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Oligomers and Polymers with Reactive Acetylenic Groups

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The problem of the synthesis and study of the properties of thermoreactive oligomers and polymers containing reactive acetylenic groups, leading to the formation of compounds with a three-dimensional structure, are examined. Pathways leading to the formation of oligomers and polymers from acetylenic monomers during their polycyclotrimerisation with retention of the residual acetylenic groups as well as the methods of synthesis of various oligomers and polymers with subsequent introduction of acetylenic groups into the latter are indicated. The possible structural transformations of the acetylenic groups during the hardening process with formation of rigid and cross-linked polymers without the evolution of volatile products are discussed. The bibliography includes 126 references.

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I. INTRODUCTION

The problems of the synthesis of oligomers and polymers with acetylenic bonds and of the preparation of materials based on them has recently been attracting increasing attention. This can be explained by the likely usefulness of acetylenic compounds for the preparation of reactive oligomers and polymers and heat resistant and thermostable materials based on them. The acetylenic group is being successfully used nowadays in various classes of thermostable polymers: polyphenylenes and carbochain polymers, polyethers and polyesters, polyamides, polyurethanes and other heterochain compounds, and polymers with a heterocyclic structure: polyimides, polyphenylquinoxalines, polydibenzoxazoles, etc.

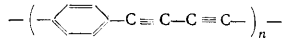
The use of the acetylenic group in the synthesis of polymers has led to considerable progress in the chemistry and technology of materials based on the polymers enumerated above. In the first place mention should be made of the decreased processing temperature, the improved solubility and fluidity of the starting materials, the possiblity of obtaining large components, and an improvement in the quality of the articles. One of the first polymers of acetylene has been "cuprene" obtained at the end of the last century by passing acetylene through a copper tube heated to 240–250 °C.[1] It did not find practical applications.

At the end of the 1960s Korshak and co-workers[2,3] achieved the polymerisation of a number of acetylenic compounds under pressure. Phenylacetylene and propargyl alcohol were polymerised and polymers with a system of conjugated double bonds were obtained. In a number of other studies[4,5], various monomers were subjected to catalytic and radiation-induced polymerisation. These investigations indicated ways of employing the acetylenic group in polymer synthesis and revealed the possibility of stabilising many polymers by binding the free radicals formed on decomposition of the polymer.

Oligomers and polymers containing acetylenic groups were first obtained by Korshak and co-workers[6,7] and also by Kotlyarevskii et al.[8] by the oxidative dehydropolycondensation of acetylenic monomers. Thus, "carbyne"—a polymer with triple carbon–carbon bonds in the chain which constitutes a new linear modification of carbon—was obtained from acetylene by this reaction; it is a black powder capable of being converted into graphite at 2300 °C.[7] The carbyne formation reaction can be represented schematically in a general form as follows:

$$n\,HC{\equiv}CH \xrightarrow{[O]} (-C{\equiv}C-)_n- \quad .$$

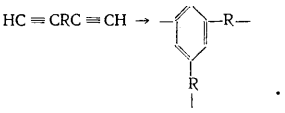
Polyacetylene having the structure



has been obtained from *p*-diethynylbenzene. The study of polyacetylenes showed that they possess semiconducting properties and exhibit photoconductivity.

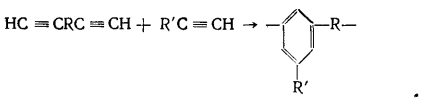
The specific synthesis of carbyne has been achieved[9] by the dehydrochlorination of poly(vinylidene chloride).

The polymerisation and oxidative dehydropolycondensation reactions of acetylenic monomers lead to the formation of linear polymers. At the end of the 1960s and the beginning of the 1970s Korshak and co-workers[10,11] developed a funamentally new method of synthesis of polymers with acetylenic groups by the polycyclotrimerisation of acetylenic compounds in which aromatic carbocycles are formed as a consequence of the interaction of three acetylenic groups and their closure to form a six-membered ring in accordance with the scheme



However, certain difficulties arise in carrying out this process with a high degree of selectivity, because all the monomers used for the polycyclotrimerisation can just as readily polymerise with the parallel formation of other unity in the chain, which is undesirable from the standpoint of the polycyclotrimerisation process. In order to carry out the polycyclotrimerisation reaction, it is necessary that at least one of the monomers involved in the process should contain two acetylenic groups. The polycyclotrimerisation reaction is usually performed in the presence of a catalyst[12–15] whose efficienty largely determines the selectivity of the process.

The joint polycyclotrimerisation in accordance with the scheme

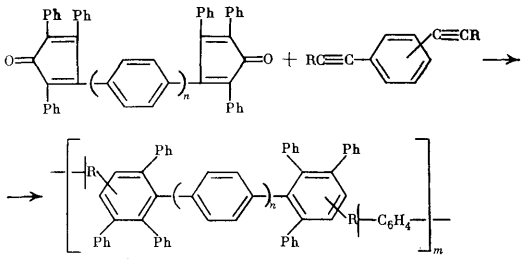


is of greatest practical interest. This reaction is based on the use of acetylenes and their derivatives and does not lead solely to the formation of polyphenylenes having various structures and containing reactive groups. The most interesting are the oligophenylenes containing residual triple bonds as functional groups, because this facilitates the subsequent, chemical modification and hardening of the polymers. The polycyclotrimerisation process makes it possible to regulate the content of the triple bonds in the polymer[15-18].

The above possibilities of the polycyclotrimerisation reaction have attracted in recent years much attention by investigators working in the field of the synthesis of polymers both in our country and abroad. A review was published in 1980 [19] which attempted to extend the fundamental approach to the introduction of the acetylenic linkage into an oligophenylene, developed by Soviet workers[20], to other classes of polymers. The studies initiated by Korshak and co-workers[10] on the polycyclotrimerisation of acetylenic compounds were subsequently extended by the same investigators to the polycyclotrimerisation of dinitriles and dicyanoesters; on this basis, a general method was developed for the synthesis of polymers[21,22], their modification, and the formation of three-dimensional networks.

Before the publication of the studies by Korshak and co-workers, isolated communications on the problems of the synthesis of acetylene-containing polyphenylenes could be found in the literature. Thus the Diels–Alder reaction of bistriphenylcyclopentadienones with diacetylenes in accordance with the scheme

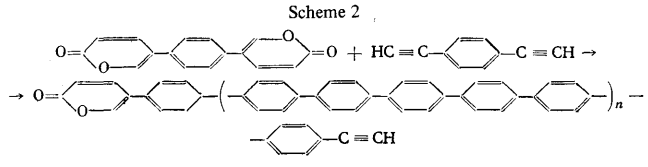
Scheme 1



has been described[23,24]. In the presence of more than a twofold excess of acetylene, the resulting polymer could contain acetylenic groups at the ends of the macromolecule.

The reaction of bispyrones with diacetylenes[24] via the scheme

Scheme 2



proceeds analogously.

At attempt has been made to obtain aromatic polymers from non-conjugated diacetylenes[26]. However, the oligomers synthesised consisted mainly of polymers having a polyene structure with small amounts of admixtures of dimers and trimers having indan, cyclophane, and arylacetylene structures.

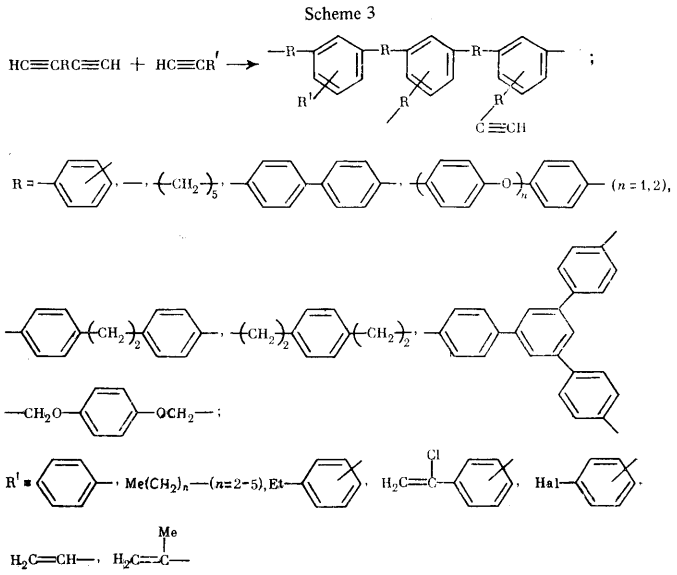
Extensive data have now accumulated on the problem of the synthesis and study of the structures and properties of oligomers and polymers containing reactive acetylenic groups; examination and survey of these data is the aim of the present review.

II. CARBOCHAIN OLIGOMERS AND POLYMERS

1. Polyphenylenes

One of the most common methods of synthesis of oligophenylenes with acetylenic groups is the polycyclotrimerisation of diethynylcompounds or their mixtures with monoethynyl compounds. The possibility of carrying a selective process under relatively mild conditions has been noted[10,27,28]. A series of syntheses in accordance with the scheme

Scheme 3



were carried out.

p-Diethynylbenzene and phenylacetylene have acquired the greatest importance as the diethynyl and monoethynyl compounds respectively. The polycyclotrimerisation reaction is usually accompanied by the conversion of the acetylenic compounds into polyenes. The catalysts of such a mixed process may be $[(EtO)_3P]_4CoBr$, $NiCl_2.2PPh_3.2NaBH_4$, and also Ziegler catalysts[20]; it has been shown that the last are the most effective and that in their presence (for specific ratios of AlR_3 and $TiCl_4$) the polycyclotrimerisation reaction becomes dominant. The oligophenylenes obtained with molecular weights in the range 1000–5000 readily dissolve in benzene, toluene, and chlorinated organic solvents.

The study of the thermal properties of the products showed that they are readily hardened[10] at temperatures in the range 150–250 °C and that the hardening process is completed at 300–350 °C. Oligophenylenes containing residual ethynyl groups are therefore capable of producing polyphenylenes with a high deformation thermal stability, the latter increasing with the number of ethynyl groups in the initial oligophenylene. The properties of the oligophenylene depend on the structure of the initial monomers, on the reaction conditions, on the type and composition of the catalyst, and the ratio of the initial monoethynyl and diethynyl monomers, etc. Certain methods of synthesis and properties of the oligophenylenes were described previously in reviews[29,30] and here we shall deal with the main new investigations.

The mechanism of the polycyclotrimerisation reaction of acetylenic compounds was investigated by statistical and thermodynamic methods and also a number of other procedures[15,16,29–36] and it was concluded that the reaction involves stepwise coordination polyaddition which differs from both polymerisation and polycondensation and is a new reaction leading to the synthesis of polymers. As a consequence of the coordination character of the process, the structure and properties of the oligomers obtained depend on the structure of the initial monomers and in the first place on the flexibility or rigidity of the interethynyl diacetylene fragment[37–40] and on steric factors[17,18,36,41], because they determine the nature of the preliminary orientation of the acetylenic molecules in the formation of the aromatic ring on the catalytic complex. The stepwise, discrete character of the process is responsible for the additivity of the influence of the ratio of the diethynyl and monoethynyl monomers, of the order of the introduction of the monomers, and of other reaction conditions on the structure and properties of the polyphenylenes[18,42–44].

The reaction mechanism was inferred with the aid of the statistical theory of branching processes based on the cascade theory[15,16,39,40,45,46]. The structure of the oligophenylenes was investigated by the method of ozonolysis[47]; it was shown that the polycyclotrimerisation of acetylenic compounds in the presence of the $Al(iso\text{-}C_4H_9)_3$–$TiCl_4$ catalytic system is a highly selective process and the influence of the polyene sections has almost no effect as a consequence of their small amount.

Taking into account the characteristics of the polycyclotrimerisation reaction, polymers with properties useful in practice, namely thermostable and mechanically strong polymers, were synthesised specifically from phenoxyacetylenes[38,48,49]. Thus, as a consequence of the presence of oxygen "hinge" atoms between the benzene rings, the polymers based on di(4-ethylphenyl) ether and 1,4-di(4-ethynylphenoxy)benzene produced specimens which are more easily worked than oligophenylenes based on *p*-diethynylbenzene and have high moduli of elasticity and high compressive strengths (reaching 1000–1400 kg cm^{-2} compared with 350 kg cm^{-2} for oligophenylenes based on *p*-diethylbenzene); the limiting deformation of these polymers without rupture and their thermal stability and heat resistance were also higher. According to thermogravimetric data, intense weight losses are observed in an inert atmosphere in the temperature range 450–600 °C.[48]

In order to modify the properties of the oligomers, oligophenylenes based on various diethynyl, triethynyl, and monoethynyl monomers were synthesised: diphenyl butadiyne[50], 4,4′-diethynylbiphenyl[48], di(4-ethynylphenyl)ethane[37], diethynyltetraphenyldisiloxane[51], vinyl- and isopropenyl-acetylenes[52,53], chlorovinylphenylacetylene[42], ethylphenylacetylene[54], tri(ethynylphenyl)benzene[41] and other triethynyl compounds.

In order to increase the thermal stability of the polymer by increasing the number of unsaturated groups in the oligophenylene and in order to be able to employ the latter as a cross-linking agent, branched oligophenylenes with double bonds were synthesised[52,53] by the partial or complete replacement of phenylacetylene (in its copolycyclotrimerisation reaction with *p*-diethynylbenzene) by alkenylacetylenes: binylacetylene or isopropenylacetylene. The reaction was carried out at −10 °C in the presence of $Al(iso\text{-}C_4H_9)_3$–$TiCl_4$, which is the most effective catalyst of the trimerisation of alkenylacetylenes[55,56]. In view of the ready structure formation in oligophenylenes with vinyl groups, a product fully soluble in organic solvents was obtained only on the basis of the ternary copolymer of *p*-diethynylbenzene, phenylacetylene, and vinylacetylene. The possibility of regulating the number of unsaturated groups in the ternary copolymers by varying the ratio of the initial components was demonstrated.

Oligophenylenes containing vinyl chloride groups have been synthesised[42]. During the preparation of *p*-diethynylbenzene from technical divinylbenzene, ethynyl(chlorovinyl)benzene remains in the reaction products as a consequence of the incomplete dehydrochlorination; it is difficult to remove completely. In order to elucidate the influence of this group on the polycyclotrimerisation product and to determine the possibility of achieving the synthesis from unpurified *p*-diethynylbenzene, the study mentioned above[42] was undertaken.

It was established that, when *p*-diethynylbenzene, phenylacetylene, and ethynyl(chlorovinyl)benzene interact, an oligomer with an increased degree of saturation of the bonds is formed as a result of the retention of the vinyl chloride group during the reaction. It was shown that phenylacetylene is more reactive towards *p*-diethynylbenzene than ethynyl(chlorovinyl)benzene. The chlorine atom in ethynyl(chlorovinyl)benzene apparently reduces (as a consequence of the inductive effect) the electron density in the triple bond of the acetylenic group relative to the electron density of the triple bond of phenylacetylene. The use of triethynyl monomers greatly improves the thermal stability of the polymers formed, whose softening temperature is in the region of intense thermal decomposition, i.e. above 500 °C.[41]

A polyphenylene and an oligophenylene have been synthesised from diacetylene and substituted acetylenes have been obtained by the polycyclotrimerisation reaction in solution in toluene at −10 °C in the presence of $Al(iso\text{-}C_4H_9)_3$–$TiCl_4$.[17,43,57]. Both synthetic diacetylene, obtained by chlorinating butynediol with thionyl chloride and subsequent dehydrochlorination by alcoholic alkali, and pyrolytic diacetylene, which is a side product in the synthesis of acetylene from natural gas, were employed in the reaction. It was shown that an aromatic polymer is formed from initial monomers without benzene rings. In the polymer obtained from diacetylene alone, each aromatic ring is formed as a result of the interaction of three diacetylene molecules. The polymer is an amorphous yellow powder containing aromatic and ethynyl groups; it softens at 150–200 °C and hardens (owing to the presence of residual ethynyl end groups) on heating; in the cross-linked state, it exhibits a high thermal stability. According to thermogravimetric data, intense weight losses are observed in air at 400–600 °C.[43]

The high chemical stability of polyphenylenes and graphite-filled plastics based on them has been demonstrated[58]. Chemically stable polymeric materials used as binders and impregnating substances in industry include furan and phenol-formaldehyde resins and compositions based on them; however, they are stable only in relation to a 70% solution of sulphuric acid. Polyphenylenes and graphite-filled plastics exhibited an effective chemical stability in relation to an 80% solution of sulphuric acid at its boiling point (120–125 °C) for 850 h and also in relation to a 93% solution of sulphuric acid. The high thermal and corrosion stabilities of polyphenylene, which can be explained by its aromatic structure, make it a promising material as a binder in the preparation of graphite-polymeric materials.

The use of the products of the copolycyclotrimerisation of *p*-diethynylbenzene and a halogenophenylacetylene showed[44] that the reactivity of *p*-diethynylbenzene is somewhat higher than that of the halogeneophenylacetylene; the oligomers are therefore enriched in *p*-diethynylbenzene fragments compared with the initial mixture.

The capacity of oligophenylenes for structure formation under the influence of ultraviolet irradiation has been studied[48,60]. It has been suggested that, in the absence of oxygen, the photoinitiated cross-linking takes place via the

residual ethynyl end-groups, as in thermal cross-linking in an inert atmosphere. In the presence of oxygen, the rate of cross-linking increases as a consequence of the oxidation of the ethynyl groups to peroxy-groups and the decomposition of the latter with subsequent recombination of the radicals. The mechanism of the photochemical cross-linking of polyphenylenes by diazides has also been described[60].

The oligophenylenes obtained by the polycyclotrimerisation reaction are characterised by the presence of residual ethynyl groups which can enter into various reactions: they can be oxidised to carboxy-groups[12], can combine with decaborane[61] to form oligophenylenecarbaboranes, and can interact with diazo-compounds[62] to form oligophenylenepyrazoles. The oligomers obtained have acquired new functional groups, which expands the synthetic possibilities in polymer chemistry.

An oligophenylenecarbaborane has been synthesised by the chemical modification of an oligophenylene containing acetylenic end-groups under the influence of decaborane[61]. It was established that, under the chosen conditions, the replacement of the ethynyl groups of the oligophenylene by carbaborane groups takes place almost quantitatively via the scheme

$$B_{10}H_{14} + PhNMe_2 \rightarrow B_{10}H_{12}(PhNMe_2)_2 \xrightarrow{HC\equiv C-} HC(B_{10}H_{10})C- + PhNMe_2 + H_2 .$$

This demonstrated that the polycyclotrimerisation of ethynyl compounds in the presence of $Al(iso\text{-}C_4H_9)_3$–$TiCl_4$ leads to the formation of oligphenylenes containing only aromatic units and residual triple bonds, which are responsible for the acquisition of a three-dimensional structure by the oligophenylene.

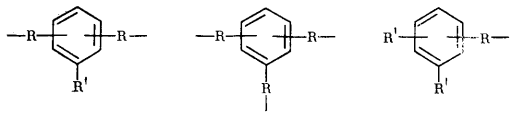
Oligophenylenepyrazoles have been obtained as a result of the modification of an oligophenylene having terminal ethynyl groups on treatment with diazomethane and bisdiazohexane and some of their properties, particularly their resistance to thermo-oxidation, have been estimated[62]. The ethynyl groups of oligophenylenes have been hydrosilyated by dihydrosilanes in order to improve their mechanical characteristics[63].

Oligophenylenes based on the dipropargyl ethers of hydroquinone and dian have been obtained recently together with phenylacetylene in the presence of cobaltocene as the catalyst[64]. The polymers exhibit an enhanced fluidity and fusibility and possess effective mechanical characteristics.

A wide range of acetylenic compounds capable of undergoing polycyclotrimerisation and copolycyclotrimerisation have been enumerated[65,66] and the importance of using effective catalytic systems has been discussed. The authors of these studies point out that many transition metal compounds used as the catalysts of the polymerisation of monoacetylenes cannot be used for polycyclotrimerisation. For example, nickel chloride in the presence of sodium tetrahydroborate leads to the formation of thermally unstable polyolefins and not aromatic structures in the polymerisation of phenylacetylene. The catalyst $Ni(CO)_2(PPh_3)_2$, which has been widely used for the polymerisation of acetylenes, leads to the formation of unsaturated linear trimers as well as trisubstituted benzenes. The reaction of phenylacetylenes and diethynylbenzene in the presence of this catalyst leads to the formation of polymers in the infrared spectra of which a band appears at 965 cm^{-1}, characteristic of a *trans*-substituted terminal double bond, which indicates the occurrence of linear polymerisation. The copolymerisation of phenylacetylene and *p*-diethynylbenzene in the presence of the carbonylphosphinenickel complex leads to the formation mainly of polyolefins instead of the required thermostable polyphenylenes.

When the $AlEt_2Cl$–$TiCl_4$ Ziegler catalyst is used under the conditions of its effective operation, only triphenylbenzene is formed from phenylacetylene, while high-molecular-weight polyphenylene polymers can be obtained by copolymerisation. The authors[65,66] believe that the main cause of the formation of polyphenylenes rather than polyolefins is the molar ratio Al/Ti = 1.5–5.0. They believe that the catalyst concentration can vary within wide limits but the molar ratio of the catalyst to the acetylene-containing monomers must be at least 1:300–1500. Chemical study of the reaction products demonstrated the absence of unsaturated double and triple bonds from the polymer. Taking these findings into account, it was established on the basis of infrared, ^1H NMR and, ^{13}C NMR spectroscopic data that the polymer contains only aromatic structures.

However, the absence of terminal acetylenic groups from the reaction products (polyphenylenes) precludes their modification; such polymers are hardened thermally at high temperatures via secondary processes involving the degradation of the oligophenylenes and the recombination of radicals. The authors[65,66] introduced the monoacetylene monomer (phenylacetylene or tolylacetylene) into the reaction with diethynylbenzene in portions, which they believe to ensure a high solubility of the resulting polymer. They suggest that the reaction proceeds via three different pathways: chain propagation, chain branching, and chain termination, to which correspond three different types of fragments.

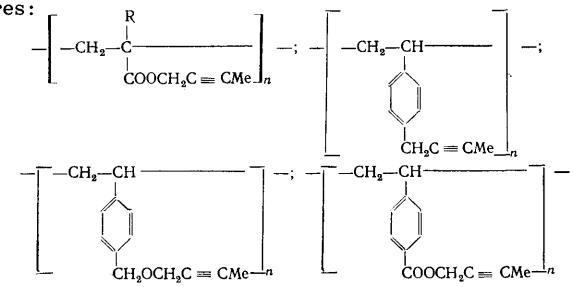


The synthesis of a polyphenylene containing residual ethynyl groups has been described[67]. Only one component, namely *p*-diethynylbenzene, was used for its synthesis; the reaction was carried out in the presence of two different catalytic systems: diethylaluminium chloride and titanium tetrachloride and nickel acetylacetonate. The authors[67] point out that the polyphenylenes which they obtained were soluble in organic solvents up to high degrees of conversion of the monomer into the polymer. For the Ziegler type catalyst, this claim conflicts with data[66] according to which a soluble polyphenylene cannot be obtained from diethynylbenzene alone.

2. Carbochain Polymers

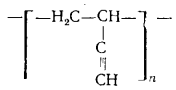
Carbochain polymers with a linear structure have been obtained, as already stated, by the oxidative dehydropolycondensation reaction[7]. By treating the polymers obtained with bistetraphenylcyclopentadienone, it is possible to increase their thermal stability and to employ them as binders, films, and coatings.

Carbochain polymers containing acetylenic groups in the side chain have been synthesised by the polymerisation of vinyl monomers[68–70] and were found to have the following structures:



Polymers of this type, soluble in organic solvents at elevated temperatures (120 °C and above), were cross-linked. It was established that the non-cross-linked polymers can combine with bromine and decaborane at the triple bonds.

Polymers with an unsubstituted acetylenic group in the side chain have also been synthesised[71]. A polymer with a triple bond linked directly to the main chain could not be obtained from a polyolefin. A polyconjugated polymer containing vinyl, allene, and acetylenic groups is formed in this case. In order to obtain a polymer containing an ethynyl side group of the type

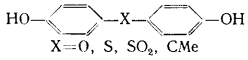


trimethylsilylvinylacetylene is usually polymerised with subsequent removal of the trimethylsilyl group.

III. HETEROCHAIN OLIGOMERS AND POLYMERS

1. Polyethers and Polyesters

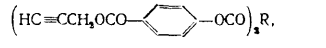
Polyethers have been obtained by the thermal polymerisation of di(4-ethynylphenyl) ether on heating to 150 °C.[72] The polymer obtained was used as a binder for composite materials. The kinetics of the thermal polymerisation of 3-ethynylphenyl phenyl ether have been investigated[73]. By treating bisphenols having the general formula



X=O, S, SO_2, CMe

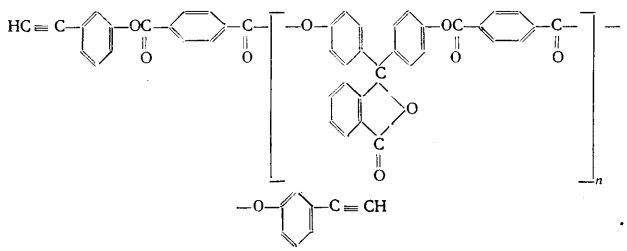
and also hydroquinone and a novolac resin with propargyl bromide in an alkaline medium, oligomers having acetylenic end-groups and capable of thermal polymerisation at 200 °C without the evolution of volatile products were obtained[74].

Oligoesters containing propargyl groups of the following type have been synthesised[75,76]: oligoesterpropargylates



and $(HC{\equiv}CCH_2OCOCH_2CH_2OCO)_2R$, oligocarbonatepropargylates $(HC{\equiv}CCH_2OCO)_2R$, and oligoesterpropiolates $(HC{\equiv}CCOOROCO)_2C_6H_4$ and $(HC{\equiv}CCOOROCO)_2C_2H_4$, where R is a diol residue. It has been shown that they harden at 200–300 °C with formation of cross-linked products and that their thermal stabilities are much higher than those of the analogous polymers with saturated bonds in the chain.

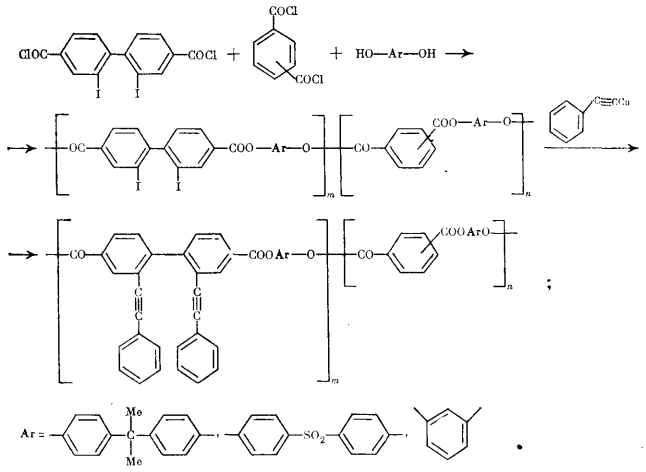
Thermostable thermoreactive aromatic polyesters containing acetylenic groups have been obtained by the polycondensation of aromatic bisphenols (phenolphthalein, phenolphthalimidine, phenolsulphonephthalein, and fluorescein) with the chlorides of isophthalic or terephthalic acid with subsequent addition of ethynylphenol[77]. When phenolphthalein is used together with terephthalic acid chloride and 3-ethynylphenol for the synthesis, the polymer has the following structure:



Glass plastics based on this polyester have a high strength and exhibit low weight losses on thermal ageing (0.4% at 250 °C for 1000 h).

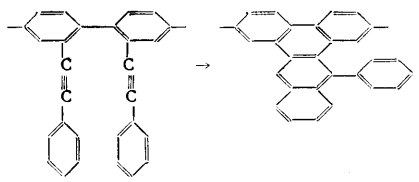
Aromatic polyesters containing phenylethynyl groups have been obtained[78] by the interfacial condensation of the dichloride of 2,2'-di-iodobiphenyl-4,4'-dicarboxylic acid and isophthaloyl or terephthaloyl chloride with bisphenols and subsequent substitution of the iodine by phenylethynyl groups in accordance with the scheme

Scheme 4



The resulting polyesters are soluble in pyridine and tetrachloroethane and harden at 200 °C in argon in the course of 30 h via an intramolecular cyclisation mechanism (Scheme 5):

Scheme 5



Polyesters containing conjugated diacetylenic groups in the chain have been synthesised by the polycondensation of the chlorides of dicarboxylic acids (succinic, azelaic, adipic, sebacic, isophthalic, and terephthalic) with 3,5-hexadiyne-1,6-diol and their photochemical and thermal behaviour has been investigated. The synthesis of epoxide resins containing ethynyl end-groups by the interaction of epoxide oligomers with aminophenylacetylene has been described[80]. The resins were hardened at 250 °C with formation of impact-resistant thermostable polymers.

2. Polyamides

Analogously to aromatic polyesters, aromatic polyamides with phenylethynyl side groups have been obtained by the low-temperature polycondensation of diamines with the dichloride of 2,2'-di-iodobiphenyl-4,4'-dicarboxylic acid or its mixture with the dichloride of biphenyl-4,4'-dicarboxylic acid in dimethylformamide (DMF) followed by the treatment of the iodine-containing polyamides with an excess of copper phenylacetylide[81]. Most of these polyamides were soluble in DMF, had softening temperatures in the range 177–247 °C, and showed weight losses amounting to 1.1–3.9% after three

days at 300 °C. It was established that the solubility of polyamides with an identical structure of the acid component of the molecule decreases in the following sequence of aromatic diamino-fragments:

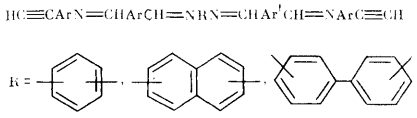


Like polyesters, these polyamides are capable of being hardened via an intramolecular cyclisation mechanism with formation of 9-phenylbenzanthracene units.

Polyamides containing tolane fragments have been obtained by the condensation of the dichlorides of isophthalic and terephthalic acids with 4,4′-diaminotolane in DMF containing LiCl.[82] Polyisophthalamides are soluble in DMF and *N*-methylpyrrolidinone with added LiCl and polyterephthalamides are soluble in sulphuric and methylsulphuric acids. According to thermogravimetric analysis, the temperature of the onset of the thermal decomposition of these polymers is 445–470 °C in air and 490–530 °C in an inert atmosphere.

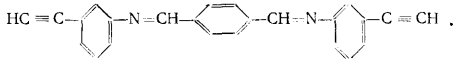
3. Polymeric Schiff Bases

Oligoimines containing acetylenic end-groups and having the following structures can be obtained by the reaction of aromatic aldehydes with aromatic diamines and subsequent treatment of the reaction product with aminoarylacetylene[83]:



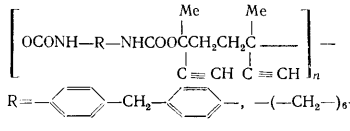
The resulting oligomers are soluble in halogenated solvents. They are capable of hardening on heating. Thus the oligoimine obtained from isophthalic dialdehyde, 1,3-di(3-aminophenoxy)benzene, and 3-aminophenylacetylene has a softening temperature of 40–45 °C and on heating to 150 °C in the absence of air for 16 h it gives rise to a hard material with a glass point T_g = 230–260 °C and remains thermally stable up to 350 °C.

Analogous oligomers have been obtained by the reaction of 3-aminophenylacetylene with terephthalic dialdehyde[84]. In particular, a product having the following structure and a melting point of 136–139 °C has been isolated:

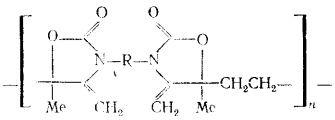


4. Polyurethanes

Acetylene-containing polyurethanes have been obtained by the polycondensation of di(4-isocyanatophenyl)methane and hexamethylene di-isocyanate with 3,6-dimethylocta-1,7-diyne-3,6-diol:[85]



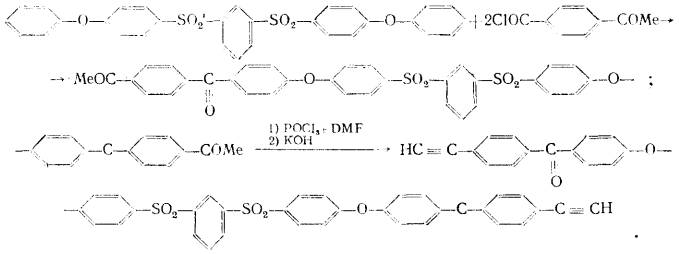
They are soluble in organic solvents and form transparent films. They have a viscosity η_{log} = 0.4–0.54 (30 °C, DMF), T_g = 135° and 54 °C, and temperatures corresponding to a 10% weight loss of 260° and 175 °C respectively. When solutions of the polyurethanes in DMF are heated, intramolecular cyclisation with formation of the corresponding polyoxazolidinones takes place:



The polymers obtained have high glass points T_g = 170–175 °C and a high temperature corresponding to a 10% weight loss (390–410 °C).

5. Polysulphones

Polysulphones with acetylenic end-groups have been obtained by the reaction of 1,3-di(4-phenoxybenzenesulphonyl)benzene with 4-acetylbenzoyl chloride via the following scheme[86]:



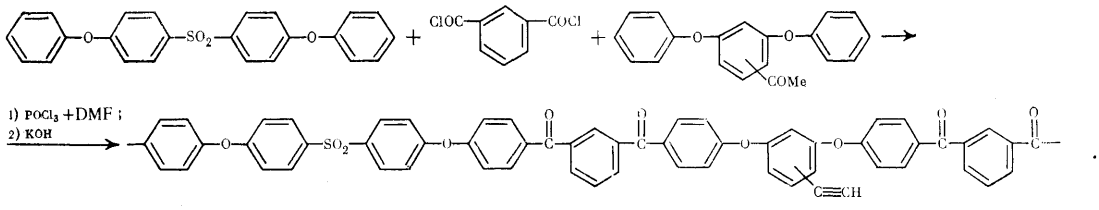
This bisacetylenic oligomer is a relatively low-melting solid soluble in the usual organic solvents: chloroform, dioxane, and tetrahyrofuran (THF). It was hardened in nitrogen at 300 °C. The authors[86] suggest that the hardening proceeds via a polycyclotrimerism with formation of polymers of the type of polyphenylenes. The hardened products have high glass points and a high thermo-oxidative stability. The weight losses at 300 °C in circulating air amounted to 4–6 wt.% after five days.

The question of the synthesis and properties of polysulphones with acetylenic groups has been examined in detail in a review[19]. Here we may mention that the synthesis of a polysulphone with an acetylenic side group via Scheme 6 is possible[87].

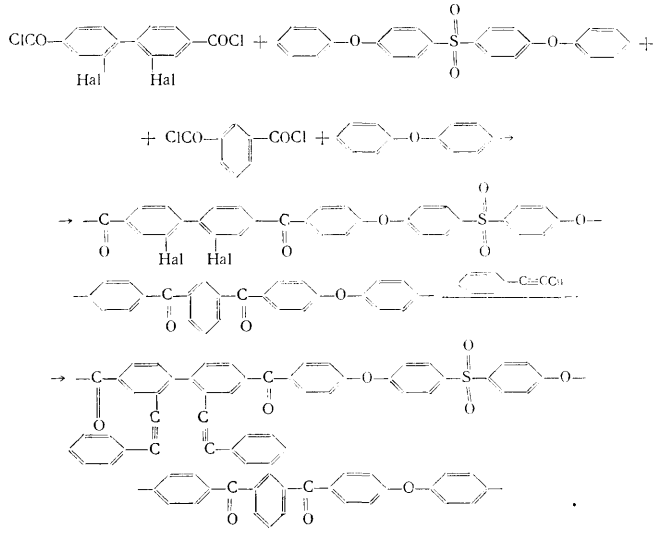
The polymers are soluble in DMF and have η_{log} = 0.23–0.43 and T_{soft} = 185–225 °C. After hardening in the presence of palladium chloride in nitrogen at 210° and 285 °C, they lost their solubility and did not soften up to 300 °C. According to thermogravimetric data, they are thermally stable in an inert atmosphere up to 550 °C and retain their thermo-oxidative stability up to 250 °C.

The sulphone oligomers have also been hardened by the intramolecular cyclisation of derivatives of 2,2′-di(phenylethynyl)biphenyl[88–92]. The oligomers were obtained via Scheme 7:

Scheme 6

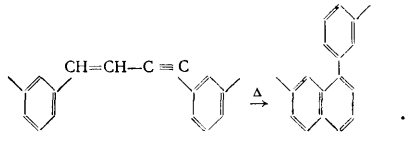


Scheme 7



After the polymers have been hardened in an inert atmosphere at 280 °C for 24 h, their thermo-oxidative stability increases and the weight losses at 300 °C in air amount to 1–2 wt.% (compared with 6–7 wt.% for the unhardened polymer).

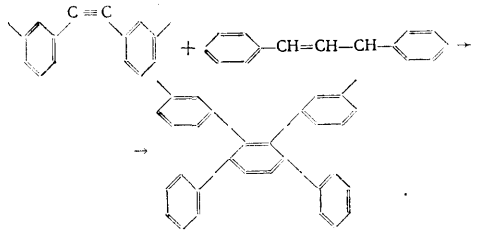
In order to achieve intramolecular cyclisation, polysulphones containing the enyne group in the polymer chain have been synthesised[93–95]:



On heat treatment, the enyne group was converted into the phenylnaphthalene group and the polysulphone was hardened. Such polymers are photosensitive but after hardening they become very brittle.

The Diels–Alder reaction has also been used to harden polysulphones[96]. Polysulphones containing tolane groups were treated with 1,4-diphenylbutadiene in accordance with Scheme 8:

Scheme 8



Among other classes of polymers, mention may be made of acetylene-containing phosphazene copolymers[97] obtained by treating polydichlorophosphazene with propargyl alcohol.

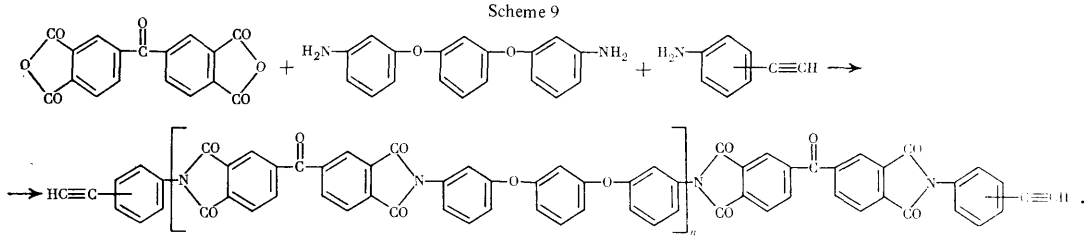
IV. HETEROCYCLIC OLIGOMERS AND POLYMERS

Polyimides, polybenzoxazoles, polyphenyltriazines, and polyphenylquinoxalines have been obtained in the series of heterocyclic polymers containing acetylenic groups.

1. Polyimides

Polyimides with ethynyl end-groups have been described in a number of communications[19,82,98–103]. They are obtained by the condensation of aromatic diamines, for example, 1,3-bis-3-aminophenoxybenzene, with aromatic tetracarboxylic acid dianhydrides, for example, benzophenonetetracarboxylic acid, and of aminophenylacetylenes with the ethynyl-substituted anhydride of an aromatic dicarboxylic acid using a two-stage method in accordance with Scheme 9:

Scheme 9



The thermal and mechanical characteristics of the polyimides have been described[19]. It is noteworthy that the glass points of the hardened polyimides are fairly high (up to 340 °C) and depend on the conditions in the subsequent (final) hardening. Graphite filled plastics with the polyimide binder retain their strength effectively at high temperatures.

Differential scanning calorimetric data[98] have demonstrated the two-stage character of the hardening of the acetylene-containing polyimides. It is believed that the $-C\equiv C-\overset{\|}{C}-$ (CH_2) groups are formed initially (at 200 °C), while in the second stage (at 240–260 °C) a third group adds on, which is accompanied by the formation of a benzene ring.

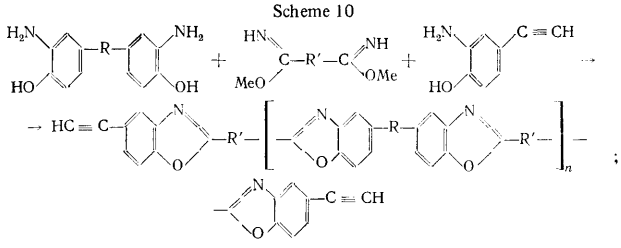
The dialkyl esters of tetracarboxylic acids can be used instead of the dianhydrides for the synthesis of polyimides with acetylenic end-groups[99], while the propargyl ester of aminobenzoic acid can be employed as the ethynyl component[102].

Branched oligoimides containing ethynyl end-groups have been obtained by the reaction of the dianhydride of benzophenonetetracarboxylic acid with aromatic triamines for the introduction of the ethynyl group into the polyimide chain by the reaction of diaminotolane with the dianhydride of pyromellitic acid has been described[82].

2. Polybenzoxazoles

Dibenzoxazole oligomers with fluorocarbon ether linkages and acetylenic end-groups have been synthesised via the Scheme[104]

Scheme 10



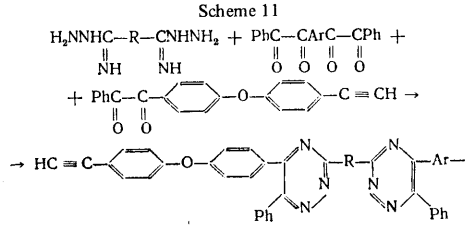
$n = 0, 1, 2$; R=—$CF_2CF_2O(CF_2)_5OCF_2CF_2$—;
R′=—$CF_2(OCF_2CF_2)_xO(CF_2)_3O(CF_2CF_2O)_yCF_2$—; $x + y = 5, 6$.

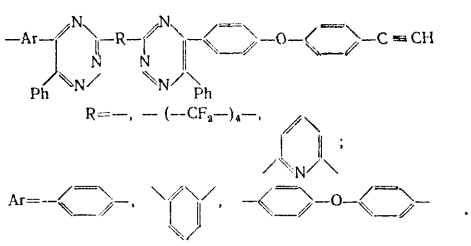
The polymers obtained had glass points ranging from −61° to −56 °C, were hardened via the acetylenic end groups at 180–200 °C, and in the hardened state began to be degraded in air at 375–400 °C.

3. Polyphenyltriazines

Oligophenyl-1,2,4-triazines containing acetylenic end-groups have been obtained by the reactions of bisamidrazones, dibenzils, and 4-(4-ethynylphenoxy)benzil via the scheme[105]

Scheme 11



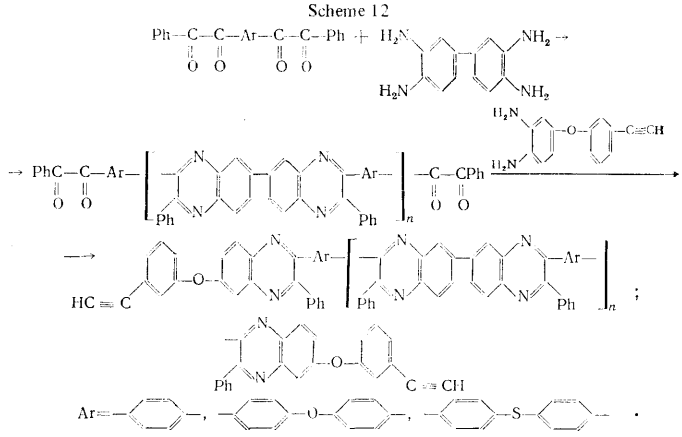


These polymers have a high thermo-oxidative stability and proved promising as binders.

4. Polyphenylquinoxalines

Polyphenylquinoxalines containing ethynyl end-groups have been obtained by a two-stage method in accordance with the scheme

Scheme 12



The scheme shows that oligomers with benzil end-groups were synthesised initially by the reaction of diaminobenzidine with an excess of an aromatic dibenzil and then a solution of 3-(3,4-diaminophenoxy)phenylacetylene was added to the reaction mixture. The polymer dissolves in THF, chloroform, dioxane, and methylene chloride; its cross-linking via the acetylenic end-groups takes place in the temperature range 200–275 °C according to differential scanning calorimetric data; the weight loss begins at 300 °C in air and at 465 °C *in vacuo*.

This and other reactions involving the formation of polyphenylquinoxalines and their properties have been described in detail in a review[9] and here we shall only note some of them. It is possible to synthesise polyphenylquinoxalines containing the 2,2′-(phenylethynyl)biphenylyl groups, which are capable of forming (via intramolecular cyclisation) 9-phenyldibenzanthracene fragments on heat treatment or exposure to radiation[108]. The viscosities of 5% solutions of the polymers obtained in chloroform at 30 °C were $\eta_{log} = 0.18–0.3$, their molecular weights ranged from 15000 to 17200, and their glass points were $T_g = 215–330$ °C. After hardening (at 245–320 °C in nitrogen), the polymers lost their solubility in sulphuric acid, which indicates the occurrence of intermolecular cross-linking.

In order to reduce the T_g of the oligomeric polyphenylquinoxalines with ethynyl end-groups, to increase the fluidity of their melts, and to decrease their hardening time, low-molecular-weight reactive plasticisers were employed:

6-(3-ethynylphenoxy)-3-[4-(3-ethynylphenoxy)phenyl]-2-phenylquinoxaline[109], 1-phenoxy-3-(3-ethynylphenoxy)-benzene, and 1,3-di(3-ethynylphenoxy)benzene[110]. The polyphenylquinoxalines with added plasticiser had T_g = 100 °C, the viscosities of their melts were reduced, and their hardening times and temperatures were lower.

V. THE HARDENING OF THE OLIGOMERS AND PRACTICAL APPLICATIONS OF THE POLYMERS

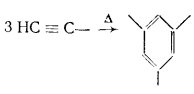
The authors of the present review believe that further progress in the field of the chemistry of polymers with acetylenic linkages will be determined not only by the synthesis of new polymers and the development and expansion of the raw materials resources but also by the development of methods which will ensure a high degree of the reaction involving the triple bond and which will increase the selectivity of the reaction with respect to the formation of aromatic rings in the three-dimensional network on hardening the polymers.

However, at the present time only a low degree of formation of aromatic rings is attained in the hardening of polymers, particularly those with rigid chains which have a high glass point, which is bound to affect their thermo-oxidative stability. Thus it has been established[111] by NMR that the ethynyl groups in polyimides with acetylenic end-groups are converted into aromatic rings to the extent of only 30%, while the remaining groups apparently give rise to olefinic fragments. The mechanisms of the hardening reactions are at present insufficiently clear and Baise[111] has pointed out the possibility of the occurrence of several different reactions of the acetylenic groups during hardening at elevated temperatures. Certain free-radical polymerisation reactions have been described. The pyrolytic cyclotrimerisation of acetylene to benzene or higher aromatic compounds may also proceed with participation of free radicals. There is also a possibility of aromatisation with conversion of acetylene-containing groups into condensed aromatic fragments.

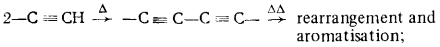
Thus the possibility of the manifestiation of a hetero-unit structure, which is in general characteristic of high-molecular-weight compounds, must be taken into account in processes involving the formation of various fragments during the hardening of compounds with acetylenic linkages[112]. The hetero-unit principle was considered previously in assessing the structures of polyphenylenes in which the main chain structures consisted of mono-, di-, and tri-substituted benzene rings (in different proportions) and also are of residual ethynyl end-groups and possibly defective polyene fragments. By altering the conditions of the synthesis, it was possible to influence within certain limits the structure of the polymer formed. The hardening conditions can also effect the character of the fragments produced.

The problems involved in the hardening of polymers with acetylenic end-groups have been considered[113]. Polymers containing acetylenic end-groups are hardened as a result of the following reactions:

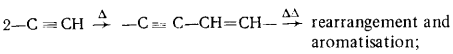
(1) trimerisation[114,115]:



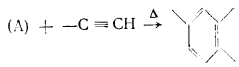
(2) Glaser coupling[116]:



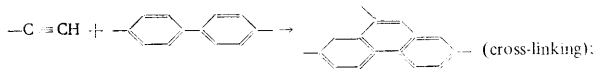
(3) Strauss coupling[117]:



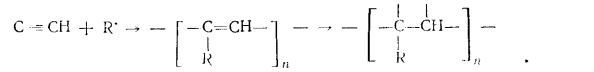
(4) Diels–Alder reaction with participation of the products (A) formed as a result of the Strauss and Glaser coupling[118]:



(5) Diels–Alder reaction in the polymer chain[118]:



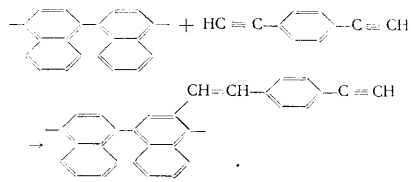
(6) free-radical polymerisation with formation of linear or branched products[118]:



The degree of reaction depends on the hardening of the polymer and on its character (thermal or catalytic)[111], but thermal hardening via the triple bonds is the most convenient method for the conversion of the oligomer into a three-dimensional polymer. Such hardening is usually carried out at 180–250 °C, where the main polymer chain is not degraded; however, it is then necessary to carry out the final hardening at 300–350 °C, since the thermal transformation of the acetylenic groups into aromatic rings takes place at 250–300 °C. This applies to the formation of a thermoreactive binder on the basis of oligophenylenes, developed in the USSR under the brand name "Reaktofen" and in the USA under the brand name "H-Resin".[119]

The oligophenylenes obtained on the basis of diethynylbenzenes are used to prepared articles by sintering, pressing, casting under pressure, and extrusion methods. These plastics can be used for a long time at 315 °C and briefly at 350 °C.[67,104,120] In order to increase the fluidity of the melt and to improve its adhesion to fillers, low-molecular-weight acetylenes are introduced into the resins[105]. Antifriction materials consisting of oligophenylenes, *p*-diethynylbenzene, and antifriction fillers, which are heat-resistant up to 380 °C, have been obtained[121].

The modification of the oligomers by the addition of low-molecular-weight oligomers has found extensive applications. There are patents for ternary and quaternary copolymers containing 25–75% of polyacetylene, obtained by the oxidative dehydropolycondensation of *p*- and *m*-diethynylbenzenes and dipropargyl ethers of phenols, together with 75–25% of low-molecular-weight acetylenes which consist of 1,4-diphenylbutadiyne, 1,3-di(phenylbutadiynyl)benzene, and others[122,123]; the copolymers are used to prepare graphite fibres. Phenol-formaldehyde resins are modified in the same way[124]. Polymers without ethynyl and other reactive groups are hardened using aromatic acetylenes. Thus the oligophenylenes obtained by the oxidative dehydropolycondensation of benzene, naphthalene, and anthracene are hardened with the aid of *p*-diethynylbenzene at 100–280 °C;[125,126] this entails the formation of insoluble and infusible products in almost quantitative yields. The study of the products of the hardening reaction for low degrees of conversion by NMR and infrared spectroscopy and also the investigation of the molecular weight distribution led to the following hardening mechanism:



Polyphenylenes can be used in the form of compositions for the construction of rocket nozzles, as ablation materials, and in composite materials together with carbon fibres for the construction of turbine blades and other devices which can operate for a long time at high temperatures and possess high resistance to wear. As a consequence of the satisfactory electrical, physical, and chemical characteristics, these polymers are promising for the preparation of electrical insulators, protective coatings, lining materials and filters in the form of compositions with metals, asbestos, and glass and carbon fibres, all components capable of being used at high temperatures[65].

The likely usefulness of polyimides with acetylenic groups as binders for carbon and glass plastics has been demonstrated[98,99]. Polyphenylquinoxalines are suitable for the preparation of adhesion materials[127] and polysulphones are capable of forming films which retain strength and flexibility after hardening[92]. Polymeric Schiff bases[83] serve as effective varnish coatings and impregnating materials and can be used to prepare semiconducting and conducting materials.

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The problems containing the employment of acetylenic compounds in the synthesis and chemical modification of polymers examined in this review are at present extremely urgent and offer much promise from the standpoint of both the preparation on their basis of traditional polymers with more effective operating characteristics and for the preparation of materials with fundamentally new properties.

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