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Communications

Cubic Nonlinear Optics of Polymer Thin Films. Effects of Structure and Dispersion on the Nonlinear Optical Properties of Aromatic Schiff Base Polymers

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The conjugated aromatic Schiff base polymers or poly(azomethines) are thermally stable film- and fiber-forming materials that exhibit good mechanical strength, thermotropic liquid crystallinity, and lyotropic liquid crystallinity in concentrated sulfuric or methanesulfonic acid.[1-3] Although these features of the aromatic poly(azomethines) have been investigated for many years,[1-3] the detailed structure and solid-state properties of this class of polymers have not been previously studied because of their general *insolubility* except in strong concentrated acids in which they rapidly degrade due to the hydrolysis of the Schiff base (—CH=N—). We recently reported the preparation of soluble complexes of a series of conjugated aromatic poly(azomethines) and their solution processing to optical-quality thin films suitable for characterization of linear optical, nonlinear optical, and electronic properties of the polymers.[4] Here, we will report on our initial study of the third-order nonlinear optical properties of two members of the conjugated aromatic poly(azomethines) to explore the effects of structure and wavelength dispersion on the cubic nonlinear optics of polymer thin films.

Our interest in these aromatic Schiff base polymers as third-order nonlinear optical materials is based in part on their unique and rich molecular structures [(—R_1—N=CH—)$_n$ and (—R_1—N=CH—R_2—CH=N—)$_n$] and their relationship to other *p*-phenylene polymers. The R_1 and R_2 groups in the Schiff base polymer backbones can be varied with considerable lattitude because of the readily obtainable diamines and dialdehydes from which the polymers are made by condensation polymerization. Thus, such a class of polymers is ideal for investigating structure–nonlinear optical property relationships. The conjugated aromatic poly(azomethines) are isoelectronic with poly(*p*-phenylenevinylene) (PPV) and derivatives whose electronic structure and nonlinear optical properties have been widely investigated.[5-9] For example, films of PPV and its 2,5-dimethoxy derivative (PDMOPV) have $\chi^{(3)}$ values, measured by third harmonic generation, of 7.8 × 10^{-12} and 5.4 × 10^{-11} esu, respectively, at 1.85 μm.[7] Highly oriented PPV films have a $\chi^{(3)}$ of 1.5 × 10^{-10} esu at 1.85 μm.[9] Similarly large third-order optical nonlinearities can be expected in conjugated aromatic poly(azomethines). On the basis of the theoretically predicted[10] anharmonicity effect on $\chi^{(3)}$, the aromatic poly(azomethines) might be

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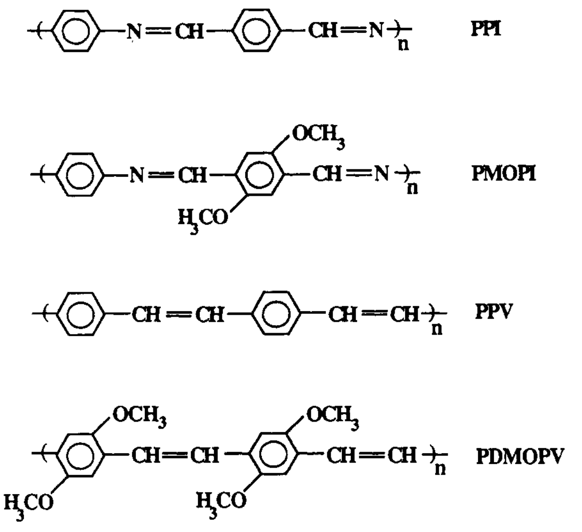
Chart I



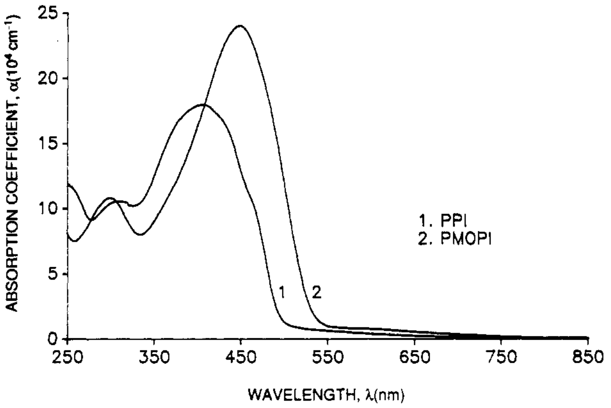


Figure 1. Optical absorption spectra of thin films of PPI and PMOPI.

expected to have larger optical nonlinearities compared to their corresponding vinylene-linked polymers due to the anharmonicity arising from a nitrogen replacing one CH in vinylene links.

This communication reports our picosecond third harmonic generation measurement of the third-order susceptibility $\chi^{(3)}$ and its wavelength dispersion in two members of the conjugated aromatic Schiff base polymers: poly(1,4-phenylenemethylidynenitrilo-1,4-phenylenenitrilomethylidyne) (PPI, Chart I) and poly(1,4-phenylenemethylidynenitrilo-2,5-dimethoxy-1,4-phenylenenitrilomethylidyne) (PMOPI, Chart I). The preparation, characterization, and thin-film processing of PPI, PMOPI, and related Schiff base polymers have previously been described.[4]

Thin films of the polymers were prepared on optically flat fused silica substrates (5 cm in diameter) from either soluble $GaCl_3$ complexes in nitromethane or di-*m*-cresyl phosphate (DCP) complexes in *m*-cresol.[4] As reported in detail elsewhere,[4] the polymer thin films prepared from these complexes are completely free of $GaCl_3$, DCP, or solvent as confirmed by infrared and electronic absorption spectroscopies and by thermal analysis, including differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Figure 1 shows the electronic absorption spectrum of the parent aromatic poly(azomethine) (PPI). This electronic spectrum shows that PPI absorbs in the visible with λ_{max} at 405 nm and an optical bandgap (E_g) of 2.50 eV. 2,5-Dimethoxy substitution of every other *p*-phenylene ring in PPI causes a significant red shift in the optical absorpion spectrum as observed in Figure 1 for the spectrum of PMOPI. The λ_{max} and E_g of PMOPI are 450 nm and 2.34 eV, respectively. The linear optical properties of PPI and PMOPI are collected in Table I. Other substitutions in the aromatic poly(azomethines) were previously observed to produce expected variation in the optical properties λ_{max} and E_g.[4]

Table I. Intrinsic Viscosity [η], λ_{max}, α, Optical Bandgap, and Resonant and Nonresonant $\chi^{(3)}$ of Schiff Base Polymers

polymer	[η],[a] dL/g	λ_{max}, nm	$10^4\alpha$,[b] cm^{-1}	E_g, eV	$10^{-12}\chi^{(3)}$ (−3ω;ω,ω,ω), esu nonresonant (at 2.38 μm)	resonant (at $3\lambda_{max}$)
PPI	1.38	405	18	2.50	1.6	16
PMOPI	1.04	450	24	2.34	7.3	54

[a] In nitromethane/$GaCl_3$ at 30 °C. [b] Absorption coefficient at λ_{max}.

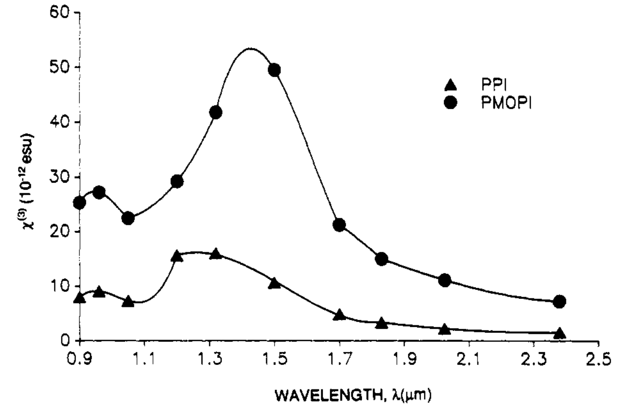


Figure 2. $|\chi^{(3)}|$ spectra of two aromatic Schiff base polymers (PPI and PMOPI). The solid lines are to guide the eye only.

The third harmonic generation (THG) measurements of the magnitude of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ were made with a picosecond laser system continuously tunable in the range 0.6–4.0 μm[11] and following the procedure previously described.[12] The THG experiments in the present study were performed at a fundamental wavelength of 0.9–2.4 μm. The reported $\chi^{(3)}$ values are average values, corrected for absorption at the third harmonic wavelength and obtained relative to the $\chi^{(3)}$ for fused silica (2.8×10^{-14} esu at 1.9 μm).[13] The error for the reported $\chi^{(3)}$ values is ±20% due mostly to the error in film thickness measurement. The repeatability of individual results for each sample was ±5%.

The wavelength dispersion of the magnitude of the third-order susceptibility $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ of PPI and PMOPI thin films in the wavelength range 0.9–2.4 μm is shown in Figure 2. The nonresonant $\chi^{(3)}$ values for PPI and PMOPI were $\sim 1.6 \times 10^{-12}$ and $\sim 7.3 \times 10^{-12}$ esu, respectively, at 2.4-μm wavelength (Table I). The magnitude of the nonresonant cubic optical nonlinearity of PMOPI is about a factor of 5 larger than that of the parent aromatic poly(azomethine) (PPI). The enhancement of the nonresonant third-order optical properties of PPI by dimethoxy substitution can be explained by the greater electron delocalization in PMOPI as evidenced by its smaller bandgap.

The $|\chi^{(3)}|$ spectra of PPI and PMOPI in Figure 2 exhibit a resonance feature that can be attributed to dispersive processes since the optical spectra of the polymers did not

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show any absorption features in the wavelength range 0.80–3 μm. The resonance peak in the $\chi^{(3)}$ spectra of PPI and PMOPI was ~1.2 and ~1.35 μm, respectively, and hence suggests a three-photon resonance as the origin of the observed peak in the wavelength dispersion of the third-order optical susceptibility. As shown in Table I, the magnitude of the three-photon resonance enhanced $\chi^{(3)}$ of PPI and PMOPI was 1.6×10^{-11} and 5.4×10^{-11} esu, respectively. Thus, three-photon resonance enhancements result in about 1 order of magnitude increase for PPI and a factor of 8 increase for PMOPI above the nonresonant optical nonlinearities for these two aromatic poly(azomethines).

Although a detailed quantitative comparison of the measured third-order optical nonlinearities of PPI and PMOPI cannot be made with those of their isoelectronic vinylene polymers PPV and PDMOPV because the complete $\chi^{(3)}$ spectrum of any of the vinylene polymers has not been reported, a qualitative comparison is in order. In the case of the Schiff base polymer PPI and its vinylene analogue PPV, the two polymers exhibit similar optical absorption spectra[4] with a $\lambda_{\max}$ at 405 nm. Therefore, a similar dispersion due to three-photon resonance can be expected in the $\chi^{(3)}$ spectrum of PPV as observed in Figure 2 for PPI. The reported $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ of PPV at 1.85 μm (7.8×10^{-12} esu) is most likely resonantly enhanced. For comparison purposes, the corresponding $\chi^{(3)}$ value of PPI at 1.83 μm is 3.3×10^{-12} esu and this value too is resonantly enhanced. In the case of PDMOPV, the reported $\chi^{(3)}$ of 5.4×10^{-11} esu at 1.85 μm is to be compared with 1.5×10^{-11} esu for PMOPI at 1.83 μm. Here, the major difference in the optical nonlinearities of PMOPI and PDMOPV can be traced to two factors. First, it should be noticed that PDMOPV at 1.85 μm is much closer to a three-photon resonance peak (~1.5 μm) than PMOPI is at 1.83 μm to its three-photon resonance at 1.35 μm. Second, the greater degree of π-electron delocalization in PDMOPV ($\lambda_{\max}$ = 500 nm) compared to PMOPI ($\lambda_{\max}$ = 450 nm) also contributes to the larger optical nonlinearity. The greater π-electron delocalization in PDMOPV is due to 2,5-dimethoxy substitution on every *p*-phenylene ring of the polymer, whereas only every other *p*-phenylene ring in PMOPI is so substituted. Thus, it can be anticipated that 2,5-dimethoxy substitution on every ring of PMOPI will further enhance the optical nonlinearity.

In summary, we have investigated the third-order nonlinear optical properties of two conjugated aromatic Schiff base polymers, PPI and PMOPI, by picosecond third harmonic generation and show that they are a new class of third-order nonlinear optical materials. The measured $|\chi^{(3)}(-3\omega,\omega,\omega,\omega)|$ spectra of PPI and PMOPI in the wavelength range 0.9–2.4 μm showed a three-photon resonance peak at 1.2 and 1.35 μm, respectively. The resulting resonance enhanced $\chi^{(3)}$ was 1.6×10^{-11} and 5.4×10^{-11} esu for PPI and PMOPI, respectively. The nonresonant $|\chi^{(3)}|$ values of PPI and PMOPI at 2.4 μm were 1.6×10^{-12} and 7.3×10^{-12} esu, respectively. These results show that a simple structural modification of PPI, as realized in its derivative PMOPI, results in a factor of 3–5 enhancement of the cubic nonlinear optical properties over the entire spectrum of $\chi^{(3)}$ investigated. Furthermore, three-photon resonance evidenced in the dispersion of $\chi^{(3)}$ enhanced the optical nonlinearities by about a factor of 10 above the off-resonance nonlinearities. Considering the many as-yet unexplored possible structural modifications afforded by the conjugated Schiff base polymers, it can be expected that larger $\chi^{(3)}$ values may be found in other derivatives.

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Comparison of Simultaneous and Preirradiation Grafting of Methyl Methacrylate onto a Porous Membrane

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Radiation-induced graft polymerization is an effective technique for tailoring existing polymers of various shapes. We adopted porous membranes in a flat sheet[1] or hollow fiber[2] as a trunk polymer and introduced the chelate-forming groups[3] and affinity ligands.[4] Radiation-induced grafting can be classified into two categories: (1) simultaneous irradiation or preirradiation grafting; (2) vapor-phase or liquid-phase grafting. In addition, the preirradiation technique can be divided into two modes: with or without exposure to air before grafting. In a previous paper,[5] porous cellulose triacetate membrane was irradiated in a nitrogen atmosphere, and after exposure to air for about 1 min, methyl methacrylate (MMA) was contacted with the membrane in vapor and liquid phases, and the water permeability of the resulting MMA-grafted membranes was then compared. When the trunk polymer had a porous structure, the grafted polymer branches were formed both on the surface of the internal macropore and in the amorphous domain of the polymer matrix. To control the water permeability of the porous functional membrane, it is important to select the grafting technique governing the location of the grafted polymer branches. We report here the comparison of the water permeability of the MMA-grafted membranes prepared by the two modes of vapor-phase grafting and discuss the location of the grafted polymer branches.

A commercially available porous cellulose triacetate (CTA) membrane (FM22, Fuji Film Co., Ltd., Japan) was used as the trunk polymer for grafting. The diameter and

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