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The Preparation, Structure, and Properties of Semiconductor Films Based on Acetylenic Polymers

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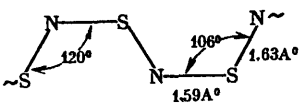
The methods of preparation of organic polymeric semiconducting materials by the catalytic polymerisation of acetylene and its derivatives are described. The characteristics of the catalyst and the influence of the conditions of synthesis on the structure, morphology, stability, and conductivity of the films as well as the questions of the ageing, stabilisation, and doping of the films and the appearance of microheterogeneities (defects) as a result of ageing and oxidation of polyacetylene are considered.
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I. INTRODUCTION

Organic materials, especially polymers, are already used in electronics, radio engineering, and electrical engineering as electrically conducting and semiconducting elements. After the discovery of semiconducting properties in polymers with a system of conjugated bonds, their investigation has been continuous since the 1950's with continued success.[1-5] The discovery in 1973 of the polymers $(SN)_n$ exhibiting metallic conductivity and not containing metal atoms led to an avalanche of investigations. It was soon found that the polysulphonitrite (polythiazide)



exhibits an intrinsic metallic conductivity and passes to the superconducting state at ~0.3 K.[6] The reports of the first organic polymer capable on doping of the transition from the semiconducting to the metallic state was a well established fact and served as a stimulus for the creation of a series of new conjugated polymers and composites based on polyacetylene, polypyrrole, polythiophen, etc., whose electrophysical properties vary within wide limits during their doping by electron acceptors or donors. However, the high conductivity and effective semiconducting properties of π-electron low-dimensional systems is not their only positive feature; they also manifest various interesting magnetic, optical, and other properties. These materials have begun to play an important role in the development of modern technological systems for the accumulation and storage of information (computers) and the transformation of solar energy,[7] in electronics (field transistors, diodes),[8] and as conductors, electrodes (accumulators, high-capacitance condensers), and as sensors of electromagnetic and acoustic radiation, and also in other branches of engineering.[9,10] The lightness and high strength, characteristic of polymeric materials, their high impact strength, their low cost, and the simplicity of the technology of the preparation of the films, fibres, and articles of complex shape make the new materials advantageous compared with traditional ones.[11]

The synthesis, properties, and applications of polyacetylene have been considered in fair detail in monographs and reviews[1-4,12-18], whose number has increased sharply in recent years.

This paper surveys the results of the latest research into the methods of synthesis and certain properties of polymers of the acetylene series with a regular structure, which are promising as "organic metals" and semiconductors. It deals mainly with the methods which make it possible to obtain films and fibrous materials; it does not include familiar methods such as dehydrogenation, dehydration, and dehydrohalogenation,[19,20] which lead to the formation of films with an irregular structure, exhibiting a low electrical conductivity.

II. THE SYNTHESIS AND PROPERTIES OF POLYACETYLENE

One of the most thoroughly investigated methods of synthesis of polyacetylene (PA) with a regular structure involves the polymerisation of acetylene on a metal complex catalytic system obtained from trialkylaluminium combined with alkoxytitanium. In 1958 Natta and co-workers succeeded in polymerising acetylene in the presence of $Al(C_2H_5)_3-Ti(OC_3H_7)_4$ catalytic system.[21,22] Systematic studies in recent years[23-25] made it possible to find new methods for the synthesis of stereoregular polyacetylene films. The $Al(Et)_3-Ti(OBu)_4$ catalytic system ensures the preparation of PA films with a predominantly (up to 98%) *cis*-structure at temperatures not above 70 °C and with mainly *trans*-structure at +150 °C.[26]

If one disregards the specific requirements which must be met by the conditions in the preparation of the catalytic system (in an inert medium in the absence of traces of moisture), the synthesis of PA itself does not present major difficulties. PA films grow on the surfaces of a concentrated catalyst solution or almost on any support wetted with a catalyst solution (preferably in toluene) in an atmosphere of purified acetylene.[25] The growth of the films can be regulated by altering the temperature and acetylene pressure during the synthesis.[24,27] Before its use, the homogeneous catalytic system is usually maintained at room temperature. The catalyst "ripening" reaction then takes place:[28]

$$Ti(OBu)_4+AlEt_3\rightarrow EtTi(OBu)_3+AlEt_2(OBu)\,,$$
$$2EtTi(OBu)_3\rightarrow 2Ti(OBu)_3+C_2H_4+C_2H_6\,,$$
$$Ti(OBu)_3+AlEt_3\rightarrow EtTi(OBu)_2+Al(Et)_2OBu\,,$$
$$EtTi(OBu)_3+AlEt_3\rightarrow EtTi(OBu)_3\cdot Al(Et)_3\,.$$

The ageing of the catalyst initially increases the activity but after a time the yield PA falls owing to the further reduction of titanium:

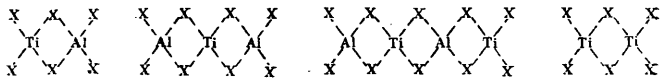
$$EtTi(OBu)_2 + Al(Et)_3 \rightarrow TiOBu + Al(Et)_2(OBu) + C_2H_4 + C_2H_6.$$

If the synthesis is carried out at a low catalyst concentration, a gel-like red product, consisting of tangled fibrils up to 800 Å in diameter, is formed. A foam-like material with a density ranging from 0.04 to 0.4 g cm^{-3} can be obtained from dilute gels by subliming the solvent at a temperature below its freezing point.[29]

The study of the dependence of the rate of formation of PA films on the catalyst concentration and acetylene pressure made it possible to find the optimum ratio of the catalyst components (Al/Ti = 4); the increase of this ratio to 10 increases the size of the fibrils.[30] The fall of the rate of reaction at the end of the process can be explained by the impairment of the diffusion of the monomer through the thickness of the film formed on the catalyst surface.[31] During synthesis, the film is formed simultaneously on the walls of the flask and on the surface of the catalytic solution, the gel accumulating in the upper layer and the PA powder settling on the bottom of the reactor. The molecular weight $\overline{M}_n$ of the powder is lower than that of the gel and decreases with increase in the catalyst concentration to 400–500.[32] The molecular weight of the gel-like PA decreases slightly with increase in the catalyst concentration and rises from 2×10^4 to 3.6×10^4 with increase in temperature from −78 °C to −10 °C. The molecular weight of the PA in the film is a factor of two smaller than in the gel.[33]

The high sensitivity of the catalysts to impurities precludes an unambiguous estimation of the influence of various factors determining $\overline{M}_n$ of polyacetylene. Low-molecular-weight products with $\overline{M}_n \cong 1200$ are formed when the synthesis is carried out in hydrogen.[15] The concentration of acetylene has a considerable influence on $\overline{M}_n$: with increase in its pressure to 760 mmHg, $\overline{M}_n$ increases to 120 000.[28,34] Apparently the inhomogeneity of the substrates, arising from the imperfection of the technique of the synthesis, is the cause of some lack of reproducibility in the properties of the polymers obtained.

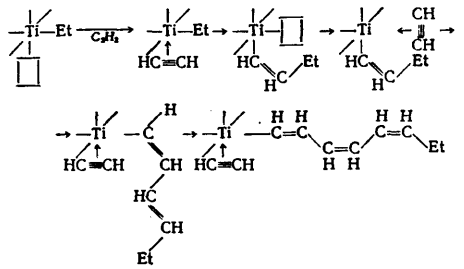
It has been suggested that the synthesis takes place on the "surface" of the catalytic clusters. Investigation by the EPR method made it possible to distinguish up to four types of complexes in the catalyst:[35]



(I) (II) (III) (IV)

The highest catalytic activity is shown by the complex (I), while the complexes (II) and (IV) are inactive. The ratios of the complexes in the catalyst depend on the Al/Ti stoichiometric ratio.

The structure of the catalyst suggests that the reaction proceeds via the *cis*-addition mechanism:



This results in the formation of PA with a *cis*-transoid structure. The formation of the *trans*-structure at high temperatures can be explained by the thermal isomerisation preceded by the crystallisation of the chains. An alternative possibility—the *trans*-dissociation of the triple bond in the catalytic complex—is sterically prohibited for the transition state;[35,36] the structure of the complex and the polymerisation kinetics have been examined in greatest detail elsewhere.[28,37]

In all the cases described above the synthesis results in the formation of fibrils[35] and the morphology of the PA films is almost independent of the conditions of synthesis. However, depending on these conditions, the diameter of the fibrils can vary from 200 to 10^4 Å and is usually 220–800 Å.[28,38] When the films are grown on supports, the size of the fibrils diminishes. The same effects have been observed in the synthesis of PA in other polymers. The size of the fibrils is particularly strongly affected by the time during which the catalyst is kept (its ageing); with increase in the ageing time, the size of the fibrils increases.[39] Detailed study of the growth of the fibril on thin films by transmission electron microscopy made it possible to observe microfibrillar branching on the main fibril (30 to 50 Å in size) and thickened regions at its entanglement sites as the presence of rings at the ends of the fibrils.

It has been shown that significant changes in the morphology of the film are not observed on isomerisation of PA. The film consists of arbitrarily arranged fibrils which are sometimes collected into larger formations.[36] The formation of the film is apparently a consequence of the interaction of the fibrils with one another via adhesion forces.

The synthesis of PA with fibrils oriented along some axis involves considerable difficulties. The simplest and most readily available method involves the stretching of the film, whereupon the fibrils are oriented predominantly along the stretching axis.[39] Crystalline specimens with a *trans*-structure, which give rise to a diffraction pattern similar to the Debye rings, are formed in the polymerisation of acetylene in a controlled shear field on a Teflon cylinder rotating at a rate of 3×10^3 rev min^{-1}.[40] It has been suggested that the polymer chain in these specimens is not oriented along the axis of the fibre. With increase in the rate of rotation of the cylinder, highly crystalline specimens are obtained in most axes of the fibril and the chains are parallel.[41] A method of preparation of macroscopic ribbon structures in a substrate rotating with a radial velocity of the mixing ring ranging from 10^7 to 10^{10} Å cm^{-1} [sic (Ed.of Translation)] which gives rise to the maximum shear stress in the future microfibrils has been described.[42] In the structures obtained, the molecular axis coincides with the axis of the fibre and the ribbon consists of a bunch of fibres. *trans*-Polyacetylene ribbons are more crystalline and the size of their domains is $(7-10) \times 10^5$ Å. A PA with a molecular weight of ~500, which can give rise to pseudo-lamellar structures, was found in the reaction medium.[42]

Oriented PA films are formed also on a polycrystalline Ziegler–Natta catalyst in solid biphenyl. The technique of deposition of the catalyst is fairly simple: on slow evaporation of the solvent from the mixture, a thin oriented layer of an active complex is produced on which a lustrous silvery PA film grows in the course of 3–5 days at −78 °C; the film is oriented in the direction of the single crystals of the support.[43]

Highly oriented PA films have been obtained by the polymerisation of acetylene which had been epitaxially oriented beforehand on the surface of crystalline benzene.[44] Oriented PA films have been synthesised on the basis of this idea using cyclohexylpropylalkoxybenzene in the liquid crystal state, in the presence of a Ziegler catalytic system at 18 °C.[45] Morphological studies have shown that the fibrils are almost fully oriented in the direction of the liquid crystal domains.[45] Anisotropic PA films have also been obtained by the polymerisation of acetylene in the nematic phase of the MBBA liquid crystal ($C_4H_9C_6H_4N-CHC_6H_4OCH_3$) in a magnetic field with a strength greater than 2500 G, but the orientation is insufficiently

pronounced.[45] Iodine-doped films having the composition $(CH)I_{0.15}$ exhibited appreciable anisotropic properties: their conductivity in the direction of the field was 1235 Ω^{-1} cm^{-1}, while at right angles to this direction it was 300 Ω^{-1} cm^{-1}.[46] X-Ray diffraction studies of the oriented films confirmed that their molecular and fibrillar axes coincide and that they have a high degree of crystallinity (~90%) and made it possible to explain features associated with the lattice parameters and the crystal system. The anisotropy of the electrical conductivity and of the optical properties of oriented films has been investigated in fair detail.[39]

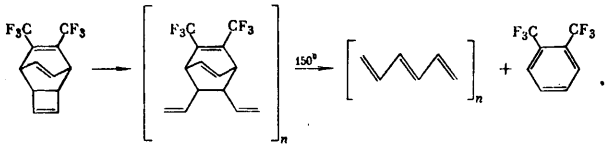
The metal complex catalytic systems are fairly varied. "Mixed systems", for example molybdenum or tungsten compounds combined with trialkylaluminium, have been used to an increasing extent in recent years for the preparation of various semiconducting polymeric materials. Lanthanide (Y, La, Pr, Gd, Tb, Dy) naphthenates or ethyl hexyl phosphates combined with triethylaluminium are effective catalysts of the stereospecific polymerisation of acetylene and its derivatives.[47] A catalyst component ratio of 1 : 5 is optimum. A polyacetylene obtained at a catalyst concentration ranging from 0.03 to 0.7 M at low temperatures contains 70% of the *cis*-isomer; according to the EPR data, there are 10^{17} paramagnetic centres per gram of the substance.[47] The results of X-ray diffraction studies (based on the characteristic $2\theta = 23.3°$ reflection), IR spectroscopic data and the initial conductivities of this specimen correspond to the values obtained for PA synthesised by other methods.[24-27] On the basis of such non-informative data, the not entirely justified conclusion has been reached[47] that the replacement of $Ti(OBu)_4$ by lanthanide compounds does not alter the PA structure.

The $AlR_3-VOCl(neopentyl)_2$ catalytic system is of great practical interest.[48] The PA obtained in its presence at −60 °C has a fibrous structure and can be processed by the usual method adopted in polymer technology. When a "mixed catalyst" is used, the particle size increases from 100 to 500 Å and the density of the film is found to increase. By filtering the suspension, it is possible to obtain a film of any size. Films on different supports, having effective adhesion properties, can be obtained by atomising the gel. The polymer can be readily doped with AsF_5, $FeCl_3$, I_2, and other electron acceptors; preliminary tests demonstrating certain advantages of such materials which are used in accumulators.[48] PA gels with analogous properties, obtained in the presence of other catalytic systems, are of great practical interest.[49] There is information in patent literature[50] about technological procedures for the preparation of PA films from gels with particle diameters in the range 0.01 − 1 mm, obtained in the presence of a "mixed catalyst" in the temperature range from −100° to −48°C. These results indicate the possibility of going over to a very simple and cheap technology involving a continuous process for the preparation of PA films.

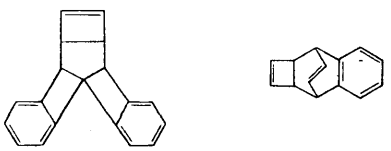
WCl_6 and $MoCl_5$, in the presence of which acetylene polymerises at 20 °C and pressures up to 14 atm, are comparatively readily available. However, the polymers obtained contain carbonyl groups, which is apparently due to the presence of oxygen, and have a low molecular weight.[51] Complex systems including tetraphenyltin in addition to WCl_6 or $MoCl_5$ are more promising for the preparation of film materials.[52] A PA film with a predominantly (to the extent of 90%) *trans*-structure and a "fibrous" morphology is formed on the surface of a concentrated solution of a vanadium catalyst. The diameter of the polymer fibrils, obtained in the presence of the $MoCl_5-Ph_4Sn$ catalyst can be varied in the range 300 − 10 000 Å; in the case of the WCl_6-Ph_4Sn catalyst, it reaches 1.2×10^5 Å.[30,52]

The study of the kinetics of the polymerisation of acetylene in the presence of $Ti(OBu)_4-Al(Et)_3$, WCl_6-Ph_4Sn, $MoCl_5-Ph_4Sn$, and $Ti(CH_2C_6H_5)_4$ catalysts showed that the rate of the process decreases in the above sequence.[31,52] Films doped with various acceptors, namely $(CHI_{0.25})_n$, $[CH(SbF_5)_{0.7}]_n$, and $[CH(CF_3SO_3H)_{0.18}]_n$, had a conductivity of 10 − 20 Ω^{-1} cm^{-1} at 20 °C.[53]

A new, novel method of synthesis of PA films in the *trans*-form involves the polymerisation of 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0]-deca-3,7,9-triene (BTFM) with opening of the ring:[54-55]



The polymerisation takes place in the presence of the $WCl_6-Sn(CH_3)_4$ catalytic system and deposits on the reactor surface. The prepolymer film splits off trifluoromethylbenzene with formation of a silvery PA film as a result of heating *in vacuo* at 100 − 150 °C. The density of the polymer reaches 1.1 g cm^{-3} and approaches the flotation density of the PA obtained by other methods. According to Leising et al.[54] and Edwards and Feast,[55] the amorphous PA obtained by this procedure has the fully *trans*-configuration and its structure is not fibrous. According to IR spectroscopic data, 1,2-bis-(trifluoromethylbenzene) residues are present in the polymer. Crystalline PA films with the monoclinic system and $\beta = 91.5°$ are obtained after prolonged heating of the prepolymer on electron microscope grids at 100 °C *in vacuo*.[56] An improvement of the method make it possible to obtain also films of fully oriented crystalline PA.[57] Subsequently methods of synthesis of polymers from other monomers were developed:[58]



On heat treatment of the prepolymer, naphthalene and anthracene are released in the former and latter case. An increase in the heat treatment temperature makes it possible to free the polymer from impurity residues.[58] According to spectroscopic data, the absorption due to the presence of sp^3-hybridised carbon is not observed in the spectra of the films; the absorption in the region of 1480 cm^{-1} in the Raman spectra of the polymers considered, due to the presence of C=C bonds, is displaced compared with the absorption observed for PA obtained by other methods (1460 cm^{-1}). It has been suggested that this is associated with a decrease in the size of the conjugation blocks. The films obtained are doped with difficulty in the gas phase owing to their high density. The conductivity of the initial films is 10^{-7} Ω^{-1} cm^{-1} and reaches 10 − 200 Ω^{-1} cm^{-1} when they are doped with bromine or iodine in solution and 2 Ω^{-1} cm^{-1} when the polymer having the composition $[CH(AsF_5)_{0.03}]_x$ is obtained.[58]

Solutions of ω-($\eta^1:\eta^5$-cyclopentadienyl)tris(η-cyclopentadienyl)-dititanium ($CpTiCl_2TiCp_2$) in hexane[59,60] and the cyclopentadienyl complex of sodium CpNa [61] exhibit a high catalytic activity. By removing the solvent slowly *in vacuo* from the PA gel formed, it is possible to obtain films with a metallic lustre. It has been suggested that the active complex has a tetrahedral structure and that the mechanism of the polymerisation is analogous to the mechanism of the polymerisation of olefins in the presence of a Ziegler − Natta catalyst.[61] The *cis*-polyacetylene films obtained at −80 °C had a conductivity of 240 Ω^{-1} cm^{-1} after doping.[60]

The classical ionic and radical polymerisation methods do not allow the preparation of high-molecular-weight polymers with a system of conjugated bonds (PCB) owing to the isomerisation of the active centres[2] associated with the polyene chain. With increase in the effective degree of conjugation, there is an appreciable change in electron affinity and the ionisation potential.[62] One of the methods

which make it possible to carry out the cationic polymerisation process involves the formation of a complex with the growing polyconjugated chain during synthesis. In practice such a process can be achieved in the presence of a large excess of a strong electron acceptor in the reaction medium. In this case, the electron density on polyene chains falls and there is a corresponding decrease in the probability of electron transfer from the chain to the active centre.

On the basis of these factors, it has been possible to synthesise PA films on the inner surface of the reactor in the temperature range from −78° to −198° when acetylene is added to arsenic pentafluoride. Soga et al.[63] and Kora and Kobayashi[64] identified the absorption band of *cis*-PA in the region of 740 cm^{-1} and of the doped complex in the region of 900 and 1370 cm^{-1}. Doped films having the composition $[CH(AsF_5)_{0.01}]_n$, obtained for the ratio $C_2H_2:AsF_5 \cong 0.1$, have an electrical conductivity of $4.8 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$.[63,64] Films of analogous composition have been obtained by the gas-phase polymerisation of vinylacetylene in the presence of SbF_5.[65,66] The conductivity of the film increased to $1 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$ with increase in the SbF_5 concentration, but the metallic state could not be attained.

Soluble polyenes, including soluble PA, have been obtained in solution in AsF_3 in the presence of AsF_5 by cationic polymerisation,[67] which was carried out at the freezing point of acetylene; films having a conductivity of $10^{-6}-10^{-7}\ \Omega^{-1}\ cm^{-1}$, characteristic of weakly doped PA with a molecular weight of $\sim 10^{-3}$, could be cast from the solution obtained. Spectroscopic studies confirmed the presence of the *cis*-structure in the polymer obtained. The possibility, in principle, of the polymerisation of acetylenic monomers (acetylene, methylacetylene, cyanoacetylene, and perfluoroacetylene) with formation of high-molecular-weight products in the presence of Group III, IV, and V metal halides has been indicated.[64] Insoluble polymers with specific conductance of $10^{-3}\ \Omega^{-1}\ cm^{-1}$, obtained at −78 °C by polymerising acetylene in the presence of AsF_5, $NaAsF_5$, SiF_4, AsF_3, BF_3, SbF_5, and PF_6, are of practical interest.[68]

Bivalent mercury compounds or organomercury derivatives are effective cocatalysts of the cationic polymerisation of acetylene and its derivatives.[69] The reactions of mercury oxide or mercury salts with protic and aprotic acids in saturated hydrocarbon media result in the formation of heterogeneous complexes, which effectively polymerise acetylene, vinylacetylene, phenylacetylene, and propargyl alcohol. Polyacetylene mainly with the *trans*-structure and a degree of crystallinity of 70% has been obtained in the form of films in the polymerisation of acetylene on the catalyst surface.[62,69] According to X-ray diffraction data, the principal reflection corresponds to the interplanar spacing $d = 3.22$ Å.[62,69] A homogeneous catalyst, whose active complex with acetylene is stable at low temperatures, has been obtained in the presence of aromatic ligands.[69] In the presence of aromatic solvents (toluene, benzene), the solvent is alkylated and subsequently copolymerises with acetylene, as a result of which the IR spectra of the films show absorption bands corresponding to the aromatic ring. The characteristic features of the polymerisation of acetylenic monomers, the influence of temperature and catalyst composition on the structure, and the properties of the polymers obtained have been investigated.[70,71] A study of the morphology of the films demonstrated the absence of fibrils.

Virtually all the methods of synthesis enumerated above, which make it possible to obtain PA with a high molecular weight, lead to the formation of insoluble polymers. Their insolubility can be explained by the formation of network structures together with the intense intermolecular interaction. The degree of cross-linking of polymers obtained in the presence of Ziegler catalytic systems is 3−5% according to NMR data,[72] which has been confirmed by the results of ozonolysis.[73] Quantum-chemical calculations have confirmed that the isomerisation process results in the formation of intermolecular bonds leading to the appearance of an unpaired electron.[74]

The easiest and most promising method of synthesis of PA with a linear structure involves the polymerisation of acetylene in the presence of Group VIII metals in combination with reductants (Luttinger catalyst).[75-77] Polyacetylene with a high degree of crystallinity has been obtained by polymerising acetylene in the presence of the $Co(NO_3)_2-NaBH_4$ catalytic system with the 1 : 2 component ratio. In order to prevent the destruction of the catalyst, both components are introduced into the substrate containing the monomer. An increase in the temperature and sodium tetrahydroborate concentration leads to the partial reduction of the polymer. The activity of nickel complexes can be greatly increased if the polymerisation is carried out in the preence of $NaBH_4$.[62,77] A crystalline polymer obtained at low temperatures contains no fibrils; the crystallites have dimensions up to 70 Å. The characteristic reflection observed at $2\theta = 23.75°$ ($d = 3.74$ Å) confirms the *trans*-structure of the polymer. Palladium complexes are ineffective in the synthesis of high-molecular-weight polymers.[62,77,78] The Luttinger catalyst makes it possible to obtain linear polymers with the *cis*-structure distinguished by a high crystallinity. The yield of PA reaches 25−30 g per gram of catalyst.

The chlorination of freshly prepared polymers at low temperatures permits the synthesis of soluble chloropolymers with a molecular weight of $(2-5) \times 10^4$.[27,79] Although the authors claim that, in contrast to hydrogenation, at a low chlorination temperature the polymer did not undergo degradation, our data[80] indicate that, when the temperature and the solvent are selected appropriately, the chlorinated polymers obtained have a molecular weight up to 2.5×10^5; the degradation is more appreciable on chlorination in the light and at an elevated temperature. The linear structure of PA is demonstrated by the fact that soluble iodinated polymers are obtained by iodinating a suspension of PA in ethanol.[80]

Systematic study of the methods of synthesis of PA made it possible to develop a fairly simple and convenient method for the preparation of films on various supports wetted with an ethereal solution of the catalyst.[79] The disadvantages of these films as well as films obtained by Shirakawa's method[24,25] are the difficulties of freeing them from catalyst residues and the dependence of the properties on the thickness of the surface.[81] The methods for the preparation of PA films by atomising in an inert gas stream PA freed from catalyst residues or by casting homogenised gels are much more practical.[49,82,83] The properties of such films depend on the conditions governing their formation. "Free" films with a thickness up to 2−3 mm are obtained by the filtration under pressure in an inert medium of a homogenised suspension containing 5−10 g $litre^{-1}$ of PA formed in organic media at low temperatures in the presence of the $Co(NO_3)_2-NaBH_4$ catalyst. The films obtained by atomisation in an inert gas stream are homogeneous and exhibit an effective adhesion to metallic, polyurethane, polyester, poly(ethylene terephthalate), polyimide, etc. supports.

The properties of the films have been described as a function of the conditions of synthesis and the composition of the catalyst.[62,84] PA suspensions undergo an appreciable change in their properties in the course of time. In an inert medium at a temperature above −20 °C, cross-linking and aggregation of the fibrils are observed, which lowers the rate of oxidation and chlorination. The morphology of the films changes especially markedly when the suspension is aged in the presence of moisture and oxygen: the diameter of the fibrils increases, their length diminishes, and breaks and nodes are formed. In contrast to this, it has been claimed[85] that a PA suspension undergoes no changes in its properties on being kept for two weeks.

The preparation of soluble polymers with a stream of conjugated bonds and a large molecular weight is especially difficult owing to the strong intermolecular interaction, but a PA with a fairly high molecular weight has been obtained in the form of finely dispersed

particles by carrying out the synthesis in the presence of the Luttinger catalyst and surface-active substances, mainly copolymers of styrene and polyethylene with poly(ethylene oxide).[86] Acetylene was added at −60 °C to the catalyst and the copolymer in solution in the cyclohexane–tetrahydrofuran mixture and the mixture was heated to −30 °C. This resulted in the formation of stable colloidal solutions with spherical particles whose size ranged from 40 to 2000 Å; the density of the films isolated was 1.15 g cm^{-3}. Colloidal PA solutions can be obtained in the presence of other polymers which prevent the aggregation of the PA molecules produced.

Polyacetylene obtained in the presence of Group VIII metals combined with $NaBH_4$ possesses virtually the same morphology as the polymer synthesised by Shirakawa's method.[25] The dimensions of the fibrils are in the range 300–800 Å and depend on the catalyst concentration, the temperature of the synthesis, and the medium.[27,87]

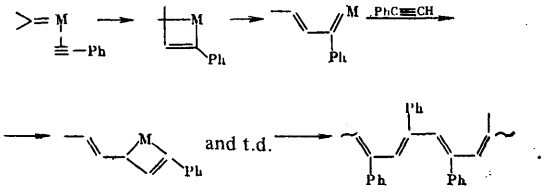
The thermogravimetric curves for the PA have two exothermic peaks at 145° and 325 °C.[16] The first corresponds to irreversible *cis–trans* isomerisation. At 325 °C hydrogen migrates, chain termination takes place, and the PA is cross-linked without the formation of volatile products; the polymer acquires a brown colour and a large number of defects appear, which is reflected in the appearance in the IR spectra of absorption bands characteristic of CH_2, CH_3, $-C=C-$, and C_6H_5 groups.[16] It has been suggested that structure formation takes place in the polymer in the temperature range 280–380 °C. The exothermic peaks in the region of 425° and 440 °C correspond to the partial decomposition of the PA; 72% of the initial mass of the PA is lost at 720 °C. The main products of the decomposition of the PA are benzene, hydrogen, and lower hydrocarbons.[15] When PA is heated in air to 90 °C, the degree of its crystallinity falls after only a few hours and a brown amorphous substance resembling cuprene is obtained when 70 h have elapsed.

III. THE SYNTHESIS AND PROPERTIES OF POLYACETYLENE DERIVATIVES

The likely usefulness of PA for the preparation of electrodes in accumulators and new semiconducting materials for the electronic industry stimulated further search for further technological materials. One of the ways in which such search is prosecuted involves the study of the polymerisation of acetylene derivatives and of the properties of the material formed.

The golden-green amorphous films of poly(hepta-1,6-diyne), obtained by the polymerisation of the corresponding monomer in the presence of a Ziegler–Natta catalyst, have the most interesting electrophysical characteristics.[88] In addition to the absorption in the region of 1610 cm^{-1}, characteristic of polyenes, the IR spectrum of this polymer exhibits absorption in the region of 910 and 1430 cm^{-1}, indicating the presence of the methylene group. A cyclic structure has been proposed for the polymer on the basis of these data. The conductivity of the freshly prepared specimens is 10^{-12} Ω^{-1} cm^{-1} and reaches 10 Ω^{-1} cm^{-1} when they are doped with AsF_5. The undoped films have a density of ~1 g cm^{-3}. A transition of the polymer to the vitreous state has been observed by differential scanning calorimetry in the temperature range from −50° to 330 °C; the first exothermic peak, associated with the *cis–trans* transition, is observed at 127 °C and the second occurs at 267 °C. The poly(hepta-1,6-diyne) films differ from the polyacetylene films by the fact that they contain no fibrils and are more sensitive to oxygen.[88]

One of the most readily available acetylene derivatives is phenylacetylene (PhA). The method for its polymerisation and the properties of polyphenylacetylene (PPhA) have been studied in fair detail and have been described[12,16,89,90] and we shall therefore consider only certain questions concerning the preparation of semiconducting materials from PhA. The polymerisation of PhA in the presence of $AlEt_3-TiCl_4$ leads to the *cis*-isomer [91] or the *trans*-isomer [92] depending on the conditions of synthesis; the pure *cis*-cisoid PPhA has a bright red colour. The crystalline insoluble *cis*-PPhA is obtained in the presence of iron acetylacetonate and trialkylaluminium.[91] The soluble *cis*-PPhA with $M_n = (1-2) \times 10^4$ is formed in the presence of $MoCl_5$ or WCl_6.[93,94] The kinetics of the polymerisation of PhA in the presence of $MoCl_5$ catalyst fixed on kaolin, talc, and aluminium and magnesium oxides have been investigated[95] and it was found that the carrier influences the structure and properties of PPhA. The molybdenum in the active centre exists in the quadrivalent state.[95] High-molecular-weight PPhA with $M_n \cong 8 \times 10^4$ has been obtained in the form of a yellow soluble powder on UV-initiated polymerisation of the monomer in the presence of tungsten or molybdenum carbonyl in a halogen-containing solvent.[96] It has been suggested that the reaction mechanism involves the elimination of carbon monoxide under the influence of UV irradiation with formation of a coordination complex between the carbonyls of the above metals and PhA. The polymer chain grows in the consecutive stages involving the formation of the metallocarbenes and metallocyclobutenes:



The films can be readily obtained from the polymer solutions.

Although the electron-initiated polymerisation of arylacetylenes is in fact fairly promising, it has been little investigated.[97,98] The PhA polymers obtained in dimethylformamide (DMF), dimethyl sulphoxide (DMSO), and acetonitrile in the presence of tetra-alkylammonium, lithium, potassium, and sodium salts or $NaNO_3$ as electrolytes have a low molecular weight (of the order of 500–3700) and a melting point ranging from 90° to 160 °C. The synthesis takes place in the cathodic space on graphite electrodes; the radical inhibitors do not influence the polymerisation but alcohols retard the process. On the basis of these data, the authors propose an ionic initiation mechanism. The yield of the polymer, in which a large amount of cyclohexadiene structures has been observed, reaches 60%.[97-100]

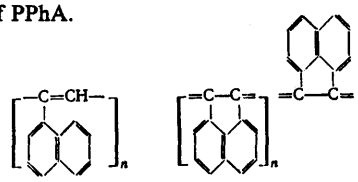
The PhA polymerises in a homogeneous catalytic system consisting of mercury compounds combined with acids in aprotic solvents.[101] The soluble polymers formed, mainly with the cisoid structure, are distinguished by a high degree of crystallinity. The films obtained from the solution of the polymer weakly doped with boron trifluoride exhibit semiconducting properties and have an electrical conductivity of the order of $10^{-6}-10^{-8}$ Ω^{-1} cm^{-1}; they lose their crystallinity on ageing. It follows from the analysis of the IR and ^1H NMR spectra that, under these conditions, cyclohexa-1,3-diene and cyclohexa-1,4-diene structures, diminishing the effective conjugation, appear in the polymers.[101,102] The stable complexes of PPhA with iodine, which are formed when PhA is polymerised at 100° to 150 °C in the presence of iodine as the catalyst, have an electrical conductivity of the order of $10^{-3}-10^{-5}$ Ω^{-1} cm^{-1}.[103]

The appeciable defects in the conjugation chain in PPhA compared with PA are caused not only by the influence of the benzene ring, which gives rise to steric hindrance to the coplanarity of the fragment of the main chain, but also by the tendency of the PPhA to isomerise. The isomerisation takes place at temperatures up to 130 °C and is accompanied by a slight decrease in the molecular weight; analogous changes have been observed to a large extent after the specimens have been kept for a long time in the light.[104,105] An appreciable decrease in $\overline{M}_n$ and the appearance of cyclohexadiene

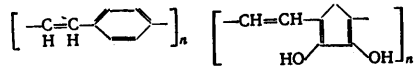
fragments have been observed at 130–280 °C.[106] Further heating leads to weight loss, which is associated with the evaporation of the low-molecular-weight products—mainly triphenylbenzene.[107] These changes result in the complication of the polymer structure, a decrease in the length of the effective conjugation, and hence an impairment of the electrical conductivity.[99] For example, the electrical conductivity of the iodine-doped crystalline *cis*-cisoid PPhA falls by several orders of magnitude after its heat treatment at 120 °C. Apparently this is why a dependence of the electrical conductivity of PPhA on its structure and molecular weight has not been observed in many investigations. On doping with iodine, the electrical conductivity of PPhA reaches 10^{-5} Ω^{-1} cm^{-1}, the *cis*-isomer being doped more readily than the *trans*-isomer. Variation of the molecular weight over the range $(7-10) \times 10^3$ does not affect the reversible incorporation of iodine and the conductivity of PPhA.

Soluble complexes of PPhA with organic electron acceptors have been obtained; their solutions absorb radiation in the range 700 to 900 mm as a function of the nature of the electron acceptor.[108] The electrical conductivity of the polymer increases after the addition of the acceptor, reaching a maximum when the content of the latter is 75 mole per cent and does not then change further. Analogous behaviour has been observed also for polystyrene.[108] The authors suggest that the acceptor forms a complex with the phenyl side groups in the polymer chain. However, a study of the kinetics of the reaction of PPhA with chloroanil and other organic acceptors demonstrated the formation of a charge-transfer complex (CTC) in the first stage of the process and the subsequent complete charge transfer with formation of a polymeric radical-cation.[109] The equilibrium constants for the complex ($K \geqslant 10^3$) have been estimated and its enthalpies have been found ($\triangle H \geqslant 8.6$ kcal $mole^{-1}$) from the activation energies ($E_{eff} = -8.6$ kcal mol^{-1}). Further studies showed that styrene does not form a CTC with iodine.[110]

Methods for the polymerisation of 1-ethynylnaphthalene[89,111] and acenaphthenediylidenes with various substituents[112] have also been investigated. The electrophysical properties of the polymers obtained have been described in fair detail[111,112] and are in the main similar to the properties of PPhA.



Polyarylacetylenes capable of forming films with metallic lustre and having a specific conductance (for undoped specimens) of 10^{-8} Ω^{-1} cm^{-1} each and having the following structure have been obtained by photoreductive condensation:[113]



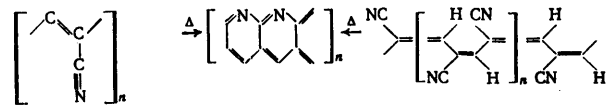
The synthesis, structures, and properties of polyarylacetylenes have been described in great detail in a review.[90]

Among other polymeric derivatives of acetylenes, poly(3,3,3-trifluoroprop-1-yne) is of interest. Trifluoromethylpropyne is polymerised in solution in DMF in the presence of $PdCl_2$ at 60 °C.[114] Liquid oligomers, which have a polyene structure according to IR and NMR spectroscopic data, are formed. A higher-molecular-weight product with $M_n \cong 10^3$ was obtained at −78 °C in the presence of butyl-lithium.[78] On heat treatment, the brown polymer powder blackens, but its conductivity $\sigma = 10^{-12}$ Ω^{-1} cm^{-1} does not change; specimens doped with iodine have a conductivity of 9.5×10^{-5} Ω^{-1} cm^{-1}. The polymer is resistant to thermal and thermo-oxidative degradation up to 240 °C. In the differential-thermal analysis of the specimen in the temperature range up to 450 °C, three exothermic peaks are observed.[78,114]

A polymer with a conductivity up to 10^{-5} Ω^{-1} cm^{-1}, described previously,[115] has been obtained by the polymerisation of propargyl chloride in the presence of $PdCl_2$.[114] The high conductivity is apparently due to the doping of the polymer by the halogen eliminated. The introduction of an excess of iodine into the polymer powder softens it and a thin film with a conductivity of 2×10^3 Ω^{-1} cm^{-1} can be obtained from it by pressing.

Like cyanoacetylene, propiolonitrile readily polymerises in the presence of various catalysts.[116] In the presence of triethylamine, a black insoluble powder is formed in high yields; in order to obtain films, the reaction is carried out in the gas phase. The BuLi catalyst in THF polymerises cyanoacetylene at −70 °C ($\overline{M}_n \cong 4800$). The effective adhesive properties of the films make it possible to grow them even on the surface of Telfon; splitting into layers on deformation of the support is not observed.[114,117,118] In the presence of $Ti(OBu)_4-AlEt_3$, the reaction involving the formation of a *cis*-transoid polymer takes place in solution in pentane at room temperature but the yield of the polymer is somewhat lower than in the presence of chromium acetylacetonate with an excess of triethylaluminium.[116] A brown polymer with a linear *trans*-transoid structure can also be obtained.

Catalysts based on $MoCl_5$ and $Sn(C_6H_5)_4$ make it possible to obtain linear products from cyanoacetylene at room temperature.[116] The polymer is not doped by electron donors but it is reversibly doped with iodine up to a content of the latter of 40 mole per cent. Its electrical conductivity then changes from 10^{-12} to 10^{-3} Ω^{-1} cm^{-1}. Differential-thermal analysis data indicate the occurrence of processes at 140°, 215°, and 255°C without change in rate. The weight loss at 1110 °C is ~50%. The study of the specimens after the heat treatment suggested that the first stage (280 °C) involves isomerisation, while at higher temperatures cyclic structures appear as a consequence of degradative processes:[114]



linear *trans*-transoid polymer

linear *cis*-transoid polymer

The cyanoacetylene polymers and copolymers exhibit semiconducting properties and are promising materials for the preparation of transistors and solar batteries.[117,118]

Polymethylacetylene has been obtained[119] by the polymerisation of methylacetylene in the presence of a Ziegler–Natta catalyst at 0 °C. The orange powder obtained is sensitive to air and does not give rise to an EPR signal even on heating to 150 °C. The results of thermogravimetric analysis indicate its vigorous decomposition at 180 °C with a weight loss of up to 90%.[119] Polymethylacetylene is doped with iodine and other electron acceptors whereupon $\sigma = 10^{-3}$ Ω^{-1} cm^{-1} is attained. The films are formed on gas-phase polymerisation of methylacetylene on the surface of the catalyst at low temperatures. The polymerisation of ethynylferrocene and methylethynylferrocene takes place readily in the presence of WCl_6-Ph_4Sn.[120]

Other acetylene derivatives containing bulky substituents, capable of fully disturbing the coplanarity of the chain, as a rule polymers with poor electrophysical properties. For example, the polymerisation of t-butyl- or n-butyl-acetylene under the influence of WCl_6 leads to the formation of light-coloured powdered products with $M_n \cong (0.8-5) \times 10^5$ which do not possess the properties of PCB.[121] Table 1 indicates certain acetylenic derivatives used as monomers for the synthesis of PSS.

IV. COPOLYMERS AND COMPOSITES BASED ON POLYACETYLENE

The search for methods of synthesis of polyenes is closely related to the modification of the properties of these polymers in order to obtain materials which are suitable for processing on the technological equipment used in the polymer industry. One of such current procedures is the preparation of copolymers of acetylene and its derivatives with other monomers used in industry and composites. Films containing 2–5% of DA, capable of being doped with electron-acceptors, have been obtained by polymerising acetylene in a matrix comprising polyethylene and copolymers of styrene with butadiene and isoprene using a Ziegler–Natta catalyst.[122,123] The dispersed doped compositions have a high surface conductivity and an improved resistance to the action of air. The number-average molecular weight of the PA composition reaches 2.5×10^4, while the weight-average molecular weight M_w is 10^5, so that we have the ratio $M_w/M_n = 4.26$.[124] The properties of the conducting composites obtained by doping the polymer with iodine and having a PA content up to 3% can be explained by a simple percolation model.[125]

Flexible elastic films can be obtained by pressing PA with ethylene–propene rubbers or by polymerising acetylene in solution in poly(vinyl chloride), polyvinylpyrrolidinone, or polyvinylbutyral; the stretching of the films promotes an increase in electrical conductivity, which can be explained by the orientation effect.[126] The most varied materials, ranging from elastic to rigid, can be obtained by polymerising acetylene in the presence of the $Ti(OBu)_4-AlR_3$ catalyst in a polybutadiene matrix with $\overline{M}_n = 2 \times 10^5$. When they were doped with lithium or iodine, a composite having a conductivity ranging from 10 to 100 Ω^{-1} cm^{-1} was obtained; the conductivity increases on stretching the specimens.[127] The morphology of the composites varies as a function of the PA content from fibrillar (for an 80% PA content) to globular (PA content less than 20%).[128] Electrically conducting compositions have been obtained by the graft polymerisation of acetylene. The addition of PA to the copolymer chain has been demonstrated.[123] The graft block-copolymer of PA and atactic polystyrene with $M_n = 10^5$, obtained in the presence of a Ziegler–Natta catalyst and containing up to 40% of PA, is capable of forming lamellar single crystals which have a hexagonal lattice whose unit cell parameters are $a = 5.12$ Å and $c = 4.8$ Å and whose size ranges from 10^3 to 10^4 Å.[129] With decreased content of the polymer-carrier, the interface necessary for the formation of the crystalline phase diminishes.

A soluble block-copolymer of PA with polyisoprene and polystyrene is obtained for a PA content up to 5% and permits the study of the behaviour of the stable PA chain in solution. Spectroscopic studies[130] have shown that in such copolymers the polyene molecule retains the properties of the homopolymer. However, there are also certain differences. Thus at room temperature rapid *cis–trans* isomerisation takes place in the copolymer. The block-copolymer is more sensitive to oxidation than PA itself and, in contrast to PA or the composite, it is capable of combining quantitatively with bromine at the double bond. NMR data have made it possible to identify segments with PA and to establish that the chain conformation is non-linear. According to electron microscopic data, the graft copolymers are characterised by the presence of separate microphases with microdomains $(1-1.5) \times 10^5$ Å in diameter.[130,131]

The PA and styrene block-copolymers have been obtained from styrene oligomers with $M_n = 10^3$ synthesised in the presence of BuLi. After the treatment of the oligomer with aluminium chloride and the addition of $Ti(OBu)_4$, acetylene was introduced into the system at a pressure of 700 mmHg. This method makes it possible to obtain also copolymers of acetylene with methylacetylene and phenylacetylene.[37] The films made of copolymers with different contents of methylacetylene have also been obtained by polymerising a mixture of monomers on a thin layer of catalyst deposited on a support.[119] The elasticity of the polymer increases with increase in the methylacetylene content whereupon the conductivity of the doped film and its stability in air diminish. With increase in the methylacetylene content in the copolymer, its morphology changes appreciably and the fibrillar structures characteristic of PA disappear.[119]

The reverse process involving the grafting of polystyrene, polyisoprene, poly(methyl methacrylate), and poly(ethylene oxide) blocks to the PA chain is carried out by polymerising the corresponding monomers on polyacetylene doped with sodionaphthalene. Films

Table 1. The polymerisation conditions and the properties of the acetylenic polymers.

Initial monomer	Polymerisation catalyst	Conductivity, Ω^{-1} cm^{-1}		Refs.
$CH_3{=}CH$	$Ti(OBu)_4{-}AlR_3$	10^{-13}–10^{-8}	(film)	[114, 119]
$CH_3C{\equiv}CH$	BuLi	10^{-13}–10^{-5}	(powder)	[78, 114]
$ClCH_2{-}C{\equiv}CH$	$PdCl_2$-pyridine	10^{-4}–10^{-3}	(powder)	[114, 115]
$HO{-}CH_2{-}C{\equiv}CH$	Hg^{2+}-acid, KOH, $PdCl_2$	10^{-10}–10^{-8}	(powder)	[62]
$CH_2{=}CH{-}C{\equiv}CH$	SbF_5	10^{-2}	(film)	[65, 66]
$C_3H_7{-}C{\equiv}CH$	$NiX_2 - NaBH_4$	—	(powder)	[75]
$C_4H_9{-}C{\equiv}CH$	WCl_6, $Ti(OBu)_4 - AlR_3$	$>10^{-14}$	(film)	[121]
$NC{-}C{\equiv}CH$	$A^-(NR_3$, BuLi) *	10^{-6}–10^{-3}	(film)	[117, 118]
$NC{-}C{\equiv}C{-}CN$	$Ti(OBu)_4 - AlEt_3$	10^{-6}	(film)	[116]
$C_6H_5{-}C{\equiv}CH$	$MoCl_6$, WCl_6, SbF_5	10^{-5}	(film)	[66, 89, 94, 114]
$C_6H_5{-}C{\equiv}C{-}C_6H_5$	electrochemical method	—	(powder)	[97]
$C_{10}H_7{-}C{\equiv}CH$	BuLi	10^{-7}	lm, powder)	[65, 66, 89, 111]
$HC{\equiv}C{-}(CH_2)_3{-}C{\equiv}CH$	$Ti(OBu)_4 - AlR_3$	10^{-13}–10^{-1}	ilm)	[88]
$R{-}OOC{-}C{=}CH(R{=}CH_3, C_2H_5)$	electrochemical method	—	(powder)	[97]

*Here A^- = anion.

with interesting magnetic properties have been obtained by copolymerising acetylene with carbon monoxide.[131] An amorphous polymer containing up to 15 mole per cent of CO and having molecular weights up to 87×10^4 can be synthesised in the presence of the $Ti(OBu)_4-4AlEt_3$ catalyst. The AsF_5-doped films had conductivities up to 200 Ω^{-1} cm^{-1}.[131] When epoxyethane is used, materials having the properties of solid electrolytes are obtained.[37] In recent years, there has been a marked growth of interest by investigators in composites containing PA. Composites containing graphite, carbon black, charcoals,[132] various network polymers, and, in particular, thermolysed polyacrylonitrile[48] have been produced. Composites obtained by polymerising acetylene on polypyrrole films are of interest; after doping, they have a conductivity of ~ 20 Ω^{-1} cm^{-1} and are fairly stable in air.[133]

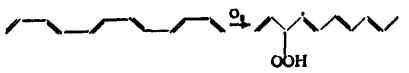
V. THE OXIDATION, REDUCTION, DOPING, AND STABILISATION OF THE FILMS

The ability of PA and other PCB to combine with 25–33 wt.% of oxygen in air is evidence of their instability, although the use of this property for special purposes can be of independent practical value. The oxidation of PA alters the chemical and physical characteristics of the material. The electrophysical and mechanical properties of films change particularly markedly.[134] On absorption of oxygen, the material becomes more brittle; the slight modification of the surface of the fibrils in consequence of the adsorption of oxygen or other acceptors greatly influences the formation of films. The films doped with acceptors are oxidised more slowly than the initial films.[135,136] The electrical conductivity of PA films increases after the absorption of oxygen up to 16 wt.% and then falls by several orders of magnitude.

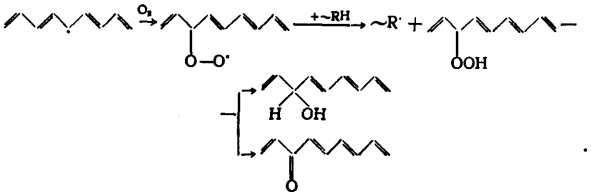
The absorption bands of the oxidised specimens in the region of 1720 and 1670 cm^{-1} correspond to the deformation vibrations of the carbonyl group in the isolated and αβ-unsaturated ketones.[138] Bands at 1109 and 1143 cm^{-1} correspond to the antisymmetric vibrations of the C–O bond in aliphatic ethers. The absorption bands in the range 1000–1300 cm^{-1} and in the region of 3420 cm^{-1} indicate the appearance of hydroperoxy- and hydroxy-groups. The absorption bands at 1370 and 890–900 cm^{-1} appear in the initial stage of the oxidation caused by the doping of the PA with atmospheric oxygen and disappear at high degrees of oxidation; the absorption in the region of 1920 cm^{-1}, attributed to the allene group, vanishes simultaneously.[136-139]

There exist several ways of adding oxygen to polyenes. Singlet oxygen can react with the olefin via the 1,2-addition mechanism with the ultimate formation of cyclic peroxides. In the case of 1,3- and 1,4-addition, other corresponding products appear. Triplet oxygen reacts with the initial radical to form a peroxy-radical capable of being converted into hydroperoxy-, carbonyl-, and hydroxy-groups as a result of further reactions.[136] The oxidation occurring in the absence of UV irradiation is a pseudofirst order reaction.

Visible light does not affect the rate of oxidation; diffusion also does not limit the rate of the process. In the oxidation of the films, an induction period, corresponding to the formation of a CTC, is observed; this is followed by two oxidative processes on the surface and in the bulk of the specimen, which lead to the appearance of an inflection in the kinetic curve. The following reaction scheme has been proposed on the basis of the studies carried out:[136,140]



The oxidation of *cis*-PA begins with the isomerisation and formation of neutral defects:



However, the scheme presented reflects inadequately the specific features of the oxidation process in view of the complex character of the reactions of oxygen with the polyconjugated system. The results of the study of the kinetics of the oxidation of PA indicate the absence of a linear relation between the decrease in the number of double bonds and the accumulation of oxidised groups.[138] The kinetics and mehcanism of the oxidation of PA have been described in detail in other communications.[30,141]

Owing to the preferential consumption of molecules with a *cis*-structure, in the initial stage of the oxidation of PA, the enrichment of the specimen in the *trans*-isomer is observed. If the temperature does not exceed 150 °C, the oxygen content of the polymer can reach 35%. With increase in temperature, thermo-oxidative degradation, in the course of which CO_2 and H_2O are evolved, takes place.[136,138] The rates of oxidation at 70 °C of PA and polymethylacetylene obtained in the presence of a Ziegler–Natta system are respectively 9.16×10^{-7} and 10^{-6} mol g^{-1} s^{-1}, while the activation energies for these processes are 9.6 and 14 kcal mol^{-1}.[142] The activation energies for the oxidation of PA measured by different workers are in the range from 11 to 20 kcal mol^{-1},[136,139,143] which is apparently associated with the different densities of the films employed. The activation energies for the formation of the complex of PA with oxygen and for its decomposition have been found respectively to be 11.52 and 13.45 kcal $mole^{-1}$ and it has been shown that water accelerates the oxidation of PA.

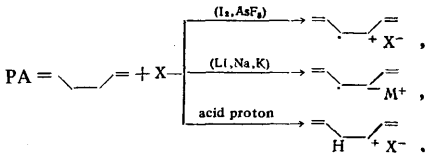
The addition of ozone to polyenes takes place at low temperatures and leads in the case of PA to the formation of an adduct in 98.5% to 99.5% yields whose decomposition results in the formation of oxalic acid diesters.[73] The activation energy for the oxidation of PA by ozone is 19.59 kcal mol^{-1}.[144] The kinetics of the oxidation and doping of polyheptadiene and PA differ somewhat.[145]

Studies of different types of stabiliser have shown that quenching agents for singlet oxygen, for example, dimethylanthracene as well as compounds decomposing peroxides do not affect the rate of oxidation of PA.[142] Sterically hindered phenols and inhibitors of the amine type, which actively capture radicals, inhibit the thermal oxidation of PA. The inhibition of the oxidation of PA also occurs on the addition of mixtures of sterically hindered phenols and peroxide-decomposing compounds which exhibit a synergistic effect. Following an increase in temperature the action of antioxidants weakens; this is believed to be caused by the surface character of the inhibition.[142] In the presence of 2,6-di-t-butylphenol, the stability of PA is retained also after doping. The kinetics of the oxidation of PA have been studied in the presence of inhibitors.[30,136] Analogous results have been obtained in the study of polymethylacetylene synthesised in the presence of a Ziegler–Natta catalyst; stabilisers of the phenolic type are effective if they are used in a complex with systems decomposing peroxides.[146]

The stability of various polymers of the acetylene series in relation to oxidation in air and UV irradiation increases in the presence of acid esters and thioesters based on Group V and VI elements, especially phosphorus, sulphur, nitrogen, etc.[141] A polyacetylene synthesised in the presence of phenols and phosphines is also less susceptible to oxidation. It is likewise resistant to the action of water, but its doped derivatives, especially those doped with electron

donors, are sensitive to moisture. The PA doped with sodium is readily hydrolysed by water, whereupon its partial hydrogenation takes place.[147] The elecrical conductivity of the films doped with electron acceptors falls in the presence of moisture owing to the hydroxylation of the PA, particularly in alkaline media. Chain protonation takes place in acid media and the stability of the films is higher than in an alkaline medium.[148,149] In strongly acid HBF_4 solutions, it is possible to dope PA irreversibly without the formation of hydroxylation products.[150,151]

Doping of *p*-type includes in essence a PA oxidation step and occurs fairly vigorously with the cooperation of various acceptors. Correspondingly, *n*-type doping includes a reduction process and occurs with the cooperation of electron donors. In early studies, the doping mechanism in the first stage was described by the scheme[36]



Here provision is made for the delocalisation of the cations and anions formed along the conjugation chain. Later this scheme was confirmed by the finding that, following the addition of external oxidants, the rate and degree of doping increase and hydroxy-groups can be detected in the PA structure.[152] As already mentioned, the ability of PA to be doped with an electron acceptor or donor is its most important characteristic, which makes it possible to employ this material as *n*- and *p*-type semiconductors, electrodes, solar energy converters, in the manufacture of accumulators, and in other technological fields. In the vertical stage of the reaction with PA, oxygen acts as an electron acceptor, which entails an increase in the conductivity and the appearance of an interfacial polarisation effect.[139]

One of the most promising methods of doping is electrochemical. The irreversibility of electrochemical doping, investigated in a number of studies,[153,154] made it possible to develop doped polyacetylene electrodes for accumulators.[155,156] In a general form, the equation for the doping process can be written as follows:

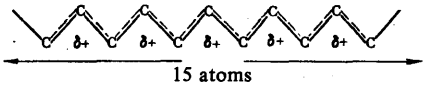
$$CH_x + yA \rightarrow [CH^{y+}(A^-)_y]_x ,$$

$$CH_x + yM \rightarrow [M_y^+(CH)^{y-}]_x ,$$

where A^- and M^+ are the univalent anion and cation respectively.

As in the oxidation reaction, a *cis*–*trans* transition is observed in the PA during the doping process and, depending on the degree of doping, three states of PA arise. In the first, semiconducting state, the concentration of the dopant is less than 1% and the material has semiconducting properties. In the second, metallic state, where the concentration of the dopant exceeds 6%, the material acquires properties characteristic of metals: high conductivity independent of temperature, paramagnetic susceptibility, and low heat capacity; its thermo-e.m.f. begins to vary linearly with temperature, etc. Finally, in the transition state, the material occupies an intermediate position between metals and semiconductors as regards its properties.

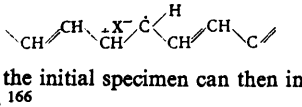
At the present time, the high conductivity of doped PA is explained mainly by the mobility of solitons. Neutral solitons, called in the chemical literature "delocalised radicals",[157] exhibit a high mobility in *trans*-PA. Positive and negative solitons (carbonium ions and carbanions) appear as a result of electron transfer to an acceptor (*p*-doping) or from a donor to the polymer (*n*-doping). The unit charge of the solitons is distributed approximately between 15 carbon atoms:



The charge on each CH group diminishes with increase in its distance from the doping ion.[158] Analysis of the IR spectra provides proof of the appearance of solitons. The vibrational models of soliton are observed at 1385 and 900 cm^{-1}, which is consistent with calculated data.[9,105] However, the properties of PA in the initial doping stage can be accounted for differently, with the aid of the theory of the formation of polarons.[159]

The general characteristics of the doping by various electron acceptors are the same. X-Ray diffraction studies on the iodine-doped PA indicate the existence of undoped regions and regions doped on the surface; furthermore, there are also complexes of PA with the dopant exhibiting metallic conductivity.[160] It has been observed by NMR that, together with complex formation, iodine adds to the double bond.[161] The doping of PA films obtained using the $Co(NO_3)_2-NaBH_4$ catalytic system is achieved both by immersing them in solutions of different acceptors and electrochemically until the attainment of a conductivity $\sigma \cong 10^3\ \Omega^{-1}\ cm^{-1}$.[162] In the doping process, the characteristic reflection of *cis*-PA with $d = 3.73$ Å disappears and reflections with $d = 8.35$ Å appear when SbF_5 is used as the dopant and $d = 8.15$ Å when AsF_5 is used; similar reflections have been noted for doped graphite ($d = 8.46$ and 8.15 Å respectively). A layered structure has been proposed for the doped specimens on the basis of these investigations.[162] When the PA film is doped with fluorosulphonic acid in the gas phase, the conductivity increases rapidly with increase in the content of the dopant y up to the critical value $y = 0.02$, after which a tendency towards saturation is observed, occurring at $y = 0.29$, whereupon σ reaches $2 \times 10^4\ \Omega^{-1}\ cm^{-1}$. At low temperatures the conductivity is independent of temperature, which can be explained by the vibrationally-excited tunnelling of the charges between the metal-like sections.[163] Detailed investigation of the doping of PA films indicate a non-uniform occurrence of this process, because the diffusion of the dopant into the relatively dense fibrils is difficult.[164]

A novel doping method involves the implantation of halogens in PA. Treatment of PA with a stream of halide ions at a dose of $10^{11}-10^{17}$ ions cm^{-2} and for an irradiation energy of 10–40 eV generates a uniform ion concentration gradient along the specimen. This film then becomes stable in air and acquires a colour ranging from red to blue depending on the irradiation energy. It has been suggested[165] that complexes having the following structure are formed in the ion implantation process:



The conductivity of the initial specimen can then increase by five orders of magnitude.[166]

The doping of PA by acids, especially those which cannot behave as oxidants is of special interest. The addition of a proton to the polyene chain with formation of a complex is suggested in this case.[167] The doped polymers have a comparatively low electrical conductivity (up to $10^{-3}\ \Omega^{-1}\ cm^{-1}$). This has been explained[167] by the appearance of steric effects, the formation of cross-links, or the addition of HCl to the double bond, which limits the length of the conjugation chain.[168] However, this evidence was in no way confirmed in the above study; furthermore, we have shown† that the addition of HCl to the double bond is not observed.

Doping with alkali metals can be carried out most readily in solution in tetrahydrofuran using sodium naphthalide or benzophenonelithium as the dopant; as in the *p*-doping process, under these conditions absorption bands in the regions of 1090 and 1480 cm^{-1}, characteristic of the *trans*-isomers, appear in the Raman

† See A.A.Matnishyan, N.M.Davtyan, and G.R.Martirosyan, Vysokomol.Soed., 1987, **29B**, 728.

spectra of *cis*-PA.[169] Doping with lithium tetrahydroaluminate in solution leads to the formation of a relatively unstable PA anion with a conductivity of 5 Ω^{-1} cm^{-1}.[170,171] In order to prepare elastic *n*-type films, PA is treated with anthraquinone derivatives combined with reductants (KBH_4, $NaHSO_3$, $NaCNBH_3$) in an aqueous medium.[172] Although the stability of the films increases in such treatment, nevertheless doping is accompanied by the partial reduction of the polymer and hence by the destruction of the conjugation regions. PA films treated with biarylyliodonium salts, whose UV irradiation leads to the doping of the exposed sections accompanied by an increase in conductivity, have found a new practical application as photo-sensitive materials.[173] The characteristic features and mechanisms of the doping of PA have been investigated in fair detail in recent years in connection with the prospect of constructing accumulators using PA films as electrodes.

Phenylacetylene is irreversibly doped with iodine, whereupon its conductivity increases from 10^{-14} to 10^{-5} Ω^{-1} cm^{-1}. The dependence of the conductivity on the iodine concentration c is of the form[159]

$$\sigma = \sigma_0 \cdot \exp[\gamma c(1-c) - \gamma/4],$$

where $\gamma \cong E/kT$.[159] An ionic mechanism of electrical conduction involving the thermally activated charge transfer model has been proposed. The current is determined by the number of charge carriers and not by their mobility.[114,174] Complexes of PPhA with various organic and inorganic acceptors were obtained. A mixture of PPhA with dichlorodicyano-*p*-benzoquinone and tetracyano-*p*-quinodimethane exhibits a high conductivity and measurements of the thermo-e.m.f. made it possible to assign it to the *n*-type.[108]

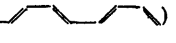
Among other polyenes, doped polyheptadiyne, polymethylacetylene, and certain polyarylacetylenes have been investigated.[112]

VI. THE STRUCTURE AND MORPHOLOGY OF POLYENES

Studies of PA films obtained both in the presence of Ziegler–Natta catalysts and Group VIII metals led to the conclusion that the *cis*-form of the polymers includes the *cis*-transoid structure



and the *trans*-cisoid structure



while the *trans*-form consists mainly of the *trans*-transoid structure[16,27]



The formation of the *cis*-cisoid structure is not ruled out either. The content of the *cis*-form in the synthesis of the polymer on the support or on the catalyst surface depends on the thickness of the film; as a consequence of the appreciable heat of reaction observed when the films are obtained by the method of Shirakawa and co-workers,[24,25] the fraction of the *cis*-isomers in thick specimens falls to 70–75% owing to their transition to the *trans*-form.[174] However, since the activation energy for the isomerisation reaction increases rapidly as the *trans*-structures accumulate and reaches 21 and 38 kcal $mole^{-1}$ for contents of the *cis*-form of 70 and 20% respectively, this explanation cannot be regarded as exhaustive.[143] If the polymerisation is carried out in the presence of the $Co(NO_3)_2$–$NaBH_4$ catalyst, the *trans*-cisoid structure is formed in appreciable amounts on the supports together with the dominant *cis*-transoid structure;[175] the fraction of the *cis*-cisoid structure is negligible. The ratio of the isomers depends greatly on the composition of the catalyst and the temperature of the synthesis (Table 2). The nature and concentration of the catalyst components also have an appreciable influence on the composition of the PA.

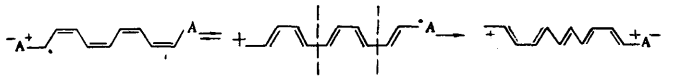
The quantitative ratios of the *cis*- and *trans*-isomers found by different workers differ significantly; this is associated with the use of different methods for the determination of the relative absorption coefficient $K_{trans/cis}$, whose values are 1.05 (Shen et al.[47]), 1.66 (Gibson et al.[176]), etc. The question concerning the mechanism of the *cis*–*trans* isomerisation is not as yet entirely clear. Probably, after the transfer of one electron to the dopant with participation of another electron and a π electron of a neighbouring carbon atom, a new double bond is formed; this process, in which the newly formed unpaired electron is involved, then develops further until the encounter with the dopant or another free electron:[177]



Table 2. The content of the *cis*-isomer (%) of polyacetylene as a function of the nature of the catalyst and the temperature of the synthesis.

Catalyst	Temperature of the synthesis, °C					Refs.
	−78	−18	0	+20	+100	
$Ti(OBu)_4$–$Al(C_2H_5)_3$	98	95	79	59	7,2	[135]
$Co(NO_3)_2$–$NaBH_4$	94	72	45	30	—	[75, 84]
WCl_6–Ph_4Sn	—	—	—	10	—	[52]
$MoCl_5$–Ph_4Sn	—	—	—	10	—	[52]
$Ti(CH_2$–$C_6H_5)_4$	—	—	—	40	—	[52]

In the presence of an acceptor, in the first stage the *cis*-transoid form is converted into the unstable *trans*-cisoid form, which constitutes an excited state of the initial form and then, as a result of rotation about two single bonds, sections with the *trans*-structures are formed:



The view has been expressed in the literature that the crystal structure of the catalyst produces a planar structure of the PA. The subsequent organisation of the polymer chains depends on the rates of polymerisation and crystallisation, changes in which can lead to sharp changes in the morphology.[38] It has been stated[38] that the concentration of the Ziegler–Natta catalyst has little influence on the PA morphology, while an increase in the ageing time leads to more appeciable changes. The influence of the catalyst on the structure and properties of PA has been investigated in greater detail.[15,16,28] Our studies have shown that the morphology of PA is influenced by the catalyst concentration and the composition of the ligand shell, but especially marked influence is shown by the nature of the metal in the catalytic cluster.[178,179]

The IR spectra of PA contain the following absorption bands: at 440 cm^{-1} (deformation vibrations of the C–C–C fragment), 740 and 1015 cm^{-1} (out-of-plane deformation vibrations of the C–H bond in the *trans*- and *cis*-forms respectively), 1118 cm^{-1} (C–C deformation vibrations), 1249 and 1329 cm^{-1} (in-plane C–H deformation vibrations), 1292 cm^{-1} (out-of-plane C–H vibrations), 3013 cm^{-1} (C–H stretching vibrations characteristic of the *trans*-structure), and 3044 and 3057 cm^{-1} (stretching vibration characteristic of the *cis*-structure).[175] The quality of the spectra increases when thin polymer films, obtained by sputtering the freshly prepared gel onto glass of the KRS type, are investigated. The doped specimens are distinguished by a characteristic absorption due to soliton modes in

the regions of 1370 and 900 cm^{-1}.[147] The photoacoustic IR spectroscopic method (PAIR) makes it possible to investigate PA powders and to detect 1150 and 1920 cm^{-1} absorption regions, which are weakly shown when other methods are used.[137] In combination with Raman spectra, the PAIR method permits a fairly profound investigation of the structures of insoluble and infusible polymers in the form of both powders and films.[17,136-139]

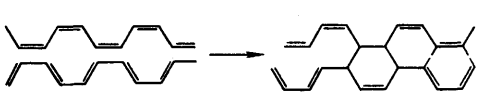
In order to determine the molecular weight and the molecular weight distribution in PA and also in order to characterise quantitatively the cross-links and other features of the structure, it is necessary to hydrogenate or chlorinate the initial polymer. These methods make it possible to convert PA into soluble derivatives. The sodium- or potassium-doped PA is hydrogenated by hydrogen at pressures up to 100 atm.[180] The PA films obtained in the presence of the $Ti(OBu)_4-AlR_3$ catalyst are treated with a solution of potassium naphthalide in THF for 1 h and are then hydrogenated for 20 h at 170–260 °C under pressure of 30 atm. The resulting product with $M_n \cong 10^4$, soluble in tetralin, is polyethylene.[180,181] A residual absorption in the region of 965 cm^{-1}, corresponding to the deformation vibrations of the C–H group and the double bond, is observed in the IR spectra. The presence of a doublet in the regions of 720 and 730 cm^{-1}, corresponding to the vibrations of the CH_2 group, makes it possible to estimate the degree of crystallinity of the specimen, which is approximately 50%. It has been suggested that a linear product is formed in the synthesis of PA in the presence of a Ziegler–Natta catalytic system,[180,182] but the considerable scatter of the yields of the soluble hydrogenation products (from 5 to 80%) suggests the appearance of cross-links in the course of the segregation of the PA.[181]

The melting point of the soluble fraction of the polyethylene obtained is 118–122 °C, the molecular weights are $\overline{M}_w$ = 6000 to 7000 and $\overline{M}_n$ = 14 100–18 700, and the ratio of the number-average and weight-average molecular weights in different specimens varies from 2.4 to 3.14.[124,130,180] Although the form of the molecular weight distribution does not change on hydrogenation of PA in the temperature range 195–260 °C,[180] nevertheless this does not rule out the possibility of cross-linking in the course of the hydrogenation process and also of the degradation of the polymer chain.

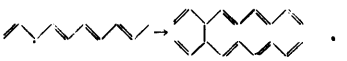
According to data obtained by the radioisotope method, the molecular weight of PA varies from 2.2×10^4 to 7.7×10^4 when the temperature of the synthesis is changed from –7° to 25 °C.[34] Polyacetylene with an end group containing tritium or labelled carbon can be obtained by adding an excess of CH_3OT or carbon-labelled CO_2 to the reaction system after the synthesis.[34,183]

Soluble derivatives of PA can be best obtained by chlorinating freshly prepared specimens in suspension in chloroform or carbon tetrachloride at low temperatures.[79] The molecular weight of the chloroform-soluble fraction of the polymer synthesised in the presence of the $Ca(NO_3)_2-NaBH_4$ catalyst is 10^4.[79] Chlorination of the freshly prepared PA suspension at low temperatures makes it possible to reduce the contribution of the possible degradation processes. However, in this case the scatter of the yields of the soluble products is observed, which is a consequence of the occurrence of secondary cross-linking processes in the ageing of the polymer. The soluble fraction of the chlorinated PA diminishes appreciably after the *cis–trans* isomerisation.[74,134]

PA can be cross-linked via the Diels–Alder reaction,[27]



or as a result of the recombination of the radical centres formed in the *cis–trans* isomerisation:



The first process is indicated by a decrease in the amount of the soluble fraction of the chlorinated polymer during the ageing of PA. The probability of the second process increases in thermal or photochemical isomerisation.[79] On oxidation or reduction of the cross-linked polymers, there is a possibility of the formation of structures of the type of Hafner salts.[27,184] The possibility of cross-linking in the course of *cis–trans* isomerisation when unpaired spins appear has been confirmed by quantitative quantum-chemical calculations for a modified diatomic overlap.[74] Attempts have been made to find a correlation between the structural defects in *trans*-PA associated with the cross-links and the vibrational spectra.[38] The attempts to characterise PA in terms of the conjugation length have shown that specimens synthesised in different laboratories have different distributions even when the same method is used. According to Raman or IR spectroscopic data, the breakdown of conjugation is not associated with oxidation in the presence of cross-links.[185] It has been suggested that this is explained by conformational defects (for example, the twisting of the chains) or the inclusion of *cis*-units in the *trans*-chain of the polyene.[185] The appearance of cross-links diminishes the length of the conjugated sections and influences greatly the mechanical and electrophysical properties of PA.[134]

Another defect influencing the properties of PA arises on partial reduction of the double bond. NMR studies using PA enriched in the ^{13}C isotope made it possible to observe a weak signal in the region of 47 p.p.m., which was attributed to methylene groups; the concentration of the latter was 3–4 mole per cent.[15] The possibility of the reduction of double bonds is also indicated by the elemental composition of PA obtained in the presence of Ziegler–Natta catalysts ($CH_{1.03}$): according to different data, the H : C ratio varies in the range from 1.01 to 1.09.[186] The signal due to the CH_2 groups is particularly strong in the ^1H NMR spectra of chlorinated PA in the range 1.2–1.6 p.p.m. Partial reduction of PA can occur even during synthesis in the presence of both Ziegler–Natta catalysts and Group VIII metals. This has also been confirmed by the results of the ozonolysis of *cis*- and *trans*-PA. The final product of the hydrolysis of the *cis*- and *trans*-isomers is the ester $CH_3COO-COOCH_3$ formed in 98.55–99.52% yield, which confirms the linearity of the structure.[73] The presence of the hydrogenated $-CH_2-CH_2-$ units and also of cross-links leads to the formation, after treatment with diazomethane, of additional esters, $CH_3OOCCH_2COOCH_3$ and $CH_3.COOCH_2COOCH_3$, in yields of 0.1–0.5 and 0.23–1.04% respectively.[73] Bearing in mind the high reproducibility of the experimental results, one can assume that an increase in the number of cross-links by a factor of 2–4 occurs during polymerisation. The appearance of defects in the PA structure, including the formation of cross-links and the occurrence of sp^3-hybridisation is indicated also by X-ray diffraction data.[39,187]

The study of electron diffraction and X-ray diffraction analysis of thin oriented PA films have revealed the presence of an orthorhombic unit cell and orientation of the chain axis along the fibrils.[185,188] In the crystalline state, the *cis*- and *trans*-isomeric forms of the chain have different symmetries and repeat distances of 4.36 Å for four CH groups and 2.46 Å two CH groups respectively. It follows from the analysis of the intensity integrals for the powder X-ray diffraction patterns in the crystalline and amorphous regions that the degree of crystallinity of the films is 70–90%. The diffuse halo (at about 4.0 Å) is close to the strong interplanar reflections at 3.81 Å for the *cis*-structures and at 3.72 to 3.56 Å for the *trans*-structures. The disorder in the amorphous region is caused by the chain ends and the sp^3-hybridisation of the carbon atoms. It follows from X-ray diffraction data that the *trans*-cell contain 7% of the structure

of the disordered *cis*-cell and that in the film there are no isolated amorphous or crystalline regions, although a PA structure with single crystals incorporated in the polymer matrix has been proposed.[27]

Doping leads to the formation of new crystal structures inserted between the planes of the initial lattice, whose contribution depends on the diameter of the fibrils, the number of cross-links, the size of the dopant, etc. The inhomogeneity caused by the slow diffusion of the dopant in the fibril also influences the final crystal structure of PA. The distances between the inclusions of the dopant, which is believed to aggregate into packs along the same axis, is between 20 and 60 Å.[187] The interplanar spacings, which are 7.95 Å for I_3^-, 8.3 Å for ClO_4^-, and 9.3 Å for $FeCl_4^-$, can be interpreted as the distances between two dopant-enriched planes separated by PA chains.[187] The X-ray diffraction parameters for different types of PA obtained by the method described above (Table 3) differ somewhat; this is associated with the nature of the catalytic system used and with the method of preparation of the specimens for the investigations. The apparent size of the crystallites, determined from the width of the reflections for PA obtained in the presence of Ziegler catalysts, is 60 Å;[189] for the PA obtained in the presence of Group VIII metals, it reaches 100 Å and more.[178,179]

Table 3. The unit cell parameters of polyacetylene.

Catalyst	Unit cell parameters, Å			Crystal system	Refs.
	a	*b*	*c*		
cis-PA					
$Ti(OBu)_4$—$Al(C_2H_5)_3$	7.68	4.46	4.48	orthorhombic	[6, 190]
»	7.61	4.47	4.39	»	[191]
»*	7.74	4.32	4.47	»	[67, 85]
$Co(NO_3)_2$—$NaBH_4$*	7.76	4.32	4.47	»	[27]
$TiO(Bu)_4$—$Al(C_2H_5)_3$**	5.12	—	4.84	hexagonal	[129]
trans-PA					
$Ti(OBu)_4$—$Al(C_2H_5)_3$	7.32	4.24	2.46	rhombic	[188]
»***	4.24	7.32	2.46	monoclinic	[39]
$Co(NO_3)_2$—$NaBH_4$	5.62 (6.62)	4.92	2.59	orthorhombic	[79, 142]
Poly-BTFM	7.32	4.24	2.46	monoclinic	[56]
Catalyst based on lanthanide metals	5.08	5.44	9.52	rhombic	[192]

*According to electron diffraction data.
**Block-copolymers of the single crystal.
***Oriented films.

The morphology of PA has been mainly investigated using scanning electron microscopes, but more extensive information has been obtained on high-resolution transmission microscopes.[193] The formation of lamellar particles of irregular shape and with a thickness of 50–100 Å, which, by joining together, form loose fibril-like structures where the chain axes are perpendicular to the fibril axes, has been noted by Wegner and co-workers.[27,79,85,194] However, it was subsequently shown fairly convincingly by electron diffraction and scanning microscope methods that the chain axes in the films are parallel to the axes of the fibrils.[190,191] It is essential to note that the study of the morphology of PA by transmission or scanning electron microscopy makes it necessary to master a fine technique of the preparation of the specimens; the frequently observed "kebab" structures[188] or lamellar formations, thickened regions comprising knots of individual fibres and appearing on doping, as well as the "string of pearls" effect are usually associated with the metal deposition technique (Au:Pd).[195] The conditions leading to photographs in which the initial morphology is masked have been discussed. The size of the fibrils can be diminished by carrying out the polymerisation in the presence of various copolymers, which prevent their formation. The morphology of PA changes in the doping process and a new highly crystalline structure appears. The pattern in the distribution of iodine, used as the dopant, indicates the absence of the segregation of particles.[196]

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The dependence of the PA structure on the composition and concentration of the catalyst, the reaction temperature, and the nature of the monomer gives rise to the hope that the possibilities for the synthesis of polymers of this class are still far from being exhausted. Further development of the synthesis of polymers of the acetylene series will depend on the practical requirements which they will have to meet in the creation of specific instruments or devices

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