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# New Heterochain Polymers Based on Cyclic Imides of Carboxylic Acids

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Results are given for the use of cyclic imides of carboxylic acids and monomers for new thermostable polyimides and polyamides. Migration copolymerisation, polycondensation, and cycloaddition of imides of aliphatic, aromatic, and unsaturated structure are discussed. A list of 159 references is included.

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## I. INTRODUCTION

Anhydrides of di-, tri-, and tetra-carboxylic acids are used as starting materials for the synthesis of most thermostable polyheteroarylenes[1-3]. Use of these monomers in reactions with aromatic di- or tetra-amines yields processable polymers resistant to chemicals and radiation, which withstand prolonged heating to 300°C. However, the preparation and especially the purification of these anhydrides is associated with several difficulties[4]. Existing methods of obtaining polymers from them also have their defects[5], primarily the hydrolytic instability of the polymers formed in the first stage, as well as the complexity of achieving 100% cyclisation in the second stage. The search for other monomers structurally analogous to anhydrides and the development of new methods for synthesising thermostable heterochain polymers are extremely urgent tasks.

Cyclic imides of carboxylic acids are of definite interest in this connection[6]. Effective procedures for their synthesis by the vapour-phase oxidative ammonolysis of alkylbenzenes have been developed recently[3,7,8]. Good yields and ease of purification guarantee important advantages in comparison with anhydrides.

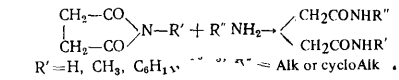
In the present Review we have attempted to summarise examples of the use of such monomers, describe new reactions in which they are used, and report the properties of the resulting polymers.

## II. POLYCONDENSATION OF CYCLIC IMIDES WITH AMINES INVOLVING CLEAVAGE OF THE IMIDE RING

It has long been known that cyclic imides of carboxylic acids are able to react with several nucleophilic compounds. Until recently, however, these reactions were not studied in relation to polymer chemistry. Many investigations during the past 10–15 years have shown a promising future for the use of these reactions in synthesising macromolecular compounds. Amines are active nucleophilic components, undergoing aminolysis with imides to give diamides.

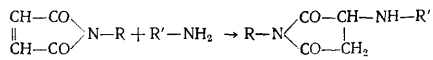
### 1. Aliphatic Imides

The first systematic investigation of the interaction of aliphatic imides with amines was undertaken by Sheremet'eva and her coworkers during the 1960s. Taking succinimides as examples, they showed[9] that amines in alcoholic solutions in the cold produce cleavage of the imide ring with formation of corresponding mono- or di-substituted diamides:

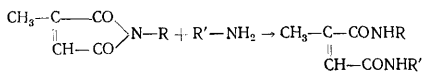


R' = H, $CH_3$, $C_6H_{11}$, ... R'' = Alk or cycloAlk.

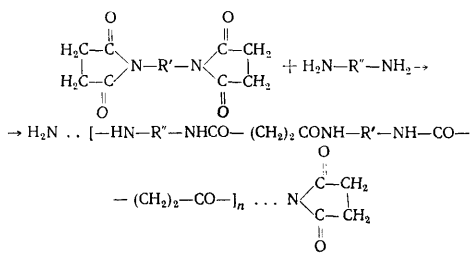
Imides of unsaturated dicarboxylic acids—maleic, citraconic, itaconic—may react differently with amines according to the conditions[9-11]. In anhydrous organic solvents only addition of ammonia and amines at the double bond takes place, with formation of corresponding derivatives of aspartic acid:



An aqueous solution of an amine causes aminolysis with formation of diamides and preservation of the double bond:



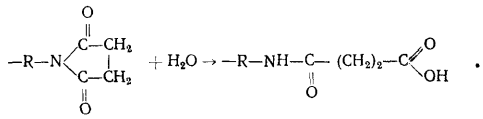
Polymers varying in chemical structure and properties can be obtained by applying these reactions to difunctional compounds. Sheremet'eva et al. were the first to show[12] that linear polyamides can be obtained by the aminolysis of disuccinimides:



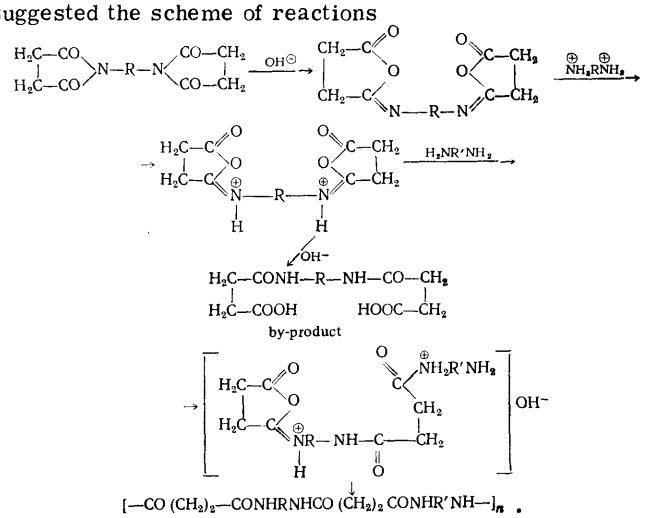
R' = $-(CH_2)_6-$; $-CH_2-C_6H_4-CH_2-$; R'' = $-(CH_2)_m-$; $-CH_2-C_6H_4-CH_2-$; $m = 2, 4, 6$.

The reaction is conducted under mild conditions, in the cold with prolonged standing of solutions or suspensions of the imides with the amines in the presence of water in such solvents as dioxan, methanol, etc. Polyamides of molecular weight 16 000–20 000 are thus obtained. Reaction does not take place in dry organic solvents even after boiling for many hours[13].

Bisimides of glutaric, aspartic, and unsaturated acids have also been used as initial monomers in this reaction[14]. Mixed polyamides are obtained from bisimides and bisamines containing substituents R′ and R″ differing in structure. Conducting the reaction at room temperature eliminates transamidation and will yield mixed polyamides of strictly specified, regular structure, in which the hydrocarbon fragments R′ and R″ are arranged in a definite sequence in the macromolecule. Termination of the growing polymer chain may result from hydrolysis:

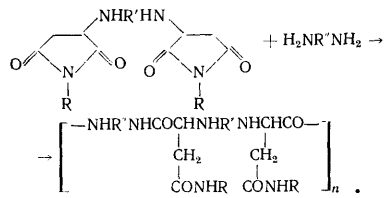


A comparative kinetic investigation of aminolysis and hydrolysis was made in the case of the action of amines on the hexamethylenebisimides of succinic and glutaric acids in order to determine the quantitative relation between these reactions[15]. For each of the bisimides the rate of aminolysis is several times greater than the rate of hydrolysis, and bisglutarimides are hydrolysed appreciably more rapidly than are bissuccinimides. Both processes—aminolysis and hydrolysis—are catalysed by hydroxide ions. The quantitative relation between hydrolysis and aminolysis depends on the pH. With succinimides both processes are second-order reactions with respect to the hydroxide ion, whereas with glutarimides they have the first order. The kinetic results obtained for succinimides suggested the scheme of reactions




Water is assumed[15] to activate both initial components. Amino-groups are converted into ammonium ions, while bisimides isomerise under the influence of hydroxide ions into bisisoimides. Azomethine groups are then protonated by the transfer of protons from ammonium ions. Under the influence of nucleophilic attack by the amine (in the main reaction) or by hydroxyl (in the secondary reaction of hydrolysis) the carbon–oxygen bond in the isoimide ring undergoes fission with formation of the main product and a by-product.

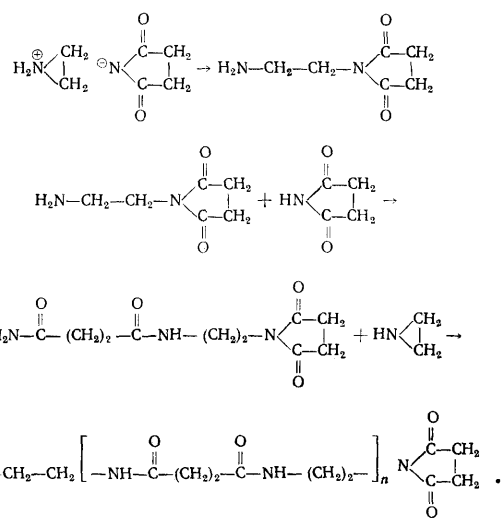
Bisimides of aspartic acid have also been used as initial monomers[16,17]:



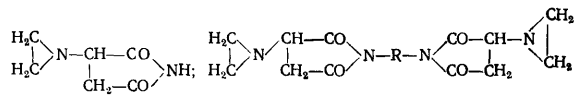
At room temperature they react with bisamides only on the addition of 20–30% of water to the solution. When the water content is increased to 50%, the viscosity of the resulting polymer is lower owing to chain termination by hydrolysis of the imide rings. Reaction does not take place in solutions of anhydrous organic solvents; but at higher temperatures (50–100°C) the polymer is formed even without the addition of water. The resulting polyamidoimides contain secondary amino-groups in the chain, which strengthen the basic character of the polymer, with consequent improvements in its solubility and its dyeability by acid dyes, while the film- and fibre-forming properties are maintained.

The aminolysis of imides by amines has been used in several other cases. This reaction forms the basis of a process for obtaining crystalline polyamides distinguished by enhanced thermal stability resulting from the regular arrangement of amide groups[18]. The initial monomers are bissuccinimides and aliphatic or aliphatic–aromatic diamines, which are heated in a sealed ampoule at 150–200°C for 1–5 h.

2,4- and 6,4-Nylons have been obtained by the action of ethylenediamine on ethylene-*NN*′-bissuccinimide and of hexamethylenediamine on hexamethylene-*NN*′-bissuccinimide respectively in a nitrogen atmosphere in a sealed ampoule at 200°C.[19] Polyamides of high molecular weight have been obtained also[20] by the aminolysis of imides by secondary amines. Thus polyethylenesuccinamides of specific viscosity 0.28 dl $g^{-1}$, beginning to decompose at 290°C, result from the interaction of succinimides with aziridine in the melt or in solution at 170°C. The reaction was assumed[20] to involve formation of an ion-pair comprising an aziridine cation and a succinimide anion:



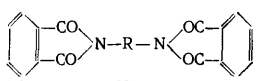
In order to combine imide and imine functional groups in the same molecule, 3-aziridin-1′-ylsuccinimide and 3,3′-diaziridinylbissuccinimides



have been prepared by the action of aziridine on maleimide and *NN*′-bismaleimides respectively. These monomers polymerise with cleavage of the imide and imine rings in the melt at 125°C to form cross-linked polymers that decompose at 300°C. Aminolysis of the imide ring has been used also to cross-link polymaleimides by treatment with aziridine or a diamine[21]. The imide ring is thus opened, and the resulting amide bonds promote formation of a three-dimensional structure in the polyamidoimide.

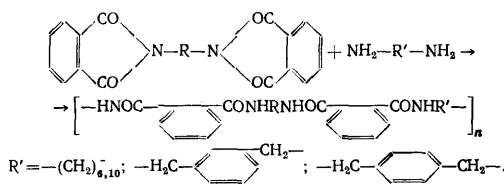
## 2. Aromatic Imides

Aromatic imides have also been used during recent years as initial monomers in the reactions of bisimides and bisamines involving cleavage of the imide ring. Investigations have been made[22–24] on the action of aliphatic and aliphatic–aromatic amines on *NN*′-disubstituted bisphthalimides



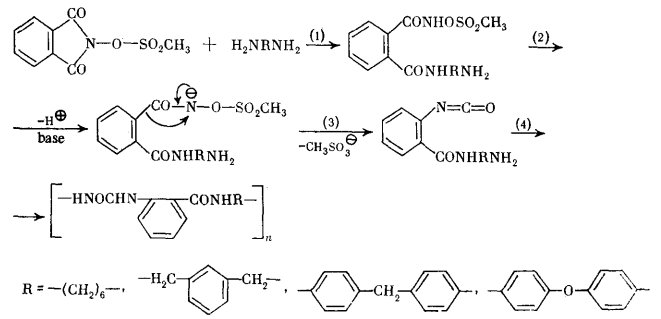
R = —$(CH_2)_n$—; —*m*-$C_6H_4$—; —*p*-$C_6H_4$—; *m*-, *p*-$(CH_2)_2C_6H_4$; *n* = 2, 4, 6.

Reaction does not take place in water or in aqueous alcohol. In dry organic solvents at 20–95°C polyamides are formed:



The yield and the viscosity of the polymers depend on the nature of the hydrocarbon substituent attached to the nitrogen, the structure of the initial bisamine, and reaction conditions. Bisimides of aromatic or aliphatic–aromatic diamines proved relatively inactive: only oligomeric amides were obtained, and in some cases formation of an amide bond was not observed at all. Alkylenebisphthalimides are considerably more reactive: they react with aliphatic bisamines under homogeneous conditions—dissolved in a mixture of chloroform and alcohol at room temperature or in dimethylformamide (DMF), at 70°C (with 30% solutions in 70 h)—to form polymers of maximum viscosity 0.18 dl $g^{-1}$ in ~40% yield. Under heterogeneous conditions—in suspension in toluene—polyamides of maximum viscosity 0.3 dl $g^{-1}$ can be obtained in ~60% yield.

The presence of strongly electron-accepting substituents attached to the imide nitrogen tends to activate phthalimides towards aminolysis[25,26]. In particular, under mild conditions *N*-methanesulphonyloxyphthalimide[25] reacts both with aliphatic and with aromatic diamines with cleavage of the ring. The reaction is assumed to involve the four stages of (1) nucleophilic attack on the carbonyl by the amine, (2) removal by a base of a proton from the *O*-sulphonylhydroxamic acid, (3) removal of a methanesulphonate anion with subsequent rearrangement, and (4) addition of an amino-group to the isocyanate:



The reaction takes place in the presence of triethylamine or pyridine in *N*-methylpyrrolidone solution at room temperature to give polyphenyleneamidoureas in high yields (94–99%) but of comparatively low viscosity (0.12–0.34 dl $g^{-1}$), which may be due to chain termination as a result of secondary intramolecular cyclisation with formation of quinazolinedione. The unsymmetrical structure of the polymer chains is responsible for the high solubility of the polyamidoureas and their relatively low softening point (143–261°C).

In contrast to *N*-substituted phthalimides, from which linear polyamides are obtained, aminolysis of the imides of aromatic tetracarboxylic acids permits the synthesis of cyclochain polymers, in particular polyimides.

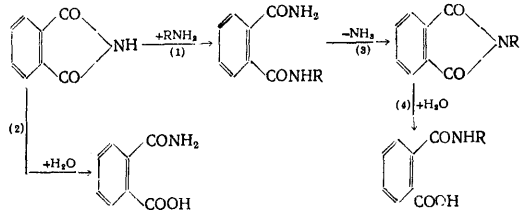
Model monofunctional compounds (phthalimide, 4-cyanophthalimide, trimellitimide, etc.) have shown[27,28] that aminolysis does not occur under mild conditions in anhydrous organic solvents (dioxan, alcohol, DMF, acetone) at 5–20°C. Yet treatment of suspensions of imides with a solution of an aliphatic or an aliphatic–aromatic amine in water or a 1 : 1 mixture of water with an organic solvent leads to rapid interaction of the initial components. The yield of solid products of aminolysis is ~90% for all the imides investigated. From the aqueous filtrate 5–10% of amido-carboxylic acids can be isolated, whose formation indicates secondary hydrolysis of the initial imide ring. Unchanged initial imide is absent from the solid products of aminolysis, the conversion products being a mono-*N*-substituted *o*-bisamide and an *N*-substituted imide. For example, interaction of phthalimide with benzylamine yields *N*-benzylphthalimide and the monobenzylated bisamide of phthalic acid, forming respectively 30 and 70 wt.% of the mixture.

From this it may be assumed that the main reaction leads to subsequent partial cyclisation of *o*-bisamide groups with evolution of ammonia and formation of imides. Indeed, if an aqueous suspension of chemically pure monobenzylphthalamide is kept at 20°C for a few hours, *N*-benzylphthalimide is obtained. Brief (30–90 min) treatment of bisamides with hot water gives the same result. Yet boiling a bisamide in such organic solvents as dioxan, benzene, and pyridine did not result in cyclisation. Nor did heating the dry bisamide at 100°C for several hours produce any chemical change. Cyclisation is observed only above 150°C.

After being heated at 170–200°C for 1 h, bisamides are converted quantitatively into *N*-substituted imides. When *o*-bisamides are boiled in water for the same time, the yield of cylised products is only 50–70% (depending on

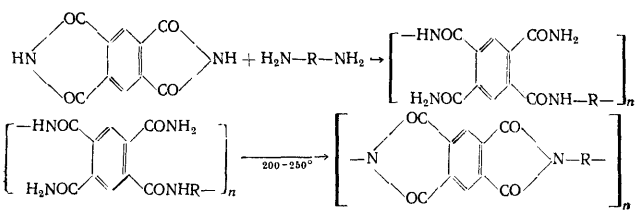
the nature of the initial bisamide). Up to 50% of ammonium *o*-amido-carboxylates, products of the hydrolysis of *N*-substituted imides, then accumulate in the aqueous filtrate[27].

Thus the reaction between an aromatic imide and an aqueous solution of an aliphatic or an aliphatic–aromatic amine can be written



The main reaction of aminolysis (1) is accompanied by slight hydrolysis of the initial imide ring (2). The *N*-substituted *o*-bisamides formed in the main reaction are partly cyclised to *N*-substituted imides (3). The ammonia thus evolved promotes partial hydrolysis of *N*-substituted imide rings to amido-acids (4). Under the given conditions the main reaction—aminolysis (1)—occurs rapidly and constitutes 90–95%, while the yield of secondary hydrolysis products in reactions (2) and (4) is small, totalling <10%. This enabled the reaction to be extended to difunctional compounds.

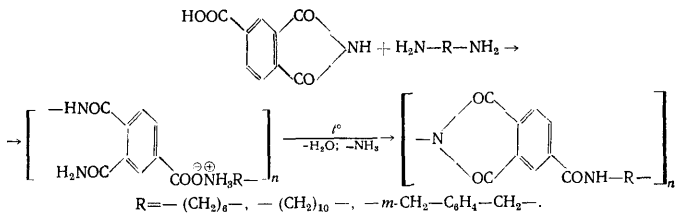
Linear polyimides are obtained[29-31] when the bisimides of pyromellitic and benzophenonetetracarboxylic acids are used as monomers with such bisamines as hexamethylenediamine, xylylenediamines, and bisaminomethylcyclohexane. The reaction takes place in two stages:



The prepolymers formed in the first stage are white powders soluble in strong mineral acids and containing polyamidoamides in the main structure. The infrared spectra of the polymers and investigations on model compounds show that the macromolecule contains also imide rings and salt groups. The first stage occurs at room temperature under heterogeneous conditions, in aqueous suspension. The reduced viscosity (measured for 0.5% solutions in concentrated sulphuric acid at 20°C) for the polyamidoamide from hexamethylenediamine and pyromellitimide was respectively 1.22, 1.08, and 0.91 dl $g^{-1}$ on preparation in water, a 1 : 1 mixture of water and DMF, and a 1 : 1 mixture of water and ethanol, and did not exceed 0.04 dl $g^{-1}$ in dry DMF, ethanol, or dioxan.

In the second stage imidisation occurs in the solid phase at 200–250°C. Cyclodeamination of polyamidoamides takes place more rapidly and at a lower temperature than cyclodehydration of the corresponding polyamido-acids. Polymers obtained from bisimides are therefore distinguished by greater completeness of cyclisation, and surpass in thermal stability polyimides based on analogous bisanhydrides[31]. The cyclised polyimides are insoluble and infusible heat-resistant dielectrics, which begin to decompose at 300–350°C.

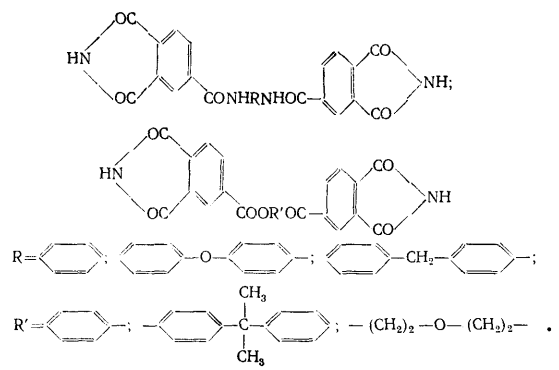
Soluble linear polyamidoimides can be obtained from trimellitimide as initial monomer treated with bisamines under analogous conditions[32]. In this case the first stage, conducted in aqueous solution at room temperature, gives oligomeric products containing amide, imide, and salt groups in the chain; in the second stage these products are heated in the melt at 200–250°C, when the salt and *o*-bisamide groups undergo polycondensation and cyclodeamination with the liberation of water an ammonia respectively to form polyamidoimides:



The resulting polymers, having $[\eta]$ = 0.40–0.75 dl $g^{-1}$, are soluble in cresol and sulphuric acid, and soften at 210–245°C.

Polymers of analogous structure with $[\eta]$ = 0.08–0.15 dl $g^{-1}$ could be obtained in a single stage by the action both of aliphatic and of aromatic bisamines (hexamethylenediamine, ethylenediamine, bis-*p*-aminophenyl ether, diphenylmethane-*pp'*-diamine) on trimellitimide in DMF, dimethylacetamide (DMA), or cresol solution at the boiling point with azeotropic removal of the water liberated[33]. The melting points of the polymers vary from 170 to 340°C depending on the structure of the initial bisamine. Thermogravimetry in a stream of nitrogen indicates that decomposition begins at ~490°C.

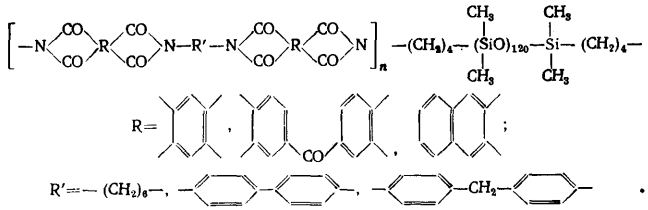
Polymers have been obtained under similar conditions from the bistrimellitimides[34]



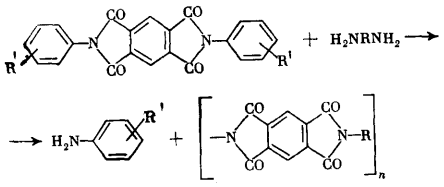
They have $[\eta] \leq 0.1$ dl $g^{-1}$, which indicates that the functional groups are relatively inactive under the given conditions. The polyetherimides, polyesterimides, and polyamidoimides formed are ordered polymers[34,35]. Regular arrangement of the structural units of macrochains ensures stronger intermolecular interaction between polar groups. This is why the ordered polymers have higher melting points and lower solubilities than similar polymers based on trimellitimide. However, ordered polymers differ little in thermal stability from unordered copolymers[35].

Block copolyimides of high molecular weight and viscosity ~1.0 dl $g^{-1}$ have been obtained[36] by the stepwise reaction of aromatic bisimides first with aliphatic or aromatic bisamines and then with polyorganosiloxanediamines. The reaction takes place in solution in hexamethylphosphoramide (HMPA) or other strongly polar solvent (tetramethylurea, dimethyl sulphoxide (DMSO), *N*-methylpyrrolidone) with the monomers held for a long time (10–20 h) first at

20 and then at 70–80°C. This involves successive addition of the amine with cleavage of the imide ring and then cyclodeamination. The products are film-forming polyimides

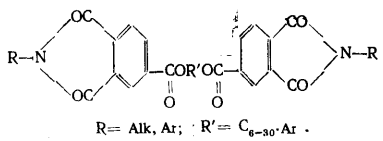


Imido–amine exchange between an *NN'*-diarylated pyromellitimide and an aromatic bisamine probably also occurs by a mechanism of successive opening and closing of the imide ring[37]. The reaction takes place in the melt at 250–300°C, with liberation of the corresponding aromatic amine and formation of an insoluble, infusible polyimide:



R= Ar R'=—$OCH_3$, —$OC_2H_5$, —OH, Hal .

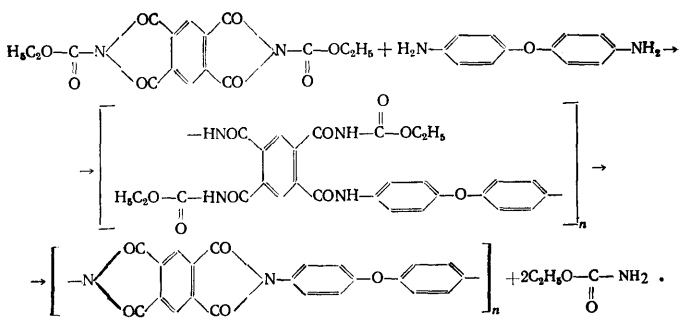
The same reaction has been applied under analogous conditions to diester–bistrimellitimides[38,39]



R= Alk, Ar; R'= $C_{6-30}$ Ar .

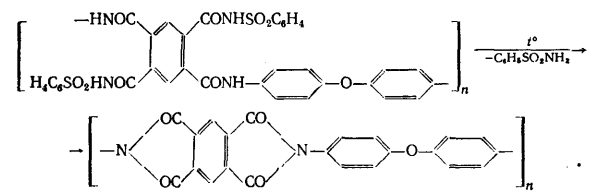
These monomers react in the melt with aliphatic, aromatic, or siloxane diamines to form soluble, fusible linear polyesterimides. The use of metals of Groups I and II–Vb or their oxides, hydroxides, imides, or salts as catalysts in this reaction enables polymers of higher molecular weight to be obtained.

The introduction of strongly electron-accepting substituents into the imide group enables the reaction to be conducted under milder conditions with formation of an easily processable and readily soluble polyamide as prepolymer. Such *N*-substituted bisimides include diethyl pyromellitimide-*NN'*-dicarboxylate[40–42], which has been subjected to two-stage polycondensation with diamines:

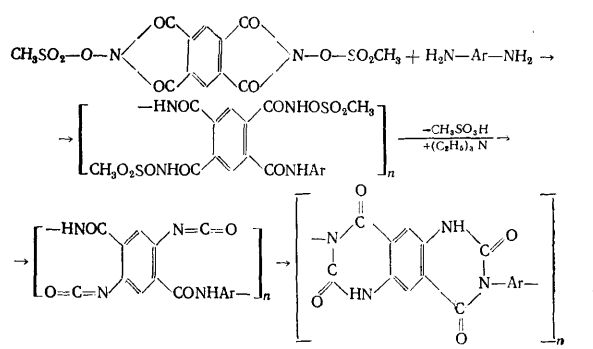


The reaction was conducted in *N*-methylpyrrolidone solution at room temperature. The suspension became homogeneous after being stirred for 1 h, but the viscosity continued to increase for 5 days, reaching 0.9 dl $g^{-1}$. A strong, flexible film was cast from the resulting polyamide solution, and was heated in a vacuum above 240°C for 5 h to form a polyimide.

A more vigorous reaction takes place between *NN'*-diphenylsulphonylpyromellitimide and bis-*p*-aminophenyl ether[43]. In solution at room temperature a polyamide of reduced viscosity up to 0.9 dl $g^{-1}$ is formed within 30–60 min. A solution of a polymer (in contrast to solutions of polyamido-acids) has a stable viscosity, but even at 20°C such a polyamide gradually cyclises in solution, a process considerably accelerated by the presence of water. Complete conversion into the polyimide occurs when the polyamide films are heated at 160°C for 10 min. Cyclisation is accompanied by the separation of benzenesulphonamide as a by-product:



An analogous reaction between *NN'*-dimethanesulphonyloxypyromellitimide and aromatic bisamines yields new polymers, containing quinazolinedione rings in the chain[44]:



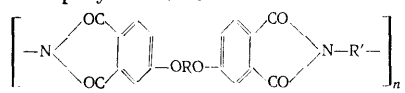
The reaction is conducted in *N*-methylpyrrolidone solution at room temperature in the presence of tertiary amines, which promote formation of the polyamidoisocyanate and subsequent isomerisation cyclisation. The polymers are obtained in theoretical yield with a specific viscosity of 0.25 dl $g^{-1}$. The comparatively low viscosity is due to separation of the polymer from the solution at an early stage. The resulting polypyrimidoquinazolinetetraones are soluble only in strong mineral acids, and are stable up to 400°C.

The above examples show that cyclic imides of aliphatic, unsaturated, and aromatic carboxylic acids are able to undergo ring cleavage on reaction with diamines. The activity of the monomers in this reaction is determined by their chemical structure and by the reaction conditions. With strongly basic aliphatic amines reaction takes place even at room temperature, when a necessary condition is often the presence of water, which probably activates both monomers. Linear polyamides are then formed from imides of aliphatic and unsaturated acids. Imides of aromatic tetracarboxylic acids yield polyamides containing *ortho* to the amide bond primary or secondary amide groups capable of cyclisation with the separation of a by-product of low molecular weight and the formation of linear polyimides. Under more severe conditions reaction takes place also with the less basic aromatic diamines, when a polyimide is obtained without separation of the prepolymer.

## III. POLYCONDENSATION WITHOUT CLEAVAGE OF THE IMIDE RING

Recently cyclic imides of carboxylic acids have begun to be used also in polycondensations. Aromatic bisimides containing hydroxyl, carboxyl, and chlorocarbonyl as reactive functional groups are often employed as monomers in polyamidation and polyesterification with bisamines, bisisocyanates, and phenolic diols. Sometimes different types of functional groups are combined in the same molecule, and homopolycondensation is effected. These reactions enable us to obtain in a single stage polyimides containing also other hetero-bonds (amide, ester, etc.), in which unstable uncyclised *o*-amido-acid units are absent. The present Review omits many examples of such reactions reported for various imides of tri- and tetra-carboxylic acids, which have been discussed previously[3], and dwells only on comparatively unknown reactions.

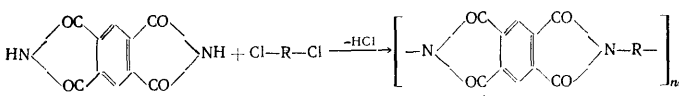
As already remarked, until not long ago imides of *o*-dicarboxylic acids were not used for the preparation of polymers. Several recent patents reveal the possibility of applying polycondensation to such monomers in order to synthesise the polyetherimides

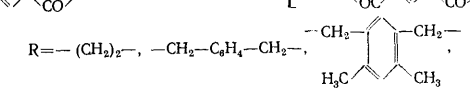


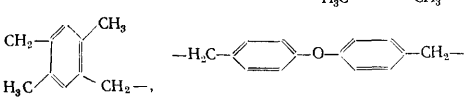
R = Arylene; R′ = Arylene, Alkylene .

Bisnitrophthalimides are condensed with alkali-metal derivatives of dihydric phenols[45,46] or metal salts of aromatic dicarboxylic acids[47]. The reaction takes place in solution in DMF at 50 °C. Bischlorophthalimides[48], bisfluorophthalimides[49], and bischloronaphthalimides[50] react similarly with alkali-metal bisphenoxides in polar solvents or their mixtures with aromatic hydrocarbons at high temperatures.

Polycondensation is applied also to unsubstituted imides of aromatic tetracarboxylic acids. Nishizaki and Fukami[51,52] were the first to suggest condensing the di-imide of pyromellitic acid with dihalides by Gabriel's reaction as a new method of synthesising polyimides:

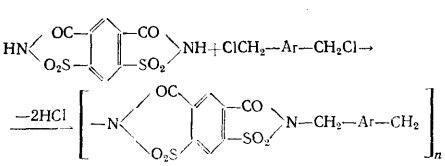


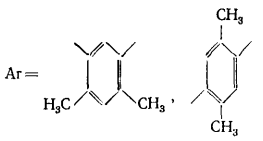




Reaction occurs in the presence of basic catalysts in solution at 70 °C to give a 50–80% yield of the polymer.

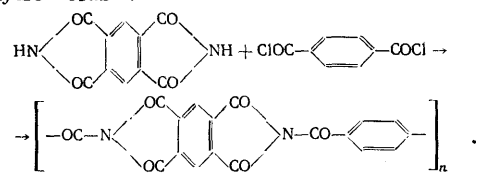
An analogous reaction has recently been reported between aromatic bischloromethyl derivatives and the bisimide of 4,6-disulphoisophthalic acid[53,54]:





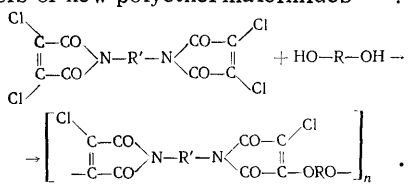
Polar amide solvents were used at the boiling point. Soluble polyimides having a specific viscosity of 0.2 dl $g^{-1}$ were obtained after 5 h.

Imides of aromatic and alicyclic acids are capable also of polycondensation with chlorides of aliphatic and aromatic dicarboxylic acids[55]:

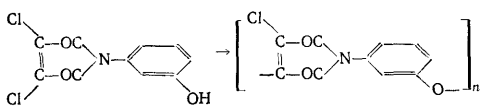


Reaction takes place in the presence of a catalyst—triethylamine, pyridine, aniline, copperII chloride, cobalt naphthenate, an organic compound of tin, or an alkali-metal salt of an organic or an inorganic acid—in solution at 80–200 °C. The yield of polyimides exceeds 90%, and their specific viscosity 0.9 dl $g^{-1}$ (for a 0.5% solution in concentrated sulphuric acid). The thermal stability of the polymers is above 350 °C.

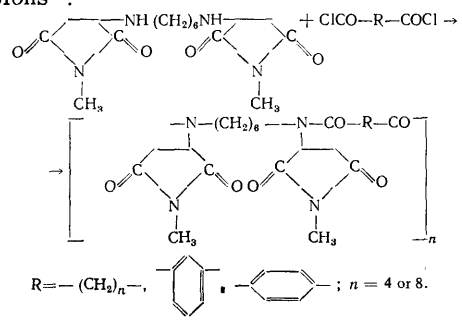
Imides of unsaturated and aliphatic acids undergo polycondensation by means of various functional substituents attached to carbon atoms. Thus the reaction of *N*-aryl-3,4-dichloromaleimides with phenols forms the basis of the synthesis of new polyethermaleimides[56,57]:



Use as initial monomers of 2,2-diphenylpropane-*pp*′-diol and a bisdichloromaleimide together with diphenylmethane-*pp*′-diamine gave a high yield of a polymer having specific viscosity 0.47 dl $g^{-1}$, capable of forming strong elastic films stable in nitrogen and in air at temperatures above 300 °C. The 3,4-dichloro-*N*-*m*-hydroxyphenylmaleimide synthesised was capable of homopolycondensation:



Bisimides of aspartic[58] and citraconic[59] acids can be used as bisamine components in polycondensation with chlorides of dicarboxylic acids. Good yields are obtained of polyamides in which all hydrogen atoms in the amino-group are replaced by imide rings capable of various conversions[60]:



R = $-(CH_2)_n-$, , ; $n$ = 4 or 8.

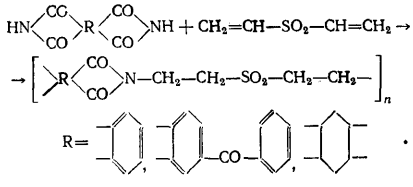
Complete aminolysis of imido-groups can be achieved by methylamine or they can be hydrolysed with alkali[60]. The main chain of the macromolecule does not break down, and new water-soluble polymers are formed.

## IV. MIGRATION COPOLYMERISATION INVOLVING THE IMIDE RING

Since the nitrogen atom in an imide of a di- or tetracarboxylic acid is adjacent to two strongly electron-accepting carbonyl groups, the proton attached to the nitrogen atom is mobile. This enables unsubstituted amides to undergo proton-transfer reactions, so that migration copolymerisation can occur without cleavage of the imide ring.

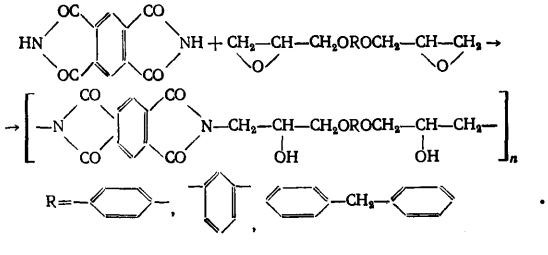
Among such reactions are the migration copolymerisation of unsubstituted bisimides of aromatic[61] and alicyclic[62] acids with dienes containing two active double bonds. Examples of such dienes that are used may contain $\alpha$ to a double bond a carbonyl group or an aromatic ring capable of activating it (e.g. divinylbenzene, diacrylates, vinyl esters of dicarboxylic acids, etc.). Reaction takes place in any suitable solvent at 80–120°C in the presence of a basic catalyst—an alkali or an alkaline-earth metal or its alkoxide, or a Grignard reagent—the quantity of which may vary from 0.0001 to 0.5 equiv. Polymers of high melting point, having specific viscosities of 0.35–0.65 dl $g^{-1}$, are formed in ~80% yield.

Russo and Mortillaro[63] suggested the use of divinyl sulphone as copolymerising diene:



The reaction is conducted in the presence of sodium t-butoxide in DMSO, DMF, or pyridine solution at 100°C. Infusible crystalline polymers of viscosity 0.09–0.23 dl $g^{-1}$, soluble only in concentrated sulphuric acid (in the case of aromatic imides) or in amide solvents (in the case of alicyclic imides), are formed in 50–80% yield. Their thermal stability is ~300°C independently of the structure of the monomer unit.

Linear polyimides containing hydroxyl groups have been obtained[64,65] from bisimides of aromatic tetracarboxylic acids and such diepoxides as the diglycidyl ethers of aromatic diols:



Reaction occurs in the presence of a tertiary amine or a quaternary ammonium salt as catalyst in solution at a high temperature. The yield of the resulting hydroxylated polyimides is 60–86%, with a specific viscosity of 0.1–0.34 dl $g^{-1}$. The polymers melt at 140–280°C, and vigorous decomposition begins at 300–400°C.

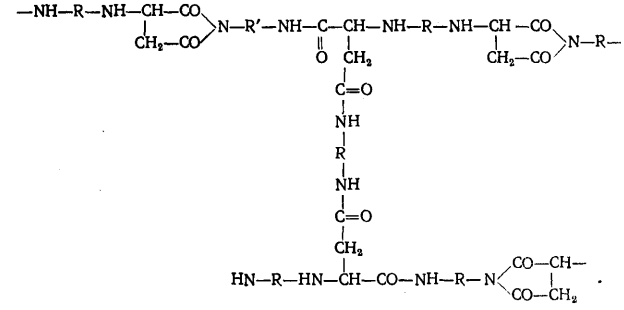
Bisimides of alicyclic tetracarboxylic acids react similarly with aliphatic and alicyclic diglycidyl ethers[66]. This gives oligomers having terminal epoxide groups, which are then hardened with anhydrides of dicarboxylic acids. In the presence of a highly effective catalyst—a chromium tricarboxylate—bisimides of aromatic or alicyclic acids may react also with epoxy-resins to form cross-linked polyimides[67].

## V. REACTIONS AT THE DOUBLE BOND IN UNSATURATED IMIDES

As already mentioned, two reactive centres—an imide ring and a double bond—are present in mono- and bisimides of unsaturated dicarboxylic acids. The double bond enables such monomers to undergo several reactions characteristic of alkenes. Disregarding vinyl polymerisation with opening of the double bond by a radical mechanism (since the literature on this topic is vast and requires separate discussion), we shall consider only certain transformations of the double bond of unsaturated imides in migration copolymerisation with nucleophilic compounds and in the Diels–Alder reaction.

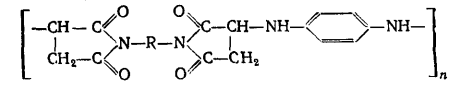
### 1. Migration Copolymerisation with Amines

In the migration copolymerisation of unsaturated imides with bisamines the chain grows by migration of hydrogen of the imide group to the double bond with the formation of secondary amine units. Polymers were first obtained in this way by Sheremet'eva[14]. When ethylene- and hexamethylene-bismaleimides are treated with such bisamines as phenylenediamine, hexamethylenediamine, ethylenediamine, and piperazine in aqueous alcohol, both reactive centres in the bisimide are involved, and a rubberlike cross-linked polymer is formed, containing imide rings and aspartamide segments in the chain

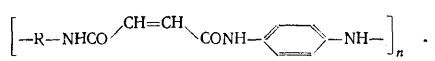


When carefully dried reagents are used in anhydrous organic solvents, the imide ring is preserved and only the double bond is involved. The linear polyaminoimides formed are soluble in several solvents, and have intrinsic viscosities of 0.05–0.18 dl $g^{-1}$. The molecular weight determined from the terminal amino-groups is 2000–9000.

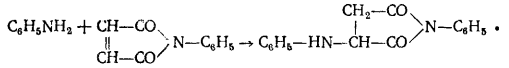
Reaction between dimaleimides and aromatic or aliphatic–aromatic diamines in the melt at 80–200°C yields[68] linear polyimides soluble in concentrated sulphuric acid and HMPA, resistant to abrupt changes in temperature, and beginning to decompose at 400°C. Such polymers comprise 85% of polyaminoimide units



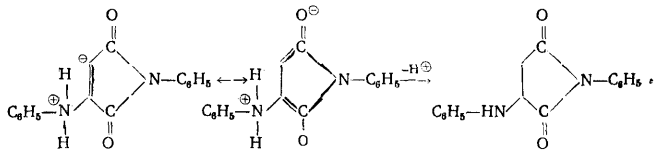
and 15% of units of structure



Study of the migration copolymerisation of bisimides of unsaturated acids with bisamines was then developed[69,70] by examining as model reaction the action of aniline on *N*-phenylmaleimide

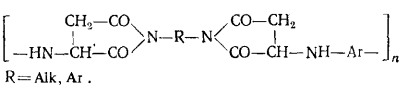


Since the reaction velocity depends on the polarity of the medium, it was supposed[69,70] that the mechanism involved a charged intermediate product stabilised by the medium:



This mechanism suggests the possibility of acid and base catalysis. Indeed, weak protic acids (acetic, propionic, formic, maleic) exhibit a considerable catalytic effect.

Extension of this reaction to difunctional compounds—bismaleimides and aromatic diamines—yields the polyimides

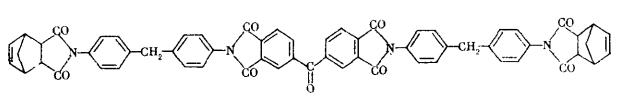


R = Alk, Ar.

Conducting the reaction in the presence of a catalyst—acetic acid—in cresol solution at 100–110°C for 3 days gives polyaspartimides as amorphous compounds softening at 210–300°C (depending on the chemical structure of the initial monomers) and having high melting points[70]. They are soluble in phenolic and amide solvents, their viscosity being $[\eta] = 0.25–0.6$ dl g$^{-1}$.

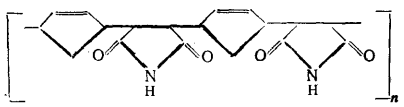
Migration polymerisation can be accomplished also in other phenolic solvents[71], benzonitrile, DMF, DMSO, nitrobenzene[72], and various phosphorus-containing compounds[73]. The use has been suggested also of such carboxylic acids as acetic, propionic, trifluoroacetic, formic, etc., which act as both solvent and catalyst[74]. Mineral acids and certain complex compounds may be used as catalysts[75].

Linear polyaminoimides obtained by the migration polymerisation of bisimides with bisamines can be hardened by heat, forming insoluble, infusible polymers of good heat and chemical resistance. The mechanism of thermosetting is not clear, but the presence of terminal amino-groups and double bonds, together with reactive secondary amino-groups and imide rings in the main chain, promotes various reactions—polymerisation, migration copolymerisation at the imide ring or the double bond, as well as other processes governed by the chemical nature of the macromolecular chain—leading initially to branching and then to cross-linking. For example, the oligomeric prepolymer[76]



containining tetrahydro*endo*methylenephthalimide fragments as end-groups, is cross-linked on heat treatment at 260–300°C, without the evolution of volatile components.

It is assumed that pyrolytic polymerisation takes place by a mechanism opposite to the Diels–Alder reaction, and the final polymer contains the units



Polyaminoimide prepolymers are most often set in the melt at 200–250°C, either in the presence or in the absence of radical or ionic catalysts. Any mono-or poly-functional compounds that react with the resin can be used in the hardening process. Thus 5—95 wt.% of the corresponding monoimides can be introduced[77,78] during setting into oligomeric prepolymers obtained from bisamines with bismaleimides, bistetrahydrophthalimides, or bistetrahydro*endo*methylenephthalimides, their addition lowering significantly the price of the required thermostable polymer. Alkene hydrocarbons or unsaturated ethers[79–81], condensation polyesters containing double bonds[82], epoxides[83], and epoxy-resins[84,85] have also been suggested as copolymerising and cross-linking additives.

The two-stage method, in which a soluble, fusible polyaminoimide obtained in the first stage is subsequently hardened, has proved extremely fruitful, and has led to the appearance of numerous patents claiming either modification of this method or new compositions that can be used as varnishes, glues, laminated materials, moulded articles, etc.[86–90] Thus products of the reaction of bismaleimides, biscitraconimides, bistetrahydrophthalimides, or bisitaconimides with di-, tri-, or tetra-amines (heated to 50–180°C in the absence of a solvent or in a polar solvent) have been proposed[91] for obtaining thixotropic aqueous suspensions of prepolymers. The resulting polymer is suspended in water and used as a paste for various purposes. After additional heat-treatment (at 250°C for 24 h) a glassfibre-reinforced plastic in which the binder is a similar composition based on diphenylmethane-*pp'*-bismaleimide and diphenylmethane-*pp'*-diamine withstands being heated at 250°C for 1000 h, with only a slight decrease in bending strength.

Prepolymers formed similarly by the migration copolymerisation of bismaleimides with bisamines in polar organic solvents can be modified, without isolation from the solutions, by the addition of anhydrides of polycarboxylic acids[92]. Some of the secondary amino-groups of the main polymer chain react, and carboxy-groups are introduced into the side-chain of the polymer. These ensure that the prepolymer becomes soluble in water on addition of a base. Such solutions have been proposed for electrodeposition on metal surfaces. The transparent protective coatings formed after further hardening at a high temperature are strong and chemically resistant.

Not only individual diamines but also oligomeric or polymeric bisamines[93,94], monoamines[95], and even ammonia[96] can be used in migration copolymerisation. The comonomers may be oligoimides[96–98] as well as bisimides. The migration copolymerisation of bisimides with bisamines and hardening are often combined into a single stage. Polymers are thus formed from mixtures of the initial monomers when heated in the melt[99–102]. To facilitate processing and lower the melting point phosphoric esters are sometimes added to the mixture[99,103]. The addition of polymerisation initiators such as dicumenyl peroxide, etc. accelerates cross-linking and lowers the setting temperature.

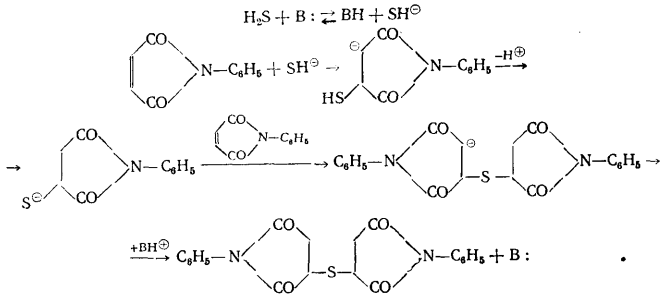
It must be noted in conclusion that the manufacture of polyaminoimides from bismaleimides and aromatic bisamines has now been established in several countries. On several criteria, including heat resistance, these polymers are little inferior to aromatic polyimides from tetracarboxylic bisanhydrides and bisamines. Yet the technology of their production and processing has several important advantages: as the prepolymers they are stable, and are easily processed by the same technology as for the usual thermosetting plastics; and the shape of articles on hardening is fixed without the evolution of volatile components[104,105].

Such a resin is manufactured in France under the trade name Kerimid. Moulding materials such as Kinnel based on it, reinforced with glass fibres, are distinguished by their heat and flame resistance, with great stability towards the action of solvents. They are intended for use in aircraft construction, electronics, and the electronic industry[106-108]. Casting and moulding compositions of self-lubricating type are manufactured, filled with powdered tetrafluoroethylene, molybdenum sulphide, graphite, or carbon fibres. Such compositions possess not only great heat resistance but also low surface friction with insignificant abrasion. At high temperatures these materials surpass steel, light alloys, and titanium in their strength characteristics.

## 2. Migration Copolymerisation with Other Nucleophiles

Nitrogen-containing compounds other than amines are also used in migration copolymerisation with unsaturated imides, e.g. urea[109], hydrazines[110], dihydrazides[111], bisaldoximes[112-114], and bisimidic esters[115]. Various sulphur-containing compounds—hydrogen sulphide[116], dithiols[117,118], disulphinic acids[119]—are also employed.

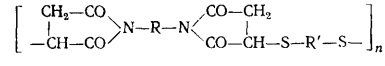
Crivello[120] was the first to examine as model reaction the action of hydrogen sulphide on *N*-phenylmaleimide in various solvents, and found the reaction to be instantaneous in solvents of basic character (DMF, DMA, pyridine). If neutral or weakly acid solvents are sued, small quantities of a tertiary amine or other base (B:) must be present as catalyst. Hence it may be concluded that the primary attack on the double bond in the maleimide is initiated by the highly nucleophilic hydrogen sulphide anion, and the mechanism of the reaction can be written



The attempt to extend this reaction to difunctional compounds has been unsuccessful: the action of hydrogen sulphide and dithiols on bisdimaleimides in polar organic solvents at room temperature produces rapid gelation. The anionic polymerisation of bisimides initiated by thiolate ions is regarded as a competing reaction leading to cross-linking. However, this side reaction could be effectively suppressed by conducting polymerisation in weakly acid media or by adding to the reaction mixture small quantities (0.5–10%) of protonating agents such as inorganic acids (sulphuric, phosphoric), carboxylic acids (acetic, formic, benzoic), phenols, or various acid salts[116]. Catalytic quantities (0.01–0.001 wt.%) of such tertiary amines as tetramethylethylenediamine, tributylamine, etc. can be used to accelerate the reaction[118].

The reaction can be conducted in the usual organic solvents, in compounds of amide type, and also in aqueous emulsion. In the last case acid and neutral alkali-metal salts are used as catalysts. The most successful media were phenol and cresol, which acted both as solvents and as protonating agents. Thus the action of hydrogen sulphide under these conditions on bismaleimides[120] or oligomeric aminoimides containing two terminal double bonds[121] will give good yields of macromolecular polyimidosulphides, clear fibrous polymers having $[\eta] = 0.1-0.63$ dl $g^{-1}$, soluble only in highly polar liquids (DMSO, DMA, hexafluoroacetone hydrate) and resistant to the usual organic solvents. They melt at comparatively high temperatures (260–300°C) and are stable up to 325°C.

Replacement of hydrogen sulphide by a dithiol will yield polyimidosulphides having the structure



in which R and R′ are different bivalent organic radicals of aliphatic, aromatic, or heterocyclic type. The properties of the polymers depend on the structure of the main chain. Thus lengthening the segments between two sulphur atoms results in lower melting points and greater solubility of the polymers in the usual organic solvents.

Block copolymers containing polyimidosulphide and polysulphide units can be obtained by using oligomeric polysulphides of molecular weight 2000–8000 as second components in migration copolymerisation with bismaleimides[122,123]. The reaction is conducted in the presence of tetramethylethylenediamine in cresol or its mixture with dichloromethane at 40°C. Polymers containing ≥70% of polysulphides are thermoplastic elastomers; with lower contents of polysulphides they can be regarded as thermoplasts modified with rubbers. The strength properties of the block copolymers deteriorate with increase in the quantity of the polysulphide component, but are little affected by its molecular mass or the nature of the polyimidosulphide block. The thermal stability of the copolymers is determined by that of the polysulphide blocks.

Linear polyimidosulphides obtained by the migration copolymerisation of unsaturated bisimides with sulphur-containing monomers are hardened at 150–300°C either purely thermally or in the presence of organic peroxides.

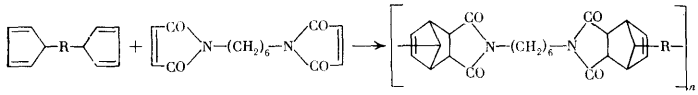
Polyimidosulphides, which are characterised by high mechanical strength and heat resistance, are recommended for the production of electrically insulating films and coatings, moulded goods, packing materials, and gas-separating membranes[117,119,124].

## 3. Cycloaddition

Reactions involving cycloaddition provide another promising and growing method for using unsaturated bisimides to obtain polyimides of various structures. The literature on this topic up to 1965 was presented in review papers[125,126] and in Korshak's monograph[127]. Therefore we shall discuss in some detail only results that have appeared during recent years.

Bismaleimides are successfully used in photochemical homopolymerisation processes involving 2 + 2 cycloaddition, which yields polyimides containing alicyclic units in the chain[128,129], and also as dienophiles in copolymerisation with dienes involving thermal Diels–Alder 4 + 2 polyaddition. The latter type of reaction permits wider variation in the chemical composition and the properties of the polymers, since both cyclic and open-chain dienes can be used. Cyclopentadiene derivatives have been investigated in the greatest detail among diverse diene components. The copolymer of *m*-phenylene-*NN'*-bismaleimide with *p*-xylylenedi-5-cyclopentadiene was first mentioned by Upsom[130], who obtained an insoluble product from the reaction in the mass. Its composition and its insolubility suggest a cross-linked copolymer containing mainly units formed by vinyl polymerisation of the bismaleimide.

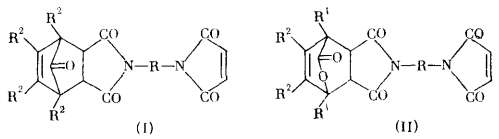
Further investigation showed[131] that Diels–Alder polyaddition uncomplicated by 1,2-polymerisation takes place in benzene and DMF solution with the formation of 1 : 1 copolymers:



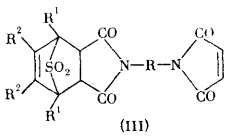
R = $-(CH_2)_6-$, $-(CH_2)_9-$, $-H_2C-C_6H_4-CH_2-$ .

The resulting polyimides probably have relatively low molecular weights, since $[\eta] = 0.1-0.22$ dl $g^{-1}$, they soften at 110–240 °C, and they dissolve in organic solvents. Raising the temperature of the reaction medium leads to the formation of polymers of lower viscosity, which indicates occurrence of the reverse Diels–Alder reaction.

Polyimides of far higher molecular mass were obtained by Kraiman[132,133] and by Chow[134,135], using as monomers adducts of bismaleimides with cyclopentadienone (I), 2-pyrone (II), and thiophen dioxide (III)

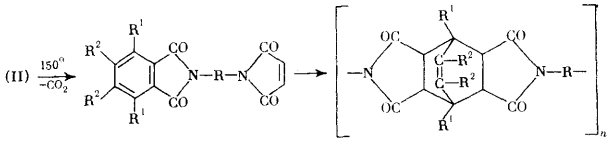


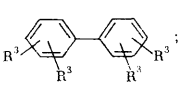
(I) (II)



(III)

Such adducts contain both dienophile and diene reaction centres, but the latter is in an inactive, "protected" state. With rise in temperature either carbon dioxide or sulphur dioxide is evolved from the adducts (I)–(III), and the liberated diene bonds copolymerise rapidly with the dienophile end of the monomer to form a polyimide:



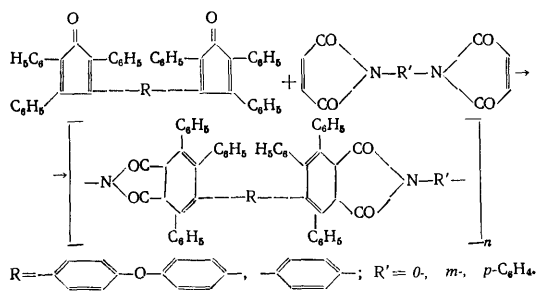
R = $-(CH_2)_n-$, *m*-, *p*-$C_6H_4-$, ;

$R^1$ = H, Alk; $R^2$ = H, Alk, Ar; $R^3$ = H, $CH_3$ .

The reaction is conducted in a solvent of high boiling point (bromobenzene, a halogenated aliphatic hydrocarbon, 1-chloronaphthalene)[132–135], when macromolecular polyimides having $[\eta] = 2.0$ dl $g^{-1}$ can be obtained in times varying from 20 min to several days depending on the temperature. Under these conditions the Diels–Alder reaction is not complicated by the secondary vinyl-type polymerisation characteristic of free cyclopentadiene.

Polymers which either melt at low temperatures or soften at high temperatures are obtained depending on the nature of the substituent R in the di-imide. The nature of the substituents $R^1$ and $R^2$ in the diene monomer has little influence on the physical properties of the polyimides. The solubility, the high heat resistance, the strength, and the good film-forming and dielectric properties enable the resulting polymers to be used as high-temperature insulating films, fibres, and thermostable and chemically resistant plastics.

Interesting polyimides, capable of aromatisation, have been obtained from bismaleimides with phenylated derivatives of cyclopentadienone. Model monofunctional compounds[136,137] and monomers[138] have shown that the reaction conforms to the scheme

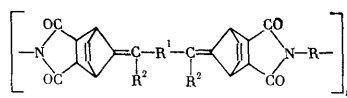


R = ; R' = *o*-, *m*-, *p*-$C_6H_4$.

Polydihydrophthalimides are formed in theoretical yield: The reaction is conducted in boiling chloronaphthalene or trichlorobenzene solution to give maximum viscosities $[\eta] = 0.3-1.0$ dl $g^{-1}$ for various polymers after 1–3 and 18–24 h respectively. The polymers are stable in air up to 300 °C. They are dehydrogenated to the corresponding aromatic polyimides by the action of bromine or by heating in nitrobenzene solution. Under these conditions, however, the degree of conversion is probably not very high, since the temperature at which decomposition of the polymer begins has changed little after modification.

Quantitative aromatisation could be accomplished[136,137] by heating a carefully ground specimen of the polymer *in vacuo* at 350 °C, when some decrease in viscosity was observed. The resulting polyimides do not lose weight in air up to 530 °C: i.e. they are comparable in thermal stability with polyimides based on pyromellitic bisanhydride and aromatic bisamines. In contrast to the latter, however, they dissolve in several organic solvents.

Cyclicdienes other than cyclopentadiene derivatives are also used as monomers copolymerising with bisimides by the Diels–Alder reaction. Thus polyimides of high molecular weight

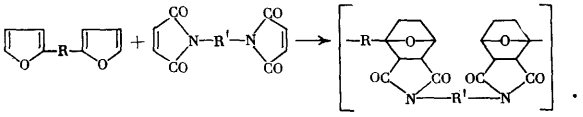


R = $-(CH_2)_n-$ ($n = 2, 3, 6$);

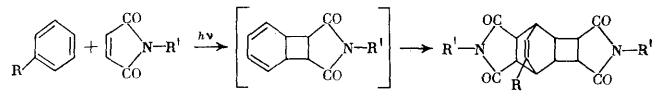
*p*- or *m*- $C_6H_4$, *p*-$C_6H_4 \cdot C_6H_4$, *m*-$CH_2-C_6H_4-CH_2$;

$R^1$ = Ar; $R^2$ = Alk, cycloAlk, Ar

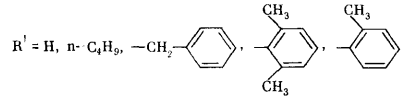
have been obtained[139] by copolymerisation with difulvenes in chloroform, DMF, or *N*-methylpyrrolidone solution at 60–70 °C. Berlin et al.[140,141] showed the possibility of using ωω′-difuran derivatives as dienes:



For a long time aromatic compounds were not used as diene components, since it was considered that they were incapable of Diels–Alder condensation. However, later investigations have shown that maleimide and certain of its *N*-substituted derivatives, on exposure to ultraviolet radiation in the presence of a sensitiser, add to benzene and its homologues to form 2:1 adducts[142–145]. It is supposed that an intermediate equimolecular adduct formed by photoinitiated 1 + 2 cycloaddition is then involved in Diels–Alder 1 + 4 cycloaddition:

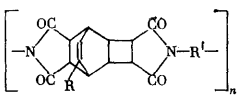


R = H, $C_nH_{2n+1}$ ($n$ = 1, 2, 10–13);



This reaction has recently been extended to bismaleimides to give corresponding macromolecular polyimides. Such polymerisation was first achieved by Stevens and Musa[146,147]. When solutions of various bismaleimides in a mixture of benzene and acetone are exposed in the presence of acetophenone to ultraviolet radiation for 18 h, the polyimides listed in Table 1 are obtained. The yield of polymer obviously depends significantly on the nature of the substituent R in the bisimide: thus the yield is 70–95% in the case of alkylenebismaleimides. The highest yield is observed with R = $[CH_2]_2$. Increasing the number of methylene units in the maleimide bridge lowers the yield, which may be due to intramolecular polymerisation of the double bonds and formation of cyclic bisimides of low molecular weight. If R = $C_6H_4$, which may be *meta*- or *para*-substituted, the yield of polymer falls to 15–30%. In such molecules the phenyl rings are probably coplanar with the maleimide rings, and this favours the appearance of low excited states which quench the photoexcitation of maleimide. Introduction of an *ortho*-substituent prevents coplanarity, and the yield of polymer then increases to 65–80%. All the polymers obtained begin to decompose at 360 °C. Since change in the chemical structure has hardly any effect on the temperature at which decomposition begins, it is assumed[147] that degradation of the polymer chains begins with thermal decyclisation by a reverse Diels–Alder reaction.

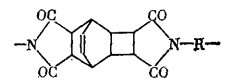
The reaction can be applied also to various homologues of benzene. Thus the use of various alkylbenzenes as comonomers[148] yields polymers of probable structure



R = $CH_3$–, $C_2H_5$–, $(CH_3)_2CH$–, $(CH_3)_3C$–;
R′ = Alkylene, Arylene.

This view is based on analogy with the condensation of maleic anhydride with monosubstituted benzenes, in which cycloaddition takes place at the bond most remote from the substituent[149,150]. However, some results[151] indicate that the site of cycloaddition depends on the reaction temperature, and mixtures of isomers—or heterounit coplymers—may be obtained.

**Table 1.** Polyimides of general formula obtained by the polyaddition of bismaleimides to benzene[147].



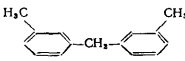
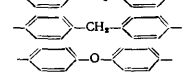
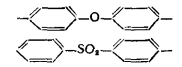
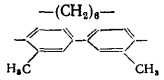
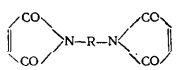
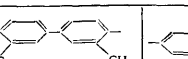
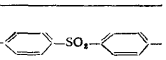
| R | Yield, % | R | Yield, % |
|---|---|---|---|
| $-(CH_2)_2-$ | 95 |  | 80 |
| $-(CH_2)_3-$ | 80 |  | 15 |
| $-(CH_2)_6-$ | 70 |  | 30 |
|  | 65 |  | 85 |

**Table 2.** Polyimides obtained by the photoaddition of alkylbenzenes to bismaleimides[146].



| Alkylbenzene | R: $-(CH_2)_6-$ | | R:  | | R:  | |
|---|---|---|---|---|---|---|
| | yield, % | $t_{soft}$*, °C | yield, % | $t_{soft}$*, °C | yield, % | $t_{soft}$*, °C |
| Benzene | 70 | 410 | 65 | 485 | 85 | 450 |
| Toluene | 40 | 380 | 45 | 390 | 89 | 400 |
| Ethylbenzene | 23 | 390 | 0 | — | 50 | 350 |
| Cumene | 28 | 390 | 0 | — | 60 | 420 |
| t-Butylbenzene | 34 | 425 | 44 | 370 | 85 | 400 |

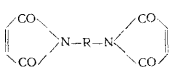
*$t_{soft}$ = temperature at which softening begins.

Table 2 gives the yield and the thermal stability of polymers obtained after the optimum time of exposure, which varied from 5 to 40 h for different imides[148]. The yield decreases significantly on passing from benzene to alkylbenzenes. On the basis of the inductive effect the reactivity should increase in the sequence—methyl < ethyl < isopropyl < *t*-butyl—but the steric effect would diminish the reactivity in the same sequence. The net effect determines the polymer yield for different hydrocarbons. The terminal members of the sequence show the same net effect of the opposing factors, so that the yields are similar. The absence of a polymer in the reaction of ethylbenzene and cumene with 3,3′-dimethylbiphenylbismaleimide may be due to greater steric hindrance caused by the *o*-methyl groups. The higher yield with the bismaleimide containing a sulphonyl group is probably due to the fortunate combination of the electron-donating power of the alkyl groups with the strong electron-accepting influence of the sulphonyl group. All

the polymers obtained are either only partly soluble or completely insoluble in organic solvents and trifluoroacetic acid.

Soluble polyimides or analogous structure can be obtained in high yields from the reaction of bismaleimides with several benzene derivatives in the presence of acetophenone in solution in excess of the aromatic hydrocarbon or in a mixture of the latter with chloroform or alcohol during ultraviolet irradiation for 18–20 h.[152–154] The yield and the viscosity of the resulting polymers depend significantly on the nature and the concentration of the monomers, the temperature, the duration of exposure, and other factors[154–156]. Table 3 shows that hexamethylene-*NN'*-bismaleimide is the most active among the bisdienophiles investigated. The reactivity of the bismaleimide decreases sharply when the aliphatic is replaced by an aromatic bridge. A possible reason is diminished conjugation of the carbonyl group with the double bond. The comparatively low viscosity of the polyimides is probably due to precipitation of the polymers because of poor solubility in the reaction medium and to cessation of chain growth at low degrees of polymerisation.

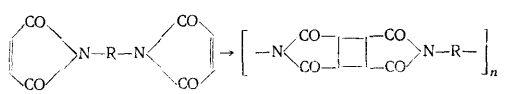
Table 3. Polyimides from aromatic derivatives and bismaleimides[152–154].



| Aromatic diene | R = $-(CH_2)_2-$ | | R = $-(CH_2)_6-$ | | R = $-(CH_2)_{10}-$ | | R =  | |
|---|---|---|---|---|---|---|---|---|
| | yield, % | $\eta_{sp}$, dl g$^{-1}$ | yield, % | $\eta_{sp}$, dl g$^{-1}$ | yield, % | $\eta_{sp}$, dl g$^{-1}$ | yield, % | $\eta_{sp}$, dl g$^{-1}$ |
| Benzene | 73 | 0.13 | 56 | 0.44 | 30 | 0.14 | 7 | 0.06 |
| Toluene | 55 | 0.12 | 73 | 0.55 | — | — | 8 | 0.03 |
| *o*-Xylene | 51 | 0.09 | 71 | 0.14 | — | — | 18 | 0.11 |
| *m*-Xylene | 68 | 0.07 | — | — | — | — | — | — |
| *p*-Xylene | — | — | 61 | 0.30 | — | — | — | — |
| Ethylbenzene | 60 | 0.12 | 80 | 0.10 | 45 | — | 10 | 0.07 |
| Cumene | 45 | 0.10 | 67 | 0.09 | 15 | 0.20 | 5 | 0.09 |
| Chlorobenzene | 19 | 0.02 | 20 | 0.04 | — | — | 7 | 0.03 |
| Diphenyl ether | 35 | 0.02 | 40 | 0.03 | — | — | — | — |

Raising the temperature and lengthening the time of irradiation increase the yield of polymers, which reaches its maximum value more rapidly the higher the temperature. With certain pairs of monomers, however, prolonged exposure at high temperatures (40–80°C) leads to diminished yields, probably because of breakdown of the thermally unstable reaction complex formed initially. Higher yields of polymer are obtained with increase in the concentration of the bismaleimide in the reaction mixture. The yield increases on addition of an inert solvent (acetone, chloroform, alcohol), because of improved solubility of the bisimide and hence the possibility of reaction occurring in more concentrated solutions.

In mixtures of solvents, however, the main reaction is accompanied by secondary homopolymerisation of the bisimide:



This leads to the formation of mixed polymers with cyclobutane rings in the chain, as is confirmed by fractionation and by infrared and nuclear magnetic resonance spectroscopy of the polymers[156].

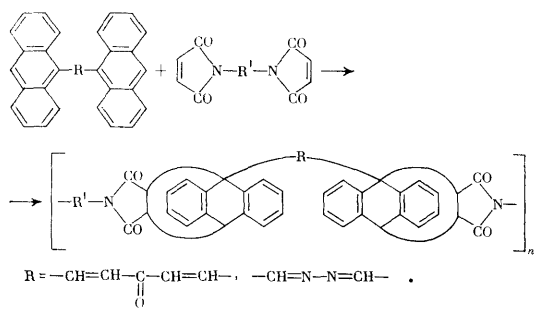
Mixed Diels–Alder polyimides have been obtained also by the copolymerisation of two aromatic dienes with bismaleimides[156,157]. The yield is 20–80%, and the intrinsic viscosity 0.01–0.15 dl g$^{-1}$. They are inferior to homopolyimides in thermal stability, and begin to decompose at 330–370°C. Increasing the content of substituted benzene segments in the chain in mixed polyimides based on benzene and alkylbenzenes produces a monotonic fall in viscosity.

An investigation of the influence of the composition of the initial mixture of aromatic hydrocarbons on the yield and the properties of the mixed polyimides has shown[157] that, according to their reactivity towards bismaleimides, they can be arranged in the sequence

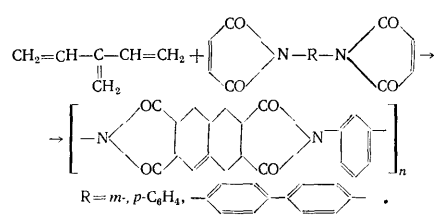
cumene ⩾ toluene > benzene ⩾ diphenyl ether > chlorobenzene.

It follows from this sequence, which coincides with that deduced from a study of homopolymerisation, that the rate of polymerisation increases when the aromatic hydrocarbon contains electron-donor substituents of small bulk, and decreases in the presence of electron-accepting substituents.

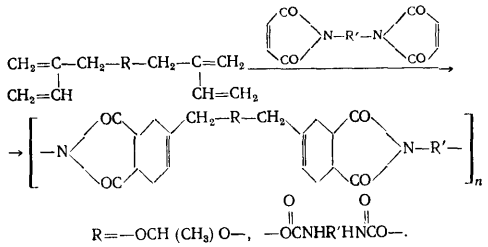
The above results show that under certain conditions many benzene derivatives are able to undergo Diels–Alder reactions with bismaleimides just as actively as cyclic dienes. Among other aromatic compounds only 9-anthraldehydebisazine and 1,5-di(anthr-9-yl)penta-1,4-dien-3-one have been mentioned[127] as developing the diene character of anthracene on reaction with bismaleimides:



Not only aromatic and cyclic derivatives but also open-chain bisdienes are used as comonomers. Thus 3-methylenepenta-1,4-diene in acetone solution at 55°C reacts rapidly with bismaleimides to give a theoretical yield of a polyimide stable up to 500°C:[158]



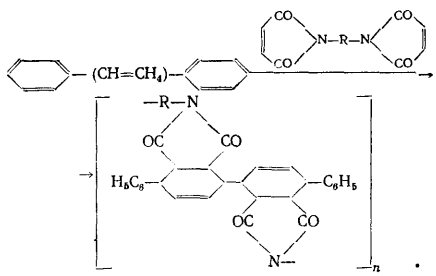
The same study used acetals and biscarbamates of 2-methylenebut-3-enol as bisbutadienes. Their polymerisation with phenylene-*m*- or *p*- or with biphenylylene-4,4′-bismaleimides in DMF solution at 100°C gave polyimides:



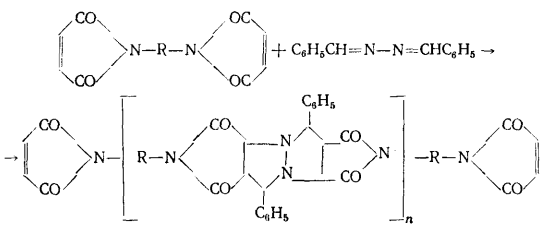
R=—OCH (CH$_3$) O—, —OCNHR′HNCO—.

The yield for polymers varying in structure was 50–76%, with $[\eta]$ = 0.05–0.20 dl g$^{-1}$ and softening temperatures from 74 to 194°C.

Another example of an acyclic diene is 1,8-diphenyloctatetraene[125,126]. Polymers were obtained from it in theoretical yield, but the reduced viscosity was insignificant:



Benzylideneazine may act as a kind of acyclic diene in Diels–Alder reactions[159], adding at the 1,3-position to bismaleimides to form polyimides:



R = (CH$_2$)$_6$, *o*-, *m*-, *p*-C$_6$H$_4$.

Polymerisation takes place in the melt at 180–190°C. The specific viscosity of the polymers is 0.13–0.30 dl g$^{-1}$, and their softening temperature 238–300°C.

Thus the Diels–Alder reaction ensures growth of the polymer chain to give linear polyimides when bisimides of unsaturated acids (mainly maleic) are treated with various dienes. The reaction takes place in solution or in the melt. The temperature and the duration of the synthesis are determined by the nature of the diene, the dienophile, and the solvent. In several cases active dienes react with bisimides under mild conditions, under which polymers of high molecular weight can be obtained. A peculiarity of this reaction is its reversibility, leading at high temperatures to formation of the initial components. Furthermore, the process is sometimes complicated by secondary 1 + 2 cycloaddition, causing cross-linking of the polymer chains.

Among the advantages of this reaction is that polyimides can be obtained with 100% imidisation. In most cases volatile reaction products are absent. These factors enable dense and non-porous polymers of high thermal stability to be obtained, which are promising for practical utilisation.

The above Review of published information shows that cyclic imides of di- and tetra-carboxylic acids are highly active monomers, and can be used in polycondensation, migration polymerisation, and cycloaddition reactions. The resulting open-chain or cyclic polymers possess several interesting properties.

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