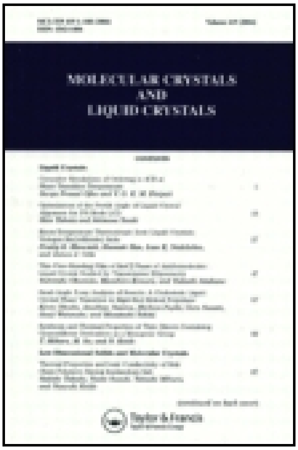

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Second Order Nonlinear Optical Properties of Polymers Containing Mesogenic Side Chains

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Second Order Nonlinear Optical Properties of Polymers Containing Mesogenic Side Chains

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Second harmonic generation is observed from poled polymer films which contain a side chain mesogen with nonlinear optical (NLO) properties. The side chain is a derivative of 4-hydroxy-4′-nitrostilbene (HNS), and the content is varied by copolymerization with methyl methacrylate. The polymer exhibits a liquid crystalline (LC) phase when the side chain content is greater than 75 mol%. LC orientation is induced by poling for the homopolymer. The second order NLO susceptibility ($\chi^{(2)}$) of the oriented homopolymer is 1.5 times larger than the estimated value when the polymer is isotropic under the same poling field. This enhancement corresponds to the large anisotropic properties of the polymer. By doping HNS to the homopolymer, the $\chi^{(2)}$ value increases with increases in the doping content up to 20 mol% where the LC orientation remains, and reaches 1.6 times the value of the undoped homopolymer.

Keywords: Second harmonic generation, side chain polymer, electric poling, liquid crystalline orientation, $\chi^{(2)}$ anisotropy, NLO compound doping

INTRODUCTION

Second order nonlinear optical (NLO) effects have been utilized in the field of opto-electronics. Recently, organic compounds with second order NLO susceptibility ($\chi^{(2)}$) much greater than those of inorganic compounds have been studied, and many organic crystals have been found to show large $\chi^{(2)}$ values.[1] However, the fabrication of NLO devices using organic crystals is restricted by the processability and transparency of organic crystals.

Polymers with large $\chi^{(2)}$ values offer some advantages over organic crystals in their processability and transparency. These polymers include guest-host polymer systems, in which NLO materials are dissolved in host polymers,[2–4] and side chain polymers, in which NLO materials are covalently attached to the polymer main chains.[5–10] A noncentrosymmetric orientational structure can be attained by electric field poling to these polymers. Guest-host polymer systems were first investigated by Meredith *et al*,[2] and have since been extensively studied by Singer *et al.*[3,4] Side chain polymers are expected to have larger $\chi^{(2)}$ than guest-host polymer systems because the content of NLO materials can be higher. Several side chain polymers have already been synthesized for nonlinear optics, and the NLO susceptibilities of these polymers remained more stable after the poling than guest-host polymer systems.[9] So far, there are not so many studies about the relationship between second order NLO properties and the content of NLO materials.

In this study, second order NLO properties of the polymers with different NLO mesogen content are investigated, as well as their liquid crystalline orientation.

EXPERIMENTAL

Materials

The molecular structures of materials investigated are shown in Figure 1. These materials were synthesized according to reported procedures.[5,7] The polymers contain a side chain mesogen with a stilbene moiety. The content of the side chain is varied by copolymerization with methyl methacrylate. Synthesized polymers were purified by reprecipitation using methanol. Further purification was done by using gel filtration column chromatography to separate low molecular compounds. 4-Hydroxy-4′-nitrostilbene (HNS) was used as an additive to the polymers. Structures of all compounds and synthetic intermediates were identified by ^{1}H NMR. Their purity was confirmed by thin layer chromatography.

Method

Polymer samples dissolved in chloroform were cast onto glass substrates with interdigital electrodes which were made of evaporated aluminum. Both the inter-

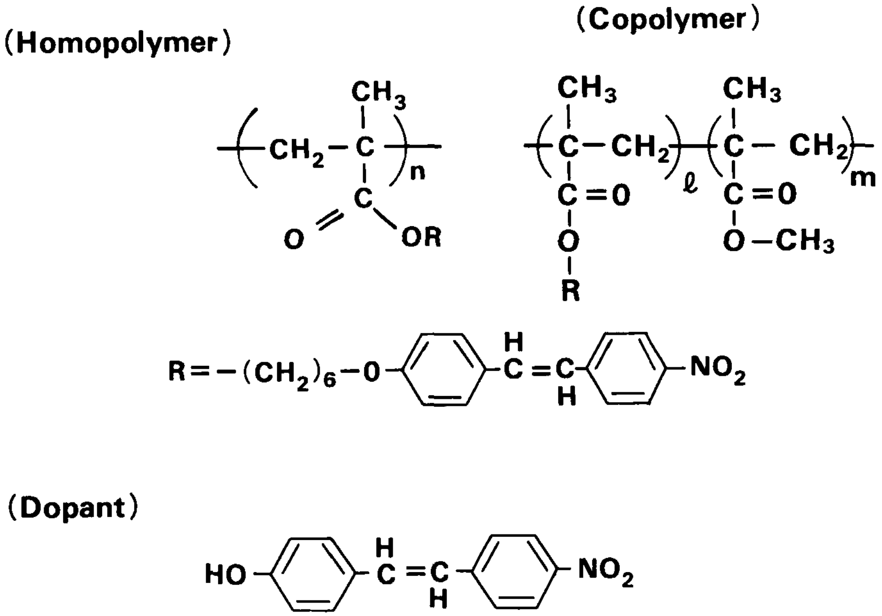

FIGURE 1 Molecular structures of materials investigated.

digital spacing and electode width were 1.0 mm. The thickness of electrodes was 0.2 μm. The cast polymer films were dried completely under a nitrogen stream. The film thickness ranged from 0.2 μm to 0.5 μm. The samples were immersed in an inert liquid which was kept at a constant temperature higher than their glass transition temperatures (Tg). After the sample temperature was equilibrated to the bath tempereature, a DC electric field was applied. The maximum field strength was 15 kV/mm. The samples were then cooled before the electric field was switched off.

The second order NLO susceptibility ($\chi^{(2)}$) was determined by second harmonic generation (SHG) measurement. A Q-switched Nd^{3+}YAG laser (DCR-11, Quanta-Ray) supplied 0.6 mJ per pulse of fundamental wave (1064 nm), which was focused on an approximately 500 μm spot on the sample. A double-quarter-wave plate was used for the variation of the laser polarization. The SH wave was collected and filtered from the fundamental wave. The SH intensity was detected by a photomultiplier tube. The signals were integrated with a boxcar averager (MODEL 4420, EG&G PARC). Verification of the SH wave was provided by measurement of the signal intensities at 532 nm and 540 nm using interference filters with a 2 nm half width. $\chi^{(2)}$ was determined relative to the known value of ${\chi^{(2)}}_{111}$ for α-quarts ($= 1.6 \times 10^{-9}$ esu) using the following equation:

$$\chi^{(2)} = 2/\pi\,(Is/Iq)^{1/2}\,\chi_q^{(2)}\,1_{cq}/1_s, \tag{1}$$

Here, I_s, I_q, 1_{cq}, and 1_s are the SH intensity from a sample, the SH intensity from α-quartz, the coherence length (20.6 μm)[11] of α-quartz and film thickness of the sample, respectively. It should be noted that equation (1) is applicable only when the film thickness is thinner than the coherence length of the sample.

The glass transition temperatures of the polymers were determined by differential scanning calorimetry (DSC) measurement. Birefringences (Δn) of films were determined from the retardations (R), which were measured using polarizing microscopy and the film thicknesses (1) by the following equation.

$$\Delta n = R/1, \tag{2}$$

Refractive indices of the polymers at the SH wavelength (532 nm) and the fundamental wavelength (1064 nm) were determined using a single-term Sellmeir equation[12] from the values at 633 nm and 1152 nm which were accurately measured with a prism coupler (Metricon PC-2000).

RESULTS AND DISCUSSION

Polymer properties

Synthesized polymers contain a side chain mesogen containing a stilbene structure with an alkoxy group as an electron donor and a nitro group as an electron acceptor. The absorption maximum of the polymers was around 350 nm. An SH wave of 532 nm is generated, when the fundamental wave is radiated. Thus, these polymers have no absorption around the SH wavelength, and there is no need to consider absorption or luminescence effects in this wavelength region.

Homopolymers exhibited a nematic liquid crystalline phase between the glass transition temperature and the clearing temperature, which was identified by observing schlieren texture. Copolymers with a side chain content below 75 mol% showed only an isotropic phase above their glass transition temperatures. Therefore, the macroscopic orientation for these copolymers is not expected.

$\chi^{(2)}$ determination

SHG was detected from all samples when they were poled in a DC field under the conditions shown in the experimental section. This indicates that the microscopic structure of side chain dipole becomes noncentrosymmetrical by applying an electric field. The coherence length (lc) of each polymer sample must be much larger than the sample thickness to determine $\chi^{(2)}$ using Equation 1. lc is defined by the following equation:

$$lc = \lambda/4(n_{2w} - n_w), \tag{3}$$

where λ, n_{2w} and n_w are fundamental wavelength, refractive index of the sample at the SH wavelength and that at fundamental wavelength, respectively. For the homopolymer, n_{2w} and n_w were determined to be 1.6022 and 1.6573, respectively as shown in the experimental section. Then the lc was evaluated to be 4.8 μm by using Equation 3. For the copolymers, lc was less than that of the homopolymer. Therefore, the sample thickness (0.2 μm − 0.5 μm) is much smaller than the lc. The SH intensity of a poled polymer film is shown as a function of the incident angle of the laser beam in Figure 2. Laser polarization and SH signal polarization were parallel to the direction of the DC field (orientational direction of side chains) and the $\chi^{(2)}$ value is the maximum value of the $\chi^{(2)}$ tensor (i.e. $\chi^{(2)}{}_{333}$). The SH power decreases with the increase in incident angle. This is because the reflectivity of the fundamental wave depends on the incident angle. Thus, the $\chi^{(2)}$ value was determined using the SH intensity at an incident angle of 0°. In Figure 2, data points seem to disaperse and show periodicity at around the small rotational angle. This is thought to relate to defects on the sample surface or small variations in thickness, because the pattern depends on the sample preparation and was independent of the polymer composition and the molecular ordering.

NLO properties of poled polymers

It is known that the $\chi^{(2)}$ value increases with an increase in the content of a NLO compound in a polymer, as is expressed in the following theoretical relationship:

$$\chi^{(2)} = Nf_w f_{2w} B\ E/kT, \tag{4}$$

Here, N is the number density of NLO molecules; B is the molecular hyperpolarizability; and f_{2w} and f_w are Lorentz-Lorentz local field factors at fundamental and

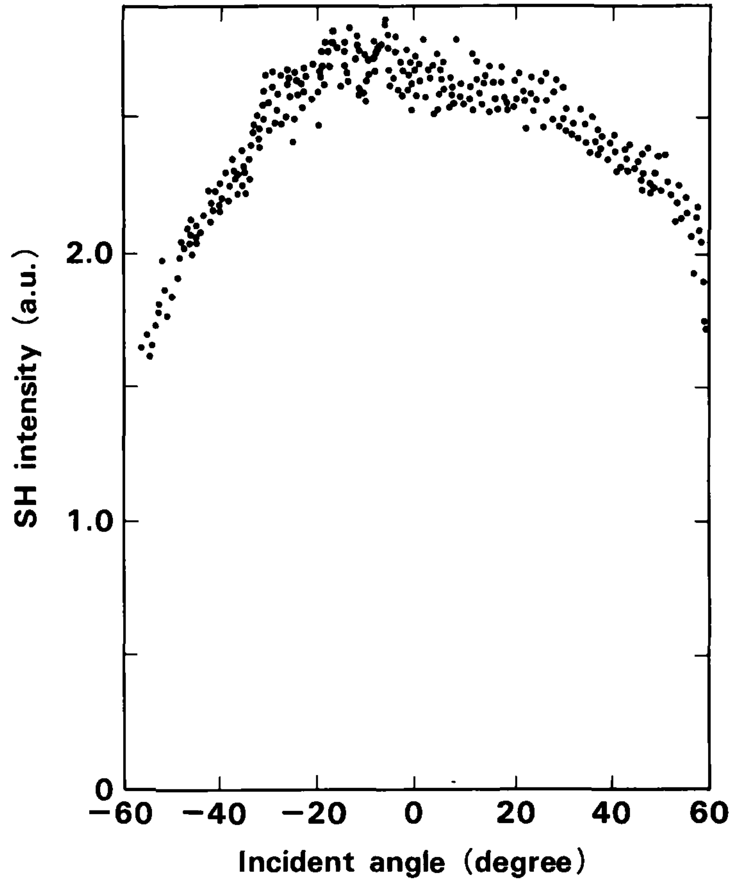

FIGURE 2 Second harmonic intensity of a poled homopolymer film as a function of incident laser beam angle. The poling field is 15 kV/mm.

SH wave frequency, respectively. However, in this equation, the NLO molecules are separated from each other, and interaction of the NLO molecules is negligible. From Equation 4, $\chi^{(2)}$ is proportional to both poling field and the content of NLO molecules.

The dependence of the side chain content on the $\chi^{(2)}$ value was investigated to clarify the effectiveness of Equation 4. The relationship between $\chi^{(2)}$ and side chain content is shown in Figure 3. The poling field was 15 kV/mm for all the samples. Sample temperatures were set at temperatures above the sample glass transition temperatures. The $\chi^{(2)}$ values increase proportionally with an increase in side chain content up to around 25 mol%. This is in accordance with the relationship shown in Equation 4, which shows negligible interaction of the side chain dipoles. Polymers with a side chain content exceeding 25%, however, do not satisfy Equation 4, and the $\chi^{(2)}$ value almost saturates. This suggests that the dipole orientation of the side chains is restricted by their interaction, and that the amount of oriented dipole is almost the same over 25 mol% despite the increase in side chain content. The $\chi^{(2)}$

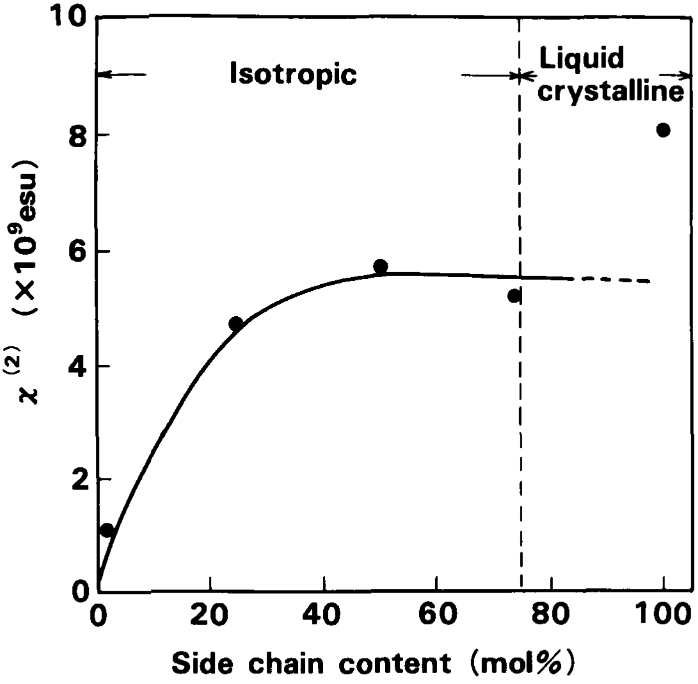

FIGURE 3 $\chi^{(2)}$ value as a function of side chain content. The poling field is 15 kV/mm. Liquid crystalline phase is obtained above the side chain content of 75 mol%. Dotted line shows the estimated $\chi^{(2)}$ value when the polymer remains isotropic under the poling field of 15 kV/mm.

value increases discontinuously for the homopolymer because of $\chi^{(2)}$ enhancement by liquid crystalline orientation, which is discussed later.

Liquid crystalline orientation

Liquid crystalline orientation induced by DC field was observed only for the homopolymer. Photographs of electric field induced oriented polymers at the diagonal position (a) and the extinction position (b) are shown in Figure 4. These photographs show that the liquid crystalline orientation is parallel to the poling field direction. It is shown that the $\chi^{(2)}$ value depends on the order parameter of NLO component as follows[4]:

$$\chi^{(2)}_{333} = \left(\tfrac{1}{5} + \tfrac{4}{7}\langle P_2\rangle + \tfrac{8}{35}\langle P_4\rangle\right), \tag{5}$$

$$\chi^{(2)}_{113} = \chi^{(2)}_{131} = \chi^{(2)}_{311} = \left(\tfrac{1}{5} + \tfrac{1}{21}\langle P_2\rangle - \tfrac{8}{70}\langle P_4\rangle\right), \tag{6}$$

where $\langle P_2\rangle$ and $\langle P_4\rangle$ are the second and the fourth order parameters, respectively. In the isotropic state where both $\langle P_2\rangle$ and $\langle P_4\rangle$ are 0, $\chi^{(2)}_{311}/\chi^{(2)}_{333}$ is $\frac{1}{3}$. On the other hand, the $\chi^{(2)}_{333}$ value is five times that of the isotropic state when the side chains are completely oriented.

The birefringence and the value of $\chi^{(2)}_{311}/\chi^{(2)}_{333}$ of the poled polymers are shown in

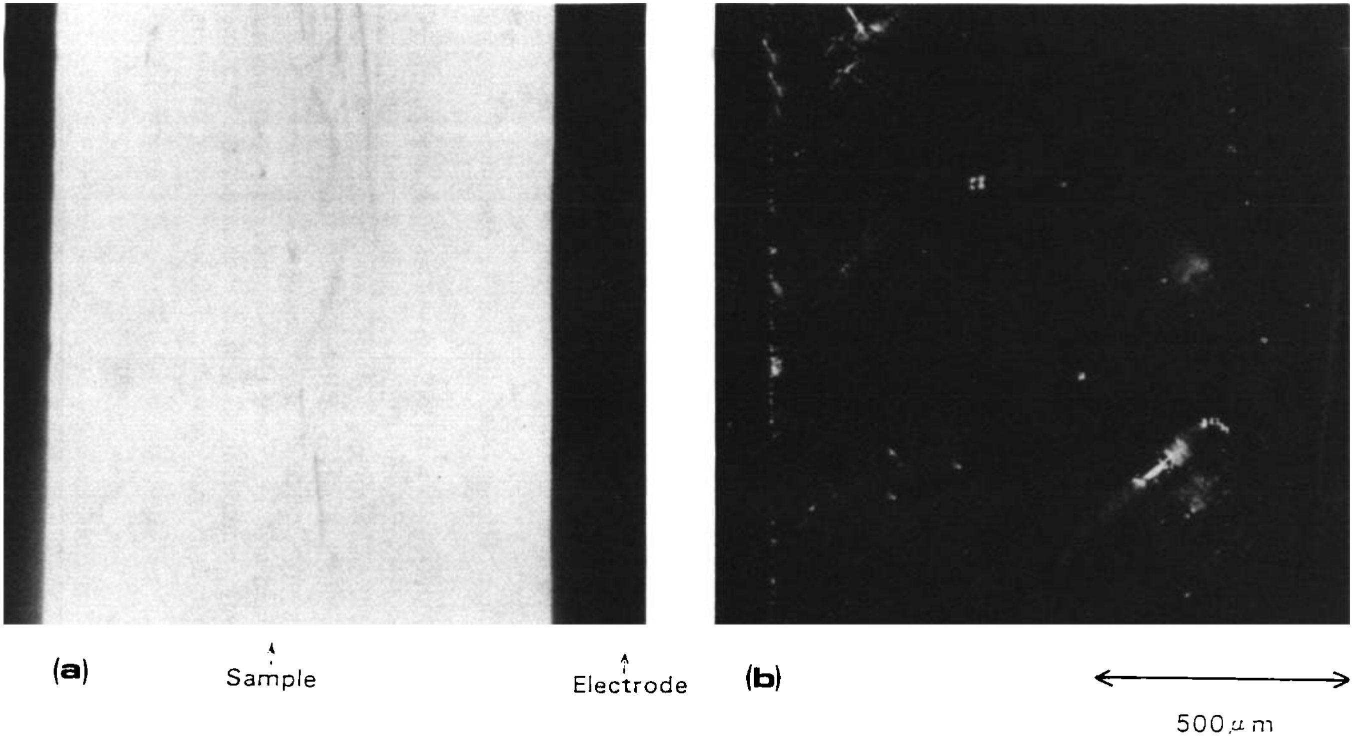

FIGURE 4 Photographs of liquid crystalline orientation of a poled homopolymer film under crossed polarizers at diagonal (a) and extinction (b) position.

Table 1. Macroscopic orientation is not observed for the copolymer samples, and the values of their Δn are much smaller than that of the oriented homopolymer (the content is 100 mol% in Table 1). $\chi^{(2)}_{311}/\chi^{(2)}_{333}$ values for isotropic samples are about $\frac{1}{3}$, which agrees well with the results from Equations 5 and 6. For the oriented homopolymer, the $\chi^{(2)}_{311}/\chi^{(2)}_{333}$ value is much lower than $\frac{1}{3}$. This indicates that liquid crystal orientation makes higher anisotropy for $\chi^{(2)}$ tensor, and enhances $\chi^{(2)}_{333}$ compared with that of the isotropic phase. As is shown in Figure 3, the $\chi^{(2)}$ value almost saturates at the side chain content of 25 mol%. This suggests that the $\chi^{(2)}$ value of the homopolymer is as much as that of 20 mol% copolymer without the enhancement by liquid crystalline orientation. The $\chi^{(2)}$ values of the oriented homopolymer and the copolymer of 25 mol% were 8.0×10^{-9} esu and 5.4×10^{-9} esu, respectively. Thus, the enhancement of $\chi^{(2)}$ by the liquid crystalline orientation is evaluated to be 1.5 times greater than that of an unoriented polymer. This is the first time that the $\chi^{(2)}$ enhancement due to liquid crystalline orientation has been observed.

NLO properties of poled homopolymer-HNS mixtures

In guest-host polymer systems, it is well known that the $\chi^{(2)}$ value is proportional to the content of guest molecules, as shown in Equation 4. In order to attain a higher $\chi^{(2)}$ value than that in the poled polymer mentioned above, HNS was doped into the homopolymer and the relationship between $\chi^{(2)}$ and the HNS content was investigated. HNS has almost the same structure as the polymer mesogen, so a high solubility of the homopolymer is expected. The $\chi^{(2)}$ value is shown as a function of poling electric field in Figure 5. The sample is the homopolymer with the HNS content of 20 wt%. Figure 5 shows that $\chi^{(2)}$ increases proportionally with the poling field. The $\chi^{(2)}$ value reaches 1.3×10^{-8} esu at a poling field of 15 kV/mm. This value exceeds by 4.5 times the analogous parameter of KDP where $\chi^{(2)}_{36} = 2.2 \times 10^{-9}$ esu. A breakdown in the electrodes occurred when the applied voltage was higher than 15 kV/mm. Higher $\chi^{(2)}$ value will be obtained if the breakdown is inhibited.

The relationship between $\chi^{(2)}$ and HNS content is shown in Figure 6. $\chi^{(2)}$ increases proportionally to the HNS content. Liquid crystalline orientation was observed for these mixtures, and the birefringence values were almost the same as that of the homopolymer shown in Table 1. This indicates that the HNS molecules and the polymer side chains are electrically poled independently and the interaction of the polymer side chain and the doped HNS is small. However, polymer samples with an HNS content greater than 20 wt% do not satisfy the relationship where two components do not mix with each other. The solubility of 20 wt% is, however,

TABLE 1

Birefringence and $\chi^{(2)}_{311}/\chi^{(2)}_{333}$ for poled polymers

Content (mol%)	25	50	75	100 (homopolymer)
Δn	<0.01	<0.01	<0.01	0.38
$\chi^{(2)}_{311}/\chi^{(2)}_{333}$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	$<\frac{1}{10}$

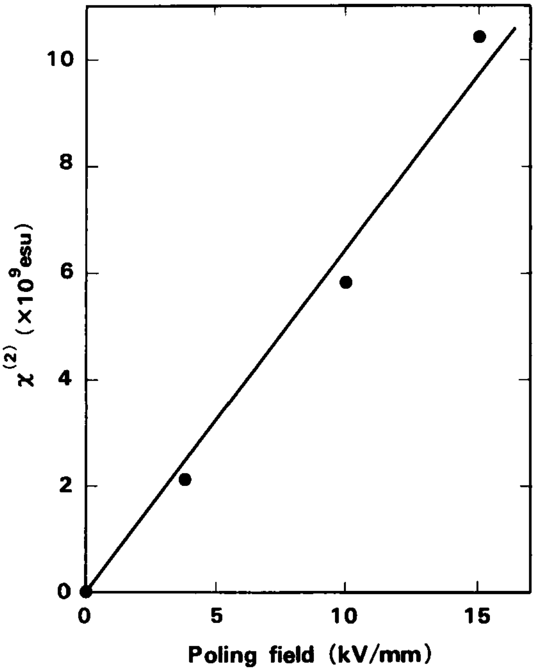

FIGURE 5 $\chi^{(2)}$ value of homopolymer doped with HNS as a function of poling field. The doping content is 20 mol%.

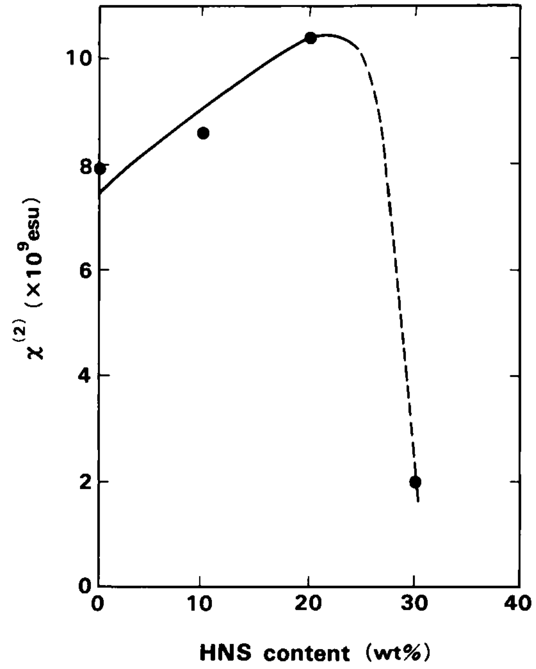

FIGURE 6 $\chi^{(2)}$ value of poled homopolymer as a function of HNS doping content. The poling field is 15 kV/mm.

larger than that of conventional guest host systems.[13] This is because the structures of side chain and HNS are almost the same. The maximum $\chi^{(2)}$ value was 1.6 times greater than that of nondoped homopolymer.

CONCLUSION

Second order nonlinear optical properties were investigated for polymers containing a side chain mesogen of a derivative of 4-hydroxy-4′-nitrostilbene (HNS). A liquid crystalline phase is observed above a side chain content of 75 mol%. It was shown that liquid crystalline orientation is obtained by poling for the homopolymer, and increases the $\chi^{(2)}$ value to 1.5 times that estimated when the polymer is unoriented under the same poling field. It was also found that doping HNS to the homopolymer is effective in raising the $\chi^{(2)}$ value up to the doping ratio of 20 mol% which results in an $\chi^{(2)}$ value of 1.6 times greater than that of the undoped homopolymer.

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