Application of Cryptand to Diazo/PVA Resists

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Photo- and thermal reaction of *p*-substituted benzene diazo compounds (SBD) with [2.2.2]-cryptand (CRP) was studied by UV spectrum and degradation temperature (D.T.). Diazo cation of *p*-chloro benzene diazo compound (ClBD) was reacted with lone pair electrons of nitrogen atom of CRP by UV spectrum data. When CRP was added, photodecomposition rate of SBD with electron withdrawing-substituent (WSBD) and of SBD with electron donating-substituent (DSBD) were accelerated two and ten times larger than that without CRP, respectively. D.T. of WSBD with CRP in solid were lower than that without CRP, but D.T. of DSBD with CRP was similar to that without CRP. Photodecomposition rate of a diphenylamine-4-diazonium sulfate salt/formaldehyde condensate (DSR) / Polyvinyl alcohol (PVA) resist with CRP was 3 times higher than that without CRP. Diazo/PVA resist with CRP will be improved in sensitivity without decreasing thermal stability.

Keywords: photosensitive diazo compound, diazo/PVA resist, cryptand, photodecomposition

1. Introduction

The *para*-substituted benzene diazo compounds (SBD) with electron-donating groups (DSBD) are used as the photo acid generator for micro resists [1], photosensitive emulsions for screen printing resists [2], and UV-fixable thermal recording papers [3,4]. SBD with electron withdrawing substituent (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 [5-9]. Thermal decomposition of less expensive β -cyclodextrin (CD) complexes with diphenylamine-4-diazonium sulfate/formaldehyde condensate / PVA resist (DSR-PVA) was suppressed [10]. The coloring of the DSR/PVA emulsion films was suppressed by inclusion of 18C6 or PEG [10].

In this report, [2.2.2]-cryptand (CRP) which the inner radius is similar than it of 18C6 was applied

to *p*-substituted benzene diazo compounds (SBD). Inclusion compound formation of cryptand in methanol was studied by UV spectrum from absorption spectra. Photo- and thermal degradation was followed by UV spectrum. Degradation temperature D.T. was measured by DTA. Stabilization energy of constitution of complex was calculated by WinMOPAC. Application of CRP to DSR / PVA resist was studied by measurement of photodecomposition.

2. Experimental

2.1 Materials

The *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 plate making and PVA emulsion for screen printing were purchased from Murakami Screen K.K. The additives used were, [2.2.2]-cryptand (CRP), boron trifluoride diethyl etherate (BF_3O) and potassium chloride, KCl of extra pure grade.

Concentrations of SBD and inclusion compounds in a methanol 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 prepared by mixing SBD with cryptand. Coating solutions of the resist were prepared by dissolving 0.6 g of the diazo compound in 100 g of the matrix PVA-emulsion in water together with the additives. The resist layers (PVA films) for photodecomposition were coated on to glass plates to a thickness of 15.3 μm .

2.2 Measurements

Thermal decomposition of SBD in methanol was monitored by the ultraviolet (UV) absorbance at λ_{max} under light-shielded conditions. Photodecomposition of SBD in methanol was conducted by irradiation by a Sunhayato Chibi Light Model BOX 1 with fluorescence light (FL-6BL). The incident energy was 2.2 mW/cm^2 . The absorbances at λ_{max} of UV spectra were measured with a Shimadzu UV-1600 PC spectrophotometer. UV spectra of the films were measured with a Shimadzu UV 1600 PC. Thermal degradation temperature was determined by TGA in solid measured with Mescience TG-DTA 2000S Analyzer.

2.3 Computational method

All geometry optimizations and calculation were carried out with semi-empirical methods at the PM5 Hamiltonian in WinMOPAC (ver.3.5.1a, Fujitsu Limited). For other parameters default values programmed in MOPAC2002 [11].

3 Results and Discussion

3.1 UV spectra of CIBD with CRP

UV spectra of CIBD in methanol with addition of various concentration of CRP are shown in Fig. 1. It has been found that the maximum absorption wavelength (λ_{max}) of CIBD ions showed no shift with CRP addition, though the λ_{max} of all the diazo compounds with 18C6 shifted to shorter wavelength [7]. The λ_{max} of CIBD with CD which include did not shift, either [12]. The inner radius of CRP is reported to be 2.4 $\text{\AA}$ [13], but the outer size

of benzene ring containing hydrogen atoms is 7.37 $\text{\AA}$. So CRP can't include the benzene ring of CIBD.

An absorbance of CIBD at λ_{max} 280 nm became lower with addition of CRP. When more than 7 times of moles of CRP was added to CIBD, the absorbance of CIBD became constant, and CIBD may be included or react with CRP.

When 1-naphthol-4-sulfonic acid (NW acid) was added to CIBD, a new absorption appeared at 380 nm due to an azo dye formed by coupling reaction. However, CIBD with CRP showed lower absorbance at 380 nm than CIBD without CRP, which indicates that CIBD reacted with CRP.

Fig. 1 UV spectra of BD in methanol in the absence and presence of cryptand (CRP) : CIBD, 1×10^{-4} mol/L, (1) CIBD + CRP (2×10^{-4} mol/L), (2) CIBD + CRP (4×10^{-4} mol/L), (3) CIBD + CRP (5×10^{-4} mol/L), (4) CIBD + CRP (8×10^{-4} mol/L), (5) CIBD + CRP (10×10^{-4} mol/L)

When CIBD was dissolved in aqueous solution containing CRP and BF_3O , the absorbance of CIBD did not change. It was considered that the lone pair electrons of CRP was coordinated by BF_3 , and an interaction between CIBD and CRP was inhibited.

Similarly, when CIBD was dissolved in an aqueous solution containing an inclusion compound of CRP with K^+ ion, the absorbance of CIBD did not changed.

3.2 Photodecomposition of SBD with CRP in methanol

An influence of CRP addition on the relationship between irradiation time and remaining weight percent of SBD in methanol is shown in Fig. 2. Photodecomposition rate of DSBD with CRP was accelerated more than that without CRP. Photodecomposition rates of CIBD (WSBD), BD and

(C_2H_5)₂NBD (DSBD) were 2, 3 and 10 times larger than that of SBD without CRP, respectively. The photodecomposition rate of DSBD with CRP was increased more than WSBD with CRP.

The photodecomposition rate of CIBD containing CRP and BF_3 was similar to that of CIBD without additives.

Fig. 2 Photodecomposition of SBD with cryptand (CRP) in methanol, SBD: 5×10^{-5} mol/L, CRP: 5×10^{-5} mol/l, Incident energy: 2.2 mW/cm^2 , (■), CIBD; (□), CIBD + CRP; (▲), BD; (△), BD + CRP; (●), (C_2H_5)₂NBD; (○), (C_2H_5)₂NBD + CRP.

3.3 Thermal decomposition in methanol

Thermal decomposition of CIBD with CRP in methanol was determined by measuring the intensity, λ_{max} at 283 nm.

Thermal decomposition rate of CIBD with CRP was two times higher than that of CIBD without CRP.

3.4 Degradation temperature of solid complex

Degradation temperature, D.T. of SBD with CRP was determined by TGA in solid state.

Relation of D.T. and weight ratio of CRP to CIBD is shown in Fig. 3. The D.T. of CIBD with CRP was lower than that without CRP, and became constant above 0.5 of weight ratio.

Hammett' plots of D.T. in solid state are shown in Fig. 4. The D.T. of SBD with CRP is lower than that without CRP. WSBD with CRP were lower than that with DSBD. It is reported [14] that the

electron transfer (by calculation) of SBD from the diazo group to the benzene ring of SBD with electron withdrawing group (WSBD) are easier than that of SBD with electron donating group (DSBD). It is considered the electron poor diazo group $N \equiv N^+$ of WSBD is easily reacted or included with electron rich cryptand.

Fig. 3 Relationship between weight ratio of cryptand (CRP) to CIBD and D.T.

Fig. 4 Hammett' plots of D.T. of various *p*-substituted diazo compounds (SBD) with cryptand (CRP) and without cryptand (CRP).

3.5 Application of CRP to DSR/PVA resists

The residual DSR with CRP in DSR/PVA film after UV irradiation was measured by UV spectrometry and the remaining weight percent of diazo

compounds was calculated. The relation of irradiation time and remaining weight percent is shown in Fig. 5. Photodecomposition rate of DSR/PVA film with CRP was accelerated more than that without CRP. When more than 30 wt% of CRP was added to DSR/PVA resist, photodecomposition rate became constant.

Fig. 5 Photodecomposition of DSR/PVA films with cryptand (CRP). Incident energy : 2.2 mW/Cm^{-2}

4. Reaction scheme

It is calculated that the CRP include K^+ ion was shown in Fig. 6-A and its stabilization energy is -62.38 kcal/mol . If CRP include diazo group (Fig.6-B), its stabilization energy is -23.86 kcal/mol by WinMOPAC calculation. But photo- and thermal decomposition of CIBD with CRP was accelerated. Photodecomposition rate of CIBD in CRP, the lone pair electrons of which coordinate to BF_3 , did not change. From these results, the diazo cation of CIBD may be react or interact to lone pair electrons of CRP.

Fig. 6 Inclusion compound model of CRP + K^+ (A) and CRP + benzene diazonium (BD) (B)

5. Conclusion

The D.T. of WSBD was lower than that of DSBD. Electron poor diazo cation easily reacted with CRP. The photodecomposition was accelerated by addition of CRP in methanol, an aqueous solution and the DSR/PVA resist. The diazo/PVA resist with CRP will be improved in sensitivity without decreasing thermal stability.

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