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Cross-Linked Polymer Materials for Nonlinear Optics. 1. UV-Cured Acrylic Monomers Bearing Azobenzene Dyes

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ABSTRACT: In this paper results are presented on two different acrylic monomers 1 and 2 that have been converted by relatively fast UV curing (90 min) at modest temperatures (ca. 60–70 °C) into highly stable nonlinear optic (NLO) materials in which loadings of NLO molecules up to 50 w/w % can be achieved. Although the azobenzene derivatives such as NLO chromophores 1 and 2 exhibit partial degradation during UV-initiated radical polymerization, the highly cross-linked formulations showed very stable second harmonic generation activities. Especially NLO chromophore 2 which has a resonantly enhanced d_{33} of 13 pm/V is stable during more than a year at room temperature and shows no relaxation for a week at 80 °C.

Introduction

The preparation of the hitherto known second-order nonlinear optic (NLO) polymer systems may occur along various routes: (i) poling of solid solutions and side-chain polymers at the T_g temperature and freezing in the orientation by cooling,[1,2] (ii) simultaneous poling and curing of a cross-linkable polymer system at elevated temperatures, for example, by cross-linking of systems based on cyanates,[3] isocyanates/OH,[4] epoxides/NH_2,[5] epoxides/OH,[6] polyimides,[7] amides with ethynyl groups,[8] or acrylates,[9] and (iii) simultaneous poling and curing of a cross-linkable polymer system at relatively low temperatures, for example, by cross-linking of systems with UV light.[10]

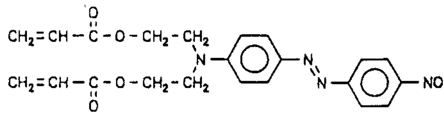
All these methods and materials have their limitations. In solid solutions the maximum attainable NLO concentration is limited to approximately 20 w/w % ($N \approx 4 \times 10^{20}$ chromophores cm^{-3} for Disperse Red 1 in PMMA)[1g,h,2b,11a] and the orientation is not stable.[5e,11] At present, side-chain NLO polymers are known that exhibit a much better orientational stability[1e,2] and that are predicted to have a nearly infinite stability (10^{11} years, $T_g \geq 140$ °C) at room temperature.[12] However, the orientation immediately decreases when the polymer is brought above its T_g.[13] This means that short excursions to high temperatures during the assembly of electronic modules in which electrooptical materials are used[14] are not possible without loss of electrooptic activity.

The use of cross-linked NLO polymers, first shown by Eich et al.,[5a] leads to a much improved stability as there was no decay in second harmonic generation for over 500 h at ambient conditions and no tendency of relaxation even at 85 °C. However, cross-linking of their systems, based on amine cross-linked epoxides, took more than 16 h at 140 °C. Very fast curing within 10 min at a relatively low temperature of 70 °C was done by Mandal et al.,[10a] who cross-linked a solution of NLO molecules with cinnamoyl side groups in a cinnamoyl side-chain photoresist, with UV light. The disadvantage was that the maximum attained concentration of the NLO compound was only 20 w/w % ($N \approx 2 \times 10^{20}$ cm^{-3}).

In this paper results are presented on two different acrylic monomers that have been converted by relatively fast UV curing (90 min) at modest temperatures (ca. 70 °C) into highly stable NLO materials in which loadings of NLO molecules up to 50 w/w % can be achieved. First, an NLO system was prepared consisting of a photoinitiator, the diacrylate 1 derived from the highly NLO active Disperse Red 19, and a UV-curable resin in which 1 could be incorporated for more than 48.5 w/w % ($N \approx 8 \times 10^{20}$ cm^{-3}).

We also synthesized a new NLO chromophore in which the nitro group was replaced by a sulfone group. This offered the opportunity to fix the NLO chromophore on both the donor and acceptor sides in the polymeric matrix to increase the stability. Similar acrylic sulfone compounds were cross-linked by Allen et al.[9] by thermally initiated radical polymerization. They found a nonzero NLO activity, even at 190 °C. Further, we coupled two chromophores with a semirigid spacer into one molecule to give 2 in order to reduce the possibilities of crystallization during spin-coating into thin films.

In a subsequent paper[33] results on thermally cross-linked polyurethanes based on the chromophore of 2 are presented.



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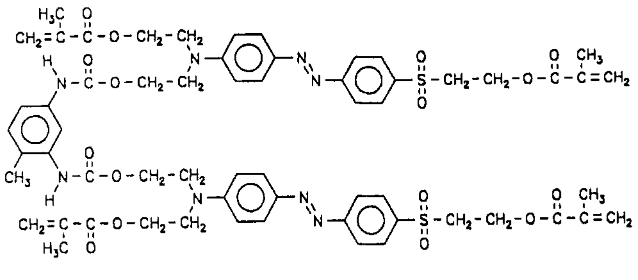

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Experimental Section

General Procedures. NMR spectra were recorded on a Varian VXR400 spectrometer (^1H resonance frequency 400 MHz, ^{13}C resonance frequency 100 MHz) using a 5-mm switchable probe and a VXR 5000 data system. TMS was used as a reference. For measurements in DMSO, as a reference the chemical shifts of deuterated DMSO were taken at 2.49 ppm for the proton spectra

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and at 39.5 ppm for the ^{13}C spectra. T_g values were determined by dielectric measurements as a function of the temperature.

All separations by column chromatography were carried out using silica gel 100, 70–230-mesh ASTM from Merck.

The rate of conversion was calculated with a relative error of about 20% from the decrease of the vibrations at 810 and 1410 cm^{-1} in the IR spectrum, taking the vibrations at 830 and 1510 cm^{-1} as a reference. The rate of isomerization/degradation of the NLO chromophore 1 was determined from the decrease of the vibrations at 860 cm^{-1} in the IR spectrum, taking the vibrations at 830 cm^{-1} as a reference.

Synthesis. 4-Nitro-4′-[*N*,*N*-bis[2-(acryloyloxy)ethyl]amino]azobenzene (1). The starting compound 4-nitro-4′-[*N*,*N*-bis(2-hydroxyethyl)amino]azobenzene (12; mp 190 °C) was obtained from Disperse Red 19 (dye content about 28%; Sigma) by Soxhlet extraction with anhydrous acetone for 24 h. A mixture of 1.2 g (3.6 mmol) of 12 and 2.5 mL of triethylamine in 40 mL of dry THF was cooled to 0 °C, and 1.65 g (18 mmol) of acryloyl chloride was slowly added over a $^1/_2$-h period, while maintaining a temperature slightly below 0 °C. After stirring at ambient temperature for 16 h, the reaction mixture was filtered and the solvent removed. A solution of the residue in dichloromethane was extracted with water and dried over magnesium sulfate. Purification was carried out by column chromatography on silica gel using a mixture of chloroform/methanol (95/5) as eluent to give 1.04 g (66%) of 1: mp 91 °C (from isopropyl alcohol); UV–vis (EtOH) λ_{max} 454 nm (log ϵ 2.25); ^1H NMR ($CDCl_3$) δ 3.81 (t, $2NCH_2$), 4.41 (t, $2CH_2OCO$), 5.87 (dd, $1H_{vinyl}$, J = 1.22 and 17.33 Hz), 6.13 (dd, $1H_{vinyl}$), 6.42 (dd, $1H_{vinyl}$, J = 1.22 and 10.5 Hz), 6.90 and 8.33 (AA′BB′, 4H), 7.92 and 7.94 (AA′BB′, 4H); ^{13}C NMR ($CDCl_3$) δ 49.8 (NCH_2CH_2O), 61.2 (NCH_2CH_2O), 111.9 (C(3,Ar′)), 122.8, 124.7, 126.1, 127.9, 131.6 (CH_2=), 144.5 (*C*(1,-Ar′)) 147.8 (CNO_2), 151.0 (*C*(4,Ar′)), 156.6 (*C*(1,Ar)), 166.0 (*C*OO).

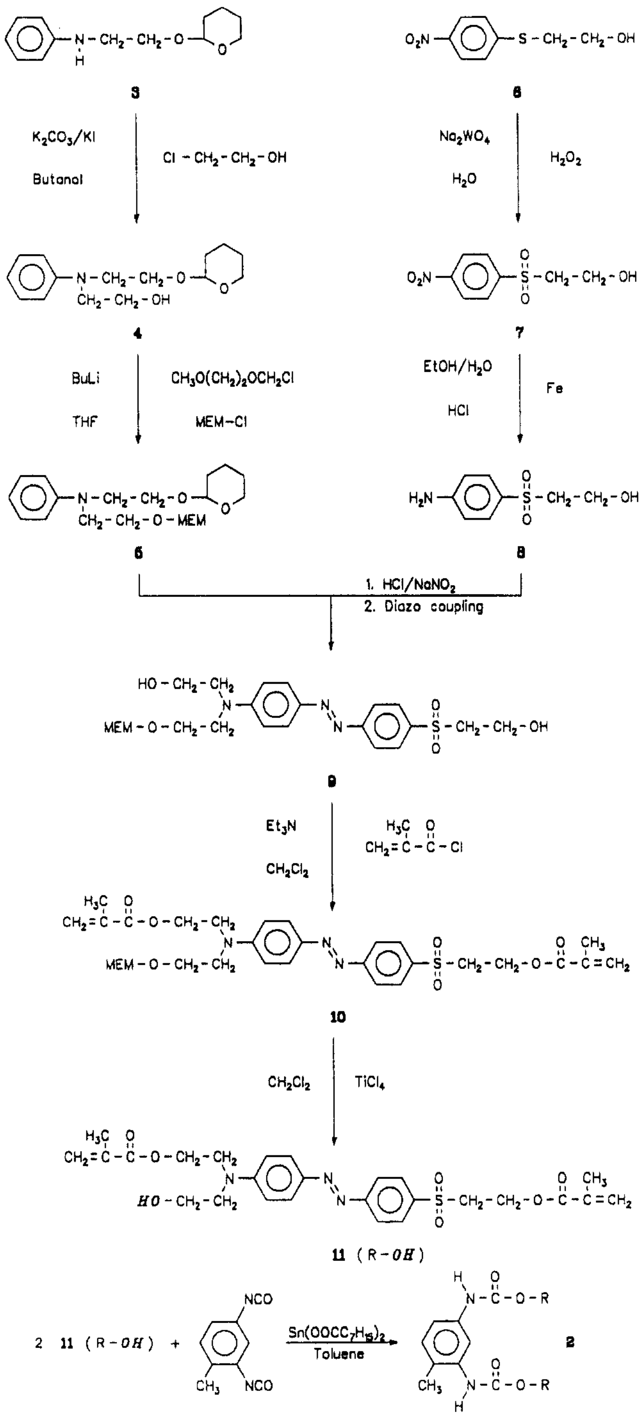
NLO Molecule 2. The synthesis of the NLO molecule 2 is shown in Scheme 1. The key intermediate 9 was synthesized via diazo coupling of the aniline derivative 5 and 1-[(2-hydroxyethyl)-sulfonyl]-4-aminobenzene (8). Hereafter methacrylation, deprotection, and coupling with toluene diisocyanate was performed to give 2.

***N*-[2-(Tetrahydropyranoxy)ethyl]aminobenzene (3).** The tetrahydropyranyl ether of 2-chloroethanol was synthesized in 87% yield from 2-chloroethanol and 3,4-dihydro-2*H*-pyran [bp 90–96 °C (11 mm) [lit.[16] bp 89–90 °C (14 mm)]]. Starting from the previous compound and aminobenzene, *N*-[2-(tetrahydropyranoxy)ethyl]aminobenzene (3) was prepared according to the method of Robello[15] in 53% yield: bp 135–145 °C (1 mm); ^1H NMR ($CDCl_3$) δ 4.63 (C(2,Pyr)*H*), 1.55 (4H), 1.73 (1H), 1.83 (1H), 3.51 and 3.89 (C(6,Pyr)H_2), 3.32 (NCH_2CH_2O), 3.68 and 3.93 (NCH_2CH_2O), 4.11 (N*H*), 6.66 (H_{ortho}), 6.72 (H_{para}), 7.19 (H_{meta}); ^{13}C NMR ($CDCl_3$) δ 19.6 (*C*(4,Pyr)), 25.3 (*C*(5,Pyr)), 30.6 (*C*(3,-Pyr)), 43.8 (CH_2N), 65.5 and 66.3 (*C*(6,Pyr) and CH_2O), 99.2 (*C*(2,-Pyr)), 113.1 (*C*(2,6)–Ar), 117.5 (*C*(4)–Ar), 129.2 (*C*(3,5)–Ar), 148.3 (*C*(1)–Ar).

***N*-[2-(Tetrahydropyranoxy)ethyl]-*N*-(2-hydroxyethyl)-aminobenzene (4).** A solution of 57.7 g (0.26 mol) of 3, 42.5 g (0.52 mol) of 2-chloroethanol, 36.1 g (0.26 mol) of potassium carbonate, 1.1 g (6.62 mmol) of potassium iodide in 150 mL of *n*-butanol was heated at reflux under nitrogen with vigorous mechanical stirring for 2 days. Subsequently, another 42.1 g (0.52 mol) of 2-chloroethanol and 15 g (0.11 mol) of potassium carbonate were added, and reflux was continued for an additional 2 days. After cooling, the solution was filtered and the solvent was removed at reduced pressure. The residual oil was chromatographed on silica gel with ethyl acetate/dichloromethane (1/2) as eluent to produce 12.1 g (17%) of 4 as a light-brownish oil: ^1H NMR ($CDCl_3$) δ [tetrahydropyranyl group: 4.58 (C(2)*H*), 1.58 and 1.70 (C(3)H_2), 1.50 and 1.80 (C(4)H_2), 1.50 (C(5)H_2), 3.47 and 3.80 (C(6)H_2)], 3.72 and 3.96 (NCH_2CH_2O), 3.64 and 3.68 (NCH_2CH_2O), 3.52 and 3.58 (CH_2CH_2OH), 3.80 (CH_2OH), 3.34 (O*H*), 6.72 ($H_{ortho,para}$), 7.22 (H_{meta}); ^{13}C NMR ($CDCl_3$) δ 19.3 (*C*(4,Pyr)), 25.2 (*C*(5,Pyr)), 30.2 (*C*(3,Pyr)), 52.1 and 55.9 (CH_2N), 61.1, 62.2 and 65.1 (*C*(6,Pyr) and CH_2O), 99.1 (*C*(2,Pyr)), 112.6 (*C*(2,6)–Ar), 116.8 (*C*(4)–Ar), 129.2 (*C*(3,5)–Ar), 148.0 (*C*(1)–Ar).

***N*-[2-(Tetrahydropyranoxy)ethyl]-*N*-[2-(2′-methoxyethoxymethoxy)ethyl]aminobenzene (5).** A solution of 24 g (0.09 mol) of 4 in 400 mL of dry THF was treated, under a nitrogen atmosphere, at −30 °C with 1 equiv of BuLi (35.8 mL of a 2.56 M solution in diethyl ether). After stirring for 30 min at 0 °C, 12.4 mL (0.11 mol) of (2-methoxyethoxy)methyl chloride [(MEM)-Cl[29]] was added. Stirring was continued for an additional 1 h at 0 °C. The reaction mixture was hydrolyzed with water, and the aqueous phase was extracted with ether. The organic extracts were combined and dried over magnesium sulfate, and the solvent was removed under reduced pressure. The residual oil (89%) was chromatographed on silica gel with ethyl acetate/dichloromethane (1/2) as eluent to yield 10 g (31%) of 5 as a pale yellow oil: ^1H NMR ($CDCl_3$) assigned signals δ 4.59 (C(2,Pyr)*H*), 3.36 (s, OCH_3), 4.72 (s, OCH_2O), 6.67 (H_{para}), 6.78 (H_{ortho}), 7.21 (H_{meta}).

Scheme 1



1-[(2-Hydroxyethyl)sulfonyl]-4-nitrobenzene (7). To a mixture of 50 g (0.25 mol) of β-hydroxyethyl 4-nitrophenyl sulfide (6), prepared according to Verhart and Tesser,[17] in 250 mL of absolute ethanol and 0.6 g of sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$) in 30 mL of water were slowly added over a $2^1/_2$-h period at 40–45 °C and over a $1^1/_2$-h period at 75–80 °C, respectively, two portions of 25 mL of concentrated hydrogen peroxide (30%). After refluxing for another 1 h, the reaction mixture was cooled to ambient temperature overnight, affording pale yellow crystals of **7** in 91% yield: mp 123–125 °C from ethanol (lit.[17] mp 128 °C); ^{1}H NMR (DMSO-d_6) δ 3.58 (t, SO_2CH_2), 3.73 (m, CH_2OH), 4.89 (t, O*H*), 8.19 and 8.44 (AA′BB′, 4H); ^{13}C NMR (DMSO-d_6) δ 54.9 and 57.2 ($SO_2CH_2CH_2O$), 124.3 (*C*(2,-Ph)), 129.5 (*C*(3,Ph)), 145.6 (CSO_2), 150.3 (CNO_2).

1-[(2-Hydroxyethyl)sulfonyl]-4-aminobenzene (8). Metod A: Reduction of 7 with Fe/HCl. By treatment of a solution of 80 g (0.35 mol) of **7** in 40 mL of 50 wt % ethanol with 4 mL of concentrated hydrochloric acid in the presence of 58 g (1.04 mol) of iron according to the method of Mahood and Schaffner,[30] 1-[(2-hydroxyethyl)sulfonyl]-4-aminobenzene (**8**) was obtained in 65% yield: mp 105–106 °C [pale yellow crystals from water/ethanol (50/50, v/v)]; ^{1}H NMR (DMSO-d_6) δ 3.23 (t, SO_2CH_2), 3.60 (m, CH_2OH), 4.78 (t, O*H*), 6.08 (s, NH_2), 6.63 and 7.47 (AA′BB′, 4H); ^{13}C NMR (DMSO-d_6) δ 55.2 and 58.2 ($SO_2CH_2CH_2O$), 112.7 (*C*(3,Ph)), 124.4 (CSO_2), 129.5 (*C*(2,Ph)), 153.5 (CNH_2).

Method B: Reduction of 7 with H_2/Pt–Al Catalyst. According to the method of Gilman,[31] 4.5 g (0.019 mol) of **7** and 0.6 g of Pt–Al catalyst (5% Pt on alumina, Type 25A, Johnson Matthey) were suspended, under a nitrogen atmosphere, in 50 mL of absolute ethanol in a hydrogenation vessel, the flask was flushed with hydrogen, and the hydrogenation was conducted at 60 °C at a slight positive pressure for 36 h until completion. After suction filtration of the hot solution, the product was isolated by removal of the solvent from the filtrate followed by crystallization from water/ethanol (50/50, v/v): yield 3.5 g (90%).

4-[(2-Hydroxyethyl)sulfonyl]-4′-[*N*-(2-hydroxyethyl)-*N*-[2-(2′-methoxyethoxymethoxy)ethyl]amino]azobenzene (9). To a solution of 6.4 g (0.0318 mol) of the aromatic amine **8** in 14 mL of 6 M HCl was added dropwise a solution of 2.4 g (0.0347 mol) of $NaNO_2$ in 15 mL of water at such a rate that the temperature did not exceed 5 °C. To the resulting diazonium salt solution was added at the same temperature a solution of 10 g (0.0283 mol) of compound **5** in 280 mL of 0.1 M HCl. After stirring for 3 h, the solution was brought to ambient temperature and neutralized with saturated sodium carbonate, and the resulting oil was taken up in dichloromethane. The organic extracts were dried over magnesium sulfate and evaporated to give 12.6 g of a red oil. Purification was performed by column chromatography on silica gel with acetone/dichloromethane (2/3) as eluent to produce 9.9 g (73%) of **9** as a red oil: ^{1}H NMR ($CDCl_3$) δ 2.80 (t, 1H), 3.06 (t, 1H), 3.31 (s, OCH_3), 3.38 (m, SO_2CH_2), 3.47 and 3.64 (m, OCH_2CH_2O), 3.70 (t, NCH_2), 3.78 (t, NCH_2), 3.89 (t, OCH_2CH_2), 3.89 (m, CH_2OH), 4.03 (m, CH_2OH), 4.73 (s, OCH_2O), 6.82 and 7.89 (AA′BB′, 4H), 7.99 (AA′BB′, 4H).

4-[[2-(Methacryloyloxy)ethyl]sulfonyl]-4′-[*N*-[2-(methacryloyloxy)ethyl]-*N*-[2-(2′-methoxyethoxymethoxy)ethyl]amino]azobenzene (10). A mixture of 9.9 g (0.0205 mol) of **9**, 4.6 g (0.0455 mol) of freshly distilled triethylamine, 30 mg of hydroquinone (inhibitor), and 100 mL of dry, distilled dichloromethane was cooled to 0 °C and treated dropwise with stirring under nitrogen with a solution of 4.7 g (0.0452 mol) of freshly distilled methacryloyl chloride in 15 mL of dichloromethane. The reaction was stirred at 0 °C for 2 h and then at 25 °C for 1 day. After washing with saturated sodium bicarbonate and water, the solution was dried over magnesium sulfate and the solvent was removed at reduced pressure. The residual oil (12.9 g) was chromatographed on silica gel with acetone/dichloromethane (gradient ranging from 1/10 to 2/3) as eluent to produce 10.3 g (81%) of **10** as a deep-red oil: ^{1}H NMR ($CDCl_3$) δ 1.71 (s, CH_3), 1.87 (s, CH_3), 3.28 (s, OCH_3), 3.43 (m, 2H), 3.48 (t, 2H), 3.59 (m, 2H), 3.65 (m, 2H), 3.73 (m, 2H), 4.32 (t, CH_2OCO), 4.46 (t, CH_2OCO), 4.65 (s, OCH_2O), 5.39 (s, $1H_{vinyl}$), 5.52 (s, $1H_{vinyl}$), 5.78 (s, $1H_{vinyl}$), 6.03 (s, $1H_{vinyl}$), 6.80 and 7.84 (AA′BB′, 4H), 7.92 (AA′BB′, 4H).

4-[[2-(Methacryloyloxy)ethyl]sulfonyl]-4′-[*N*-[2-(methacryloyloxy)ethyl]-*N*-(2-hydroxyethyl)amino]azobenzene (11). A solution of 10.3 g (16.7 mmol) of **10** in 150 mL of dry, distilled dichloromethane was cooled to 0 °C and treated under nitrogen with 12.4 g (4 equiv) of $TiCl_4$. The reaction mixture was stirred overnight at 25 °C. After washings with ammonia and water, the aqueous layer was extracted with chloroform. The combined organic extracts were dried over magnesium sulfate and evaporated at reduced pressure. The residual oil (8.2 g) was column chromatographed on silica gel using acetone/dichloromethane (1/5) as eluent to give 4.8 g of crude **11**. Repeated column chromatography on silica gel using the same eluent yielded 3.8 g (44%) of pure **11** as a deep-red oil: ^{1}H NMR ($CDCl_3$) δ 1.77 (s, CH_3), 1.92 (s, CH_3), 3.53 (t, SO_2CH_2), 3.66 (t, NCH_2), 3.82 (t, NCH_2), 3.86 (m, CH_2OH), 4.39 (t, CH_2OCO), 4.49 (t, CH_2OCO), 5.44 (s, $1H_{vinyl}$), 5.55 (s, $1H_{vinyl}$), 5.83 (s, $1H_{vinyl}$), 6.09 (s, $1H_{vinyl}$), 6.85 and 7.85 (AA′BB′, 4H), 7.92 and 7.96 (AA′BB′, 4H) ; ^{13}C NMR (DMSO-d_6) δ 17.4 and 17.9 (CH_3), 49.1, 52.7, 54.0, 58.0 (2C), 61.7, 111.7 (*C*(3,Ar′)), 122.2, 125.6, 129.0, 126.0, and 126.1 ($=CCH_3$), 134.9 and 135.6 ($CH_2=$), 139.1 and 142.7 (*C*(1,Ar′) and *C*(4,Ar)), 151.7 and 155.5 (*C*(4,Ar′) and *C*(1,Ar)), 165.7 and 166.5 (*C*OO).

Reaction Product 2 from 4-[[2-(Methacryloyloxy)ethyl]sulfonyl]-4′-[*N*-[2-(methacryloyloxy)ethyl]-*N*-(2-hydroxyethyl)amino]azobenzene (11) and Toluene Diisocyanate (TDI). A solution of 0.55 g (1.04 mmol) of **11**, 1.3 mL of tin octoate, and a few mg of IONOL (2,6-di-*tert*-butyl-4-methylphenol; Fluka) in 65 mL of dry toluene was treated with a solution of 0.52 mmol of TDI in 7.5 mL of dry toluene and heated at reflux temperature for 1 h. After removal of the solvent, the residue was purified by column chromatography on silica gel using a mixture of chloroform/acetonitrile/methanol (88/10/2, v/v/v) as eluent to give 0.62 g (76%) of crude **2** (mixture of the 2,4- and 2,6-isomers). By repeated column chromatography, 83 mg of the 2,4-isomer could be isolated: ^{1}H NMR ($CDCl_3$) δ 1.78 (s, $2CH_3$), 1.92 (s, CH_3), 1.94 (s, CH_3), 2.18 (s, CH_3), 3.55 (t, $2SO_2CH_2$), 3.80 (m, $4NCH_2$), 4.40 (m, $4CH_2OCO$), 4.50 (t, $2CH_2OCO$), 5.45 (s, $2H_{vinyl}$), 5.59 (s, $2H_{vinyl}$), 5.84 (s, $2H_{vinyl}$), 6.10 (s, $1H_{vinyl}$), 6.13 (s, $1H_{vinyl}$), 6.66 (bs, 1H), 6.89 and 7.89 (AA′BB′, 8H), 7.07 and 7.18 (AB, 2H), 7 .19 (bs, 2H), 7.83 (bs, 1H), 7.94 and 8.00 (AA′BB′, 8H).

Processing. In a typical procedure, a 10 wt % solution containing the acrylic NLO monomer, an acrylic diluent, and a photoinitiator [ratio acrylics/initiator (96/4, w/w)] in dry acetone was used to spin-coat (Convac. Type ST 145) over indium tin oxide (ITO) glass substrates (2.5 × 2.5 cm^2) at 600 rpm for 2 s and, subsequently, 2000 rpm for 40 s. Prior to use, the glass substrates were cleaned by treatment with a 5 wt % soap solution in an ultrasone bath for 1 h, rinsed with distilled water and acetone, respectively, and finally treated in an ultrasone bath for $^1/_2$ h in acetone and dichloromethane, respectively.

Poling and Cross-Linking. For second harmonic generation (SHG) measurements films were poled with a tungsten wire corona electrode ($\phi = 50\ \mu m$) during cross-linking. As was recently shown by Ratsavong et al.,[26] we also noticed that the use of a thicker corona wire resulted in lower SHG signals. The ITO-glass substrate was placed as the ground electrode of the poling equipment under a CO_2 atmosphere at room temperature. The corona current through the film was measured by the potential drop over a 3-MΩ resistance between the ITO and the earth. Prior to poling and photo-cross-linking, the substrate was flushed with carbon dioxide, after which precuring for 5–30 min was carried out using an experimental, metal-doped, high-pressure mercury lamp (HOK-7; Philips) as a light source for cross-linking and a filter system. Beyond the filter system the energy density on the sample amounted to 80 mW/cm^2 at a wavelength of 360 nm, causing an increase of temperature up to 50 °C. Then, while proceeding with photo-cross-linking, a voltage was applied on the corona wire varying from +5 to +10 kV and from −5 to −10 kV in such a way that the corona current was approximately 8 μA. This caused a further increase of temperature up to 60–70 °C. After radiation for 90 min (including precure), the UV light source was switched off. Next, when the temperature had dropped below 50 °C, the poling field was turned off and the substrate was allowed to cool to ambient temperature.

Second Harmonic Measurements. Second harmonic measurements were done in transmission according to Singer et al.[1b] with the 1064-nm wavelength of a Nd:YAG laser (pulse length 10 ns, 10 Hz, 10–20 mJ/pulse, or 200 ns, 2 kHz, 2.7 mJ/pulse) and quartz or KDP as the reference material. The intensity of the second harmonic signal ($I^{2\omega}$) was recorded as a function of the incident angle of the fundamental. The d_{33} was calculated according to Singer et al.[1b] using the d_{11} value of quartz or the d_{36} value of KDP (0.45 pm/V) as a reference, assuming d_{13} =

$1/3d_{33}$ and accounting for the absorption at 532 nm similar to Mortazavi et al.[1k] The refractive index of the films on glass was measured by ellipsometry at 633 nm. With this value the refractive indices at 532 and 1064 nm were estimated as $n_{532} = n_{633} + 0.05$ and $n_{1064} = n_{633} - 0.05$ to take account of the dispersion of the refractive index.

Electrooptic Experiments. Films were spin-coated onto ITO-glass substrates (cf. processing) and cured without poling for 0 to 60 min with filtered UV light. After depositing a semitransparent gold electrode on top of the film, the film was contact-poled with 500 kV/cm at room temperature. The electrooptic (EO) signal was measured in transmission until a saturated value, similar to that of Khanarian et al.[32] Details of the electrooptical technique used are presented in the subsequent paper.[33] After switching off the poling field, the EO coefficient was determined.

Results and Discussion

Syntheses. 4-Nitro-4′-[*N,N*-bis[2-(acryloyloxy)ethyl]-amino]azobenzene (1) was synthesized by reaction of 4-nitro-4′-[*N,N*-bis(2-hydroxyethyl)amino]azobenzene (Disperse Red 19) with acryloyl chloride.

The synthesis of the NLO molecule **2** is shown in Scheme 1. The key intermediate, the azo dye monomer **9**, was synthesized in 73% yield via diazo coupling of the aniline derivative **5** and 1-[(2-hydroxyethyl)sulfonyl]-4-aminobenzene (**8**).

Following the method of Robello,[15] the required aniline derivative **5** was obtained by two consecutive N-alkylations of aniline in refluxing *n*-butanol using an alkyl chloride, potassium carbonate as acid acceptor, and potassium iodide as a catalyst. Reaction of aniline with the *O*-tetrahydropyranyl derivative of 2-chloroethanol[16] afforded *N*-[2-(tetrahydropyranoxy)ethyl]aminobenzene (**3**) in 53% yield. Via an analogous route the latter was converted to **4** by treatment with 2-chloroethanol, *albeit* the yield was much lower (17%). Ultimately, protection of the alcohol group in **4** using (2-methoxyethoxy)methyl chloride produced the aniline derivative **5** in poor yield (31%).

Starting with β-hydroxyethyl 4-nitrophenyl sulfide (**6**), the corresponding sulfonyl derivative **7** was obtained in almost quantitative yield (91%) by catalytic oxidation in the presence of sodium tungstate using hydrogen peroxide.[17] Reduction of the nitro group in **7** was achieved using iron and aqueous acidified ethanol to provide a 65% yield of 1-[(2-hydroxyethyl)sulfonyl]-4-aminobenzene (**8**).

Reaction of the azo dye monomer **9** with a small excess of methacryloyl chloride in the presence of triethylamine afforded the methacryl group-functionalized azo dye **10** in excellent yield (81%). Lewis acid-catalyzed deprotection of **10** in the presence of $TiCl_4$ produced the acrylic monomer **11**. Ultimately, the hydroxyl group of the latter was reacted with toluene diisocyanate to give **2** which was homopolymerized and copolymerized with a commercial aromatic acrylate, *viz.*, Photomer 3016 from Harcros, using a free-radical initiator and UV light to produce cross-linked polymers useful for nonlinear optics.

UV Processing. Monomer **1** being a crystalline, cross-linkable, acrylic material with a NLO chromophore with a high β-value was used for the preparation of a NLO polymer system by UV irradiation at low temperature. To examine the effect of various process parameters on the final cross-linked NLO polymer system, experiments were carried out in which monomer composition, concentration of the photoinitiator, and irradiation conditions were varied.

To prevent crystallization, monomer **1** was mixed with a highly viscous UV-curable resin, Photomer 3016 from Harcros. Photomer 3016 being a difunctional acrylated epoxy based on an aromatic epoxy resin showed a very good solubility toward the monomers used. As a result, clear films could be made from monomer **1** and Photomer 3016 (up to 50/50 w/w %, $N \approx 8 \times 10^{20}$ cm^{-3}) in the presence of a photoinitiator. If the films were cured immediately after spin-coating, they remained clear. Without cross-linking, however, they crystallized slowly into opaque films within 2 h.

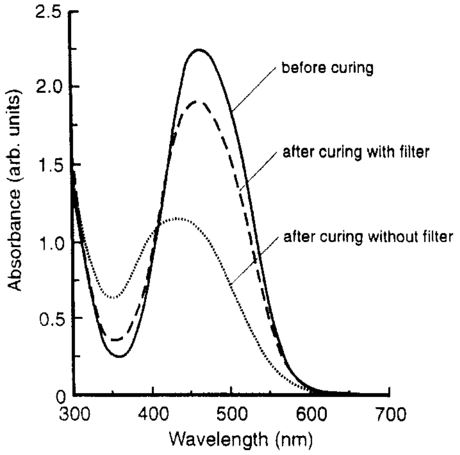


Figure 1. Change in the CT band of a film consisting of 40 w/w % **1**, 56 w/w % Photomer 3016, and 4 w/w % isopropylthioxanthone after 90 min of UV curing with and without a filter.

Monomer **2**, designed for stable NLO and good spin-coating properties, for example, no crystallization, could be spin-coated to clear films that indeed did not crystallize, not even after prolonged aging at room temperature. It was cured both in the presence and in the absence of diluent Photomer 3016 to give clear, transparent thin films.

Thin transparent films (0.3–2 μm) on various substrates such as indium tin oxide (ITO) glass, KBr tablets, or glass of the appropriate formulations were formed by spin-coating from 10 wt % solutions. UV cross-linking was performed in an inert atmosphere (CO_2) to prevent radical inhibition by oxygen from air. For this purpose a nitrogen atmosphere could not be applied because of unstable corona discharges during poling. After cross-linking, all films were insoluble in various solvents such as acetone, ethanol, or DMF.

For the UV-initiated radical polymerization, photoinitiators were used having an activation wavelength that was within the transmission window of the used monomers and the filter, *vide infra*, *viz.*, 2-methyl-1-[4-(methylthio)-phenyl]-2-morpholinopropanone-1 (Irgacure 907; Ciba-Geigy) or isopropylthioxanthone (ITX). In the latter case the NLO molecule was used as the coinitiating amine that is normally required to be present.[18]

Degradation. Azobenzenes, like compounds such as **1** and **2**, are known to undergo a reversible trans–cis isomerization by UV radiation.[19–21] The cis isomer is stabilized, if the azobenzene is part of a side-chain polymer.[22,23] As the cis isomer has a much lower NLO activity, trans–cis isomerization has to be avoided as much as possible.

We could sharply reduce the decrease of the CT band of the trans isomer, as seen from Figure 1, by using filtered UV light with an intensity of 80 mW/cm^2 at 360 nm for curing, allowing no transmission > 400 nm.

The decrease in the CT band of **1** was attended with a decrease of a 860-cm^{-1} absorption band in the FTIR spectrum, as shown in Figure 2. By comparing the IR spectra of analogous compounds, like azobenzene, 4-aminoazobenzene, 4-nitroazobenzene, and others, it was concluded that this absorption band is likely derived from the out-of-plane deformation of two neighboring H atoms

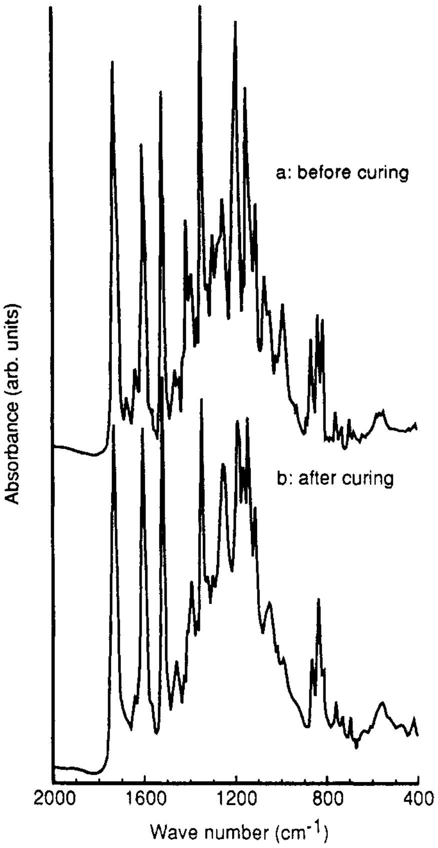


Figure 2. FTIR absorption spectrum of a film consisting of 45 w/w % 1, 45 w/w % Photomer 3016, and 10 w/w % Irgacure 907 before (a) and after (b) 60 min of UV curing with filtered UV light.

at the nitrophenyl ring. The H atoms of the other phenyl group absorbed at 830 cm^{-1} and showed no decrease during polymerization. Also the absorption of the NO_2 group at 1350 cm^{-1} decreased. Therefore, as no new sharp peaks appeared in the FTIR spectrum during cross-linking, the decrease in the CT band is likely due, partly or even totally, to degradation of the NLO chromophore. Bellobono et al.[24] and Lückemeyer et al.[25] also found degradation of azobenzenes due to radicals produced by UV light. For monomer 2, however, the absorption of the hydrogen atoms at the phenyl–SO_2– occurred at 845 cm^{-1} and was nearly completely covered by the peak at 830 cm^{-1}. As a consequence, the degradation could not be monitored by FTIR.

Study of the Cross-Linking. The UV cross-linking was studied because it is of crucial importance to the formed NLO materials. First, there will be an optimal range in the cross-linking density where poling is most effective, as both the electrical conductance and the dipole mobility will decrease with increasing conversion. Second, the UV-curing process has to be optimized to get high conversions without much secondary photoinduced processes that azobenzenes like 1 and 2 are known to exhibit. Third, the total process should take place within reasonable time to be economically acceptable.

By Means of FTIR. The conversion of the formulations as a function of curing time was followed by the decrease in the absorption at 810 cm^{-1} (=CH_2 out-of-plane deformation) in the FTIR spectrum. As the total conversion and curing rate strongly depend on the film thickness, the formulations were spin-coated on KBr tablets to give identical film thicknesses in all experiments.

Experiments 1 and 2 from Table 1 show that there is a concomitant decrease of conversion and degradation both in the presence and absence of the UV filter. From experiments 3–6 it can be seen that the conversion decreases as the concentration of NLO monomer in the sample increases. This can be explained by an effective quenching of the photoinitiator by the NLO chromophore. The quenching effect is confirmed by the fact that the observed curing rate is very low compared to common UV formulations where cross-linking takes place in the order of seconds. Further, again it is observed that the decrease of the NLO chromophore degradation is attended with the decrease in the conversion.

Table 1. Conversion and Decrease of the IR 860-cm^{-1} Absorption of the NLO Chromophore of Various Formulations of 1 and 2 and Acrylic Diluent (Photomer 3016) after Various Times of Curing with Filtered UV Light: No Transmission > 400 nm

		% convn			% decrease IR 860 cm^{-1}		
exp	composition (w/w %) monomer/P3016/PI[a]	60 min	90 min	120 min	60 min	90 min	120 min
	Monomer 1						
1[b]	40/56/4 ITX	85	91		50	58	
2	40/56/4 ITX	30	39		6	10	
3	10/79/11 ITX	87	92		71	84	
4	20/69/11 ITX	67	82		28	46	
5	30/59/11 ITX	37	56		12	16	
6	40/49/11 ITX	33	43		8	10	
7	20/76/4 ITX	69	78		30	46	
8	20/72/8 ITX	71	84		30	43	
9	48.5/48.5/3 Irg	56			19		
10	47.5/47.5/5 Irg	68			26		
11	45/45/10 Irg	80		91	41		58
12	25/73/2 Irg	76			32		
13	25/65/10 Irg	94			65		
	Monomer 2						
14	49/49/2 Irg		86		c		
15	96/–/4 ITX	c			c		
16	96/–/4 Irg	c			c		

[a] Photoinitiator. [b] No filter used. [c] Estimation not possible.

The conversion nor the decrease of the NLO chromophore concentration is hardly affected by the concentration of the photoinitiator ITX, as seen from experiments 7 and 8.

Using photoinitiator Irgacure 907, there is a definite dependence of the polymerization rate on the photoinitiator concentration, experiments 9–13, and the polymerization is faster than using ITX. But here too, higher conversions are accompanied by larger decreases in the NLO chromophore concentrations.

In conclusion, the bleaching process during polymerization of the NLO chromophore 1 and Photomer 3016 is coupled with the conversion so that always high conversions are attended with high levels of degradation.

Monomer 2, experiment 14 in Table 1, polymerizes faster than monomer 1, experiment 9. This might be due to a different effectivity in the quenching of the photoinitiator by 1 and 2.

Monomer 2 was also homopolymerized, experiments 15 and 16 in Table 1. The UV–vis absorption spectrum showed nearly no change after curing for 90 min with filtered UV light, whereas in the FTIR spectrum the absorption at 810 cm^{-1} was hardly visible.

By Means of the Maximal Attainable r_{33}. As there is little decrease in the NLO chromophore concentration during curing of monomer 2, *i.e.*, bleaching, the EO coefficient is proportional to the number of dipoles that is available to be directed in the electric field. So, the EO coefficient will decrease as a function of the cross-linking density, due to fixation of the NLO chromophore or due to an increase of the T_g of the network. To get an indication of the degree of cross-linking of monomer 2, films were

Table 2. Curing Times *before* Contact Poling, Poling Temperature (T_p), and Electrooptic Coefficient (r_{33}) of Various UV-Cured Films and a Solid Solution of 2, Poled with 500 kV/cm

exp	sample	composition (w/w %)	curing time (min)	T_p (°C)	r_{33} (pm/V)	N[c] (10^{20} cm^{-3})
17	2/ITX	96/4	0	25	*a*	9.4
18	2/ITX	96/4	5	25	15.6	9.4
19	2/ITX	96/4	60	25	1.6	9.4
20	PMMA/2[b]	86/14		105	2.1	1.4

[a] Conduction too high to pole. [b] Solid solution. [c] Calculated assuming a matrix density of 1 g/cm^3.

Table 3. SHG Signals of Various Formulations of 1 and 2 (cf. Table 1)

exp	composition (w/w %) monomer/P3016/PI[a]	d_{33} (pm/V)	d_{33} relaxed (pm/V)
	Monomer 1		
2	40/56/4 ITX	34	23
9	48.5/48.5/3 Irg	8	*b*
	Monomer 2		
14	49/49/2 Irg	13	13
16	96/–/4 Irg	43[c]	8

[a] Photoinitiator. [b] Not measured. [c] Immediately after poling.

contact-poled after curing, and, subsequently, the electrooptical coefficient (r_{33}) was measured at 633 nm, directly after poling. The results are compiled in Table 2.

Without curing the conduction of the film was too high for poling.

After curing for 5 min a film was obtained with a T_g of 55 °C. The EO coefficient amounted to 15.6 pm/V, experiment 18. This film was compared with a film from a solid solution of 14 wt % of 2 in PMMA poled at 105 °C, r_{33} = 2.1 pm/V. After correction for the concentration and temperature ($r_{33} \propto N/T$: N, number of NLO chromophores; T, temperature in Kelvin), a value of 18.3 pm/V was calculated for 96 w/w % NLO chromophores poled at 25 °C under the assumption that the densities and refractive indices of the films are the same. Robello et al.[24b] also give for the same chromophore as a side chain in PMMA ($N = 7.0 \times 10^{20}$ cm^{-3}, V_p = 890 kV/cm, and T_p = 120 °C) a r_{33} value of 12.9 pm/V at 633 nm. So, within the curing period of 5 min nearly all the NLO dipoles in the UV-cured film can still be poled at room temperature. Interestingly, the EO coefficient of the solid solution of 2 in PMMA was much more stable than the coefficient of solid solutions of the well-known Disperse Red 1 in PMMA. The higher stability might be due to the higher molecular volume of 2.[11b]

After curing of 2/ITX for 60 min, the T_g increased to 80 °C, experiment 19, and a r_{33} value of only 1.6 pm/V was measured.

Thus, a certain degree of cross-linking occurred so that approximately only 9% of the NLO chromophores was available to be poled at room temperature. This implies that poling has to be carried out between 5 and 60 min of curing.

Poling and Second Harmonic Generation (SHG) Measurements. For SHG measurements films were spin-coated on ITO-glass substrates and after 30 min of precure simultaneously poled and cured for 60 min using a wire corona electrode. The SHG measurements were done in transmission normally 1 day after poling and were performed with a Q-switched Nd:YAG laser at 1064 nm so the calculated d_{33} is resonantly enhanced. The results are compiled in Table 3.

Formulation 2 from Table 1, simultaneously poled and cured for 90 min, showed SHG signals that were not stable during the measurement when the rotation of the sample was stopped at an angle of maximum second harmonic intensity. Very rapidly, within 1 min, a decrease was observed to approximately 10% of the initial value. This might be due to heating of the sample by absorption of a fraction of the laser light raising the temperature above the T_g of the NLO material. As a matter of fact, the laser power was rather high: pulse length 200 ns, 2 kHz, 2.7 mJ/pulse. When using a lower power input (pulse length 10 ns, 10 Hz, 10–20 mJ/pulse), there was no indication of a decrease of the intensity. When kept at room temperature and measured on the rotating sample, the d_{33} value decreased to only 67% of its initial value (34 pm/V) in 395 days.

Formulation 9, simultaneously poled and cured for 90 min, showed stable SHG signals of 8 pm/V during the measurement. This formulation should possess a much higher T_g than formulation 2 because of the higher conversion of over 80%.

When UV curing was performed under poling conditions, the decrease of the CT band of the NLO chromophore was much more pronounced than without poling, especially in the poling area. This might be caused by the orientation of the molecules,[1k] but degradation due to effects of the corona discharges cannot be excluded. Herminghaus et al.,[27] for instance, found that PVA was insoluble after corona poling.

As was recently noticed by other investigators,[1c,d,24b,28] we also experienced that poling with a negative corona (ITO-glass positive) induced more degradation than did a positive corona and incidentally complete bleaching occurred in the former case.

Monomer 2 in formulation 14 showed a very stable SHG signal of 13 pm/V. The d_{33} did not relax in 451 days at room temperature, and aging at 80 °C for a week showed no significant decrease of the SHG signal. Here again, however, a substantial decrease occurred in the CT band during poling.

The pure monomer 2, in formulations 15 and 16, having an initial d_{33} value of 43 pm/V, showed no stable SHG signals, being most probably due to the rather low T_g value of 80 °C. During the measurements the SHG signal relaxed to 8 pm/V (82% decrease) at room temperature.

Recently, the UV cross-linking, at room temperature, of several acrylics containing NLO chromophores was also studied by Robello et al.[10f] both as dopant and as matrix itself. When using dopant systems, the maximum attainable concentration was only 23 w/w % ($N \approx 4 \times 10^{20}$ cm^{-3}). In all cases the NLO activity was not stable. A gradual decrease to zero at room temperature was observed. Even in case of homopolymerization the d_{33} was only 0.7 pm/V at 1.06 μm after poling and cross-linking.

The great differences between the results found in this paper and the results found by Robello et al.[10f] may be attributed to the following facts. First of all, they polymerized only for a few seconds strictly at room temperature and in the case of homopolymerization they did not use a photoinitiator. Therefore, the conversion, and thus the T_g of the materials, was low. Second, they attached the NLO chromophore only with one side to the polymer network. Last, they used contact poling instead of corona poling, applying a much lower field.

Conclusions

The UV polymerization of NLO materials 1 and 2 used in formulations with an acrylic resin and a photoinitiator showed much lower polymerization rates, on the order of 30 min or more to reach complete conversion, than is usual in UV curing where complete conversion is reached on the order of seconds. The conversion rate decreases with increasing NLO chromophore concentration which is probably due to effective quenching of the photoinitiator by the NLO chromophore. Moreover, the NLO chromophore undergoes a substantial bleaching of the CT band during the curing process, *albeit* UV-filtered light is used. This bleaching is attributed to degradation of the azobenzene chromophore. Therefore, the NLO activity is always low: in the case of stable orientation due to degradation of the chromophore and in the case of little degradation due to relaxation of the orientation. In spite of these disadvantages the highly cross-linked formulations showed very stable SHG activities. Especially, NLO chromophore **2**, which has a resonantly enhanced d_{33} of 13 pm/V, is stable during more than a year at room temperature and shows no relaxation for a week at 80 °C. This means that fixing the NLO chromophores on two sides of the polymer matrix gives very stable NLO materials. However, the azobenzenes such as NLO chromophores **1** and **2** are most probably not compatible with UV-initiated radical polymerization.

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