

# Study on third-order nonlinear optical properties of a soluble poly(*p*-phenylene vinylene) derivative

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A soluble poly(2-methoxy-5-decoxy)-*p*-phenylene vinylene (PMODOPV) was synthesized via dehydrochlorination reaction and characterized by UV-visible absorption spectrum. The results showed that PMODOPV had a broad optical absorption band in the range of 450–550 nm and the optical band gap was calculated to be around 2.12 eV. The third-order nonlinear optical susceptibilities ( $\chi^{(3)}$ ) of PMODOPV films implanted by 30-keV  $N^+$  ions in the dose range of  $3.8 \times 10^{15}$ – $9.6 \times 10^{16}$  ions/cm<sup>2</sup> were measured by degenerate four-wave mixing (DFWM) technique. The results demonstrated that the resonant and off-resonant  $\chi^{(3)}$  values were all enhanced significantly by means of ion implantation. The maximum resonant  $\chi^{(3)}$  value of  $9.67 \times 10^{-9}$  esu at 532 nm and off-resonant  $\chi^{(3)}$  value of  $2.49 \times 10^{-10}$  esu at 1.064  $\mu\text{m}$  were obtained when the ion dose was  $3.8 \times 10^{16}$  ions/cm<sup>2</sup>.

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Recently,  $\pi$ -conjugated polymers with large  $\pi$ -electron delocalization have received much attention because of their larger and ultra faster nonlinear optical (NLO) response due to the distortion of  $\pi$ -conjugated electronic charge distribution along the main chain<sup>[1–3]</sup>. Poly(*p*-phenylene vinylene) (PPV) and its derivatives are typical  $\pi$ -conjugated polymers that have been described in the literature for the possibility of using them in light-emitting device and large-area multicolor display, while the reports on their NLO properties are less actually<sup>[4,5]</sup>. On the other hand, the NLO susceptibilities of PPV and its derivatives are too small to achieve practical applications<sup>[6,7]</sup>. Based on these situations, we synthesized and characterized a soluble poly(2-methoxy-5-decoxy)-*p*-phenylene vinylene (PMODOPV), and  $N^+$  ion implantation was carried out in order to enhance its third-order NLO susceptibility ( $\chi^{(3)}$ ) in this paper.

The overall synthetic route to PMODOPV was as follows. 1-decoxy-4-methoxy-benzene was synthesized from the reaction of 4-methoxyphenol with *n*-decanyl bromide in the presence of sodium alkoxide. The monomer, 2-decoxy-5-methoxy-*p*-bis (chloromethyl) benzene was then prepared by chloromethylation of its precursor in the system of formaldehyde, hydrochloric acid and a little paraformaldehyde in dioxane solution. The polymer was synthesized by condensation polymerization of monomer and tert-butoxide potassium in tetrahydrofuran and a solid product with deep red color was obtained (yield: 56%). The molecular structure of PMODOPV is shown in Fig. 1.

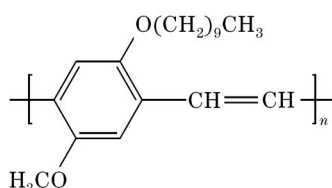


Fig. 1. Molecular structure of PMODOPV.

The PMODOPV films were prepared on quartz glass plates at room temperature by spin coating with the solution of PMODOPV in chloroform for a thickness of about 800 nm (measured by American Dektak-3 film-thickness meter). The PMODOPV films were implanted by 30-keV  $N^+$  ions with the dose in the range of  $3.8 \times 10^{15}$ – $9.6 \times 10^{16}$  ions/cm<sup>2</sup> followed by thermal annealing at 100 °C for about 2 h in the vacuum. UV-visible absorption spectrum was recorded on a Hitachi U-2001 UV-visible spectrometer. The  $\chi^{(3)}$  values were measured by degenerate four-wave mixing (DFWM) system shown in Fig. 2, where BS1, BS2, BS3, and BS4 were beam splitters;  $M_1$ ,  $M_2$ , and  $M_3$  were fully reflecting mirrors; D1 and D2 were pyroelectric detector and silicon detector, respectively;  $I_f$ ,  $I_b$ ,  $I_p$ , and  $I_s$  were forward pump beam intensity, backward pump beam intensity, probe beam intensity, and signal beam intensity, respectively. The pulse laser beam came from an American Spectra Physics GCR-170 Nd:YAG laser (pulse-width 10 ns, repetition-frequency 10 Hz).

UV-visible absorption spectrum of PMODOPV is shown in Fig. 3. It is obvious that there exists a broad optical absorption band in the range of 450–550 nm assigned to  $\pi \rightarrow \pi^*$  transition of  $\pi$ -conjugated structure followed by a red shift of absorption maximum from 400 to 497 nm in comparison with unsubstituted PPV because

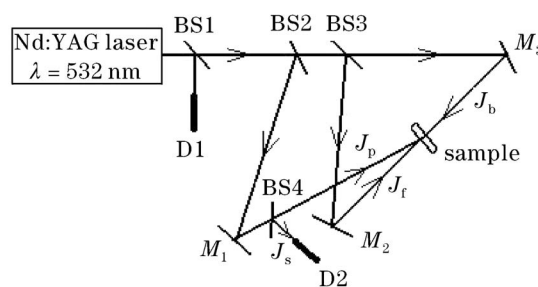


Fig. 2. DFWM experiment setup.

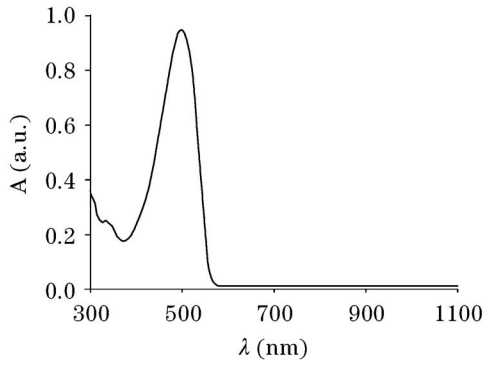


Fig. 3. UV-visible absorption spectrum of PMODOPV.

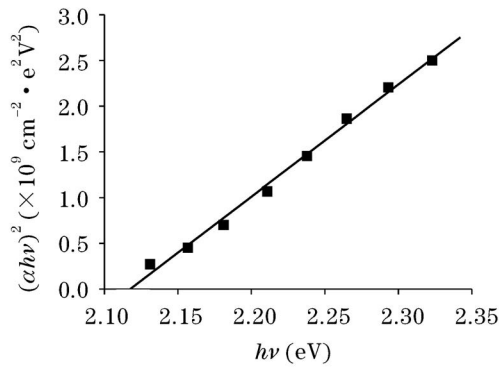


Fig. 4. Plot of  $(\alpha h\nu)^2$  versus  $h\nu$  for PMODOPV film.

of the presence of strong electron-donating groups<sup>[8]</sup>. The optical absorption maximum of PMODOPV shifting to higher wavelength compared with that of unsubstituted PPV suggests a decrease in the optical band gap. The optical band gap ( $E_g^{opt}$ ) can be estimated by studying the dependence of absorption coefficient ( $\alpha$ ) on incident photon energy ( $h\nu$ ). For most of the amorphous semiconducting materials,  $\alpha$  is given by<sup>[9]</sup>

$$(\alpha h\nu)^2 = C(h\nu - E_g^{opt}), \tag{1}$$

where  $C$  is a constant. Figure 4 shows the plot of  $(\alpha h\nu)^2$  versus  $h\nu$  for PMODOPV film and the extrapolation yields an  $E_g^{opt}$  value of 2.12 eV. It indicates that PMODOPV synthesized in this paper has a narrower optical band gap and is suitable for potential application in NLO materials.

The  $\chi^{(3)}$  value can be determined by comparing the measured signals for sample films with that for carbon disulfide as reference under the same experimental conditions with the following formula<sup>[10]</sup>

$$\chi^{(3)} = \left( \frac{I_s}{I_{CS_2s}} \right)^{1/2} \frac{L_{CS_2}}{L} \left( \frac{n}{n_{CS_2}} \right)^2 \chi_{CS_2}^{(3)}, \tag{2}$$

where  $L$  is the thickness and  $n$  is the linear refractive index. The  $\chi_{CS_2}^{(3)}$  value is measured to be  $1.70 \times 10^{-12}$  esu at 532 nm, and the same result has been reported elsewhere<sup>[11]</sup>. With the measurement and calculation, the resonant  $\chi^{(3)}$  value at 532 nm and off-resonant  $\chi^{(3)}$  value at 1.064  $\mu\text{m}$  of PMODOPV film with the increase of ion dose are obtained.

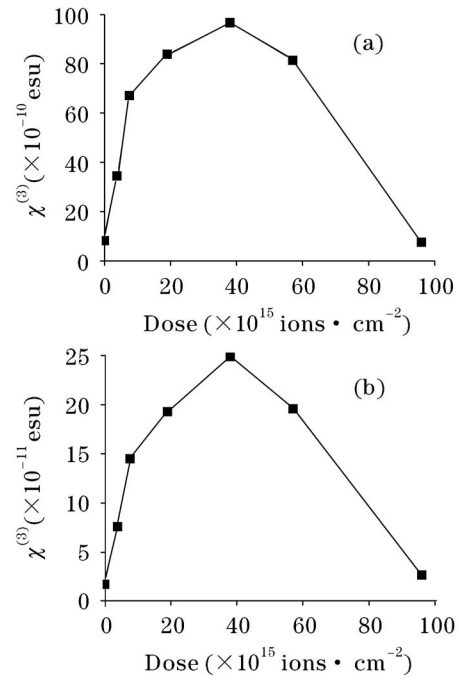


Fig. 5.  $\chi^{(3)}$  value plotted against  $N^+$  ion dose for PMODOPV film at 532 nm (a) and 1.064  $\mu\text{m}$  (b).

The resonant  $\chi^{(3)}$  value at 532 nm plotted against  $N^+$  ion dose with the energy of 30 keV for PMODOPV film is shown in Fig. 5(a). It is found that the  $\chi^{(3)}$  value of pristine film is  $8.27 \times 10^{-10}$  esu and shows a rapid increase once the film is bombarded by  $N^+$  ions and achieves the maximum value of  $9.67 \times 10^{-9}$  esu which is almost eleven times larger than that of pristine film at an ion dose of  $3.8 \times 10^{16}$  ions/cm<sup>2</sup>. The  $\chi^{(3)}$  value begins to decrease at a slower rate with further increase in ion dose and attains a minimum value of  $7.58 \times 10^{-10}$  esu when the ion dose is up to  $9.6 \times 10^{16}$  ions/cm<sup>2</sup>.

Figure 5(b) shows the off-resonant  $\chi^{(3)}$  value at 1.064  $\mu\text{m}$  plotted against  $N^+$  ion dose with the energy of 30 keV for PMODOPV film. It is obvious that the trend of variation of  $\chi^{(3)}$  value in the off-resonant region is very similar to that in the resonant region with the increase of ion dose. The  $\chi^{(3)}$  value of pristine film is  $1.76 \times 10^{-11}$  esu and increases fleetly until a maximum value of  $2.49 \times 10^{-10}$  esu is reached at an ion dose of  $3.8 \times 10^{16}$  ions/cm<sup>2</sup> followed by a slower decrease. The  $\chi^{(3)}$  value is decreased to  $2.68 \times 10^{-11}$  esu when the ion dose is  $9.6 \times 10^{16}$  ions/cm<sup>2</sup>. We also find that the increasing extent of  $\chi^{(3)}$  value in off-resonant region is more than that in resonant region, which reflects that  $N^+$  ion implantation makes more remarkable contributions to the enhancement of  $\chi^{(3)}$  value in off-resonant region than that in resonant region.

In summary, we have synthesized and characterized a soluble poly (2-methoxy-5-decoxy)-*p*-phenylene vinylene (PMODOPV) successfully. UV-visible absorption spectrum shows that PMODOPV has remarkable optical absorption at the wavelength in the range of 450–550 nm and a narrower optical band gap of 2.12 eV is also observed. DFWM measurement shows that the resonant  $\chi^{(3)}$  value of  $8.27 \times 10^{-10}$  esu at 532 nm and off-resonant  $\chi^{(3)}$  value of  $1.76 \times 10^{-11}$  esu at 1.064  $\mu\text{m}$  of pristine

PMODOPV film are obtained, and they are all enhanced significantly in virtue of  $N^+$  ion implantation. When the ion dose was  $3.8 \times 10^{16}$  ions/cm<sup>2</sup>, the resonant  $\chi^{(3)}$  value at 532 nm and off-resonant  $\chi^{(3)}$  value at 1.064  $\mu\text{m}$  are increased to  $9.67 \times 10^{-9}$  esu and  $2.49 \times 10^{-10}$  esu, respectively. It demonstrates that the  $N^+$  ion implantation has a strong effect on the  $\chi^{(3)}$  value of  $\pi$ -conjugated polymer not only in resonant region but also in off-resonant region, which provides a new method to achieve NLO polymer materials with larger  $\chi^{(3)}$  value for promising all-optical devices.

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