Measurement of Acid Diffusion from a Photoacid Generator in Polymer Solids by using Nile Blue A Base

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In chemically amplified resists, acid diffusion from a photo-acid generator (PAG) is one of the important factors which control their efficiency. This paper reports observation and estimation of the acid diffusion from PAG (p-nitrobenzyl 9,10-dimethoxyanthracene-2-sulfonate, NAS, or 2,4-dinitrobenzyl tosylate, DNBT) in polymer solids (PMMA or PEMA) by using a diffusion-controlled acid-base reaction. Nile Blue A base used as a basic indicator changes its absorption peak by protonation. The rate constants and hence the diffusion coefficients of acids from the PAG in polymer solids were estimated from second-order reaction kinetics.

Keywords: Chemical amplification, Photo-acid generator, UV spectrum, Acid diffusion, Nile Blue A base, PMMA, PEMA

1. Introduction

Chemically amplified resists[1,2] have emerged as one of the most sensitive resists for deep UV, e-beam, and X-ray lithographies. Its concept is that the quantum yield of a photo-induced reaction is amplified effectively by an acid-catalyzed chain reaction in the resist. This means that a resist of this type is affected by the movement of an acid in it. So, the acid diffusion from a photo-acid generator (PAG) is regarded as one of important factors which control sensitivity, resolution, contrast, and other properties of chemically-amplified resists.

The estimation of diffusion coefficients of acids in polymer solids has been carried out by scanning electron microscope (SEM) observation after exposure and development of positive resists.[3,4] This method utilizes acid-catalyzed reactions, and the result includes the effect of chemical reaction factor. The

diffusion area of acids from PAG and kinetic chain length of chemically-amplified photocrosslinking reaction of a photosensitive polyimide were also evaluated from the extent of reaction[5].

In order to remove the influence of chemical reaction factor, we have tried to observe and estimate acid diffusion coefficients in polymer solids by using a diffusion-controlled acid-base reaction. We use Nile Blue A base (NBA_b) as a basic indicator. It is so reactive with acidic substances that its protonation proceeds irreversibly resulting in NBA cation (NBA⁺) except under basic condition.[6]

Figure 1 Absorption spectra of NBAb in PMMA before and after exposure, and during PEB at 110°C. Arrows show the direction of change during PEB. PEB times are shown beside the arrow.

Its UV absorption spectrum also changes with the protonation (Figure 1). The absorbance, film thickness and molar extinction coefficient, ϵ , give values of each initial concentration of an acid or NBAb, and the change in concentrations of NBAb and NBA⁺. As a result second-order reaction plots and rate constants can be obtained. The rate constant, k ($M^{-1} s^{-1}$), for a bimolecular diffusion-controlled reaction like this system, is given by Smoluchowski equation[7,8] :

$$k = 4\pi RDN_A \quad (1)$$

where R (cm) is the radius of the reaction sphere, D ($cm^2 s^{-1}$) is the sum of the diffusion coefficients of two reacting species, and N_A is Avogadro's number divided by 10^3 . Thus we obtain k and D and discuss acid diffusion in polymer solids.

In the present paper, the diffusion of acid from PAG after post-exposure baking (PEB) is studied by using the reaction of the acid with NBAb. Poly(methyl methacrylate) (PMMA) and poly(ethyl methacrylate) (PEMA) are used as polymer matrices to investigate influence of glass transition temperature (T_g). p-nitrobenzyl 9,10-dimethoxyanthracene-2-sulfonate (NAS) and 2,4-dinitrobenzyl tosylate (DNBT) are

Figure 2 Second-order plots for the reaction NBAb with the acid from NAS in PMMA at 115°C.

used as PAG to investigate the influence of the size of counter ions.

2. Experimental

Materials. Acetonitrile (AcCN) was supplied by Dojin Co. and used after dehydration with molecular sieves. Other solvents used in this study were supplied by Wako Pure Chemical Co. Dichloromethane and tetrahydrofuran (THF) were used after distillation. Nile Blue chloride was supplied by Sigma Chemical Co, and transformed to Nile Blue A base by the extraction into benzene from its aqueous alkaline solution. PMMA (Wako Pure Chemical Co.) was used after reprecipitation. PEMA, polymerized

previously in our laboratory[9], was used after reprecipitation. NAS[10] and DNBT[11] were synthesized according to the methods described in the literatures. IR and NMR spectra of the products were ascertained with a infrared spectrophotometer (JASCO Model IR-700) and a NMR spectrometer (JEOL JNM-GX400 FT-NMR), respectively. Other materials were from commercial sources and used without further purification.

Film Preparation and UV Exposure. A polymer was dissolved into NBAb solution in AcCN, and then PAG solution in AcCN was added. The polymer film was cast from this solution in teflon pan. It was dried at 50°C for 40 h and at 55°C for 1.5 h in vacuo. In addition, it was dried at 119°C for PMMA or at 75°C for PEMA each for 1.5 h in vacuo. The film thickness was measured with a micrometer (Mitsutoyo 293 Series). Films were exposed to a filtered 250-W high-pressure mercury lamp at 436 nm for 2 h in case of NAS and at 350~400 nm for 7 h for DNBT.

Measurement of Absorption Spectra during Post-exposure Bake (PEB). The PEB of films was carried out in a heating furnace (Yamato Muffle Furnance FP22) or in a thermostat (Oxford Model DN-704), and the changes in their UV spectra during heating were recorded on a UV-VIS spectrophotometer (Jasco Model V-570). PMMA films were finally heated at 130°C and for PEMA at 100°C in order to evaluate the initial concentration of photo-generated acid from the NBAb concentration at complete reaction.

The heating at 130°C for 1 h of a film containing NAS and NBAb without exposure to the mercury lamp showed substantially no absorption change, which assures no occurrence of thermal protonation of NBAb in the present experimental conditions.

3. Results and Discussion

Absorption Spectra of NBAb and Second-order Plots. The absorption peak of NBAb in Figure 1 decreases and that of NBA⁺ increases with the extent of post-exposure bake (PEB). It shows that the acid produced from NAS as a PAG and not having reacted with NBAb directly during exposure diffuses during the PEB to react with NBAb. The mechanism of photo-acid generation from NAS[12] and DNBT[11] has been already described.

When NBAb with the initial concentration, a_0 , and the acid with the initial concentration, b_0 , react, the rate of the increase in the product (NBA⁺) concentration, x , is given by eq 2,

$$\frac{dx}{dt} = k(a_0 - x)(b_0 - x) \quad (2)$$

where k ($M^{-1} s^{-1}$) is the second-order rate constant. Eq 2 is transformed to eq 3.

$$kt = \frac{1}{(a_0 - b_0)} \ln \frac{1 - (x/a_0)}{1 - (x/b_0)} \quad (3)$$

The absorbance of such spectra as in Figure 1, film thickness, ϵ_{NBAb} ($3.6 \times 10^4 \text{ cm}^{-1} M^{-1}$ at 504 nm in PMMA) give values of a_0 , b_0 and x in the right-hand side of eq 3.

The second-order plots according to eq 3 for the reaction of NBAb with the acid from NAS in PMMA at 115°C are shown in Figure 2. They give almost straight line, and the rate constants, k , can be obtained from the linear approximation of the slope. The value of k for the reactions in PMMA films with various initial concentrations of NBAb, a_0 , became almost constant for the region of $a_0 \geq 4.0 \times 10^{-4} M$, but it scattered with large errors when a_0 is below $4.0 \times 10^{-4} M$. So, the initial concentration of a_0 in the following measurements was set to be in the range of $4 \sim 7 \times 10^{-4} M$.

Temperature Dependence of Second-order Plots. The second-order plots according to eq 3 for the reactions of NBAb with the acid from NAS in PMMA and PEMA at different PEB temperatures are shown in

Figure 3. The slopes of these plots, k , increase with the increase in PEB temperature. It shows the temperature dependence of acid diffusion in polymer solids.

The reaction proceeds in the second-order kinetics when the PEB temperature, T , is above T_g of the polymer (PMMA: 105°C[13], 110°C[14], PEMA: 65°C[13]) where acid diffuses, but at $T < T_g$ it deviates from the second-order kinetics. This slowing down in rates during the reaction is a characteristic phenomenon to the reaction in an amorphous solid below T_g [15] and shows that acid diffusion is not constant owing to a lack of free volume necessary for the acid to diffuse. On the other hand, the diffusion proceeds according to the second-order kinetics at $T > T_g$ owing to enough free volume for the acid to diffuse constantly. Thus, the plots in PMMA at 75°C deviate from a straight line but those in PEMA at 75°C, on the other hand, fit with a straight line. Figure 4 shows Arrhenius plots for k . When second-order plots deviate from a straight line, we evaluated k from the initial slope of the plots for 0~1500 sec where they seem comparatively straight. The Arrhenius plots for both PMMA and PEMA show bending points, which reflect the influence of T_g . The values of activation energy below and above T_g were obtained from the slopes in Figure 4 and are summarized in Table 1.

Diffusion Coefficients. In the present study, eq 1 can be replaced by eq 4,

$$k = 4\pi(R_{acid} + R_{NBAb})(D_{acid} + D_{NBAb})N_A \quad (4)$$

where we approximately regard R_{acid} and R_{NBAb} as the radius of the rigid sphere model of each moiety. If the acid from PAG exists and diffuses as a simple proton in polymer solids, eq 4 is replaced by eq 5 since $R_{acid} \ll R_{NBAb}$ and $D_{acid} \gg D_{NBAb}$.

$$k = 4\pi R_{NBAb} D_{acid} N_A \quad (5)$$

From the values of k obtained and R_{NBAb} (3.2 Å)[16], D_{acid} can be estimated to be in the range of 10^{-13} - 10^{-15} cm² s⁻¹. The diffusion

Figure 3 Second-order plots for the reaction of NBAb with the acid from NAS in PMMA(▲●■◆) and PEMA(△○□◇) at different PEB temperatures indicated in Figure.

Figure 4 Arrhenius plots for second-order rate constants for the reaction of NBAb with the acid from NAS in PMMA(◆) and PEMA(▲).

Table 1 Activation energy, E , for the reaction of NBAb with the acid from NAS in polymer solids.

Matrix	$T_g/^\circ\text{C}$	$E/\text{kJ mol}^{-1}$	
		$T < T_g$	$T > T_g$
PMMA	110	74	142
PEMA	75	43	97

Table 2 Initial rate constants, k , and corresponding diffusion coefficients, D , for the reaction of NBAb with acids from NAS and DNBT in PMMA at PEB temperatures indicated.

PAG	a_0 for NBAb/ 10^{-4}M	b_0 for NBAb/ 10^{-4}M	$k/\text{M}^{-1}\text{s}^{-1}$ at		$D/10^{-15}\text{cm}^2\text{s}^{-1}$ at		$E/\text{kJ}\cdot\text{mol}^{-1}$
			75°C	90°C	75°C	90°C	
NAS	5~6	1.6~1.8	0.44	1.4	1.8	5.6	74
DNBT	4~5	0.7	1.6	3.6	6.6	15	79

mechanism is divided into two cases. When the size of the penetrant is much less than the average hole size in the polymer, it is suggested that diffusion occurs through localized activated jumps from one pre-existing cavity to another. As the size of the penetrant increases or the hole size decreases, this mechanism may cease to be dominant since there are fewer cavities available to accommodate the penetrant molecule. This suggests that diffusion process should become more dependent on the free volume and local chain dynamics of the matrix polymers. Since temperature dependence of the local free volume changes at the glass transition temperature, the change in slope of the Arrhenius plots will be anticipated.[15,17]

Diffusion of simple gases like He or O_2 belongs to the former. If an acid exists and diffuses in polymer solids as a simple proton, its size is so small that it must diffuse like simple gases. But the acid observed in the present study is influenced by T_g of the matrix polymers in its second-order plots and Arrhenius plots. So it is regarded to belong to the latter. Besides, though diffusion coefficients of simple gases in polymer solids are generally in the range of $10^{-5} - 10^{-9}\text{cm}^2\text{s}^{-1}$ [17], those of the acid from NAS in the present study are in the range of $10^{-13} - 10^{-15}\text{cm}^2\text{s}^{-1}$. These suggest that the acid from NAS does not exist or diffuse in polymer solids as a simple proton but diffuses under some interaction with the counter ion, polymer side chain, and so on. Figure 5 shows the difference between the diffusion of acids from NAS and DNBT in PMMA in second-order plots, which gives

Figure 5 Second-order plots for the reaction of NBAb with the acids from different PAG (NAS($\diamond$, $\square$) or DNBT($\blacklozenge$, $\blacksquare$)) in PMMA. PEB temperatures are 75°C($\diamond$, $\blacklozenge$) and 90°C($\square$, $\blacksquare$).

suggestion that the acids in polymer solids should have interaction with their counter ions and their diffusion increases with the decrease in size of their counter ions.

The initial rate constants, k , and corresponding diffusion coefficients for the plots in Figure 5 are summarized in Table 2. The conditions of $R_{\text{acid}} \ll R_{\text{NBAb}}$ and $D_{\text{acid}} \gg D_{\text{NBAb}}$ might not hold in the present case, but the results in Table 2 at least suggest $D_{\text{acid}} > D_{\text{NBAb}}$ since D depends on the size of counter ions of PAG, and they can be used for order estimation of diffusion coefficients in the present system. The order of magnitudes for diffusion coefficients obtained in the present study is near to translational diffusion coefficients of fluorescence dyes whose number of fused-aromatic rings are more than three observed with nonradiative energy

transfer[18] and near-field scanning optical microscopy (NSOM)[19]. These also support the above suggestion of the concern of counter ions for the acid diffusion from photo-acid generators. In the present study, average intermolecular distance between the acid and NBAb is estimated to be in the range of 10 - 15 nm according to Poisson statistics.[20]

4. Conclusion

We observed diffusion of the acids from PAG in PMMA and PEMA by using diffusion-controlled acid-base reaction with NBAb. The method consists of measuring the decrease in absorption spectra of NBAb. It is suggested that the acid diffusion in polymer solids is influenced by T_g of polymer matrices and counter-ion size. The obtained diffusion coefficients are in the range of 10^{-13} - 10^{-15} cm² s⁻¹.

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6. References

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