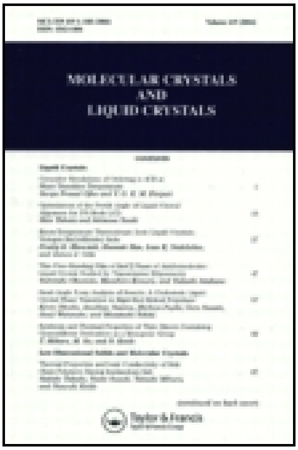

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Doping of Photochromic Dye to Polymer Substrates by Vaporization of the Dye in a Vacuum

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Polystyrene (PS) were doped with the photochromic dye, cis-1,2-dicyano-1, 2-bis(2,4,5-trimethyl-3-thienyl)ethene (CMTE), using a simple vacuum process, termed the "vapor transportation method." CMTE-doped PS molds showed photochromism. The CMTE-doped PS molds were examined by Optical microscopy and SEM/Energy dispersive X-ray (EDX) elemental analysis. Optical microscopy and sulfur (S) elemental analysis confirmed formation of CMTE-doped regions with rapid CMTE concentration decreases at the CMTE-doped region/PS substrate interfaces, although the doping temperature was much higher than the glass transition temperature (T_g) of PS.

Keywords: interface; photochromic dye; polymer; vacuum; vapor

INTRODUCTION

Photochromic compound, diarylethenes, have the advantages of thermal irreversibility, fatigue-resistance, and high sensitivity [1] to fabricate optical devices, such as memory media for optical recording [2,3] and optical switching [4,5]. For fabrication of these devices, formation

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processes of organic thin films or thin layers with photochromic compounds are the key techniques. However, the most common process, "wet process," with organic solvents (e.g. dipping, casting, spin-coating, and ink-jetting) has difficulty in removing solvent from films, causing Reyleigh scattering and small cracks by irradiation with focused light [6]. In addition to these disadvantages, photochromic molecules tend to aggregate in the films [2] formed by the wet process.

To remove these problems, we have developed the "vapor transportation method" [6–10] using the vacuum technique, which can form functional molecule-doped polymer regions on polymer substrates [6,7]. In addition, we have already shown that the molecules of the diarylethene derivative cis-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl) ethene (CMTE) can be doped selectively into polystyrene (PS) regions of PS-*block*-PMMA substrates [8,9], showing that how our simple method can provide a unique surface modification process for polymer substrates. In this paper, we examined the CMTE-doped region/PS substrate interfaces by Optical microscopy and SEM/Energy dispersive X-ray (EDX) elemental analysis to investigate specific CMTE diffusivity into PS molds.

EXPERIMENTAL

CMTE (Tokyo Chemical Industry Co., Ltd.) was used as a photochromic compound without further purification. Pellets of polystyrene (PS) (Aldrich Chemical Co., Inc.; M_w, 280,000) were purified by reprecipitating twice from 1,2-dichloroethane solution to methanol, and then molded in a cylindrical shape 2.5 mm in diameter and 3 mm in length. PS was also molded in quartz cells with an inner thickness of 0.5 mm and an inner width of 9.0 mm for doping CMTE at 140°C (in particular, above 130°C, to avoid marked plastic deformation).

The molded substrates were loaded into Pyrex glass tubes with a small amount of CMTE (5 mg), and the pressure in the tube was reduced to the base pressure of 2×10^{-6} Pa, using a vacuum pump [6,8,9]. To seal an ampoule at the cutting point, a gas burner was used to fuse the cut end. These ampoules containing 5 mg of CMTE were heated uniformly at temperatures between 110°C and 140°C.

To analyze the depth and interfacial structure of the CMTE-doped regions of molds, samples were prepared by trimming the substrate perpendicular to the surface of the longitudinal molds with razor blades. After UV irradiation for 2 minutes, samples were observed with an Olympus BH2-RFCA optical microscope. The optical microscope was also used to examine the interfacial structure of the CMTE-doped PS mold surrounded by the quartz cell. To examine the interface structures of the CMTE-containing region of the molds in detail, the surfaces of samples, trimmed using razor blades, were smoothed using an ultramicrotome (Ultracut UCT, Leica) with a glass knife, and then treated by osmium coating, using a plasma coating device (PMC-5000; Meiwa-Shoji Co. Ltd.) with an ampoule chamber of osmium oxide. Field Emission Scanning electron microscopy (FESEM) equipped with energy dispersive X-ray spectroscopy (EDX) was operated at an acceleration voltage of 15 kV. Mapping images and intensity profiles of sulfur in these samples were obtained.

RESULTS AND DISCUSSION

The color of CMTE-doped PS molds changed from light yellow to reddish brown when irradiated with UV light for 2 min. This change confirmed that the chemical structures of CMTE doped in the molds were transformed from the open to the closed ring form by UV irradiation [9]. In contrast, the color of these molds changed from reddish brown to light yellow when irradiated with visible light for 2 min. These results implied that CMTE molecules retain their own photochromic properties inside the polymer molds; our new method simple adds the photochromic properties of CMTE molecules to their surfaces.

Optical microscopy was used to observe the interfacial structures between CMTE-doped regions and the PS substrates. Figures 1(a) and (b) show low magnification images of CMTE-doped PS molds exposed to CMTE vapor at 110°C for 26 h and 120°C for 6 h, respectively. The interfacial regions of the doped CMTE were determined from their color. Figure 1 shows reddish brown regions the interfaces

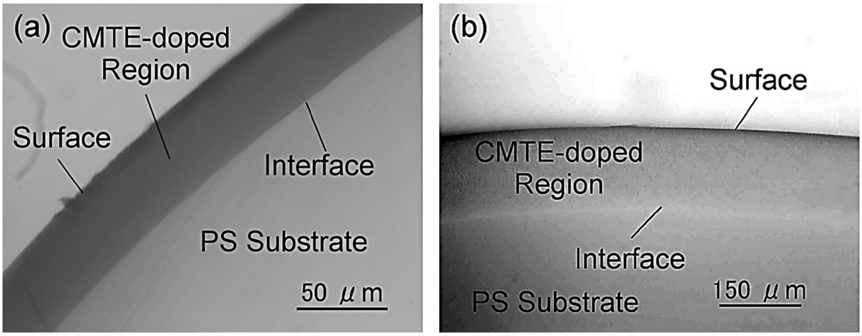

FIGURE 1 Low magnification images of CMTE-doped polymer molds observed by optical microscopy: (a) PS molds exposed to CMTE vapor at 110°C for 26 h; and (b) PC molds exposed to CMTE vapor at 120°C for 6 h.

of which have rapid CMTE concentration decreases. Assuming that their interfaces have the rapid concentration decreases, the depths of CMTE-doped PS treated at 110°C for 26 h and 120°C for 6 h were estimated to be 43.7 μm and 150 μm, respectively.

Next, the interfacial structures in CMTE-doped PS molds were examined with FESEM/EDX. Figures 2 (a), (b), and (c) show PS

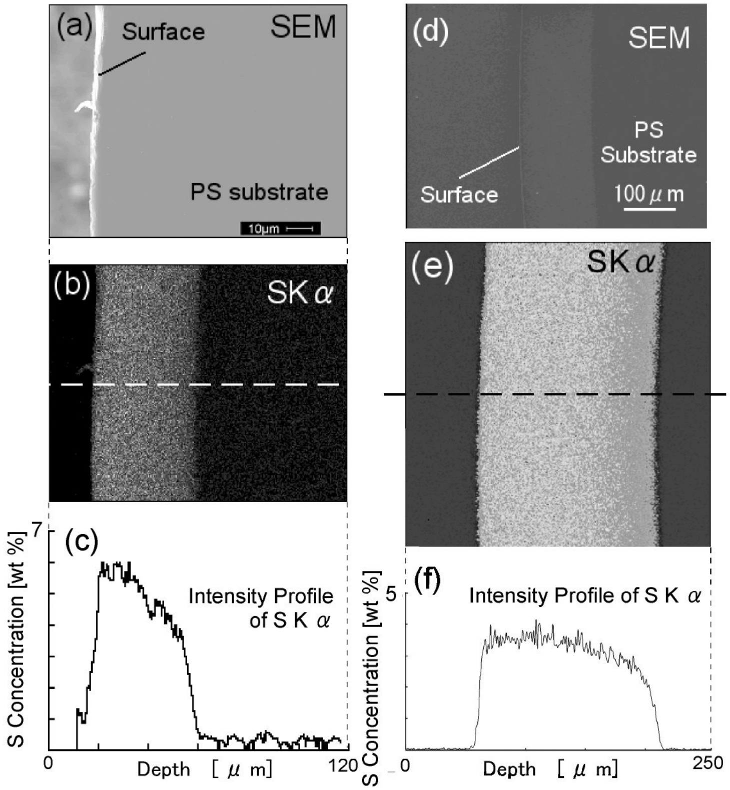

FIGURE 2 SEM images, S Kα images, and intensity profiles of cross-sections of CMTE-doped PS molds by SEM equipped with EDX elemental analysis. SEM/EDX was operated at an acceleration voltage of 15 kV. Figures 2(a), (b), and (c) show PS molds exposed to CMTE vapor at 110°C for 26 h (the same as Figures 1(a)). Figures 2(d), (e), and (f) show PS molds treated at 120°C for 6 h. Figures 2(a) and (d) are SEM images. Figures 2(b) and (e) are S Kα images. Figures 2(c) and (f) show intensity profiles of S Kα. Dashed lines in both Figures 2(b) and (e) show the locations from which the intensity profiles of S Kα in Figures 2(c) and (f) were taken, respectively. The white areas on the S Kα images in Figures 2(b) and (e) indicate the presence of CMTE molecules in PS molds.

substrate exposed to CMTE vapor at 110°C for 26 h (same as Figure 1(a)). Figures 2 (d), (e), and (f) show CMTE-doped PS treated at 120°C for 6 h (same as Figure 1(b)). Figures 2 (a) and (d) are SEM images, and Figures 2 (b) and (e) are images of S Kα. Figures 2 (c) and (f) present the intensity profiles of S Kα. As a single CMTE molecule contains two sulfur (S) atoms [9] and these polymer molds do not contain S atoms, we expected to detect S Kα element signals in doped CMTE of the sample in Figures 2 (a) and (d) with SEM/EDX elemental analysis. The SEM images in Figures 2 (a) and (d) do not show the presence of CMTE-doped interfacial regions clearly. However, the white areas in S Kα images in Figures 2 (b) and (e) demonstrate the presence of CMTE molecules in the PS substrate. In Figure 2 (c), the width of the doped CMTE in PS was measured as 47.8 μm. The intensity of S Kα decreased gradually from the surface to a depth of 41.4 μm, and then dropped abruptly at an interfacial distance of 6.4 μm. The intensity profile of S Kα in Figures 2 (c) and (f) agreed with the depth of the region shown the S Kα images in Figures 2 (b) and (e) and with the results of optical microscopy, which suggested that the depth of the CMTE-doped region can be distinguished by simple optical observation. Figure 2 (c) shows that the interface of the CMTE-doped PS substrate has a rapid concentration decrease. Figure 2 (f) shows that the thickness of the CMTE-doped region was 150 μm, which was longer than that in Figure 2 (c), and that the interface also has a rapid concentration decrease structure. Figure 3 shows a CMTE-doped polymer mold when CMTE was doped at 140°C for 72 h. Although the doping temperature was 40°C higher than the glass

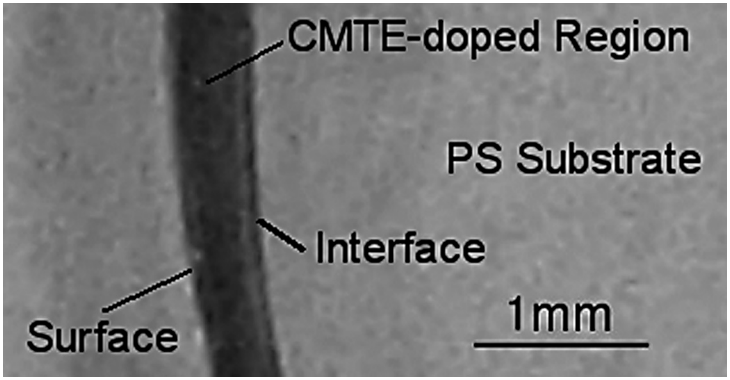

FIGURE 3 Low magnification images of CMTE-doped polymer molds surrounded by a quartz cell observed by optical microscopy. CMTE was doped at 140°C for 72 h.

transition temperature (T_g) of PS ($T_g = 100°C$), the average thickness of the CMTE-doped region was 500 μm and the interface also had a rapid concentration decrease. These results indicated that, when CMTE was doped to deeper levels, a CMTE-doped region with a rapid concentration decrease extended deeper from the surface, although the doping temperature was 10–40°C higher than the T_g of PS.

If doping of CMTE molecules follows Fick's laws of diffusion, then we should see a profile of S Kα with a gradual concentration gradient [11] instead of a rapid concentration decrease. At present, our results suggest that Fick's laws of diffusion do not govern doping of CMTE into polymer substrates: doping behavior is not mediated by conventional thermal diffusion (there was an interaction between CMTE molecules and PS during diffusion).

In contrast, when fluorescent dyes DCM, Alq_3 and Coumarin 314 were doped to PS at temperatures higher than 130°C, the dye-doped region had a concentration gradient [10]. In that case, when the doping temperatures were higher than 130°C, PS molds showed marked plastic deformation. This phenomenon enhanced doping of these dyes, causing conventional thermal diffusion at temperatures much higher than T_g of PS. These results indicated that diffusion behavior of CMTE into PS was quite unique. However, the CMTE diffusion mechanism into PS using our method in detail is now under investigation.

CONCLUSIONS

CMTE-doped PS molds were formed by the "vapor transportation method." The CMTE-doped PS molds showed "photoisomerization." Interfacial structures of CMTE-doped polymers were examined by a combination of optical microscopy and SEM/EDX analysis. Rapid CMTE concentration decreases were observed at the interfaces of these polymers. As the doping temperatures were higher, much higher than the T_g of PS, the interfaces still kept the rapid CMTE concentration decreases and the CMTE-doped regions moved deeper from the surface, indicating that the CMTE doping behavior was not mediated by conventional thermal diffusion. Since our method can form CMTE-containing thin "films" with obvious CMTE-doped region/polymer substrate interfaces on the substrates, it will be effective for fabricating organic optical memory media and optical switching devices.

In future studies, we will investigate the CMTE diffusion mechanism into PS in detail. We will also investigate methods to control the thickness and interface structures when organic compounds with low molecular weights were doped to polymer substrates by adjusting the optimal combination between polymer substrates and organic compounds to provide a new fabrication process for organic opto-electronic devices.

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