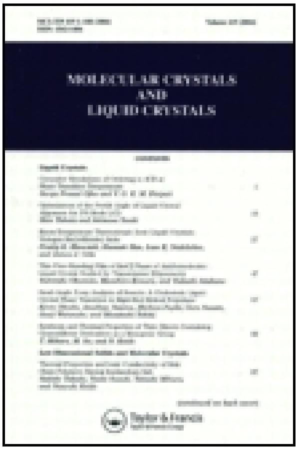

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Formation of Surface Relief Grating upon Light Irradiation in Conducting Polymer and Photochromic Polymer Composite System

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The formation of surface relief grating upon light irradiation on a composite film of conducting polymer with rigid main chain structure and acrylate polymer containing azo-substituent with soft main chain structure has been studied. The diffraction efficiency of the photo-induced grating decreases with increasing concentration of conducting polymer with respect to the polyacrylate in the concentration range higher than 3%. This implies that the height of surface relief on the film is lowered upon doping conducting polymer, which is confirmed by an atomic force microscope observation. It has been found, however, that the formation of surface relief grating is promoted by slight doping of conducting polymer (<3%) and progresses even after stopping light irradiation on the composite film. Anomalous angular dependence of photoluminescence from the composite film having relief grating on it has also been found.

Keywords: azobenzene polymer; conducting polymer; surface relief grating; photoluminescence

INTRODUCTION

Recently, holographic recording of surface relief grating has been reported on the polymer film containing photochromic azobenzene-substituents, which can be effectively realized using two interfering beams of a low power laser light even at room temperature [1,2]. This one-step holographic recording has potential application in electrooptics and optical storage.

On the other hand, conducting polymers having a highly extended π-electron system in the main chains have also attracted considerable attention from fundamental and practical points of view. Especially highly fluorescent conducting polymers such as poly(2,5-dialkoxy-p-phenylenevinylene) (RO-PPV) and poly(9, 9'-dialkylfluorene) have been investigated as active materials for electroluminescence (EL) devices, in which spectral narrowing of photoluminescence (PL) and the lasing effect have also been observed

[3-6]. Recently, we have reported the PL narrowing and evolution of sharp emission lines upon optical excitation in synthetic opals made of SiO_2 spheres infiltrated with conducting polymer, in which the periodic structure of the order of optical wavelength in opal should be strongly coupled to the emission characteristics [7].

In this paper, we investigate the formation of surface relief grating on a composite film of conducting polymer with rigid main chain structure and acrylate polymer containing azo-substituent with soft main chain structure.

EXPERIMENTAL

Figure 1 shows molecular structures of acrylate azo-polymer and conducting polymer, poly (2-methoxy-5-dodecyloxy-*p*-phenylenevinylene) (MDDO-PPV). These polymers were dissolved in chloroform as the common solvent and spin coated on a glass substrate. In order to remove residual solvent, the polymer thin film was heated above the glass transition temperature in vacuum. Figure 2 shows optical absorption spectrum of the azo-polymer/MDDO-PPV composite film. The azo-polymer originally has an absorption band centered at 480nm, which originates from the azobenzne substituents. This dominant absorption band in azo-polymer is completely overlapped on that in MDDO-PPV which corresponds to π-π^* transition of the π-conjugated main chain.

The grating was recorded using a simple interferometric geometry as shown in Fig.3. Recording light source is Ar^+ laser at a wavelength of 488 nm. The polarization of two recording lights were circularly polarized using a $\lambda/4$ plate. In order to monitor the grating formation, the intensity of diffracted beam of a He-Ne laser light at 633nm was measured by a powermeter. The surface profile of the recorded relief grating was investigated by an atomic force microscope (AFM), JSTM-4200A (JOEL). Absorption and photoluminescence spectra were measured using a diode array spectrophotometer (HP, 3452A) and a CCD multichannel spectrometer (Hamamatsu, PMA-11), respectively.

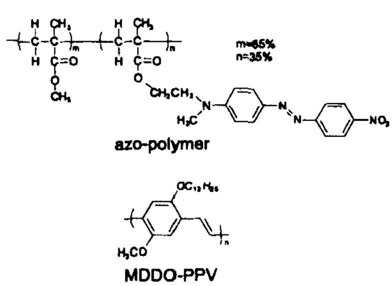

FIGURE 1 Molecular structures of azo-polymer and conducting polymer used in this study.

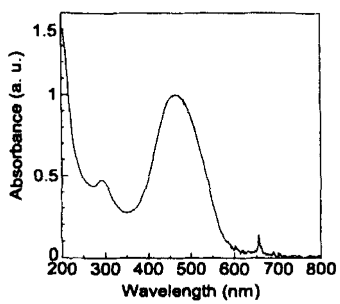

FIGURE 2 Absorption spectrum of azo-polymer doped with MDDO-PPV (5mol%).

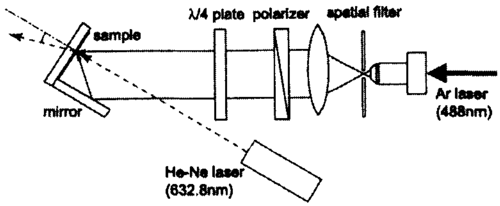

FIGURE 3 Experimental geometry for recording the surface relief grating.

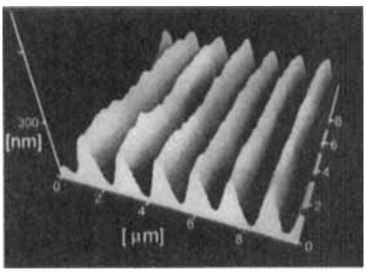

FIGURE 4. Atomic force microscope profile of the formed surface gratings on the azo-polymer/MDDO-PPV composite film (3mol%).

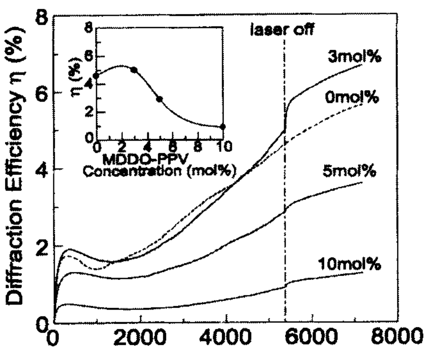

FIGURE 5. Time dependence of diffraction efficiency in the formed grating as a function of the mol concentration of MDDO-PPV in the composite. The inset indicates diffraction efficiency of the formed relief grating as a function of MDDO-PPV concentration.

RESULTS AND DISCUSSION

Grating formation

Using two interfering beams of a recording light (488nm), surface relief grating can be recorded on a pure azo-polymer film. Also on the azo-polymer film doped with the conducting polymer MDDO-PPV, surface relief grating could be formed as the same manner as that on the pure azo-polymer, as shown in Fig.4. The surface of the film is periodically lifted according to the distribution of the light intensity due to the interference.

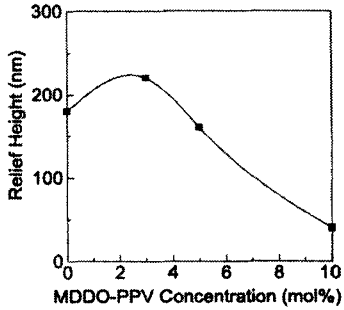

FIGURE 6 The dependence of the relief height of formed surface grating on the MDDO-PPV concentration.

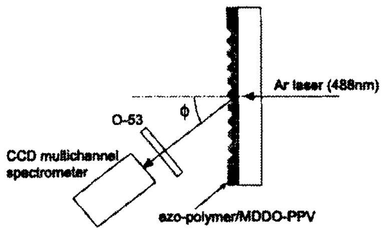

FIGURE 7 Measurement geometry for the angular dependence of PL spectra.

Figure 5 shows time dependence of the diffraction efficiency η of the formed relief grating as a function of the concentration of MDDO-PPV. Just after starting an irradiation of recording light, the grating structure was formed, and the diffraction efficiency gradually increases by sequential light irradiation. However, the diffraction efficiency of photo-induced grating decreases with increasing the concentration of the doped MDDO-PPV in the concentration range higher than 3mol% as shown in the inset of Fig.5. However, it should be noted that, in the low concentration range of MDDO-PPV, the diffraction efficiency slightly increases upon doping with conducting polymer. These concentration dependence of diffraction efficiency should be associated with the change in the relief height of the grating on the film upon doping with conducting polymer. This height change was confirmed by an AFM observation, in which, although the profile of the surface relief remains unchanged, only the height of the relief decreases. Figure 6 shows the relief height directly estimated from the AFM profile as a function of the MDDO-PPV concentration. At the concentration range below 3mol%, the surface relief becomes higher with increasing the concentration of MDDO-PPV. Above 3mol%, however, the relief height decreases monotonously, which corresponds to the decrease in the diffraction efficiency shown in Fig.5. The concentration dependence of the relief height may be attributed to the suppression of the main chain migration due to the rigidity of the conjugated main chain of MDDO-PPV.

It should be also noted from Fig.5 that the diffraction efficiency continuously increases even after the laser irradiation is removed. In addition, the efficiency of the MDDO-PPV doped azo-polymer stepwise increases upon stopping the recording. Especially this anomalous increase in the diffraction efficiency is most remarkable in the film of MDDO-PPV concentration of 3mol%.

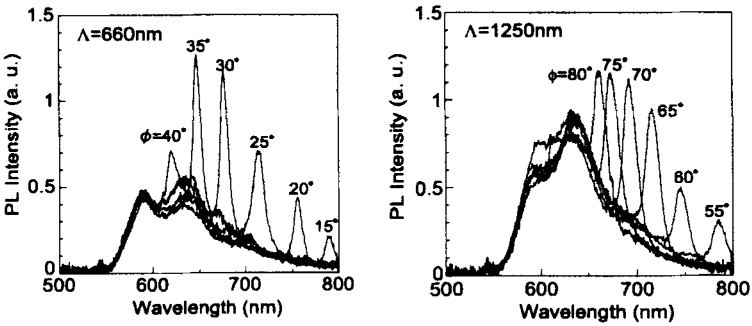

FIGURE 8 Photoluminescence spectra emitted from the composite films having surface relief grating with the periodicity of (a) 660nm and (b)1250 nm as a function of the monitoring angle ϕ.

<u>Photoluminescence from composite film having surface relief grating</u>

MDDO-PPV is known to show PL with high quantum efficiency. The composite film of azo-polymer and MDDO-PPV also shows intense PL in spite of the low concentration of PPV. In such composite film with surface relief grating, the emission characteristics of PL should be influenced by the periodic structure of the relief grating. We have investigated angular dependence of the PL intensity emitted from the MDDO-PPV in the composite film having surface relief grating. Measurement geometry is shown in Fig.7. Excitation beam of 488nm in wavelength was irradiated for PL from the rear side of the film (from the glass substrate side) and the PL spectra were monitored from the polymer side.

Figures 8 (a) and (b) show PL spectra of the composite films having surface relief grating with the periodicity of 660 and 1250 nm, respectively. As is evident from these figures, sharp peaks superimposed on an original PL spectra of MDDO-PPV are observed and the peak positions depend on the monitoring angle ϕ which determines the direction of the photodetector with respect to the normal direction of the film surface.

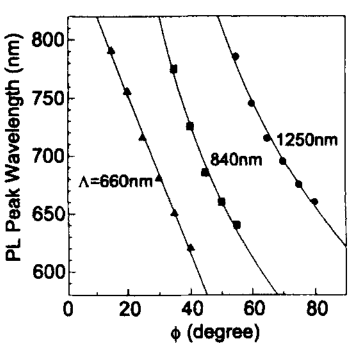

FIGURE 9 Wavelength at which the PL peak is observed as functions of the monitoring angle ϕ and the periodicity of the recorded relief grating Λ.

Figure 9 shows the wavelength at which the PL peaks appear as functions of ϕ and the periodicity of the recorded relief grating Λ.

It should be noted that these emission peaks are not associated with a simple diffraction of PL by the surface grating formed on the film. In general, diffraction angle ϕ_d of the grating should be determined by the grating periodicity Λ and the wavelength of the light λ in accordance with the relation, $\phi_d = \mathrm{Sin}^{-1}(\lambda/\Lambda)$. That is, ϕ_d increases with decreasing Λ and for the longer λ. In the case of the azo-polymer studied here, however, the angle ϕ, at which the PL peaks are observed, monotonously decreases with shifting the peak wavelength toward longer and upon the reduction of the grating periodicity. Namely, directional characteristics of PL emission from the film with surface grating can not be explained in terms of a simple diffraction theory. The detailed characteristics and mechanism of the anomalous angular dependence of PL is now under study.

CONSLUSION

The formation of surface relief grating on a composite film of conducting polymer MDDO-PPV and acrylate polymer containing azo-substituent was investigated. The diffraction efficiency of the grating depends on the concentration of doped MDDO-PPV. In the concentration range of MDDO-PPV higher than 3mol%, the diffraction efficiency decreased with increasing MDDO-PPV concentration because of the suppression of the relief height. However, the formation of surface relief was promoted by slight doping of conducting polymer (<3%) and progressed even after stopping irradiation of laser light. Anomalous angular characteristics of photoluminescence from the composite film having surface relief grating on it was also observed.

Acknowledgement

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