

# Crosslinkable, Nonlinear Optical Copolymers: Processing, Corona Poling, and Second Harmonic Generation Studies

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## SYNOPSIS

Polymethacrylate copolymers, containing nonlinear optically active 4'-dialkylamino-4-nitroazobenzene side groups and crosslinkable 2-butenyl side groups were synthesized and characterized. Films of these copolymers can be thermally crosslinked at elevated temperatures and photochemically crosslinked by exposure with UV light. Both methods allow the control of the crosslinking density. A precrosslinking step, prior to the corona-poling step, can be applied to optimize alignment and relaxation of the chromophores. During corona-poling, the temperature dependence of the second harmonic generation (SHG) of an Nd-YAG laser (1.064  $\mu\text{m}$ ) was studied for films with different degrees of precrosslinking. Depending on the conditions of precrosslinking, the SHG signal intensity and the alignment stability can be maximized. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

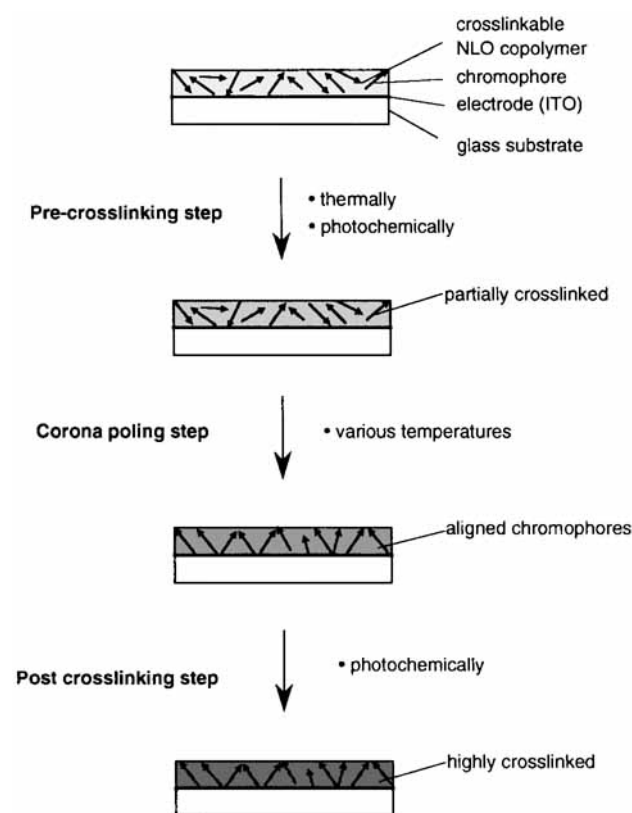
Second order nonlinear optical (NLO) polymers require a noncentrosymmetric order. One commercially attractive possibility to align chromophores into a noncentrosymmetric order is the application of a strong external electric field.<sup>1-5</sup> In order to prevent relaxation of the chromophores after poling, polymers with high glass-transition temperatures ( $T_g$ ) or chemically crosslinked systems have been investigated.<sup>6-15</sup> Even in NLO polymers with high  $T_g$  it was observed that the second order nonlinearity decreased after storing at room temperature.<sup>6,7</sup> A much more stable alignment can be achieved in chemically crosslinked networks. For example, a thermally crosslinkable mixture of multifunctional epoxy monomers and nitrophenylamine chromophores showed good long-term stability.<sup>8,9</sup> The film thickness and crosslinking reaction is usually more difficult to adjust and control if a low molar mass monomer mixture is used. Therefore several photocrosslinkable NLO polymers have been studied.<sup>12-14</sup> In these examples, the corona-poling step

was done prior to the photocrosslinking reaction. We reported recently on photocrosslinkable methacrylate copolymers based on 2-butenyl and benzophenone side-groups<sup>15</sup> in which the photocrosslinking reaction and corona poling were done simultaneously.

In this paper, we explore the concept of using precrosslinked NLO polymers in the corona-poling step. A precrosslinking step has the advantage that alignment and relaxation of the chromophores can be optimized by the crosslink density. Scheme 1 illustrates the various steps for such a process. A photochemically or thermally crosslinkable NLO polymer is spin coated on an ITO-glass substrate. In a precrosslinking step, the film is partially converted to a desired crosslink density. The noncentrosymmetric alignment is achieved by a corona-poling step at elevated temperatures. By optimization of precrosslink density and corona-poling conditions a stable alignment can be already obtained at this processing stage. It is also possible to further enhance the alignment stability in an additional photochemical crosslinking step.

The experiments reported in this paper were conducted on a series of polymethacrylate copolymers **1a–1d**, containing nonlinear optically active 4'-dialkylamino-4-nitroazobenzene side groups and

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**Scheme 1** Representation of processing steps for crosslinkable NLO copolymers. Precrosslinking step thermally or photochemically. Corona-poling step at various temperatures. Postcrosslinking step photochemically.

crosslinkable 2-butenyl side groups.<sup>16,17</sup> The chemical structure and copolymer composition are shown in Figure 1. Films of these copolymers can be thermally crosslinked at elevated temperatures and photochemically crosslinked by exposure with UV light. During the corona-poling process, the temperature dependence of the second harmonic generation (SHG) of an Nd-YAG laser (1.064  $\mu\text{m}$ ) was studied for films with different degrees of precrosslinking.

## EXPERIMENTAL

### Materials

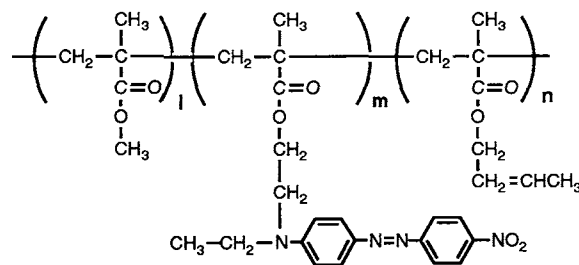
Nonstabilized 2-butenyl methacrylate was supplied by Kuraray Co., Ltd. and used without further purification. Methyl methacrylate was used after distillation to remove the inhibitor. 4'-[(2-Methacryloxyethyl)ethylamino]-4-nitroazobenzene was synthesized as previously described.<sup>15</sup> 2,2'-Azobis(2-methylpropanitrile) (AIBN; Eastman Kodak

Co.) was recrystallized from ethanol and stored at 0°C. *m*-Benzoylbenzophenone was synthesized after a procedure described previously<sup>18</sup> and recrystallized from a hexane and benzene mixture (1 : 1). Tetrahydrofuran (THF) was distilled over potassium and stored under argon. All other solvents and chemicals were used as received.

### Polymer Synthesis

The copolymers **1a–1d** were obtained by a free radical solution polymerization in dioxane with AIBN as initiator. The concentration of monomers was about 30–40% (w/v) and the [monomers] to [AIBN] molar ratio was about 1000. Monomer feed ratio, yields, and copolymer composition are summarized in Table I. As an example for the general copolymerization procedure, the synthesis of copolymer **1b** is described.

**Copolymer 1b:** 2.0 g (5.24 mmol) of 4'-[(2-methacryloxyethyl)ethylamino]-4-nitroazobenzene; 2.0 g (14.3 mmol) of 2-butenyl methacrylate; 3.0 g (30 mmol) of methyl methacrylate; and 6.5 mg of AIBN were dissolved in 17.5 mL of dioxane. The reaction mixture was treated with a gentle stream of argon. After sealing, the mixture was heated to 52°C for 24 h. The resulting homogeneous viscous solution was cooled and added dropwise into 400 mL of methanol to precipitate the polymer. After two additional precipitations from dichloromethane solution into methanol, the copolymer was extracted under reflux with methanol until the methanol ex-



	l	m	n
<b>1a</b>	0.91	0.09	0
<b>1b</b>	0.61	0.09	0.30
<b>1c</b>	0.40	0.11	0.49
<b>1d</b>	0.28	0.11	0.61

**Figure 1** Chemical structure of thermally and photochemically crosslinkable NLO copolymers **1a–1d**.

**Table I** Monomer Feed Ratio, Yield, and Copolymer Composition

Polymer	Feed Ratio (mol %) <sup>a</sup>			Yield (%)	Composition (mol %) <sup>b</sup>		
	L	M	N		l	m	n
<b>1a</b>	90.5	9.5	0	52	91.4	8.6	0
<b>1b</b>	60.5	10.6	28.9	57	60.7	9.3	30.0
<b>1c</b>	44.4	11.2	44.4	35	40.0	11.1	49.3
<b>1d</b>	29.5	11.7	58.8	46	28.1	11.2	60.7

<sup>a</sup> Feed ratio of monomers, L: methyl methacrylate; M: 4'-[(2-methacryloxyethyl)ethylamino]-4-nitroazobenzene; N: 2-butenyl methacrylate.

<sup>b</sup> Copolymerization ratio, determined by NMR.

tract became colorless. The polymer was dried at 40°C in vacuum for 48 h. Yield: 4.0 g (57 wt %). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ (ppm) = 0.81 (brs); 0.98 (brs); 1.1–1.4 (m); 1.6–1.9 (m); 3.56 (brs, OCH<sub>3</sub> + N—CH<sub>2</sub>—CH<sub>3</sub>); 3.64 (brs, N—CH<sub>2</sub>—CH<sub>2</sub>—O); 4.13 (brs, N—CH<sub>2</sub>—CH<sub>2</sub>—O); 4.36 (brs, O—CH<sub>2</sub>—CH=CHCH<sub>3</sub>); 5.5 (brs, O—CH<sub>2</sub>—CH=CHCH<sub>3</sub>); 5.7 (brs, O—CH<sub>2</sub>—CH=CHCH<sub>3</sub>); 6.83 (brs, aromatic of monomer **1**); 7.92 (brs, aromatic of monomer **1**); 8.29 (brs, aromatic of monomer **1**); IR (film on NaCl): 1730, 1672, 1600, 1517, 967 cm<sup>-1</sup>.

### Characterization

Differential scanning calorimetry data were obtained on a Mettler DSC 30 using a heating rate of 10°C/min. The molecular weight and molecular weight distributions were measured with chloroform as eluent. A Spectra-Physics LC-GPC system and a Spectra UV-100 detector was used. The columns (Polymer Standards Service) were calibrated with polystyrene standards. UV-VIS spectra were measured with a Perkin-Elmer Lambda-9 spectrometer. NMR spectra were measured with a 400 MHz instrument from General Electric. Deuterated chloroform was used as a solvent. The copolymer composition was determined by NMR spectroscopy using separated signals of each monomers. Refractive indices were measured with a Metricon Prism Coupler Model-2010 at 632.8 nm. Spin-coated thin films on a silicon substrate were used for the measurements.

### Film Preparation

Thin films were prepared from a solution of approximately 10 wt % of copolymer in benzene. The solution was first filtered through 0.2 μm Teflon filter and then spun at 900–1000 rpm. Quartz sub-

strates were used for absorption measurements. Silicon wafers were used for refractive index measurements. For corona poling, indium–tin–oxide (ITO) coated conductive glass plates were used.

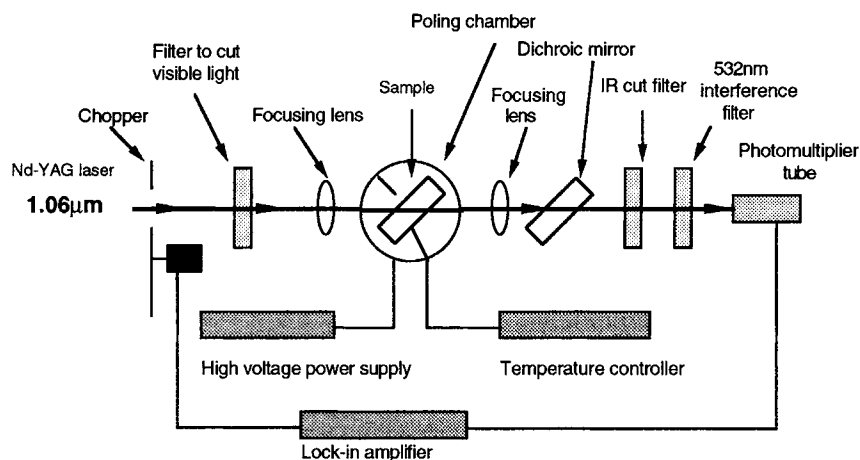
### SHG Measurement During Corona Poling

A corona discharge poling process of spin-coated films on ITO glass substrates was used to noncentrosymmetrically align the chromophores. The experimental set-up is given in Figure 2. The sample stage employs a stainless needle at high static potential that is positioned about 2 cm above a grounded ITO substrate on which the copolymer film was coated. The sample is positioned on a temperature-variable hot stage in a stainless chamber that allows work under inert atmosphere. The sample is positioned at 45° to the incident 1.064-μm Nd-YAG laser (Spectra Physics Model 3800S), that focused on the sample with *p*-polarization. The sample was heated at the rate of 1°C/min with an electric field of 3–6 kV and a current of 2–4 μA. The fundamental wave was blocked by IR cut filters and a 532-nm interference filter. The second harmonic signal was detected by a photomultiplier tube and amplified.

## RESULTS AND DISCUSSION

### Preparation and Properties of Crosslinkable NLO Copolymers

The methacrylate copolymers **1a–1d** studied in this paper are based on methyl methacrylate, a nonlinear optical active azobenzene monomer and a crosslinkable 2-butenyl monomer (Fig. 1). The copolymers were synthesized by a free-radical polymerization using AIBN as initiator. All synthesized copolymers were completely soluble in organic solvents such as



**Figure 2** Schematic drawing of experimental set-up for second harmonic generation measurement at various temperatures during corona poling.

benzene or chloroform, indicating that no crosslinking occurred during copolymerization. The results of GPC, DSC, and refractive index investigations of the copolymers **1a–1d** are summarized in Table II. The molecular weights and molecular weight distributions were measured by GPC calibrated with polystyrene standards. All copolymers had a mono-modal distribution. The number average molecular weight was on the order of 150,000–270,000 g/mol and the weight average molecular weight was on the order of 400,000–560,000 g/mol. All polymers are amorphous. The  $T_g$  depends on the copolymer composition and is dominated by the 2-butenyl methacrylate content.  $T_g$  decreases with an increasing amount of 2-butenyl methacrylate. Refractive indices of copolymers are much higher than polymethyl methacrylate (PMMA) ( $n = 1.49$  at 632.8 nm). This is a consequence of the strong absorption associated with the NLO chromophore at 478 nm. For copolymers with a similar content of NLO side groups, the refractive indices increase with an increasing amount of 2-butenyl groups.

### Thermal Precrosslinking

Copolymers with 2-butenyl side groups **1b–1d** can be thermally crosslinked in an inert atmosphere without decomposition at temperatures between 150 and 180°C. Depending on time and temperature the crosslink density can be varied. Films that are slightly swellable or completely nonswellable in chloroform are obtained. In an experiment under the same conditions, copolymer **1a**, which contains no 2-butenyl side group, was, after annealing at 150°C, still completely soluble in chloroform. This indicates that the copolymer crosslinking reactions occur through the 2-butenyl carbon—carbon double bond. Table III lists  $T_g$  of precrosslinked films after curing at various conditions. The  $T_g$  of the precrosslinked systems depend on the curing time and are 2–7°C higher compared to the starting copolymers. With increasing curing time a slight increase in  $T_g$  was observable. The  $T_g$  signal generally broadens with increasing curing time and was not clearly detectable for films cured at 180°C for 24 h.

**Table II** Results of GPC, DSC, and Refractive Index Investigations

Polymer	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	$M_w/M_n$	$T_g$ (°C) <sup>a</sup>	RI <sup>b</sup>
<b>1a</b>	263	496	1.88	120 <sup>c</sup>	1.598
<b>1b</b>	176	415	2.36	97 <sup>d</sup>	1.600
<b>1c</b>	146	392	2.69	87 <sup>d</sup>	1.603
<b>1d</b>	272	559	2.05	82 <sup>d</sup>	1.606

$M_n$  and  $M_w$  values determined by GPC, polystyrene standards, UV detection.

<sup>a</sup> Determined by DSC, heating rate: 10°C/min.

<sup>b</sup> Refractive index at 632.8 nm.

<sup>c</sup> Second heating after rapidly quenching with liquid nitrogen.

<sup>d</sup> First heating.

**Table III**  $T_g$  of Precrosslinked Films After Curing at Various Conditions

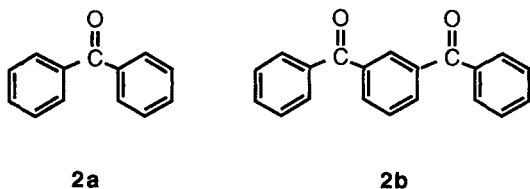
Curing Time (h)	$T_g$ ( $^{\circ}\text{C}$ )			
	<b>1b</b>		<b>1d</b>	
	150 <sup>a</sup>	180 <sup>a</sup>	150 <sup>a</sup>	180 <sup>a</sup>
0	97	97	82	82
3	97	98	82	82
7	98	100	82	85
16	102	105	85	89
24	102	— <sup>b</sup>	88	— <sup>b</sup>

<sup>a</sup> Curing temperature ( $^{\circ}\text{C}$ ).<sup>b</sup> Not clearly detectable.

It is possible to lower the curing temperature and to enhance the curing speed by the addition of a free radical initiator such as AIBN. The crosslinking density can be controlled by the amount of initiator, the curing temperature, and curing time. Copolymer films of **1b–1d** with 2–15 wt % AIBN were cured at 70, 100, and 130 $^{\circ}\text{C}$ . Almost independent of the initiator concentration, no crosslinking occurred at 70 $^{\circ}\text{C}$ . All films were still soluble in chloroform. The copolymers **1b–1d** doped with 4 wt % of AIBN crosslinked at 100 $^{\circ}\text{C}$  became already insoluble in chloroform after curing for 30 min. At a curing temperature of 130 $^{\circ}\text{C}$  the crosslink reaction is faster. The fact that the samples exposed to 70 $^{\circ}\text{C}$  are still not crosslinked reveals that the crosslink reaction with AIBN occurs above  $T_g$  of the doped polymer. DSC measurements on these precrosslinked films did not show well-defined glass transitions.

### Photochemical Precrosslinking

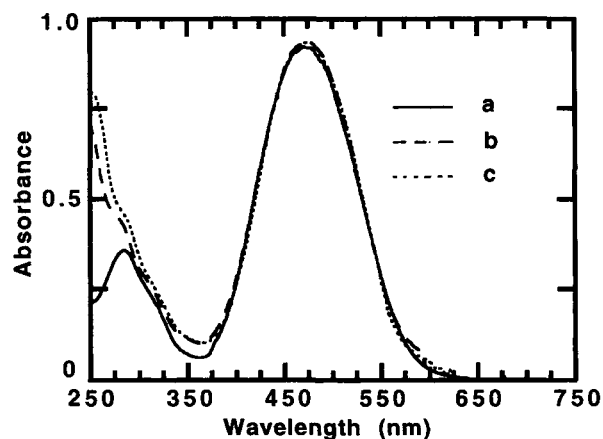
The photoreaction of 2-butenyl methacrylate containing copolymers doped with benzophenone derivatives yield also to crosslinked polymers.<sup>17,18</sup> Two benzophenone photoinitiators **2a** and **2b** (Fig. 3), were used in this study. Benzophenone **2a** represents a monofunctional photoinitiator, whereas **2b**

**Figure 3** Chemical structure of photoinitiators **2a** and **2b**.

is bifunctional. The precrosslinking density can be adjusted by the exposure time and the photoinitiator concentration. Absorption spectra of films of **1b** doped with 10 wt % of **2a** or **2b** on a quartz substrate are shown in Figure 4. The absorption maxima of the copolymers are at 478 nm and the absorption minimum is around 350–375 nm. Due to the small  $n - \pi^*$  absorption of the benzophenone derivatives, the absorbance of doped films around 360 nm is slightly higher compared to the nondoped films. It is interesting to note that optically clear films with no phase separation up to 50 wt % of **2b** could be prepared by spin coating. Films of **1b–1d** doped with 30 wt % **2a** or **2b** were mainly studied. The benzophenone derivatives act as plasticizer and lower  $T_g$  to room temperature. After 7 h irradiation at 30–35 $^{\circ}\text{C}$  (at 366 nm with a 100 W Hg lamp), the films became completely insoluble and nonswellable in chloroform. After this exposure most of the benzophenone photoinitiator had reacted. In some experiments the small amount of nonreacted benzophenone derivative was removed by sublimation prior to corona poling. After the removal of benzophenone **2a**, no specific carbonyl vibration at 1661  $\text{cm}^{-1}$  of IR spectra was observed. In the case of films with the bifunctional benzophenone **2b**, a peak at 1661  $\text{cm}^{-1}$  was still observable. This indicates that the photoinitiator is covalently incorporated on one part of the molecule.

### Corona Poling and SHG Measurements

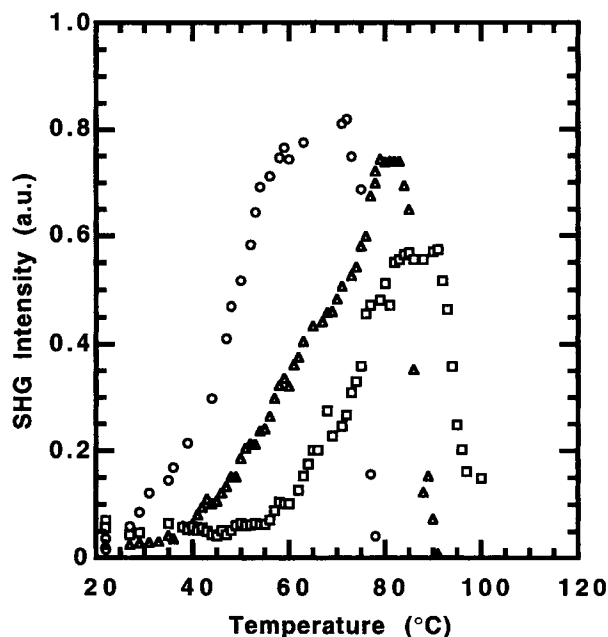
SHG was measured *in situ* during the corona-poling process while heating the samples as film on an ITO

**Figure 4** Absorption spectra of spin-coated films of **1b** on a quartz substrate (film thickness: 1.0–1.1  $\mu\text{m}$ ): (a) without photoinitiator; (b) with 10% w/w **2a**; (c) with 10% w/w **2b**.

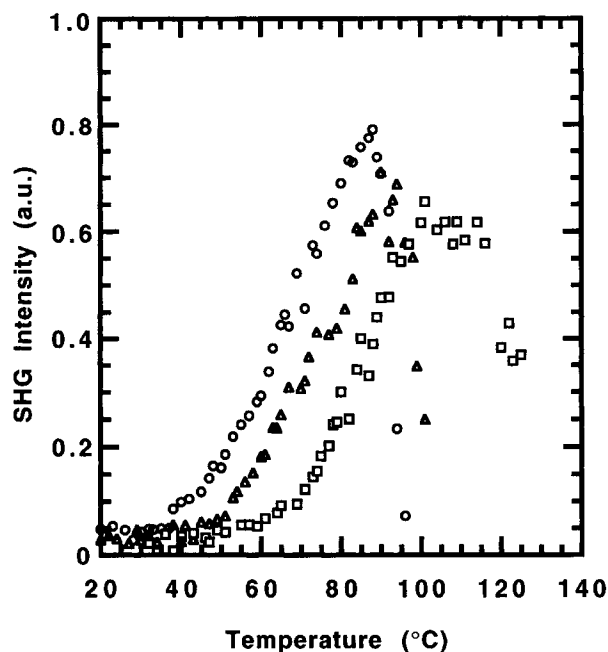
glass substrate between room temperature and 140°C. The corona-poling field was about 4–6 kV/2–3  $\mu$ A. Thermally and photochemically precrosslinked films of **1b–1d** with different crosslinking degree were investigated. The results were compared with nonprecrosslinked copolymers.

The SHG intensity of the noncrosslinked films of copolymers **1a–1d** started to increase at room temperature when the electric field was applied. This means that the NLO chromophores are mobile at room temperature although the  $T_g$  of the copolymers is much higher (82–120°C). The maximum SHG values of the copolymers were found at 98°C for **1a**, 76°C for **1b**, 63°C for **1c**, and 58°C for **1d**. These values are about 15–20°C below  $T_g$  of the copolymers. Above these temperatures, the SHG intensity decreased. This decrease is due to the increased mobility of the side group chromophores even below  $T_g$ . In some cases film damage at the high temperatures occurred under high electric fields. These observations confirm that corona poling is most effective below  $T_g$ .<sup>19</sup>

For thermally precrosslinked copolymers, SHG intensity started to increase at temperatures above room temperature. The onset temperature is dependent on curing temperature, curing time, and content of 2-butenyl side groups. As an example, Figure 5



**Figure 5** Intensity of SHG signal versus temperature for thermally crosslinked films of **1b** (heating rate: 1°C/min); curing temperature is 180°C. Cure time (○) 0 h; (△) 4 h; (□) 16 h.



**Figure 6** Intensity of SHG signal versus temperature for photochemically crosslinked films of **1b** doped with 30 wt % of **2b** (unreacted **2b** was removed by sublimation after exposure): (heating rate: 1°C/min); exposure time (○) 0 h; (△) 4 h; (□) 16 h.

shows the intensity of SHG signals of films of **1b** precrosslinked at 180°C for 4 h and 16 h. The results are compared to a nonprecrosslinked film of **1b**. During poling, the temperature was increased at about 1°/min. The onset temperature of the SHG signal shifts to higher values with longer curing times. The higher crosslink density restricts the mobility and does not allow the alignment of the chromophores below the onset temperature. The maximum SHG intensity for these systems seems to drop with increasing precrosslinking. This can be attributed to the restricted mobility of the chromophores in a higher crosslinked network structure. Further increase in temperature results in a decay of the SHG intensity and damage of the film.

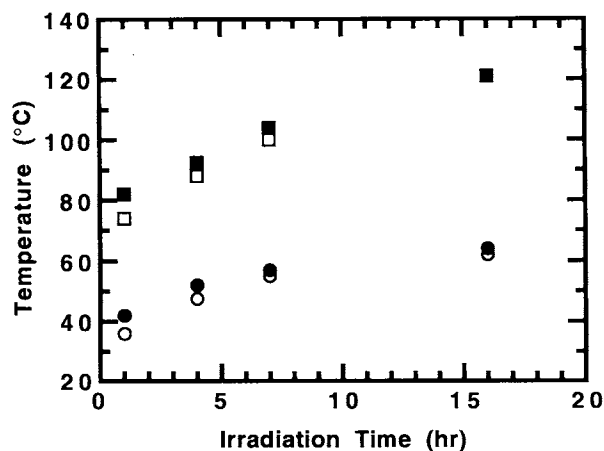
Similar experiments were performed with photochemically precrosslinked films of **1b–1d** doped with 30 wt % **2b**. UV light at a wavelength of 366 nm and an intensity of 3–5 mW/cm<sup>2</sup> was used for the photoreaction. It is possible to remove unreacted **2b** from the film at 95°C for 1 h under a reduced pressure. The results of SHG measurements are shown in Figure 6. The onset temperatures of irradiated films are between 50–65°C and increase with irradiation time. If benzophenone, which acts

as plasticizer, is not removed, the SHG onset temperatures are about 15–20°C lower and the temperatures of maximum SHG intensity are 20–40°C lower.

The onset temperatures and the temperatures of maximum SHG signal intensity for copolymers **1b** and **1d** are plotted in Figure 7 as a function of the irradiation time. In these experiments 30 wt % of **2b** were used and the unreacted amount was removed after exposure. The onset temperatures as well as the maximum temperatures for the SHG signal increased with increasing irradiation time. The lower  $T_g$  of **1d** compared to **1b** is also reflected, particularly at short irradiation times.

### Alignment Stability

Thermally and photochemically precrosslinked films were corona-poled at a few degrees below the determined temperature for the maximum SHG intensity and slowly cooled to room temperature in the presence of the corona field. A film of **1b** cured at 180°C for 7 h was used as an example for a thermally precrosslinked case. As a photochemically precrosslinked film, **1b** with 30 wt % of **2b** irradiated for 7 h was used. For both samples, the SHG intensities did not change after poling for more than 4 weeks at room temperature. In comparison, the SHG intensity of noncrosslinked films decayed to half of their original value after 2 weeks. The alignment stability of the NLO chromophore is related to the



**Figure 7** Onset temperature of SHG signal for photo-crosslinked films of (●) **1b** and (○) **1d** and temperature of maximum SHG signal for photocrosslinked film of (■) **1b** and (□) **1d** as a function of exposure time. Film thickness was 1.5–2.0  $\mu\text{m}$  (unreacted **2b** was removed by sublimation after exposure).

determined onset temperature of SHG intensity. The differences of the  $T_g$  of the noncrosslinked and crosslinked copolymers that are within 10°C, cannot solely explain the stability difference. This suggests that the formed network structure and the local environment of the chromophores play an important factor for the alignment stability.

### CONCLUSIONS

Noncentrosymmetrically aligned copolymers with 4'-dialkylamino-4-nitro-azobenzene side groups as a NLO chromophore and a 2-butenyl side group as a crosslinkable unit display SHG. In order to stabilize the SHG signal, these polymers can be precrosslinked prior to corona-poling thermally at temperatures between 150 and 180°C, or around 100°C with the aid of a free radical initiator and photochemically by UV irradiation if benzophenone derivatives are added. The  $T_g$  are a function of the copolymer content of 2-butenyl methacrylate and the crosslink density.

Investigations of the SHG signal intensity during the corona-poling process revealed that the signal intensity and stability can be optimized if the copolymers are precrosslinked prior to the corona-poling process. NLO chromophores are mobile at room temperature in the noncrosslinked films, although the  $T_g$  is between 82 and 120°C. Nonlinear optical properties were measured by the Mach-Zehnder interferometric method. The  $d_{13}$  value for copolymer **1b** without precrosslinking was 5 pm/V at 633 nm. The second order EO coefficient is dependent on the poling and crosslinking conditions. Because of the restricted mobility of the chromophore in higher crosslinked samples, the  $d_{13}$  values are lower. The onset temperature of the SHG signal shifts to higher values for films with increased precrosslink density. The higher crosslink density restricts the mobility and does not allow the alignment of the chromophores below this onset temperature. Films poled at optimized precrosslinking and poling temperature showed no decay of the initial SHG intensity after storing for 4 weeks at room temperature.

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