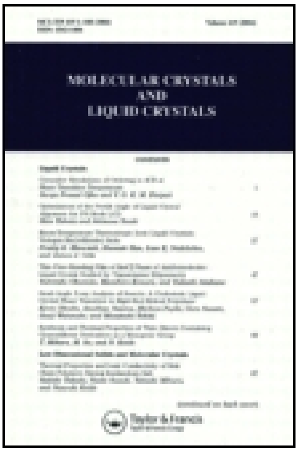

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The Chemical Modification of Polydiacetylenes: The Interaction of Nitrogenous Reagents with Single Crystals of Poly-1,6-di-N-Carbazolyl-2,4-Hexadiyne (DCH)

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The chemical modification of polydiacetylenes is discussed as an approach to the modification of the electronic structure of this novel class of crystallographically ordered conjugated polymers. Single crystals of poly-1,6-di-N-carbazolyl-2,4-hexadiyne react with either $NO_2^+BF_4^-$ or fuming HNO_3 (gas or liquid) to introduce nitro groups in the 3 and 6 positions of carbazole rings. These reactions do not result in highly conductive materials. Poly-DCH crystals are inert to NOCl and concentrated HNO_3 under conditions described herein.

INTRODUCTION

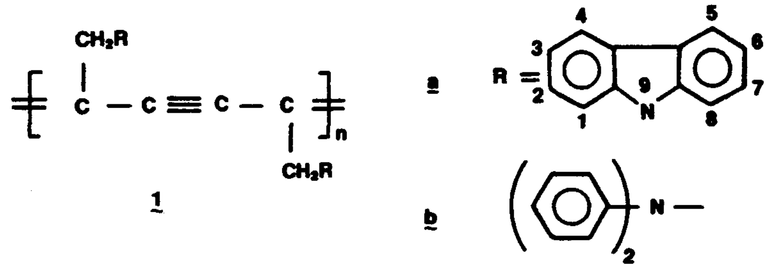
The polydiacetylenes (PDA,1) are a class of crystallographically ordered polymers with conjugated backbones.[1,2] Topics of current interest in these novel materials include optical and electronic phenomena[1,2] and their chemical modification.

Associated with the conjugated backbone is a nonlocalized electronic structure manifested in an intense visible absorption spectrum. The visible absorption spectra of PDA crystals may be classified into two types: "blue" spectra with the most intense absorption observed between 620–660 nm and "red" spectra with the most intense absorption observed between 540–570 nm. Both "blue" and "red" spectra may be observed in certain thermochromic PDA, especially those with urethane side groups. Recently, the differences between PDA exhibiting "blue" and "red" spectra has been correlated with the crystallographic volume of the polymeric repeat unit with smaller volume systems displaying lower energy "blue" spectra.[4] The electronic structure which leads to the PDA absorption spectrum also has associated with it a third order nonlinear coefficient ($\chi^{(3)}$) which has the largest value for any nonresonant system reported to date. The response time of the nonresonant $\chi^{(3)}$ is in the femtosecond regime.[5]

Given the above-cited interest in optical and electronic phenomena in PDA, it is of interest to inquire into approaches to the modification of the PDA electronic structure. Recently it has been observed that certain PDA interact with certain electrophilic reagents, and chemical reaction with the conjugated backbone, modifying the electronic structure, has been deduced.[6–10] This PDA chemical reactivity is the subject of the remainer of the discussion herein.

THE CHEMICAL REACTIVITY OF POLYDIACETYLENES

The PDA derived from 1,6-di-N-carbazolyl-2,4-hexadiyne (DCH, 1a)[6–10] and 1,1,6,6-tetraphenylhexadiynediamine (THD, 1b)[10] provide examples in which reagents diffuse into macroscopic single crystals to yield modified materials which are homogeneous on examination by various electron microscopy techniques. The chemical reactivity observed to date of these PDA with related aromatic amine side groups seems to be controlled by crystal morphology and side chain energy levels. In particular, it has been suggested[10] that the first oxidation potential of the side group may be a figure-of-merit to correlate such reactivity. Hence, poly-THD, whose diphenylamine side chain is more easily oxidized than a carbazole group is more reactive to bromine than poly-DCH.[10]



SCHEME 1

The interaction of poly-DCH with bromine[6–10] has been found to be of particular interest. Crystallographic order is retained for materials which have gained 3–8 Br atoms per polymer repeat unit. For materials which have gained *ca.* 6 Br atoms for polymer repeat, the lattice constants of the modified polymer reveal an expansion of the poly-DCH lattice in the two directions perpendicular to the polymer chain.[11] From solid state ^{13}C-CP-MAS NMR studies,[8,11] it was deduced that for materials which had gained *ca.* 6 Br atoms per repeat, the PDA backbone structure was extensively converted to a mixed polyacetylene. For materials which have gained either *ca.* 6 or *ca.* 8 atoms per repeat unit, the carbazole groups are selectively brominated in the 3,6 positions.[8,9,11] For materials which have gained *ca.* 8 Br atoms per repeat unit, solid state NMR studies[8,11] indicate extensive addition of Br to the backbone and disruption of conjugation. Additionally, the NMR studies[8] indicate the presence of small concentrations of butatriene segments in the Br_8 material.

Chlorine is more reactive than bromine toward poly-DCH single crystals while iodine is markedly less reactive.[9] In contrast to bromine, chlorine interacts with poly-DCH to introduce Cl atoms only in the carbazole group and not on the backbone, as deduced by ^{13}C CP-MAS NMR studies.[12]

While interactions with the PDA backbone were deduced for both poly-DCH and -THD, significant enhancements of dc conductivity, relative to the pristine polymers, have not been observed to date in halogenation experiments.

POLY-DCH AND NITROGENOUS REAGENTS

Motivations for the study of reactions of poly-DCH with the nitrogen-containing reagents to be described in this section include the desire to extend the scope of the chemical reactivity summarized above and the possibility of the "doping"[7] of a PDA to a crystalline conductive polymeric material. The latter possibility has not yet been achieved in our work. Herein, we describe the reactivity of poly-DCH single crystals with a variety of reagents primarily of the NO-NO_2-types. Since the morphology of poly-DCH crystals is such that chemical reactivity would initially occur in the side chain carbazole group,[6] our strategy called for the use of reagents which might oxidize the carbazole group to its cation-radical. This ion-radical would then be reduced by electron transfer from the conjugated backbone leaving the PDA valence band *p*-doped.[13]

Reagents containing NO-moieties investigated include nitrosyl chloride, aqua regia, and nitrosyl tetrafluoroborate. Poly-DCH crystals were inert to both dense vapor (74 hour exposure at 20°Ce and liquid (4 hours at −5°C) nitrosyl chloride. Aqua regia, reputed to contain NOCl as an active component, was found to be primarily a chlorinating reagent, although some nitration also occurred.[9] When poly-DCH crystals were exposed to a 14-fold molar excess of nitrosyl tetrafluoroborate in nitromethane solution, no hint of reaction was evident after 24 hours at 20°C. This mixture was heated at reflux for five days to give a heterogeneous solid which showed black ends on otherwise pristine poly-DCH crystals; unreacted NO^-BF_4 remained in the reaction solution.

At 20°C over a period of 4 hours, poly-DCH crystals are inert to the usual concentrated HNO_3 (69–71% HNO_3 by weight). However, exposure of poly-DCH crystals to red fuming HNO_3 (≥90% HNO_3 by weight) or its dense vapor results in 40–70% weight gains. The resultant materials are soluble in solvents such as dimethylsulfoxide indicating backbone cleavage. By x-ray powder diffraction, these materials are largely amorphous. A sample prepared using nitric fumes which had gained 61% in weight (observed elemental analysis: C, 49.32; H, 2.80; N, 12.52, corresponding to $C_{30}H_{20}N_{6.5}$) revealed broad x-ray reflections as 12, 4.82, 3.24, and 3.14 Å. The FTIR spectrum reveals absorption at 1511, 1342, 796, 751, and 720 cm^{-1}. Using 9-ethyl-3,6-dinitrocarbazole as a model compound, the FTIR[6] and ^{13}C NMR (solution and solid state) spectra[12] indicate nitro substitution in the 3 and 6 positions of the carbazole ring; the triple bond is not detected in the NMR spectra of the nitrated poly-DCH.[12]

Exposure of poly-DCH crystals to 10–27 fold molar excesses of nitronium tetrafluoroborate in boiling nitromethane for 24 hours led to homogeneous black materials which had gained 10–50% in weight. X-ray powder diffraction of these materials revealed a broad amorphous hump with reflections at d = 9.49, 4.84, and 3.13 Å. The FTIR spectrum resembled those of 9-ethyl-3,6-dinitrocarbazole[6] and poly-DCH exposed to nitric fumes with absorption at 1525, 1480, 1343, 1315, 902, 861, 849, 818, 793, 749, 718, 664 and 650 cm^{-1}; 3,6-dinitro substitution of the carbazole rings is thus indicated. The specific dc resistivity of these materials was not less than 10^7 ohm-cm. To achieve less resistive materials related to poly-DCH by charge-transfer doping, it may be necessary to find an oxidant which does not introduce polar substituents such as nitro groups. A large local dipole scatters electronic carriers in a one-dimensional material.

Poly-DCH crystals appear somewhat more reactive to $NO_2^+BF_4^+$ than to $NO^+BF_4^-$. These reagents are reported to have comparable reduction potentials, *ca.* +1.50 volts vs. NHE.[14] Such a potential is clearly sufficient to oxidize an alkylcarbazole in solution.[15]

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