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Canal polymerization

1. 1,3-Butadiyne in perhydrotriphenylene

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Summary

The canal polymerization of 1,3-butadiyne in perhydrotriphenylene (PHTP) and the synthesis of 1,3-butadiyne and perhydrotriphenylene are described. Depending on the experimental method, two types of inclusion compound crystals are obtained. Resonance Raman and uv-visible absorption spectroscopy indicate the backbone to be of the ene-yne type.

Introduction

One of the goals of the conducting polymers effort at Los Alamos National Laboratory is to generate well defined polymers with linear chains of high chemical and steric regularity(1,2). Inclusion polymerization in PHTP has been shown to produce polymers of high stereochemical regularity (3,4). Knowledge of the stereochemistry of the polymer may allow correlation of its electrical conductivity and, perhaps, its electronic properties with the structure of the macromolecule. To this end, polymerization of individual polymer chains in a well defined canal of a crystalline host material is one of the better ways to avoid cross-links, side reactions, or by-product formation. Furthermore, these polymers are easily separated from the host by selective dissolution since their solubilities usually differ greatly from those of the hosts. It is possible that ultimately the study of the "canal" polymers will provide useful information on the properties of single polymer chains.

In this paper, we describe our initial work on canal polymerization of 1,3-butadiyne in PHTP host. More detailed accounts of this work will be published later.

Experimental

Trans-anti-trans-anti-trans perhydrotriphenylene was prepared by the method of Farina, et. al. (4,5). Dodecahydrotriphenylene (10g, Aldrich, as received) and 10% palladium on activated carbon (3g, Aldrich) in 600ml n-heptane were rocked for 170 hours at 300^{o}C, under 1400 psig of hydrogen. The PHTP was then recrystallized two times from n-heptane. 1,3-Butadiyne was prepared according to the method of Armitage, et al.(6). 1,4-Dichloro-2-butyne (12.5g, Aldrich, as received) was diluted with 12ml dioxane and added slowly to a solution of 12g KOH in 120 ml water at 95^{o}C, under nitrogen. 1,3-Butadiyne gas was collected in a trap at -78°C, transferred to a vacuum line and purified by distillation from a -78 to -198°C trap at 10^{-4} torr. 1,3-Butadiyne was kept cold and away from air to prevent explosion.

The inclusion compounds were formed by two methods, resulting in two types of crystals, types I and II. Type I crystals resulted when a large excess of 1,3-butadiyne was placed over PHTP crystals so that the inclusion compound actually recrystallized out of the monomer. This takes place over several days at -10°C. Type II crystals formed when a small excess of liquid 1,3-butadiyne was placed over PHTP, allowing the canals to fill by diffusion at -10 to -20°C. The polymerization was subsequently done either thermally at -10°C to 100°C, or by ^{60}Co radiation, using dosages of 125, 250, and 950 krad.

In the case of radiation polymerization, the excess 1,3-butadiyne was removed before irradiating. In the case of thermal polymerization, the excess was not removed when the temperature was at -10°C. The polymerization began in the canals at -10°C within 24 hours and was continued for 7 days. The 1,3-butadiyne outside the canals did not polymerize and was removed before further polymerization at 25°C or 100°C for 24 hours.

The uv-visible spectrum was measured on a Perkin Elmer model 330, the IR spectrum on a Perkin Elmer model 283. PHTP-polybutadiyne or polybutadiyne dispersions in very thin KBr pellets were used in both cases. Raman spectroscopy was performed on single crystals using a SPEX 1403 monochromator, equipped with a Nicolet 1180E data station. A right angle geometry was used with <1mw of an Ar^+ laser at 457.9 nm with resolution at $3cm^{-1}$.

Results and Discussion

Type I crystals, prepared by recrystallizing PHTP in liquid 1,3-butadiyne, formed clear needle-like single crystals which extinguished cleanly under polarized light. Polymerization begins rapidly upon formation of the crystals at -10°C so no crystals with unpolymerized monomer have been isolated. Some of these crystals melted at the melting point of PHTP, 128°C, and some at 159°C. After polymerization, type I crystals contained 8.5% polymer by weight, which corresponds to about an 85% filling of the PHTP canals, estimating the identity period of 1,3-butadiyne in the canal to be equal to that of PHTP(4). Type II crystals, on the other hand, which were formed by diffusion of the monomer directly into the canals, were opaque and had roughened surfaces. These all melted at 127 to 128°C and contained only about 1% polymer, corresponding to about 10% filling of the canals. Upon melting, in both types of crystals, liquid PHTP flowed away from the polymer, leaving a polymer which did not melt up to 420°C. Reactivity of the polymer towards light and air would be expected, leading to insoluble, infusible material formation. These two types of crystals are shown in Fig 1.

Both type I and type II crystals undergo thermal and radiation-induced polymerization, with the color of the PHTP inclusion crystals progressing from yellow to orange, then red and finally brown. The polymer obtained by dissolving away the PHTP of a single crystal with hexane is shown in Fig. 2. It consists of long fibers oriented parallel to what was the long axis of the crystal.

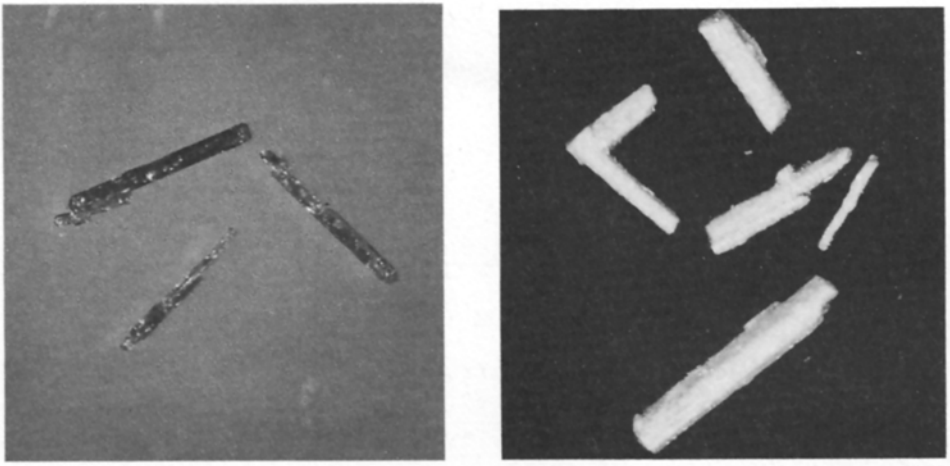

Figure 1A - Polybutadiyne-PHTP Type I single crystals formed by recrystallization out of monomer.
1B - Polybutadiyne-PHTP Type II crystals prepared by diffusion of monomer into host canals.

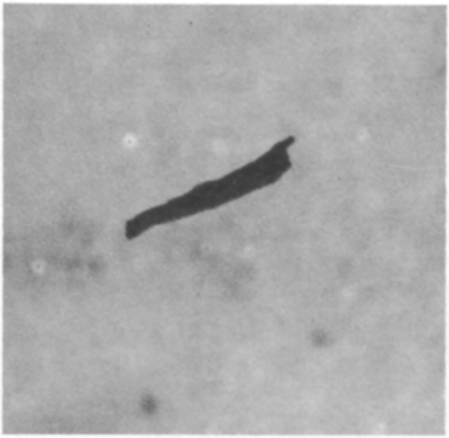

Figure 2 - Polymer remaining after dissolving PHTP with hexane

Resonance Raman experiments with 457.9 nm excitation resulted in the spectrum in Fig.3 for both types of crystals. The peaks at 1270, 1523 and 2124 cm^{-1} correspond very well to the 1254, 1525 and 2104 cm^{-1} positions reported for another diacetylene polymer(7). The assignments for these features (7,8) are given in Table 1, along with our assignments for the remaining features.

The band positions unambiguously show that we do indeed have polymerized diacetylene with a conjugated ene-yne type backbone(8). The most

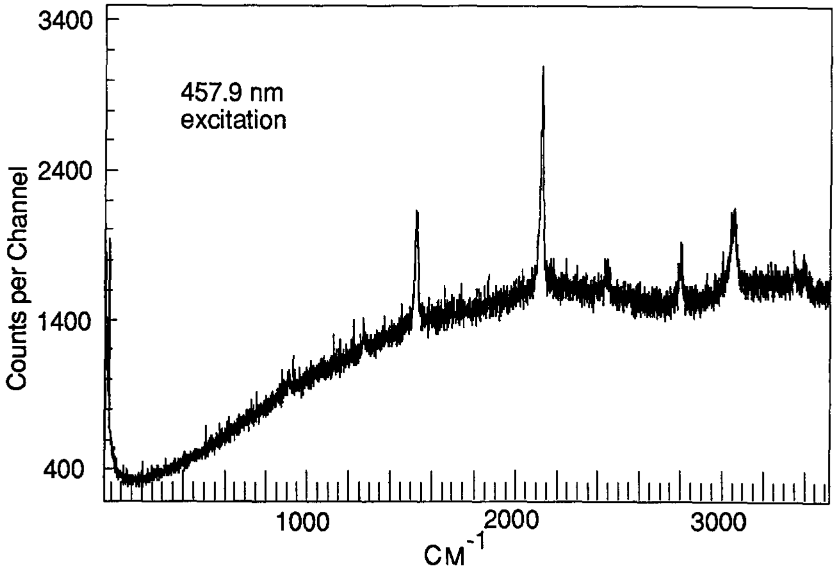

Figure 3 - Resonance Raman spectrum of canal polymerized polybutadiyne

TABLE 1

Peak (cm^{-1})	Assignment	
907	vCHdef, C-H deformation	
1270	vC-C, C-C stretch	Conjugated
1523	vC=C, C=C stretch	
2124	vC≡C, C≡C stretch	
2440	vCHdef + vC=C	Combination
2801	vC=C + vC-C	Combination
3054	2vC=C and/or C-H stretch	
3401	vC-C + vC≡C	Combination

prominent feature above the v(C≡C) stretch at 2124 cm^{-1} is at 3054 cm^{-1} and we believe that this may be due to a C-H stretching fundamental and/or overtone of the v(C=C) stretch. Based on the position of both the v(C=C) and the v(C≡C), and with the use of the equations of Shand, et. al.(9), we estimate the chain segment to be 7-8 repeat units. The assignments of the 907, 1270 and 3054 cm^{-1} features to a C-H deformation, a C-C stretch, and a C-H stretch are all in analogy to polyacetylene spectra(10). Since other polydiacetylenes reported to date have other more complex R groups attached to the polymer backbone, neither the C-H deformation nor the C-H stretch would appear in their resonance Raman spectra. While the appearance of combination and overtone features is ubiquitous in resonance Raman spectra, we nevertheless consider the highest frequency assignments as tentative until further comparative work among analogous diacetylene polymers is performed.

The UV-Vis spectrum of radiation polymerized single crystals is shown in Fig. 4. The longest wavelength absorption peak occurs at about 465 nm. The broadening of the peak is probably due to the inability to obtain a good dispersion in KBr. When we correlate this absorption peak to the longest wavelength absorption of diacetylene oligomers of known lengths, as reported by Bitler and Wudl(11), it appears the chain length is about 19 unsaturated bonds or 9 to 10 diacetylene repeat units. (This number can only be considered approximate since solution effects cannot be duplicated.) This estimation is in fairly good agreement with our Raman results, which indicate an ene-yne chain segment of 7 to 8 repeat units. Using the method of Exarhos, et. al., (6) a 465 nm absorption peak indicates an ene-yne chain segment of about 8 repeat units.

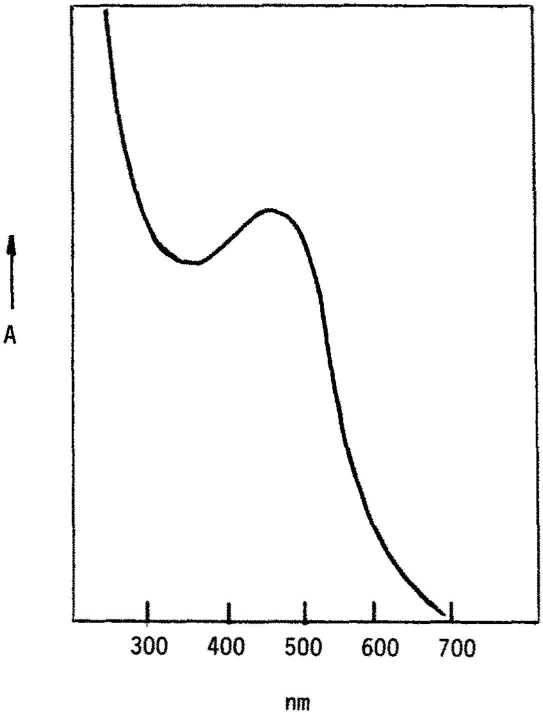

Figure 4 - UV-visible absorption spectrum of polybutadiyne-PHTP Type I crystals/KBr.

The presence of pendant acetylenic groups is indicated by peaks in the IR spectrum at 3300, 2160 and 640 cm^{-1}. The peak at 2160 is quite weak and not detectable in some samples. Peaks indicative of the conjugated ene-yne polymer backbone are seen at 1625 (broad), 1235, and 880 cm^{-1}. The presence of the acetylenic C-H stretch is somewhat surprising since it seems to be inconsistent with the clear indication of an ene-yne backbone without any pendant acetylenic groups from our Raman data. We feel the answer may be linked to the rather short ene-yne conjugation lengths (7-8 units) that we measure. It could be that these 7-8 unit segments are interrupted by a polyene segment that is formed by just one of the acetylene groups of the diacetylene, leaving the other pendant.

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