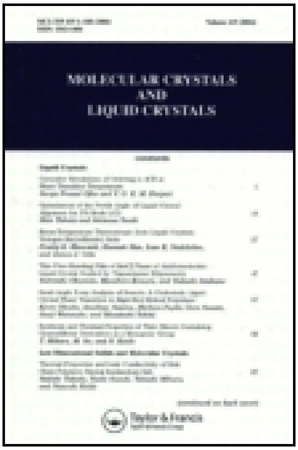

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Third-Order Nonlinear Optical Properties of Dye-Attached Polymers

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Several dye-attached polymers are synthesized and their third-order nonlinear optical susceptibilities $\chi^{(3)}$ are evaluated from third harmonic generation (THG). The attached dyes possess π-electron conjugated systems, which differ in their skeleton, π-conjugated length, and substituting groups. The largest $\chi^{(3)}$ obtained here is of the order of 10^{-11} esu for a polyamic acid with π-conjugated systems consisting of four aromatic rings bonded through carbon–carbon or nitrogen–nitrogen double bonds. $\chi^{(3)}$ exhibits a power law dependence on π-conjugated length with an exponent of about 4. It is also demonstrated that the existence of electron acceptors and donors is effective in increasing third-order optical nonlinearity.

Keywords: nonlinear optics, third harmonic generation, dye, polyamic acid, polyimide, π-conjugation, acceptor, donor

INTRODUCTION

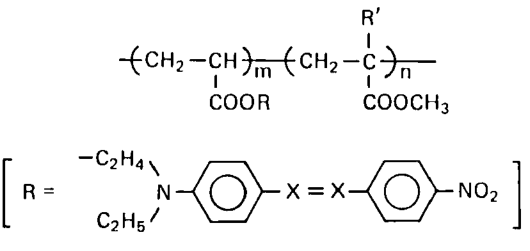
π-Electron conjugated organic systems are potentially important for various optical devices because of their large nonlinearity and fast response times. Typically, π-electron conjugated polymer crystals such as polydiacetylene have been investigated as third-order nonlinear optical materials. However, amorphous polymers could prove to have better processability, mechanical properties and transparency than polymer crystals like polydiacetylene. Thus, the third order nonlinear optical susceptibility $\chi^{(3)}$ has been recently evaluated for various amorphous polymers such as polysilane,[1] polygermane,[2] poly-*p*-phenylenebenzobisthiazole (PBT),[3] dye-attached polymer,[4] and polyarylene vinylene.[5,6] Large $\chi^{(3)}$ amorphous polymers require the introduction of a high concentration of nonlinearity generating units into the polymer chain.

In this study, two types of amorphous polymers were synthesized with π-electron conjugated systems in their main chain or side chain. One example is a dye pendant polymer where an azo or stilbene dye was introduced as the side chain of a methacrylate or acrylate polymer, which are known to have good transparency; polymethylmethacrylate (PMMA) is used for plastic optical fibers.[7] The azo and stilbene dyes have π-electron conjugated systems with acceptor and donor substituent groups at both ends of their molecules, where intramolecular charge transfer occurs. The other example is polyamic acid and polyimide with a π-electron conjugated system in the main chain. The π-electron conjugated system is not an intramolecular charge transfer system, unlike the azo and stilbene dyes described above. Polyamic acid and polyimide are popular as high thermal resistant polymers and have been investigated for optical waveguides.[8,9] $\chi^{(3)}$ was evaluated for films of the two types of polymer. The dependence of $\chi^{(3)}$ on the molecular structure and π-electron conjugated length incorporated into a polymer is also discussed.

EXPERIMENTAL

The synthesized polymers with azo and stilbene dye as their side chain are shown in Figure 1. A-MMA and A-MA are copolymers of an azo dye attached to an acrylic monomer with methylmethacrylate and with methylacrylate, respectively. S-MMA is a copolymer of a stilbene dye attached to a monomer and methylmethacrylate. The dyes all have a nitro group as an electron acceptor and an amino group as an electron donor. The polymers were obtained by radical copolymerization. The molar ratios of the dye monomer in the copolymers were identified by nuclear magnetic resonance (NMR) spectroscopy. Copolymers with a higher azo dye content were obtained with methylacrylate (A-MA) rather than with methylmethacrylate (A-MMA). The highest dye contents were 25.9, 45.1, and 24 mol% in A-MMA, A-MA, and S-MMA, respectively. These polymers were soluble in conventional solvents. They were deposited on glass substrates by a spinning technique. The thickness of the films ranged from 0.2 μm to 0.3 μm.

The synthesized polyamic acids and polyimides are shown in Figure 2. Polyamic acids were obtained by the reaction of carboxylic acid anhydride with a diamine. A relatively long π-electron conjugated system exists in diamine compounds. The π-conjugated system is not an intramolecular charge transfer system, because it



A–MMA	X = N	R' = CH$_3$
A–MA	X = N	R' = H
S–MMA	X = CH	R' = CH$_3$

FIGURE 1 Synthetic polymers with azo and stilbene dyes as side chains.

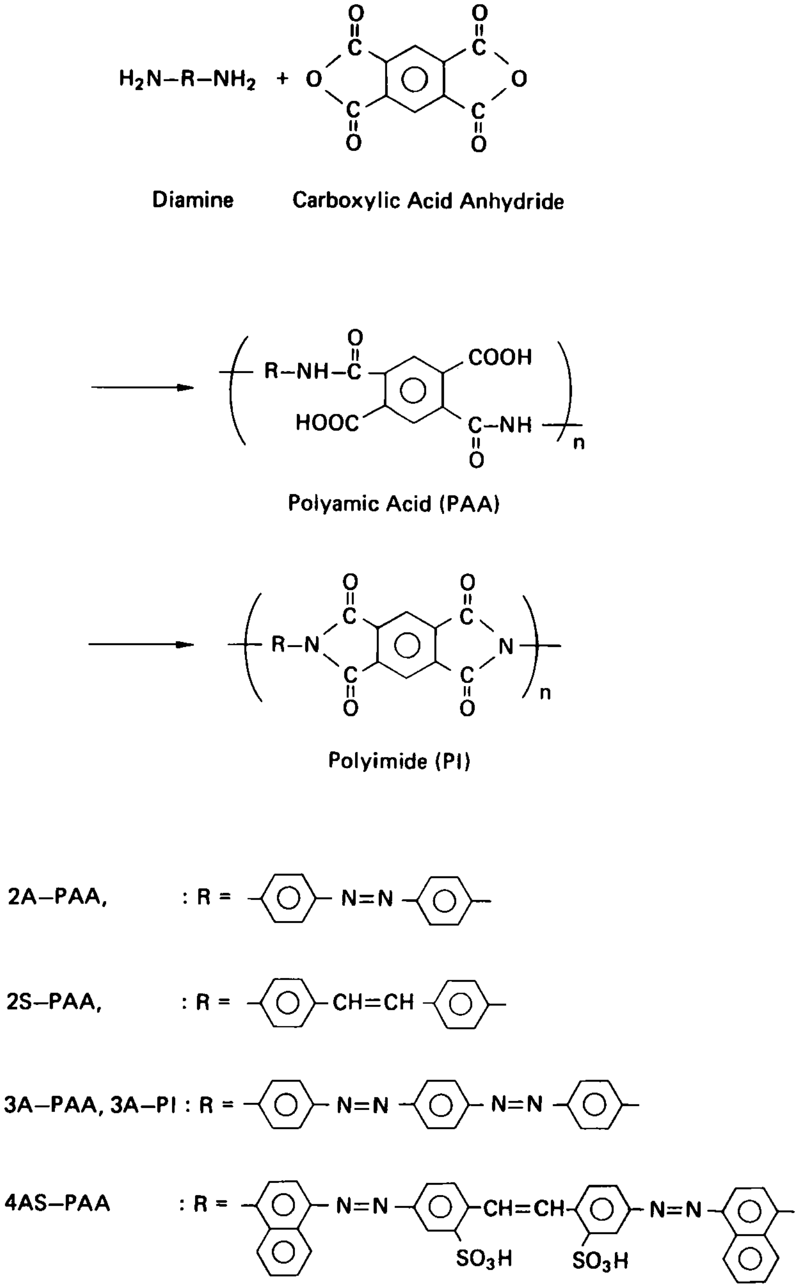


FIGURE 2 Synthetic polyamic acids and polyimides.

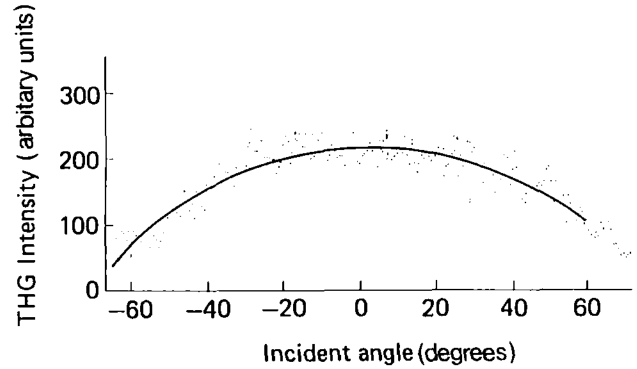


FIGURE 3 THG intensity as a function of incident angle.

does not have either a strong acceptor or a strong donor at the ends of the molecular chain. The diamines (or their ammonium salts) used for the synthesis are commercially available. The reaction was carried out under previously described conditions.[10] Films of polamic acids for $\chi^{(3)}$ evaluation were easily obtained using a spinning technique. Film thickness was 0.2 μm to 0.3 μm. Polyimides were obtained by heating under previously described conditions.[10] However, the polyamic acid 4AS-PAA was not converted to polyimide under the same conditions.

$\chi^{(3)}$ was evaluated from THG as follows.[11] THG intensities were measured at a fundamental wavelength of 1.85 μm to 2.15 μm, which was obtained by wave mixing a Q-switched Nd:YAG laser beam and tunable dye laser beam. The sample was mounted on a goniometer and rotated about an axis perpendicular to the laser beam. The generated third harmonic wave was passed through the fundamental wave cutting filter, a monochromator, and was detected by a photomultiplier tube. If film is thicker than the coherence length, a Maker fringe pattern is observed.[12] However, in this case, the thickness is much less than the coherence length, so the intensity is a monotonic function of the incident angle as shown in Figure 3. The $\chi^{(3)}$ value was calculated using Equation 1, where l is the sample thickness, $\chi_s^{(3)}$ is the $\chi^{(3)}$ of the standard sample, fused silica, and $l_{c,s}$ is its coherence length. $I_{3\omega}$ and $I_{3\omega,s}$ are the peak intensity values in the polymers and fused silica.

$$\chi^{(3)} = (2/\pi)\chi_s^{(3)}(I_{3\omega}/I_{3\omega,s})^{1/2}(l_{c,s}/l) \qquad (1)$$

RESULTS AND DISCUSSION

Figure 4 shows the $\chi^{(3)}$ of three copolymers containing azo or stilbene dyes at 1.9 μm. In the three copolymers, $\chi^{(3)}$ increases linearly with dye monomer content. The values are of the order of 10^{-12} esu. The largest $\chi^{(3)}$ obtained here was 3.2 × 10^{-12} esu, which is comparable to the $\chi^{(3)}$ of poly-*p*-phenylenebenzobisthiazole and polysilane.[1,3] The azo pendant polymers have larger $\chi^{(3)}$ values than the stilbene polymers. Similar results are obtained at other wavelengths as shown in the wavelength dependence in Figure 5. Figure 5 also shows little change at wavelengths

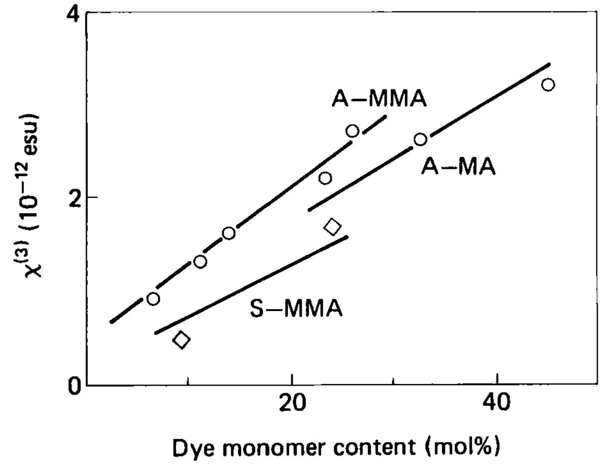


FIGURE 4 $\chi^{(3)}$ of three copolymers containing azo or stilbene dyes at 1.9 μm as a function of dye monomer content.

longer than 2.05 μm. This means that the $\chi^{(3)}$ in this region, which is of the order of 10^{-12} esu, does not include any significant enhancement such as is observed in polydiacetylene due to a resonant effect.[13] Figure 6 shows absorption spectra of dye pendant copolymer thin films. Absorption tails extend to around 600 nm, so the small increase in $\chi^{(3)}$ at shorter wavelengths near 1.8 μm is probably due to the resonant effect. The wavelength of 600 nm is equivalent to the third harmonic of the fundamental wave at 1.8 μm.

$\chi^{(3)}$ values of polyamic acids and a polyimide are shown in Table I at 1.9 μm.

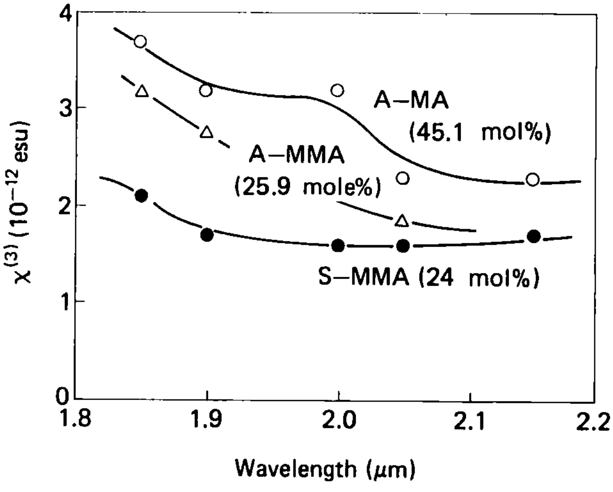


FIGURE 5 $\chi^{(3)}$ of three copolymers containing azo or stilbene dyes as a function of wavelength.

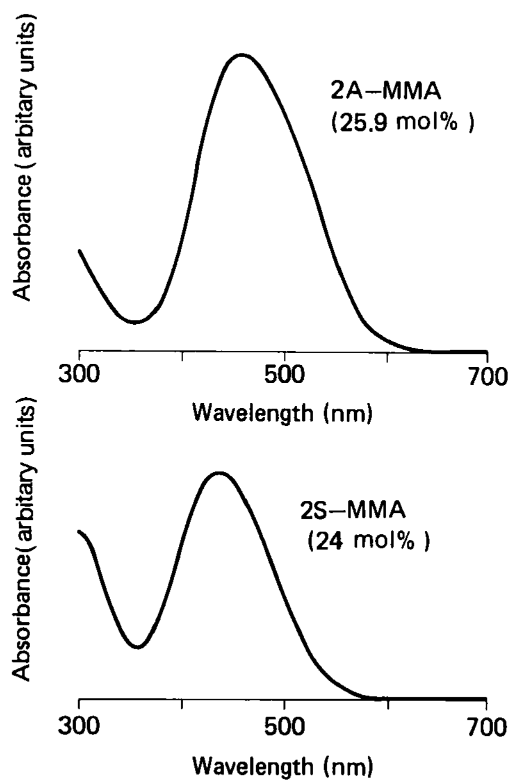


FIGURE 6 Absorption spectra of dye pendant copolymer thin films.

The wavelength dependence of $\chi^{(3)}$ is small in these polymers. The largest $\chi^{(3)}$ is 1.2×10^{-11} esu for 4AS-PAA. This is very large among processable polymer films. Polyamic acid with phenyl azobenzene (2A-PAA) has a larger $\chi^{(3)}$ than stilbene (2S-PAA). This is consistent with the results obtained for dye pendant polymers described above. The phenyl azobenzene structure is thought to be more useful for generating optical nonlinearity than the stilbene structure. This is probably because it has a better conformation for polarization, in other words a planar

TABLE I

$\chi^{(3)}$ of polyamic acids and polyimides at 1.9 μm.

Polymer	$\chi^{(3)}$ (10^{-12} esu)
2S-PAA	0.54
2A-PAA	0.73
3A-PAA	2.7
4AS-PAA	12
3A-PI	2.8

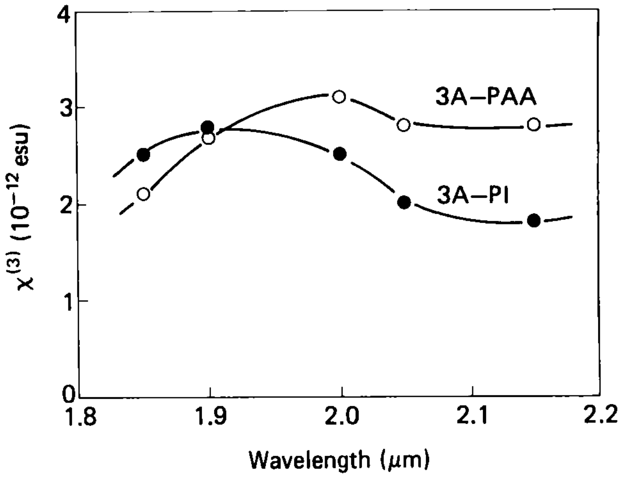


FIGURE 7 Comparison of $\chi^{(3)}$ in polyamic acid 3A-PAA and polyimide 3A-PI at wavelengths from 1.85 μm to 2.15 μm.

structure could be easily obtained for a phenyl azobenzene skeleton. Figure 7 compares $\chi^{(3)}$ in polyamic acid 3A-PAA and polyimide 3A-PI at wavelengths from 1.85 μm to 2.15 μm. The conversion from polyamic acid to the polyimide slightly decreases $\chi^{(3)}$ at wavelengths longer than 2.05 μm, where the wavelength dependences of $\chi^{(3)}$ are very small. This is probably because the π-electron conjugated length is scarcely extended by the conversion. In addition, imide rings are supposed to act as electron acceptors.

A comparison of polyamic acids 2S-PAA, 2A-PAA, 3A-PAA, and 4AS-PAA reveals the dependence of $\chi^{(3)}$ on the conjugated π-bond length. The $\chi^{(3)}$ of 2S-PAA and 2A-PAA, which are π-electron conjugated systems containing two benzene rings bonded through a carbon–carbon (—CH=CH—) or nitrogen–nitrogen (—N=N—) double bond, is of the order of 10^{-13} esu. 3A-PAA with three benzene rings and 4A-PAA with four rings (two benzene rings and two naphthalene rings) have $\chi^{(3)}$ of the order of 10^{-12} esu and 10^{-11} esu, respectively. If the π-conjugated length is assumed to be approximately equivalent in a 1,4-substituted naphthalene ring and benzene ring for these π-conjugation systems, and also in carbon–carbon and nitrogen-nitrogen bonds, then the dependence of $\chi^{(3)}$ on π-conjugated length is given by the open circles in Figure 8. It shows that lg $\chi^{(3)}$ vs. lg n is approximately linear. The power law dependence of $\chi^{(3)}$ on the conjugated length n has an exponent of 3.5. The number densities of π-conjugated groups in the all polymers are different. Thus, the $\chi^{(3)}$ value was calculated at a number density of 6×10^{20} cm^{-3} assuming the relative density is 1 in all polymers. They are shown as closed circles in Figure 8. The power law dependence has an exponent of 4.5. This value is close to the theoretically predicted value for conjugated linear chains such as polyenes.[14,15]

A comparison of the $\chi^{(3)}$ values of dye pendant polymer A-MMA and polyamic

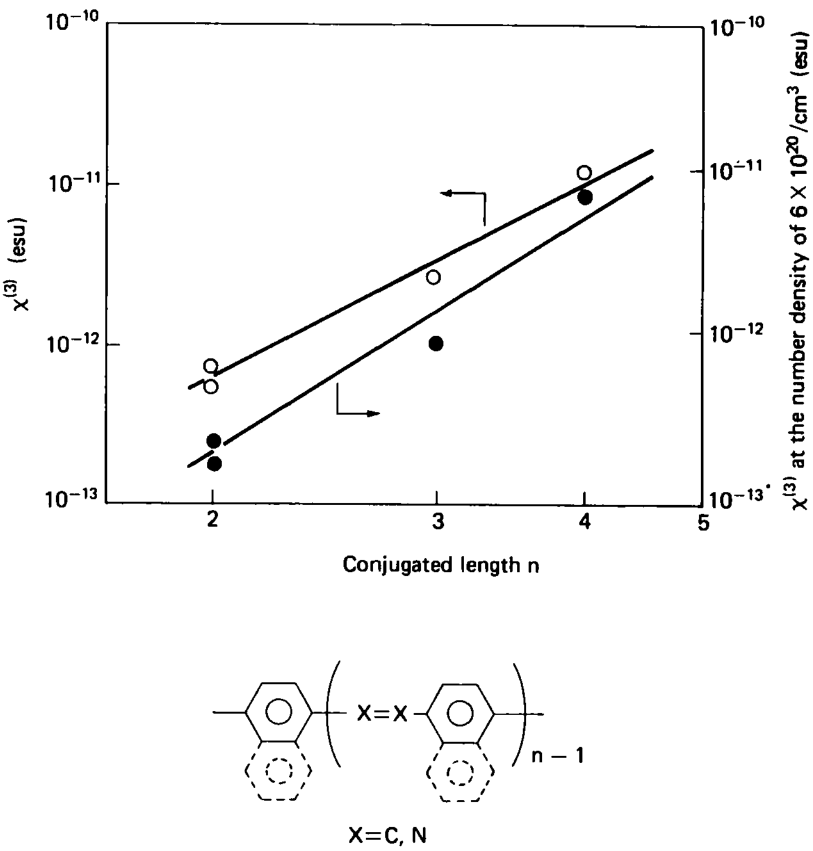


FIGURE 8 Dependence of $\chi^{(3)}$ on pi-conjugated length (open circles); $\chi^{(3)}$ at the number density of 6×10^{20} cm^{-3} as a function of conjugated length (closed circles).

acid 2A-PAA reveals the effect of intramolecular charge transfer. These polymers have a π-conjugated system of two benzene rings bonded through a nitrogen–nitrogen bond (i.e. a phenyl azobenzene unit). The $\chi^{(3)}$ values are 2.7×10^{-12} esu and 7.3×10^{-13} esu in A-MAA (25.9 mol%) and 2A-PAA, respectively. It is four times larger in A-MMA than in 2A-PAA. On the other hand, the density of the phenyl azobenzene unit in the polymer, which is calculated on the assumption that the relative density is 1, is 9.2×10^{23} cm^{-3} in A-MMA, and 1.4×10^{24} cm^{-3} in 2A-PAA. The density of A-MMA is two-thirds that of 2A-PAA. Therefore, by taking into consideration the difference in number density of the phenyl azobenzene unit, the third-order optical nonlinearity of A-MMA becomes about six times as large as that of 2A-PAA. This is due to the difference in substitution groups between them, that is A-MMA possesses an electron donor and an acceptor at the ends of the phenyl azobenzene, but 2A-PAA does not. It is concluded that the intramolecular charge transfer derived from substituted donor and acceptor groups contributes to the increase in third order optical nonlinearity.

CONCLUSION

Several processable polymers with a high $\chi^{(3)}$ were obtained; these possess nonlinearity generating units in their side chain or main chain. This shows that a large $\chi^{(3)}$ can be achieved even in relatively short π-conjugated system. A comparison of $\chi^{(3)}$ of these polymers revealed the dependence of $\chi^{(3)}$ on the π-conjugated length. The fact that the existence of electron acceptor and donor groups substituted at both ends of a π-electron conjugated system increases the third order optical nonlinearity was also confirmed. These polymers are easy to process and have good transparency; thus they are suitable for device applications. The $\chi^{(3)}$ is still lower than that in π-conjugated polymer crystals such as polydiacetylene. Further studies will develop higher $\chi^{(3)}$ materials by incorporating units possessing greater optical nonlinearity.

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