Polymer Bulletin 38, 265–272 (1997)

Polymer Bulletin

Synthesis and free radical polymerization of 4-{1′-(2″-methacryloyloxyethoxy)-5′-naphthyliminomethylidene}-4′-nitrostilbene for nonlinear optical applications

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Received: 14 October 1996/Accepted: 11 December 1996

Summary

4-{1′-(2″-Methacryloyloxyethoxy)-5′-naphthyliminomethylidene}-4′-nitrostilbene **6** was prepared by the reactions of methacryloyl chloride with 4-{1′-(2″-hydroxyethoxy)-5′-naphthyliminomethylidene}-4′-nitrostilbene **5**. Compound **5** was synthesized from 4′-methyl-4-nitrostilbene by several reaction steps. Monomer **6** was polymerized with DTBP as a radical initiator to obtain polymer with 4-(1′-oxy-5′-naphthyliminomethylidene)-4′-nitrostilbene, 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 120°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). Recently we have prepared polymethacrylate containing NLO-phore composed of three conjugated phenyl groups in the side

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chain (29) and these polymers show a thermal stability up to 300°C with a T_g of 165°C, which is a promising material for NLO device applications. However, examples of NLO-polymers with the chromophoric side chain composed of four conjugated phenyl groups are seldom found in the literature. Thus, it is of interest to prepare polymethacrylate containing four conjugated phenyl groups as the NLO-phore in the side chain. In this work we prepared polymethacrylate with the NLO-phore 4-(1′-oxy-5′-naphthyliminomethylidene)-4′-nitrostilbene, 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 4-{1′-(2′′-Methacryloyloxyethoxy)-5′-naphthyliminomethylidene}-4′-nitrostilbene **6**. We now report the results of the initial phase of the work.

Experimental

Materials

2-Iodoethanol, p-tolualdehyde, 4-nitrophenylacetic acid, 5-amino-1-naphthol (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^0 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. Di-tert-butyl peroxide (DTBP) was washed successively with aqueous silver nitrate, water, and dried with anhydrous magnesium sulfate.

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 (30) 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 4.72 (s, benzylic 2H), 7.42-8.55 (m, aromatic 10H). 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). ^{1}H 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.

4-(1'-Hyroxy-5'-naphthyliminomethylidene)-4'-nitrostilbene **(4)**

Compound **4** was prepared by a known method (28) from 4'-nitro-4-stilbenecarboxaldehyde and 5-amino-1-naphthol in absolute ethanol, and recrystallized from acetone. Yield=90%; mp: 245-246°C (dec). ^{1}H NMR (DMSO-d_6) δ 6.63-8.68 (m, aromatic 17H); IR (KBr) 3400 (s, O-H), 1613, 1592 1583(s, C=C), 1497, 1330 (vs, N=O) cm^{-1}. UV/Vis (chloroform) λ_{max}=359 nm, ε =17940. Anal. Calcd for $C_{25}H_{18}N_2O_3$: C, 76.13; H, 4.60; N, 7.10. Found: C, 76.24; H, 4.68; N, 7.16.

4-{1'-(2''-Hydroxyethoxy)-5'-naphthyliminomethylidene}-4'-nitrostilbene **(5)**

4-(1'-Hyroxy-5'-naphthyliminomethylidene)-4'-nitrostilbene (5.52 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 4.60 g (75% yield) of pure product **5**. Mp: 204-205°C (dec). ^{1}H NMR (DMSO-d_6) δ 3.63-3.95 (m, 2H, -CH_2-O-), 3.95-4.38 (m, 2H, Ph-O-CH_2-), 6.43-8.77 (m, 17H, aromatic); IR (KBr) 3530 (w, O-H), 1618, 1592 (s, C=C), 1508, 1343 (vs, N=O) cm^{-1}. UV/Vis (chloroform) λ_{max}=362 nm, ε=38575. Anal. Calcd for $C_{27}H_{22}N_2O_4$: C, 73.96; H, 5.05; N, 6.39. Found: C, 73.88; H, 5.13; N, 6.34.

4-{1'-(2''-Methacryloyloxyethoxy)-5'-naphthyliminomethylidene}-4'-nitrostilbene **(6)**

A solution of methacryloyl chloride (2.09 g, 20 mmol) in 10 mL of chloroform was slowly added dropwise to a solution containing 4-{1'-(2''-hydroxyethoxy)-5'-naphthyliminomethylidene}-4'-nitrostilbene (2.19 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. Thus the obtained product was recrystallized twice from ethanol/acetone (90/10, vol/vol) yielded 1.72 g (68% yield) of pure product **6**. Mp: 130-131°C (dec). ^{1}H NMR (DMSO-d_6) δ 1.47-2,20 (m, 3H, $-CH_3-$), 3.96-4.93 (m, 4H, $-O-CH_2-CH_2-O-$), 5.43-5.83 (s, 1H, vinylic), 5.83-6.14 (s, 1H, vinylic), 6.56-8.43 (m, 17H, aromatic); IR (KBr) 3020 (w, =C-H), 2918 (w, C-H), 1714 (s, C=O), 1618, 1593 (s, C=C), 1509, 1339 (vs, N=O) cm^{-1}. UV/Vis (chloroform) λ_{max}=359 nm, ε=18960. Anal. Calcd for $C_{31}H_{26}N_2O_5$: C, 73.50; H, 5.17; N, 5.53. Found: C, 73.60; H, 5.24; N, 5.46.

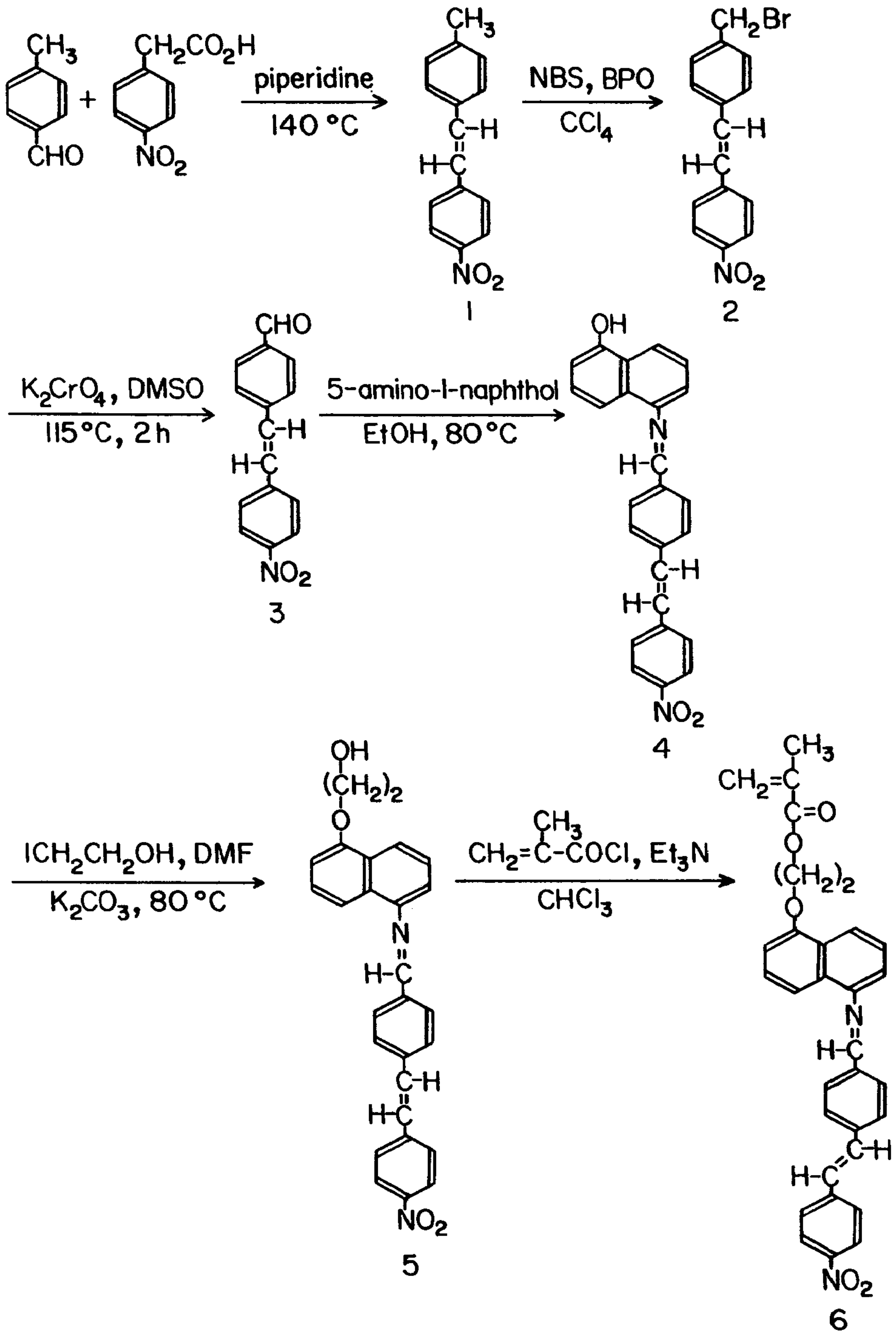
Radical polymerization of monomer **6**

A representative radical polymerization procedure was as follows: In a polymerization tube were placed 0.76 g (1.5 mmol) of **6**, 2.2 mg (0.015 mmol) of DTBP, 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 120°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 0.70 g (92% yield) of polymer **7**. IR (KBr) 2930 (m, C-H), 1715 (s, C=O), 1588 (s, C=C), 1337 (vs, N=O) cm^{-1}. UV/Vis (chloroform) λ_{max}=354 nm. Anal. Calcd for $(C_{31}H_{26}N_2O_5)_n$: C, 73.50; H, 5.17; N, 5.53. Found: C, 73.62; H, 5.26; N, 5.62.

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 (30) 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 (31) by oxidation of the corresponding benzyl bromide **2**. 4-(1′-Hyroxy-5′-naphthyliminomethylidene)-4′-nitrostilbene **4** was prepared by the reaction of 4′-nitro-4-stilbenecarboxaldehyde **3** with 5-amino-1-naphthol, and reacted with 2-iodoethanol to yield 4-{1′-(2′′-hydroxyethoxy)-5′-naphthyliminomethylidene}-4′-nitrostilbene **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. The IR spectra confirmed the chemical structures, exhibiting all the absorption bands attributable to the functional groups comprising the compounds. Monomer **6** shows olefinic protons at δ = 5.43-5.83 (broad singlet, 1H, vinylic) and δ = 5.83-6.14 (broad singlet, 1H, vinylic) in its ^{1}H NMR spectrum. The same monomer sample showed strong absorption bands at 1714, 1593, and 1339 cm^{-1} indicating the presence of carbonyl, olefinic, and nitro groups, respectively. Compound **6** showed strong uv absorption bands near 359 nm by the chromophore 4-(1′-oxy-5′-naphthyliminomethylidene)-4′-nitrostilbene in the side chain measured in chloroform. Monomer **6** is soluble in common organic solvents such as acetone and DMSO, but is slightly soluble in ethanol and diethyl ether.

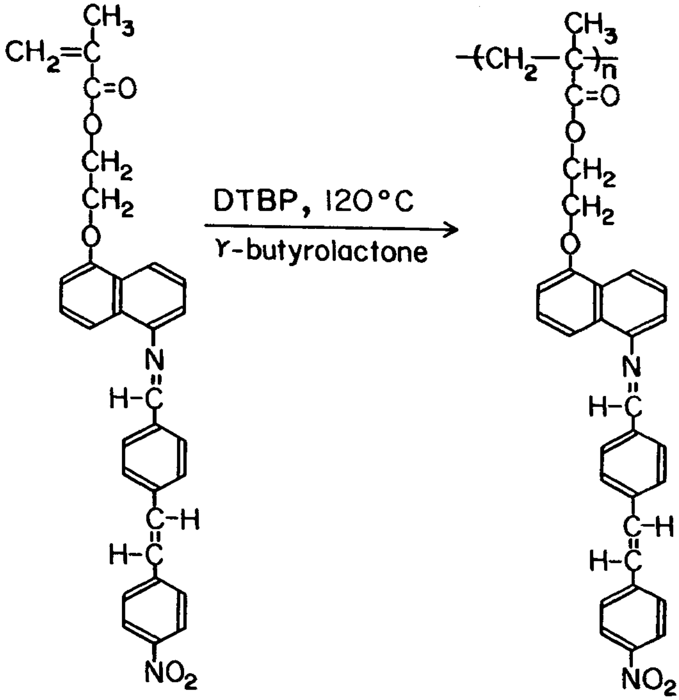

piperidine
140 °C
NBS, BPO
CCl_4
1
2
K_2CrO_4, DMSO
115°C, 2 h
5-amino-1-naphthol
EtOH, 80°C
3
4
ICH_2CH_2OH, DMF
K_2CO_3, 80 °C
$CH_2=C(CH_3)-COCl$, Et_3N
$CHCl_3$
5
6

Free radical polymerization of monomer **6**

4-{1′-(2″-Methacryloyloxyethoxy)-5′-naphthyliminomethylidene}-4′-nitrostilbene **6** was polymerized with DTBP as radical initiator to obtain the polymer **7** (Scheme 2). Polymerizations were carried out in γ-butyrolactone solution at 120°C. The polymerization results are summarized in Table 1. Monomer **6** was quite reactive toward radical initiator and polymerized readily by DTBP. In most cases, conversions were quite high (>90%) as shown in Table 1. However, polymerization of mononmer **6** with AIBN only gave a low polymer yield. 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 absorption bands near 354 nm by the chromophore 4-(1′-oxy-5′-naphthyliminomethylidene)-4′-nitrostilbene 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.

Properties of polymers

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.



6 **7**

Table 1. Free radical polymerization of **6** by DTBP in γ-butyrolactone at 120°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	88
6	0.38	2.0	20	92

[a] **6**=4-{1′-(2′′-Methacryloyloxyethoxy)-5′-naphthyliminomethylidene}-4′-nitrostilbene.

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 double phase degradation patterns, probably due to the presence of multiple benzene rings in the pendant group. The polymer showed a good thermal stability and were not decomposed below 300°C as shown in Table 2. The T_g values of the polymers obtained from DSC thermograms were around 120°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	120	307	376	498	3.53

Conclusion

We prepared a new methacrylate monomer **6** containing highly dipolar electronic system composed of four conjugated phenyl groups. Methacrylate compound **6** was polymerized radically to obtain the novel polymethacrylate **7** containing 4-(1′-oxy-5′-naphthyliminomethylidene)-4′-nitrostilbene, 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 peak around 120°C, which is acceptable for NLO device applications. 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.

Acknowledgement

This work was supported by the Korea Science and Engineering Foundation.

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