

## Thermally induced spectral diffusion for photoautomerization systems in polymer matrices

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Thermally induced spectral diffusion of a spectral hole was investigated using photoautomerization systems in various polymers. The broadening rates were correlated with the packing densities of the matrix polymers calculated by Bondi in the form of a Doolittle-type equation. The result was interpreted as the result of redistribution of entropically oriented free volume. The origin of the two-level system in amorphous polymers was discussed. The free volume is thought to be the origin of the intrinsic two-level system.

### I. INTRODUCTION

Anomalous properties of glasses at low temperature have attracted much interest for a long time.<sup>1-4</sup> The most adopted model to explain the anomalies in glasses is the two-level system (TLS) model.<sup>1</sup> Though the model can explain the anomalies phenomenologically, the microscopic explanation has been an unresolved problem.<sup>1,5-7</sup> A hole burning spectroscopy is a direct method of investigating the low-energy excitations of host-guest systems at low temperature. The most interesting feature of the spectroscopy is its ability of energetically marking the sites hidden in the inhomogeneous distribution. The hole, a shadow image in the absorption spectrum of removed molecules, acts as a tracer. The hole shape becomes a very sensitive probe for investigating the change of the microscopic environment. When temperature increases, the hole area becomes small and the hole width broadens. The changes are partially reversible. When the sample is recooled to the initial temperature, the hole area and the hole width are recovered. The irreversible decrease of the hole area, which we call the thermally induced hole filling (TIHF), in many amorphous systems obeys to the law of square root of the excursion temperature. This can be expressed not by a single activation process but by a uniform distribution of activation barriers of TLS potentials.<sup>8,9</sup> It is directly shown that the distribution starts from very low energy of at least  $10\text{ cm}^{-1}$  by Köhler and Friedrich.<sup>8</sup> The irreversible broadening of hole width, which we call thermally induced spectral diffusion (TISD), is not necessarily correlated with TIHF and is much more complex than TIHF.<sup>10-13</sup> Köhler and co-workers formulated the changes quantitatively by a combination of three independent processes: one-phonon tunneling process, two-phonon Raman scattering process, and an activation process.<sup>10,11</sup> Though their model succeeded in expressing the temperature dependence of TISD and TIHF quantitatively, the physical origin of TLS has not yet been clear. In this paper, the thermally induced change of spectral holes has been investigated using photoautomerization systems in various polymer matrices. We made attention on the packing density, which is one of the most fundamental parameters derived only from topological orienta-

tion, independent of the chemical structure of the molecule. The quantitative relation between the amount of free volume and the thermally induced change of spectral holes is discussed.

### II. EXPERIMENT

Tetraphenoxypthalocyanine (TPPc), tetratertiarybutylphthalocyanine (TBPc), and tetraphenylporphine (TPP) were used for guest molecules. Poly(*o*-methylstyrene) (*o*-MePS), poly( $\alpha$ -methylstyrene) ( $\alpha$ -MePS), poly(methylmethacrylate) (PMMA), polystyrene (PS), poly(isobutylene) (PIB), polyethylene (PE), and poly(4-methylpentene-1) (P4MP1) were used for matrix polymers. We selected the polymers, the packing densities of which were calculated by Bondi.<sup>14,15</sup> The dye concentrations were about  $10^{-3}$  mol/l. Dyes and polymers were thoroughly dissolved in appropriate solvents. The solvents and solutes were separated by evaporation or reprecipitation and the mixtures were dried in vacua. And then the samples were melted on a hot plate to take away the solvent thoroughly and pressed by hands between a pair of slide glasses and left to cool. Some samples had strong association peaks. But the association does not influence the change of holes because the associated dyes become inactive for hole burning and the change of a hole reflects only the change of environment

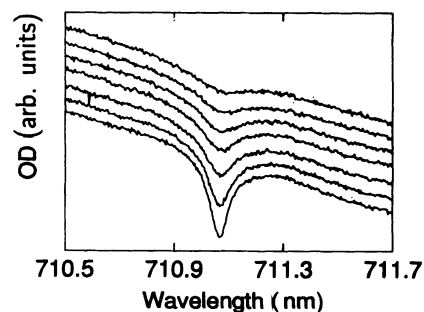


FIG. 1. Thermally induced change of a spectral hole burned in TPPc/PS. The burn and the excursion temperatures were 6.4, 18.4, 30, 40, 50, 60, and 77 K. Each base line was shifted for the clarity.

around molecularly dispersed dyes. Usual temperature cycle experiments were carried out. Samples were cooled in a gas flow type cryostat (Oxford CF1204). Holes were burned by a pulsed dye laser (Lambda Physik FL2002) excited by a XeCl excimer laser (Lambda Physik EMG50) at 4–6 K. They were burned at near the top or longer wavelength side of the  $Q$  band. The burning

powers were typically  $40 \mu\text{W}/\text{mm}^2$ , and the radiating times were 10–50 sec. There was no obvious dependence of burning efficiency on the matrices. Samples were heated up to the excursion temperatures and held at the temperature. They were recooled to the initial temperature and hole spectra were measured, the light source was the output of a 500 W Xe lamp monochromated by a 0.85 m

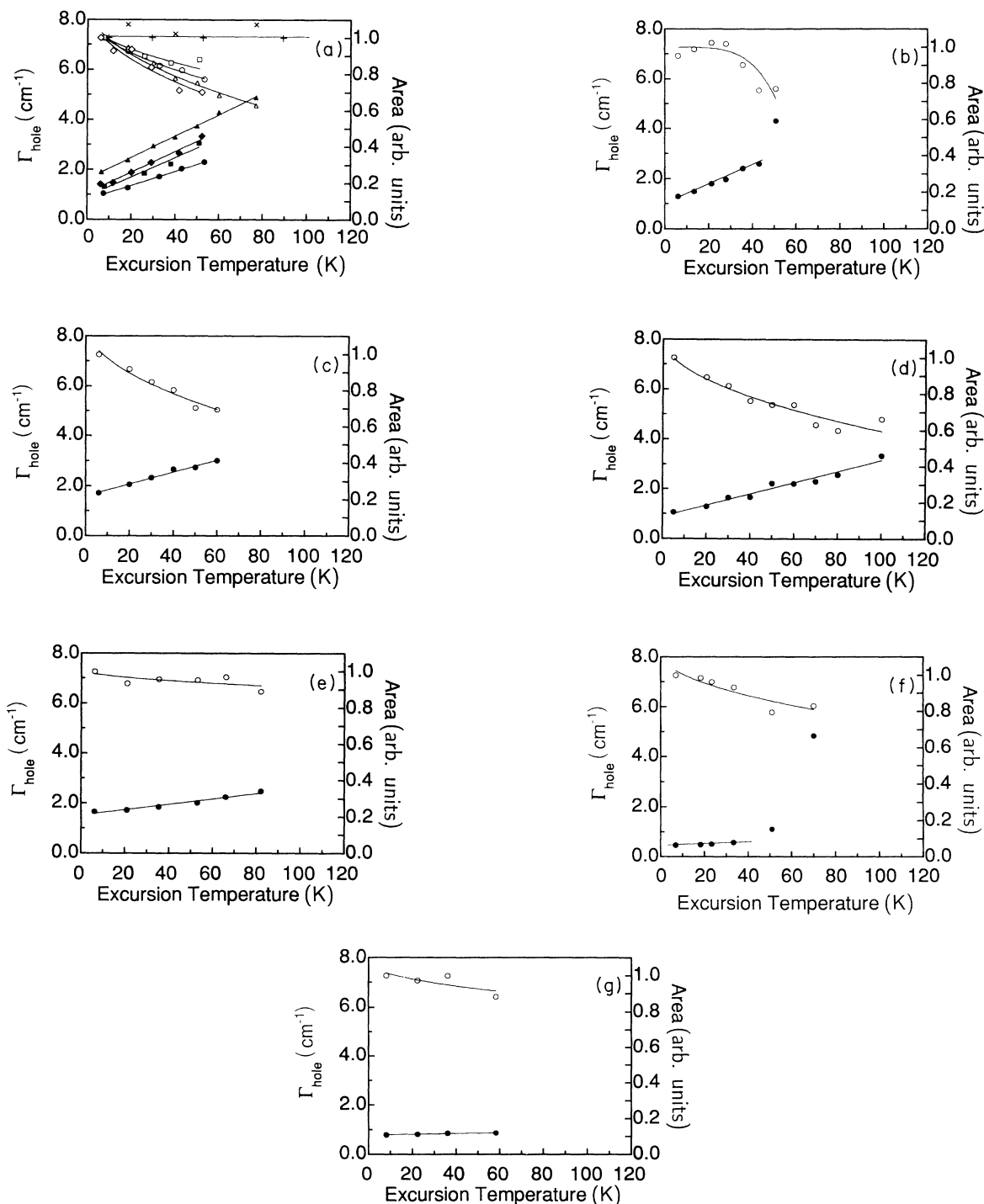


FIG. 2. Thermally induced change of width of the ZPH (filled symbols), area of the ZPH (open symbols), and PSH (crossed symbols). (a) OEP/PS (●,○), TBPC/PS (▲,△), TPPc/PS (■,□, +), and TPP/PS (◆,◇,×); (b) TPP/P4MP1; (c) TPPc/o-MePS; (d) TPPc/α-MePS; (e) TBPC/PMMA; (f) TBPC/PE; (g) TBPC/PIB.

double monochromator (SPEX 1403). The monochromated light was sufficiently weak that the temporal change of hole shapes could be ignored within our experimental accuracy. Each cycle of annealing and measuring was completed within a few tens of minutes. An example of the thermally induced change of a spectral hole burned in a TPPc/PS is shown in Fig. 1. The values of width and area were obtained by Lorentzian fitting the holes. Since the burning conditions were not optimized, the initial widths were not intrinsic ones. But the terms varying with the temperatures were independent of the burning conditions. The changes of width and area are shown in Figs. 2(a)–2(g).

TIHF in amorphous polymers is known to obey to the law of the square root of the excursion temperature as

$$\frac{A(T)}{A_0} = \frac{\sqrt{T^*} - \sqrt{T}}{\sqrt{T^*} - \sqrt{T_b}}, \quad (1)$$

where  $A(T)$  is the hole area after temperature cycle to the excursion temperature  $T$ ,  $A_0$  is the initial hole area,  $T^*$  is the system temperature defined by Köhler and Friedrich, and  $T_b$  is the burning temperature.<sup>9</sup> TISD in polymers at low temperature is known to be linearly dependent on the excursion temperature. The irreversible broadening rates  $K$  were obtained from the slope of the equations as

$$K = \frac{d\Gamma_{\text{hole}}}{dT}. \quad (2)$$

The used dyes, the matrices, the Bondi's packing density ( $\rho$ ), the inhomogeneous width ( $\Gamma_{\text{inh}}$ ),  $K$ ,  $T^*$ , and the upper bound of the investigated excursion temperature ( $T_u$ ) are shown in Table I. Though holes were observed after a temperature cycle above  $T_u$ , fitting became worse and the obtained values of  $T^*$  and  $K$  were not reliable. The investigated excursion temperature region were not intrinsic to the samples but dependent on the experimental conditions. Some data [quinizarin ( $Q$ )/PMMA, free base phthalocyanine ( $H_2Pc$ )/PMMA, and  $H_2Pc$ /PE]

were collected from Refs. 12 and 13. The hole widths increased steeply over 40 K in PE and P4MP1 matrices. It is noteworthy that the value of  $Q$ /PMMA is similar to that of TBPc/PMMA, though the hole burning mechanism is an intermolecular proton transfer for quinizarin whereas it is an intramolecular proton transfer for phthalocyanine. The fairly large discrepancy between the broadening rate of TBPc/PE in our experiment and  $H_2Pc$ /PE in the reference is thought to be mainly due to the experimental accuracy. The broadening rate of TBPc/PIB would also be overestimated by a similar reason.

### III. RESULTS AND DISCUSSION

#### A. Hole filling

The change of the area of PMMA, PE, and PIB matrices were less than other systems. It is difficult to quantitatively discuss the difference of  $T^*$  over 1000 K within our experimental accuracy. The change of area for the P4MP1 matrix was a little dispersive but was considered to be small up to 40 K and suddenly decreased. The critical behavior would be attributed to some thermally activated process having a distinct activation energy. Fearey and Small pointed out that a broad spectral diffusion, the diffusion width of which was several times larger than the hole width, could be detected as a decrease of the hole area,<sup>16</sup> whereas spectral diffusion itself conserved the hole area.<sup>17</sup> It is informative to investigate TIHF of the phonon side hole (PSH). Because the width of PSH is much larger than the width of zero-phonon hole (ZPH) and smaller than the inhomogeneously broadened width, change of PSH is a good probe for investigating the broad spectral diffusion. An example of hole spectra is shown in Fig. 3. The total hole area was numerically integrated. The initial area ratio of the ZPH to the sum of ZPH and PSH was 30%. The total hole area was conserved within a few percent up to 90 K cycles and suddenly disappeared at some temperature be-

TABLE I. List of the values of  $K$ , the inhomogeneous width ( $\Gamma_{\text{inh}}$ ), the packing density ( $\rho$ ) calculated by Bondi (Refs. 14 and 15) for the investigated dyes and polymers, and the upper bound of the investigated excursion temperature range ( $T_u$ ). The values with an asterisk are taken from Refs. 12 and 13.

Matrix	$\rho$	Guest	$K$ ( $10^{-2} \text{ cm}^{-1} \text{ K}^{-1}$ )	$\Gamma_{\text{inh}}$ ( $\text{cm}^{-1}$ )	$T^*$ (K)	$T_u$ (K)
P4MP1	0.606	TPP	2.7	320		40
PS	0.636	OEP	2.9	190	530	55
		TBPc	4.5	360	800	75
		TPPc	4.7	400	360	60
		TPP	4.5	310	320	50
		$H_2Pc$	2.1*			
o-MePS	0.644	TPPc	2.4	300	360	60
$\alpha$ -MePS	0.660	TPPc	2.1	310	460	80
PMMA	0.660	TBPc	1.0	350	10 500	80
		$H_2Pc$	0.85*	360		
		$Q$	1.1*	360		
PE	0.710	TBPc	0.22	200	900	40
		$H_2Pc$	0.08*			
PIB	0.715	TBPc	0.18	240	2 600	60

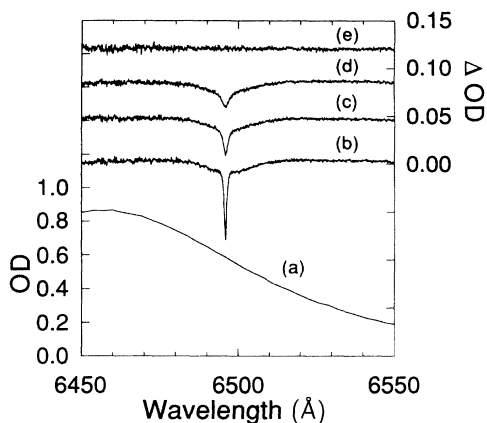


FIG. 3. Thermally induced change of a hole burned in TPP/PS. The burn and the excursion temperatures were 9, 53, 89, and 183 K. The area ratio of the ZPH to the sum of the ZPH and PSH at 9 K was 30%. The area of the sum of ZPH and PSH was mostly conserved after a 52 K cycle, whereas the area of ZPH was decreased by 30%.

tween 100 and 180 K, whereas the area of the ZPH itself was decreased about 30% (10% of the initial total hole area) after the 50 K cycle, which was out of our experimental accuracy. Another example is the case of TPPc/PS [Fig. 2(a)]. In both cases of TPPc and TPP, the area loss of the ZPH was compensated by PSH. This is direct evidence that the TIHF of the ZPH was due to broad TISD. Furthermore, the area of PSH suddenly decreased above 100 K, which meant that the photoproduct states were uniformly filled, contradicting the spectral diffusion process. The center protons of the used dyes are in small cages of phthalocyanine or a porphine ring and shielded from the environmental disturbance. We believe that TIHF of the total hole above 100 K would be due to thermally activated backreaction due to rotation of the center protons, whereas TIHF of the ZPH below 100 K would be due to relaxation process of the local environment of the amorphous impurity-matrix systems.

### B. Spectral diffusion

For the series of TBPC doped systems, the values of  $K$  were well correlated with the packing densities of the matrix polymers calculated by Bondi (Fig. 4). Those for TPPc, TPP, H<sub>2</sub>Pc, and  $Q$  were also mostly on the same curve.

According to Köhler and Friedrich, the change of hole width due to tunneling is

$$\Delta\Gamma_{\text{hole}} = \frac{1}{2} CPk(T - T_b) \int_0^{\infty} dx \frac{x \operatorname{sech}^2 x}{\cosh x \sinh x} \quad (3)$$

Here,  $k$  is the Boltzmann constant,  $T$  is the excursion temperature,  $T_b$  is the burning temperature,  $C$  is the coupling constant between TLS and a dye molecule, and  $P$  is the distribution of TLS states.<sup>10,11</sup> These parameters depend on the physical picture of TLS, what the TLS is, and how the TLS couples with the dye molecules. The value of  $K$  for OEP/PS was smaller than those for the

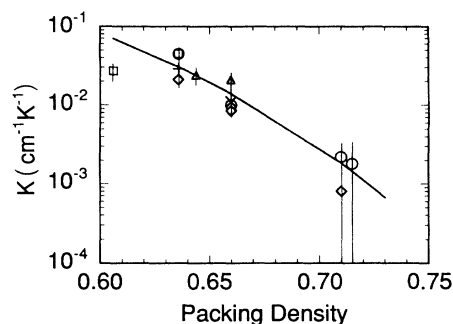


FIG. 4. Dependence of the values of  $K$  on the packing density of the matrix polymers (+: OEP; ○: TBPC; △: TPPc; □: TPP; ◇: H<sub>2</sub>Pc; ×:  $Q$ ). Matrix polymers were P4MP1, PS, o-MePS,  $\alpha$ -MePS, PMMA, PE, and PIB from left to right. The data for H<sub>2</sub>Pc and  $Q$  were collected from Refs. 12 and 13. The line is a theoretical fit according to Eq. (8) where  $K_0 = 1800$  and  $\xi v^*/v_0 = 4$ .

others. TISD comes from a change of the distribution of the perturbation by reorientations of the matrix molecules. On the other hand, an inhomogeneous distribution is determined by the maximal set of the possible static orientation. If the interaction contributing to TISD and an inhomogeneous distribution was common, it would be reasonable to consider that they are correlated with each other. Indeed, both  $K$  and  $\Gamma_{\text{inh}}$  for OEP/PS was smaller than it was for other dyes in PS (Table I). The inhomogeneous widths for other used systems were mostly the same and the normalization would have been automatically achieved. The inhomogeneous width for H<sub>2</sub>Pc was ambiguous because it was not easily dissolved and the PHB active band was hidden in the large association peak. The independence of  $K$  for the PS matrix of the guest dye molecules shows that  $C$  is mostly independent of the series of the studied dye molecules. The correlation between  $K$  and  $\rho$  shows that  $P$  should be determined by the packing density. We will introduce a free volume model to account for the relation.

The basic principle is the entropical transport of the free volume. The free volume is frozen at low temperature. Once temperature is increased, the frozen free volume is partially melted and the fluctuation of the free volume increases. When the fluctuated free volume exceeds over some critical value ( $v^*$ ), molecules jump in the voids and the free volume is transported. If the temperature is lowered in succession, the transported free volume is frozen. The heating and the cooling are so slow that the change of the system is isothermal and we always measure the new equilibrium states. Each transport would lead to change of the strain field. In the first approximation, each of them acts as a source of the elastic dipole field. The dyes feel the change of strain field averaged within a shell where the elastic interaction can reach. The change of the strain field gives an additional hole width, which is TISD. Because dipole interaction is a fairly long-range interaction, the interacting shell could be extended in space as large as needed to explain the size of spatially extended  $i$ -TLS.<sup>18</sup> The role of the free volume

in the burning process of a nonphotochemical hole was first pointed out by Shu and Small.<sup>19</sup> We have also investigated nonphotochemical hole burning in some polymer matrices and observed a correlation between the packing density and the burning efficiency.<sup>20</sup> In the Shu-Small model, the origin of the motion of the free volume is local annealing due to *i*-TLS transition which is triggered by electronic excitation. However, the role of the free volume and *i*-TLS should be modified in a thermal process. We think that the transfer of the free volume itself is the *i*-TLS transition.

We assume that  $P$  is proportional to the number of the distribution of the free volume. The system is divided into small units with neglecting their molecular individualities and they are numbered. Let the number of monomer units in the  $i$ th unit be  $n_i$ . And let the molar free volume in the  $i$ th unit be  $v_i$ . We have

$$\sum_i n_i = N, \quad (4)$$

$$\gamma \sum_i v_i n_i = v_f, \quad (5)$$

where  $N$  is the total number of the monomer units and  $v_f$  is the total free volume in the system.  $\gamma$  is a ratio of the amount of the free volume contributing to the redistribution of the total free volume. The free volume is an excess of unpacked volume over a critical value, which can be transported without change of the free energy. Cohen and Grest called it as a liquidlike free volume. The unpacked volume which does not excess over  $v^*$  is frozen at low temperature and is called as a solidlike one. The number of partition is

$$\Omega = N! / \prod n_i! . \quad (6)$$

By maximizing  $\Omega$ , assuming that  $N$  and  $v_f$  are constant, and passing to the continuum limit for the  $v_i$ , an average distribution function of free volume is obtained as<sup>21</sup>

$$p(v) = \left[ \frac{\gamma}{v_f} \right] \exp \left[ -\gamma \frac{v}{v_f} \right]. \quad (7)$$

Here, we make an assumption that the total free volume is proportional to the unpacked volume ( $v_u$ ). Then Eq. (4) is replaced by

$$p(v) = \left[ \frac{\xi}{v_u} \right] \exp \left[ -\xi \frac{v}{v_u} \right], \quad (8)$$

where  $\gamma/\xi$  is the ratio of the total free volume to the unpacked volume. We assume that the dyes coupled with TLS via elastic interaction. The dependence of  $C$  on the chemical structure of polymers and the size of voids was assumed to be weaker than the exponential dependence of size distributions. The fraction of the number of the free volume contributing to TISD is obtained by integrating  $p(v)$  over from  $v^*$  to infinity. The value of  $v_u$  is calculated from Bondi's packing density as

$$v_u = v_0(1 - \rho), \quad (9)$$

where  $v_0$  is the total volume. The coupling constant  $C$  and other numerical terms are lumped into a constant  $K_0$ . Now we can obtain  $K$  as

$$K = K_0 \exp \left[ -\xi \frac{v^*}{v_0(1 - \rho)} \right]. \quad (10)$$

The curve plotted in Fig. 1 is

$$K = 1800 \exp[-4/(1 - \rho)].$$

By setting the values of Eq. (10) to Eq. (8) and integrating from  $v^*$  to infinity, the fraction of the freely redistributing free volume (liquidlike free volume) to the total free volume at very low temperature was estimated as  $10^{-4} - 10^{-6}$ .

#### IV. CONCLUSION

Thermally induced change of spectral holes was investigated for photoautomerization systems in various polymer matrices. TIHF of PSH could be mostly ignored up to 100 K, where TIHF of ZPH obeyed the law of the square root of the excursion temperature. The rate of TISD was well correlated with the packing density of the matrix polymer. The free volume model of TISD was derived. The free volume was defined as a part of the unpacked volume. It fluctuates at low temperature. When temperature is raised and the fluctuation of it exceeds a critical value, molecular transport occurs. Using a standard method of statistical physics, a Doolittle-type equation was derived. In view of the free volume model, TLS transition is considered to be a fluctuation of the free volume. The fraction of the number of the free volume contributing to TLS transition to the total free volume was estimated to be about  $10^{-4} - 10^{-6}$ .

<sup>1</sup>*Amorphous Solids-Low Temperature Properties*, Vol. 24 of *Topics in Current Physics*, edited by W. A. Phillips (Springer, Berlin, 1981).

<sup>2</sup>A. C. Anderson, *Phys. Rev. B* **34**, 1317 (1986).

<sup>3</sup>U. Buchenau, M. Prager, N. Nücker, A. J. Dianoux, N. Ahmad, and W. A. Phillips, *Phys. Rev. B* **34**, 5665 (1986).

<sup>4</sup>C. Laermans and A. Vanelstraete, *Phys. Rev. B* **34**, 1405 (1986).

<sup>5</sup>M. H. Cohen and G. S. Grest, *Phys. Rev. Lett.* **45**, 1271 (1980).

<sup>6</sup>E. J. Cotts, A. C. Anderson, and S. J. Poon, *Phys. Rev. B* **28**, 6127 (1983).

<sup>7</sup>J. P. Sethna and K. S. Chow, *Phase Trans.* **5**, 317 (1985).

<sup>8</sup>W. Köhler and J. Friedrich, *J. Chem. Phys.* **88**, 6655 (1988).

<sup>9</sup>W. Köhler and J. Friedrich, *Phys. Rev. Lett.* **59**, 2199 (1987).

<sup>10</sup>W. Köhler and J. Friedrich, *Europhys. Lett.* **7**, 517 (1988).

<sup>11</sup>W. Köhler, J. Zollfrank, and J. Friedrich, *Phys. Rev. B* **39**, 5414 (1989).

<sup>12</sup>G. Schulte, W. Grond, D. Haarer, and R. Silbey, *J. Chem.*

- Phys. **88**, 679 (1988).
- <sup>13</sup>W. Köhler and J. Friedrich, *Ber. Bunsenges. Phys. Chem.* **91**, 858 (1987).
- <sup>14</sup>A. Bondi, *J. Phys. Chem.* **28**, 649 (1967).
- <sup>15</sup>A. Bondi, *Physical Properties of Molecular Crystal, Liquid and Glass* (Wiley, New York, 1968).
- <sup>16</sup>B. L. Fearey and G. J. Small, *Chem. Phys.* **101**, 269 (1986).
- <sup>17</sup>J. Friedrich, D. Haarer, and R. Silbey, *Chem. Phys. Lett.* **95**, 119 (1983).
- <sup>18</sup>B. L. Fearey, T. P. Carter, and G. J. Small, *Chem. Phys.* **101**, 279 (1986).
- <sup>19</sup>L. Shu and G. J. Small, *Chem. Phys.* **141**, 447 (1990).
- <sup>20</sup>J. Takahashi, J. Tsuchiya, and K. Kawasaki (unpublished).
- <sup>21</sup>M. H. Cohen and G. S. Grest, *Phys. Rev. B* **20**, 1077 (1979).