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# Synthesis and cationic polymerization of ethyl vinyl ethers containing the NLO-phores *p*-oxybenzylidenemalononitrile and *p*-oxybenzylidenecyanoacetate in the side chain

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## Summary

p-(2-Vinyloxyethoxy)benzylidenemalononitrile 3 and methyl p-(2-vinyloxyethoxy)benzylidenecyanoacetate 4 was prepared by the condensations of p-(2-vinyloxyethoxy)benzaldehyde 2 with malononitrile and methyl cyanoacetate, respectively. Monomers 3 and 4 were polymerized with cationic initiators to obtain polymers with the NLO-phores p-oxybenzylidenemalononitrile and p-oxycyanocinnamate in the side chain. The resulting polymer 6 was soluble in acetone but the polymer 5 was not soluble in common solvents. The inherent viscosities of polymer 6 were in the range of 0.20-0.30 dL/g in acetone. Solution-cast films were clear and brittle, showing $T_g$ values in the range of 61-70°C.

## Introduction

Functional polymer of nonlinear optical (NLO) activity have long been the subject of curiosity and have caused recent interest (1-5). It is well known that organic and polymeric materials with highly dipolar electronic systems exhibit NLO properties. Compared to other organic and inorganic substances, NLO polymers offer many advantages such as high nonlinear optical activity, light weight, chemical resistance, and good processability. A potentially NLO polymer must contain a highly polarzable π-electronic systems and these polymers have to be mechanically very strong. There are tremendous challenges in designing and synthesis of polymers of large NLO effects. Various polymers with the NLO-phores in the side chain such as poly(meth)acrylates (6-11) and polystyrene (12) were reported. Polyesters (13-17), polyurethanes (18), polyamides (19-21), and poly(phenyleneethynylenes) (21) containing the chromophoric main chain were also prepared. However, examples of polyalkyl vinyl ethers with the chromophoric side chain prepared directly by polymerization of alkyl vinyl ethers are not shown in the literature.

In this work we investigated the polymerization of ethyl vinyl ethers containing the NLO-phores p-oxybenzylidenemalononitrile and p-oxybenzylidenecyanoacetate in the side chain. The present report describes the synthesis and cationic polymerization of p-(2-vinyloxyethoxy)benzylidenemalononitrile 3 and methyl p-(2-vinyloxyethoxy)benzylidenecyanoacetate 4.

## Experimental

### *Materials*

The reagent grade chemicals were purified by distillation of recrystallization before use. 2-Chloroethyl vinyl ether was distilled. Sodium iodide was dried for 4h at 100°C under vacuum. Acetone was purified by drying with anhydrous potassium carbonate, followed by distillation under reduced pressure. p-Hydroxybenzaldehyde was recrystallized from water and dried under vacuum. Malononitrile was recrystallized from water and distilled from phosphorus pentoxide. Methyl cyanoacetate was purified by drying with anhydrous sodium sulfate and distilled. n-Butanol was dried with anhydrous magnesium sulfate and distilled under nitrogen. 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. Chloroform was washed with water to remove the ethanol and refluxed with phosphorus pentoxide, followed by fractional distillation. Boron trifluoride etherate was treated with a small amount of diethyl ether and distilled under reduced pressure.

### *Measurements*

IR spectra were taken on a Hitachi Model 260-30 infrared spectrophotometer. Proton-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°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.

### *Preparation of 2-Iodoethyl Vinyl Ether* 1

Anhydrous sodium iodide (45 g, 0.30 mol) was dissolved in 320 mL of dry acetone contained in a 500 mL round-bottom flask fitted with a reflux condenser protected by a calcium chloride tube, and heated on a heating mantle for 1 h with stirring. 2-Chloroethyl vinyl ether (25.0 g, 0.23 mol) was added to the mixture, and refluxed for an additional 25 h with stirring to complete the reaction. The resulting solution was cooled to room temperature and filtered with suction. The sodium chloride on the filter was washed with 55 mL of acetone anf the filtrate was concentrated by distillation of about 260 mL of the solvent. The residue was poured into 260 mL of water contained in a separate funnel, which was shaken. The lower layer was washed successively with 55 mL of 10% sodium bisulfite solution, 55 mL of 5% sodium bicarbonate, and 30 mL of water. It was dried with anhydrous magnesium sulfate(1.8 g) and fractionated under reduced pressure to give 32.8 g (72% yield) of 1. Bp: 50-52°C (20 mmHg). Proton-NMR ($CDCl_3$) δ 6.22-6.57 (q, 1H), 3.50-4.37 (m, 4H), 2.82-3.47 (t, 2H). IR (neat) 3105, 3034, 2960, 2922, 2845 (C-H), 1635, 1612 (C=C) $cm^{-1}$.

### *Preparation of p-(2-Vinyloxyethoxy)benzaldehyde* 2

4-Hydroxybenzaldehyde (12.2 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 acetone under nitrogen. The mixture was refluxed in an oil bath kept at 60°C for 72 h under nitrogen. The resulting solution was cooled to room temperature, filtered, and the inorganic salts were washed with 50 mL of acetone. Rotary evaporation of acetone gave crude product, which on vacuum distillation yielded 16.3 g (85% yield) of pure product 2. Bp: 72-74°C (0.2 mmHg). Compound 2 was crystallized in the refrigerator (6°C). Proton-NMR (acetone-$d_6$) δ 9.89 (1H, s), 7.63-7.99 (2H, m), 6.87-7.28 (2H, m), 6.32-6.73 (1H, q), 4.18-4.48 (2h, m), 3.70-4.17 (4H, m). IR (neat) 3119, 3068, 2940, 2878, 2833 (C-H), 1694, 1603, 1579 (C=C) $cm^{-1}$.

*Preparation of p-(2-Vinyloxyethoxy)benzylidenemalononitrile* 3

Piperidine (0.13 g, 1.5 mmol) was added to a solution of p-(2-vinyloxyethoxy)benzaldehyde 2 (5.38 g, 28 mmol) and malononitrile (1.98 g, 30 mmol) in 50 mL of n-butanol with stirring at 0°C under nitrogen. After stirring for 1 h at 0°C, the product was filtered and washed with 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 5.38 g (80% yield) of 3. Mp: 80-82°C. Proton-NMR (acetone-$d_6$) δ 7.75-8.13 (3H, m), 6.83-7.28 (2H, m), 6.30-6.73 (1H, q), 4.20-4.51 (2H, m), 3.76-4.21 (4H, m). IR (KBr) 3105, 3067, 2938, 2869 (C-H), 2230 (CN), 1628, 1603, 1579 (C=C) $cm^{-1}$. Anal. Calcd for $C_{14}H_{12}N_2O_2$:C, 69.99; H, 5.03; N, 11.66. Found: C, 69.90; H, 5.08; N, 11.58.

*Preparation of Methyl p-(2-Vinyloxyethoxy)benzylidenecyanoacetate* 4

Piperidine (0.17 g, 2.0 mmol) was added to a solution of p-(2-vinyloxyethoxy)benzaldehyde 2 (5.77 g, 30 mmol) and methyl cyanoacetate (2.98 g, 30 mmol) in 45 mL of n-butanol with stirring at 0°C under nitrogen. The resulting solution was stirred for 1 h at 0°C and 10 h at room temperature. After cooling in an ice bath, the product was filtered and washed with successively with cold n-butanol (30 mL), water (50 mL), and cold n-butanol (20 mL). The obtained pale yellow product was recrystallized from n-butanol to give 5.90 g (72% yield) of 4. Mp: 95-97°C. Proton-NMR (acetone-$d_6$) δ 7.84-8.25 (3H, m), 6.93-7.29 (2H, m), 6.32-6.75 (1H, q), 4.25-4.50 (2H, m), 3.87-4.24 (4H, m), 3.88 (3H, s). IR (KBr) 3103, 3016, 2957, 2930 (C-H), 2220 (CN), 1726 (C=O), 1618, 1588 (C=C) $cm^{-1}$. Anal. Calcd for $C_{15}H_{15}NO_4$:C, 65.92; H, 5.53; N, 5.13. Found: C, 65.85; H, 5.49; N, 5.18.

*Cationic Polymerization of p-(2-Vinyloxyethoxy)benzylidenemalononitrile* 3 *and Methyl p-(2-Vinyloxyethoxy)benzylidenecyanoacetate* 4

A representative cationic polymerization procedure (the case of 4) was as follows: A solution of 4 (0.71 g, 2.6 mmol) in dichloromethane (2.2 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 0.0029 mL (0.026 mmol) of boron trifluoride etherate was added to the solution. After 10 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 0.61 g (86% yield) of polymer 6; $\eta_{inh}$ = 0.22 dL/g (c 0.5 g/dL in acetone at 25°C). 5: 100% yield. IR (KBr) 3013, 2925, 2857 (C-H), 2220 (CN), 1598, 1576, 1553 (C=C) $cm^{-1}$. Anal. Calcd for$(C_{14}H_{12}N_2O_2)_n$: C, 69.99; H, 5.03; N, 11.66. Found: C, 69.90; H, 5.12; N, 11.57. 6: Proton-NMR (acetone-$d_6$) δ 7.47-8.18 (3H, m), 6.58-7.33 (2H, m), 3.22-4.54 (8H, s), 1.33-2.20 (2H, m). IR (KBr) 3032,2942, 2938, 2848 (C-H), 2218 (CN), 1720 (C=O), 1584, 1556 (C=C) $cm^{-1}$. Anal. Calcd for $(C_{15}H_{15}NO_4)_n$: C, 65.92; H, 5.53; N, 5.13. Found: C, 65.83; H, 5.45; N, 5.21.

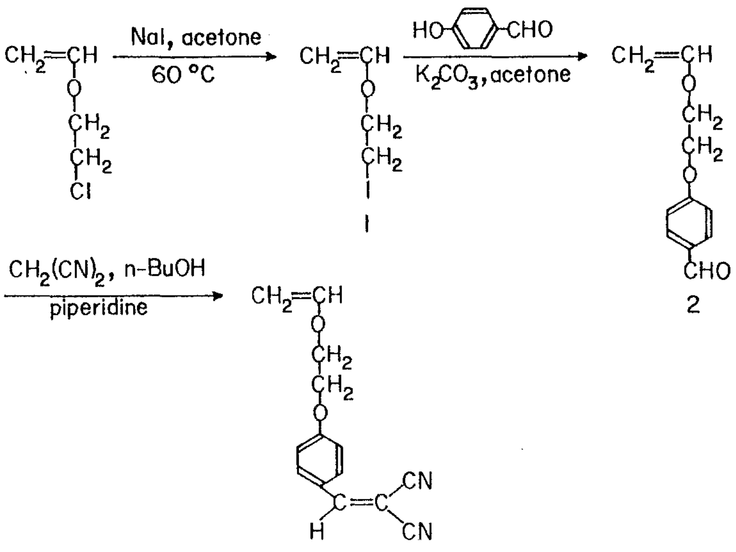
## Results and Discussion

*Synthesis of monomer* 3 *and* 4

2-Iodoethyl vinyl ether 1 was prepared by the well known halogen exchange reaction (22) from 2-chloroethyl vinyl ether and sodium iodide, and reacted with 4-hydroxybenaldehyde to yield p-(2-vinyloxyethoxy)benzaldehyde 2 (23). p-(2-vinyloxyethoxy)benzylidenemalononitrile 3 and methyl p-(2-vinyloxyethoxy)benzylidenecyanoacetate 4 were synthesized by the condensation of 2 with malononitrile or methyl cyanoacetate, respectively (24). The chemical structure of the compounds was confirmed by proton-NMR, IR spectra, and elemental analysis. Spectral data indicated that 4 was a mixture of the cis- and trans-isomer.

*Cationic Polymerization of monomer* 3 *and* 4

p-(2-Vinyloxyethoxy)benzylidenemalononitrile 3 and methyl p-(2-vinyloxyethoxy)benzylidenecyanoacetate 4 were plymerized in solution at -60°C with boron trifluoride etherate as cationic initiator to obtain the polymers 5 and 6. The polymerization results are summarized in Table 1.



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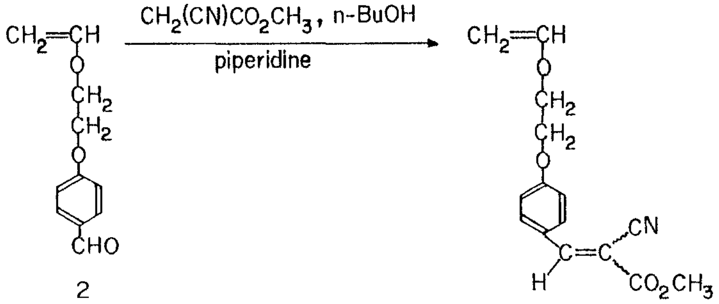

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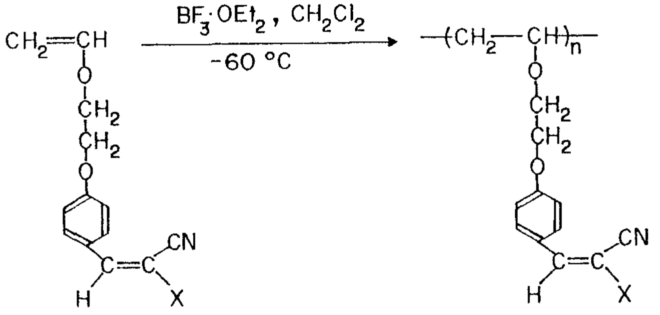
Table 1. Cationic polymerization of 3[a] and 4[b] under various conditions.

| Monomer | Solvent | Monomer/Solvent (mol/1 L) | Initiator to Monomer (mol%) | Temp (°C) | Time (h) | Yield (%) | $\eta_{inh}$[c] (dL/g) |
|---|---|---|---|---|---|---|---|
| 3 | $CH_2Cl_2$ | 1.05 | 1.0 | -60 | 10 | 100 | - |
| 3 | $CH_2Cl_2$ | 0.92 | 0.8 | -60 | 16 | 100 | - |
| 3 | $C_6H_5CH_3$ | 1.00 | 1.0 | -60 | 20 | 100 | - |
| 3 | $C_6H_5CH_3$ | 0.85 | 0.8 | -30 | 12 | 100 | - |
| 4 | $CH_2Cl_2$ | 1.18 | 1.0 | -60 | 10 | 86 | 0.22 |
| 4 | $CH_2Cl_2$ | 0.95 | 0.8 | -60 | 20 | 88 | 0.26 |
| 4 | $C_6H_5CH_3$ | 1.00 | 1.2 | -60 | 20 | 92 | 0.30 |
| 4 | $C_6H_5CH_3$ | 0.88 | 1.0 | -30 | 16 | 90 | 0.28 |

[a] 3 = p-(2-Vinyloxyethoxy)benzylidenemalononitrile.
[b] 4 = Methyl p-(2-Vinyloxyethoxy)benzylidenecyanoacetate.
[c] Inherent viscosity of polymer: Concentration of 0.5 g/dL in acetone at 25°C.



3, X=CN
4, X=$CO_2CH_3$

5, X=CN
6, X=$CO_2CH_3$

Monomer 3 and 4 were quite reactive toward cationic initiator and polymerized readily. The polymerizability of monomer 3 toward cationic initiator was very high and polymerized quantitatively at low temperature. The chemical structure of the polymers were confirmed by proton-NMR, IR spectra, and elemental analyses. In most cases, conversions were quite high, but the molecular weights were rather low as indicated by the inherent viscosities.

The polymer 6 was soluble in common solvents such as acetone, chloroform and DMSO, but was not soluble in methanol and diethyl ether. However, polymer 5 was not soluble in common organic solvents, probably due to the high molecular weight and/or the high crystallinity by the presence of polar symmetric dicyano substituents in the side chain. The inherent viscosities of polymer 6 were in the range of 0.20-0.30 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. The glass transition temperature ($T_g$) of the polymers was around 61-70°C. These $T_g$ values are higher than those for poly(ethyl vinyl ether) (-43°C), probably due to the presence of polar pendant

| Polymer | $T_g$[a], °C | Degradation temp, °C[b] | | | Residue[b] at 700°C, % |
|---|---|---|---|---|---|
| | | 5%-loss | 20%-loss | 40%-loss | |
| 5 | 70 | 254 | 316 | 365 | 29.5 |
| 6 | 61 | 330 | 367 | 394 | 27.4 |

[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.

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.

Table 2. Thermal properties of polymer 5 and 6.

In conclusion, we prepared clean poly(ethyl vinyl ether) 5 and 6 containing the NLO phores p-oxybenzylidenemalononitrile or p-oxybenzylidenecyanoacetate in the side chain by the cationic polymerization of the vinyl monomer 3 and 4, respectively. The resulting substituted poly(ethyl vinyl ether) 6 was soluble in acetone, but dicyano-substituted polymer 5 was not soluble in common solvents. Polymer 5 and 6 showed sharp $T_g$ peaks around 61-70°C in their DSC thermograms. Copolymerization with other monomers and measurements of NLO activity are in progress, and the results will be reported later.

## Acknowledgements

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