Extraordinary Large Refractive Index Change of Poly(phenylene vinylene) Derivatives induced by Photo- or Quantum Beam Irradiation

Takashi Yamashita, Kota Shinohara, Yosuke Nakatoh, Yusa Muroya and Kunihiro Okano

Faculty of Science and Technology, Tokyo University of Science
2641 Yamazaki, Noda, Chiba 278-8560, Japan

Poly(phenylene vinylene) structure is one of the chromophore with large two photon absorption (TPA) cross section, which is expected as the materials for high density optical data storage with the TPA induced reaction. Photo-irradiation to a poly(phenylene vinylene) derivative changes the refractive index of the polymer by the magnitude as high as 0.7. The mechanism involves photo-induced electron transfer from the TPA dye to matrix for the reaction of a distyrylarene derivative. The refractive index of the polymer also can be changed by the electron beam irradiation.

Keywords: refractive index / two photon absorption / photo optical effect / distyrylarene derivative

1. Introduction

Two photon absorption dyes attract much attention because they are applicable to 3-D micro-fabrication 3-D optical memories and so on, because their photochemical reactivity depends on the square of incident light intensity, and so photochemical reaction preferentially occurs at the focal point.\(^1\)

Various functions should be incorporated in materials in order to building up those two photon absorption induced functional materials besides the two photon absorption dyes. However, it is difficult to design a dye which possesses all of the function from two photon absorption to property change through chemical reaction. And so it is important to design the combination of several molecules having various individual functions. Perry et al reported distyrylarene derivatives as the dyes of large two photon absorption cross section\(^2\), which was one of the reliable candidates of initiator of the reaction.

Recently we have reported the photo-optical effect of a mixed sample of distyrylarene derivatives as two photon absorption dyes, sulfonium salt as photo acid generator, and Rhodamine B base as environment chromic dye.\(^3\)

In this paper refractive index change of a poly(phenylene vinylene) derivative was investigated by laser irradiation or electron beam irradiation.

2. Experimental

2.1 Materials

Preparation of bis(dibuthylaminostyryl)benzene (DBASB) was reported in the previous paper.\(^3\) Solvents were of spectral grade purchased from Wako pure chemical Co. Ltd., which were used as received. Chemical structures of the materials are shown in Fig 1.
2.2 Photoirradiation and electron beam irradiation

Photoirradiation of solution was performed by 420nm light, whose intensity was 400µW/cm². Electron beam irradiation was performed with an accelerator whose acceleration voltage is 1 MeV and electric current is 1 mA.

3. Results and Discussion

3.1 Optical properties of DBASB and DEO-PPV

Fig 2 shows the absorption spectra of DBASB and DEO-PPV either in solution or in solid state film. Absorption maximum of the DBASB is 420 nm, and the absorption of DEO-PPV is red-shifted compared to that of DBASB in solution, then the absorption of DEO-PPV film further red shifted. Fluorescence of DBASB is observed at 510 nm, and fluorescence shoulder is observed about 600 nm for DEO-PPV in addition to emission maximum below 500 nm.

The absorption of DEO-PPV non-linearly decreases upon photoirradiation, with threshold of 10mW of irradiation power density. Fig. 3 shows the refractive index and extinction coefficient of the DEO-PPV before photoirradiation. The magnitude of refractive index change is as large as 0.7.

The refractive index of the DEO-PPV rapidly decreased upon EB irradiation, showing this material is useful for refractive index lithography.

5 References