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Polymerisation of Acetylenes. The Structure and Electrophysical Properties of Polyvinylenes

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The literature data on the radical and ionic linear polymerisation of mainly mono- and di-substituted acetylenes with a single carbon-carbon triple bond are considered and the known mechanisms of the acetylene polymerisation processes are discussed. Much attention is devoted to the copolymerisation of acetylenes with monomers of different types. The results of studies on molecular, supermolecular, and electronic structures of polyvinylenes are compared with their electrophysical properties. The bibliography includes 475 references.

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I. INTRODUCTION

There has been a considerable growth of interest in recent years in the study of the polymerisation reactions of acetylenic compounds which make it possible to synthesise linear and cyclic compounds with a wide variety of structures. Different aspects of the problem have been described in a number of reviews and monographs[1-25].

The aim of the present review is to consider the latest advances in the synthesis of linear polymers based on mono- and di-substituted acetylenic monomers with a single C≡C bond. A review of studies on the polymerisation of diacetylenes was published previously[26]. To facilitate the description and in view of the fact that the polymerisation mechanism has not been established in many cases, a systematic account is given of the available data in accordance with the initiator or catalysts employed in the synthesis of the polymers.

The unusual features of the reactivities of alkynes are determined largely by the high electron density in the triple bond, the cylindrical symmetry of the electron distribution relative to the molecular axis, and the weak polarisability of π electrons, which hinders electrophilic attack and facilitates nucleophilic attack on the triple bond[27]. Because of the above characteristics, alkynes readily form π complexes[15] and metal acetylides[15,27]. Thus one may expect the polymerisation of alkynes to occur most readily under the influence of anionic and complex catalysts based on transition metal compounds. On the other hand, one should bear in mind that the ease of elimination of the acetylenic proton promotes chain termination and transfer, while strong bases induce the acetylene–allene rearrangement[27,28].

The relative weakness of the multiple carbon–carbon bonds compared with a single bond is the driving force of the polymerisation of unsaturated compounds. The polymerisation usually leads to a decrease of entropy and sometimes also the enthalpy of the system[29]. In the polymerisation of acetylenes, the change in the enthalpy of the system is a consequence of the replacement of the triple bonds by the more stable double bonds and the stabilisation of the resulting polyconjugated system[30]. The conjugation energy per unit in the polyvinylene (polyacetylene) chain is a function of the number of units and increases continuously up to the limiting value of 0.55 β, where β is the resonance integral or 10 kcal. The overall enthalpy of polymerisation of acetylene to give a polymer stabilised by conjugation should be 46 kcal mole^{-1}.[31] According to an estimate[30], the negative entropy of polymerisation of acetylene is −34.5 e.u.

II. RADICAL POLYMERISATION

1. Thermal Initiation

The reactions of phenylacetylene (PA) have been investigated in greatest detail. From approximately 120°C, amorphous, soluble, and coloured linear polyene is formed from PA (together with 1–25% of triphenylbenzenes)[32-41]. The molecular weight of the polymer $\overline{M}_n$ depends little on the polymerisation conditions[33,42]. An approximately twofold increase of the number-average degree of polymerisation (up to $\overline{P}_n = 26$) has been observed in the polymerisation of PA in the presence of polyphenylvinylene (poly PA) obtained beforehand[43,44]. The polymerisation of PA under pressure (80–200°C, 1000–6000 atm) proceeds at a much higher rate than under normal pressure, but the degree of polymerisation hardly changes[45,46].

The thermal polymerisation of PA can be explained satisfactorily in terms of a bimolecular initiation mechanism[36,37]. It is believed that there is a possibility of the formation under these conditions of the two most stable biradicals: triplet (*trans*-1,4) and singlet (*cis*-1,3). The first leads to mainly the chain propagation of the linear polymer and the second the formation of triphenylbenzenes. The polymerisation reaction is of second or higher order with respect to the monomer (2 in nonane and cyclohexane[37,47], 2.20 in xylene[36], and 2.32 in benzene[48]). The deviation towards the trimolecular reaction is probably associated with the formation of considerable amounts of cyclic trimers on bimolecular initiation and first-order termination. The rate of polymerisation in bulk is proportional to the concentration of PA, possibly in consequence of the gel effect. The activation energies for the polymerisation process E_a are respectively 26.8 and 33.67 kcal mole^{-1} in bulk[36] and in solution[37,47]. The termination of the growing macroradical probably occurs

via degradative chain transfer to the monomer. Chain termination in the course of intramolecular cyclisation has also been postulated[47].

Pyridylacetylenes[49] and 5-ethynyl-2-methylpyridine polymerise similarly to PA.[36] The polymerisation of 5-ethynyl-2-methylpyridine[36] (125–175°C, solution in *p*-xylene) is of second order with respect to the monomer (E_a = 20.4 kcal mole^{-1}).

A soluble polymer with $\overline{M}_n$ = 950 has been obtained from *p*-dimethylaminophenylacetylene (150°C, 24 h) in 66.5% yield; *p*-nitrophenylacetylene (200°C, 4 h) gives rise to a partly soluble polymer in 97% yield and *o*-nitrophenylacetylene polymerises explosively at 150°C.[50] The polymerisation of *o*- and *p*-nitrophenylacetylenes takes place under the influence of cold plasma[51].

Acetylenic derivatives of condensed aromatic hydrocarbons (ethynylnaphthalene[52], 9-ethynylanthracene[53], 9-ethynyl phenanthrene[54], 5-ethynylacenaphthene[55], the 1,2-dihalogenoacenaphthylene dehydrohalogenation product[56], and *N*-ethynylcarbazole[57]) polymerise comparatively readily at 100–220°C (9-ethynylanthracene even at room temperature).

Under normal pressure, propargyl alcohol does not polymerise up to 200°C, but at an elevated pressure (6000 atm) it is converted into a polyene in 11% yield at a temperature as low as 120°C.[58] With increase of temperature, the yield of the insoluble product formed as a result of cross-linking via intermolecular elimination of water also rises. Intramolecular and intermolecular cross-linking processes have also been observed in the polymerisation of propiolic acid under pressure[59–61]. The polymerisation of the ethers formed by the interaction of propargyl alcohol with phenol and its *m*-methyl- and *p*-*t*-butyl derivatives takes place with an induction period, which diminishes with increase of reaction temperature (45 h at 160°C, 1 h at 250°C) and leads to low-molecular-weight products[62]. *N*-Propargylmorpholine also polymerises with an induction period[63]. With increase of the length of the alkyl group, the yield of poly-(*N*-alkyl-*N*-propargylamines) (polymerisation in bulk at 200–250°C, $\overline{P}_n$ = 5–9) diminishes, probably owing to a steric effect and a change in the polarisability of the triple bond[64].

A substituted polyene with $\overline{M}_n$ = 2700 is formed from ethynyltriphenylgermane at 180°C.[65]

Phenoxyacetylene polymerises spontaneously even at room temperature. The resulting polyene chains are cross-linked via a Diels-Alder reaction to hydroaromatic derivatives, which are aromatised by the elimination of phenol[66]. E_a 23.1 kcal mole^{-1} for phenoxyacetylene and free-radical initiators do not influence its spontaneous polymerisation[67,68]. Phenylthioacetylene is less reactive and *p*-nitrophenoxyacetylene is much more reactive in polymerisation than phenoxyacetylene[67,68]. The structures of the polymerisation products of 2-methoxy-1-phenylacetylene[66] and ethoxyacetylene[66,69] have not been determined.

In contrast to arylacetylenes, alkylacetylenes polymerise under more severe conditions[46,70,71]. Cyclohexylacetylene oligomers with $\overline{M}_n$ = 400–500 (E_a = 32.7 kcal mole^{-1}) have been obtained at a temperature in excess of 230°C.[70] It has been suggested[72] that the thermal polymerisation of alkylacetylenes occurs only in the presence of an admixture of allenes, which initiate the process. But-2-yne gives rise (250°C, 23.5 kbar) to an insoluble resin containing non-conjugated double bonds according to infrared spectroscopic data, which may indicate the formation of a ladder structure[73].

Disubstituted acetylenes polymerise at higher temperatures than the monosubstituted derivatives. For example, tolane polymerises at 300–400°C [74,75] and $\overline{M}_n$ for the polymers increases from 850 to 1200 when the temperature rises from 300 to 400°C. A bimolecular initiation mechanism has been suggested.

The dimethyl and diethyl esters of acetylenedicarboxylic acid polymerise at temperatures in excess of 200° and 300°C respectively[76]. The polymerisation of β-iodophenylacetylene is extremely complex and is accompanied by the evolution of iodine[77,78].

When diiodo and dichloro-maleic anhydrides or diiodo-*N*-phenylmaleimide were dehalogenated, the products were polymers resulting from the dissociation of the triple bond in the hypothetical anhydride of acetylenedicarboxylic acid or its analogue[79].

2. Polymerisation in the Presence of Initiators

The initiated radical polymerisation of acetylenes has no advantages over the purely thermal process. This is indicated by the extremely limited selection of initiators, a significant contribution of thermal processes in many instances, hindering the study of the reaction kinetics, the low conversion of the monomer, the low molecular weight of the resulting polymer, and the contamination of the polymer by the initiator decomposition products.

The initiators employed were benzoyl peroxide (BP),[45,80–111] lauroyl peroxide[88,112], t-butyl peroxide[45,58,107–110], azobisisobutyronitrile (ABIN),[45,89–94,96–98,100–102,104–106,111–118], triisobutylboron[45], triisopropylboron[43,44,112,119–122], and triethylboron[123]. The benzoyl peroxide initiator does not undergo simple thermal dissociation (60–80°C) and is involved in a chain reaction with monomer molecules. It has been shown for PA [84,124] that two radicals are formed under these conditions, one of which propagates the polymerisation and the other abstracts hydrogen from the monomer with formation of benzoic acid and an inactive radical; this is confirmed by the kinetics of the decomposition of benzoyl peroxide in PA, deuterophenylacetylene, and methylphenylacetylene. ABIN does not undergo chain decomposition in the presence of PA.[111] The formation of isopropyl hydroperoxide on polymerisation of PA in the presence of triisopropylboron and oxygen appears to indicate a radical process mechanism[119]. In the absence of oxygen, PA does not polymerise under the influence of triethylboron.

The rate of polymerisation of PA is proportional to the concentration of the monomer and the initiator (benzoyl peroxide), one polymer molecule being formed on decomposition of one peroxide molecule[84,85]. With increase of temperature (60–130°C), the rate of polymerisation rises appreciably and $\overline{M}_n$ varies in the range 600–1500.[85] It is suggested[125] that E_a for the radical-initiated polymerisation of acetylenes should equal the decomposition energy of the initiator (about 21 kcal mole^{-1} in the polymerisation of PA).

Benzoquinone inhibits the polymerisation of PA under the influence of benzoyl peroxide, which is probably associated with the suppression of the above initiation reaction by benzoquinone[84]. On the other hand, benzoquinone apparently does not inhibit the growing radical, since the radiation-induced and ABIN-initiated polymerisation of PA proceeds also in the presence of benzoquinone[111]. The rate of polymerisation of PA in the presence of triisopropylboron is of first order with respect to the monomer. The initiator concentration hardly affects the yield of the polymer, which is strongly influenced by the reaction temperature. The break in the $\lg k - 1/T$ curve,

where k is the effective polymerisation rate constant, corresponds to activation energies of 78 and 29 kcal mole^{-1}, which has not been explained[43,119,120,122].

The rate of polymerisation of ethynylferrocene in the presence of benzoyl peroxide, lauroyl peroxide, and triisopropylboron in bulk at 140–200°C is proportional to the monomer concentration and $E_a \simeq 10$ kcal mole^{-1}. Up to 190°C, the concentration of benzoyl peroxide (0.2–1.6%) does not affect the yield of the polymer. The conversion passes through a maximum at 190°C and for soluble fractions $\bar{P}_n = 4$–7.[86,87,112] In contrast to benzoyl peroxide[126], t-butyl peroxide did not oxidise ethynylferrocene and did not cause the degradation of the polymer under the conditions employed (160–180°C; molar ratio initiator : monomer = 0.25 : 1).[107–110] It is suggested that the radical formed on decomposition of the initiator abstracts from the monomer the mobile acetylenic hydrogen. The monomeric radical is stabilised in the form of the dimer (diferrocenylbutadiyne) which polymerises and is methylated owing to the decomposition of some of the butoxy-radicals.

It has been shown for 1-chloro-1'-ethynylferrocene[88] that the chlorine atom located in a heteroannular position relative to the ethynyl group greatly reduces the capacity of the monomer for polymerisation. A linear polyene structure, which may be crossed-linked via chlorocyclopentadienyl rings, has been proposed for the polymer.

Propiolaldehyde polymerises via the mechanism[114]

$$n\mathrm{HC{\equiv}C{-}CHO} \xrightarrow[1.9\%]{\text{AIBN } 60^\circ,\ 19\text{h}} -[-\mathrm{HC{=}C(CHO){-}}]_n- \ .$$

Propargyl acrylate[89–93], methacrylate[90–92], crotonate[92], itaconate[91], and acetate[94] were polymerised in bulk and in solution under the influence of ABIN and benzoyl peroxide at 60–80°C. For the first three monomers, the rate of reaction is proportional to the initiator concentration raised to a power of 0.7 and 0.8 in the presence of benzoyl peroxide and ABIN respectively and to the monomer concentration raised to a power of 1.6 in both cases; E_a = 16–21 kcal mole^{-1}. For conversions up to 20–30%, polymerisation takes place via the dissociation of the double bonds, after which the triple bonds also react with the consequent formation of three-dimensional systems.

Vinylacetylene polymerises in the gaseous state at 250–400°C in the presence of small amounts of oxygen[127,128]. The rate of reaction is proportional to the monomer concentration raised to the power 1.94; E_a = 25.3 kcal mole^{-1}. The polymerisation of vinylacetylene in the presence of benzoyl peroxide takes place in a more complex manner[80,81]. Oligomers (ABIN; $\bar{P}_n = 4$–15) of divinylacetylene were obtained; oxygen accelerates the process and oxidises the polymer[116,117].

Numerous studies have been made on the polymerisation of ethynyldimethylvinylmethanol and its esters and ethers. Polycyclobutene[1,5,129] or polycyclopentene[11,94–104,118] structures, resulting from cyclopolymerisation involving the double and triple bonds, were proposed for the resulting polymers. Other investigators believe that the polymerisation proceeds only with participation of the double bonds[105,106] or with participation of the double bonds in the isopropenylacetylene series and with formation of cyclopentene rings in the vinylacetylene series[130].

A soluble polytolane was obtained in low yield under the influence of a shock wave. It is suggested that this involves a special type of polymerisation—"polymerisation in the shock wave"[131].

3. Radiation-Induced Initiation and Photoinitiation

The radiation-induced polymerisation of PA has been investigated in greatest detail. It has been carried out over a wide range of temperatures (between −196° and 100°C) in bulk and in solution under the influence of initiating radiation at different dose rates (36–10^6 r min^{-1}) and over a wide range of doses (10^6–10^8 r). Radiation polyPA—a yellow-orange amorphous product, soluble in many organic solvents, with a softening temperature of about 200°C, and with $\bar{M}_n \simeq 1200$—was obtained in a yield of 10–12%. The radiation-chemical yield of the polymer G (the number of polymerising monomer molecules per 100 eV) is 8–9 [124,125,132–134] for irradiation with accelerated electrons (1.6 M eV) and 8–13, [135,136], 13–30, [137] and 30–40 [138] for irradiation with cobalt-60 γ-rays.

The mechanism of the radiation-induced polymerisation of PA is determined largely by the process temperature. Gol'danskii and coworkers[124,125,132–134] suggested that PA polymerises via a radical mechanism in both liquid and solid phases. Japanese investigators[118] believe that ionic polymerisation takes place at low temperatures; the possibility of an "electronic" mechanism is not ruled out either[139].

The rate of polymerisation of PA is proportional to the rate of initiation, i.e. to the dose rate. The same dependence has been observed in the polymerisation of propiolic acid and its salts[60,140–143], propargyl alcohol[138,144–146], and propargyl bromide[138,148,149]. This indicates the absence of bimolecular termination of the macroradicals when a radical process mechanism is postulated, which can be accounted for by the loss of activity by the growing radical owing to the increase of the degree of delocalisation of the unpaired electron. Instead of separating the chain propagation and termination reactions, it was suggested that a single polymer chain "decay" process be considered[125]. Subsequently this hypothesis was refined; the importance of the mobile acetylenic hydrogen, terminating both the material and the kinetic chain in consequence of the formation of an inactive radical, was noted[134]. Another important characteristic of the radiation-induced polymerisation of PA is the low value of E_a (~700 cal mole^{-1}) and hence the virtual independence of the rate of the process of temperature, which is characteristic of the ionic polymerisation of olefins.

In the presence of oxygen, the yield of polyPA increases by a factor of 1.2–2.[120,132,133] The polymerisation is not inhibited by radical process inhibitors (benzoquinone), possibly owing to the fact that the interaction of the inhibitor with radicals at a high steady-state concentration, i.e. with delocalised macroradicals which have lost their activity, is the most likely process. When PA was polymerised in solution in nonane or ethyl acetate, an appreciable deviation from additivity was noted, which indicates an effective transfer of the irradiation energy absorbed by the solvent to the monomer[124,132]. A specific feature of the polymerisation of PA in the liquid phase is the independence of the yield of the polymer of dose rate (for a given dose)[125], which is characteristic of the radiation-induced solid-phase polymerisation of vinyl monomers. For polyPA's, $\bar{M}_n$ is almost independent of the polymerisation temperature, the rate of initiation, the form of the initiating radiation, the monomer concentration, and the phase state. The use of radiation-induced initiation made it possible to graft PA to fibreglass[149].

The radiation-induced polymerisation of alkylacetylenes (propyne, hex-1-yne, oct-1-yne, and cyclohexylacetylene) proceeds similarly[124,132–135]. The rate of reaction is

proportional to the dose rate: $E_a \simeq 1$ kcal mole^{-1} and $\bar{P}_n = 10-13$. A white insoluble thermostable polymer, resistant to the action of concentrated acids and alkalis, was obtained in the polymerisation of perfluorobut-2-yne under the influence of cobalt-60 γ-radiation[150] or electrons with energies in the range 0.5–4 MeV.[151]

Radiation-induced initiation has many advantages compared with thermal initiation and photoinitiation in the case of propiolic acid and its salts (fewer side reactions, the radiolysis of the monomer does not exceed 1–1.5%).[60,140-143] For a dose of 124 Mr about 30% of amorphous polymeric acid with $\bar{M}_n = 3000$ and $G = 35-40$ is formed. According to infrared spectroscopic data, the *trans*-transoid configuration of the polyene chain arises in solid-phase polymerisation and the *trans*-cisoid configuration arises in liquid-phase polymerisation. At −196°C polymerisation does not occur and, on increase of temperature to between −120° and −100°C, postpolymerisation is observed. The reactivity of propiolate salts is determined by the stability of the crystal lattice (the radius and valence of the cation).

In the study of the radiation-induced polymerisation of 59 different acetylenic monomers, polymeric products were obtained only from acetylenedicarboxylic acid and neopentylene dipropiolate[13].

An ethynylferrocene polymer with $\bar{M}_n = 1000-3000$ was obtained in a yield of about 4% (γ-irradiation, 270 Mrad).[152]

The photopolymerisation of PA,[153] methyl 4,4-dimethylpent-2-ynoate[154], tolane[155], and propargyl bromide[148] has been investigated very inadequately.

III. IONIC POLYMERISATION

1. Cationic Polymerisation

An unsuccessful attempt to polymerise vinylacetylene and 3-ethylvinylacetylene in the presence of BF_3 and $AlCl_3$ was reported in 1959.[156] However, later it proved possible to polymerise both vinylacetylenes RC≡CCH=CH$_2$†, where R=R, Et, Me$_2$(OMe)C, or CH$_2$=OMe [BF_3,[157,158] BF_3.OEt$_2$,[159-161] CCl_3COOH,[158,161] CF_3COOH,[158] H_2SO_4,[159] and $SnCl_4$ [159,160]] as well as other acetylenic monomers: pent-1-yne [$SnCl_4$ [162]], phenylacetylene [BF_3,[163] BF_3.OEt$_2$,[39,164] CF_3COOH,[39,164] CCl_3COOH,[155,166] $SnCl_4$,[162] and AlX_3 with $X_3 = Cl_3$, $EtCl_2$, Et_2Cl, or Et_3 [167]], 9-ethynylanthracene [$TiCl_4$ [53]], *p*-methoxyphenylacetylene [BF_3.OEt$_2$ and CF_3COOH [38,164]], Me$_2$NC≡CC(O)R with R = H or Me [$TiCl_4$, $SnCl_4$, H_2SO_4, HBF_4, BF_3.OEt$_2$, Et$_3$N.HBr, or CF_3COOH [168]], and ROC≡CH with R = Me, or iso-Bu [Friedel-Crafts catalysts[169]].

In the reaction of acetylene containing a powerful electron-accepting substituent (NC−C≡CH) using $TiCl_4$, Co(Acac)$_3$ (Acac = acetylacetone), and $AlEt_3$ as catalysts, a polymer is formed only in the last case, its yield being much lower than in the Ziegler polymerisation[169]. PA reacts with $SnCl_4$ to form a stable complex; polymerisation takes place after the addition of hydrochloric acid, which behaves as a cocatalyst[162].

The main product formed in the reaction of PA in the presence of CCl_3COOH (in benzene at 30–55°C) is 1-phenylvinyl trichloroacetate formed as a result of the addition of CCl_3COOH to the C≡C bond of the monomer. Acetophenone and about 3% of a low-molecular-weight linear polymer with a conjugated system were also detected.

† The catalysts are indicated in square brackets.

It has been suggested[165] that the catalyst participates in the reaction in a dimeric form $(HA)_2$ and forms with the monomer an intermediate of the solvated ion pair type (A = anion):

$$HC{\equiv}CPh + 2\,(HA)_2 \rightleftarrows (CH_2{=}\overset{+}{C}PhA^-HA)\cdot(HA)_2.$$

This ion pair leads to the formation of low-molecular-weight products and initiates the polymerisation of PA:

$$(CH_2{=}\overset{+}{C}PhA^-HA)\cdot(HA)_2 + HC{\equiv}CPh \rightarrow (CH_2{=}CPhCH{=}\overset{+}{C}PhA^-HA)\cdot(HA)_2;$$
$$(CH_2{=}CPh{-}[{-}CH{=}CPh{-}]_n{-}CH{=}\overset{+}{C}PhA^-HA)\cdot(HA)_2 \rightarrow$$
$$\rightarrow (CH_2{=}CPh{-}[{-}CH{=}CPh]_{n+1}A + (HA)_2 + HA.$$

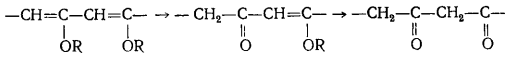
The reaction of PA with CCl_3COOH in nitroethane solution is of first order with respect to the monomer and of third order with respect to the catalyst, about 15% of a linear polymer with $\bar{P}_n = 5-10$ being formed together with acetophenone (about 85% of the reaction product)[166]. The lifetime of the ionic substances involved in the reaction in benzene is probably much shorter than in nitroethane.

An analogous linear polymer was also obtained in the polymerisation of PA in the presence of BF_3.OEt$_2$ or CF_3COOH in methylene chloride[39,164]. Here $E_a = 9.7$ kcal mole^{-1} at 0° and 25°C and is independent of the molar ratio of the catalyst and the monomer. In the chain termination reaction, the polymer forms a protonated 1 : 1 complex with an excess of the acid as a result of the interaction of the polymeric cation with the CF_3COO^- counter-ion or another proton transfer reaction. The formation of the complex together with the dependence of the rate constants for the elementary reaction steps (with the exception of initiation) on the length of the polymer chain[39] constitutes the main difference between the polymerisation of PA and that of vinyl monomers.

When PA was polymerised under the influence of BF_3 at room or a reduced temperature in n-hexane, methylene chloride, or 2-bromopropane, a fraction partly soluble in organic solvents was obtained together with a soluble fraction having $\bar{M}_n \simeq 3000$. A linear structure was attributed to both fractions on the basis of infrared spectroscopic data[163]. A linear polymer with $\bar{M}_n = 1000-2000$ was also obtained in the polymerisation of PA in the presence of $AlHal_nR_{3-n}$ in solution or in a suspension in toluene at 30°C [167] or in solution in n-hexane in the presence of $TiCl_4$.[170] The activity of $AlCl_nR_{3-n}$ falls to zero in consequence of the decrease of its electrophilic properties when $n \rightarrow 0$. The yield of the polymer, amounting to 18, 39, and 55% in polymerisation in methylene chloride in the presence of $AlBr_3$, $TiCl_4$, and BF_3 fell when the reaction was carried out under the influence of BF_3.OEt$_2$, $SnCl_4$, and VCl_3 and also in solution in hexane.

In the presence of BF_3.OEt$_2$, *p*-methoxyphenylacetylene forms polymers giving rise to protonated complexes on reaction with an acid. When CF_3COOH was used, only low-molecular-weight products were obtained[38,164]. In the polymerisation of 9-ethynylanthracene, the conversion of the monomer and $\bar{M}_n$ of the products increase with the temperature of the synthesis (the experiments were performed at approximately 20°C and at −70°C).[53] In the course of polymerisation, the active centre isomerises, which leads to the appearance in the polymer chain of allenic 1,6- units and structures (apart from the main 1,2-structures) formed via the Diels–Alder reaction between the growing end of the macromolecule and the initial monomer.

In ether, hexane, or methylene chloride at −78°C, alkoxyacetylenes give rise to linear oligomers with $\bar{M}_n$ = 500–600, which are converted into polyketones on subsequent treatment with hydrochloric acid[169]:



Vinylacetylene and its derivatives polymerise[157-161] as a result of the simultaneous dissociation of double and triple bonds with formation of ladder polymers, while only double bonds are involved in the radical process.

The decrease of the reaction rate with time, usually observed in the cationic polymerisation of acetylenes, is not associated with side reactions of the monomer and is due to the deactivation of the catalyst on formation of the catalyst–polymer complex[171]. Because of this, the polymerisation is carried out in the presence of large amounts of catalyst or at elevated temperatures, which promote the dissociation of the complex.

2. Anionic Polymerisation

As noted above, the tendency of alkynes to interact with nucleophilic agents should make them more reactive in anionic polymerisation compared with radical and cationic polymerisation. This is confirmed by the anionic polymerisation of tolane under mild conditions[172], while its thermal polymerisation produces a polymer only at high temperatures[74,75]. Activated electrophilic acetylenes (hexafluorobut-2-yne[173-177], methyl esters of propiolic[178,179], acetylenedicarboxylic, and phenylpropiolic acids, ethyl tetrolate[179], acetylpropiolic anhydride which polymerises also in the presence of alkali[179,180], cyanoacetylenes[181-184], dicyanoacetylene[185], propiolaldehyde[186], propiolamide, tetrolamide, and *N*-methylpropiolamide[187]) polymerise even under the influence of weak nucleophilic agents such as cyanide, thiocyanate, and halide salts.

With increase of the electrophilicity of the substituents at the triple bond (phenylpropiolonitrile[188], cyanoacetylene[181-184,189], and dicyanoacetylene[185,190]), the reactivity of the monomers rises: phenylpropiolonitrile does not change in the presence of tertiary amines, while dicyanoacetylene polymerises readily in their presence even at −73°C.

A method has been proposed for the polymerisation of dialkylamides of acetylene-α-carboxylic acids having the general formula $RC{\equiv}CC(O)NR'_2$ (propiolic or tetrolic acid is best) in aprotic solvents [dimethylformamide (DMF), dimethyl sulphoxide (DMSO), or hexamethylphosphoramide (HMPA)] in the presence of 5–10 mole % of PhSNa, t-BuOK, and tertiary amines with formation of polymers having $\bar{M}_n$ = 2000–3000.[191] The introduction of electron-donating substituents into the propiolamide molecule decreases the reactivity of the monomer; only resinous substances are formed as the products[187].

The reactivity of alkynes has been found to decrease in the following sequences:

$$HC{\equiv}CH > MeC{\equiv}CH > EtC{\equiv}CH^{192} \text{ and}$$
$$MeOOCC{\equiv}CCOOMe > HC{\equiv}CCOOMe > MeC{\equiv}CCOOEt > PhC{\equiv}CCOOMe^{179}.$$

The dimethyl ester of acetylenedicarboxylic acid polymerises even in the presence of a weak nucleophilic agent such as Cl^-, while the methyl ester of phenylpropiolic acid forms a polymer in approximately 1% yield only in the presence of PhSNa.

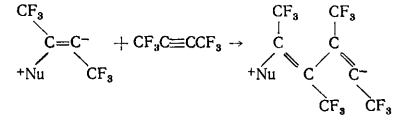
Together with the formation of a linear polyene, the occurrence of cyclotrimerisation processes has been noted[178,188,193-195]. A cyclic trimer is formed on polymerisation of propiolonitrile in the presence of BuLi, but not when sodionaphthalene is used[188]. For the ratio PA : n-BuLi > 20 in HMPA, triphenylbenzene was obtained instead of the linear polyPA.[195]

The polyene structure $-[-CH{=}C(CONH_2)-]_n-$ (polymerisation in bulk in the presence of triethylamine[189]) as well as the heterochain structure $-[-CH{=}CHCONH-]_n-$ (polymerisation in DMF solution in the presence of anhydrous NaCN[187]) has been proposed for polypropiolamide. The structure of polymers corresponding to the dissociation of monomer triple bonds only and analogous to the first of the two described above is produced on polymerisation of the dialkylamides of tetrolic and propiolic acids[196]. In this case the formation of a heterochain polymer is impossible owing to the absence of a mobile hydrogen atom in the amide group. Propiolaldehyde may be converted both into the copolymer $-[-HC{=}C(HCO)-]_x-[-OCH(C{=}CH)-]_y$ (at −40°C in the presence of NaCN in DMF[186] or at 0°C in the presence of pyridine in THF[114]) and into the homopolymer $-[-OCH(C{=}CH)-]_{x+y}-$ (at −78°C in the presence of pyridine or NaCN in THF[186]).

We shall consider in greater detail certain general features and characteristics of the elementary stages of the anionic polymerisation of acetylenes.

Initiation. Tolane[172], tetrolonitrile[197,198], phenylpropiolonitrile[188], dimethylaminopropynol and 4-dimethylaminobut-3-yn-2-one[168], benzoylpropiolic anhydride[180], acetylpropiolic anhydride[179,180], and dicyanoacetylene[185,190] have been polymerised using for initiation electron transfer from a metalloaromatic complex to the monomer. Such initiation takes place instantaneously and is accompanied by the formation of coloured products.

Polymerisation in the presence of phosphines[185,186,199], amines[184,185,189,199-203], and ammonia[189] presupposes a Zwitter-ionic initiation mechanism, which has been proposed, for example, for the polymerisation of propiolonitrile in the presence of triethylamine[184]. The formation of a dipolar ion is also postulated in the polymerisation of hexafluorobut-2-yne in the presence of Ph_3P, Et_2PH, and Me_3N[199]:



where Nu is a nucleophile.

In the presence of aromatic bases (pyridine, acridine, 3-aminopyridine, etc.), propargyl halides initially form quaternary salts, which then polymerise in the presence of the excess base[204]. Propargyl halides also polymerise in the presence of trialkylarsines, trialkylphosphines, or triarylphosphines[204].

Polar initiators, causing the dissociation of the triple bond of the monomer with formation of carbanions, constitute a large group of substances. The organometallic compounds in this class initiate the polymerisation of disubstituted acetylenes[168] and cyanoacetylenes[185,188,190,197,198]. Weak nucleophilic agents such as alkali metal salts and alkoxides initiate similarly the polymerisation of disubstituted[174-176,179,187,189] and monosubstituted acetylenes[178,180-184,186,187,196]. The polymerisation in the presence of alkali metal salts proceeds simultaneously via radical-anions and carbonium ions[179,205].

An unusual type of initiation reaction is observed in the polymerisation of monosubstituted acetylenes under the influence of strong nucleophilic agents: of 5-ethynyl-2-methylpyridine in the presence of a suspension of sodium[193]; of the mixed anhydrides of acetylene-α-carboxylic and other carboxylic acids[180]; of PA [194,206,207] and cyanoacetylene[183,184,208] in the presence of n-BuLi; of methyl-, ethyl-, and phenyl- acetylenes[192] and *p*-nitrophenylacetylene[50,209] in the presence of the lithium and sodium salts of DMSO. In this case the acidic acetylenic hydrogen atom is substituted by the metal and chain propagation takes place via the insertion of the monomer in the carbon-metal bond. This mechanism is supported by the polymerisation of acetylenes in the presence of alkali metal acetylides[183,192].

Whereas in non-polar solvents (benzene and toluene) and weakly solvated polar solvents PA does not polymerise in the presence of n-BuLi and gives rise to lithium phenylacetylide in HMP, n-BuLi adds to PA apparently with formation of butylstyryl-lithium, which behaves as the polymerisation initiator[195].

It has been suggested that the polymerisation of ferrocenylacetylene in the presence of a dispersion of sodium, which could not be achieved in the presence of n-BuLi, sodio-dimethyl sulphoxide, and sodionaphthalene, involves the initial dimerisation of the monomer with formation of diferrocenylbutadiyne and subsequent conversion into a ladder polymer[107-110].

Chain propagation. As in the anionic polymerisation of vinyl monomers, for acetylenes there probably exist various types of chain propagation active centres with different reactivities. A study of the polymerisation of acetylenes in DMSO showed[192] that chain propagation takes place at active centres which consist of a solvated complex of the carbanion and the monomer. The addition of a highly dissociated salt ($NaNO_3$, NaI) to the system hindered or stopped the polymerisation. A large excess of the salt suppressed also the initial coordination of the acetylide and the monomer. The results led to the conclusion that chain propagation in a highly solvating medium with a fairly high dielectric constant ($\epsilon \geqslant 23$) takes place preferentially via free anions.

The lack of experimental data on the synthesis of stereoregular polyenes even when the polymerisation is initiated by n-BuLi in a hydrocarbon medium is particularly noteworthy. Individual oligomeric stereoisomers[188] were detected in the polymerisation products of phenylpropiolonitrile in the presence of n-BuLi and sodionaphthalene in THF, which shows that the reaction is not stereospecific.

Chain termination. Chain termination may be due to various causes. A mass-spectrometric study of polyhexafluorobut-2-yne[210], obtained in the presence of CsF, showed that the process is initiated by the F^- ion, while proton transfer from the solvent to the carbanion is responsible for chain termination. Another type of chain termination has been observed in the polymerisation of DC≡C–CN.[181,183] According to infrared spectroscopic and NMR data for the low-molecular-weight fraction, the active centre is destroyed as a result of the transfer of deuterium from the monomer to the carbanion.

The absence of factors leading to chain termination presupposes the formation of "live" polymers. Indeed polyacetylene obtained in the presence of the sodium salt of DMSO retains for a long time the ability to form block copolymers with acrylonitrile, ethyl methacrylate, and styrene[192]. The activity series for the vinyl monomers then corresponds to the corresponding series for their anionic homopolymerisation.

Certain experimental facts suggest a decrease of the reactivity of the "live" polymer with increasing length of the polymer chain and an increase of the length of the polyene chain in equilibrium with the monomer when the temperature of the reaction mixture is reduced. Consequently even in "live" polymerisation chain propagation may cease as a result of the attainment of thermodynamic equilibrium in the system‡. In this case the change in the rate of polymerisation during the reaction can be explained only by the enhancement of the resonance stabilisation of the anion in the course of the propagation of the conjugated chain[23]. Calculations[202,212-214] confirmed these conclusions.

On the other hand, the observed self-inhibition in the polymerisation of phenylacetylene in the presence of n-BuLi in HMPA has been attributed to the formation of polymer-donor and monomer-acceptor charge-transfer complexes and not to kinetic termination or deactivation of the growing centre[195].

IV. POLYMERISATION OF ACETYLENES UNDER THE INFLUENCE OF TRANSITION METAL COMPOUNDS

Since cyclic and linear oligomerisation and polymerisation of acetylenes frequently accompany one another, the choice of reaction conditions is important for specific synthesis. This section deals mainly with studies whose aim has been to synthesise high-molecular-weight (oligomeric) linear polyene systems.

1. Catalysis by Transition Metal Salts and Their Complexes

Various reactions of acetylenes in the presence of copper(I) salts accompanied by the formation of cuprene analogues insoluble in organic solvents have been studied for a long time[2,6,215]. It has been suggested that polymerisation involving the conversion of PA into a soluble polyene with $M_n = 7000$ in the presence of CuO at 250–350°C proceeds via a stage involving the formation of a linear conjugated polyene which is converted into a three-dimensional product as a result of an intermolecular Diels-Alder reaction[216].

It has recently been established[217] that amine complexes of univalent and bivalent copper salts [CuCl, $Cu(OOCCH_3)_2$] polymerise butyne-2,4-diol and the diacetate derived from it. Linear polymerisation is accompanied by the intermolecular elimination of water or acetic anhydride. The complex spontaneous polymerisation of phenoxyacetylene is apparently accelerated in the presence of CdI_2.[66]

PA has been polymerised in the presence of rhodium salts [$RhCl_2$,[218] $RhCl_3$,[219,220] $RhCl_3.3H_2O$,[221,222] and $Rh(NO_3)_3$[219]], while in the presence of the complex $RhCl.(PPh_3)_3$ PA,[223,224] hexafluorobut-2-yne[225], and α-ethynylnaphthalene[226] have been polymerised. The reaction is of first order with respect to the monomer and

‡ The reversible nature of the polymerisation of acetylene was also observed on carrying out the reaction in the presence of a complex catalyst, where the degree of polymerisation increased with increase of the pressure in the system[211].

the catalyst[219,221], reaching a maximum value in the medium with the dielectric constant $\epsilon = 10$.[219] The activation energy for chain propagation remains constant (approximately 15 kcal mole^{-1}) in media with $\epsilon < 10$, increasing to 20.8 kcal mole^{-1} with increase of ϵ from 10 to 25.1. The dielectric constant was altered by carrying out the polymerisation in different solvents (benzene and its mixtures with ethanol, DMF, and DMSO). Consequently the coordination between the catalyst and solvent molecules determines the polymerisation process. With increase of the concentration of alcohol, there is merely an increase of the number of active centres, which leads to a rise of the rate of reaction without a change in the activation energy. DMF and DMSO, which have been used to obtain media with high dielectric constants, forms stable complexes with the catalysts, which results in an increase of the activation energy and a decrease of the rate of the process.

PA and methylacetylene polymerise over $PdCl_2$ [227] or its complexes with benzonitrile[227,228] and DMSO;[228] poly-(α-ethynylnaphthalene) has been obtained in the presence of the complex $(PdCl_2.PPh_3)_2$.[226] In solutions of rhodium and palladium salts, both catalytic and noncatalytic reactions of acetylenes are possible. The linear oligomerisation of vinyl- and phenyl-acetylenes with formation of σ-organo metallic polyenes has been observed by Temkin and Flid and coworkers[220]. The products are $Cl_mM-[C(R)=CR'-]_{n-1}-CH(R)C(O)R'$ in aqueous solutions and $ClPd-[C(R)=CR'-]_{n-1}-C(R)=C(R')Cl$ with $n = 18-20$ in non-aqueous solutions.

PolyPA with $\bar{M}_n = 3400$ has been synthesised in 67% yield at 20°C in the presence of $[Mo(OCH_3)_2Cl_2]_2$, obtained by dissolving $MoCl_5$ in absolute methanol[229].

The complexes of nickel cyanides with heterocyclic aromatic amines[230] or complexes of the type $NiX_2.(PR_3)_2$, where X = SCN, Cl, Br, or I and R = alkyl, cycloalkyl, aryl, or arylalkyl, have been used to synthesise linear polymers based on various mono- and di-substituted acetylenes[112,226,231-234]. An increase of the catalytic activity of the complexes has been observed in the series $NiCl_2 < NiBr_2 < NiI_2$, PA forming mainly a linear polymer, while propynol gives approximately equal amounts of linear polymers and aromatic trimers[231]. The polymerisation of the dibutyl ester of ethynylboronic acid in the presence of $NiBr_2(PPh_3)_2$ is accompanied by degradative-hydrolytic processes leading to a three-dimensional polymer with the probable structure $[-\overset{|}{C}=\overset{|}{C}-B(OH)OBu]_n$.[235]

In contrast to the complexes $NiX_2.(PPh_3)_2$ discussed above, in the presence of $(PPh_2)_2Ni(C_5H_7O_2)_2$ ethynylferrocene polymerises with difficulty and the structure of the polymer differs from that of the polyethynylferrocenes obtained in the presence of triphenylphosphine complexes or radical initiators[112]. The platinum complexes $(Ph_3P)_2.Pt(R)Cl$ (R = Cl or H), in the presence of which PA,[234,236] 2-methylbut-3-yn-2-ol[237,238], and α-ethynylnaphthalene[226] polymers have been obtained, are less active in the polymerisation of acetylenes.

2. Group VI–VIII Metal Carbonyls

A number of nickel[25,239-243], chromium, molybdenum, and tungsten[242,244] carbonyls or their complexes, for example $Mo(CO)_6$, $Mo(CO)_5.PPh_3$, $Mo(CO)_3.3PyH$, $Ni(CO)_2.(PPh_3)_2$, etc. have been used in the polymerisation of various acetylenic monomers. The polymerisation of 35 different mono- and di-substituted acetylenes in the presence of the complex $Ni(CO)_2.(PPh_3)_2$ has been studied in greatest detail[239,240,245]. The preferential formation of benzene derivatives or linear oligomers of the type $RC\equiv C-[-C(R)=CH-]_n-CH=CHR$ and $RC\equiv C-[-C(R)=CH-]_n-C(R)=CH_2$, where $n = 0-10$, was determined mainly by the nature of the substituent at the triple bond[239]. Whereas monosubstituted acetylenes with lower alkyl aryl, vinyl, $HOCH_2$, EtOOC, RCO, and RO substituents underwent only cyclotrimerisation, acetylenes with higher alkyl substituents yielded mainly linear oligomers. Only a linear dimer has been obtained from cyclohexylacetylene, while a number of monosubstituted (t-butylacetylene, propargyl chloride, propargyl acetate, cyanoacetylene, 5-chloropent-1-yne, and propiolic acid and its amide) and disubstituted acetylenes (with the exception of but-2-yne-1,4-diol and but-2-yn-1-ol) failed to react. With decrease of the reactivity of the monosubstituted acetylenes (ethers and esters, ketones, vinylacetylene > arylacetylenes > alcohols > higher alkynes > lower alkynes, acetylene ≫ acids), there was an increase of the yield of the linear polymerisation products.

A relation between the rate of reaction and the yield of the polymers on the one hand and the polarity and other properties of the solvents employed in the reaction on the other has not been found in the polymerisation of PA and hept-1-yne[240]. Water, dioxan, THF, acetic acid, and butan-2-one are unsuitable as solvents owing to their ability to form strong coordinate bonds or to decompose the catalyst irreversibly. The reaction is very sensitive to temperature and mixing.

The activity of the catalyst and the direction of the reaction depend also on the nature of the ligands bound to nickel. The replacement of the group R = OPh by R = C_2H_4CN in $Ni(CO)_2.(PR_3)_2$ favours linear polymerisation, while $Ni(CO)_4$ is altogether inactive in the polymerisation of monosubstituted acetylenes[240,246]. However, monomers (propargyl esters of propiolic and undec-10-ynoic acids) are capable of forming activated cyclic intermediates with $Ni(CO)_4$ polymerise in the presence of this complex[246].

In the polymerisation of PA in the presence of arene-metal tricarbonyls $ArM(CO)_3$, where Ar = toluene or mesitylene and M = Cr, Mo, or W, the reaction is fastest in the presence of molybdenum catalysts in hot aromatic solvents or in bulk at room temperature[242,243], giving a quantitative yield of a linear polyphenylacetylene with a molecular weight of 12 000 (according to gel-chromatographic data).

3. Organic Compounds of Group V-VIII Metals

Under the influence of triphenylchromium, hexafluorobut-2-yne forms only linear polymers[241]. On the other hand, when "dimesitylcobalt"[247] and "diphenylcobalt"[248], which are intermediates in the reaction of cobalt bromide with mesityl- and phenyl-magnesium bromides, are used, but-2-yne and hex-3-yne give rise to a mixture of linear polymers and cyclic trimers. The yield of the polymer and cyclic trimer is directly proportional to the initial concentration of the monomer, but the polymer : cyclic trimer ratio changes at a low temperature from 1 : 17 to 5 : 1 on passing from but-2-yne to hex-3-yne[247]. This is probably associated with the increased steric hindrance in the cyclotrimerisation of hex-3-yne. The yield of poly(hex-3-yne) increases with increase of the concentration of the monomer and falls with increase of temperature, the polymerisation involving a catalytic mechanism under any conditions[248].

Analogous active intermediates are probably formed also when the Iotsich reagents RC≡CMgX are treated with cobalt and nickel chlorides[249].

Acetylenes polymerise in the presence of dicyclopentadienylvanadium[250] and complexes of heterocyclic aromatic amines with dicyclopentadienylnickel[230]. Mainly trialkylbenzenes are formed from propyne, pent-1-yne, and hex-1-yne, PA gives a linear polymer, while disubstituted acetylenes (hept-3-yne, but-2-yne-1,4-diol, and tolane) remain unchanged under these conditions[250]. In the presence of diacrylonitrile- and diacrolein-nickel, phenylacetylene, propargyl alcohol, phenylpropiolaldehyde, and propiolate and acetylenedicarboxylate esters react vigorously to form polymeric products[251].

It has been established[234,236-238] that bistriphenylphosphine complexes of σ-organometallic derivatives of nickel and platinum $(PPh_3)_2Ni(C{\equiv}CPh)_2$, $(PPh_3)_2Pt\langle^{CH}_{CPh}\|$, and *cis*- and *trans*-$(PPh_3)_2Pt(C{\equiv}CPh)_2$ catalyse the polymerisation of monosubstituted acetylenes (PA and 2-methylbut-3-yn-2-ol) in bulk and in solution. The less active platinum complexes, in the presence of which the reaction occurs at a fairly high temperature (110–193°C) and is therefore complicated by the thermal polymerisation of the monomer, make it possible to obtain almost exclusively linear polymers. Vinyl-, isopropenyl-, phenyl-, divinyl-, and vinylisopropenyl- acetylenes have been recently polymerised in the presence of the diarene complexes $M(AlCl_4).2C_6H_6$ (M = Co or Ni [252,253])—the so called "alkyl-free organometallic catalysts"[254].

The polymerisation of acetylenes under the influence of catalytic systems based on π-allyl transition metal complexes is of considerable interest. Such complexes were proposed for the first time for the polymerisation of monosubstituted acetylenes by Japanese investigators[255].

In the presence of the π-allylmetal halides $[\pi\text{-(allyl)}.MX]_n$, where allyl = C_3H_5 (allyl), C_4H_7 (but-2-enyl), or C_5H_9 (pentenyl), M = Ni or Pd, X = Cl, Br, or I, and n = 1 or 2, alkylacetylenes (hex-1-yne, hept-2-yne, and oct-4-yne) cyclotrimerise and arylacetylenes (PA) oligomerise[256,257]. The activity in cyclotrimerisation falls in the above series of allyl derivatives.

Polyvinylenes have been obtained from methyl-, phenyl-, vinyl-, and vinylpropenyl-acetylenes under the influence of $(\pi\text{-}C_4H_7NiX)_2$, where X = I or Cl.[258] The reaction takes place quantitatively under mild conditions (25°C, 2 h, molar ratio monomer : catalyst = 30–50) and vinyl- and vinylpropenylacetylenes polymerise exclusively via the triple bond.

PA [259,260] and cyanoacetylene[261] in the presence of di-(π-allyl)nickel and PA in the presence of di-(π-but-2-enyl)nickel[260] form a mixture of cyclic trimers and linear polyenes. The maximum conversion of cyanoacetylene in the temperature range between −30° and 30°C occurs at 30°C. The yield of both the polyene and the cyclic trimer diminishes as the temperature is reduced[261,262].

The polymerisation of vinyl- and isopropenyl-acetylenes in the presence of di-(π-allyl)nickel gives rise to a mixture of soluble and insoluble products[263]. Above 0°C, the main reaction product from isopropenylacetylene is a soluble polymer, while below 0°C an insoluble polymer is formed. The soluble polymer loses its solubility after isolation. The polymerisation involves preferentially the isopropenyl group in the 1,2-position, together with the dissociation of the triple bonds and the formation of small blocks of conjugated double bonds. A polymer consisting mainly allenic units has been obtained from vinylacetylene via the 1,4-addition mechanism. Polymerisation via the triple bond also takes place to a slight extent.

The activity of the π-allyl complexes of nickel decreases in the sequence[257,258] $(\pi\text{-}C_4H_7NiI)_2 > (\pi\text{-}C_4H_7NiCl)_2 > (\pi\text{-}C_4H_7)_2Ni$. The influence of electron-donating (phosphines and amines) and electron-accepting (nickel trichloroacetate, $AlBr_3$, and $TiCl_4$) additives on the polymerisation reaction is extremely varied. In the presence of pyridine and DMF (in the stoichiometric amount or in excess relative to the catalysts), the overall yield of acetylene oligomerisation products in the presence of the $[\pi\text{-(allyl)}MX]_n$ catalysts falls, the cyclotrimerisation processes being retarded in the first place. Triphenylphosphine exhibits a weaker inhibiting activity than amines. Complexes containing more than three PPh_3 molecules per metal atom greatly activate the cyclisation of alkynes[257]. On passing from $(\pi\text{-}C_4H_7NiI)_2$ to its complex with one molecule of $Ni(OCOCCl_3)_2$ (the latter does not catalyse the reactions of acetylenes), triphenylbenzene is formed preferentially from PA instead of the linear polymer. On the other hand, when $(\pi\text{-}C_4H_7NiCl)_2$ is replaced by its complex with 1.5 molecules of $Ni(OCOC.Cl_3)_2$, the rate of cyclotrimerisation of hept-2-yne decreases without a change in the mode of the process[256]. A retardation of the polymerisation of vinylacetylenic hydrocarbons under the influence of Lewis acids has also been noted[258].

When di-(π-allyl)nickel is used, the influence of the additives varies depending on the nature of the monomer. The presence of phosphines does not influence the direction of the reaction of cyanoacetylene and the yield of reaction products[261,262]. On the other hand, the addition of PPh_3 and $TiCl_4$ alters the mode of polymerisation of isopropenylacetylene: the triple bond is dissociated instead of the double bond. The replacement of $(C_3H_5)_2Ni$ by $(C_3H_5NiBr)_2$ has a similar effect[263].

4. Ziegler–Natta Catalysts

The most common organometallic complex catalysts, or Ziegler–Natta catalysts, which are widely used in the polymerisation of olefins, have also found applications in the polymerisation of acetylenes. Depending on the nature of the acetylenic monomer and the reaction conditions, the process can be driven towards the preferential formation of cyclic trimers (benzene derivatives)[7,14,17,18,25] or linear polymers[7,17,18,264-271]. The available data about the influence of reaction conditions on the structural specificity of the polymerisation process are extremely contradictory. When alkynes were polymerised under the influence of catalytic systems based on organoaluminium compounds and titanium derivatives, the maximum yields of cyclic trimers were obtained in the presence of $TiCl_4$.[272-280] It was also noted[281,282] that the reaction in the presence of $TiCl_3$ leads to the formation of linear polymers only, which is inconsistent with other data (see below).

Substituents at the titanium atom have a much stronger influence on the direction of the process than changes in the aluminium component. The $Et_3Al\text{–}(C_5H_5)_2TiX_2$ catalytic systems, where X = Cl or OBu, are relatively ineffective in the linear polymerisation of PA.[283] When $TiCl_4$ in the complex with R_3Al (where R = Et or iso-Bu) is replaced by $Ti(OR')_4$ (where R' = Et or Bu), the catalytic system becomes inactive in the cyclotrimerisation reaction[282,284-286]. On the other hand, systems of the type $R_2AlCl\text{–}Ti(OR')_4$ are active in cyclotrimerisation and

polymerisation[284,286]. These data suggested that, in order to obtain benzene derivatives from acetylenes under the influence of typical Ziegler–Natta catalysts, a halogen atom combined with a transition metal[275] or in one of the catalyst components[284] is necessary. On the other hand, when Et_3Al is replaced by Et_2AlCl in the complex with $Fe(DMG)_2$ (where DMG = dimethylglyoxime), the system becomes almost inactive in the polymerisation of PA.[286] Similarly the effectiveness of the alkylaluminium component in the complex with $Fe(DMG)_2.2X$ (where X = PyH or NH_3) in the linear polymerisation of α-ethynylnaphthalene decreases in the sequence[287] $Et_3Al > (iso\text{-}Bu)_3Al > Et_2AlCl$. A change in the transition metal can affect both the proportions and the structures of the linear and cyclic polymerisation products.

The catalytic activity of the complex catalyst with Et_3Al in the polymerisation of α-ethynylnaphthalene[288] decreases in the following sequence as a function of the transition metal: $Co(Acac)_3 > Fe(Acac)_3 > Cr(Acac)_3 > Ti(OBu)_4 > VO(Acac)_2$, while in the polymerisation of PA [285] the sequence is $Co(Acac)_3 > Cr(Acac)_3 > VO(Acac)_2 > Ti(OBu)_4 > TiCl_2(C_5H_5)_2$.

Whereas the polymerisation of ethynylferrocene in the presence of the $R_3Al–Ti(OBu)_4$ catalytic system leads to the formation of polyenes with $\overline{M}_n$ = 1000–3500,[285] there is no polymerisation under the influence of $Et_3Al–TiCl_4$,[289] while in the presence of $(iso\text{-}Bu)_3Al\text{-}VO(Acac)_2$ insoluble and infusible products were obtained; according to infrared spectroscopic data, such products are not formed as a result of the dissociation of the triple bond[290].

The complexes $(iso\text{-}Bu)_3Al–VOCl_3$ and $(iso\text{-}Bu)_2AlCl–VOCl_3$ are less active than $(iso\text{-}Bu)_3Al–TiCl_4$, probably in consequence of the interaction of the oxygen p electrons with the vacant orbitals of vanadium, which lowers its capacity for coordination. The coordination saturation of the vanadium atom on passing from $VOCl_3$ to $V(Acac)_3$ in the above complexes makes them inactive in the formation of linear and cyclic products[291,292]. The reduced activity of the vanadium complexes compared with the titanium complexes is also associated with the greater stability of the former[292]. The stereospecificity of the $(iso\text{-}Bu)_3Al–TiCl_4$ system demonstrated in relation to 1,3,5- and 1,2,4-tri-n-butylbenzenes formed on polymerisation of hex-1-yne, is much higher than that of $(iso\text{-}Bu)_3Al–VOCl_3$,[291] which agrees with the relative stereospecificities of the analogous systems in the polymerisation of propene[293].

Electron-donating additives (PyH, NH_3, THF, etc.) have a marked influence on the properties of catalysts; a limited influence of PyH and Et_3N on the yield and proportions of the final products in the polymerisation of ethynylferrocene has been noted[286]. A decrease of the yields and molecular weights of the PA [283,287,294] and p-iodophenylacetylene[77] polymers have been observed when modified systems comprising Et_3Al with $Fe(DMG)_2.2D$ (where D = PyH or NH_3) and $TiCl_3.D_n$ (where D = PyH and n = 1 or 2) were used. The use of δ-$TiCl_3$ (this modification contains up to 27% $AlCl_3$) instead of α-$TiCl_3$ in the complex with Et_3Al leads to an appreciable increase of the yield of cyclic trimers[294]. The activity of the complex falls with increase of the coordinating capacity of the electron-donating additive[287]. In this connection it is interesting to note that, when the catalytic complex is prepared under appropriate conditions, the acetylenic monomer may form part of the complex as an electron-donating additive[295].

The virtually constant activity of iron, cobalt, and nickel chelate complexes in the polymerisation of acetylenic compounds (regardless of the structure of the ligand) and the influence on the process of the electron-donating additives bound to the catalyst show that the coordination of the monomer or the polymer to the transition metal atom is a significant factor in polymerisation in the presence of Ziegler–Natta catalysts[283,287].

The ratio of the components of the catalytic system is very important for the specific synthesis of linear and cyclic products. This is not surprising, since the formation of the active catalytic complex is associated primarily with alkylation and the change in the valence state of the transition metal[296,297]. Thus, in polymerisation in the presence of the $R_3Al–TiCl_4$ catalytic system, the maximum yield of the cyclotrimerisation products derived from a number of alkynes was noted for the molar ratio Al:Ti = 1–3 (with R = iso-Bu),[276] 3 (with R = Et),[298] 3 (with R = iso-Bu),[282,291,292,299,300] and 2–4 (with R = Et).[274] Whereas in the polymerisation of PA in the presence of $Et_3Al–TiCl_4$ the maximum yield of linear polymers was reached for Al:Ti > 4,[274] in the presence of $(iso\text{-}Bu)_2AlCl–TiCl_4$ linear polymers were not obtained for any Al:Ti ratios in the range from 1/3 to 8;[284] in the presence of $Et_2AlCl–TiCl_4$ with Al:Ti = 3–7 the yield of triphenylbenzenes falls sharply and the main reaction product is a linear polymer[273]. On the other hand, other investigators believe that the optimum ratio for the formation of linear polymers is Al:Ti = 1–3.[269,301–303] In the presence of the $R_3Al–Ti(OBu)_4$ system where R = Et or iso-Bu, no changes were observed in ethynylferrocene for the molar ratio Al:Ti = 1. For higher Al:Ti ratios, up to 20, mainly a linear polymer is formed. On passing from R_3Al to Et_2AlCl and for the molar ratio Al:Ti = 5, only a cyclic trimer is formed[286]. Poly-α-ethynylnaphthalene and polyPA have been obtained in the presence of $Et_3Al–Ti(OBu)_4$ for Al:Ti ratios of 2.86 [288] and 4 [285] respectively. The replacement of $TiCl_4$ by $TiCl_3$ increases the activity of the system in linear polymerisation reactions over a wide range of Al:Ti ratios (from 1 to 10),[75,77,268,272,283,304–309] the use of δ-$TiCl_3$ resulting in an increase of the polymerisation rate constant approximately by a factor of 5 compared with α-$TiCl_3$.[308]

When the nature of the transition metal is altered, the optimum ratio of the catalytic system components for the preferential formation of linear or cyclic products changes. This is mainly because of the ease of reduction of a particular metal. Indeed vanadium halides react with aluminium alkyls much more readily than do titanium halides[296]. In conformity with this finding, the optimum ratios in the polymerisation of hex-1-yne in the presence of $(iso\text{-}Bu)_3Al–TiCl_4$ and $(iso\text{-}Bu)_3Al–VOCl_3$ are respectively Al:Ti = 3 and Al:V = 1.5. With increase of the latter ratio, the yield of the linear polymer rises sharply for an overal conversion of 100%.[291] However, as in the case of olefins[297,298], there are no unambiguous data concerning the valence state of the transition metal in the catalytic complex in the polymerisation of acetylenes. For example, it is believed that the maximum activity of the system with respect to cyclotrimerisation corresponding to Al:Ti = 3 is determined by Ti^{2+} [274] or Ti^{3+}.[292]

The data concerning the influence of solvents on the structure of the reaction products are also contradictory. Donda et al.[274] believe that aromatic solvents promote the cyclisation of PA in the presence of $Et_3Al–TiCl_4$. According to the results of Reikhsfel'd and coworkers[282,310], the nature and amount of the solvent, which is inert with respect to the catalyst (benzene, n-heptane, cyclohexane, n-octane, and isooctane), do not influence the overall yield and the proportions of the 1,2,4- and 1,3,5-trisubstituted benzenes formed in the polymerisation of a number

of alkynes in the presence of (iso-Bu)$_3$Al–TiCl$_4$. In the presence of the same catalytic system, no difference was observed between the polymerisations of α-ethynylanthracene in n-heptane and toluene[53]. On the other hand, the yield of cyclic trimers in the polymerisation of PA in the presence of Et$_3$Al–TiCl$_3$ is determined by the type of solvent employed[308]: other conditions being equal, mainly linear polymers (in yields of 84–98%) are formed in aromatic solvents (benzene, toluene, and *o*-dichlorobenzene), while in aliphatic solvents (n-heptane, cyclohexane, and dichloroethane), the products are cyclic trimers (23–90%).

The range of monomers polymerised in the presence of Ziegler–Natta catalysts is fairly extensive: propyne[272,290,295,298], but-1-yne[298 304 311], pent-1-yne[75], hex-1-yne[268,282,284,291,292,304–306,311,312], dodec-1-yne[311], 3,3-dimethylbut-1-yne[299], 3-methylpent-1-yne[313], 4-methylhex-1-yne[306], vinylacetylene[284,300,301], isopropenylacetylene[273], PA,[170,274,283,285,287,295,307,308,314,315], *o*- and *p*-nitro, -chloro-, and -methyl-phenylacetylenes[214], phenyldeuteroacetylene[316], α- [288] and β-ethynylnaphthalenes[303], 9-ethynylanthracene[53], ethynylferrocene[286], cyanoacetylene[317], α-furylacetylene[300], isobutoxyacetylene[318], phenoxyacetylene[302], trimethyl- and triethyl-silylacetylenes[319,320], but-2-yne[298], dec-5-yne[298], methylphenylacetylene[316], and β-iodophenylacetylene[75,77]. Propargyl bromide and 5-ethynyl-2-methylpyridine do not polymerise—the former monomer decomposes the catalyst, while in the presence of the latter the catalyst is not deactivated. According to Makovetskii et al.[300], the pyridine substituent weakens the capacity of the triple bond for coordination. Disubstituted acetylenes show a greater tendency towards the formation of cyclic trimers than monosubstituted derivatives[276,294,316], which can probably be explained by the greater steric hindrance in the formation of the linear polymer chain. When the temperature was reduced, a decrease of the conversion of the monomers[269,283,284,286,291,302,307] and an increase of the relative content of cyclic trimers in the reaction products[294,316] were observed. The yield of cyclic trimers also increases with increase of the degree of conversion of monomers[294,316].

It is known[296,297] that not only the ratio of the components of the catalytic complex but also the state of aggregation of the catalyst and its degree of dispersion in the solvent have a major influence on the structure and properties of the products obtained. In their turn, these parameters depend in many respects on the conditions in the preparation of the catalytic complex (the order in which the components are introduced, the rate of stirring, the temperature and duration of interaction, the absence or presence of a solvent, the absolute amounts of the components, etc.). Thus in the polymerisation of PA in the presence of Et$_3$Al–α-TiCl$_3$ the order in which the components of the catalytic system, the solvent, and the monomer are mixed has hardly any influence on the rate of reaction. However, when δ-TiCl$_3$ is used, a change in the order in which the reactants are introduced (a change from the sequence TiCl$_3$ + Et$_2$Al solution + monomer to the sequence TiCl$_3$ + monomer + Et$_3$Al solution) alters sharply the polymerisation kinetics[316]. In the latter case the monomer is probably actively involved in the formation of other catalytic active centres. This may be promoted by the AlCl$_3$ present in relatively large amounts as an impurity in δ-TiCl$_3$. Similarly the purity of the metal alkyl has a definite influence on the degree of reduction of the transition metal (for example, one must take into account the virtually unavoidable admixture of the highly reducing aluminium hydride in the initial aluminium alkyl component). It is extremely probable that the contradictory nature of many of the data discussed is in fact in many respects determined by the different conditions used in the preparation of the catalyst components and the catalytic complexes based on them as well as different process conditions.

5. Other Catalysts

The linear polymerisation and cyclotrimerisation of acetylenes is catalysed by many systems comprising Group VIII transition metal compounds (with the exception of iron) or their complexes, for example NiCl$_2$, CoBr$_2$, PbCl$_2$, Ru(SCN)$_2$, OsCl$_2$, [Ni(C$_2$H$_4$CN)$_3$.P]$_2$, PdCl$_2$.[P(Bu-n)$_3$]$_2$, and NiCl$_2$.[P(Pr-n)$_3$]$_3$ in combination with hydrides of Group I–IV elements (NaBH$_4$, KBH$_4$, LiH, LiAlH$_4$, B$_2$H$_6$, SiH$_4$, SnH$_4$, etc.)[224,241,321–326].

The systems comprising cobalt, platinum, palladium, and osmium proved to be the most active in the polymerisation of hept-1-yne. The valence of the metal is unimportant, but the effectiveness of the organometallic complex is greater than that of an inorganic salt. At high temperatures the process is catalysed even in the absence of a reducing agent[326].

Acetylenes also polymerise under the influence of palladium on charcoal[327] and catalytic systems consisting of an iron halide (FeX$_n$, where X = Cl or Br, and n = 2 or 3), and alkali metal acetylide, and a ketone[328,329].

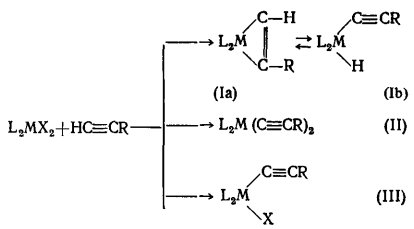
6. The Mechanisms of the Polymerisation Reactions of Acetylenes in the Presence of Transition Metal Compounds

Several mechanisms have been proposed for the cyclic oligomerisation and linear polymerisation of acetylenes, which reflect primarily the wide variety of the catalytic systems employed. However, the contradictory nature or lack of some data on the kinetics and mechanisms of the processes, frequently caused by experimental difficulties (the high rates and heats of reaction[240,330]), make these mechanisms merely hypothetical.

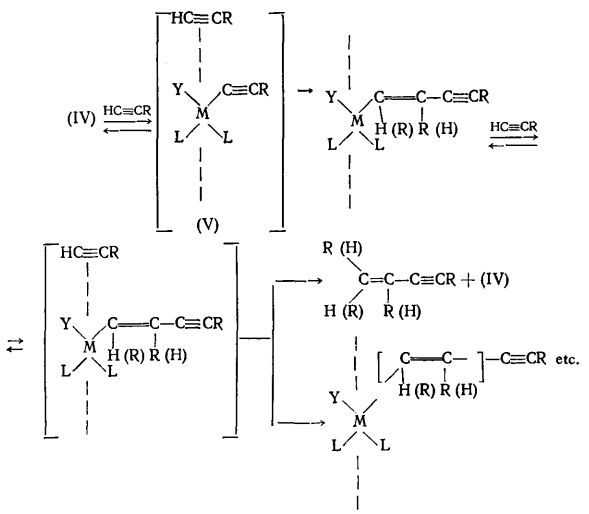
Despite the wide variety of transition metal compounds which catalyse the polymerisation of acetylenes, the first stage in the linear polymerisation and cyclotrimerisation is believed to be coordination of acetylenes to the transition metal of the π-complex type[15,25].

According to Meriweather et al.[240], when Ni(CO)$_2$.(PR$_3$)$_2$ is used, the actual catalyst of the polymerisation of acetylenes is the complex $(R_3P)_2Ni\begin{matrix}C-H\\ \|\\ C-R'\end{matrix}$, in equilibrium with the hydride acetylide (R$_3$P)$_2$Ni(H)C≡CR′. The advantages and disadvantages of this mechanism have been discussed in detail in the literature[14,15,25]. Whereas intermediate acetylides have not been detected in the case of nickel catalysts, a number of acetylides have been isolated in the presence of the less active triphenylphosphine complexes of platinum[236–238]. Possibly the formation of acetylides determines the induction period in

polymerisation[234]. The "organometallic" mechanism based on these data can be represented as follows[112,226,236]:

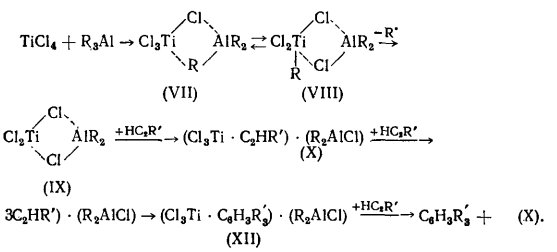


We put (Ib) = (II) = (III) = $L_2M\langle^{C\equiv CR}_{Y}$ = (IV), where M = metal, L = ligand, R = alkyl or aryl, Y = H or C≡CR, and X = Cl, Br, I, or SCN.



The reaction of the phosphine complex of the metal with the alkyne results in the formation of one of the active intermediate products (I)–(III) or their mixture, (IV). Then (IV) reacts rapidly and reversibly with another alkyne molecule to form (V). In the π-complex (V), the triple bond interacts with the p_z orbital of the bivalent metal in such a way that the z axis passes through the centre of the triple bond and the alkyne is disposed parallel to the plane of the complex. The presence in the system of a new π-linked acetylenic unit (V), acting as a kind of Lewis base, compensates the weak shift of the π-electron cloud of the σ-linked acetylenic unit and leads to the formation of (VI). The growth of the polymer chain takes place via the insertion of the coordinated monomer molecule in the ≡C–M bond.

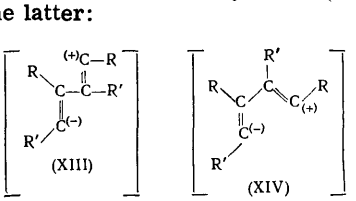
On the basis of the investigations made, Reikhsfel'd and Makovetskii suggested[14,282] that, regardless of the type of catalyst used, the cyclotrimerisation of acetylenes proceeds via a coordination mechanism similar to that proposed earlier for the formation of benzene or cyclooctatetraene derivatives in solutions of nickel complexes[15]. When account is taken of later refinements[292], the proposed mechanism is as follows. When the alkyne RC≡CH molecule interacts with the Ti^{3+} ion, forming part of the two-metal complex with aluminium in proportions of 1 : 1, the complex (VII) is formed with a bridge bond via the R group. The presence of this bond is necessary for the reversible alkylation of titanium to the complex (VIII). The alkylation of titanium is promoted by the fact that the bridge bond via the chlorine atom is energetically more favourable than the bridge bond via the alkyl group. The complex (VIII) contains the extremely unstable Ti–R bond, which dissociates with formation of the complex (IX). The latter reacts with an alkyne molecule to form a new complex (X), which contains, like complex (IX), a coordination-unsaturated titanium atom. In the attack on the complex (X) by two alkyne molecules, an octahedral complex (XI) is produced. According to kinetic data (the second order of the cyclotrimerisation reaction with respect to the monomer[313]), the last stage determines the rate of the entire process. The next stage is the intramolecular exchange of the chlorine atom for the alkyne with a nearly coplanar disposition of all three alkyne molecules and subsequent formation of a benzene ring from them. This liberates two coordination sites in the octahedron, which rearranges back to a square form (XII) with a molecule of the benzene derivative as the ligand. The latter is displaced by a new alkyne molecule with formation of the initial complex (X):



The mechanism discussed above is based primarily on the independence of the cyclotrimerisation reaction (observed by the authors) in different solvents and the identical reactivities in this process of acetylenes with substituents having the opposite effects on the electron density of the triple bond. On the other hand, the mechanism does not explain the simultaneous formation of linear as well as cyclic oligomers and the influence of the nature of the solvent on the ratio of the cyclic and linear products noted in many instances[274,294,308]. The formation of asymmetric 1,2,4-trisubstituted benzenes, the yield of which is sometimes equal to or greater than that of the symmetrical 1,3,5-isomer[277,278,294,308], is also difficult to account for in terms of the "coordination" mechanism. The first order (with respect to the monomer) of the PA cyclotrimerisation reaction[294,308] in the presence of the $Et_3Al–TiCl_3$ system is not consistent with the many-centre character of the "coordination" mechanism.

Many investigators have developed the anionic-coordination mechanism of cyclotrimerisation and linear polymerisation of acetylenes, proposed for the first time by Natta et al.[332]

According to Lutz[14,298], the alkyne is polarised after chemisorption on the catalyst surface. Chain propagation proceeds via the Al–C bond and the direction of the reaction is determined by the configuration of the intermediate complex—(XIII) or (XIV); a linear polymer is formed in the presence of the former and a cyclic trimer in the presence of the latter:

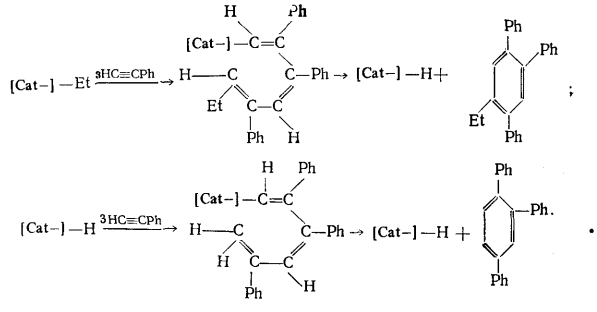


The high selectivity of the cyclisation of disubstituted acetylenes is associated with steric factors. However, this mechanism does not explain the cyclotrimerisation of monosubstituted acetylenes occurring in many instances with high yields.

A study of the reaction of acetylene in the presence of the $Et_3Al-TiCl_4$ system established[333] that ethylbenzene is formed together with benzene. A control experiment showed that the former is not a product of the direct alkylation of benzene under the influence of Et_3Al. This suggested that the cyclotrimerisation proceeds with participation of the M–C bond and the intermediate formation of linear products.

There is no doubt that, as in the polymerisation of olefins in the presence of Ziegler–Natta catalysts, the reactions of acetylenes are initiated by the insertion of the monomer molecule in the M–C bond of the complex catalyst. It has been established by NMR for the $Me_2AlCl-(C_5H_5)_2TiCl_2$ catalytic system[334] that PA is inserted in the Ti–Me bond. The monomer, activated on formation of the π-complex[15], undergoes the *cis*-dissociation of the triple bond during the addition to the M–C bond, as shown by the chain structures of the polyenes synthesised[335–337]. Measurements of the electrical conductivities of reaction mixtures with different compositions have shown that the PA polymerisation reactions in the presence of many Ziegler catalysts are ionic[285].

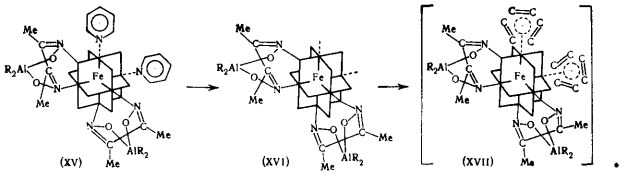
Data obtained in two investigations[294, 308] on the polymerisation of PA in the presence of $Et_3Al-TiCl_3$ are consistent with the anionic-coordination mechanism. The independence of the rate constant for the polymerisation of PA in n-heptane of the yield of cyclic trimers and the first order of the reaction with respect to the monomer show that the mechanism of the formation of cyclic products in the polymerisation of PA in the presence of Ziegler systems is determined by the abstraction of the linear trimer from the catalystic centre with ring closure and not by the simultaneous step involving the interaction of three monomeric units:



The presence of the ethyl group in triphenylbenzenes confirms this mechanism. The preferential formation of cyclic products when the polymerisation is carried out in aliphatic hydrocarbons and of linear polymers in aromatic solvents is associated with the donor–acceptor interaction of the aromatic solvents with the growing chain, which hinders the formation of a conformation suitable for cyclisation. Furthermore, one cannot rule out the possibility of the formation of complexes by aromatic solvents with the titanium component of the catalyst[49, 338–341], which would also hinder cyclisation. The strong inhibiting effect of Et_3Al on the cyclisation process may be explained as follows: by the capture of the end of the polyene chain due to the counteraction by the free Et_3Al on the $TiCl_3$ surface; by the donor–acceptor interaction of Et_3Al with the polyene chain; by the possibility of the formation of Et_3Al as an agent transferring to the chain the secondary active centres [Cat–]–Et, on which the growing chains have an "alkyl" tail which sterically hinders cyclisation.

However, one should note that the homogeneous catalytic system $R_3Al-NiCl_2$ is formed in both aliphatic and aromatic solvents, while polarisation takes place only in the latter[288]. The aromatic solvent probably plays in this case the role of a ligand with π-donor properties, increasing the possibility of dative interaction between the transition metal and acetylene.

Simionescu et al.[226] consider the complex $Fe(DMG)_2 \cdot 2PyH$ as an octahedral chelate system, which gives rise to a new complex (XV) by reaction with R_3Al. The formation of (XV) was confirmed experimentally by the detection of the RH produced. The aluminium in (XV) decreases the electron density of the Fe–N chelate linkage, which is enhanced by the π-electron system of PyH. In this connection, one should consider the above activity series of aluminium alkyl components[226, 287, 288]. On heating (90°C, 15 min), the complex (XV) is converted into the polymerisation catalyst (XVI) proper. The electron deficiency of the Fe–N linkage is compensated in (XV) by the six alkyne molecules forming two three-unit aromatic systems of type (XVII). The subsequent dissociation of the triple bond leads to the formation of the polyene:



In contrast to the polymerisation mechanisms already examined, where chain propagation takes place (by analogy with vinyl polymerisation) as a result of the addition of the triple bond to the active terminal bond, in the presence of $RhCl.(PPh_3)_3$ PA behaves as a bifunctional monomer. C≡C and ≡C–H behaves as functional groups. Chain propagation is the result of the successive addition of the ≡C–H bond in one monomer molecule to the C≡C bond in another under the coordinating influence of rhodium, as shown by the formation of *trans*-1,4-diphenylbutenyne[223].

The catalytic activity of π-allyl compounds is apparently in many respects determined by their stability, which depends on the nature of the metal and the ligands linked to it[254]. The presence of π-allyl groups is not an obligatory condition for the activity of the complex; the creation of a specific state of the transition metal and a definite degree of its stabilisation are important[257]. The oligomerisation of acetylenes on π-allyl halides is described by first-order kinetic equations with respect to the monomer. The reaction order with respect to the catalyst varies as a function of its nature: it is 0.5 in cyclotrimerisation on π-crotylnickel chloride and unity on the monomeric π-pentenylnickel iodide[257]. The acetylenic monomer initially displaces the allyl ligand from the catalyst (identification of diallyl) with formation of formally univalent (from π-allylmetal halides)[260, 261] or zerovalent nickel[256, 257]. Linear polymerisation takes place via the insertion of the monomer in the M–C σ bond and subsequent chain transfer to the monomer[257, 260] or via insertion in the metal hydride linkage[261].

The hypothetical mechanism of catalysis by a Group VIII transition metal salt and a hydride reducing agent presupposes the reduction of the ion to the lowest valence state with formation of the metal hydride, which in its

turn gives a complex with two and more monomer molecules[325]. In this complex the metal atom behaves as an agent transferring hydrogen from one monomer molecule to another.

In the light of recently published interesting data on the polymerisation of a number of acetylenes in the presence of Group VIB arenemetal tricarbonyls[242,243], the "cyclobutadiene" mechanism[15], which has not apparently been considered for the explanation of the linear polymerisation of acetylenes, has attracted attention. An intermediate ladder compound having the cyclobutane structure, which is rapidly and quantitatively converted into linear polyPA following the addition of the catalyst, has been isolated from the products of the initial stage of the polymerisation of PA. Dewar hexamethylbenzene has been detected in the reaction medium in the polymerisation of but-2-yne[242,243]. These findings suggested that a series of consecutive [2 + 2] cycloadditions initially result in the formation of ladder polymers, which are then converted into higher-molecular-weight linear products, probably via a series of metathetical reactions of the olefins with subsequent isomerisation of the electronic structures of the final compounds.

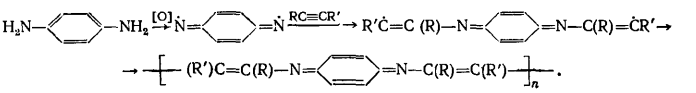
V. COPOLYMERISATION OF ACETYLENES

The copolymerisation of various acetylenic monomers with one another is closest to the homopolymerisation of acetylenes as regards the process mechanism and the properties of the products. As in homopolymerisation, in the copolymerisation of alkynes in the presence of radical initiators[38], cationic catalysts[342], homogeneous and heterogeneous Ziegler–Natta catalysts[343], and catalytic systems comprising Group VIII transition metal compounds and the hydrides of Group I–IV elements[323,324], only copolymers with a low molecular weight have been obtained regardless of reaction conditions. Possibly alternating copolymers are formed in the copolymerisation of *p*-chlorophenylacetylene with *p*-methoxyphenylacetylene and of cyanoacetylene with phenoxyacetylene[38].

The thermal copolymerisation of mono-,and di-acetylenes (PA and *p*-diethynylbenzene) in the range 150–300°C leads to infusible insoluble, and thermally stable copolymers with low electrical resistivities[32–34]. In the catalytic copolymerisation of mono- and di-ethynyl derivatives, the structure of the product is determined by the nature of the diacetylene monomer and the reaction conditions. Whereas the copolymers of PA with *p*-diethynylbenzene contain polyene sections (polyenisation process) together with polyphenylene sections (polycyclotrimerisation process)[26,330,344–348], hepta-1,6-diyne copolymerises with PA under the same conditions via the C≡C bond of the intermediate hept-1,6-diyne dimer, namely 5-(pent-1-ynyl)indane[330,346–349]. Unusual copolymers consisting of polyene or polyene and acene fragments are formed in the homopolymerisation of propargyl propiolate in the presence of $Ni(CO)_4$ [246] or on thermal homopolymerisation of conjugated diynes[26].

The product of the radiation-chemical reaction obtained on irradiation of an acetylene–carbon tetrafluoride mixture by fast electrons at room temperature is apparently a polyvinylene in which some of the hydrogen atoms in the chain have been substituted by fluorine atoms[350]. The fluorine content in the polymer increases with increase of the CF_4 concentration in the initial mixture and varies from 14 to 40 wt.% when the $CF_4 : C_2H_2$ ratio changes from 1 : 1 to 50 : 1 respectively.

The introduction of acetylenic monomers into the reaction system where aromatic compounds undergo polycondensation via a radical mechanism leads to the formation of soluble coloured paramagnetic copolymers. Thus macromolecules containing aromatic and acetylenic units have been obtained by the reduction of aromatic bisdiazonium salts with titanium trichloride in the presence of phenylacetylene, propargyl alcohol, and acetylenedicarboxylic acid[351–353]. The oxidation of aniline and *p*-phenylenediamine by cerium(IV), iron(III), and vanadium(V) salts in the presence of propargyl alcohol, acetylenedicarboxylic acid and its dimethyl ester gives rise to a copolymer via the mechanism[354]



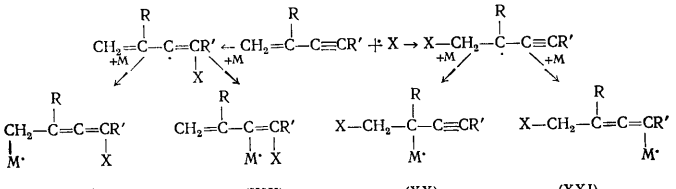
Copolymers containing polyphenylene and polyvinylene fragments are formed when the acetylenic monomer is introduced into the lithium–*p*-dichlorobenzene system in THF solution[355].

The block copolymerisation of polyvinylenes (polyacetylene, polyPA, and polytolane) with electron-accepting vinyl monomers (maleic anhydride, fumaronitrile, and acrylonitrile), occurring in solution and in the melt at 180–200°C, has been investigated[356–360]. A reaction mechanism has been proposed, consisting in the thermal excitation of the charge-transfer complex of the polymer and the monomer to a triplet state at the initiation stage followed by the decomposition of the complex with hydrogen transfer and the formation of polymeric radicals activated by paramagnetic centres and behaving as centres for the growth of macrochains. When polyarylvinylenes are added to vinyl monomers in catalytic amounts, the homopolymerisation of the latter is initiated[361–363].

However, the copolymerisation of acetylenes with olefinic monomers is of greatest theoretical and practical interest. The theoretical interest arises primarily from the determination of the causes of the deactivation of the growing centre on polymerisation of acetylenes and the practical interest is due to the creation of new types of polymeric materials combining the properties of conjugated (high thermal stability and resistance to thermal oxidation, semiconducting properties) and saturated polymers (solubility, fusibility, etc.). It has been noted[364–366] that the set of properties characteristic of polyconjugated systems is manifested to a much greater extent when the conjugated blocks in the macromolecule are separated by fairly long non-conjugated sections. It has been suggested that the copolymers of dicyanoacetylene with vinyl monomers be used in articles where both semiconducting properties and thermal stability are needed (thermoelectric devices, transistors, solar batteries, the casings of rockets, etc.)[367] and that the copolymers of polyvinylenes with ethylene and propene be used for the manufacture of synthetic paper[368].

Studies on the synthesis of rubbers with unsaturated units to facilitate their vulcanisation have been made for a long time[369–371]. The aim of many, particularly the early investigations of the copolymerisation of ethynyldimethylvinylmethanol with dienes[372–377], vinylpyrrolidinone, vinylcaprolactams[378], and 2-methyl-5-vinylpyridine[379] has been to obtain the final products. Price and McKeon[156] proposed the following mechanism for the

copolymerisation of vinylacetylenes with acrylonitrile, styrene, isobutene and 2-vinylpyridine (M):



(XVIII) (XIX) (XX) (XXI)

R=R′=H; R=H, R′=Et; R=Me, R′=H; R=Me, R′=Et.

The polymerisation takes place mainly with formation of structures of type (XX), but the monomers with R = Me and R′ = H are partly converted also into structures of type (XIX) or (XXI) [(XVIII)] respectively.

The radical copolymerisation of isoprene with vinylacetylene takes place preferentially and with trimethylvinylethynylsilane exclusively via the double bond of the acetylenic monomer[380]. According to infrared spectroscopic data, isopropenyl- and vinyl-acetylenes are combined into ternary copolymers with ethylene and propene as a result of the dissociation of the triple bond when the reaction is carried out in the presence of $EtAlCl_2$–$VOCl_3$ (or VCl_4).[381,382] According to the available data on the cationic polymerisation of vinylacetylene[158–161], the copolymerisation of vinylacetylene with isobutene in the presence of BF_3 [369] also probably proceeds via the triple bonds of the acetylenic monomer.

Thus the problem of the structures of the copolymers of the vinyl- and isopropenyl-acetylene series is controversial. As for the data on the homopolymerisation of monomers of this type discussed above, the formation of soluble products is attributed both the the involvement in the reaction of only double or triple bonds of one molecule of the acetylenic monomer[130,126] and of the triple bond of one molecule and the double bond of another[130,378]. In the former case linear and in the latter cyclolinear copolymers should be formed.

The copolymerisation of *p*-ethynylstyrene with styrene[113,383] or of propargyl esters of acrylic, methacrylic, and itaconic acids with *N*-vinylpyrrolidinone and *N*-vinylcaprolactam[89,384,385] in the presence of radical initiators probably proceeds preferentially via the double bonds. The number of triple bonds involved in the reaction increases with increasing temperature of the synthesis and at advanced stages of the reaction, which results in the formation of cross-linked products. Under the same conditions, 1,4-di-*p*-chlorophenoxybut-2-yne does not copolymerise with styrene[82].

The explosive copolymerisation of ferrocenylacetylene with chloroprene which could not be prevented by the addition of hydroquinone and which was accompanied by the liberation of iron and HCl, has been observed at 85–90 °C. Under the same conditions, ferrocenylacetylene and isoprene failed to react. It is suggested[386] that the degradative processes are associated with the intermediate formation of an unstable α-chlorovinylferrocene.

Dehalogenation of dihalogenomaleic anhydride in the presence of vinyl monomers can serve as a method for the preparation of copolymers with the acetylenedicarboxylic anhydride units[79]. The synthesis of ternary copolymers has been described: acetylene–ethylene–propene[387,388], acetylene–methylacetylene–propene[389], ethynyldimethylvinylmethanol–butadiene–styrene (or acrylonitrile)[370,390], CH_2=C(R)C≡CH (where R = H, alkyl, cycloalkyl, or aryl) with 1-mono-olefins[381,382] and other similar systems[391], hex-1-yne–cyclohexane–sulphur dioxide[392], and PA–cycloheptene–sulphur dioxide[392].

In the statistical copolymerisation of acetylenes, the preferential interaction of the vinyl monomer is usually noted[388,393–396], which is due to the different reactivities and coordination capacities of the comonomers. Possibly the formation of the copolymer only at a high concentration of the Ziegler catalytic system is associated with the latter factor[397]. However, PA is more active in radical copolymerisation with vinyl chloride[398], vinylidene chloride[399,400], acrylonitrile[401], and maleic anhydride[402].

The alternating copolymerisation of PA [403] and its *p*-dimethylamino-derivative[50,404] with maleic anhydride presupposes, like the alternating copolymerisation of vinyl monomers, the preliminary formation of donor–acceptor complexes of the comonomers. The change in the composition of the copolymer as a function of the proportion of the monomers in the initial mixture shows, according to the author[402], that maleic anhydride does not form a stable complex with PA. On the other hand, thermochemical studies and ESR, NMR, and infrared spectroscopic data have shown[360,405,406] that the copolymerisation of PA with maleic anhydride proceeds with formation of polyphenylene blocks. One cannot rule out the possibility that the first reaction stage consists mainly in the formation of poly-PA with subsequent addition of maleic anhydride units.

The block copolymers of acetylenic monomers can be obtained in different ways. When PA was added to live polyisoprene with a molecular weight up to 500 000, a block copolymer with the molecular weight of the polyene block up to 10 000 was obtained[407]. The opposite sequence is also possible: the addition of monomers to live polyacetylene chains[192]. When ethylenic and acetylenic monomers were introduced alternately into the reactor containing complex initiators, it was possible to obtain copolymers containing up to 10% of acetylenic hydrocarbons[388,389]. Block copolymerisation can occur also with simultaneous supply of the comonomers to the catalyst, as happens in the interaction between acetylenes and olefins in the presence of Et_3Al–$TiCl_3$ [408] or $(iso\text{-}Bu)_3Al$–$VOCl_3$.[409–411] The intense colour of the copolymer after the complete separation of the ferrocenylacetylene homopolymer suggests the possible block copolymerisation also of the ferrocenylacetylene–isoprene pair in the presence of radical initiators and $(iso\text{-}Bu)_3Al$–$TiCl_4$.[397,412] The possibility of the formation of block copolymers of olefins with acetylenes even at a low concentration of the latter is due, according to Matkovskii[413] primarily to the preferential adsorption of acetylenes by the active centres and the difference between the rate constants for the homopolymerisation of the comonomers. Dimethyl- and ethylmethyl-ethynylmethylamines deactivate the active centres much more markedly than PA, probably owing to the additional involvement of the amino-group in the reaction[411]. An increase in the content of the acetylenic comonomer in the initial mixture reduces the rate of copolymerisation, the yield of the copolymer, and its molecular weight[409–411].

The ability of cyanoacetylene to polymerise under the influence of amines[189] has been used to synthesise graft copolymers. The reaction was carried out by adding cyanoacetylene to a solution of the polymeric initiator, which consisted of a homopolymer of 2-vinylpyridine or the copolymers of 4-vinylpyridine and 2-dimethylaminoethyl methacrylate with vinyl monomers[184].

Thus, despite the inhibiting properties of acetylenic monomers in radical[401,414,415] and ionic[409–411,413] polymer-

Table 1. Conditions governing the preparation of binary acetylenic copolymers.

Acetylenic comonomer	Second comonomer	Initiator	Solvent	Temperature, °C	References
1	2	3	4	5	6
Acetylene[a]	Propyne	$NiCl_2$—$NaBH_4$, $PtCl_4$—B_2H_6, $OsCl_3$—$LiAlH_4$	THF, acetonitrile	26—35	323
	But-1-yne	$NiBr_2$—$NaBH_4$	THF	26	323
	Hept-1-yne	$CoCl_2$—$NaBH_4$, $PhCl_3$—LiH	THF	26—35	323
	Phenylacetylene	$Pd(NO_3)_2$—SiH_4	Ethanol	40	323
	Propargyl alcohol	$RuCl_3$—KBH_4	Dioxan, ethanol	35	323
	Ethylene	(iso-Bu)$_3$Al - $VOCl_3$	n-Heptane	20	410
	Propene	Et_3Al—$TiCl_3$	n-Heptane	50	409
		Et_3Al—$3TiCl_3 \cdot AlCl_3$	n-Heptane	70	388
		Et_3Al—$3TiCl_3 \cdot AlCl_3$	Petrol	50	388
		$TiCl_3$—$LiAlH_4$	Petrol	150—160	389
	Buta-1,3-diene	Et_2AlCl - Ni naphthenate	Toluene	20—30	395
		Et_3Al—$TiCl_4$	n-Heptane	~50	417
	Styrene	Et_3Al—$TiCl_4$	Chlorobenzene	70—75	418
Propyne	But-1-yne	(iso-Bu)$_3$Al - VCl_3	Benzene	12.8	343
	Pent-1-yne	(iso-Bu)$_3$Al - VCl_3	Benzene	12.8	343
	Propene	Et_2AlCl—$CrCl_3$[b]	—	77	389
	Isobutene	BF_3	Petroleum ether	—60	394
	Buta-1,3-diene	Et_3Al—$TiCl_3$	n-Heptane	50	408
	SO_2	H_2O_2	Paraldehyde	~20	419
But-1-yne	Phenylacetylene	Et_3Al—$TiCl_3$	Benzene	30	343
	Isobutene	BF_3	Petroleum ether	—10	394
	SO_2	H_2O_2	Paraldehyde	~20	419
Pent-1-yne	Isobutene	BF_3	Petroleum ether	—10	394
	SO_2[c]	H_2O_2	Paraldehyde	~20	419
	SO_2[d]	Ascaridol	Ethanol	~20	421
3-Methylbut-1-yne	Isobutene	BF_3	Petroleum ether	—10	394
Hex-1-yne	Methyl acrylate	BP	—	60	401
	Acrylonitrile	BP	—	60	401
	SO_2	H_2O_2	Paraldehyde	~20	419
Vinylacetylene	Isobutene	BF_3	—	—100	369
	Acrylonitrile	AIBN	—	60	156
Isopropenylacetylene	Acrylonitrile	AIBN	—	60	156
	2-Vinylpyridine	AIBN	—	60	156
Propargyl alcohol	Vinyl chloride	AIBN	THF	70	398
Propiolaldehyde	Styrene	AIBN	—	60	422
	Methyl methacrylate	AIBN	Benzene	60	423
Cyanoacetylene	Phenoxyacetylene	—	—	43	38
	Acrylonitrile	NaCN	DMF	—40 — ~20	183
Phenylacetylene	Ferrocenylacetylene	$AlCl_3$	n-Heptane	—70	342
	Ethylene	Et_3Al—$TiCl_3$	n-Heptane	50	408
		(iso-Bu)$_3$Al - $VOCl_3$	n-Heptane	20	411
	Propene	Et_3Al—$3TiCl_3 \cdot AlCl_3$	n-Heptane	70	388
		Et_3Al—$MoCl_3(MoCl_5)$	n-Heptane	100	418
	Isobutene	$AlCl_3$	EtCl	—78	393
	But-1-ene	Et_3Al—$TiCl_3$	n-Heptane	60—65	418
	Pent-1-ene	Et_3Al—$TiCl_3$	Benzene	50—70	418
	Styrene	AIBN	—	60	424, 425
		BP	—	60	414
		1-Azobiscyclo-hexane-1-carbonitrile	—	60	401
	Vinyl chloride	AIBN	THF	70	398
	Vinylidene chloride	Radical	—		399, 400
	Methyl acrylate	BP	—	60	401, 414
	Methyl methacrylate	AIBN	—	60	424—426
		AIBN, photochemically	—		427
		—	—	150	428
	Ethyl methacrylate	AIBN	—	60	429
	n-Propyl methacrylate	AIBN	—	60	429
	n-Butyl methacrylate	AIBN	—	60	429
	Isobutyl methacrylate	AIBN	—	60	429
	Vinyl acetate	BP	—	60	414
	Maleic anhydride	—	—	150	360, 405, 406
		^{60}Co γ-radiation	Acetone	30	402
		AIBN	Acetophenone	98	403
		AIBN, photochemically	Ethyl methul ketone	4—6	403
		—	—	98	403
	Acrylonitrile	BP	—	60	401, 414
	2-Vinylpyridine	BP	—	60	414
	Fumaronitrile	—	—	170	405, 406
	SO_2	H_2O_2	Paraldehyde	~20	419
		Ascaridol	Ethanol	~20	421
n-$RC_6H_4 \equiv CH$	*p*-Methoxyphenylacetylene (R = Cl)	*t*-Butyl peroxide	—	120	38
	Styrene (R = Me, MeO, Cl, Br, or NO_2)	AIBN	—	60	424
	Methyl methacrylate (R = Me, MeO, Cl, Br, or NO_2)	AIBN	—	60	424
	Maleic anhydride (R = Me_2N)	AIBN	Benzene	60	50, 404

Table 1 (continued).

Acetylenic comonomer	Second comonomer	Initiator	Solvent	Temperature, °C	References
1	2	3	4	5	6
Ferrocenylacetylene	Isobutene	BF_3	CH_2Cl_2	−40	430
	Isoprene	(iso-Bu)$_3$Al – $TiCl_4$, t-butyl peroxide or Co(Acac)$_2$	Toluene o-Xylene	20 150	397 412
2-Ethyl-1-vinylacetylene	Acrylonitrile	AIBN	—	60	156
	2-Vinyl pyridine	AIBN	—	60	156
diphenylacetylene	Styrene	BP	—	60	401
	Methyl acrylate	BP	—	60	401
	Acrylonitrile	BP	—	60	401
Hexafluorobut-2-yne	1-Chloro-1-fluoro-ethylene	$(NH_4)_2S_2O_8$—$Na_2S_2O_5$	Emulsifier	20	431
	1,1-Difluoro-3-methylbutadiene	$K_2S_2O_8$; pH = 10.2	»	50	431
Dicyanoacetylene[b]	Styrene	AIBN	THF	55	99, 367
Butyne-1,4-diol	Acrolein	p-$MeC_6H_4SO_3H$	—	~20	432
		$BF_3 \cdot OEt_2$, $SnCl_4$, $FeCl_3$	—	20	433
ROOC — C≡C — COOR′	Vinyl chloride (R = Me, R′ = H)	BP	Methanol	60	434
	Methyl acrylate (R = Me, R′ = H)	BP	Benzene	60	434
	Vinyl acetate (R = R′ = Me)	BP	—	60	434
	Isobutene (R = R′ = Et)	H_2O_2	—	60	434
	Vinyl chloride (R = R′ = Et)	H_2O_2	—	60	434
	Ethyl vinyl ether (R = R′ = Et)	BP	—	60	434
	Methyl methacrylate (R = R′ = Et)	BP	—	60	434
	Vinyl acetate (R = R′ = Et)	BP	—	60	434
p-Diethenylbenzene	Styrene	AIBN	—	60	435
	Methyl methacrylate	AIBN	—	60	435

[a] There is a possibility of the copolymerisation of acetylene with mono-olefins at 40–150°C in DMF under the influence of catalytic systems, consisting of inorganic and organic cobalt or nickel salts and alkali metals or their acetylides[416], and also of the copolymerisation of acetylene or other alkynes with dienes in hydrocarbon solvents at 50°C under pressure in the presence of catalysts of the Ziegler–Natta type[417].

[b] Transition metal halides mixed with lithium and aluminium alkyls, aluminium halide alkyls, or aluminium hydrides can serve as catalysts[389].

[c] Copolymers of hept-1-yne have also been obtained under these conditions[419,420].

[d] Copolymers of non-1-yne, cyclohexylpropyne, and pentadec-1-yne have also been obtained under these conditions[421].

[e] The copolymerisation with other monomers under the influence of radical or ionic initiators is also possible[367].

isation of vinyl monomers, it has been possible to obtain different types of copolymers of acetylenes with olefins (Table 1).

From kinetic studies of the radical polymerisation of styrene and methyl methacrylate in the presence of PA and its derivatives, Higashiura and Oiwa[424,426] regard acetylenes as highly effective inhibitors and not as comonomers. The inhibiting activity of acetylenes is associated primarily with the resonance stabilisation of the terminal growing chain radical and the activity of the acetylenic radicals should decrease sharply with increase in the size of the conjugated block to which the active centre is linked. Bearing in mind that the probability of the formation of radicals of this type should depend on the concentration of the acetylenic monomer in the reaction mixture and on the corresponding reaction rate constants, Uzbekova and Razumovskii investigated the radical copolymerisation of *p*-diethynylbenzene[435] and PA [425] with styrene and methyl methacrylate using reaction mixtures with a low content of the acetylenic monomer. Their data show that the acetylenes investigated can be regarded as comonomers with a weak inhibiting activity.

Zaitsev et al. proposed an equation for the determination of the composition of the copolymer[436], taking into account the characteristics of the radical copolymerisation of acetylenes noted above, i.e. the difference between the reactivities of the radicals —CH=ĊR and —CH=C(R)—ĊH=CR:

$$\frac{d[M]}{d[X]} = \frac{r_X[X]/[M] + r_X r_M + r_M[M]/[X] + 1}{2r_X[X]/[M] + 1}, \qquad (1)$$

where $r_M = k_{MM}/k_{MX}$, $r_X = k_{XX}/k_{XM}$, and M and X are respectively the vinyl and acetylenic monomer. Table 2 shows (the copolymerisation conditions are indicated in Table 1) that the copolymerisation constants r_M calculated from the classical equation and from Eqn. (1) on the basis of the same experimental data hardly differ, while the values of r_X differ appreciably, as was to be expected.

Table 2. The copolymerisation constants for acetylenic and vinyl monomers.

Acetylenic comonomer (X)	r_X	Vinyl comonomer (M)	r_M	References
n-Butylacetylene	0	Methyl acrylate	11.2±2	401
	0	Acrylonitrile	5.4±0.3	401
Vinylacetylene	0.60±0.02	Acrylonitrile	0.13±0.01	156
	0.13	Isobutene	8.0	369, 400
Isopropenylacetylene	0.47±0.01	Acrylonitrile	0.33±0.01	156
	0.55±0.01	2-Vinylpyridine	1.65±0.05	156
Propargyl alcohol	1.0	Vinyl chloride	2.3	398
Propiolaldehyde	0.21	Styrene	0.32	422
	0.27±0.04	Ditto	0.62±0.02	401
	0.47±0.1	Methyl methacrylate	0.65±0.02	436
	0.20±0.02		1.5±0.03	427
Phenylacetylene	—	Ditto	0.81±0.1	425
	0.05	"	0.85±0.1	436
	0.23±0.03	Ethyl methacrylate	2.1±0.1	429
	0.22±0.02	n-Propyl methacrylate	1.4±0.1	429
	0.21±0.02	n-Butyl methacrylate	1.7±0.2	429
	0.27±0.02	Isobutyl methacrylate	1.9±0.1	429
	0.36±0.02[a]	Styrene	0.34±0.1	425
	0.84±0.1	"	0.36±0.04	436
	0.33±0.05	Acrylonitrile	0.26±0.03	401
	0.69±0.04	"	0.30±0.02	436
	0.2±0.05	2-Vinylpyridine	4.0±0.7	414
	0.32±0.15	"	4.0±0.2	436
	3.0	Vinyl chloride	0.2	398
	1.4	Vinylidene chloride	0.1	399, 400
	0.50±0.05	Maleic anhydride	0.05±0.05	402
2-Ethyl-1-vinyl-acetylene	0.63±0.4	Acrylonitrile	0.17±0.01	156
	0.6±1	2-Vinylpyridine	1.5±0.5	156
Diphenylacetylene	0	Methyl acrylate	55±5	401
	0	Acrylonitrile	13.6±1.0	401
Dicyanoacetylene	0	Styrene	1.4	99
p-Diethyny benzene	—	Methyl methacrylate	0.606±0.15[b]	435
	—	Ditto	0.60±0.1	436
	0.74±0.02[a]	Styrene	1.18±0.1[b]	435
	0.87±0.1	"	1.15±0.1	436

[a] Calculated by Zaitsev et al.[436] from the data of Uzbekova and coworkers[425,435].

[b] r_M was calculated from the differential equation for the composition of a copolymer of bifunctional monomers[437].

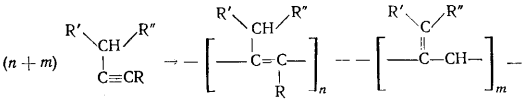
VI. THE STRUCTURES AND ELECTROPHYSICAL PROPERTIES OF ACETYLENIC POLYMERS

The data on the kinetics of the polymerisation of a number of acetylenes discussed above indicate a monomolecular mechanism of chain termination and the independence of the molecular weight of the conditions of the synthesis. Regardless of the chemical nature of the acetylenic monomers and the methods used to polymerise them, polymers with low molecular weights are usually obtained ($\overline{M}_n$ does not exceed 1000–5000). These facts demonstrate the inactivation of the reactive centre during the polymer chain propagation process.

On the one hand, the active centre of the growing chain is linked directly to the conjugated system, so that the reactivity must be evidently influenced by factors which determine the mobility and degree of delocalisation of π electrons. Indeed theoretical calculations based on models involving a conjugated reaction centre[201,212–214,438] confirmed that the delocalisation of the charge or the radical over the conjugation chain with increasing length of the polymeric molecule are the cause of the kinetic deactivation of the active centres. On the other hand, the active radical formed, for example, on dissociation of the triple bond is located in the p_{xy} orbital in the plane perpendicular to that of the conjugated p_z orbitals. In this case the active radical must be appreciably localised in the last unit of the growing chain owing to the weak overlapping of the electronic wave functions and its reactivity should not therefore depend on the chain length.

Thus the mechanism of the delocalisation of the unpaired electron of the growing polymeric radical in radical polymerisation or of the ionic charge in the ionic polymerisation of acetylenes is not self-evident. Therefore, the possibility of the intermolecular inactivation of the reactive centre is postulated together with the intramolecular inactivation[23].

The breakdown of the continuity of the conjugation chain may lead to a growth of the polymer chain which virtually rules out the inactivation of the growing macroradical. Thus the polymerisation of alkylacetylenes containing mobile hydrogen atoms in the α-position relative to the triple bond is accompanied by hydrogen transfer from the alkyl side group to the main chain and the formation of alkylidene side groups[268,305,439,440]:



As a result of the breakdown of the continuity of the conjugated chain, weakly coloured high-molecular-weight polymerisation products are formed.

Long conjugation chains with a coplanar disposition of the C=C bonds are probably unfavourable on thermodynamic and kinetic grounds. The conjugated fragments of macromolecules tend to assume an arrangement relative to one another at an angle in the range $0° < \theta < 90°$C. The macromolecules formed are not planar: they can have different steric conformations in which the exchange interaction of the π electrons diminishes with increase of $\cos^2\theta$. Therefore, in order to estimate the conjugation chain lengths in the macromolecules, the concept of "effective conjugation" or of "block conjugation" has been introduced; it is conventionally expressed in terms of the number of conjugated structural elements having a coplanar arrangement and an electronic absorption or luminescence spectrum analogous to that of the corresponding polymeric homologue as regards the position of the maximum[23,336]. The size of the conjugated block depends on the conditions of the synthesis, but changes little with increase in the length of the macromolecule. The conjugated blocks in polyPA, obtained by thermal polymerisation in bulk at 150°C and in the presence of the Et_3Al–$TiCl_3$ catalytic system in benzene at 70°C, consist of 3–5 and 4–8 units respectively[336,441,442].

The monomeric units in polyPA are combined "head-to-tail"[443–445]. Polyenes obtained under different conditions differ from one another by the position of the substituents both in relation to the double bond and in relation to the chain itself[19,40,224,336,337,446,447]. Four types of chain conformation are possible for polymers of the polyPA type: *trans*-*s*-transoid, *trans*-*s*-cisoid, *cis*-*s*-cisoid, and *cis*-*s*-transoid. For a free rotation of 180° about the single bond, there is a possibility of a transition from the *s*-transoid form to the *s*-cisoid form and converseley. It was found experimentally[336] that polyPA obtained by thermal polymerisation has mainly the *trans*-*s*-cisoid conformation (the angle of rotation about the single bond is $\varphi = 120°$C) with an admixture of the *cis*-structure. The fractions of the polyPA obtained in the presence of Et_3Al–$TiCl_3$ can have the *cis*-*s*-cisoid and *cis*-*s*-transoid conformations (φ = 140–150° and <80° respectively). According to calculated data[447], the *cis*-*s*-cisoid conformation ($\varphi = 110°$) is energetically favoured for polyPA. The discrepancy between the calculation and experiment in the last two instances has been attributed by the

author[447] to intermolecular interaction. The benzene-soluble polyPA and poly-(α-ethynylnaphthalene) fractions, obtained in the presence of $Fe(DMG)_2.2PyH + Et_3Al$, have the *cis*-*s*-transoid conformation, while block polymerisation of PA and α-ethynylnaphthalene leads to products having the *trans*-transoid structure[337].

Molecules with the *cis*-*s*-cisoid conformation can give rise to close packing of the same type as in molecular crystals. The distances between the molecules are then still so large that intermolecular delocalisation cannot be appreciable. The macromolecules with the *cis*-*s*-transoid conformation are more close packed. Accordingly, Ziegler polyPA is characterised by the presence of crystalline formations (degree of crystallinity about 30%), while thermal polyPA is amorphous[40,448]. Together with the soluble Ziegler polyPA having the *cis*-*s*-transoid conformation and a yellow colour, which has already been considered, a small amount (about 5%) of a red product with a high degree of crystallinity (>70%) and insoluble in organic solvents at room temperature is formed. This product is an assembly of macromolecules with the *cis*-*s*-cisoid structure firmly fixed to the surface of the catalyst. The helical molecular chain contains three monomeric units per repeat period with benzene rings slightly inclined relative to the chain axis. The crystal lattice consists of chains located one above the other without displacement; the packing coefficient is 0.8.[449]

Possibly all the isomeric polyene structures discussed above exist in the helical form and are characterised by a greater (for the *cis*-form) or smaller (for the *trans*-form) packing density. Helical chain conformations impart an ordered structure to the macromolecules, which enables them to be distributed in crystal matrices[337]. The helical structure of the linear conjugated polyhexafluorobut-2-yne is probably responsible for the white colour of this polymer[450].

It has been suggested on the basis of the number and intensity of the diffraction lines and in view of the identity of their periodicities[337] that more ordered packing of the macromolecules is achieved at lower temperatures of the synthesis and that the packing in crystalline matrices depends more on the structure of the main polymer chain than on the nature of the substituent.

The non-stereospecificity of anionic polymerisation noted above can be attributed both to the non-stereospecificity of the addition of the anion to the triple bond and to the isomerisation of the growing anion or the macromolecules when they are isolated and investigated. It is known[224,446,447] that heat treatment or treatment with solvents causes the isomerisation of polyPA. The *cis*–*trans* isomerisation of polyacetylene has been observed on decomposition of catalysts of the Ziegler–Natta type by a mixture of methanol and hydrochloric acid[451] and as a result of the heat generated by a laser source in the recording of Raman spectra[452]. The ratio of the *cis*-transoid and *trans*-transoid structures apparently depends primarily on the temperature of the addition of the first monomeric unit to the catalyst, i.e. on the formation of the complex (XVII). If the transition (XVI) → (XVII) takes place at a low temperature (−78°C), then fully *cis*-transoid poly-(α-ethynylnaphthalene) is formed not only at −78°C but also at a polymerisation temperature of 25°C.[226]

Thus the configuration of the polyene is determined mainly by the composition of the catalyst and the temperature of the synthesis; a *cis*-transoid configuration presupposes the *cis*-dissociation of the triple bond in the polymerisation process. On the other hand, according to electron microscope data, the supermolecular structure of polyenes changes very little with the temperature of the synthesis and is almost independent of the type of the catalyst and its concentration[337,451].

Regardless of the nature of the aromatic substituent, all the polyenes investigated form only globular structures with dimensions up to 300–700 nm. More complex morphological formations in the form of rods or other structures have not been observed even for *cis*-transoid polymers with the highest degree of crystallinity[337,453,454]. The characteristics of the molecular, the supermolecular, and the electronic structures of acetylenic polymers discussed above determine their semiconducting properties[22,112,120,226,455–458].

The dark and photoelectric conductivities of soluble polyvinylenes do not usually exceed $10^{-12}\ \Omega^{-1}\ cm^{-1}$ regardless of the nature of the initial monomer and the polymerisation conditions. The mobility is of an electronic type; as a rule, one is dealing with *p*-type conductivity with a mobility of $10^{-4}\ cm^2\ V^{-1}\ s^{-1}$.[456,459] When a polymer–electron acceptor heterophase system is formed, it is possible to increase greatly the photoconductivity of the system relative to the level of the photoconductivity of both the polymer and the acceptor[460–465]. Not only the corresponding low-molecular-weight compounds but also polymeric compounds, for example the products of the nitration of PA and tolane polymers, can be used as electron acceptors even under the conditions of electrophotography. In the presence of polymeric acceptors, the system exhibits film-forming properties and an improved thermal stability in addition to the enhanced photosensitivity[466,467].

Possibly the increase of photoelectric sensitivity is associated with the spectral sensitisation of the acceptor by the polyene system. Since the spectral sensitisation constitutes the most important procedure for varying the spectral photosensitivity and increasing the integral photosensitivity of silver halides in photography and of zinc oxide in electrophotography, the spectral sensitisation of the photoconductivity of inorganic semiconductors by conjugated polymers is of great interest[468–471]. The electrical conductivity of polymers is defined by the relation[455]:

$$\sigma = q\mu n = q\mu N e^{-E/2kT} ,$$

where q is the elementary charge of the current carriers (electrons), μ the mobility of the carriers, n the number of carriers per unit volume, N the concentration of π electrons, and E the activation energy for conduction (the gap between the valence and conductivity bonds under the conditions of the band mechanism of conduction).

The activation energy is determined mainly by the electron–electron repulsion in the polymer chain; it amounts to 2.5 and 2.4 eV respectively for PA and tolane polymers[472]. The gap may be reduced only when the electron–electron interaction in the polymer chain is weakened, which involves the withdrawal of electrons from the chain under the influence of, for example, electron-accepting side groups[473]. With increase of the degree of conjugation of the cyclic benzene side groups with the main chain, which is achieved by the high-temperature sublimation of the polymer (500°C, 10^{-5} mmHg), the mobility of the holes in the sublimed films of PA and tolane polymers increases from 2×10^{-4} to 0.1 and from 2×10^{-4} to 0.3 $cm^2\ V^{-1}\ s^{-1}$ respectively, while the activation energy for conduction diminishes to 1.4 and 1.3 eV.[472,474,475]

The activation energies for conduction and the mobilities obtained for the sublimed polyphenylvinylene films are probably close to the theoretical limit. Indeed, with

decrease of the electron–electron repulsion in the polymer chain under the influence of electron-accepting side group substituents, the concentration of carriers also falls, i.e. the compensation effect comes into force[456].

The mobility of the charge carriers is determined by the intermolecular transitions of these carriers between the conjugated regions. Their low mobility in conjugated polymers in the acetylenic series is due primarily to the low degree of overlapping of the atomic wave functions at the sites corresponding to the breaks in conjugation. Branching and cross-linking in macromolecular chains should therefore lead to a decrease of the activation energy for conduction and to an increase of the mobility of the carriers. Ladder and graphite-like structures can be regarded as limiting cases of the structures of regularly cross-linked polymers.

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The data examined demonstrate an extremely vigorous development in recent years of research on the polymerisation processes of acetylenic compounds. This is associated primarily with efforts directed towards the creation of new organic semiconducting materials. A number of mechanisms have been proposed for the thermal and catalytic polymerisation of acetylenes, which may be regarded as merely hypothetical in view of the contradictory nature or lack of convincing data for the kinetics and mechanisms of the processes. An unambiguous answer to the question of the causes responsible for the deactivation of the growing active centre in the polymerisation of acetylenes has not yet been obtained. There is no doubt that further study of the copolymerisation of alkynes is of interest from both theoretical and practical points of view. We share Myl'nikov's view that "together with the importance of seeking new semiconducting organic polymers there is an urgent necessity for a more detailed investigation of the specific physical structure as solids with a simultaneous development of methods for their purification and for the determination of the impurities"[458]. However, the activation energies for conduction and charge carrier mobilities greater than about 1 eV and about 1 $cm^2\ V\ s^{-1}$ respectively should not probably be expected even for well ordered polyvinylene systems with a linear structure. Studies involving both the synthesis of regular ladder and graphite-like systems and an increase in the photoconductivity of organic semiconductors under the influence of electron acceptors are possibly the most promising in this sense.

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