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Characteristic Features of the Polymerisation of Acetylene and Its Derivatives

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The requirements which must be met by polymers with a conjugation system, used as organic semiconductors, are analysed. The characteristic features of ionic, radical and stereospecific polymerisation of acetylene and its derivatives are considered and the mechanisms of the destruction of the active centres in the ionic polymerisation as well as the methods of preparation of high-molecular-weight polymers are discussed.
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I. INTRODUCTION

The polymerisation of acetylene and its derivatives is one of the fundamental methods for the synthesis of polymers with a conjugation system (PCS), which are beginning to be used at the present time as organic semiconductors and metals. Studies on the creation of organic semiconductors based on PCS can be referred to two periods. During the first period (from the beginning of the 1950s until the middle 1970s), hundreds of PCS of different structure were synthesised and extensive experimental data on their properties were accumulated. The polymers obtained had a whole series of interesting physicochemical and electrophysical characteristics. Some of them have found practical applications as thermostable materials and stabilisers in relation to the thermo-oxidative degradation of saturated polymers[1-7]. The work of A.A.Berlin has made an enormous contribution to the development of this field. During this period, the first semiconductor devices and photosensitive materials were created. However, the properties of the PCS did not satisfy the requirements of modern electronics, for which much more ordered polymers with a much higher molecular weight, forming films or crystals, are essential. The materials developed did not therefore find extensive practical applications.

The beginning of the second period of the synthesis of organic semiconductors and metals based on PCS is associated with the work of Wegner, Shirakava, and Heeger.

In 1968–1971 Wegner[8-10] demonstrated for the first time the possibility of creating polyconjugated single crystals based on substituted diacetylenes. The polymerisation was carried out in the solid phase with thermal, thermochemical, and radiation initiation. Later, whole series of single crystals of polydiacetylenes of different structure were synthesised. The study of the electrophysical and optical characteristics of the polymers obtained showed that they can be used as materials for non-linear optics. It was also shown that they are semiconductors with a high mobility of charge carriers. According to the estimates of different workers, the mobility of the carriers is in the range 10^3–10^5 $cm^2 V^{-1} s^{-1}$.

In 1971–1975 Shirakava and co-workers[11-13] were the first to synthesise a free highly ordered polyacetylene film on the surface of the $Al(C_2H_5)_3$–$Ti(OBu)_4$ catalytic system. The authors showed that a film in the *cis*-form is formed at −78 °C. Isomerisation to the more stable *trans*-form takes place either directly during the synthesis or during subsequent heat treatment. The films obtained have a metallic lustre and a conductivity between 10^{-9} Ω^{-1} cm^{-1} (for the *cis*-form) and 10^{-5} Ω^{-1} cm^{-1} (for the *trans*-form).

In 1977–78 Heeger and co-workers[14,15] established that the conductivity of polyacetylene films doped with powerful electron donors or acceptors increases by 12 orders of magnitude (from 10^{-9} Ω^{-1} to 10^3 Ω^{-1} cm^{-1}). The conductivity of an oriented polyacetylene film doped with AsF_5 was found to be 2×10^3 Ω^{-1} cm^{-1}.

These studies aroused enormous interest among physicists and chemists working in the field of organic semiconductors. They demonstrated the possibility, in principle, of creating organic metals and semiconductors whose properties are comparable to those of the corresponding inorganic materials. During this period, the number of studies on the synthesis and properties of PCS began to increase sharply. At the present time, many laboratories both in this country and abroad are engaged in research into this field. During recent years, a whole series of PCS which exhibit metallic conductivity on doping with powerful electron donors or acceptors have been synthesised. These are polyacetylene[11-15], polyphenylene[16-18], polypyrrole[19,20], poly(phenylene sulphide)[21,22], and polyheptadiyne[23]. This list is probably incomplete because the search for new polymers is still being continued. The study of the electrophysical characteristics of these polymers showed that, depending on the nature and concentrations of the doping agents, it is possible to obtain *n*- and *p*-type semiconductors or materials with metallic conductivity, which can find practical applications in new semiconductor devices, energy photoconverters, and organic accumulators and in the future also as substitutes for metals.

Analysis of the literature data shows that PCS must satisfy certain requirements in their practical utilisation as organic semiconductors and metals.

1. The polymers must have high molecular weights and must have a continuous conjugation chain.
2. The polymers must form films or crystals which are homogeneous and whose mechanical characteristics and purity satisfy the requirements of modern electronics.
3. In order to obtain specified electrophysical characteristics, it is essential to introduce into the polymers powerful electron donors and acceptors, which must be distributed uniformly throughout the bulk of the materials.
4. A high conductivity can be expected only for PCS in which the chemical structure and superstructure do not prevent intermolecular interactions.

5. The materials synthesised must retain their mechanical and electrophysical characteristics for a long time.

This review analyses the characteristic features of the polymerisation of acetylene and its derivatives and prsents certain experimental results in the synthesis of PCS.

II. POLYMERISATION METHODS

As already stated, studies on the polymerisation of monomers with a triple bond have been prosecuted since the end of the 1950s. In recent years a number of new original and review publications have appeared on the synthesis of PCS.[24–29] Analysis of the experimental results for the synthesis of high-molecular-weight polymers permits the conclusion that the classical methods of ionic and radical polymerisation do not lead to high-molecular-weight PCS; the latter can be obtained only in the presence of certain complex catalysts and variable-valence metal salts.

1. Ionic Polymerisation

We shall consider in greater detail the mechanism of the ionic polymerisation of acetylene derivatives. It follows from the literature data compiled in a review[24] that the anionic and cationic polymerisations of acetylene derivatives lead to the formation of polymers with a degree of polymerisation $n \cong 10$. In a study of the anionic polymerisation of phenylacetylene in the presence of butyl-lithium in hexamethylphosphoramide we showed[30,31] that the low molecular weight of the polyphenylacetylene formed is associated with electron transfer from the active centre to the conjugated chain:

$$R-(-CH=\underset{\displaystyle R'}{\underset{|}{C}}-)_{n-1}-CH=\underset{\displaystyle R'}{\underset{|}{C}}{}^{-} \overset{K_n^p}{\rightleftarrows} R-(-\dot{\underset{\displaystyle R'}{\underset{|}{C}}}=\underset{\displaystyle R'}{\underset{|}{C}}-)_{n-1}-CH=\underset{\displaystyle R'}{\underset{|}{C}}\cdot \quad .$$

This reaction results in the formation of a radical at the end of the chain and a radical-anion delocalised over the conjugation chain. Subsequently the radical is destroyed via a linear or quadratic mechanism, while the radical-anion is detected by ESR for a long time. The equilibrium constant of this reaction depends on the electron affinity of the radical formed and of the conjugated chain. The electron affinity of the radical is independent of the chain length, because the orbital in which it is located is orthogonal with respect to the orbitals of the conjugated chain. On the other hand, the electron affinity of the conjugated chain increases with chain length[32]. The probability of electron transfer (or the isomerisation of the active centres) should therefore increase with increasing degree of polymerisation.

Analogous features have been observed also in the cationic polymerisation of acetylene derivatives with the sole difference that the electron is transferred from a polyene chain to an active centre with formation of a radical at the end of the chain and a radical-cation delocalised over the conjugation system:

$$R-(-CH=\underset{\displaystyle R'}{\underset{|}{C}}-)_{n-1}-CH=\underset{\displaystyle R'}{\underset{|}{C}}{}^{+} \overset{K_n^p}{\rightleftarrows} R-(-\dot{\underset{\displaystyle R'}{\underset{|}{C}}}=\underset{\displaystyle R'}{\underset{|}{C}}-)_{n-1}-CH=\underset{\displaystyle R'}{\underset{|}{\dot{C}}} \quad .$$

The equilibrium constant of this reaction depends on the difference between the ionisation potentials of the polyene chain and the radical formed. The ionisation potential of the radical is independent of chain length, while that of the conjugation system decreases with increasing chain length[32]. In the cationic polymerisation of acetylene derivatives the probability of electron transfer (the isomerisation of active centres) should therefore also increase with increasing degree of polymerisation.

The equilibrium constants of the electron transfer reactions in the anionic and cationic polymerisation of acetylene and phenylacetylene, calculated from data quoted in a handbook[32], are listed in Table 1. Evidently the anionic and cationic polymerisation of acetylene should be accompanied by the isomerisation of the active centres already in the first 2–3 units. In the polymerisation of phenylacetylene the isomerisation of the active centres should begin after the attainment of a degree of polymerisation $n \cong 5$–10. The increase of the degree of polymerisation on passing from acetylene to phenylacetylene is associated with the fact that the benzene ring stabilises the ion at the end of the chain.

The kinetics of the ionic polymerisation of acetylene derivatives have been analysed[33] taking into account the isomerisation reactions of the active centres and it was shown that the molecular weight distribution of the polymers formed is described by the equation

$$\rho(n) = f(n) \cdot \left(\prod_{i=1}^{n} \frac{1}{1+f(i)} \right) , \qquad (1)$$

where $f(n) = (k_t/k_p M)K_n^p$, k_t is the rate constant for the linear termination of radicals, k_p the chain propagation rate constant, M the concentration of the monomer, and K_n^p the equilibrium constant of the electron transfer reaction.

Table 1. The equilibrium constants of the electron transfer reaction.

n	Anionic polymerisation		Cationic polymerisation	
	polyacetylene	polyphenylacetylene	polyacetylene	polyphenylacetylene
2	$7.95\cdot10^{-11}$	$7.85\cdot10^{-19}$	$2.35\cdot10^{2}$	$7.9\cdot10^{-13}$
3	$1.58\cdot10^{-9}$	$6.41\cdot10^{-12}$	$5.26\cdot10^{8}$	$3.3\cdot10^{-6}$
4	$1.7\cdot10^{12}$	$4.16\cdot10^{-8}$	$5\cdot10^{27}$	$4.55\cdot10^{-2}$
5	$4\cdot10^{17}$	$5\cdot10^{-5}$	—	$2.2\cdot10^{1}$
6	—	$9.5\cdot10^{-4}$	—	$1.05\cdot10^{3}$
7	—	$1.41\cdot10^{-2}$	—	$1.59\cdot10^{4}$
8	—	$9.7\cdot10^{-2}$	—	$1.1\cdot10^{5}$
9	—	0.312	—	—
10	—	2.16	—	—

Table 2 lists the number-average ($\bar{\Pi}_n$), weight-average ($\bar{\Pi}_w$), and z-average ($\bar{\Pi}_z$) degrees of polymerisation and the ratios $\bar{\Pi}_w/\bar{\Pi}_n$ and $\bar{\Pi}_z/\bar{\Pi}_w$ calculated by Eqn.(1) for the anionic polymerisation of phenylacetylene. Table 2 shows that, regardless of the ratio of the chain termination and propagation rate constants, low-molecular-weight polymers with a narrow weight distribution are formed. An increase of molecular weight can be achieved by decreasing the termination rate constant or by introducing into the acetylene molecule a substituent which stabilises the ion on the end of the chain.

From the ionic polymerisation scheme discussed above, it follows that the formation of high-molecular-weight polymers is possible only in the absence of the isomerisation reactions of the active centres. One of the possible polymerisation pathways without the isomerisation of the active centres may involve the formation of complexes with a conjugation

system directly in the course of chain propagation. We shall examine the mechanism of such a process in relation to the cationic polymerisation of acetylene derivatives. The reaction system should contain, apart from the monomer and initiator, the molecules of a powerful electron acceptor capable of forming stable donor–acceptor or radical-ion complexes with the polyene chain. In this case the propagation of the conjugation chain will be accompanied by the formation of complexes between the macromolecules and the acceptor molecules in which the electron density is displaced in the direction away from the polyene chain. Such macromolecules are incapable of giving up an electron to the active centre. In the prence of a sufficient number of electron acceptor molecules the cationic polymerisation should therefore proceed without the isomerisation of the active centres. Since strong Lewis acids behave simultaneously as electron acceptors and initiators of cationic polymerisation, when the process described above is carried out with their participation there is no need to employ an initiator and a separate complex-forming agent. The polymerisation is performed in the presence of large amounts of Lewis acids and the rate of initiation is regulated by introducing a specific amount of a cocatalyst. It is only necessary that the formation of complexes between the Lewis acids and the monomer should not prevent the chain propagation reaction.

Table 2. Parameters of the anionic polymerisation of phenylacetylene*.

	E_R = 1.6 eV					E_R = 1.3 eV				
k_t/k_pM	$\bar{n}_n$	$\bar{n}_w$	$\bar{n}_z$	$\frac{\bar{n}_w}{\bar{n}_n}$	$\frac{\bar{n}_z}{\bar{n}_w}$	$\bar{n}_n$	$\bar{n}_w$	$\bar{n}_z$	$\frac{\bar{n}_w}{\bar{n}_n}$	$\frac{\bar{n}_z}{\bar{n}_w}$
10^3	5.805	5.870	5.935	1.011	1.010	3.451	3.523	3.594	1.020	1.020
10^2	6.675	6.757	6.837	1.012	1.011	3.901	3.929	3.952	1.007	1.006
10	7.845	7.953	8.059	1.014	1.013	4.084	4.109	4.137	1.006	1.006
1	9.465	9.619	9.767	1.016	1.015	4.528	4.588	4.646	1.013	1.012
10^{-1}	11.83	12.06	12.29	1.020	1.019	5.065	5.111	5.157	1.009	1.009
10^{-2}	15.47	15.88	16.27	1.026	1.024	5.717	5.782	5.846	1.011	1.011
10^{-3}	21.58	22.38	23.12	1.037	1.033	6.562	6.642	6.720	1.012	1.011
10^{-4}	32.92	34.75	36.43	1.055	1.048	7.690	7.793	7.849	1.013	1.012
10^{-5}	56.79	61.69	66.16	1.086	1.072	9.252	9.399	9.541	1.015	1.015
10^{-6}	114.7	130.0	143.7	1.130	1.105	11.50	11.72	11.94	1.019	1.018

*E_R = electron affinity of the radical formed on electron transfer.

An analogous process can be carried out also in the anionic polymerisation of acetylene derivatives but in this case powerful electron donors must be used as substances functioning simultaneously as an initiator and a complex-forming agent. Such substances can be alkali metals.

Analysis of the model kinetics of ionic polymerisation with complex formation shows that the molecular weight distribution of the polymers formed is described by the equation

$$\rho(n) = f(n) \cdot \left[\prod_{i=1}^{n} \frac{(1 + K_{n-1}^{K})}{(1 + K_n^{K}) + f(i)} \right], \qquad (2)$$

where K_n^c is the complex formation equilibrium constant. It follows from Eqn.(2) that, when the equilibrium complex formation constant K_n^c is much greater than the equilibrium constant of the electron transfer reaction K_n^p, the polymerisation proceeds without the isomerisation of the active centres.

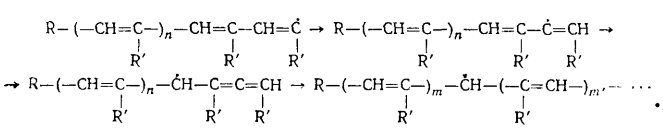
The possibility of obtaining polyacetylene films doped with AsF_5 directly in the course of the synthesis was first demonstrated in 1980.[34] The process was carried out by mixing gaseous acetylene and AsF_5 at different pressures and temperatures. Using an analogous procedure, we synthesised[35,36] SbF_5-doped films of polyacetylene and polyvinylacetylene with conductivities up to $10^{-2}\ \Omega^{-1}\ cm^{-1}$; the study of the polymerisation of vinylacetylene in the presence of various acceptors showed that the yield of the polymer decreases in the following sequence: $SbF_5 > H_2SO_4 > TiCl_4 > SnCl_4 >$ polyphosphoric acid[35,36].

The results show that the ionic polymerisation of acetylene derivatives in the presence of large amounts of a complex-forming agent is likely to be useful for the synthesis of organic semiconductors and metals because the complex formation process virtually constitutes doping of the polymer and makes it possible to obtain in a single stage highly conducting materials in the form of films. Such processes can be readily carried under technological conditions and make it possible to obtain films on various surfaces.

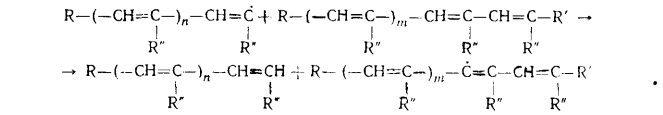
2. Radical Polymerisation

We believe that the radical polymerisation of acetylene derivates suffers from no fundamental limitations to the formation of high-molecular-weight polymers. However, it is known[6] that PCS are effective inhibitors of thermal and thermo-oxidative degradation, i.e. exhibit an enhanced affinity for radicals. In the radical polymerisation of acetylene derivatives there is therefore a possibility of the occurrence of side reactions the most important of which are as follows:-

(a) intramolecular isomerisation of the chain propagating radical:



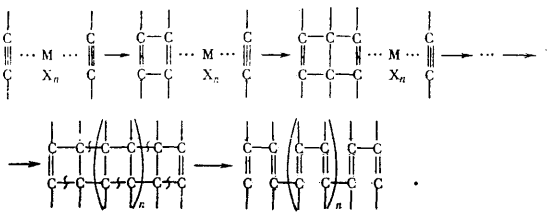
(b) intermolecular interaction of the chain propagating radical with the conjugated macromolecule via an addition or substitution mechanism:



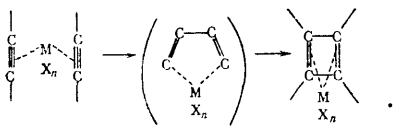
During these reactions, radicals delocalised over the conjugated system are formed and chain propagation ceases. The contribution of these reactions to the polymerisation process depends on the chemical structure of the monomer, the concentration, the temperature and the state of aggegation. The most suitable process for the formation of high-molecular-weight polymers is probably solid-phase polymerisation at low temperatures such as the polymerisation of single crystals of substituted diacetylenes. In solution, high-molecular-weight polymers are formed only when the polymerisation is accompanied by breaks in the conjugation in the system. For example, the polymerisation of vinylacetylene monomers[37,38] proceeds statistically at the double bond in the 1–4 positions. The breaks in the conjugation chain make it possible to obtain polymers with molecular weights of 10^4–10^6.[39,40] Subsequent heat treatment leads to rearrangements and the formation of a conjugated polymer.

3. Polymerisation of Acetylene and Its Derivatives in the Presence of Complex Catalysts and Variable-Valence Metals

There are few literature data on this problem, but the existing results suggest that, in the presence of these catalytic systems, the possibility of obtaining high-molecular-weight polymers is also associated with the absence of isomerisation reactions of the active centres. The polymerisation of phenylacetylene in the presence of metal carbonyls and various additives has been investigated[41-43]. The authors suggested that the chain propagation proceeds with formation of four-membered rings, which then isomerise to a polyconjugated polymer via the mechanism

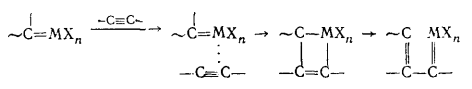


This mechanism is based on data concerning the formation of cyclobutadiene complexes in the presence of metal carbonyls. For example, it has been shown[47] that diphenylacetylene forms a cyclobutadiene complex in the presence of derivatives of iron tricarbonyl:



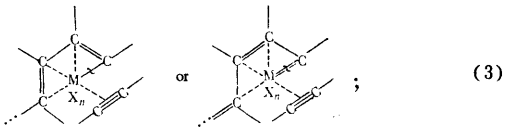
In the course of the reaction it is sometimes possible to detect intermediates. It is seen from the above scheme that the formation of high-molecular-weight polymers is associated with the formation of non-conjugated ladder macromolecules in the first stage.

An intereresting polymerisation mechanism has been proposed in a large series of studies by Masuda and co-workers[28,29,45-47], who investigated the polymerisation of acetylene derivatives in the presence of various metal chlorides and carbonyls. They showed that the polymerisation of phenylacetylene in the presence of $W(CO)_6$ in CCl_4 under the influence of ultraviolet radiation makes it possible to obtain polymers with a molecular weight $\overline{M}_n \cong 80\,000$–$100\,000$, while 2-chlorophenylacetylene gives rise to polymers with $\overline{M}_w \cong 400\,000$ in the presence of $Mo(CO)_6$ under ultraviolet irradiation. The same workers showed that, by selecting the appropriate solvent, it is possible to obtain a polyphenylacetylene with $\overline{M}_n \cong 100\,000$ also in the presence of metal chlorides and their complexes. It has been suggested that the polymerisation proceeds via a stage involving the formation of a four-membered metal-containing cyclobutene unit:

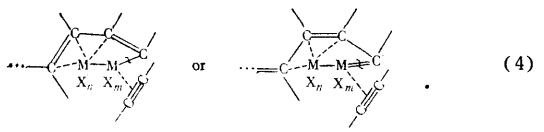


We believe that the formation of high-molecular-weight polymers in the polymerisation of acetylene derivatives in the presence of complex catalyst and variable-valence metals is associated with the tendency of the polyconjugated macromolecules formed to produce donor–acceptor complexes. It has already been stated than an increase in the conjugation chain length entails a decrease of the ionisation potential and an increase of the electron affinity of the macromolecules. Therefore, regardless of the nature of the active centre and its linkage with the catalyst, the growing macromolecule also tends to form a coordinate bond with the catalyst. The strength of this bond should increase with increasing chain length.

In order to obtain high-molecular-weight polymers, it is necessary that the complex formed should not prevent the chain propagation reaction. Otherwise, cyclobutadiene and benzene derivatives or low-molecular-weight polymers are formed. The reaction complex can be illustrated schematically as follows:-



(3)



(4)

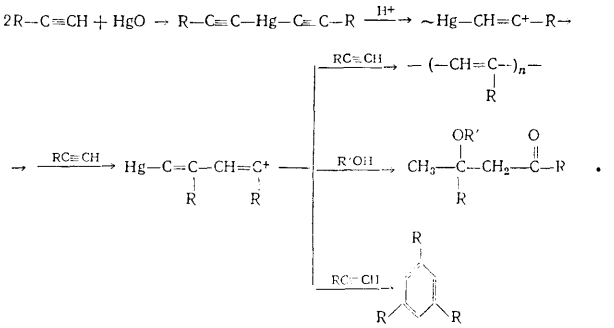
In such a complex the active centre is fixed on the catalyst via an additional coordinate bond with the conjugated system, which prevents its isomerisation and destruction. The available scattered literature data[48,49] concerning the structure of such complexes suggest that the preferential formation of high-molecular-weight polymers is observed when the catalytic centre contains several metal atoms [see Scheme (4)]. On the other hand, if the catalytic centre contains one metal atom, then low-molecular-weight products are formed [see Scheme (3)].

We investigated the polymerisation of acetylene, vinylacetylene, and their derivatives in the presence of palladium salts, mercury(II) oxide in conjunction with Lewis acids, and Ziegler and Latinger catalysts[50].

The catalytic system based on soluble palladium salts with ligands (pyridine and dimethylformamide) ensures a high yield of polymers in the polymerisation of propargyl derivatives, particularly with electron-accepting substituents[51,52]. The polymers obtained from bromo-substituted propargyl derivatives and their copolymers with diethylbenzene and divinylethynylmethanol have a conductivity of 10^{-8}–10^{-4} Ω^{-1} cm^{-1}. The covalently bound bromine atom in these polymers is apparently fairly labile and can be split off directly in the course of synthesis, forming complexes with the conjugation system.

The catalytic system consisting of a mixture of mercury(II) oxide and Lewis acids initiates a process which combines the features of ionic and coordination polymerisation. It proved to be effective in the polymerisation of acetylene and its derivatives. The polymerisation of acetylene in the presence of the homogeneous mercury(II) oxide–boron trifluoride etherate catalytic system has been studied for various component ratios. A soluble complex with an absorption maximum at 390 nm is formed in the first stage. At a concentration of the components of 10^{-4} M, the formation of a complex is observed immediately after the addition of the acetylene solution. The polymer is precipitated as a red-brown deposit which blackens on standing and contains residues of the catalyst. In the polymerisation of gaseous acetylene in the presence of a layer of catalysts deposited on a support, it was possible to grow films several millimetres thick. The polymerisation of vinylacetylene in the presence of the same catalytic system begins at a temperature as low as −70 °C. The yield of the polymer increases with increase of temperature.

Despite their inertness, propargyl derivatives polymerise almost quantitatively and the first stage involves the formation of mercury bisacetylides, which subsequently catalyse the polymerisation[50]. The polymerisation of phenylacetylene also proceeds via a stage in which mercury bisacetylide is formed. The mercury bisacetylide isolated is soluble in the monomer and has a high catalytic activity. It has been suggested that the polymerisation proceeds via a cationic mechanism. The formation of a σ-complex of mercury with the acetylenic bond loosens the latter and facilitates attack by the proton. In a simplified form the process can be represented by the following scheme:



In the presence of alcohol, it was possible to isolated the dimeric cation termination product, namely 3-methoxy-1,3-diphenyl-1-butanone, which confirms the validity of the above scheme.

It has been shown[27] that the $Co(NO_3)_2$–$NaBH_4$ catalytic system makes it possible to obtain a highly ordered polyacetylene, the degree of crystallinity of which is higher than that of the substance obtained by the Shirakava method. Polyacetylene films of any size on various surfaces can be obtained in the presence of this system†.

III. CONCLUSION

The data examined in this review show that a qualitative leap forward has been achieved in recent years as regards the creation of organic semiconductors and metals based on polymers with a conjugated system. Methods have been developed for the preparation of polymers in the form of films whose conductivity increases by 10–16 orders of magnitude after the interaction of powerful electron donors or acceptors. The electrophysical characteristics of polyacetylene, polyphenylene, and certain other polymers already make it possible to devise on their basis accumulators, photoconverters, and semiconductor devices.

Analysis of the mechanisms of the ionic, radical, and stereospecific polymerisation of acetylene derivatives has shown that the destruction of the active centres is associated with a decrease of the ionisation potential and an increase of the electron affinity of the polymer chain. Ionic polymerisation in the presence of a complex-forming agent and polymerisation in the presence of metal complex catalysts are most promising for the preparation of organic semiconductors and metals. The results presented suggest that procedures for the preparation of organic semiconductors whose parameters will enable them to compete with the corresponding inorganic materials will be developed in the next few years.

† See V.M.Kobryanskii and A.A.Matnishyan, "Materialy III Vsesoyuznogo Nauchnogo Seminara 'Ionika Tverdogo Tela'" (Proceedings of the IIIrd All-Union Scientific Seminar 'The Ionics of the Solid State'), Vilna, 1983, p.5.

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