Translated from *Uspekhi Khimii* **58** 1006–1031 (1989) U.D.C. 541.64

Thermostable and fire-resistant polymers based on chloral and its derivatives

V V Korshak (deceased), A L Rusanov
Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow

ABSTRACT. The possible ways of using chloral and its derivatives as monomers for the synthesis of fire-resistant and thermostable carbochain and heterochain polymers are examined. Questions concerning the synthesis from chloral of the polyfunctional monomers used to prepare polyheteroarylenes with specific properties are given an especially detailed consideration.

The bibliography includes 170 references.

Contents

I. Introduction 588
II. Chloral homopolymers and copolymers 588
III. Chloral-based condensation monomers 590
IV. Condensation polymers based on chloral derivatives 594

I. Introduction

The development of raw materials for the synthesis of polymers and materials derived from them is a key problem which in many respects determines the successful and intensive development of the chemistry and technology of high-molecular-weight compounds. The problem of ensuring the supply of monomers for the development of polymers with specific properties—fire resistance, thermal stability, etc.—in which considerable progress has been made during the last decade, is especially acute.[1]

The use of chloral, which is produced on a large scale,[2,3] its output in 1970 in the USA being at the level of 50 000 tonnes annually, as the raw material for the synthesis of monomers of this kind is therefore of considerable interest. Chloral is the starting material for the synthesis of pharmaceuticals, especially pure chloroform, herbicides (sodium trichloroacetate, dichloral-urea) and insecticides of the type of chlorophos.[3] However, the principal application of chloral has always been the manufacture of DDT [4]—a widely used insecticide, whose world production in 1956 was 80 000 tonnes.[5] Between 1942 and 1974, 4.5 million tonnes of DDT were used in the fight against agricultural pests throughout the world[6] and during the antimalarial compaign over a period of many years the application of DDT saved more than 1 billion people from malaria.[7] Furthermore, it helps to eradicate diseases such as the plague, typhoid, sleeping sickness, yellow fever, leishmaniasis, colorado tick fever, etc.[7]

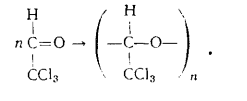
During the last 20–25 years, an acute controversy has developed concerning the toxic effect of DDT on the human organism which it enters as a result of being incorporated in the "food chain", including plants and animals used by man, as a result of which the World Health Organisation forbade the use of this preparation as an insecticide or in any other way leading to the possibility of its being incorporated in the "food chain". Furthermore, many pests (about 200 species) have developed resistance to DDT as a result of its frequent application. Consequently in all the major states a programme for the gradual replacement of DDT has been put in train and in 1963 its manufacture and the associated manufacture of chloral already began to decrease.[3,7] Nevertheless the output of these products has continued to be considerable (mainly for the use of DDT in developing countries[7]) and the manufacturing capacity for chloral and DDT available in the world is capable of meeting the highest requirements for these products.

In view of the foregoing, the use of chloral and DDT for the synthesis of polymers with specific properties appeared extremely attractive.

The promising nature of this aspect has been partly demonstrated in a number of studies[8–11] but none of them reflect the set of possibilities inherent in the use of these compounds—direct or indirect—in the chemistry and technology of polymers. Within the framework of this review, we have attempted to consider as widely as possible the ways of utilising chloral and DDT for the preparation of thermostable and fire-resistant polymers.

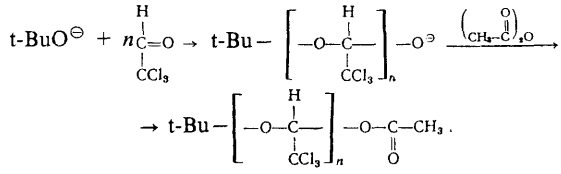
II. Chloral homopolymers and copolymers

Since the polymerisation of aldehydes, involving the partial dissociation of a carbon–oxygen bond, is a familiar reaction in the synthesis of polymers,[12] it is quite natural that the polymerisation of chloral became the first application of this product in the chemistry of polymers.[12–15] Vogl showed that chloral can polymerise via both anionic and cationic mechanisms:

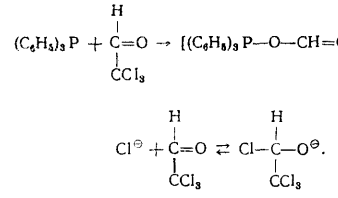


The tendency of aldehydes to polymerise is correlated with the polarisation of the double bond of the carbonyl group, which is reflected in the position of the C=O band in the IR spectrum. Aldehydes in which the absorption frequency of the carbonyl group is above 1750 cm^{-1} and especially chloral readily polymerise via an anionic mechanism on treatment with nucleophiles.[16] The most widely used initiators are alkali metal alkoxides, tertiary amines, tertiary phosphines, quaternary ammonium and phosphonium salts, as well as organometallic compounds. Even when comparatively weak nucleophiles are employed, the anionic polymerisation takes place at a high rate and leads to the formation of polychloral in a high yield. For example, the block polymerisation of chloral using 0.2 mol% of lithium t-butoxide as the initiator leads to the

formation of polychloral in 85% yield after 3 min.[17] A study of the mechanism of chain propagation by stopping the polymerisation at early stages of the process showed that it proceeds via the mechanism[18,19]



When triphenyl phosphite is used as the initiator,[20] the polymerisation reaction proceeds, according to Hoffmann and Diehr,[21] in conformity with the following scheme:



In the presence of anionic initiators, chloral is polymerised by a special method. It consists in carrying out the initiation at a temperature above the limiting value followed by the polymerisation after cooling below the limiting temperature.[14,15,17] This process makes it possible to obtain polychloral in the form of desirable materials.

The cationic polymerisation of chloral can be initiated only by strong Lewis and Brønsted acids (BF_3, CH_3SO_3H, H_2SO_4); the rate of polymerisation is then significantly lower—when 2 mol% CH_3SO_3H is used as the initiator at −5 °C for 300 h, the degree of conversion is only 40%. A noteworthy exception is observed in polymerisation initiated by $AlCl_3$ and $SbCl_2$; in these cases, polychloral was obtained in a high yield, but there are doubts about the purely cationic nature of this process which might have been initiated also by chlorine.[12]

Polychloral is completely insoluble in organic solvents because of its isotactic structure,[12,22] demonstrated by X-ray diffraction, ^{13}C NMR, and ^{35}Cl NQR and caused by the large bulk of the trichloromethyl side groups. The same fragments which are responsible for the high chlorine content in polychloral give rise also to the virtual incombustibility of this polymer.

The mechanical, electrical, and thermal properties of polychloral have been examined.[23] The polymer is characterised by moderate crystallinity; its density is 1.9 g cm^{-3} and its refractive index is $n_D^{25} = 1$. Its thermal expansion coefficient is 4×10^{-5} K^{-1}. Polychloral fibres have a tensile strength of the order of 40 mPa and an elongation on rupture of the order of 25%. The coefficient of friction of polychloral, both static and dynamic, is 0.55.

The dielectric constant of polychloral at room temperature is 2.8, its scattering factor is 0.003, and its electrical resistivity is 4×10 Ω cm.

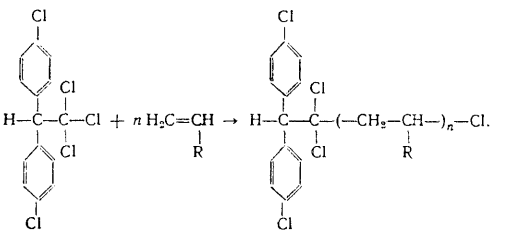
The thermal stability of polychloral obtained as a result of polymerisation is low (220 °C); as for other polyacetals, regardless of the methods of polymerisation subsequent treatment leads to the formation of more stable end groups. Thus the comparatively low thermal stability of the polychloral obtained by the anionic mechanism is due to the presence of alkoxy-end groups with which the depolymerisation process begins. The mechanism of the degradation of the polychloro-compound has been investigated in fair detail.[24] Thermogravimetric analysis of polychloral showed that the unstabilised polychloral is degraded at comparatively low temperatures. The bimodal and even trimodal character of the differential thermogravimetric analysis curves indicate the presence of two or three polychloral fractions with different end groups.[24]

The methods for the introduction of more stable end groups during and after the polymerisation of chloral include the use of the corresponding chain transfer agents, decomposing counterions etc. as well as different versions of the treatment of the polymer already obtained. Thus, when the polymerisation is initiated by triphenylphosphine and the polymer is subsequently treated with PCl_5 in CCl_4, polychloral acquires a greater thermal stability. On heating in an atmosphere of nitrogen at a rate of 20 K min^{-1}, this type of polychloral begins to degrade at 250 °C and the maximum rate of degradation is attained at 340 °C. Thus correctly stabilised polychloral has the same thermal stability as the industrial (i.e. stabilised) polyoxymethylene.

Polychloral does not melt without decomposition. Its hypothetical melting point (~460 °C), which is far removed from its degradation temperature, has been obtained by extrapolating the melting points of chloroal–formaldehyde complexes.[23]

The copolymers of chloral with other monomers have attracted much attention among investigators; copolymers of this product with a wide variety of comonomers have been described in the patent literature. However, one should note that the copolymerisation reactions of chloral with mono- and di-chloroacetaldehydes,[25] aliphatic and aromatic isocyanates,[26–28] ketones, formaldehyde, and trioxane have been studied in greatest detail. The copolymers of chloral with monochloroacetaldehyde are soluble in chloroform, while its copolymers with dichloroacetaldehyde are insoluble. None of the copolymers melt below the thermal degradation temperature and their thermal stabilities are intermediate between those characteristic of the corresponding homopolymers.

Yet another possible application of chloral in polymerisation processes is associated with the presence in it of the trichloromethyl group, which plays the role, under certain conditions, of an active centre at which radical processes take place. Thus the telomerisation of ethylene, propene, butene, and a number of other polymers using DDT has been examined:[29]



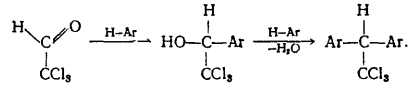
The presence of trichloromethyl substituents in the chloral homopolymers and copolymers leads to the possibility, by analogy with the process examined above,[29] of modifying these polymers by the graft polymerisation reactions. According to a number of investigators,[30–32] such reactions should proceed especially effectively in the presence of metal carbonyls. The radical formation process in the systems considered usually involves electron transfer from the transition metal to the halogeno-derivative; the metal then passes to a higher oxidation state and the halogen-derivative decomposes into ionic and radical fragments.[32]

Despite the availability of the starting material, the chloral homopolymers and copolymers as well as their modification products have not found practical applications. The condensation polymers, obtained from chloral derivatives and DDT, are more promising in this respect.

III. Chloral-based condensation monomers

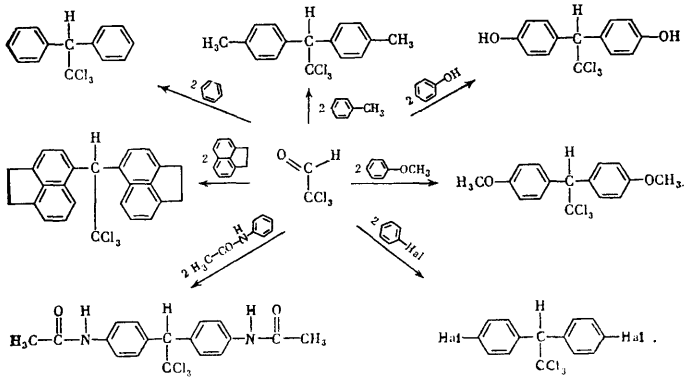
The majority of syntheses of condensation monomers using chloral are based on the well known reactions of this compound with aromatic hydrocarbons, aromatic alkyl-substituted hydrocarbons, and aromatic hydrocarbons containing various functional groups[2] with subsequent reactions of the diaryltrichloroethanes obtained in this way via the central chloroethane fragments and the aromatic rings.

The condensation reactions between chloral and aromatic hydrocarbons and their derivatives, leading to the formation of diaryltrichloroethane derivatives, are carried out in the presence of an acid catalyst and proceed with formation of intermediate carbinols:[33]

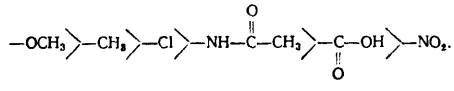


Concentrated H_2SO_4 or its monohydrate, HCl, HF, P_2O_5, H_2PO_4, Lewis acids, and a number of other acid agents are usually employed as catalysts.[2]

In a series of numerous reactions of chloral with aromatic hydrocarbons and their derivatives, the greatest interest attaches, from the standpoint of the synthesis of condensation monomers, to the reactions of chloral with benzene,[34] toluene,[35] acenaphthene,[36] phenol,[37] anisole,[38] acetanilide,[39] and halogenobenzenes—especially chlorobenzene[40] and fluorobenzene.[41] Thes reactions take place in accordance with an idealised scheme and lead to the formation of the target 2,2-diaryl-1,1,1-trichloroethanes in high yields:

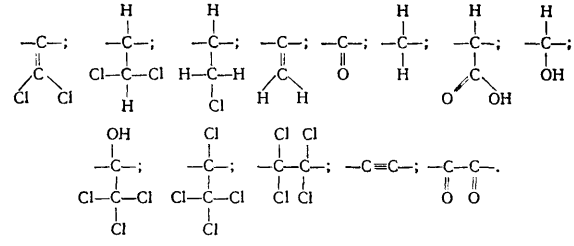


The ease of the reaction of substituted benzenes with chloral varies, in the first place, as a function of the electronic influence of the substituents. According to Yasue and Takai,[42] the reactivity of aromatic rings in reactions with chloral diminishes in the following sequence as a function of the nature of the substituent:

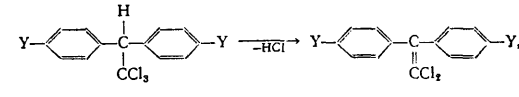


The reactions of 2,2-diaryl-1,1,1-trichloroethanes are carried out in the following ways: (a) the reactions of central 1,1,1-trichloroethane groups; (2) the substitution of the hydrogen atoms in the aromatic rings of diarylchloroethanes and their derivatives with respect to the central group; (3) the reactions of the functional groups, introduced into the aromatic rings of diaryltrichloroethanes and their derivatives with respect to the central group.

The central trichloroethane groups can undergo various reactions leading to their transformation into groups such as 1,1-dichloroethylene, 1,1-dichloroethane, 1-chloroethane, ethylene, carbonyl, methylene, carboxy-, hydroxy-, trichloroethanol, 1,1,1,2-tetrachloroethane, 1,1,2,2-tetrachloroethane, acetylene, α-dicarbonyl, etc.:



In a series of numerous reactions of the 1,1,1-trichloroethane groups, their dehydrochlorination reactions have been most thoroughly investigated,[43] especially in relation to the following series:

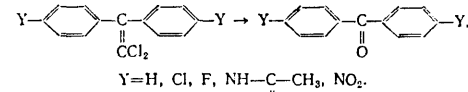


Y=H, Cl, CH_3, OCH_3, OH, NH_2.

The main dehydrochlorinating agents are alcoholic alkali,[35,40] liquid ammonia,[44] methylamine,[44] LiCl in dimethylformamide (DMF),[45] MOH or M_2CO_3 (M = K or Na) in DMF,[46] and tertiary and heterocyclic amines.[4]

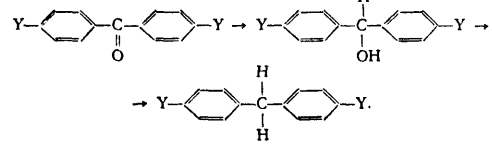
A semiquantitative kinetic study of the dehydrochlorination of various 2,2-diaryltrichloroethanes by KOH in 90% ethanol at the boiling points of the solutions has been carried out[47] and it has been shown that the process proceeds quantitatively and that only one mole of HCl is split off at 80 °C. The kinetics of the dehydrochlorination reaction of diaryltrichloroethanes (which are related to DDT) using NaOH were investigated in a later study.[48] It was found that these processes are second order reactions and proceed via the E_2 mechanism.

In a series of different reactions of the 1,1-dichloroethylene groups, the most thoroughly investigated and most widely used process is their oxidation to keto-groups:[49,50]



Y=H, Cl, F, NH—C(=O)—CH_3, NO_2.

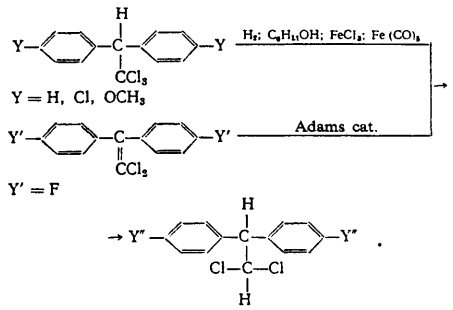
The commonest oxidants of the 1,1-dichloroethylene groups are CrO_3/AcOH, HNO_3/AcOH, and $K_2Cr_2O_7$/AcOH. The diaryl ketones obtained in this way are reduced to the corresponding diphenylmethanols[51,52] and diarylmethanes:[53,54]



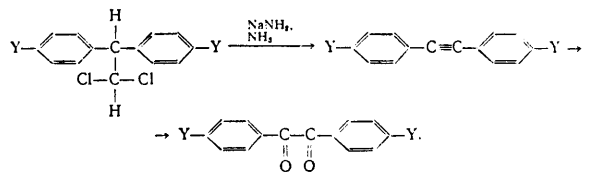
Sodium amalgam[51] and $LiAlH_4$ [52] are used to reduce diaryl ketones to diphenylmethanols; the reduction of diaryl ketones to diarylmethanes is achieved successfully by catalytic hydrogenation using Pd/C [53] or NiRe [54] as catalysts.

Reactions of the 1,1,1-trichloroethane group such as its hydrolysis with formation of 1,1-diarylacetic acids and their subsequent decarboxylation also lead to derivatives of the diphenylmethane series;[55] the same sequence of reactions can be achieved with compounds of the 2,2-diaryl-1,1-dichloroethylene series.[55]

An interesting aspect of the reactions of 1,1,1-trichloroethane groups consists of their reduction processes.[56] In particular, the reduction of 2,2-diaryl-1,1,1-trichloroethanes to 2,2-diaryl-1,1-dichloroethanes has been achieved in cyclohexanol at 110–150 °C using $FeCl_3$ or $Fe(CO)_5$ as catalysts.[55,56] Analogous products have been obtained by reducing 2,2-diaryl-1,1-dichloroethylenes in the presence of the Adams catalyst:[41]

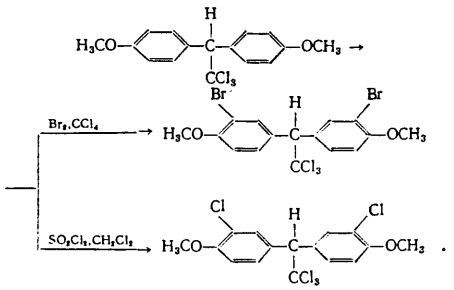


1,2-Diarylacetylenes, subsequently oxidised to benzils,[59] have been obtained by dehydrochlorinating 1,1-dichloroethanes on treatment with $NaNH_2$ in liquid ammonia[57] and also by catalytic dehydrochlorination in the presence of $Mo(CO)_6$:[58]

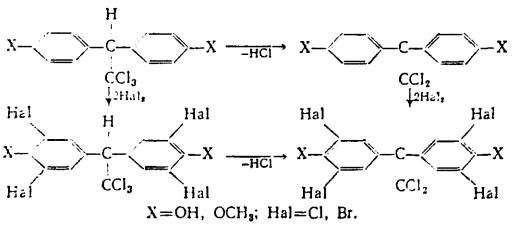


These reactions take place with a change in the carbon skeleton of the molecules, but the isomerisation mechanisms have not been established to this day. A number of reactions of 2,2-diaryl-1,1,1,2-tetrachloroethanes, obtained by chlorinating 2,2-diaryl-1,1,1-trichloroethane derivatives,[50] include a similar isomerisation:[60–65]

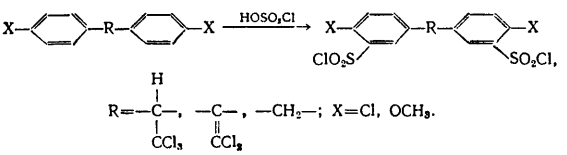
In a series of reactions involving the substitution of hydrogen atoms in the aromatic rings of diaryltrichloroethanes and their derivatives substituted in the central group, the halogenation,[66–69] sulphonylchlorination,[70,71] and nitration[72–75] processes occur most widely. The halogenation of 1,1,1-trichloro-2,2-di(*p*-methoxyphenyl)ethane, namely bromination with bromine in CCl_4 and chlorination with SO_2Cl_2 in methylene chloride, has been described:[66]

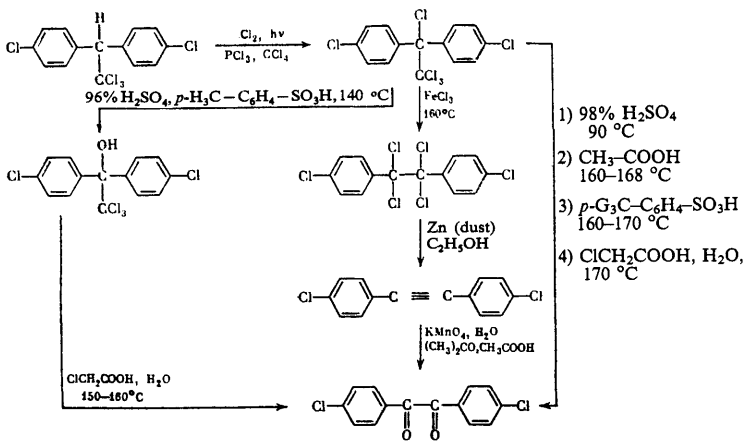


Bisphenols containing an even greater number of chlorine atoms have been obtained by halogenating 1,1,1-trichloro-2,2-di-(4-hydroxyphenyl)ethane with subsequent dehydrochlorination[67–69] or, in the reverse sequence, by dehydrochlorination and then halogenation:

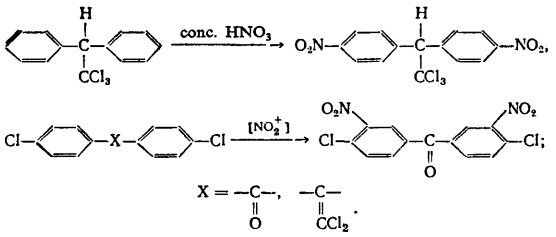


The sulphonylchlorination of the simplest chloral derivatives—DDT, 1,1-dichloro-2,2-di(*p*-chlorophenyl)ethylene, 4,4′-dichlorodiphenylmethane, and 1,1-dichloro-2,2-di(*p*-methoxyphenyl)ethylene [70–71]—led to the corresponding disulphonyl chlorides:

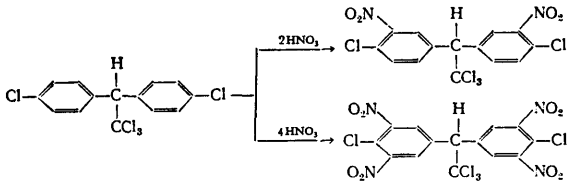




The nitration of diaryltrichloroethanes and their derivatives substituted in the central group has been achieved for a wide range of objects—1,1,1-trichloro-2,2-diphenylethane,[72] 1,1-dichloro-2,2-di(*p*-chlorophenyl)ethylene,[73] 4,4′-dichlorobenzophenone,[73] and DDT:[74,75]



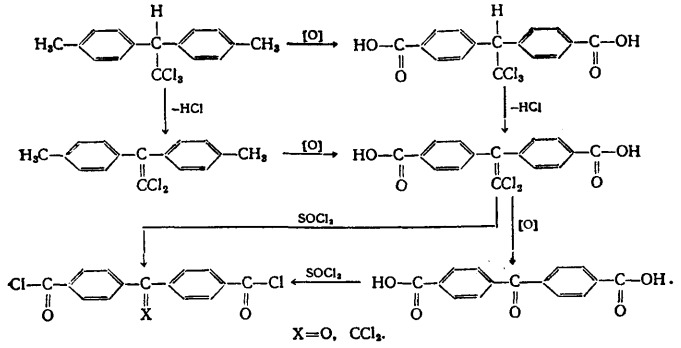
Depending on the conditions under which they are carried out, the latter processes lead to 1,1,1-trichloro-2,2-di(4-chloro-3-nitrophenyl)-ethane or 1,1,1-trichloro-2,2-di(4-chloro-3,5-dinitrophenyl)ethane:



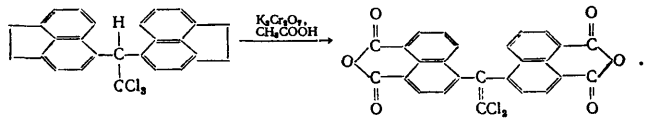
On reaction with caustic alkalis in alcoholic solutions, these compounds are converted into the corresponding dichloroethylene products, which are then oxidised to benzophenone derivatives.[75]

The reactions of the functional groups introduced at various stages of the processes into the aromatic rings of diaryltrichloroethanes and their derivatives substituted in the central group have developed considerably. In particular, diaryltrichloroethanes containing alkyl substituents in the aromatic rings have been oxidised with formation of the corresponding dicarboxylic[76] and tetracarboxylic[36] acids. Thus the oxidation of 1,1,1-trichloro-2,2-di(*p*-tolyl)ethane afforded 2,2-di(*p*-carboxyphenyl)-1,1,1-trichloroethane,[76] which was then made to undergo reactions involving the central group with formation of 2,2-di(*p*-carboxyphenyl)-1,1-dichloroethylene[77] and benzophenone-4,4′-dicarboxylic acid.[78] The same dicarboxylic acids have been obtained by oxidising 1,1-dichloro-2,2-di(*p*-tolyl)ethylene.[77,78]

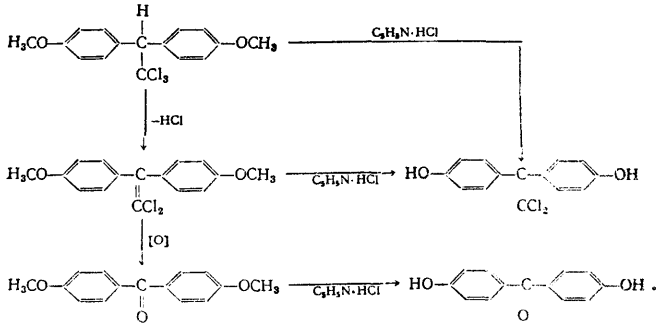
The dicarboxylic acids obtained were converted into the corresponding dichlorides:[77,78]



2,2-Di(4-acenaphthenyl)-1,1,1-trichloroethane was oxidised in a glacial acetic acid using $K_2Cr_2O_7$ or $Na_2Cr_2O_7$ as oxidants.[36] The simultaneous occurrence of the oxidation reactions of the alkylene fragments of the acenaphthenyl units, the conversion of the *peri*-dicarboxy-groups into anhydrides, and the dehydrochlorination of the trichloroethane "bridges" to the 1,1-dichloroethylene bridges were then observed:



The principal reactions of 1,1,1-trichloro-2,2-di(*p*-methoxyphenyl)ethane and its derivatives substituted in the central group involve the conversion of the methoxy-groups into hydroxy-groups on treatment with pyridine hydrochloride:[68,79]

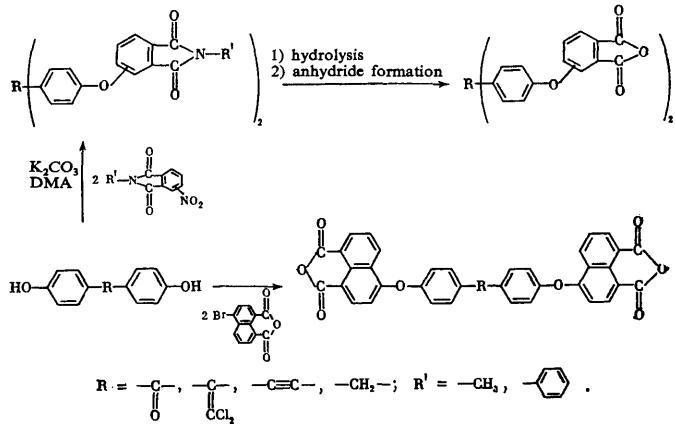


The dehydrochlorination of the 1,1,1-trichloroethane groups to 1,1-dichloroethylene groups takes place simultaneously under the reaction conditions (210 °C).

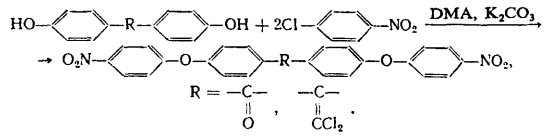
Similar reactions have been used to convert 2,2-di(3-halogeno-4-methoxyphenyl)-1,1,1-trichloroethane into 2,2-di(3-halogeno-4-hydroxyphenyl)-1,1-dichloroethylene:[66]



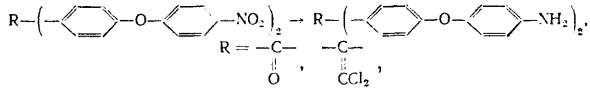
The reactions of the hydroxy-groups of bisphenols involve primarily their conversion into bisphenoxides, which interact vigorously with activated aromatic halogeno- and nitro-compounds. Thus the reaction of bisphenoxides with *N*-substituted 4-nitrophthalimides yielded diimides containing ether linkages; the hydrolysis of these diimides led to the formation of bisphthalic acids, which were then converted into bisphthalic anhydrides.[80–82] Bisnaphthalic anhydrides containing ether linkages were obtained by the reaction of bisphenoxides containing methylene and carbonyl central groups with 4-bromonaphthalic anhydride:[83]



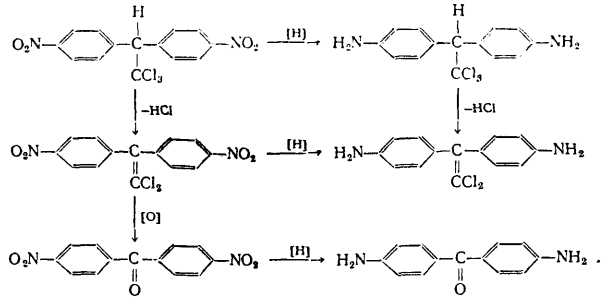
Aromatic dinitro-compounds, each containing two diaryl ether units, have been obtained by the reaction of bisphenoxides with *p*-chloronitrobenzene in dimethylacetamide (DMA) in the presence of K_2CO_3:[84]



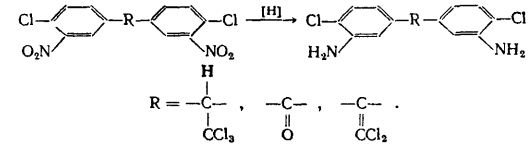
The reduction of nitro-groups to amino-groups has been the main pathway in the chemical reactions of nitro-groups present in various derivatives of chloral and DDT. The catalytic reduction of 4,4′-di(*p*-nitrophenoxy)arylenes to the diamines,[84] i.e.



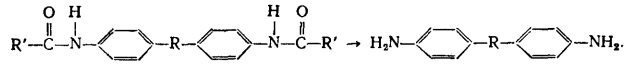
has not been the only reaction of this kind. The simpler dinitro-chloral derivatives 1,1,1-trichloro-2,2-(*p*-nitrophenyl)ethane,[72] 1,1-dichloro-2,2-di(*p*-nitrophenyl)ethylene,[72] and 4,4′-dinitrobenzophenone[74] have also been reduced catalytically:



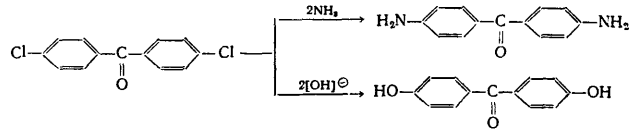
The same type of reaction has been carried out likewise for di(4-chloro-3-nitrophenyl)arylenes:[75,85,86]



An alternative method of synthesis of aromatic diamines from chloral derivatives is the hydrolysis of the bisamides:[87]



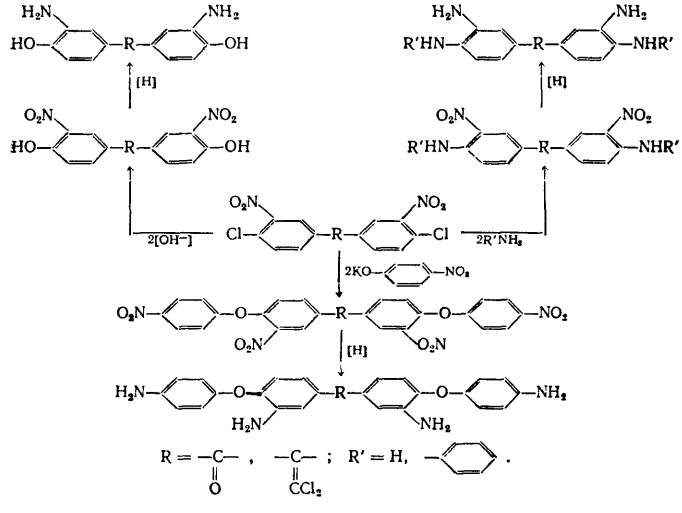
The reactions involving the substitution of halogen atoms in activated aromatic dihalogeno-compounds also constitute an extremely effective approach to the synthesis of diamines. A simple method of synthesis of diamines, for example from 4,4′-dichlorobenzophenone,[73,88] using NH_3 and different catalysts, has thus arisen:



The hydrolysis of the same compound[89,90] with aqueous NaOH using different catalysts, for example CuCl and Cu_2O,[90] led to the formation of 4,4′-dihydroxybenzophenone.

The introduction of nitro-substituents increases sharply the mobility of the chlorine atoms in the aromatic rings of DDT and the products of its reactions via the central group, making them more reactive even compared with the chlorine atoms in di(4-chlorophenyl) sulphone.[91] This fact determines the possibility of the successful use of such products directly in polycondensation processes and also of carrying out various reactions involving the chlorine atoms. In particular, the reactions of such compounds with ammonia and aromatic amines, leading to the corresponding bis(*o*-nitroanilines) and bis(*o*-nitrodiphenylamines), are of considerable interest.[86,92] The chlorine atoms in compounds of this kind are very readily hydrolysed by alkalis;[73] this has been used, in particular, to synthesise 4,4′-dihydroxy-3,3′-dinitrobenzophenone,[73] and they also interact with potassium *p*-nitrophenoxide, forming, for example, 3,3′-dinitro-4,4′-di(*p*-nitrophenoxy)benzophenone.[93]

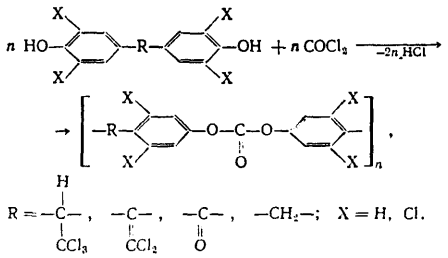
The reduction of the nitro-groups in dinitrodiamines leads to the formation of unsubstituted[86] and *NN*′-diphenyl-substituted[92] bis(*o*-phenylenediamines); the reduction of nitro-groups in bis(*o*-nitrophenols) affords bis(*o*-aminophenols),[73] while the reduction of nitro-groups in 3,3′-dinitro-4,4′-di(*p*-nitrophenoxy)-benzophenone leads to the formation of 3,3′-diamino-4,4′-di(*p*-aminophenoxy)benzophenone:[93]



Analysis of the entire foregoing data enables one to claim that a wide range of varied di- and tetra-functional monomers have been obtained from chloral and DDT. Some of them are of considerable interest from the standpoint of the properties of the polymers based on them and also from the standpoint of their availability and potential cost.

IV. Condensation polymers based on chloral derivatives

In the series of condensation polymers based on chloral and DDT derivatives, polycarbonates obtained in accordance with the scheme



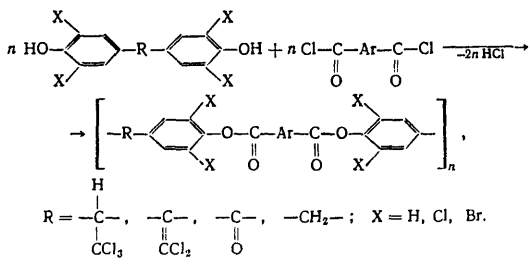
were the first to attract the attention of investigators.[94-98] Since polycarbonates based on 4,4'-dihydroxybenzophenone and di(4-hydroxyphenyl)methane were examined previously,[94-98] in the present review attention is concentrated on polymers derived from bisphenols containing 1,1,1-trichloroethane and 1,1-dichloroethylene central groups.

The first mention of the use of 1,1,1-trichloro-2,2-di(*p*-hydroxyphenyl)ethane and 1,1-dichloro-2,2-di(*p*-hydroxyphenyl)ethylene to obtain polycarbonates (as comonomers of bisphenol A) dates back to 1964,[99] when a group of Polish investigators synthesised copolycarbonates by interfacial polycondensation. The subsequent research by the same group of investigators[68,69] led to a series of interesting results, referring, in particular, to the synthesis of homopolycarbonates from 1,1-dichloro-2,2-di(*p*-hydroxyphenyl)-ethylene.[69] Comparison of the properties of homopolycarbonates based on 1,1-dichloro-2,2-di(*p*-hydroxyphenyl)ethylene, 1,1,1-trichloro-2,2-di(*p*-hydroxyphenyl)ethane, and bisphenol A[100,101] showed that the homopolymer based on 1,1-dichloro-2,2-di(*p*-hydroxyphenyl)ethylene is characterised by a more interesting set of thermal and deformation-strength properties. At approximately 20 °C, the thermal stability of this polymer exceeds that of the industrial polycarbonate obtained from bisphenol A and is superior to it as regards its strength characteristics and, by virtue of the large content (25%) of chlorine, as regards its fire resistance. Further increase in the chlorine content in polycarbonates leads, on the one hand, to a further increase of the thermal stability and fire resistance, but, on the other hand, it entails a sharp diminution of the elasticity of the polymers. Furthermore, systems containing 1,1,1-trichloroethane groups are characterised by a reduced thermal stability—after prolonged exposure to temperatures in the range 100–300 °C they evolve HCl, which is probably associated with the dehydrochlorination of the trichloroethane groups.

The valuable set of properties of the polycarbonates based on 1,1-dichloro-2,2-di(*p*-hydroxyphenol)ethylene combined with the high hydrolytic stability of chlorine-containing polycarbonates[102] have been responsible for the further development of studies in this field,[44,103-108] which were completed by the development of a high-quality thermoplastic.

The thermal stability of the unstabilised and stabilised homopolycarbonates and copolycarbonates as well as their fire resistance have attracted special attention.[109] The study of the chemical composition of the gases evolved on combustion of this polycarbonate[110] and tests on mice using the technique involving the pyrolysis of the polymers in air[111,112] showed that they are characterised by the smallest combustibility, smoke evolution, and toxicity among all the known thermoplastics.

Together with the polycarbonates considered above, polyarylates obtained from the same bisphenols and aromatic dicarboxylic acid dichlorides have aroused considerable interest:[113]

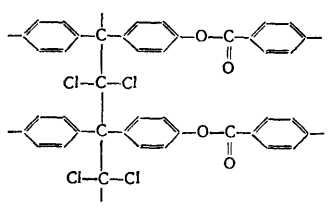


By virtue of the considerations described above in relation to polycarbonates, in the present review attention is concentrated on polyarylates derived from bisphenols containing 1,1,1-trichloroethane and 1,1,1-dichloroethylene central groups, in particular from 1,1-dichloro-2,2-di(*p*-hydroxyphenyl)ethylene.[108,114-118] The synthesis of these polymers using the dichlorides of the commonest aromatic dicarboxylic acids—isophthalic and terephthalic—as acid components was achieved by interfacial polycondensation[108,114-16] and also by the acceptor-catalytic polyesterification in solution.[108,118] Polyarylates have been obtained as homopolymers as well as copolymers using bisphenol A as the comonomer.[119,120] The polyarylates obtained are satisfactorily soluble in chlorinated hydrocarbons; they form films and coatings with effective mechanical, dielectric, and optical properties.[116,121] Homopolyarylates based on 1,1-dichloro-2,2-di(*p*-hydroxyphenyl)ethylene are characterised by significantly better thermal and electrophysical characteristics than polymers based on other bisphenols.

In terms of their thermal stability and fire resistance, polyarylates based on 1,1-dichloro-2,2-di(*p*-hydroxyphenyl)ethylene are superior to industrial polyesters and polycarbonates. The maximum temperature of the long-range use of polyarylate is 180 °C, whilst that of the short-term use is 260 °C. The onset of thermal degradation in air is observed at 360 °C according to the results of dynamic thermogravimetric analysis (DTGA), the weight loss after 150 h at 200 °C amounting to 1%. Their dielectric and mechanical properties do not change after heating at 180 °C for 1000 h.

The properties of polyarylate films can be significantly improved by heat treatment for 2–5 h at 180–250 °C. Thus the heat-treated films become much more chemically stable and lose their solubility in chlorinated hydrocarbons.

These changes in properties are probably associated with the partial "cross-linking" via the dichloroethylene groups:[108,118]



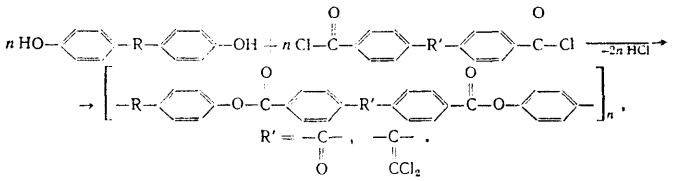
which has also been noted for polycarbonates.[104]

Polyarylates sensitive to UV radiation[122,123] as well as electret[124] and coloured[125] polyarylates have been obtained from 1,1-dichloro-2,2-di(*p*-hydroxyphenyl)ethylene.

The attempts to use the polyarylates synthesised as pigmented and non-pigmented coatings[126] to protect pipes transporting hot liquids at 150–200 °C showed that, after use for 2 years, these coatings retain excellent thermal and chemical characteristics as well as good adhesion to metallic surfaces.

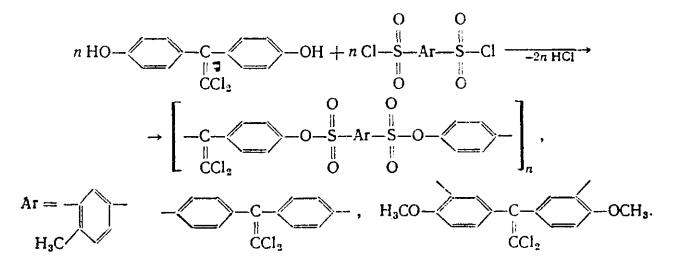
The polyarylates can also be used as constructional materials in the production of components for electrotechnical and radiotechnical purposes.

Together with the bisphenol derivatives of chloral and DDT, the dichlorides of aromatic dicarboxylic acids—benzophenone-4,4′-dicarboxylic acid and 2,2-di(*p*-carboxyphenyl)-1,1-dichloroethylene, which are also chloral derivatives, have been used to synthesise polyarylates:



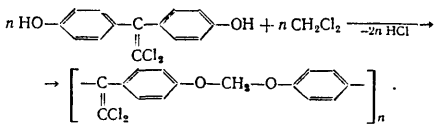
Since polyarylates based on the dichloride of benzophenone-4,4′-dicarboxylic acid were examined in detail previously,[113] in the present review attention is concentrated on polymers based on the dichloride of 2,2-di(*p*-carboxyphenyl)-1,1-dichloroethylene.[118,127–133] These polymers were obtained by interfacial polycondensation[127,128] and acceptor-catalytic polycondensation[118,128–131] methods. According to a number of workers,[118,127–133] the polyarylates synthesised dissolve readily in methylene chloride, chloroform, tetrachloroethane, tetrahydrofuran (THF), and other solvents. Films characterised by a higher fibre resistance and capacity for long term use at 200 °C have been obtained by casting from solutions of these polymers in chloroform. According to Taova et al.,[133] the 1,1-dichloroethylene group has a positive influence on the thermal characteristics of polyarylates.

Together with polyarylates, polysulphonates obtained by the reaction of bisphenols with disulphonyl chlorides have also attracted much attention of investigators; here at least one of the comonomers was a chloral or DDT derivative. In particular, the interaction of 1,1-dichloro-2,2-di(*p*-hydroxyphenyl)ethylene with various disulphonyl chlorides, carried out under the conditions of interfacial polycondensation using phase transfer catalysts afforded polysulphates with comparatively high molecular weight characteristics:[108,117,134,135]



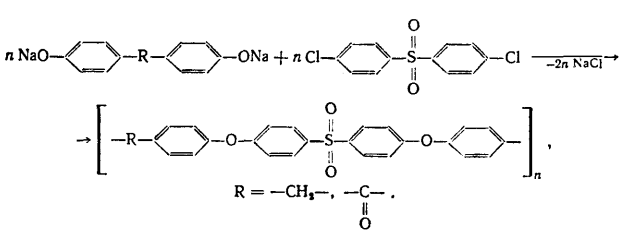
Polysulphonates are superior to the corresponding polyarylates in the first place as regards solubility; in the series of polymers represented by the scheme above,[37] the highest solubility is that of the polysulphonate based on the 1,1-dichloro-2,2-di(3-chlorosulphonyl-4-methoxy)ethylene; this polymer is readily soluble in acetone, cyclohexanone, and xylene,[134] which is due to the presence in it of *ortho*-methoxy-substituents and *meta*-phenylene rings in the main chains of the macromolecules. Polysulphonates with the highest molecular weights are obtained using triethylbenzylammonium chloride or bromide as the phase transfer catalyst. The polysulphonates then form films characteristic by a high fibre resistance as a consequence of the presence in the polymer of a large amount of chlorine and sulphur. The film forming properties of polysulphonates improve significantly when part of the disulphonyl chloride is replaced by isophthaloyl chloride (20 mol%) or terephthaloyl chloride (30 mol%).[136] The thermal decomposition of polysulphonates modified in this way begins at 330 °C; the modification improves the adhesion properties of the polysulphonates, their solubility in the available organic solvents, their resistance to the action of acids and alkalis, and their elastic properties. The mechanical properties of the modified polysulphonates do not change at a temperature of approximately 180 °C.

Together with the synthesis of various types of polyesters, chloral and DDT derivatives have been used successfully to synthesise polyethers. Thus 1,1-dichloro-2,2-di(*p*-hydroxyphenyl)ethylene has been used to synthesise polyformals—the products of the condensation of bisphenols with methylene chloride:[137]



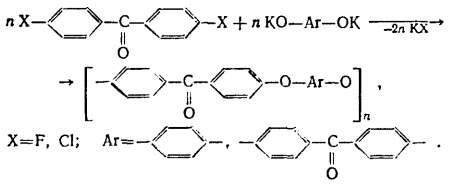
A polyformal was synthesised by the reaction of 1,1-dichloro-2,2-di(*p*-hydroxyphenyl)ethylene with methylene chloride in *N*-methyl-2-pyrridinone (MP) in the presence of NaOH.[137] The polyformal thus obtained contained 10–15% of cyclic oligomers. Comparison of the characteristics of the polyformal with those of the analogous polymer obtained from bisphenol A showed that their mechanical properties are comparable but the system containing the 1,1-dichloroethylene group is more heat resistant (by approximately 25 °C) and more fire resistant. The glass point of the polyformal synthesised from 1,1-dichloro-2,2-di(*p*-hydroxyphenyl)ethylene is 120 °C and its oxygen index is 43.

The first attempts to synthesis fully aromatic polyethers using chloral and DDT derivatives as the monomers were associated with the development of processes for the interaction of di(4-chlorophenyl) sulphone with different bisphenols,[138,139] especially with di(4-hydroxphenyl)methane and 4,4′-dihydroxybenzophenone:

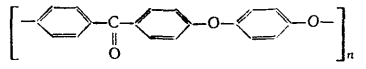


Later studies in this field were associated with the use of 1,1-dichloro-2,2-di(*p*-hydroxyphenyl)ethylene as the bisphenol.[140,141] In the series of these polymers, systems based on 4,4′-dihydroxybenzophenone, characterised by the glass point T_g = 205 °C, attracted most attention by investigators. The possibility of using chloral and DDT derivatives as dihalogeno-components of the reaction attracted even more interest. In particular, polyethers based on 4,4′-dichloro- and 4,4,′-difluorobenzophenone are of considerable

interest.[142,143] These polymers are obtained in accordance with the scheme[144–146]



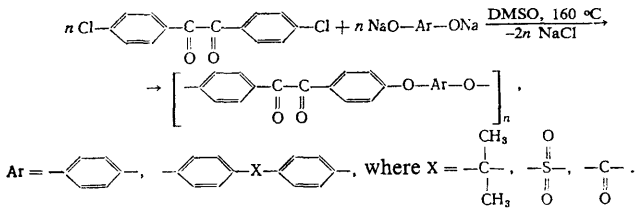
The crystallinity of the polymers formed, referred to as polyetherketones, makes it necessary to synthesise them at high temperatures (up to 335 °C) in solvents such as sulpholan[144] and diphenyl sulphone.[145] One of the representatives of polymers of this class, corresponding to the formula



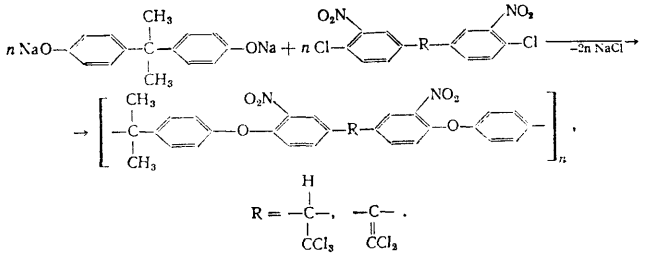
and characterised by T_g = 145 °C and the melting point T_m = 334 °C, was first introduced by the ICI Company in 1982.[143]

Using 4-hydroxythiophenol as the diol component, polythioetherketones were obtained.[147] These are crystalline polymers with $[\eta] \geqslant 0.4$ dl g^{-1} and having a high thermal and chemical stability and effective mechanical properties. The use of *p*-dimercaptobenzene led to polysulphideketones[148] with good thermal characteristics.

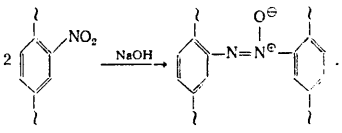
The attempt to use a DDT derivative such as 4,4′-dichlorobenzil as the dihalogeno-reactant[149] led to the formation of oligomeric polyethers, which has the consequence, according to Lesiak and Nowakowski,[149] of the reduced reactivity of 4,4′-dichlorobenzil due to the non-coplanarity of its molecules:



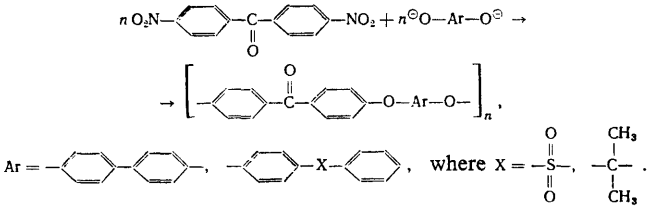
Polymers with extremely low molecular weights have been obtained by the reaction of bisphenol A with 1,1-dichloro-2,2-di(*p*-chlorophenyl)ethylene and 1,1,1-trichloro-2,2-di(*p*-chlorophenyl)ethane;[91,150] high-molecular-weight polyethers have been synthesised only as a result of the activation of the chlorine atoms by introducing nitro-substituents into the monomers:[91,150]



However, it is noteworthy that, when the polycondensation is carried out at high temperatures (more than 80 °C), insoluble products are formed. According to Adam and Husein,[91] this is a consequence of side reactions involving nitro-groups—for example, their coupling in an alkaline medium with formation of intermolecular azoxy-"cross-links":

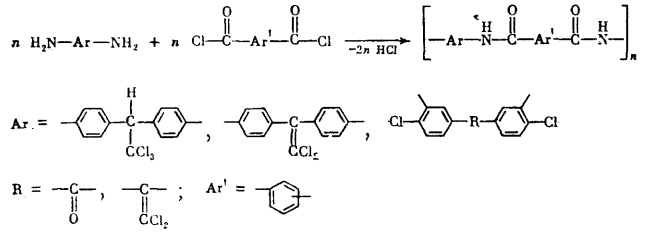


An alternative nucleophilic aromatic nitro-substitution process[151] led to the formation of high-molecular-weight unsubstituted aromatic polyethers based on chloral derivatives: the interaction of 4,4′-dinitrobenzophenone with alkali metal bisphenoxides under the conditions of nucleophilic aromatic nitro-substitution, i.e.



afforded polyetherketones with [η] for solutions in *N*-MP in the range 1.07–1.32 dl g^{-1}.[152] The polyetherketones synthesised are readily soluble in DMF, DMA, and MP. They have melting points in the range 195–255 °C, appreciably below their decomposition temperatures. These are the reasons why materials with a high thermal stability can be obtained from polyetherketones.

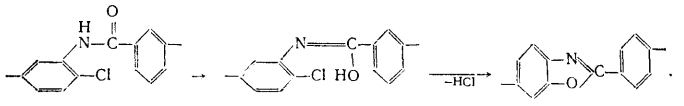
Aromatic polyamides have been obtained both from diamino-derivatives of chloral and DDT,[153–156] i.e.



and from the acid dichloride of 2,2-di(*p*-carboxyphenyl)-1,1-dichloroethylene.[157–159]

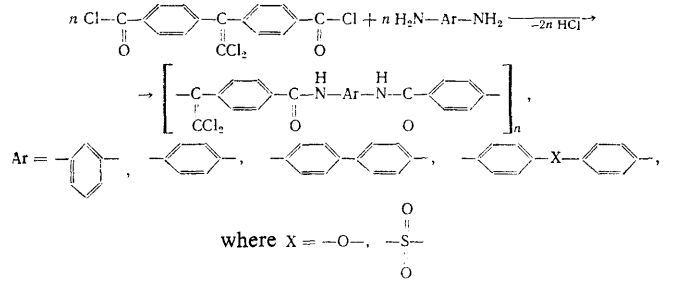
The initial studies on the synthesis of polyamides from the diamino-derivatives of chloral and DDT were performed using 2,2-di(*p*-aminophenyl)-1,1,1-trichloroethane and 2,2-di(*p*-aminophenyl)-1,1-dichloroethylene[153,154] under the conditions of polycondensation in solution[153] and interfacial polycondensation.[154] This yielded comparatively high-molecular-weight and fire-resistant but sparingly soluble polymers. The change to diamines with less symmetrical structures—3,3′-diamino-4,4′-dichlorobenzophenone and 2,2-di(3-amino-4-chlorophenyl)-1,1-dichloroethylene[155,156]—led to the possibility of obtaining polyamides with improved solubility in organic solvents. A detailed study of the dependence of the principal characteristics of polyamides on their structure[155,156] showed that polymers with 1,1-dichloroethylene groups dissolve somewhat better than systems with carbonyl groups in the main macromolecular chain and that the introduction of chlorine into the aromatic rings imparts a greater fire resistance to the polymers than the introduction of the same amount of chlorine in the form of dichloroethylene groups. Polyamides containing carbonyl groups are less fire

resistant than the analogous systems containing 1,1-dichloroethylene groups but are more heat resistant and more thermostable than the latter. An interesting feature of polyamides containing chlorine atoms as *ortho*-substituents relative to the amide group is their ability to undergo intramolecular dehydrochlorination at elevated temperatures (> 300 °C), which leads to the formation of benzoxazole rings:[160,161]



Overall the polyamides considered are of definite practical interest due to the availability of the initial compounds and to their set of valuable properties of the polymers.

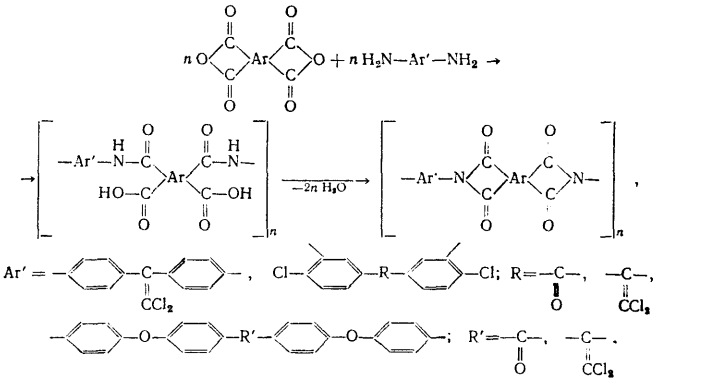
Polyamides based on the acid dichloride of 2,2-di(*p*-carboxyphenyl)-1,1-dichloroethylene,[157–159] obtained in accordance with the scheme



using low-temperature polycondensation in solution[157] and emulsion polycondensation[159] methods, are also extremely interesting from the practical point of view.

The polyamides obtained are high-molecular-weight polymers readily soluble in DMA and MP and with limited solubility in DMF, hexamethylphosphoramide (HMP), and pyridine. They all have a relatively high heat resistance and thermal stability—their softening temperatures reach 310 °C and the temperatures corresponding to a 10% weight loss are in the range 360–405 °C. The high chlorine content in the polyamides (~ 13–18%) is responsible for the self-quenching capacity of these systems. Films obtained from them are not inferior as regards strength to films based on the polyamide of the "phenylon" type. The polyamide obtained using *meta*-phenylenediamine and known under the name "Dneprolon-M" is especially promising.[158]

The use of chloral and DDT derivatives for the synthesis of linear heterocyclic polymers has attracted much attention of investigators in recent years. Among them, the commonest are aromatic polyimides,[1] many of which have been obtained from compounds such as 4,4'-diaminobenzophenone, di(4-aminophenol)methane, etc. i. e. monomers which, as has been shown above, can be obtained from chloral and DDT. Since the methods of synthesis and properties of such polymers have already been examined in detail,[1] in the present review attention is concentrated on polymers which had not been described hitherto. Polyimides based on aromatic diamino-derivatives of chloral and DDT have been obtained by their interaction under mild conditions with the dianhydrides of tetracarboxylic acids in dipolar aprotic solvents with subsequent catalytic conversion of poly(*o*-carboxy)amides into imides in accordance with the scheme



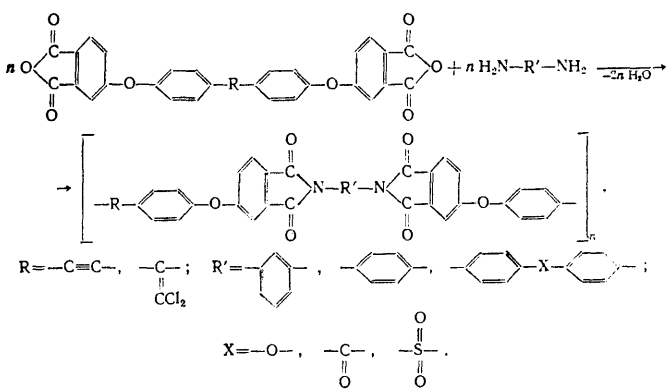
Chloral and DDT derivatives such as 2,2-di(4-aminophenyl)-1,1-dichloroethylene,[162] 3,3'-diamino-4,4'-dichlorobenzophenone, and 2,2-di(3-amino-4-chlorophenyl)-1,1-dichloroethylene[155] have been used in a number of studies[155,156] as the diamines. The commonest bisphthalic anhydrides—the anhydrides of pyromellitic and benzophenone-3,3'-4,4'-tetracarboxylic acids and the 3,3',4,4'-tetracarboxy-derivative of diphenyl sulphone—served as the comonomers of these diamines. The polymers based on 2,2-di(4-aminophenyl)-1,1-dichloroethylene were obtained in the form of comparatively high-molecular-weight {[η] = 1.0–1.4 dl g^{-1}}, heat-resistant (T_{soft} > 280 °C), and fire-resistant [oxygen index (OI) = 36–40] systems which are, however, soluble only in H_2SO_4 and a 3 : 1 tetrachloroethane (TCE)–phenol mixture. The transition from these polymers to polyimides based on 3,3'-diamino-4,4'-dichloroarylenes[155] led, by analogy with a similar structural change in polyamides (see above), to the formation of systems with a significantly greater solubility in organic solvents. Analysis of the dependence of the properties of these polymers on their structure showed that polyimides based on 2,2-di(3-amino-4-chlorophenyl)-1,1-dichloroethylene exhibit the highest solubility and fire resistance, while the best thermal characteristics are those of polyimides based on 3,3'-diamino-4,4-dichlorobenzophenone. The improved capacity of such polymers for being worked into articles is determined not only by their solubility in organic solvents but also by the comparatively mild pressing conditions. Polyimides of this type with the most rigid chains, namely polypyromellitimides, which can be worked by pressing at a temperature exceeding 350 °C, behave under these conditions as thermoreactive systems; intermolecular HCl elimination processes take place during pressing, which results in the formation of "cross-linked" structures characterised by an increased heat resistance.

Diamines containing ether linkages and other groups, for example 4,4-di(*p*-aminophenoxy)benzophenone, have been used to synthesise polyimides.[84] The polyimides obtained from this monomer are high-molecular-weight crystalline systems, whose structure is similar to that of polymers regarded as promising film and constructional materials.[163,164]

Aromatic tetraamino-derivatives of DDT, especially 3,3',4,4'-tetraaminobenzophenone, have been used to obtain polyimides containing *N*-phthalimide *ortho*-substituents.[165] The synthesis of such polyimides reduces to treating the tetraamines with twice the molar amounts of cyclic dicarboxylic acid anhydrides and equimolar

amounts of the dianhydrides of tetracarboxylic acids with subsequent catalytic conversion of the prepolymers thus obtained into imides. The difference between the nucleophilicities of the reaction centres of the aromatic tetramines makes it possible to vary the isomeric composition of the polyimides by altering the sequence in which the mono- and di-anhydrides are introduced into the reaction.[165] When 3,3′,4,4′-tetraaminobenzophenone, phthalic anhydride, and various bisphthalic anhydrides were used as the initial compounds, polyimides containing *N*-phthalimide *ortho*-substituents were obtained; these polymers are readily soluble in amide and phenolic solvents and this is combined with high thermal stabilities and heat resistances, differing little in this respect from polyamides based on other di(*o*-phenylenediamines).[165] Fundamentally different results were obtained when 3,3′-diamino-4,4′-di(*p*-aminophenoxy)benzophenone was used as the initial tetramine.[93] The synthesis of polyimide with the initial introduction of phthalic anhydride yields polymers containing predominantly the *N*-(*p*-phenoxy)phthalimide *ortho*-substituents. These polymers exhibit a solubility, unique for polymers of this class, in DMF, DMA, MP, HMP, dimethyl sulphoxide (DMSO), phenolic solvents, tetrachloroethane, chloroform, and cyclohexanone. Their softening temperatures are in the range 245–290 °C and the temperatures corresponding to a 10% weight loss, determined by the DTGA method, are 440–490 °C.

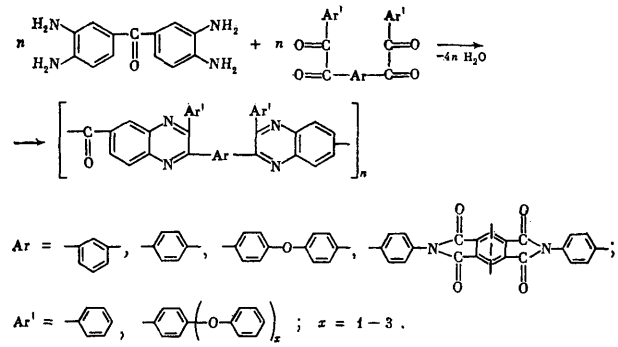
A series of polyimides have also been obtained from non-traditional tetracarboxylic acid dianhydrides derived from chloral and DDT. Thus the synthesis of polyimides from the dianhydrides of di(*o*-dicarboxyphenoxyphenyl)acetylene and 1,1-di(*o*-dicarboxyphenoxyphenyl)-2,2-dichloroethylene has been described. The dianhydrides were made to react with aromatic and aliphatic diamines in organic solvents or in the melt in accordance with the scheme



Polymers based on *m*-phenylenediamine, having T_g = 219–247 °C, temperatures of the onset of thermal degradation in the range 470–500 °C (in air) and 470–545 °C (in N_2), and OI = 45–56 and giving rise to coke residues in the range 64–73%, have been studied in greatest detail.

Polyquinoxalines based on DDT derivatives, in the first place on 3,3′,4,4′-tetraaminobenzophenone,[166–170] whose interaction with various bis(α-diketones) has been achieved in accordance with the scheme below, have attracted much attention of investigators.

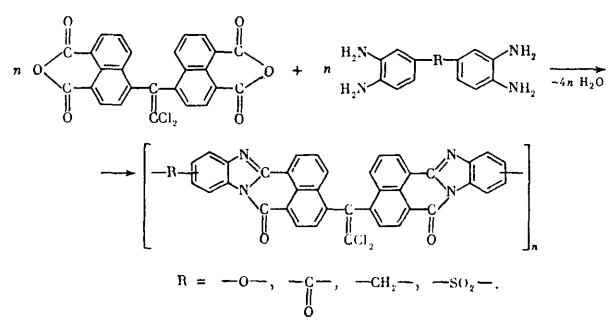
Scheme



High-molecular-weight polymers have been obtained under the usual conditions[167] of the synthesis of polyquinoxalines—low-temperature polycondensation in protic solvents or in the presence of protic additives. Their heat resistance exceeds by 10–25 °C the analogous systems based on di(3,4-diaminophenyl) ether and they have a high thermal stability under the conditions of dynamic and isothermal thermogravimetric analysis being at the same time readily soluble in phenolic and chlorinated solvents, which makes it easy to work them and convert them into articles. In particular, strong films have been obtained from them. They lose between 5.8 and 32.1% of the initial weight depending on their structure and the duration of thermal ageing at 316 °C.

Carboplastics and adhesives capable of being used for a long time at 316 °C and superior, as regards the retention of their strength characteristics during thermal ageing, to the analogous systems based on 3,3′-diaminobenzidine have been obtained from polyphenylquinoxalines synthesised from 3,3′,4,4′-tetraaminobenzophenone.[168,169]

Finally, chloral and DDT derivatives have been used by a number of investigators also for the synthesis of ladder polyheteroarylenes, among which polynaphthoylenebenzimidazoles have been studied in greatest detail. In particular, polymers of this type have been obtained by the reaction of the dianhydride of 2,2-di(4,5-dicarboxynaphthyl)-1,1-dichloroethylene with bis(*o*-phenylenediamines) in phenolic solvents (phenol, *m*-cresol), preferably using benzoic acid as the catalyst:



A characteristic feature of the polynaphthoylenebenzimidazoles thus obtained is ready solubility not only in acid but also in phenolic solvents, which makes it easier to work them and convert them into articles.

The list of uses, presented in this review, of chloral and DDT derivatives in the synthesis of new polymers and materials based on them indicates exceptionally interesting possibilities in the development of this field. The ease of reaction of chloral and DDT

derivatives via the central group, via the functional groups in the aromatic rings, etc. makes it possible to obtain a large number of a wide variety of monomers which are in their turn responsible for a valuable set of properties of the polymers based on them. The possibility of synthesising from available starting materials of high-molecular-weight compounds with improved thermal stability and fire resistance and combined with an improved solubility and capacity for being worked may provide an important stimulus for the intensification of studies in the field under consideration.

References

1. V V Korshak *Termostoikie Polimery* (Thermostable Polymers), Izd. Khimiya, Moscow, 1969
2. F I Luknitskii *Chem. Rev.*, 1975, **75**(3) 259
3. L A Oshin (Editor), Handbook *Promyshlennye Khlororganicheskie Produty* (Industrial Organochlorine Products), Izd. Khimiya, Moscow, 1978
4. N N Mel'nikov, V A Nabokov, E A Pokrovskii *DDT—Svoistva i Primenenie* (DDT—Properties and Applications), GNTIKhL, Moscow, 1954
5. P Karrer *Lehrbuch der Organischen Chemie* (Translated into Russian), GNTIKhL, Leningrad, 1960
6. N N Mel'nikov, A I Volkov, O A Korotkova *Pestitsidy i Okruzhayushchaya Sreda* (Pesticides and the Environment), Izd. Khimiya, Moscow, 1977
7. Z Poller *Chemistry on the Way to the Third Millenium* (Translated into Russian), Izd. Mir, Moscow, 1982
8. T Lesiak, J Nowarkowski *Polimery*, 1980, **25**(3) 81
9. T Lesiak, J Nowarkowski *Polimery*, 1981, **26**(1) 1
10. V V Korshak, A L Rusanov, S Kh Fidler, et al *Plastmassy*, 1984, (10) 32
11. E R Kekharsaeva et al. *Plastmassy*, 1985, (2) 9
12. O Vogl *Encyclopedia of Polymer Science and Engineering*, Wiley, New York, 1985, Vol. 1, p. 623
13. O Vogl, US P. 3 454 527, 1969
14. O Vogl, H C Miller, W H Sharkey *Macromolecules*, 1972, **5**(5) 656
15. O Vogl, K Hatada *J. Polym. Sci., Polym. Lett. Ed.*, 1975, **B13** 609
16. O Vogl, W M D Brayant *J. Polym. Sci.*, 1964, **A2**(10) 4633
17. K Hatada et al. *Vysokomol. Soedin., Ser. A*, 1977, **19**(9) 1987
18. O Vogl *Chemist*, 1985, **62**(9) 16
19. A Abe, K Tasaki, K Inomata, O Vogl *Macromolecules*, 1986, **19**(11) 2707
20. O Vogl, US P. 3 775 371, 1973
21. H Hoffmann, H J Diehr *Tetrahedron Lett.*, 1962, **13** 583
22. G Wasai, T Iwata, M Kuragano, et al *Kogyo Kagaku Zasshi*, 1964, **67** 1920
23. P Kubisa, L S Corley, T Kondo, et al. *Polym. Eng. Sci.*, 1981, **21** 829
24. L S Corley, O Vogl *J. Macromol. Sci., Chem.*, 1980, **14** 1105
25. G H McCain, D E Hudgin, I Rosen, *ACS Polymer Prepr.*, 1965, **6** 659
26. G Odian, L S Hiraoka *J. Polym. Sci.*, 1970, A1, **8**(5) 1309
27. P Kubisa, T Teshirogi, K Hatada, et al. *Makromol. Chem.*, 1980, **181**, 2267
28. P Kubisa, L S Corley, O Vogl, *J. Macromol. Sci., Chem.*, 1980, **181** 2267
29. E C Ladd, US P. 2 609 402; *Chem. Abs.*, 1953, **47** 11 252
30. R Kh Freidlina, A B Belyavskii *Dokl. Akad. Nauk SSSR*, 1959, **127**(6) 1027
31. R Kh Freidlina, A B Belyavskii *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1961, (1) 177
32. C H Bamford, in *Reactivity, Reaction Mechanisms, and Structure in Polymer Chemistry* (Edited by A D Jenkins et al.) (Translated into Russian), Izd. Mir, Moscow, 1977
33. F D Chattaway, R J K Muir *J. Chem. Soc.*, 1934 701
34. A Bayer *Ber. Bunsenges. Phys. Chem.*, 1872, **5** 25
35. O Fisher *Ber. Bunsenges. Phys. Chem.*, 1874, **7** 1191
36. V V Korshak, A L Rusanov, et al. *Dokl.Akad.Nauk SSSR*, 1988, **299**(1) 131
37. M Ter Meer *Ber. Bunsenges. Phys. Chem.*, 1874, **7** 1200
38. E Jager *Ber. Bunsenges. Phys. Chem.*, 1874, **7** 1197
39. E Graef, A Burger *J. Am. Chem. Soc.*, 1946, **68** 2400
40. O Zeidler *Ber. Bunsenges. Phys. Chem.*, 1874, **7** 1180
41. H L Bradlow, C A Werf *J. Am. Chem. Soc.*, 1947, **69** 662
42. M Yasue, Y Takai *Yakugaku Zasshi*, 1957, **77** 829; *Chem. Abs.*, 1957, **52** 116
43. M Trojna, J Hubacek *Chem. Listy*, 1957, **51** 752
44. M R McLaury, et al *J. Polym. Sci., Polym. Chem. Ed.*, 1980, **18**(8) 2501
45. W K S Cleveland, J I Webb, C M Orlando US P. 4 117 018, 1978
46. P L Kinson, C B Guinn, US P. 4 073 814, 1978
47. B Brand, S Busse-Sundermann *Ber. Bunsenges. Phys. Chem.*, 1942, **75**(12) 1819
48. S J Cristol *J. Am. Chem. Soc.*, 1945, **67**(9) 1494
49. H Haller, P Bartlett, N Drake, et al *J. Am. Chem. Soc.*, 1945, **67**(9)
50. O Grummitt, A Buck, A Jenkins *J. Am. Chem. Soc.*, 1945, **67**(1) 155
51. H Wichelhaus *Ber. Bunsenges. Phys. Chem.*, 1889, **22** 988
52. L H Conover, D S Tarbell *J. Am. Chem. Soc.*, 1950, **72**(8) 3586
53. H L Bradlow, C A Werf *J. Am. Chem. Soc.*, 1947, **69**(6) 1254
54. M Levine, S C Temin *J. Org. Chem.*, 1957, **22**(1) 85
55. W C White, T R Sweeny *US Public Health Rpts.*, 1945, **60** 66; *Chem Abs.*, 1945, **39** 1676
56. E C Chukovskaya, R Kh Freidlina, N A Kuz'mina *Synthesis*, 1983, (10) 773
57. A I Kovredov, Zh S Shaugumbekova, A V Kazantsev, L I Zakharkin *Zh. Obshch. Khim.*, 1979, **49**(7) 1534
58. N A Kuz'mina et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, (6) 1443
59. S S Tomar, N K Ray, S K Mukerjee *Agric. Biol. Chem.*, 1974, **38** 1067
60. W L Walton *J. Am. Chem. Soc.*, 1947, **69**(6) 1544
61. O Neilands, J Kreieberga, US P 3 935 239; *Chem. Abs.*, 1976, **85** 5370
62. I N Uspenskaya, G V Motsarev *Khim. Promst.*, 1975, (3) 181
63. H F Wilson, W E Craig US P 2 812 280; *Chem. Abs.*, 1958, **52** 7357
64. G T Barry, R Boyer *Can. J. Res.*, 1943, **26B** 518
65. W Voegtli, H Muhr, P Läuger *Helv. Chim. Acta*, 1954, **37**(6) 1627
66. T Lesiak, J Nowakowski, Polish P. 216 194, 1979
67. S Porejko, Z K Brzozowski, S Maczenski, Z Wielgosz, Polish P. 48 893, 1964
68. S Porejko et al *Chim. Ind. (Milan)*, 1964, **92**(3) 243
69. S Porejko, Z Wielgosz *Polimery*, 1968, **13**(2) 55
70. J Nowakowski *Zh. Org. Khim.*, 1981, **17**(7) 1482

71. Z K Brzozowski, B Zurakowska *IUPAC Macro-83, Bucharest,* 1983, VIII-26, p. 343
72. S Kirkwood, P H Phillips *J. Am. Chem. Soc.*, 1947, **69**(4) 934
73. G S Mironov, V A Ustinov, M I Farberov *Zh. Org. Khim.*, 1972, **8**(7) 1509
74. J Forest, O Stephenson, W A Waters *J. Chem. Soc.*, 1946, (5) 333
75. O G Backeberg, J L O Marais *J. Chem. Soc.*, 1945, **54**(11) 803
76. V T Dorofeev, V N Sokolenko USSR P. 793 989; *Byull. Izobret.*, 1981, (1) 92
77. A M Kharaev, E R Kekharsaeva, G B Shustov, V T Dorofeev *Polikondensatsionnye Protsessy i Polimery* (Polycondensation Processes and Polymers), Izd. Kabardino-Balkar. Gos. Univ., Nal'chik, 1984, p. 51
78. V T Dorofeev, A A Matnish'yan, M G Mordzon, S G Grigoryan *Reaktivy i Osobo Chistye Veshchestva* (Reagents and Specially Pure Substances), Izd. NIITEKhim, Moscow, 1980, No. 6
79. T Lesiak, J Nowakowski, Polish P. 219 827, 1979
80. B G Clayton, F G Wiliams, US P. 3 944 517
81. B G Clayton, F G Williams, US P. 3 956 222
82. T Takekoshi, J E Kochanowski, J S Manello, M J Webber *J. Polym. Sci., Polym. Chem. Ed.*, 1985, **23**(6) 1759
83. Z Jedlinski, U Gaik, B Kowalski, Polish P. 131 685
84. V V Korshak, A L Rusanov, Yu N Margalitadze, N Z Makharashvili *Vysokomol. Soedin., Ser. B*, 1988, **30**(3) 114
85. T Lesiak, J Nowakowski *J. Prakt. Chem.*, 1979, **321**(6) 921
86. P Montagne *Ber. Bunsenges. Phys. Chem.*, 1915, **48** (10) 1027
87. A Burger, E Graeff, M S Bailey *J. Am. Chem. Soc.*, 1946, **68**(9) 1725
88. V V Voronenkov, E A Lazurin *Zh. Org. Khim.*, 1971, **7**(8) 1764
89. G S Mironov, I V Budnii, K A Chernyakovskaya, M I Farberov *Zh. Org. Khim.*, 1972, **8**(3) 597
90. V A Ustinov, G S Mironov, V V Kepeikin, et al., USSR P. 529 149; *Chem. Abs.*, 1976, **85** 192 378
91. G A Adam, N Husein *Br. Polym. J.*, 1979, 190
92. F Consonna *Gazz. Chim. Ital.*, 1904, **34** 374
93. V V Korshak et al. *Dokl. Akad. Nauk SSSR*, 1986, **289**(2) 367
94. H Schnell *Chemistry and Physics of Polycarbonates* (Translated into Russian), Izd. Khimiya, Moscow, 1967
95. O V Smirnova, S B Erofeeva *Polikarbonaty* (Polycarbonates), Izd. Khimiya, Moscow, 1972
96. V V Korshak, S V Vinogradova *Neravnovesnaya Polikondensatsiya* (Non-equilbrium Polycondensation), Izd. Nauka, Moscow, 1972
97. D W Fox *Encyclopedia of Chemical Technology*, Wiley, New York, 1982, Vol. 18, p. 479
98. D W Fox *ACS Polym. Prepr.*, 1986, **27**(1) 474
99. Z Dobkowski, B Krajewski, Z Wielgosz *Polimery*, 1970, **15**(8) 428
100. Z Sobiczewski, Z Wielgosz *Plast. Kautsch.*, 1968, **15** 176
101. Z Sobiczewski, Z Wielgosz, K Janicka *Plast. Kautsch.*, 1969, **16** 99
102. Z Boromowska, Z Wielgosz *Polimery*, 1970, **15** 12
103. S Porejko, Z Wielgosz *Polimery*, 1971, **16** 495
104. S Porejko, Z Wielgosz *Polimery*, 1972, **17** 76
105. Z Boromowska, Z Wielgosz *Polimery*, 1975, **20** 1
106. W K S Cleveland, I L Webb, C M Orlando, US P. 4 117 018, 1978
107. A Factor, C M Orlando *J. Polym. Soc., Polym. Chem. Ed.*, 1980, **18**(2) 579
108. Z K Brzozowski *Polimery*, 1984, **29** 415
109. K N Sannes, A Factor, US P. 4 118 370, 1978
110. J C Cornahan, A M Colley *ACS Polym. Prepr.*, 1972, **20**(2) 353
111. G L Nelson, E J Hixson, E P Denike *J. Combust. Toxicol.*, 1978, **5** 222
112. C J Hilado, C L Slattengren, A Fryst, et al. *J. Combust. Toxicol.*, 1976, **3** 270
113. V V Korshak, S V Vinogradova *Poliarilaty* (Polyarylates), Izd. Nauka, Moscow, 1964
114. Z K Brzozoski, J Kielkiewicz, Z Gozlowski *Angew. Makromol. Chem.*, 1975, **44** 1
115. J Kielkiewicz, S Porejko *Angew. Makromol. Chem.*, 1979, **78** 75
116. Z K Brzozowski, J Kaczorowski, C Traczewski *Prepr. Int. Symp. Macromolec. Helsinki*, 1972, Vol. 4, Sec. 3, p. 373
117. Z K Brzozowski *XXXI IUPAC Macromolecular Symposium. Merseburg (GDR), 1987*, Microsymp. I. Abstracts, p. 60
118. A M Kharaev et al *Vysokomol. Soedin., Ser. A*, 1986, **28**(6) 1325
119. Z K Brzozowski, J Kielkiewicz, S Porejko, J Kaczorowski, US P. 3 887 522, 1975
120. Z K Brzozowski, J Kielkiewicz, S Porejko, J Kaczorowski, B. P. 1 384 975, 1975
121. Z K Brzozowski, J Petrus, J Dubczynski *J. Macromol. Sci., Chem.*, 1979, **A13**(17) 887
122. Z K Brzozowski *Chem. Prum.*, 1976, **26** 315
123. Z K Brzozowski, B Jozwik *J. Photochem.*, 1986, **35**(3) 341
124. Z K Brzozowski, J Kielkiewicz, K Bukat, et al. *II Internat. Conf. Symp.*, 1979, 3B
125. Z K Brzozowski, J Kielkiewicz, K Goslanka *Plast. Kautsch.*, 1979, 26
126. Z K Brzozowski, S Porejko, J Kaczorowski, J Kielkiewicz US P. 3 856 558, 1975
127. A K Mikitaev et al. *Vysokomol. Soedin., Ser. B*, 1983, **25**(12) 916
128. A I Kharaev, E R Kekharsaeva, G B Shustov, V T Dorofeev *Polikondensatsionnye Protsessy i Polimery* (Polycondensation Processes and Polymers), Izd. Karbardino-Balkar. Gos. Univ., Nal'chik, 1984, p. 51
129. S V Plyasovskaya, M A Voronina, L D Khokhlyavina *Vopr. Khim. Khim. Tekhnol.*, 1983, **72** 43; *Chem. Abs.*, 1984, **101** 171 863
130. A M Kharaev et al. *Vysokomol. Soedin., Ser. A*, 1986, **28**(6) 1325
131. A K Mikitaev et al *Vysokomol. Soedin., Ser. A*, 1984, **26**(6) 1207
132. E R Kekharsaeva, A K Mikitaev, G B Shustov, et al. *Plast. Massy*, 1985, (7)
133. A Zh Taova, S F Koshieva, A M Kharaev, Z M Betrozova *Polkondensatsionnye Protsessy i Polymery* (Polycondensation Processes and Polymers), Izd. Kabardino-Balkar. Gos.Univ., Nal'chik, 1985, p. 133; *Ref. Zh. Khim.*, 1986, 14S347
134. Z K Brzozowski, B Zurakowska *IUPAC Macro-83, Bucharest,* 1983, VII-26, p. 343
135. Z K Brzozowski, B Jozwik, K Wojhar, P Priffer *IUPAC Macro-83, Bucharest*, 1983, CII-27, p. 347
136. Z K Brzozowski, P Kaminski *Pr. Nauk. Inst. Technol. Org. i Tworzyw. Sztucz. Wrocl.*, 1985, (39) 25; *Ref. Zh. Khim.*, 1986, 15S189
137. F J Williams, A S Hay, H M Relles, et al. *New Monomers and Polymers* (Edited by B M Culbertson et al.), Plenum Press, New York–London, 1984
138. R N Johnson *J. Polym. Sci.*, 1967, A1, **5**(4) 1237

139. A S Hay *Adv. Polym. Sci.*, 1967, **4** 496
140. Z K Brzozowski, G Rokicki, B Pogorzelska-Marciniak *Angew. Makromol. Chem.*, 1976, **43** 59
141. Z K Brzozowski, J Kielkiewicz *Polimery*, 1973, **18** 315
142. R A Clendinning, A G Farnham, R N Johnson *ACS Polymer Prepr.*, 1986, **27**(1) 478
143. J B Rose *ACS Polymer Prepr.*, 1986, **27**(1) 480
144. R N Johnson et al. *J. Polym. Sci.*, 1967, A1, **5**(9) 2375
145. T A Attwood, P C Dawson, J L Freeman, et al. *Polymer*, 1981, **22** 1096
146. D R Kelsey US P. 4 638 944
147. I Fukawa, H Komeda, H Sakurai *Japanese Appl.* 61-143 438; *Ref. Zh. Khim.*, 1987, 12S521
148. I Fukawa, H Komeda, H Sakurai *Japanese Appl.* 61-200 127; *Ref. Zh. Khim.*, 1987, 17S440
149. T Lesiak, J Nowakowski *Vysokomol. Soedin., Ser. B*, 1980, **22**(7) 498
150. G A Adam, M A Husoin, M M Barbooti *Thermochim. Acta*, 1980, **37** 173
151. T Takekoshi *Polymer J.*, 1987, **19**(1) 191
152. E Radlmann, W Schmidt, G E Nischk *Makromol. Chem.*, 1969, **130** 45
153. Z K Brzozowski, A Grabowska-Rostek, Z Przybysz *J. Macromol. Sci., Chem.*, 1981, **A16**(7) 1193
154. Z K Brzozowski, Z Przybysz, A Grabowska-Rostek *J. Macromol. Sci., Chem.*, 1981, **A16**(7)
155. V V Korshak, A L Rusanov, S Kh Fidler, et al. *Trudy X Mezhdunarodnogo Mikrosimpoziuma po Polikondensatsii. Solnechnyi Bereg (NRB). 1985* [Proceedings of X International Microsymposium on Polycondensation. Slanchev Brjag (Bulgaria). 1985], Izd. Bolg. Akad. Nauk 1986, p. 123.
156. V V Korshak, A L Rusanov, N Z Makharashvili, G V Kazakova *Plast Massy*, 1987, (11) 18
157. V T Dorofeev, V N Sokolenko, I A Oleksyuk, L A Seredina *Vysokomol. Soedin., Ser. B*, 1978, **20**(10) 737
158. A I Burya et al. *Vopr. Khim. Khim. Tekhnol.*, 1979, (57) 109
159. V T Dorofeev *Vysokomol. Soedin., Ser. B*, 1981, **23**(12) 925
160. A C Karydas, W T Whang, E M Pearce *J. Polym. Sci., Polym. Chem. Ed.*, 1984, **22**(3) 847
161. E M Pearce *Polym. Prepr. Jpn.*, 1983, **32**(5) 975
162. V V Korshak, A L Rusanov, S Kh Fidler, et al. *Vysokomol. Soedin., Ser. B*, 1985, **27**(3) 220
163. P M Hergenrother *Angew. Makromol. Chem.*, 1986, **145/146** 323
164. P M Hergenrother *Polymer J.*, 1987, **19**(1) 73
165. V V Korshak et al *Faserforsch. Textiltechn.*, 1978, **29**(11/12) 649
166. W Wrasidlo, J M Augl *Macromolecules*, 1970, **3**(5) 544
167. P M Hergenrother *J. Macromol. Sci. Rev.*, 1971, **C6**(1) 1
168. P M Hergenrother *J. Appl. Polym. Sci.*, 1974, **18** 1779
169. P M Hergenrother *Polym. Eng. Sci.*, 1976, **16**(5) 303
170. J M Augl, J V Duffy *J. Polym. Sci.*, 1971, **A9** 1343