Synthesis of a Novel Difunctional NLO Azo-Dye Chromophore and Characterizations of Crosslinkable Copolymers with Stable Electrooptic Properties

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ABSTRACT: The synthesis and the nonlinear optical (NLO) properties of crosslinkable copolymers based on a novel NLO azo-dye chromophore bearing two functions: one used the free-radical copolymerization, that is, the methacrylate group, and the other one used for the crosslinking process, that is, the carboxylic acid function, are described. Copolymerization of this new monomer with glycidyl methacrylate leads to novel soluble crosslinkable NLO copolymers bearing free epoxy and carboxylic groups. The poling process, before crosslinking, is achieved at a temperature (T_p) close to the glass transition temperature, T_g (<70°C), of the copolymers. At this temperature, no reaction takes place between epoxy and carboxylic acid functions. In fact, crosslinking begins to start at a higher temperature, T_c ($T_c \gg T_p \approx T_g$). After the optimization of the poling and crosslinking processes, the NLO crosslinked polymer with 30 mol % of the chromophore exhibits a T_g of 157°C and a high quadratic susceptibility (d_{33}) of 30 pm/V at 1320 nm. This coefficient is stable at 85°C for several weeks. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 974–982, 1999

Key words: difunctional azo-dye chromophore; glycidyl methacrylate copolymer; crosslinkable electrooptic polymers; thermally stable electrooptic properties

INTRODUCTION

There is a great potential for the use of polymer materials for communication systems both as passive and active components. In the last area, many works showed that specific polymers provide good opportunities to build optical components such as electrooptic modulators.^{1–3} Modulators are one of the main elements of a telecommunication optical network. It is well known that

some highly conjugated molecules, with a high dipole moment in the molecular plane, yield strong electronic nonlinear optical (NLO) effects. To give rise to quadratic NLO properties (such as, e.g., the Pockels effect), molecules (such as organic chromophores) must be acentric toward the electric field. For this reason, a planar-conjugated molecular group is inserted between a powerful electrodonor group and a powerful electroacceptor group. These molecules are grafted onto the polymer backbone to form side-chain NLO polymer materials. To make a noncentrosymetric material, a strong electric field is applied on the polymer film at a temperature close to the glass transition temperature (T_{σ}) of the polymer to pole NLO groups.

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At the beginning of the 1990s, a full polymer Mach–Zehnder modulator was reported by Möhlmann.⁴ The main problem of this kind of material is the decay over time of the NLO effect due to relaxations of the dipole alignment, induced during poling, and this is the main cause which hinders the development of polymer electrooptic modulators. Only a few laboratories are specifically working on these relaxation phenomena.⁵ It is worthwhile to note that a thoroughly stable electrooptic coefficient is needed in the range of -20 to $+85^{\circ}$ C.

To enhance the stability of the poled structure, some authors tried to lock the NLO orientation by using a polymer structure yielding a high glass temperature, such as polyimide⁶ and maleimide, or by using interpenetrating networks⁸ (IPNs). High T_{σ} 's improve the stability of the NLO properties; however, a slight decrease of the electrooptic coefficient still occurs after a long time. Moreover, a very high poling temperature and then a high thermal stability of the chromophore are required for the processing of NLO polyimide materials.⁹ Crosslinking of functional moieties contained in the polymer close to the NLO chromophore could be a second way to enhance the stability of the NLO materials. Crosslinking using a sol-gel technique¹⁰ or photocrosslinking¹¹ processes have been already described. However, photocrosslinking with an azo-dye chromophore induces a photofading effect and, thus, the NLO properties were dramatically reduced.¹² On the other hand, other works were devoted to the simultaneous curing and poling of multifunctional¹³ NLO groups such as double-end crosslinkable (DEC) NLO $chromophores^{14}$ or thermosetting resins based on epoxy prepolymers bearing NLO groups¹⁵ or on NLO polyurethane prepolymers.¹⁶ However, these processes need very careful adjustments of the poling-curing technique.

In the following work, we performed a new method which results in the crosslinking between the NLO chromophore and the polymer backbone. In the first step, a difunctional NLO azo-dye-chromophore is synthesized: one function is involved in a free-radical copolymerization and the second one is used during the crosslinking process. In the second step, this NLO chromophore is copolymerized with another monomer bearing a functional group which will react with the crosslinking group of the chromophore at a temperature (T_c) much higher than the poling temperature (T_p) . Before carrying out the synthesis of such a copoly-

mer, we also took into account all the requirements needed for the waveguide fabrication and the electrooptic effect. Thus, we take care of the different NLO group synthesis steps which will not yield the cancellation of the electrooptic coefficient and, of course, will not hinder the following chemical reactions such as those of grafting, polymerization, and anchoring. These last points are the main difficulties toward the realization route of a stable electrooptic polymer.

Because difunctionalized NLO groups are not available, we undertook to design such a NLO group and then a new polymer, taking into account the synthesis requirements. The first requirement concerns the crosslinking function, which, after the poling process, must not lower the hyperpolarizability of the NLO chromophore.

Second, the other specifications concern the NLO group properties. Thus, the chromophore has to yield a large hyperpolarizability and bear a polymerizable group such as a methacrylic moiety. The chemical structure of this electrooptic monomer is given by the following formula:



Nitro- and tertiary amines were chosen as efficient acceptor and donor groups, respectively, and placed at the end of the π -extended molecule in order to obtain a large electrooptic coefficient. Moreover, the carboxylic group (crosslinking group) is placed on one of the aromatic groups in order to perform anchoring after the poling process. Because of its location and its electronic configuration, the anchoring function retains a high level of the hyperpolarizability. This monomer can undergo free-radical copolymerization with the methacrylic monomer bearing the second crosslinking function. This function could be an epoxy one. We describe in this article the synthesis of a difunctional monomer, its copolymerization with glycidyl methacrylate (GMA), and the poling and crosslinking processes to yield electrooptic copolymers with stable NLO properties.

EXPERIMENTAL

Instrumentation

¹H-NMR spectra were recorded on a Bruker WP200 spectrometer with TMS as the reference.

Chemical shifts are reported in ppm: s = singlet, d = doublet, t = triplet, q = quadruplet, and m = multiplet. IR spectra were obtained on a Nicolet 510P FTIR spectrometer with an accuracy of 2 cm⁻¹. Solid samples in KBr pellets were used. Differential scanning calorimetry (DSC) analyses were performed on a Perkin-Elmer DSC4 apparatus at a heating rate of 5°C/min (for the melting point) and 40°C/min (for the T_g measurement) under nitrogen. The T_g was defined as the midpoint of the transition. Ultraviolet-visible (UVvis) spectra were taken on a Varian Super Scan3 spectrophotometer. Thermogravimetric analyses (TGA) were performed on a TA Instrument TGA 51 apparatus with a heating rate of 10°C/min under nitrogen. The weight-average molecular weight (M_w) and index of polymolecularity (Ip) of the copolymers were determined by size-exclusion chromatography (SEC) with a Spectra Physics Winner Station apparatus equipped with two columns, PLgel 3 μ m Mixed-E (300 mm length), from Polymer Laboratories using poly(methyl methacrylate) (PMMA) standards. The detection was achieved with a Spectra Physics SP8430 differential refractometer using tetrahydrofuran (THF) as the eluent (1 mL/min).

Materials

2-(N-Ethylanilino)ethanol (from Aldrich, France) and 2-amino-5-nitrobenzoic acid (from Lancaster, France) were used as received. Methacryloyl chloride and GMA (from Aldrich) were distilled just prior to use. 2,2'-Azobisisobutyronitrile (AIBN) was purified by crystallization, twice, from methanol. All other solvents and reagents (from Aldrich) were analytical grade and were used without further purification.

Synthesis of 2(N-ethylanilino)ethyl Methacrylate (I)

Under argon, 8.7 g (5.27 mmol) of 2-(*N*-ethylanilino)ethanol, 5.33 g of triethylamine (5.27 mmol), and 10 mg of hydroquinone were dissolved in 150 mL chloroform. To this mixture cooled at 0°C, 6.05 g (5.79 mmol) of methacryloyl chloride was added dropwise. Then, the solution was stirred 17 h at 40°C. After cooling at room temperature and washing twice with 150 mL of water, the organic layer was dried over anhydrous sodium sulfate. The solvent was evaporated and the product obtained was purified by column chromatography [silica gel (Chromagel Silice 60 A.C.C.), dichloromethane/pentane (7/3 v/v)]. After vacuum drying, an oily product was obtained. Yield 8.0 g (65%).

¹H-NMR [CO(CD₃)₂]: $\delta = 1.20$ (t, J = 7.0 Hz, 3H, -NCH₂<u>CH3</u>); 1.95 [s, 3H, =C(CH3)CO₂--]; 3.45 (q, J = 7.0Hz, 2H, -N<u>CH2</u>CH₃); 3.70 (t, J = 6.2 Hz, 2H, -N<u>CH2</u>CH₂O--); 4.31 (t, J = 6.2 Hz, -NC H₂<u>CH2</u>O--); 5.60 [m, 1H, CH2=C(CH₃)--]; 6.1 [m, 1H, <u>CH2</u>=C(CH₃)--]; 6.8 (m, 2H, Ar. ring); 7,3 (m, 3H, Ar. ring).

Synthesis of 4'-[*N*-(2-methacryloxy ethyl)-*N*ethyl]amino-4-nitro-2-carboxyazobenzene (<u>II</u>)

In a 250-mL one-necked flask, 4.68 g (2.57 mmol) of 2-amino-5-nitrobenzoic acid was added to a solution of 50 mL of NaOH (0.5N). To dissolve the acid, it was necessary to warm the solution to 70°C. Then, 11 mL of concentrated hydrochloric acid (10N) was slowly added. The solution was cooled at 0°C and 1.77 g (2.57 mmol) of sodium nitrite in 4 mL water was added gradually with stirring to obtain the diazonium salt. After 1 h at $0-5^{\circ}C$, the solution was filtered and 6 g (2.57 mmol) of methacrylate I was added dropwise to the filtrate with stirring at 0°C. The mixture was further stirred overnight at 20°C. The precipitate was collected by filtration, washed with water, and purified by column chromatography [silica gel (Chromagel Silice 60 A.C.C.), dichloromethane/diethyl ether (9/1 v/v)]. After vacuum drying, a deep purple powder was obtained. Yield 5.8 g (53%).

$$\begin{split} & \text{Mp} = 115^{\circ}\text{C}.\ ^{1}\text{H-NMR}\ (\text{CDCl}_{3})\text{:}\ (\text{cf. Scheme 1})\ \delta \\ &= 1,32\ (\text{t, J} = 7.0\ \text{Hz},\ 3\text{H, Ha})\text{;}\ 1.93\ (\text{s, 3H, He})\text{;}\\ & 3.62\ (\text{q, J} = 7.0,\ 2\text{H, Hb})\text{;}\ 3.81\ (\text{t, J} = 5.9\ \text{Hz},\ 2\text{H,}\\ & \text{Hc})\text{;}\ 4.41\ (\text{t, J} = 5.9,\ 2\text{H, Hd})\text{;}\ 5.60\ (\text{m, 1H, Hf})\text{;}\ 6.1\\ & (\text{m, 1H, Hf})\text{;}\ 6.85\ (\text{d, J} = 8.9\ \text{Hz},\ 2\text{H, Hh})\text{;}\ 7.77\ (\text{d,}\\ & \text{J} = 8.8\text{Hz},\ 2\text{H, Hi})\text{;}\ 8.08\ (\text{m, 1H, Hj})\text{;}\ 8.34\ (\text{m, 1H,}\\ & \text{Hk})\text{;}\ 9.1\ (\text{m, 1H, Hl})\text{;}\ 14.1\ (\text{broad signal, Hg}).\ \text{UV-vis}\ (\text{ethanol})\text{:}\ 520\ \text{nm}\ (\lambda_{\text{max}})\text{;}\ \text{IR}\ (\text{cm}^{-1})\text{:}\ 3450\ \text{cm}^{-1}\\ & (\text{m, }\nu_{\text{st}}\ -\text{OH}),\ 2980-2960\ \text{cm}^{-1}\ (\text{w, }\nu_{\text{st}}\ -\text{CH}),\\ 1724\ \text{cm}^{-1}\ (\text{s, }\nu_{\text{st}}\ \text{C=O}\ \text{ester}),\ 1700\ \text{cm}^{-1}\ (\text{s, }\nu_{\text{st}}\ \text{C=O},\ \text{acid}),\ 1635\ \text{cm}^{-1}\ (\text{w, }\nu_{\text{st}}\ \text{CH}_{2}\ -\text{C}),\ 1605\ \text{cm}^{-1}\ (\text{s, }-\text{CH}\ -\text{CH}\ -\text{of}\ \text{Ar. ring}),\ 1518\ \text{cm}^{-1}\ (\text{s, }\nu_{\text{asym}}\ -\text{NO}_{2}),\ 1337\ \text{cm}^{-1}\ (\text{s, }\nu_{\text{sym}}\ \text{NO}_{2})\text{;}\ 1165\ \text{cm}^{-1}\ (\text{s, }\nu_{\text{st}}\ -\text{C-O}\ -\text{C}),\ 835\ \text{cm}^{-1}\ (\text{m, }\nu_{\text{oop}}\ \text{CH}_{2}\ -\text{C}).\\ \end{split}$$

Copolymerization Procedures

The synthesis of copolymers **P-III**, containing 30 mol % of monomer **II**, is described below as a representative example: a 100-mL Schlenk flask equipped with an argon outlet and a magnetic



Scheme 1 Synthesis of difunctional NLO azo-dye chromophore II.

stirrer was charged with 30 mL of THF, 1.311 g (9.23 mmol) of GMA, 1.686 g (3.96 mmol) of monomer \underline{II} , and 216 mg (1.319 mmol/10 mol %) of AIBN. This mixture was placed under an argon atomosphere, stirred, and kept at 60°C for 36 h. Then, the copolymer was purified by two reprecipitations from THF/methanol and dried until a constant weight in a vacuum at 40°C. Yield 2.09 g (70%).

¹H-NMR (CDCl₃): $\delta = 0.6-1.5$ (m, --CH₂--C(<u>CH3</u>)-, from monomer **II** and GMA; --NCH₂<u>CH3</u>, monomer **II**); 1.7-2.2 [m, --<u>CH2</u>--(CH₃)-, from monomer **II** and GMA]; 2.5, 2.75, and 3.15 (m, --CH₂--<u>CH</u>--<u>CH2</u>, protons of epoxy ring from GMA); 3.4-4.5 (m, -O--CH₂--<u>CH</u>/, GMA, CH₃<u>CH2NCH2CH2</u>-O-, monomer **II**); 6.9 (m, H of Ar. ring, ortho of amino group); 7.75 (m, H of Ar. ring, meta of amino group); 8.3 (m, H of Ar. ring, meta of NO₂); 8.5 (m, H of Ar. ring, ortho of NO₂); 9 (m, H of Ar. ring, ortho of CO₂H). IR (KBr): 3450 cm⁻¹(m, ν_{st} --OH), 2980-2960 cm⁻¹ (w, ν_{st} --CH--), 1730 cm⁻¹ (s, ν_{st} C=O ester), 1601 cm⁻¹ (s, -CH=CH-- of Ar ring), 1518 cm⁻¹ (s, ν_{asym} --NO₂), 1340 cm⁻¹ (s, ν_{sym} NO₂); 1136 cm⁻¹ (s, ν_{st} -C-O-C--), 903 cm⁻¹ (w, ν_{st}, -C-O-C-, epoxy ring).

Analyses and physical characteristics of the synthesized copolymers are given in Table I.

Polymer Films Preparation and Poling Procedure

The copolymers were dissolved in 1,1,2-trichloroethane. The solutions, 140 g/L, were filtered through a $0.2-\mu m$ PTFE membrane and were spin-coated (speed: 1500 rpm) onto glass or quartz substrates. Prebaking of the samples was done immediately after spin coating at 80°C for 1 h. The film having a thickness of 1.5 μ m was poled by applying a corona voltage around 5 kV at 1 cm of the film. While the electric field was maintained, the sample was placed on a hot stage at the temperature of poling, T_p , for 15 min. Thereafter, anchorage of the chromophores occurs when the film is heated at the crosslinking temperature, T_c , for 20 min. The film was cooled to room temperature before removing the electric field. The second-order NLO properties of the poled polymer were measured according to methods already described.¹⁷

RESULTS AND DISCUSSION

Synthesis and Copolymerizations of Difunctional NLO Azo-dye Chromophore II

The synthetic route to the difunctional electrooptic monomer is shown in Scheme 1. The key step

Polymer	Initial Mol Fraction of Chromophore	Final Mol Fraction of Chromophore ^a	Yield (%)	T_g (°C)	${M_w}^{ m d}$ (Ip)	Refractive Index ^e (1.32 μ m)
P-I	0.10	0.08	73	$50^{ m b}$	9300	1.54
				(94 ^c)	(2.1)	
P-II	0.20	0.17	73	$40^{ m b}$	12,300	1.57
				(112^{c})	(2.8)	
P-III	0.30	0.30	70	$65^{ m b}$	16,500	1.62
				(157^{c})	(4.1)	
P-IV	0.40	0.35	70		25,400	
					6.1	
P-V	0.50	0.40	72		16,900	
					4.9	

Table I Analyses and Physical Characteristics of NLO Crosslinkable Polymers

^a Determined by ¹H-NMR.

^b T_g of copolymer observed during the first run from 50 to 200°C at 40°C min. ^c T_g of the crosslinked copolymer found during the second run from 50 to 200°C at 40°C/min.

^d PMMA standards.

^e Refractive index determined from prism-coupling method.

of the synthesis of the chromophore, II, is the formation. in situ, of the diazonium ion of 2-amino-5-nitrobenzoic acid. The diazotization is carried out, first, in basic medium, to dissolve the 2-amino-5-nitrobenzoic acid and then the chlorohydric acid and, at last, sodium nitrite was added to generate the diazonium salt. Diazotizations and azo-cou-



Scheme 2 Chemical structure of crosslinkable NLO copolymer.

pling reactions need to be carried out at as low a temperature as possible (generally 0–5°C).¹⁸ The electrophilic substitution between the diazonium salt and the aromatic amine takes place selectively in the *para* position of the aromatic ring of I. Indeed, the two ¹H-NMR signals of the aromatic protons of **I**, at 6.8 (2H) and 7.3 ppm (3H), become two characteristic doublets of a para substitution, one located at 6.85 ppm (Hh) and the other at 7.77 ppm (Hi) (see Fig. 1).

The azo-dye monomer II was copolymerized with GMA under free-radical conditions with AIBN as the inititiator at 60°C. At the end of the copolymerization, all the copolymers are soluble in THF and 1,1,2-trichlororethane. The physical characteristics of the polymers are gathered in Table I. The molar compositions of the polymers were evaluated by ¹H-NMR. Thus, the intensity of the signal in the aromatic range corresponding to the protons of the chromophore moiety (δ from 6.8 to 9 ppm, 7H) was compared to the three well-defined intensities of the signals of the epoxy-ring protons, located between 2.5 and 3.15 ppm (3H). As shown in Table I, the molar fractions of the chromophore in the polymers are close to the initial fractions, indicating similar reactivity ratios of the two methacrylic monomers. This result is corroborated by a recent study of Navarro-Rodriguez et al. in which the reactivity ratios, r_1 and r_2 , determined by the Fineman-Ross method, of MMA and GMA were 0.4 and 0.62, respectively.¹⁹ The yields of the free-radical copolymerizations are close to 70%. Copolymers P-I,



Figure 1 ¹H-NMR (CDCl₃) of the difunctional NLO azo-dye chromophore <u>II</u>.

P-II, and **P-III**, just before crosslinking, exhibit very interesting low T_g 's (from 40 to 65°C). So, the poling process can be achieved at a sample temperature, T_p , in the range of 70–80°C. The T_g 's of the crosslinked copolymers increase with increase of the chromophore content from 94°C for **P-I** to 157°C for **P-III**.

The refractive index of a polymer is a function of the chromophore content: The higher the mol % of the chromophore, the higher the refractive index. The T_5 , T_{10} , and T_{20} , which are the temperatures at 5, 10, and 20% weight loss (measured by TGA), are 255, 280, and 300°C, respectively, for

polymer **P-III**. These temperatures correspond to the thermal degradation of the azo-dye chromophore.

Poling and Crosslinking Procedure for the Polymer P-III

First, the characteristic temperatures (T_p and T_c) were determined, on a polymer film (1.5 μ m), in order to begin the poling process and afterward the anchoring process. The poling process is achieved at a sample temperature, T_p , close to the T_g 's of the copolymer. As the T_g of copolymer **P-III**



Figure 2 Normalized OD versus time at different temperatures of the epoxy absorption band at 903 cm⁻¹ for the electrooptic polymer **P-III** containing 30 mol % of the NLO unit.

is 65°C, the poling of the chromophores can be achieved at 70°C under an electric field applied by the corona method for 15 min. The next step is the anchoring process, which has to be done at a temperature, T_c , higher than the poling one. On the other hand, the two functions must not react at the poling temperature to ensure an optimum chromophore orientation in the electric field. Therefore, the anchoring kinetic is studied to determine the more efficient temperature to achieve the crosslinking between the NLO poled molecules and the epoxy function of the copolymer. By FTIR, crosslinking can be assayed by diminution of the epoxy-ring vibrational mode at 903 cm⁻¹. A plot of the normalized optical density (OD) at 903 cm^{-1} versus the time at different temperatures is shown in Figure 2.

These curves show that crosslinking does not occur at the poling temperature ($T_p = 70^{\circ}$ C). On the other hand, the reaction involving epoxy and carboxylic functions is thoroughly achieved, for example, after 20 min at 150°C. It can be noticed that the epoxy functions are more consumed than are the carboxylic functions involved, which is due to other chemical reactions between hydroxy and epoxy groups or hydroxy and carboxylic groups.²⁰ Consequently, some dissolving tests are performed after heating the electrooptic film. The insolubility of the polymer, in THF, is observed after a few minutes at 150°C. Then, the crosslinking occurs at this temperature and not at the poling temperature.

NLO Properties and Thermal Stability

Electrooptic characterizations were evaluated in order to determine the electrooptic yield and the thermal stability of the NLO properties. The dichroic spectrum of the **P-III** film (thickness 1.5 μ m) for each of the process steps is given in Figure 3. An expected decrease is observed of the OD due to the corona poling. The absorption maxima of the copolymer are slightly blue-shifted. This hypsochromic effect is due to the anchorage of the chromophore into the copolymer backbone.

To determine the electrooptic coefficient, the measurements of the second harmonic generation (SHG) were performed by a 1320-nm laser source. The d_{33} coefficient reaches 30 pm/V at 1320 nm, which is a good level to exploit the NLO effects. The temporal stability of the polymer film was studied by the decay of the SHG signal, $I_{2\omega}$, as a function of temperature, and Figure 4 shows the behavior of the SHG yield by the copolymer, **P**-**III**, after crosslinking, and by the well-known MMA-Dispersed RED1 grafted copolymer (MMA-DR1) with a chromophore molar fraction of 0.3.²¹

As a result of the anchoring process, the new electrooptic polymer retains a high NLO level over a range of temperatures up to 120° C, whereupon the SHG signal decreases. Other studies²¹ confirmed the high and stable electrooptic coefficient of this copolymer. Thus, the coefficient r_{33} reaches 12 pm/V at 1320 nm, which makes it possible to exploit the stable Pockels effects in order to perform high bit rate optical modulation in integrated optics. Furthermore, the electrooptic coefficient, r_{33} , is stable at 85°C for several weeks.¹⁷



Figure 3 UV-visible spectra of the electrooptic polymer **P-III** (1) after baking, then (2) after the poling process and (3) after the anchoring process.



Figure 4 Second harmonic generation signals from 1320 nm of polymer **P-III** and a classical electrooptic polymer based on the Disperse Red 1 chromophore (30 mol %) versus temperature.

CONCLUSIONS

In this article, the design and the realization of an efficient method to thermally stabilize electrooptic polymers were reported. As a matter of fact, the relaxation of chromophores remained the main problem which hinders the use of electrooptic polymers. To prevent this phenomenon, one of the best methods seems to be the anchoring of the chromophore after the poling process. The difficulty of this method is probably the synthetic route of the electrooptic copolymer because it has to preserve the anchoring function without canceling the electrooptic yield. This work consisted of designing and making a polymer which fulfills all the requirements needed. The synthesis of such a polymer was described. A new NLO azodye chromophore including a carboxylic function and a methacrylic moiety was synthesized. Then, polymerization was performed with a comonomer bearing a side-chain epoxy function. This functional group is expected to react with the carboxvlic function of the chromophore at the end poling process. In such a way, NLO groups can be locked in the electric field direction. With a polymer containing 30 mol % of the chromophore, this method offers the opportunity to make a thermally stable electrooptic polymer with an electrooptic coefficient of 12 pm/V at 1320 nm stable at 85°C for several weeks.

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REFERENCES

- Polymers in Lightwave, Integrated Optics, Technology and Applications; Hornak, L. A., Ed.; Marcel Dekker: New York, 1992.
- Polymers for Second Order Nonlinear Optics; Lindsay, G. A.; Singer, K. D., Eds.; ACS Symposium Series 601; American Chemical Society: Washington, DC, 1995.
- Robello, D. R. In Desk Reference of Functional Polymers, Syntheses and Applications; Arshady, R., Ed.; American Chemical Society: Washington, DC, 1997; Chapter 3.6, p 505.
- (a) Möhlmann, G. R. Proc ECOC'90, 1990, 833; (b) Möhlmann, G. R. Synth Met 1990, 37, 207.
- (a) Tsutsumi, N.; Matsumoto, O.; Sakai, W. Macromolecules 1997, 30, 4584; (b) Kaatz, P.; Prêtre, P.; Meier, U.; Stalder, U.; Bosshard, C.; Günter; P.; Zysset, B.; Stähelin, M.; Ahlheim, M.; Lehr, F. Macromolecules 1996, 29, 1666.; (c) Prêtre, P.; Kaatz, P.; Bohren, A.; Günter, P.; Zysset, B.; Ahlheim, M.; Stähelin, M.; Lehr, F. Macromolecules 1994, 27, 5476.
- 6. (a) Miller, R. D.; Burland, D. M.; Jurich, M.; Lee, V. Y.; Lundquist, P. M.; Moylan, C. R.; Twieg, R. J.; Thackara, J. I.; Verbiest, T.; Sekkat, Z.; Wood, J.; Aust, E. F.; Knoll, W.; ACS Symposium Series 672; American Chemical Society: Washington, DC, 1997; p 100; (b) Yu, D.; Li, W.; Gharavi, A.; Yu, L. ACS Symposium Series 672; American Chemical Society: Washington, DC, 1997; p 123; (c) Man, H. T.; Chiang, K.; Haas, D.; Teng, C. C.; Yoon, H. N. SPIE Proc 1990, 1213, 7; (d) Saadeh, H.; Gharavi, A.; Yu, D.; Yu, L. Macromolecules 1997, 30, 5403; (e) Jen, A. K.-Y.; Chen, T.-A.; Cai, V. P.; Liu, Y.-J.; Drost, J.; Minimi, R. M.; Dalton, L. R.; Bedworth, P.; Marder, S. R. Mater Res Soc Symp Proc 1995, 392, 33; (f) Marestin, C.; Mercier, R.; Sillion, B.; Chauvin, J.; Nakatani, K.; Delaire, J. A. Synth Met 1996, 81, 143; (g) Yu, D.; Yu, L. Macromolecules 1994, 27, 6718; (h) Chen, T. A.; Jen, A.K-Y.; Cai, Y. Macromolecules 1996, 29, 535.
- (a) Ahlheim, M.; Lehr, F. Macromol Chem Phys 1994, 195, 361; (b) Ahlheim, M.; Lehr, F. Macromol Chem Phys 1995, 196, 243; (b) Verbiest, T.; Samyn, C.; Van Beylen, M.; Persoons, A. Macromol Rapid Commun 1998, 19, 349.
- (a) Marturunkakul, S.; Chen, J. E.; Xi, L.; Liang, X. L.; Jeng, R. J.; Senguta, S. K.; Kumar, J.; Tripathy, S. K. Polym Prepr 1994, 35, 134; (b) Xie, H.-Q.; Liu, Z.-H.; Liu, H.; Guo, J.-S. Polymer 1998, 39, 2393; (c) Xie, H.-Q.; Huang, X.-D.; Guo, J.-S. J Appl Polym Sci 1996, 60, 537; (d) Li, M.; Srikanth Sharma, P. R.; Frisch, H. L. J Polym Sci Part A Polym Chem Ed. 1998, 36, 553.
- (a) Chen, T. A.; Jen, A. K.-Y.; Cai, Y. J Am Chem Soc 1995, 117, 7295; (b) Verbiest, T.; Burland, D. M.; Jurich, M. C.; Lee, V. Y.; Miller, R. D.; Volksen, W. Macromolecules 1995, 28, 3005.

- (a) Sung, P.-H.; Hsu, T.-F. Polymer 1998, 39, 1453;
 (b) Jeng, R. J.; Chen, Y. M.; Chen, J. I.; Kumar, J.; Tripathy, S. K. Polym Prepr 1993, 34, 292;
 (c) Kang, S. J.; Lee, H.-J.; Kim, H. K.; Park, J. T.; Choi, S.-K. Polym Bull 1995, 35, 599.
- (a) Masse, C. E.; Conroy, J. L.; Cazeca, M.; Jiang, X. L.; Sandman, D. J.; Kumar, J.; Tripathy, S. K. J Appl Polym Sci 1996, 60, 513; (b) Bosc, D.; Boutevin, B.; Granier-Azema, D.; Rousseau, A. Polym Bull 1992, 29, 289–293; (c) Mandal, B. K.; Kumar, J.; Huang, J.-C.; Tripathy, S. Makromol Chem Rapid Commun 1991, 12, 63; (d) Mandal, B. K.; Chen, Y. M.; Lee, J. Y.; Kumar, J.; Tripathy, S. Appl Phys Lett 1991, 58, 2459.
- (a) Boutevin, B.; Granier-Azema, D.; Rousseau, A.; Bosc, D.; Guilbert, M.; Foll, F. Polym Bull 1995, 34, 309; (b) Kato, M.; Kanda, K.; Kimura, T.; Matsuda, H.; Nakanishi, H. Polym Bull 1996, 36, 407; (c) Kato, M.; Hirayama, T. Macromol Rapid Commun 1994, 15, 741.
- (a) Kato, M.; Ohara, H.; Fukuda, T.; Matsuda, H.; Nakanishi, H. Macromol Chem Phys 1998, 199, 881; (b) Boogers, J. A. F.; Klaase, P. Th. A.; de Vlieger, J. J.; Alkema, D. P. W.; Tinnemans, A. H. A. Macromolecules 1994, 27, 197; (c) Tapolsky, G.; Lecomte, J.-P.; Meyrueix, R. Macromolecules 1993, 26, 7383.
- (a) Dalton, L. R.; Wu, B.; Harper, A. W.; Ghosn, R.; Ra, Y.; Liang, Z.; Montgomery, R.; Kalluri, S.; Shi, Y.; Steier, W. H.; Jen, A. K.-Y. ACS Symposium Series 601; American Chemical Society: Washington, DC, 1995; p 158; (b) Xu, C.; Wu, B.; Todorova,

O.; Dalton, L. R. Macromolecules 1993, 26, 5303–5309.

- (a) Zentel, R.; Jungbauer, D.; Twieg, R. J.; Yoon, D. Y.; Willson, C. G. Makromol Chem 194, 859 1993; (b) Kitipichai, P.; Laperuta, R.; Korenowski, G. M.; Wnek, G. E. J Polym Sci Part A Polym Chem Ed 1993, 31, 1365; (c) Kitipichai, P.; Laperuta, R.; Korenowski, G. M.; Wnek, G. E. Polym Prepr 1991, 32, 146; (d) Boogers, J. A. F.; Klaase, P. Th. A.; de Vlieger, J. J.; Tinnemans, A. H. A. Macromolecules 1994, 27, 205–209.
- (a) Zhu, J.; Chen, J.; He, M.; Dalton, L. R.; Garnier, S. M.; Chen, A.; Steier, W. H. Polym Prepr 1998, 39, 1; (b) Tang, H.; Cao, G.; Taboada, J. M.; Chen, R. T. J Polym Sci Part B Polym Phys 1997, 35, 2385; (c) Ra, Y. S.; Mao, S. S. H.; Wu, B.; Guo, L.; Dalton, L. R. Polym Prepr 1997, 38, 86.
- Liang, J.; Levenson, R.; Rossier, C.; Toussaere, E.; Zyss, J.; Rousseau, A.; Boutevin, B.; Foll, F.; Bosc, D. J Phys III Fr 1994, 4, 2441.
- Zollinger, H. Color Chemistry; Syntheses, Properties, Applications of Organic Dyes and Pigments; VCH: Weinheim, Germany, 1987.
- Navarro-Rodriguez, D.; Rodriguez-Gonzalez, F. J.; Romero-Garcia, J.; Jimenez-Regalado, E. J.; Guillon, D. Eur Polym J 1998, 34, 1039.
- (a) Madec, P. J.; Marechal, E. Makromol Chem 1983, 184, 343; (b) Madec, P. J.; Marechal, E. Makromol Chem 1983, 184, 357.
- Bosc, D.; Foll, F.; Liang, J.; Rousseau, A.; Boutevin, B. Fr. Telecom Patent EP 641 808, March 8, 1995; Chem Abstr 123, 170624.