthrene positions. In its turn, each of the 100 curves is averaged over 50 random starting positions of oxygen molecules.

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