Synthesis of Highly Crosslinked Poly(vinyl ethers) Containing the Nonlinear Optical Chromophore Oxybenzylidenemalononitrile and Oxycyanocinnamate

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Nonlinear optical (NLO) materials based on organic compounds have long been the subject of curiosity and extensively studied over the past decade because of their potential applications in the field of telecommunications, optical signal processing, optical switching, etc.[1-6] It is well known that organic and polymeric materials with highly dipolar electronic systems exhibit NLO properties. The organic materials seem to be superior because of their higher nonlinear optical activity and faster response time than the inorganic ones. Among the organic materials the NLO polymers are receiving great attention, mainly because they offer many advantages such as mechanical endurance, light weight, chemical resistance, and good processability to form optical devices.[7] A potential NLO polymer must contain a highly polarizable dipolar electronic systems and these polymers have to be mechanically very strong with a high T_g. There are tremendous challenges in designing and synthesis of polymers with large NLO effects. Polyesters,[8-12] polyurethanes,[13-15] polyamides,[16,17] and poly(phenylenecthynylenes)[18] containing the chromophoric main chain were prepared. Various polymers with the NLO-chromophores in the side chain such as poly(meth)acrylates[19-27] and polystyrene[28] were also reported. Recently we have explored utilizing poly(vinyl ethers) as a new optical polymer system for second-order NLO applications. We prepared poly(alkyl vinyl ethers)[29-34] containing various NLO-chromophore in the side chain. Poly(vinyl ethers) exhibited a thermal stability up to 300 °C with a T_g of 60-90 °C, which is rather low for electrooptic applications. The thermal and mechanical stability, and long-term stability of NLO polymers are improved by crosslinking. Trollsas and coworkers prepared crosslinked pyroelectric polyacrylates for second-order nonlinear optics.[35-37] Thermosetting polyurethanes containing NLO-chromophore were synthesized by Dalton etc.[38,39] Recently self-crosslinkable copolymer of polymethacrylate was synthesized by Kim etc.[40,41] NLO-functionalized epoxy polymers crosslinked by sol-gel technique showed good thermal stability.[42] However, examples of crosslinked poly(vinyl ethers) containing a chormophoric side chain prepared directly by the polymerization of monomeric vinyl ethers are not shown in the literature. Thus, it is of interest to prepare crosslinked poly(vinyl ethers) having a NLO-phore in the side chain. We therefore developed a series of crosslinkable divinyl ether monomers having NLO-phore in side chain and polymerized by cationic initiators.[43] This work is now extended to the construction of another crosslinked poly(vinyl ethers) containing NLO-phore from trivinyl

ethers. The present report describes the synthesis and cationic polymerization of tetrafunctional trivinyl ether compounds 2,3,4-tri-(2'-vinyloxyethoxy)benzylidenemalononitrile (**2a**) and methyl 2,3,4-tri-(2'-vinyloxyethoxy)benzylidenecyanoacetate (**2b**).

Experimental Section

Materials. The reagent grade chemicals were purchased from Aldrich and purified by either distillation or recrystallization before use. 2-Chloroethyl vinyl ether was distilled under vacuum. Sodium iodide was dried for 4h at 100 °C under vacuum. 2,3,4-Trihydroxybenzaldehyde was used as received from Aldrich. Malononitrile was recrystallized from water and distilled from phosphorus pentoxide. *n*-Butanol was dried with anhydrous magnesium sulfate and distilled under nitrogen. *N,N*-Dimethylformamide (DMF) was purified by drying with anhydrous calcium sulfate, followed by distillation under reduced pressure. Piperidine was dried with calcium hydride and fractionally distilled. Dichloromethane was dried with calcium chloride, distilled over anhydrous calcium sulfate, and stored in a brown bottle with 4A molecular sieves. 2-Iodoethyl vinyl ether was prepared according to the procedure previously described.[29]

Measurements. IR spectra were taken on a Shimadzu FT IR-8201PC infrared spectrophotometer. ^{1}H NMR spectra were obtained on a Varian EM 360L NMR (60 MHz) and Varian 300 MHz spectrometer. Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer. The glass transition temperatures (T_g) were measured on a DuPont 910 differential scanning calorimeter under nitrogen atmosphere. DuPont 951 thermogravimetric analyzer with a heating rate of 10 °C/min up to 700 °C was used for the thermal degradation study of polymers under nitrogen. Melting points were measured in Buchi 530 melting point apparatus and are corrected. Viscosity values were obtained by using a Cannon-Fenske viscometer.

2,3,4-Tri-(2'-vinyloxyethoxy)benzaldehyde (1). 2,3,4-Trihydroxybenzaldehyde (3.08 g, 0.02 mol), anhydrous potassium carbonate (24.9 g, 0.18 mol), and 2-iodoethyl vinyl ether (14.9 g, 0.075 mol) were dissolved in 90 mL of dry DMF under nitrogen. The mixture was refluxed in an oil bath kept at 80 °C for 25 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

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magnesium sulfate. Rotary evaporation of diethyl ether gave crude product, which was recrystallized from *n*-butanol yielded 5.83 g (80% yield) of pure product **1**. Mp 50-51 °C. ¹H NMR (CDCl₃) δ 3.95-4.60 (m, 18H, 3 CH₂=, 3 -O-CH₂-CH₂-O-), 6.43-6.582 (m, 3H, 3 =CH-O-), 6.75-7.79 (m, 1H, aromatic), 7.58-7.62 (d, 1H, aromatic), 10.31 (s, 1H, -CHO). IR (KBr) 3110, 3042 (w, =C-H), 2955, 2906, 2885 (m, C-H), 1673 (vs, C=O), 1614 (vs, C=C), 1582 (s, C=C) cm⁻¹.

2,3,4-Tri-(2'-vinyloxyethoxy)benzylidenemalononitrile (2a). Piperidine (0.04 g, 0.5 mmol) was added to a solution of 2,3,4-tri-(2'-vinyloxyethoxy)benzaldehyde **1** (3.64 g, 10 mmol) and malononitrile (0.73 g, 11 mmol) in 50 mL of isopropyl alcohol with stirring at 0 °C under nitrogen. After stirring for 6 h at 0 °C, the reaction mixture was cooled to -10 °C for crystallization. The product was filtered and washed successively with cold isopropyl alcohol (20 mL), water (10 mL), and cold isopropyl alcohol (10 mL). The obtained pale yellow product was recrystallized from isopropyl alcohol to give 3.13g (76% yield) of **2a**. Mp 56-57 °C. ¹H NMR (CDCl₃) δ 3.90-4.48 (m, 18H, 3 CH₂=, 3 -O-CH₂-CH₂-O-), 6.45-6.58 (m, 3H, 3 =CH-O-), 6.78-6.82 (d, 1H, benzylic), 8.08-8.11 (d, 1H, aromatic), 8.32 (s, 1H, aromatic). IR (KBr) 3120, 3056 (w, =C-H), 2936, 2882 (m, C-H), 2223 (s, CN), 1624 (s, C=C), 1571 (vs, C=C) cm⁻¹. UV/Vis (chloroform) λ_max=354 nm, ε=25800. Anal. Calcd for C₂₂H₂₄N₂O₆: C, 64.06; H, 5.87; N, 6.79. Found: C, 64.14; H, 5.85; N, 6.86.

Methyl 2,3,4-tri-(2'-vinyloxyethoxy)benzylidenecyano-acetate (2b). Piperidine (0.04 g, 0.5 mmol) was added to a solution of 2,3,4-tri-(2'-vinyloxyethoxy)benzaldehyde **1** (3.64 g, 10 mmol) and methyl cyanoacetate (1.09 g, 11 mmol) in 50 mL of isopropyl alcohol with stirring at 0 °C under nitrogen. After stirring for 5 h at 0 °C, the reaction mixture was cooled to -10 °C for crystallization. The product was filtered and washed successively with cold isopropyl alcohol (15 mL), water (10 mL), and cold isopropyl alcohol (10 mL). The obtained pale yellow product was recrystallized from isopropyl alcohol to give 3.87g (87% yield) of **2b**. Mp 60-62 °C. ¹H NMR (CDCl₃) δ 3.89 (s, 3H, -CO₂CH₃), 3.91-4.44 (m, 18H, 3 CH₂=, 3 -O-CH₂-CH₂-O-), 6.46-6.58 (m, 3H, 3 =CH-O-), 6.77-6.82 (d, 1H, benzylic), 8.17-8.21 (d, 1H, aromatic), 8.78 (s, 1H, aromatic). IR (KBr) 3134, 3078 (w, =C-H), 2933, 2852 (m, C-H), 2222 (s, CN), 1720 (vs, C=O), 1632, 1611 (s, C=C), 1582 (vs, C=C) cm⁻¹. UV/Vis (chloroform) λ_max=345 nm, ε=25200. Anal. Calcd for C₂₃H₂₇NO₈: C, 62.02; H, 6.11; N, 3.14. Found: C, 62.10; H, 6.15; N, 3.18.

Cationic Polymerization of Monomers 2a-b. A representative cationic polymerization procedure (the case of **2a**) was as follows: A solution of **2a** (1.24 g, 3.0 mmol) in dichloromethane (3.0 mL) was placed in a rubber septum stopper capped glass ampule under nitrogen. The resulting solution was flushed with nitrogen for 20 min. The ampule was then placed in an ethanol-acetone bath kept at -60 °C under nitrogen, and 0.0034 mL (0.03 mmol) of boron trifluoride etherate was added to the solution. After 1 h the ampule was taken out and the polymerization mixture was poured

into 500 mL of methanol and stirred. The precipitated polymer was collected and dried under vacuum to give 1.22 g (98% yield) of polymer **3a**. IR (KBr) 2920, 2848 (m, C-H), 2224 (s, CN), 1574 (s, C=C) cm⁻¹. Anal. Calcd for (C₂₂H₂₄N₂O₆)ₙ: C, 64.06; H, 5.87; N, 6.79. Found: C, 64.14; H, 5.81; N, 6.85. **3b**: IR (KBr) 2922, 2840 (m, C-H), 2222 (w, CN), 1726 (vs, C=O), 1582 (s, C=C) cm⁻¹. Anal. Calcd for (C₂₃H₂₇NO₈)ₙ: C, 62.02; H, 6.11; N, 3.14. Found: C, 62.10; H, 6.18; N, 3.19.

Results and Discussion

Synthesis of compound 2a and 2b. 2,3,4-Tri-(2'-vinyloxyethoxy)benzaldehyde (**1**) was prepared by reaction of 2-iodoethyl vinyl ether with 2,3,4-trihydroxybenzaldehyde. Tetrafunctional monomers of 2,3,4-tri-(2'-vinyloxyethoxy)benzylidenemalononitrile (**2a**) and methyl 2,3,4-tri-(2'-vinyloxyethoxy)benzylidenecyanoacetate (**2b**) were prepared by the condensations of **1** with malononitrile or methyl cyanoacetate, respectively. Compounds **2a-b** were obtained in high yield and were purified by recrystallization in *iso*propyl alcohol for polymerization. The chemical structure of the compounds was identified by proton-NMR, IR spectra, and elemental analysis. All the analytical data confirmed the expected chemical structure. Compound **2** showed strong uv absorption bands near 350 nm by the chromophore oxybenzylidenemalononitrile or oxycyanocinnamate in the side chain measured in chloroform.
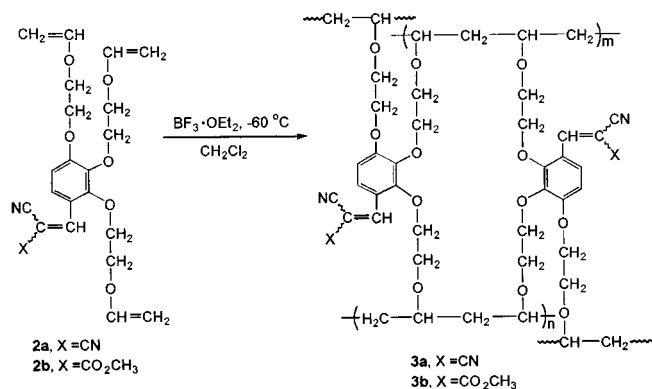
Cationic Polymerization of Monomers 2a and 2b. Trivinyl ether compounds **2a-b** were polymerized in solution at -60 °C with boron trifluoride etherate as cationic initiators to obtain the polymers **3a-b**. The polymerization results are summarized in Table 1. Monomers **2a-b** were quite reactive toward cationic initiators and polymerized readily with high yields. The chemical structures of the polymers were identified by IR spectra and elemental analyses. The IR spectra confirmed the chemical structures, exhibiting all the absorption bands attributable to the functional groups comprising

Scheme 1

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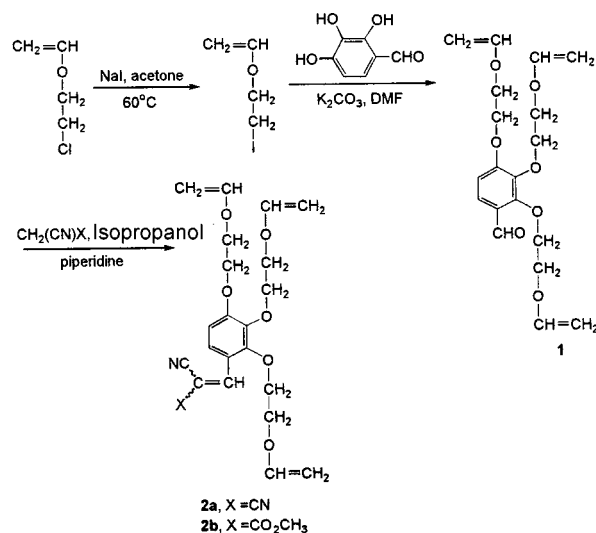
the polymers. The three vinyl ether groups participated in the vinyl polymerization, and cationic polymerization of **2a-b** led only to optically transparent swelling poly(vinyl ethers) **3a-b** containing oxybenzylidenemalononitrile and oxycyanocinnamate in the side chain, which is presumably effective chromophore for second-order nonlinear optical applications. The trisubstituted electron-poor terminal olefin did not participate in the cationic vinyl polymerization. Polymers **3a-b** were not soluble in any organic solvents due to cross-linking. Thus, we have found a unique polymerization system that lead to cross-linked poly(alkyl vinyl ethers) having NLO-phore in the side chain by cationic initiators. These polymerization systems can be applied to the synthesis of new crosslinked NLO polymers. Previously we have prepared bifunctional vinyl ethers containing p-oxybenzylidenemalononitrile and p-oxycyanocinnamate and polymerized them with cationic initiators to give poly(vinyl ethers).[2] Cationic polymerizabilities of trifunctional trivinyl ether compounds **2a-b** are higher than those of p-substituted bifunctional vinyl ether compounds.

Properties of Polymers. The polymers **3a-b** were not soluble in common solvents such as methanol, ethanol, diethyl ether, benzene, toluene, acetone, methyl ethyl ketone, cyclohexanone, dichloromethane, chloroform, DMF, and DMSO due to crosslinking. Polymers **3a-b** isolated from methanol were amorphous materials. The thermal behavior of the

Table 2. Thermal properties of polymers **3**

Polymer	T_g^a, °C	Degradation temp., °C[b]			Residue[b] at 700 °C, %
		5%-loss	20%-loss	40%-loss	
3a	-	323	370	421	1.3
3b	-	332	371	412	0.7
P(2,4-DVEBM)[c]	-	329	389	497	1.3
P(2,4-DVEBC)[d]	-	332	367	415	4.3
P(3,4-DVEBM)[e]	-	300	343	385	2.3
P(3,4-DVEBC)[f]	-	299	342	364	2.0
P(2,5-DVEBM)[g]	-	327	386	488	1.7
P(2,5-DVEBC)[h]	-	328	367	414	2.3

[a]Determined from DSC curves measured on a DuPont 910 differential scanning calorimeter with a heating rate of 10 °C min under nitrogen atmosphere. [b]Determined from TGA curves measured on a DuPont 951 thermogravimetric analyzer with a heating rate of 10 °C min under nitrogen atmosphere. [c]P(2,4-DVEBM)=Poly[2,4-di-(2'-vinyloxyethoxy)benzylidenemalononitrile]. [d]P(2,4-DVEBC)=Poly[methyl 2,4-di-(2'-vinyloxyethoxy)benzylidenecyanoacetate]. [e]P(3,4-DVEBM)=Poly[3,4-di-(2'-vinyloxyethoxy)benzylidenemalononitrile]. [f]P(3,4-DVEBC)=Poly[methyl 3,4-di-(2'-vinyloxyethoxy)benzylidenecyanoacetate]. [g]P(2,5-DVEBM)=Poly[2,5-di-(2'-vinyloxyethoxy)benzylidenemalononitrile] [h]P(2,5-DVEBC)=Poly[methyl 2,5-di-(2'-vinyloxyethoxy)benzylidenecyanoacetate].

polymers were investigated by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) to determine the thermal degradation pattern and glass transition temperature (T_g). The results are summarized in Table 2. Polymers **3a-b** showed a good thermal stability and did not decompose below 320 °C. The polymers show a double phase degradation pattern in their TGA thermograms, probably due to cross-linking. Thermal stability of polymers **3a-b** were similar to those of the polymers from trifunctional divinyl ethers as shown in Table 2. Cross-linked polymers **3a-b** showed broad endothermic bands around 100-200 °C without any characteristic T_g peaks in DSC thermograms.

In summary, we pepared two trivinyl ether compounds **2a-b** having highly polarizable π-conjugated dipolar electronic system. The trivinyl ether compounds were polymerized by cationic initiator to yield crosslinked poly(vinyl ethers) **3a-b** containing oxybenzylidenemalononitrile or oxycyanocinnamate, which is potential effective NLO-chromophore for second-order nonlinear optical applications in the side chain. Monomers **2a-b** were quite reactive toward cationic initiators and polymerized readily in high yields within 3 hr. Cationic polymerizabilities of tetrafunctional trivinyl ether compounds **2a-b** were higher than those of p-disubstituted bifunctional derivatives. Polymers **3a-b** were not soluble in any organic solvents due to cross-linking. The polymers showed a thermal stability up to 320 °C in TGA thermograms, which is acceptable for electrooptic device applications. We are now in the process of extending the polymerization system to the synthesis of other type of crosslinked NLO polymers, and the results will be reported at a later date.

Scheme 2

2a, X=CN
2b, X=CO$_2$CH$_3$

3a, X=CN
3b, X=CO$_2$CH$_3$

Table 1. Cationic polymerizations of **2a-b**[a] by BF$_3$ in CH$_2$Cl$_2$ at -60 °C

Monomer	Monomer/Solvent (mol 1 L)	Initiator to Monomer (mol%)	Time (h)	Yield (%)
2a	1.00	1.0	1	98
2a	0.75	0.8	2	96
2a	0.67	0.8	1	95
2a	0.50	0.6	2	90
2b	1.00	1.0	1	92
2b	0.75	0.8	2	88
2b	0.67	0.8	1	86
2b	0.50	0.6	3	85

[a]2a = 2,3,4-Tri-(2'-vinyloxyethoxy)benzylidenemalononitrile; 2b = Methyl 2,3,4-tri-(2'-vinyloxyethoxy)benzylidenecyanoacetate.

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