

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

Takatoshi Miyaji, Chiaki Azuma and Shigeo Nakamura*

The University of the Air, Setagaya-ku, Tokyo 154-0002, Japan

FAX: +81-3-5486-7730

*Faculty of Engineering, Department of Applied Chemistry, Kanagawa University, Kanagawa-ku, Yokohama 221-8686, Japan

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 150W xenon lamp were observed. That is, the irradiation of UV-light at 390nm in the DMF solution of MMA/AZ-copolymer at 2.8×10^{-4} M (for a unit of AZ in the polymer), the fluorescent intensity of the peak at 480nm by the excitation at 390nm decreased monotonously.

Fluorescent changes of the copolymers by UV-irradiation in solid state were also studied. The fluorescent spectra of the MMA- or St/AZ-copolymers have a maximum at 542nm by excitation at 515nm. The fluorescent intensities of the polymer increase with irradiation of UV-light at 420nm. When the polymer was irradiated by UV-light at 330nm, the fluorescent intensity from the polymer excited by UV-light at 515nm decreased. The intensity increased with increasing the proportion of AZ unit in the copolymers. The changes of the intensities of the St/AZ-copolymer were smaller than that of the MMA/AZ-copolymer.

Key words: Photo-fluorescent change, UV-Irradiation, Azomethine copolymer, Vinylguanamine, π -electron conjugated system

1. INTRODUCTION

The synthesis of various polymers¹ having *s*-triazine moiety have been widely studied for the high performance polymers as EL materials¹, photochromic polymers¹ and nonlinear optic materials². 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-irradiation³.

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 purity reagents (99.0wt% ϕ) were used without further purification.

2.2 Synthesis

Copolymerization of Methylmethacrylate (MMA) or Styrene (St) with Vinylguanamine(VG): As an example, 0.6855g (5mmol) of 2-vinyl-4,6-diamino-1,3,5-triazine, 4.50g (45mmol) of methylmethacrylate and 5ml of N,N-dimethylformamide were added into 200ml of a

three necked flask equipped with a thermometer, a Liebig condenser and a drying glass tube containing calcium chloride. The flask stirred with a magnetic stirrer was heated at 80°C under N₂, and then added 60mg (0.37mmol) of 5,5'-azobisisobutyronitrile. The mixture was stirred for 3hr at 80°C. The mixture was poured into 500ml of methanol, then stirred for 1hr. 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 dL/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 St/VG=90/10, 96/4, 98/2.

Table I Synthesis of the copolymer

| Monomer | Polymer (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 |
| St/VG | 70/30 | 36.4/63.6 |
| | 90/10 | 86.9/13.1 |
| | 96/4 | 88.9/11.1 |
| | 98/2 | 95.8/4.2 |

Reaction of the copolymer with p-dimethylaminobenzaldehyde: As an example, 0.1g of the copolymer, 1ml of dioxane and 2.06g (1ml) of polyphosphoric acid placed into a glass sample tube were heated at 80°C. After 3hr, 0.1492g (1mmol) of *p*-dimethylaminobenzaldehyde was added to the mixture, and then heated for 21hr. The mixture was poured into

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

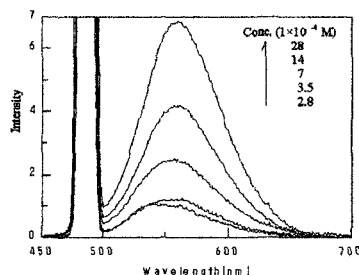


Figure 3 The fluorescent spectra excited at 480nm of the MMA-copolymer solution (MMA/AZ=90/10) of concentrations at 28, 14, 7, 3.5, and 2.8 $\times 10^{-4}$ M

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 due to form an excimer between two AZs by the UV-light.

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

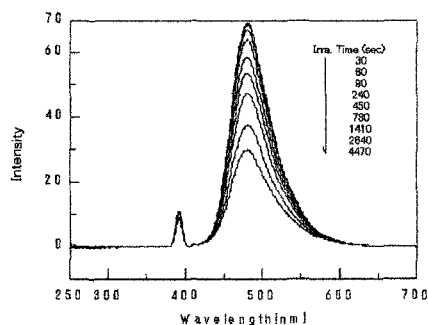


Figure 4 The change of the fluorescent spectra of the MMA/AZ-copolymer (MMA/AZ=90/10) solution by UV-Irradiation at 390nm

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 471nm by the excitation at 420nm also the maximum at 542nm by the excitation at 515nm 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 478nm excited at 390nm in the DMF solution is shifted to 471nm in the solid state, because of an effect solvent, as shown on 0 sec in Figure 1 and 5. The fluorescent spectra excited at 420nm shows a shoulder peak around 540nm in Figure 5. The peaks at 540nm of the fluorescent spectra excited at 420nm and at 542nm in the fluorescent spectra excited at 515nm in the solid

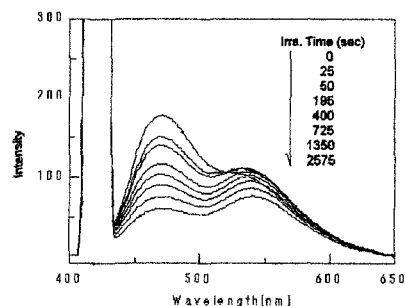


Figure 5 The change of the fluorescent spectra excited at 420nm of the MMA-AZ-copolymer (MMA/AZ=90/10) by UV-irradiation at 420nm in solid state

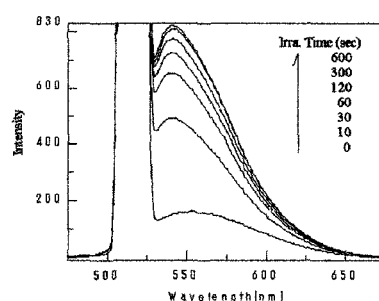


Figure 6 The change of the fluorescent spectra excited at 515nm of the MMA-AZ-copolymer (MMA/AZ=90/10) by UV-irradiation at 420nm in solid state

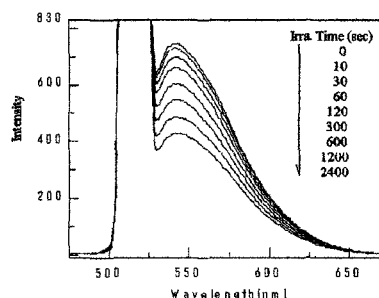


Figure 7 The change of the fluorescent spectra excited at 515nm of the MMA-AZ-copolymer (MMA/AZ=90/10) by UV-irradiation at 330nm in solid state

state, respectively, would be observed by the formation of the excimer between AZs.

The changes of the fluorescent intensities excited at 420nm of the copolymers by UV-irradiation at 420nm 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 515nm using the MMA/AZ-copolymers were also investigated by the UV-irradiation with 150W xenon lamp, as shown in Figure 6 and 7. When the MMA/AZ-copolymer (MMA/AZ=90/10) in the solid

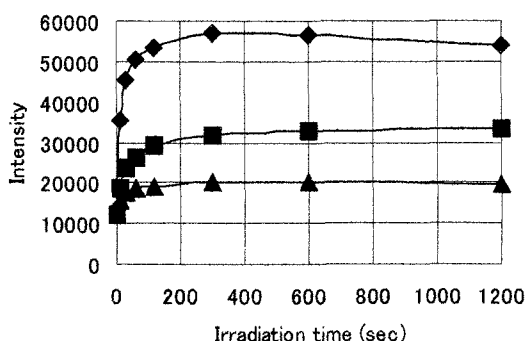


Figure 8 The fluorescent change of the copolymers with the MMA/AZ-ratios of (◆) 90/10, (■) 96/4, and (▲)98/2 by UV-irradiation at 420nm in solid state

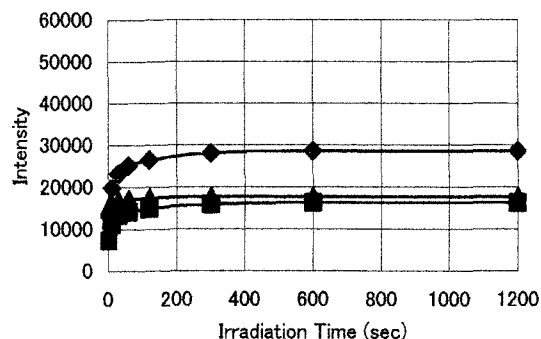


Figure 10 The fluorescent change of the copolymers with the St/AZ-ratios of (◆) 90/10, (■) 96/4, and (▲)98/2 by UV-irradiation at 420nm in solid state

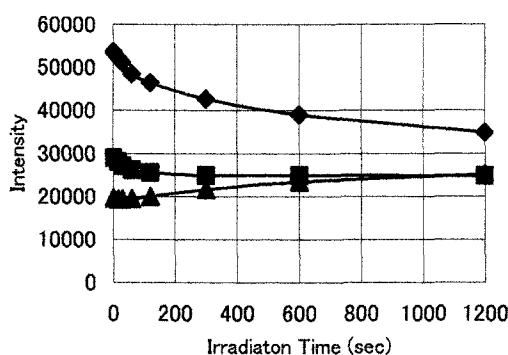


Figure 9 The fluorescent change of the copolymers with the MMA/AZ-ratios of (◆) 90/10, (■) 96/4, and (▲)98/2 by UV-irradiation at 330nm in solid state

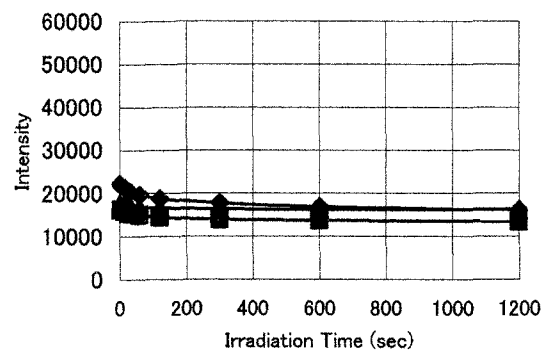


Figure 11 The fluorescent change of the copolymers with the St/AZ-ratios of (◆) 90/10, (■) 96/4, and (▲)98/2 by UV-irradiation at 330nm in solid state

state was irradiated by UV-light at 420nm, the fluorescent intensities increased monotonously. Then the fluorescent intensities of the copolymer decreased with UV-irradiation at 330nm. 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 542nm 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/AZ=90/10 has higher magnitude of both the increase and the decrease of the intensity than that of the other MMA/AZ-copolymers. The St/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 480.3nm of the fluorescence spectra and at 393.4nm 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

maximum fluorescent intensity at 478nm excited at 390nm in the DMF solution by UV-irradiation at 390nm was observed.

In the solid state, the maximum of the fluorescent spectra is shown at 471nm by the excitation at 420nm also at 542nm by the excitation at 515nm. When the MMA/AZ-copolymers in the solid state were irradiated by UV-light at 420nm, the fluorescent intensities excited at 420nm decreased, and the fluorescent intensities excited at 515nm increased monotonously. After the UV-irradiation at 420nm to the copolymer, the increased intensities at 515nm decreased with UV-irradiation at 330nm. The St/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.

REFERENCE

- [1] Oishi Yoshiyuki: *Kobunshi gakkaiishi*, **48**, 274-278 (1999)
- [2] L. Xiang et al.: *Chem. Phys. Lett.* **338**, (2001) 167-172, Hisamoto Yonehara et al., *J. Mater. Chem.*, **4** (10), 1571-1577 (1994)
- [3] Takatoshi Miyaji, Chiaki Azuma and Shigeo Nakamura: "Monograph on Photonics Science and Technology", Ed. by Hiroyuki Sasabe, Chitose Printing Co. Chitose (2003) pp.65-74
- [4] Paul W. Morgan, Stephanie L. Kwolek, and Terry C. Pletcher: *Macromolecules*, **20**, 729-739 (1987)