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Synthesis, electroconductivity and third-order nonlinear optical property of poly(2-isopropoxy-5-methoxy-1,4-phenylenevinylene)

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Summary

Asymmetrically disubstituted poly(2-isopropoxy-5-methoxy-1,4-phenylene-vinylene), PIMPV, was prepared in thin films via organic-soluble precursor polymer method. These polymer films could be easily stretched up to 7 times, and the drawn films of the PIMPV could be doped with $FeCl_3$ and I_2 to give conductivities of 26.9 and 11.3 Scm^{-1}, respectively. The third-order nonlinear optical susceptibility of the polymer was determined using third harmonic generation(THG) method at 1907 nm, fundamental wavelength. Measured $\chi^{(3)}$ $(-3\omega: \omega, \omega, \omega)$ value was 3.7×10^{-12} esu.

Introduction

Organic polymers as potential candidates for applications in optical devices are very attractive because of their large optical nonlinearity, fast response time and low absorption loss as compared with inorganic materials. Among organic nonlinear materials, conjugated polymers with extensive π-electrons delocalization are important because of the large π-electrons contribution to optical nonlinearity.

Especially, poly(1,4-phenylenevinylene) (PPV) and its derivatives have been attracting considerable interest in recent years because of their electrical and nonlinear optical (NLO) properties (1,2). These polyconjugated polymers can be readily prepared in high molecular weight through the water-soluble precursor route. These water-soluble precursor polymers can be transformed into organic-soluble precursor polymers by treatment with methanol. Both of the water-soluble and organic-soluble non-conjugated precursor polymers are cast into films and then converted into extended π-conjugated structures by thermal elimination reaction. Substitution on the phenylene ring of PPV with different types of electron-donating and electron-withdrawing groups has a significant influence on the electronic and morphological structures of the resulting polymer and, thus affects the electrochemical and optical properties (3,4,5). The presence of strong electron donors leads to the reduction in band gap and ionization potential of the conjugated polymers, to facilitate oxidation with weak oxidants such as I_2 and $FeCl_3$. For example, poly(2,5-dimethoxy-1,4-phenylenevinylene) (PDMPV) can be doped with I_2 to give electrical conductivity in the order of 10^0 to 10^2 Scm^{-1} (6), whereas the precursor polymer of PDMPV can not be drawn to any extent during or prior to the elimination reaction. Drawability of a precursor polymer is an important factor in conductivity because an oriented film shows a significantly enhanced conductivity value on doping along the drawn direction. Generally, the conductivities of

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drawn polymer films are 10 times higher than those of undrawn ones. The asymmetric introduction of methoxy and isopropoxy substituents on the phenylene ring of PPV can be important in manipulating the oxidation potential and especially, packing ability in a more controlled way.

In this study, we report some results of the electrical conductivities and the third harmonic generation measurement on thin films of PIMPV which electron-donating alkoxy groups are asymmetrically substituted. We also examine the polymer structure and coplanarity of PIMPV main chain by using NMR spectroscopy and molecular modeling.

Experimental

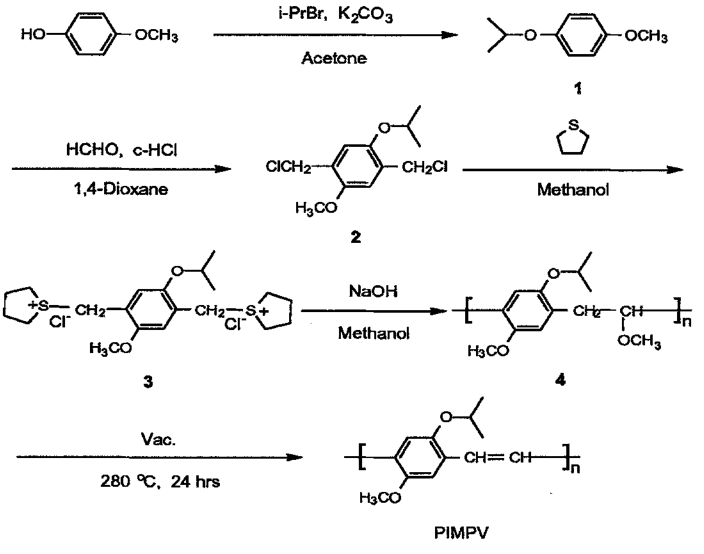
Monomer synthesis

1-Isopropoxy-4-methoxybenzene **1** was prepared by reacting the 4-methoxyphenol (0.16mol) with isopropylbromide (0.24mol) in acetone for 24 hrs. Colorless liquid was obtained and the yield was 70%. ^{1}H-NMR ($CDCl_3$, ppm) : d=6.8(s, 4H), 4.4(m, 1H), 3.8(s,3H), 1.3(d, 6H) and 7.24($CHCl_3$ from solvent).

2-Isopropoxy-5-methoxy-1,4-bis(chloromethyl)benzene **2** was synthesized by reacting **1** (0.09mol) with the mixture solution of formaldehyde(56mL) and conc-HCl(46.4mL) in dioxane solvent for 20 hrs at 100 °C. The yield was 40%. ^{1}H-NMR ($CDCl_3$, ppm) : d=7.0(d, 2H), 4.7(d, 4H), 4.6(m, 1H), 3.9(s, 3H), 1.4(d, 6H) and 7.24($CHCl_3$ from solvent).

The compound **2** (0.02mol) and excess tetrahydrothiophene were reacted at 50 °C in 20 mL of methanol for 20hrs. The reaction solution was concentrated by distilling out a part of the solvent and unreacted tetrahydrothiophene, and was poured into acetone at 0 °C. The precipitate was washed with acetone and dried. The yield of 2-isopropoxy-5-methoxy-1,4-phenylenedimethylene bis(tetrahydrothiophenium chloride), **3**, was 76%. ^{1}H-NMR (D_2O, ppm) : d=7.1(d, 2H), 4.6(m, 1H), 4.4(d, 4H), 3.8(s, 3H), 3.5~3.3(m, 8H), 2.3~2.1(m, 8H), 1.2(d, 6H) and 4.6(HDO from solvent). The syntheic route and structure of PIMPV are shown below.

Synthetic scheme



Polymerization

The monomer sulfonium salt solution (1.0M) in methanol was polymerized in an NaOH solution (1.0M) under nitrogen atmosphere at 0 °C. A few minutes later, green yellowish gel was formed. To transform this water soluble precursor polymer to organic soluble precursor polymer, methanol was added to reaction mixture. At first, gel was dissolved in methanol, after a few hours, yellowish gel particles were precipitated. It was filtered, washed with methanol and then dried under vacuum at room temperature. This polymer can be dissolved in methylenechloride, THF, acetone, etc. This organic-soluble precursor polymer was dissolved in methylenechloride, and then precursor polymer film was obtained by casting from this solution. For THG measurement, it was spin-coated on the BK-7 glass with 1,300 rpm. These precursor polymers were subjected to thermal elimination in vacuo at 280 °C for 24 hours to transform into the final polyconjugated polymer film. If desired for conductivity study, the precursor poymer films were uniaxially drawn at 120 °C using a zone-heating apparatus.

Analysis

^{1}H-NMR spectra were recorded on a Brucker AM 200 spectrometer. FT-IR spectra were obtained with Bomem Michelson series FT-IR spectrophotometer and UV-visible spectra were measured by Shimadzu UV-3100S. GPC analysis was performed on THF solution using a Waters Associates 440. Differential scanning calorimetry (DSC) and thermogravimetric analysis(TGA) were performed under nitrogen atmosphere at a heating rate of 10 °C/min with Dupont 9900 analyzer. Electrical conductivities were measured by using a four-in-line probe configuration on which resistance measurements were performed using a Keithley 197 digital multimeter. Thicknesses of spin-coated polymer films were measured by using Alpha step 200.

$\chi^{(3)}$ measurement

Third harmonic generation (THG) was performed to determine $\chi^{(3)}$ value of the PIMPV. Q-switched Nd:YAG laser which generates 1064 nm was used as a light source. The pulse duration and repetition rate were 8 ns and 10 Hz, respectively. The laser beam of 1064 nm was converted into 1907 nm using H_2 Raman cell to perform this measurement in transparent region which corresponds to the nonresonant region of three-photon resonance.

Results and Discussion

Once the film was cast from water-soluble precursor polymer solution, it could not be completely redissolved in water and organic solvents, even though IR spectra showed that only a very small amount of insoluble vinylene units were present in the film. So, it is very difficult to identify the structures of PPV derivatives by solution NMR spectroscopy. In order to confirm the precursor polymer structure, we converted the water-soluble precursor poymer into the organic-soluble precursor polymer. We obtained the fine ^{1}H-NMR spectrum of 4 which shows all of the corresponding peaks of the polymer (Figure 1). The two peaks which appear at 3.5~3.8 ppm are assigned to protons of methoxy group substituted on the phenylene ring. This splitting is explained by two possible position of methoxy group in polymer main chain. To confirm this result, we obtained ^{1}H-NMR spectrum of symmetrically substituted organic soluble precursor polymer of PDMPV. It also shows splitted peaks at 3.5~3.8 ppm. We can determine x and y values of PIMPV precursor polymer from the integrals of the splitted peaks. Determined x and y values are 0.61 and 0.39, respectively.

The number average and weight average molecular weights of organic soluble precursor polymer which were calculated from GPC data are 4.39 x 10^5, and 5.18 x 10^5

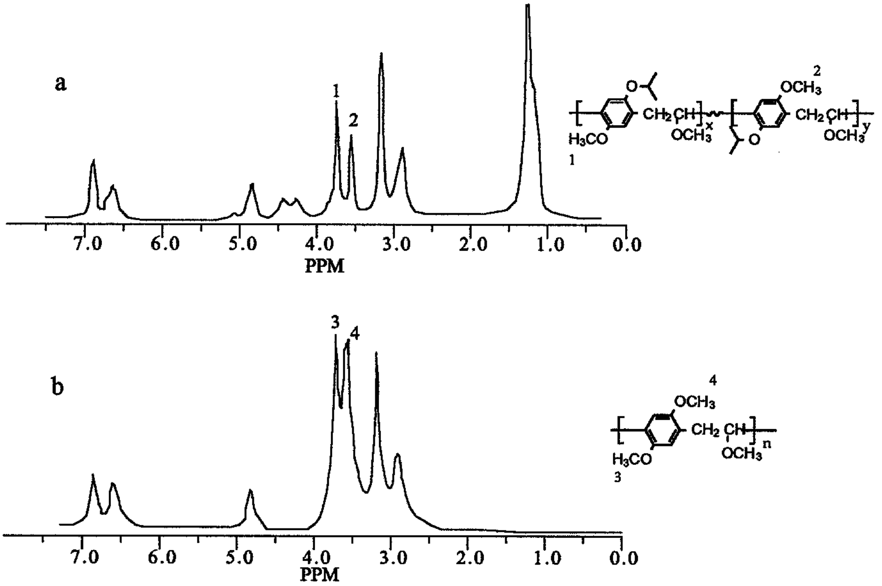


Figure 1. ^{1}H-NMR spectra of a) PIMPV precursor polymer and b) PDMPV precursor polymer in $CDCl_3$

respectively. Especially, the polydispersity value was 1.18 indicating that PIMPV polymer is almost monodisperse.

Thermal analyses of the elimination reaction of the precursor polymer **4** by TGA and DSC (Figure 2) with a heating rate of 10 °C/min indicated that one major weight loss

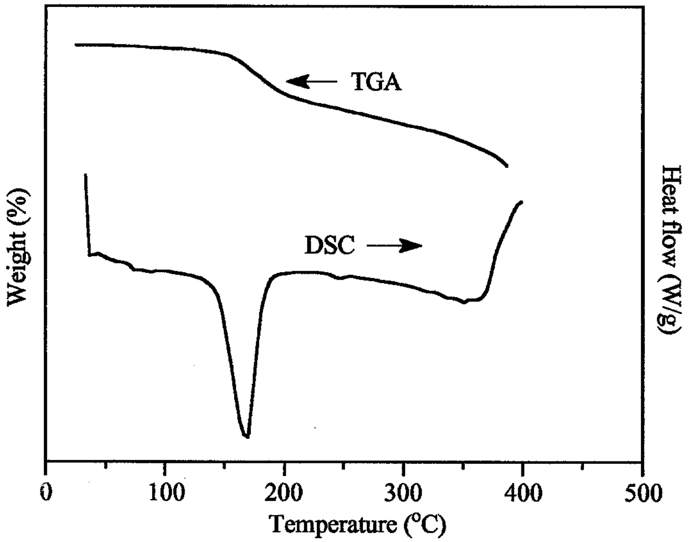


Figure 2. DSC and TGA thermograms of PIMPV precursor polymer

occurs at 120 °C ~ 170 °C. This endotherm corresponds to the elimination of methanol. DSC thermograms of water-soluble precursor polymers show two major weight losses at two different temperatures (5). The low temperature endotherm corresponds to the loss of water. But this low temperature endotherm due to loss of water around at 100 °C disappeared in DSC thermogram of our organic-soluble precursor polymer.

The film of PIMPV exhibits a strong IR absorption at 959 cm^{-1} indicating that the vinylene =CH bonds formed in the elimination reaction were entirely of trans configuration. A broad absorption peak at 3200~3600 cm^{-1} which appears in the spectrum of the water-soluble precursor polymer due to absorbed water, does not appear in the IR spectrum of organic-soluble precursor polymer. The profiles of the IR spectra of PIMPV and its precursor, not given in this article, are similar to those for other PPV derivatives (5).

Figure 3 shows UV-visible spectra of PIMPV and its precursor polymer. The uneliminated polymer film displayed absorption maximum at 300 nm, which is associated with partially formed stilbene and other units containing delocalized π-electrons. When the film was thermally eliminated, the absorption maximum for $\pi-\pi^*$ transition and the absorption edge were red-shifted to 460 nm and 600 nm, respectively. There is no absorption at 600~700 nm. This indicates that this polymer film is nonresonant at 636 nm wavelength used in third harmonic generation experiment.

Electrical conductivities of the polymers were measured using a four-in-line technique. On doping with I_2 vapor and $FeCl_3$ solution, the polymer films became black and highly electroconducting. The conductivities of undrawn and drawn (L/L_0=7) films of PIMPV when doped with I_2 were 0.91 and 11.3 Scm^{-1}, respectively and those for undrawn and drawn (L/L_0=7) $FeCl_3$-doped films were 0.61 and 26.9 Scm^{-1}, respectively. The conductivity values of drawn films are 10 times higher than those of undrawn ones.

As mentioned before, the dimethoxy substituted PPV film could not be drawn because of its dense packing ability between polymer chains due to symmetrical structure. On the other hand, asymmetrically disubstituted PIMPV could be readily stretched. However, the conductivity value of I_2-doped PIMPV film is lower than that of PDMPV. This can be

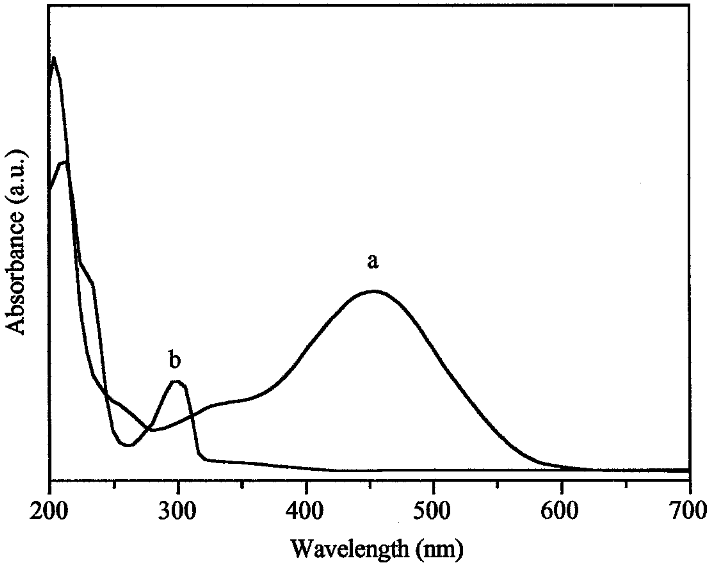


Figure 3. UV-visible spectra of a) PIMPV and b) PIMPV precursor polymer

attributed to following reason : a molecular model of the coplanar conformation of the 2-isopropoxy-5-methoxyphenylene-trans-vinylene unit indicates that the hydrogen atoms of isopropoxy group and of trans-vinylene are located too close each other to avoid such a steric repulsion, and thus the coplanar conformation has to be destroyed, leading to less efficient π-delocalization.

To determine the third order nonlinear optical susceptibility of PIMPV film, the third harmonic generation (THG) intensity of polymer(undrawn) was measured in function of the angle of incidence. THG from the BK-7 glass substrate was also measured as a reference. Figure 4 shows Maker-fringe patterns of the polymer and BK-7 glass substrate. The $\chi^{(3)}$ value of the PIMPV was calculated by comparing the measured THG peak intensity of the film and that of the substrate using the equation reported elsewhere, assuming the film thickness to be much thinner that the coherence length of the film(7,8). We also assumed that the effect of the refractive index difference between the PIMPV and the substrate for $\chi^{(3)}$ calculation is negligible. Measured $\chi^{(3)}$ value and film thickness of PIMPV were 3.7 x 10^{-12} esu and 0.36 μm, respectively. This $\chi^{(3)}$ value is slightly smaller than that of PDMPV, $5.4\text{x}10^{-11}$ esu at 1.85μm reported by Kaino et al(9). This result is explained by following two reasons. One is band gap energy difference of the polymers. It is well known that $\chi^{(3)}$ value is in inversely proportional to the sixth power of band gap energy (10). The edge position decreases from 610 nm of PDMPV to 590 nm of PIMPV, which indicates a increase in band gap energy. The other is the effect of NLO chromophore density. The NLO chromophore density of PIMPV is smaller than that of PDMPV because the numbers of repeating unit per unit volume of PIMPV polymer are less than those of PDMPV polymer. This is well consistent with the fact that the packing ability between PIMPV polymer chains, due to the bulky isopropoxy groups, is lower than that of PDMPV, even though PIMPV has a advantage of drawability compared with PDMPV.

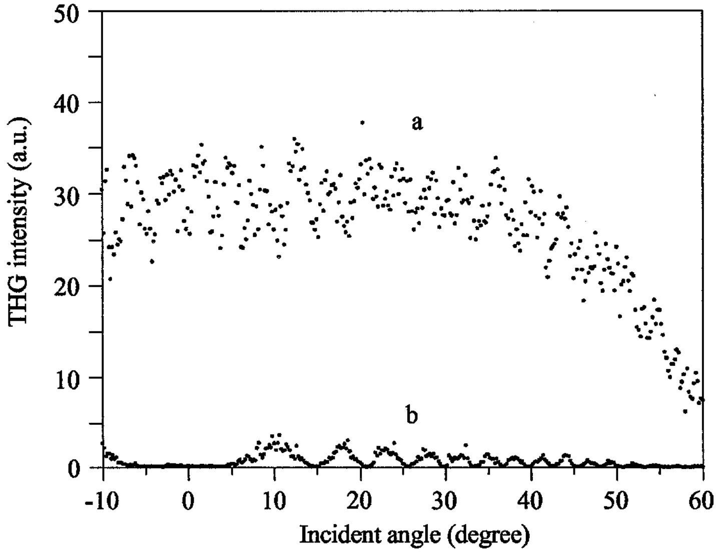


Figure 4. Maker-fringe patterns of a) PIMPV and b) BK-7 glass

Acknowledgement

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