Photorefractivity Based on Photoinduced Ionic-conductivity Changes with Crowned Spirobenzopyran

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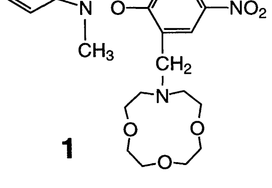
Significant light diffraction by photorefractive effect has been realized with composite films consisting of a nonlinear optical compound, crowned spirobenzopyran, a polymeric lithium salt, and poly(methyl methacrylate), based on a mechanism of photochemical ionic-conduction control by the photochromic crown ether.

Photorefractivity, which was discovered with inorganic crystals,[1] often happens by spatial modulation of refractive index of nonlinear-optical materials by charge redistribution. Considerable attention has been focused on organic photorefractive materials, taking advantage of their much higher processibility and diversity than the inorganic materials.[2,3] In general, the organic photorefractive materials consist of nonlinear-optical, charge-generating, charge-transporting, and charge-trapping compounds and a binder polymer, or polymers containing their corresponding functional groups. In photorefractive organic materials, space-charge formation, which brings about ordered orientation of the nonlinear-optical moiety, is performed by photoinduced redistribution (charge generation followed by electric-field-induced drift) of electronic carriers i.e., electrons or holes. Photoinduced redistribution of ionic carriers, i.e., cations or anions, should afford such space-charge formation inducing photorefractive effect.

We have been engaged in the design of photoresponsive ion-conducting materials involving photochromic crown compounds.[4-6] For instance, a spirobenzopyran incorporating a crown ether moiety at the 8-position (**1**), what we call crowned spirobenzopyran, can isomerize photochemically between its spiropyran and merocyanine forms.[7] By the photoisomerization of crowned spirobenzopyran, photochemical control of cation-binding ability of its crown moiety is feasible, based on intramolecular interaction between a crown-complexed cation and a phenolate anion in the merocyanine form. This photochemical control of cation-binding ability by **1**, in turn, can afford photoinduced ionic-conductivity changes, when the photochromic crown compound is contained in ion-conducting composite polymers.[4]



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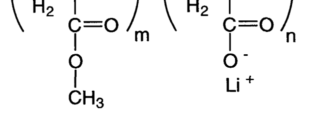

PMMA-Li m : n = 4 : 1

It is thus expected that the present ionic-conductivity switching system of crowned spirobenzopyran induces photorefractive effect by redistribution of ionic species. Here we wish to report photorefractive effect involving the photochemical control system of cation-binding ability of crowned spirobenzopyran **1**.

Composite films which consist of 4'-(*N,N*-dimethylamino)-benzylidene-2-methyl-4-nitroaniline (DBMNA, 43.5 wt%) as the nonlinear optical compound, crowned spirobenzopyran **1** (2.2 wt%) as the photocontrol agent of ionic conductivity, a lithium salt (0.2 wt%) as the ion-conducting species, and poly(methyl methacrylate) (PMMA, 54.3 wt%) as the binder polymer, were hot-pressed between two indium-tin-oxide-coated (ITO) glasses with a polyamide spacer of 100 μm. Diffraction efficiencies of the composite films were measured by a four-wave mixing system using writing (5 mW) and reading (0.5 mW) beams of He-Ne lasers. The diffraction efficiency was increased with a raise in the applied electric field (Figure 1). No significant diffraction

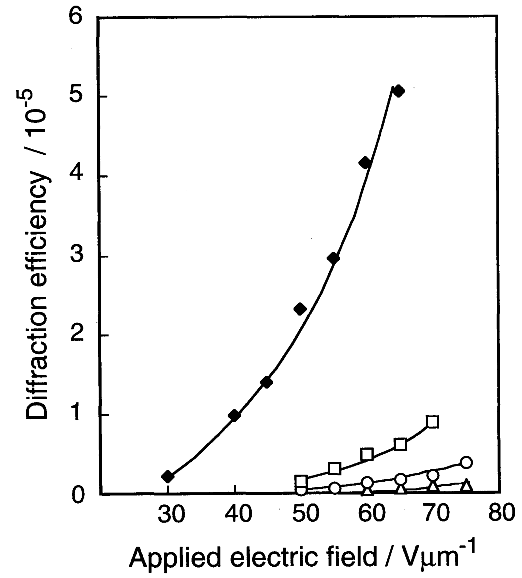

Figure 1. Dependence of diffraction efficiency on applied electric field in four-wave mixing experiment for DBMNA/**1**/lithium salt/PMMA.
Lithium salt : LiCl (△), $LiClO_4$ (○), $CH_3(CH_2)_{16}CO_2Li$ (□), and PMMA-Li (◆).

was observed without the applied electric field or without any lithium salt or/and the nonlinear-optical compound in the composite film. It is therefore obvious that some refractive-index change derived from the photoisomerization between spiropyran and merocyanine forms of **1** itself is not the main reason for such significant diffraction as seen in the present system. An alternative reason for the photoinduced diffraction is photorefractive effect based on space-charge formation caused by the photoinduced cation-complexing-ability change of crowned spirobenzopyran.[4]

The composite films as cast were dark red with an absorbance of about 0.045 at 633 nm, so **1** is considerably isomerized to its corresponding merocyanine form even under dark conditions and the crowned merocyanine can bind Li^+ strongly in composite films. In a separate experiment, irradiation of visible light (>500 nm) on a composite film decreased the absorbance at 633 nm to 0.023. This means that visible light causes back isomerization of the crowned merocyanine to **1**, thus releasing Li^+ from the crown ether moiety. In a control composite film containing a spirobenzopyran derivative without crown ether moiety instead of **1**, there is little photoinduced change of absorbance at 633 nm. It is thus considered that the photoinduced change of cation-complexing ability of **1** and thereby of cation mobility leads to the space-charge formation for photorefractive effect. If this is the case, suppressed mobility of a counter anion of a lithium salt should increase the contribution of cation-mobility changes to the ionic-conductivity changes, based on the mechanism for cation-complexing-ability change of crowned spirobenzopyran, thus enhancing the photoinduced space-charge formation and thereby the diffraction. As expected, the employment of large counter anions, which have relatively low mobility, raised the diffraction efficiency as also demonstrated in Figure 1. Specifically, drastic diffraction enhancement was attained in the single-ionic conducting system where only the cation takes part in the ionic conduction,[4] that is, polyanions such as PMMA-Li that can be obtained by partial hydrolysis of PMMA with lithium methoxide.

A direct evidence for the photorefractivity in the present system is self diffraction by two-beam coupling measurements.[2] The composite films were irradiated by two writing beams of an equal light intensity (5-mW He-Ne laser) with an electric field applied (Figure 2). On applying the electric field, one of the writing beam (probe light) was enhanced in the intensity, while the other writing beam (pump light) was weakened. The gain (loss) in the intensity on the two-beam coupling experiment is a proof for the photorefractive origin in the present system based on photoinduced ionic-conductivity switching by crowned spirobenzopyran.

Thus, the present system has realized a photorefractive system using photoresponsive ionic conduction. At the moment, the diffraction efficiencies in this ion-conducting system are not so high as those in electron(or hole)-conducting system.[8] However, since ion-conducting system allows direct space-charge formation by ion migration, efficient photorefractive systems may be expected by using photoresponsive ionic conductors similar to the present system containing a photochromic crown compound.

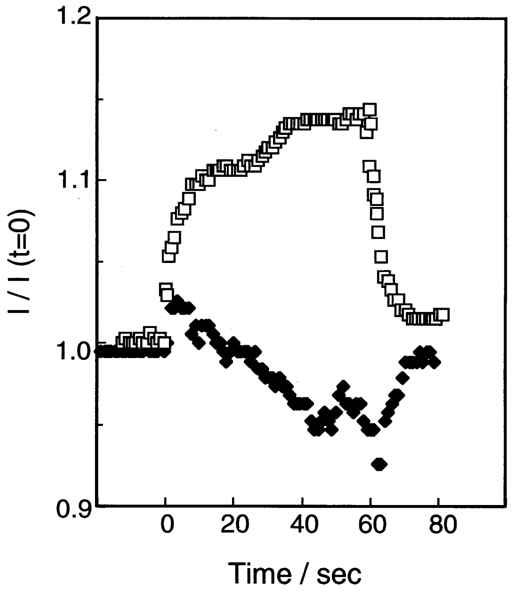

Figure 2. Two-beam coupling experiment for DBMNA/**1**/PMMA-Li/PMMA system.
The intensity of diffracted lights (□ : probe; ■ :pump) was monitored as an electric field (75 Vμm^{-1}) was switched on at t=0 and off at t=60 s.

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