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Novel Photo-responsive Polymer Based on Diarylethene

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Photochromic diarylethene, which shows photoreversible ring-closing and opening reactions as illustrated in Fig. 1, has various unique characteristics such as fatigue resistivity, thermal stability in both sides of the photochromic reaction scheme, and also photo-responsibility in the solid phase.[1,2] Upon the photochromic reactions, not only the absorption spectrum but also various other properties change reversibly, such as dielectric constant, photoluminescence, photoconduction, electrochemistry, dielectric constant, and even magnetic properties.[3-6] These photo-responsibility of diarylethene can be applied for the functional switching materials and devices.

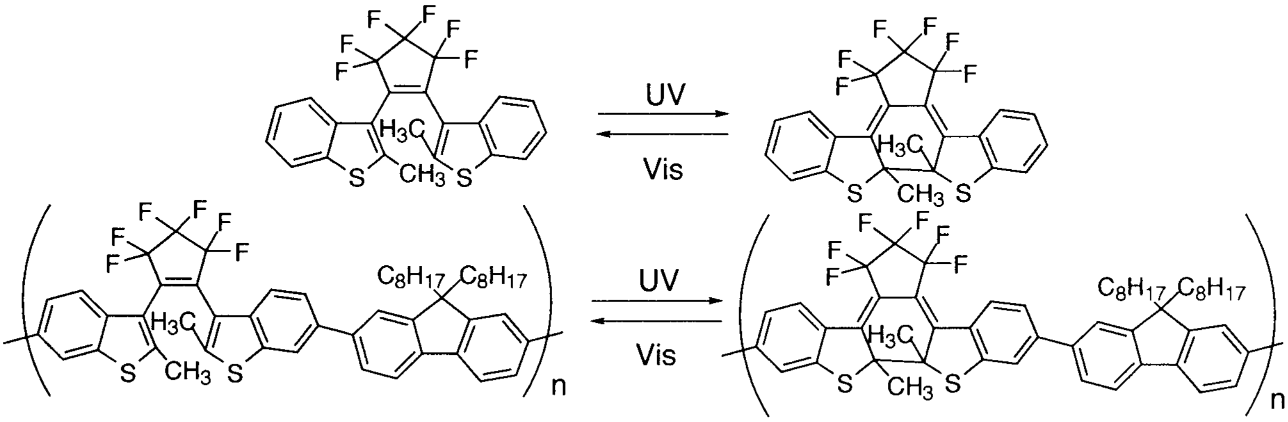

Figure 1. Photochromis of BFCP and polymer **1**

Since the bis(benzothiophen-3-yl) perfluorocyclopentene, BFCP in Fig. 1, has 3-rinked benzothiophene units, two aromatic moiety are less conjugated each other. While, bond alternation is possible in the ring-closed form in which two aromatic moiety are connected each other with the trans-cisoid type 1,4-butadiene structure. Therefore, conjugated polymer based on the bis(benzothiophen-3-yl) perfluorocyclopentene is possible to exhibits drastic changes in the optical and electrical properties upon photochromic reactions of the diarylethene units. In the present study, novel photo-responsive polymer was prepared on the basis of photochromic

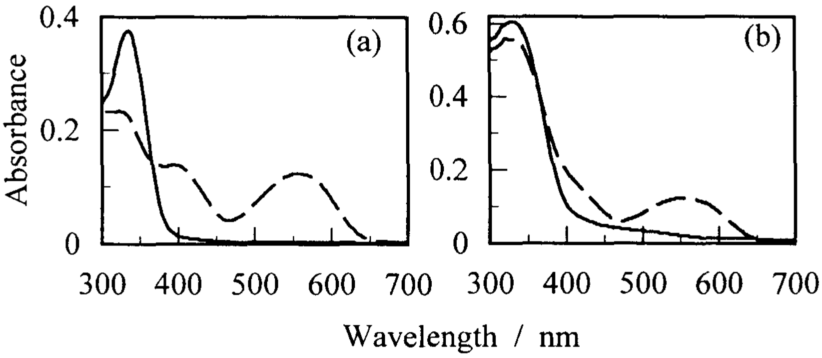

Figure 2. UV-vis absorption spectra of (a) polymer 1 in THF solution and (b) spin coated film of polymer 1 . solid line: in the original state, where all of the diarylethene units are in the open-ring form, broken line: at the photostationary state under irradiation with 313 nm.

diarylethene and dialkylfluorene.

The polymer 1 of which molecular structure is also shown in Fig. 1 was prepared by Ru-complex catalyzed coupling reaction of two components. The polymer was purified carefully by Shoxlet extraction with methanol, and by reprecipitation from chloroform/methanol for three times. The resulting polymer has about 4600 of molecular weight and was soluble in various kinds of organic solvents such as chloroform and THF. Clear transparent film was prepared by spin-coating method onto the quart plate.

Figure 2 shows photochromic behavior of polymer 1 in solution and also in the spin-coated film. In the original state, strong absorption band was observed at about 334 nm. After the UV light irradiation, the original pale yellow film turned to violet and clear absorption band was newly observed at 560 nm, which is characteristic band for the ring-closed form of the diarylethene sites.

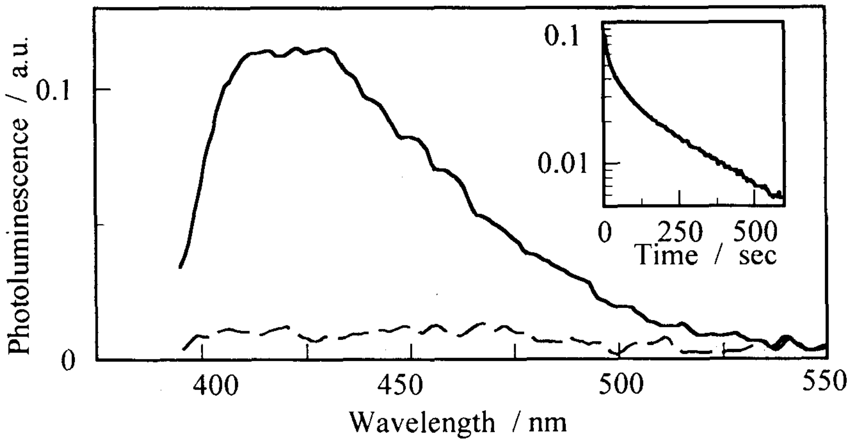

Figure 3. Photoluminescence spectra of polymer 1 film. solid line: in the original state, broken line: at the photostationary state. (inset: decay profile of the PL intensity)

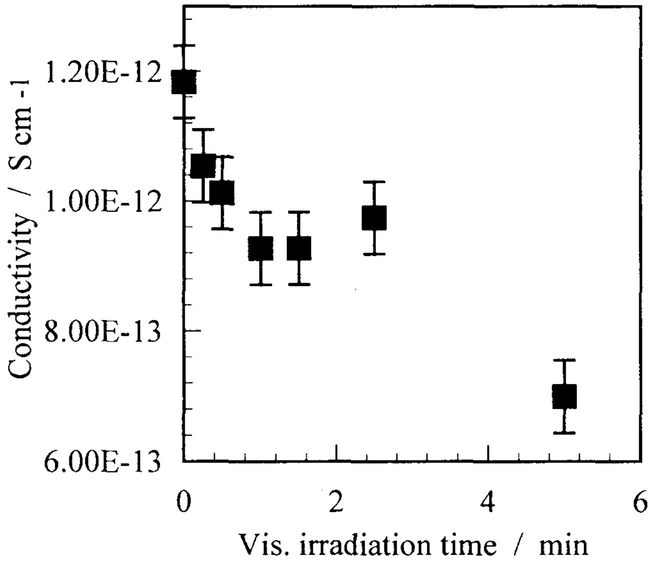

Figure 4. Change in conductivity of polymer 1 film upon visible light irradiation

After the irradiation the visible light of wavelength longer than 480 nm original yellow film was recovered and the absorption band at 560 nm disappeared. This photochromic cycles can be repeated for more than 20 cycles and no marked degradation was observed. The maximum conversion of the photochromic site was about 40 % in solution and about 14% in solid film. As shown in Fig. 3, polymer 1 showed clear photoluminescence at about 410 nm, where the excitation wavelength was 365nm, isosbestic point of the photochromic reaction. The emission intensity decreased rapidly as shown in the inset of Fig. 3. After about 5 min, the emission was totally quenched. It should be noted that, although the photoluminescence was 100 % quenched, only about 14% of the diarylethene sites turned to the closed-ring form even at the photostationary state. This remarkable non-linear phenomenon can be explained by the term of the efficient excitation energy transfer in the polymer chain. That is, the small amount of the ring-closed form sites which have second absorption band at about 400 nm acts efficiently as the energy acceptor and the emission quencher.

The conductivity of the polymer 1 also changed as shown in Fig. 4. The conductivity was about 1.2×10^{-12} S cm^{-1} in the 35% ring closed state, photostationary state achieved in the solution phase, and it decreased to 5.3×10^{-13} S cm^{-1} upon irradiation of the visible light. It should be noted that effects of the photoconductivity and persistent photoconductivity seem to be not dominant in this experiment since the resistance increased after the light irradiation. The conductivity was stable in the non-irradiated state, which suggests that the photochromic reaction of the diarylethene sites take dominant role in this photo-induced change in the electrical conductivity. Since the ring-closed form site has the extended conjugation system on the main chain, ring-closed form site seems to contribute to the larger conductivity. It should be noted that, the 35% of the photochromic reaction conversion seems to be enough large for the percolation threshold. That is, the electrical conductivity seems to be determined not by the low conjugated open ring form sites but by the highly conjugated closed ring form sites.

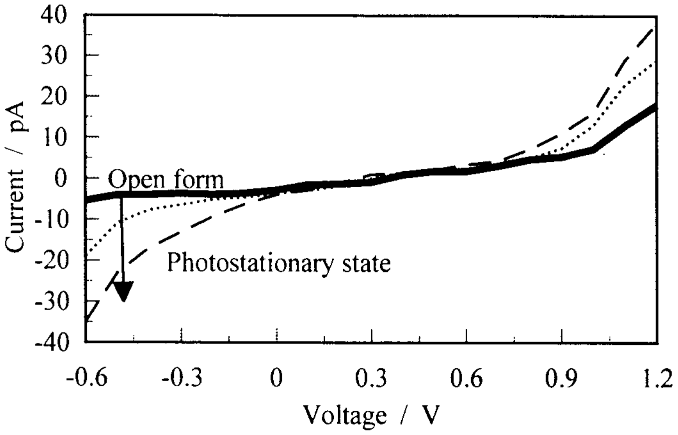

Figure 5. Current-voltage characteristics of Al/polymer 1/ITO cell before and after UV light irradiation.

Figure 5 shows I-V characteristics of the Al/polymer 1/ITO type junction device. In this sample, the Al electrode was evaporated onto the polymer 1 film on the ITO electrode. In the original state, the IV curve showed clear current rectification and the forward current was observed when positive bias was applied to the ITO electrode. After the UV light irradiation the reverse biased current was found to increase. Since the increased current was stable under the dark condition, this photo-responsibility should be explained by the photoisomerization reaction of the diarylethene sites in the polymer 1 main chain. That is, electronic state of the ring-closed form diarylethene act as the inter-gap state in the junction characteristics at Al-polymer interface and photochromic reaction in small amount of the diarylethene sites seems to results in the drastic increase in the leaking reverse direction current.

References

1) M.Irie and M.Mohri : *J.Org.Chem.* 53, 803 (1988).
2) T.Kawai, T.Koshido and K.Yoshino : *Appl.Phys.Lett.* 67, 795 (1995).
3) T.Kawai, T.Koshido, M.Nakazono and K.Yoshino : *Chem.Lett.* 697 (1993).
4) T.Koshido, T.Kawai and K.Yoshino : *J.Phys.Chem.* 16, 6110 (1995).
5) T.Koshido, T.Kawai and K.Yoshino : *Synth.Met.* 73, 257 (1995).
6) T.Kawai, N.Fukuda, D.Groschl, S.Kobatake and M.Irie : *Jpn.J.Appl.Phys.*, 38, L1194 (1999).