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Synthesis and free radical polymerization of *p*-(2-methacryloyloxyethoxy)-*N*-(4-nitrostilbenzylidene)aniline for nonlinear optical applications

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Summary

p-(2-Methacryloyloxyethoxy)-N-(4-stilbenzylidene)aniline 6 was prepared by the reactions of methacryloyl chloride with p-(2-hydroxyethoxy)-N-(4-stilbenzylidene)aniline 5. Monomer 6 was polymerized with radical initiators to obtain polymer with p-oxy-N-4-(stilbenzylidene)aniline, which is presumably effective chromophore for second-order nonlinear optical applications in the side chain. The resulting polymethacrylate 7 showed a thermal stability up to 300 °C in TGA thermogram, and the T_g value obtained from DSC thermogram was 166°C, which is acceptable for NLO device applications.

Introduction

Functional materials of nonlinear optical (NLO) activity based on organic compounds have long been the subject of curiosity and have caused recent intrest 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 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. Polyesters (8-12), polyurethanes (13), polyamides (14-15), and poly(phenyleneethynylenes) (16) containing the chromophoric main chain were prepared. Various polymers with the NLO-phores in the side chain such as poly(meth)acrylates (17-22), polystyrene (23), and poly(alkyl vinyl ethers) (24-27) were also reported. Robello (17) prepared polyacrylates bearing aminonitrostilbene and azo dyes in the side chain. Recently polymethacrylates containing mesogenic (carbazoylmethylene)aniline and 4-nitrobenzylideneaniline groups in the side chain were also reported by Uryu etc (28). However, examples of NLO-polymers with the chromophoric side chain composed of three conjugated phenyl groups are seldom found in the literature. Thus, it is of interest to prepare polymethacrylate containing three conjugated phenyl groups as the NLO-phore in the side chain. In this work we prepared polymethacrylate with the NLO-phore p-oxy-N-(4-nitrostilbenzylidene)aniline, which is presumably effective chromophore for second-order nonlinear optical applications in the side chain. The present report describes the synthesis and radical polymerization of p-(2-methacryloyloxyethoxy)-N-(4-nitrostilbenzylidene)aniline **6**. We now report the results of the initial phase of the work.

Experimental

Materials

2-Iodoethanol, p-tolualdehyde, 4-nitrophenylacetic acid, 4-aminophenol (Aldrich) were used as received. Carbon tetrachloride was refluxed with phosphorus pentoxide under nitrogen and distilled. 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. Dimethyl sulfoxide (DMSO) was dried over 4 A° molecular sieves for several days and distilled under vacuum. N,N-Dimethylformamide (DMF) was purified by drying with anhydrous calcium sulfate, followed by distillation under reduced pressure. Chloroform was washed with water to remove the ethanol, dried with anhydrous potassium carbonate, refluxed with anhydrous calcium chloride, and distilled. Methacryloyl chloride was distilled and used immediately. Triethylamine was refluxed over potassium hydroxide and distilled. γ-Butyrolactone was dried with anhydrous magnesium sulfate and fractionally distilled under nitrogen. Piperidine was dried with calcium hydride and fractionally distilled. α,α′-Azobisisobutyronitrile (AIBN) was recrystallized from methanol and dried under reduced pressure at room temperature.

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.

4′-Methyl-4-nitrostilbene (1)

Compound 1 was prepared by a known method (29) from p-tolualdehyde and 4-nitrophenylacetic acid, and recrystallized from ethanol. Mp: 139-140°C. ^{1}H NMR (acetone-d_6) δ 2.33 (s, benzylic 3H), 7.04-7.95 (m, aromatic 8H), 8.05-8.35 (d, aromatic 2H). IR (neat) 3075, 3015 (w, =C-H), 1626, 1592, (s, C=C), 1512, 1347 (vs, N=O) cm^{-1}. Anal. Calcd for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.47; N, 5.86. Found: C, 75.42; H, 5.51; N, 5.90.

4′-Bromomethyl-4-nitrostilbene (2)

4′-Methyl-4-nitrostilbene (13.6 g, 0.057 mol), N-bromosuccinimide (10.7 g, 0.060 mol), and benzoyl peroxide (0.14 g) were dissolved in 90 mL of CCl_4 under a nitrogen atmosphere. The mixture was refluxed with vigorous stirring at 85°C for 12 h under nitrogen. The resulting solution was cooled to room temperature, filtered with suction, and rinsed with 30 mL of CCl_4. The yellow solid on the filter was washed thoroughly with water to remove succinimide. The product was recrystallized from ethanol yielded 14..1 g (78% yield) of pure product 2. Mp: 127-128°C. ^{1}H NMR (acetone-d_6) δ 2.33 (s, benzylic 3H), 7.04-7.95 (m, aromatic 8H), 8.05-8.35 (d, aromatic 2H). IR (neat) 3020 (w,

=C-H), 1628, 1586 (s, C=C), 1508, 1328 (vs, N=O) cm^{-1}. Anal. Calcd for $C_{15}H_{12}BrNO_2$: C, 56.63; H, 3.80; N, 4.40. Found: C, 56.56; H, 3.76; N, 4.45.

4'-Nitro-4-stilbenecarboxaldehyde **(3)**

A mixture of 11.5 g (0.036 mo) of 4'-bromomethyl-4-nitrostilbene and 10.5 g (0.054 mol) of potassium chromate in 55 mL of DMSO was refluxed with vigorous stirring at 115 °C for 2 h under nitrogen. Extraction was performed on the resulting black solution thrice with 250 mL of diethyl ether. The organic layer was concentrated by distillation of the solvent. The residue was precipitated into 300 mL of water contained in a round bottomed flask, which was stirred. The precipitated yellow product was filtered with suction and washed successively twice with 100 mL of water and 100 mL of n-hexane. Thus obtained product was recrystallized from ethanol yielded 7.3 g (80% yield) of pure product **3**. Mp: 199-200°C (dec). ^1H NMR (acetone-d_6) δ 9.99 (s, -CHO), 7.18-8.37 (m, aromatic 10H). IR (neat) 1687 (vs, C=O), 1598, 1565 (vs, C=C), 1505, 1334 (vs, N=O) cm^{-1}. UV/Vis (chloroform) λ_{max}=354 nm, ϵ =23630.Anal. Anal. Calcd for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.38; N, 5.53. Found: C, 71.21; H, 4.36; N, 5.56.

p-Hydroxy-N-(4-nitrostilbenzylidene)aniline **(4)**

Compound **4** was prepared by a known method (10) from 4-nitrobenzaldehyde and 4-aminophenol in absolute ethanol, and recrystallized from acetone. Yield=90%; mp: 215-216°C (dec). ^1H NMR (DMSO-d_6) δ 6.77-7.46 (m, aromatic 4H), 7.66 (s, aromatic 1H), 7.76-8.19 (m, aromatic 6H), 8.22-8.52 (d, aromatic 2H), 8.75 (s, -N=CH-), 9.48 (s, -OH); IR (KBr) 3420 (s, O-H), 1614, 1578 (C=C), 1498, 1338 (vs, N=O) cm^{-1}. UV/Vis (chloroform) λ_{max}=356 nm, ϵ=26300. Anal. Calcd for $C_{21}H_{16}N_2O_3$: C, 73.24; H, 4.68; N, 8.13. Found: C, 73.28; H, 4.64; N, 8.16.

p-(2-Hydroxyethoxy)-N-(4-nitrostilbenzylidene)aniline **(5)**

p-Hydroxy-N-(4-nitrostilbenzylidene)aniline (4.82 g, 0.014 mol), anhydrous potassium carbonate (5.80 g, 0.042 mol), and 2-iodoethanol (3.58 g, 0.021 mol) were dissolved in 25 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 100 mL of water, stirred, filtered, and the obtained brown product was washed with 100 mL of water. Thus obtained product was recrystallized from ethanol yielded 3.92 g (72% yield) of pure product 5. Mp: 172-173°C (dec). ^1H NMR (DMSO-d_6) δ 3.47-3.89 (m, 2H, -CH_2-O-), 3.90-4.15 (m, 2H, Ph-O-CH_2-), 4.16-4.61 (m, 1H, -OH), 6.65-8.89 (m, 15H, aromatic); IR (KBr) 3538 (s, O-H), 3078 (=C-H), 2954, 2928 (w, C-H), 1618, 1588 (vs, C=C), 1508, 1342 (vs, N=O) cm^{-1}. UV/Vis (chloroform) λ_{max}=355 nm, ϵ=29320. Anal. Calcd for $C_{23}H_{20}N_2O_4$: C, 71.12; H, 5.19; N, 7.21. Found: C, 71.18; H, 5.24; N, 7.28.

p-(2-Methacryloyloxyethoxy)-N-(4-nitrostilbenzylidene)aniline **(6)**

A solution of methacryloyl chloride (2.09 g, 20 mmol) in 10 mL of chloroform was slowly added dropwise to a solution containing p-(2-Hydroxyethoxy)-N-(4-nitrostilbenzylidene)aniline (1.94 g, 5.0 mmol) and triethylamine (2.53 g, 25 mmol) in 25 mL of chloroform at 0°C under nitrogen atmosphere. The mixture was stirred for 24 h at room temperature under nitrogen. The resulting solution was cooled to room temperature and concentrated by distillation of the solvent. The residue dissolved in 60 mL of water, stirred, and filtered with suction. The yellow solid on the filter was washed thoroughly with water to remove salts. The product was recrystallized twice from ethanol/acetone (90/10, vol/vol) yielded 1.48 g (65% yield) of pure product **6**. Mp: 178-180°C (dec). ^1H NMR (DMSO-d_6) δ 1.73-2,41 (m, 3H, -CH_3-), 3.99-4.57 (m, 4H, -O-CH_2-CH_2-O-), 5.53-5.78 (m, 1H, vinylic), 5.93-6.20 (m, 1H, vinylic), 6.57-8.67 (m, 15H, aromatic); IR (KBr) 3018 (w, =C-H), 2963, 2924, 2870 (w, C-H), 1710 (s, C=O), 1618, 1592 (s, C=C), 1505, 1338 (vs, N=O) cm^{-1}. UV/Vis (chloroform) λ_{max}=353 nm, ϵ=46830. Anal. Calcd for $C_{27}H_{24}N_2O_5$: C, 71.04; H, 5.30; N, 6.14. Found: C, 71.11; H, 5.25; N, 6.18.

Radical polymerization of monomer 6

A representative radical polymerization procedure was as follows: In a polymerization tube were placed 0.68 g (1.5 mmol) of **6**, 2.5 mg (0.015 mmol) of AIBN, and 3.6 mL of γ-butyrolactone under nitrogen. The resulting solution was degassed by a freeze-thaw process and sealed under vacuum. The polymerization tube was placed in an oil bath kept at 65°C. After 24 h the polymer solution was poured into 300 mL of methanol and stirred for 1 h. The precipitated polymer was collected by filtration with suction, followed by washing with 50 mL of methanol. Thus obtained polymer was dried under vacum to give 0.63 g (92% yield) of polymer **7**. IR (KBr) 3010 (w, =C-H), 2912, 2855 (m, C-H), 1717 (s, C=O), 1613, 1584 (s, C=C), 1502, 1333 (vs, N=O) cm^{-1}. UV/Vis (chloroform) λ_{max}=353 nm. Anal. Calcd for $(C_{27}H_{24}N_2O_5)_n$: C, 71.04; H, 5.30; N, 6.14. Found: C, 71.13; H, 5.38; N, 6.22.

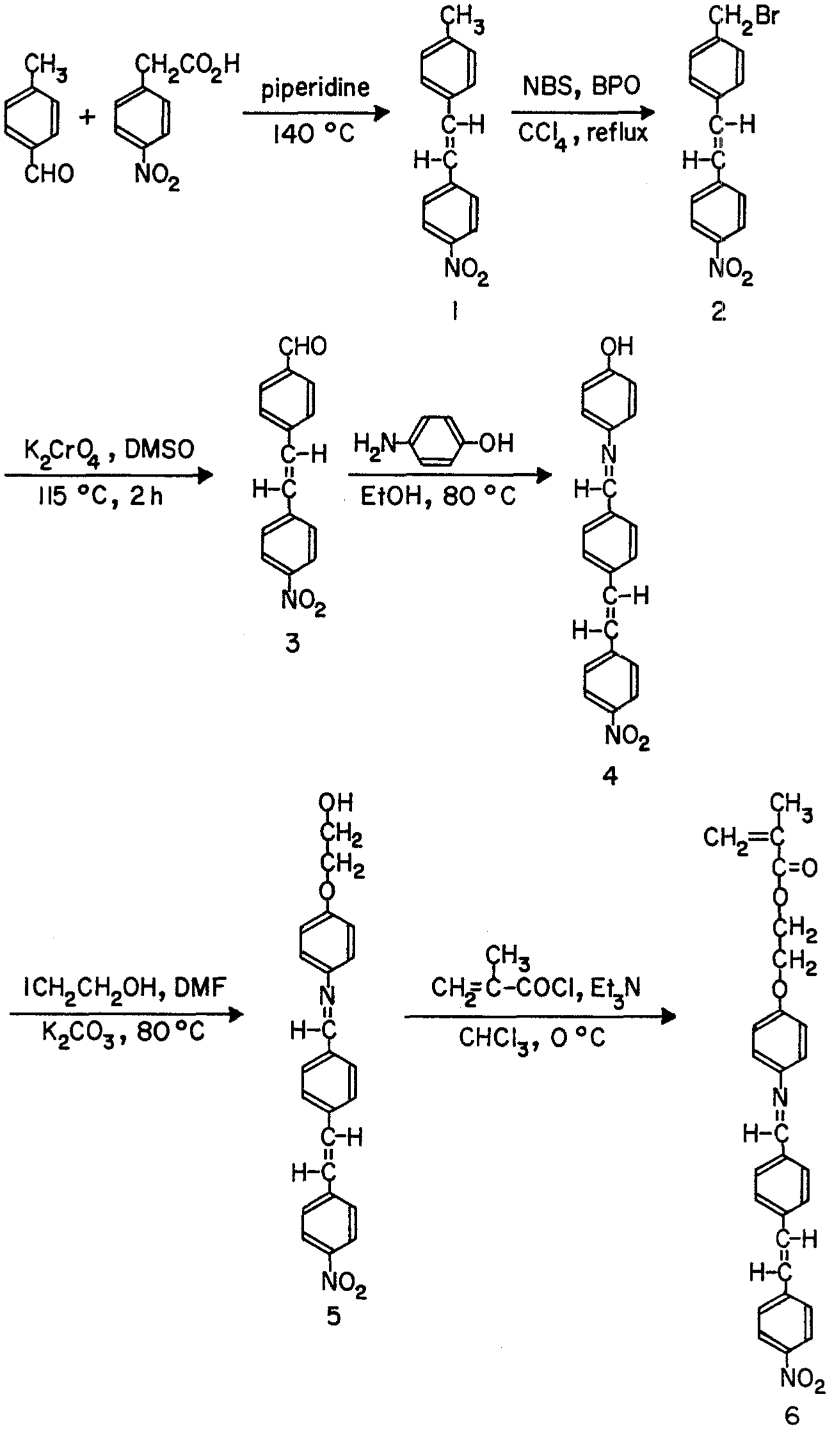
Results and Discussion

Synthesis of monomer 6

4′-methyl-4-nitrostilbene **1** was synthesized by the condensation of 4-nitrophenylacetic acid with p-tolualdehyde according to a literature procedure (29) and recrystallized from ethanol. Bromination of compound **1** by N-bromosuccinimide (NBS) yielded 4′-bromomethyl-4-nitrostilbene **2**. 4′-Nitro-4-stilbenecarboxaldehyde **3** was synthesized, according to a known method (30) by oxidation of the corresponding benzyl bromide **2**. p-Hydroxy-N-(4-nitrostilbenzylidene)aniline **4** was prepared by the reaction of 4′-nitro-4-stilbenecarboxaldehyde **3** with p-aminophenol, and reacted with 2-iodoethanol to yield p-(2-hydroxyethoxy)-N-(4-nitrostilbenzylidene)aniline **5**. The methacrylate **6** was synthesized from methacryloyl chloride and compound **5** following established literature procedure (28). In dilute chloroform solution, the title compound was obtained in moderate yield (Scheme 1). The chemical structures of the compounds were confirmed by ^{1}H NMR, IR, UV-Vis, and elemental analyses. Monomer **6** shows olefinic protons at δ = 5.53-5.78 (m, 1H, vinylic) and δ = 5.93-6.20 (m, 1H, vinylic) in its ^{1}H NMR spectrum. The same monomer sample showed strong absorption bands at 1710, 1592, and 1338 cm^{-1} indicating the presence of carbonyl, olefinic, and nitro groups, respectively. Compound **6** showed strong uv absorption bands near 353 nm by the chromophore p-oxy-N-(4-nitrostilbenzylidene)aniline in the side chain measured in chloroform. Monomer **6** is moderately soluble in common organic solvents such as acetone and DMSO, but is slightly soluble in ethanol and diethyl ether.

Free radical polymerization of monomer 6

p-(2-Methacryloyloxyethoxy)-N-(4-nitrostilbenzylidene)aniline **6** was polymerized with AIBN as radical initiator to obtain the polymer **7** (Scheme 2). Polymerizations were carried out in γ-butyrolactone solutuin at 65 °C. The polymerization results are summarized in Table 1. Monomer **6** was quite reactive toward radical initiator and polymerized readily. In most cases, conversions were quite high (>90%) as shown in Table 1. The chemical structure of the polymer **7** was identified by IR, UV-Vis spectra and elemental analyses. The IR spectrum confirmed the chemical structures, exhibiting all the absorption bands attributable to the functional groups comprising the polymer. The polymer **7** showed strong absorption bands at 1717, 1584, and 1333 cm^{-1} in its IR spectrum indicating the presence of carbonyl, olefinic, and nitro groups, respectively. The same polymer sample showed strong uv absor-


piperidine
140 °C
NBS, BPO
CCl4, reflux
1
2
K2CrO4, DMSO
115 °C, 2 h
H2N–C6H4–OH
EtOH, 80 °C
3
4
ICH2CH2OH, DMF
K2CO3, 80 °C
CH2=C(CH3)–COCl, Et3N
CHCl3, 0 °C
5
6

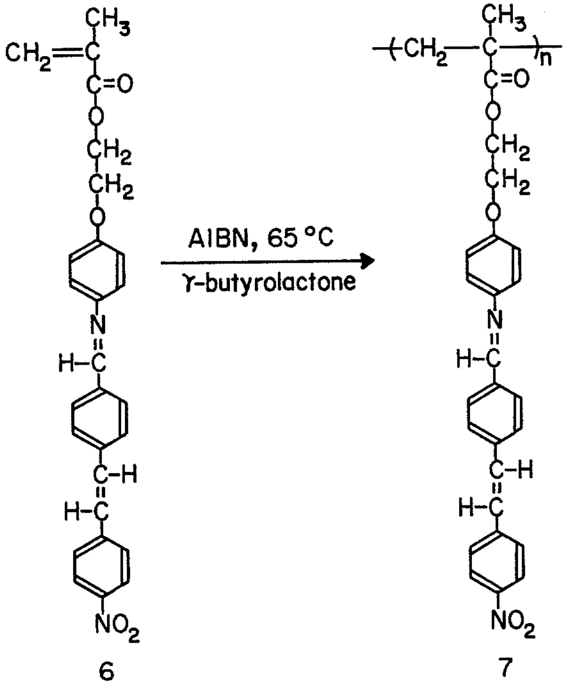


Table 1. Free radical polymerization of **6** by AIBN in γ-butyrolactone at 65 °C

Monomer[a]	Monomer/Solvent (mol/L)	Initiator to Monomer (mol%)	Time (h)	Yield (%)
6	0.42	1.0	24	92
6	0.33	1.0	20	91
6	0.50	0.8	24	90
6	0.38	2.0	20	92

[a] **6** = p-(2-Methacryloyloxyethoxy)-N-(4-stilbenzylidene)aniline.

ption bands near 353 nm by the chromophore p-oxy-N-(4-nitrostilbenzylidene) aniline in the side chain as in the monomer **6**. These spectral evidences indicate that the radical polymerization proceeded cleanly via vinyl type polymerization. Cross-linking through the internal double bonds are obviously not favored for steric reasons. The polymer **7** was not very soluble in common organic solvents, probably due to the presence of polar and bulky pendant group and/or high molecular weight. The thermal behavior of the polymer was investigated by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) to determine the thermal degradation pattern and T_g. The results are summarized in Table 2. TGA thermograms showed triple phase degradation patterns, probably due to the presence of three benzene rings in the pendant group. The polymer showed a thermal stability up to 300°C in TGA thermogram. The T_g values of the polymers obtained from DSC thermograms were around 166°C, which is acceptable for NLO device applications. These T_g values are higher than those for poly(methyl methacrylate) (105°C), probably due to the presence of polar and bulky pendant group.

Table 2. Thermal properties of polymer **7**

Polymer	T_g, °C	Degradation temp, °C			Residue at 700°C, %
		5%-loss	20%-loss	40%-loss	
7	165	308	400	484	3.44

Conclusion

We prepared new monomer **6** containing highly dipolar electronic system composed of three conjugated phenyl groups. The methacrylate compound was polymerized radically to obtain the novel polymethacrylate **7** containing p-oxy-N-(4-nitrostilbenzylidene)aniline, which is presumably effective chromophore for second-order nonlinear optical applications in the side chain. The resulting substituted polymethacrylate **7** was not soluble in common organic solvents, probably due to the presence of polar and bulky pendant group and/or high molecular weight. The polymer showed a thermal stability up to 300 °C, showing T_g peaks around 166 °C. Copolymerization with other monomers such as methyl methacrylate to increase solubility and measurements of NLO properties are in progress, and the full accounts of the work will be reported later.

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