

Communications to the Editor

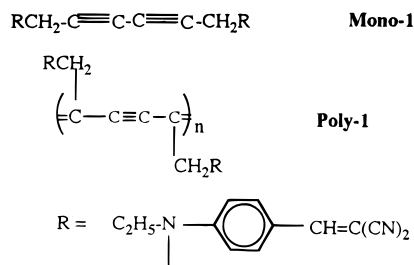
Side Group Interactions in a Polydiacetylene Single Crystal

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Herein we describe unusual features in the Raman and anisotropic reflection spectra of the new polydiacetylene (PDA) crystal from 1,6-diethyl-(1,6-bis-*p*-benzylidenemalononitrile)-2,4-hexadiyldiamine (Mono-1). As a consequence of synthesis by



topochemical and topotactic solid-state polymerization, PDA are available, in optimal cases as the present, as macroscopic polymer single crystals¹ and hence are among the best defined polymers. While much information about the optical properties of PDA is available,¹ fundamental understanding of the optical properties is largely lacking. Since solid-state spectral and electronic properties are structure-dependent, we also report the crystal structure of Mono-1 and its topochemical and topotactic conversion to the PDA Poly-1. Since Mono-1, like related monomers,² requires thermal polymerization and is not converted to polymer in a preparatively useful way by ionizing radiation, we report

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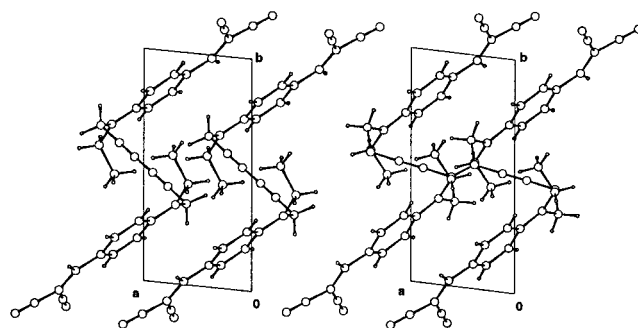


Figure 1. Projections of the crystal structures of Mono-1 (left) and Poly-1 (right) down the crystallographic *c* axes.

the first crystallographic study of the topotactic conversion of a monomer to a polymer with complete structure solution at intermediate steps in the process. Previous structural studies of this type have been reported for [2 + 2] photocycloadditions.³

Mono-1 was synthesized in three steps from *N*-ethyl-*N*-prop-2-ynylaniline (see Supporting Information). Single crystals were grown from acetone solution and polymerized at temperatures between 110 and 130 °C. The crystal structure of Mono-1 is shown in Figure 1a (left).⁴ The monomer stacking distance, *d*, 4.9976 Å, the angle between the diacetylene rod and the stacking axis, ϕ , 45.0°, and the distance between the C-1 and C-4' reacting atoms, *R*, 3.50 Å, are nearly identical with the ideal criteria (5 Å, 45°, <4 Å) for solid-state polymerization.^{5,6} We attempted to convert the single crystal of monomer to polymer by heating it at 120 °C for extended periods.⁴ After 46 days, the monomer crystal had converted completely to polymer, and the results of the structure determination are presented in Figure 1b (right). The shortest contact between polymer chains is a weak hydrogen bond between a cyano nitrogen atom and the methylene group attached to the polymer backbone [C···N, 3.40 Å; C–H···N, 128.3°; C≡N···H, 156.3°]. While single-crystal-to-single-crystal polymerizations of diacetylene monomers are well-known, the opportunity to study such a transformation in a radiation-stable phase is rare. Hence we determined the structure of the mixed crystal at five intermediate stages of conversion as well. This solid-state reaction proceeds smoothly at 120 °C over a 7-week period of heating. During the conversion, (a) the crystals converted

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(4) X-ray structure analyses: Enraf-Nonius CAD-4 diffractometer, graphite-monochromated Cu K α radiation ($\lambda = 1.54178$ Å). Structures were solved by direct methods (SIR92) and refined by full-matrix least squares by using anisotropic displacement parameters for C and N (CRYSTALS). For Mono-1 at 294 K: *a* = 4.9976(9), *b* = 10.802(4), *c* = 12.494(4) Å; $\alpha = 81.28(3)$, $\beta = 82.87(3)$, $\gamma = 83.31(2)^\circ$; *V* = 658.2(3) Å³; space group *P*1; *Z* = 1; *D*_{obs} = 1.18(1) g·cm⁻³; *D*_{calc} = 1.182 g·cm⁻³; *R* = 0.0652; *R*_w = 0.0860 for 1905 observed reflections and 164 refined parameters. For Poly-1 at 294 K: *a* = 4.9052(3), *b* = 10.921(1), *c* = 11.833(2) Å; $\alpha = 87.90(1)$, $\beta = 86.45(1)$, $\gamma = 83.132(7)^\circ$; *V* = 627.90(14) Å³; space group *P*1; *Z* = 1; *D*_{obs} = 1.24(1) g·cm⁻³; *D*_{calc} = 1.239 g·cm⁻³; *R* = 0.0781; *R*_w = 0.1087 for 1950 observed reflections and 164 refined parameters. Data were also collected on five intermediate stages of conversion after heating the original crystal at 120 °C and cooling to ambient. The five experiments and their degrees of conversion as obtained by refinement of crystallographic occupancy parameters for monomer and polymer, are as follows: 1:2d, 16%; 2:4d, 39%; 3:7d, 42%; 4:14d, 73%; 5:25d, >97%. Data for these five experiments, as well as data for Mono-1 and Poly-1, are available in Supporting Information as CIF files.

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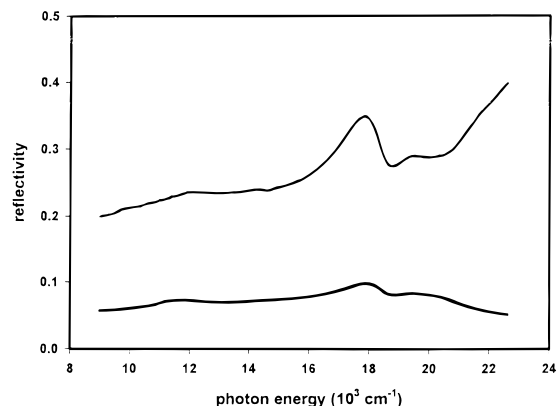


Figure 2. Polarized specular reflection spectra of the (001) face of a single crystal of Poly-1 at 298 °K. The upper spectrum is obtained with light polarized along the pseudo-polymer long axis principal direction and the lower with light polarized along the principal direction perpendicular thereto.

topotactically⁷ to polymer in a roughly linear fashion; (b) the cell constants of the monomer ($P\bar{1}$) gradually changed to those of the polymer ($P\bar{1}$); (c) both monomer and polymer coordinates were resolvable only for the C-1 atoms at intermediate levels of conversion of 16, 39, 42, and 73% (changes in the positions of other atoms were $< \sim 0.3$ Å); and (d) the intensity data overall dropped by 15% at the initial stages of reaction and remained at a lower level until reaction was complete. At $>97\%$ conversion, intensities were still $\sim 6\%$ low, but returned to initial values after a final 21 days of annealing at 120 °C. This study represents a unique characterization of the events associated with the onset of disorder as well as the conditions required for successful annealing of a thermal, topotactic solid-state polymerization.

Polarized specular reflection spectra (9000–24 000 cm^{-1} , Figure 2) were obtained from the (001) face of a Poly-1 crystal at ambient temperature. Features typical of PDA were observed from 16 000 to 42 000 cm^{-1} . In this region, the response is that characteristic of the “blue-shifted” series of polydiacetylenes.⁸ For pseudo-long-axis polarization, the peak is found near 17 800 cm^{-1} (~ 571 nm), similar to the PDA crystal of 1,1,6,6-tetraphenylhexadiyndiamine (THD).⁹ The peak about 1500 cm^{-1} to higher energy corresponds to vibrational fine structure associated with the double bond of the conjugated backbone, and the strong feature beginning at 21 000 cm^{-1} is associated with the side group. Significant anisotropy is apparent from the spectrum in the perpendicular direction. However, heretofore unobserved structure for PDAs is observed in *both* principal directions from approximately 12 000 to 16 000 cm^{-1} . A quite broad band with

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some apparent structure is observed with maximum intensity polarized along the principal direction most nearly parallel with the polymer spine. However, the dichroism suggests that the transition is polarized in a direction from the side groups of one polymer toward the spine of an adjacent one. The appearance of a band to the red of the usual PDA absorption, its width, its lack of vibronic structure, and its apparent polarization suggest that the band arises from possibly more than one charge-transfer transition where the conjugated spine of one polymer chain serves as the donor to the side group of an adjacent polymer chain. Such features to the red of the usual PDA absorption have not been previously reported.

Raman spectra reveal information about vibrational modes coupled to electronic states. The Raman spectra of Mono-1 and Poly-1 were recorded on polycrystalline samples using 1064-nm light. In addition to the diacetylene shift at 2259 cm^{-1} , noteworthy lines are observed at 2212 (conjugated CN) and 1563 cm^{-1} (aromatic ring) in the monomer. In the spectrum of Poly-1, in addition to the strong lines expected^{10,11} for normal modes associated with triple and double bond stretching at 2115 and 1502 cm^{-1} , significant lines are observed at 2211 and 1562 cm^{-1} . The similarity of these shifts to those found in the monomer leads to the same assignment. This is unusual, because in the absence of situations such as possible Fermi resonance,^{10,11} vibrations associated with side groups are usually *not* detected in Raman spectra of PDA. Qualitatively, observation of side group vibrations in the Raman spectrum suggests a backbone-side group interaction in Poly-1 that has not been previously reported for earlier studied PDA.

The observation of a charge-transfer spectrum in Poly-1 suggests that additional physical studies of this material as well as synthesis of other related materials will produce further interesting polymeric materials which will exhibit equally unusual optical and electronic phenomena, likely including ground-state electron transfer involving conjugated backbone-side group interactions.

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Supporting Information Available: CIF files for Mono-1, Poly-1, and five intermediate structure determinations on partially reacted crystals; syntheses of Mono-1 and precursor materials (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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