

Synthesis of and the Second-Harmonic Generation by a Poly[(2-methoxy-5-{2-(4-nitrophenyl)ethenyl}-1,4-phenylenevinylene)-co-(1,4-phenylenevinylene)]

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A poly[(2-methoxy-5-{2-(4-nitrophenyl)ethenyl}-1,4-phenylenevinylene)-co-(1,4-phenylenevinylene)] [poly(MNEPV-co-PV)] containing 30 mol % of the styryl-substituted 1,4-phenylenevinylene units was prepared via an organic-soluble precursor polymer. The precursor polymer, poly[{2-methoxy-5-(2-(4-nitrophenyl)ethenyl)-1,4-phenylene-1-(benzyloxy)ethylene}-co-{1,4-phenylene-1-(benzyloxy)ethylene}], was cast into a thin film from its solution in 1,1,2,2-tetrachloroethane. The thin film was formed on a poling device and heated stepwise to 235 °C at a field strength of 10⁵ V/cm to thermolyze it to the final, poled polyconjugated poly(MNEPV-co-PV). The second harmonic generation of the poled film was measured at room temperature in transmission with a Y-cut quartz plate as reference using a Nd:YAG laser beam of 1064 nm at an angle of 90° to the film. The $\chi^{(2)}$ value thus obtained was 2.0 × 10⁻⁸ esu and the value remained the same for more than a month even when the film was subjected to a thermal history up to 100 °C.

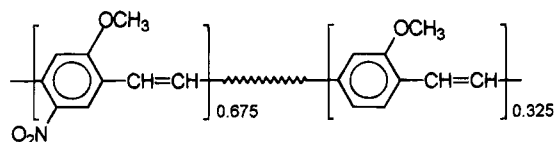
Introduction

Recently, many organic polymers carrying dipolar chromophores have been studied for their second-harmonic generation (SHG) or other optical properties related to second-order optical nonlinearity.¹⁻³ To achieve noncentrosymmetric structure, one usually has to pole the polymers in a strong poling field near the glass transition temperature (T_g) of the polymers. Maintenance of the poled structure, however, is rather difficult even at room temperature because of the relaxation of the polymer chains and chromophoric units either in the main chain or in a side chain. One of the most widely investigated methods to prevent the relaxation of poled state is to cross-link the chains during or after poling to form three-dimensional networks.⁴⁻⁶ The most important shortcomings to this approach are difficulty in controlling the cross-linking reactions and the great difficulty in obtaining uniform crosslinks.

Attaching electron donor and acceptor groups onto poly(1,4-phenylenevinylene), PPV, is expected to result in materials that can maintain the poled state unrelaxed once properly poled, because PPV has a highly rigid backbone due to its polyconjugated structure. PPV and its derivatives have been the subject of many recent

studies regarding their structures and electrical⁷⁻¹¹ and optical properties.¹²⁻¹⁶ These polyconjugated polymers can be prepared via either water⁷⁻¹⁰ or organic-soluble^{17,18} precursor polymers. This synthetic approach enables us to obtain the polymers in a variety of forms such as films or fibers.

One¹⁹ of our recent papers describes the synthesis of and second harmonic generation (SHG) by a thin poled film of a poly[(2-methoxy-5-nitro-1,4-phenylenevinylene)-co-(2-methoxy-1,4-phenylenevinylene)] (1), poly(MNPV-co-MPV)).



1, poly(MNPV-co-MPV)

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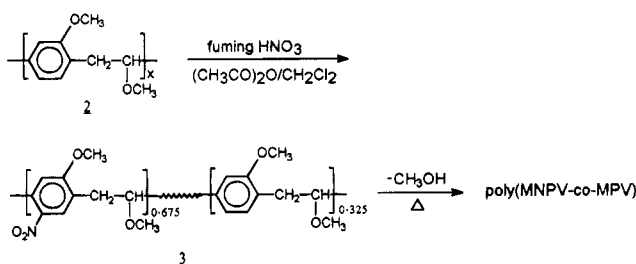
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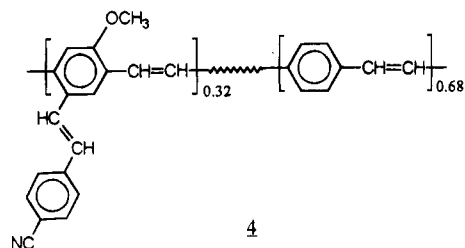
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This copolymer was synthesized by thermolysis of the following organic-soluble precursor polymer prepared by nitration of poly(2-methoxy-1,4-phenylene-1-methoxyethylene) (**2**).



The second-order susceptibility ($\chi^{(2)}$) of this polymer obtained from the SHG measurement for the 1064 nm fundamental beam was 1.0×10^{-8} esu. Moreover, the SHG activity of the polymer did not decay at all for more than 100 days even when the sample had a thermal history up to 100 °C (described further in the Results and Discussion). To obtain the final film of polyconjugated polymer **1** in a poled state, a thin film of the precursor polymer **3** was subjected to thermolysis by stepwise heating in a strong electric field. Although there have been many reports¹²⁻¹⁶ on the third harmonic generation (THG) of PPV and substituted PPVs, our investigation¹⁷ of the SHG activity of polymer **1** demonstrates one of the first successful attempts to obtain a PPV derivative in a poled state.

We²⁰ also have recently reported the synthesis and nonlinear optical (NLO) properties of the following polymer, **4**, that has an electron-withdrawing nitrile group attached to its β -styryl side branches. The electron-donating methoxy group is located on the same phenylene ring as the substituted styryl group. Since



the distance between the dipolar centers is greater than in polymer **1**, this structure was expected to result in a greater 2nd-order NLO activity. However, the improvement was marginal most probably due to less efficient poling arising from an increased rotational barrier of the bulky dipoles across the main chain. The value of the electrooptic coefficient obtained for **4** was 1.2 pm/V for an incident wavelength of 633 nm.

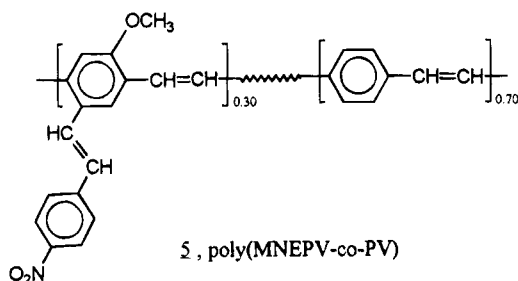
In connection with the present PPV-based polymer systems it should be added that Hall et al.¹⁵ reported earlier the synthesis and basic characterizations of relatively rigid dipolar AB polyesters that should be useful as nonlinear optical materials. They contain highly dipolar *p*-phenyleneazo groups²¹ or quino-dimethane units²² or *p*-oxy- α -cyanocinnamate units.²³

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Williams et al.²⁴ also have shown earlier that similar dipolar polyesters reveal a high nonlinear optical effect.

In this report, we would like to describe the synthesis of poly[2-methoxy-5-(2-(4-nitrophenyl)ethenyl)-1,4-phenylenevinylene]-co-(1,4-phenylenevinylene) (**5**), poly-



(MNEPV-co-PV), in a poled state and its SHG for the 1064 nm fundamental laser beam at an angle of 90° to the transverse poled film. A thin film of this polymer was obtained in a poled state by carrying out thermolysis of its organic-soluble precursor polymer in an electric field. Other characteristics of the precursor polymer **10** and polymer **5** are also described in this report.

Experimental Section

The numbers denoting compounds and polymers are the same as those shown in Scheme 1.

Synthesis of Precursor Polymer 8. The synthetic procedure for the preparation of precursor **8** from the two bisulfonium salts **6** and **7** has been described in detail in our previous publication.²⁵

Synthesis of Poly[2-methoxy-5-(2-(4-nitrophenyl)ethenyl)-1,4-phenylene-1-benzyloxy-ethylene]-co-(1,4-phenylene-1-benzyloxyethylene) (10**).** After precursor polymer **8** was prepared from **6** (1.500 g, 1.94×10^{-3} mol) and **7** (1.366 g, 3.89×10^{-3} mol) in a mixed solvent (30 mL) of H₂O and DMF (v/v = 1/1), the mixture was subjected to dialysis against distilled water for 3 days using a dialysis tube (Sigma, molecular weight cutoff at 12 000).²⁵ To this dialyzed solution was added slowly with rigorous stirring an aqueous solution of sodium *p*-toluenesulfonate (3.3 g in 20 mL), which precipitated out polymer **9**. The precipitate was washed thoroughly with distilled water. Polymer **9** thus obtained was dissolved in 250 mL of benzyl alcohol. The solution was kept at 50 °C for 2 days. The reaction mixture was then poured into 700 mL of cold methanol. The precipitate formed was washed further with cold methanol, yielding 0.631 g (40%) of **10**. Its inherent viscosity for a solution of 0.2 g/dL in 1,1,2,2-tetrachloroethane was measured at 30 °C using a Ubelhode type viscometer. The value obtained was 1.390 dL/g.

Anal. Calcd for **10**: C 80.70, H 6.16, N 1.60, S 0 %. Found: C 78.59, H 5.91, N 1.71, S 1.45%. ¹H-NMR (CDCl₃) δ 8.13 (Ar H in nitrobenzene moiety), 6.9–7.5 (Ar H and CH=CH), 4.5 (–CH–), 4.2 (–OCH₂Ph), 3.8 (–OCH₃), 3.0 (–CH₂–). IR spectrum (neat film) 3050 (Ar C–H stretching), 2950 (alkenyl C–H stretching), 2860 (aliphatic C–H stretching), 1454 (Ar C=C stretching in the styryl unit), 1516 and 1347 (N–O stretching), 986 (*trans*-vinylene =C–H out-of-plane bending), 735 cm⁻¹ (Ar C–H out-of-plane bending in benzyl ring).

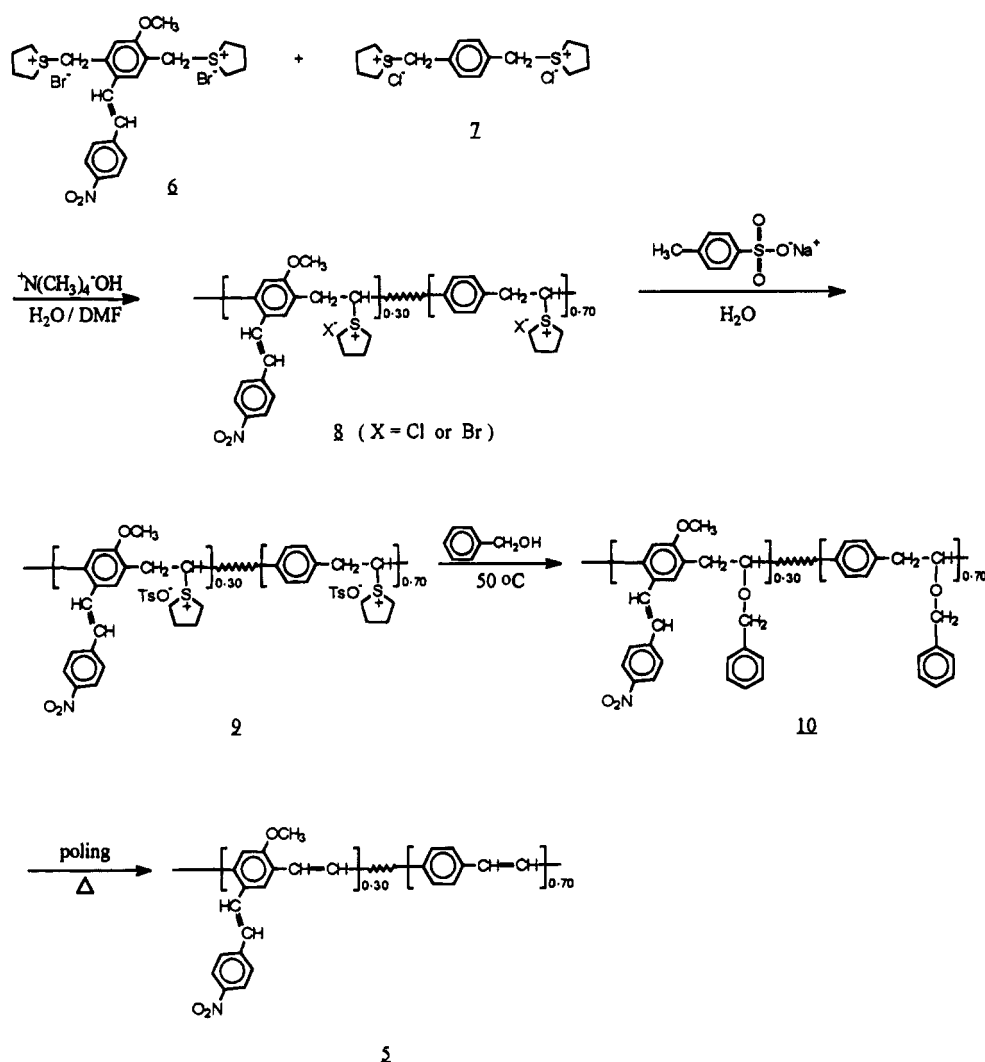
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Scheme 1. Synthetic Route to Polymer 5



Synthesis of Poly[2-methoxy-5-(2-(4-nitrophenyl)ethenyl)-1,4-phenylenevinylene]-co-(1,4-phenylenevinylene) (5). Polymer 10 (0.5 g) was dissolved in 50 mL of 1,2-dichloroethane. The solution was then filtered through a Teflon syringe filter (Aldrich, pore size, 0.45 μm). *n*-Hexane was added to the filtrate precipitating out the polymer. After being dried, the polymer was redissolved in 5 mL of 1,1,2,2-tetrachloroethane and the solution was refiltered. A film was cast from this solution, and it was subjected to stepwise heating on a hot stage which is described in the following section and summarized here: 25 $^\circ\text{C}$ \rightarrow 110 $^\circ\text{C}$ /30 min \rightarrow 130 $^\circ\text{C}$ /30 min \rightarrow 165 $^\circ\text{C}$ /10 min \rightarrow 235 $^\circ\text{C}$ /40 min \rightarrow room temperature. The heating rate was maintained constant at 5 $^\circ\text{C}/\text{min}$.

Anal. Calcd for polymer 5 assuming that it contains 70 mol % of 1,4-phenylenevinylene units based on its nitrogen content: C 82.9, H 5.26, N 2.68%. Found, C 83.2, H 5.04, N 2.68%. IR (neat film): 3030 (Ar C-H stretching), 2950 (alkenyl C-H stretching), 2850 (aliphatic C-H stretching), 1614 (C=C stretching in backbone), 1590 (Ar C-C stretching), 1515 and 1340 (N-O stretching), 970 cm^{-1} (*trans*-vinylene =C-H out-of-plane bending).

Preparation of Poled Film of Polymer 5.¹³ The solution of polymer 10 in 1,1,2,2-tetrachloroethane mentioned above was spread on a KOH-washed Corning glass (No. 7059) plate (2.5 \times 2.5 cm, 1 mm thick) on which a thin (about 1000 \AA thick) layer of chromium had been deposited at 10^{-6} Torr in a thermal evaporator. The metal film deposited on the optical flat was separated into two electrodes by a 150 μm gap in the middle. The two electrodes were attached to the chromium layer and fixed with an epoxy resin. The cell was placed in a

spin coater and a thin film of polymer 10 was coated in the central gap. One¹⁹ of our recent reports shows the detailed layout of the poling device.

The whole cell was placed in the heating block of a hot stage (Mettler FP 82) and heated stepwise under a nitrogen atmosphere as described above while the applied electric field between the two electrodes was maintained at 1.0×10^5 V/cm. The heating rate was controlled at 5 $^\circ\text{C}/\text{min}$. The thickness of the final film was 0.33 μm . Such a contact poling method provides us with a transversely poled film.

Measurement of Refractive Index. The refractive index of polymer 5 was measured by ellipsometry²⁶ (Rudolph Co. S2000 spectroscopic ellipsometer) over the wavelength range 350–700 nm at intervals of 5 nm. The refractive index value of polymer 5 at 1064 nm was estimated from the data using the Sellmeier equation:^{27,28}

$$n^2 = C + \frac{B\lambda^2}{\lambda^2 - A}$$

where n is the refractive index and A , B , and C are constants. The value obtained for 1064 nm is 1.5453, whereas the experimental value at 532 nm is 1.7059.

Measurement of Second-Harmonic Generation.^{29,30} A Q-switched Nd:YAG laser ($\lambda = 1064$ nm; Spectron Laser

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System Model SL 800) was used in this investigation. The pulse width and interval were 7 ns and 10 Hz, respectively. A photomultiplier tube (Hamamatsu Co. R 105) and a BOXCAR (Stanford Research System Model SR 250) were used in signal amplification and detection. The monochromator utilized was supplied by American Holographic Inc. (Model MM-10). The sample cell was fixed normal (90°) to the direction of the incident beam. The beam's polarization was parallel to the poling direction, i.e., the static electric field direction. The SHG activity of the polymer film detected at 532 nm was estimated by comparing its SH intensity with that of quartz. The experimental setup for the measurement was described in detail in our previous article.¹⁹ To check the stability of the laser, SHG by a Y-cut quartz crystal (2.0 mm thick) was recorded at 532 nm. The quadratic susceptibility (d_{11}) value of Y-cut quartz crystal was taken to be 0.8×10^{-9} esu.²⁹

The coherence length and the relative envelope intensity were determined following established methods.^{29,30} The coherence length of the polymer film was found to be $1.656 \mu\text{m}$. For quartz, a value of $20.64 \mu\text{m}$ for the 011 orientation was utilized.^{29,30}

Identification and Characterization of Intermediates and Polymers. Elemental analyses were performed by the Korea Basic Science Center—Seoul Branch using a Carlo ERDA EA 1108 elemental analyzer. The NMR and IR spectra of intermediates and polymers were recorded on a Bruker AM 300 NMR spectrometer and Mattson's Alpha Centauri FT-IR spectrophotometer, respectively. The UV-vis spectra were obtained on a Hewlett-Packard 8452A spectrophotometer. Thermal properties were studied under a nitrogen atmosphere on a DuPont 910 DSC instrument and a Mettler 3000 thermogravimetric analyzer at a heating rate of $10^\circ\text{C}/\text{min}$.

Results and Discussion

Synthesis and Characterization of Polymer 5.

The synthetic route to poly(MNEPV-co-PV) (5) shown in Scheme 1 is given in the Experimental Section. A mixture of the bis-sulfonium salt monomers 6 and 7 in the mol ratio of 33:67 was polymerized at room temperature in a mixed solvent of water and *N,N*-dimethylformamide (DMF).^{25,31–34} The polymerization was catalyzed by tetramethylammonium hydroxide. The precursor polymer 8, thus obtained, was dialyzed for 3 days against distilled water using a dialysis tube with a molecular weight cutoff at 12 000. The precursor polymer solution was slowly added to an aqueous solution of sodium *p*-toluenesulfonate, precipitating out polymer 9 in which *p*-toluenesulfonate is the counterion. Polymer 9 was dissolved in and reacted with benzyl alcohol at 50°C , converting it into polymer 10. The inherent viscosity value of 10 measured at 30°C in 1,1,2,2-tetrachloroethane was 1.39 dL/g , which indicates that it is of high molecular weight.

In the IR spectrum (Figure 1) of polymer 10, we can identify sharp doublet absorptions at 1516 and 1347 cm^{-1} for the N–O stretching vibration modes of the NO_2 groups and another sharp absorption at 968 cm^{-1} arising from C–H out-of-plane bending mode of the *trans*-stilbene-like structure. The peak for the out-of-plane bending mode of the C–H bonds in the monosubstituted benzene rings appears at 735 cm^{-1} . The NMR

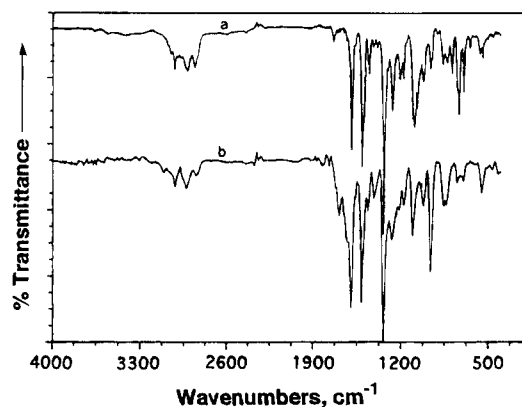


Figure 1. FT-IR spectra of (a) precursor polymer 10 and (b) final polymer 5.

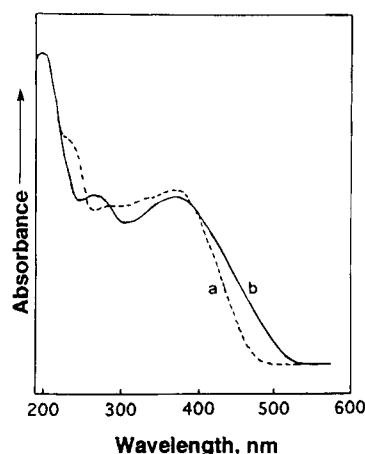


Figure 2. UV-vis spectra of (a) precursor polymer 10 and (b) final polymer 5.

spectral data given in the Experimental section also agree very well with those expected for the structure of 10.

The UV-vis spectrum of polymer 10 is shown in Figure 2a. The absorption peak observed in the longest wavelength region occurs around $\lambda_{\text{max}} = 370 \text{ nm}$, and its absorption edge is 472 nm . This absorption arises from the $\pi-\pi^*$ transition of the *trans*-1-methoxy-4'-nitrostilbene moiety³⁵ in the polymer. The results of elemental analysis indicate that the polymer 10 contains a relatively low level ($\sim 6 \text{ mol } \%$) of the unsubstituted sulfonium salt of polymer 9. This implies that most, but not all, of the sulfonium groups in polymer 9 were replaced with benzyl alcohol to produce polymer 10. The composition of 10 estimated by the results of elemental analyses agrees very well with that of 5 estimated by its nitrogen content. Polymer 10 was found to be soluble at room temperature in many chlorinated organic solvents such as dichloromethane, chloroform, 1,1,2,2-tetrachloroethane, and 1,2-dichloroethane.

The thermal properties of polymer 10 were studied under a nitrogen atmosphere by differential scanning calorimetry (DSC) and thermogravimetry analysis (TGA) methods. The DSC and TGA thermograms are given in Figure 3. According to the DSC thermogram, a sharp thermolysis endotherm begins at about 155°C and then a broad endotherm follows ending at about 220°C . We

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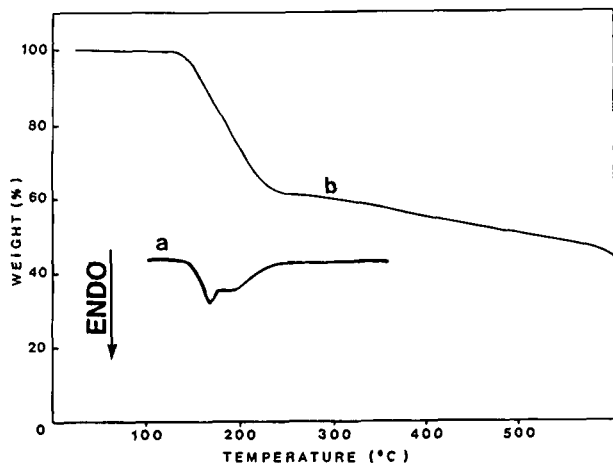


Figure 3. Thermal properties of precursor polymer **10**: (a) DSC thermogram and (b) TGA thermogram obtained under nitrogen atmosphere at a heating rate of 10 °C/min.

believe that the first endotherm corresponds to the thermolysis reaction and the second to an overlapping of the thermolysis reaction by the evaporation of benzyl alcohol (bp 205 °C), produced in the thermolysis of **10**. The TGA thermogram (Figure 3), at a heating rate of 10 °C/min, of polymer **10** indicates that the weight loss begins at about 150 °C and the thermolysis is over at about 230 °C. These results coincide with those of the DSC analysis. After that, there is a continuous slow weight loss, up to a decomposition temperature of about 580 °C. The DSC thermogram exhibited no glass transition up to the decomposition temperature.

A thin film of polymer **10** in a contact poling device was subjected to thermolysis to the final polymer **5** in an external field of 10⁵ V/cm, as detailed in the Experimental Section. Our previous article²⁵ described a synthetic method of preparing **5** directly from the water-soluble precursor polymer **8**. This direct thermolysis of **8** to **5**, however, generates HX (X = Cl and/or Br) gases, which can damage the electrodes in the poling device. To avoid this problem, we prepared polymer **5** via the precursor polymer **10**, which evolves noncorrosive benzyl alcohol during the thermolysis reaction. Finally, the polymer film was kept at 235 °C for 40 min. The composition of **5** was estimated from the nitrogen content obtained by elemental analysis and was found to contain 30 mol % of the β -styryl-substituted phenylenevinylene unit.

The IR spectrum of **5** is compared with that of precursor **10** in Figure 1. The absorption peak at 970 cm⁻¹, due to the out-of-plane bending mode of C-H in the *trans*-vinylene unit, increased in intensity because of the newly generated *trans*-vinylene structure along the main chain. In addition, the newly formed vinylene units along the backbone causes a new absorption peak at 1614 cm⁻¹, which arises from the aliphatic C=C stretching mode. Since thermolysis of **10** removes the benzyloxy unit, the peak at 735 cm⁻¹ arising from the aromatic C-H out-of-plane bending vibration of the monosubstituted benzene structure has disappeared.

Figure 2 compares the UV-vis spectrum of polymer **5** with that of the precursor polymer, **10**. The position of λ_{\max} for polymer **5** in the 350–400 nm region remains practically unchanged. However, its absorption edge has moved from 472 to 515 nm. Moreover, the peak shape has broadened noticeably. We³⁶ earlier observed

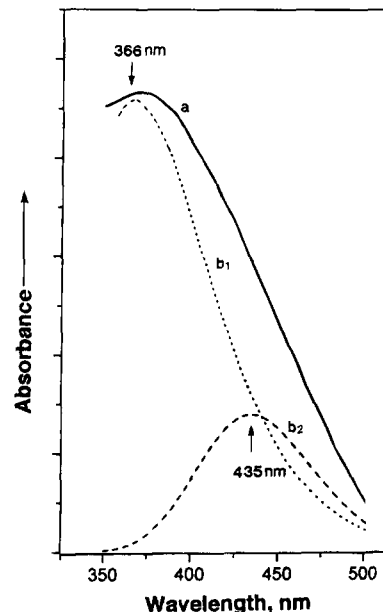


Figure 4. Resolution of (a) the original UV-vis spectrum of polymer **5** into two (b₁ and b₂) spectra; b₁ corresponds to the absorption of main chain and b₂ to that of stilbene structure.

that similar copolymers without the nitro group in the β -styryl side chain show two distinctive but overlapped absorptions over this wavelength range for two different π - π^* transitions: one for the main chain π -system in the longer wavelength region and another for the π -system of the stilbene-like moiety in the shorter wavelength region. Therefore, assuming that a similar overlapping of the two different absorption peaks occurs in the present case too as well, we have tried to resolve the absorption peak. The results are shown in Figure 4. It appears that the peak is composed of two peaks whose λ_{\max} positions are located at 366 and 435 nm, respectively. The first peak corresponds to the absorption arising from the π - π^* transition of the *trans*-4-methoxy-4-nitrostilbene moiety³⁵ and the second corresponds to the absorption due to the the π - π^* transition of the main chain π -system. We^{20,25} have observed the exact same phenomenon for poly[2-(4-cyanophenyl)ethenyl-5-methoxy-1,4-phenylenevinylene] (PCEMPV) and for copolymers similar to **5** prepared directly from polymers similar to **9**. PCEMPV²⁰ showed a broad UV-vis absorption peak whose λ_{\max} was located at 340 nm. This absorption peak was resolved into two peaks with λ_{\max} 's at 338 and 345 nm.

Second-Harmonic Generation by Polymer 5. The second-harmonic generation by a thin film (0.33 μm) of polymer **5** was measured in transmission with Nd:YAG laser beam of wavelength 1064 nm at an angle of 90° to the film.^{29,30} The laser beam was polarized parallel to the poling direction. The determination of the relative second-order nonlinear optical susceptibility was performed by the analysis of the Maker fringes.^{29,30,36}

A solution of the precursor polymer **10** in 1,1,2,2-tetrachloroethane (10% by wt/vol) was spin-coated in a poling device's central gap (150 μm), on a glass plate whose surface was coated with chromium except in the gap area.¹⁹ The whole optical flat was placed on a hot-stage and heated stepwise as described in the Experi-

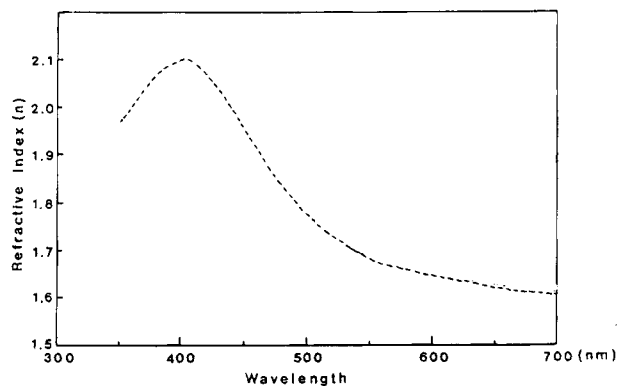


Figure 5. Dependence of refractive index of polymer **5** on wavelength.

mental Section while the poling field was kept constant at 1.0×10^5 V/cm. The SHG activity of the film was estimated by comparing its SH intensity at 532 nm with that of a Y-cut quartz crystal.

The coherence length of polymer **5** determined following the established method^{29,30} was 1656 nm, which is virtually the same as the value of 1657 nm for polymer **1**.¹⁹ The refractive indexes of polymer **5** for the wavelengths of 532 and 1064 nm were 1.7059 and 1.5453, respectively. The value at wavelength 1064 nm was estimated from the values (Figure 5) measured from 350 to 700 nm using the Sellmeier equation.^{27,28}

The value of the sample's quadratic susceptibility tensor (d_{33}) was estimated using the following, well-known equation:^{29,30}

$$d_s = d_q \{I_{M,s}(0)/I_{M,q}(0)\}^{1/2} (l_{c,q}/l_{c,s})(\eta_s/\eta_q)^{1/2}$$

where subscripts s and q stand for the sample and for the quartz, respectively. $I_M(0)$ and l_c denote the relative envelope intensity at 0° , and the coherence length for normal incidence, respectively. The values of η were estimated using the following equation:^{29,30}

$$\eta = \frac{(\eta_\omega + 1)(n_{2\omega} + 1)(n_\omega + n_{2\omega})}{n_{2\omega} P^2(0) R(0)}$$

where the n 's are refractive index values at 1064 and 532 nm. $P(0)$ and $R(0)$ are the projection factor and multiple reflection factor at 0° , respectively; these are equal to unity.

The values used for the Y-cut quartz crystal are as follow:^{22,23}

$$n_\omega = 1.5470; n_{2\omega} = 1.5341$$

$$d_{11} = 0.8 \times 10^{-9} \text{ esu}; l_{c,q} = 20.64 \mu\text{m}$$

The value of d_{33} for polymer **5** thus estimated is 1×10^{-8} esu, i.e., the $\chi^{(2)}$ value of the present polymer film is 2×10^{-8} esu. This value is of the same order of magnitude as the d_{22} value (0.74×10^{-8} esu) of LiNbO₃ and almost 1 order of magnitude smaller than its d_{33} value (9.8×10^{-8} esu).³⁷ As described in the Introduction section, the d_{33} value of polymer **1** reported earlier by us¹⁹ was just half of the present value. In other words, the d_{33} value of the present polymer, **5**, is twice

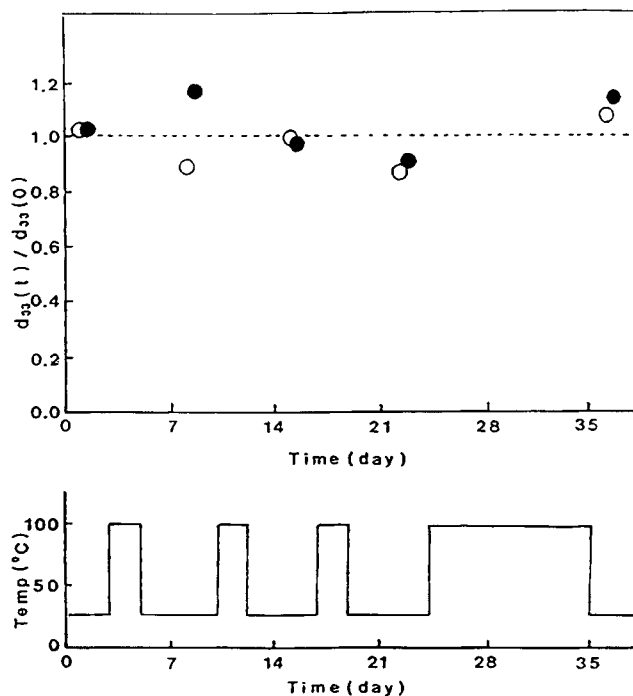


Figure 6. SHG intensity of polymer **5** at room temperature (○) and after heat treatment as shown in the lower diagram (●).

the value of the previous polymer **1**. There are at least three major reasons for the less than expected improvement in changing the structure from polymer **1** to **5** by interposing a styryl group between the nitro group and the main chain: (1) the overall content of the 2-methoxy-5-(*p*-nitrostyryl)phenylene unit in **5** is lower than that of nitromethoxyphenylene unit in **1** (30 vs 68%);¹⁹ (2) polymer **1** contains electron-donating methoxy-substituted phenylenevinylene comonomer units, whereas polymer **5** contains only unsubstituted phenylenevinylene comonomer units; and (3) the dipole orientation or poling may be more difficult for polymer **5** than for polymer **1**, because **5** requires the rotation of much bulkier structural units than **1**.

Nevertheless, the d_{33} value obtained for polymer **5** is the largest ever reported for a PPV derivative. Moreover, it should be noted that the poling electric field that we applied to our sample, 10^5 V/cm, was relatively weak, and is 1 order of magnitude smaller than the electric field conventionally used. Furthermore, the SH signal remained constant over a period of more than one month for a sample kept at room temperature and also for the one having a thermal history up to 100 °C, as shown in Figure 6. Earlier we¹⁹ reported that the SHG by polymer **1** remained unchanged for more than 100 days even when the sample had a thermal history up to 100 °C.

Conclusion

We have succeeded in preparing a new poled poly-(1,4-phenylenevinylene) copolymer, **5**, containing comonomer units carrying an electron donor (OCH₃ group) and an electron acceptor (NO₂ group) across a stilbene moiety. A thin film of this polymer shows a large SHG ($\chi^{(2)} = 2 \times 10^{-8}$ esu) and, moreover, exhibits no relaxation for a prolonged period of time (> 1 month) for a sample kept at room temperature and also for the

(37) Boyd, R. W. *Nonlinear Optics*; Academic Press: San Diego, 1992.

one having a thermal history up to 100 °C. Optimization of the thermolysis and poling conditions, such as varying heating rate and using a stronger poling field, is expected to enhance the dipole alignment, leading to a much higher SH activity.

The remarkable stability of the poled dipoles is ascribed to the rigid nature of the polyconjugated main chain of the present polymer, **5**. Furthermore, polymer **5** did not show any glass transition up to its decomposition temperature when its thermal behavior was examined by DSC. We believe, therefore, that the poled

polymer would reveal a stability in its SHG property even at higher temperatures.

The approach to obtain stable, poled polyconjugated polymer films through the precursor route discussed in this article will certainly provide us with a wide variety of materials having improved SHG when the chemical structure of the polymer is properly modified.

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