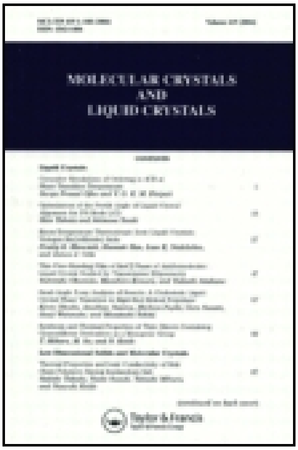

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SOLID STATE POLYMERIZATION AND THE CHEMICAL REACTIVITY OF SOLID POLYDIACETYLENES

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Abstract The term "design" of a solid state polymerization, taken to imply the necessary crystallographic and mechanistic considerations, is introduced with a view toward discovery and development of new lattice controlled processes. Using examples from known solid state polymerizations, a qualitative discussion of several crystallographic and mechanistic issues is presented. With the caveat that such issues may not be easily separated, a central conclusion appears to be that mechanistic problems associated with initiation and propagation steps may hold the key to progress in this area. While chlorine, aqua regia, and nitric acid convert single crystals of poly-1,6-di-N-carbazolyl-2,4-hexadiyne (DCH) to amorphous solids, bromination, which proceeds more rapidly as temperature is lowered, results in a crystalline solid. These reactions are anisotropic and their products are characterized by spectroscopic and crystallographic techniques. It is concluded that the initial reactivity is controlled by carbazole energy levels, rather than those of the conjugated backbone.

INTRODUCTION

This work summarizes our experimental studies and current thinking on approaches to new fully ordered conjugated polymers via solid state polymerization. Our efforts are motivated by the need for such polymers beyond the polydiacetylenes (PDAs) for novel electronic and optical properties.[1,2] Moreover, current theoretical speculation concerning the electronic structure of presently unknown one- (polyyne), two-, and three-dimensional conjugated polymers should stimulate new synthetic work directed toward such materials, especially their structurally ordered forms.[2,3]

We further report initial observations on the controllable chemical reactivity of the PDA poly-1,6-(di-N-carbazolyl) 2,4-hexadiyne (DCH). These results reveal an additional vector in PDA research that is anticipated to lead to new and useful modified PDAs.

The thread that links these topics is that the solid state reactions observed are controlled by impurities and defects in these organic solids.

"DESIGN" OF A SOLID STATE POLYMERIZATION

Just as the term "design" of an organic metal[4] implies the crystallographic and physical constraints necessary for the achievement of the metallic state in organic systems, so "design" of a solid state polymerization is taken to mean the necessary crystallographic and mechanistic considerations needed to achieve a new lattice-controlled complete polymerization. Just as discussions of the "design" of an organic metal mention the necessary considerations, but fail to address issues such as kinetic control of phase formation, so it seems likely that discussions of the "design" of a solid state polymerization will have analogous shortcomings. Nevertheless, it is important to make a new beginning along such lines. An earlier discussion[5] of "ground rules" for solid state polymerization also emphasized additional issues such as mobility of monomer in the solid and diffusion controlled versus lattice controlled polymerization.

Early discussions of the "design" of an organic metal were facilitated by the initial experimental observations on the prototype, TTF-TCNQ. Analogously, the existence of crystallographic and mechanistic information on the topochemical polymerizations of, *e.g.*, nickel *bis* (cyanoethylphosphine) dihalides,[6] S_2N_2,[7] and especially conjugated diacetylenes, provides a most valuable data base for further discussion. Indeed, the wealth of information concerning the latter process allows the statement that diacetylene polymerization is better investigated and understood than any other polymerization reaction at present.[8]

Crystallographic Considerations

The crystallographic issues in a discussion of a new solid state polymerization of necessity begin with the topochemical principle, a structurally-based concept which emphasizes lattice regularity rather than lattice imperfections for reactivity and which notes that reaction occurs with a minimum of atomic or molecular movement.[9] For carbon-carbon bond formation to occur, it is well documented that the atoms which will form the covalent bond are typically about 4.0Å, a C----C van der Waals contact distance, in the reactant crystal structure.

A comprehensive review of the crystallography of diacetylene monomers has recently appeared.[10] The central conclusion of the analysis of existing structural data for reactive monomeric diacetylenes is that the distance between the reacting carbon atoms is less than 4.0Å. The only exception to this conclusion to date is DCH which undergoes a phase transition in the course of its polymerization.

In the general case involving new polymerizations, the strategy of using selective nonbonded interactions to orient reactive moieties within a reasonable distance of one another seems most appropriate at present. This strategy was adopted in the solid state approach to asymmetric synthesis[11] and earlier in the studies of "crystal engineering" as applied to solid state photodimerization.[12] The point is further illustrated by two current approaches to the polymerization of monoacetylenes.

B.M. Foxman and his collaborators have initiated a detailed study of the structures and reactivity of metal propiolates.[6,13] Following up on the report of H_3C .... CH_3 contacts of ca. 3.9Å in the crystal structure of bis (acetato) tetraaquonickel (II), they have synthesized numerous metal propiolates and have found several different types of short contacts between digonal carbons in these monomer structures. To date, polymerization of metal propiolates by heat and ^{60}Co gamma radiation has resulted in the conversion of crystalline monomers to amorphous polypropiolates.

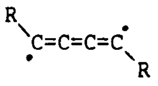
The tactic of structure control by replacement of a methyl group by the HC≡C- moiety will find broader applicability in the search for polymerizable monoacetylenes. The X-ray powder pattern of propargyl 3,5-dinitrobenzoate is superimposable on that of the ethyl ester.[14] The reported structure[15] of the latter provides a structural interpretation for the lack of solid state reactivity[14] of the propargyl ester to heat and gamma radiation.

Hydrogen bonding has been used to orient the potentially reactive acetylene carbons of propiolamide ($HC{\equiv}C\text{-}CONH_2$) and the semicarbazone of propiolaldehyde ($HC{\equiv}C\text{-}CH{=}N\text{-}NH\text{-}CONH_2$).[16] The reported[17] crystallographic information on propiolamide revealed an infinite array of C(1) .... C(2') contact at 3.82Å. The crystal structure of the semicarbazone[16] reveals an infinite molecular chain with three unique C(1) .... C(2') contacts at distances of 3.64, 3.66, and 3.77Å. Yet vacuum sublimed samples of these compounds are markedly less reactive to ^{60}Co gamma radiation than diacetylenes such as DCH or the metal propiolates cited above. Clearly, in these cases, short crystallographic contact distances between potentially reacting carbons is not sufficient to guarantee significant reactivity toward gamma radiation.

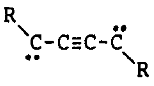
Initiation, Propagation, and Termination in Crystalline Monomers

A central conclusion of the above brief examination of crystallographic issues is that, while selective nonbonded interactions may be used to get reactive moieties close to each other, mechanistic considerations may outweigh the crystallographic ones. Mechanistic aspects of solid state polymerization are now taken up, again with special reference to diacetylene polymerization.

For initiation, it appears likely that a diacetylene converts to species such as the diradical (DR) or the dicarbene (DC):



DR

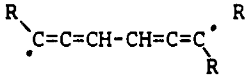


DC

Qualitatively, because fewer pi-bonds are broken in its formation, the DR would be expected to be of lower energy than DC. The generation and role of these species in chain propagation have been extensively studied, primarily by H. Sixl and collaborators.[18]

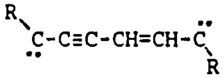
Certain diacetylenes (*e.g.* PTS, the bis-tosylate of 1,6-dihydroxy-2,4-hexadiyne) may be polymerized thermally (PTS is also readily polymerized by ultraviolet light and gamma radiation) while others are melt stable (*e.g.* TCDU, the biphenyl urethane of 1,12-dihydroxy-5,7-dodecadiyne) and require radiation, most conveniently ^{60}Co gamma radiation, to be polymerized. Following ideas of chemical reactivity derived from the perspective of the conservation of orbital symmetry, chemists regard thermally- and radiation-induced reactions as quite distinct. The observed reactivity patterns of diacetylenes, as regards the nature of the initiating stimulus, remain puzzling.

In the interest of identifying monomer structures related to diacetylenes which might lead to new examples of fully ordered conjugated polymers, the structures of DR and DC species which might be obtained from an assortment of monomers have been discussed in terms of their generation and possible patterns of reactivity.[19] For a molecule such as R-C≡C-CH=CH-C≡C-R, the following DR and DC species may be written:



$\overset{R}{\underset{\bullet}{C}}=C=CH-CH=C=\underset{R}{C}^{\bullet}$

DR



$\overset{R}{\underset{\bullet\bullet}{C}}-C\equiv C-CH=CH-\overset{\bullet\bullet}{\underset{R}{C}}$

DC

Further reaction of DR would lead to an atactic polymer formed by a nontopochemical process. Formation of DC requires H shifts. Relevant synthetic work directed toward this and related monomers remains to be undertaken.

Even in a crystal with reactive moieties near each other, the initiation of reaction need not occur in the ordered crystal structure. We have observed that, while vacuum sublimed crystals of propiolamide and propiolaldehyde semicarbazone are unreactive to ^{60}Co gamma radiation, polymerization is initiated in crystals of these compounds grown in chlorinated solvents.[16] Chloroform is present in crystals of the semicarbazone to the extent of 0.4 mole percent, *i.e.* one molecule out of 250 in the crystal is the solvent located in a defect. The model for reactivity of these crystals includes initiation by excited or ionized solvent as well as termination of excited species by quenching.[16] Earlier, the solid state polymerization of trithiane proceeded to a greater extent for both thermal and radiation polymerization with crystals grown from chloroform than with sublimed crystals.[20]

A central problem associated with chain propagation may occur for monomers in which the hybridization of the atoms involved in covalent bond formation changes in the reaction, *e.g.* sp^2 to sp^3 in vinyl polymerization and sp to sp^2 in diacetylene polymerization. Because van der Waals distances change to covalent bond distances in such reactions, it had been argued that the formation of crystalline polymers without lattice disruption might be out of the question.[21] The formation of amorphous polymer from crystalline monomer has been widely observed for vinyl monomers.[21] While PDA single crystal formation precludes the generality of the above argument, it could be widely applicable.

In this context, the following question is appropriate. Does the observation of the transformation of crystalline monomer to amorphous polymer[6,13,21] imply that the chain propagation problem discussed above is operative? That need not be the case. A counter example would be a propagating chain where an intermediate might undergo stereomutation. Examples might include acetylene and vinyl polymerization where lack of stereochemical homogeneity would likely preclude complete crystallographic order. This situation has been observed for several vinyl polymerizations.[21]

Two recent reviews[18,22] discuss diacetylene chain propagation for both thermal and photo processes. DCH polymerization presents an interesting problem with respect to crystallography of the final polymeric product. Polymerization of DCH either thermally or with ^{60}Co gamma radiation gives the same phase of crystalline polymer. With radiation, this transformation is single crystal monomer to single crystal polymer via an intermediate phase.[10] In contrast, the thermal process give rise to a fibrous polymer which is not a fully ordered single crystal due to nucleation of separate polymer domains.[23] Hence, the nature of the solid state transformation depends on the stimulus in this and other examples.

The above discussion of "design" of a solid state polymerization has emphasized qualitative mechanistic and structural considerations. Its primary intent is to stimulate experimentation in new classes of monomers. The generation of new reactive intermediates for initiation remains an important challenge. It would appear that good rationales for first order control of crystal structure are available, but that fine tuning may prove complex. A central conclusion appears to be that mechanistic issues associated with initiation and propagation may hold the key to new classes of fully ordered polymers with the caveat that mechanistic and crystallographic issues may not be easily separated in systems of interest.

THE CHEMICAL REACTIVITY OF SOLID POLYDIACETYLENES

Due to their van der Waals tight packed structures, the interaction of reactive gases and liquids with single crystal PDAs often results in reaction only at the crystal surfaces.[16] Such experimentation is typically motivated by the success in rendering the partially crystalline polyacetylene $(CH)_x$, also a conjugated system, conductive by means of reactive "dopants" and the anticipated ease of ionization of the PDA backbone from the reported solid state ionization energies.[24] Hence, a rich chemistry of solid PDAs does not exist at the present time, especially from the perspective of the crystallographic definition of reaction products. It was concluded that the oxygen molecules which interact with poly-PTS reside on the surface or in defects.[25] Exposure of poly-4-BCMU to iodine resulted in a lower uptake of iodine for single crystals than for amorphous samples; only an electrical characterization of these materials was given.[26]

In the course of our studies of the ion implantation of PDAs, a process which converts them into conductive materials,[27] single crystals of poly-DCH were exposed to bromine at temperatures of 20-25° for twenty-four hours. After isolation, the crystals were bronze in appearance rather than the brassy color of pristine poly-DCH and their weight had increased by 125 percent corresponding to about six Br atoms per repeat unit in the polymer. X-ray powder diffraction of this brominated poly-DCH revealed numerous reflections suggesting a crystal-crystal transformation via a liquid-solid reaction. Poly-DCH interacts with either liquid or gaseous chlorine to introduce 13-14 Cl atoms per repeat unit and is nitrated by either nitric acid or nitric fumes. Aqua regia is primarily a chlorinating agent for poly-DCH. X-ray powder diffraction of the products of these latter reactions, which appear to be homogeneous on microscopic examination, reveals that the structural change which has occurred is single crystal to amorphous solid. These observations are to be contrasted with the results of the interaction of antimony pentahalides with single crystal poly-DCH which reveal a heterogeneous process.[16]

Information on the nature of the bronze crystals, which is the appearance of poly-DCH which has gained 3-6 Br atoms per repeat unit, was obtained by means of a variety of spectral and diffraction techniques. Figure 1 displays the solid state electronic spectrum of material which has gained ca. 6Br, recorded by diffuse reflectance, of a one percent by weight dispersion in sodium chloride. The features at visible wavelengths are reminiscent of PDAs and those in the ultraviolet are those of the carbazole side chain. Since Figure 1 reveals absorption at 6328Å, the resonance Raman spectrum was recorded. The observed Raman shifts of 2108, 1487, 1472, 1458, 1429, 1330, and 1236 cm^{-1} are similar to those of pristine poly-DCH.[27] A luminescence process, which has also been detected in fluorescence measurements, accompanies the Raman scattering process.

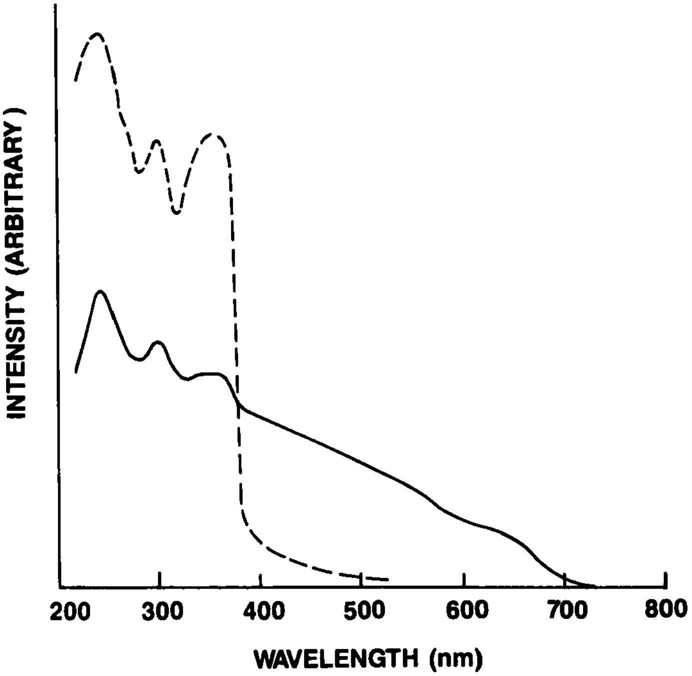


FIGURE 1 Solid state spectrum of poly-DCH which has gained 6 Br atoms per repeat unit (——) and 3,6-dibromocarbazole (----).

In the course of attempting to control the crystallographic transformation, it was found that the bromination proceeds more rapidly as the temperature is lowered. In 75 minutes at -5°, poly-DCH gains 60% in weight while at 20°, a 30% weight gain is observed. Both samples in these experiments are heterogeneous; that is, both pristine poly-DCH and the new phase are observed upon microscopic examination. In two hours at -5°, the product isolated is completely transformed to a new phase, while the product of the experiment at 20° remains heterogeneous. We have deduced two factors which can account for the faster bromination at lower temperatures. The density of bromine, hence its concentration, increases ($3.10 g/cm^3$ at 25°; $3.19 g/cm^3$ at 0°) as temperature is lowered; this is the minor factor. We thus ascribe a complex of the donor-acceptor type between a donor carbazole in poly-DCH and an acceptor bromine as the source of the inverted temperature behavior:

$$Cz + Br_2 \overset{K}{\rightleftharpoons} [Cz{\bullet}Br_2] \longrightarrow Cz\text{-}Br$$

The complex $Cz{\bullet}Br_2$ is a key intermediate in carbon-bromine bond formation. A decrease in K as T increases accounts for the observed behavior. Direct evidence for complexes as intermediates in ionic bromination has recently been published.[28] Complex formation has been invoked in bromine gas-organic solid reactions,[29] and gas-solid reactions of aromatic hydrocarbons with halogens lead to substitution in the positions expected for an electrophilic process.[30]

Fourier transform infrared (FTIR) spectra of brominated and nitrated poly-DCH and relevant model molecular compounds reveal that the inital positions of substitution on the carbazole ring are the 3 and 6 positions. Analysis of the aromatic C-H out-of-plane deformation vibrations is particularly useful for this purpose, as revealed in Figure 2 which shows a close correspondence of this portion of the FTIR spectrum for nitrated poly-DCH and the molecular model compound N-ethyl-3,6-dinitrocarbazole. Comparison of the FTIR spectra of brominated poly-DCH and

1,3,6,8-tetrabromocarbazole reveals that substitution of the carbazole ring beyond dibromination does not occur. These conclusions are independently confirmed by ^{13}C CP-MAS NMR spectra of these materials.[31]

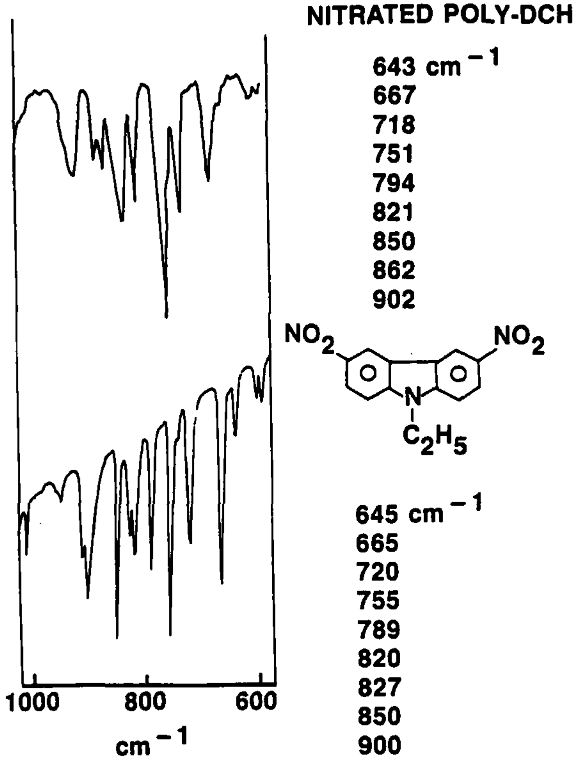


FIGURE 2 Fourier transform infrared spectra of nitrated poly-DCH and a model compound in the region of the aromatic out-of plane CH deformation vibrations.

The crystallographic consequences of the interaction of bromine with poly-DCH have been probed via rotation and Weissenberg photographs. The crystallites of poly-DCH, which has gained ca. 6Br atoms per repeat unit, appear similar to the straws in a broom. Precession photographs reveal a repeat along the chain axis of 4.85±0.1Å, consistent with the preservation of a PDA structure. Weissenberg photographs do not permit a clear interpretation of the lattice in other directions. Additional detail is presented in an accompanying article.[32]

Microscopic examination of poly-DCH crystals which have been exposed to bromine for one hour at either -5° or 25°, i.e. conditions which lead to heterogeneous material, reveals that reaction begins by the diffusion of bromine into the ends of the crystal, rather than reaction on the faces of the length of the needle-like crystals. From the known morphology of poly-DCH crystals,[23,33] it follows that the initial interaction of bromine occurs at those faces which expose the planes of carbazole groups rather than with those faces parallel to the direction of the conjugated chain. In addition to these observations in heterogeneous brominated poly-DCH crystals, every other situation where a heterogeneous product is isolated from interaction of poly-DCH with a given reagent, microscopic examination reveals that reaction begins at the ends of the crystal. Hence, the gas-solid and liquid-solid reactions noted herein for poly-DCH are anisotropic. Previously, the anisotropic reaction of ammonia with substituted benzoic acid and anhydride crystals has been observed[34] and anisotropic reaction of chlorine with phenols has been discussed.[35]

The above description of the anisotropic reaction of bromine with poly-DCH was confirmed by rotation and Weissenberg photographs of heterogeneous crystals. In these experiments, elaborated in the accompanying article, separate X-ray photographs were obtained from an apparently pristine area in the center of a crystal and the end of the crystal.

It should not be construed that bromine diffuses into every poly-DCH crystal to the same extent. Indeed, if a batch of brominated poly-DCH is added to carbon tetrachloride, a very small number of crystals float. Microscopic examination of these crystals reveals no evidence of reaction. Further, batches of brominated poly-DCH may be fractionated by density. For example a 72 mg. sample of poly-DCH which had gained ca. 4.5 Br atoms per repeat unit was fractionated using $CHBr_3/CCl_4$ mixtures. In this manner was isolated 24mg with $d < 1.93$ g/cm^3, 33 mg with $d = 1.931$-1.933, and 13mg with $1.933 < d < 1.978$ g/cm^3. Using a poly-DCH unit cell volume of 1040Å^3 [16] and a volume of 30Å^3 for covalent Br,[36] densities of 1.89, 2.00 and 2.09 g/cm^3 may be calculated for poly-DCH which has gained 4,5, and 6 Br atoms per repeat unit, respectively. A sample of poly-DCH which has gained ca. 6Br atoms per repeat unit had an observed density of 2.104 g/cm^3

Since exposure of poly-DCH to dense bromine vapor at 25° for three months does not lead to a detectable weight gain, the general question of the reactivity of this polymer is of interest. Monomeric DCH, whose crystal structure is similar to the polymer,[10] is transformed to an amorphous solid by exposure to bromine vapor; a weight gain of 260% is noted. The polymer is clearly markedly less reactive than the monomer. Poly-PTS is inert to refluxing bromine[37] and monomer extracted poly-TCDU is rendered amorphous by bromine vapor.

Any approach to understanding the reactivity of poly-DCH should begin with its energy levels. Figure 3 displays the absolute energy levels of poly-DCH, as deduced by Bassler and coworkers,[38] along with the highest filled levels of carbazole from the work of Nielsen, et al.[39] It is relevant to deduce from Figure 3 that, in comparison to the PDAs such as PTS and those with urethane side chains such as TCDU, the filled level of carbazole is relatively near the top of the poly-DCH valence band and the first singlet excited state of carbazole is near the excitonic level and bottom of the conduction band. Earlier,[16] the oxidation of the PDA backbone in the interaction of thermally polymerized DCH with antimony pentahalides was interpreted to involve initial electron transfer with the carbazole side chain. In the present experiments, the carbazole energy levels, not those of the conjugated backbone, and crystal morphology are clearly important considerations in understanding the reactivity, especially with bromine.

While it is already apparent that not all PDAs will exhibit the reactivity of poly-DCH, we expect that other PDAs will show related types of reactivity under appropriate kinetic and morphological conditions. The existence of many new examples of PDAs modified via gas-solid and liquid-solid reactions is readily conceivable.

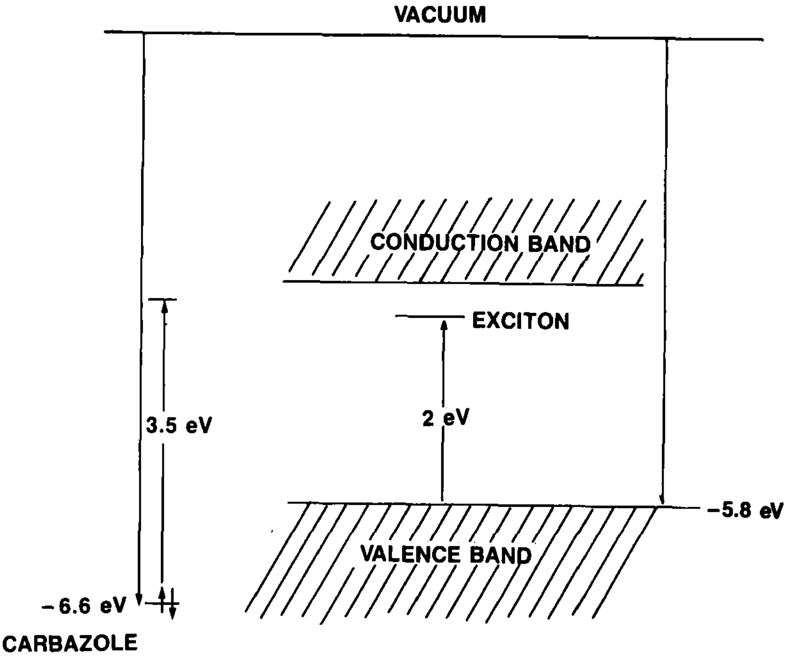


FIGURE 3 Absolute energy levels of poly-DCH (from ref. 38) with the levels of carbazole (from ref. 39) superimposed.

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