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Trends in the development of polycondensation and condensation polymers

S V Vinogradova, V A Vasnev

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Abstract. New trends in the development of polycondensation methods, elucidation of the main principles of macromolecular design of polymeric chains and preparation of novel promising condensation polymers are considered and analysed. The bibliography includes 152 references.

I. Introduction

Polycondensation is one of the most important methods for the synthesis of polymers. This is based on an elementary substitution reaction and opens up access to an immense variety of polymers — from linear aliphatic compounds to complex fused aromatic and heterocyclic systems including highly branched dendritic polymers.

Starting from 1833,[1] polycondensation has invariably attracted the keen attention of investigators. At present, this branch of polymer chemistry is being intensely developed owing to the discovery of hitherto unknown reactions leading to the formation of high-molecular-mass compounds. However, a search for alternative polycondensation routes and their intensification, elaboration of principles of macromolecular design, preparation of novel promising polymeric materials and detailed analysis of their properties still remain topical problems. These trends are considered in the present review.

II. Novel types of polycondensation

Studies aimed at the search for ways of involvement of less reactive starting compounds and new types of monomers in known polycondensation processes have been carried out since the 1980 – 1990's. These processes include carbonylation polycondensation,[2–12] polycondensation of monomers that undergo ring–chain isomerisation,[13–19] polynitrosubstitution,[20–22] radical-ion polycondensation in the presence of samarium iodide,[23–29] catalytic polycondensation of arylene halides, [30–43] *etc*. Some of these processes will be considered in the subsequent sections.

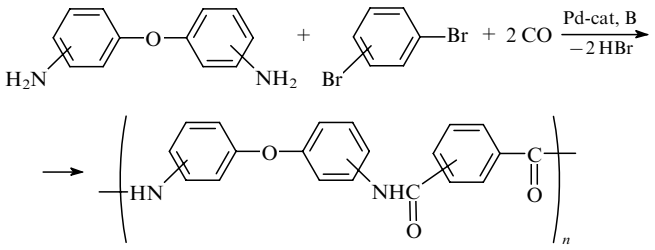
S V Vinogradova, V A Vasnev A N Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, 119991 Moscow, Russian Federation. Fax (7-095) 135 50 85. Tel. (7-095) 135 92 25 (S V Vinogradova), (7-095) 135 92 12. E-mail: vasnev@ineos.ac.ru (V A Vasnev)

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1. Carbonylation polycondensation

The recently discovered carbonylation polycondensation reaction [2–12] is based on the use of carbon monoxide and aromatic dihalogen derivatives instead of conventionally employed dicarboxylic acids or their activated derivatives (most commonly, dichlorides). These compounds react with dinucleophiles (*e.g.*, diamines, dihydrazides, diphenols, aminophenols, *etc*.) in the presence of palladium catalysts to yield the corresponding high-molecular-mass products, *viz*., polyamides, polyhydrazides, polyarylates, *etc*. This approach to the synthesis of polymers directly from CO and aryl halides is attractive, since the latter are readily available by direct halogenation of aromatic compounds and are rather stable, and carbon monoxide is very cheap. In contrast, aromatic dicarboxylic acid chlorides are hydrolytically unstable and the acids themselves are synthesised in many steps. This approach was used in the synthesis of, *e.g.*, polyamides (Scheme 1).

Scheme 1



B is a base.

Carbonylation polycondensation was used in the synthesis of aromatic, aliphatic-aromatic and silicon-containing polyamides. Using polycondensation of *m*-dibromobenzene, 4,4′-diaminodiphenyl oxide and CO as an example, it was shown that the best results were obtained if the reaction was carried out in *N*,*N*-dimethylacetamide (DMA) (115 °C, 1.5 h) using the $[PdCl_2(Ph_3P)_2]-Ph_3P$ complex as a catalyst and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base.[4] The reaction rate and the length of the polymeric chain increase if diiodoarenes are used instead of dibromides.[5] Thus the polycondensation of *m*-diiodobenzene with 4,4′-diaminodiphenyl oxide at a CO pressure of 0.1 MPa yields a polyamide with a molecular mass (*M*) of 24 000 at 90 °C in 2 h, whereas the molecular mass of a polymer prepared from *m*-dibromobenzene does not exceed 14 000 after 6 h. Moreover, the molecular mass of the polymer formed is even higher (up to 91 000 kDa) if the reaction is carried out in the presence of a 5% excess of the diamine.

Carbonylation polycondensation was used in the synthesis of polyarylates and aliphatic-aromatic polyesters.[4–6] In the former case, the solutions of the polymers formed had a logarithmic viscosity of up to 0.69 dl g^{-1} in *o*-chlorophenol, in the latter case, the viscosity was 0.18–0.36 dl g^{-1} (see Refs 6 and 7). The polycondensation of 4,4′-dibromodiphenyl oxide with 2,2-bis(4-hydroxyphenyl)propane in an atmosphere of CO in chlorobenzene as a solvent was carried out at 115 °C using a DBU–K_2CO_3 mixture as a base and various palladium derivatives {*e.g.*, the $[PdCl_2(Ph_3P)_2]$–PPh_3 complex} as catalysts and was complete within 3 h. The M_n and M_w values for the polyacrylate were equal to 70 000 and 88 000, respectively; the logarithmic viscosity (η_{log}) in chlorobenzene was 0.51 dl g^{-1}.

The best results in the synthesis of polyhydrazides from dibromoarenes, dicarbohydrazides and CO were obtained when the polycondensation was performed in DMSO or DMF (T = 95 °C) in the presence of $Pd(Ph_3P)_4$ and DBU.[8] A polymer with η_{log} = 0.65 dl g^{-1} was prepared starting from 4,4′-dibromodiphenyl oxide, CO and terephthalohydrazide.[8]

High-molecular-mass polyether ketoamides were synthesised using Pd-catalysed polycondensation of dibromoarenes containing etheroxo groups with aromatic diamines and CO.[9] Reactions of diiodoarenes with bis(*o*-aminophenols) and CO yield polyhydroxyamides with molecular masses M_w = 34 000–49 000 and M_n = 13 000–31 000; their thermal polycyclisation (T = 250–300 °C) gave the corresponding polybenzooxazoles.[10]

Tetraiodobenzene, tetraiodo-*p*-xylene, 3,3′,4,4′-tetraiododiphenyl sulfone and 1,4-dibromo-2,5-diiodobenzene were used as the halogen derivatives in the synthesis of polyimides.[4, 11] Thus a polyimide with M_w = 28 000 and M_n = 17 000 was synthesised in 95% yield from 1,2,4,5-tetraiodobenzene and 5-amino-3-(4-aminophenyl)-1,1,3-trimethylindane under CO pressure of 0.78 MPa in the presence of DBU, 6 mol.% of the complex $[PdCl_2(Ph_3P)_2]$ and 12 mol.% of triphenylphosphine (DMA, 115 °C, 24 h).
High-molecular-mass polyamidoimides were prepared from 4-chloro-*N*-(4-iodophenyl)phthalide, bis(aminophenyl) oxide and carbon monoxide using carbonylation polycondensation in DMA or *N*-methylpyrrolidone (*N*-MP) (T = 100 °C) in the presence of a palladium catalyst.[12]

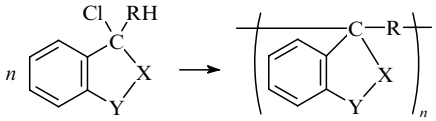
However, the attempts to replace expensive palladium catalysts by nickel catalysts [2] were unsuccessful. Obviously, the search for inexpensive efficient catalytic systems for the carbonylation polycondensation is a problem for future studies.

Thus, carbonylation polycondensation opens up new prospects for the synthesis of diverse polymers. It may be hoped that in the near future it will be used not only for preparation of novel polymers, but also for optimisation of synthetic procedures.

2. Polycondensation of monomers that undergo ring–chain isomerisation

Electrophilic substitution of monomers that undergo ring-chain isomerisation (or tautomerisation) is a new approach to the synthesis of aromatic polymers. Carboxylic acid pseudochlorides are examples of such non-traditional monomers.

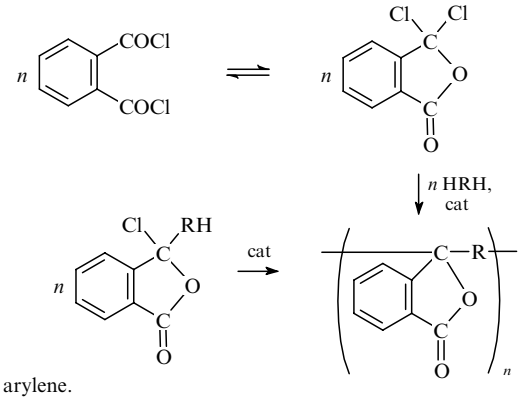
According to the scheme:



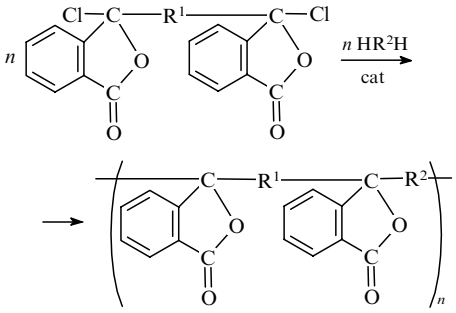
R is arylene; X = O, NAlk, NAr; Y = CO, SO_2

the growth of the polymeric chain results from the formation of a C–C bond between the carbon atoms of aromatic and heterocyclic (phthalide, phthalimidine and sulfophthalimide) nuclei. Such a polycondensation can be used for the preparation of polyarylenephthalides (X = O, Y = CO), polyarylenephthalimidines (X = NAr, Y = CO) and polyarylenesulfophthalides (X = O, Y = SO_2).

The synthesis of polyarylenephthalides from carboxylic acid pseudochlorides and their properties have been studied in much detail.[13–19]



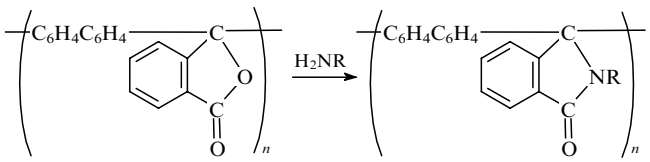
R is arylene.



R^1,R^2 are arylenes.

Chlorinated hydrocarbons (dichloromethane, dichloroethane, *etc.*) or nitrobenzene were used as solvents; the latter proved to be the most versatile. The temperature was varied from 770 to 140 °C; metal halides (*e.g.*, $ZnCl_2$, $AlCl_3$, $AlBr_3$, $FeCl_3$, $InCl_3$, $SbCl_5$, *etc.*) (0.01–1.5 mol per chloride group) were used as catalysts.[13] For example, the reaction occurs selectively and yields a polymer with M = 46 000–60 000 under conditions that are optimum for the synthesis of poly-*p*-diphenylenephthalide from 4-(3-phthalyl-3-chloro)biphenyl (monomer concentrations, 2–3 mol $litre^{-1}$, $SbCl_5$ (7 mol.%–10 mol.%) or $InCl_3$ (3 mol.%–10 mol.%) as a catalyst, nitrobenzene, 100–110 °C. The same reaction was performed in the so-called 'precipitation system', *i.e.,* in the presence of $AlCl_3$ in dichloroethane (20 °C, 24 h).[15] In the early steps, this reaction occurs in a homogeneous medium and then the polymer formed is precipitated to give a product with a higher molecular mass.

The presence of reactive groups in polyarylenephthalides opens up broad prospects for further chemical modifications at the lactone ring. Thus reactions of these polymers with amines yield *N*-substituted polyarylenephthalimidines:[17, 18]

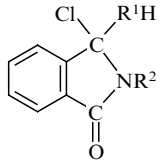


R = Me, Bu^n, C_8H_{17}, $C_{18}H_{37}$, Ph, C_2H_4OH, *etc.*

The properties of these compounds depend on the nature of the substituent at the nitrogen atom. With an increase in the length of the aliphatic substituent (from C_1 to C_{18}), the softening temperatures of the polymers decrease from 390 to 80 °C and the decomposition temperatures decrease from 360 to 260 °C. The possibility of thermal dehydration of polybiphenylene-*N*-(β-hydroxyethyl)phthalimidine, which yields an insoluble structurised polymer, has been demonstrated. A polymer which contains

phenyl substituents at the nitrogen atom manifests the best thermal characteristics: its softening temperature and the temperature of the onset of decomposition are equal to 450 and 475 °C, respectively. Thermolysis of polyterphenylenephthalide at 390–450 °C results not only in the cleavage of its polymeric chain but also in its structurisation.[16]

Polyarylenephthalimidines can also be synthesised by direct polycondensation of monomers of appropriate structures.



R^1 is arylene; R^2 = Alk, Ar.

It has been noted that, unlike the synthesis of polyarylenephthalides, the polycondensation in nitrobenzene cannot be realised with $SbCl_5$ and $InCl_3$ as catalysts. High-molecular-mass polyarylenephthalimidine could only be prepared in a reaction catalysed by $AlCl_3$ (2.5–3.5 equiv.).[18]

The synthesis of high-molecular-mass polyarylenesulfophthalides with phenylene fragments alternating with sulfophthalide groups in the main chains of the macromolecules has been carried out.[19] High reactivity of the sulfophthalide groups is a characteristic feature of these polymers. For example, the opening of the sulfophthalide ring under the action of aqueous solutions of alkalis results in quantitative formation of the corresponding polysulfonic acid salts. Such sulfonic acids can be regarded as a special type of polyelectrolyte, *viz*., aromatic polymers with side ionogenic sulfonate groups. In addition, the presence of triphenylmethane fragments determines the unusual optical properties of these compounds.[19]

Thus, the use of monomers of carboxylic acids of the pseudochloride type, which undergo ring-chain isomerisation, in the synthesis of polymers opens up attractive prospects for the development of novel polymers. The materials thus prepared combine high thermal and chemical stabilities with excellent solubilities in organic solvents, good physicomechanical characteristics and various unique properties.

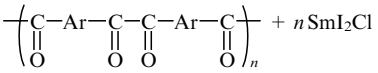
Studies in this area were begun in the 1990's and are ongoing. They are aimed predominantly at the in-depth analysis of specific (thermal, electrical, optical, *etc*.) properties of these polymeric systems.

3. Radical-ion polycondensation in the presence of samarium iodide

The efficient syntheses of organic compounds using bivalent metal halides of the lanthanide family, which are known to be potent reductants, have been documented relatively recently.[23] The use of such compounds as reaction initiators and coreactants ensures highly selective reactions under mild conditions and at high rates. SmI_2, which possesses an unusually high redox potential (for compounds soluble in organic solvents) is the most reactive amongst bivalent lanthanide halides.

Thus α-diketones are synthesised from aromatic acid chlorides and SmI_2 within several minutes in THF at room temperature (yields 70%–80%).[24] The use of aromatic dicarboxylic chlorides in such reactions is a relatively simple route to the synthesis of poly-α-diketones.[25–27]

$$n\,\mathrm{ClOCArCOCl} + n\,\mathrm{SmI_2} \longrightarrow$$



Ar = *m*-C_6H_4, *p*-C_6H_4, $C_6H_4OC_6H_4$, $C_6H_4C(CF_3)_2C_6H_4$, *etc*.

Based on the literature data of the mechanism of condensation of acid chlorides in the presence of SmI_2,[25] it may be supposed that it is radical ions generated under the action of compounds with high redox potentials that are the reactive species in the polycondensation. Their dissociation yields acyl radicals which are rapidly reduced into acyl anions; the latter react with the second acid chloride group to give α-diketone fragments:

$$\mathrm{a-A-a} + \mathrm{SmI_2} \longrightarrow [\mathrm{a-A-a}]^{\bullet -}\mathrm{SmI_2^+},$$

$$[\mathrm{a-A-a}]^{\bullet -}\mathrm{SmI_2^+} \longrightarrow [\mathrm{a-A-a}]^{\bullet -} + \mathrm{SmI_2^+},$$

$$[\mathrm{a-A-a}]^{\bullet -} \longrightarrow \mathrm{a-A^{\bullet}} + \mathrm{a^-},$$

$$\mathrm{a-A^{\bullet}} + \mathrm{a-A^{\bullet}} \longrightarrow \mathrm{a-A-A-a},$$

$$\mathrm{SmI_2^+} + \mathrm{a^-} \longrightarrow \mathrm{SmI_2a},$$

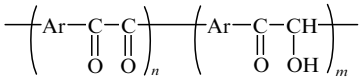
$$\mathrm{a-A^{\bullet}} + \mathrm{SmI_2} \longrightarrow \mathrm{a-A^-SmI_2^+},$$

$$\mathrm{a-A^-SmI_2^+} + \mathrm{a-A-a} \longrightarrow \mathrm{a-A-A-a} + \mathrm{SmI_2a}.$$

a = Cl, F; A = −C(O)ArC(O)−.

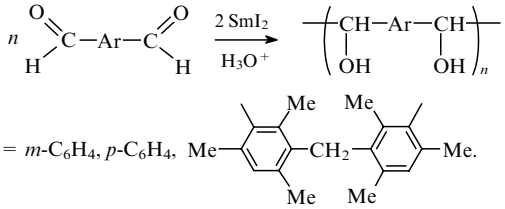
Thus, such a polycondensation can be termed as radical-ion polycondensation.

Studies of the pattern of this process have shown that the structures and yields of the polymers formed strongly depend on the reaction conditions, *viz*., the order of addition of the reagents, their ratios, concentrations and reaction time.[27] The units in these polymers often possess different structures; they contain hydroxymethylene groups along with α-diketone groups as a result of partial reduction of the carbonyl group by samarium iodide.



Polymers devoid of hydroxy ketone groups could be prepared only by adding a solution of SmI_2 in a THF–methyl iodide mixture to a solution of a dicarboxylic acid dichloride in THF (0.3–0.03 mol litre^{-1}, SmI_2 : substrate = 2.8 : 1.0, 30 °C, 20 min). The addition of a dicarboxylic acid dichloride to a solution of SmI_2 (4 : 1) yielded polymers with different-unit structures, the content of the diketone and hydroxyketone groups being the same.[27]

Radical-ion polycondensation in the presence of SmI_2 was also used in the synthesis of polypinacones from aromatic dialdehydes.[28]



In this case, the polymers had relatively low molecular masses (12 000–15 000).

The presence of reactive functional groups, *viz*., keto and hydroxy groups, in poly-α-diketones and polypinacones, opens prospects for their further chemical modification. For example, zirconocene dichloride reacts with the hydroxy ketone groups of the polymer to form covalent bonds owing to the presence of the hydroxy groups and coordination compounds due to interaction with the keto groups. Such polymers hold promise as catalysts for certain organic reactions.[29]

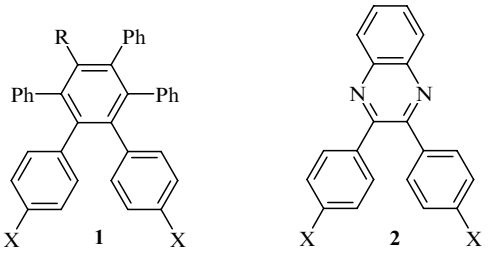
4. Polycondensation with arylene halides catalysed by palladium and nickel complexes

Since the 1990's, the need for polymeric materials with specific properties, such as electroconductivity, photo- and electroluminescence, third-order nonlinear optical activity, *etc*., has stimu-

lated studies on polycondensation of aromatic dihalides with alkenes and alkynes, aromatic diboronic acids, aromatic organometallic compounds, *etc*. Dehydrohalogenation and dehalogenation reactions, which are catalysed by palladium and nickel complexes and result in the formation of the C–C bond, are usually referred to as cross-coupling reactions. They were used in the synthesis of polyaryleneethynylenes $(-Ar-C\equiv C-)_n$,[30–36,42] polyconjugated polyarylenevinylenes $(-Ar-CH=CH-)_n$[30,32,34,37–40] as well as carbo- and heterocyclic polyarylenes.[32,41]

The use of aromatic halides, which are much more accessible than the monomers used in conventional polycondensation processes, is the advantage of this method. As a rule, polyconjugated polymers are poorly soluble in organic solvents due to high rigidity of their macromolecules, which significantly restricts their practical applications. Pd- and Ni-catalysed polycondensation circumvents this limitation, since side substituents or bulky groups can easily be introduced into the starting aromatic halides or ethynyl derivatives, which favour their solubility.[30,33,34]

Thus relatively short-chain polyaryleneethynylenes (M = 5800–8000) readily soluble in amide solvents were prepared from dibromides and diiodides derived from branched aromatic heterocyclic compounds (hexa- and pentaphenylarylenes, compounds **1**), quinoxalines, compounds **2**, phenylimidazoles



R = H, Ph (**1**); X = Br, I.

and diethynyl aromatic compounds in the presence of palladium catalysts (DMA, 90 °C, 6–8 h).[30,33]

Pd-Catalysed polycondensation was used in the synthesis of some novel regular polyaryleneethynylenes from dibromides and substituted diethynyloligothiophenes, -anthracenes and -benzenes. Such polymers (especially those containing anthracene fragments) are characterised by high quantum yields of luminescence.[31]

The synthesis of polyarylenevinylenes was carried out using ethylene and divinylbenzene as the starting monomers.[37,38]

The reaction of *p*-divinylbenzene with dialkoxy-substituted *p*-diiodobenzene derivatives gave polymers (M_w = 32 000–62 000) of the general formula

$$-\!\left(CH{=}CHC_6H_4CH{=}CHC_6H_2(OR)_2\right)_n-,$$

R = C_mH_{2m+1}, m = 4, 7, 8, 12, 16,

which are readily soluble in organic solvents and manifest liquid crystalline properties.[40]

Homopolycondensation of dibromotetraarylethylenes in the presence of a Ni(0) complex prepared *in situ* from anhydrous $NiCl_2$, Ph_3P, bipyridyl and Zn in a dipolar aprotic solvent (100 °C, 2 h) resulted in polyarylenevinylenes containing phenyl substituents in the vinylene group:[43]

$$-\!\left[C_6H_4C(Ar){=}C(Ar)C_6H_4\right]_n-,$$

Ar, phenyl; 2,4,6-triphenylphenyl; 2,4,6-tris(biphenylyl)phenyl.

Polymers that contain branched polyphenyl substituents usually possess fairly high quantum yields of luminescence (22%–23%).

A series of unsaturated polymers of the polycinnamide type

$$-\!\left(ArCH{=}CHCONHAr'NHCOCH{=}CH\right)_n-$$

have been synthesised[30] from aromatic *N*,*N*′-arylenediamides and arene dihalides in the presence of palladium catalysts. Thus a high-molecular-mass polymer with M_n = 93 000 and M_w = 488 000 has been synthesised from 4,4′-diiododiphenyl oxide and bisacrylamide with Ar′ = *p*-$C_6H_4OC_6H_4$-*m*.

Polycondensation cross-coupling with the use of transition metal complexes as catalysts allows preparation of various carbo- and heterochain polymers (*e.g*., substituted polyphenylenes, polyimides, polyether ketones, polythiophenes, *etc*.) (for review, see Ref. 41).

The above-described polycondensation, which occurs under relatively mild conditions, opens up new prospects for the synthesis of structurally diverse polymers. However, it demands further investigation, especially as regards the synthesis of polymers with high molecular masses, primarily of linear polyconjugated polymers possessing valuable electrical and optical properties. Systematic development of this approach aimed at the design of branched conjugated dendritic polymers and investigation of their optical properties is of special interest. And, of course, special attention should be given to the search for, and development of, novel efficient catalytic systems for cross-coupling reactions including catalytically active and selective metal–polymer composites.

5. Polycondensation in non-traditional media

It is known that many polycondensation processes demand large amounts of toxic or flammable organic solvents which are often nonrecoverable. In this context, a search for alternative reaction media is a topical ecological and economical problem. Therefore, supercritical carbon dioxide[44] and the so-called 'ionic liquids'[45,46] have attracted considerable attention in recent decades.

Supercritical carbon dioxide is interesting in that it manifests the properties of an inert solvent for numerous substances, on the one hand, and can be completely removed from the reaction mixture as a gas upon depressurisation, on the other hand.[44]

Ionic liquids usually represent organic salts or mixtures of organic and inorganic salts which exist in a liquid ionic state at, or close to, room temperature. Their main characteristic features include low vapour pressure, non-inflammability and the possibility to be repeatedly regenerated. Other advantages include high chemical and thermal stability; they are also good solvents for a broad range of compounds. Their melting points vary over a wide range — from −90 to 200 °C; in addition, these compounds manifest catalytic activity and other valuable properties.[45,46]

From the above, it follows that supercritical carbon dioxide and ionic liquids are promising media for polycondensation, however, their application is still poorly explored.[46,47] In contrast to polymerisation, there are very few examples of the use of supercritical carbon dioxide in polycondensation.[44] A recently published paper[47] is devoted to the use of this compound as a medium in the synthesis of polyimides based on a 4,4′-(hexafluoropropane-2,2-diyl)diphthalic dianhydride and 4,4′-(hexafluoropropane-2,2-diyl)aniline or diaminofluorene. This reaction was carried out at 130–180 °C for 3–6 h and under a CO_2 pressure of 32.5 MPa. It is noteworthy that polycondensation in CO_2 of a very high degree of purity [>99.997%, $c(H_2O)$ = 0.001%] yielded a polymer with a logarithmic viscosity as low as 0.14 dl g^{-1}, whereas polycondensation in the presence of small amounts of water gave higher-molecular-mass polymers. This suggests that in this case CO_2 plays a dual role of a solvent and a catalyst. Indubitably, polycondensation in supercritical CO_2 demands further investigation.

Some recently published papers describe polycondensation in ionic liquids.[48,49] These studies were the first to demonstrate the possibility in principle to perform the synthesis of condensation

polymers (polyimides and polyamides) in ionic solvents which are alternative to conventional organic solvents, and sometimes manifest catalytic activity, as in the synthesis of polyimides. 1,3-Dialkylimidazolium [bromide (**1**) and tetrafluoroborate], 1,3-dibutylimidazolium salts, *etc*., were used as the reaction media. The polycondensation of 1,4,5,8-naphthalenetetracarboxylic dianhydride with 5-amino-2-(4-aminophenyl)benzoimidazole in ionic liquid **1** at 180 °C with the concentrations of the starting compounds varying from 0.4 to 0.6 mol litre^{-1} afforded high-molecular-mass polynaphthoyleneimides (the logarithmic viscosity of a solution of the polymer in sulfuric acid was $\sim$ 0.6 dl g^{-1}). Polycondensation in an ionic liquid was successfully employed in the synthesis of high-molecular-mass aromatic polyamides. It is noteworthy that the rate of the polycondensation and the molecular mass of the polymer formed strongly depend on the nature of the ionic liquid cations. Using the synthesis of polyterephthalamide of 5-amino-2-(4-aminophenyl)benzoimidazole as an example, it was demonstrated that the ionic liquid used can be repeatedly regenerated.[48]

These data should be regarded as an initial step in the study of polycondensation in ionic liquids, which proved to be highly promising and deserving of further investigation.

* * *

On the whole, the novel types of polycondensation considered in this section significantly extend the range of its applications in the synthesis of high-molecular-mass compounds. Such methods open up new ways to the preparation of important special-purpose polymers needed in small amounts to suit the specific areas of their application.

III. Macromolecular design of condensation polymers

1. Construction of a polymeric chain in the course of polycondensation

A search for ways to a directed design of polymeric chains is the main challenge in polycondensation, since it is the only possibility to obtain materials with predetermined properties. This problem can be solved using different approaches. One of them is variation of the chemical structure of the monomers, which is widely employed at present (see Section III.3). The other consists of synthesis of copolymers or polymers from non-symmetrical monomers. This route is especially important, since it allows broad variations of specific characteristics of polymeric systems. However, this approach requires directed design of a polymeric chain, which is impossible without knowledge of the fundamental principles of formation of such chains in the course of polycondensation, *i.e*., the principles of macromolecular design.

Non-equilibrium acceptor-catalytic polyesterification was used as a model system. It is a detailed study of this type of polycondensation that has made it possible to establish the basic principles of macromolecular design, particularly with respect to different mechanisms of alternation of co-monomers and non-symmetrical monomers along the polymeric chain.[50–53] Copolycondensation of two co-monomers, *viz*., $y-M_2-y$ and $y-M_3-y$, *e.g*., 2,2-bis(4-hydroxyphenyl)propane, hexamethylene glycol, *etc*., with an intermonomer $x-M_1-x$ (*e.g*., terephthalic dichloride, *etc*.) entails different alternations of monomers along the polymeric chain in regularly alternating (RA), block (BL) and statistical (ST) modes.

$$2\,x-M_1-x + y-M_2-y + y-M_3-y \longrightarrow$$

$$\longrightarrow -(M_1-M_2-M_1-M_3)_n- \quad \text{RA}$$

$$\longrightarrow -(M_1-M_2-M_1-M_2-M_1-M_3-M_1-M_2-M_1-M_3)_n- \quad \text{ST}$$

$$\longrightarrow -(M_1-M_2)_n-(M_1-M_3)_m- \quad \text{BL}$$

x, y are terminal functional groups.

If polycondensation involves two monomers, one of which has a non-symmetrical 'head' and 'tail' structure (*e.g.,* β-hydroxyethyl ether of a diphenol), the limiting cases entail either regular alternation of the 'head-to-tail', 'head-to-tail' (HTHT) or 'head-to-head', 'tail-to-tail' (HHTT) types or statistic alternation.

$$x-M_1-x + y-M_2M_3-y \longrightarrow$$

$$\longrightarrow -M_1-M_2M_3-M_1-M_3M_2-M_1-M_2M_3-M_1-M_3M_2- \quad \text{HHTT}$$

$$\longrightarrow -M_1-M_2M_3-M_1-M_2M_3-M_1-M_2M_3- \quad \text{HTHT}$$

$$\longrightarrow -M_1-M_2M_3-M_1-M_2M_3-M_1-M_3M_2-M_1-M_2M_3- \quad \text{ST}$$

Prior to these studies, there was an erroneous concept that blocks built up of a more reactive monomer are formed in the initial steps of the reaction, provided the co-monomers possess different reactivities, which results in block-copolymers. If the reactivities of non-symmetrical monomers are different, it is the more reactive groups that react in the first step thus leading to the formation of 'head-to-head' or 'tail-to-tail' structures, which favours the formation of regular polymers consisting predominantly of these fragments.[54, 55] However, this hypothesis does not take into account the violation of the rule of non-equivalence of the functional groups, which is extremely important for polycondensation. This has led to formulation of improper rules.

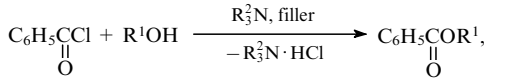
The generalisation of numerous experimental results, which take into account kinetic theory,[50–53] has made it possible to formulate the basic principles of a macromolecular design for non-equilibrium polycondensation. The presence of all monomers (irrespective of their reactivities) in the initial steps of the reaction favours the formation of statistical polymers, and deviation from this type of structure is related to a change in the reactivities of the functional groups of the intermonomer (symmetrical monomer). Gradual introduction of co-monomers into the reaction zone is not sufficient for the synthesis of block-copolymers.

In the case of one-step reactions, gradual addition of a symmetrical intermonomer into the solution of co-monomers favours the formation of block-copolymers (*i.e*., regular polymers of the HHTT type); the lengths of the blocks (*i.e*., the ratios of the 'head-to-head', 'tail-to-tail' fragments) reflect the differences in the reactivities of the co-monomers used. The prerequisites for the formation of block-copolymers by one-step non-equilibrium copolycondensation in a homogeneous system include noticeably different reactivities of co-monomers and the introduction of the intermonomer into the reaction zone at a rate lower than its reaction with the more reactive co-monomer. The passage of a one-step polycondensation to two-step and multistep processes significantly extends the potential of macromolecular synthesis and allows preparation of block-copolymers made up of blocks of required lengths. Using this approach, one can control the microstructure of a polymeric chain and thus regulate the properties of the polymers formed.

Further progress in the development of novel types of polycondensation, of non-equilibrium matrix polycondensation in

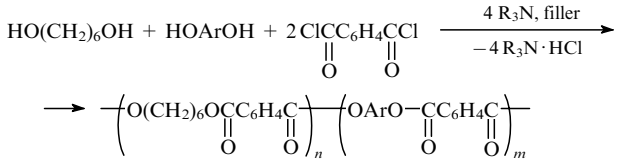
particular, has established a number of characteristic features, *e.g.*, the effect of a heterogeneous matrix on the formation of copolymer microstructure and other properties of polymeric systems.[3, 56–60] In contrast to polymerisation in the presence of fillers, which has been studied in great detail,[61, 62] polycondensation and polyaddition in the presence of a dispersed solid phase were first described in the 1970's. The subjects of these studies were polysiloxanes,[63] polyurethanes [64] and epoxide oligomers.[65] It was not until the 1990's that systematic studies of non-equilibrium polycondensation in the presence of fillers, such as graphite and molybdenum disulfide, were begun.[3, 56, 57]

Studies of model esterification



R^1 = Bu^n, Ph; R^2_3N = Et_3N, Py.

and copolyesterification



have shown that polyesters prepared in benzene in the presence of graphite had much higher molecular masses than polymers synthesised in the absence of graphite (Table 1), because the filler plays the role of a heterogeneous matrix. This influences the reactivities of functional groups and the ratios of chain propagation and termination rates.

Table 1. Effect of a matrix (graphite) on the molecular mass of a polyarylate prepared from 2,2-bis(4-hydroxy-3-chlorophenyl)propane and terephthalic dichloride.[56]

Matrix (mass %)	S [a] /m^2 g^{-1}	$[\eta]$ [b] /dl g^{-1}	$M \times 10^{-3}$
–	–	0.68	30
30	9.5	0.87	53
30	14.0	0.92	60
60	14.5	1.15	70

[a] Specific surface of the matrix. [b] The viscosity η was measured in THF at 25 °C.

In the absence of a filler in non-polar solvents (*e.g.*, benzene), the reactivity of phenol exceeds that of n-butanol 200-fold. The copolymers formed upon gradual introduction of terephthaloyl dichloride into the reaction zone have a block structure and are characterised by a microheterogeneity coefficient $K_m = 0.23$.†

In the presence of graphite (80 mass%), which has a specific surface of 14 m^2 g^{-1}, the activity of phenol in the acylation by aromatic acid chlorides is 3 times lower than in the absence of a filler, while that of butanol increases nearly 1.5-fold under similar conditions. As a result, the difference in the activities of phenolic and alcoholic groups decreases from 200- to 40-fold, *i.e.*, the difference in the reactivities of aromatic and aliphatic hydroxy groups is levelled off. As a result, the K_m value of copolymers of hexamethylene glycol and 2,2-bis(4-hydroxy-3-chlorophenyl)propane with terephthaloyl dichloride obtained in the presence of a filler is 0.53 rather than 0.23, *i.e.,* the structure of the copolymer becomes more statistical.

† The microheterogeneity coefficient K_m reflects the degree of orderliness of the copolymer units. At $K_m = 1$, the units of a macromolecular chain are distributed statistically, whereas at $K_m \neq 1$ the copolymer has a block structure, the size of its blocks increasing with a decrease in K_m.

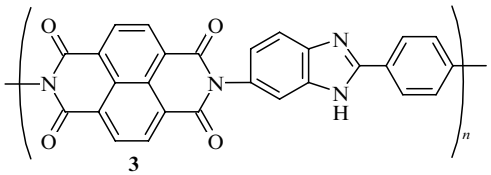
The changes in the reactivities of these components are caused by sorption, by the filler, of the active complexes formed. Since the acylation mechanisms of phenol and butanol are different, *viz.*, general basic (phenol) and nucleophilic (butanol),[66] the effects of graphite on each of these catalytic pathways are oppositely directed. It is this factor that influences the microstructure of the copolymers formed. The polycondensation in the presence of graphite also has a beneficial effect on the properties of the filled compositions formed. Apparently, this is due to the fact that the growth of macromolecules in a non-polar solvent in the presence of the filler largely occurs on its surface, which ensures more uniform distribution of graphite within the polymer in comparison with an analogous mixture prepared by simple mechanical blending of the components.[56]

As can be seen from Table 2, the 'synthetic' composition of a copolyester surpasses the corresponding 'mechanical' mixture in softening temperature, thermal stability, specific impact strength and specific electroconductivity. In addition, it has lower values of friction and wear factors.[56]

Table 2. Properties of compositions based on 2,2-bis(4-hydroxy-3-chlorophenyl)propane polyterephthalate prepared using different methods.[56]

Characteristics	Mechanical blending	Synthesis in the presence of a filler (graphite, 30 mass %)
Softening temperature /°C	220	260
Thermolysis (350 °C, vacuum),		
[CO] /10^3 mol $unit^{-1}$	9	1
[CO_2] /10^3 mol $unit^{-1}$	63	2
Specific impact strength /kJ m^{-1}	45	118
Specific electroconductivity /10^{13} Ω^{-1} m^{-1}	1	500

Interesting results were obtained when non-equilibrium acceptor-catalytic copolyesterification was carried out in the presence of hetero- and carbochain polymeric matrices.[58–60] These included 'active matrices', *i.e.*, polymers containing oxygen or nitrogen atoms in the main chain which can form hydrogen bonds with hydroxyl-containing monomers, such as polyphenylquinoxaline (a polyether based on 2-phenylquinoxaline), polynaphthoyleneimidobenzoimidazole **3** [a polyimide based on naphthalene-1,4,5,8-tetracarboxylic dianhydride and 5-amino-2-(4-aminophenyl)benzoimidazole], polyethylene oxide



3

and 'inert matrices', which do not react with monomers (*e.g.*, hyper-cross-linked polystyrene). The latter had a well-developed internal surface of their granules and differed from one another in pore size and structure of the cross-linking reagent (the cross-linking bridges are $-CH_2-$ or $-CH_2C_6H_4CH_2-$ groups, the pore sizes vary from 10 to 850 Å).

The results obtained suggest that the microstructures of the copolyesters formed with polymeric matrices introduced into the reaction system depend on the following factors, *viz.*, the presence and accessibility of nucleophilic sites which influence the kinetic parameters of intermonomer–co-monomer interactions, the convergence of reactivities of bisphenol and glycol, the presence and

sizes of pores in matrices and the ratios of sizes of pores and co-monomer molecules.

If porous matrices are used, two processes may occur simultaneously, which have opposite effects on the formation of the copolymer microstructure, *viz*., gradual desorption from the surface of the matrix, which results in an increase in K_m, and selective desorption of monomers from matrix pores, which decreases K_m (the so-called 'sponge effect'). Depending on the ratios of pore sizes of polymeric matrices to the molecular sizes of the co-monomers, one of these processes will predominate, which is reflected on the degree of the block structure of the copolymer formed. The use of polymeric matrices differing in the physicochemical properties of their particles opens up new possibilities for the synthesis of copolymers, since this allows purposeful variation of the microstructure of the chain formed and, correspondingly, the properties of the target product.

Thus it was found that copolymers having different microstructures [*e.g*., block ($0.3 < K_m < 1$) or statistical ($K_m = 1$)] can be prepared by copolycondensation of terephthaloyl dichloride with 2,2-bis(4-hydroxy-3-chlorophenyl)propane and hexaethylene glycol in the presence of triethylamine (benzene, 40 °C) at different concentrations of polyphenylquinoxaline or hypercross-linked polystyrene.[58, 59] Some examples of microstructures of copolyterephthalates prepared with the use of polymeric matrices are given in Table 3.

Table 3. Microheterogeneity coefficients of copolyterephthalates obtained in the presence of polymeric matrices (62 mass % Et_3N, benzene, 40 °C).[59]

Co-monomers	Matrix	K_m
DCD – HMG	PPQO	1.11
DCD – HMG	PEO	0.50
DCD – HMG	PS 10	0.89
DCD – HMG	PS 75	0.25
DMD – HMG	PS 10	0.92
DMD – HMG	PS 850	0.26
PP – DCD	PS 10	0.89
PP – DCD	PS 850	0.72

Notes. Abbreviations: HMG, hexamethylene glycol; DCD, 2,2-bis(4-hydroxy-3-chlorophenyl)propane; DMD, 2,2-bis(4-hydroxy-3-methylphenyl)propane; PP, bis(4-hydroxyphenyl)fluorene; PPQO, polyphenylquinoxaline; PS 10, polystyrene (pore size 10 – 15 Å); PS 75, polystyrene (pore size 75 – 85 Å); PEO, polyethylene oxide; PS 850, polystyrene (pore size 850 – 950 Å).

It may thus be expected that the use of polymeric matrices in polycondensation can in principle result in the manifestation of such effects as changes in the local concentrations of functional groups of reactants and 'sponge effects', *i.e*., initial sorption of monomers by the matrix with subsequent gradual desorption over the course of the reaction. This accounts for the changes in the reactivities of functional groups and conformations of molecules and for enhanced interactions of the macromolecules formed with the matrix.

In predicting the further fate of matrix-assisted polyesterification, one may suppose that one of the trends will be directed towards increasing the conformational specificity of this reaction. This will enable improvement of the microstructure of the polymeric chain if conformationally regular polymers are synthesised.

Polymeric matrices were also used for polycyclocondensation of tetracarboxylic dianhydrides with diamines.[67] In this case, amorphous cardo polyimides prepared from pyromellitic dianhydride and 3,3-bis(4-aminophenyl)phthalide or diphenyl oxide-3,3′,4,4′-tetracarboxylic dianhydride and 9,9-bis(4-aminophenyl)-fluorene, which are readily soluble in organic solvents and in reaction media, were used as matrix polymers.

Polyimides based on diphenyl oxide-3,3′,4,4′-tetracarboxylic dianhydride and 4,4′-diaminodiphenyl oxide or 5-amino-2-(4-aminophenyl)benzoimidazole and a polyimide from pyromellitic dianhydride and 9,9-bis(4-aminophenyl)anthrone were the target polymers. Their processability into films from solutions or into moulded articles from melts is difficult (or virtually impossible) because of their insolubility and high softening temperatures.

Sequential polycyclisation of these monomers in fusible catalytic media containing *p*-nitrotoluene (or diphenyl sulfone) and benzoic acid together with matrix cardo polyimides synthesised in previous steps in the same medium yielded novel polymeric systems. The latter differ from the corresponding crystalline polyimides synthesised by standard methods both in structures and properties (solubility, thermal stability, strength, *etc*.), which extends the range of their processability and practical applications. The data obtained demonstrate a high degree of control over the properties of these polymer – polymeric systems. Copolymers having both block and statistical structures should be formed, although this suggestion needs further verification.

The widening of the scope of these investigations is of indubitable interest. First of all, one should pay attention to the formation of systems from other classes of polymers and soluble matrix polyimides and the use of other polymers as matrices. It can be expected that the rate of formation of such polymers, their molecular masses and structures will be controlled, which will enable the preparation of finely dispersed homogeneous products and, if necessary, molecular composites. This offers an opportunity to improve the properties and processabilities of incompatible or partly compatible polymers in comparison with mixtures obtained by simple mechanical blending of the corresponding components.[67]

2. Polycondensation – polymerisation systems

The good solubility of polyheteroarylenes containing cardo and fluorine-containing groups in both common organic solvents and some unsaturated monomers has prompted an interesting route to the synthesis of novel polycondensation – polymerisation systems. Radical polymerisation and copolymerisation of (meth)acrylates, fluoro(meth)acrylates, styrene, acrylonitrile and other monomers in the presence of variable amounts of polyheteroarylenes (cardo and fluorine-containing polyimides, polyarylates, *etc*.) were used for the synthesis of novel soluble high-molecular-mass products.[68 – 72]

Together, the results obtained suggest that the transfer of a growing chain to the benzene nuclei of polyheteroarylenes in the radical polymerisation of unsaturated monomers in the presence of soluble polyheteroarylenes is not the only way to the synthesis of copolymers.[71] The mechanism of formation of such condensation – polymerisation systems is not finally elucidated, although the very fact of their synthesis is extremely important. The copolymers formed differ significantly from the corresponding carbochain polymers in solubility and enhanced thermal, mechanical, thermofrictional, *etc*., characteristics even at low concentrations of a polyheteroarylene[69 – 71] (Table 4). Such polymeric systems are distinguished for better solubility, and, in some

Table 4. Some properties of polymeric systems prepared upon polymerisation of methyl methacrylate in the presence of a polyarylate from 4,4′-hexafluoropropane-2,2-diyldiphenol and terephthalic acid.[70]

Concentration of polyarylate (mass%)	η_{log} /dl g^{-1}	T_g /°C	Characteristics of films		
			σ /MPa	ε (%)	$10^3 E$ /mPa
0	3.85	110	40	20	1.08
4	5.80	130	60	4	2.20
100	0.60	215	55	75	1.83

Note. σ, breaking strength; ε, relative elongation at breaking point; E, elasticity modulus.

cases, enhanced strength properties in comparison with starting polyheteroarylenes.

The possibility in principle to perform anionic polymerisation of ε-caprolactam in the presence of aromatic polyimides as macromolecular activators has been demonstrated.[72] The involvement of five-membered imide rings of polyheteroarylenes in the reaction enables the synthesis of novel polycondensation–polymerisation systems, *e.g.*, partly cross-linked graft copolymers with enhanced thermal and tribological characteristics and high water resistance as compared with ordinary polycaprolactam.

The design of novel polymeric systems based on polyheteroarylenes and epoxide polymers can also be related to such 'symbiotic' polymer formation.[73,74] In particular, a combination of cardo polyheteroarylenes [*e.g.*, poly(phenolphthalein terephthalate)] with epoxide oligomers upon moderate heating is a promising approach to their reprocessing into monolithic articles. The chemical reaction of an epoxy oligomer with a polyarylate, which occurs by the insertion (and opening) of the oxirane ring into the ester bond, results in the formation of a network structure, which manifests a set of specific properties. Enhanced (in comparison with classical compositions based on oligoepoxides) thermal durability is the main advantage of such compositions. Reactions of cardo polyimides with oligoepoxides favour the synthesis of novel polymeric materials which manifest good thermal, strength and electroinsulating properties.[74]

It may be hoped that the above-described processes hold great promise in the directed control of the properties of carbo- and heterochain polymers.

The polymer formation described above should more correctly be referred to as a 'symbiotic' process, since the reactants eventually complement the useful properties of each other. There is no doubt that this trend requires further development and perfection.

3. Variations of chemical structures of monomers

Rapid progress in high-tech branches of modern industry and growing demands for novel materials pose the problem to the polymer chemist of design of high-molecular-mass compounds possessing enhanced specific properties, such as thermal stability, high working capacity under extreme operating conditions and excess loads, photochemical stability, optical conductivity, low permittivity, *etc*. The variability and versatility of polycondensation opens new ways to the synthesis of such polymeric materials. The use of monomers with appropriate chemical structures leading to directed variation of the structures of the polymeric chains of condensation polymers is a promising approach to the macromolecular design of the latter.

a. Ring–chain polyheteroarylenes

The structures of ring–chain polyheteroarylenes possessing a set of useful properties have been much attended to in the past decade. Preparation of modified polyheteroarylenes which, contrary to infusible and insoluble polymers, manifest better solubility in organic solvents, thus favouring their processing into finished articles, is a topical problem in this area.

Studies carried out in the 1980's have shown that introduction of cardo groups into various polyheteroarylenes using the corresponding monomers is an effective route to improve their solubility.[3,75] This can also be attained due to the presence of 'hinge' and side groups in the resulting macromolecules and the nonsymmetrical structure of the polymeric chain.[3,75,76] Of particular interest is construction of a polymeric chain structure which combines the enhanced solubility of a polymer with advanced thermal characteristics and, in some cases, new specific properties conferred on the polymer.

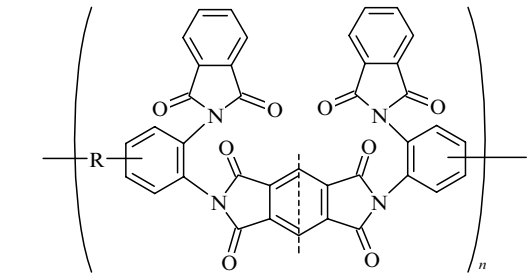
The introduction of phenyl substituents into the macromolecules of ring–chain polyheteroarylenes has proved a promising approach to increase their solubility, thermal plasticity and resistance against thermooxidation.[77] For example, polymers prepared from 5,6-diphenylbenzene-1,2,3,4-tetracarboxylic dianhydride and *p*- and *m*-phenylenediamines or 4,4′-diaminodiphenyl oxide soften at temperatures above 400 °C and lose 5% of their mass in air at 487, 523 and 591 °C, respectively. These polymers are soluble in a broad range of organic solvents, *e.g.*, *sym*-tetrachloroethane (TCE), *N*-MP, DMSO, DMA, DMF and *m*-cresol.

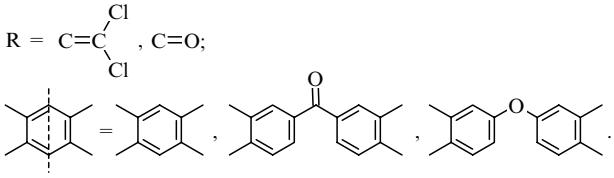
A series of novel soluble phenylated polyimides have been prepared starting from 4-(4-benzoylphenyl)-3,5,6-triphenylbenzenedicarboxylic dianhydride and various aromatic diamines. These polymers are amorphous, have glass transition temperatures (T_g) of 345–395 °C and lose 10% of their mass in air at 565–624 °C. The significant interval between their decomposition and glass transition temperatures enables their successful processing by pressing. Strong films prepared from polymer solutions are characterised by dielectric constants varying from 2.72 to 3.00.[78] Starting from 1,4-bis[2,3,4,5-tetraphenyl-6-(4,5-dicarboxy-1-naphthyl)phenyl]benzene dianhydride and benzidine or 3,3′,4,4′-tetraaminobiphenyl, soluble thermostable polynaphthylimide and the so-called polynaphthoylenebenzoimidazole, respectively, which manifest high luminescence efficiency due to the presence of aromatic groups, have been synthesised.[79] Methoxy- and phenoxy-substituted polyimides were synthesised based on 3,5-diaminoanisole,[80] 3-amino-5-(4-aminophenoxy)diphenyl ether,[81] 3,5-diaminodiphenyl oxide[82] and aromatic tetracarboxylic dianhydrides.

In the majority of cases, phenoxy-substituted polyimides manifest better solubilities in comparison with methoxy-substituted and unsubstituted analogues. A phenoxy-substituted polyimide containing hexafluoroisopropylidene groups manifests the best solubility.[82] Phenoxy-substituted polyimides based on tetracarboxylic dianhydrides containing 'hinge' groups are also easily soluble in common organic solvents. They are characterised by a large interval between the decomposition and glass transition temperatures and high thermal stabilities.[83] Polynaphthylimides and polyperylenimides possessing enhanced solubilities were synthesised from phenoxy-substituted diamines.[84]

The reaction of 2,6-diamino-4-hydroxytoluene and bis(3,5-diamino-4-hydroxyphenyl) oxide with tetracarboxylic dianhydrides gave a series of novel hydroxy-containing polyimides possessing good thermal characteristics. These polyimides are subject to further chemical modification. For example, the action of acryloyl chlorides yields photosensitive polymers.[85,86] Some soluble film-forming sulfur-containing polyimides[87–89] were synthesised from aromatic diamines containing phenylsulfonyl, phenylthio and benzothiazole-3-ylthio groups.

An interesting case of a chemical modification of polyimides has been described which includes incorporation of side phthalimide fragments into the polymer. These polymers were synthesised based on bis(phthalic anhydrides), bis(*o*-phenylenediamines) and chloral derivatives followed by reaction with phthalic anhydride.[90]





Polyimides with these structures are easily soluble in organic solvents, they manifest high thermal characteristics and fire-resistance. Polymers containing 1,1-dichloroethylene groups undergo structurisation upon thermal treatment, which renders them insoluble.

Polyimides containing phthalimide substituents were also prepared starting from 2,4-diamino-6-phthalimidotoluene and bisphthalic anhydrides[91] as well as from 2,4,6-triaminotoluene by sequential treatment with equimolar amounts of phthalic and bisphthalic anhydrides.[92] All the polymers thus modified are readily soluble in *N*-MP, DMF and a TCE–phenol mixture. Their softening temperatures are 270–360 °C; 10% mass loss temperatures are 400–450 °C.

The presence of side functional substituents has a beneficial effect on the properties of other polyheteroarylenes as well having ring–chain structures. For example, polyquinoxalines containing diarylether substituents[93,94] combine good processability with high thermal stability and low (in comparison with phenylquinoxaline) dielectric permittivity.[94]

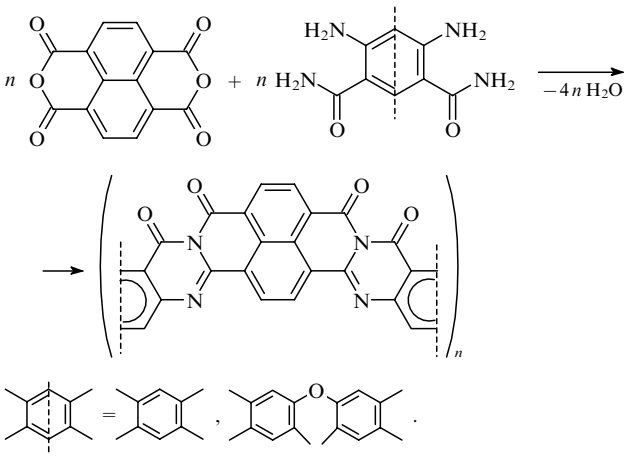
The presence of fluorine-containing (*e.g.*, trifluoromethyl, hexafluoroisopropylidene, trifluoromethylphenoxide, *etc.*) groups is also beneficial as regards the properties of different polyheteroarylenes.[95–102] Thus polyimides based on 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]hexafluoropropane and aromatic diamines[87] are easily soluble not only in *m*-cresol, but also in chloroform, dichloromethane, DMF, DMA and *N*-MP. Their softening temperatures are 200–220 °C, while their 5% mass loss temperatures in air are around 500 °C. These polyimides are readily processed into strong monolithic articles and films by moulding, extrusion and casting from solutions. Apart from high solubility, heat resistance, thermal stability and easy processability, phenyl-substituted polyimides of 4,4′-bis[tetraphenyl(4,5-dicarboxy-1-naphthyl)phenyl]benzophenone containing trifluoromethyl and hexafluoroisopropylidene groups have low dielectric constants (2.85 and 2.8, respectively).[96]

There is evidence that electric conductivities of these polymers change on going to fluorine-substituted polyimide derivatives. Thus substitution of fluorine for four hydrogen atoms in the benzene nuclei of polyimides decreases their dielectric permittivities, whereas substitution of one atom increases them.[100] Substitution of a methyl group for a trifluoromethyl group decreases the dielectric permittivity. Dielectric permittivities of fluorine-containing polyimides vary from 2.58 to 2.85, whereas those of ordinary polyimides are equal to 2.9–3.4.

A search for new routes to the synthesis of novel promising low-permittivity polymeric materials for microelectronics has been a challenge to polymer chemists in the past decade. The main approaches to the design of polymeric film materials manifesting low permittivities on the basis of various condensation polymers are considered in a recent review.[98] According to computer prognoses,[101] significant advances in this area can be achieved through the use of phenylated polyphenylenes devoid of polar groups. Different modifications of such polymers can result in materials with dielectric constants of 2.50–2.60.

Significant progress has been achieved in recent years in the synthesis of soluble polynaphthyl- and polyperylenimides containing six-membered imide rings. These polymeric systems possess enhanced thermal and chemical stabilities, optical conductivity, unusual electrographic properties and easy processability into articles by conventional methods.[103]

In addition to the broad potential of chemical modification of the known classes of ring–chain polyheteroarylenes by changing the framework of their polymeric chains, attempts are being made to modify the polymers through the formation of new heterocycles in the chain. For example, the use of bisnaphthalic anhydrides and bisanthranylamides in the synthesis of polymers has made it possible to prepare a novel class of thermostable polyheteroarylenes, *viz.*, polynaphthoylenequinazolones with six-membered heterocycles.[104]



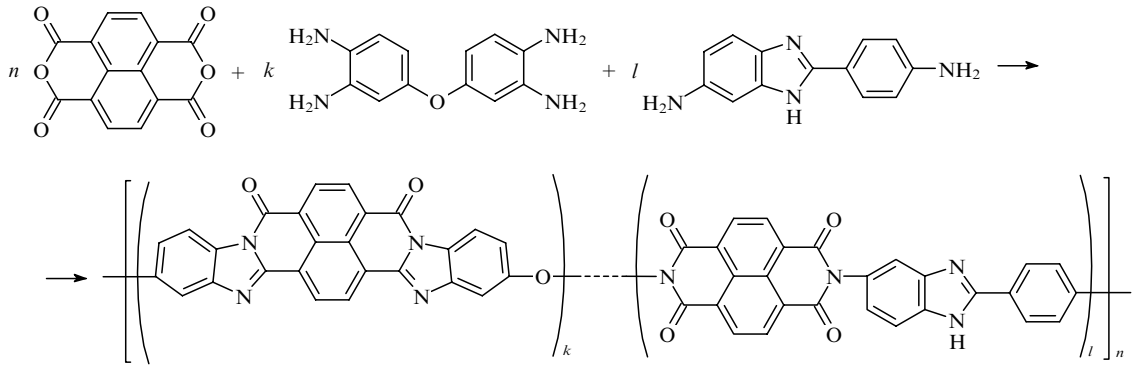
Properties of ring–chain polyheteroarylenes strongly depend on the composition of the basic polymeric chain, which determines its rigidity and flexibility.[105] The design of polymeric chains with high thermodynamic rigidity (*i.e.*, containing maximally straightened polymeric chains) is determined by the necessity to create thermostable, high-strength and high-modulus materials. Rigid-chain (the Kuhn segment is 320×10^{-8} cm) high-molecular-mass ($M = 1\,200\,000$) polynaphthoyleneimidobenzoimidazole **3** (see above) presents special interest in this respect.

Isotropic films of this polymer, which have been given the name 'iplon', are endowed with unique deformation characteristics: their breaking stress at specific elongation of $\varepsilon = 40\%$ and the elasticity modulus of $E = 46\,000$ kilogram-force cm^{-2} is $\sigma = 4700$ kilogram-force cm^{-2} (see Ref. 106). Their orientation (60%) gave anisotropic films with $\sigma = 9300$ kilogram-force cm^{-2}, $\varepsilon = 10\%$ and $E = 200\,000$ kilogram-force cm^{-2}.

With regard to these parameters, 'iplon' has no analogues among other heterocyclic non-composite polymeric materials. Approaches to further enhancing the strength characteristics of polynaphthoylenebenzoimidazole films have already been outlined. These include additional incorporation of rigid rod-like fragments into their polymeric chains. To meet this goal, a series of copolymers based on 1,4,5,8-naphthalenetetracarboxylic dianhydride, 5-amino-2-(4-aminophenyl)benzoimidazole and rod-like aromatic diamines have been synthesised.[107] The breaking strengths of oriented films of a copolymer based on 4,4′-diaminobiphenyl (30 mol.%) reaches 1.5×10^4 kilogram-force cm^{-2}, the elasticity modulus being 38×10^4 kilogram-force cm^{-2}.

Molecular composites, which represent mixtures of rigid-chain and flexible-chain polymers, are promising materials with enhanced physicomechanical characteristics. In such composites, rigid-chain components play the role of a reinforcing filler, which is dispersed at the molecular level in a flexible-chain polymer, which represents a permanent matrix. This allows fine attenuation of the microstructures of these polymeric systems (in comparison with mechanical mixtures) by synthesising block-type molecular composites with the corresponding structures. A series of block copolymers including those based on rigid-chain polynaphthoyleneimidobenzoimidazole with a Kuhn segment of 320×10^{-8} cm and flexible-chain polynaphthtoylenebenzoimidazole with a Kuhn segment of 50×10^{-8} cm have been synthesised specially for this purpose (Scheme 2).[108] These polymers manifest high physicomechanical characteristics ($\sigma = 4100$ kilogram-force cm^{-2}, $\varepsilon \approx 20\%$, $E = 82\,000$ kilogram-force cm^{-2}). Electron-microscopic studies have shown that at the molecular level the flexible matrix is reinforced by a rigid-chain block. The data on the molecular composites based on rigid-chain polybenzobisazoles have been generalised in a review.[109] It is reported that these composites are the most promising materials for those fields where low mass, high strength, thermal and chemical stability, and transparency with respect to radio waves are critical.

Scheme 2



Publications of the past decade consider miscellaneous properties of ring–chain polyheteroarylenes and various aspects of their applications in diverse branches of modern engineering, such as antifriction and self-lubricating plastics, composite materials, films, membrane and foamed materials, fibres, wave guides, adhesives, photoresists, *etc*.[3, 77, 79, 98, 103, 104, 109–115]

b. Polyarylenes

Recent investigations into the synthesis and chemical modification of polyarylenes,[116–119] polyaryleneethynylenes and polyarylenevinylenes[30–32, 120–124] attract considerable attention. In particular, the Diels–Alder homocondensation of 2,5-diphenyl-3,4-bis[4-(phenylethynyl)phenyl]cyclopentadienone was used for the preparation of a highly branched thermostable polyphenylene with M_w 160 000 that was readily soluble in organic solvents.[116] Polycyclocondensation of 4,4′-bis(4-acetylphenoxy)diphenyl sulfone was used in the synthesis of polyphenylenes containing acenaphthyl groups. Their subsequent dehydrogenation to acenaphthylenyl fragments gave a structurised polymer. The polymers containing reactive acenaphthylene groups are promising for production of thermostable plastics.[113]

The Diels–Alder reaction was used in the synthesis of hexafluoroisopropylidene-containing phenyl-substituted polyphenylenes which combine high thermal stability with solubility in organic solvents and have low dielectric constants.[119] Diethynylarenes and tolanes containing phenylated cyclopentadiene substituents[120–122] and other similar starting reagents[123, 124] were used, as in the synthesis of a series of thermostable thermoset phenylated polyphenylenes containing acetylene fragments under similar conditions. Some representatives of this class are easily soluble in organic solvents, have low dielectric constants[120] and manifest strong fluorescence.[121]

Polyconjugated polyaryleneethynylenes were synthesised by reaction of the corresponding dibromoarylenes and diethynylarenes in the presence of palladium or nickel complexes.[30–32] The fluorescence maxima of the polymers formed lie in the yellow-to-blue region.

A series of investigations of various physical characteristics of phenyl-substituted polyphenylenes, such as electrical birefringence,[125] hydrodynamic, optical and conformational characteristics[126] and radiation-induced conductivity,[127] have been carried out. No doubt, further development of the synthesis of high-molecular-mass polymers and in-depth study of their specific properties are topical.

The progress in investigations aimed at the synthesis of condensation polymers considered above would be impossible without further achievements in the chemistry of monomers based on readily available raw materials, *e.g*., 2,4,6-trinitrotoluene and chloral. Thus a series of aromatic diamines have been synthesised from 2,4,6-trinitrotoluene in order to obtain the corresponding ring–chain polyheteroarylenes containing methoxy-, fluoromethoxy-, phenoxy-, hydroxy-, sulfur-containing and other side groups.[80, 82, 83, 87–89] Diverse polyarylenes are accessible from arylene dihalides that can be prepared from chloral.[33, 128, 129]

c. Polyarylene ethers

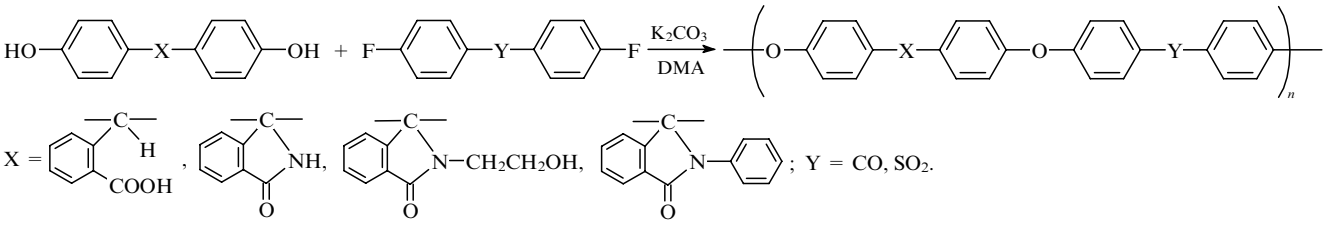
A series of recently published papers are devoted to the directed design of polymeric chains of polyarylene ethers. These polymers have attracted much attention since the 1960–1970's and are considered to be promising themoplastic materials owing to their high thermal stabilities and numerous valuable construction properties.[130] However, these compounds are not very heat-resistant, which inevitably poses the problem of their further modification. An analysis of the main regularities of their formation and effect of their molecular masses (*i.e*., the lengths of the polymeric chains) on their physicochemical properties is yet another central task.

Polyarylene ethers are usually synthesised by nucleophilic substitution of arylene dihalides with alkali metal phenolates or by electrophilic substitution (*e.g*., by reaction of aromatic dicarboxylic acid dichlorides with diaryl ethers in strongly acidic media). A recent study[131] aimed at the synthesis of polyarylene ether ketones from 4,4′-difluoro- or 4,4′-dichlorobenzophenone and cardo-type bisphenolates (phenolphthalein, phenolfluorene, phenolanthrone, phenolphthalein anilide) has significantly extended the knowledge of the pattern of this polycondensation process, enabled its optimisation and estimation of the effects of the chemical structures of the monomers on the properties of the polymers. In addition, it has enabled the synthesis of polymers with controllable molecular masses from 10 000 to 100 000 and above.[131]

The introduction of bulky cardo groups into macromolecules enhances considerably their thermal stabilities, so that glass transition temperatures of the above-mentioned polymers are 230–240 °C. They are amorphous, readily soluble and thermostable. The presence of the constituent cardo groups also favours the enhanced breaking stress and elasticity moduli of the films prepared from them.[132] The physicomechanical properties of polymers prepared from phenolphthalein and 4,4′-difluorobenzophenone were virtually unchanged starting from M = 40 000–60 000. In this range, poly(ether ketones) are easily molded from melts owing to their good fluidity. Such polymers were used for the preparation of unfilled monolithic materials as well as fiber glass and black-reinforced plastics possessing uniquely high specific impact strength. Thus the impact strength of an unfilled uncut specimen was 92 kJ m^{-2}.

Phthalide groups were also introduced into polyarylene ether ketones using an alternative procedure which employs a highly reactive difluoroderivative, *viz*., {3,3-bis[4-(4-fluorobenzoyl)phenyl]phthalide}.[133] This compound and various bisphenolates were used as starting materials in the synthesis of novel polyarylene ether ketones with softening temperatures up to 250 °C. It is noted that monolithic samples of cardo copolyarylene ether ketones containing 4,4′-propane-2,2-diyldiphenol fragments manifest uniquely high impact strength with incision (up to 44 kJ m^{-2}).[134]

Scheme 3

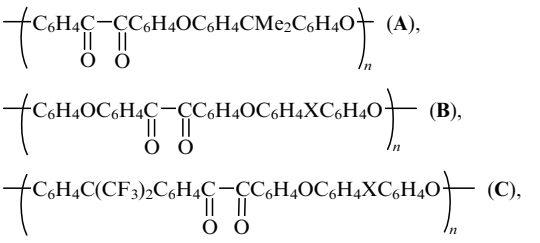


A series of crystallisable cardo copolyarylene ether ketones have been synthesised; their crystallisation is determined by the simultaneous presence of cardo bisphenols and hydroquinone (or 4,4′-dihydroxybiphenyl) fragments.[135,136] The glass transition temperatures of these compounds reach 250 °C, whereas the melting temperatures lie in the range of 300–350 °C.

Further developments in the field of chemistry of polymers will be directed at the incorporation of reactive groups into polymeric chains.[137–145] The development of methods for the synthesis of monomers containing functional groups (carboxy, alcoholic and phthalimide) is currently under way (Scheme 3).[137–139] Side groups in polyarylene ethers synthesised from these monomers allow their further chemical modification.

The polymers obtained have high softening temperatures (up to 260–290 °C); derivatives containing free carboxy groups are soluble in DMA, pyridine, cyclohexanone, THF and dioxane, and insoluble in chlorinated hydrocarbons. It is noted that the range of solvents for these polymers is wide and includes non-polar or low polarity solvents owing to the ability to form hydrogen bonds and to be involved in intra- and intermolecular interactions.[140] Polyarylene ethers containing free carboxy groups present interest as polyelectrolytes and polymeric composites.[139]

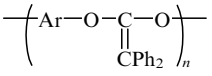
The use of difluoroarylenes containing α-diketone fragments as monomers has enabled the synthesis of the corresponding polyarylene ether ketones:[26,140–143]



X = CMe_2, $C(CF_3)_2$, *etc.*

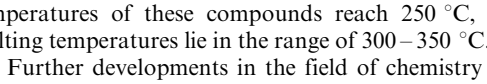
The glass transition temperatures of the polymers **B** and **C** vary in the range 165–245 °C, their 10% mass loss temperatures in air lie around 460–540 °C, and their dielectric constants vary from 2.90 to 3.25. These polymers are soluble in organic solvents.[142,143] The presence of α-diketone fragments in these macromolecules opens up new ways to their further conversion into, *e.g.*, linear polymers containing quinoxaline and triazine fragments or into cross-linked polymeric structures containing interchain quinoxaline fragments. It may be expected that the thermal and mechanical characteristics of these polymers will be enhanced in comparison with the original ones.

Chemical modification of polyarylene ethers can also be achieved through the introduction of double and triple bonds into their structures. The reaction of 1,1-dichloro-2,2-diphenylethylene with bisphenols was used in the synthesis of oligomers of the general formula:



Ar = $C_6H_4CMe_2C_6H_4$, $C_6H_4C(O)C_6H_4$,

which are promising candidates for thermoset fire-resistant materials.[144] Polycondensation of various bisphenols with difluoroarylenes containing acetylene groups was used for the preparation of unsaturated polyarylene ether ketones.[145]



X = CO, COCO; Ar = $C_6H_4CMe_2C_6H_4$, $C_6H_4CMePhC_6H_4$, *etc.*

Their thermal treatment is accompanied by structurisation at the triple bonds and results in enhancement of their thermal characteristics.

Thus, the studies of polyarylene ethers are mainly directed at the perfection of their synthesis and the design of novel promising polymeric structures. A search for hitherto unknown activators of electrophilic monomers employed in the synthesis of polyarylene oxides is currently under way. Thus it was found that the acyclic and heterocyclic groups present in arylene dihalide molecules activate halogen atoms. This line of research, which holds much promise both for the optimisation of nucleophilic substitution and for the preparation of novel polymeric systems possessing valuable properties, has been considered in a special review.[146]

IV. Conclusion

Because of the limited size of the present review, we cannot dwell further on all recent achievements in polycondensation and encompass the whole range of novel polymers synthesised by this method, since such examples are too numerous. The advances in the study of carborane-[147] and sulfur-containing[148] condensation polymers and polyorganophosphazenes[149,150] have been adequately covered in recently published papers. Suffice it to mention yet another promising trend which has been successfully developed over the past decade, *viz.*, design and investigation into highly branched dendritic polymers which are considered in detail in special reviews.[151,152]

In conclusion, it should be noted that polycondensation is still a very diverse and intensively explored area of research which is being further developed, being aimed at a search for novel polymer-forming reactions, methods for macromolecular design in polycondensation processes and purposeful design of polymeric chains for the most promising classes of polymers with the ultimate goal of conferring novel useful properties to existing polymers and of preparing new polymer systems. There is every reason to believe that future studies will provide interesting new data in this field of polymer chemistry.

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