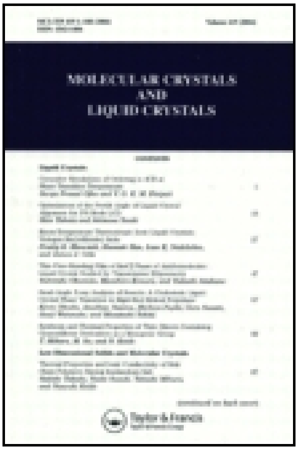

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# Synthesis and Electro-Optic Properties of Novel T-Type Polyurethane with High Thermal Stability of Second Harmonic Generation

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# Synthesis and Electro-Optic Properties of Novel T-Type Polyurethane with High Thermal Stability of Second Harmonic Generation

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*2,5-Di-(2′-hydroxyethoxy)benzylidenemalononitrile* (**3**) *was prepared and polyadded with 3,3′-dimethoxy-4,4′-biphenylenediisocyanate to yield novel T-type polyurethane* **4** *containing 2,5-dioxy benzylidenemalononitrile group as a nonlinear optical (NLO)-chromophore, which constituted parts of the polymer backbones. Polyurethane* **4** *was soluble in common organic solvents such as acetone and N,N-dimethylformamide. It showed a thermal stability up to 280°C in thermogravimetric analysis thermogram and the glass-transition temperature* ($T_g$) *obtained from differential scanning calorimetry thermogram was around 146°C. The second harmonic generation (SHG) coefficient* ($d_{33}$) *of poled polymer film at* $1064\,cm^{-1}$ *fundamental wavelength was around* $5.59 \times 10^{-9}$ *esu. The dipole alignment exhibited high thermal stability up to* $T_g$*, and there was no SHG decay below 140°C because of the partial main-chain character of the polymer structure, which was acceptable for nonlinear optical device applications.*

**Keywords:** 2,5-Di-(2′-hydroxyethoxy)benzylidenemalononitrile; differential scanning calorimetry (DSC); NLO; poling; polyurethanes; relaxation of dipole alignment; SHG coefficient; thermogravimetric analysis (TGA)

## INTRODUCTION

Recently there has been an extensive research effort in the synthesis of nonlinear optical (NLO) materials because of their potential applications in the field of electro-optic devices. Inorganic materials have

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Address correspondence to Ju-Yeon Lee, Institute of Functional Materials, Department of Chemistry, Inje University, 607 Obang-dong, Gimhae 621-749, Korea. E-mail: chemljy@inje.ac.kr many disadvantages such as slow response time and degradative photorefractive effects, which limit their applications. NLO polymers, on the other hand, are considered candidate materials, mainly because they offer many advantages such as light weight and good processability to form optical devices [1]. Stabilization of electrically induced dipole alignment is important considerations in the developments of NLO polymers. Two approaches have been proposed to minimize the randomization. One is to use crosslinking method [2] and the other is to utilize high $T_g$ polymers such as polyimides [3,4]. Polyurethanes with a NLO chromophore, whose dipole moment is aligned transverse to the main chain backbone, showed large second-order nonlinearity with enhanced thermal stability [7,8]. Main-chain NLO polymers [5] have good thermal stability of dipole alignments, but they often do not dissolve in organic solvents. Side-chain NLO polymers [6] have the advantages such as good solubility, homogeneity and high level of NLO chromophore, but they often suffer from poor stability of dipole alignments at high temperatures. In this work we have prepared novel T-type polyurethanes containing the dioxybenzylidenemalononitrile groups as NLO-chromophores. We selected 2,5-dioxy benzylidenemalononitrile groups as NLO-chromophores because they have a large dipole moment and are rather easy to synthesize. Furthermore, the 2,5-dioxybenzylidenemalononitrile groups constitute novel T-type NLO polyurthanes (see Fig. 1c), in which the pendant NLO-chromophores are part of the polymer backbones. These mid-type NLO polymers are expected to have the advantages of both main-chain and side-chain NLO polymers; stabilization of dipole alignment and good solubility.

## EXPERIMENTAL

### Materials

Synthetic methods of diol **3** and polymer **4** are summarized in Schemes 1 and 2. Compound **3**: Mp = 138–140°C. $^1$H NMR (acetone-$d_6$) $\delta$ 3.74–3.94 (m, 4H, 2 $-CH_2-OH$), 3.94–4.12 (m, 2H, $-OH$), 4.12–4.22 (m, 4H, 2 $-O-CH_2-$), 7.15–7.32 (m, 2H, aromatic), 7.75 (s, 1H, aromatic), 8.58 (s, 1H, $-Ph-CH=$). IR (KBr) 3516, 3233 (s, O–H), 3045 (m, =C–H), 2941 (m, C–H), 2233 (m, CN), 1576 (s, C=C) cm$^{-1}$. Anal. Calcd for $C_{14}H_{14}N_2O_4$: C, 61.31; H, 5.14; N, 10.21. Found: C, 61.41; H, 5.22; N, 10.28. Polymer **4**: Inherent viscosity ($\eta_{inh}$) $= 0.29\,dL\,g^{-1}$ ($c = 0.5\,g\,dL^{-1}$ in $m$-cresol at 25°C). $^1$H NMR (DMSO-$d_6$) $\delta$ 3.88 (s, 6H, 2 $-OCH_3$), 4.17–4.53 (q, 8H, 2 $-O-CH_2-CH_2-O-$), 7.16–7.39 (d, 6H, aromatic), 7.57–7.76 (d, 2H, aromatic), 8.20 (d, 1H, aromatic), 8.47 (s, 1H, aromatic), 8.59–8.66 (d, 1H, N-H), 9.02 (s, 1H, N–H).

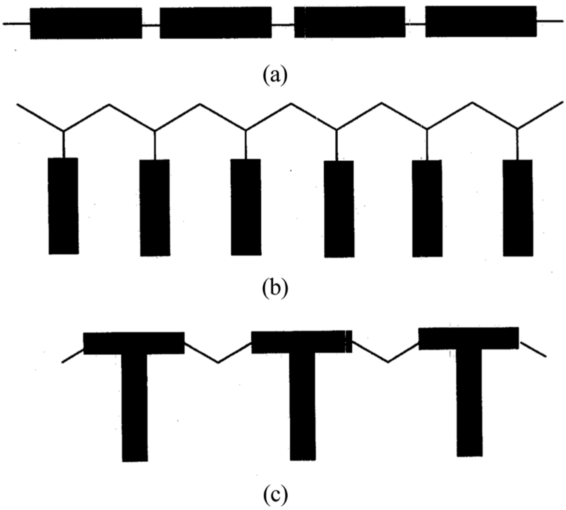
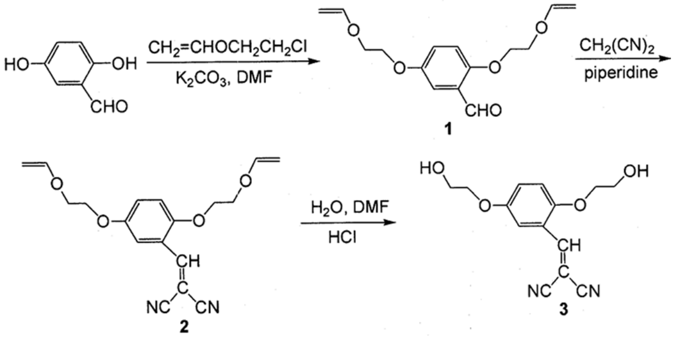


**FIGURE 1** (a) Main-chain NLO polymers, (b) side-chain NLO polymers, and (c) T-type NLO polymers.

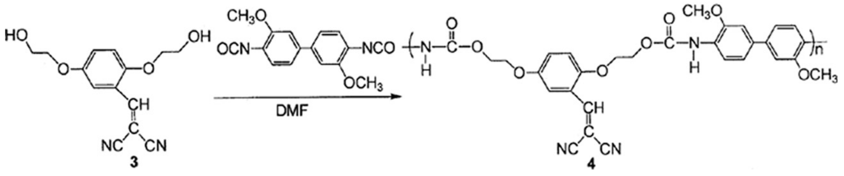
IR (KBr) 3420 (m, N–H), 2941 (m, C–H), 2233 (m, CN), 1728 (s, C=O), 1583 (s, C=C) $cm^{-1}$. Anal. Calcd for $(C_{30}H_{26}N_4O_8)_n$: C, 63.15; H, 4.59; N, 9.82. Found: C, 63.25; H, 4,64; N, 9.88.

## SHG Measurements

The alignment of the NLO-chromophore of the polymers was carried out by corona poling method. The refractive index of the polymer sample was measured by the optical transmission technique [9].



**SCHEME 1** Synthetic method of diol **3**.



**SCHEME 2** Synthetic method of polymer **4**.

Second harmonic generation (SHG) measurement was carried out one day after poling. A continuum PY61 mode-locked Nd:YAG laser ($\lambda = 1064\,\mathrm{nm}$) with pulse width of 40 ps and repetition rate of 10 Hz was used as the fundamental light source and Y-cut quartz was used as reference. A 3-mm-thick Y-cut quartz crystal (a piece of quartz plate whose plane is perpendicular to the crystalline y-axis and the thickness of the plate is 3 mm and $d_{11} = 0.3\,\mathrm{pm/V}$) was used as a reference for determining the relative intensities of the SH signals generated from the samples.

The Maker Fringe pattern was obtained from measuring the SHG signal at 0.5° intervals using a rotation stage. SHG coefficients ($d_{33}$) were derived from the analysis of measured Maker-fringes [10].

## RESULTS AND DISCUSSION

### Synthesis and Characterization of Polymer 4

The synthetic route for compound **3** is presented in Scheme 1. Polymer **4** was prepared by the polyaddition reaction between a diol **3** and 3,3′-dimethoxy-4,4′-biphenylenediisocyanate (DMBPI) in a dry DMF solvent (see Scheme 2). We obtained polyurethanes with similar molecular weights and compositions. The striking feature of this polymerization system is that it gives unprecedented novel T-type NLO polymers, in which the pendant NLO chromophores are part of the polymer backbones. In this way the mid-type NLO polymers can have the advantages of both main-chain and side-chain NLO polymers simultaneously. The chemical structure of the polymer was identified by $^1$H NMR and IR spectra, and elemental analysis. $^1$H NMR spectrum of the polymer showed a signal broadening due to polymerization, but the chemical shifts are consistent with the proposed polymer structures. The signal at 8.59–8.66 ppm assigned to the amine proton indicates the formation of urethane linkage. The IR spectra of the same polymer samples also show a strong carbonyl peak near 1728 cm$^{-1}$ indicating the presence of urethane bond. The number-average molecular weights ($M_n$) of the polymers were determined to be 14600 ($M_w/M_n = 1.93$) for polymer **4**. The polymer **4** was soluble in common solvents such as acetone, DMF, and DMSO, but was not soluble in methanol and diethyl ether. The inherent viscosity value was around 0.29 dL/g. Polymer **4** showed strong absorption near 407 nm by the NLO-chromophore 2,5-dioxybenzylidenemalononitrile group. We now have well defined T-type polyurethanes, and we investigate their properties in the following section.

## Thermal Properties of Polymers

The thermal behavior of the polymers was investigated by TGA and DSC to determine the thermal degradation pattern and $T_g$. Polymer **4** showed a thermal stability up to 280°C according to their TGA thermograms. The initial weight loss in the polymers begins at 294°C. The $T_g$ values of the polymer **4** measured by DSC were around 146°C. This is relatively high value compared to those of common polyurethanes and probably attributed to the rigid biphenyl unit in the polymer backbone. The TGA and DSC studies showed that the decomposition temperature of the polymer **4** was higher than the corresponding $T_g$. This indicates that high-temperature poling for a short term is feasible without damaging the NLO chromophore.

## Electro-Optic Properties of Polymers

The electro-optic properties of polymers were studied by the SHG method. To induce noncentrosymmetric polar order, the spin-coated polymer films were corona-poled. As the temperature was raised gradually to 155°C, 6.5 kV of corona voltage was applied and kept that temperature for 30 min. After the electric poling, the dipole moments of the NLO-chromophores were aligned and UV-Vis spectrum of polymer **4** exhibited a slight blue shift and a decrease in absorption due to birefringence. The estimated order parameter value Φ was 0.14 ($\Phi = 1 - A_1/A_0$, where $A_0$ and $A_1$ are the absorbances of the polymer film before and after poling, respectively). The decrease in absorbance after poling was an indicator of the dipole alignment. The refractive index of the sample was measured by the optical transmission technique [9]. The transmittance of thin film includes on the information of the thickness, refractive index and extinction coefficient of that. Thus, we can determine these parameters by analyzing the transmittance. SHG measurements were performed at a fundamental wavelength of 1064 nm using a mode locked Nd-YAG laser. Nonlinear optical properties of polymer **4** are summarized in Table 1. In order

**TABLE 1** Nonlinear Optical Properties of Polymer **4**

| Polymer | $\lambda_{max}$[a] (nm) | $d_{33}$[b] (esu) | $\Phi$[c] | $d_{31}$[b] (esu) | film thickness[d] (μm) | $n$ |
|---|---|---|---|---|---|---|
| **4** | 407 | $(5.59 \pm 0.28) \times 10^{-9}$ | 0.14 | 0.51 | $(2.28 \pm 0.16) \times 10^{-9}$ | $n_1 = 1.58$<br>$n_2 = 1.64$ |

[a] Polymer film.

[b] SHG coefficients ($d_{33}$) were derived from the analysis of measured Maker-fringes [10].

[c] Order parameter $\Phi = 1\text{-}A_1/A_0$, where $A_0$ and $A_1$ are the absorbances of the polymer film before and after corona poling, respectively.

[d] Film thickness was detennined by the optical transmission technique [9].

to determine the microscopic second-order susceptibility of the polymer, the angular SHG dependence was recorded. Figure 2 shows the angular dependence of SHG signal in a poled polymer **4**. The SHG values were compared with those obtained from a Y-cut quartz plate. SHG coefficients ($d_{33}$) were derived from the analysis of measured Maker-fringes with Pascal fitting program according to the literature procedure [10]. The values of $d_{33}$ and $d_{31}$ for polymer **4** were $(5.59 \pm 0.28) \times 10^{-9}$ and $(2.28 \pm 0.16) \times 10^{-9}$ esu, respectively. Since the second harmonic wavelength was at 532 nm, which is not in the absorptive region of the resulting polyurethane, there was not resonant contribution to this $d_{33}$ value. To evaluate the high-temperature

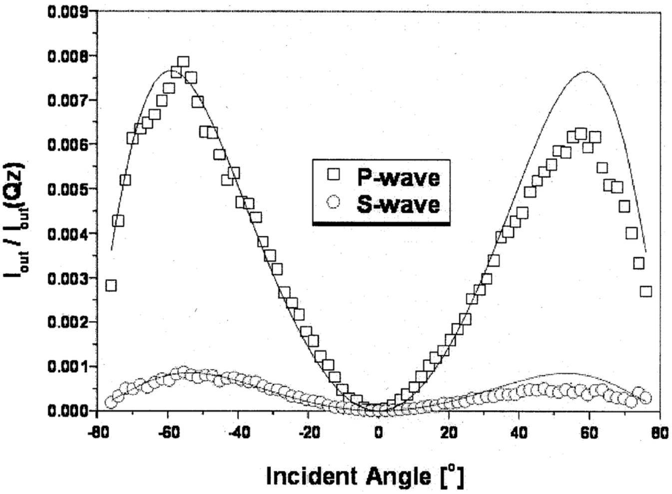


**FIGURE 2** Angular dependence of SHG signal in a poled film of polymer **4**.

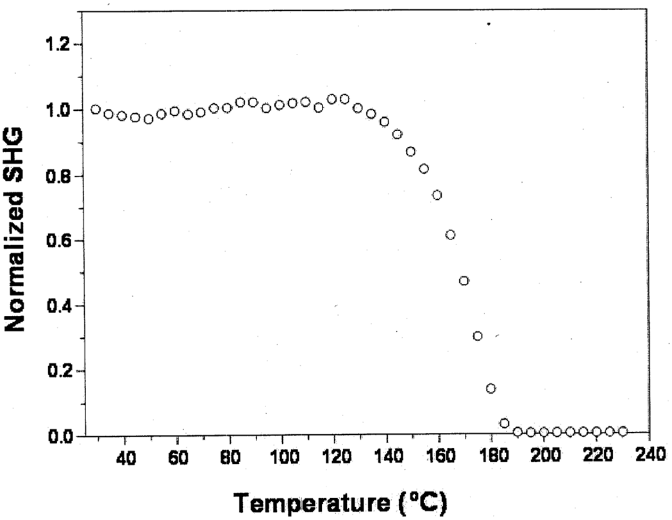


**FIGURE 3** Normalized SHG signal of polymer **4** as a function of temperature at a heating rate of 10°C/min.

stability of the polymers, we studied the temporal stability of the SHG signal. In Figure 3 we present the dynamic thermal stability study of the NLO activity of the film of polymer **4**. To investigate the real-time NLO decay of the SHG signal of the poled polymer films as a function of temperature, *in situ* SHG measurements were performed at a heating rate of 10°C/min from 30°C to 250°C. The polymer film **4** exhibited a thermal stability up to $T_g$ and no significant SHG decay was observed below 140°C. In general side chain NLO polymers lose thermal stability below $T_g$. The stabilization of the dipole alignment is a characteristic of main-chain NLO polymers. The high thermal stability of second harmonic generation of polymer **4** was due to the stabilization of dipole alignment of NLO chromophore, which stemmed from the partial main chain character of the polymer structure. Thus, we obtained a new type of NLO polyurethane having the advantages of both main-chain and side-chain NLO polymers: stabilization of dipole alignment and good solubility.

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