Polymer Bulletin 35, 33–40 (1995)

Polymer Bulletin

# Preparation of poly(alkylvinylether)s for nonlinear optical applications

## Synthesis and cationic polymerizations of 3′,5′-dimethoxy-4′-(2-vinyloxyethoxy)-4-nitrostilbene and 3′,5′-dimethoxy-4′-(2-vinyloxyethoxy)-2,4-dinitrostilbene

**Ju-Yeon Lee**

Department of Chemistry, Inje University, Aebang-dong, Kimhae 621-749, Seoul, Korea

Received: 23 January 1995/Revised version: 3 March 1995/Accepted: 7 March 1995

## Summary

3′,5′-Dimethoxy-4′-(2-vinyloxyethoxy)-4-nitrostilbene 2 and 3′,5′-dimethoxy-4′-(2-vinyloxyethoxy)-2,4-dinitrostilbene 5 were prepared by the reactions of 2-iodoethyl vinyl ether with 3′,5′-dimethoxy-4′-hydroxy-4-dinitrostilbene 1 and 3′,5′-dimethoxy-4′-hydroxy-2,4-dinitrostilbene 4, respectively. Monomers 2 and 5 were polymerized with cationic initiators to obtain polymers with the NLO-phores 3′,5′-dimethoxy-4′-oxy-4-nitrostilbene and 3′,5′-dimethoxy-4′-oxy-2,4-nitrostilbene in the side chain. The resulting polymer 3 and 6 were soluble in DMSO and DMF. The inherent viscosities of polymers were in the range of 0.28-0.33 dL/g in DMSO. Polymers 3 and 6 showed good thermal stabilities in their TGA thermograms, and the $T_g$ values from DSC thermograms were in the range of 81-87°C.

## Introduction

Functional polymers 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 polarizable 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 (6-12) and polystyrene (13) were reported. Polyesters (14-18), polyurethanes (19), polyamides (20-21), and poly(phenyleneethynylenes) (22) containing the chromophoric main chain were also prepared. Dix etc. (23) prepared poly(ethyl vinyl ether) partly grafted with azo dyes by the reaction of poly(2-chloroethyl vinyl ether) with 4′-amino-4-nitroazobenzene. However, examples of polyalkyl vinyl ethers with the chromophoric side chain prepared directly by the polymerization of monomeric alkyl vinyl ethers are seldom found in the literature. Recently we have prepared clean poly(ethyl vinyl ethers) containing the NLO-phores p-oxybenzylidenemalononitrile, methyl p-oxybenzylidenecyanoacetate (24), and 4′-oxy-4-nitrostilbene (25) in the side chain by cationic polymerization of the corresponding monomers. This work is now extended with the synthesis and characterization of another poly(ethyl vinyl ethers) containing the NLO-phores 3′,5′-dimethoxy-4′-oxy-4-nitrostilbene and 3′,5′-dimethoxy-4′-oxy-2,4-dinitrostilbene in the side chain. The present report describes the synthesis and cationic polymerization of 3′,5′-dimethoxy-4′-(2-vinyloxyethoxy)-4-nitrostilbene 2 and 3′,5′-dimethoxy-4′-(2-vinyloxyethoxy)-2,4-dinitrostilbene 5. We now report the results of the initial phase of the work.

## Experimental

### *Materials*

2-Chloroethyl vinyl ether, 3,5-dimethoxy-4-hydroxybenzaldehyde, p-nitrophenylacetic acid, piperidine, and 2,4-dinitrotoluene (Aldrich) were used as received. Sodium iodide was dried for 4 h at 100 °C under vacuum. Acetone was purified by drying with anhydrous potassium carbonate, followed by distillation under nitrogen. N,N-Dimethylformamide (DMF) was purified by drying with anhydrous calcium sulfate, followed by distillation under reduced pressure. Dichloromethane washed with concentrated sulfuric acid and then with water, dried with anhydrous calcium chloride, refluxed with calcium hydride, and distilled under nitrogen before use. Toluene was washed with cold concentrated sulfuric acid and then with water, aqueous 5% sodium bicarbonate, again with water, dried with anhydrous calcium sulfate, refluxed with phosphorus pentoxide, and distilled. 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. $^1$H NMR spectra were obtained on a Varian EM 360L NMR spectrometer (60 MHz). UV-VIS spectra were obtained on a Kontron UVikon 860 spectrophotometer. 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*

Anhydrous sodium iodide (45.0 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). $^1$H NMR ($CDCl_3$) δ 6.22-6.57 (q, =CH-O-), 3.50-4.37 (m, $CH_2$= and -O-$CH_2$-), 2.82-3.47 (t, -$CH_2$-I). IR (neat): 3105, 3034, 2960, 2922, 2845 (m, C-H), 1635, 1612 (vs, C=C) cm$^{-1}$.

### *Preparation of 3′,5′-dimethoxy-4′-hydroxy-4-nitrostilbene* (1)

Compound 1 was prepared by a known method (26) from 3,5-dimethoxy-4-hydroxybenzaldehyde and p-nitrophenylacetic acid, and recrystallized from ethanol. Mp: 186-187°C. $^1$H NMR (acetone-d$_6$) δ 6.76-7.03 (d, aromatic 2H), 7.43-7.70 (d, aromatic 4H), 8.10-8.80 (m, aromatic 3H). IR (neat) 3536 (s, O-H), 3010 (m, =C-H), 2936, 2832 (m, C-H), 1630, 1596, 1587 (vs, C=C), 1508, 1329 (vs, N=O) cm$^{-1}$.

*Preparation of 3′,5′-dimethoxy-4′-hydroxy-2,4-dinitrostilbene* (**4**)

Compound **4** was prepared by a known method (26) from 3,5-dimethoxy-4-hydroxybenzaldehyde and 2,4-dinitrotoluene, and recrystallized from DMSO. Mp: 272-273°C (dec). $^1$H NMR (acetone-d$_6$) δ 3.81 (s, 2CH$_3$O-), 6.94 (s, aromatic 2H), 7.26-7.47 (d, aromatic 2H), 8.03-8.71 (m, aromatic 3H). IR (neat) 3460 (s, O-H), 3124, 3080, 3008 (m, =C-H), 2940, 2840 (m, C-H), 1628, 1603, 1595 (vs, C=C), 1514, 1340 (vs, N=O) cm$^{-1}$.

*Preparation of 3′,5′-dimethoxy-4′-(2′-vinyloxyethoxy)-4-nitrostilbene* (**2**)

3‘,5’-Dimethoxy-4‘-hydroxy-4-nitrostilbene (8.14 g, 0.027 mol), anhydrous potassium carbonate (11.19 g, 0.081 mol), and 2-iodoethyl vinyl ether (7.92 g, 0.040 mol) were dissolved in 50 mL of dry DMF under nitrogen. The mixture was refluxed in an oil bath kept at 80°C for 6 h under nitrogen. The resulting solution was cooled to room temperature, diluted with 200 mL of water, filtered, and the obtained yellow product was washed successively with 200 mL of diethyl ether, 200 mL of water, and 100 mL of cold ethanol. After separation of the organic layer, the aqueous layer was extracted with 200 mL of diethyl ether two times. Rotary evaporation of the solvent under reduced pressure gave yellow product, which was washed with water (150 mL) and cold ethanol. Recrystallization from ethanol yielded 9.03 g (90% yield) of pure product **2**. Mp: 109-110°C. $^1$H NMR (acetone-d$_6$) δ 3.83 (s, 2 CH$_3$O-), 3.84-4.33 (m, CH$_2$= and -O-CH$_2$-CH$_2$-O-), 6.26-6.69 (q, =CH-O-), 6,90 (s, aromatic 2H), 7.27 (s, aromatic 2H), 7.49-7.82 (m, aromatic 2H), 7.91-8.26 (m, aromatic 2H). IR (KBr) 3001 (m, =C-H), 2939, 2830 (s, C-H), 1630, 1599, 1582 (vs, C=C), 1507, 1325 (vs, N=O) cm$^{-1}$. UV/Vis (chloroform) $\lambda_{max}$=370, ε=21,930. Anal. Calcd for C$_{20}$H$_{21}$NO$_6$: C, 64.68; H, 5.70; N, 3.77. Found: C, 64.74; H, 5.66; N, 3.71.

*Preparation of 3′,5′-dimethoxy-4′-(2′-vinyloxyethoxy)-2,4-dinitrostilbene* (**5**)

3‘,5’-Dimethoxy-4‘-hydroxy-2,4-nitrostilbene (9.35 g, 0.027 mol), anhydrous potassium carbonate (11.19 g, 0.081 mol), and 2-iodoethyl vinyl ether (7.92 g, 0.040 mol) were dissolved in 50 mL of dry DMF under nitrogen. The mixture was refluxed in an oil bath kept at 80°C for 10 h under nitrogen. The resulting solution was cooled to room temperature, diluted with 200 mL of water, filtered, and the obtained yellow product was washed successively with 200 mL of diethyl ether, 200 mL of water, and 100 mL of cold ethanol. Recrystallization from ethanol yielded 10.34 g (92% yield) of pure product **5**. Mp: 139-140°C. $^1$H NMR (acetone-d$_6$) δ 3.81 (s, 2 CH$_3$O-), 3.82-4.30 (m, CH$_2$= and -O-CH$_2$-CH$_2$-O-), 6.19-6.62 (q, =CH-O-), 6,86 (s; aromatic 2H), 7.37 (s, aromatic 2H), 7.98-8.68 (m, aromatic 3H). IR (KBr) 3063 (m, =C-H), 2960, 2938, (m, C-H), 1643, 1617, 1593, 1588 (vs, C=C), 1518, 1503, 1343, 1324 (vs, N=O) cm$^{-1}$. UV/Vis (chloroform) $\lambda_{max}$=395, ε=11,150. Anal. Calcd for C$_{20}$H$_{20}$N$_2$O$_8$: C, 57.69; H, 4.84; N, 6.73. Found: C, 57.77; H, 4.78; N, 6.66.

*Cationic polymerization of* **2** *and* **5**

A representative cationic polymerization procedure (the case of **2**) was as follows: A solution of **2** (0.74 g, 2.0 mmol) in dichloromethane (2.5 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 -30°C under nitrogen, and 0.0034 mL (0.030 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 DMSO into methanol to give 0.67 g (90% yield) of polymer **3**; $\eta_{inh}$=0.30 dL/g (c 0.5 g/dL in DMSO at 25°C). **3**: $^1$H NMR (DMSO-$d_6$) δ=0.76-1.93 (m, $-CH_2-$), 3.05-4.35 (m, $-CH-O-CH_2-CH_2-O-$ and 2 $CH_3O-$), 6.45-7.50 (m; aromatic 4H), 7.52-8.75 (m, aromatic 4H). IR (KBr) 3068 (w, =C-H), 2936, 2871, 2840 (s, C-H), 1628, 1595, 1578 (vs, C=C), 1508, 1341 (vs, N=O) cm$^{-1}$. UV/Vis (chloroform) $\lambda_{max}$=374. Anal. Calcd for $(C_{20}H_{21}NO_6)_n$: C, 64.68; H, 5.70; N, 3.77. Found: C, 64.77; H, 5.64; N, 3.84. **6**: $^1$H NMR (DMSO-$d_6$) δ=0.82-1.94 (m, $-CH_2-$), 3.06-4.35 (m, $-CH-O-CH_2-CH_2-O-$ and 2 $CH_3O-$), 6.50-8.37 (m, aromatic 7H). IR (KBr) 3078 (m, =C-H), 2932, 2860, 2828 (s, C-H), 1620, 1596, 1575 (vs, C=C), 1518, 1502, 1344 (vs, N=O) cm$^{-1}$. UV/Vis (chloroform) $\lambda_{max}$= 399. Anal. Calcd for $(C_{20}H_{20}N_2O_8)_n$: C, 57.69; H, 4.84; N, 6.73. Found: C, 57.78; H, 4.76; N, 6.67.

## Results and discussion

### *Synthesis of monomer* 2 *and* 5

3′,5′-Dimethoxy-4′-hydroxy-4-nitrostilbene **1** and 3′,5′-dimethoxy-4′-hydroxy-dinitrostilbene **4** were synthesized by the reactions of 3,5-dimethoxy-4-hydroxybenzaldehyde with p-nitrophenylacetic acid and 2,4-dinitrotoluene respectively, according to a literature procedure (26), and recrystallized from ethanol and DMSO. 2-Iodoethyl vinyl ether was prepared by the well known halogen exchange reaction (27) from 2-chloroethyl vinyl ether and sodium iodide, and reacted with 3′,5′-dimethoxy-4′-hydroxy-4-nitrostilbene **1** and 3′,5′-dimethoxy-4′-hydroxy-2,4-dinitrostilbene **4** to yield 3′,5′-dimethoxy-4′-(2-vinyloxyethoxy)-4-nitrostilbene **2** and 3′,5′-dimethoxy-4′-(2-vinyloxy-ethoxy)-2,4-dinitrostilbene **5** (18). The chemical structures of the compounds were confirmed by $^1$H NMR, IR, UV-Vis spectra, and elemental analyses. Spectral data indicated that stilbene compounds **2** and **4** were isolated as the trans-isomers. Compounds **2** and **4** showed strong uv absorption bands near 375-395 nm measured in chloroform.

### *Cationic polymerization of monomer* 2 *and* 5

3′,5′-Dimethoxy-4′-(2-vinyloxyethoxy)-4-nitrostilbene **2** and 3′,5′-dimethoxy-4′-(2-vinyloxyethoxy)-2,4-dinitrostilbene **5** were polymerized in solution at -30 °C with boron trifluoride etherate as cationic initiator to obtain the polymers **3** and **6** (Scheme 1 and Scheme 2). The polymerization results are summarized in Table 1. Monomers **2** and **5** were quite reactive toward cationic initiator and polymerized readily at low temperature. The chemical structures of the polymers were confirmed by $^1$H NMR, IR, UV-Vis spectra, and elemental analyses. Polymers **3** and **6** showed strong uv absorption bands near 374-399 nm by the chromophores 3′,5′-dimethoxy-4′-oxy-4-nitrostilbene and 3′,5′-dimethoxy-4′-oxy-2,4-dinitrostilbene in the side chain measured the chloroform. Spectral data indicated that the internal double bond in stilbene moiety did not participate in the vinyl polymerization. In most cases, conversions were quite high, but the molecular weights were rather low as indicated by the inherent viscosities. The polymers **3** and **6** were soluble in DMF and DMSO, but were not soluble in methanol and diethyl ether. The inherent viscosities of polymers were in the range of 0.28-0.33 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. TGA thermograms showed double phase degradation patterns, probably due to the presence of two benzene rings in the pendant group.

Table 1. Cationic polymerization of 2[a] and 5[b] under various conditions.

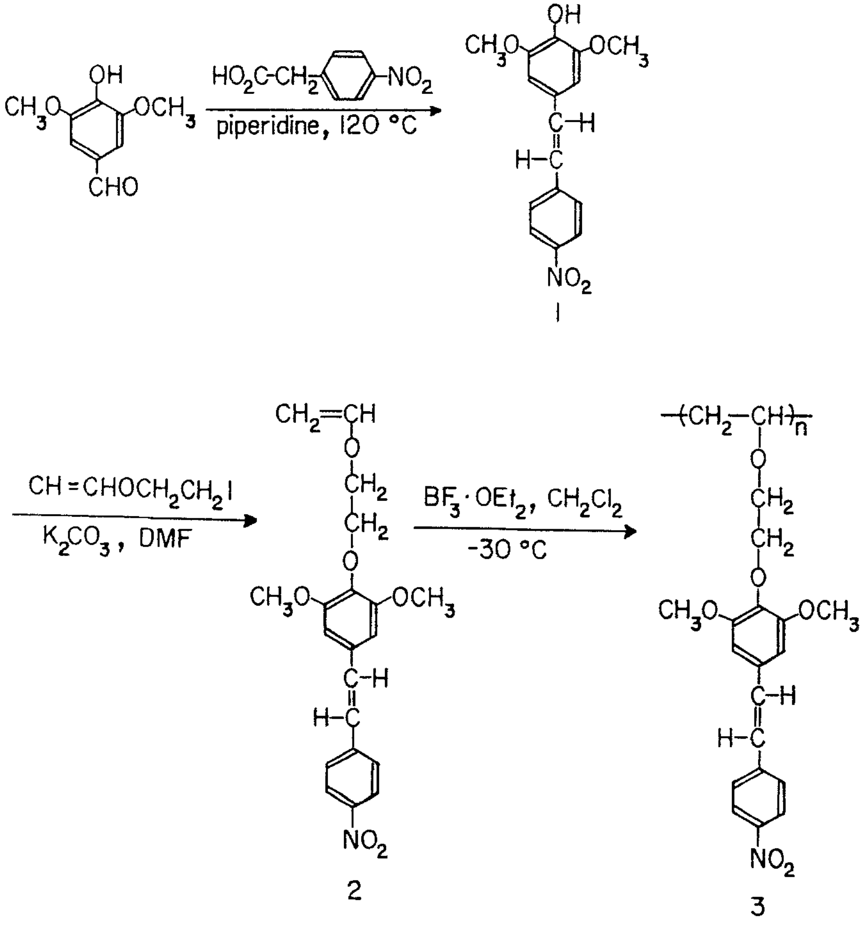
| Monomer | Solvent | Monomer/solvent (mol/1 L) | Initiator[c] to monomer (mol-%) | Temp (°C) | Time (h) | Yield (%) | $\eta_{inh}$[d] (dL/g) |
|---|---|---|---|---|---|---|---|
| 2 | $CH_2Cl_2$ | 0.80 | 1.5 | -30 | 10 | 90 | 0.30 |
| 2 | $CH_2Cl_2$ | 0.57 | 1.2 | -60 | 16 | 86 | 0.28 |
| 2 | $C_6H_5CH_3$ | 0.80 | 1.5 | -30 | 12 | 88 | 0.32 |
| 2 | $C_6H_5CH_3$ | 0.67 | 1.2 | -60 | 20 | 90 | 0.33 |
| 5 | $CH_2Cl_2$ | 0.59 | 1.5 | -30 | 10 | 95 | 0.32 |
| 5 | $CH_2Cl_2$ | 0.80 | 1.2 | -60 | 20 | 92 | 0.30 |
| 5 | $C_6H_5CH_3$ | 0.67 | 1.5 | -30 | 20 | 90 | 0.28 |
| 5 | $C_6H_5CH_3$ | 0.80 | 1.8 | -60 | 24 | 95 | 0.31 |

[a] 2 = 3′,5′-Dimethoxy-4′-(2-vinyloxyethoxy)-4-nitrostilbene.

[b] 5 = 3′,5′-Dimethoxy-4′-(2-vinyloxyethoxy)-2,4-dinitrostilbene.

[c] Initiator: Boron trifluoride etherate.

[d] Inherent viscosity of polymer: Concentration of 0.5 g/dL in DMSO at 25 °C.



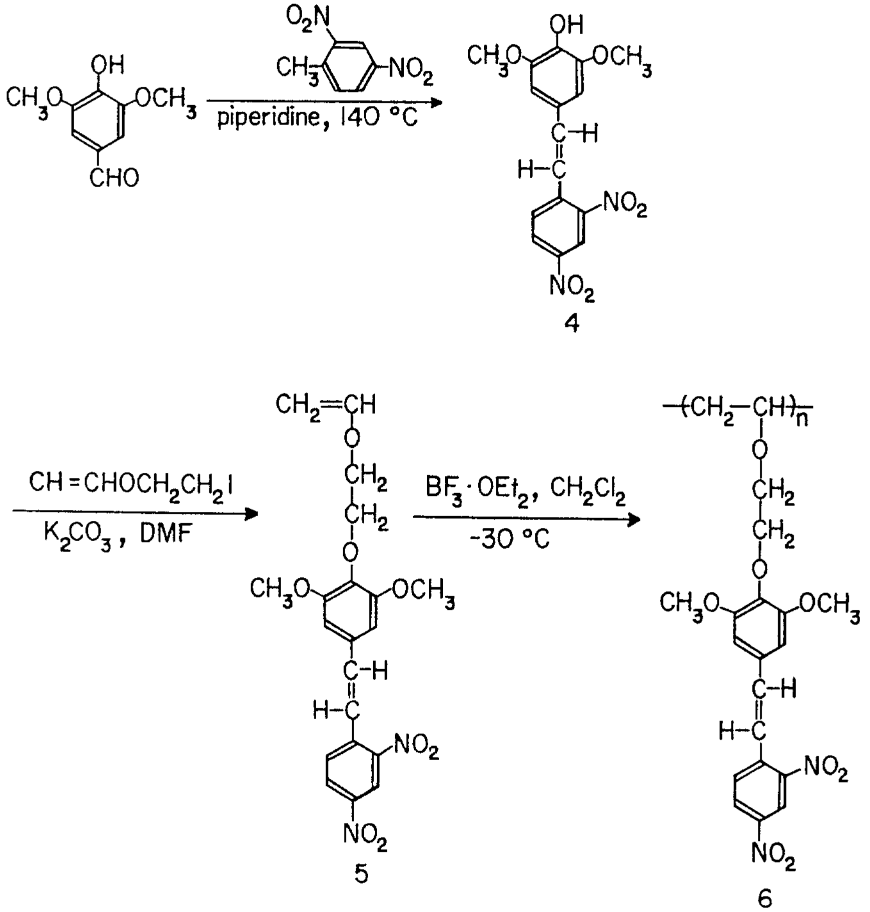


Table 2. Thermal properties of polymers 3 and 6.

| Polymer | $T_g$[a], °C | Degradation temp in °C[b] | | | Residue[b] at 700 °C, % |
|---|---|---|---|---|---|
| | | 5%-loss | 20%-loss | 40%-loss | |
| 3 | 87 | 310 | 354 | 484 | 10.5 |
| 6 | 81 | 289 | 320 | 443 | 7.0 |

[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.

Polymers 3 and 6 showed a good thermal stability and were not decomposed below 300°C as shown in Table 2, which is acceptable for NLO device application. The $T_g$ values of the polymers obtained from DSC thermograms were around 81-87°C.These $T_g$ values are higher than those for poly(ethyl vinyl ether) (-43°C), probably due to the presence of polar and bulky pendant group. Polymers **3** and **6** did not exhibit any characteristic liquid crystalline properties, probably because that the alkyl chain of pendant group are rather short. In summary, we prepared clean poly(ethyl vinyl ethers) **3** and **6** containing the NLO phores 3′,5′-dimethoxy-4′-oxy-4-nitrostibene and 3′,5′-dimethoxy-4′-oxy-2,4-dinitrostibene in the side chain by the cationic polymerization of the corresponding vinyl monomers **2** and **5**. The resulting substituted poly(ethyl vinyl ethers) **3** and **6** were soluble in DMF and DMSO, but were not soluble in methanol and diethyl ether. Polymer **3** and **6** showed thermal stabilities up to 300°C, which is acceptable for NLO device application, showing $T_g$ peaks around 81-87 °C. Copolymerization with other monomers to increase the $T_g$ values and measurements of NLO activity are in progress, and the results will be reported later.

## Acknowledgements

This work was supported by the Korea Science and Engineering Foundation (951-0305-009-2).

## References

1. Williams DJ (1984) Angew Chem Int Ed Engl 23: 69
2. Prasad PN, Ulrich DR (ed) Nonlinear Optical and Electroactive Polymers. Plenum Press, New York 1987
3. Chemla DS, Zys J (ed) Nonlinear Optical Properties of Organic Molecules and Crystals, vol 1, 2. Academic Press, New York 1987
4. Heeger AJ, Orestein J, Ulrich DR (ed) Nonlinear Optical Priperties of Polymers, Mater Res Soc Symp Proc vol 109
5. Shen YR (1984) The Principles of Nonlinear Optics. Wiley, New York
6. Robello DR (1990) J Polym Sci Part A Polym Chem 28: 1
7. Nijhuis S, Rikken GLJA, Havinga EE, Hoeve WT, Wynberg H, Meijer EW (1990) J Chem Soc Chem Commun: 1093
8. Ni Z, Leslie TM, Padias AB, Hall HK (1991) Macromolecules 24: 2100
9. Rondou P, Beylen MV, Samyn C, S'heeren G, Persoons A (1992) Makromol Chem 193: 3045
10. S'heeren G, Persoons A, Rondou P, Wiersma J, Beylen MV, Samyn C (1993) Makromol Chem 194: 1733
11. McCulloch IA (1994) Macromolecules 27: 1697
12. Baehr C, Glusen B, Wendorff JH, Staring EG (1994) Makromol Chem Rapid Commun 15: 327
13. Vanermen G, Samyn C, S'heeren G, Persoons A. (1992) Makromol Chem 193: 3057
14. Stenger-Smith JD, Fisher JW, Henry RA, Hoover JM, Lindsay GA, Hayden LM (1990) Makromol Chem Rapid Commun 11: 141
15. Fuso F, Padias AB, Hall HK (1991) Macromolecules 24: 1710
16. Stenger-Smith JD, Fisher JW, Henry RA, Hoover JM, Nadler MP, Nissan RA, Lindsay GA (1991) J Polym Sci Part A Polym Chem 29: 1623
17. Francis CV, White KM, Newmark RA, Stephens MG (1991) Macromolecules 26: 4379
18. Wright ME, Mullick S, Lackritz HS, Liu L-Y (1994) Macromolecules 27: 3009
19. Boogers JAF, Klaase PTA, Vlieger JJD, Tinnemans AHA (1994) Macromolecules 27: 205
20. Lindsay GA, Stenger-Smith JD, Henry RA, Hoover JM, Nissan RA (1992) Macromolecules 25: 6075
21. Xu C, Wu B, Dalton LR, Ranon PM, Shi Y, Steier WH (1992)

Macromolecules 25: 6716
22. Kondo K, Okuda M, Fugitani T (1993) Macromolecules 26: 7382
23. Campbell D, Dix LR, Rostron P (1993) Eur Polym J 29: 249
24. Lee JY (1994) Polym Bull in press.
25. Lee JY (1994) Polym Bull in press.
26. Cullinane NM (1923) J. Chem Soc 123: 2053
27. Moore AHF (1963) Org Syn Coll Vol 4: 84