# Photo-Fluorescent Behaviors of MMA or St-Copolymers having Azomethine Side Chain Groups Synthesized by the Reaction of Coploy-Vinylguanamine Units with $p$-Dimethylaminobenzaldehyde 

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#### Abstract

The MMA or St/vinylguanamine-copolymers having azomethine side chain group (AZ) were synthesized by the reaction of the guanamine unit with p-dimethylaminobenzaldehyde and were irradiated by UV-light in the solution or the solid state. The changes of the fluorescent intensity of the copolymers irradiated with the UV-light using 150 W xenon lamp were observed. That is, the irradiation of UV-light at 390 nm in the DMF solution of MMA/AZ-copolymer at $2.8 \times 10^{-4} \mathrm{M}$ (for a unit of AZ in the polymer), the fluorescent intensity of the peak at 480 nm by the excitation at 390 nm decreased monotonously.

Fluorescent changes of the copolymers by UV-irradiation in solid state were also studied. The fluorescent spectra of the MMA- or $\mathrm{St} / \mathrm{AZ}$-copolymers have a maximum at 542 nm by excitation at 515 nm . The fluorescent intensities of the polymer increase with irradiation of UV-light at 420 nm . When the polymer was irradiated by UV-light at 330 nm , the fluorescent intensity from the polymer excited by UV-light at 515 nm decreased. The intensity increased with increasing the proportion of $A Z$ unit in the copolymers. The changes of the intensities of the $\mathrm{St} / \mathrm{AZ}$-copolymer were smaller than that of the MMA/AZ-copolymer. Key words: Photo-fluorescent change, UV-Irradiation, Azomethine copolymer, Vinylguanamine, $\pi$-electron conjugated system


## 1. INTRODUCTION

The synthcsis of various polymers ${ }^{1}$ having $s$-triazinc moiety have been widely studied for the high performance polymers as EL materials ${ }_{3}$ photochromic polymers ${ }^{1}$ and nonlinear optic materials ${ }^{2}$. On the other hand, few investigations about the azomethine groups from a reaction of guanamines being an $s$-triazine group with aromatic aldehydes have reported, because of their low reactivity. Recently, we have already reported that the reaction of guanamine on the side chain of MMA or St-copolymers with benzaldehyde easily takes place in polyphosphoric acid. The copolymer having the azomethine side chain group with $p$-dimethylaminophenyl group shows unique fluorescent properties by UV-irradiation ${ }^{3}$.
In this paper, we report about the photo-fluorescent properties of the copolymer having the azomethine group in the solution and the solid state by UV-irradiation.

## 2. EXPERIMENTAL

### 2.1 Materials

Vinylguanamine, 5,5'-azobisisobutyronitrile were purified by recrystallization from methanol. N,N-Dimethylformamide (DMF) were purified by vacuum distillation. All other higher puerility reagents ( $99.0 \mathrm{wt} \%>$ ) were used without further purification.

### 2.2 Synthesis

Copolymerization of Methylmethacrylate (MMA) or Styrene (St) with Vinylguanamine (VG) : As an example, 0.6855 g ( 5 mmol ) of 2 -vinyl-4,6-diamino-1,3,5-triazine, 4.50 g ( 45 mmol ) of methylmethacrylate and 5 ml of $\mathrm{N}, \mathrm{N}$-dimethylformamide were added into 200 ml of a
three necked flask equipped with a thermometer, a Licbig condenscr and a drying glass tube containing calcium chloride. The flask stirred with a magnetic stirrer was healed al $80^{\circ} \mathrm{C}$ under $\mathrm{N}_{2}$, and then added 60 mg ( 0.37 mmol ) of 5,5 'azobisisobutyronitrile. The mixture was stirred for 3 hr at $80^{\circ} \mathrm{C}$. The mixture was poured into 500 ml of methanol, then stirred for Ihr . The precipitate was corrected by filtration and dried under vacuum. The polymer was purified with methanol and tetrahydrofuran. The copolymer was obtained with $75.8 \%$ of the yield and shows $0.11 \mathrm{dL} / \mathrm{g}$ of the reduced solution viscosity.

Six types of the copolymers are prepared by the combination of the units and the ratio, as follows: MMA/VG $=90 / 10,96 / 4,98 / 2$ and $\mathrm{St} / \mathrm{VG}=90 / 10,96 / 4$, 98/2.

| Monomer | Colymer (m/n) |  |
| :---: | :---: | :---: |
|  | feed ratio | determination |
| MMA/VG | 90/10 | 90.9/10.0 |
|  | 96/4 | 94.3/5.7 |
|  | 98/2 | 98.2/1.8 |
|  | 70/30 | 36.4/63.6 |
| St/VG | 90/10 | 86.9/13.1 |
|  | 96/4 | 88,9/11.1 |
|  | 98/2 | 95.8/4.2 |
| Reaction of | the | copolymer | p-dimethylaminobenzaldehyde : As an example, 0.1 g of the copolymer, 1 ml of dioxanc and 2.06 g ( 1 ml ) of polyphosphoric acid placed into a glass sample tube were heated at $80^{\circ} \mathrm{C}$. After $3 \mathrm{hr}, 0.1492 \mathrm{~g}$ ( 1 mmol ) of $p$-dimethylaminobenzaldehyde was added to the mixture, and then heated for 21 hr . The mixture was poured into

300 ml of methanol having 15 ml of triethylamine, and then stirred for 1 hr . The precipitate was corrected by filtration, washed with methanol and dried under vacuum. The yield of the yellowish polymer powder was $100 \%$. The conversion of the guanamine units to the AZ in the copolymers was observed to be of $100 \%$ by IR spectroscopy. IR: $\left(-\mathrm{COOCH}_{3}\right) 1730 \mathrm{~cm}^{-1}$, ( $s$-triazine) $1670 \mathrm{~cm}^{-1},(-\mathrm{HC}=\mathrm{N}) 1615 \mathrm{~cm}^{-1}, \quad\left(\mathrm{C}_{6} \mathrm{H}_{4}\right)$ and $1350 \mathrm{~cm}-1$, NMR: $\left(-\mathrm{OCH}_{3}\right) 3.6 \mathrm{ppm},(-\mathrm{HC}=\mathrm{N}-) 5.4 \mathrm{ppm}$, (phenyl-) 6.6 and 7.1 ppm

### 2.3 UV-irradiation

The UV-irradiations of the polymer on the solution or the solid state were carried out with a 150 W xenon lamp equipped in a JASCO FP-6500 Spectrophotometer. After the UV-irradiation, the fluorescent spectra were taken directly in the spectrophotometer.

### 2.4 Characterization

IR spectra were measured by using Shimadzu FTIR-4200 on KBr disks. Fluorescent spectra of the polymer were measured with the fluorescent spectrophotometer in the solid state in a powder cell and in the solution state at the concentration of $2.8 \times 10^{-4} \mathrm{M}$. The fluorescent intensity of the copolymers in the solid state were estimated by a computational treatment removing the reflection influence. A molecular orbital calculation of azomethine model compounds was carried out by AM1 method (keyword: MM/AMI PRECISE CHARGE) in CAChe.
3. RESULTS AND DISCUSSION
3.1 The fluorescent properties of the copolymers in DMF solution


First we investigated about the fluorescent properties of the MMA/AZ-copolymer (MMA/AZ $=90 / 10$ ) in the DMF solution of a concentration at $2.8 \times 10^{-4} \mathrm{M}$. As shown in Figure 1, the maximum at 480.3 nm in the fluorescent spectra and at 393.4 mm in the excitation spectra were observed. It is known that aromatic azomethine compounds do not form a planer structure among aromatic rings and azomethine group ${ }^{4}$. Accordingly most of aromatic azomethine compounds cannot probably have a strong fluorescence in case of the molecule obtained from the aromatic rings with low molecular weight because the extent of the $\pi$-electron conjugated system in the molecules is limited. The geometry of the model AZ was optimized by AM1 method. The model $A Z$ is simulated to have 56.45 degree for the dihedral angles among $5 \mathrm{~N}-6 \mathrm{C}-8 \mathrm{~N}-10 \mathrm{C}$, as shown in Table II. This result suggests that the AZ molecule would not have a $\pi$-conjugated planarity needed for a strong fluorescence. The calculation of the protonated $A Z$ was carried out, because of the possibility of $A Z$ partially protonated by the polyphosphoric acid used as the reaction solvent. The dihedral angle among $5 \mathrm{~N}-6 \mathrm{C}-8 \mathrm{~N}-10 \mathrm{C}$ of the protonated model molecule is -0.04 degree. This means the protonated molecule


Figure 1 The excitation and fluorescent spectra of the MMA/AZ-copolymer (MMA/AZ $=90 / 10$ ) solution


Table II Selected Angle of AZ optinized by Molecuiar Orbital Calculations ${ }^{\text {( }}$ Selected atoms
(1) The non-protonated model $A Z$
$8 N-10 \mathrm{C}-12 \mathrm{C}-18 \mathrm{C}$
$5 \mathrm{~N}-6 \mathrm{C}-9 \mathrm{~N}-10 \mathrm{C}$

| (2) The protonated model AZ |  |
| :--- | :--- |
| $8 \mathrm{~N}-10 \mathrm{C}-12 \mathrm{C}-18 \mathrm{C}$ |  |
| $5 \mathrm{~N}-6 \mathrm{C}-8 \mathrm{SN}-10 \mathrm{C}$ |  |
| 1) The molecular orbital calculations were carned out by AM1 method |  |



Figure 2 The fluorescent spectra excited at 390 nm of the MMA/AZ copolymer (MMA/AZ $=90 / 10$ ) added (1) formic acid, (2) non-additives and (3) KOH into the solution
would have a $\pi$-conjugated planarity. The fluorescent spectra of the polymer solutions in the presence of formic acid or potassium hydroxide were measured to confirm the result of the calculation. The intensity increased with the addition of formic acid and decreased with the addition of potassium hydroxide, as shown in Figure 2. These results suggest that the molecule has a plancr structure in the presence of acid. Consequently, it is probably that the pristine copolymer can fluoresce on account of remaining some polyphosphoric acid in the system.

The fluorescent spectra excited at 485 nm have a small peak with the maximum at 560 nm . The fluorescent intensities of the copolymer increased with increasing the proportion of the $A Z$ on the copolymer side chain or the concentration of the copolymer (MMA/AZ $=90 / 10$ )


Figure 3 The fluorescent spectra excited at 480 nm of the MMA-copolymer solution (MMA/AZ $=90 / 10$ ) of concentrations at 28 , $14,7,3.5$, and $2.8 \times 10^{-4} \mathrm{M}$
in the solution. The results on the behavior in the change of the concentration of the MMA-copolymer are shown in Figure 3. The increase of the fluorescent intensities would occur duc to form an excimer between two AZs by the UV-light.

The change of the fluorescent spectra excited at 390 mm having the maximum at 478 mm was shown by a UV-irradiation at 390 nm of UV-light with a 150 W xenon lamp. The intensities decreased with the UV-irradiation, as shown in Figure 4.


Figure 4 The change of the fluorescent spectra of the MMA/AZ-copolymer (MMA/AZ $=90 / 10$ ) solution by UV-Irradiation at 390 mm
3.2 The fluorescent properties of the copolymer in solid state

The fluorescent spectra of the MMA/AZ-copolymer (MMA/AZ $=90 / 10$ ) are shown in Figure 5 and 6 (the spectra at 0 sec in the Figures). The maximum of the fluorescent spectra is shown at 471 nm by the excitation at 420 nm also the maximum at 542 nm by the excitation at 515 nm is shown. The fluorescent properties of the St-copolymers are the same as that of the MMA-copolymer. The maximum of the fluorescent spectra at 478 nm excited at 390 nm in the DMF solution is shifted to 471 nm in the solid state, because of an effect solvent, as shown on 0 sec in Figure 1 and 5. The fluorescent spectra excited at 420 nm shows a shoulder peak around 540 nm in Figure 5. The peaks at 540 nm of the fluorescent spectra excited at 420 nm and at 542 nm in the fluorescent spectra excited at 515 nm in the solid


Figure 5 The change of the fluorescent spectra excited at 420 nm of the MMA-AZ-copolymer (MMA/AZ $=90 / 10$ ) by UV-irradiation at 420 mm in solid state


Figure 6 The change of the fluorescent spectra excited at 515 nm of the MMA-AZ-copolymer (MMA/AZ $=90 / 10$ ) by UV -irradiation at 420 nm in solid state


Figure 7 The change of the fluorescent spectra excited at 515 nm of the MMA-AZ-copolymer (MMA/AZ $=90 / 10$ ) by UV-irradiation at 330 nm in solid state
state, respectively, would be observed by the formation of the excimer between AZs.

The changes of the fluorescent intensities excited at 420 nm of the copolymers by UV-irradiation at 420 nm were observed. The intensities of the MMA- or St/AZ-copolymers decreased, as shown in Figure 5. However, the increase of the intensity by the UV-irradiation cannot be observed, although the copolymers were attempted with UV-irradiations by a lot of wavelengths.

The changes of the fluorescent intensities excited at 515 nm using the MMA/AZ-copolymers were also investigated by the UV-irradiation with 150 W xenon lamp, as shown in Figure 6 and 7. When the MMA/AZ-copolymer (MMA/AZ $=90 / 10$ ) in the solid


Figure 8 The fluorescent change of the copolymers with the MMA/AZ-ratios of (*) 90/10, (■) 96/4, and ( $\mathbf{\Delta}$ )98/2 by UV-irradiation at 420 nm in solid state


Figure 9 The fluorescent change of the copolymers with the MMA/AZ-ratios of ( $\leqslant$ ) $90 / 10$, ( ${ }^{\text {( }}$ ) $96 / 4$, and ( $\mathbf{A}$ ) $98 / 2$ by UV-irradiation at 330 nm in solid state
state was irradiated by UV-light at 420 nm , the fluorescent intensities increased monotonously. Then the fluorescent intensities of the copolymer decreased with UV-irradiation at 330 nm . The other MMA/AZ-copolymers (MMA/AZ $=94 / 6,98 / 2$ ) were also irradiated under the same condition. The plots of the area intensities of the peak at 542 nm against the irradiation time were illustrated in Figure 8 and 9. Where, the strong peaks at the shorter wavelength to be the reflections peaks, as shown in Figure 5-7, are eliminated by a computational treatment. As the result of the irradiation, the MMA/AZ-copolymer in the case of MMA $A Z=90 / 10$ has higher magnitude of both the increase and the decrease of the intensity than that of the other MMA/AZ-copolymers. The SU/AZ-copolymers (St/AZ $=90 / 10,94 / 6,98 / 2$ ) have also the same phenomena by UV-irradiation as shown in Figure 10 and 11. However, the St/AZ-copolymers have low magnitude of the change, compared with the MMA/AZ -copolymers.

## 4. CONCLUSION

The maximum at 480.3 nm of the fluorescence spectra and at 393.4 nm of the excitation spectra of MMA/AZ-copolymer (MMA/AZ $=90 / 10$ ) in the DMF solution was observed. The copolymers are considered to be partially protonated by polyphosphoric acid used as the reaction solvent, due to the results of the molecular orbital calculation on the model AZ and the behavior of the fluorescent spectra in the DMF solution in the presence of formic acid. The decrease of the


Figure 10 The fluorescent change of the copolymers with the St/AZ-ratios of ( $\bullet$ ) 90/10, (輏) $96 / 4$, and ( $\mathbf{\Lambda}$ ) $98 / 2$ by UV-irradiation at 420 nm in solid state


Figure 11 The fluorescent change of the copolymers with the St/AZ-ratios of ( $-90 / 10$, $96 / 4$, and ( $\mathbf{\Delta}) 98 / 2$ by UV-irradiation at 330 nm in solid state
maximum fluorescent intensity at 478 nm excited at 390 nm in the DMF solution by UV-irradiation at 390 nm was observed.

In the solid state, the maximum of the fluorescent spectra is shown at 471 nm by the excitation at 420 nm also at 542 nm by the excitation at 515 nm , When the MMA/AZ-copolymers in the solid state were irradiated by UV-light at 420 nm , the fluorescent intensities excited at 420 nm decreased, and the fluorescent intensities excited at 515 nm increased monotonously. After the UV-irradiation at 420 nm to the copolymer, the increased intensities at 515 nm decreased with UV-irradiation at 330 nm . The $\mathrm{St} / \mathrm{AZ}$-copolymers have the same phenomena on the UV-irradiation. The MMA/AZ-copolymers show high magnitude on the intensity change by UV-irradiation, compared with that of the St/AZ-copolymers.

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