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New NLO-functionalized poly(1,4-phenylenevinylene) derivative containing dinitrobenzene moiety as electron acceptor

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Summary

New NLO-functionalized poly(1,4-phenylenevinylene) (PDNAPV) containing 2,4-dinitroanilino group, was synthesized through organic-soluble precursor pathway. The prepared polymer was characterized with NMR, FT-IR, UV-visible and other spectroscopic methods to identify its properties. The result from the thermal analyses and spectroscopic techniques showed that the precursor was converted into PDNAPV around at 200°C without any decomposition of 2,4-dinitroanilino group. The second-order NLO coefficient ($\chi^{(2)}$) of poled PDNAPV film was determined by second-harmonic generation technique. The resonant $\chi^{(2)}$ value was 26 pm/V and the resonance-corrected value ($\chi^{(2)}(0)$) was 12 pm/V, which was stable at room temperature for a month

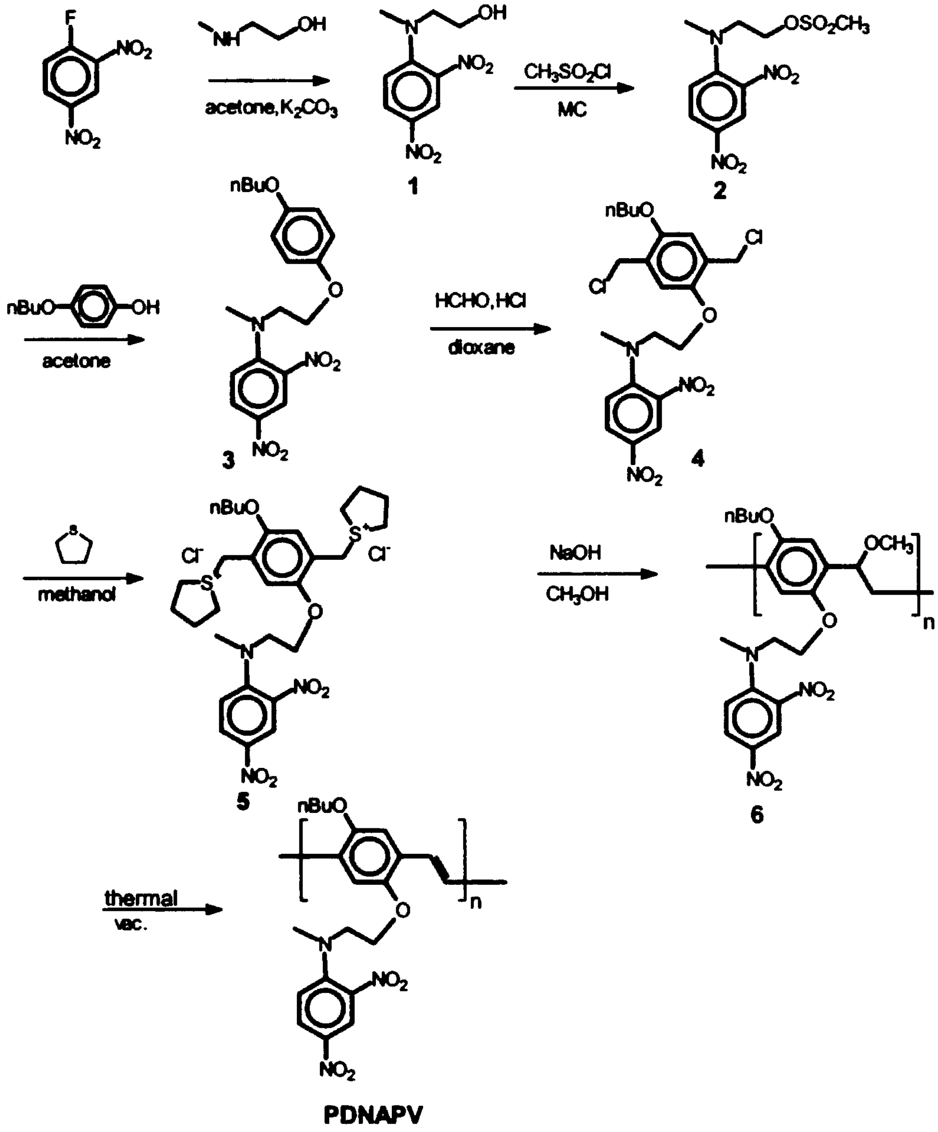
Introduction

To date many researches about polymeric materials have been done for electro-optic devices because of their advantages over inorganic ones. [1-2] Large nonlinear optical (NLO) activity and thermal stability at high temperature should be achieved for actual device application. There have been several ways to functionalize polymers as NLO materials. Firstly, blending NLO chromophores with polymer was used for polymeric NLO devices.(host/guest system) [3-4] Because of poor thermal stability of NLO activity, however, there have been much interest in binding NLO chromophore covalently to hard polymer backbone. [5-8] Polymers which show high glass transition temperature were used as a backbone to which NLO chromophore was attached.

Recently poly (1,4-phenylenevinylene) (PPV) derivatives have received much attention because of their great importance in the area of optical signal processing and

(PPVs) containing electron donor and acceptor in main chain showed very stable electro-optic properties. The nonlinearity, however, was not large because of synthetic difficulty to introduce a powerful electron donor in the PPV backbone. [15] Hence we incorporated the Disperse Red 1 as NLO chromophore to the side chain of PPV backbone. However Disperse Red 1 showed large absorption in visible region, especially at 532nm. Since the absorption in visible region lowers device efficiency, short absorption edge was required for actual application. [16,17] Compared to previous incorporated chromophore to the PPVs, 2,4-dinitroanilino group should give lower absorption edge and high NLO activity because of the strong acceptor strength of 2,4-dinitrobenzene groups. In this study, we are to discuss about the synthesis and characterization of poly(2-butoxy-5-(2-[(2,4-dinitrophenyl)methylamino] ethoxy)-1,4-phenylenevinylene) (PDNAPV) and about its NLO properties.

Experimental Part



Scheme 1. Synthetic scheme of PDNAPV

Synthesis of monomer

*2-[(2,4-Dinitrophenyl) methylamino[ethan-1-ol (**1**)*

A mixture of 2,4-dinitro-fluorobenzene (10g, 54mmol), potassium bicarbonate (7.5g, 54mmol) and N-ethanolamine(3.3g, 54mmol) was dissolved in acetone. The solution was refluxed for 8 hours and then cooled to room temperature. The product was extracted with ethyl acetate. Yellowish oil was obtained and it was further purified with column chromatography. The yield was 9.9g (76%).

^{1}H-NMR (200MHz, $CDCl_3$): δ 8.60(d, 1H), 8.15(q, 1H), 7.18(d, 1H), 3.88(d, 2H), 3.57(d, 2H), 2.96(s, 3H), 2.18(s. 1H)

*2-[(2,4-Dinitrophenyl) methylamino] ethyl methylsufonate (**2**)*

Compound **1** (9.9g, 41mmol) and methanesulfonyl chloride (4.7g, 41mmol) was dissolved in methylenedichloride and equivalent triethylamine (4.2g, 41mmol) was added dropwisely. After the addition of triethylamine, the reaction solution was refluxed for 1 hour. The crude product was extracted with methylene dichloride to give orange-yellow colored solid. The resulting solid was recrystalized in methanol several times. The product yield was 11.9g (91%).

^{1}H-NMR (200MHz, $CDCl_3$,): δ 8.63(s, IH), 8.23(q, 1Ha), 7.17(d, 1H), 4.20(t, 2H), 3.71(d, 2H), 3.03(s, 3H), 2.98(s, 3H)

*2,4-Dinitrophenyl-[2-(4-butoxyphenoxy)ethyl]methylamine (**3**)*

Compound **2**(10.0g, 31mmol), potassium bicarbonate (4.3g, 31mmol) and 4-butoxyphenol (5.2g, 31mmol) were dissolved in 50mL of acetone. The reaction solution was refluxed for 12 hours. After extraction and evaporation, yellow solid was obtained. The crude product was purified through recrystallization in methanol. The yield was 7.73g (64%).

^{1}H-NMR (200MHz, $CDCl_3$): δ 8.62(d, 1H), 8.19(q, 1H), 7.22(d, 1H), 6.74(d, 4H), 4.16(t, 2H), 3.86(t, 2H), 3.73(t, 2H), 3.03(s, 3H), 1.73(m, 2H), 1.40(m, 2H), 0.93(t, 3H).

*[2-(2,5-Bis(chloromethyl)-4-butoxyphenoxy)ethyl](2,4-dinitrophenyl)methylamine (**4**)*

Compound **3** (6.0g, 15.4mmol) was added in the mixture of 8.0mL of formaldehyde aqueous solution and 8.0mL of aqueous hydrochloric acid solution. The mixture was refluxed in the flow of dry hydrochloric gas. After 8 hours passed, The solution was cooled to room temperature and poured into cold sodium hydroxide solution (1.0N). The product was extracted with methylene dichloride and yellow solid was obtained after the evaporation of solvent.. The product yield was 4.64g (62%).

^{1}H-NMR (200MHz, $CDCl_3$): δ 8.65(d, 1H), 8.25(q, 1H), 7.28(d, 1H), 6.86(d, 2H), 4.60(s, 2H), 4.39(s, 2H), 4.25(t, 2H), 3.95(t, 2H), 3.79(t, 2H), 3.07(s, 3H), 1.76(m, 2H), 1.48(m, 2H), 0.95(t, 3H)

*2-Butoxy-5-(2'-[(2,4-dinitrophenyl)methylamino]ethoxy)-1,4-phenylenedimethylene-bis(tetramethylene suffionium chloride) (**5**)*

Compound **4** (40g, 8.2mmol) and excess tetrahydrothiophene (2.2mL, 25mmol) were reacted for 24 hours in methanol at 50°C. The desired monomer salt **5** was obtained by concentrating of the solution, precipitating in cold acetone, filtration and vacuum drying. The product yield was 3.65g (67%)

^{1}H-NMR (200MHz, $CDCl_3$): δ 8.43(d, 1H), 8.15(q, 1H), 7.31(d, 1H), 7.06(d, 2H), 4.53(s, 2H), 4.33(s, 2H), 4.09(t, 2H), 3.91(t, 2H), 3.77(t, 2H), 3.21(m, 8H), 2.88(s, 3H), 2.21(m, 8H), 1.63(m, 2H), 1.32(m, 2H), 0.81(t, 3H).

*Precursor polymer of PDNAPV (**6**)*

Compound **5** (1.0g, 1.51mmol) was dissolved in 2mL, of methanol, and then 1.5mL of IN sodium hydroxide aqueous solution was added. After keeping in methanol for 1 day at room temperature, yellow precipitate was formed, and washed with excess of methanol. The resulting precipitate was further purified through the repeating reprecipitation in methanol.

Instrumentation and Apparatus

^{1}H-NMR spectra were recorded on a Bruker AM 200 spectrometer. FT-IR spectra were obtained with Bomem Michelson series FT-IR spectrophotometer and UV-visible spectra of polymer samples were measured with Shimadzu UV-3100S. Thermogravimetric analyses (TGA) were performed with Dupont 9900 analyzer under nitrogen atmosphere at a heating rate of 10°C/min. Differential scanning calorimetry (DSC) data were obtained on Perkin-Elmer DSC-7 with a heating rate of 10°C/min. The second-order nonlinearity of these polymer samples was measured by second harmonic generation (SHG) method using 1064nm laser radiation. A polarized Q-switched Nd:YAG laser with a 8ns pulse width and a 10Hz repetition rate was used as the light source. The second harmonic signal was detected by a photomultiplier tube and averaged over 300 pulses in a boxcar integrator.

Results and Discussion

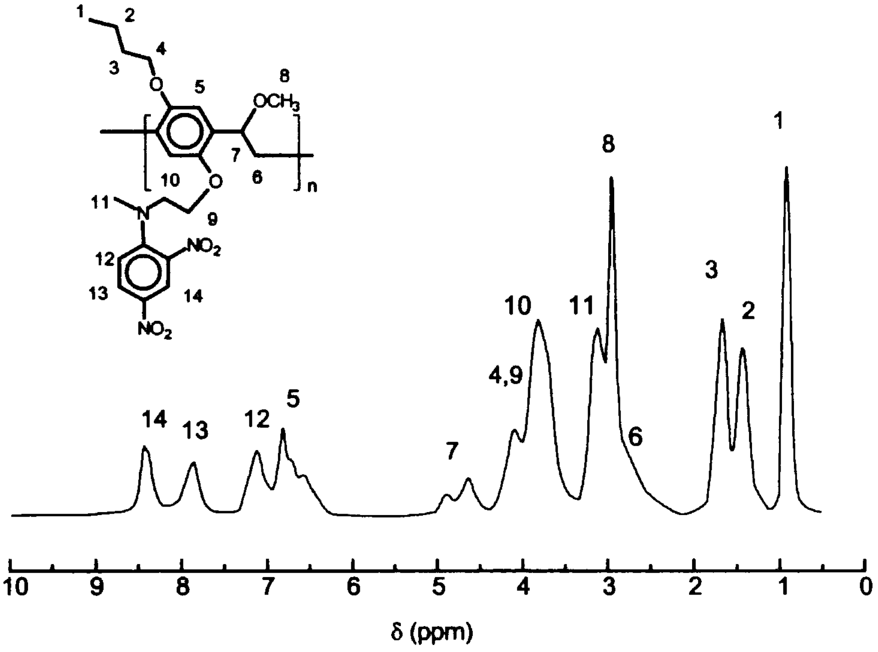


Figure 1. ^{1}H NMR spectrum of PDNAPV precursor polymer

The synthetic pathway of PDNAPV is shown in *Scheme 1.* 2,4-Dinitro-anilino chromophore was prepared via the nucleophilic substitution of the fluorine atom activated by the electroaccepting 2,4-dinitrobenzene group by N-ethanolamine. The chromophore was bound to the 4-butoxyphenol, followed by the chloromethylation in the presence of excess formaldehyde and hydrochloric acid. The resulting bischloromethylated compound was then converted to the tetrahydrothiophenium salt monomer (5). [18] In general, the PPV structure should be rigid and insoluble to make it hard to process into the proper form. [19] So we used the organic-soluble precursor route for better processibility. The molecular weight of precursor polymer was determined with the GPC with the reference to the polystyrene. The number-averaged molecular weight was 237,200g/mol and weight-averaged one 512,000g/mol. The resulting precursor polymer was soluble in organic solvents such as tetrahydrofuran, methylene dichloride, 1,2-dichloroethane. The NMR spectrum of precursor polymer is shown in Figure 1. The peaks among 6 to 9 ppm correspond to the aromatic protons of 2,4-dinitroanilino and butoxy-substituted benzene. Generally, new peak corresponding benzylic proton should appear after the polymerization in this type precursor of PPVs. [20] We can see that peak around 4.7ppm. Other peaks are denoted in Figure 1.

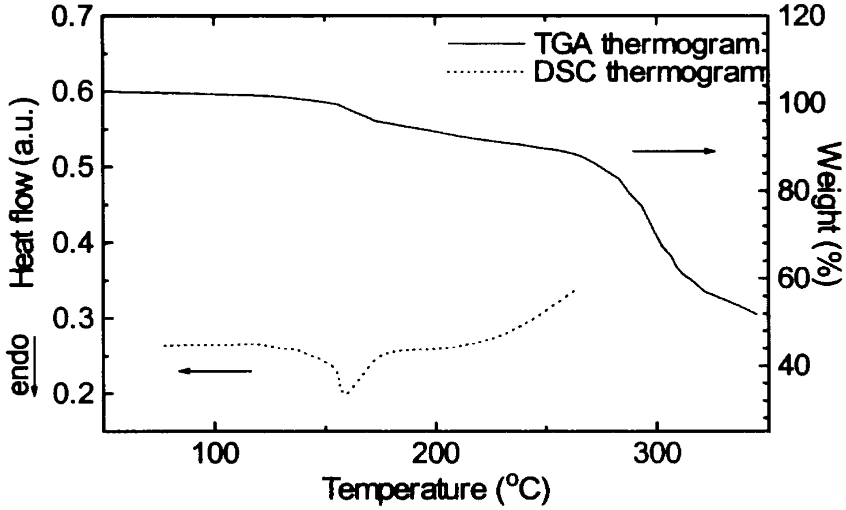


Figure 2. TGA and DSC thermograms of precursor polymer of PDNAPV

In order to get the information about the elimination reaction, several tools including UV-visible, FT-IR spectroscopy and thermal analyses were used. Among them the thermal analyses give important information about the conversion of precursor polymer into conjugated PPV structure because weight loss and endothermic reaction occurred as methanol was eliminated. In the TGA thermogram, two large weight losses were observed around at 160°C and at 270°C. The former is corresponding to the elimination of methanol from precursor polymer and the latter to the decomposition of NLO chromophore, i.e. 2,4-dinitro-anilino moiety. In Figure 2, we could observe that the precursor polymer maintained about 92% of original weight until 200°C. Formula weights of repeating unit of precursor polymer and PDNAPV are 445.47 and 413.43, respectively. Therefore, the theoretical weight loss due to elimination reaction would be 92.8% assuming other decomposition reaction wouldn't occur. This agreement between theoretical and experimental values could be evidence that the elimination occurred around at 160°C. In DSC thermogram, we also observed the endothermic peak around at 160°C corresponding to the elimination of methanol as in other PPVs through same type precursor. So we performed the elimination process at 200°C for 1 hour. The abrupt weight loss that started at 270°C should be from the decomposition of attached NLO chromophore since PPV chain itself showed stability up to 500°C without large weight loss. At 350°C residual weight decreased to 52% of original weight. We could calculate the attached NLO chromophore fraction from formula weights of PDNAPV and 2,4-dinitro-aniline moiety. The calculated weight loss is 51%, which corresponds well to residual percentage at 350°C.

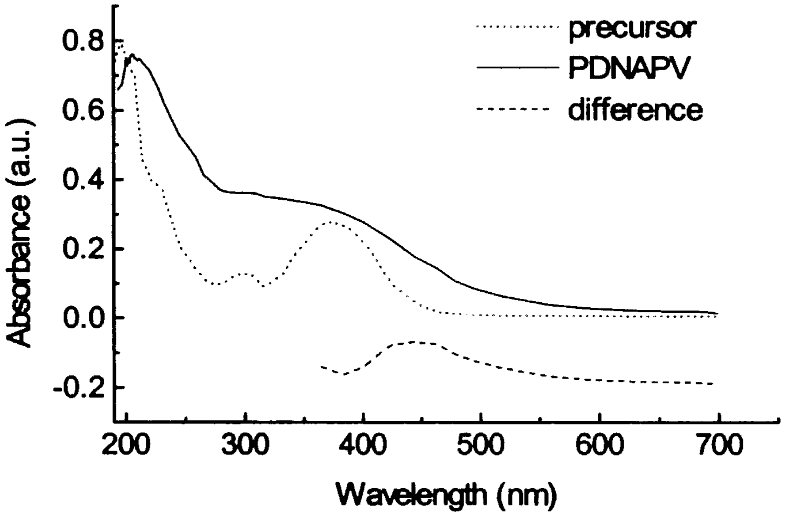


Figure 3. UV-visible spectra of precursor and PDNAPV

We also observed the UV absorption of the polymer films before and after the elimination process. (Figure 3) The thermolysis of the precursor polymer at 200°C yields π-conjugation to show new absorption band in UV region. [21] Since the new absorption superimposes that of 2,4-dinitroanilino group, we got the difference between absorption before and after elimination reaction. In the difference of both spectra, we could observe that the new absorption band appeared at 450nm after elimination. In general, dialkoxy substituted PPVs showed their characteric absorption band from π-conjugation around at 450nm. Hence the generation of the new absorption is another evidence for the conversion to PDNAPV. In FT-IR spectra of precursor and PDNAPV, absorption peak appeared at 960cm^{-1} corresponding to the trans-vinylene stretching, which also indicates the formation of the conjugated structure. [22,23]

After precursor polymer was dissolved in 1,2-dichloroethane, it was spin-cast onto indium-tin oxide(ITO)-coated glass to give pinhole free, yellow transparent film. The thickness of the films could be controlled around 1μm by adjusting solution concentration and spinning speed. After formation of thin films, the resulting samples were submitted to the poling process to get noncentrosymmetry. Second-order nonlinearity could be observed only if the centrosymmetry should be broken from some reasons. [24,25] In inorganic crystals, spontaneous aligning of the dipole along the crystal axis breaks the centrosymmetry. In organic polymers, however, artificial ordering should be required to obtain second-order NLO activity. Corona electrical poling that used in this study was one of the general tools for it. Positive charged corona was generated from 20μm thick tungsten wire and accumulated onto the surface of polymer films. The potential difference between grounded ITO electrode and polymer surface induced the electric field that acts as the ordering force of dipoles. To make dipole rotate in proper direction and to prevent the decomposition of NLO chromophore, we performed poling process through several steps. We elevated the temperature of polymer films up to 120°C and applied 4kV to tungsten wire. Most dipole should be oriented in this stage and elimination reaction should not occur since it started around 160°C. After 1 h, we raised temperature to 200°C accompanying the elimination reaction holding electric field. The polymer film was cooled to room temperature after 1 hour passed and finally the electric field was turned off.

Table I. Comparing NLO properties of PBDR1PV and PDNAPV

Polymer	${}^{a}\alpha$ (cm^{-1})	$\chi^{(2)}$ (pm/V)	${}^{b}\lambda_{max}$ (nm)	${}^{c}\chi^{(2)}(0)$ (pm/V)
PBDR1PV	1.9×10^{3}	100	486	20
PDNAPV	2.5×10^{2}	23	373	12

[a] Absorption constant at 532nm (absorbance per thickness)
[b] Absorption maxima of NLO chromphore
[c] Nonresonant value calculated with two-level model

To measure the second-order NLO properties of the polymeric films, we used the second-harmonic generation (SHG) technique with fundamental wavelength of 1064nm (Nd:YAG) with angular dependence method. [26] We obtained second-order NLO coefficient ($\chi^{(2)}$) by previous methods reported by Herman *et al.* [27] The measured $\chi^{(2)}$ is 26pm/V, which is higher than most NLO-functionalized PPVs. [12] PDNAPV showed somewhat lower nonlinearity than that of poly(2-butoxy-5-(2'-{ethyl-[4′-[4′-nitrophenylazo] -phenyl]-amino}-ethoxy)-1,4-phenylenevinylene) (PBDR1PV). For actual application, however, the nonresonant value is important. We applied two-level model to deduce the nonresonant value ($\chi^{(2)}(0)$). [28] Table I summarized the results of PBDRIPV and PDNAPV. Especially, PDNAPV showed lower absorption constant (α) at 532nm and shorter absorption maxima than those of PBDR1PV, even though the $\chi^{(2)}(0)$ value is a little bit lower. The nonlinearity of PDNAPV was very stable at room temperature for one month without detectable decay. It should be from the rigidity of PPV backbone.

CONCLUSION

New poly(1,4-phenylenevinylene) derivative containing 2,4-dinitroanilino group was prepared successfully. This precursor route gave good films of optical quality and polymers of high molecular weight (around 500,000g/mol). It also showed lower absorption at 532nm. The PDNAPV films showed high 2nd-order NLO coefficient ($\chi^{(2)}$) value of 26 pm/V when poled, and nonresonant value ($\chi^{(2)}(0)$) of 12 pm/V after the correction by the two-level model. Its nonlinearity was stable at room temperature for a month without any significant decay.

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