Poly(pyridine-2,5-diyl) Containing Indigo Unit and Optical Third Harmonic Generation from Its Film

Takakazu YAMAMOTO,* Kenichi KIZU, Tsukasa MARUYAMA,
Naoki OOBA,[†] Satoru TOMARU,[†] and Kenji KUBOTA[††]
Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 227
† NTT Opto-Electronics Laboratories, Nippon Telegraph and
Telephone Corporation, Tokai, Ibaraki 319-11
†† Faculty of Engineering, Gunma University, Tenjincho, Kiryu 376

A copolymer of pyridine-2,5-diyl and indigo-6,6'-diyl has been prepared by dehalogenation polycondensation using Ni(0) complex. The copolymer forms a good film, and the film shows the three-photon resonant third-order nonlinear susceptibility $\chi^{(3)}$ of about 10^{-11} esu at absorption of poly(pyridine-2,5-diyl) unit.

Nonlinear optical properties of π-conjugated polymers and colorants are subject of recent interest, and a number of papers have been published on the nonlinear optical properties of the materials.[1] However, nonlinear optical properties of π-conjugated polymers containing color center have not been reported. We now report optical third harmonic generation, THG, from poly(pyridine-2,5-diyl) PPy containing a color center, indigo unit.

Dehalogenation polycondensation of 2,5-dibromopyridine with Ni(0) complex Ni(0)L$_m$ (a mixture of bis(1,5-cyclooctadiene)nickel(0) and 2,2'-bipyridyl)[2] in the presence of 0.25 molar ratio of 6,6'-dibromoindigo gives a deep green copolymer in 90% yield after work up in a manner similar to that previously reported;[2]

$$\text{(1)}$$
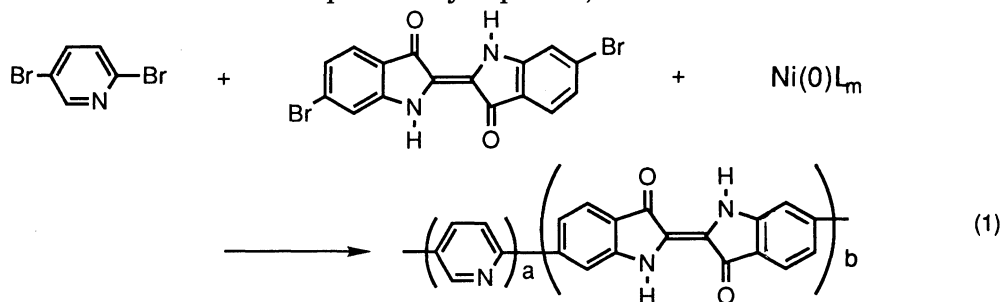
The IR and UV-visible spectra of the copolymer are reasonable for its structure. The UV-visible spectrum shows two absorption bands at 370 nm (absorption due to the PPy or oligo(pyridine-2,5-diyl) unit)[2] and 645 nm (absorption due to indigo unit) in formic acid in an

absorbance ratio of about 10:1. The λ_{max}value of 370 nm essentially agrees with the λ_{max} value of PPy (373 nm),[2] whereas the absorption band of indigo (615 nm)[3] is somewhat shifted to longer wavelength by attachment of the PPy or oligo(pyridine-2,5-diyl) unit. The ratio (a:b in Eq. 1) between the pyridine-2,5-diyl unit and indigo-6,6'-diyl unit estimated from the relative absorbance ratio (10:1) and molecular absorption coefficients of the pyridine unit in PPy (ε = 20000)[2] and indigo (ε = 9400)[3] roughly agrees with the feeding ratio of the two monomers: (a:b)$_{estimated}$ = 10/20000:1/9400 = 4.7:1. The copolymer has molecular weight of 14000 as determined by light scattering method.[4]

Casting the formic acid solution of the copolymer on a Pyrex glass plate and removal of formic acid under vacuum give a film with good optical and mechanical properties. Figure 1 shows UV-visible absorption spectrum and $\chi^{(3)}$ profile of the copolymer film with thickness of 0.25 μm. The $\chi^{(3)}$ value is enhanced up to 10^{-11} esu by three-photon resonance at the absorption region of PPy, and is more than 10^{-12} esu even in the nonresonant region of PPy. Both values are comparable to those of π-conjugated polymers with sufficiently long π-conjugation system. The present observation on THG as well as the

Fig. 1. (a) UV-visible absorption spectrum (-) and (b) $\chi^{(3)}$ profile of the copolymer film (o).

excellent dispersion of the color center in the polymer material, in contrast to difficulty to disperse well colorants like indigo in polymer materials, is expected to give a new basis to design polymer-based $\chi^{(3)}$ materials and control optical properties of the materials.
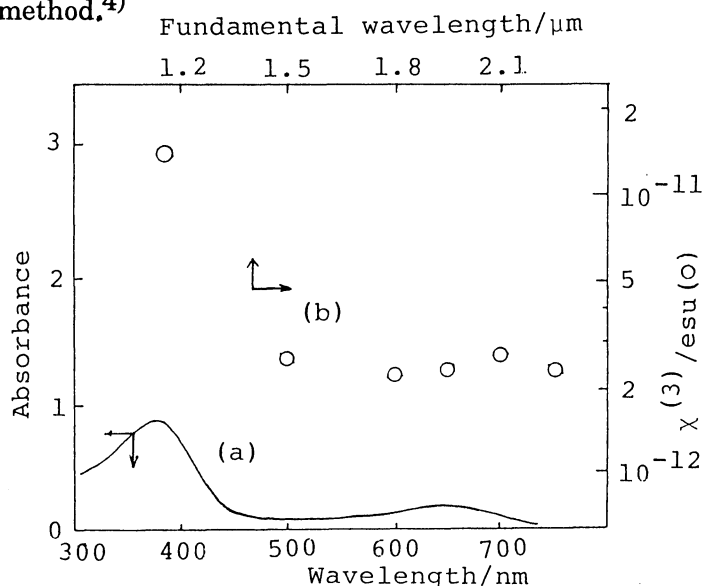
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