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THE CHEMICAL MODIFICATION OF POLY-1,6-DI-N-CARBAZOLYL-2,4-HEXADIYNE: DIFFRACTION, MICROSCOPY, AND MAGNETISM STUDIES

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Abstract X-ray rotation photographs of brominated poly-1,6-di-N-carbazolyl 2,4-hexadiyne (DCH) reveal a chain axis repeat distance indicative of the preservation of a polydiacetylene (PDA) structure. Weissenberg photographs of a partially reacted poly-DCH crystal display evidence of the formation of a new crystalline phase. Electron microscopy of chemically modified poly-DCH reveals preservation of a fibrous morphology. The modified polymers do not appear sensitive to electron beam radiation during image formation. The reaction of poly-DCH with bromine has been monitored by electron spin resonance spectroscopy. The g-value increases significantly in the course of the bromination. Static susceptibility measurements of poly-DCH and other PDAs reveal that they are primarily diamagnetic materials.

INTRODUCTION

In the accompanying article,[1] our discovery of the controlled chemical modification of the polydiacetylene (PDA) from 1,6-di-N-carbazolyl-2,4-hexadiyne (DCH) was reported. As a result of the polymer crystal habit, the reactions are anisotropic, and in its initial stages, the reactivity is likely controlled by side chain energy levels rather than by those of the conjugated backbone. In the case of the reactions of poly-DCH with bromine, crystal-crystal transformations accompanying the chemical reaction are observed. In the interest of a detailed description of the crystal-crystal transformation, the X-ray diffraction studies reported herein were undertaken. Morphological aspects of the fibers of chemically modified poly-DCH were probed by both scanning (SEM) and transmission electron microscopy (TEM). Finally, paramagnetic species in poly-DCH and its chemically modified forms, as well as other PDAs, were probed in static magnetic susceptibility and electron spin resonance (ESR) studies.

X-RAY DIFFRACTION STUDIES

Since the presence of at least twenty reflections in the X-ray powder diffraction of a sample of poly-DCH which had gained ca. 6 Br atoms per polymer repeat unit indicated a highly crystalline material, photographic studies of these crystals were undertaken to seek a more detailed description of them.

The crystallites of samples of poly-DCH which have gained ca. 6 Br per repeat resemble the straws in a broom. From rotation photographs of such crystals, a polymer repeat of 4.85 ± 0.1 Å may be deduced, and this reveals preservation of a PDA structure.[2] A representative rotation photograph is presented in Figure 1; the spots in Figure 1 are clearly more diffuse than those of the pristine polymer. This pattern is typical of poly-DCH samples which have gained 3-6 Br atoms per repeat.[3] Corresponding Weissenberg photographs confirm that the crystallites are well aligned in the chain direction but are poorly correlated perpendicular to that axis.

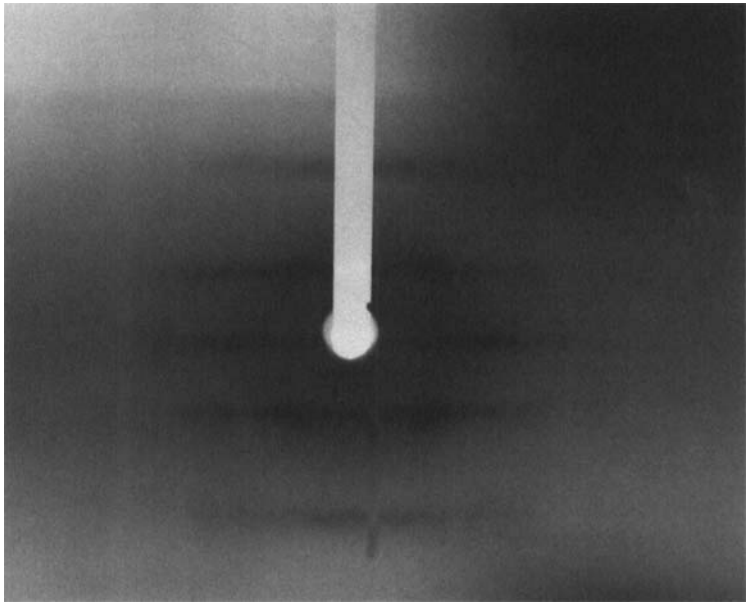

FIGURE 1 Rotation photograph, taken with CuK_α radiation, of a brominated (ca. 6 Br per repeat) poly-DCH crystal.

Information about the effects of the diffusion of bromine into the poly-DCH lattice may be obtained from the photographic study of a partially reacted crystal,[1] schematically shown with only the end reacted in Figure 2.

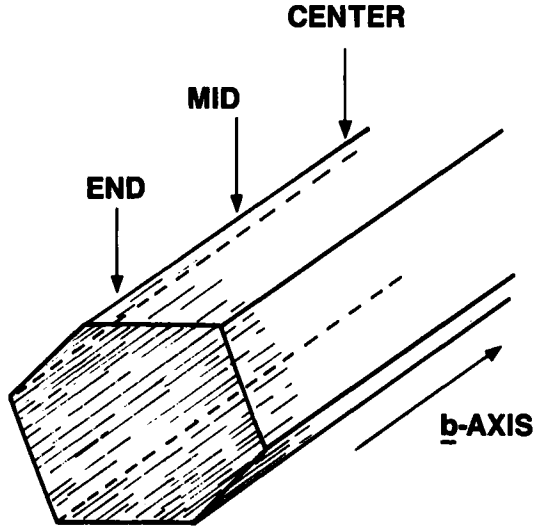

FIGURE 2 Schematic representation of a partially reacted poly-DCH crystal.[4] The shading indicates where reaction is visually observed.

With reference to Figure 2, separate X-ray photographs were obtained from areas designated "center," "mid," and "end." Rotation photographs in the "center" area, which appears pristine on microscopic examination, reveal a strong similarity to the pristine lattice with spots slightly less well defined than those of a pristine crystal. A zero-level Weissenberg photograph from the area designated "mid" provides direct evidence of the formation of a new crystalline phase. This photo (Figure 3) shows the spots of the unreacted phase which are less well defined than those in a pristine crystal, and very diffuse new lines indicative of the new phase.

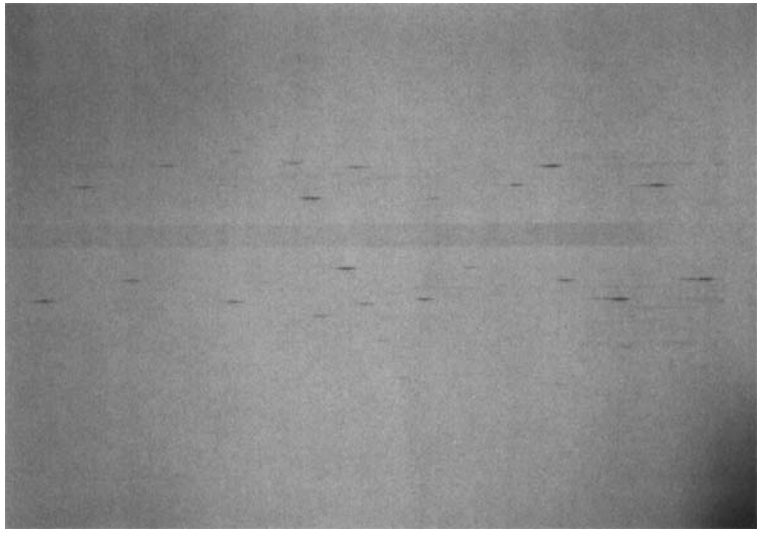

FIGURE 3 Weissenberg photograph (zero level) from the area of Figure 2 labeled "mid".

ELECTRON MICROSCOPY

Scanning Electron Microscopy (SEM)

Pristine, brominated, and nitrated poly-DCH were examined by SEM techniques at a variety of magnifications. It was observed that the overall fibrous morphology of poly-DCH is maintained after chemical modification. The fibers of the modified polymer appear swollen in comparison to those of the pristine material. Figure 4 shows a sample of brominated poly-DCH which has gained 107% in weight.

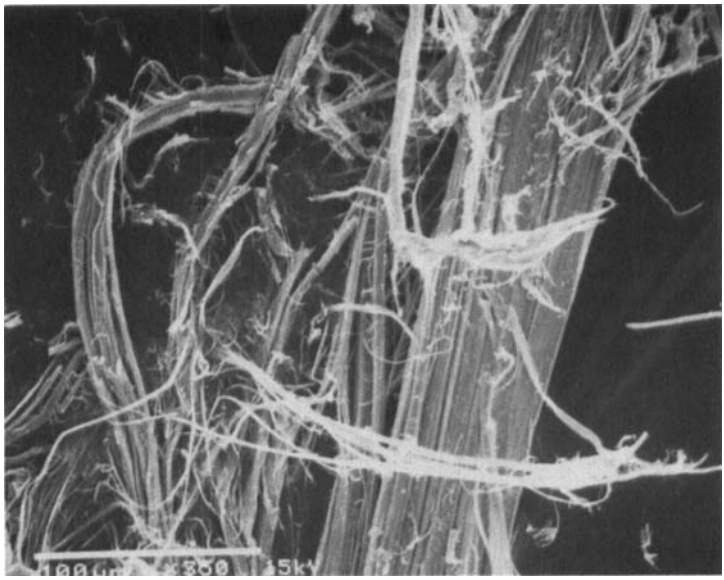

FIGURE 4 SEM of brominated poly-DCH (gain of ca. 5.7 Br atoms per repeat), 350x.

Transmission Electron Microscopy (TEM)

The micromorphology of brominated poly-DCH was investigated using bright field TEM. Samples were prepared by ultrasonication of the polymer dispersion in xylene, N,N-dimethylformamide, or dioxane. Drops of supernatant liquid were removed and allowed to evaporate on an uncoated gold grid. Typical areas examined reveal agglomerations of fibrous bundles with diameters in the range 30-50 nm. Figure 5 shows a sample which has gained ca. 4 Br atoms per

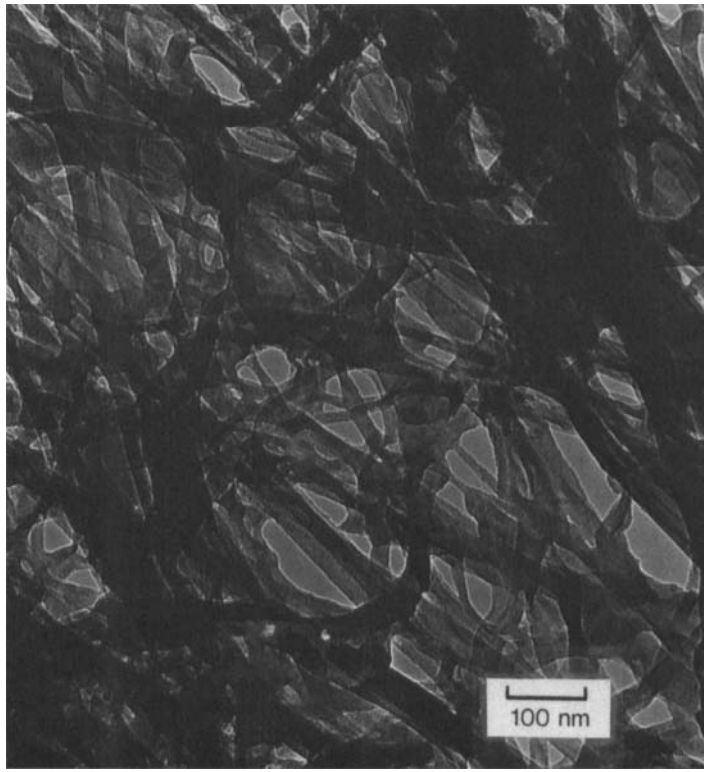

FIGURE 5 Brominated (ca. 4 Br per repeat) poly-DCH on a gold grid (120,000x).

repeat unit at a magnification of 120,000 x. The modified polymers exhibit no observable sensitivity to electron beam irradiation during image aquisition.

Selected area diffraction patterns were collected from several areas of the specimen. Experimentally derived d-spacings are compatible with those obtained by X-ray diffraction. These diffraction studies are continuing.

MAGNETISM

Both ESR and static techniques were used to characterize the paramagnetic species present in the materials under investigation.

Electron Spin Resonance (ESR)

Poly-DCH has an ESR spectrum at 20°C which has a linewidth of 20 gauss and g = 2.00292 for samples with the principal axis of each crystal perpendicular to the magnetic field. The paramagnetic species presumably arise from radiation damage during or after polymerization. For samples of poly-DCH heated at 100° for 15 minutes, the change in ESR signal intensity at 20° after heating is less than one percent.

ESR was used to monitor the reaction with bromine. Interestingly, the signal decreased in the course of the reaction. At -2 to -4°, the first order rate constants were $1.2\text{-}1.7 \times 10^{-2}$/min. over a time of 80 minutes. At this time, the linewidth decreased to 17 gauss and g = 2.0069. At a reaction time of greater than 120 minutes, the second ESR signal decreases at a rate of 2.1×10^{-3}/min. In a time

of 16-20 hours, the ESR signal is reduced to ca., one tenth of its original intensity.

The observation[1] that reaction of poly-DCH with bromine proceeded more rapidly as the temperature is lowered was interpreted in terms of the intermediacy of a donor-acceptor complex between a carbazole moiety and bromine as a precursor to carbon-bromine bond formation. If the proposed complex involved electron transfer, it might be expected that the concentration of paramagnetic species would initially increase and then decrease. Our observation of only a steadily decreasing decreasing ESR signal intensity argues against such an electron transfer process.

The room temperature ESR spectrum of a sample of brominated poly-DCH which has gained 113 percent in weight (i.e. about 5.75 Br atoms per repeat unit) reveals at least two lines with estimated g-values of 2.0041 and 2.0080. These g values and the change in g value in the course of bromination noted above suggest the involvement of a heavy atom, likely Br, with the observed paramagnetic species. Our ESR studies of these materials are continuing.

Static Susceptibility

Static susceptibility studies were performed with a SQUID device over the temperature range 6-300°K at a field of 10^4 oersteds. In addition to poly-DCH and a brominated (113 percent weight gain) poly-DCH, data were taken for the PDA from the 1,6-bis-p-toluenesulfonate of 2,4-hexadiyne (PTS). These materials were found to be diamagnetic with weak paramagnetism noted at low temperatures, in accord with earlier observations on PDAs.[5] Accordingly, data processing

followed a Curie law treatment for the molar susceptibility ($\chi_m = A + C/T$). The table displays the values of A and C obtained.

TABLE Magnetic susceptibility of polydiacetylenes.

PDA	$Ax10^6$, emu	$Cx10^6$, emu/°K
PTS	-190.3	92.4
DCH	-239.9	494.5
$DCHBr_{5.75}$	-411	3257.6

The values for the core diamagnetism in the table are in satisfactory agreement with those calculated from Pascal's constants for the PDA repeat unit. Previously, a study of diamagnetic anisotropy in urethane substituted PDAs appeared.[6] With reference to the table, the larger paramagnetic term for DCH versus PTS probably follows from the fact that DCH is polymerized by ^{60}Co gamma radiation and PTS is thermally polymerized.

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