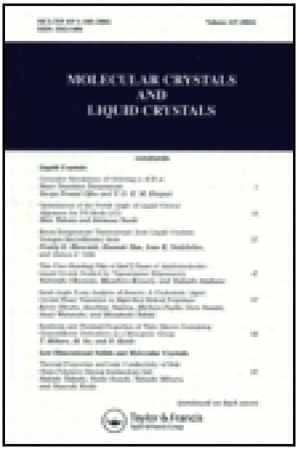

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Synthesis of Poly(1,4-Phenylenevinylene) Derivatives Containing NLO Chromophore within Side Chains

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SYNTHESIS OF POLY(1,4-PHENYLENEVINYLENE) DERIVATIVES CONTAINING NLO CHROMOPHORE WITHIN SIDE CHAINS

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ABSTRACT Poly(1,4-phenylenevinylene) derivative, 58-poly(NO2STMPV-co-IMPV), consisting of poly[2-methoxy-5-{3-(4-nitrostilben-4'-yl-oxy)propoxy}phenylenevinylene] (poly(NO2STMPV)) and poly(2-isopropoxy-5-methoxy-1,4-phenylenevinylene) (poly(IMPV)) was synthesized through the Wessling's precursor method. Films of the precursor copolymers were eliminated either by way of thermal treatment or using strong acidic conditions. The electrical conductivities of $FeCl_3$-doped 58-poly(NO2STMPV-co-IMPV) were found to be between 10^{-1} - 10^{-4} S/cm. The second-order nonlinear optical susceptibility (d_{33}) of this copolymer was about 2.0 pm/V.

INTRODUCTION

There has been considerable interest in organic nonlinear optical(NLO) materials because of their potential application to electro-optic devices.[1] In particular, organic polymers hold the promise to surpass the performance of traditional electronic crystals, such as $LiNbO_3$, used for the integrated optical modulators. There are many second-order NLO polymers, however their temporal stability after poling has been one of the major problems. Two ways have been reported to increase the temporal stability of the poled state. In the first approach, a high T_g polymer was used as the polymeric backbone to produce enhanced temporal stability.[2] Second, the main chain NLO polymers combined with the thermally induced crosslinking unit were used to give the temporal stability.[3]

Poly(1,4-phenylenevinylene) derivatives may be used as a candidate material for the NLO device applications because of their high rigid backbone structure and thus enhanced stability. Recently, PPV derivatives having second-order NLO chromophore were synthesized by using the water-soluble precursor method, and their poled samples were shown to be very effective in increasing their temporal stability.[4] However, low reactivity of the derivatized monomers involved caused problems such as low molecular weight and low content NLO dye in polymers produced. Also, because of the ionic conductivity of the polyelectrolyte-type precursor polymers, poling at high electric field becomes difficult. It is well known that ionic precursor of poly(2,5-dialkoxy-1,4-phenylenevinylene) reacts with alcohol to form a non-ionic precursor having a good solubility in common organic solvents.[5]

In this paper describes the synthesis, physicochemical and thermal characterization, and the second-order NLO activity of a new poly(1,4-phenylenevinylene) copolymer having nitrostilbene chromophores within side chains which derived from non-ionic polymer precursor.

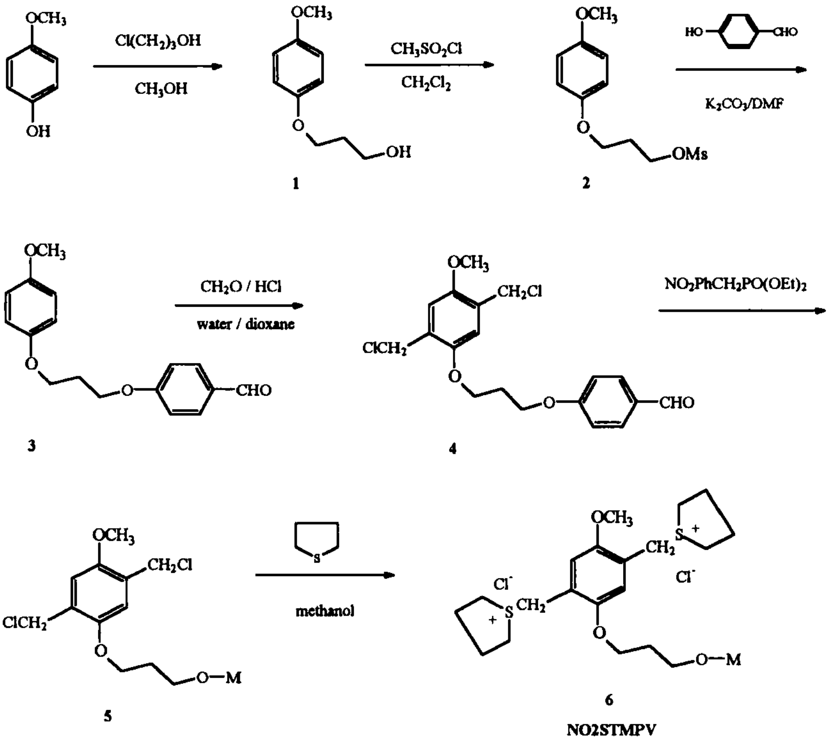
SYNTHESIS

The overall reaction for the preparation of bissulfonium salt monomer and the polymers is outlined in SCHEME I and II. 4-Methoxyphenol was alkylated by the reaction of 3-chloropropanol in strong basic condition. The compound **1** was treated with methanesulfonyl chloride to produce the mesylated compound **2**. Aldehyde derivatives **3** was obtained by a subsequent substitution reaction of compound **2** with p-hydroxybenzaldehyde. The bischloromethyl compound **4** was prepared by the chloromethylation reaction using formalin and dry hydrogen chloride. The stilbene compound **5** was obtained by the reaction of diethyl p-nitrobenzylphosphonate carbanion with aldehyde group of compound **4**. The sulfonium salt monomer **6** was made by reacting compound **5** with excess terahydrothiophene for 5 days in methanol. The monomer **6** in water/methanol/dimethylformamide mixture can be polymerized by addition of a 1.0 N NaOH aqueous solution at 0 °C. For copolymers composed of the resulting monomer **6** and dialkoxy-substituted monomer IMPV, total moles of the two monomers were kept constant, but their mole ratios were varied. Polymer solutions produced were dialyzed in the water/methanol using dialysis tube with molecular cut-off at 12,000. After 3 days, the precipitated polymers were collected and redissolved in 1,2-dichloroethane. The cast polymer films were subjected to thermal elimination in vacuum (10^{-2} torr) at 200 °C for 5 hrs or acid catalyzed elimination using the HCl gas.

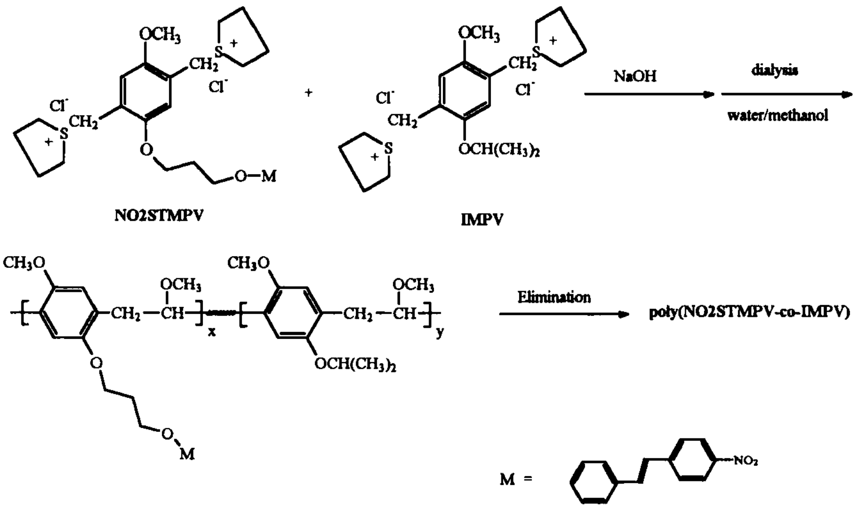
RESULT AND DISCUSSIONS

The ^{1}H-NMR spectrum shown in FIGURE 1 agrees with the anticipated spectrum of the bissulfonim monomer. The two doublet peaks near 7.5 ppm and 7.1 ppm were due to the two vinyl protons of side chain stilbene group and the broad proton peaks near 3.5 ppm and 2.2 ppm can be assigned to the protones in the tetrahydrothiophene rings.

SCHEME I



SCHEME II



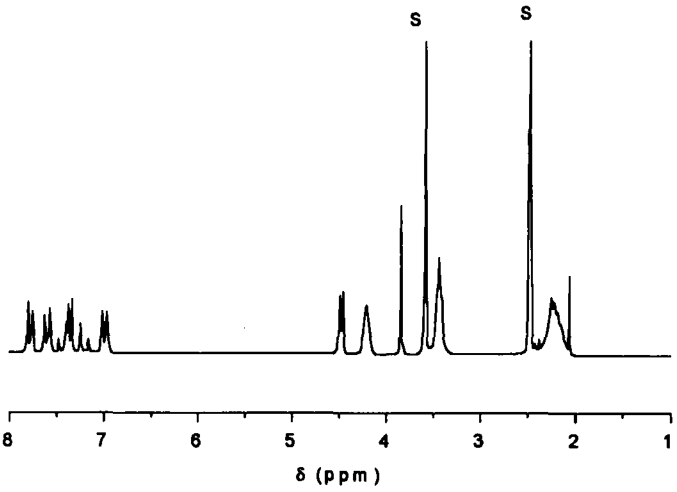


FIGURE 1 ^{1}H-NMR spectrum of the monomer (NO2STMPV).

FIGURE 2. shows the FT-IR spectra of the 58-poly(NO2STMPV-co-IMPV) containing 58 mol % of NO2STMPV unit. A sharp absorption of organic soluble precursor polymer at 964 cm^{-1} is due to trans vinylene =CH bending mode of stilbene double bond. This absorption peak increased after the elimination, especially under the dry HCl atmospheres. Very strong absorption peaks at 1,508cm^{-1} and 1,338cm^{-1} due to the stretching vibration of nitro group , respectively, are not changed by the elimination reaction. These results indicate that more conjugated polymer was obtained under strong acidic conditions. No thermal decomposition of NLO dye was observed during the elimination reaction.

The weight average molecular weight of the precursors for poly(NO2STMPV) and the 58-poly(NO2STMPV-co-IMPV) were about 77,000 and 340,000, respectively. Both precursors were readily soluble in methylene chloride and dichloroethane. The precursor film of the homopolymer was very brittle. However, 58-poly(NO2STMPV-co-IMPV) copolymer film was very flexible and readily drawn up to draw ratio of 5.4.

TABLE 1 shows the draw ratios and the maximum conductivity values of FeCl$_3$-doped copolymer after elimination. The electrical conductivity of the drawn film is increased about 10 times in comparison with the undrawn one. In particular, the conductivity values of the drawn and undrawn copolymer films which were eliminated under the

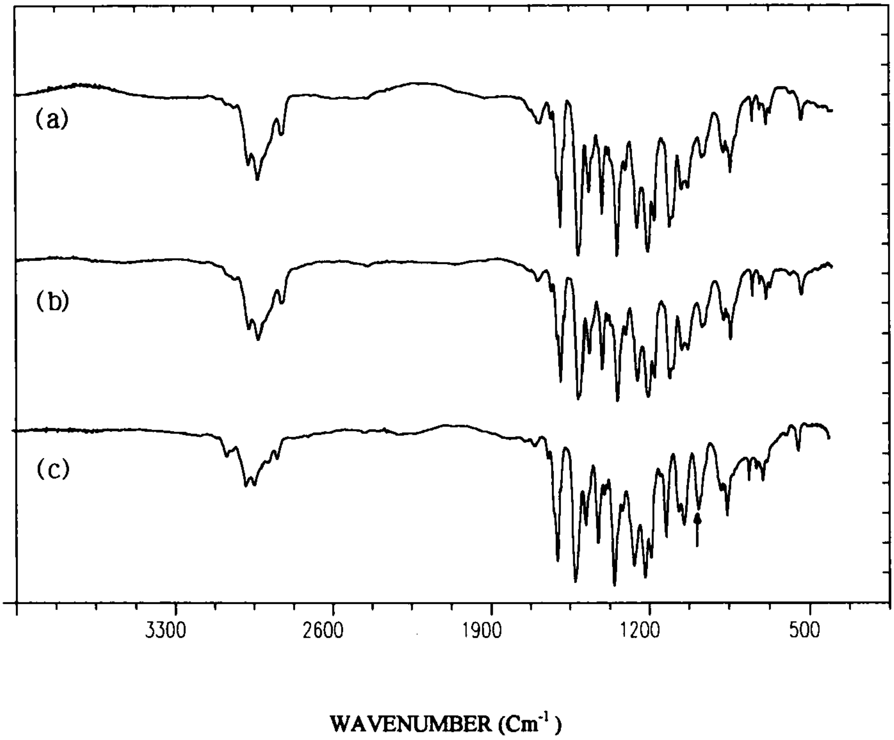


FIGURE 2 FT-IR spectra of the 58-poly(NO2STMPV-co-IMPV); (a) organic soluble precursor, (b) after thermal elimination at 200 °C for 5 hrs in vacuum, (c) after elimination at 120 °C for 5 hrs under dry HCl gas.

strong acidic conditions were significantly increased compared with those of the thermally eliminated films without the acid catalyst. Thus the thermal elimination under the acidic conditions was a very effective way to transform the organic soluble precursor into the π-conjugated polymers.

TABLE 1 Electrical conductivity of 58-poly(NO2STMPV-co-IMPV)

Polymers	NO2STMPV:IMPV in feed (actual)	Draw Ratio (l/l_0)	Conductivity (S/cm)
58-Poly(NO2STMPV-co-IMPV)$^{(a)}$	50:50(58:42)	1.0	4.0×10^{-4} $^{(b)}$
		5.4	7.4×10^{-3} $^{(b)}$
		1.0	1.6×10^{-2} $^{(c)}$
		5.4	4.7×10^{-1} $^{(c)}$

(a) Numerical value for mol % of NO2STMPV. (b) Elimination reaction was executed at 200 °C for 5 hrs in vacuum. (c) Elimination reaction was executed at 120°C for 5 hrs under dry HCl gas vacuum.

In order to investigate thermal property and thermal elimination condition for poling, DSC analysis of organic soluble precursor copolymer, 58-poly(NO2STMPV-co-IMPV), was performed. As shown in FIGURE 3, first-run curve shows the glass transition temperature (Tg) at 75 °C and the thermal elimination at 175 °C. The Tg from second-run curve was shifted to 137 °C. The eliminated polymer was decomposed at 250 °C due to NLO chromophore within side chains. Corona poling was done using the wire corona poling set-up with thermal elimination at 193 °C. Strong acid could not be used as the complete elimination catalyst because the acid evoked the breakdown due to the corrosion of transparent indium-tin oxide (ITO) electrode.

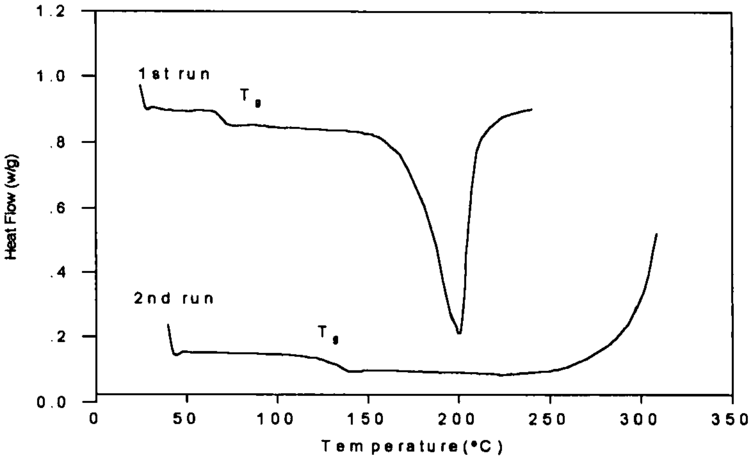


FIGURE 3 DSC thermograms of the organic soluble precursor polymer for 58-poly(NO2STMPV-co-IMPV) (10 °C/min, N_2 atmosphere)

The second-order nonlinear optical coefficient (d_{33}) of 58-poly(NO2STMPV-co-IMPV) was measured by comparing the strength of SHG signal for the sample with that of the Y-cut quartz. The d_{33} value of the copolymer was about 2.0 pm/V. More detailed study on second order NLO properties of these polymers by modifying the elimination condition or substituents is planned.

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