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Extending the Diacetylene Polymerization Concept — A Reactive Intermediate Analysis

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EXTENDING THE DIACETYLENE POLYMERIZATION CONCEPT -- A REACTIVE INTERMEDIATE ANALYSIS

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Abstract. In the interest of identifying monomer structures which might lead to further examples of fully crystalline conjugated polymers, the structures of diradical (DR) and dicarbene (DC) species which might be obtained from an assortment of monomers more extended in length than diacetylenes are qualitatively discussed in terms of their generation and possible reactivity patterns.

The solid state polymerization of diacetylene monomers is by now a model process for the production of macroscopic fully ordered crystals of conjugated polymers.[1] Beyond the interesting process of their formation, the polydiacetylenes exhibit optical and electronic properties which are clearly of fundamental interest, as well as potentially technologically useful. It is therefore appropriate to seek related monomer molecular structures and inquire into their possible solid state reactivity in the hope of finding further examples of fully crystalline conjugated polymers.

It is a straightforward exercise to list numerous molecular structures of conjuated monomers which are greater in length than diacetylenes. To proceed further, it is appropriate to recognize that species such as the diradical (DR) and dicarbene (DC), listed in Scheme 1 with R as a generalized substituent, are the likely initiating species.[1,2] DR and DC are not resonance structures, as they have different numbers of unpaired electrons. Qualitatively, DR would be expected to be lower in energy than DC because fewer pi bonds are broken in its formation. The oligomers of DR and DC, as well as more complex species, are the key species in the propagation of the polydiacetylene chain.[2] Hence, this work seeks to analyze the DR and DC species from monomer molecular structures with more extended conjugated systems than the diacetylenes. The assumptions implicit in the analysis are: (1) only the DR and DC intermediates are relevant; (2) only their 1,n (where n is the number of carbons in the conjugated chain) addition reactions are important; and (3) in an experimental system, monomer crystal structure may be controlled to give the appropriate orientation for 1,n addition polymerization. Where appropriate, comparison is made to existing experimental work.

DR AND DC INTERMEDIATES FROM EXTENDED MONOMERS

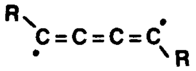
The simplest cases of monomers more extended than diacetylenes are those from tri- and tetra-acetylenes, and experimental study of examples of both of these cases has been reported.[3,4] For 1,6 addition, the DR and DC intermediates are given in Scheme 1. Interestingly, 1,4 addition polymerization is the observed reactivity pattern in the case where structural information, _i.e._ lattice constants, is available.[3] The 1,6 addition polymerization of a triacetylene remains an unobserved reactivity pattern. The structure of the product of the tetraacetylene is uncertain.[4]

Scheme 2 shows the DR and DC intermediates for monomers in which two acetylenic groups are substituents at the end of a _trans_ polyene chain. Two distinct situations arise. While DR intermediates are straightforwardly written, they are bi-allenic in character, and their polymerization would lead to a repeating allene structure. If formed, this polymer would be atactic and would form by a nontopochemical process, since the planar backbone of the conjugated monomer would lead to nonplanar intermediates and product. This conclusion may also be applied to other structures in the Schemes where bi-allene structures are relevant.

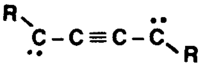
The DC intermediates written for direct excitation have five coordinate carbons. If, as shown in Scheme 2, these may isomerize via the 1,3 H shift, DC intermediates with normal carbon valences are arrived at. It may be possible to synthesize the latter DC intermediates via suitable carbene precursors. This situation also holds for the monomer in Scheme 2 where a butadiene moiety is replaced by a butatriene, with the exception that the DC intermediate

SCHEME 1

- **DIACETYLENE POLYMERIZATION**



Diradical (DR)

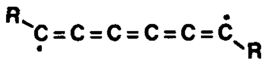


Dicarbene (DC)

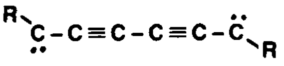
Reference 1 and 2

- **TRIACETYLENE POLYMERIZATION**

For 1,6 Addition,

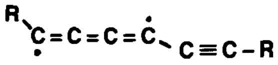


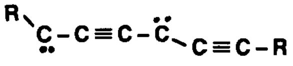
DR



DC

1,4 Addition is Experimentally Observed. Reference 3

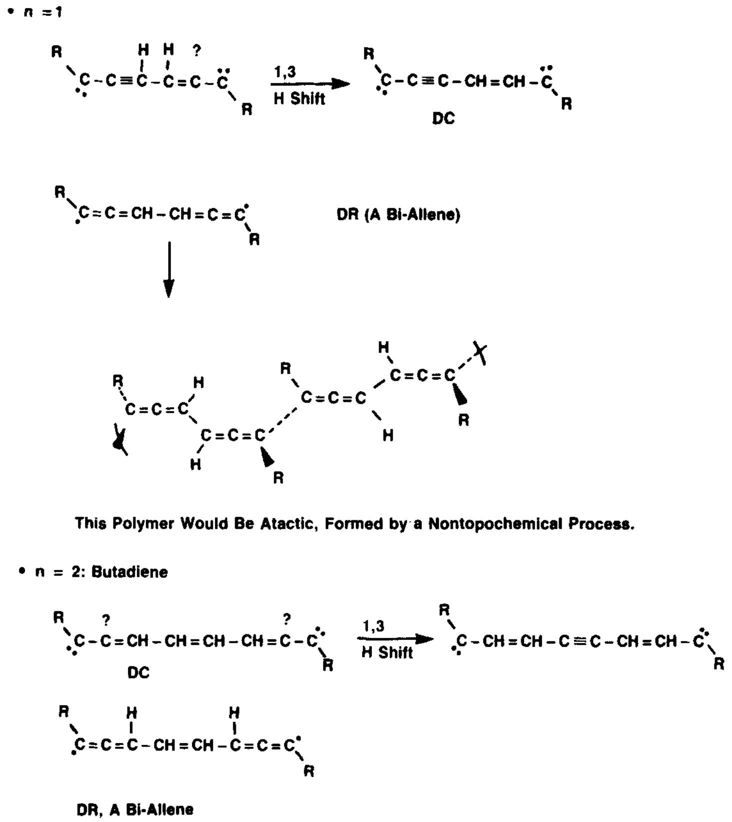




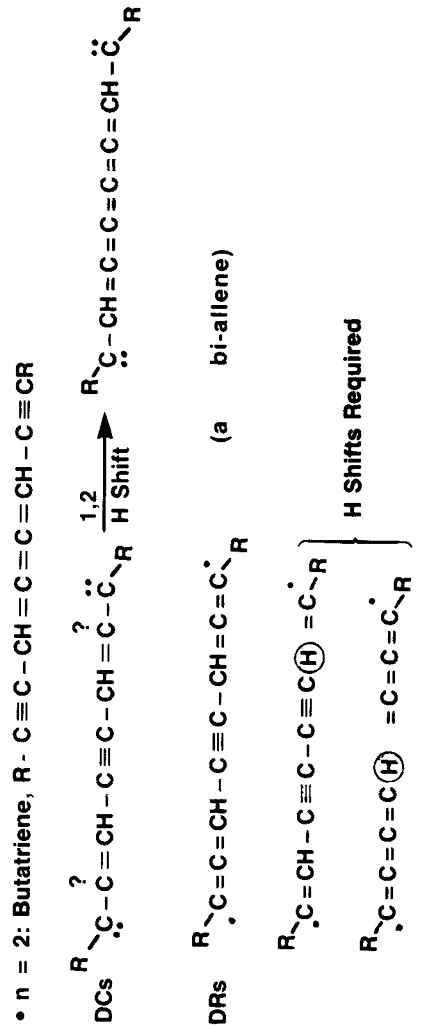
- **TETRAACETYLENES (See Reference 4)**

SCHEME 2

POLYMERIZATION OF $R-C\equiv C(CH=CH)_nC\equiv C-R$



SCHEME 2 (CONTINUED)



now requires a 1,2 H shift.

Proceeding to consider the case in which the acetylenic groups are para substitutes on a aromatic ring (Scheme 3), both DR and DC species are quinodimethanylic in character involving loss of aromaticity. Experimentally,[5] the ultraviolet photopolymerization of 1,4-diethylnylnaphthalene has been studied. The polymer characterized is formed by polymerization of only one of the acetylenic groups with the remaining acetylene acting as a substituent.[5b] The polymerization is light-initiated and controlled by diffusion processes within locally melted regions of the crystal leading to a disordered product.[5c]

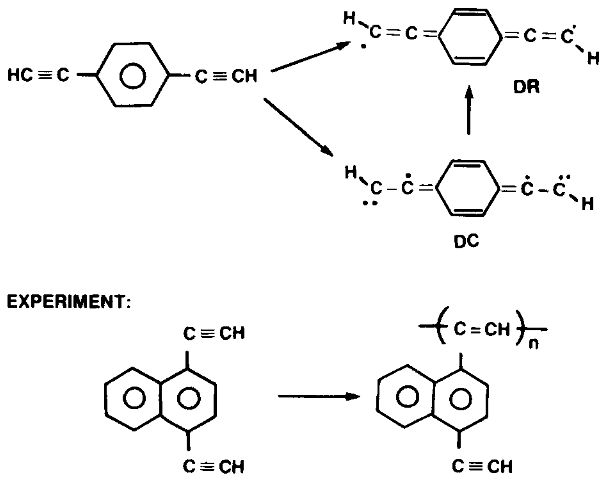
Scheme 4 contains several additional extended DR and DC species. If the DR species derived from p-diethynylbenzene is extended by replacing allenic with butatrienic groups, a planar DR species may be written, but it is not apparent which neutral molecule would lead to that DR. Two isomeric DC species with aromatic rings related to this DR may be written. Again, it may be possible to synthesize suitable carbene precursors to these DC intermediates. The monomer structure, in which a p-styryl group is placed between two acetylene groups, leads to an allenic DR in which the benzenoid ring loses aromaticity.

DISCUSSION

The above analysis emphasizes DR and DC species formed directly from a given monomeric structure. In experimental studies of diacetylene initiation and propagation, the species from the dimer has been observed,[2,6] but usually not those from a monomer. The above analysis is justified since a monomer is a molecular crystal and initially a monomer molecule must be excited. Moreover, if dimer DR and DC structures for the extended monomers discussed above are written, the conclusions are the same for those of the monomer.

The qualitative conclusion that a DR form is lower in energy than a DC form in diacetylenes need not be the case in more extended structures. It has been concluded[2] from ESR spectra of oligomerized photo-products of the diacetylene PTS that the structure of the propagating chain changes from DR-like to DC-like at a critical chain length of n=6.

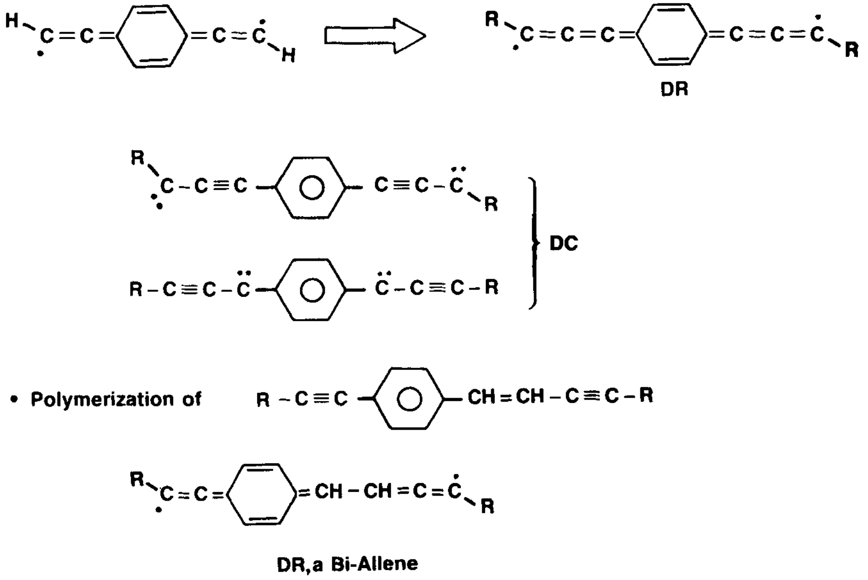
SCHEME 3
POLYMERIZATION OF p - DIETHYNYLAROMATICS



The Polymer is Formed in a Nontopochemical Process. (Reference 5)

SCHEME 4

- Replace the Bi-Allene of Scheme 3 with a Butatriene



In Scheme 4, the DC structures may be lower in energy than the corresponding DR because the aromatic structure of the ring is retained in the former.

In summary, the analysis of DR and DC species derived from conjugated monomers more extended than simple diacetylenes leads to the expectation that DR species formed by direct excitation which have bi-allenic character will lead to atactic polymers formed by a nontopochemical process. If intramolecular hydrogen shifts occur, DC species which are constitutionally isomeric to the DR species could conceivably polymerize in a topochemical process to give new examples of fully ordered conjugated polymers. Intramolecular hydrogen shifts are known in solid state photochemistry.[7] Experimentally, it is of interest to learn if the situation is controlled by thermodynamic or kinetic considerations. It is also of interest to attempt to direct generation of such DC species through synthesis of suitable carbene precursors. While the analysis presented herein discusses only DR and DC species, experimentally it is certainly possible that initiation could be caused by ionization leading to ion-radicals.

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