Free Volume Distribution of Poly(alkyl methacrylate)s and the Effect of Inclusion

Takashi Yamashita, Nao Yoshida, Noubaki Wada

*Department of Pure and Applied Chemistry, Faculty of Science and Engineering,
Tokyo University of Science
2641 Yamazaki, Noda 278-8501, Chiba, Japan*

Free volume distribution of poly (methyl methacrylate) and their alkyl ester derivatives was determined with photo-reactive probe techniques. With azobenzene as the photochromic probe, fairly large part of the free volume in PMMA is found to be the more reactive cavity than the reaction in solution, while there is some fraction of free volume whose quantum of the photoreaction is zero. With the increase in the alkyl chain length, increase in the average free volume is observed. The average free volume becomes smaller for branched alkyl esters due to occupation by the dangling chain. Inclusion complex with β -cyclodextrin makes the free volume distribution monodispersely, while the distribution is wide with γ -cyclodextrin inclusion complex.

Keywords: Free volume distribution, methacrylate, inclusion, photo-reactive probe

1. Introduction

Most of organic photo-functional materials use the reactions in polymer solids, and the reactions in solid state polymer are different from those in solutions, due to the restriction of molecular mobility, inhomogeneity of the matrix, existence of various relaxations, and so on. Those reactions take place in the nano-sized free volume in polymer, which plays a great role to control the solid state photo reactions.

We have investigated the free volume in polymer with photo reactive probes or fluorescence probes to obtain the information on the nano space. Recently we have successfully obtained the information on the free volume distribution in poly(methyl methacrylate) in the term of quantum yield distribution of the photo-reactive probes. This is one of the most powerful ways to estimate the inhomogeneity of solid state polymer, which critically control the reaction, diffusion, and relaxation of guest molecules to perform the photo-functions.

2. Experimental

2.1 Sample preparation

Azobenzene was purchased from Tokyo Kasei Kogyo Co., and was purified by recrystallization from ethanol. Methyl methacrylate (MMA, Tokyo Kasei Kogyo Co.) was distilled under vacuum before use. Sample polymer films were prepared by heating a mixture of 0.1mol/l α,α -azobisisobutyronitrile, azobenzene and methyl methacrylate (MMA) up to 50°C for 14 hours to polymerize in bulk state.

The prepared films were annealed by heating to certain temperatures for 1 hour in an oven, then they were cooled to room temperature for overnight or quenched rapidly.

3. Results and Discussion

3.1 Quantum yield distribution of AZB in PMMA

Fig 1 shows the spectral change of AZB in ethanol solution under photoirradiation at 317 nm. Decrease in the absorption band at 310 nm is observed accompanied by increase in the absorption at 450nm, showing that *trans* to *cis* photoisomerization of the AZB occurred. Isosbestic points at 236nm, 268nm and 372nm are also observed

Progress in the photoisomerization under steady

Figure 1 Change in the absorption of AZB in ethanol solution under photoirradiation at 325 nm.

Figure 2 Quantum yield distribution of AZB in ethanol solution and in PMMA solid.

state photoirradiation is described as Eq. (1), where, C_{trans} and C_{cis} [mol l⁻¹] are the concentration of photochromic molecules, ϵ_{trans} and ϵ_{cis} [M⁻¹cm⁻¹] are their molar extinction coefficients at the photo irradiating wavelength, and $\phi_{trans \rightarrow cis}$ and $\phi_{cis \rightarrow trans}$ are the quantum yields of the photoreaction, respectively. S [cm²] is the sample area, l [cm] is the sample thickness, I_0 [Einstein cm⁻²s⁻¹] is the incident light intensity, and OD is the optical density of the sample, i.e. total optical density both *trans* and *cis* form. Eq.1 can be transformed into Eq.2 using the OD of the sample, where OD_0 and OD_∞ are the optical density at photo irradiation wavelength before irradiation and after photo stationary state, respectively.

$$\begin{aligned} & -\frac{d(10^{-3} C_{trans} S l)}{dt} \\ &= I_0 S \frac{\epsilon_{trans} C_{trans}}{\epsilon_{trans} C_{trans} + \epsilon_{cis} C_{cis}} (1 - 10^{-OD}) \phi_{trans \rightarrow cis} \\ & - I_0 S \frac{\epsilon_{cis} C_{cis}}{\epsilon_{trans} C_{trans} + \epsilon_{cis} C_{cis}} (1 - 10^{-OD}) \phi_{cis \rightarrow trans} \quad (1) \end{aligned}$$

$$\begin{aligned} \frac{dOD}{dt} &= 10^3 I_0 (\epsilon_{trans} \phi_{trans \rightarrow cis} + \epsilon_{cis} \phi_{cis \rightarrow trans}) \\ & \times (1 - 10^{-OD}) \left(\frac{OD_\infty}{OD} - 1 \right) \quad (2) \end{aligned}$$

The ϵ_{trans} and ϵ_{cis} , molar extinction coefficients of *trans* and *cis* forms, respectively, were obtained by the "two wavelength irradiation method", which can obtain the molar extinction coefficients of

unstable isomers without their isolation. Fitting experimentally obtained OD change to the eq2 gives the quantum yield of photochromic reaction of AZB.

Fig 2 shows the quantum yield distribution of AZB in ethanol and in PMMA solid. The figure shows that the quantum yield of photoisomerization of AZB in PMMA is 0.08. On the other hand, OD change of AZB in PMMA under photoirradiation could not fit to the theoretical curve of Eq(2). Then we deconvoluted the observed OD change assuming the quantum yield distribution obeys Gaussian. The quantum yield of photoisomerization of AZB in PMMA has wide distribution from 0 to 0.2. Quantum yields of certain reaction should be usually specific to a molecule, and so the distribution of the quantum yield should be attributed to the effect of polymer matrix surrounding the AZB molecules. In other word, the distribution of the quantum yield reflects inhomogeneity of free volume in matrix polymer.

A certain fraction with quantum yield of zero exists, which corresponds to the molecules in a free volume whose size is smaller than the critical free volume required for the photochromic reaction. Fairly large part of the distribution has the quantum yield larger than that in solution, to our interest. This can be explained that a molecule in large vacancy reacts faster than that in solution because the molecule does not affected by even small solvent molecules. In other words, the

large vacancy acts as a nano scale reactive flask in polymer solid.

3.2 Effect of Polymer Structure

Fig 3. shows the quantum yield distribution of photochromic reaction of AZB in poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA) and poly(butyl methacrylate) (PnBuMA) in order to compare the effect of matrix. The average quantum yields for the photoreaction are 0.089, 0.10, and 0.11 for PMMA, PEMA, and PnBuMA, respectively. Figure 3

The figure shows that quantum yield increases as the increase in the alkyl chain length. In addition, only PnBuMA has narrow distribution, different from others. Table 1 summarizes quantum yields of photochromic reaction, Φ , half width value, H , glass transition temperature T_g ,

Figure3 Quantum yield distribution of photochromic reaction of AZB in PMMA, PEMA, and PnBuMA.

Table 1. Photophysical constants and polymer properties of photochromic reaction of AZB in various poly(alkyl methacrylate)s. quantum yields of photochromic reaction, Φ , half width value, H , glass transition temperature T_g , and density of the polymers, ρ .

	Φ	H	T_g	ρ
PMMA	0.089	0.084	105	1.15
PEMA	0.100	0.083	65	1.1
PnBuMA	0.110	0.004	20	1.05

and density of the polymers, ρ . The average quantum yields are explained that they are dependent to average free volume contents, which are in turn dependent to matrix polymer density. The narrow distribution of PnBuMA is explained by its T_g , namely, the photoreaction of AZB in PnBuMA had took place in the anisotropic state (melting state) of the matrix polymer because T_g of PnBuMA is below room temperature (20°C). The free volume distribution is thought to be averaged in the melting state above T_g by the fast molecular motion and exchange of free volume.

Fig 4 shows the quantum yield distribution of AZB in various methacrylate polymers with branched alkyl groups, namely, poly methacrylates with isopropyl (PiPrMA), tert-butyl (PtBuMA), and iso-butyl (PiBuMA) groups.

Figure 4. Quantum yield distribution of photochromic reaction of AZB in PiPrMA, PtBuMA, and PiBuMA

Table 2. Photophysical constants and polymer properties of photochromic reaction of AZB in various branched poly(alkyl methacrylate)s. quantum yields of photochromic reaction, Φ , half width value, H , glass transition temperature T_g , and density of the polymers, ρ .

	Φ	H	T_g
PIPrMA	0.041	0.017	75
PIBuMA	0.046	0.008	54
PIBuMA	0.05	0.008	

The average quantum yields of photochromic reaction of AZB are 0.041, 0.046, and 0.050 in PiPrMA, PtBuMA, and PiBuMA, respectively. These average quantum yields are also thought to be dependent to the matrix polymer density, but those data are not available. Half-width values for the distribution are relatively small compared to those of linear alkyl esters. The half-width value narrowing is thought to be the effect of the blanch ester chain, whose dangling chains fill the free volume of the polymer to decrease average quantum yields and make the space relatively homogeneous.

3.3 Effect of Inclusion

Nano-space in solid state polymer shown in Fig 2 is interesting because a part of the nano space provides guests high photo reactivity, and which can improve photo-functional materials based on solid state reactions in polymers.

In order to establish such nano-space with homogeneity and high efficiency, host compounds is incorporated in polymer to include AZB in the cavity. Figure 5 shows the structure of γ -cyclodextrin, whose cavity can include AZB. Both β -cyclodextrin and γ -cyclodextrin is used as the host of AZB, and the host-guest complexes are dispersed in PMMA, shown in Figure 6.

Figure 5. Structure of γ -cyclodextrin.

Figure 7 shows NMR spectra of the AZB and β -CD before and after complexation. The protons 3, and 5 of β -CD, which locate inside of the cavity (Figure 8) shift to the higher magnetic fields after mixing AZB and β -CD, showing the AZB is included in the CD cavity.

Figure 6. Structure of β -CD and γ -CD.

Figure 7. NMR spectra of β -CD in the presence of AZB (Upper), and without AZB (lower).

Figure 8. Steric structure of a unit of CD. Protons 3 and 5 locate inside the CD cavity.

Figure 9 UV spectra of AZB, g-CD, and the mixture of AZB and g-CD.

On the other hand, no spectral change in NMR was observed for the mixture of AZB and γ -CD, possibly due to small interaction between the host and guest due to the larger cavity size. Figure 9 shows the UV spectra of the mixture of AZB and γ -CD. The absorption of AZB shifts to the longer wavelength region after addition of γ -CD, showing that AZB is included in CD cavity.

Figure 10 shows the quantum yield distribution of the photoreaction of AZB-CD inclusion, which are dispersed in PMMA matrix. With β -CD, the photochromic reaction proceeded quite homogeneously as same as the reaction in solution even dispersed in inhomogeneous amorphous polymer solid. The homogeneity of the reaction is achieved by the separation of AZB

Figure 10 Quantum yield distribution of photochromic reaction of AZB in PMMA, AZB/ β -CD complex in PMMA, and AZB/ γ -CD in PMMA

by the CD cavity. Many advanced photo resists for microlithography is based on the chemical amplification today, and the homogeneity of acid diffusion is critical to achieve fine resolution. Using β -CD complex homogeneous photoreaction is achieved, but the average quantum yield is not so high, possibly due to the restriction of local free volume around AZB. In order to study cavity size effect on the photochemistry of AZB/CD complex, the photoreaction of AZB in γ -CD was investigated.

Distribution of the quantum yield of the photochromic reaction of AZB included in γ -CD and dispersed in PMMA is relatively narrow compared to that without CD, but the reaction is not perfectly homogeneous (Fig 10). One of the reasons may be because AZB is excluded from the CD cavity that the situation becomes similar to the sample which AZB is dispersed in PMMA. However the assumption is not true because the quantum yield distribution should be the same as that of AZB/PMMA sample if the AZB is excluded, but there are no AZB component whose quantum yield is larger than 0.11. This shows the quantum yield distribution of AZB/ γ -CD/PMMA does not reflect the distribution of AZB in PMMA. One of the most possible explanation is that the γ -CD cavity is so large that the inside of the cavity is no more homogeneous than β -CD, because AZB molecules locate inhomogeneously inside of the cavity or PMMA polymer chain partially penetrates into the cavity to bring inhomogeneity.

3.4 Effect of Thermal Treatment

Figure 11 shows the change in the quantum yield distribution of AZB/ β -CD complex in PMMA, shown in Figure 10. The quantum yield is so homogeneous that the distribution is negligibly small. Apparent distribution of the photoreaction of AZB/ β -CD in PMMA in Figure 11 is contributed to the effect of experimental condition and the horizontal axis of the figure is too expanded.

Average quantum yield of AZB/ β -CD in PMMA is 0.06 just after bulk polymerization, however the average quantum yield increased to 0.066 and 0.065 after annealing at 80°C and 100°C, respectively. The average quantum yield became 0.06 again after thermal treatment above T_g of PMMA (150°C). These phenomena can be

explained in relation to the relaxation of polymer chain during annealing.

Figure 11 Change in the quantum yield distribution of AZB in β -CD in PMMA

The AZB/ β -CD complex after bulk polymerization may be distorted caused by the internal pressure during polymerization of MMA. Polymer chain relaxation during thermal treatment up to 100°C also relaxed the distortion of CD to increase the average quantum yield of photoreaction of AZB. However, the thermal treatment above T_g makes CD distorted again.

These phenomena are quite contrast to the case of AZB/PMMA. Average quantum yield of AZB relatively decreases during thermal treatment due to the relaxation and molecular packing of polymer chain, which also decreases the quantum yield distribution. Thermal treatment above T_g decreases the average quantum yield and increased the distribution again because the polymer chain becomes random state above T_g .

This difference in the thermal treatment effect is explained that the AZB/PMMA gives the information on the bulk region, while AZB/ β -CD/PMMA gives the information on vacant region.

4 Conclusion

Quantum yield distributions of AZB in PMMA and various methacrylate polymer were measured to find the distribution reflect homogeneity of polymer matrix. Average quantum yield

distribution corresponds to the polymer density, and the distribution width reflects the state of polymer. Quantum yields of AZB in methacrylate polymers with blanched alkyl esters were relatively small compared to those in liner alkyl esters due to spatial filling by the dangling chains. β -CD inclusion makes the quantum yield distribution perfectly homogeneous, while with γ -CD the distribution is still inhomogenous due to penetration of polymer chain.

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