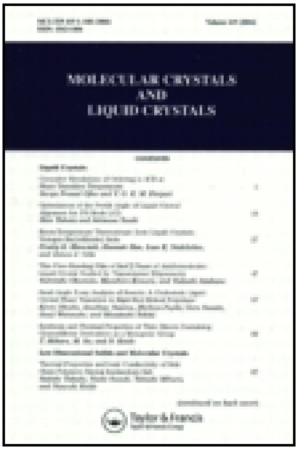

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Phase-Matched Second Harmonic Generations in Poled Polymer Films Based on Poly (methyl methacrylate) Containing a p-Aminophenyl-cyclobutenedione Moiety as the Side Chains

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PHASE-MATCHED SECOND HARMONIC GENERATIONS IN POLED POLYMER FILMS BASED ON POLY (METHYL METHACRYLATE) CONTAINING A p-AMINOPHENYL-CYCLOBUTENEDIONE MOIETY AS THE SIDE CHAINS

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Abstract Poled polymer films containing a nonlinear optical active moiety (cyclobutenedione derivative) as the side chains were prepared and applied to frequency doublings in guided-wave structures. A (p-aminophenyl) cyclobutenedione containing monomer, 1-{4-[N-(2-methacryloyloxyethyl)-N-methyl-amino]-phenyl}-2-methylamino-cyclobutene -3,4-dione [CD1-MA] was newly synthesized. For less than 20 wt% concentration, amorphous copolymers of CD1-MA with methyl methacrylate showed the glass transition at around 125°C. The copolymers were crystalline at higher dye concentrations. The d_{33} value of the poled polymer film with 10 wt% of CD1-MA concentration was estimated as 8.1 pm·V^{-1} by the Maker fringe method. Second harmonic waves of Nd:YAG laser (1064 nm) were observed in three-layer optical waveguides (air / poled polymer / pyrex glass) for the collinear type and the Cerenkov type phase matchings.

INTRODUCTION

Recently, much more attentions are focused on the nonlinear optical (NLO) properties of organic materials.[1-3] Second-order NLO properties of organic molecules are characterized by molecular hyperpolazability β_m and the most of the organic molecules with high β_m values so far reported belonged to a series of aromatic compounds with electron donating and electron accepting groups in the suitable positions.

We have demonstrated that a series of phenyl-cyclobutenedione derivatives with electron donating groups in the appropriate positions showed very high β_m values.[4-6] For example, a derivative of N,N-dimethyl -

aniline with a 1-cyclobutene-3,4-dione unit at the para-position showed about 4 times as large β_m values as that of N,N-dimethyl-p-nitroaniline. This result should be attributed to the large electron accepting ability of cyclobutenedione rings. Moreover, considering other unique features, that is, cut-off wavelength are shorter than their counterparts with nitro-substituent, modifications of chemical structures are easier because cyclobutenedione unit is divalent, and so on, the cyclobutenedione derivatives are one of the most promising candidates for application to NLO materials synthesized.

In addition, noncentrosymmetrically arrangements of NLO molecules are indispensable particularly for application of second-order NLO devices. Among many system to arrange NLO molecules noncentrosymmetrically[1-3,7], poled polymers [8,9] are the most fascinating systems because guided-wave structures made of poled polymer systems have some advantages for the application of optical frequency doublers or signal processors.[1,10,11]

For the initial period of the studies on the poled polymer systems, "guest" NLO active molecules were simply dispersed or, in other word, doped in "host" polymeric materials. We have succeeded to observe second harmonic (SH) wave of Nd:YAG laser (1064 nm), which emitted from slab type poled polymer (poly methyl methacrylate : PMMA) dispersed with a phenyl-cyclobutenedione derivatives.[12] However, generally the guest-host type systems have some limitations on the dye-doping concentrations and the long term stabilities, and these phenomena were also found in our system.

More advanced poled polymer systems were investigated.[1,13] These material systems were characterized with regards that the dye molecules were chemically bonded to the base materials. This is not only a superior solution for the phase separation of the dye molecules from the "host" materials, but also a effective approach to afford the long-term stabilities in the polymer systems.

In this paper, a new methacrylate type monomer having p-amino-phenyl-cyclobutenedione unit, 1-[4-(N-methacroyloxyaminoethyl-N-ethyl) aminophenyl]-2-methylamino-cyclobutene-3,4-dione [CD1-MA] , was newly synthesized and copolymerized with methyl methacrylate. The NLO properties of the copolymers afforded by the corona-poling treatments were discussed, and phase matched SH waves from the poled polymer waveguides were investigated.

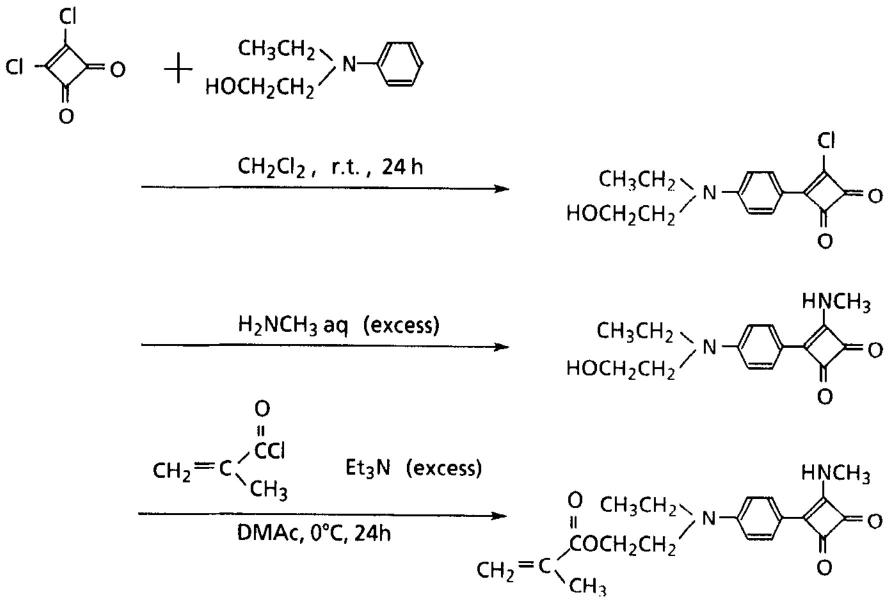
MATERIALS FOR POLED POLYMERS

The polymerizable dye used in the present work, 1-{4-[N-(2-methacryloyloxylethyl)-N-ethylaminol]-pheny}-2-methylamino-cylobutene-3,4-dione [CD1-MA] was synthesized according to the three step reactions as shown in scheme 1. The chemical structure was confirmed by means of IR spectroscopy, NMR spectroscopy and elemental analysis.

Another dye compound containing p-aminophenyl-cyclobutenedione unit for the guest molecule in poly (methyl Methacrylate) host material, 1-{4-[N-(2-methoxylethyl)-N-methylamino]-phenyl}-2-(N-2-hydroxybutyl)amino-cyclobutene-3,4-dione [CD2] as shown in Scheme 2 was obtained by the condensation reaction of (R)-(-)-2-amino-1-butanol with corresponding p-aminophenyl-cyclobutenedione containing chloride. Among the candidates, the compound was chosen in the viewpoint from the dispersibility in poly (methyl methacrylate) [PMMA] . Molecular hyperpolarlizability β_m of CD2, determined by the solvatochromic method, was about 4 times as large as that of N,N-dimethyl-p-nitroaniline. The PMMA used in the guest-host systems commercially available one from Wako Pure Chemical Inc. (η_{inh}=0.5 in N,N-dimethylacetamide).

The copolymers of [CD1-MA] with methyl methacylate (MMA) were synthesized in dimethylsulfoxide at 70 °C for 4 hours in the presence of azobis (isobutylonitrile) as the radical initiating reagent (1 wt% of total monomer was used). Inducing ratio of cyclobutenedione (CD) unit in the polymer were adjusted by controlling the molecular ratio of [CD1-MA] to MMA in feed.

Table 1 is summarizing the results of the polymer synthesis together with the thermal properties of the copolymers. The concentration of p-aminophenyl-cyclobutenedione unit in the copolymers were in good agreements with the corresponding expected values calculated from the feeding ratio. The copolymers had amorphous nature when the concentration of CD1-MA unit were lower than 20 wt%, whereas they were crystalline at higher dye concentrations. These results suggest that the interaction between the dye moiety were innegligible at high dye concentrations. The amorphous copolymers had their glass transition temperatures in the range of 100-130 °C.



[CD1-MA]

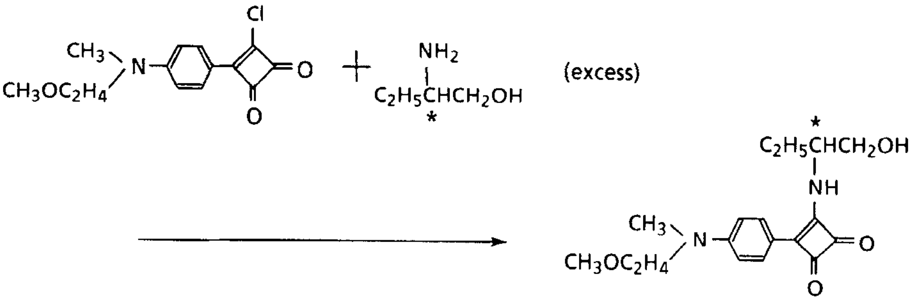
over all yield 12 %

m.p. 157-159 °C

λ_{max} = 400.6 nm in DMAc

($\varepsilon = 4.0 \times 10^5$)

Scheme 1



[CD2-MA]

m.p. 136-136.5 °C

Scheme 2

TABLE I Synthesis and thermal properties of poly (CD1-MA-co-MMA).

CD1-MA concentration in feed (wt%)	Contents of CD1 unit calc.[a] (wt%)	Contents of CD1 unit found[b] (wt%)	η_{inh}[c] (dl/g)	Glass transition temperature[d] (°C)	Melting temperature[d] (°C)
1	0.66	0.53	1.10	125	
5	3.3	2.8	0.87	130	
10	6.6	6.0	0.87	130	
15	10	10.6	0.74	120	
20	13.3	11.9	0.79	140	
50	33.1	35.8	0.34		151
100	66.4		0.26		179
(dope-type)[e]	6.8		0.50[f]	105	

a) Formular weight of CD unit was estimated to be 227.24 ($C_{13}H_{11}N_2O_2$)*.

b) Determined from absorbance of polymer solutions in N,N-dimethyl acetamide.

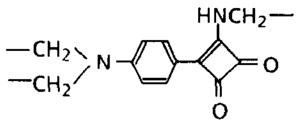
c) Measured in N,N-dimethyl acetamide at a concentration of 0.5 g/dl at 30 °C.

d) Determined by differential scanning calorimetry.

e) 10 wt% of CD2 was used.

f) Inherent viscosity of PMMA used.

*



NONLINEAR OPTICAL PROPERTIES OF POLYMER FILMS

Preparation of copolymer films

Thin films of the amorphous copolymers having uniform thickness were fabricated by means of the spin-coating method from solutions in 4-methyl-2-pentanone on well-cleaned pyrex glass substrates of 1mm thickness. The thin films thus prepared were dried in a oven at 80 °C for 24 hours or longer. Figure 1 shows the absorption spectra of the spin-coated films of the copolymers, poly (CD1-MA-co-MMA). The smooth spectra showing the linear relationship between absorbance per unit thickness and CD1 dye concentrations suggest the uniform constitutions of the copolymers. Because the absorption in the wavelength range longer than 470 nm are negligible, the copolymers can be applied to frequency doubling devices for blue lights.

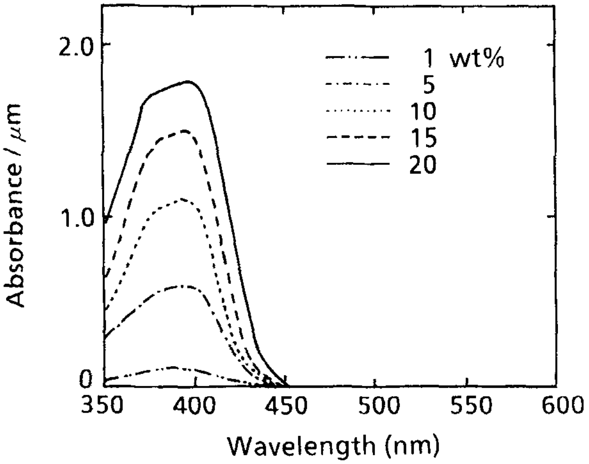
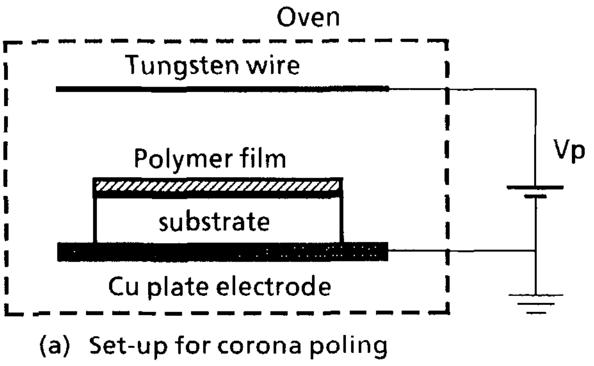


FIGURE 1 Absorption spectra of copolymer thin films with different CD1-MA concentrations. Vertical axe shows absorbance per unit thickness (μm).

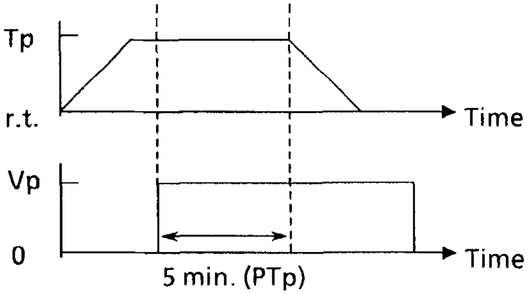
Orientational control of CD1 moiety

The uniaxial alignments of the dye-moiety in the copolymer films were performed by corona-poling method illustrated in Figure 2. The typical poling procedure was as follows. The copolymer thin film on the substrate was placed on a copper plate electrode and a DC electric voltage (Vp) of 5 kV on the distance of 1 cm was applied through a tungsten wire fixed above the sample for 5 minutes (PTp) at a temperature (Tp) of 130 °C. Then the samples were gradually cooled down to the room temperature under keeping applied voltage.

The nonlinear optical coefficient d_{33} of the poled polymer films were determined by the Maker fringe method[13], using refractive indices measured by m-line method and d_{11} (0.4 pm/V) of quartz plate as a reference. Because of the experimental restriction that the heating oven used for the poling treatments and the optical measurement systems were placed independently, the period of time of about 10 minutes for the sample



(a) Set-up for corona poling



(b) Time sequence on corona poling

FIGURE 2 Corona poling method used in this work.

replacement were unavoidable. The term "initial" used hereinafter in this paper does mean "10 minutes" after the poling procedures.

Since the poling procedures are critical for the nonlinear optical properties of resultant poled polymers, the poling conditions such as the poling temperature (Tp), applied voltage during poling (Vp) and period of time of poling (PTp) were examined (The abbreviations in the nestings are the same as that used in figure 2).

Figure 3 shows the relationships between Tp and Vp when the leaky currents on poling (Ip) were maintained equal to 1 μA. The copolymer used was the one containing 10 wt% of CD1-MA unit. On elevating Tp, Vp was decreased because the corona discharging process, which should enhance Ip,

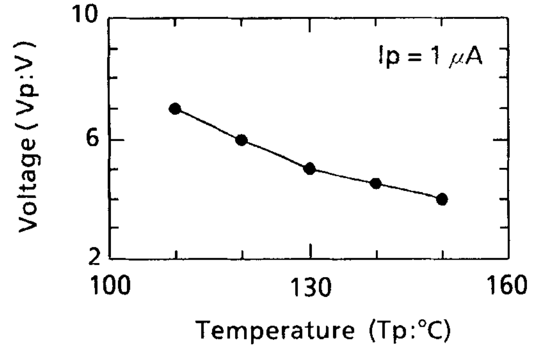


FIGURE 3 Relationship between poling temperature Tp and poling voltage applied under poling current of 1 μA.

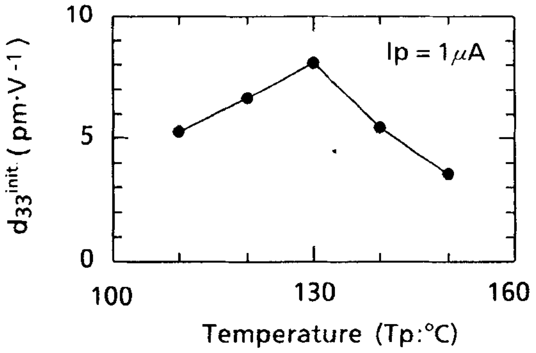


FIGURE 4 Relationship between poling temperature Tp and initial nonlinear optical coefficient d_{33} under poling current of 1 μA.

became faster. Ip of greater than 1 μA were undesirable because the film surface were damaged (the whitenings of the samples were observed).

Figure 4 shows the relationship between Tp and initial value of nonlinear optical coefficient d_{33} ($d_{33}^{init.}$). It was observed that the d_{33} value was decreased when Tp was higher than 130 °C, because applicable Vp was diminished while the disturbance of molecular orientations by heat were enhanced. Maximum $d_{33}^{init.}$ value achieved in these experiments was 8.1 $pm \cdot V^{-1}$.

In the next stage, the effect on the contents of the dye unit in the copolymers for the initial value of d_{33} ($d_{33}^{init.}$) was investigated. As shown in figure 5, the d_{33} was increased proportionally with CD1-MA contents in the range less than 10 wt% with the following saturation at higher concentrations. The reason why the d_{33} did not increase at the range of CD1-MA concentrations of 10 - 20 wt% is not clear, but it seems to be concerning with the crystallinity at higher concentrations. That is, it should be due to the interactions between the dye moieties which should stand up against the molecular reorientations occurred during the poling treatments.

The effect of PTp on the d_{33} value was examined. Some preliminary investigations revealed that PTp of 5 minutes was enough and prolonged PTp gave no effects on d_{33}.

Based on these results, poling conditions,that is, Vp = 5 kV, Tp = 130 °C and PTp = 5 minutes, were determined and further investigations were carried out by using the copolymer containing 10 wt% of CD1-MA unit.

Stability of oriented CD1 moiety

Stability of the d_{33} value was measured and the results were compared to the case of the formerly reported dope type system, where [CD2] guest molecules were dispersed in the PMMA host material. Figure 6 shows the dependence of d_{33} on the time passed after the poling, where the contents of the dye moieties in the two systems were equal at the point of the numbers of p-aminophenyl-cyclobutenediones in the unit volumes. In both cases, rather fast decreases of d_{33} values were observed during one or a few days following final low level d_{33} values. The final constant d_{33} values ($d_{33}^{const.}$) remained unchanged over a month at room temperature.

Quantitative expression for time-dependent d_{33} values can be given phenomenologically by a biexponential formula as shown in equation (1).

$$d_{33}=A\,e^{-t/\tau 1}+B\,e^{-t/\tau 2}+C\,e^{-t/\tau 3}\quad(\tau 1<\tau 2<\tau 3)\qquad(1)$$

In equation (1), the first term represents the fastest relaxation which is not clarified. And $\tau 3$, the time constant for the slowest relaxation process, should be taken as month-order or year-order in our experiment. In Table 2, $\tau 2$ values for the two systems shown in figure 6 were listed together with $d_{33}^{init.}$, $d_{33}^{const.}$ and their ratio. The $\tau 2$ value for the copolymer systems was found to be about 20 times larger than that of the doped polymer system. In

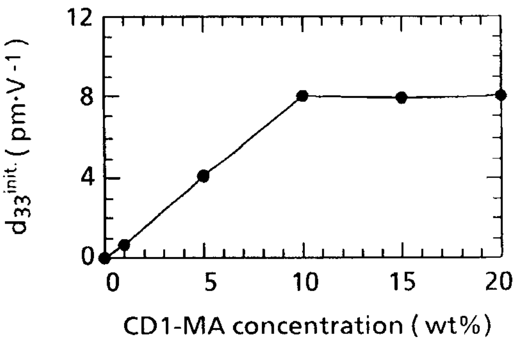


FIGURE 5 Relationship between nonlinear optical coefficient d_{33} and CD1-MA concentrations in the poled polymers.

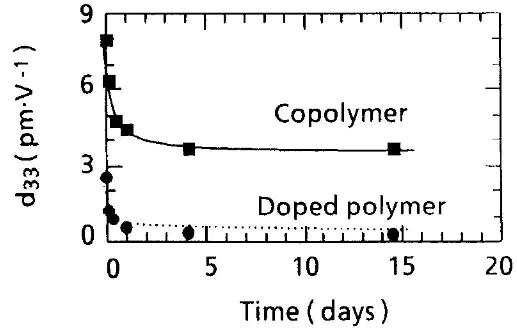


FIGURE 6 Nonlinear optical coefficient d_{33} as functions of times for poled polymer. The contents of CD moiety in the two systems were almost equal and the concentration was 6.5 ± 0.5 wt%.

TABLE II Second harmonic coefficient d_{33} and decay parameter.

Type	$\tau 2$ (days)	$d_{33}^{init.}$ (pm·V-1)	$d_{33}^{const.}$ (pm·V-1)	$\frac{d_{33}^{const.}}{d_{33}^{init.}}$
Copolymer	2.439	8.06	3.63	0.45
Doped polymer	0.12	2.52	0.3	0.12

many previous papers, the decreases in d_{33} values of poled "dye-side-chain" type polymers were slow in comparison with doped polymer systems[13] as in our present study. In consequence, the copolymer type showed moderately high d_{33}^{const} value of 3.7 pm·V^{-1}.

PHASE-MATCHING PROPERTIES IN WAVEGUIDE

Preparation of tapered waveguide

Phase matched SHG was realized by adjusting thickness of the optical waveguides. Because it is very difficult to adjust the exact phase matching thickness, tapered waveguides are often useful. Up to date, two-step spin-coating method has been carried out to prepare the tapered films for waveguides.[10] In this time, we applied dip-coating method to preparation of tapered films for waveguides.

Dip-coated films with tapered thickness were fabricated by controlling of dipping speed, viscosity and so on. Figure 7 shows relation between lateral position and film thickness of a tapered film fabricated by dip-coating method. Linear tapered films with smooth inclination were obtained within wide area.

The coupling efficiency (20 %) of prism and propagation loss (5.6 dB·cm^{-1}) in tapered dip-coated film were better than them (10 %, 14.3 dB·cm^{-1}) in spin-coated films. From these results, we found out dip-coating film was superior to spin-coating film as waveguide.

Thus copolymer thin films by dip-coating method were used for tapered slab type waveguide in corona-poling.

Collinear type phase-matched SHG

The collinear type phase-matching in the poled polymer waveguide are obtained at film thicknesses of the cross points in mode dispersion curves. Because each CD1 molecules tend to align perpendicular to the substrate surface, the TM waves were chosen for the fundamental wave (Nd:YAG laser, $\lambda = 1064$ nm) with the SH wave ($\lambda = 532$ nm). The refractive indices n_f^{ω} and $n_f^{2\omega}$ of the poled polymer film at the wavelength of 1064 nm and 532 nm were 1.495 and 1.512 for TM polarized lights, respectively. Figure 8 shows TM mode dispersion curves for the fundamental and SH waves. At the cross points, $\Delta\beta = \beta_{2\omega} - 2\beta_{\omega} = 0$, that is, $N_{eff}^{\omega} = N_{eff}^{2\omega}$ is satisfied. Here, β_{ω}

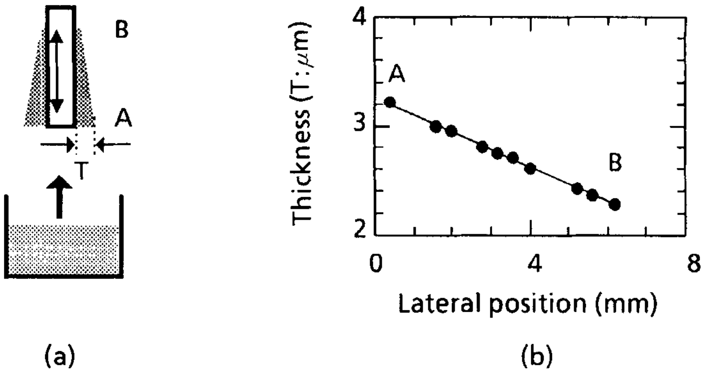


FIGURE 7 (a) Dip-coating method. (b) Relationship between lateral position and film thickness of a tapered film fabricated by dip-coating method.

and $\beta_{2\omega}$ are propagation constant in the waveguides, $N_{eff}^{\ \omega}$ and $N_{eff}^{\ 2\omega}$ effective refractive index of fundamental and SH wave, respectively.

In the conversion from TM^{ω} to $TM^{2\omega}$, SHG output power $P_{2\omega}$ in the optical waveguide is given by[11]

$$P_{2\omega} = \frac{\omega^2 d_{33}^{\ 2} \mu_0^3}{4 W \varepsilon_0} (N_{eff}^{\omega})^6 P_{\omega}^{\ 2} S^2 L^2 \, sinc^2(\frac{\Delta\beta L}{2}) \qquad (2)$$

where, ω is the angular frequency, P_{ω} the fundamental input power, ε_0 the free space permittivity, μ_0 the magnetic permeability, W the beamwidth of the guided wave, L the interaction length, S the spatial coupling of the field distributions. Among several phase matching conditions available, cross point from TM_0^{ω} to $TM_2^{2\omega}$ expected to show the highest conversion efficiency, based on the estimation of the theoretical conversion efficiencies by equation (3). Under the phase matching condition, the film thickness and effective refractive index were calculated at 2.523 μm and 1.486, respectively.

The TM mode SHG signal of collinear type from poled polymer slab type waveguides were measured by the experimental setup as shown in

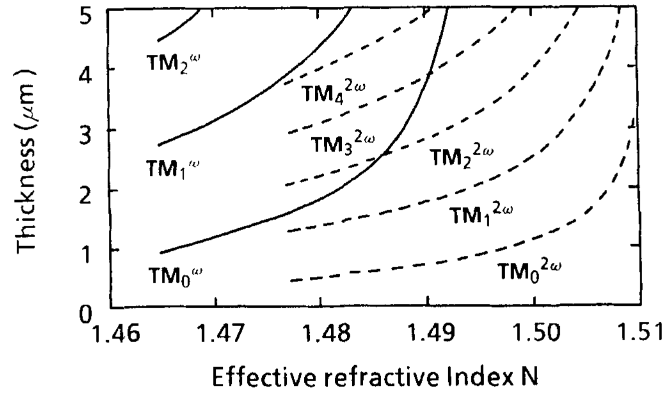


FIGURE 8 Mode dispersion curves of poled polymer for TM mode. The solid and dash line denote the mode dispersions of the fundamental and the second harmonic waves, respectively.

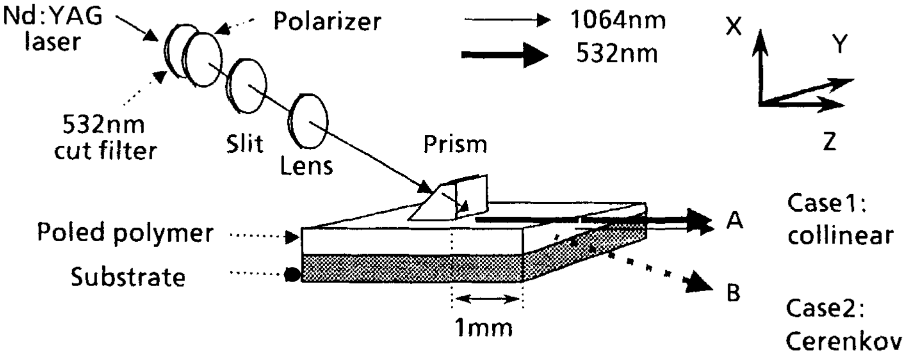


FIGURE 9 Experimental set-up for phase-matched SHG measurements in poled polymer waveguides.

figure 9. Where, fundamental wave of pulsed Nd:YAG laser (1064 nm) was launched by coupling prism. Fundamental wave and SH wave (532 nm) were both end-fired at the point A as shown in case 1. The experimental adjustment of film thickness for the phase matching was carried out by the positioning of the slab type waveguide with a gradual change in the

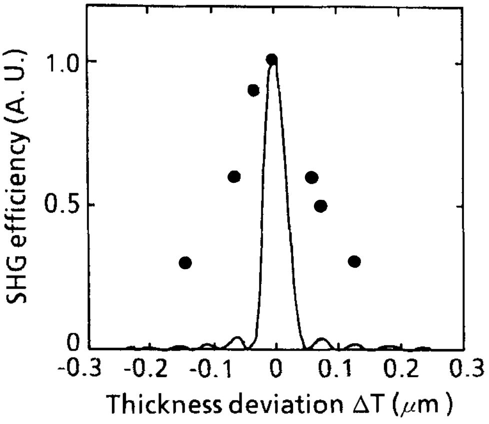


FIGURE 10 Relationship between thickness deviation and SHG conversion efficiencies on collinear type phase-matching. Black circle denotes measured data. Solid line denotes theoretical line calculated by equation (2).

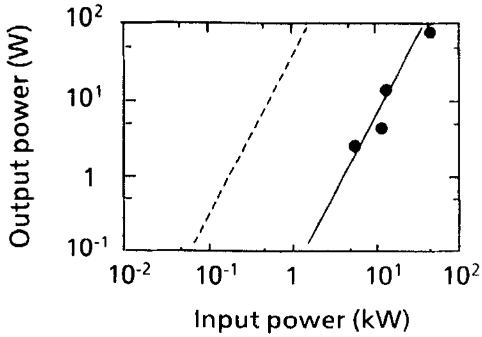


FIGURE 11 Relationship between input power of fundamental wave and output power of SH wave generated on collinear type phase-matching. white circle denotes measured data. Dash line denotes theoretical line calculated by equation (2).

thickness along the Y-direction. SH wave were detected through 1064 nm cut-filter together with 532 nm bandpass-filter.

Figure 10 shows measured SHG conversion efficiency as a function of thickness with calculated curve. SH wave could be observed in waveguide thickness of narrow range (about 0.2 μm). Especially, theoretical half-value width at the peak on the collinear type was very narrow and about 0.05 μm. Maximum collinear type SHG conversion efficiency was obtained at the film thickness of 2.53 μm which was in good agreement with the theoretical calculation.

Figure 11 shows a linear line with slope 2 in logarithmic plotting between the fundamental input and SH output together with the calculation. The conversion efficiency of 4.3×10^{-8} %·W^{-1} by experiment was much lower than the predicted value of 3.3×10^{-5} %·W^{-1} by the calculation. The main reasons for the low efficiency is uncertainty of the control on the film thickness. In addition, coupling loss at the prism-waveguide interface, propagation loss in the waveguide and the scattering occurring at the terminal edge are also point out.

Cerenkov type phase-matched SHG

The phase-matching condition between the fundamental guided mode and the second harmonic radiation mode (leaky mode) can be automatically satisfied by adjusting waveguide parameter such as thickness, molecular orientation, refractive indices and so on. We can observe Cerenkov type SHG at the phase-matching thickness in connection with the condition, $n_S^{2\omega} > N_{eff}^{\omega} > n_S^{\omega}$, as shown in figure 8.

In the conversion from TM$^{\omega}$ to radiation mode, SHG output power $P_{2\omega}$ of the optical waveguide is as follows.[15]

$$P_{2\omega} = \left| d_s I_s + d_W I_W \right|^2 P_{\omega}^{\ 2} \frac{\beta}{\rho} \left(\frac{n_{o2s}}{n_{e2s}} \right)^2 2L\pi \tag{3}$$

Where d_S and $d_W(d_{33})$ are nonlinear d constant of the substrate and the waveguide layer, respectively. I_S and I_W are the overlap integrals between a polarization wave of an angular frequency 2ω and radiation mode in the substrate and the waveguide layer, respectively. β and ρ are propagation constant of a radiation mode and wave number in x direction shown in figure 9 of a radiation mode, respectively. n_{o2S} and n_{e2S} are refractive index of the

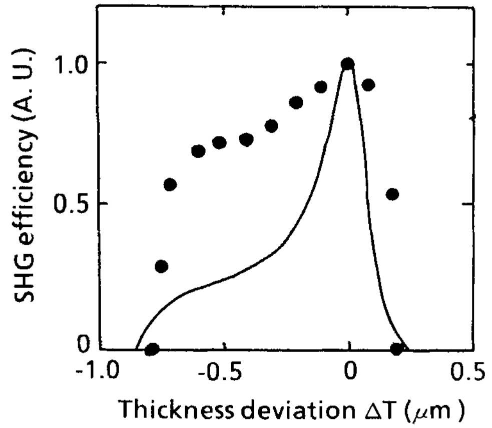


FIGURE 12 Relationship between thickness deviation and SHG conversion efficiencies on Cerenkov type phase-matching. Black circle denotes measured data. Solid line denotes theoretical line calculated by equation (3).

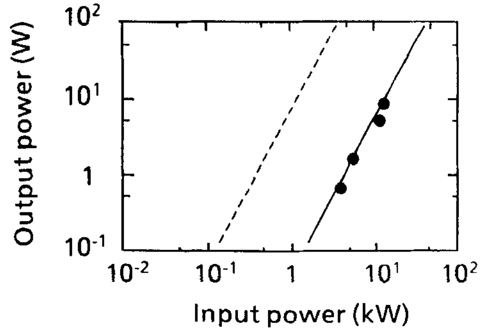


FIGURE 13 Relationship between input power of fundamental wave and output power of SH wave generated on Cerenkov type phase-matching. Black circle denotes measured data. Dash line denotes theoretical line calculated by equation (3).

poled polymer at the wavelength of 532 nm for TE and TM polarized light, respectively. Among many phase matching conditions, the conversion between TM_1^{ω} and the radiation mode gave the most strong SHG according to the estimation of the theoretical efficiencies by equation (3). In this case, the optimal film thickness and effective refractive index were given as 3.544 μm and 1.474, respectively.

The TM mode SHG signal by Cerenkov type phase matching were measured by using the experimental setup of case 2 shown in Figure 9, where the fundamental wave was emitted from the point A, but SH signals (532nm) the point B.

Figure 12 shows measured SHG conversion efficiency as a function of thickness with theoretical calculation. SH wave could be observed in the range of wide waveguide thickness (about 0.7 μm). Maximum Cerenkov type SHG conversion efficiency was obtained at the film thickness of 3.502 μm which was in good agreement with the theoretical calculations.

Figure 13 shows a linear line with slope 2 in logarithmic plotting between the fundamental input and SH output together with the calculations. The conversion efficiency of 3.3×10^{-8} %·W^{-1} by measurement was much lower than the predicted value of 7.4×10^{-6} %·W^{-1} by the calculation. The difference between calculated and measured conversion efficiencies on Cerenkov type SHG is smaller than that on collinear type SHG. This suggests that phase-matching condition of Cerenkov type is gentler than that of collinear type.

CONCLUSIONS

A new polymerizable dye for nonlinear optical materials, 1-{4-[N-(2-methacryloyloxyethyl)-N-ethylamino]-phenyl}-2-methylamino-cylobutene-3,4-dione [CD1-MA] was synthesized and their copolymers with methyl methacrylate were prepared. The copolymer film containing 10wt% of the CD1-MA unit showed the d_{33} value of 8.1 pm·V^{-1} just after the poling, and time-dependent change in the d_{33} value was much less than the corresponding host-guest (dye-doped) material. The second harmonic generations (SHG) utilizing two different phase-matching methods, the collinear type phase-matching and the Cerenkov type radiation, were both observed in the three-layer optical waveguide (air / poled polymer / pyrex glass) with tapered thickness fabricated by the dip-coating method. The conversion efficiencies from the fundamental to SH wave were estimated to be in the order of 10^{-8} %·W^{-1}. The value was still small from the expectation (~10^{-5} %·W^{-1}). We could estimate high conversion efficiencies though d_{33} values were small compared with others data presented previously.[16,17] The reason should be attributed to the precise control of waveguide thickness. We can conclude that the precise control of the device configurations, as well as the use of poled polymers with high d_{33} values, should be of great importance for the application of the frequency doubling devices.

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