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13. ABSTRACT (Maximum 200 Words)

Polymeric systems have been established as useful materials for second order nonlinear optical (NLO) processes, viz. frequency doubling, linear electro-optic effect, frequency mixing and parametric oscillation. Crosslinked systems are reported to exhibit stable second order properties. The system can be poled and photocrosslinked in the poled state to yield a material with stable optical nonlinearity. This approach is based on the inter- and intra- molecular photocrosslinking reactions of a photoreactive functionalized polymer. Since the second order susceptibility is directly proportional to the concentration of the nonlinear species and the temporal stability is dependent on the mobility of the nonlinear species in the polymer matrix, large and stable second order NLO properties are expected from these photocrosslinked polymers. In this communication, we report the synthesis and detailed characterization of this class of polymer.

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New Photocrosslinkable Polymers for Second Order Nonlinear Optical Processes

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New photocrosslinkable polymers for second-order nonlinear optical processes

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Introduction

Polymeric systems have been established as useful materials for second-order nonlinear optical (NLO) processes, viz. frequency doubling, linear electro-optic effect, frequency mixing and parametric oscillation[1]. These polymers are prepared either by incorporating nonlinear species into a polymer matrix (guest-host systems) or by covalent attachment of the nonlinear species to a polymer backbone or side chains (functionalized systems). The functionalized systems permit higher amount concentration of nonlinear species into the polymer (for larger nonlinear susceptibility), and possess restricted molecular mobility (for increased stability). Problems of phase segregation are also avoided leading to excellent film homogeneity and optical clarity (for lower scattering loss). Typical organic second-order nonlinear species consist of at least one of each donor and acceptor groups attached to a π-moiety, e. g., 4-nitroaniline. Second-order NLO effect in polymers is observed only when the nonlinear species assemble in a noncentric organization. This can be achieved by aligning the nonlinear species in the polymer matrix using an external electric field, a process commonly known as poling. Poled functionalized polymers, in general, exhibit excellent NLO properties such as high electro-optic coefficient and low optical loss, but show poor temporal stability due to the deorientation of the nonlinear species after the electric field is withdrawn[2].

Crosslinked polymer systems have been reported to exhibit stable second-order properties[3,4]. Recently, we reported, for the first time, a new class of crosslinked system by processing nonlinear species with a polymer like a guest-host system. The guest NLO molecule and the host polymer contained functionalized groups through which crosslinking may be introduced. The system can be poled and photocrosslinked in the poled state to yield a material with stable optical nonlinearity[5,6]. More recently, we reported a different approach for obtaining a crosslinked polymeric system with high amount concentration of nonlinear species by photochemical reaction[7]. This approach is based on the inter- and intramolecular photocrosslinking reactions of a photoreactive functionalized polymer (Fig. 1). The photocrosslinking reaction can be performed at a wavelength depending on the absorption profile of the photoreactive groups which are pendant to the polymer chains. Since the second-order susceptibility is directly proportional to the concentration of the nonlinear species and the temporal stability is dependent on the mobility of the nonlinear species in the polymer matrix,

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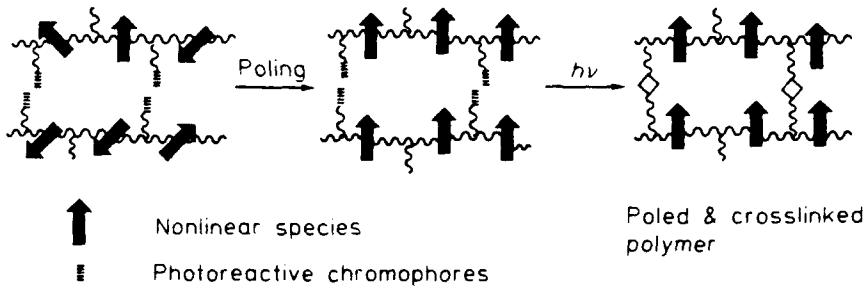
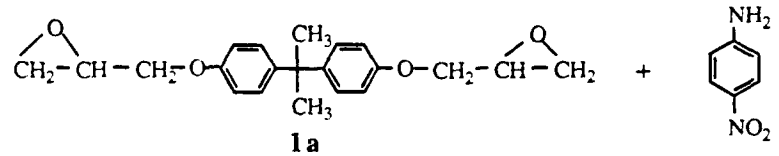


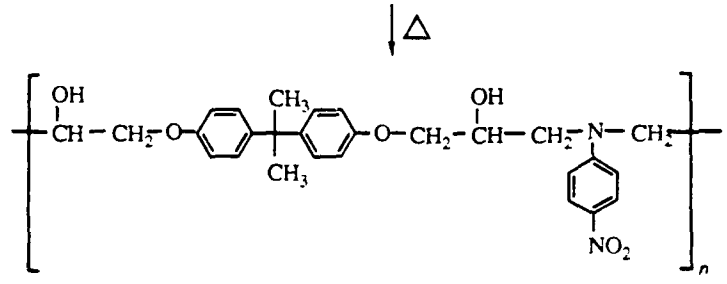
Fig. 1. Schematic of a new approach for the preparation of stable second-order nonlinear optical polymers

large and stable second-order NLO properties are expected from these photocrosslinked polymers. In this communication, we report the synthesis and detailed characterization of this class of polymer.

Scheme 1:



1a



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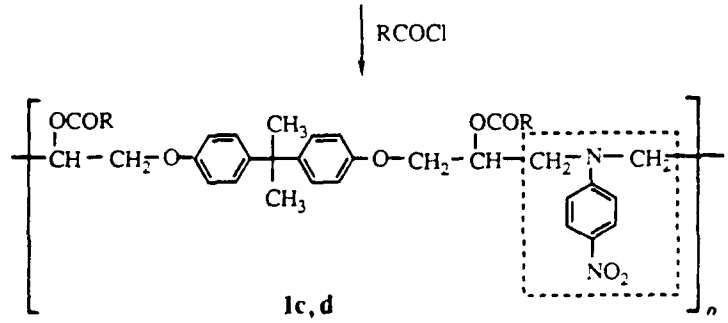


1c, d

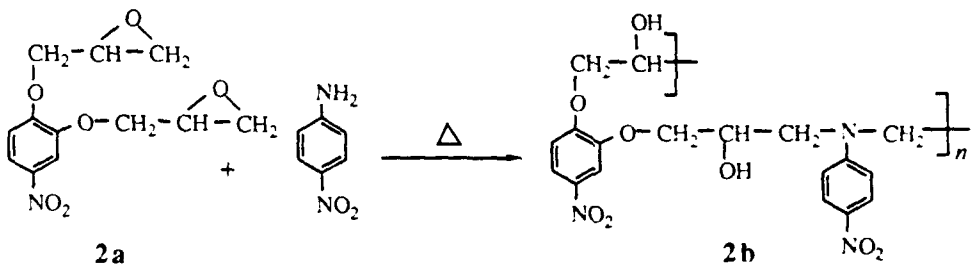
	R
1c	C_6H_5-CH=CH-
1d	C_6H_5-CH=CH-CH=CH-

Results and discussion

The synthesis of the photocrosslinkable polymers involves two steps; the synthesis of functionalized NLO prepolymer and the chemical attachment of photoreactive groups. The prepolymers were prepared by reacting an epoxy and an amino compound consisting of the nonlinear species. Epoxy compounds with and without the nonlinear species **1a** and **2a**, respectively, have been used to investigate the effect of concentration of the nonlinear species on the second-order susceptibility. Appropriate photoreactive groups were then attached to the prepolymers **1b** and **2b** by esterification of hydroxyl groups using the acid chloride of the photoreactive chromophores. Two photoreactive groups, cinnamoyl and cinnamylideneacetyl differing in reactivities have been used to investigate the photocrosslinkable behavior. The synthetic route for obtaining the photocrosslinkable polymers **1c**, **1d**, **2c** and **2d** is schematically shown below (the nonlinear species is indicated by the dotted line).

The epoxy compound **1a** contains no nonlinear species. Hence polymers **1c** and **1d** have a low concentration (≈ 21 wt.-%) of nonlinear species (*Scheme 1*). On the other hand, polymers **2c** and **2d** are loaded with relatively higher concentration of nonlinear species (52 wt.-% and 48 wt.-%, respectively) due to the presence of the nonlinear species in the epoxy compound **2a**, as well (*Scheme 2*).

Scheme 2:

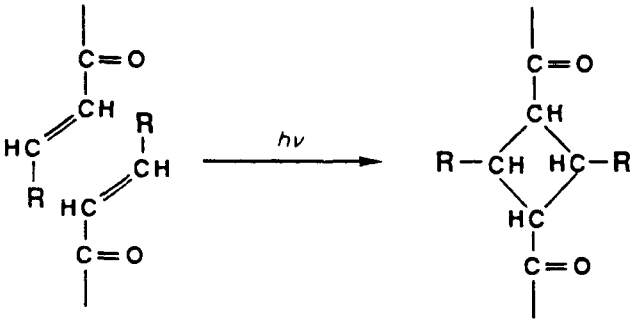


	R
2c	C_6H_5-CH=CH-
2d	C_6H_5-CH=CH-CH=CH-

All polymers are soluble in common organic solvents and form excellent optical quality films from solution in an organic solvent or mixture of organic solvents. Electric field poling is effective at a temperature close to the glass transition temperature (T_g) of the polymer. The nonlinear species can be frozen-in into the preferred orientation

by photocrosslinking. Efficient photocrosslinking reaction occurs at a wavelength close to the absorption maximum of the photoreactive groups. For example, polymers containing cinnamoyl and cinnamylideneacetyl groups, with absorption maxima at 280 nm and 320 nm, respectively, can be crosslinked within a short exposure time at 254 nm and 366 nm, respectively. Typical 2 + 2 photodimerization of carbonyl group activated double bond is shown in *Scheme 3*[8]. In the present work the concept has been estalished with a simple nonlinear species, 4-nitroaniline. Further investigation on photocrosslinking behavior and NLO properties of this and other systems, where the nonlinear species has considerably larger molecular hyperpolarizability (e.g., donor, acceptor derivatized azo, stilbene and azomethine dyes), will be published elsewhere.

Scheme 3:



Experimental part

Instrumentation

^{1}H NMR spectral data were obtained on a Bruker WP-270 NMR spectrometer. IR spectra were taken on a Bruker-IFS-113V FT-IR spectrophotometer. Ultraviolet-visible (UV-VIS) spectra were recorded on a Perkin-Elmer-559 spectrophotometer. The heats of phase transitions were determined with the aid of a DuPont 2910 differential scanning calorimeter under a flow of nitrogen, with a heating rate of 10 K/min. Number- and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) of the polymers were determined with a Waters 510 HPLC unit combined with a Waters 410 differential refractometer using chloroform as an eluent. The gel-permeation chromatography (GPC) calibration is based on polystyrene standards. The used column set consisted of Waters styragel 100, 500, 1 000 and 10 000 Å.

Materials

4-Nitroaniline (Aldrich), 4-nitropyrocatechol (Aldrich), and cinnamoyl chloride (Aldrich) were used without further purification. Bisphenol-A diglycidylether[a] (**1a**) was obtained from a commercial source (Shell, Epon-828) and used as received. 4-Nitropyrocatechol diglycidylether[b] (**2a**) was prepared following the procedure described for **1a**[9]. Cinnamylideneacetyl chloride was synthesized according to the method described in the literature[10]. Tetrahydrofuran (THF) (Aldrich) and triethylamine (Aldrich) were distilled under nitrogen before use.

Polymers **1c** *and* **1d**: 7.5 g of **1a** and 3 g of 4-nitroaniline were heated at 140 °C for 4 h and 160 °C for 3 h in a sealed tube. The prepolymer **1b** was powdered and unreacted 4-nitroaniline was removed from the crude mixture by vacuum sublimation at 140 °C for 1 h. Yield: 10 g (95%); glass transition temperature T_g = 54 °C.

[a] Systematic IUPAC name: 2,2-bis[4-(2,3-epoxypropoxy)phenyl]propane.
[b] Systematic IUPAC name: 3,4-bis(2,3-epoxypropoxy)nitrobenzene.

In one reaction, 3,5 g of cinnamoyl chloride in 15 mL of tetrahydrofuran (THF) was added dropwise to a solution of 3,5 g of **1b** and 10 mL of triethylamine in 15 mL of THF, and stirred for 24 h at room temperature. The dark brown solution was precipitated into 800 mL of methanol. The polymer **1c** was filtered, washed with methanol and dried under reduced pressure at room temperature. Yield: 4,2 g (78%); T_g = 78 °C; $\bar{M}_n$ = 2500; $\bar{M}_w$ = 8500.

IR (KBr): 1242 (s; C—O—C), 1510, 1327 (s; NO_2), 1713 cm^{-1} (s; CO).

UV-VIS (film): 279 (wavelength of maximum absorption λ_{max} (cinnamoyl)); 375 (λ_{max} (NLO)); 480 nm ($\lambda_{cut\ off}$).

^{1}H NMR ($CDCl_3$): δ = 1,61 (s, 6H, CH_3); 3,57–4,20 (m, 4H, OCH_2; 4H, NCH_2; 2H, CH); 6,55–7,95 (m, 22H, ArH; 4H, CH=CH).

$C_{45}H_{42}O_8N_2$ (738)	Calc.	C 73,17	H 5,69	N 3,79
	Found	C 73,14	H 5,11	N 3,05

In a second reaction, 4 g of cinnamylideneacetyl chloride in 15 mL of THF was added dropwise to a solution of 4 g of **1b** and 10 mL of triethylamine in 15 mL of THF and stirred for 24 h at room temperature. The dark brown solution was precipitated into 900 mL of methanol. The polymer **1d** was filtered, washed with methanol and dried under reduced pressure at room temperature. Yield: 5 g (76%); T_g = 94 °C.

IR (KBr): 1235 (s; C—O—C), 1510, 1321 (s; NO_2), 1708 cm^{-1} (s; CO).

UV-VIS (film): 315 (λ_{max} (C_6H_5CH=CHCH=CHCOCl)); 375 (λ_{max} (NLO)); 460 nm ($\lambda_{cut\ off}$).

^{1}H NMR ($CDCl_3$): δ = 1,65 (s, 6H, CH_3); 3,62–4,30 (m, 4H, OCH_2; 4H, NCH_2; 2H, CH); 6,51–8,05 (m, 22H, ArH; 8H, CH=CH).

$C_{49}H_{46}O_8N_2$ (790)	Calc.	C 74,43	H 5,82	N 3,54
	Found	C 74,27	H 5,75	N 3,19

Polymers **2c** *and* **2d**: 8 g of **2a** and 4 g of 4-nitroaniline were heated at 140 °C for 1 h and 160 °C for 10 h in a sealed tube. Prepolymer **2b** was purified by vacuum sublimation at 140 °C for 1 h. Yield: 11,5 g (96%); T_g = 36 °C.

In one reaction, 4 g of cinnamoyl chloride in 15 mL of THF was added dropwise to a solution of 4 g of **2b** and 10 mL of triethylamine in 15 mL of THF and stirred for 24 h at room temperature. The dark brown solution was precipitated into 800 mL of methanol. The polymer **2c** was filtered, washed with methanol and dried under reduced pressure at room temperature. Yield: 4,5 g (68%); T_g = 78 °C; $\bar{M}_n$ = 1500; $\bar{M}_w$ = 2500.

IR (KBr): 1279 (s; C—O—C), 1518, 1327 (s; NO_2), 1719 cm^{-1} (s; CO).

UV-VIS (film): 284 (λ_{max} (cinnamoyl)); 374 (λ_{max} (NLO)); 480 nm ($\lambda_{cut\ off}$).

^{1}H NMR ($CDCl_3$): δ = 3,59–4,22 (m, 4H, OCH_2; 4H, NCH_2; 2H, CH); 6,48–7,95 (m, 17H, ArH; 4H, CH=CH).

$C_{36}H_{31}O_{10}N_3$ (665)	Calc.	C 64,96	H 4,66	N 6,32
	Found	C 63,22	H 4,59	N 6,03

To produce polymer **2d**, 4 g of cinnamylideneacetyl chloride in 15 mL of THF was added dropwise to a solution of 4 g of **2b** and 10 mL of triethylamine in 15 mL of THF and stirred for 24 h at room temperature. The dark brown solution was precipitated into methanol (900 mL). The polymer **2d** was filtered, washed with methanol and dried under reduced pressure at room temperature. Yield: 4,6 g (65%); T_g = 88 °C.

IR (KBr): 1279 (s; C—O—C), 1518, 1343 (s; NO_2), 1711 cm^{-1} (s; CO).

UV-VIS (film): 318 (λ_{max} (C_6H_5CH=CHCH=CHCOCl)); 385 (λ_{max} (NLO)); 480 nm ($\lambda_{cut\ off}$).

^{1}H NMR ($CDCl_3$): δ = 3,55–4,28 (m, 4H, OCH_2; 4H, NCH_2; 2H, CH); 6,55–8,11 (m, 17H, ArH; 8H, CH=CH).

$C_{40}H_{35}O_{10}N_3$ (717)	Calc.	C 66.95	H 4.88	N 5.86
	Found	C 66.43	H 4.69	N 5.44

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