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Advances in the Polycondensation Methods for the Synthesis of Thermostable Polymers

S.V.Vinogradova and V.V.Korshak

The review deals with the properties and the methods of synthesis by non-equilibrium condensation of heat resistant and thermostable polymers which have found considerable practical application in various branches of engineering. The bibliography includes 42 references.

The growing requirements for polymeric materials by many branches of modern engineering have, in the last decade, attracted much attention to polymers with enhanced heat resistant and thermostable properties. Heat resistance will be understood as the limiting temperature at which the polymer can retain a particular mechanical strength and thermal stability is defined as the limiting temperature which a given polymer can withstand without chemical change, mainly decomposition.

Classical examples of thermostable polymers known for a long time are, for example, polytetrafluoroethylene and organosilicon polymers of the polydimethylsiloxane type. However, despite their high thermal stability, they cannot be used successfully in many cases.

Recently it has become necessary to obtain new types of heat resistant materials which retain high strengths under load at elevated temperatures. Promising materials of this kind are polymers the macromolecules of which consist of aromatic or heterocyclic units. However, since the chains of such a structure are very rigid, many of these polymers cannot be used as starting materials for the preparation of films, fibres, and other articles for which a certain elasticity is needed. Therefore a natural solution of the problem was to synthesise polymers the macromolecules of which contain, in addition to the rigid phenylene and heterocyclic rings, more flexible bonds for example, esters and ether bonds.

The principal method for the synthesis of the majority of the known heat resistant and thermostable polymers is polycondensation, primarily non-equilibrium polycondensation. Until recently polycondensation methods, unlike polymerisation techniques, were not subdivided into various types. When fairly extensive experimental data on various polymerisation processes were accumulated and treated from a general standpoint, various types of the process became distinguishable, such as radical, cationic, anionic, and ionic–coordination polymerisation, each of which became established in polymer chemistry and occupies an honourable place among its techniques.

A similar development is being undergone by polycondensation reactions too. A general treatment of extensive experimental data on polycondensation makes it possible to subdivide polycondensation processes into at least two different types, namely equilibrium and non-equilibrium polycondensation processes which differ in the types of reaction occurring[1,2].

A principal feature of non-equilibrium polycondensation is the absence of degradation of the polymer by a low-molecular-weight polycondensation product and in most cases the absence from the polycondensation process also of other degradative exchange reactions.

Since the equilibrium constant for the process

$$A + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} C + D$$

is defined by the equation

$$K = \frac{k_1}{k_2} = \frac{[C][D]}{[A][B]},$$

it follows that high equilibrium constants should be characteristic of irreversible processes and hence also of non-equilibrium polycondensation, i.e. $k_1 \ll k_2$, or $k_1 \to \infty$, or an infinitesimal value of k_2.

The absence from the polycondensation process of degradative exchange reactions, which is responsible for the irreversibility of the process, may be due to various causes: (a) owing to the occurrence of the process at fairly low temperatures where exchange reactions do not take place at all and the starting materials are sufficiently reactive to form the polymer under such conditions; (b) owing to the formation in the polycondensation process of a polymer with a chemical structure such that it is incapable of degradative reactions with a low-molecular-weight polycondensation product, with the starting materials, or with the growing or completed macromolecules.

In contrast to equilibrium polycondensation, which has been investigated fairly thoroughly, non-equilibrium polycondensation is a little known process. Reactions of this type have been investigated only in recent years. So far comparatively few cases of non-equilibrium polycondensation have been studied in detail and the main features of these processes are still not altogether clear, although a fairly large number of cases of non-equilibrium polycondensation are known. Table 1 presents a far from complete list of such reactions, many of which have been used successfully for the synthesis of heat resistant polymers. It is not possible to examine them all in detail in this review, but some of them will be considered.

One of the classes of heat resistant and thermostable polymers to which much attention has been drawn in the last decade are heterochain esters of dihydric phenols—polyarylates. Polyarylates of dicarboxylic aromatic acids have the most interesting properties[3]. Table 2 presents data on the softening temperatures and the thermal stability of some of these polymers, which show that these are highly heat resistant and thermostable macromolecular compounds[4-7].

Since in the synthesis of polyarylates one of the reaction components is a dihydric phenol the hydroxy-groups of which are less reactive to acids than those of aliphatic polyhydric alcohols, it proved useful to employ the chlorides of dicarboxylic acids as the acid reagents in the synthesis of polyarylates[3]. The use of acid reagents of this type made possible successful polycondensation in solution and at interfaces. In general the availability of these two methods of polycondensation is important for the synthesis of heat resistant high-melting polymers, since polycondensation can be continued to a high degree of completion of the process without decomposition of the polymer formed: because of the high melting point of many heat resistant

polymers, including polyarylates, polycondensation in the melt would have to be carried out at 300–500°C and sometimes at even higher temperatures.

Thus the main method for the synthesis of heat resistant polyarylates is the reaction of dicarboxylic acid chlorides with dihydric phenols, which can be achieved in three versions.

(a) By the interaction of the dicarboxylic acid with the dihydric phenol in solution at an elevated temperature:

$$x\,ClOCRCOCl + x\,HOArOH \rightarrow [-OCRCOOArO-]_x + 2x\,HCl.$$

(b) By the interaction of the dicarboxylic acid with the dihydric phenol in solution at room or a relatively low temperature in the presence of a tertiary amine:

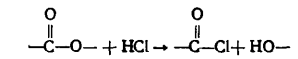
$$x\,ClOCRCOCl + x\,HOArOH \xrightarrow{NR'_3} [-OCRCOOArO-]_x + 2x\,NR'_3 \cdot HCl.$$

(c) By the interfacial polycondensation of the dicarboxylic acid chloride with the dihydric phenol:

$$x\,ClOCRCOCl + x\,HOArOH + 2x\,NaOH \rightarrow [-OCRCOOArO-]_x + 2x\,NaCl.$$

Until recently the polycondensation of dicarboxylic acid chlorides with dihydric phenols, carried out at high temperatures, was automatically classified as an equilibrium polycondensation process. However, studies in recent years at the Institute of Organic Derivatives of the Elements of the USSR Academy of Sciences in collaboration with the Laboratory of the Kinetics of Polymerisation Processes at the Institute of Chemical Physics of the USSR Academy of Sciences showed that this is not so.

The equilibrium in the reaction



was studied using as an example the interaction of hydrogen chloride with the polyarylate of terephthalic acid and 9,9-di-(4-hydroxyphenyl)fluorene and with model compounds such as 9,9-di-(4-benzoxyphenyl)fluorene and phenyl benzoate[8]. The reactions were carried out at 220°C in ditolylmethane in a stream of dry hydrogen chloride and also under pressure, which ensured the presence in the reaction mixture of a definite amount of hydrogen chloride.

Table 1. Examples of starting materials employed in non-equilibrium polycondensations and the types of polymers thus obtained

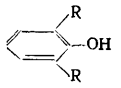
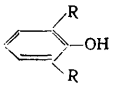
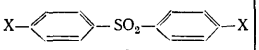
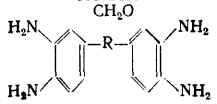
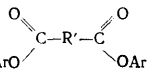
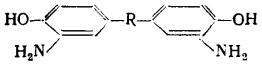
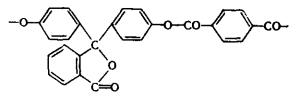
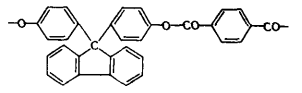
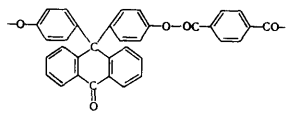
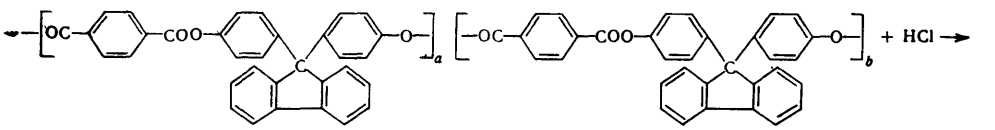
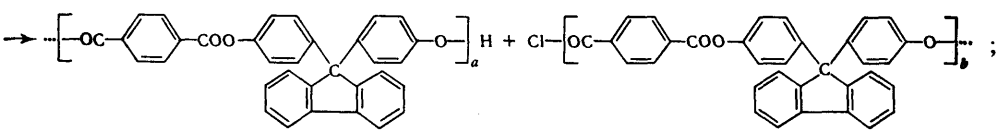
First component	Second component	Type of compound formed
ClOCRCOCl	HOArOH	polyarylate
ClO_2SRSO_2Cl	HOArOH	polysulphonate
$RPOCl_2$	HOArOH	polyphosphonate
ClOCRCOCl	$H_2NR'NH_2$	polyamide
ClO_2SRSO_2Cl	$H_2NR'NH_2$	polysulphonamide
ClOCOROCOCl	$H_2NR'NH_2$	polyurethane
ClOCRCOCl	HOOCR'COOH	polyanhydride
ClO_2SRSO_2Cl	HArH	poly(arylene sulphone)
$NaOArONa$	XArX	polyether
		polyether
$NaOArONa$		polyethersulphone
HArH	ClRCl	polyarylenealkane
C_6H_6	C_6H_6	polyphenylene
HOOCRCOOH	H_2NNH_2	polyaminotriazole
HC≡CH	HC≡CH	poly-yne (carbyne)
CH_2O	HArOH	polyphenol
		polybenzimidazole
	ClOCR'COCl	polybenzoxazole

Table 2. Polyarylates

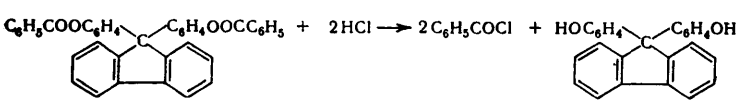
Repeating unit	Softening temp., °C (from thermo-mechanical curve)	Temp. of onset of decomposition, °C (inert medium)
	340	350—360
	350	350—360
	360	350—360

It was found that, on heating 1 M solutions of the polymer in an open system in a stream of dry hydrogen chloride for 5 h at 220°C, the molecular weight of the polymer remained unchanged. When phenyl benzoate and 9,9-di-(4-benzoxyphenyl)fluorene were heated under the same conditions, neither phenol nor benzoyl chloride were detected in the reaction mixture. This showed that the following reactions do not occur:





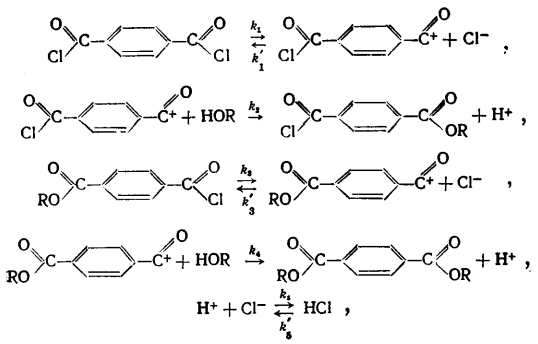
$C_6H_5COOC_6H_5 + HCl \rightarrow C_6H_5COCl + C_6H_5OH$;



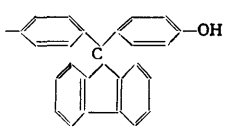
On the other hand, measurement of the equilibrium constant for the reaction of phenyl benzoate with hydrogen chloride in a closed system showed that at 40°C it is 2.35×10^{-4} and at 220°C 4.48×10^{-3}. Values of the same order of magnitude were also found by Polish investigators in a study of the equilibrium in the reaction of 2,2-di-(4-hydroxyphenyl)propane and its dichloroformate derivative in nitrobenzene at 60°, 80°, and 100°C.[9]

The equilibrium constants for equilibrium polycondensation processes are known to amount usually to several units. Thus the above data show that the equilibrium in the interaction of dicarboxylic acid chlorides with dihydric phenols is strongly displaced to the right. This suggests that the interaction is largely a non-equilibrium process for the low-molecular-weight polycondensation product.

More detailed studies were also made at the Institute of Organic Derivatives of the Elements and the Institute of Chemical Physics of the kinetics of the interaction of terephthalic acid chloride with 9,9-di-(4-hydroxyphenyl)fluorene under conditions typical for the synthesis of polyarylates by high-temperature condensation, namely in the temperature range 150–200°C using ditolylmethane, dowtherm†, and nitrobenzene as solvent[10]. It was found that the order of the reaction based on initial rates is 1.5: the reaction is first order with respect to the dihydric phenol and of order 0.5 with respect to the acid chloride. Analysis of the kinetic data and measurements of the conductivity of the system showed that the interaction has the following ionic mechanism:



where R =



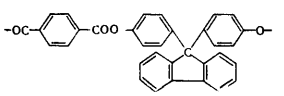
or the residue of the macromolecule.

The first reaction stage is equilibrium ionisation of one of the acid chloride groups. The resulting acylium ion interacts with the phenol or recombines with a chloride anion. The second stage is the equilibrium ionisation of the acid chloride group in a mixed ester–acid chloride species and its further interaction with the phenol.

Despite the fact that the polycondensation of dicarboxylic acid chlorides with dihydric phenols is, as mentioned above, an irreversible process for the low-molecular-weight polycondensation product (hydrogen chloride), the chain propagation reaction is nevertheless accompanied also by various degradative exchange reactions between the polymer molecule formed and the starting materials and also between the macromolecules themselves, because the process is carried out at an elevated temperature. Owing to the higher stability of polyarylates to chemical processes as compared with other types of polyesters, these reactions take place to a lesser extent in the above series of polyesters but they do occur and must be taken into account in an examination of the general features of the formation of polyarylates by high-temperature polycondensation.

† A eutectic mixture of phenyl ether and biphenyl (Ed. of Translation).

Table 3. Degradation of the polyarylate



by various reagents

Duration of degradation, h	η_{intr} in tricresol before and after degradation					
	hydroxyphenylfluorene		ClOC–⟨⟩–COCl		isophthalic acid	
	argon	HCl	argon	HCl	argon	HCl
0	0.80	0.8	0.80	0.80	0.80	0.80
2	0.74	0.60	0.77	0.74	0.80	0.72
4	0.71	0.50	0.75	0.65	0.73	0.67
10	0.58	0.40	0.69	0.46	0.65	0.59
20	0.49	—	0.63	—	0.64	—

* The degradation was carried out in a 10% solution of the polymer in ditolylmethane at 220°C.

Table 3 presents the results obtained for the degradation of poly[9,9-di-(4-hydroxyphenyl)fluorene terephthalate] by various chemical agents, from which it is clear that polyarylates do undergo exchange reactions[11]. It is interesting that the low-molecular-weight polycondensation product (hydrogen chloride) catalyses all types of degradative exchange processes in the synthesis of polyarylates by high-temperature polycondensation. It is also noteworthy that a tendency has been found for a narrowing of the molecular weight distribution of polyarylates (Table 4) as a result of degradative exchange reactions during polycondensation on heating[12].

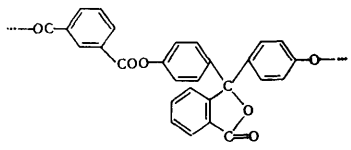
Table 4. Variation of the coefficient of polydispersity (M_w/M_n) of the polyarylate as a result of degradation at 220°C

Degrading agent	Duration of reaction, h	Gas stream	M_w/M_n
None	0		2.09
Hydroxyphenylfluorene	10	HCl	1.22
Hydroxyphenylfluorene	10	Ar	1.68
Hydroxyphenylfluorene	20	Ar	1.48
ClOC–⟨⟩–COCl	20	Ar	1.45

Very interesting results were obtained at the Institute of Organic Derivatives of the Elements of the USSR Academy of Sciences in studies on the effect of the reaction medium on the synthesis of heat resistant polyarylates. In particular, it was established that the physicomechanical

properties of the polyarylate of isophthalic acid and phenolphthalein, the so called polyarylate F-1, depend appreciably on the solvent in which the polycondensation is carried out[13].

The chemical structure of the polyarylates of phenolphthalein and aromatic dicarboxylic acids is responsible for the high rigidity of the macromolecules:



Therefore in the synthesis of phenolphthalein polyarylate in ditolylmethane, which does not dissolve the polymer formed, the free energy of formation of coiled macromolecules should be lower than the free energy of formation of extended macromolecules (there are fewer points of contact between the coiled macromolecule and the insoluble polymer). This leads to preferential synthesis of the globular forms of the macromolecule, which is responsible for the globular type of the supermolecular structure of the phenolphthalein polyarylate synthesised in ditolylmethane. On the other hand, in the synthesis of phenolphthalein polyarylate in good solvents, for example, in 1-chloronaphthalene or nitrobenzene, extended macromolecules are formed preferentially. As a result packets of macromolecules and other fibrillar supermolecular structures arise. Polymers with this structure naturally possess better physicomechanical properties than the corresponding polymer with a globular supermolecular structure, as can be seen from the data presented in Table 5.[13]

Table 5. Properties of polyarylate F-1

Property	Medium in which polymer was obtained		
	ditolylmethane	1-chloronaphthalene	
Supermolecular structure	globular	fibrillar	
Molecular weight	28 000	28 000	48 000
Softening temperature, °C	270	290	300
Tensile strength, kgf cm^{-2}	640	740	780
Elongation on rupture, %	10—20	80	100
Specific impact strength, kg cm cm^{-2}	2—3	10	20

Thus in the synthesis of polymers with rigid macromolecular chains, which are, incidentally, typical for many heat resistant polymers, it is necessary to choose the correct reaction medium bearing in mind its effect on the selection of particular macromolecular conformations during the synthesis itself. In the synthesis of heat resistant polymers capable of crystallisation, the polycondensation conditions are sometimes very important. This will be illustrated by the synthesis of the crystallisable polyarylate of 9,9-di-(4-hydroxyphenyl)-10-anthrone and terephthalic acid[14]. Table 6 shows that, by varying the reaction temperature, it is possible to obtain either a crystalline or an amorphous polymer, which in turn affects its properties[14]. In the synthesis of crystallisable polymers it is necessary to take into account also other factors in the reaction conditions, such as the rate of heating and cooling of the reaction mass, the concentration of the reaction mixture, and methods for the isolation and purification of the polymer.

For polyarylate as an example, we considered one of the cases of non-equilibrium polycondensation which leads to heat resistant and thermostable polymers, the process involving heating in an organic solvent. Below we shall return to several cases of the synthesis of heat resistant polymers under such conditions.

In the last decade the synthesis of heat resistant polymers by non-equilibrium polycondensation under mild temperature conditions, virtually without heating, has attracted much attention. This process became possible owing to the discovery of methods for the synthesis of polymers such as interfacial polycondensation and low-temperature polycondensation in solution.

Table 6. Effect of the conditions of synthesis of the polyarylate obtained from hydroxyphenylanthrone and terephthalic acid on its properties and structure

Polycondensation conditions			η_{intr}, dl g^{-1} (Ph-TCE)*	Softening temp., °C (in a capillary)	Organic liquid dissolving the polymer	Structure
°C	duration, h	medium				
220	11—12	Sovol	0.42	does not melt, darkens at 450°	mixture of phenol and TCE	crystalline
220	10	1-chloro-naphthalene	0.90	ditto	ditto	ditto
250	5	" "	1.70	380—400	tricresol, TCE, dichloroethane, $CHCl_3$, CH_2Cl_2, dioxan, cyclohexanone, etc.	amorphous structure predominates
320	1	Sovol	0.68	350—380	ditto	amorphous

* Ph = phenol and TCE = tetrachloroethane.

We shall not consider in detail interfacial polycondensation as a non-equilibrium polycondensation method since this has been extensively discussed in recent years[15,16]. We shall only note that its essential feature involves reaction between the starting materials when the solution of one of the active initial components (for example the dicarboxylic acid chloride) in an organic solvent is brought into contact with an aqueous (usually alkaline) solution of the second component (for example a diamine or a dihydric phenol). The reaction takes place at atmospheric pressure, at a low, usually room temperature and is very rapid. Under optimum conditions, the yield of polymers synthesised by this method is a rule high and so is the molecular weight. The range of heat resistant polymers synthesised by this method is fairly wide. These are heat resistant polyamides, polyarylates, polyanhydrides, polysulphonamides, polyamidoarylates, etc., based mainly on compounds with aromatic rings in the molecules:

$$x\,\mathrm{ClOCRCOCl} + x\,\mathrm{H_2NR'NH_2} \xrightarrow{\mathrm{NaOH}} [-\mathrm{OCRCONHR'NH}-]_x + 2x\,\mathrm{NaCl},$$

$$x\,\mathrm{ClSO_2RSO_2Cl} + x\,\mathrm{H_2NR'NH_2} \xrightarrow{\mathrm{NaOH}} [-\mathrm{SO_2RSO_2NHR'NH}-]_x + 2x\,\mathrm{NaCl},$$

$$x\,\mathrm{ClOCRCOCl} + x\,\mathrm{HOArOH} \xrightarrow{\mathrm{NaOH}} [-\mathrm{OCRCOOArO}-]_x + 2x\,\mathrm{NaCl},$$

$$x\,\mathrm{ClOCROOCl} + x\,\mathrm{HOOCRCOOH} \xrightarrow{\mathrm{NaOH}} [-\mathrm{OCRCOOOCRCOO}-]_x + 2x\,\mathrm{NaCl}.$$

The method of the so called low-temperature polycondensation in solution is extremely interesting. One must stipulate immediately that, when non-equilibrium polycondensation including low-temperature polycondensation is

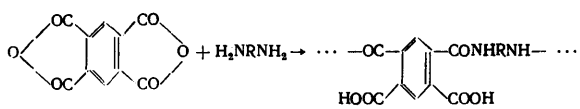
carried out in an organic solvent, different versions are possible: (a) both the starting materials and the resulting polymer are readily soluble in the reaction medium and the polycondensation really takes place in solution; (b) the starting materials are soluble in the reaction medium, while the polymer is only partially soluble or altogether insoluble; (c) the starting materials are only partially soluble or completely insoluble in the reaction medium, while the polymer is soluble.

Despite the fact that in the last two cases the process takes place under heterogeneous conditions, nevertheless these methods are also known in the literature as polycondensation in solution, although it will of course be more correct to regard them as simply polycondensation in an organic solvent. The most favourable conditions for the synthesis of heat resistant high-melting polymers are, of course, usually those where the polymer is formed and is readily soluble in the reaction medium, since this makes it possible to manufacture articles from the polymer (films, fibres) directly from the reaction solution, omitting the preliminary isolation of the polymer itself.

Polycondensation in solution at low temperature (room temperature or slightly above) of the order of 50°C proved to be possible owing to the use of reactive starting materials—such as acid chlorides and anhydrides—and special reaction media of activators. Thus low-temperature polycondensation of dicarboxylic acid chlorides with dihydric phenols at room temperature or with slight heating to about 50°C has been achieved by carrying out the reaction in the presence of a tertiary amine[15,17-49]:

$$x\,\mathrm{ClOCRCOCl} + x\,\mathrm{HOArOH} \xrightarrow{2x\,NR'_3} [-\mathrm{OCRCOOArO}-]_x + 2x\,NR'_3 \cdot HCl.$$

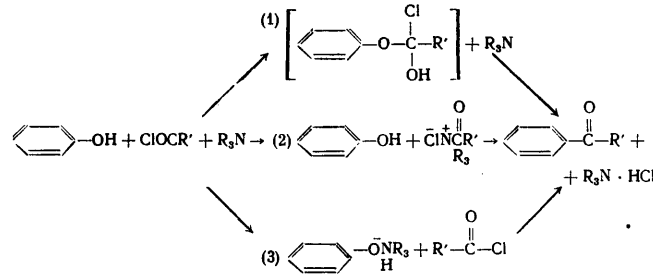
The conversion of dicarboxylic acid chlorides into polyamides by reaction with diamines can be successfully carried out in an amide solvent, for example dimethylacetamide[20-22]. In two-stage syntheses of heat resistant and thermostable polymers such as polyimides, the first stage, involving the formation of a high-molecular-weight polyamidoacid, has been successfully achieved in solvents such as dimethylacetamide, dimethylformamide, and dimethylsulphoxide[23,24]:



In a two-stage synthesis of polyoxadiazoles good results are obtained when the first reaction stage, involving the formation of a polyhydrazide, is carried out under conditions of low-temperature polycondensation in hexamethylphosphoramide (HMPA)[25]:

$$\mathrm{ClOCRCOCl} + H_2NHNOCR'CONHNH_2 \xrightarrow{HMPA} \cdots\!-\!OCRCONHNHCOR'CONHNH-\!\cdots$$

We shall consider briefly certain features of the formation of polymers by low-temperature polycondensation in solution. Despite the fact that the acylation of phenols by carboxylic acid chlorides in the presence of tertiary amines is widely used in practical organic chemistry, the problem of the role of the base in this process has still not been solved. In principle, several hypotheses concerning the role of the base in the acylation of phenols are possible[15]: (1) the first reaction step is the formation of a complex of the acid chloride and phenol which breaks down under the action of the base to form an ester bond; (2) the base forms a reactive complex with the carboxylic acid chloride the reaction of which with phenol yields an ester bond; (3) a reactive complex of the base and phenol is formed and then readily reacts with the carboxylic acid chloride:



At present it is still impossible to state a preference for a particular mechanism. However, studies aimed at solving this problem are being carried out, in particular at the Institute of Organic Derivatives of the Elements of the USSR Academy of Sciences. At the present stage of the investigation we believe that the first reaction stage most probably takes place via mechanism (2), but this is still a very arbitrary assumption and the elucidation of the problem requires further study.

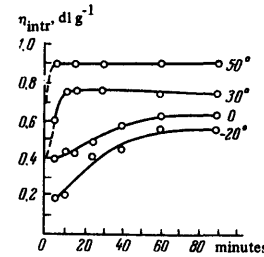


Figure 1. Variation of the intrinsic viscosity of polyarylate F-2 solution in tetrachloroethane with time for different polycondensation temperatures

Very few data have been published on the rate of low-temperature polyesterification in solution. However, there is no doubt that it is fairly high, since in most cases the reaction reaches completion in a very short time.

Fig. 1 presents data on the variation of the molecular weight of polyarylate F-2 in the polycondensation of terephthalic acid chloride with phenolphthalein in dichloroethane solution in the presence of triethylamine at various temperatures (concentration of acid chloride 0.2 M, molar ratio acid chloride : phenolphthalein : triethylamine = 1 : 1 : 2).[17] They indicate a high rate of this reaction. Indeed at 50°C the increase in the molecular weight and the formation of the polymer cease roughly five minutes from the start of the reaction. Even when the polyesterification is carried out at -20°C, the formation of the polymer is virtually complete after 1 h.

The low-temperature polycondensation of terephthalic acid chloride with phenolphthalein takes place in a very interesting way in the presence of a tertiary amine in acetone, which does not dissolve the resulting polymer[18]. Here after the first minute of polycondensation the yield of the polyarylate (the polymer is precipitated as it is formed) is already 95%. At the same time the molecular weight of the polymer increases considerably when the reaction is

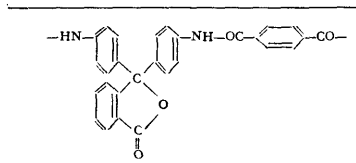
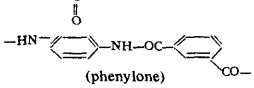
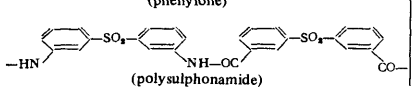
continued. It goes on increasing to almost the same extent when the precipitated polymer is separated after the first minute of the process, washed free of the starting materials with acetone, and treated with a fresh portion of pure acetone.

This is undoubtedly evidence that in the synthesis of the polyarylate in acetone the molecular weight of the polymer may increase as a result of reactions of the terminal groups of the polymer chains even after the precipitation of the polymer. Probably this is favoured by the high polarity of the acetone and its consequent high solvating power, which facilitates the interaction between the terminal groups of the polymer chains.

Successful low-temperature polyesterification is also dependent on the purity of the starting materials and the tertiary amine, the relative amounts of the starting materials, their concentration in solution, and other factors[26]. Polymers with highest molecular weights are obtained when carefully purified starting materials are introduced into the reaction in equimolar proportions.

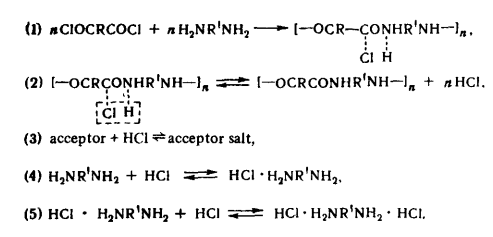
Low-temperature polyamide formation, used successfully in particular for the synthesis of heat resistant aromatic polyamides such as, for example, polyphenyleneisophthalamide[21,22], polyamides based on anilinephthalein, anilinofluorene, etc. has also been developed in recent years[27]. Table 7 lists certain examples of these polyamides obtained at the Institute of Organic Derivatives of the Elements of the USSR Academy of Sciences by Sokolov and coworkers[28].

Table 7. Aromatic polyamides

Polymer	Softening temp.*, °C	Temp. of onset of weight loss in air, °C
	390	450
 (phenylone)	280	—
 (polysulphonamide)	278	—

* Determined from thermomechanical curves

The polycondensation of dicarboxylic acid chlorides with diamines in solution may involve several competing reactions[15,20]:



(1) $n\,ClOCRCOCl + n\,H_2NR^1NH_2 \longrightarrow [-OCR(Cl\,H)CONHR^1NH-]_n$,

(2) $[-OCR(Cl\,H)CONHR^1NH-]_n \rightleftharpoons [-OCRCONHR^1NH-]_n + n\,HCl$,

(3) acceptor + HCl ⇌ acceptor salt,

(4) $H_2NR^1NH_2 + HCl \rightleftharpoons HCl \cdot H_2NR^1NH_2$,

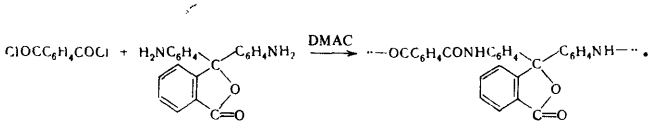
(5) $HCl \cdot H_2NR^1NH_2 + HCl \rightleftharpoons HCl \cdot H_2NR^1NH_2 \cdot HCl$,

(6) ClOCRCOCl + acceptor ⇌ saltlike product.

The first three reactions favour the formation of the polymer, while the last three lead to the breakdown of the equimolar proportions of the starting materials and stimulate the termination of the growing polymer chain, i.e. reduce the molecular weight of the polyamide. The ease of their occurrence is determined both by the chemical nature of the starting materials employed and the process conditions.

The role of the substance binding the hydrogen chloride evolved in low-temperature polyamide formation may be fulfilled by tertiary and secondary amines, the initial diamines themselves, and weakly basic organic solvents.

Low-temperature polyamide formation in solution is rapid. This can be inferred if only from the fact that the polycondensation of isophthalic acid chloride with anilinephthalein[20] at −30°C is terminated after several minutes:



$ClOCC_6H_4COCl + H_2NC_6H_4C(O)(C{=}O)C_6H_4NH_2 \xrightarrow{DMAC} \cdots OCC_6H_4CONHC_6H_4C(O)(C{=}O)C_6H_4NH\cdots$

The rate of low-temperature polycondensation is of course determined largely by the chemical nature of the starting materials. For example, according to the data of Sokolov and coworkers[28], the time required for the formation of a polyamide from isophthalic acid and di(aminophenyl)sulphone by low-temperature polycondensation is about 30 min, while in the case of poly-*m*-phenyleneisophthalamide it is about 1 h.

Table 8. Low-temperature polyamide formations

Starting materials		Solvent	η_{intr}, dl g^{-1}	Remarks
acid chloride	diamine			
Isophthalic	Anilinephthalein	DMAC*	1.14	solid acid chloride used in reaction
"	"	DMF**	polymer is not formed	ditto
"	"	DMAC	0.22	acid chloride introduced into reaction as soln. in DMAC
Terephthalic	"	"	1.45	solid acid chloride used in reaction
Isophthalic	*m*-phenylenediamine	"	1.52	ditto
"	*p*-phenylenediamine	"	1.60	"
"	*m*-phenylenediamine	"	0.40	acid chloride introduced into reaction as soln. in DMAC
"	"	DMF	0.08	solid acid chloride used in reaction

* DMAC = dimethylacetamide.
** DMF = dimethylformamide.

The products of low-temperature polyamide formation are greatly influenced by the order and method of the introduction of the starting materials into the reaction. When the process is carried out in dimethylacetamide, best results are obtained by adding the solid acid chloride (Table 8) to a solution of the diamine in dimethylacetamide, since it is then probably possible to avoid or weaken many undesirable side processes, which are stimulated by the amide solvent[20,22,24].

NN-Diethylacetamide, hexamethylphosphoramide, and *N*-methylpyrrolidinone can also be used as solvents for low-temperature polyamide formation. On the other hand, when the process is carried out in diethylformamide, high-molecular-weight polyamides are not as a rule obtained. Sokolov and coworkers explained this by the fact that in dimethylformamide side reactions predominate over the main process[29].

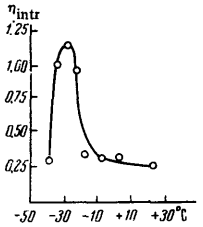
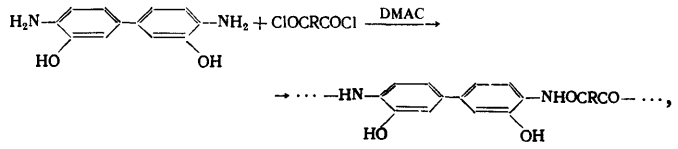


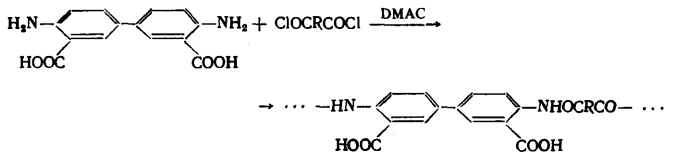
Figure 2. Variation of the viscosity of the polyamide obtained from isophthalic acid chloride and anilinephthalein with polycondensation temperature

The molecular weight of the polyamide synthesised by low-temperature polycondensation is significantly influenced by the reaction temperature. Fig. 2 shows that in the polycondensation of isophthalic acid chloride with anilinephthalein in dimethylacetamide a polymer with the highest molecular weight is formed at −30°C.[20] According to the data of Savinov and Sokolov[22], poly-*m*-phenyleneisophthalamide with the highest molecular weight is produced when the reaction is performed in dimethylacetamide at 0°C. According to Morgan's data[15], highest molecular weights are achieved in the polycondensation of terephthalic acid chloride and *trans*-2,5-dimethylpiperazine in chloroform at or below room temperature.

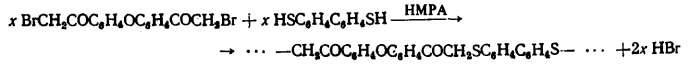
Other low-temperature polycondensations in solution are not unaffected by temperature either. Thus the optimum temperature for the polycondensation of the acid chloride of di-(4-carboxyphenyl) ether with the dihydrazide of the same acid in hexamethylphosphoramide is 0–5°C.[25] Polyhydroxyamides have been synthesised at somewhat higher temperatures, approximately between 17° and 40°C, from 3,3′-dihydroxybenzidine and the chlorides of various dicarboxylic acids in dimethylacetamide[30,31]:



and also by the condensation of 4,4′-diaminobiphenyl-3,3′-dicarboxylic acid and an acid chloride:

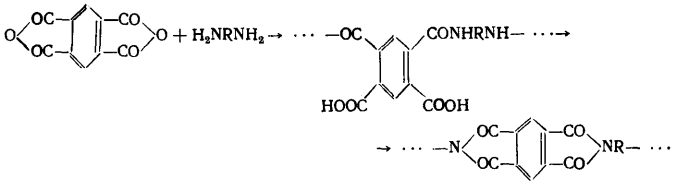


Probably an increase of reaction temperature, leading to an increase of the rate of the main reaction, is desirable in the case of less reactive diamines such as dihydroxy- and dicarboxy-diamines. On the other hand, in the polycondensation of still less reactive di-(4-bromoacetylphenyl) ether with 4,4′-dimercaptobiphenyl in hexamethylphosphoramide, it is desirable to increase the reaction temperature at a certain stage from 20°C to as much as 100°C in order to obtain a polymer with a higher molecular weight[32].



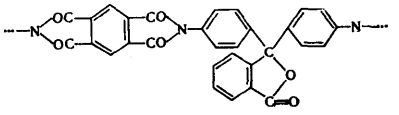
The rule of the equivalence of functional groups, which consists in the fact that polymers of high molecular weight are obtained when the starting materials are reacted in stoichiometric proportions, operates in most cases of low-temperature polycondensation.

Among heat resistant and thermostable polymers, cyclochain polymers have attracted much attention recently. Because of their infusibility and insolubility, the only reasonable and useful method of synthesis of many of them was until recently two-stage polycyclisation with formation in the first reaction stage of a high-molecular-weight intermediate which is soluble and therefore can be processed, for example a polyamidoacid in the case of polyimides and polyhydrazides in the case of polyoctadiazoles, which after the formation of the appropriate article are cyclodehydrated to give polymers with a cyclochain structure:



Apart from the evident advantages of this method—for example, articles can be manufactured from infusible and insoluble polyimides—in many cases the final stage of polymerisation has certain disadvantages also, namely (1) the difficulty of obtaining high-molecular-weight polymers in a block or in a thick sheet because of the vigorous hydrolysis of the polyamidoacid by the water evolved in its cyclisation, (2) the degradation of polyimides by the solvents remaining in the polymer even after heat treatment at elevated temperatures, and (3) the necessity to employ high temperatures (frequently of the order of 300°C) and a high vacuum to obtain polyimide articles with satisfactory physical properties.

Recently methods have been found at the Institute of Organic Derivatives of the Elements of the USSR Academy of Sciences for the preparation of heat resistant soluble polyimides, their synthesis involving the use of starting materials containing a central carbon atom in a bulky cyclic group[32–35]. The solubility of such polyimides, in particular anilinephthalein polyimides,



and their stability at high temperatures in many solvents led to a different method for their synthesis—single-stage high-temperature polycondensation in solution[31,34].

Table 9. Synthesis of polyimides by single-stage polycondensation in solution

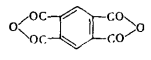
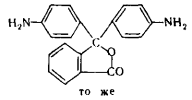
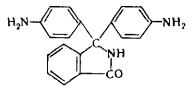
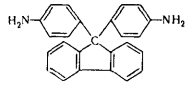
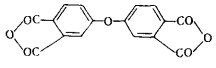
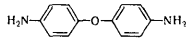
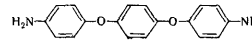
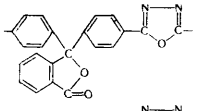
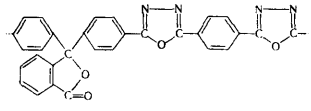
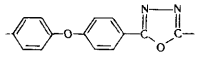
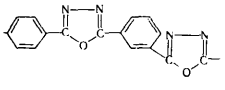
Reaction conditions: starting materials: dianhydride	diamine	solvent	concn. of soln. M	reaction temp., °C	duration of reaction, h	η_{intr} of 0.5% soln. at 25°, dl g^{-1}
		nitrobenzene	0.40	210	7	1.65
ditto	то же	benzonitrile	0.40	195	8	1.14
—"—	—"—	1-chloro-naphthalene	0.40	200	8	0.63
—"—		sulpholane	0.40	200	4	0.68
—"—		nitrobenzene	0.30	210	7	1.18
		"	0.12	200	7	0.65
		"	0.40	210	10	0.98
ditto		"	0.40	210	17	0.58

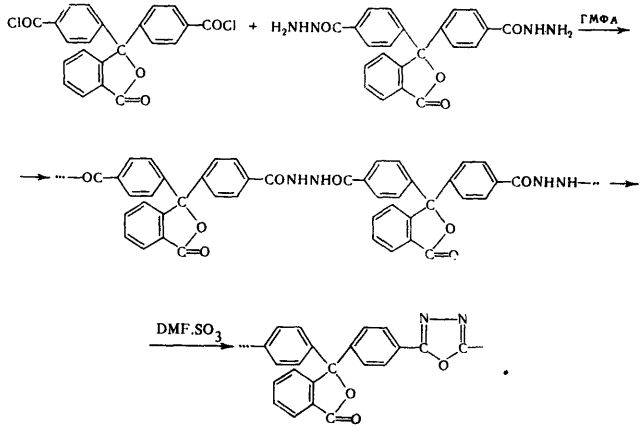
Table 10. Poly-1,3,4-oxadiazoles

Structure of elementary unit	Softening temp., °C	Temp. of onset of decomp. in air, °C
	390	400 (3 deg min^{-1})
	390	450 (3 deg min^{-1})
	370	420 (10 deg min^{-1})
	does not soften before decomp.	450 (10 deg min^{-1})

In the synthesis of such a polyimide by high-temperature polycyclisation in nitrobenzene the initial product is an amidoacid, which, being insoluble in the reaction medium, is precipitated. The subsequent polymerisation (polycyclisation) reaction takes place at 160–210°C and is accompanied by quantitative conversion of the insoluble amidoacid into soluble polyimide. In this method of synthesis of polyimides the difficulties associated with the degradation of the polyamidoacids and polyimides are eliminated and it is no longer necessary to subject the polyimide articles to high-temperature vacuum treatment.

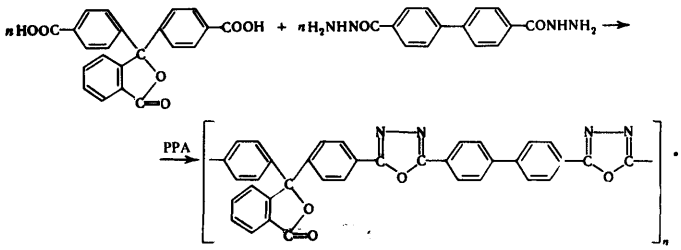
The single-stage method for the separation of soluble polyimides based on anilinephthalein was also extended successfully to the synthesis of high-molecular-weight polyimides based on various tetracarboxylic acid and diamines (Table 9).

We shall consider briefly yet another class of heat resistant and thermostable polymers with a cyclochain structure—polyoxadiazoles. Table 10 lists as an illustration the softening temperatures and the temperatures corresponding to the onset of decomposition of certain polyoxadiazoles [36,37]. They can be synthesised by two-stage methods and also in one stage. Using the two-stage method of synthesising polyoxadiazole, particularly from di-(4-carboxyphenyl) ether, Korshak et al. [25] obtained good results when the first stage, involving the polycondensation of the acid chloride of di-(4-carboxyphenyl) ether with its dihydrazide, was carried out in hexamethylphosphoramide. In the second stage, involving the conversion of the polyhydrazide into polyoxadiazoles, the polymer is usually heated in a vacuum under very severe conditions (about 300°C, 25–30 h). However, it has recently been shown, for polyoxadiazoles obtained from diphenylphthalide-4,4′-dicarboxylic acid as an example, that polyhydrazides can be cyclodehydrated successfully at atmospheric pressure under milder conditions, namely by heat treatment at 100°C for 5 h, when the complex of an amide solvent, for example dimethylformamide (DMF) or dimethylacetamide with sulphur dioxide, is to be used as the cyclodehydrating agent [36,38]:



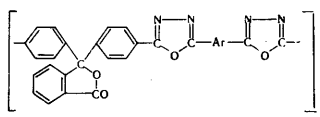
It was noted that polyoxadiazoles may be synthesised also in one stage. Here the process is carried out in polyphosphoric acid (PPA). In a study of the synthesis of soluble polyoxadiazoles based on diphenylphthalide-4,4′-dicarboxylic acid very good results were obtained using this method.

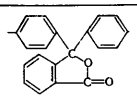
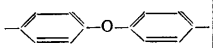
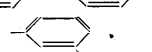
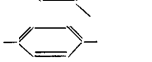
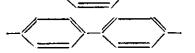
In this case the acid and the hydrazide are allowed to react in equimolar proportions. For example,:



The reaction is carried out gradually by heating the reaction mixture to 140°C and maintaining it at this temperature for several hours.

Table 11. Intrinsic viscosities of polyoxadiazoles obtained by various methods



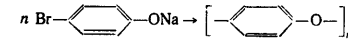
Ar	η_{intr} of 0.5% soln. in 3:1 trichloroethane: phenol mixture, dl g^{-1}		
	thermal cyclodehydration of polyhydrazides	chemical cyclodehydration of polyhydrazides in the presence of DMF.O_3	polycondensation in PPA*
	0.67	0.55	3.00
	1.10	0.90	3.50
	0.70	0.60	1.00
	0.58	0.70	1.90
	0.89	0.80	4.75

* PPA = polyphosphoric acid (Ed. of Translation).

Table 11 presents the results obtained in the synthesis of polyoxadiazoles from diphenylphthalide-4,4'-dicarboxylic acid by various methods. They show that polycondensation in polyphosphoric acid yields high-molecular-weight polymers [36].

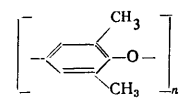
In recent years considerable progress has been achieved also in the synthesis of aromatic polyethers and polysulphones. Despite the fact that these materials are less heat resistant than aromatic polyamides, polyesters, and particularly polymers with a cyclochain structure, they nevertheless have valuable properties; they are heterochain polymers with reasonably good heat resistant properties. Therefore we shall consider briefly their synthesis.

For a long time considerable difficulties were encountered in the synthesis of aromatic polyethers. It was impossible to obtain polymers with a high molecular weight. Recently, various methods have been employed in their synthesis. Thus, a method has been described for the preparation of a polyether with a 1,4-phenyl structure from sodium *p*-bromophenoxide by a modified Ullman condensation:

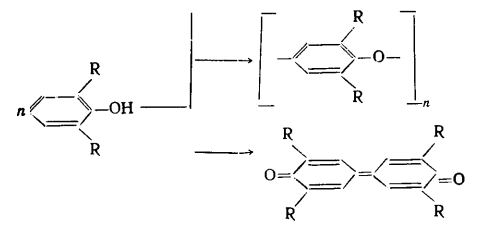


Copper(I) chloride combined with various organic bases (pyridine, *NN*-dimethylformamide, *NN*-dimethylacetamide) is employed as a catalyst. The reaction is carried out at 200°C in dimethoxybenzene, nitrobenzene, or benzophenone with careful exclusion of oxygen and moisture. Since the polymer obtained has the capacity to form fibres, its molecular weight is fairly high. It is also fairly heat resistant: it can be moulded at 300–350°C. [39]

A new variety of non-equilibrium condensation, namely oxidative dehydropolycondensation, proved to be a very interesting procedure for the preparation of aromatic polyethers. The General Electric Company manufactures by this method on an industrial scale a polyether with the following structure:



Its glass point is 205°C and the crystals melt at 267°C. According to thermogravimetric data, the degradation of the polymer in an inert atmosphere begins at about 400°C. Its synthesis became possible when it was established that certain 2,6-disubstituted phenols react by the following mechanism in the presence of oxygen with an amide complex of copper as catalyst:



With 2,6-dimethylphenol, the process takes place readily giving a polymer with a high molecular weight, while the yield of side products is very low. In general the formation of polymers of this type by oxidative dehydropolycondensation is successful when the dimensions of the constituents in the *ortho*-position are small.

On the other hand, if one of the substituents is, for example, a t-butyl group or both substituents are isopropyl groups, the corresponding diphenoquinone is formed preferentially and not the polymer. Substituents which increase the oxidative potential of the phenol retard the polycondensation. Thus, whereas 2,6-dimethylphenol readily undergoes polycondensation at room temperature, the polycondensation of 2-chloro-6-methylphenol requires a temperature of 60°C and for comparable rates of the process with 2,6-dichlorophenol a still higher temperature is needed [39].

Copper chloride in pyridine is usually employed as a catalyst for the oxidative dehydropolycondensation of 2,6-disubstituted phenols; other primary, secondary, or tertiary amines may be used instead of pyridine.

An interesting case of non-equilibrium polycondensation developed in recent years is the polycondensation of the phenoxides of dihydric phenols with aromatic dihalogeno-derivatives in which the halogens are labile because of the presence of electronegative substituents in the molecule [40–42].

An example of this type of reaction is that of the phenoxide derived from dian‡ with di-(4-chlorophenyl) sulphone in dimethyl sulphoxide, which leads to the formation of the so called "polysulphone" (this product was developed and is manufactured by the Union Carbide Company):

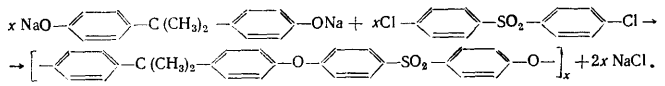


Table 12. Synthesis of polysulphone from di-(4-chlorophenyl) sulphone

Dian salt	Solvent	Duration of reaction, h	Reaction temp., °C	η_{intr} of soln. with 0.2 g/100 ml $CHCl_3$	Yield, %
Na	dimethyl sulphoxide	1	160—165	1.0	>99
K	dimethyl sulphoxide	4	195—200	0.65	>99
Na	sulpholane	3	200—210	0.75	>99
Na	diphenyl sulphone	11	230—250	0.40	—
Na	di-n-propyl sulphoxide	3.5	200—210	0.08	98
Na	benzophenone	8.5	220—230	—	53

The glass point of this polymer, which is fairly thermostable, is 195°C. On heating in an inert atmosphere for 30 min at 400°C, it remains unchanged. The heat resistance of polymers of this type can be varied by altering their chemical structure. For example, the glass point of the corresponding polymer obtained from di-(4-hydroxyphenyl) sulphone is 245°C. In general polycondensation of this type is carried out at elevated temperatures in anhydrous dipolar aprotic solvents, among which dimethyl sulphoxide and sulpholane (1,1-dihydroxytetrahydrothiophen) proved to be the most effective. Probably highly polar solvents of this type not only dissolve the polymer formed but also promote a higher rate of reaction, as it were catalysing the process. On the other hand, Table 12 shows that less polar organic solvents do not facilitate the reaction [40]. Johnson et al. [40], who made a detailed study of the interaction of the phenoxides derived from dihydric phenols with dihalogeno-compounds, noted that the reaction is sensitive to admixtures of water and other nucleophilic substances, because these interfere with the synthesis of a polymer having a high molecular weight. Polymers with the highest molecular weight are obtained when the starting materials enter into the reaction in equimolar proportions. The rate of this reaction depends on the basicity of the phenoxide obtained from the dihydric phenol and the electronegativity of the substituent in the dihalogeno-derivative. The reactivity of dihydric phenols evidently varies in inverse proportion to their acidity.

Thus alkali metal phenoxides derived from di(hydroxyphenyl) sulphone, which is a comparatively acid dihydric phenol, reacts much more slowly with di-(4-chlorophenyl) sulphone than the corresponding phenoxides obtained from dian. The reactivity of aromatic dihalogeno-derivatives (Table 13) is determined both by the nature of the activating group and the halogen: difluoro-compounds are more reactive than dichloro-compounds [40]. Sodium and potassium phenoxides may be employed in the reaction. The phenoxides of other metals (lithium, calcium, or magnesium) derived from dian are not suitable because of their insolubility in dimethyl sulphoxide [40].

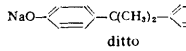
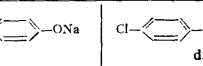
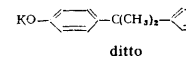
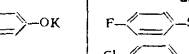
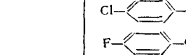
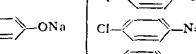
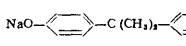
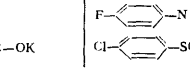
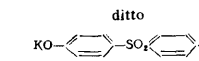
It is clear from the foregoing that many types of heat resistant and thermostable polymers are successfully obtained by the polycondensation method. Non-equilibrium polycondensation processes are the most important. Most of these are reactions discovered and investigated in recent years. There is no doubt that a more profound study of such reactions and the discovery of their mechanisms constitute the tasks of the immediate future.

‡ Di-(*p*-hydroxyphenyl)dimethylmethane (Ed. of Translation).

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Table 13. Reactivities of the starting materials in the synthesis of polysulphones in dimethyl sulphoxide

Phenoxide from dihydric phenol	Dihalogeno-derivative	Reaction conditions: conc., %	duration of reaction, h	reaction temp., °C	η_{intr}, dl g^{-1}
		20	4	135	0.71
ditto	ditto	40	1	160	1.35
		20	0.5	25—145	0.94
ditto		10	18	135	0.16
»		20	0.5	135	1.0
		40	6	160	0.26
ditto		40	<1	25—160	1.5
		20	29	150	0.2

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Institute of Organic Derivatives of the Elements, USSR Academy of Sciences, Moscow