입체 장애 구조를 가진 이중 기능성 2-(2'-비닐옥시에톡시)-1-나프틸메틸리덴말로노니트릴의 합성 및 중합거동

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Synthesis of Sterically Hindered Bifunctional 2-(2'-Vinyloxyethoxy)-1-naphthylmethylidenemalononitrile and Its Polymerization Behaviors

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요 약: 2-(2'-비닐옥시에톡시)-1-나프탈데히드 **(1)**를 말로노니트릴과 축합반응시켜 2-(2'-비닐옥시에톡시)-1-나프틸메틸리덴말로노니트릴 **(2)**를 합성하였다. 이중 기능성 비닐 에테르 단량체 **2**는 입체방해효과 때문에 자유라디칼 개시제에 의해서는 호모중합 또는 전자가 풍부한 에틸 비닐 에테르와 전자가 부족한 벤질리덴말로노니트릴과의 공중합은 진행되지 않았다. 그러나 화합물 **2**는 양이온 개시제에 의해서는 중합이 잘 진행되어 효과적인 비선형광학 발색단으로 예상되는 2-옥시-1-나프틸메틸리덴말로노니트릴을 측쇄에 포함하는 중합체 **3**을 형성하였다. 중합체 **3**은 아세톤같은 상용 용매에 잘 녹았으며 고유점도는 0.25-0.30 dL/g을 보였다. 아세톤 용액으로부터 얻어진 중합체 필름은 불투명하고 취약성을 보였다. 중합체 **3**은 300℃까지 열안정성을 보였으며 DSC로부터 얻어진 유리전이온도는 82℃였다.

ABSTRACT: 2-(2'-Vinyloxyethoxy)-1-naphthylmethylidenemalononitrile **(2)** was prepared by the condensation of 2-(2'-vinyloxyethoxy)-1-naphthaldehyde **(1)** with malononitrile. Bifunctional vinyl ether monomer **2** did not homo- or copolymerize with electron-rich ethyl vinyl ether and electron-poor benzylidenemalononitrile by free radical initiators due to the steric hindrance. However, compound **2** polymerized well by cationic initiators to give polymer **3** having 2-oxy-1-naphthylmethylidenemalononitrile, which is presumably effective NLO-chromophore for second order nonlinear optical applications. Polymer **3** was soluble in common solvents such as acetone and DMSO, and the inherent viscosities of the polymers were in the range of 0.25-0.30 dL/g. Films cast from acetone solution were cloudy and brittle. Polymer **3** showed a thermal stability up to 300 ℃ with a T_g of 82 ℃ in DSC thermogram.

INTRODUCTION

It is well known that electron-rich alkyl vinyl ethers do not radically homopolymerize, but co-polymerize with vinyl monomers of electron deficient character such as vinylidene cyanide,[1] 2-vinylcyclopropane-1,1-dicarbonitrile,[2] alkyl *a*-cyanoacrylates,[3-5] alkyl vinyl ketones,[6] maleic

anhydride,[7,8] and others by radical initiation. Cycloadditions frequently accompanied these polymerizations and most of the cyclic adducts are cyclobutane compounds. For example, alkyl vinyl ethers readily form cyclobutane adducts with a variety of electron-poor olefins such as tetracyanoethylene[9] and tricyanoethylene.[10] 3,4-Dihydro-2H-pyrans are formed in the reactions of alkyl vinyl ethers with alkyl a-cyanoacrylates, dimethyl dicyanofumarate,[11] and alkyl vinyl ketones.[6] These facile reactions proceed through an electron donor-acceptor (EDA) complex, which generates zwitterion or diradical tetramethylenes as initiating species.[12] It has also been reported that trisubstituted electron-poor olefins such as benzylidenemalononitrile and ethyl benzylidenecyanoacetate do not homopolymerize, but copolymerize with vinyl acetate, styrene, acrylonitrile, or methyl acrylate by radical initiators.[13-19] The captodative olefins with geminal electron-withdrawing and electron-donating groups have a strong tendency to polymerize spontaneously due to the resonance stabilization of radical species.[20,21] The question remains as to whether certain bifunctional monomers composed of both electron-rich alkyl vinyl ether and electron-poor trisubstituted olefin moieties can be polymerized by radical initiation. Recently we have prepared p-(2-vinyloxyethoxy)benzylidenemalononitrile and methyl p-(2-vinyloxyethoxy)benzylidenecyanoacetate, and polymerized by radical initiators.[22-24] These bifunctional ethyl vinyl ethers polymerized quantitatively with radical initiators to give swelling polymers that were not soluble in organic solvents due to cross-linking. Sterically hindered 3,5-dimethoxy-4-(2'-vinyloxyethoxy) benzylidenemalononitrile does not homopolymerize radically, but copolymerize with ethyl vinyl ether by radical initiation.[25] This work is now extended with the synthesis and

radical polymerizations of another sterically hindered ethyl vinyl ethers containing electron acceptors. In this work we prepared 2-(2'-vinyloxyethoxy)-1-naphthylmethylidenemalononitrile **(2)** and investigated its polymerization behaviors.

EXPERIMENTAL

Materials. The reagent grade chemicals were purchased from Aldrich and purified by either distillation or recrystallization before use. 2-Chloroethyl vinyl ether was distilled. Sodium iodide was dried for 4h at 100 ℃ under vacuum. Acetone was purified by drying with anhydrous potassium carbonate, followed by distillation under reduced pressure. 2-Hydroxy-1-naphthaldehyde was recrystallized from ethanol and dried under vacuum. 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. γ-Butyrolactone was dried with anhydrous magnesium sulfate and fractionally distilled under nitrogen. a, a'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol and dried under reduced pressure at room temperature. Boron trifluoride etherate was treated with a small amount of diethyl ether and distilled under reduced pressure. 2-Iodoethyl vinyl ether was prepared according to the procedure previously described.[26]

Measurements. IR spectra were taken on a

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Hitachi Model 260-30 infrared spectrophotometer. ^{1}H NMR spectra were obtained on a Varian EM 360L NMR spectrometer (60 MHz). 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 in a nitrogen atmosphere. DuPont 951 thermogravimetric analyzer with a heating rate of 10 ℃/min up to 700 ℃ 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-(2'-Vinyloxyethoxy)-1-naphthaldehyde (1). 2-Hydroxy-1-naphthaldehyde (17.2 g, 0.10 mol), anhydrous potassium carbonate (18.0 g, 0.13 mol), and 2-iodoethyl vinyl ether (25.7 g, 0.13 mol) were dissolved in 180 mL of dry DMF under nitrogen. The mixture was refluxed in an oil bath kept at 80 ℃ for 10 h under nitrogen. The resulting solution was cooled to room temperature, diluted with 220 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 on vacuum distillation yielded 19.8 g (82% yield) of pure product 1. Mp=68-69 ℃. ^{1}H NMR (acetone-d$_6$) δ 3.92-4.69 (m, 6H, CH$_2$=, -O-CH$_2$-CH$_2$-O-), 6.35-6.77 (q, 1H, =CH-O-), 7.35-8.32 (m, 5H, aromatic), 9.09-9.33 (m, 1H, aromatic), 10.83 (s, 1H, -CHO). IR (KBr) 3040 (w, =C-H), 2940, 2016, 2866 (m, C-H), 1666 (vs, C=O), 1614, 1591 (vs, C=C) cm^{-1}.

2-(2'-Vinyloxyethoxy)-1-naphthylmethylidenemalononitrile (2). Piperidine (0.13 g, 1.5 mmol) was added to a solution of 2-(2'-vinyloxyethoxy)-1-naphthaldehyde 1 (6.78 g, 28

mmol) and malononitrile (1.98 g, 30 mmol) in 50 mL of n-butanol with stirring at 0 ℃ under nitrogen. After stirring for 1 h at 0 ℃, the product was filtered and washed successively with cold n-butanol (80 mL), water (30 mL), and cold n-butanol (20 mL). The obtained pale yellow product was recrystallized from n-butanol to give 6.50 g (80% yield) of 2. Mp=84-85 ℃. ^{1}H NMR (acetone-d$_6$) δ 3.94-4.69 (m, 6H, CH$_2$=, -O-CH$_2$-CH$_2$-O-), 6.38-6.78 (q, 1H, =CH-O-), 7.39-8.28 (m, 6H, aromatic), 8.71 (s, 1H, Ph-CH=). IR (KBr) 3018 (m, =C-H), 2928, 2875 (m, C-H), 2230 (s, CN), 1622, 1576 (vs, C=C) cm^{-1}. Anal. Calcd for C$_{18}$H$_{14}$N$_2$O$_2$: C, 74.47; H, 4.86; N, 9.65. Found: C, 74.56; H, 4.78; N, 9.74.

Cationic Polymerization of Monomer (2).
A representative cationic polymerization procedure was as follows: A solution of 2 (0.75 g, 2.6 mmol) in dichloromethane (2.0 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 ℃ under nitrogen, and 0.0029 mL (0.026 mmol) of boron trifluoride etherate was added to the solution. After 15 h the ampule was taken out and the polymerization mixture was poured into 500 mL of methanol. The precipitated polymer was collected and reprecipitated from acetone into methanol to give 0.66 g (88% yield) of polymer 3; η_{inh} = 0.28 dL/g (c 0.5 g/dL in acetone at 25 ℃). ^{1}H NMR (acetone-d$_6$) δ 1.33-2.35 (m, 2H, -CH$_2$-), 3.33-4.57 (m, 5H, -O-CH$_2$-CH$_2$-O-CH-), 6.90-8.03 (m, 1H, aromatic), 8.17-8.65 (m, 1H, aromatic). IR (KBr) 3010 (w, =C-H), 2918, 2850 (s, C-H), 2222 (s, CN), 1612, 1585, 1556 (vs, C=C) cm^{-1}. Anal. Calcd for (C$_{18}$H$_{14}$N$_2$O$_2$)$_n$: C, 74.47; H, 4.86; N, 9.65. Found: C, 74.58; H, 4.82; N, 9.73.

RESULTS AND DISCUSSION

Synthesis of Monomer 2. 2-Iodoethyl vinyl ether was prepared by the well known halogen exchange reaction[26] from 2-chloroethyl vinyl ether and sodium iodide, and reacted with 2-hydroxy-1-naphthaldehyde to yield 2-(2'-vinyloxyethoxy)-1-naphthaldehyde **(1)**.[27] 2-(2'-Vinyloxyethoxy)-1-naphthylmethylidenemalono-nitrile **(2)** was synthesized by the condensation of **1** with malononitrile.[28] The chemical structure of the compounds was confirmed by ^{1}H NMR, IR spectra, and elemental analysis. Monomer **2** shows olefinic protons at $\delta = 6.38-6.78$ (q, 1H, vinylic) in their ^{1}H NMR spectra.

Free Radical Polymerization of Monomer 2. 2-(2'-Vinyloxyethoxy)-1-naphthylmethyli-denemalononitrile **2** did not homopolymerize with free radical initiators probably due to the steric hindrance. Compound **2** also did not copo-lymerize with electron-rich ethyl vinyl ether or electron-poor benzylidenemalononitrile by radi-cal initiators such as AIBN, BPO, and DTBP (Table 1). All the attempts to secure a copoly-mer sample have failed so far. In contrast, we have prepared a series of simple vinyl ethers containing electron acceptors and polymerize them with radical initiators to give highly cross-linked poly(vinyl ethers).[22-24] We also found that sterically hindered 3,5-dimethoxy-4-(2-vinyl-oxyethoxy)benzylidenemalononitrile did not homopolymerized by radical initiators,[25] as the presently investigated compound **2**. However, it copolymerized radically with ethyl vinyl ether to give cross-linked copolymers. The inability of homo- or copolymerization of **2** by radical initia-tor seems to be due to the higher sterically hin-dered structure of **2**.

Cationic Polymerization of Monomer 2. Compound **2** polymerized well by cationic initia-tors such as boron trifluoride to give polymer **3**
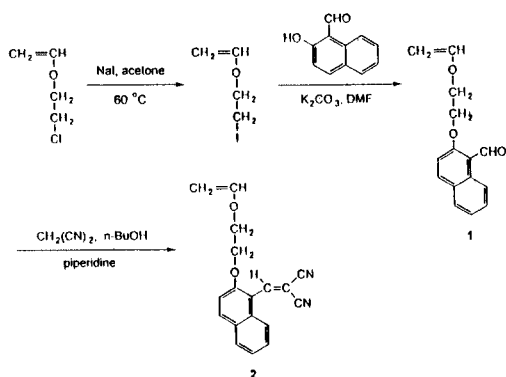
Scheme 1

Table 1. Polymerizations of 2^a Under Various Conditions

monomer	monomer /solvent (mol/1 L)	initiator to monomer (mol%)	temp. (℃)	time (h)	yield (%)	η_{inh}^b (dL/g)
2	1.30, CH₂Cl₂	BF₃, 1.0	-60	15	88	0.28
2	1.00, CH₂Cl₂	BF₃, 0.8	-30	12	85	0.26
2	1.00, CH₂Cl₂	BF₃, 1.5	-60	20	88	0.24
2	1.67, CH₂Cl₂	BF₃, 1.5	-60	20	92	0.25
2+EVE^c	1.30^e	AIBN, 1.0	65	12	nil	-
2+EVE^c	1.67^e	AIBN, 1.5	65	24	nil	-
2+BMN^d	1.30^e	AIBN, 1.0	65	12	nil	-
2+BMN^d	1.67^e	AIBN, 1.5	65	24	nil	-

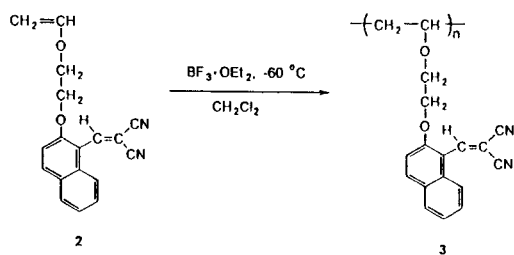^{a} **2** = 2-(2'-Vinyloxyethoxy)-1-naphthylmethylidenemalononitrile.
^{b} Inherent viscosity of polymer: Concentration of 0.5 g/dL in acetone at 25 ℃.
^{c} EVE: Ethyl vinyl ether.
^{d} BMN: Benzylidenemalononitrile.
^{e} Solvent: γ-Butyrolactone.

having 2-oxy-1-naphthylmethylidenemalononitrile, which is presumably effective NLO-chromo-phore for second order nonlinear optical applica-tions. Cationic polymerization was carried out in dichloromethane solution with boron trifloride as cationic initiator at -60 ℃. The polymerization results are summarized in Table 1. Monomer **2** was very reactive toward cationic initiators and polymerized readily. The chemical structure of the polymers were confirmed by ^{1}H NMR, IR spectra, and elemental analyses. IR spectra con-firmed the chemical structures, exhibiting all

Scheme 2

Table 2. Thermal Properties of Polymer 3

polymer	T_g^a, ℃	degradation temp, ℃^{b}			residue^b at 700 ℃, %
		5%-loss	20-loss	40%-loss	
3	82	298	343	389	3.3

^{a} Determined from DSC curves measured on a DuPont 910 differential scanning calorimeter with a heating rate of 10 ℃/min under nitrogen atmosphere.

^{b} Determined from TGA curves measured on a DuPont 951 thermogravimetric analyzer with a heating rate of 10 ℃/min under nitrogen atmosphere.

the absorption bands attributable to the functional groups comprising the polymers. Spectral data indicated that the terminal naphthylidenyl group did not participate in the cationic vinyl polymerization. In most cases, conversions were quite high, but the molecular weights were rather low as indicated by the inherent viscosities.

Properties of Polymers 3. The polymer **3** was soluble in common solvents such as acetone, methyl ethyl ketone, dichloromethane, chloroform, DMF, and DMSO, but was not soluble in methanol, ethanol, and diethyl ether. Polymer **3** was light yellow colored amorphous mterial. The inherent viscosities of polymer **3** measured in acetone solution at 25 ℃ were in the range of 0.25-0.30 dL/g indicating moderate molecular weights. The thermal behavior of the 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. Polymer **3** exhibited a thermal stability up to 300 ℃ in TGA thermogram, which is acceptable for electrooptic device applications. The glass transition temperature (T_g) of the polymer was around 82 ℃ in DSC thermogram. These T_g values are higher than those for poly(ethyl vinyl ether) (-43 ℃), probably due to the presence of polar pendant group. Solution-cast films were clear and brittle, which could be due to the

rather low molecular weight and/or high concentration of dipole moment, and therefore NLO activity has not been measured yet.

CONCLUSIONS

Bifunctional monomer 2-(2′-vinyloxyethoxy)-1-naphthylmethylidenemalo-nonitrile **2** did not homo- or copolymerize with electron-rich ethyl vinyl ether and electron-poor benzylidenemalononitrile by free radical initiators presumably due to the extensive steric hindrance. However, it polymerized well by cationic initiators to give amorphous polymer **3** having 2-oxy-1-naphthylmethylidenealononitrile, which is a potential NLO-chromophore for electrooptic device applications. The resulting substituted poly(vinyl ether) **3** was soluble in common organic solvents. Polymer **3** showed a thermal stability up to 300 ℃ with a T_g of 82 ℃. We are now exploring further the polymerization of other donor-acceptor systems and the results will be reported later.

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