

Nonlinear Optical Properties of Solution of the Substituted Polyaniline

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SYNOPSIS

Nonlinear optical properties of solution of substituted polyaniline (PANI), such as polytoluidine (POT), Br-POT, and Br-PANI, were measured by the degenerate four-wave mixing (DFWM) method as a function of the concentration of solution and the protonation state. The observed nonlinear optical properties are intrinsic and might be related to the resonance effect and the photoexcitation of the molecule on the quinoid ring of the poly-emeraldine chain. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Organic polymeric systems containing π -electron conjugated structure show strong nonlinear optical effects because of the large π -electron contribution to the third harmonic susceptibility.¹ The promise of conducting polymers that are fast-response nonlinear optical materials has been recently emphasized because of its application for fast optical switches, transient nonlinear memories, and optical transistors.^{2,3} Polyaniline (PANI) is a unique class of conducting polymers in that the chemical and physical properties are controlled by both the oxidation state and the protonation state.^{4,5} Epstein et al.⁶ reported the photoinduced absorption (at 0.9, 1.4, and 3.0 eV) and photoinduced bleaching (at 1.8 eV) for the emeraldine base form of PANI. It was suggested that the photoinduced absorption and photoinduced bleaching are related to nonlinear optical properties of PANI. Moreover, Wong et al.⁷ measured the third harmonic generation of the base form of PANI by the degenerate four-wave mixing (DFWM) method. Wan et al.⁸ measured the third nonlinear susceptibility of the thin film of the base form of PANI by the Maker Fringe method. Furthermore, we have studied the nonlinear optical

properties of solution of PANI in NMP solvent in detail.⁹ However, the origin of the third-order optical nonlinearity of PANI is not well understood.

In this paper, the third-order nonlinear optical effects of the substituted PANI obtained by the DFWM method is reported and the origin of its nonlinear optical properties is discussed.

EXPERIMENTAL

Polyaniline (PANI) and polytoluidine (POT) were synthesized by the MacDiarmid method.¹⁰ Br-PANI and Br-POT were obtained by reaction of the solution of PANI and POT in NMP solvent with Br₂H₂O. Resulted products were filtered and dried under vacuum chamber at 60°C, followed by treatment with NH₃H₂O to convert to neutral. Substituted PANI obtained in this paper was characterized by elemental analysis, FTIR, and UV-visible spectrum, which will be reported elsewhere.¹¹ The solution of neutral POT, Br-POT, and Br-PANI in NMP solvent was made by the adding of its neutral powder into the NMP solvent to produce a blue solution, while the solution of POT, Br-POT, and Br-PANI with a different protonation state was adjusted by adding hydrochloric acid with a high concentration. The protonation state of solution was controlled by the pH value measured with a pH meter (S-10A model).

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General speaking, the third nonlinear optical effect is characterized by a microscopic hyperpolarizability, γ , and a corresponding bulk susceptibility, $\chi^{(3)}$. The third-order nonlinear optical effect can be best understood in the general picture of four-wave mixing (FWM).¹² Three input waves, $E(\omega_1)$, $E(\omega_2)$, and $E(\omega_3)$, interact in a medium to generate a coherent phase-matched output at $E(\omega_4)$, where

$$E(\omega_4) = \chi^{(3)}(-\omega_4, \omega_1, \omega_2, \omega_3)E(\omega_1)E(\omega_2)E(\omega_3)$$

The measurement of $E(\omega_4)$ at a known input field $E(\omega_1)$, $E(\omega_2)$, and $E(\omega_3)$ and known polarization yields information about $\chi^{(3)}$. In third harmonic generation (THG), $\omega_1 = \omega_2 = \omega_3$ and $\omega_4 = 3\omega$. In other words, one passes a beam of frequency ω through the medium, and interaction of three photon fields from the same beam generates a coherent output $E(3\omega)$. The measurement of third harmonic generation can yield $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$. In DFWM, one generally uses two counterpropagating beams at $E_1(\omega)$ and $E_2^*(-\omega)$; a third beam, $E_3(\omega)$, incident at a small angle with respect to $E_1(\omega)$ generates a phase conjugated $E_4^*(-\omega)$ that counterpropagates with respect to $E_3(\omega)$. $E_4^*(-\omega)$ is proportional to $\chi^{(3)}(-\omega, \omega, -\omega, \omega)$.

The nonlinear optical properties of solution of substituted PANI in NMP were measured by the DFWM method. For ideal conditions, the diffraction efficiency of a weak and thin grating is given by¹³

$$\eta = \frac{d}{4} (\Delta K^2 + k^2 \Delta n^2) \quad (1)$$

Here d is the thickness of the sample, $k = 2\pi/\lambda$ is the circular wavenumber, and ΔK and Δn are the amplitudes of the spatially modulated absorption coefficient for the field strength and refractive index, respectively. It has been demonstrated that the diffraction efficiency is related to the third harmonic susceptibility, as shown¹³:

$$\chi^{(3)} = \frac{n^2 - \Delta n}{Z_0 I} - i \frac{n^2 \Delta K}{Z_0 I K} \quad (2)$$

where $Z_0 = 120 \pi \Omega$ is the wave impedance and I is the irradiance of the light. It should be noted that eq. (3) is correct only when the following conditions are satisfied:

$$n^2 \gg \frac{K^2}{k^2} \quad \text{and} \quad \left| \frac{\Delta K}{K} \right| \gg \left| \frac{\Delta n}{n} \right| \quad (3)$$

Thus, it is possible to obtain the third harmonic susceptibility of the tested sample if the diffraction efficiency of the tested and standard samples can be measured at the same measuring conditions. The measurements of the diffraction efficiency have been carried out by dye laser with a repeat frequency of 10 Hz and with pulse width of 7 ns operating at the wavelength of 5850 Å at power density of 5 MW/cm². All nonlinear optical measurements were performed at room temperature and a sample cell with 1.0 mm thick was used. To avoid measuring error, the laser energies were controlled to refrain from the saturated excitation and to measure the diffraction signal of all samples at the same conditions. The diffraction signal from the sample was measured by a photoelectric diode with high speed and it was treated by a signal average meter (EG & G 4203 Model). All measured results indicate that the diffraction signal observed is due to the substituted PANI since no diffraction signal from NMP solvent itself was observed.

RESULTS AND DISCUSSION

1. Absorption Spectra

It has been reported that two peaks at 320 nm (A) and at 630 nm (B) for the base form of PANI were observed.¹⁴ It was demonstrated that peak A was due to the π - π^* transition on the polymer chain of PANI, whereas peak B was due to excitation of the quinoid segment of polyemeraldine.¹⁵ Typical UV-visible absorption spectra for a neutral solution of substituted PANI in NMP solvent at 250–850 nm are shown in Figure 1. One can see that peak A for all substituted PANI reported in this paper was located at 320 nm. This suggests that the π - π^* transition is independent of the substitution on the PANI ring. On the other hand, peak B is shifted from 630 to 580, 620, and 625 nm for Br-POT, POT, and Br-PANI, respectively. These results suggest that substituted fashion on PANI rings affects only the excitation of quinoid segment of PANI. As mentioned before, the fundamental wavelength of 5850 Å was used, which is located at absorption peak B, to measure the nonlinear optical properties of substituted PANI. Therefore, the resonance effect contributed to third harmonic susceptibility should be considered.

2. Concentration of Solution

A typical relationship between the relative intensity of the diffraction signal and the concentration of

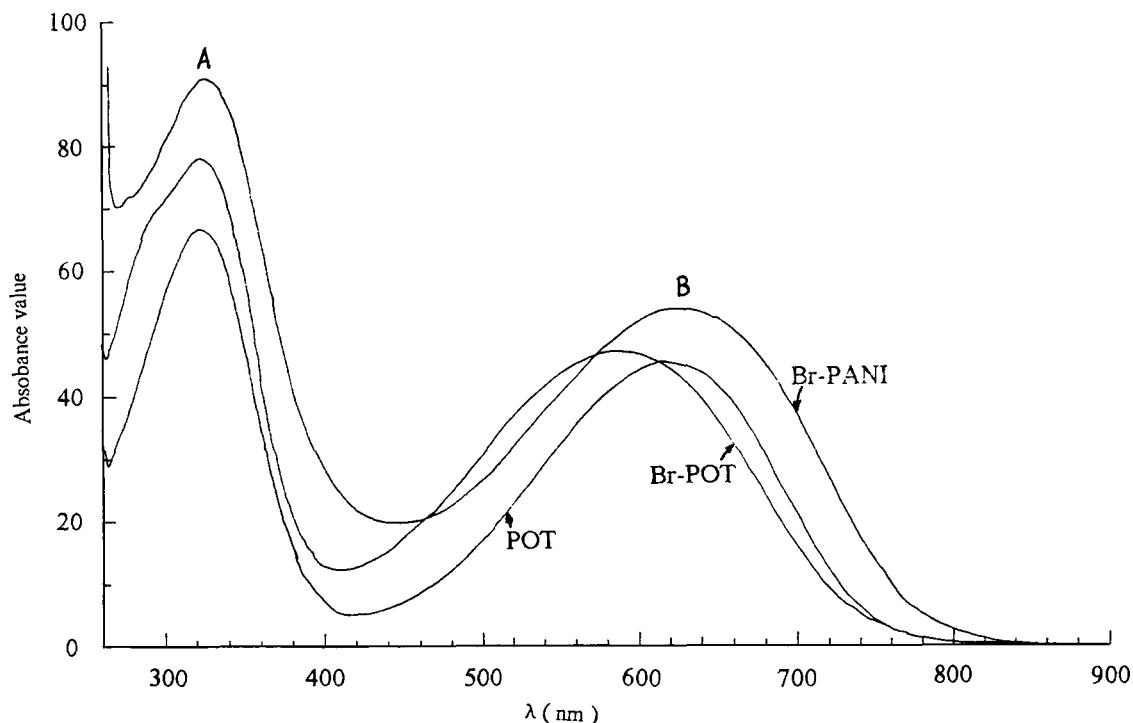


Figure 1 UV-visible absorption spectra of solution for neutral-substituted PANI in NMP solvent POT (2.25×10^{-4} mol/L), Br-POT (1.25×10^{-4} mol/L), and Br-PANI (3.75×10^{-3} mol/L).

solution for POT, Br-POT, and Br-PANI in NMP is shown in Figures 2–4, respectively. As one can see, a saturated phenomenon for the intensity of the diffraction signal of the POT, Br-POT, and Br-PANI was observed, i.e., the relative intensity of the diffraction signal increases with increase of the concentration when the concentration of the solution is lower than the critical concentration, while it is

independent of the concentration of solution as the concentration of the solution is higher than this critical concentration. The critical concentration for POT, Br-POT, and Br-PANI was observed at 7×10^{-4} , 1.0×10^{-3} , and 1.4×10^{-3} mol/L, respectively. The saturated phenomenon of the intensity of diffraction single with the concentration of the solution is consistent with observations obtained

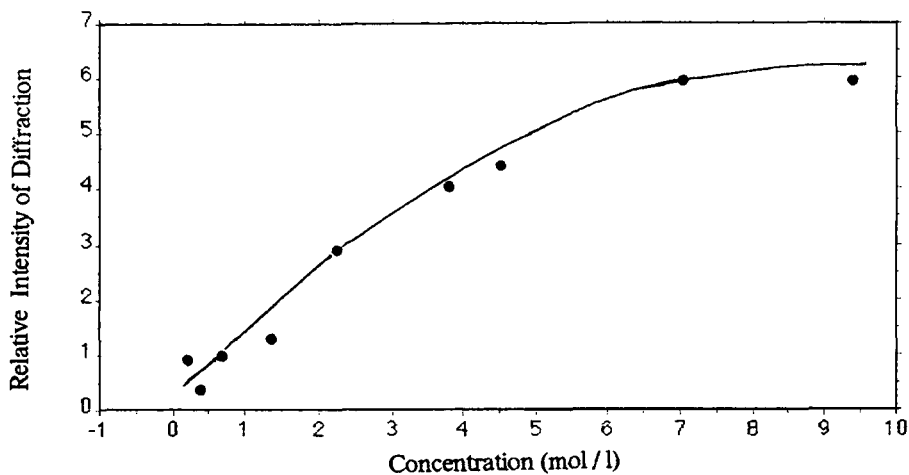


Figure 2 Dependence of the concentration of solution on the relative intensity of the diffraction signal for POT solution in NMP.

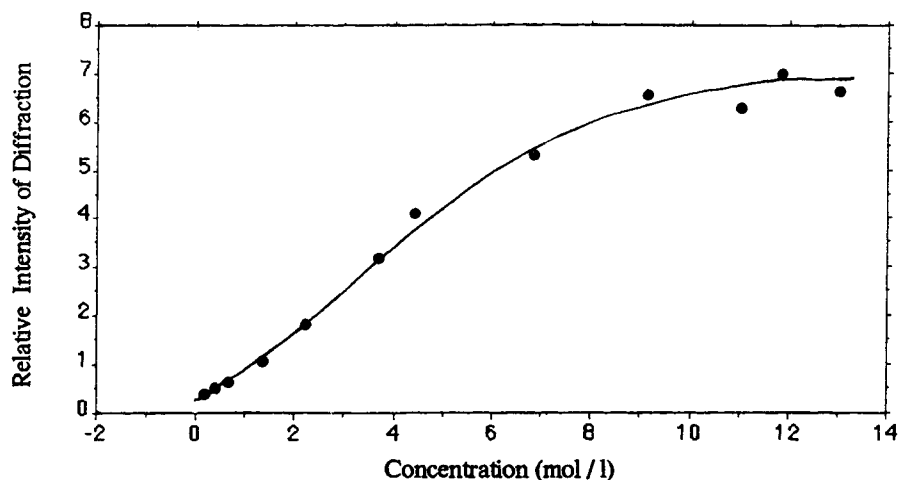


Figure 3 Dependence of the concentration of solution on the relative intensity of diffraction signal for Br-POT solution in NMP.

from PANI.⁹ The saturated diffraction intensity with the concentration of the solution might be due to the following facts: the first fact might be a resonance effect because of the fundamental wavelength of 5850 Å located at the absorption peak B. This is consistent with observations that the absorption of peak B increases with increase of the concentration.¹⁶ The second fact might be due to a deviation of the apparent concentration from the real concentration of solution because the absorption value at 630 nm does not obey Beer's law when the concentration is higher due to that the concentration of the solution made in the experiment is lower than that calculated by the weight used.¹⁶ However, the critical concentration for substituted PANI is higher than that of PANI.⁹ In addition, it was noted that

the relative intensity of the diffraction signal of PANI is higher than that of substituted PANI when the concentration of the solution was the same. The relative intensity of the diffraction signal at the same concentration was shown in the order of PANI > POT ~ Br-POT > Br-PANI, and $\chi^{(3)}$ is about 10^{-11} – 10^{-12} esu determined by SO₂ as the standard sample. As known, the third harmonic susceptibility of π -conjugated polymers strongly depends on the delocalization of electrons.¹⁷ Therefore, it is reasonable to expect that the third harmonic susceptibility of POT should be lower than that of PANI because the localization extent of electrons in POT is higher than that of PANI, which is supported by the fact that the conductivity of POT at room temperature is lower than that of PANI.¹⁸

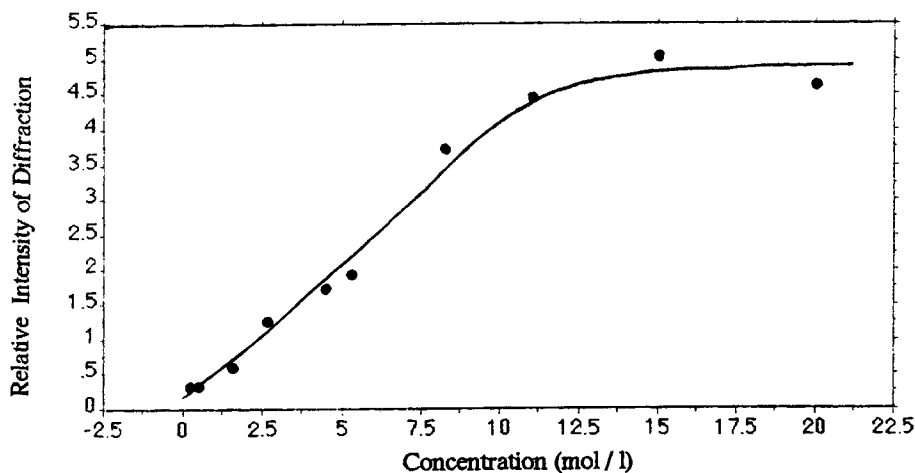


Figure 4 Dependence of the concentration of solution on the relative intensity of diffraction signal for Br-PANI solution in NMP.

3. Protonation State

It has been demonstrated that an insulator-to-metal transition occurred when the base form of PANI was protonated by aqueous acid solution¹⁹ and the nonlinear optical properties of solution of PANI in NMP depends on the protonation state.⁹ Thus, it is necessary to measure the effect of the protonation state on the relative intensity of the diffraction signal of substituted PANI. At pH values of 1–14, a typical dependence of the protonation state on the relative intensity of the diffraction signal for POT and Br-POT is shown in Figures 5 and 6, respectively. For the POT sample, a maximum relative intensity of the diffraction signal at pH 8–9 was observed, whereas for the Br-POT sample, a maximum relative intensity of the diffraction signal at pH 6 was observed. This behavior is also consistent with observations obtained from PANI,⁹ where a maximum magnitude was observed at pH 7. Therefore, these results indicate that the maximum magnitude corresponding to the intensity of the diffraction signal depends on the substitution on the PANI rings.

Heeger et al.²⁰ suggested that prior to charge injection by photoexcitation of electron-hole pairs, all the oscillator strength is in the interband absorption, $h\omega_3$ (or $h\omega_1$, $h\omega_2$, etc.). These shifts in oscillator strength occur on a time scale of $\sim 10^{-13}$ s. Based on Heeger et al.'s suggestion, thus, the nonlinear optical properties observed for conducting polymers may be related to photoexcitation of soliton, polaron, and bipolaron. However, our experimental results show that the relative intensity of the diffraction signal for substituted PANI decreases with increase of the protonation state when it was protonated by

aqueous acidic solution, as shown in Figures 5 and 6. This is inconsistent with suggestions proposed by Heeger et al.²⁰ We believe that this may be due to that only soliton, polaron, and bipolaron in Heeger et al.'s suggestion are considered to contribute to third harmonic susceptibility. In fact, $\chi^{(3)}$ measurement by DFWM or nonlinear refractive index determination can be complicated by contributions due to resonant excitations that can create excited-state species, thermal effects, and density changes.^{21,22} As described above, moreover, a resonance effect should be considered because the fundamental wavelength used for measurement of nonlinear optical properties was located near absorption peak B. Furthermore, the relative intensity of the diffraction signal for both PANI and substituted PANI decreases with increase of the protonation state. This is consistent with the fact that the absorption of peak B of PANI decreases with increase of the protonation state¹⁶ and it disappeared when PANI was fully protonated, which is called the emeraldine salt form of PANI. Therefore, it is reasonable to believe that the nonlinear optical properties of substituted PANI observed are related to the resonance effect and the photoexcitation of the quinoid ring on the polyemeraldine chain.

CONCLUSION

In summary, the third nonlinear optical properties of the solution of substituted PANI in NMP solvent strongly depends on the concentration of solution and the protonation state as well as the substitution on the PANI chain. The observed nonlinear optical

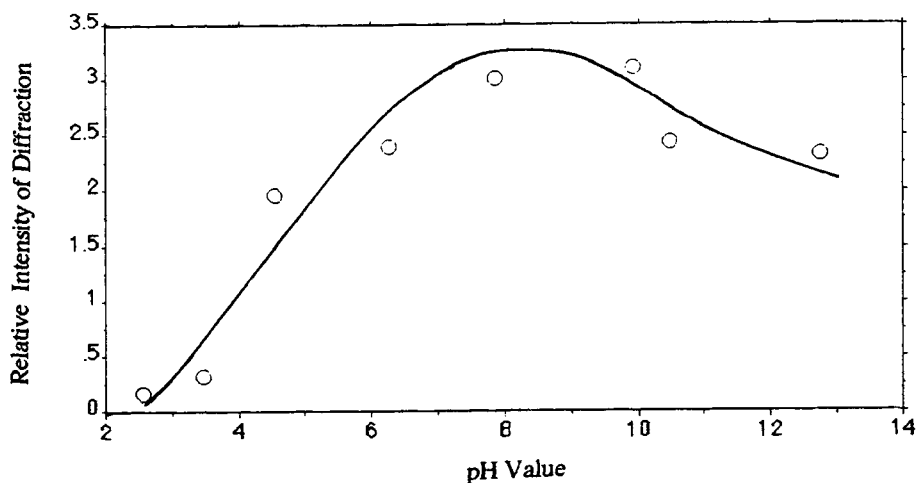


Figure 5 Dependence of the protonation state on the relative intensity of diffraction signal of POT solution in NMP.

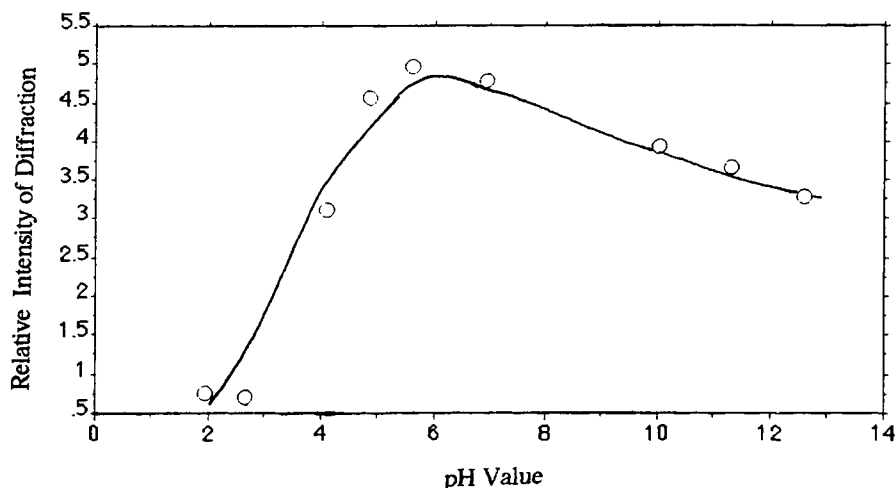


Figure 6 Dependence of the protonation state on the relative intensity of diffraction signal of Br-POT solution in NMP.

properties of substituted PANI are intrinsic and might be related to the resonance effect and the photoexcitation of the quinoid ring on the poly-emeraldine chain.

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