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Evidence for Second-Order Optical Nonlinearity in γ -Ray Induced Partially Cross-Linked Polyacrylonitrile

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The first direct evidence for second-order nonlinearity in partially cross-linked polyacrylonitrile is reported. The cross-linking in γ -ray-induced polymerized neat acrylonitrile is well supported by UV–vis spectroscopy, FTIR, and ¹³C CP/MAS solid-state NMR. The second harmonic generation (SHG) powder test was employed to access the preliminary information about the occurrence of second-order nonlinear effect. The second harmonic generation is accomplished without the application of an external electric field, thus illustrating the importance of structural changes imparted by high-energy photon flux. Second-order nonlinearity in the present case is expected due to the small π conjugation imparted by cross-linking through —C=N across polymeric chains coupled with the noncentrosymmetric molecular structure. Second harmonic intensity as high as 80% of that for powder urea has been observed.

Introduction

Advances in nonlinear optics hold promise for important applications in optical information processing, telecommunications, and integrated optics. To perform various optical operations, the second- or third-order nonlinear optical response of a material for an electric field at optical or radio frequency is required. Electrooptic devices employing the second-order nonlinear response provide many basic functions in modulation and frequency conversion. Organic materials, in recent years, have proved to be one of the promising nonlinear materials mainly because of the feasibility of molecular engineering, ultrafast responses with large optical nonlinearities and easy processability favoring existing technology.^{1–5} The nonlinear effects in organic polymers are dominated by polarizability of electrons in π orbitals,^{6,7} which makes them more suitable in high-speed applications such as high data rate electrooptic modulation.⁸ Unfortunately, most of the polymers are isotropic in nature and second-order nonlinearities are generally achieved by incorporating optical chromophores within the polymer where electric field induced SHG is usually observed.^{9–11} Electric poling generally causes the preferable macroscopic alignment of chromophore charge transfers over to generate electric dipole transitions and the origin of noncentrosymmetry could be attributed to the presence of isolated hyperpolarizable constituent chromophores. However, this method leads to several thermal reactions of chromophores, particularly during the poling of high-temperature polymer systems. Improved thermal and mechanical stability as well as long-term properties of NLO materials has been observed by cross-linking.¹² An alternative approach, LB film technique, for controlling the noncentrosymmetry with the controlled dimensions and a high degree of molecular order has recently been suggested.^{13–15}

Polyacrylonitrile (PAN) is an important polymer and has mainly been commercially used as a textile fiber since 1960. Recently, PAN has also been discovered as a precursor for the synthesis of carbon fiber, which is the basis of “advanced composites” used in aeronautic and aerospace applications.¹⁶ The pyrolysis of PAN leads to a conjugated imine system and has been reported to exhibit third-order nonlinearities.¹⁷

In this paper, we present the first direct evidence for second-order nonlinearity in partially cross-linked polyacrylonitrile, an abundant and flexible material that can be of immense technological interest in fabricating NLO devices. More specifically, we illustrate that a partially cross-linked PAN can exhibit second-order effects without the application of an external electric field. This is particularly significant, as it is difficult to achieve stable polar order in the absence of poling for most of the polymeric NLO materials. For example, SHG signals from solution-cast thin films of the hemicyanine–amylose supramolecule without any external poling have been reported.¹⁸

Experimental Section

The analytical grade acrylonitrile was distilled and neat monomer was sealed in a glass tube. The tube was exposed to γ radiation from a ⁶⁰Co source at room temperature. The polymer thus formed is further irradiated by the heavy doses of γ radiation. The irradiation time was varied from 24 to 168 h for the constant dose rate of 2000 rad/min. Both dose rate and irradiation time can be used to modulate the extent of cross-linking, although the accurate control at precise location (site specific) is difficult. The partially crystalline yellow polymer powder obtained was then characterized.

XRD of the PAN sample was recorded on Phillips PW 1729 diffractometer using Cu K α radiation. Optical absorption spectra were collected on a Hewlett-Packard 8452 diode array spectrophotometer with 2 nm spectral resolution at room temperature in the range 300–800 nm. The solutions were prepared by dissolving 1 mg of polymer in 5 mL of DMF at 40° C under

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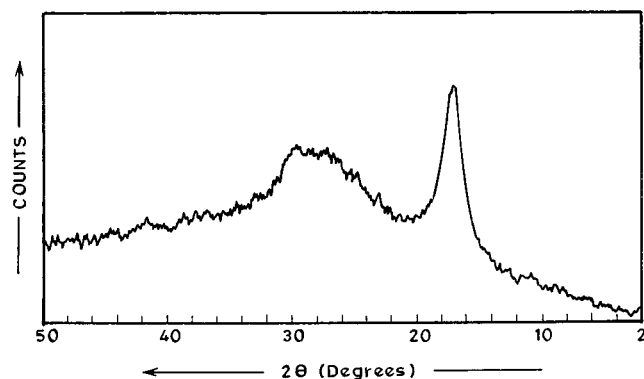


Figure 1. Typical XRD pattern of PAN after γ -irradiation for 96 h.

constant stirring. The infrared spectrum of the polymer in the transmission mode was obtained on a Perkin-Elmer 1600 FTIR spectrophotometer. The sample pellet was prepared by mixing 1 mg of polymer in 150 mg of KBr powder. ^{13}C CP/MAS solid-state NMR spectra were recorded on Bruker high-resolution FT-NMR spectrometer operated at 125 MHz for carbons. Cross polarization was achieved by a constant pulse of 1 ms. Samples were scanned at 4 and 6 kHz to recognize sidebands from the actual signals. Sample was accumulated for 800 scans at ambient temperature.

The second harmonic (SH) measurements were carried out by powder method.¹⁹ The PAN powder was pressed in the form of a pellet and was sandwiched between two microscope slides with the spacer. The experimental setup consisted of a TEM₀₀ mode Q-switched Nd:YAG laser with a pulse duration of 17 ns and repetition rate of 1 Hz. The laser beam with the spot size of 6 mm was incident on the pellet after filtering the stray radiation of the flash lamp. The second harmonic signal in the forward direction of the beam propagation was collected by a photomultiplier tube (EMI 6255QB) and the signal amplitude was measured by a fast storage oscilloscope (TEK 466); urea in the powder form was used as a reference.

Results and Discussion

Figure 1 shows the typical X-ray profile of PAN, indicating the intense maximum centered at $2\theta \sim 17^\circ$ corresponding to a 5.2 Å lateral repeat distance, which can be best interpreted as the (100) diffraction of an hexagonal lattice.²⁰ Thus, the PAN chains appear to have a nearest chain to chain distance of 5.2 Å. The crystalline domain size, 18 nm, was estimated using a Scherrer relation. A broad asymmetric peak in the range 20–30° is usually attributed to the off-equatorial scattering of PAN.

The optical absorption spectra of PAN samples recovered after various doses of γ radiation are depicted in Figure 2. All samples exhibit a band around 280 nm, which is attributed to the $\pi-\pi^*$ electronic transition of the nitrile group and has been suggested to be due to the absorption of complicated associates consisting of three nitrile groups. The bathochromical shift of this band with respect to its position corresponding to nonassociated nitrile groups has been explained on the basis of strong dipole-dipole interaction between nitrile groups of different macromolecules. This band is reported to be observed at about 270 nm for linear PAN in the form of films and in solution.²¹ This red shift in the absorption maximum suggests conjugated π segments in the PAN structure. High UV absorbance as well as a red-shifted absorbance maximum observed for PAN recovered from exposure times of 72 h (Figure 2b) and 96 h (Figure 2c) is indicative of the increased extent of $-\text{C}=\text{N}$ π conjugation.²² Further, the appearance of a broad absorbance

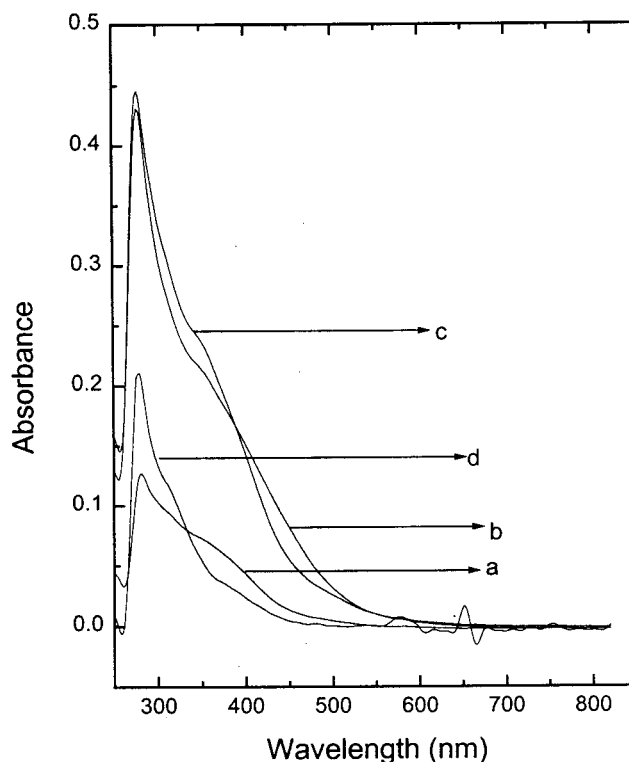


Figure 2. UV-vis absorption spectra of PAN samples recovered after different γ -radiation exposure time (a) 48 h; (b) 72 h; (c) 96 h; (d) 120 h.

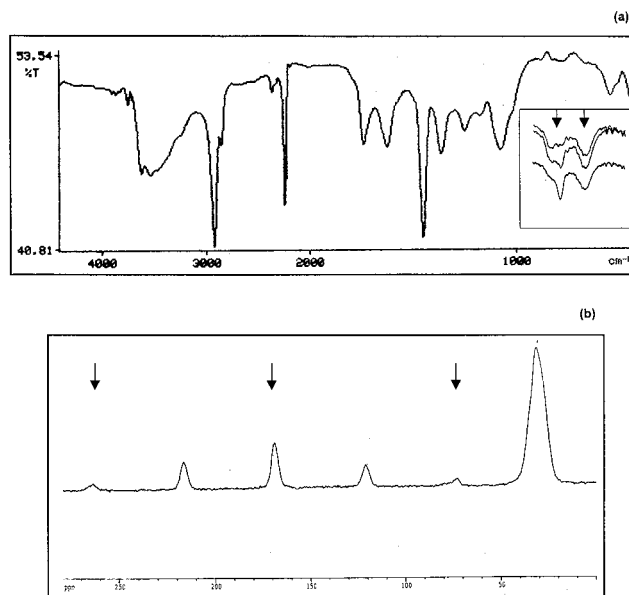
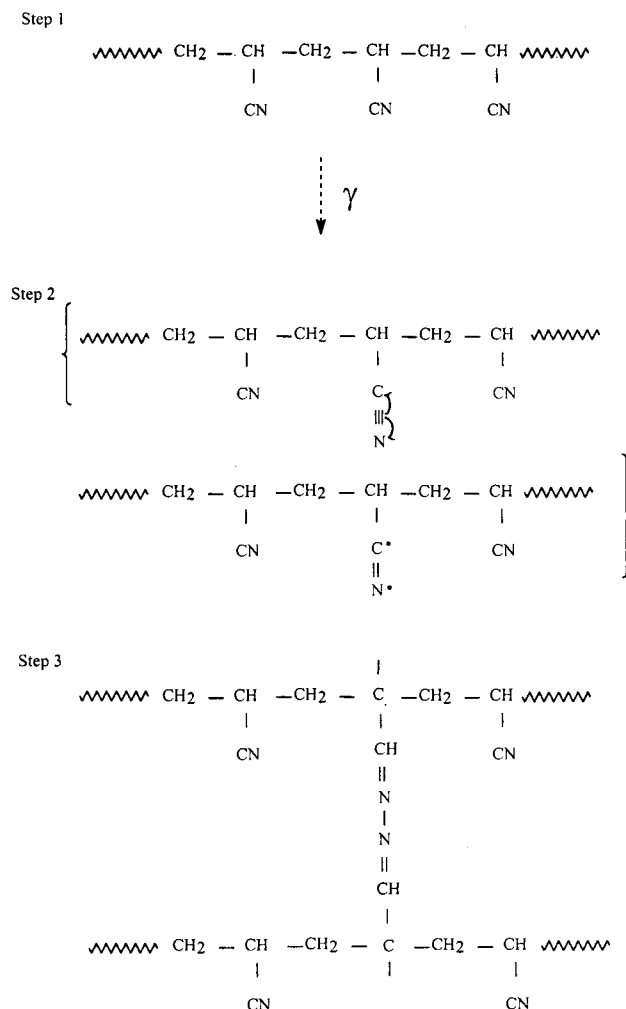


Figure 3. Identification of cross-linking in γ -ray induced polymerized acrylonitrile. (a) FTIR spectrum of the sample after 96 h of exposure with the dose rate of 2000 rad/min. The inset shows characteristic bands (indicated by arrows 1741 and 1621 cm^{-1}) of $-\text{HC}=\text{N}-\text{N}=\text{CH}-$ conjugation for increasing exposure time, viz. 48, 72, and 120 h (corresponding to the curves in the upward direction, respectively). (b) CP/MAS spectrum of the same sample scanned at room temperature. Contact time for CP = 1 ms. Arrows indicate spinning sidebands.

developed in the range 350–450 nm also reflects the formation of $\text{C}=\text{N}$ π electron conjugation system.

Figure 3a illustrates the FTIR of PAN. The σ bands at 2927, 2858, and 1454 cm^{-1} are undoubtedly assigned to $\nu_a(\text{CH}_2)$, $\nu_s(\text{CH}_2)$, and $\delta(\text{CH}_2)$ respectively, while the π band at 1364 cm^{-1} is most likely the $\gamma_w(\text{CH}_2)$ mode, which is much stronger. This is expected, as there can be an increase in the dipole moment

SCHEME 1



of the CH_2 group due to the influence of the neighboring $-\text{CN}$ group on the electronic structure.²³ The σ band at 2244 cm^{-1} is due to a nitrile group and a doublet in the range $1620\text{--}1750\text{ cm}^{-1}$ can be ascribed to the formation of $-\text{HC}=\text{N}-\text{N}=\text{CH}-$ conjugation across the polymeric chains.

The cross-linking of PAN is further confirmed by the ^{13}C CP/MAS solid-state NMR spectra presented in Figure 3b. The CP/MAS spectrum contains well-resolved resonances for the backbone ($28\text{--}42\text{ ppm}$, overlapping methylene and methine) and the side chain nitrile ($115\text{--}127\text{ ppm}$) corresponding to linear PAN. ^{13}C resonances are strongly influenced by the electronegativity of the functional groups. The downfield peak at around 216 ppm here can be interpreted in terms of $-\text{C}=\text{N}$ conjugation across the polymeric chains. The cross-linking in polymeric chains is expected to proceed in the sequence shown in Scheme 1. Linear PAN is formed in the first step followed by homolytic radical formation on $-\text{C}\equiv\text{N}$ group (second stage). The $-\text{C}\equiv\text{N}$ consisting of weaker π bonding is more susceptible to forming radicals, which results in the cross-linking of two polymeric chains through the nitrile group. Hence, the actual resonance of $-\text{C}=\text{N}$ ($145\text{--}165\text{ ppm}$) appears still in the downfield region due to the deshielding caused by nitrogen linking at $-\text{C}=\text{N}$ across the polymeric chain.

The plot of the generated second harmonic intensity vs input fundamental laser intensity exhibits a quadratic dependence (Figure 4). For normal incidence, the transmitted second harmonic intensity is found to be quadratically dependent on incident intensity whereas the absorption at the fundamental and

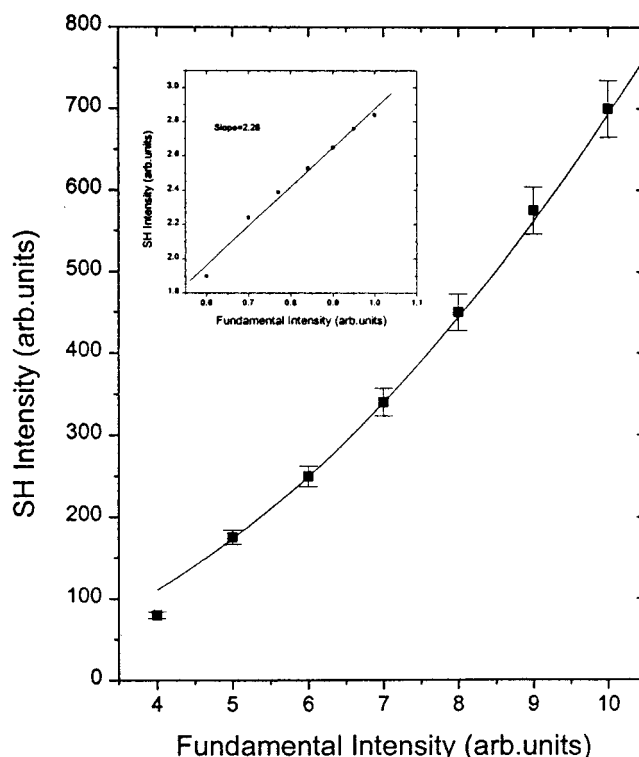


Figure 4. Intensity dependence of $I(2\omega)$ on $I(\omega)$. The solid line is the quadratic fit for the sample prepared by 96 h of exposure with the dose rate of 2000 rad/min. The inset depicts the logarithmic plot. This dependence has been fitted to the straight line with the slope of 2.28.

the extinction coefficient at the second harmonic are negligible.¹⁹ The wavelength of the SH signal is measured to be 532 nm with a grating monochromator in a separate measurement. The fundamental laser wavelength (1064 nm) as well as the SH wavelength lies well in the nonresonant region of PAN. The logarithmic plot fitted to the straight line (Figure 4 inset, slope = 2.28) is also indicative of second harmonic generation.

It is well-known that the quadratic nonlinearity in organic materials originates from asymmetric molecular electron distribution in the presence of an intense optical field such as a laser beam. Virtually all organic NLO materials contain π bonds and optical nonlinearities corresponding to highly delocalized π electrons, the basic criterion for the second harmonic generation being the noncentrosymmetrical molecular arrangement in the bulk. This loss of centrosymmetry in polymers is achieved by the application of an external electric field and the directional bias imparted by substituent groups across the π bond. The occurrence of SH signal, in the present case, without the application of external electric field can be explained on the basis of two reasons: first, PAN is known to possess high, persistent electrical polarization arising from the strong dipole moment of the nitrile groups and the quasi crystalline structure.²⁴ The hexagonal structure of PAN implies noncentrosymmetric molecular arrangement in the crystalline domain. Second, the cross-linking through $-\text{C}=\text{N}$ in the present case develops a repeated molecular conjugated system across the polymeric chains with two π bonds. Because of the intermolecular attraction between PAN macromolecules, the crystalline phase favors conjugation. Although, the mechanism of self-poling in the present medium is not very clear at this moment, it is likely that the π conjugation developed in the crystalline domain is capable of providing directional bias resulting from the aligned strong polar nitrile groups as well as the rigidity of PAN macromolecules, which makes the contribution of delocalized

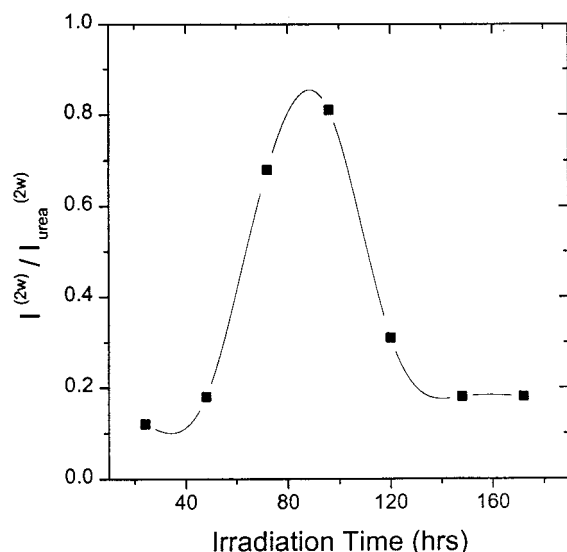


Figure 5. Variation of normalized second harmonic intensity ($I^{2\omega} / I_{urea}^{2\omega}$) with the irradiation time in hours (dose rate of 2000 rad/min).

π electrons nonzero in the presence of intense optical field. Further, it is possible that the delocalization of these π electrons, along this bond length alteration may induce collective effects, producing a significant second-order nonlinear response in the partially cross-linked PAN. We believe that the second-order nonlinearity in the present case is due to the small π conjugation imparted by cross-linking through $-C=N$ across polymeric chains coupled with noncentrosymmetric molecular structure.

The SH signal is observed to increase with an increase in the irradiation dose initially and then drops drastically, as indicated in Figure 5. As the formation of $-C=N$ proceeds via cross-linking with the irradiation time, the SH intensity is found to increase initially. Further irradiation may result in cleavage of the $-C=N$ bonds of the cross-links, which explains the decrease in the NLO activity upon long exposure time. The reduced UV absorption observed for lower irradiation time (Figure 2a) and higher irradiation time (Figure 2d) associated with the blue shift in the absorbance maximum verifies the above interpretation. This is well supported by the decrease in peak absorbances of IR bands appearing due to $-C=N$ conjugation (Figure 3a inset). Although, the SH intensity measured is as high as 80% of that for powder urea, it is rather low in comparison with some of the systems. For example, powder SHG efficiencies nearly 13, 62, and 200 times that of urea were found for 3-aminoxanthone (3-aminoxanthene-9-one),⁵ Z-1-ferrocenyl-2-(p-nitrophenyl)ethylene and E-1-ferrocenyl-2-(N-methylpyridinium-4-yl)ethylene iodide.³ Low SH powder efficiency in this particular system is likely to be due to the partial cross-linking and small crystalline domain.

Conclusions

Polyacrylonitrile on exposure to heavy doses of γ -irradiation leads to a material capable of unusual second-order optical

nonlinearities arising from the delocalization of π electron conjugation imparted by cross-linking through $-C=N$ across polymeric chains coupled with noncentrosymmetry in the crystalline PAN domain. Self-poling in this nonlinear medium is unknown at this stage. A significant second harmonic intensity of nearly 80% of that of powder urea has been observed, which can be significantly improved by growing single crystals of the same material.

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