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# Preparation of a novel Y-type nonlinear optical polyester with high, second harmonic generation thermal stability

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## Abstract

2,4-Di-(2′-hydroxyethoxy)benzylidenemalononitrile was prepared and condensed with terephthaloyl chloride to yield a novel Y-type polyester containing dioxybenzylidenemalononitrile, nonlinear optical chromophores as part of the polymer backbone. The resulting polymer was soluble in common organic solvents such as acetone and *N*,*N*-dimethylformamide and displayed thermal stability up to 300 °C with a glass-transition temperature of ∼94 °C. The second harmonic generation coefficient ($d_{33}$) of poled polymer film at the 1064 nm fundamental wavelength was $6.48 \times 10^{-9}$ esu. The dipole alignment exhibited high thermal stability even at 10 °C higher than $T_g$ and there was no second harmonic generation decay <105 °C due to the partial main-chain character of the polymer structure.

*Keywords:* Nonlinear optics; Polyester; Differential scanning calorimetry (DSC); Thermogravimetric analysis (TGA); SHG coefficient; Relaxation of dipole alignment

## 1. Introduction

Nonlinear optical materials have been extensively studied over the past decade because of their potential applications in the field of electro-optic devices [1]. It is well known that organic and inorganic materials with high dipolar electronic systems exhibit large NLO effects. Organic materials display higher optical nonlinearity and faster response times than their inorganic counterparts; among organic materials, NLO polymers are receiving great attention of late, mainly because they offer many advantages such as mechanical endurance, low mass, high chemical resistance and good processability in terms of their use in electro-optic devices [2−4]. A potential NLO polymer must contain highly polarizable conjugated electronic systems and has to be mechanically very strong and thermally stable with a high $T_g$. In the development of NLO polymers, stabilization of dipole alignment is an important criteria; in this context, two approaches to minimize randomization have been proposed namely, the use of cross-linking [5−9] and the utilisation of high $T_g$ polymers such as polyimides [10−13]. Various polyesters with NLO chromophores in the main chain [14] or side chain [15−17] have been prepared and their NLO properties studied. Main-chain NLO polymers have good thermal stability of dipole alignments, but they often do not dissolve in organic solvents, and their intractability makes them unusable to fabricate stable films. Side-chain NLO polymer systems have the advantages such as good solubility, homogeneity and high loading level of NLO chromophores, but they often suffer from poor stability of dipole alignments at high temperatures. Recently we have reported novel polyurethanes [18,19], polyimides [20], and polyesters [21] with enhanced thermal stability of dipole alignment.

In this work we prepared novel polyester containing 2,4-dioxybenzylidenemalononitrile group as a NLO chromophore. We selected the latter because it has a large dipole moment and is rather easy to synthesize. Furthermore, 2,4-dioxybenzylidenemalononitrile group constitutes a novel Y-type NLO polyester (Fig. 1c), and this Y-type NLO polyester has not been reported in the literature. Thus, we synthesized a new type of NLO polyester, in which the pendant NLO chromophores are components of the polymer backbone. This mid-type NLO

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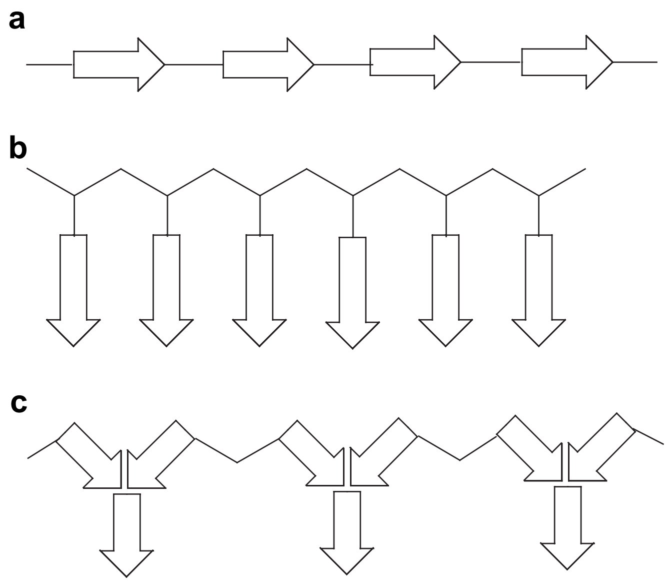


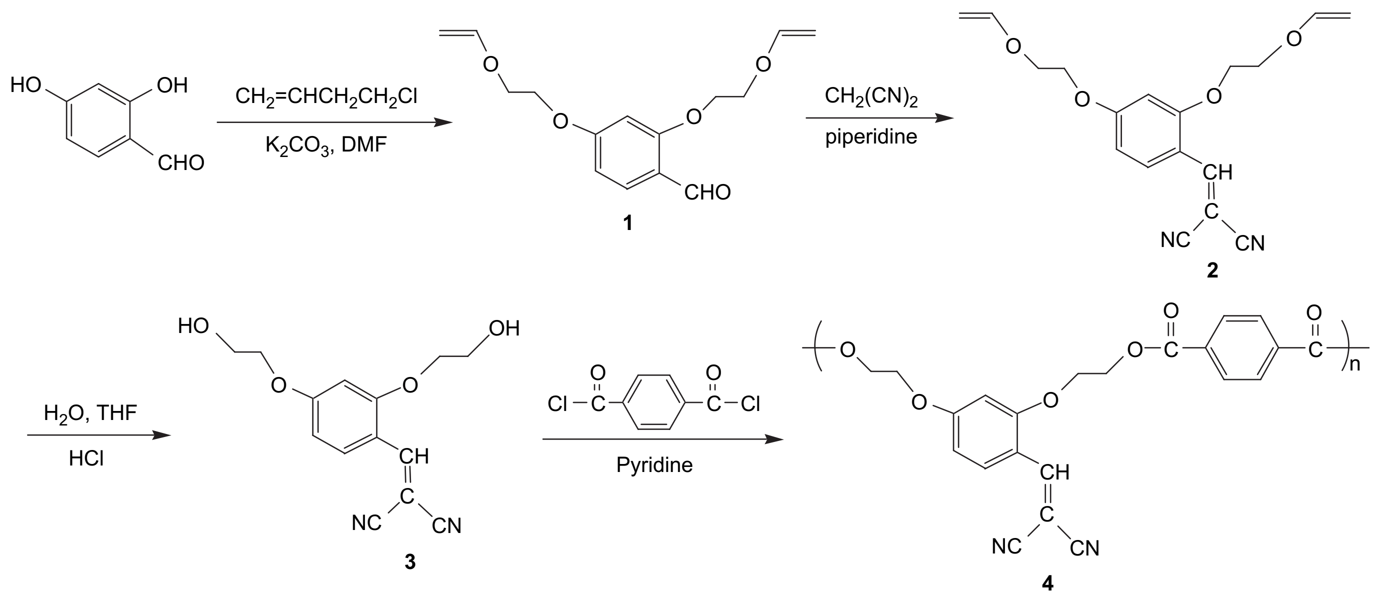
Fig. 1. (a) Main-chain NLO polymers, (b) side-chain NLO polymers, and (c) Y-type NLO polymers.

polymer is expected to have the advantages of both main-chain and side-chain NLO polymers namely stabile dipole alignment and good solubility. After confirming the structure of the resulting polymer we investigated its properties such as solubility, $T_g$, thermal stability, second harmonic generation activity and relaxation of dipole alignment. We now report the results of the initial phase of the work.

## 2. Results and discussion

### 2.1. Synthesis and characterization of polymer **4**

2,4-Di-(2′-vinyloxyethoxy)benzaldehyde (**1**) was prepared by the reaction of 2-chloroethyl vinyl ether with 2,4-dihydroxybenzaldehyde. 2,4-Di-(2′-vinyloxyethoxy)benzylidenemalononitrile (**2**) was prepared by the condensation reaction of **1** with malononitrile. Compound **2** was hydrolyzed to yield compound **3**. Diol **3** was condensed with terephthaloyl chloride (TPC) in a dry DMF solvent to yield polyester **4** containing the NLO chromophore, 2,4-dioxybenzylidenemalononitrile group. The synthetic route for polymer **4** is presented in Scheme 1. Polymerization results are summarized in Table 1. The polymerization yield was around 92%. The chemical structure of the resulting polymer was confirmed by $^1$H NMR, IR spectra, and elemental analysis. Elemental analysis results fit the polymer structures. $^1$H NMR spectrum of the polymer showed a signal broadening due to polymerization, but the chemical shifts are consistent with the proposed polymer structure. The IR spectrum of the same polymer sample shows a strong carbonyl peak near 1722 cm$^{-1}$ indicating the presence of ester bond. The same polymer sample also showed a strong nitrile peak near 2224 cm$^{-1}$. These results are consistent with the proposed polymer structure, indicating that the NLO chromophore remained intact during the polymerization. The molecular weight was determined by GPC using polystyrene as the standard and tetrahydrofuran (THF) as the eluent. The number average molecular weight ($M_n$) of polymer **4** was 17,200 ($M_w/M_n = 1.92$). The structural feature of this polymer is that it has pendant NLO chromophores, which are parts of the polymer main chains. Thus the resulting polymer **4** is a mid-type of side-chain and main-chain NLO polymer, and is expected to have both their merits. Polymer **4** is soluble in common solvents such as acetone, DMF, and DMSO, but is not soluble in methanol and diethyl ether. The inherent viscosity was around 0.30 dL/g. Polymer **4** showed strong absorption near 377 nm by the NLO chromophore 2,4-dioxybenzylidenemalononitrile. We now have well defined polyester **4** and investigated its properties.



Scheme 1. Synthesis of diol **3** and polymer **4**.

Table 1
Polymerization of **3**[a] with TPC[b] in pyridine

| Monomer | Monomer/ solvent (mol/L) | Diol **3** to RNCO (mol/mol) | Time (h) | Yield (%) | $\eta_{inh}$[c] (dL/g) | $M_n$ | $M_w$ | PD[d] |
|---|---|---|---|---|---|---|---|---|
| **3**, TPC | 0.67 | 1.0 | 10 | 90 | 0.30 | 17,200 | 33,100 | 1.92 |
| **3**, TPC | 0.80 | 1.0 | 12 | 92 | 0.29 | 17,800 | 33,600 | 1.89 |

[a] **3** = 2,4-Di-(2′-hydroxyethoxy)benzylidenemalononitrile.
[b] TPC = terephthaloyl chloride.
[c] Inherent viscosity of polymer: concentration of 0.5 g/dL in DMSO at 25 °C.
[d] PD = polydispersity.

### *2.2. Thermal properties of polymer **4***

The thermal behavior of the polymers was investigated by TGA and DSC to determine the thermal degradation pattern and glass-transition temperature. The results are summarized in Table 2. Polymer **4** showed a thermal stability up to 300 °C according to its TGA thermogram. The initial weight loss in the polymers begins near 276 °C. The $T_g$ value of polymer **4** measured by DSC was around 94 °C. The TGA and DSC studies showed that the decomposition temperature of the polyester **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.

### *2.3. Nonlinear optical properties of polymer **4***

The NLO properties of polymer **4** were studied by the SHG method. To induce noncentrosymmetric polar order, the spin-coated polymer film was corona-poled. As the temperature was raised gradually to 100 °C, 6.5 kV of corona voltage was applied and kept at that temperature for 30 min. The poling was confirmed by UV–vis spectrum. Polymer **4** showed strong absorption near 377 nm by the NLO chromophore 2,4-dioxybenzylidenemalononitrile group. After electric poling, the dipole moments of the NLO chromophores were aligned and the UV–vis spectrum of polymer **4** exhibited a decrease in absorption due to birefringence. From the absorbance change, the order parameter of the poled film could be estimated, which is related to the poling efficiency. The estimated order parameter value $\Phi$ was equal to 0.19 for polymer **4** ($\Phi = 1 - A_1/A_0$, where $A_0$ and $A_1$ are the absorbances of the polymer film before and after poling, respectively). The refractive index of the sample was measured by the optical transmission technique [22]. The transmittance of thin film includes information on the thickness, refractive index and its extinction coefficient. Thus, we can determine those parameters by analyzing the transmittance. SHG measurements were performed at a fundamental wavelength of 1064 nm using a mode-locked Nd-YAG laser [23–26]. In order to determine the microscopic second-order susceptibility of the polymer, the angular SHG dependence was recorded. Fig. 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. To calculate the $d_{31}$ and $d_{33}$ values, both s-polarized and p-polarized IR laser were directed to the samples and recorded. Nonlinear optical properties of polymer **4** are summarized in Table 3. SHG coefficients ($d_{33}$) were derived from the analysis of measured Maker-fringes with the Pascal fitting program according to the literature procedure [26]. The values of $d_{31}$ and $d_{33}$ for polymer **4** were $2.21 \times 10^{-9}$ and $6.48 \times 10^{-9}$ esu, respectively. Since the second harmonic wavelength was at 532 nm, which is not in the absorptive region of the resulting polymer, there was not resonance contribution to this $d_{33}$ value. In the isotropic model, the ratio of $d_{33}/d_{31}$ is predicted to be about 3. Our $d_{33}/d_{31}$ value of 2.93 is in good agreement with the predicted value. The electro-optic coefficient ($r_{33}$) of corona-poled polymer film measured by simple reflection technique [27] was around 18 pm/V at 633 nm.

Table 2
Thermal properties of polymer **4**

| Polymer | $T_g$ (°C) | Degradation temperature (°C) | | | | Residue at 800 °C (%) |
|---|---|---|---|---|---|---|
| | | Initial loss | 5% loss | 20% loss | 40% loss | |
| **4** | 94 | 276 | 308 | 396 | 465 | 42.6 |

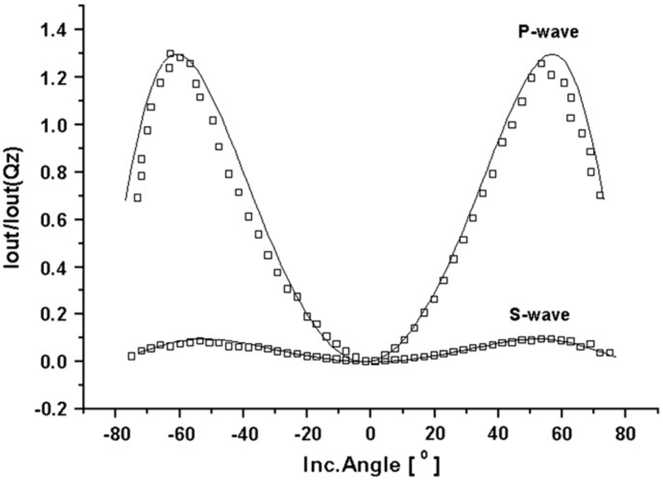


Fig. 2. Angular dependence of SHG signal in a poled film of polymer **4**.

To evaluate the high-temperature stability of the polymers, we studied the temporal stability of the SHG signal. In Fig. 3, we present the dynamic thermal stability study of the NLO activity of the film **4**. To investigate the real time NLO decay of the SHG signal of the poled polymer film as a function of

Table 3
Nonlinear optical properties of polymer **4**

| Polymer | $\lambda_{max}$[a] (nm) | $d_{33}$[b] (esu) | $\Phi$[c] | Film thickness[d] (μm) | $d_{31}$[b] (esu) | $n$ |
|---|---|---|---|---|---|---|
| **4** | 377 | $(6.48 \pm 0.12) \times 10^{-9}$ | 0.19 | 0.53 | $(2.21 \pm 0.08) \times 10^{-9}$ | $n_1 = 1.57$<br>$n_2 = 1.65$ |

[a] Polymer film after corona poling.
[b] SHG coefficients ($d_{33}$) were derived from the analysis of measured Maker-fringes [26].
[c] Order parameter $\Phi = 1 - A_1/A_0$, where $A_0$ and $A_1$ are the absorbances of the polymer film before and after corona poling, respectively.
[d] Film thickness was determined by the optical transmission technique [22].

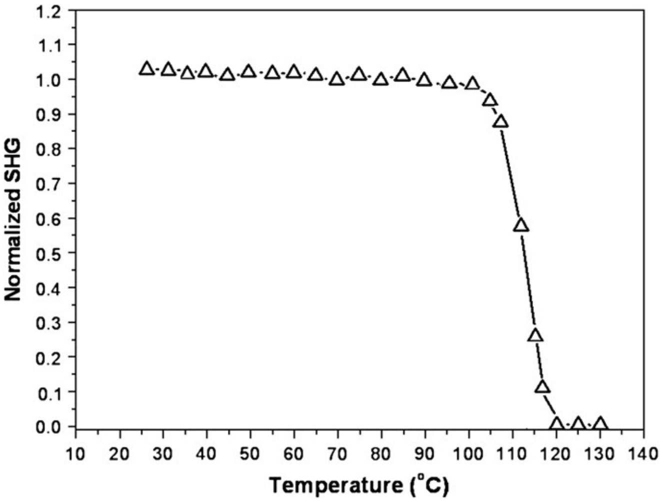


Fig. 3. Normalized SHG signal of polymer **4** as a function of temperature at a heating rate of 10 °C/min.

temperature, in situ SHG measurements were performed at a heating rate of 10 °C/min from 30 to 150 °C. The polymer film exhibited high thermal stability even at 10 °C higher than $T_g$ and no significant SHG decay was observed below 105 °C. In general, side-chain NLO polymers lose thermal stability of dipole alignment below $T_g$. Stabilization of dipole alignment is a characteristic of main-chain NLO polymers. The exceptional 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. The polymer also showed good long-term thermal stability of $d_{33}$ except for the small activity loss within a few days after poling, which is acceptable for NLO device applications. Thus, we obtained a new type of NLO polyester having the advantages of both main-chain and side-chain NLO polymers/stabilization of dipole alignment and good solubility.

## 3. Conclusions

A novel, Y-type polyester **4** with pendant NLO chromophores as part of the polymer main chains was synthesized. The mid-type NLO polyester is soluble in common organic solvents and polymer **4** displayed thermal stability up to 300 °C and a $T_g$ of ~94 °C. The SHG coefficient ($d_{33}$) of corona-poled polymer film was $6.48 \times 10^{-9}$ esu. The striking feature of this polymer is that it exhibits SHG stability even at 10 °C higher than $T_g$ and no significant SHG decay was observed below 105 °C. The high thermal stability stems from stabilization of the dipole alignment of the NLO chromophore.

## 4. Experimental

### 4.1. Materials

The reagent grade chemicals were purchased from Aldrich and purified by either distillation or recrystallization before use. 2,4-Dihydroxybenzaldehyde and 2-chloroethyl vinyl ether were used as received. Terephthaloyl chloride (TPC) was purified by sublimation under vacuum. Malononitrile was recrystallized from water and distilled under reduced pressure. Piperidine was treated with potassium hydroxide and then distilled over barium oxide to remove trace amounts of water. DMF was purified by drying with anhydrous calcium sulfate, followed by distillation under reduced pressure.

### 4.2. Measurements

IR spectra were taken on a Shimadzu FT IR-8201PC infrared spectrophotometer. $^1$H NMR spectra were obtained on a Varian 300 MHz NMR spectrometer. UV–vis absorption spectra were measured on a Shimadzu UV-3100S spectrophotometer. Elemental analyses were performed using a Perkin–Elmer 2400 CHN elemental analyzer. $T_g$ was measured on a TA 2920 differential scanning calorimeter in a nitrogen atmosphere. DuPont 951 thermogravimetric analyzer with a heating rate of 10 °C/min up to 800 °C was used for the thermal degradation pattern of polymer under nitrogen. The number average molecular weight ($M_n$) and weight average molecular weight ($M_w$) of the polymer were estimated by gel permeation chromatography (GPC) (columns styragel HR5E4E; solvent THF). Melting points were measured with a Buchi 530 melting point apparatus and are corrected. Viscosity values were obtained by using a Cannon-Fenske viscometer.

### 4.3. Film preparation and SHG measurements

The polymer film was prepared from a 10 wt% by weight polymer solution in DMF deposited on an indium–tin oxide (ITO) covered glass. The film was spin cast at room temperature in the range 1000–1200 rpm. The films were dried for 12 h under vacuum at 60 °C. The alignment of the NLO chromophore of the polymers was carried out by corona poling method. The poling was performed in a wire-to-plane geometry under in situ conditions. As the temperature was raised gradually to 5–10 °C higher than $T_g$, 6.5 kV of corona voltage was applied and this temperature was maintained for 30 min. The film was cooled to room temperature in the presence of the electric field. Finally, the electric field was removed. The refractive index of the sample was measured by the optical transmission technique [22]. Second harmonic generation (SHG) measurement was carried out one day after poling. A continuum PY61 mode-locked Nd/YAG laser ($\lambda = 1064$ 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 poled polymer film was mounted on the rotator coupled to a step motor. The output signals from the photodiode and PMT were detected as a function of the incident angle. 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 $d_{11} = 0.3$ 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 by 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 [23–26].

### *4.4. Preparation of 2,4-di-(2′-vinyloxyethoxy)benzaldehyde (**1**)*

2,4-Dihydroxybenzaldehyde (13.8 g, 0.10 mol), anhydrous potassium carbonate (82.9 g, 0.60 mol) and 2-iodoethyl vinyl ether (49.5 g, 0.25 mol) were dissolved in 400 mL of dry DMF under nitrogen. The mixture was refluxed in an oil bath kept at 80 °C for 15 h under nitrogen. The resulting solution was cooled to room temperature, diluted with 300 mL of water, and extracted with 300 mL of diethyl ether three times. The organic layer was washed with saturated aqueous sodium chloride solution, and dried with anhydrous magnesium sulfate. Rotary evaporation of diethyl ether gave crude product, which was recrystallized from 1-butanol yielding 25 g (yield 90%) of pure product **1**. M.p.: 68–69 °C. $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 4.03–4.35 (m, 12H, $2CH_2{=}$, 2–O–$CH_2$–$CH_2$–O–), 6.50–6.62 (m, 4H, 2=CH–O–, aromatic), 7.82–7.86 (d, 1H, aromatic), 10.35 (s, 1H, –CHO). IR (KBr) (cm$^{-1}$): 3100, 3082 (w, =C–H), 2954, 2875 (m, C–H), 1674 (vs, C=O), 1615 (vs, C=C), 1575 (s, C=C).

### *4.5. Preparation of 2,4-di-(2′-vinyloxyethoxy)benzylidenemalononitrile (**2**)*

Piperidine (0.13 g, 1.5 mmol) was added to a solution of 2,4-di-(2′-vinyloxyethoxy)benzaldehyde **1** (8.35 g, 30 mmol) and malononitrile (2.18 g, 33 mmol) in 170 mL of 1-butanol with stirring at 0 °C under nitrogen. After stirring for 4 h at 0 °C, the reaction mixture was cooled to −10 °C for crystallization. The product was filtered and washed successively with cold 1-butanol (80 mL), water (30 mL), and cold 1-butanol (20 mL). The obtained pale yellow product was recrystallized from 1-butanol to give 8.81 g (yield 90%) of **2**. M.p.: 70–71 °C. $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 4.02–4.40 (m, 12H, $2CH_2{=}$, 2–O–$CH_2$–$CH_2$–O–), 6.45–6.71 (m, 4H, 2=CH–O–, aromatic), 8.17–8.34 (t, 2H, aromatic). IR (KBr) (cm$^{-1}$): 3117, 3037 (w, =C–H), 2943, 2887 (m, C–H), 2222 (s, CN), 1611 (s, C=C), 1566 (vs, C=C). Anal. Calcd for $C_{18}H_{18}N_2O_4$: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.38; H, 5.65; N, 8.46.

### *4.6. Preparation of 2,4-di-(2′-hydroxyethoxy)benzylidenemalononitrile (**3**)*

Aqueous hydrochloric acid (1.5 M, 30 mL) was slowly added to a solution of 2,4-di-(2′-vinyloxyethoxy)benzylidenemalononitrile (**2**) (8.48 g, 0.026 mol) in 60 mL of dry THF with stirring under nitrogen at 0 °C. The mixture was stirred at 80 °C for 8 h under nitrogen. The resulting solution was extracted with diethyl ether (80 mL) three times. The organic layer was washed successively with saturated sodium chloride, sodium hydrogen carbonate, and water, followed by drying with anhydrous magnesium sulfate. Rotary evaporation of diethyl ether gave crude product. The obtained pale yellow product was recrystallized from ethyl acetate to give 6.13 g (yield 86%) of **3** (Scheme 1). M.p.: 148–149 °C. $^1$H NMR (acetone-$d_6$) $\delta$ (ppm): 2.78–2.84 (m, 2H, –OH), 3.87–3.98 (m, 4H, 2–$CH_2$–OH), 4.18–4.29 (m, 4H, 2–O–$CH_2$–), 6.73–6.82 (m, 2H, aromatic), 8.18–8.26 (d, 1H, aromatic), 8.43 (s, 1H, –Ph–CH=). IR (KBr) (cm$^{-1}$): 3394 (s, O–H), 3043 (w, =C–H), 2953 (m, C–H), 2220 (m, CN), 1607, 1576 (vs, C=C). Anal. Calcd for $C_{14}H_{14}N_2O_4$: C, 61.31; H, 5.14; N, 10.21. Found: C, 61.38; H, 5.23; N, 10.12.

### *4.7. Synthesis of polyester **4***

A representative polycondensation procedure was as follows: Terephthaloyl chloride (2.03 g, 0.01 mol) and diol **3** (2.74 g, 0.01 mol) were dissolved in 30 mL of anhydrous pyridine under nitrogen. The resulting solution was refluxed in an oil bath kept at 80 °C under a nitrogen atmosphere. After heating for 10 h with stirring the resulting polymerization solution was poured into 400 mL of methanol. The precipitated polymer was collected and reprecipitated from DMSO into methanol. The polymer was further purified by extraction in a Soxhlet extractor with diethyl ether and dried under vacuum, yielding 3.64 g (90% yield) of polymer **4**. Inherent viscosity ($\eta_{inh}$) = 0.30 dL/g ($c$ = 0.5 g/dL in DMSO at 25 °C). $^1$H NMR (DMSO-$d_6$) $\delta$ (ppm): 4.42–4.56 (s, 4H, 2–$CH_2$–O–), 4.58–4.76 (d, 4H, 2Ph–O–$CH_2$–), 6.75–6.95 (m, 2H, aromatic), 7.95–8.13 (s, 5H, aromatic), 8.17–8.3 (s, 1H, aromatic). IR (KBr) (cm$^{-1}$): 3040 (w, =C–H), 2959 (m, C–H), 2224 (s, CN), 1722 (vs, C=O), 1608 (s, C=C). Anal. Calcd for $(C_{22}H_{16}N_2O_6)_n$: C, 65.34; H, 3.99; N, 6.93. Found: C, 65.42; H, 3.88; N, 6.97.

## Acknowledgements

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