Translated from *Uspekhi Khimii*, **44**, 502-530 (1975) U.D.C. 547.91; 547.928

Problems of the Chemistry of Thermostable Organic Polymers

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The effect of π-electron delocalisation, due to polyconjugation in macromolecular structures, on the thermal and thermo-oxidative stability of polymers is surveyed, and data are given indicating that thermal oxidation is activated by the centres produced by the rupture of strained chemical bonds during thermolysis. Certain general problems and advantages in the synthesis of polyconjugated thermostable oligomers and high polymers are discussed. A list of 76 references is included.

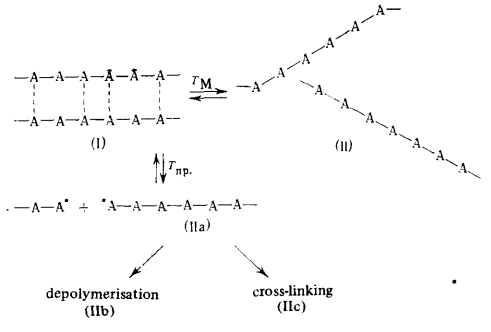
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I. INTRODUCTION

The action of heat on a polymeric material may cause processes of two kinds, resulting in reversible and irreversible changes in its physicochemical properties. The first type involves phase transitions or variation in molecular mobility in amorphous regions of polymers. Such changes are taken to characterise the deformative thermal stability or thermophysical stability of polymers and polymeric materials. Irreversible change in the physicomechanical properties of polymers, in contrast, are mostly due to chemical changes in the polymer caused by the temperature and the environment. Such changes are related to the chemical thermal stability or thermochemical stability. In the absence of a reactive environment, e.g. oxygen, thermochemical degradation may be more or less reversible, although the attainment of complete reversibility is in practice difficult owing to the finite probability of anomalous recombination and cross-linking. The variation in the thermophysical stability of polymeric materials during processing and service is due in most cases to degradation and cross-linking: i.e. it is connected with their chemical thermal stability. Therefore the thermochemical stability may well be the main property from which the temperature range for practical application of the polymer can be assessed.

There are thus two states that are most dangerous in use—melting (or softening) and degradation of the polymer (beginning at a limiting temperature T_{lim})—a situation which is shown clearly by the scheme



The thermal conditions for the transition from (I) to (II) or to (IIa) are governed by the decrease in free energy $\Delta G = \Delta H - T\Delta S$, and are characterised at equilibrium by the phase transition or chemical conversion temperature $T_{tr} = \Delta H/\Delta S$. The temperature T_{tr} is obviously higher the smaller are H_{tr} and ΔS. Such conditions can be realised in polymer systems whose macrochains contain no weak chemical bonds and are characterised by strong intermolecular interaction (H_I small), as well as by a slightly larger S_{II} than S_I. This is possible in rigid systems, when the decrease in chain length on degradation produces a sharp drop in flexibility, and also during cross-linking processes.

Although the above considerations relate to thermal transformations in polymers, they have some significance for thermal oxidation processes initiated by the rupture of chemical bonds. The irreversible character of thermal oxidation and cross-linking complicate the thermodynamic treatment of the relation between the structure and the thermochemical stability of polymers, bringing a kinetic examination of the process to the forefront.

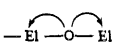
Since the thermochemical stability of polymers at high temperatures (at or above 300°C) depends primarily on the strength of the chemical and intermolecular bonds and on the molecular mobility of the structural units, we must consider the effect of electron delocalisation along the chains of the macromolecules on the thermal stability of polymeric materials. Further justification for such an approach to the problem of thermal stability is that the character of the electron delocalisation (conjugation) along large segments of polymer chains should influence not only the strength of the bonds linking them but also the molecular mobility and intermolecular interaction.

The Reviewer has repeatedly pointed out that enhancing the thermal stability (chemical and physical) of organic polymers requires the "designing" of macromolecules having a developed system of conjugation by π-electron delocalisation[1-3]. Electron delocalisation can be shown to determine the thermal stability not only of so called organic polymers but also of polymers with inorganic chains. Indeed, the data in Table 1, gathered from several sources[4,5], show that in all cases the strength of a bond is improved by its polarisation and many-centred character. From this it may be concluded that macromolecules of highly thermostable polymers can be constructed in three main ways.

1. Formation of a polyconjugated system of multiple bonds and aromatic and/or heterocyclic rings. The polymer chain then contains extended segments in which a

particular type of π-conjugation is established. Such systems possess considerable rigidity, and form stable supermolecular structures [6].

2. The building up of macromolecules by means of "quasi-cumulene" [7] dative bonds formed by the delocalisation of p-electrons of one heteroatom into d- or p-electron vacancies of another element attached to it, e.g.



Such compounds include polysiloxanes and other organometallic [8,9] and inorganic [10,11] polymers. With substances of this type (in any case those with p,d-conjugation) chain flexibility does not create conditions preventing delocalisation, since flexibility is realised not so much by rotation about valency bonds as by the deformation of bond angles [7]. Thus high elasticity can be combined here with thermochemical stability of the polymeric material.

Table 1. Effect of delocalisation of π- and p-electrons on bond energy.

Bond	Conjugation	Energy, kcal mole^{-1}	Bond	Conjugation	Energy, kcal mole^{-1}
$C_{aliph}-C_{aliph}$	—	83.0	$C_{aliph}-Si$	—	78.0
$C_{arom}-C_{arom}$	$\pi-\pi$	98.0 (105)	Si—O	$p-d_v$	106.0
$C_{aliph}-\ddot{N}H$	—	82.0	B—N	$p-p_v$	115.0
$C_{arom}-\ddot{N}H$	$p-\pi$	110.0	B—O	$p-p_v$	113.0
$C_{aliph}-\ddot{O}$	—	93.0			
$C_{arom}-\ddot{O}$	$p-\pi$	107.0			

Arrows: .....delocalisation of π-electrons;
----delocalisation with displacement of p-electron density;
d_v, p_v electron vacancies.

3. Formation of block-copolymer structures including fragments of π-electron conjugation [1] and organometallic or inorganic fragments with p,d-delocalisation of valency electrons. Such structures may be expected to exhibit an interesting combination of the physicomechanical properties characteristic of polyconjugated polymer systems and compounds with dative bonds [2].

In this Review we shall examine certain problems associated with the thermal stability of organic polymers containing more or less extended fragments of π-conjugation.

II. PECULIARITIES OF THE STRUCTURE AND THE THERMOCHEMICAL STABILITY OF POLYCONJUGATED SYSTEMS

It has now been shown that the high thermochemical stability of polyconjugated polymer systems is due to processes which, in the absence of oxygen, tend to extend the polyconjugated chain. The ultimate results of such changes is the formation of graphite, amorphous carbon, or products of similar electronic structure. Special allowance must be made for this fact in the study of degradative changes in polyheteroarylenes.

The conversion of "saturated"† into polyconjugated polymers and then into graphite or amorphous carbon is accompanied by a decrease in the free energy of the system. Thus calculations show [12] that, in the thermal degradation of polyethylene and several other high polymers, graphitisation is considerably more advantageous thermodynamically than are other chemical changes. This leads to the following consequences.

1. The use of polyconjugated systems to obtain thermostable materials becomes increasingly advisable the closer such polymers approach graphite in structure and thermodynamic characteristics.

2. The widely held view that the primary structure of a polymer gives adequate criteria for judging its thermal stability cannot be regarded as correct. In fact, the energetic advantage of conversion to more extensive conjugation indicates that assessment of the thermochemical stability of a polymer should be based not so much on the specified (initial) structure of a polymer as on allowing for the chemical changes and the nature of the final products formed by the action of heat and of the environment.

For example, such polymers as cellulose, poly(vinyl alcohol), poly(vinyl acetate), polyacrylonitrile, etc. are able to form highly thermostable films and fibres as a result of degradative processes yielding polyconjugated systems, and at 2000°C forming graphite structures [3,13]. This applies also to the almost colourless polytetraphenylphenylene [14], in which the arrangement of phenylene units is non-coplanar owing to the large number of substituents. When a film of this polymer is heated, it splits off benzene, and becomes coloured, less soluble, and paramagnetic. It is not surprising, therefore, that the weight losses rapidly approach a limit on heating (400–500°C) and that the material withstands prolonged heating, especially in the absence of oxygen.

3. Since growth of the polyconjugated chain during the thermolysis of polyconjugated systems entails considerable contractions and is accompanied by degradative processes, it is reasonable to pay special attention to the synthesis of polyconjugated polymers of ladder and block–ladder structure [15,16], as well as polymer chains with regularly alternating branches, including polyconjugated fragments. The increasing interest taken in the synthesis and investigation of such structures thus becomes understandable [17].

Polyconjugated systems are characterised by the formation of stable association complexes by intermolecular donor–acceptor interaction. Such aggregates probably constitute a microphase, impair the solubility of the polyconjugated system, and raise the softening or flow point above those of saturated analogues [6].

It has been shown experimentally that polyconjugated polymers belong structurally to microheterogeneous systems, since association complexes (d = 10–50 nm) pack into larger spherical supermolecular structures (d = 1–5 μm) (Fig. 1). [6] Although the question of special intermolecular forces in polyconjugated polymers and their decisive importance in the physics and chemistry of the systems was considered as long ago as 1958, [2] due attention was not paid to it by research workers until recently, when the problem was again raised in connection with the study of the formation of polyconjugated chains [7] and the structure of organic semiconductors [18–20].

† "Saturated" polymers are those not containing π-bonds conjugated through large fragments or throughout the macromolecule.

In order to elucidate this matter a calorimetric determination was made of the conjugation energy, and the contribution to it of intermolecular π-electron interaction in individual and polymeric hydrocarbons—oligoarylvinylenes and polyarylenes—was calculated[6]. The difference between the total conjugation energy and that in the benzene rings was adopted as the criterion for assessing the intermolecular exchange interaction of π-electrons of polyconjugated chains; it was termed the "structure stabilisation energy" ΔH_π.

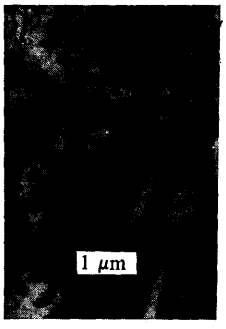


Figure 1. Electron micrograph of unshadowed platinum–carbon replica with amorphous benzene–naphthalene copolymer.

An additional contribution of 6.0–12.0 kcal mole^{-1}, appreciably exceeding known conjugation energies (2–4 kcal mole^{-1}) for buta-1,3-diene and its vinylogues, was found for individual polyene hydrocarbons containing terminal phenyl groups. It would have been wrong to attribute this difference to intramolecular delocalisation. It is more reasonable to suppose that the observed values are due mainly to intermolecular exchange interaction. On passing to polymers having a conjugated system the values of ΔH_π may exceed those found for the corresponding model systems, and may reach hundreds of kilocalories calculated for the average macromolecule. The above properties of polyconjugated systems indicate considerable intermolecular interaction and a tendency for their macromolecules to associate. The presence of strong intermolecular interactions in polyconjugated systems is largely responsible for their thermal stability, rigidity, and several other specific properties.

Existing data indicate the high radical reactivity of polyconjugated systems and its activation by paramagnetic centres present in them ("local activation effect")[6,21]. This is why self-inhibition is observed in the thermal (and at lower temperatures also in the thermo-oxidative) degradation of polyconjugated systems or "saturated" polymers capable of conversion into the former when heated[22,23]. Thus the polyconjugated polyphenylacetylene undergoes thermo-oxidative degradation considerably more slowly and to a considerably less extent than does its hydrogenated analogue, polystyrene (Fig. 2)[22,23]. With rise in temperature self-inhibition of the thermal degradation of polyconjugated systems is exhibited as far as extensive carbonisation of the polymer. The rate of the process is diminished by three-dimensional cross-linking of the polyconjugated system. The opposite results are observed with thermo-oxidative degradation: insoluble and infusible network polymers are less thermostable than their fusible and soluble analogues (Fig. 3).

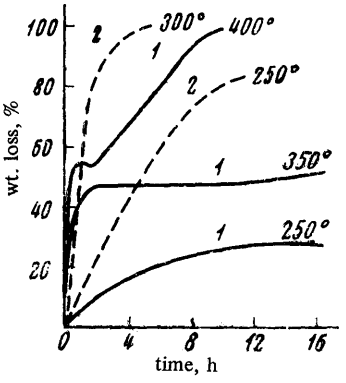


Figure 2. Thermo-oxidative degradation of: 1) polyphenylacetylene ($\overline{M}_n$ = 5000); 2) polystyrene (9000).

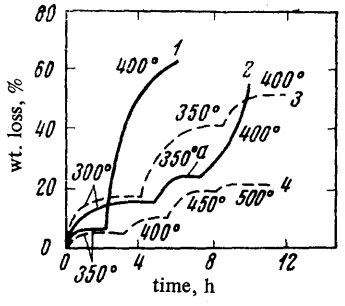


Figure 3. Weight-loss curves for: 1) three-dimensionally cross-linked insoluble block copolymer of poly-5-ethynyl-2-methylpyridine ($\overline{M}_n$ = 1700) with *p*-diethynylbenzene in air; 2) poly-5-ethynyl-2-methylpyridine (soluble fraction) in air (a = point corresponding to conversion into insoluble, infusible polymer); 3) as (2) in argon; 4) block copolymer in argon.

The probable explanation of such specific behaviour is that degradation of a polyconjugated system starts with the cleavage of weak bonds primarily in segments of disrupted conjugation. The resulting radicals can react to form a thermodynamically more stable polyconjugated structure. This process entails increased contractions and internal stresses which, at temperatures close to the carbonisation point, are able in turn to cause the local rupture of bonds. The macroradicals formed during degradation become stuck in the rigid polymer, with a greater loss of mobility the more rigid the polymer framework. The presence of radical centres having a relatively low ionisation potential catalyses the thermal oxidation. Oxygen may then be activated by the formation of charge-transfer complexes.

A different picture is observed in the thermal degradation of polyconjugated systems in the absence of oxygen, when the retained radicals probably act as traps binding active centres of the breakdown products responsible for the development of degradative processes. Convincing evidence of the creation of active centres during thermolysis is provided by our observation of reactivity in three-dimensionally cross-linked polymers (phenol–formaldehyde resites, polymers and copolymers of *p*-diethynylbenzene) thermolysed at 450–500°C. Such polymers exhibit semiconductor properties and are typical polyconjugated systems; they contain fused aromatic structures with paramagnetic centres at concentrations of $10^{19}-10^{20}$ spins g^{-1} and a narrow electron spin resonance signal (a singlet) of line width 3–4 Gauss [3,18]. Thermolysis products freshly prepared in a vacuum of $10^{-3}-10^{-5}$ mmHg possessed several specific properties: (i) their thermal oxidation passed at 300°C into combustion [24]; (ii) they were effective catalysts for the radical polymerisation of acrylates and several other electron-accepting monomers (Fig. 4) [25]; and (iii) keeping the thermolysates in oxygen, argon, or a vacuum, or the presence in the polymers of plasticisers capable of inactivating radicals (e.g. diphenylenemethanediols or phenolic alcohols in the case of phenol–formaldehyde oligomers), produces a decrease in the number of paramagnetic centres and sharp drops in the rate of oxidation of the thermolysates and in their catalytic activity towards radical polymerisation (Figs. 5 and 6).

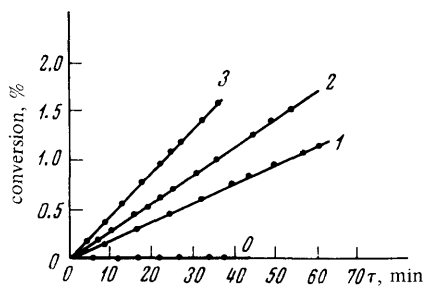


Figure 4. Variation of rate of polymerisation of methyl methacrylate catalysed by 2% of a dephenolated thermolysed phenol–formaldehyde resite with content of paramagnetic centres in the latter (spins g^{-1}): 0) no catalyst; 1) 2×10^{18}; 2) 1.7×10^{21}; 3) 5×10^{21}.

Similar regularities have been observed in the thermal and thermo-oxidative degradation of heterochain polyconjugated systems. An example is provided by results [3,26] obtained for polydiphenylamine, whose rate of degradation above 400°C is very low both in argon and in oxygen. Only on the initial portions of the rate curves are significant weight losses observed, as a consequence of the volatility of fractions of lower molecular weight and fragments of linear polymer molecules formed on degradation. The initial losses therefore increased as the molecular weight of the polymer fell from 2000 to 800. The process in argon slowed down as the polymer was "sewn up" and lost solubility during degradation (Fig. 7).

Degradation in oxygen exhibits more complicated kinetics. After formation of a three-dimensional structure and complete loss of solubility the process accelerates, owing to exothermic reactions involving oxygen and the contribution of the thermomechanical degradation of stressed structures. Polydiphenylamine remains completely soluble in polar solvents on the initial, non-stationary section, while its molecular weight increases to 6000–8000. After this, as the start of accelerated breakdown is approached, the solubility of the polymer diminishes rapidly.

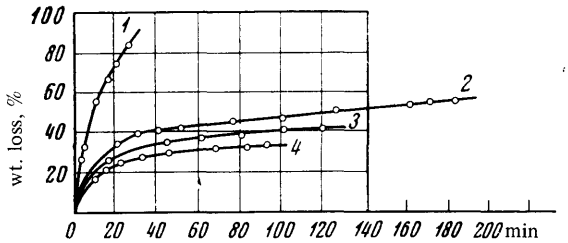


Figure 5. Thermo-oxidative degradation at 300°C and 1 atm of a thermolysed resite: 1) "freshly thermolysed" resite; 2) resite after 12 h in oxygen; 3) resite after 36 h in oxygen; 4) phenol containing the resite.

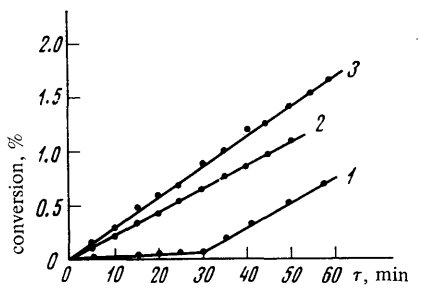


Figure 6. Catalytic activity, in the polymerisation of methyl methacrylate, of a thermolysed resite after exposure to air for (min): 1) 60; 2) 30; 3) 10.

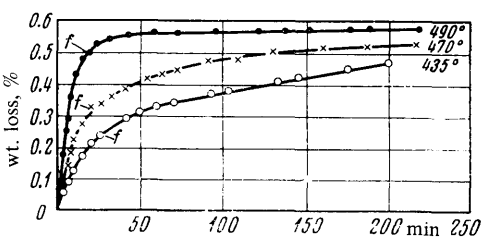


Figure 7. Weight losses in the thermal degradation of polydiphenylamine ($\overline{M}_n$ = 820) in argon.

Analysis showed that the main gaseous products of the degradation of polydiphenylamine in air were carbon and nitrogen dioxides. Degradation evidently begins with addition of an oxygen molecule at a double bond in the quinonimine structure and formation of a cyclic peroxide, which decomposes with the evolution of nitrogen dioxide.

Kinetic data indicate that the concentration of paramagnetic centres increases during the initial stages of degradation in air, then decreases, and again begins to rise almost simultaneously with the appreciable increase in rate of decomposition (Fig. 8). The variation in the concentration of paramagnetic centres in argon resembles the corresponding weight-loss curves [26].

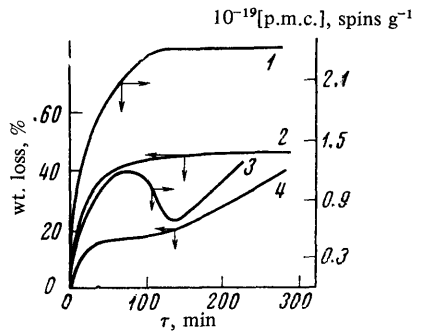


Figure 8. Variation in concentration of paramagnetic centres [p.m.c.] and weight losses in the thermolysis and thermal oxidation of polydiphenylamine: 1) [p.m.c.] in argon at 490°C; 2) loss in weight in argon at 490°C; 3) [p.m.c.] in air at 412°C (the polymer loses solubility and fusibility at the point of inflexion); 4) loss in weight in air at 412°C (as for curve *3*).

If a specimen is first heat-treated in argon until solubility is lost, and then placed in oxygen, the concentration of paramagnetic centres in the polymer falls rapidly, while its rate of decomposition increases autocatalytically. Preliminary thermal oxidation, on the other hand, improves the thermal stability of the polymer (Fig. 9).

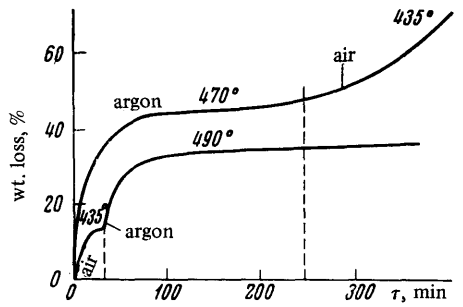


Figure 9. Rate of loss in weight when polydiphenylamine is heated in argon and in air.

This rule is probably explained by the increased concentration of active radicals trapped in the thermolysis of polydiphenylamine and their destruction ("burning out") in the preliminary thermal oxidation of the polymer. The broadening of the e.s.r. signal with the appearance of a fine structure indicates that the centres formed differ in nature from those in the original polymer associated with low-lying triplet levels. Condensation takes place more rapidly in oxygen, and the time for formation of a completely cross-linked structure is shortened. In the initial stages of formation of the network the paramagnetic centres are able to react with active radicals and be used up. As the structure becomes more rigid the rate of formation of new active radicals (by the rupture of stressed bonds) rises, and the concentration of paramagnetic centres reaches a limiting value.

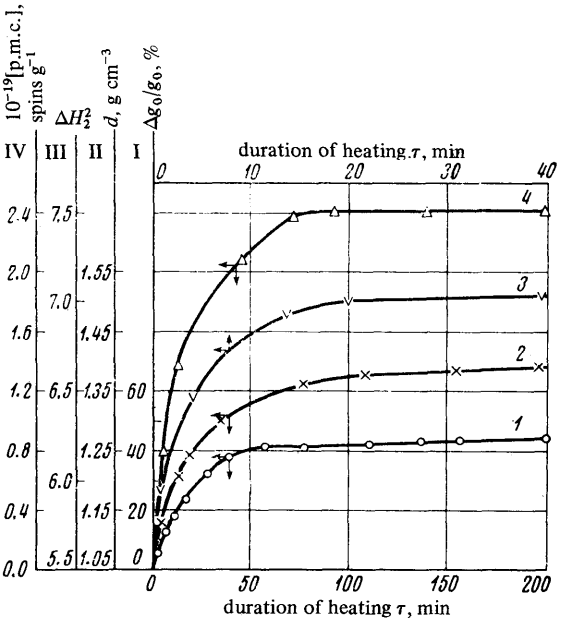


Figure 10. Rate of loss in weight and change in properties of thermolysate of polydiphenylamine ($\overline{M}_n$ = 2000) in argon at 470°C: 1) loss in weight; 2) density; 3) second magnetic moment of n.m.r. spectra; 4) concentration of paramagnetic centres from e.s.r. data.

The correctness of the above ideas can be confirmed by data indicating a correlation of the rate of thermal degradation of polydiphenylamine with the rate of increase in density, the increase in the concentration of paramagnetic centres, and the decrease in the molecular mobility of the polymer during its heat-treatment (Fig.10).

The limitation of the degradation curve of polydiphenylamine under isothermal conditions, which is general for polyconjugated systems [20,21], coincides with the completion (under the given conditions) of rearrangement of the polymer structure and formation of more thermostable fragments of fused aromatic rings. This process may be repeated with rise in temperature, which is responsible for the stepwise form of the weight-loss curves.

Thus the presence of oxygen should help to "burn-out" the most stressed portions with the formation of more

stable structures. Fig. 9 shows that preliminary treatment of polydiphenylamine in air at 435°C improves significantly its thermal stability in argon at 490°C, whereas heat-treatment of the polymer in argon diminishes its thermo-oxidative stability. In the latter case the structure formed on heat-treatment contains reaction centres, which in an oxygen atmosphere are able to react even during the formation of the network.

The whole of the above discussion indicates that the active centres produced in the thermolysis of cross-linked polymers act as initiators. Formation of the thermolysates probably involves relaxation processes leading to a decrease in the active surface area and partial destruction of paramagnetic centres. The presence in the polymer of substances of low molecular weight, capable of reacting with the radicals formed and exerting a plasticising action, enhances the probability of destruction of the radicals that have "stuck", and this improves the thermo-oxidative stability of the polyconjugated polymer [22-24].

Thus trivial considerations of the "cage" effect as a factor inhibiting a chain process cannot be used to describe the high-temperature degradation of rigid cross-linked and polyconjugated systems. The above results must be taken into account in developing methods for the synthesis and stabilisation of thermostable organic polymers.

III. SYNTHETIC PATHS TO THERMOSTABLE ORGANIC POLYMERS

When considering the formation of macromolecules of polyconjugated polymers, we must take into account the great tendency of these substances to form stable association complexes by intermolecular exchange interaction of unpaired electrons delocalised along the conjugated chain and π-electrons of multiple bonds [6]. In the absence of steric hindrance, therefore, chain growth in such macromolecules is accompanied by their aggregation and consequent impairment of the solubility of the resulting polymer. A direct consequence of this is diminished accessibility of reactive groups to the reagent and a change in their reactivity owing to resonance stabilisation caused by intra- and inter-molecular delocalisation of π-electrons [3,6]. The above specific features of the formation of polyconjugated macromolecules make it difficult to obtain polymers of high molecular weight and to process them into various goods and materials. This gives rise to difficulties in synthesising soluble or fusible conjugated oligomers and high polymers, capable of conversion into three-dimensionally cross-linked, parquet, and ladder polymers at the processing stage. These difficulties can be overcome by the use of reagents yielding polyconjugated macromolecules having side chains or groups that prevent dense packing of the chains. Methods based on the synthesis of polyconjugated systems containing polar and in particular ionogenic groups, responsible for specific solvation and solubility of the polymer in polar media, are also gaining importance.

Polyconjugated systems of high molecular weight (e.g. polyheteroarylenes) are often obtained also by a two-stage method involving the formation of soluble polymers, in which π-electron delocalisation is confined to small structural units, with subsequent conversion into polyconjugated systems by intramolecular reactions.

In view of the tendency of polyconjugated molecules to associate, which impedes or excludes their processing as solutions or melts, conversion of a high polymer into a polyconjugated system during synthesis may be advisable if the structure of the macromolecules of the resulting polyconjugated high polymer is unfavourable to their dense packing. Thus the problem of the controlled synthesis of highly thermostable organic polymers capable of being processed can be solved only if the specific structure and properties of polyconjugated polymers are taken into account. The considerable progress made in this field supports the principle that the study of polymers having a developed system of π-electron conjugation forms the scientific foundation for highly thermostable polymers.

The above specific aspects of the formation and structure of polyconjugated systems suggest the following main routes for the synthesis of oligomers and high polymers suitable for service at high temperatures and subject to radiation.

1. Synthesis of soluble and fusible oligomers with a polyconjugated system and the development of methods for their conversion into three-dimensional or planar network structures without significant disturbance of polyconjugation or the creation of molecular defects. Attainment of this aim requires the presence in the macromolecules of side-groups preventing dense packing but able under conditions of thermolysis (or radioysis) to bind macromolecules without any appreciable contribution of degradtive processes causing weight losses, increased contraction, and stresses.

2. Preparation of soluble compounds of high molecular weight with valency saturated chains and containing groups necessary for the formation of polyconjugated systems by intramolecular cyclisation and elimination, and in several cases structural units with π-electron conjugation. A polymer suitable for processing can be obtained at the synthesis stage only if the macromolecules contain either substituents that prevent dense packing or ionogenic groups.

3. Discovery of methods for synthesising block copolymers containing various polyconjugated fragments or connecting portions of "saturated" and of polyconjugated structure. Block copolymers containing organometallic blocks and fragments of π-electron (e.g. aromatic) polyconjugation may become especially important. In the last case not only plastics but also elastomers combining high thermal stability with strength may be obtained.

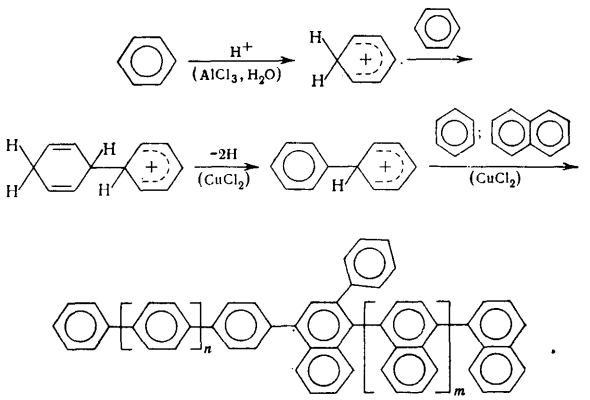
1. Polyconjugated Oligomers

Soluble oligomers suitable for the production of thermostable network polymers have been successfully synthesised in the cases of polyconjugated systems containing aromatic or heterocyclic rings joined either directly or through heteroatoms (polyheteroarylenes).

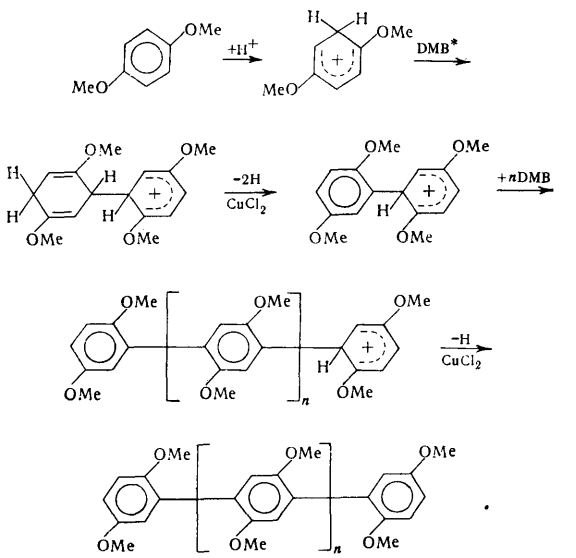
Among polyconjugated carbon-chain compounds, special interest attaches to branched oligoarylenes [27-29] and ladder oligomers of disubstituted buta-1,3-diyne [30-33]. Soluble and fusible (up to 250–400°C) oligoarylenes ($\overline{M}_n$ = 1000–3000) have been obtained by the cationic dehydrocopolycondensation of benzene with aromatic hydrocarbons in the presence of Lewis acids and dehydrogenating agents [copper(II) chloride, nitrobenzene, etc.].

The impossibility of synthesising high-molecular-weight polyarylenes in the melt and in solution is probably due to the above inactivation, characteristic of polyconjugated systems, of the reaction centre in donor–acceptor complexes formed by the growing polymer chains. Soluble and fusible polymers of naphthalene and anthracene, their

copolymers with benzene [27,28], and also polymers and copolymers of bi- and ter-phenyls [29], possess thermochemical stability in air up to 500 and in an inert gas up to 900°C. The probable mechanism of the oxidative polycondensation of aromatic hydrocarbons can be represented by a scheme analogous to that of Kovačic [34]:



Polycondensation in the presence of oxidants and Lewis acids has recently been extended to quinol and its derivatives, which has led to the synthesis of soluble oligoquinones and oligoalkoxyphenylenes having $\overline{M}_n$ = 1000 to 1500:



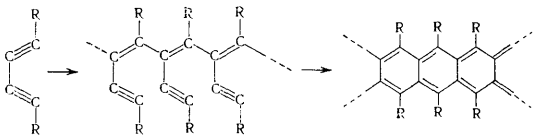
*p-dimethoxybenzene

Such polymers are stable in air up to 350°C, and are of considerable interest for the preparation of thermostable plastics and electron-exchange materials of high capacity (9–17 mg-equiv.g^{-1}). [35]

Various modifications of the Wurtz–Fittig, Ullmann, and several other reactions have been used to prepare soluble polyarylenes from aromatic monomers containing phenyl, methyl, and nitro-substituents [3,14].

A promising route to oligoarylenes suitable for processing is the high-temperature (340–450°C) dehydropolycondensation of acenes and their derivatives in the presence of conjugated paramagnetic polymers, which serve as activators. The soluble oligoanthracene obtained in this way is superior in thermal stability to the analogue synthesised by the use of Lewis acids [36,37].

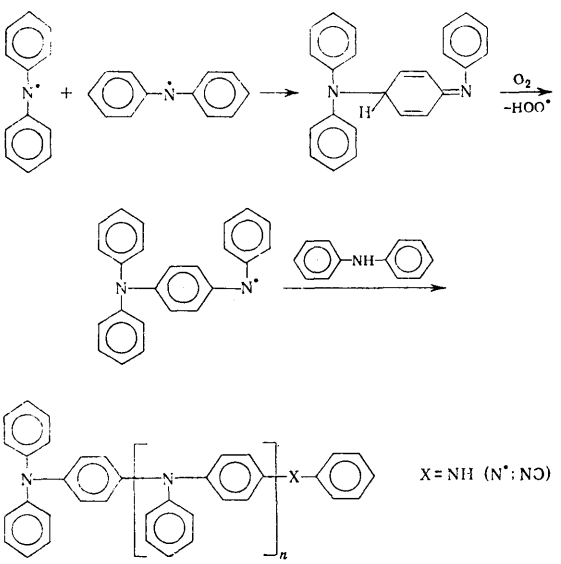
The synthesis of soluble polyconjuated oligomers having a ladder structure is of considerable interest. Such substances have been obtained by the thermal (195–400°C) and the catalytic [with $(C_4H_9)_3Al + TiCl_3$ at 50–70°C] polymerisation of 1,4-diphenyl- and 1,4-dimethyl-buta-1,3-diynes [30–32]:



(R = Ph, Me, etc.)

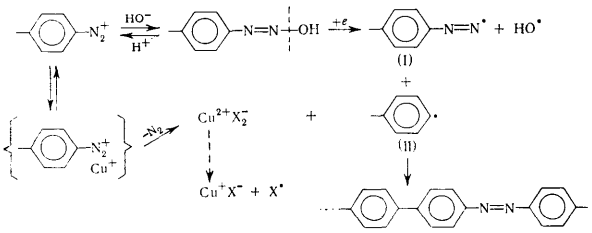
A ladder oligodiphenylbutadiyne having $\overline{M}_n$ = 3000–5000 dissolves readily in aromatic hydrocarbons, chloroform, dioxan, etc. Treatment of films of cyclised oligodiphenylbutadiyne at 1000–3000°C was accompanied by relatively small (15–35%) weight losses and yielded carbon having a graphitic structure. The electrical conductivity of the products at 300°C was 1.7–15 ohm^{-1} cm^{-1}, and the activation energy of conduction 0.04–0.06 eV. Products of the high-temperature treatment of oligodiphenylbutadiyne did not lose weight when heated in air to 700°C.

The oxidative polycondensation of secondary aromatic amines opens up interesting potentialities for the directed synthesis of polyconjugated systems [38–40]. It has been established experimentally that the oxidation of amines by oxygen in the melt at 200–250°C yields soluble, fusible oligomers of $\overline{M}_n$ = 1500–3000, possessing high thermochemical stability (temperature of progressive decomposition 450–500°C) and able to inhibit the thermo-oxidative and radiation degradation of carbocyclic and heterocyclic polymers. Available data suggest that polyarylenepolyamines are formed by the scheme

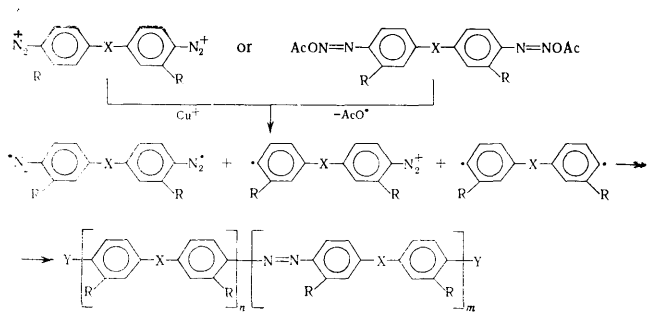


The polydeazotisation of aromatic bisdiazonium salts and bisnitrosoacylamines [41,42] shows great promise for the synthesis of soluble and fusible polyconjugated oligomers. This reaction is an example of non-equilibrium polycondensation by a radical mechanism. The deamination of

aromatic bisdiazonium salts in the presence of reductants probably has the mechanism [42,43]



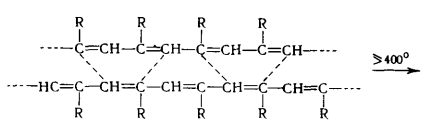
Interaction of radical centres of the growing chain with chloride ions in the redox reaction complex leads to chain termination. This liberates an electron, which is captured by the oxidised copper cation. Chain growth can cease only by conversion of the end of the growing polymer molecule into an inactive, stable radical having a considerable proportion of quinonoid structure. The content of combined nitrogen in the resulting oligomers varies with their structure from 1–2% to 7–8%. Bisdiazonium salts or bisnitrosoacylamines containing loosening phenyl, alkyl, or ionogenic groups in the aromatic ring must be used to obtain soluble oligoazoarylenes of $\overline{M}_n$ = 4000–8000:

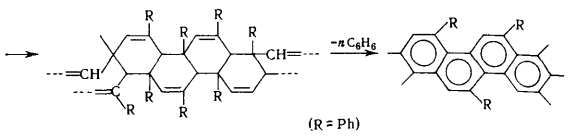


where X represents O, S, CH_2, or a single bond and R = H, Alk, Ar, COOH, OH, SO_3H, NO_2, or NHCOR.

Oligoazoarylenes are similar to oligophenylenes or the corresponding oligoarylenes in thermochemical stability [41,49]. Surprisingly, the elementary composition of oligoazoarylenes varies little when they are heated to 500–700°C, and azo-groups conjugated with benzene rings are preserved in the oligomer up to 700–1000°C. Polydeazotisation can be used to obtain oligoheteroarylenes containing metallocene groups [44]. Such polymers possess high thermochemical stability in an inert atmosphere (up to 700–800°C), but in the presence of oxygen they are degraded at 350°C.

The possibility of improving the thermal stability while maintaining solubility by appropriate heat-treatment of polyconjugated oligomers containing loosening fragments is based on controlling the fragments of a fused aromatic containing loosening groups [23,32,45]. Thus heating polyphenyl(phenoxy or pyridyl)acetylenes at 350–400°C for a short time ($1\frac{1}{2}$–2 h) converts them into soluble, dark-coloured oligomers containing fused aromatic structures [22,32]. This involves degradation with partial elimination of side radicals: e.g. in the thermolysis of polyphenylacetylene





the loss in weight at 400°C is 50% (H_2, C_6H_6, and $C_{12}H_{10}$ are eliminated), and the resulting black polymer retains solubility and possesses higher thermal stability (Fig. 11), electrical conductivity [2,45], and concentration of paramagnetic centres (the last by 10^3) than the initial polymer.

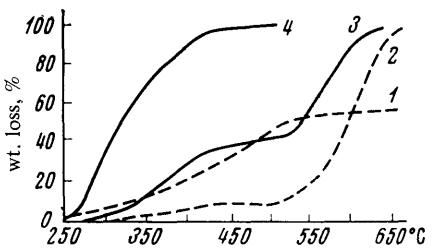
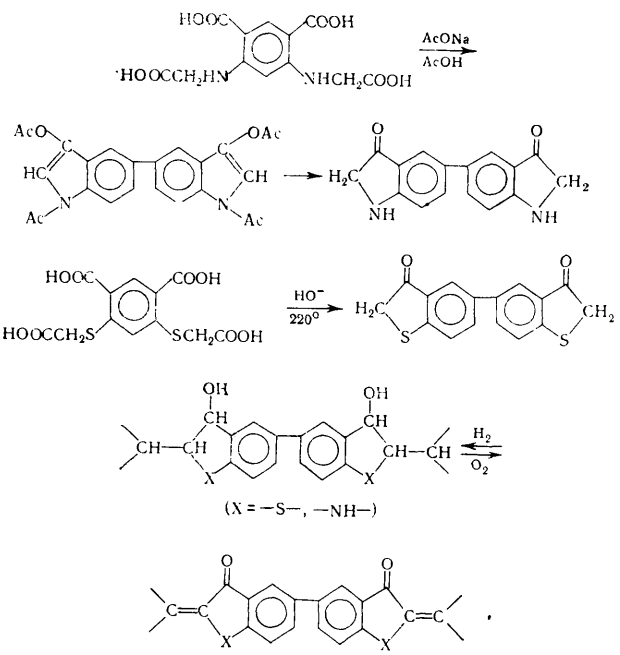
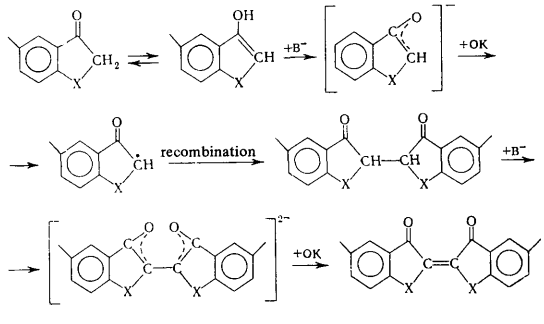


Figure 11. Thermal and thermo-oxidative degradation of soluble polyphenylacetylenes prepared in: 1) vacuum at 400°C; 2) presence of oxygen at 400°C; 3) presence of oxygen at 150°C; 4) vacuum at 150°C. At point *a* the polymer loses its fusibility and solubility [cf. Figs. 3 and 8].

The recently developed principle of the reversible conversion of insoluble into soluble polymers by redox reactions in polyconjugated oligomers and polymers [46,47] is also acquiring great importance. This method is analogous to vat dyeing, and the first "vat polymers" have been polyindigoids. Polyindigo and polythioindigo have been synthesised by oxidative polycondensation [42,46,47]



Electron spin resonance spectra obtained during the process and investigation of the products formed by termination of the growing chains on a stable radical (1,1-diphenyl-2-picrylhydrazyl) suggest the mechanism



B = base; OK = oxidant (O_2; etc.)

for the oxidative polymerisation of indoxyl and its analogues [42].

Polyindigo and polythioindigo are oligomeric polyconjugated systems of $\overline{M}_n = 4000$ possessing the magnetic and semiconducting properties usual for substances of this type. Polymeric indigoids (especially polythioindigo) also exhibit high thermal stability (up to 400–500°C) and are easily reduced by dithionite to the leuco-form, which is soluble in alkaline aqueous solution. Oxidation of the leuco-form in air yields polyindigo again. These transitions are reversible [42]. Vat dyeing with polymeric indigoids improves the thermal stability and the strength of several synthetic fibres (Fig. 12). Polyindigoids are promising also for obtaining heat-resistant coatings and as resins possessing electron-exchange and catalytic properties.

In connection with the above it is becoming urgently necessary to seek new synthetic routes to soluble oligomeric homo- and hetero-arylenes, e.g. oligoarylenazomethines [45,48], oligoarylenacetylenes [50,51], and several other polyconjugated oligomers.

2. Conversion of Polyconjugated Oligomers into Network Polymers

The transition from polyconjugated oligomers to polymeric materials and articles requires the development of rational methods permitting the conversion, at the processing stage, of fusible compositions into thermostable products possessing a specified set of physicomechanical properties. We shall now consider processes that have been suggested for "hardening" polyconjugated systems.

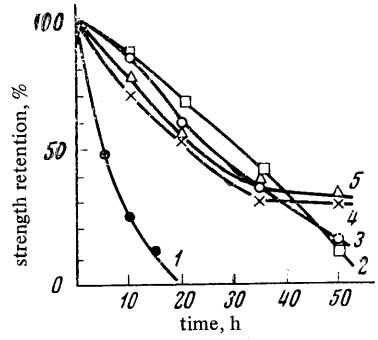
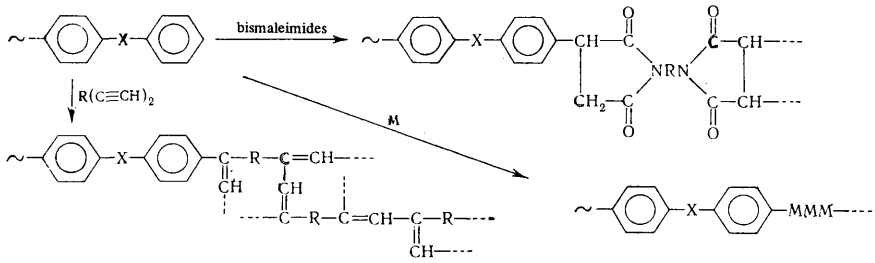


Figure 12. Strength of fibre based on a bicyclic lactam and caprolactam in air at 200°C after stabilisation with: 1) control; 2) thioindigo; 3) indigo; 4) polythioindigo; 5) polyindigo.

(*a*) Interaction of polyconjugated oligomers with compounds containing multiple bonds

Polyarylphenylenes, polyarylenes, and polyheteroarylenes containing paramagnetic centres have been shown in a series of studies [52–56] to be capable of spontaneous three-dimensional block copolymerisation at 150–200°C with *p*-diethynylbenzene and with bismaleimides of aromatic diamines or their analogues ("quasi-radical block polymerisation"). The polyconjugated oligomers containing paramagnetic centres initiate polymerisation of the electron-accepting monomers [25,54,56,57]:



X = $-C_6H_4-$, $-N{=}N-$, $>CO$, $>SO_2$, etc.; R = arylene; M = monomer

The discovery of this reaction, specific to polyconjugated systems, permitted the synthesis of thermostable soluble and three-dimensionally cross-linked block copolymers. The systems of compatible polyconjugated polymer and monomer (in several cases the latter was the solvent) were so chosen that compositions based on them possessed fluidity at the high temperature required to form the article. It is especially noteworthy that the "hardening" of a composition by quasi-radical block copolymerisation does not require the use of special

catalysts and is not accompanied by separation of products of low molecular weight, which might complicate the processing technology and impair the properties of the material.

The mechanism of quasi-radical block copolymerisation has been investigated on the systems formed by polyphenylacetylene with maleic anhydride and with methyl metacrylate[56-58]. Nuclear magnetic resonance shows that the first step is formation of a charge-transfer complex between the polyconjugated oligomer and the monomer:

$$P\uparrow\!---\!\downarrow P \overset{K_e}{\rightleftarrows} P\uparrow + M \overset{K_1}{\rightleftarrows} [P\uparrow\!---M]$$
(donor-acceptor complex)

where P↑---↓P represents associated polyphenylene macromolecules containing paramagnetic centres (the symbol ↑ denotes the presence of unpaired electrons), M a monomer molecule, and P the polyconjugated polymer. The complex [P↑---M] can be formed only if polyconjugated system and monomer are densely "packed" and if the electrophilic character of the latter is enhanced. Under otherwise similar conditions, therefore, the π-complex formation that limits polymerisation will depend on the structure and the configuration of the polyconjugated system and the monomer. The reaction is most probably initiated by thermal excitation of the reactants to a biradical state, followed by isomerisation to monoradicals, which carry on the chain polymerisation in contact with the surface of particles of the polyconjugated system. Formation of a block copolymer is evidently a consequence of termination or transfer of the growing chain. Such a mechanism can be represented to a first approximation by the scheme

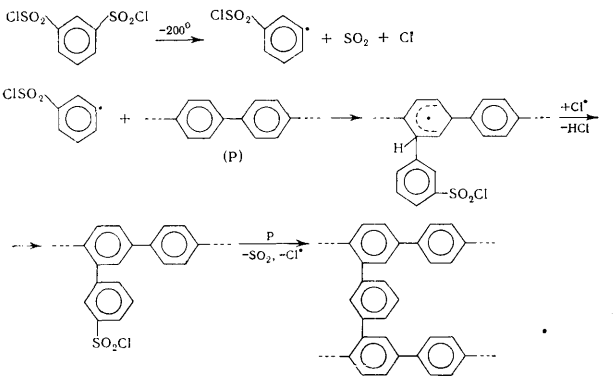
$$[P\uparrow\!---M] \overset{+M(k_i)}{\rightleftarrows} [P\uparrow\!---M\!---M] \xrightarrow{E(k_t)} [P\uparrow\!---M_1\!---M_2]$$
$$[P\uparrow\!---M_1] \xrightarrow{+M(k_p)} [P\uparrow\!---M_1MMM^{\cdot}] \xrightarrow{+M_nMMM^{\cdot}(k_t)} P\uparrow + [M]_n$$
$$P\uparrow + MMMM \overset{k't}{\rightarrow} P\uparrow - MMMM \ .$$

According to this scheme, raising the temperature and conducting the reaction in a homogeneous melt or solution should increase the yield of the block copolymer. When an insoluble polymeric polyconjugated system is used as catalyst, e.g. the pyrolysate of a phenol–formaldehyde resite[25,59], and the process is carried out at a moderate temperature ($\leq 100°C$), a stereoregular homopolymer is formed. It follows also from the scheme that the reaction velocity should be proportional to the concentration of the polyconjugated system raised to a degree $n < 1$ and to that of the monomer raised to a degree $n > 1$. All these suggestions showed good agreement with experiment[29].

The use of soluble and fusible compositions of polyarylenes with various cross-linking agents as binders for plastics reinforced with carbon or asbestos fibres will yield thermostable materials suitable for prolonged service at 300–350°C.[20] Such polymer systems are promising also for the production of thermostable coatings and adhesives.

(*b*) Formation of networks in polyconjugated oligomers by radical substitution

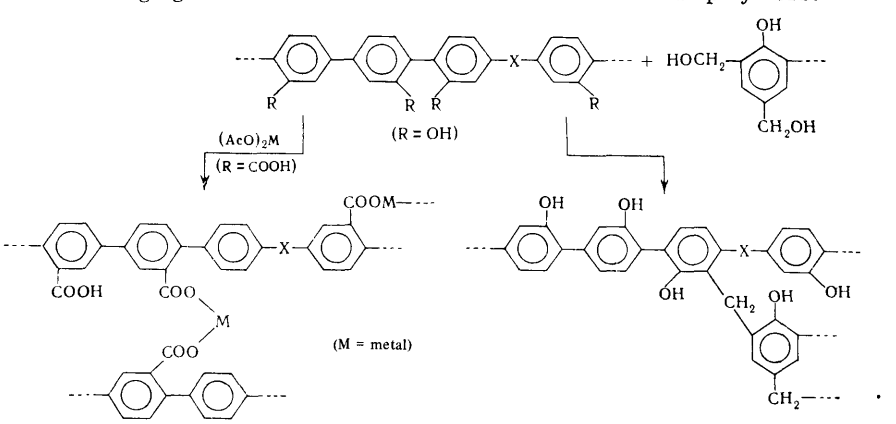
This method is based on the interaction of polyconjugated systems with aryl radicals formed by the high-temperature (150–200°C) degradation of aromatic disulphonyl dichlorides and certain other compounds:



Among the many possible cross-linking agents benzene-*m*- and *p*-disulphonyl dichlorides have acquired practical importance[60]. This reaction has recently been proposed for the synthesis of oligophenylene ($\overline{M}_n = 1775$), which can then be cross-linked or processed[61]. The reaction is accompanied by chlorination and the separation of by-products, which in several cases makes processing difficult and the method less promising than quasi-radical block copolymerisation. Nevertheless, high-strength asbestos and carbon plastics have been obtained by the use of benzenedisulphonyl dichlorides with additional heat-treatment[60,61].

(*c*) Conversion of polyconjugated oligomers into three-dimensionally cross-linked polymers by reactions of functional groups

Polyphenylenes and polyazophenylenes containing hydroxyl or carboxyl react with hydroxymethyl derivatives of phenols, phenol–formaldehyde resols, epoxide oligomers, metal salts, etc. to form infusible thermostable "cross-linked" polymers:



This method of "hardening" polyconjugated polymer systems has certain advantages over radical substitution (e.g. absence of chemically aggressive reaction products), but requires the presence of functional groups in the polyconjugated macromolecules. Known methods for the synthesis of carbon-chain oligomers depend on the use of aromatic or hydroaromatic hydrocarbons as starting material. Their conversion into polymers capable of being "hardened" by interaction with the above condensing agents requires the introduction of hydroxy-,[61] carboxy-,[2] or amino-groups into the aromatic rings.

In this connection considerable interest attaches to the polydeazotisation of aromatic bisdiazonium salts described earlier, which enables us to pass directly to oligoarylenes and oligoheteroarylenes containing almost any functional groups in the polyconjugated macromolecules, and to convert them into various types of network polymers[2,42].

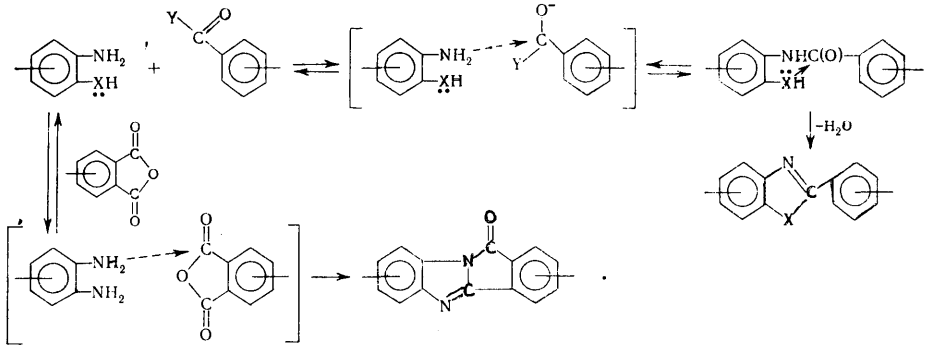
3. Synthesis of Polyconjugated Polymers of High Molecular Weight

The chemistry of polyconjugated polymers indicates that polyconjugated systems of high molecular weight can be produced only when difficulties in the growth of chains of continuous polyconjugation have been overcome. This can be achieved when there is maximum exclusion of π-electron delocalisation through large fragments of the macromolecules at the stage of chain growth, since only then are the possibilities of intermolecular aggregation and inactivation of the reaction centre diminished (see earlier). When the aim is to obtain a soluble high-molecular polyconjugated substance, it is also necessary to design the macromolecules to contain loosening groups or variegated fragments preventing dense packing of the chains.

These problems are solved most simple for "saturated" high polymers, capable of passing into polyconjugated systems by intramolecular detachment[2,18]. Examples of such processes are the thermo-oxidative dehydration of polysaccharides, dehydrocyclisation of polyacrylonitrile, dehydrochlorination of poly(vinyl chloride), and dehydration of poly(vinyl alcohol).

Considerably later (from 1960) an analogous method was applied to polycondensations yielding polypyromellitimide and several other polyheterocycloarylenes[63], and from 1966 to the synthesis of phenylated polyphenylenes[27,29]. Chain growth in the synthesis of polyheterocycloarylenes leads to the formation of compounds (e.g. polycarboxyamides, poly-*OO*-carboxyaminoamides) in which π-electron conjugation is confined to aromatic rings and groups attached directly to them. Polycondensation under mild conditions in a strongly polar medium at 20 to 70°C therefore yields initially chains of high molecular weight, which are then converted into polyconjugated high polymers by intramolecular cyclisation and detachment. Such conversion can be effected during synthesis or during subsequent processing of the prepolymer into articles.

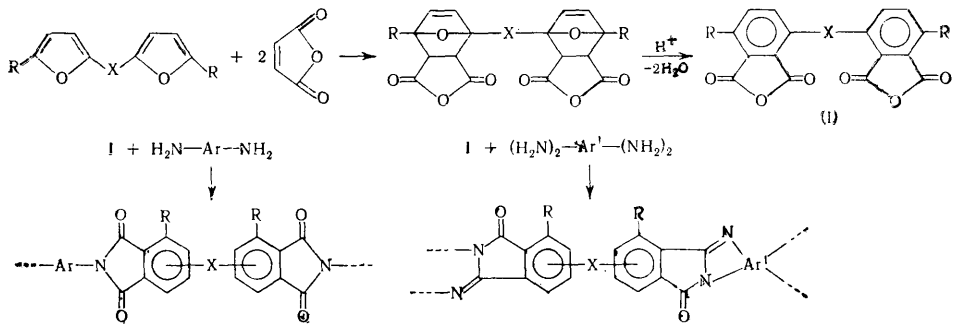
Loosening groups, e.g. phenyl, must be introduced into the chain in order to obtain soluble, almost completely cyclised polyheterocycloarylenes. Aromatic polyimides, polybenzimidazoles, polybenzoxazoles, polyimidazopyrrolones, polybenzimidazobenzophenanthrolines, polyquinoxalines, and many other polyheteroarylenes have been synthesised in this way[17,63]. The generality of the principle underlying the synthesis of high polymers having conjugated aromatic and heterocyclic ring systems is illustrated by the scheme



(X = NH, O, S, CONH, COO; Y = Cl, OR, CHO)

A promising line of advance in the field of polyheterocyclic polyconjugated systems is the synthesis of soluble polyimidazopyrrolones, polybenzimidazobenzophenanthrolines (pyrrones), and polyquinoxalines of semi-ladder, ladder, and block–ladder structure[1,17]. Solutions of pyrrones have been used to obtain strong and highly thermostable fibres, films, and foam plastics which are stable in an inert atmosphere up to 800°C and whose physicomechanical properties remain unchanged on irradiation with a dose of 10^4 Mrad.[16,17]

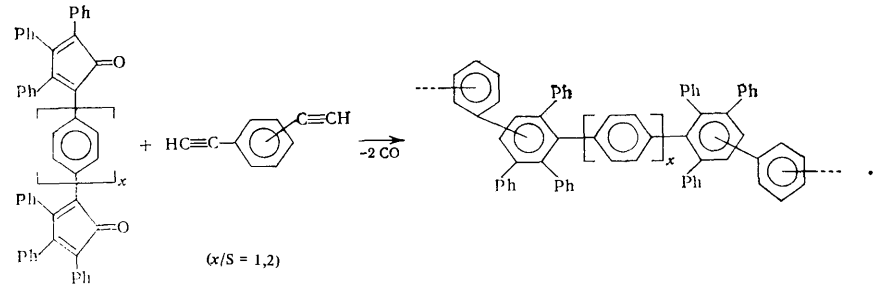
A recent advance of interest in developing the chemistry of polyheteroarylenes is the synthesis of polyimides and polyimidazopyrrolones from aromatised diadducts of maleic anhydride and various bisdienophilic compounds, e.g.[64]



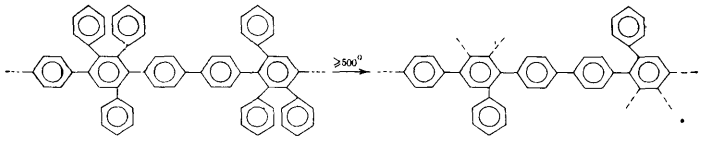
(R = H, Ar; X = —CH=NArN=CH—; —Ar— —CH_2OOCArCOOCH_2—)

Investigation of the cyclopolycondensation of dianhydrides of tetracarboxylic acids with di- and tetra-amines has shown[64,65] that the most complete cyclisation is attained when the process is conducted as a single stage in polyphosphoric acid at 200–250°C. In the intramolecular cyclisation of the initially formed polyamino-acids and especially polyaminoamides the relative immobility of structural units in the chain evidently impedes the contact of reactant groups, which limits development of the conjugated chain and increases the proportion of weak bonds in the polymer. On the other hand, two-stage cyclopolycondensation is in practice unsuitable for obtaining thick articles, for cementing monolithic materials, or for producing reinforced plastics, since cyclisation occurs at a relatively high temperature and is accompanied by the evolution of volatile products. It is therefore very urgent to solve the problem of obtaining heterocyclochain polyconjugated systems that are soluble but yet of sufficiently high molecular weight. Polymers containing fragments that destroy the symmetry of the structure and diminish the density of packing of the macromolecules satisfy these conditions[6,63]. Interesting possibilities are opened up by the use of "reactant plasticisers" to facilitate the flow of pyrrones and their cross-linking during injection moulding and extrusion[66] and by the use of oligomeric analogues for the processing of pyrrones.

Aromatic carbocyclic–chain polyconjugated systems of high molecular weight have recently been acquiring increasing importance, as have the heterocyclic–chain type. Thus the polyaddition of diacetylenic aromatic hydrocarbons (e.g. *p*-diethynylbenzene) to bistetraphenylcyclopentadienones (tetracyclones) in toluene at 180–250°C gives a quantitative yield of a benzene-soluble, amorphous, weakly coloured polyphenylpolyphenylene[14]:



The molecular weight of the phenylated polyphenylene is 20 000–100 000. In nitrogen at 575°C the polymer loses 30–35% of its weight, and passes into an insoluble brown product which in an inert environment is stable up to 800°C. This involves dephenylation and cross-linking[14]:



Paramagnetic centres appear in the polymer during heat-treatment and dephenylation, and its electrical conductivity increases.

The observed regularities are easily explained by the non-coplanarity of the aromatic rings in the polyphenylpolyphenylenes, which prevents conjugation from extending to more than two benzene rings. Favourable conditions are thereby created for the formation of a polymer of high molecular weight, which itself should not be regarded as thermostable. On thermolysis, however, the detachment of bulky groups changes the conformation of the chain with the appearance of a more coplanar polyconjugated polyphenylene; this is responsible for the thermal stability and other properties of the final material. Thus the example of phenylated polyphenylene bears an analogy to very many facts known for various polyheteroarylenes and heterocyclic–chain polymers.

Together with the data surveyed earlier, all this suggests that polyconjugation plays a decisive part in the formation of thermostable polymers and their subsequent transformations when subjected to powerful influences.

IV. ROLE OF POLYCONJUGATION IN THE THERMAL STABILITY OF POLYMERIC MATERIALS

We have come a long way and attained very considerable results during the fifteen years since the first publication establishing the concept of polyconjugation and its application to the synthesis of thermostable and semiconducting polymers [2]. The number of investigations inclined to accept these ideas and using them to develop rational methods for obtaining polymeric materials possessing high strength and thermal stability is now increasing [48,67,68].

However, several workers [69,70] approach the problem of the thermal stability of polymeric substances without taking into account intra- and inter-molecular π-electron delocalisation, i.e. in disregard of the main concepts of the chemistry and physics of polyconjugated systems. These investigators consider the difference in chemical nature between rings and other groups in the units, the configuration of the chains, and intermolecular interaction in the initial polymers. They completely ignore the role of π-electron delocalisation (conjugation) through fragments or through the chain of the macromolecules and its contribution to the intermolecular interaction and supermolecular structuring of polymeric substances. Further, they disregard the fact that the thermal stability of a material is determined in many cases not so much by the nature of the initial polymer as by the structure of the polymeric product formed by the action of thermal and other powerful factors. Yet, as shown above, it is electron delocalisation in the chains of the initial polymer and its thermal conversion products which determines the internal energy and the stability of the material under severe processing and service conditions.

It must be especially borne in mind that complicated chemical and structural changes take place in an organic polymer at high temperatures. These are responsible for (i) the growth of fragments of fused aromatic or heteroaromatic rings, with a consequent decrease in the internal energy and increase in the thermal stability of the system, and (ii) the associated increase in rigidity of the macromolecular chains and formation of three-dimensionally cross-linked polyconjugated structures. The latter processes (ii) are accompanied by increases in contraction and internal stresses, and they activate local thermal cracking of the most stressed bonds. Thus the chemical and structural changes observed in a polymer subjected to high temperatures are a prerequisite for the formation of reactive σ-radicals, as in mechanical degradation of macromolecular substances [71].

Further cross-linking with the accumulation of σ-radicals is probably the main reason for the poor stability of many cyclochain polymers under oxidising conditions at high temperatures. Thermal oxidation in such systems is initiated by reactions of σ-radicals, formed and "frozen" in the network, with oxygen at the surface of the specimen. The heat thus evolved activates neighbouring bonds and groups with the subsequent development of degradative processes. Owing to the restricted molecular mobility of the network, moreover, part of the heat evolved on interaction between oxygen and the radical cannot be dissipated in thermal lattice vibrations, and may be emitted as chemiluminescence [72], which also activates the development of thermal oxidation, as has recently been shown for the chemiluminescent initiation of polymerisation [73].

It is also possible that "hot" radicals [74] play a definite part in this process. The evolution of heat and the autocatalytic character of the high-temperature oxidation of rigid network polymers (polyconjugated systems) may be responsible for the observed thermal ignition of thermolysed resites [24]. This suggestion is supported by the above correlation of the increase in density and decrease in molecular mobility of the cross-linked thermolysate with increases in the degree of conversion and in the rate of thermal oxidation, and also by the catalysis of radical polymerisation by resite specimens that have been thermolysed at 450°C. The hypothesis is supported also by the loss of ignitability and catalytic activity which we have observed [24] after blocking of the active centres of these substances.

The views and experimental facts considered in this Review indicate that organic polymers with high resistance to thermal oxidation cannot be synthesised on the basis of rigid-chain, ladder, parquet, or network structures not containing fragments that increase the thermal mobility of the molecular framework. A directly opposite point of view is often adopted on this matter.

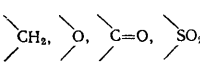
The concept of polyconjugation and the ideas underlying the chemistry and physics of polyconjugated systems are applicable also to aromatic carbon-chain and heterochain polymers. Such substances as phenol–formaldehyde resites, aromatic polyamides, polyimides, etc. are usually regarded as saturated polymers comprising aromatic rings separated by the particular groups. Such polymers surpass acyclic analogues in strength and thermal stability, and in several cases (polypyromellitimides) are closely similar to polyphenylenes and polycycloheteroarylenes containing large fragments of continuous conjugation. Hence it is deduced that the thermal stability of organic polymers is due to the presence of stable rings and the consequent rigidity of the macromolecular chains [14,69,70]. Such ideas hardly touch the essence of the phenomenon, although they reflect certain of its consequences.

Table 2. Polyconjugation in aromatic polyamides [75].

No.	Molecular structure	η_{sp}	Long-wavelength absorption λ_{max}, nm	10^{-15} [p.m.c.], spins g^{-1}
1	Benzanilide	—	276	**
2	Terephthalamide	—	304	**
3	*m*-Phenylenanilide	—	300	**
4	Poly-*m*-phenylenisophthalamide	0.88	280	4.6
5	Poly-*m*-phenyleneterephthalamide	0.58	300	8.2
6	Poly-*p*-phenylenisophthalamide	1.22	305	9.2
7	Poly-*p*-phenyleneterephthalamide	1.27	330	16.0
8	Poly-*p*-phenyleneterephthalamides differing in mol.wt.	0.04	314	2.2
9		0.14	318	5.6
10		0.35	330	12.3
11*		1.27	330	16.0
12*		1.27	330	24.6

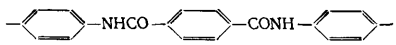
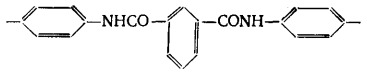
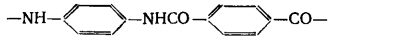
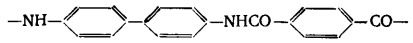
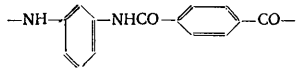
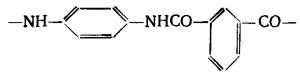
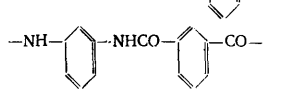
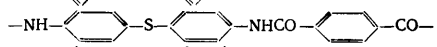
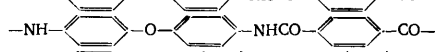
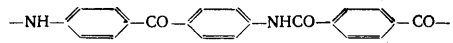
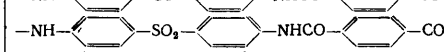
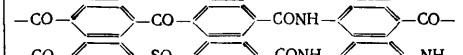
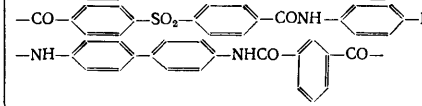
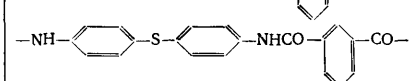
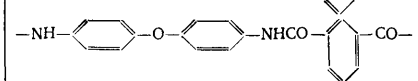
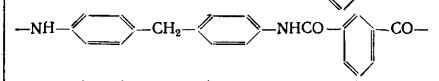
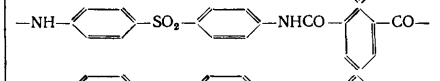
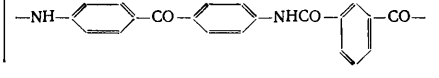
*Specimens 11 and 12 were obtained by precipitating polymer 7 from dilute solution in sulphuric acid (with water and ethylene glycol respectively). This considerably diminished the crystallinity of the polymer.
**Not detected.

Recent quantum-chemical and spectral investigations have shown that aromatic polyamides, polyimides, and other types of polyheteroarylenes are polyconjugated polymers [75]. The presence of the bridging groups



does not exclude π-electron delocalisation through extended fragments of the macromolecule[75]. Such polymers showed high π-electron exchange interactions along the chain, bathochromic shifts in the ultraviolet absorption spectra with increase in length of the macromolecule, and also the narrow e.s.r. singlet, with the g-factor of a free electron and becoming more intense with increase in molecular weight, that is characteristic of polyconjugated systems (Tables 2 and 3). The same work has established that the presence of *meta*-substituted aromatic units (e.g. in polyisophthalamides), like the presence of electron-accepting bridging groups in the amine component, diminishes the polyconjugation effect by changing the electron configuration of the molecules. All this is consistent with existing views on polyconjugation and on the properties of polyconjugated polymer systems[18,41,76].

Table 3. Long-wavelength absorption bands of various polyamides[75].

No.	Polyarylenamide	λ_{max}, nm
1		304
2		280
3		330
4		345
5		300
6		305
7		280
8		360
9		330
10		320
11		330
12		300
13		320
14		305
15		330
16		330
17		310
18		300
19		290
20		330

It is interesting that the thermal stability and several physical properties of aromatic polyamides and polyimides correlate with their effective conjugation, to which attention has been directed repeatedly[17,18,22]. The effect of polyconjugation may not be apparent in the initial state of polymers containing disconnected aromatic or heteroaromatic rings systems, as in several saturated acyclic polymers capable of eliminating groups when sufficiently stressed. Under various powerful influences, however, such systems are converted into polyconjugated systems with more or less substantial structuring and contraction, depending on the nature and structure of the polymers and the conditions of treatment.

We have thus directed attention to the role of polyconjugation—electron delocalisation through extended fragments of macromolecules and their association complexes—which in the Reviewer's opinion determines the thermal stability and other properties of polymers. This does not mean, of course, that the Reviewer denies the connection discussed in the literature between the structure of a unit, the presence of so called "weak bonds", and thermal stability, or the effect of chain rigidity on the resistance to degradation and the strength of polymers. However, none of this represents a foundation on which specific aspects of the degradation of highly thermostable polymers could be understood, and methods developed for their planned synthesis.

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