Effect of Polyethers for Photo and Thermal Decomposition of Photosensitive Diazo Compounds

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Inclusion compound formation of polyethylene glycol (PEG) with p-substituted benzene diazo compounds (SBD) in aqueous solutions was decided from activation energy (E_a) of thermal decomposition, dissociation constant K_d by Lineweaver-Burk plot modified with Michaelis-Menten formula and degradation temperature D_t , and compared with constitution of complex by WinMOPAC calculation. Thermal decomposition rate of p-chlorobenzene diazo compound (ClBD) with PEG was accelerated as with β cyclodextrine (CD) which include the benzene ring of the diazo compound. K_d of ClBD with PEG was larger than that with CD. PEG is not a ring, but a linear molecule. D_t of SBD with PEG in solid was higher than that without PEG300. Effect of molecular weight of PEG for D_t was, in a decreasing order, no additives ~ PEG 300 < PEG600 < PEG 1000 ~ PEG 2000. Thermal decomposition of a diphenylamine-4-diazonium sulfate salt/formaldehyde condensate (DSR) / Polyvinyl alcohol (PVA) resist with PEG was accelerated. Photo decomposition of DSR/PVA resist with PEG 300 and 600 was also accelerated. Benzene diazo compound with PEG 300 was more stable than neat BD from by WinMOPAC calculation.

Keywords: photosensitive diazo compound, 18-crown-6, polyethylene glycol 300, β cyclodextrin,

1. Introduction

The para-substituted benzene diazo compounds (SBD) with electron-donating groups (DSBD) are used as the photoacid generator for micro resists [1], photosensitive emulsions for screen printing resists [2], and UV-fixable thermal recording papers [3-5]. SBD with electron withdrawing substituted (WSBD) were used for acid generators for cationic polymerization. 18-Crown-6 (18C6) complexes with benzene diazonium cation improve photo and thermal stability of diazo compounds [6-11]. Thermal decomposition of less expensive β -cyclodextrin (CD) complexes with diphenylamine-4-diazonium sulfate/formaldehyde condensate / PVA resist (DSR-PVA) was suppressed [11]. DSBD with CD will be improved thermal stability without decreasing sensitivity [12]. The coloring of the DSR/PVA emulsion films was suppressed by inclusion of 18C6 or PEG [11].

In this report, inclusion compound formation of polyethylene glycol (PEG) with p-substituted

benzene diazocompounds (SBD) in aqueous solutions was decided from activation energy (E_a) of thermal decomposition, dissociation constant K_d by Lineweaver-Burk plot modified with Michaelis-Menten formula, and degradation temperature D_t and compared with constitution of complex by WinMOPAC calculation. Application of PEG to DSR / PVA resist was studied by measurement of thermal and photo decomposition.

2. Experimental

2.1 Materials

p-Substituted benzene diazonium tetrafluoroborates (SBD) were precipitated by adding hydrogen tetrafluoroborate to an aqueous solution of the corresponding benzene diazonium chloride prepared from p-substituted aniline. The solid product was recrystallized from ethanol. The conventional DSR photosensitive diazo resin for screen plating and PVA emulsion for screen printing were

purchased from Murakami Screen K.K. The additives used were, PEG300, PEG600, PEG1000, PEG2000 and CD of extra pure grade.

Concentrations of SBD and inclusion compounds in an aqueous solution were 2.5×10^{-4} mol/l, $1.25 \times 10^{-3} \sim 1.25 \times 10^{-2}$ mol/l, respectively. Solid for thermal analysis was formed by dissolving SBD in liquid PEG300 or melted SBD with PEG 1000 or PEG2000.

2.2 Measurements

Thermal decomposition of SBD in an aqueous solution was monitored by measuring the UV absorption intensity at $\lambda_{\max}$ under light-shielded conditions. Photo decomposition of SBD in an aqueous solution was conducted by irradiation with a Toshiba Super High-Pressure Mercury lamp SHL100. The incident energy was 3.1 mW/cm^2 . The absorbances at $\lambda_{\max}$ of UV spectra were measured with a Shimadzu UV-1600 PC spectrophotometer. Thermal degradation temperature was determined by TDA and TGA in solid measured with a Shimadzu ETG-60 Analyzer.

2.3 Computational experiment

Calculation was performed with WinMOPAC ver. 3.5.1a (served by Fujitsu Co. Ltd.) in a personal computer. This software combined a graphical user interface for Z-matrix and MOPAC2002 [13] for calculating engine. The EF routine and MOZYME [13] routine were used for optimizer. The Parametric Method 5 (PM5) was used. For other parameters default values programmed in MOPAC2002 were used.

In order to build a structure of PEG600, a molecular dynamics simulation program of Chem3D Pro ver.10.0 (served by CambridgeSoft) was used. The obtained structure at 300K was optimized with MOZYME routine of MOPAC2002.

3 Results and Discussion

3.1 Inclusion compound formation

3.1.1 Thermal decomposition

Thermal decomposition reaction is as follows:

D : Diazocompound

I : Inclusion compound

P : Product

Dissociation constant $K_d = [\text{D}][\text{I}] / [\text{D} \cdot \text{I}]$

Overall rate of decomposition V

$$V = k_1[\text{D}] + k_2[\text{D} \cdot \text{I}]$$

$$= k_1[\text{D}] + k_2[\text{D}][\text{I}] / K_d$$

$$= (k_1 + k_2[\text{I}] / K_d)[\text{D}]$$

k_1 : rate constant of free (dissociated) D

k_2 : rate constant of complexed D

Apparent rate constants of decomposition of D in the absence and presence of I are defined as k_{un} and k_{obs} , respectively.

$$V = k_{un}[\text{D}] = k_1[\text{D}]$$

Net rate constant of complexed D, $k_{obs} - k_{un}$

Lineweaver-burk plot modified with Michaelis-Menten formula [14,15] is shown as follow

$$1 / (k_{obs} - k_{un}) = K_d / k_2 \cdot 1 / [\text{I}] + 1 / k_2 \quad (2)$$

Para-chlorobenzene diazo compound (ClBD) (2.5×10^{-4} mol/l) complex formed by adding 1.25×10^{-3} and 1.25×10^{-2} mol/l (5 and 50 times of ClBD) of PEG300 was thermally decomposed in an aqueous solution. After thermal decomposition, remaining free ClBD and complexed ClBD was

Fig.1 Arrhenius plots of the rate constants of the neat ClBD and ClBD complexes with PEG300 or 18C6 : ●: ClBD (2.5×10^{-4} mol/l), ○: ClBD + PEG 300 (1.25×10^{-2} mol/l), □: ClBD + 18C6 (1.25×10^{-2} mol/l)

determined photochemically by measuring the intensity of maximum absorption band at 283 nm.

Thermal decomposition of neat (or free) ClBD and complexed ClBD with PEG in aqueous solutions was first-order decomposition.

The plots of the rate constants of ClBD ($k_{un} = k_1$) and complexed ClBD (k_{obs}) with 50 times of PEG 300 versus $1/T$ (Arrhenius plot) are shown in Fig.1.

The plot of 1:50 (molar ratio) showed a straight line, though there was observed a deviation from the line on the plot of the 1:5 PEG complex. In order to compare with 1:50 18C6 complexes, the Arrhenius plot of 18C6 complex is also shown in Fig.1. There is a bending point of the plots of 1:50 18C6 complexes of ClBD. It was reported, there is the bending point of a plots of 18C6 complexes of benzene diazo compound in methanol [7]. ClBD dissociates from 18C6 above 48°C, which causes the diazonium moiety free from the ligand through the entropic effect [7].

Activation energies (E_a) were obtained from the plots and are shown in Table 1.

Table 1. Activation Energy (E_a) and dissociation constant (K_d) of p-chlorobenzene diazonium (ClBD) and PEG - or 18C6-complexed ClBD in an aqueous solution

Diazo compound	E_a (kJ mol ⁻¹)	K_d .
ClBD	120	----
18C6-complexed ClBD <50°C	230 (5.48×10^{-4}) ^a	
>50°C	72	----
PEG-complexed ClBD	72	0.16
CD-complexed ClBD	----	6.5×10^{-4}
		(2.4×10^{-3}) ^b

a : 50°C[6], b : 26°C[15]

E_a 's of PEG-complexed ClBD and 18C6-complexed ClBD (above 50 °C) were 72KJ mol⁻¹. Rate constant, k , of the former compound was larger. Thermal decomposition of ClBD was accelerated, when complexed with PEG containing hydroxy groups at the chain ends. The thermal and photo decompositions of diazocompound were not accelerated by the PEG with methoxy end-groups [16]. PEG includes the benzene ring of diazo compound similarly as CD.

E_a of 18C6-complexed ClBD (below 50 °C) was 230 KJ mol⁻¹ and larger than that of neat ClBD, 120

KJ mol⁻¹. Since 18C6 includes the diazo group of diazo compound below 50 °C[7], the thermal decomposition was suppressed.

3.1.2 Dissociation constant

Dependence of net decomposition rate constant of the complex, k_{obs} - k_{un} , on the concentration of PEG300 used as the inclusion compounds is shown in Fig.2.

Dissociation constant (K_d) of ClBD complex with PEG300 was decided by Lineweaver-Burk plots modified with Michaelis-Menten formula shown in Equation (2).

ClBD (9.0×10^{-4} mol/l) with PEG300 (5~10 times ClBD) or with CD (0.5~10 times) were thermally decomposed at 40°C.

Plots of the net rate constant (k_{obs} - k_{un}) against additive concentrations of PEG was found to show a saturation phenomena. The reciprocal of net rate constants is linearly proportional concentration of additive concentration of PEG300 as shown in Fig.3.

From this result, it was considered that PEG formed a complex with ClBD.

Fig.2 Dependence of decomposition rate constant on the concentration of PEG300 [ClBD : 9×10^{-4} mol/l aqueous solution] 40°C

Fig.3 The relation of the reciprocal of net rate constant of CIBD complex and the reciprocal of PEG300 concentration

Dissociation constants, K_d , was decided from the slope of the the plots and is shown in Table 1. K_d of CD-complexed CIBD is shown in Table 1. K_d of PEG 300 was larger than that of CD. PEG 300 is not a ring, but a flexible linear molecule, so the PEG-complexed CIBD in an aqueous solution was unstable.

3.1.3 Degradation temperature of solid complex

Degradation temperature, D_t , of SBD complexes with PEG of various molecular weights was determined by TDA and TGA measured in solid. Molecular-weight effects of PEG on D_t of the complexes of benzene diazo compound (BD), CIBD and DSR are shown in Fig. 4.

D_t 's of BD and CIBD with PEG 300 were lower than those without PEG300, respectively. D_t 's of DSR with PEG were higher than that without PEG, in an increasing order : no additives ~ PEG 300 < PEG600 ~ PEG1000 ~ PEG 2000. Plots of D_t against molecular weight of BD and DSR were found saturations over molecular weight 600.

PEG600, PEG1000 and PEG 2000 were solid at room temperature. When BD and DSR are included by PEG with molecular weight over 600, they are stable. PEG300 with 6-10 oxygens simi-

larly as 18C6, is liquid and hygroscopic.

Fig. 4 Molecular weight effects of PEG on D_t of PEG-complexes SBD

Diazo compounds are thermally decomposed easily in aqueous solutions, and it is considered that diazo compounds are unstable in presence of hygroscopic PEG300.

3.1.4 Estimation of the constitution of the complex by WinMOPAC calculation

Optimized structures and the heat of formation of PEG300, PEG600, BD and the complex were calculated with WinMOPAC. Calculated heat of formation of BD, PEG300, PEG600 were 1038, -1213, -2434 kJ/mol, respectively. The heat of formation of PEG300-complexed BD and PEG600-complexed BD were -308 and -1492 kJ/mol, respectively. Optimized structure of PEG300-complexed BD and PEG600-complexed BD were shown in Fig.5.

The heat of formation of PEG-complexed BD was smaller than the sum of the heat of formation of starting materials. The stabilization energy of PEG300-complexed BD and PEG600-complexed BD were estimated -133 and -96 kJ/mol, respectively. These results support the formation of in-

clusion compound of PEG with BD.

The calculated optimized structure of PEG-complexed BD suggests, when molecular weight of PEG increases, the influence of hydroxyl end group of PEG becomes less predominantly. Therefore Dt of PEG600-complexed BD is higher than that of PEG300-complexed BD.

Fig. 5 Optimized structure of PEG-complexed BD ;(a): PEG300- complexed BD, (b): PEG600complexed BD

3.2 Application of PEG for Diazo/PVA resist

The PVA films containing diphenylamine-4-diazonium sulfate /formaldehyde condensate (DSR) and PEG (thickness 250 μ m) were stored at 50 $^{\circ}$ C in the dark, and absorbance at λ max (380 nm) of UV spectra was measured every 24 hr.

The thermal decomposition of DSR with PEG of the solid films were studied as shown in Fig.6.

The relative thermal decomposition rate of the films was, in a decreasing order; PEG300 > PEG 600 > PEG1000 > PEG 2000 ~ no additives, and corresponded directly to the reciprocal of molecular weight.

Although DSR with PEG600 was shown to be stable in solid by the experimental data of Dt, the DSR/PVA film was unstable PVA by hygroscopic PEG. for long storage. As thermal decomposition of diazo compounds is ionic reaction, it was accelerated by hygroscopic PVA.

The DSR/PVA films with or without PEG were irradiated with a mercury lamp, and the absorbance at λ max of UV spectra was measured every min. The photodecomposition of the films is shown in Fig. 7.

Fig.6 The thermal decomposition of DSR/PVA film with PEG, Temperature:50 $^{\circ}$ C. Thickness 250 μ m

Fig.7 Photodecomposition of DSR/PVA films with PEG

The relative photodecomposition rates of the DSR/PVA were, in a decreasing order : PEG300 > PEG600 > PEG1000 > no additives ~ PEG 2000. DSR/PVA films with PEG were accelerated except

PEG2000.

The diazo group is bonded with hydroxy group of PEG like a diazo group bonded with a hydroxy group of CD [15]. The diazo included with PEG generates nitrogen gas and an alkoxy and a phenyl radicals via homolysis by irradiation. The homolysis is accelerated by formation of loose complex with PEG [16].

4. Conclusion

PEG300 formed with CIBD a weak complex in aqueous solution. Degradation temperatures of SBD with PEG in solid were higher than that without PEG. The DSR/PVA films with PEG 300 did not show long shelflife, though they showed high sensitivity.

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References

1. K.Harada, M.Kushida, K.Saito, K.Sugita and H.Iida, "Micro- and Nanopattering Polymers" H.Ito, E.Reichmanis, O.Naramasu and T.Ueno, eds., ACS Symp. Ser.706, Amer. Chem. Soc., Washington, D.C., 1998, pp. 126-133
2. K.Harada, M.Kushida, K.Saito, K.Sugita and H.Iida, *J. Imaging Sci. and Technol.*, **46**, 159 (2002)
3. T.Usami, T.Tanaka and S.Ishige, *Electrophotography*, **26**, 115 (1987)
4. Y.Yoshida and S.Tatsuta, *Electrophotography*, **26**, 120
5. R.A.Bartsch, H.Chen, N.F.Haddoch and P.N.Juri, *J. Am. Chem. Soc.*, **98**, 6753 (1976)
6. T.Kuokkanen and P.O.I.Virtanen, *Acta Chem. Scand., ser. B*, **33**, 725 (1976)
7. K.Harada, M.Kushida and K.Sugita, *J. Soc. Photogr. Sci. Technol. Japan*, **46**, 600 (1993)
8. K.Harada, K.Sugita and H.Iida, *J.Imaging Sci. and Technol.*, **38**, 13 (1994)
9. H.Nakazumi, I.Szele, K.Yoshida and H. Zollinger, *Helvetica Chimica ACTA*, **66**, 1721 Y.Yoshida and S. Tatsuta, *Electrophotography*, **26**, 120 (1987)
10. H.Nakazumi, T. Kitao and H.Zollinger, *J. Organic Chem.* **52**, 2828 (1987)
11. K.Harada, M.Kushida, S.Miyagawa, S.Takahara and K.Sugita, *J.Photopolym.Sci.Technol.*, **18**, 187 (2005)
12. K.Harada, W. Aimaiti, M.Nakada, Y. Morihiro, T.Narita, R.Aoki.M.Kushida and K.Sugita, *J.Photopolymer. Sci. Technol.*, **19**, 129 (2006)
13. J. J. P. Stewart, *Int. J.Quant.Chem.*, **58**, 133 (1996)
14. H.Lineweaver and D.Burk, *J.Am.Chem.,Soc.*, **56**, 658 (1934)
15. K.Fukunishi, J.Hira, H.Yamaoka and M. Nomura, *J. Chem. Soc. Perkin Trans. I*, p.991 (1985)
16. K.Harada, M.Kushida, K.Saito and K.Sugita, *Advances in Imaging Materials and Process*, (Proc.of 13th Inter'I Conf. on Photopolymers; H.Ito, P.Rao Varanasi, M.M. Kojasteh and R.Chen, Eds., Soc. Plastics Eng. Inc., Mid Hudson Section, Hopewell Junction, NY, 2003) pp.369-373