Kinetics of Diacetylene Polymerization: An FT-Raman Study

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ABSTRACT: Changes in the FT-Raman spectrum of 1,4-bis(3-quinolyl)buta-1,3-diyne (DQ) as a function of γ-ray dosage is used to monitor the degree of monomer to polymer conversion in a solid-state topochemical polymerization reaction. The relative intensities of the characteristic C≡C peaks in the nonresonant FT-Raman spectra provide a nondestructive quantitative means to measure the conversion from monomer to polymer.

Introduction

Poly(diacetylenes) (PDAs), a class of polymers with extensive π-conjugation along the backbone, are obtained by topochemical 1,4-addition polymerization of disubstituted diaceytlenes[1,2] (Figure 1). Polymerization is carried out by subjecting the monomer crystals to thermal annealing, UV radiation, or high-energy radiation. The phenomenon of monomer to polymer crystal phase transition has been extensively studied in the PDAs. As the polymerization reaction proceeds, a homogeneous solution of the polymer chains is formed in the solid monomer matrix. The polymers are usually brightly colored and, in general, insoluble in common organic solvents in which the monomers are soluble.[3] The difference in the degree of solubility of the monomer and the polymer in common solvents has been utilized to extract the unreacted monomer from the partially polymerized samples and to obtain a measure of the monomer to polymer conversion.[4] Other techniques such as differential scanning calorimetry and photoacoustic spectroscopy have also been used to study the kinetics of diacetylene polymerization.[5,6]

As polymerization proceeds, the optical properties of the polymer begin to dominate even at very low conversion because of the extended π-conjugation along the backbone. PDAs have become a subject of great interest due to their novel linear[7] and nonlinear[8] optical properties, which arise from the conjugated backbone. A firm understanding of electron delocalization along the backbone of the conjugated polymers and the interaction of electron densities of side groups and the backbone may further help in modifying the electroactive properties of these ordered conjugated polymers.

Raman spectroscopy has been extensively used to study the electronic and vibrational structure of conjugated polymers.[9] There is considerable lowering of the IR and Raman vibrational frequencies of the C≡C and C=C bonds of the PDA backbone compared to those of the monomer because of the backbone π-conjugation in the PDAs.[10] IR spectroscopy has been used to estimate the percentage conversion for some unsymmetric diacetylenes.[11] However, in a majority of the cases, the PDA backbone vibrational transitions are IR inactive due to the symmetric nature of the functional groups along the backbone. Raman spectroscopy, on the other hand, has wide applicability to probe the vibrational structure of the backbone in these conjugated symmetric polymers. By employing resonance Raman spectroscopy, where excitation is carried out in or near the absorption band in the visible, the vibrational signatures of the backbone can be distinguished from those of the side groups, which is not easily done with IR spectroscopy.[10]

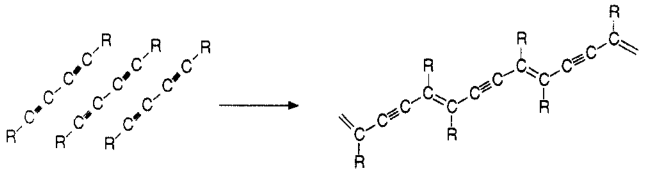

Figure 1. Topochemical solid-state polymerization of diacetylenes (1,4-addition). R stands for a substitute group in the monomer and in the polymer.

Resonance Raman spectroscopy can be used to obtain detailed information about (i) the backbone electronic structure of the intermediate species involved in the reaction process,[12-15] (ii) the influence of the polarizing environment on conjugation along the backbone,[16,17] (iii) the stress and strain dependence on the vibrational frequencies of the backbone in crystals and fibers,[18,19] (iv) the excited-state properties of the backbone,[20] and (v) the delocalization parameter along the PDA backbone.[21] Examination of the backbone vibrational frequencies for PDAs in good and poor solvents and thermochromic single crystals was used to conclude that the chromic phenomenon in these systems is related to the order–disorder transition along the backbone.[22-25] Recently, Raman spectroscopic studies established the differences between the bulk and surface phases in PDA crystals.[26,27] In addition, surface Raman spectroscopy has been used to study the disorder to order transformation in going from mono- to multilayer poly(diacetylenes).[28,29]

Information regarding the relative composition of the monomer and the polymer, however, could not be obtained due to the overwhelmingly high sensitivity of the polymer backbone vibrational bands toward the resonant laser excitation which overshadows the vibrational bands corresponding to the monomer. Nonresonant FT-Raman spectroscopy could yield accurate information regarding the relative compositions of the monomer and the polymer as the C≡C vibrations in both are treated on the same footing. The differences in the triple-bond stretching frequencies and the relative peak intensities for the monomer and the polymer chain can be made use of to

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elucidate the amount of polymer present in a given sample. The objective of this study is to demonstrate the ability of nonresonant FT-Raman spectroscopy to nondestructively measure the degree of polymer content in partially polymerized diacetylene samples.

Talwar et al. have recently reported the synthesis and preliminary investigation of the electronic spectra of poly-[1,4-bis(3-quinolyl)buta-1,3-diyne] (PDQ). This fascinating new PDA has heteroaromatic side groups directly attached to the backbone.[30,31] Substantial π-conjugation between the side group and the backbone was anticipated in this partially polymerizable system. This polymer can be dissolved in certain protic solvents and shows very large solvatochromic shifts. This partially polymerizable diacetylene is used as a testbed for the present investigation. Here, we report the FT-Raman spectrum of DQ and the evolution of the Raman spectra of corresponding polymers at various levels of polymer conversion. Comparison with a fully polymerizable prototypical poly(diacetylene), poly-[1,6-bis((*p*-tolylsulfonyl)oxy)-2,4-hexadiyne] (PTS), is also presented.

Experimental Section

Monomer, DQ, was synthesized as reported earlier.[30,32] Partially polymerized samples of DQ (PA-DQ) were obtained by γ-ray irradiation, thermal annealing, or UV irradiation of the polycrystalline samples of DQ monomer. Monomer-free polymer, PDQ, was obtained by extracting the unreacted monomer using dichloromethane as the monomer solvent from the partially polymerized samples. Percent polymer conversion was measured by gravimetry and UV–visible absorption spectrophotometry. The Raman spectra were recorded by a Perkin-Elmer 1760X FTIR spectrophotometer with a FT-Raman accessory in a 180° optical collection geometry. The excitation was achieved at 1.064 μm wavelength and 100 mW of laser power with a CW Nd:YAG laser. The scattered radiation from the sample is reflected into the FTIR spectrometer and is detected by a liquid nitrogen cooled InGaAs detector. A wavenumber resolution of 2 cm^{-1} was set for all the measurements. A scan speed of 0.1 cm/s was used, and the total accumulations of 32 scans were done for all samples. Relative intensity of the polymer and the monomer vibrational bands is the ratio of polymer peak height to the corresponding monomer peak height multiplied by a factor of 10.

Results and Discussion

FT-Raman spectra of polycrystalline samples of monomer (DQ), partial polymer (PA-DQ), and monomer-free polymer (PDQ) are shown in Figure 2. Frequencies corresponding to the principal Raman vibrational bands of DQ, PA-DQ, and PDQ are given in Table I. DQ shows vibrational bands at 2220 cm^{-1} ($\nu_{C\equiv C}$) and a doublet at 1617 and 1596 cm^{-1} (double bonds of the quinolyl side groups). PA-DQ shows bands at 2218 and 2123 cm^{-1} corresponding to the stretching vibrations of C≡C of the DQ monomer and the polymer backbone, respectively. These characteristic peaks have been used in the quantitative assessment of the monomer to polymer conversion. In a typical resonance Raman spectrum of a partially polymerized diacetylene even at very low conversion, the monomer C≡C band is absent.[10]

Two strong bands at 1473 and 1455 cm^{-1} and a weak band at 1493 cm^{-1} are observed in the C=C stretching vibration region. The bands corresponding to the C=C bond symmetric stretch of the quinolyl groups are very weak and present for the PA-DQ. PDQ shows one band at 2107 cm^{-1}, corresponding to the vibration of the backbone C≡C bond in the monomer-free polymer. The Raman spectrum of PDQ is characterized by the presence of two other strong bands at 1472 and 1444 cm^{-1}. The peak at 1444 cm^{-1} corresponds to the C=C bond of the polymer backbone. This peak continuously shifts to lower wavenumbers depending upon the degree of polymer conversion. Vibrational frequency (in wavenumbers) of the double bond decreases with increasing conjugation. A value of 1450 cm^{-1} has been projected as the lowest limit for the vibrational frequency of an extensively conjugated double bond in polyconjugated macromolecules.[33] In a nonresonant Raman spectrum (λ_{ex} = 1064 nm), the vibrational frequency for C=C of the backbone in PDQ appeared at a frequency of 1444 cm^{-1}, and in a resonant Raman spectrum (λ_{ex} = 514.5 nm), a strong vibrational band for C=C of PDQ appeared at a frequency of 1430 cm^{-1}.[34] These two values are the lowest frequencies observed for a double-bond vibration in a poly(diacetylene). The lowering of the observed vibrational frequency from the projected limiting vibrational frequency for a double bond ($\nu_{C=C}$) suggests the possibility of π-conjugation between the backbone double bonds and the quinolyl side groups in PDQ.

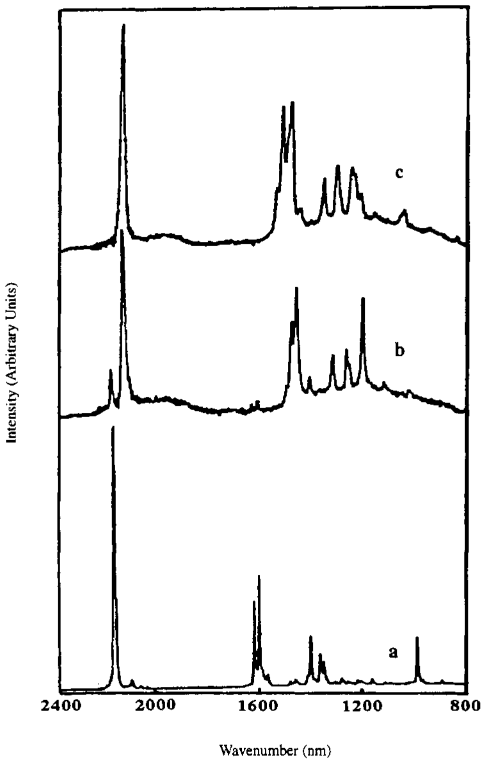

Figure 2. FT-Raman spectra of (a) DQ, (b) PA-DQ (~22%), and (c) PDQ (λ_{ex} = 1064 nm, no. of scans = 32, resolution = 2 cm^{-1}).

Table I. Principal Raman Vibrational Bands of DQ, PA-DQ, and PDQ[a]

monomer (DQ)	partial polymer (PA-DQ)	monomer-free polymer (PDQ)
2220 (s)	2218 (w), 2123 (s)	2107 (s)
1617, 1596 (m)	1620, 1599 (vw)	
1415, 1382, 1368 (w)	1493 (w), 1473 (s)	1493 (w), 1472 (s)
	1455 (s), 1408 (w)	1444 (s)
	1329, 1279 (m)	
	1221 (s)	1195 (w)
1030 (w)	1148 (w)	1038 (w)

[a] s = strong, m = medium, w = weak, vw = very weak.

The variation in the Raman spectral profile of the monomer was studied as a function of γ-ray dosage. The changes in the peak intensities of the band in the 2220–2100 and 1620–1590 cm^{-1} regions with increasing dosage are shown in Figures 3 and 4, respectively. It is observed that the relative intensity of the 2220 cm^{-1} peak decreases and that of the 2123 cm^{-1} peak increases as a function of

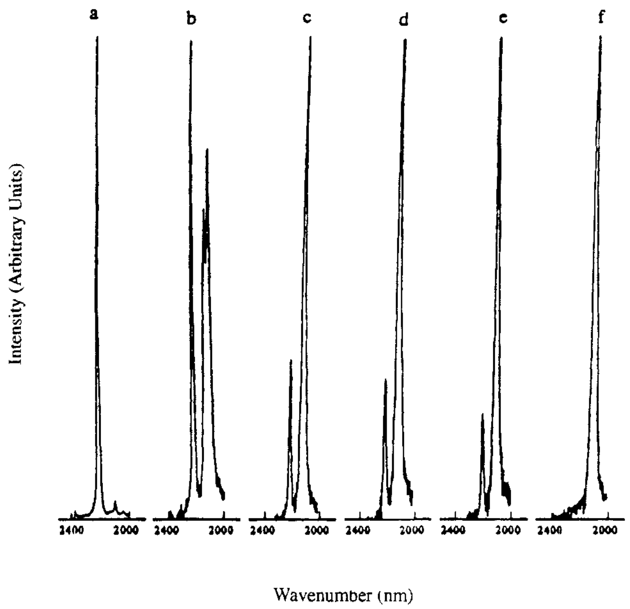

Figure 3. Changes in the relative intensities of the 2220 cm^{-1} ($\nu_{C\equiv C}$ of monomer) and 2123 cm^{-1} ($\nu_{C\equiv C}$ of polymer) bands as a function of γ-ray dosage in the partial polymer of PDQ: (a) 0 Mrad; (b) 18 Mrad; (c) 59 Mrad; (d) 84 Mrad; (e) 140 Mrad; (f) 100% polymer.

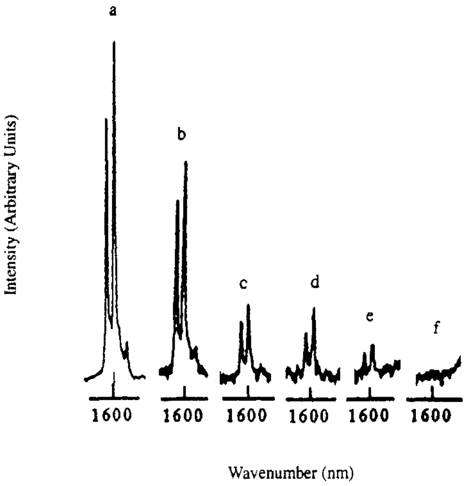

Figure 4. Changes in the intensities of the 1620 and 1590 cm^{-1} bands (corresponding to the quinolyl double bonds) as a function of γ-ray dosage in the partial polymer of PDQ: (a) 0 Mrad; (b) 18 Mrad; (c) 59 Mrad; (d) 84 Mrad; (e) 140 Mrad; (f) 100% polymer.

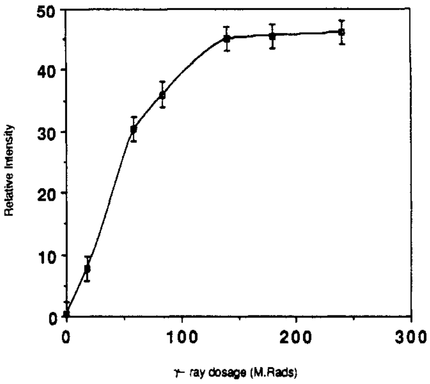

Figure 5. Plot of relative intensities of the 2123 cm^{-1} band with respect to the 2220 cm^{-1} band as a function of γ-ray dosage in PDQ (relative intensity = ratio of polymer peak height to monomer peak height multiplied by 10).

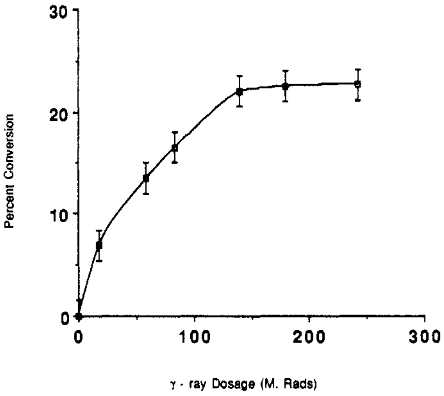

Figure 6. Plot of percent polymer conversion as a function of γ-ray dosage in PDQ.

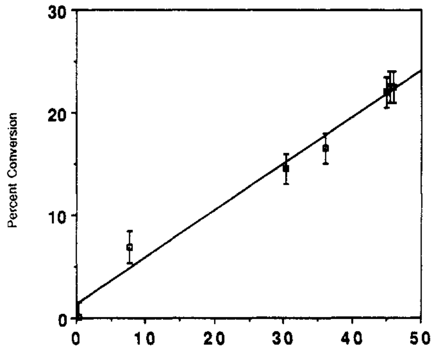

Figure 7. Plot of percent polymer conversion vs relative intensities of the 2123 and the 2220 cm^{-1} bands in PDQ (relative intensity = ratio of polymer peak height to monomer peak height multiplied by 10).

increasing dosage, an indication of increasing conversion of monomer into polymer. The plot of the relative intensities of the 2123 cm^{-1} peak (polymer) with respect to the 2220 cm^{-1} peak (monomer) as a function of total dosage is shown in Figure 5.

The plot of polymer conversion *vs* total dosage is shown in Figure 6 from a gravimetric analysis of the extracted partially polymerized samples. From Figures 5 and 6, it is possible to establish a relationship between the polymer conversion and the relative intensities of the $C\equiv C$ bond stretching vibrational bands of the monomer and the polymer (Figure 7). From this relationship, it is possible to obtain the percent polymer content in any given sample of PA-DQ, irrespective of the mode of polymerization, by measuring the relative intensities of the 2220 and 2123 cm^{-1} Raman bands. In principle, it is possible to establish such a relationship for any given monomer by recording the FT-Raman spectra of the partial polymer. The supporting data needed to obtain such a master calibration curve for any given monomer is its percent conversion curve from the gravimetric analysis. This is a general method to determine the percent polymer conversion of any given diacetylene system. The shape of the master calibration curve is expected to be different for different diacetylenes depending on the rate of polymerization, individual response of the monomeric and polymeric vibrational bands to the excitation frequency, and changes in the polarizability of the medium. Figure 8 illustrates the FT-Raman spectra of the monomer, the partial polymer, and the monomer-free polymer of the prototypical diacetylene PTS. As discussed before, the partial polymer spectrum shows the presence of both the monomer and the polymer $C\equiv C$ stretching bands not seen in the conventional resonance Raman spectroscopy. The percent polymer conversion in the partial polymers of PTS was determined through gravimetric analysis. Further, complete polymerization in this system is established by the

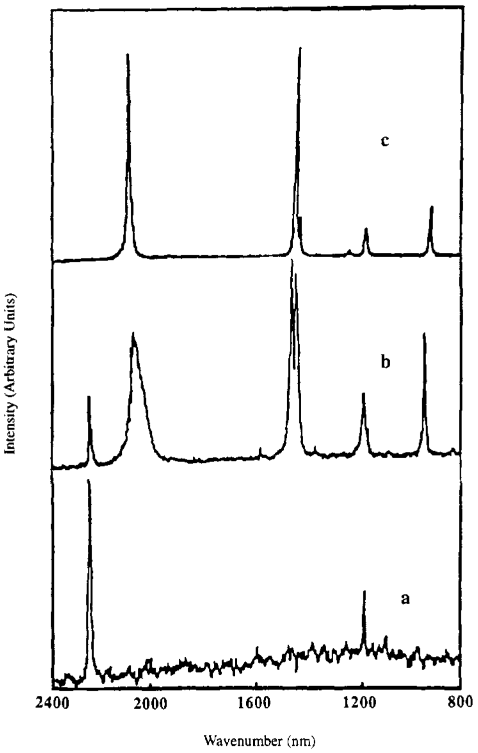

Figure 8. FT-Raman spectra of (a) PTS, (b) partial polymer of PTS (~10%), and (c) completely polymerized PTS (λ_{ex} = 1064 nm, no. of scans = 32, resolution = 2 cm^{-1}).

absence of the monomer peaks from the fully polymerized sample without monomer extraction.

Conversion in the DQ crystals could be achieved only up to 25% in any mode of polymerization.[34] However, the monomer peaks at 2220, 1617, and 1596 cm^{-1} showed a dramatic decrease in the relative intensities even at 25% conversion (Figure 2b). This can be understood in terms of (i) unequal response of the monomer and the polymer vibrational bands to the excitation frequency and (ii) the stringent electronic symmetry requirements associated with the Raman-active functional groups.

FT-Raman spectra of partial polymers of DQ (Figure 2b) and partial polymer of PTS (Figure 8b) recorded with a nonresonant excitation frequency of 1064 nm show vibrational bands corresponding to the monomer as well as the polymer. The intensities of the polymeric vibrational bands are, however, disproportionately higher than that of the monomeric vibrational bands in the case of both PTS and PDQ. To explain such unusually strong response of the polymeric vibrational bands, we consider the possibility of partial resonant enhancement as the absorption edge (~850 nm for PDQ) of the polymers is somewhat closer to the excitation frequency (1064 nm) than that of the monomer (360 nm for DQ). If the results are dominated by resonance enhancement, the overwhelmingly strong response of the polymeric vibrational bands renders the monomeric peaks almost invisible even at very low conversion (1%). The fact that both the monomeric and polymeric vibrational bands show up in the FT-Raman spectra of all the partial polymers suggests only a partial influence of this resonant enhancement.

Another factor that leads to reduction in the relative peak height of the monomeric vibrations is the lattice distortion during the polymerization reaction that leads to physical changes at the molecular level. Topochemical polymerization reaction in diacetylenes, in general, is known to cause a mismatch between the monomer lattice and the growing polymer lattice. This mismatch induces a strain in the crystal that often leads to distortion of the remaining monomer lattice. The reaction subsequently comes to a halt as the distorted monomer lattice does not satisfy the crystal packing parameters of a reactive lattice. It is a general contention that the presence of a methylene spacer next to the diacetylene moiety would facilitate the polymerization reaction by relaxing to some extent the mechanical strain that develops during the polymerization process. DQ molecules are very rigid without any methylene groups and form a tight stack in the crystal lattice. The quinolyl rings are determined to be coplanar from the single-crystal X-ray structure of DQ.[35] The triple bonds in DQ are IR inactive and highly Raman active. This reflects the electronically symmetric nature of the triple bonds in the polymerizable monomer lattice. During the polymerization reaction, the transient mechanical strain between the monomeric lattice and the growing polymeric lattice could lead to a distortion in the packing of the unreacted segments of the monomeric lattice. Distortion in the crystal packing probably results in the rotation of quinolyl rings with respect to the diacetylenic moiety. Such a rotation would partially break up the electronic symmetry of the triple bonds in the monomer, and the triple bonds become relatively less Raman active. Attempts to study the crystal structure of 25% partial polymers were unsuccessful. However, the powder X-ray diffraction studies on partial polymers of DQ showed substantial changes in the reflections corresponding to monomeric crystal lattice during the polymerization reaction.[36] Partial resonant enhancement of the polymeric vibrations and a partial loss in the electronic symmetry of the monomeric triple bonds are believed to result in a relatively high intensity ratio of polymeric vibrations to monomeric vibrations.

Factors responsible for the disappearance of the Raman bands in going from 100% to 78% monomer are at present unclear. Degradation of DQ monomer can be ruled out as a possibility for the disappearance of monomer vibrations in the partially polymerized samples. The unreacted monomer could be recovered quantitatively upon extracting the partially polymerized samples with appropriate solvent. It was found that the recovered monomer has spectral and physical characteristics identical to those of the original monomer sample. The recovered monomer crystals also undergo topochemical polymerization.

We have reported on the evolution of the FT-Raman spectra of an unusual poly(diacetylene) as a function of γ-ray dosage. Comparison with the prototypical poly(diacetylene) PTS has been made. Significant π-conjugation between the backbone and the side groups is established for PDQ. A relationship between the peak ratio of the characteristic monomer and the polymer vibrational bands and the percent polymer conversion is established for DQ. This approach has general applicability and may be used to obtain the percent polymer conversion irrespective of the mode of polymerization in a nondestructive analysis.

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References and Notes

(1) Wegner, G. *Z. Naturforsch.* **1969**, *24b*, 824.
(2) Cantow, H. J., Ed. *Polydiacetylenes*; Springer-Verlag: New York, 1984 (*Adv. Polym. Sci.* **1984**, *63*, 1).
(3) Bloor, D.; Change, R. R. *Polydiacetylenes*; *NATO ASI Ser. E* **1985**, 1.

(4) Chance, R. R.; Patel, G. N. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 859.

(5) Chance, R. R.; Patel, G. N.; Turi, E. A.; Khanna, Y. P. *J. Am. Chem. Soc.* **1978**, *100*, 1307.

(6) Chance, R. R.; Shand, M. L. *J. Chem. Phys.* **1980**, *72*, 948.

(7) Schott, M.; Wegner, G. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic Press: New York, 1987; Vol. 2, pp 3–49.

(8) Carter, G. M.; Chen, Y. J.; Rubner, M. F.; Sandman, D. J.; Thakur, M. K.; Tripathy, S. K. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic Press: New York, 1987; Vol. 2, pp 85–120.

(9) Kurti, J.; Kuzmany, H. *Phys. Rev. B* **1992**, *44*, 595.

(10) Batchelder, D. N.; Bloor, D. *Advances in Infrared and Raman Spectroscopy*; Wiley-Heyden: New York, 1984; pp 133–209.

(11) Matsuda, H.; Nakanishi, H.; Hosomi, T.; Kato, M. *Macromolecules* **1988**, *21*, 1238.

(12) Melvegar, A. J.; Baughman, R. H. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 603.

(13) Tieke, B.; Bloor, D. *Makromol. Chem.* **1979**, *180*, 2275.

(14) Bloor, D.; Kennedy, R. J.; Batchelder, D. N. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1355.

(15) Bloor, D.; Ando, D. J.; Hubble, C.; Williams, R. L. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 779.

(16) Sandman, D. J.; Chen, Y. J. *Polymer* **1989**, *30*, 1027.

(17) Sandman, D. J.; Chen, Y. J. *Synth. Met.* **1989**, *28*, D613.

(18) Mitra, V. K.; Risen, W. M., Jr. *J. Chem. Phys.* **1977**, *66*, 2731.

(19) Batchelder, D. N.; Bloor, D. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 569.

(20) Batchelder, D. N.; Bloor, D. *J. Phys. C: Solid State Phys.* **1982**, *15*, 3005.

(21) Baughman, R. H.; Witt, J. D.; Yee, K. C. *J. Chem. Phys.* **1974**, *60*, 4755.

(22) Zheng, L. X.; Benner, R. E.; Vardney, Z. V. *Phys. Rev. B* **1990**, *42*, 3235.

(23) Swiatkiewicz, J.; Mi, X.; Chopra, P.; Prasad, P. N. *J. Chem. Phys.* **1987**, *87*, 1882.

(24) Shand, M. L.; Chance, R. R.; Le Postollec, M.; Schott, M. *Phys. Rev. B* **1982**, *25*, 4431.

(25) Morrow, M. E.; Dye, R. C.; Eckhardt, C. J. *Chem. Phys. Lett.* **1989**, *158*, 499.

(26) Hankin, S.; Sandman, D. J. *Macromolecules* **1991**, *24*, 4983.

(27) Hankin, S.; Sandman, D. J.; Yost, E. A.; Stark, D. J. *Synth. Met.*, in press.

(28) Chen, Y. J.; Carter, G. M.; Tripathy, S. K. *Solid State Commun.* **1985**, *54*, 19.

(29) Chen, Y. J.; Tripathy, S. K.; Carter, G. M.; Elman, B. S.; Koteles, E. S.; Georger, J., Jr. *Solid State Commun.* **1986**, *58*, 97.

(30) Talwar, S. S.; Kamath, M.; Das, K.; Sinha, U. C. *Polymer Commun.* **1990**, *31*, 198.

(31) Talwar, S. S.; Kamath, M.; Babu, K. N. *Mater. Res. Soc. Symp. Proc.* **1990**, *173*, 583.

(32) Kamath, M. Ph.D. Dissertation, Indian Institute of Technology, Bombay, 1989.

(33) Kuzmany, H. *Frontiers of Polymer Research*; Plenum Press: New York, 1991; pp 289–296.

(34) Babu, K. N. Ph.D. Dissertation, Indian Institute of Technology, Bombay, 1992.

(35) Das, K.; Sinha, U. C.; Kamath, M.; Talwar, S. S. *Acta Crystallogr.* **1990**, *C46*, 2126.

(36) Babu, K. N.; Kamath, M.; Talwar, S. S., manuscript under preparation.