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# Structural Course of the Polymerisation of Diynes

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Examination of the available information shows that polymers of diverse structure—linear (with polyene and cumulene fragments), cyclolinear (including ladderlike), and three-dimensional—can be obtained by the polymerisation of diynes having conjugated and non-conjugated triple bonds. The structural course of the process is determined by the nature of monomer and catalyst and the conditions. Linear organometallic polymers, whose main chain comprises alternating double bonds and atoms of Group IV elements, can be obtained by the polyaddition of hydrides of these elements to $\alpha\omega$-diynes. A list of 58 references is included.

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## I. INTRODUCTION

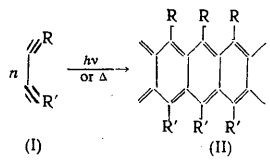
The polymerisation of acetylenic compounds, especially diynes, has been much less studied than that of alkenes and dienes. During recent years, however, polymers based on acetylenic monomers have been attracting increasing attention from research workers in connection with the intensive search for new materials possessing high thermal and thermo-oxidative stability with specific magnetic, catalytic, electrophysical, and other properties.

Whereas the polymerisation of mono- and di-substituted derivatives of acetylene usually leads to the formation of substituted polyenes (Ref.1 and Ref.2, p.378) and/or substituted cyclomers (Ref.2, p.327, and Refs.3 and 4), diynes having conjugated and non-conjugated acetylenic bonds may yield polymers in which the main chain of the macromolecule has a polyene, cumulene, or aromatic cyclic (including ladderlike) structure.

## II. SYNTHESIS OF POLYMERS FROM DIYNES WITH CONJUGATED TRIPLE BONDS

It has been discovered comparatively recently[5-11] that certain crystalline monomers of the type R.[C:C]$_2$.R′ (diacetylenic dicarboxylic acids, alkadiynediols, diurethanes, anacycline), which are stable in solution or in a melt, become coloured when illuminated or when heated rapidly to a temperature below the melting point. The colour is red — violet, dark blue, or black depending on the nature of the substituents R and R′, and more or less soluble polymers are formed with degrees of polymerisation of 3 — 20.

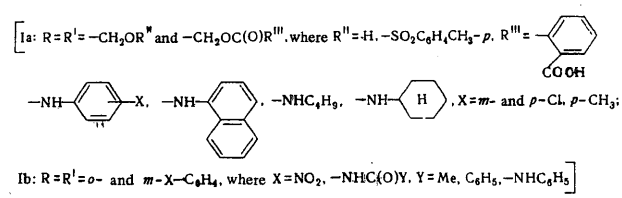
From a study of the ultraviolet spectra of the resulting polymers and the discovery of phthalic acid among their oxidative decomposition products it was suggested[5-8] that the energy communicated to the monomer in the crystalline state, i.e. with a parallel arrangement of the diyne chains, was used to serve only one pair of $\pi$-electrons in each triple bond. This destroyed the rigidity of the diyne molecule, and polymers having a substituted acene structure were formed:



(I) (II)

This interpretation, which disregarded the specific nature of the substituents R and R′, has found a place in subsequent reviews[12,13].

More detailed investigation of reactions of this type has shown[14-17] that in general such behaviour is exhibited only by those diynes which, because of the nature of their substituents



can form hydrogen bonds or develop dipole — dipole interactions.

Solid-phase polymerisation requires that the triple bonds in the monomer molecules should be arranged in such a way that the process can occur without any great change in the crystal lattice of the monomer. For this reason *ortho*-substituted compounds of type (Ib) are sometimes less reactive than the corresponding *meta*-derivatives, while *para*-isomers of (Ib) do not undergo polymerisation at all[17]. The modification of R.C:C.C:C.R (where R = $CH_2$.O.CO.NH.$C_6H_5$) free from dioxan also does not polymerise, since dioxan is responsible for the necessary packing of the monomer molecules in which the phenylurethane groups are bound by hydrogen bonds to neighbouring diyne and dioxan molecules[18].

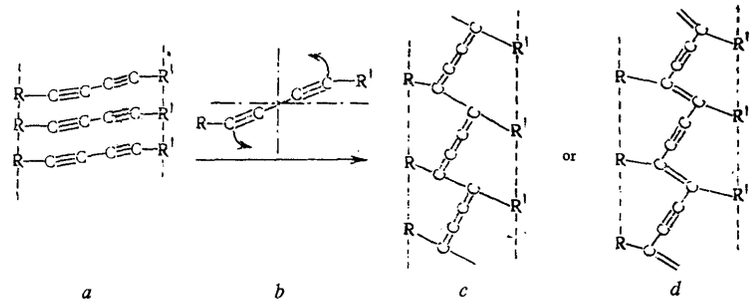



**Figure 1.**

Individual molecules are evidently regularly arranged in the crystal lattice of the monomers in the form of a "ladder" (Fig.1*a*), the "rungs" of which are formed by diyne fragments, and the "uprights" by hydrogen bonds or groups with strong dipole — dipole interaction (shown by the broken lines in Fig.1). Reaction occurs as a result of the rotation of each individual "rung" about its centre (Fig.1*b*) or shearing of the whole "ladder", while the separate "crossbars" are joined by 1,4-addition to form three cumulative double bonds in the unit[14-17] (Fig.1*c*) or perhaps an enyne structure[18] (Fig.1*d*).

Polymer systems obtained by the polycondensation of diynediols with di-isocyanates or dichlorides of dicarboxylic acids exhibit analogous structural changes to those observed in the polymerisation of monomeric diacetylenic derivatives in the solid state[19]:

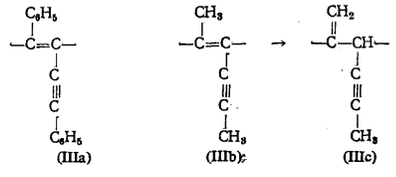
$$\mathrm{HO{-}X{-}(C{\equiv}C)_2{-}X{-}OH + OCN{-}Y{-}NCO \rightarrow}$$
$$\rightarrow \ldots{-}O{-}X{-}(C{\equiv}C)_2{-}X{-}OC\,(O)\,NH{-}Y{-}NHC\,(O){-}\ldots,$$

where $X{=}CH_2$, $CH_2(OCH_2CH_2)_2$; $Y{=}$ $(CH_2)_6$, $p\text{-}C_6H_4CH_2C_6H_4\text{-}p$.

$$\mathrm{HO{-}CH_2(C{\equiv}C)_2CH_2{-}OH + ClC\,(O)\,(CH_2)_4C\,(O)\,Cl \xrightarrow[-HCl]{\text{pyridine}}}$$
$$\rightarrow \ldots{-}O{-}CH_2(C{\equiv}C)_2\,CH_2{-}O{-}C\,(O)\,(CH_2)_4\,C\,(O){-}\ldots$$

In the case of polymers the replacement of a diyne by a cumulene or an enyne group leads to intermolecular cross-linking. Since the reaction is catalysed by radical initiators (benzoyl peroxide and azoisobutyronitrile) and is retarded by radical inhibitors (quinol), while ionic systems have no effect on the process, a radical mechanism of polymerisation is extremely probable.

The thermal and catalytic polymerisation of conjugated diynes follows a different course in solution or in a melt. The polymerisation of diphenylbutadiyne (I: R = R′ = $C_6H_5$) on the tri-isobutylaluminium — titanium tetrachloride catalytic system yields a linear polymer with a substituted polyene structure (IIIa), but on thermal polymerisation in the melt, i.e. above the melting point of the monomer, a block copolymer is formed consisting of substituted polyene (IIIa) and acene (II: R = R′ = $C_6H_5$) fragments (deduced from the results of ultraviolet, infrared, nuclear magnetic resonance, and electron spin resonance spectroscopy, luminescent, thermochemical, and X-ray examination, and also study of the chemical reactions of the products)[1,20-29].



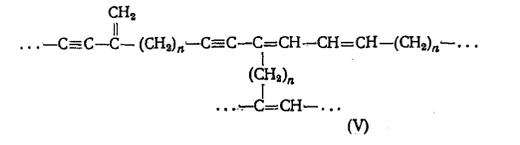

Heat-treatment and bromination, which cause intramolecular cyclisation of polydiphenylbutadiynes, increase the number of acene segments in the macromolecule[30], but in no case is a polymer obtained having a completely acene (ladderlike) structure.

The thermal polymerisation of dimethylbutadiyne (I: R = R′ = $CH_3$), like that of diphenylbutadiyne, involves predominantly formation of a block copolymer, consisting of (II: R = R′ = $CH_3$) and (IIIb) units. However, this is accompanied by the production of not more than 3% of methylene side-groups (IIIc) because of intramolecular isomerisation[31], which is responsible for the ready oxidisability and subsequent cross-linking.

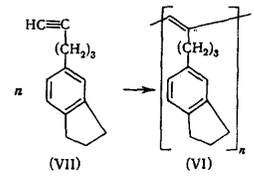
## III. POLYMERISATION OF DIYNES WITH NON-CONJUGATED TRIPLE BONDS

The course of the polymerisation of diynes of the type HC:C.X.C:CH (IV) is determined by the nature of the group X separating the triple bonds and by the reaction conditions.

The polymerisation of diynes (IV) in which X = $[CH_2]_n$ (where $n = 2-5$) on the complex catalytic system $Ni(CO)_2.2(C_6H_5)_3P$ leads to the formation of compounds of high molecular weight[32]. The high-melting insoluble polymer from hexa-1,5-diyne (IV: X = $[CH_2]_2$) has the structure (V)




as a result of simultaneous linear polymerisation and dehydropolycondensation. Hepta-1,6-diyne (IV: X = $[CH_2]_3$) gives (together with the aromatic trimer 1,3-di(indan-5-yl) propane) a 75 — 80% yield of a soluble resinous product of degree of polymerisation <20, which infrared spectroscopy shows to be a substituted polyene (VI). This structure results from polymerisation at the triple bond of the dimer (VII) obtained initially[32]:



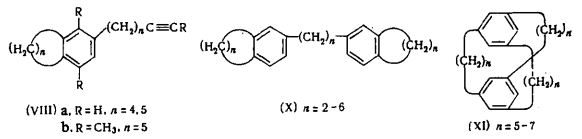
The number of 1,2,4-trisubstituted aromatic groups in polyocta-1,7-diyne is less than in polyhepta-1,6-diyne. Under these conditions nona-1,8-diyne forms only an insoluble polymer containing no aromatic groups. Copolymers of diynes with equimolecular quantities of hept-1-yne contain both aromatic groups and conjugated double bonds.

Thus the number of aromatic groups in products of the polymerisation of non-conjugated diynes of the type (IV) on the catalytic system $Ni(CO)_2.2(C_6H_5)_3P$ decreases in the sequence

hepta-1,6-diyne > octa-1,7-diyne ≫ hexa-1,5-diyne, nona-1,8-diyne

This may be determined by the conformations of the intermediate complexes of the diynes with the catalyst.

The polymerisation on the catalyst $Hg[Co(CO)_4]_2$ of diynes (IV) in which X = $[CH_2]_n$ and $n$ = 4, 5 leads to the formation of a small quantity of dimers (VIIIa; R = H, $n$ = 4, 5)



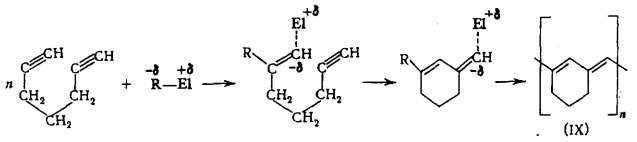
(VIII) a. R = H, $n$ = 4, 5
b. R = $CH_3$, $n$ = 5

(X) $n$ = 2-6

(XI) $n$ = 5-7

and soluble polymers, whereas undeca-2,9-diyne yields only insoluble products under the same conditions[33]. The corresponding dimer from this latter compound (VIIIb: R = $CH_3$, $n$ = 5) is obtained in 44% yield under conditions of high dilution[33]. The dimer (VIII) formed initially is evidently converted by polymerisation at the triple bond into a polymer of structure analogous to that suggested in Ref.32.

According to American workers[34] hepta-1,6-diyne (IV: X = $[CH_2]_3$) is converted on Ziegler — Natta catalysts by a mechanism of intra- and inter-molecular polymerisation into a polymer whose absorption spectra and chemical reactions (dehydrogenation, halogenation, and ozonolysis) suggest a cyclic polyene structure (IX):



(IX)

Under the same conditions octa-1,7-diyne and nona-1,8-diyne (IV: X = $[CH_2]_4$ and $[CH_2]_5$) give mainly cross-linked polymers. The soluble products of the polymerisation of octa-1,7-diyne contain seven-membered rings in the main chain, formed similarly to the rings in (IX), and perhaps long side-chains as a consequence of independent linear polymerisation at triple bonds. Of the monomer units in the soluble portion of polynona-1,8-diyne 25 — 30% contain one unchanged acetylenic group[34].

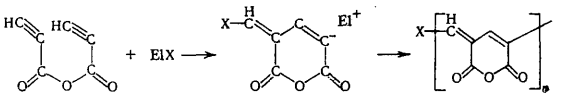
These results contradict those obtained by other investigators[33,35,36]. The polymerisation of hepta-1,6-diyne on the catalytic system $(C_2H_5)_3Al - TiCl_4$, as on the catalyst $Ni(CO)_2.2(C_6H_5)_3P$, gives a polymer having the structure (VI)[35]; but octa-1,7-diyne[33] and nona-1,8-diyne[33,36] form small amounts of cyclic trimers (X) and (XI) together with soluble and insoluble polymers. Since the infrared and nuclear magnetic resonance spectra of the trimers were identical with those of the polymers, the polymerisation of non-conjugated alkadiynes on Ziegler — Natta catalysts was supposed[33,36] to involve polycyclotrimerisation.

The copolymerisation of hepta-1,6-diyne with phenylacetylene probably yields a structure in which (VI) and $CH{:}C(C_6H_5)$ units alternate[35].

As with the polydimethylbutadiyne discussed above structure (V( should be characterised by migration of a hydrogen atom from the methylene side-group into the main-chain, which is responsible for the ready oxidisability of the resulting structure of type (IIIc). In fact, if freshly isolated polyhepta-1,6-diyne contains ~2% of oxygen, subsequent treatment and storage lead to an increase in the oxygen content to 10% and a loss of solubility by the polymer[35].

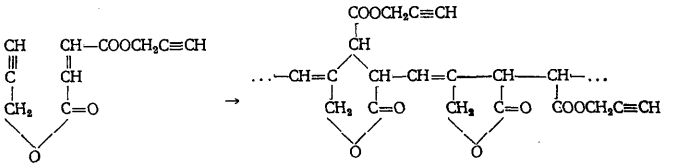
Acetylenic $\alpha$-carboxylic acid anhydrides of general formula R.C:C.CO.O.CO.C:C.R (R = H, Alk, Ar) in the presence of anionic catalysts in an inert organic solvent at 50 — 100°C give black polymeric powders; these are insoluble in water and in most organic solvents but soluble in dimethylformamide[37]. The yield of polymer (3 — 92%) increases with rise in temperature and increase in duration of the process. In dimethylformamide halide ions are active catalysts — even such a weak nucleophile as the chloride ion[38].

The polymerisation of propiolic anhydride (IV: X = CO.O.CO) involves an intramolecular cyclisation step by a mechanism analogous to that discussed above for hepta-1,6-diyne:



where El = Na, K and X = CNS, CN, Hal. Contamination with propiolic acid inhibits polymerisation and depresses the molecular weight of the resulting polymers[37-39]. Acetylenic $\alpha$-carboxylic acid anhydrides do not undergo polymerisation with cationic, radical, or thermal initiation (with respectively the ether complex of boron trifluoride, benzoyl peroxide, and a toluene solution at 100°C)[39].

Diprop-2-ynyl maleate (IV: X = $CH_2.O.CO.CH{:}CH.CO.O.CH_2$), in the presence of radical initiators in bulk and in solution at 70 — 130°C, is converted by inter- and intramolecular interaction between double and triple bonds into a polymer containing lactone units in the main chain[40]:



Diethynylarenes can be regarded as monomers intermediate in structure and properties between conjugated and non-conjugated diynes. A study of the crystal optics and spectra in the solid-phase polymerisation of single crystals of $p$-diethynylbenzene (IV: X = $p$-$C_6H_4$), initiated by ultraviolet radiation and by cobalt-60 $\gamma$-rays at ~20° and 77°K, has shown[41-43] that the polymer chains grow along a definite axis ($N_p$) of the refractive-index ellipsoid of the monomer crystal, which forms an angle of about 53° with the plane of the benzene rings.

Polymerisation involves predominantly one acetylenic group in each $p$-diethynylbenzene molecule (Fig.2). The chain evidently grows "head to tail", since a "head to head" construction requires that the inner carbon atoms of the triple bonds should come closer together, which is hardly possible in a crystal.

The reason why the crystal lattice of the monomer remains undisturbed is that the acetylenic groups of different molecules are close together, and the regrouping of atoms required for polymerisation is accomplished both by the formation from a triple bond of a longer double bond and also perhaps by some displacement of the molecules or deflection of acetylenic groups. These displacements accompanying polymerisation lead to the accumulation of mechanical stresses near the end of the polymer chain in the crystal, which causes the chain to terminate. The mechanical stresses produced may also be responsible for the absence of branching in the growing chain and the participation in polymerisation of only one acetylenic group from each molecule.

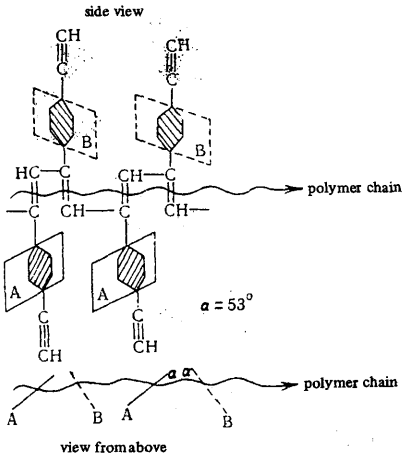



Figure 2.

Polymers of different structure are obtained when the process is conducted in solution or in a melt, as with the polymerisation of conjugated diynes.

The thermal (100 — 300°C) or catalytic polymerisation of *p*-diethynylbenzene, or its copolymerisation with phenylacetylene, diphenylacetylene, and several other acetylenic derivatives, yields insoluble and infusible polymers, probably of planar or three-dimensional structure[44-47].

In the presence of cobalt and other transition-metal complexes, diethynyl compounds (IV: X = $[p\text{-}C_6H_4]_n$, $p\text{-}C_6H_4.El.C_6H_4\text{-}p'$; $n$ = 1 — 3, El = O, Se, etc.) in bulk or solution form by polycyclotrimerisation polymers with aromatic groups in the main chain[48-50].

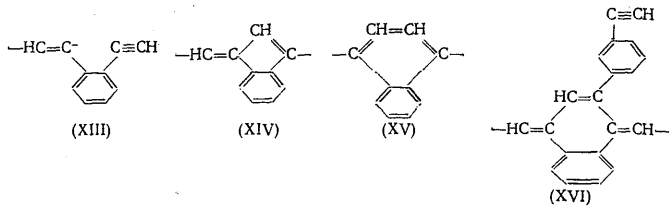
The copolymerisation of mono- and di-ethynyl derivatives enables the degree of branching in the products to be controlled. Copolycyclotrimerisation can in general be represented by the scheme

$$HC{\equiv}C{-}X{-}C{\equiv}CH + HC{\equiv}CR \rightarrow \left[\begin{array}{c} -Ar- \\ | \\ R \end{array}\!\!\begin{array}{c} \\ \\ \end{array}\!\!\begin{array}{c} -Ar- \\ \\ \end{array}\right]_n$$

(XII)

The actual structure is probably more complicated than (XII). Thus a study by infrared spectroscopy and ozonolysis of the copolymerisation of *p*-diethynylbenzene with phenylacetylene on the tri-isobutylaluminium — titanium tetrachloride catalytic system has established[51] that the soluble copolymerisation products contain polyene segments together with phenylene fragments, independently of the initial molar ratio of monomers and components of the catalytic system.

A polymer consisting of the units (XIII) — (XVI)[52]




has been obtained by coordination, radical, and cationic polymerisation of *o*-diethynylbenzene (IV: X = $o\text{-}C_6H_4$)—on the systems $R_2AlCl - TiCl_4$, $R_3Al - TiAcac$, $R_2AlCl - TiAcac$, and $RAlCl_2 - TiAcac$ (R = $C_2H_5$; Acac = acetylacetonate); isobutyronitrile; and titanium tetrachloride respectively. The polymer obtained in the presence of titanium tetrachloride contained no cyclic groups; with radical and coordination polymerisation the degree of cyclisation of the polymer was respectively 30% and 50 — 70%. The polymer evidently consists mainly of (XIII) and (XIV) units, and the chain grows by "head to head" addition — e.g. (XV), (XVI).

## IV. SYNTHESIS OF ORGANOMETALLIC POLYMERS BY POLYADDITION

The method for obtaining linear organometallic polymers is based[53-55] on the quite easy addition to a carbon — carbon triple bond of hydrides of Group IV elements in which all but two hydrogen atoms have been substituted by organic groups. The polyaddition of the "dihydrides" $RR'ElH_2$ to $\alpha\omega$-diynes can be represented by the scheme

$$n\,RR'ElH_2 + n\,HC{\equiv}C{-}X{-}C{\equiv}CH \rightarrow n\left[\begin{array}{c} R \\ | \\ -El- \\ | \\ R' \end{array}\!\!-CH{=}CH{-}X{-}C{\equiv}CH\right] \rightarrow$$

(XVII)

$$\left(\begin{array}{c} R \\ | \\ -El- \\ | \\ R' \end{array}\!\!-CH{=}CH{-}X{-}CH{=}CH-\right)_n$$

(XVIII)

where R, R' = Alk, Ar; El = Si, Ge, Sn; X = $[CH_2]_n$, $p\text{-}C_6H_4$, ElRR'. Since a triple bond is considerably more reactive than a double bond under the conditions of synthesis, the intermediate compound (XVII) probably passes into the polymer (XVIII)[55]. The properties of the resulting polymers (high decomposition temperatures, their infrared spectra, electrical conductivities, and activation energies of conduction) indicate that *d*-orbitals of the elements are involved in chemical bond formation[54].

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The information surveyed above shows that polymers varying widely in structure — linear (with polyene and cumulene units), cyclolinear, ladderlike, and three-dimensional — can be obtained from diynes depending on the nature of the monomer, the catalyst, and the conditions of polymerisation.

Since diacetylenic derivatives are able to form polymeric products not only by addition polymerisation at the carbon — carbon triple bonds but also in other ways — the most important of which are addition of unsaturated

compounds (1, 3- and 1, 4-cycloaddition[56,57]) and oxidative dehydropolycondensation[58]—further study of the reactions of diynes leading to the formation of polymers of diverse structure is desirable and promising.

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