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Novel Photoactivatable Nonlinear Optical Polymers: Poly[((4-azidophenyl)carboxy)ethyl methacrylate]

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ABSTRACT: A methacrylate polymer carrying azidobenzoate groups was prepared, and its nonlinear optical properties were studied. It was found that poly[(4-azidophenyl)carboxy)ethyl methacrylate] film irradiated by UV light under an electric field showed larger second harmonic generation (SHG) than one without irradiation. This is the first photoactivatable nonlinear optical polymer. The increase of SHG by irradiation was explained by the increase of the β value because a photoreaction changes the azido groups to amino and azo groups.

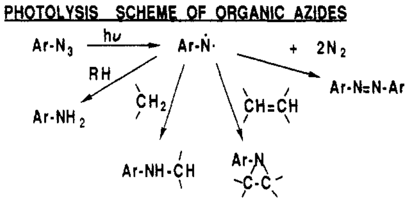
Introduction

Organic materials are known to possess much larger nonlinear optical coefficients and faster response times than inorganic ones. Polymers are generally more easily processed than organic materials such as single crystals and Langmuir–Blodgett films. Glassy polymers are widely used in optics industry owing to their uniform and amorphous nature, while crystalline polymers are nonuniform and less transparent due to scattering. It is known that some amorphous polar polymers, when poled under a high voltage, possess optical quality comparable to that of materials currently used in electrooptic devices such as $LiNbO_3$.[1] Therefore, a glassy and polar polymer is superior as a second-order nonlinear optical material.

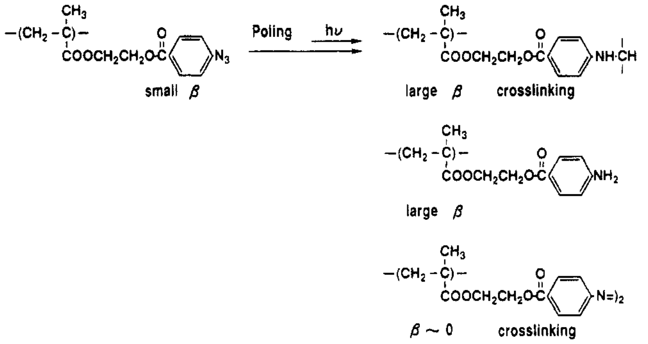
Recently, several nonlinear optical polymers with organic photosensitive molecules have been reported, which are susceptible to photoreactions such as photobleaching of chromophore-doped polymers[2] and photo-cross-linking of a polymer having cinnamoyl groups.[3] They possess good processability for patterning as well as good nonlinear optical properties. By using direct beam drawing or photomask patterning techniques, a waveguide with a desired pattern can easily be prepared from films of these polymers. In the case of a photobleachable polymer, second-harmonic generation (SHG) activity of the irradiated part is decreased, while that of unirradiated part remains unchanged, which leads to a positive type NLO materials. By using photo-cross-linking, the irradiated part is expected to exhibit slower temporal decay leading to a negative type NLO material. However, the nonlinearity of these materials is not essentially raised by UV irradiation.

It is known that an azidobenzoate group can be converted to primary, secondary, and tertiary aminobenzoate and azobenzoate groups by hydrogen abstraction, coupling, and insertion into double bonds, when irradiated with light of an appropriate wavelength, 260–380 nm, as shown in Scheme I.[4] When an azido group changes to an amino or imino group by UV irradiation, the reactant should have a larger β value. If a polymer with an azidobenzoate unit forms a cross-linked structure, as shown in Scheme II, the decay of the irradiated part is slowed down. Therefore, a film of this type of polymer is expected to assume a larger nonlinearity and an increased stability of chromophore alignment when photoirradiated under an electric field.

Scheme I



Scheme II



Here we report the preparation of poly[((4-azidophenyl)carboxy)ethyl methacrylate] and the photoreaction behavior and optical and nonlinear optical properties of a film of this polymer.

Experimental Section

((4-Azidophenyl)carboxy)ethyl Methacrylate, AZ (Scheme III). 4-Aminobenzoic acid (0.050 mol) in aqueous HCl solution (concentrated HCl/water = 20 mL/200 mL) was reacted with aqueous sodium nitrite (0.055 mol) at −10 to 0 °C for 15 min, followed by aqueous sodium azide (0.060 mol) at room temperature for 1 h, to yield 4-azidobenzoic acid (yield 84%). 4-Azidobenzoic acid (0.04 mol) was converted to 4-azidobenzoyl chloride by reacting with excess thionyl chloride (150 mL). After unreacted thionyl chloride was removed by evaporation under reduced pressure, 2-hydroxyethyl methacrylate was added to an acetonitrile solution of 4-azidobenzoyl chloride in the presence of triethylamine. ((4-Azidophenyl)carboxy)ethyl methacrylate was obtained by the reaction at reflux temperature for a few hours (yield 82% of pale yellow oil).

((4-(*N,N*-Dimethylamino)phenyl)carboxy)ethyl Methacrylate, DA. (*N,N*-Dimethylamino)benzoyl chloride was ob-

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Scheme III

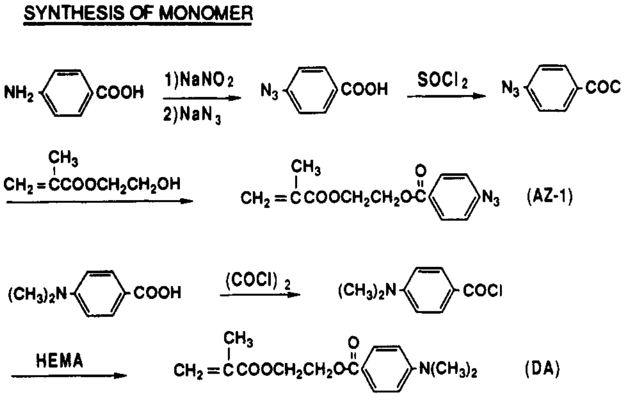

Table I
Polymerization of the 4-Substituted (Phenylcarboxy)ethyl Methacrylates[a]

code	yield, %	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
AZ-1	38	39 000	110 000	2.8
DA	42	20 000	34 000	1.7

[a] Conditions: 1 mol % AIBN on monomer, 10 wt % monomer on solvent, THF, 60 °C, 6 h.

tained by the reaction of (*N,N*-dimethylamino)benzoic acid (0.04 mol) with excess oxalyl chloride (150 mL). (*N,N*-Dimethylamino)benzoyl chloride was reacted with 2-hydroxyethyl methacrylate (0.04 mol) in the presence of triethylamine in acetonitrile to yield (((*N,N*-dimethylamino)phenyl)carboxy)ethyl methacrylate as above. The crude product was purified by recrystallization in an ethanol/methanol mixture to obtain a white powder (yield 68%). Polymerizations of methacrylate monomers were conducted in a glass ampule under a dry nitrogen atmosphere using AIBN as an initiator. The polymerization condition was shown in Table I. The structures of the monomer and polymer were identified by ^{1}H NMR (JOEL FX-200) spectra. ^{1}H NMR (in DMSO-d_6): AZ δ 1.92 (s, 3 H, $CH_2{=}C(C\mathit{H}_3)$–), 4.50 (m, 4 H, –$COOC\mathit{H}_2C\mathit{H}_2OCO$—Ar), 5.63 (s, 1 H, trans $C\mathit{H}_2{=}$), 6.06 (s, 1 H, cis $C\mathit{H}_2{=}$), 7.18, 7.98 (dd, 4 H, Ph, J = 8.7 Hz); DA δ 1.90 (s, 3 H, $CH_2{=}C(C\mathit{H}_3)$–), 3.00 (s, 6 H, –$PhN(C\mathit{H}_3)_2$), 4.44 (s, 4 H, –$COOC\mathit{H}_2CH_2OCO$—Ar), 5.63 (s, 1 H, trans $C\mathit{H}_2{=}$), 6.05 (s, 1 H, cis $C\mathit{H}_2{=}$), 6.71, 7.87 (dd, 4 H, Ph, J = 9.3 Hz). UV–visible absorption spectra of the compounds were measured on a Jasco Ubest-30 spectrometer in methanol. The β values were determined by the MOPAC PM3 program. The molecular weights of the polymers were determined by GPC based on polystyrene standards. The glass transition temperatures of the polymers were measured by DSC (Rigaku TAS-200).

Thin polymer films on ITO or a fused-silica glass plate were prepared by spin coating. After drying in a vacuum oven at 50 °C, a high voltage was applied to the films by the corona poling method (~50 MV/cm). Some polymer films were irradiated for 15 min using a high-pressure mercury lamp (Sen Tokusyu Kogen HB-450, HL-450, 450 W) during the application of the electric field. The refractive indices of the polymer were measured by the *m*-line method.[5] The SHG characteristics were measured after irradiation by a pulsed neodymium-YAG laser (Quantel, 1.064 μm, 10 ns/pulse, 0.8 ± 0.2 mJ/pulse, 10 Hz) using the Maker fringe method,[6,7] according to the schematic setup for SHG measurement in Figure 1.

Results and Discussion

It is known that azidobenzoate is converted to aminobenzoate and azobenzoate groups by UV irradiation. The β values of 4-amino-, 4-(*N,N*-dimethylamino)-, 4-azido-, and 4-azobenzoic acids were determined by the MOPAC PM3 program as 5.83, 6.457, 0.787, and 0.648 × 10^{-30} esu. Therefore, it was expected that the β value could be increased by converting an azido group to an amino group by photoirradiation, assuming that monomeric β values are equal to the polymeric ones and frequency dispersion of β is ignored.

((4-Azidophenyl)carboxy)ethyl methacrylate (AZ) and ((4-(*N,N*-dimethylamino)phenyl)carboxy)ethyl methacrylate (DA) were polymerized by the radical initiator. The polymers were abbreviated as AZ-1 and DA polymers, respectively. The yields and molecular weights of the polymers are listed in Table I. The ^{1}H NMR spectra of the AZ monomer and AZ-1 polymer are shown in Figure 2. The aromatic protons of the polymer have almost the same chemical shifts as those of the monomer. Therefore, the AZ was polymerized without decomposition of an azido group by the radical initiator.

The IR spectra of the AZ-1 polymer film prepared on KBr were measured before and after UV irradiation. The peak at 2150 cm^{-1} arisen from the $-N_3$ unit had almost disappeared after irradiation by the light for 15 min, while other signal changes in the IR spectra were negligible, as shown in Figure 3a,c. Besides IR spectral changes, the film showed a new absorption in the Raman spectrum at 1578 cm^{-1}, which is attributed to $-N{=}N-$ stretching of the azobenzoate group. The AZ-1 polymer after UV irradiation was abbreviated as the AZ-2 polymer. On the other hand, in comparing Figure 3a,b, it is found that corona poling of the AZ-1 polymer led only to a small spectral change. The DA polymer had almost the same IR spectrum as the AZ-1 polymer except for the absence of the azido absorption at 2150 cm^{-1} (Figure 3d).

The poling apparatus equipped with a high-pressure mercury lamp is shown in Figure 4. The poling and irradiation of the polymer film is shown schematically in Figure 5. The polymer films were first heated to 60 (for AZ-1 polymer) or 70 °C (for DA polymer), and an electric field (4.5 kV) was applied for 25 min. Some films were irradiated under high voltage by a UV lamp for 15 min. The poled polymer was cooled to room temperature before switching off the electric field. Figure 6a shows the change in the UV–visible spectrum of the polymer film by poling in the absence of UV irradiation. The absorption peak at 340 nm was decreased by poling. This spectral change can be attributed to the alignment of azidobenzoate units but not to their decomposition, because the azido group in the film was unchanged by only poling, as was shown by the IR spectrum in Figure 3b. Therefore, the order parameter was determined to be 0.142, which is the degree of alignment of the benzoate unit, $\Phi = 1 - (A_{\perp}/A_0)$, where $A_{\perp}$ is the absorbance perpendicular to the poling direction of a poled film, and A_0 is the absorbance of an unpoled film.[8]

As shown in Figure 6b, the polymer film (AZ-2) after poling under UV irradiation exhibited new absorptions around 300 and 400 nm, which are assigned to aminobenzoate and azobenzoate units,[9] respectively. The absorption of the azidobenzoate group at 340 nm became only a shoulder of the large peak of 300 nm, indicating the decrease of azido units in the polymer, which is consistent with the results of IR measurement. The order parameters of the AZ-2 polymer and DA polymer could not be determined by the measurement of UV–visible spectra, because the absorption of the aminobenzoate unit overlapped that of the ITO glass, although the UV–visible spectrum of the DA polymer film was not shown.

The second-order nonlinear optical *d* coefficient can be estimated using the oriented gas model[10] and the order parameter as follows:

$$d_{33} = N\beta f(2\omega)f(\omega)^2\langle\cos^3\theta\rangle/2 \qquad (1)$$

where N is chromophore density, 30×10^{20} units/cm^3, and f is the Lorentz local field factor, $(n^2 + 2)/3$; i.e., $f(2\omega) = 1.522$ and $f(\omega) = 1.493$ determined from the refractive indices in Table II. Here θ is the angle between the dipole

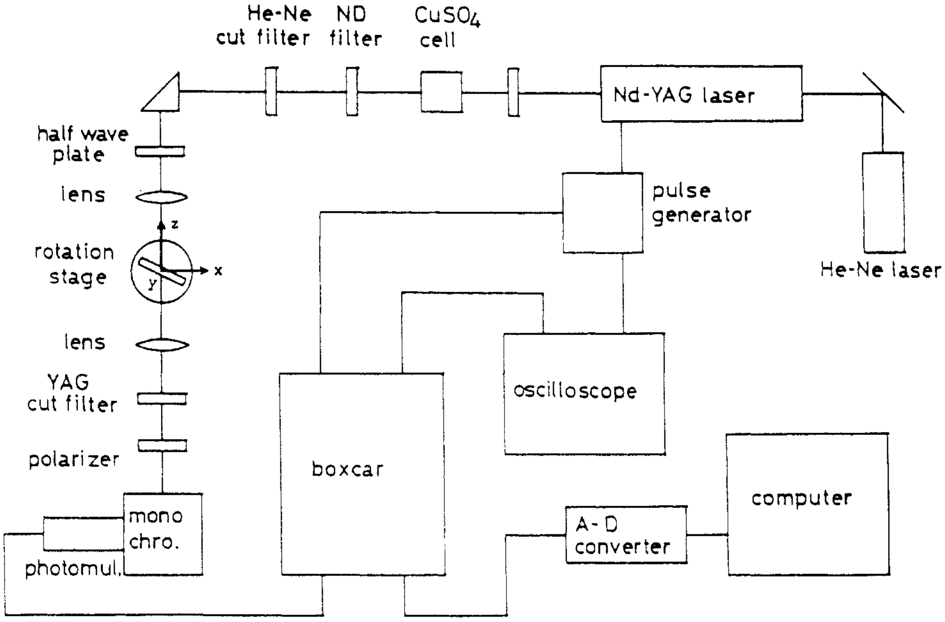

Figure 1. Schematic experiment setup for SHG measurement.

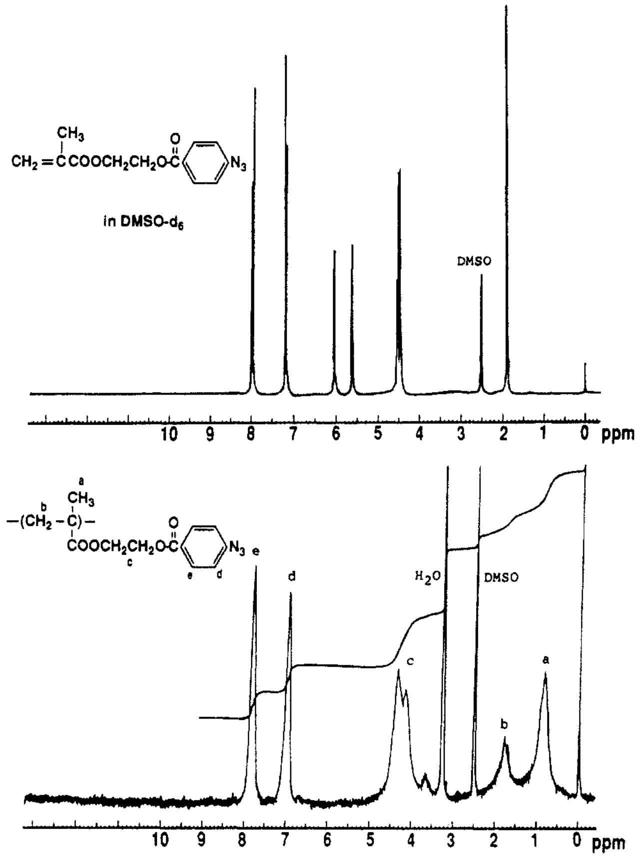

Figure 2. ^{1}H NMR spectra of ((4-azidophenyl)carboxy)ethyl methacrylate (AZ) and the polymer (AZ-1).

moments of each chromophore molecule and the poling direction, and $\langle \cos^2 \theta \rangle$ is obtained from $\Phi = (3\langle \cos^2 \theta \rangle - 1)/2$.[8] The value of $\langle \cos^3 \theta \rangle$ was determined to be 0.293 assuming a Langevin function. The β of 4-azidobenzoic acid, 0.787×10^{-30} esu, was used for the AZ-1 polymer. By substitution of these values into the eq 1, d_{33} of the AZ-1 polymer was calculated to be 0.49 pm/V. Similarly, the d_{33} value of the DA polymer film was 4.0 pm/V assuming that the order parameter of the DA polymer is equal to that of the AZ-1 polymer. Since the order parameter depends on the dipole moment, the real d_{33} of the DA polymer was expected to be larger than that evaluated by the oriented gas model.

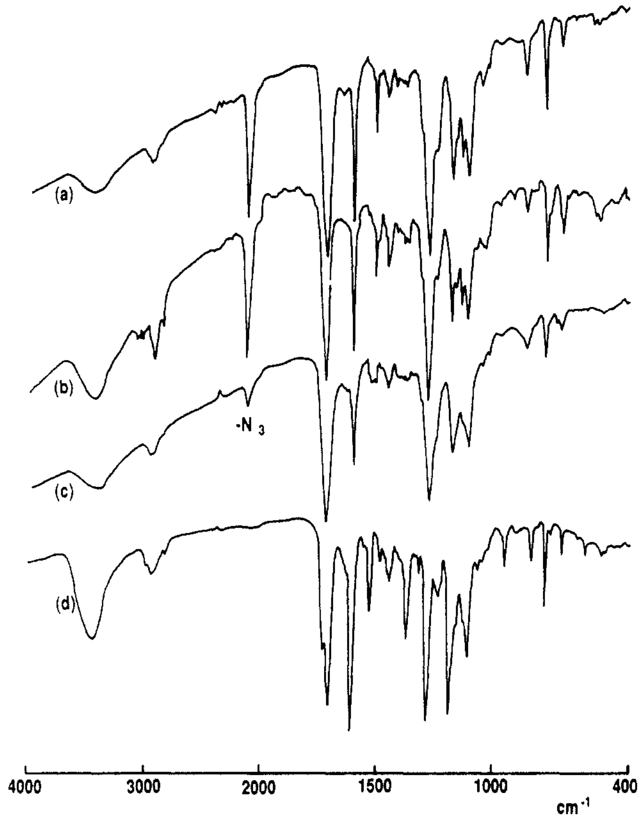

Figure 3. IR absorption spectra of the azido- (AZ-1, AZ-2) and (((*N,N*-dimethylamino)phenyl)carboxy)ethyl methacrylate (DA) polymers: (a) AZ-1 polymer film on KBr tablet without poling; (b) AZ-1 polymer powder in KBr tablet after pliing; (c) AZ-2 polymer film on KBr tablet without poling; (d) DA polymer powder in KBr tablet.

The nonlinear optical *d* coefficients were measured from the Maker fringe pattern using a neodymium-YAG laser as the incident light. Figures 1 and 7a show the schematic setup for SHG measurement. The *d* coefficients obtained are listed in Table III. The d_{33} of AZ-1, AZ-2, and DA were 0.31, 3.6, and 7.2 pm/V, respectively. The AZ-2 polymer exhibited a d_{33} value about 10 times those for AZ-1 s. This result confirmed the previous expectation that azidobenzoate units were converted to units similar to aminobenzoate having larger β values upon UV irradiation. Therefore, the polymer can be described as a

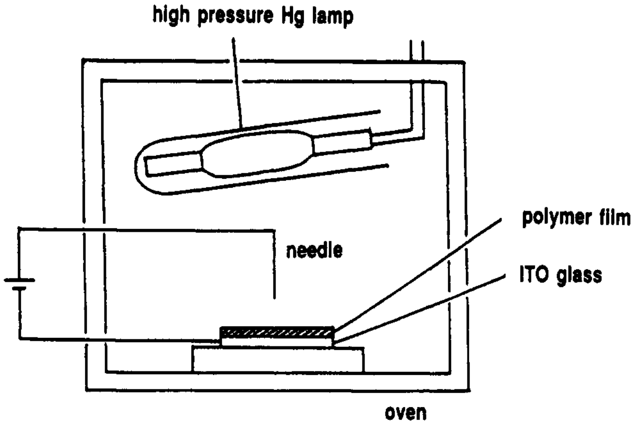

Figure 4. Poling apparatus equipped with high-pressure mercury lamp.

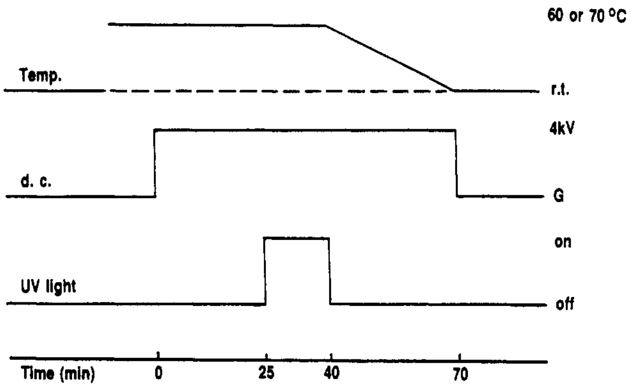

Figure 5. Schematic diagram of the poling process.

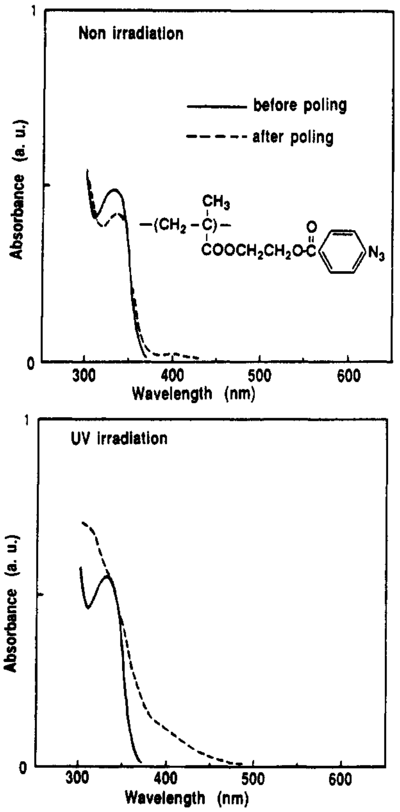

Figure 6. UV-visible absorption spectra before and after poling process: (a, top) without UV irradiation (AZ-1); (b, bottom) with UV irradiation (AZ-2).

Table II
Refractive Indices and T_g of the Polymers

code	refractive indices 1064 nm	632.8 nm	532 nm	T_g, °C
AZ-1	1.573	1.593	1.605	54
AZ-2	1.574	1.592	1.602	78
DA	1.570	1.592	1.613	65

Table III
d Coefficients of the Polymers

code	d_{33}, pm/V	d_{31}, pm/V
AZ-1	0.31	0.14
AZ-2	3.6	0.95
DA	7.2	2.8

photoactivatable nonlinear optical polymer. The *d* value of the AZ-2 polymer was half that of DA. The *d* value difference of the two polymer films can indicate that (1) all azido groups in the film did not convert to amino groups but partially to azobenzoate groups and (2) the DA film possessed a larger order parameter because its dipole moment, 5.9 D, was larger than the 1.80 D for AZ-1 (as calculated by MOPAC). Therefore, the observed *d* value of the AZ-2 polymer is reasonable.

The cross-linking reaction on photolysis was indicated by the rise of T_g of the film by 24 deg by irradiation (Table II) and also by its insolubility. However, the AZ-2 polymer swelled 157 wt % in chloroform and 480 wt % in dimethyl sulfoxide, indicating that the cross-linking is insufficient to prevent the movement of the side chains.

The decay of the relative SH wave intensities of both the polymers poled in the presence and absence of UV irradiation is plotted in Figure 8. Both polymers exhibited a decrease in the intensity with time, which is similar to other un-cross-linked polymers previously reported, in spite of the cross-linking. Apparently, our attempt to fix each chromophore using two chemical bonds formed by photoreaction under poling resulted in insufficient cross-linking and/or cross-linking mainly between polymer backbone chains by way of dehydrogenation of nitrene from the polymer main chain. No complete prevention of thermal relaxation of chromophore alignment was reported using cross-linking of the polymer,[11,12] except for the thermal cross-linking of epoxy resins.[13,14]

A possibility of patterning on a waveguide was examined using the photoactivatable nonlinear optical AZ-1 polymer film. A photomask was set on the film before photoirradiation during poling. The polymer film was irradiated by UV light through the photomask under an electric field. A needle electrode was set 8 mm above the film as shown in Figure 7b. The film plate was held on the stage of the SHG measurement system with an incline of about 60°. The SH wave intensities were measured by irradiating the YAG laser while moving the film plate at right angles to the incident beam. The incident beam diameter was about 100 μm. The unmasked area exhibited a higher SH wave intensity than the masked area, as shown in Figure 9. The needle electrode was at the right side of the figure. The SH wave intensity decreased with an increase of the distance from the needle. In the area with the pattern space of 200 μm, a good resolution was obtained. On the other hand, when the space became 100 μm, an overlapped profile was observed due to the large beam diameter of 100 μm. It is expected that a higher resolution can be obtained by using a narrower beam.

The photolysis of azido groups may generate gaseous nitrogen; however, no void due to gas generation was observed in the polymer film by microscopic examination. The AZ-1 and AZ-2 polymers showed almost the same refractive indices at any wavelength from 532 to 1064 nm. These properties are advantageous to photofabrication of optical waveguides, such as a periodically domain inverted structure, owing to the low scattering between the domains.

In a preliminary experiment to measure propagation loss using the prism sliding method,[15] almost the same

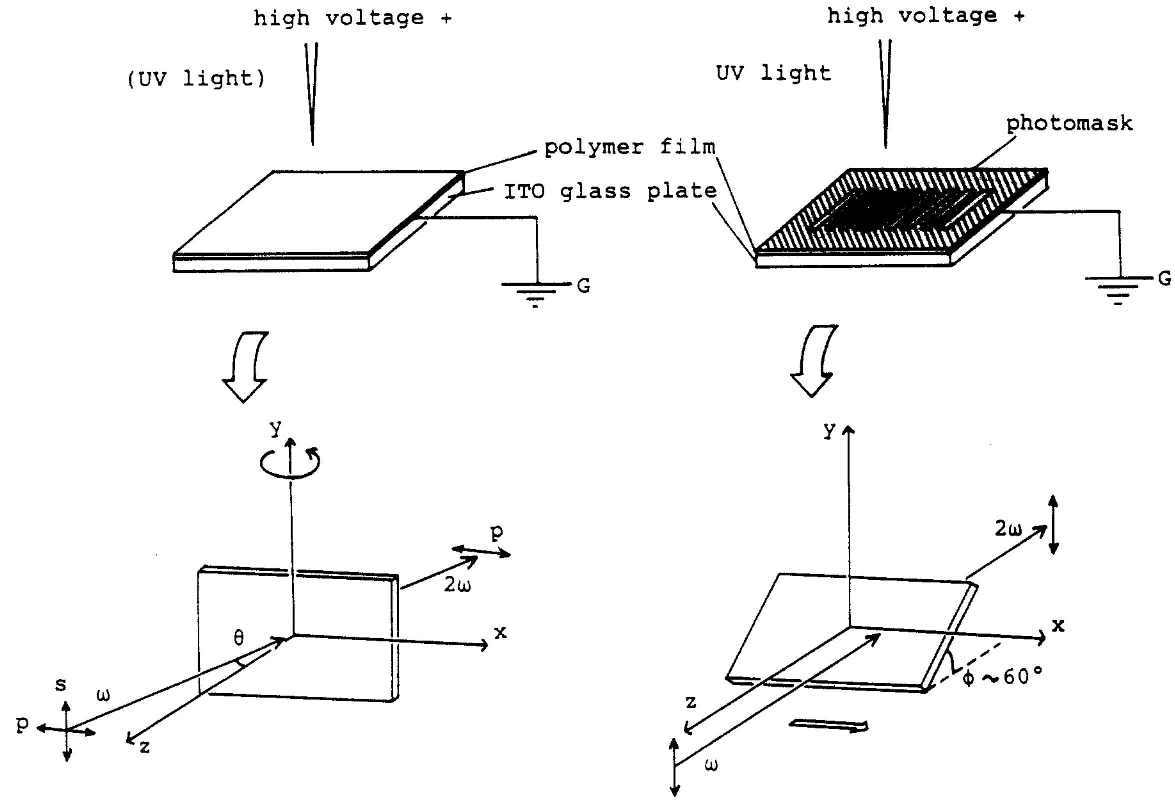

Figure 7. Schematic setup for SHG measurement: (a, left) maker fringe measurement; (b, right) photomask patterning measurement.

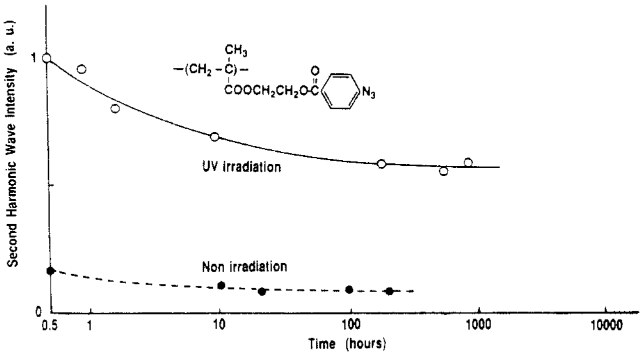

Figure 8. Temporal decay curve of SH wave intensities.

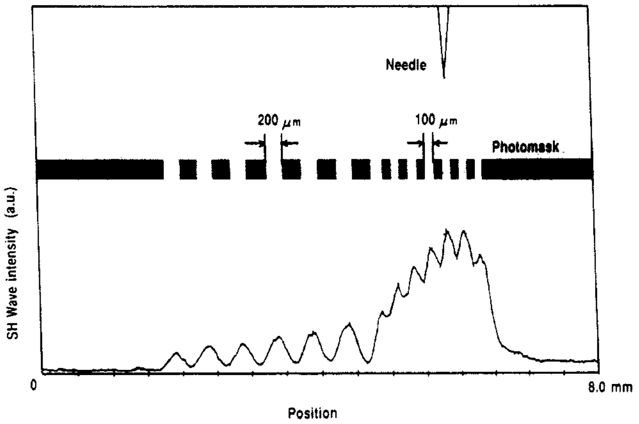

Figure 9. SH wave intensity in the polymer film using photomask.

values of about 5 dB/cm at 632.8 nm were obtained for both UV-irradiated and nonirradiated films.

In conclusion, it was found that the methacrylate polymer carrying an azidobenzoate group exhibited an increase in nonlinear optical *d* coefficients on irradiation by a high-pressure mercury lamp under poling. The increase of the *d* value was explained by the change of an azido group to an amino group having a larger β value. This type of a polymer can be described as a photoactivatable nonlinear optical polymer. Using the photoactivatable nonlinear optical polymer, photomask patterning was accomplished.

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