ADVANCES IN INTERFACIAL POLYCONDENSATION

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I. INTRODUCTION

Polycondensation is an important method for obtaining various high-molecular compounds. It can be used to prepare both heterochain compounds (polyamides, polyesters, polypeptides, polyanhydrides, polysulphides, polysiloxanes, etc.) and carbon-chain compounds (polymethylenes, polyarylenealkyls, phenol–formaldehyde resins, etc.).

Until recently, polycondensation was carried out mainly as an equilibrium process, *i.e.* under conditions of the reversible interaction of the resulting polymer with the starting materials and with reaction products of low molecular weight[2]. Such equilibrium polycondensation was usually undertaken in a homogeneous medium, *i.e.* in a solvent boiling at a sufficiently high temperature or in a melt of the polymer and the monomers.

The laws of equilibrium polycondensation have been examined in detail and elucidated in various reviews and monographs[1–6]. Considerably less research has been done on the process of polycondensation under conditions which exclude reversible reactions, such that the whole process has the character of an irreversible, non-equilibrium change. It has been suggested[7] that such a case of polycondensation should be termed "non-equilibrium polycondensation". Not very many cases of non-equilibrium polycondensation are yet known. Among them are the formation of polyaminotriazoles by the polycondensation of dicarboxylic acids with hydrazine[8], and also the formation of polyamides and polyesters by the interfacial polycondensation of dichlorides of dicarboxylic acids with diamines and diphenols[9,10]. Several polyamides and polyesters have been obtained in this way.

The polycondensation of acid dichlorides with diamines or diphenols is carried out at the boundary between two immiscible liquids, *e.g.* water and a hydrocarbon or halogenated hydrocarbon. This has been termed interfacial polycondensation or polycondensation at the phase boundary[9,10].

Interfacial polycondensation opened up new opportunities for the synthesis of polymers and therefore immediately attracted the attention of investigators. After a short interval of time a large number of papers appeared dealing with the laws of interfacial polycondensation and its application to the synthesis of various high polymers.

The method of polycondensation at the phase boundary is based on the well-known Schotten–Baumann benzoylation reaction[11]. The production of polymers from the dihalide of a dicarboxylic acid together with another bifunctional compound (a diamine, diamide, dihydric phenol, etc.) was known long ago. Thus Michler and Zimmermann[12] first found in 1881 that a polyamide is formed by the reaction of *m*-phenylenediamine with carbonyl chloride in chloroform solution. Somewhat later Einhorn[13] described a method for obtaining polyesters by stirring a 20% solution of carbonyl chloride in toluene with an alkaline aqueous solution of a dihydric phenol (quinol, resorcinol, catechol). This method for obtaining polymers represents essentially what is now termed the method of interfacial polycondensation. However, Einhorn's work was forgotten, and only recently has this method again attracted the attention of scientists. It became clear that interfacial polycondensation opens up new possibilities for the synthesis of high polymers, by greatly extending the range of suitable monomers and making it possible to utilise monomers of high melting point as well as those which are unstable, and represents a great new advance in the development of a

science of polymeric reactions. We therefore considered it useful to review and summarise published data on this question, and this is the purpose of the present survey.

II. MECHANISM OF INTERFACIAL POLYCONDENSATION

As in other cases, a polymer macromolecule formed by interfacial polycondensation passes through three different stages in the course of its formation[3]: (1) the start of the growth of the macromolecule chain; (2) the growth of the macromolecule chain; (3) the cessation of the growth of the macromolecule chain or its termination.

Each of these stages has a characteristic feature distinguishing it from the corresponding stages both of polymerisation and of equilibrium polycondensation.

1. Start of Macromolecular Chain Growth

A macromolecular chain is initiated by the reaction of an acid dichloride with a diamine or a dihydric phenol:

$$ClCORCOCl + H_2NR'NH_2 \rightarrow ClCORCONHR'NH_2 + HCl.$$

In this stage of the reaction, if it occurs at the beginning of the process, when no film of polymer is yet present at the interface, polymer formation either occurs at the surface of separation or is displaced deeper into the phase which is the better solvent for the starting materials. This is usually the hydrocarbon phase.

Acylation in homogeneous medium[14-17] of both aliphatic and aromatic amines, as well as the acylation of alcohols and phenols, occurs by a nucleophilic substitution mechanism and is a well studied reaction.

Morgan and Kwolek[10,18] consider that interfacial polycondensation, *e.g.* polyamide formation, occurs according to the following equation[18]:

$$ClCO(CH_2)_8COCl + H_2N(CH_2)_6NH_2 \rightarrow$$

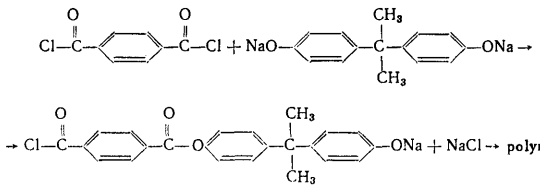
$$ClCO(CH_2)_8\underset{Cl}{CO}-\underset{H}{N}(CH_2)_6NH_2 \xrightarrow{\text{diamine}}$$

$$\rightarrow ClCO(CH_2)_8CONH(CH_2)_6NH_2 + \overset{\text{salts of the diamine}}{\longrightarrow} \text{polymer}.$$

Here a protonated amide is formed, from which the proton is easily removed by the action of a base. An amino-group in the diamine molecule or at the end of the oligomeric chain can also serve as acceptor for the proton. Water also can act as a proton carrier. The protonated amino-group can be easily reconverted into a free amino-group by contact with an inorganic base in the aqueous phase:

$$\cdots-NH_2\cdot HCl + NaOH \rightarrow \cdots-NH_2 + NaCl + H_2O.$$

The formation of polyesters[10,18,19] by interfacial polycondensation differs in several features from the production of polyamides. Thus reaction between dihydric phenols and halides of dibasic acids takes place very slowly at room temperature if the phenol is not present in the form of the phenoxide ion. Morgan[10] assumes that the production of polyesters from acid dihalides and dihydric phenols occurs *via* a nucleophilic attack of the phenoxide on the chloride of the dibasic acid, as represented by the following equation:



The characteristic feature of interfacial polycondensation is its heterogeneous nature;—the presence in the reaction zone of two immiscible solutions of reactants. When solutions of the two starting materials come into contact, the reactants as well as the solvents tend to move in opposite directions. Thus the diamine tends to pass from the aqueous phase into the organic phase, while the chloride of the dicarboxylic acid tends to pass into the aqueous phase. The diamine is readily soluble in nearly all the organic solvents employed (the partition coefficient $C_{H_2O}/C_{solvent}$ of the diamine in the solvent systems employed varied from 400 to 1);[18], but the acid chloride is in most cases almost insoluble in the aqueous phase. Polymer formation obviously takes place in the organic phase close to the boundary between the mutually immiscible solvents. This conclusion follows from several indirect observations, *e.g.* the reactions of unifunctional compounds in water–organic solvent systems, and also from direct observations on the formation of a polymer film by interfacial polycondensation[10,18].

Morgan[10,18] considers that polycondensation is initiated by the diamine coming into contact with the acid halide in the organic phase. The halide concentration considerably exceeds that of the diamine, which is apparently acylated at both ends, forming oligomers.

2. Growth of Macromolecular Chain

Chain growth takes place by reaction between the oligomers formed and the starting materials:

$$ClCORCONHR'NH_2 + ClCORCOCl \rightarrow ClCORCONHR'NHCORCOCl + HCl$$

$$ClCORCONHR'NHCORCOCl + H_2NR'NH_2 \rightarrow ClCORCONHR'NHCORCONHR'NH_2 + HCl$$

$$ClCORCONHR'NHCORCONHR'NH_2 + ClCORCOCl \rightarrow$$

$$\rightarrow ClCORCO[NHR'NHCORCO]_3Cl + HCl.$$

Here, depending on the phase in which reaction takes place, the end-groups of the polymer will be those of the starting material initially in the phase in which the reaction occurs. Since it apparently takes place more often in the hydrocarbon phase, the terminal groups will be acid chlorides in this case: *i.e.* the polymer will have the structure

$$ClCORCO[NHR'NHCORCO]_xCl.$$

Subsequent quantities of diamine, which diffuse into the organic phase, collide with the layer of oligomers having acid chloride end-groups and with the chloride of the dicarboxylic acid (Fig. 1). Reaction takes place by irreversible combination of the oligomers with the diamine. The concentration and the size of the oligomers increase until a high-polymer film is formed. Thus the polymer is obviously formed by reaction of the diamine with an oligomer and not with a fresh molecule of acid chloride.

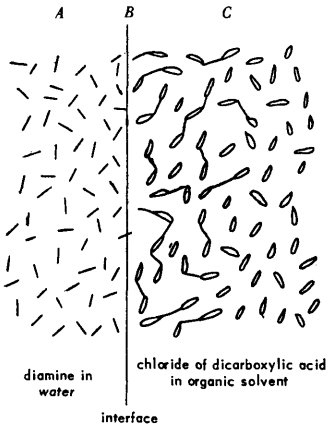


Fig. 1. Diagram of the initial relationship between reactants in the interfacial formation of a polyamide.[10,18]

It is probable that, during this period of rapid reaction, oligomers having protonated amino-groups can also diffuse from the organic into the aqueous phase, where the free amino-groups are regenerated by removal of the proton by an inorganic base; in addition, oligomers having free amino-groups can diffuse into the organic phase together with the diamines. The diffusion of the polymeric chains, however, is comparatively slow. The diffusion of reactants through the film does not cease, but merely slows down, after formation of the high-polymer film, as can be seen from a diagram of film growth with time (see Fig. 2).

Other views also exist as to the location of interfacial polycondensation. Thus Sokolov and Kruglova[20] consider that the reaction occurs neither in the aqueous nor in the organic phase, but in the polymer film itself.

In the case of polyesterification the interfacial polycondensation occurs somewhat differently, since the starting materials used in this case have rather different properties from those employed for the production of polyamides. The poor solubility of diphenoxides in the organic phase[10,18] and of the dicarboxylic acid chloride in the aqueous phase, produces a different mechanism for interfacial polyesterification compared with that of polyamide formation.

Several workers[10,18] assume that in the preparation of polyesters by interfacial polycondensation the film is formed initially in the organic phase, but subsequent film growth occurs from the aqueous phase side (Fig. 2). This mechanism is consistent with the investigations of Eareckson[19], who found that polyphenylene esters are best prepared in a rapidly stirred system of solvents containing detergents, which produces a large reaction surface. In this way the maximum possible quantity of polymer is kept in contact with the interface, and the acid chloride encounters the smallest obstacles to passing into the reaction zone[10,18]. Since the acid chlorides must react at the phase surface and be in a region of high ionic concentration, the less readily hydrolysed chlorides of aromatic acids give polymers of higher molecular weight than do readily hydrolysable aliphatic acid chlorides[10,18,19]. The reaction of polyesterification at the interface between two immiscible phases is considerably accelerated in the presence of catalysts such as quaternary ammonium salts and bases, which is apparently due to the formation of phenoxides soluble in the organic phase[21,22].

During interfacial polyesterification the inorganic base in the aqueous phase not only combines with the acid produced in the course of the reaction but also takes part in the formation of the phenoxides which react with the halides of dicarboxylic acids to form the polyesters.

3. Cessation of Growth of Macromolecules or Chain Termination

The stopping of chain growth for one reason or another determines the molecular weight of the resulting polymer, and this stage is therefore very important. In the case of interfacial polycondenstion, chain growth may cease for the following reasons:

(1) As a result of hydrolysis of terminal acid chloride groups:

$$\ldots\text{—RCOCl}+\text{H}_2\text{O}\rightarrow\ldots\text{—RCOOH}+\text{HCl}.$$

(2) As a result of the combination of acid with terminal amino-groups:

$$\ldots\text{—RNH}_2+\text{HCl}\rightarrow\ldots\text{—RNH}_2\cdot\text{HCl}.$$

(3) As a result of the conversion of phenoxides into phenols:

$$\ldots\text{—RC}_6\text{H}_4\text{ONa}+\text{HCl}\rightarrow\ldots\text{—RC}_6\text{H}_4\text{OH}+\text{NaCl}.$$

(4) As a result of the reaction of a terminal group with a unifunctional compound:

$$\ldots\text{—RCOCl}+\text{H}_2\text{NR}'\rightarrow\ldots\text{—RCONHR}'+\text{HCl}$$
$$\ldots\text{—RNH}_2+\text{ClCOR}'\rightarrow\ldots\text{—RNHCOR}'+\text{HCl}$$
$$\ldots\text{—RC}_6\text{H}_4\text{ONa}+\text{ClCOR}'\rightarrow\ldots\text{—RC}_6\text{H}_4\text{OCOR}'+\text{NaCl}$$
$$\ldots\text{—RCOCl}+\text{NaOC}_6\text{H}_5\rightarrow\ldots\text{——RCOOC}_6\text{H}_5+\text{NaCl}.$$

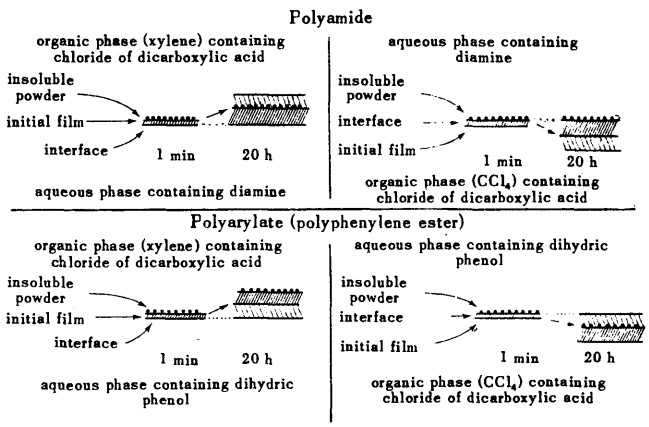


Fig. 2. Diagrams of growth of polymeric film (polyamide and polyester) at the interface between two liquids.[18]

Such unifunctional compounds can probably include also the partly saponified acid chloride:

$$\ldots -RNH_2+ClCOR'COOH \rightarrow \ldots -RNHCOR'COOH+HCl,$$

and also the basic salt of the diamine:

$$\ldots -RCOCl+H_2NR'NH_2\cdot HCl \rightarrow \ldots -RCONHR'NH_2\cdot HCl+HCl,$$

or the monophenoxide of a dihydric phenol:

$$\ldots -RCOCl+NaOC_6H_4OH \rightarrow \ldots -RCOOC_6H_4OH+NaCl.$$

(5) The impurities in the chloride of adipic acid can include its anhydride, which will terminate the chain by the reaction:

$$CO(CH_2)_4CO+H_2NR-\ldots \rightarrow HOOC(CH_2)_4CONHR-\ldots$$

(6) Apart from the above chain-terminating reactions, chain growth may stop owing to inhibition of the entry of one of the original monomers through the polymer film which is being formed, as a result of which the polymer molecules terminate in the same groups:

$$ClCORCO[NHR'NHCORCO]_x Cl \quad \text{or} \quad H_2NRNH[COR'CONHRNH]_x H$$

or

$$HOC_6H_4O[CORCOOC_6H_4O]_x H.$$

These macromolecules are unable to react with the starting materials of similar chemical nature to their end-groups, *i.e.* with those among which they find themselves. Similarly, they cannot react with one another.

III. KINETICS AND FUNDAMENTAL LAWS

Special difficulties occur in the study of the kinetics of interfacial polycondensation, since the process occurs with high reaction velocities. The quantity of diamine or diphenoxide which can be transferred to the organic phase determines the reaction velocity at any concentration of the reactants, so that the rate of reaction is ultimately governed by the rate of diffusion of monomers from one phase to the other[10,18]. The rate constants of the reactions of aliphatic acid chlorides with primary diamines are very high, their order of magnitude in homogeneous solution being 10^2–10^4 litre × × mole^{-1} sec^{-1}, *i.e.* similar to the rate of chain propagation in the radical polymerisation of vinyl compounds[18]. The reaction velocity of interfacial polycondensation is considerably higher than the rate of mixing of the reactants. Morgan and Kwolek[18] found the rate constant for the formation of polyamides in the water–chloroform system to be 570 litre mole^{-1} sec^{-1}.

Fainberg and Mikhailov[23] worked out a technique for studying the kinetics of interfacial polycondensation based on measurement of the electrical conductivity of the aqueous phase (the diamine solution). Entelis *et al.*[24] think it possible to investigate the kinetics of this reaction by utilising the chemiluminescence which they observed to accompany condensation between a toluene solution of adipoyl chloride and an aqueous solution of hexamethylenediamine.

Interfacial polycondensation makes it possible to obtain polymers of higher molecular weight than have been obtained by other methods of polycondensation. Conix[21] prepared polyphenyl esters with a mean molecular weight of 250 000. Schnell[22] reported having prepared polycarbonates with molecular weights up to 200 000, and Wittbecker and Morgan[10] have described polyurethanes having molecular weights up to 1 000 000.

The yield and the molecular weight of polymers obtained by interfacial polycondensation are greatly affected by the temperature and the duration of the reaction, the presence of excess of the starting materials, the concentration of the latter, the presence of emulsifiers, and other factors.

1. Effect of Temperature

A characteristic feature of interfacial polycondensation is that it occurs at relatively low temperatures. The molecular weight and the yield of polyamides and polyesters are affected in a similar way by the reaction temperature[25,26] (see Figs. 3 and 4), an increase in temperature leading to a decrease in the molecular weight of the polymers. This phenomenon is obviously associated with the increased rate of hydrolysis of the chlorides of dicarboxylic acids at higher temperatures[27] (Fig. 5), which leads to chain termination.

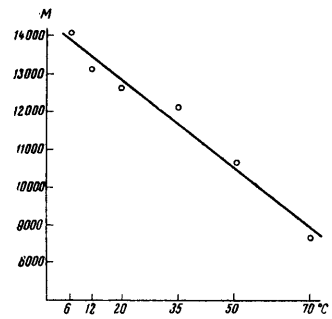


Fig. 3. Variation of the molecular weight of polyhexamethyleneadipamide with the temperature of interfacial polycondensation.[25]

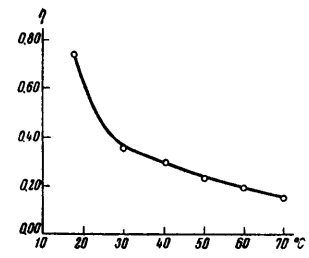


Fig. 4. Variation of the reduced viscosity of polyester with the temperature of interfacial polycondensation of isophthaloyl chloride and bisphenol A.[26]

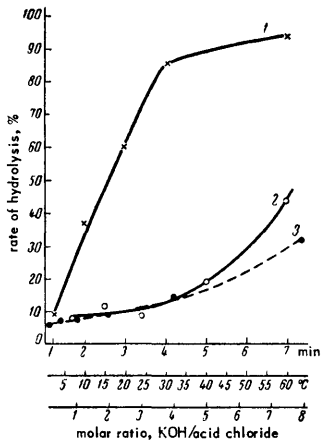


Fig. 5. Variation of the rate of hydrolysis of adipoyl chloride in benzene solution (0.15M) with: 1) time of hydrolysis at 25°; 2) temperature of reaction (reaction time 1 min); 3) quantity of caustic potash (reaction time 1 min at 25°).

The rate of hydrolysis of the carbonyl chloride end-groups on the growing macromolecule should be similarly increased, resulting in the formation of carboxyl groups at the ends of the chain, which are inactive in this reaction:

$$ClCORCO[NHR'NHCORCO]_xCl + 2H_2O \rightarrow HOOCRCO[NHR'NHCORCO]_xOH + 2HCl.$$

In addition, it is possible that chain termination may result from the formation of the monochloride of the dicarboxylic acid:

$$H_2NR'NH[CORCONHR'NH]_xH + 2ClCORCOOH \rightarrow$$
$$\rightarrow 2HCl + HOOCRCO[NHR'NHCORCO]_{x+1}OH$$

The yield of polymer, however, is only slightly affected by a rise in reaction temperature at the phase boundary from 20° to 70°.[26] Similar results were obtained by Sundet *et al.*[28] for the formation of polysulphonamides. At -40° high-molecular-weight polymers can be obtained[29].

2. Effect of Reaction Time

Since polycondensation at a phase boundary takes place rapidly, polymer formation occurs within very short intervals of time (2–10 min). Increasing the reaction time above ~10 min does not produce any increase in the yield or molecular weight of the polymers[25,26].

Table 1[25] shows that the bulk of the polymer is formed within the first few minutes of the reaction. Nor does the molecular weight change when the duration of the process is increased. An increase in the rate of stirring of the reaction system substantially increases both the yield and the molecular weight of the polymer[25,26,29]. This effect has been studied also by Akutin and Rodivilova[31].

TABLE 1. Effects of time and rate of stirring on the molecular weight and yield of polyamide[25] (concentration of reactants 0.15M).

Time of stirring, min	Yield, %	Viscosity of 0.5% solution in cresol	Molecular weight
Rapid stirring (~7 500 rev/min)			
0.5	34	0.71	19 000
1.0	45	0.69	18 500
1.5	42	0.71	19 000
3.0	49	0.68	18 700
6.0	46	0.72	19 200
12.0	43	0.73	19 700
Slow stirring (~1 000 rev/min)			
3.0	25	0.46	12 500
10.0	32	0.53	14 300
12.0	33	0.46	12 500
90.0	33	0.49	13 200

3. Effect of an Excess of One Reactant

If polymers of high molecular weight are to be formed by carrying out the reaction in a melt, equimolecular proportions of the starting materials must be present. If excess of one of the reactants is present, the molecular weight of the polymer falls sharply[32–35].

When, however, polycondensation is carried out at the interface between two phases, several workers[7,25,29,36] have shown that the relative proportions of the starting materials has no effect on the molecular weight of the resulting polymers in nearly all cases other than polyesters[26,38]. Thus in the preparation of polyamides[7,25,29] polysulphonamides[36], and polyureas[37], for example, an excess of any of the reactants up to 100–300 mole% does not lead to any lowering of the molecular weight of the resulting polymers. Fig. 6 shows the results obtained by Korshak *et al.*[7]

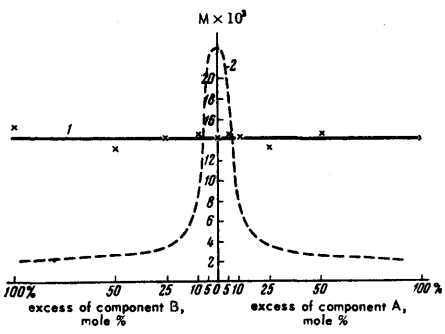


Fig. 6. Dependence of the molecular weight of polyhexamethyleneadipamide on the excess of starting materials: 1) in interfacial polycondensation (non-equilibrium); 2) in equilibrium polycondensation (in the melt); A — hexamethylenediamine; B — adipic acid.[7]

In contrast to this, with polyesters [26,38] an excess of one of the reactants lowers the molecular weight (Fig. 7 [38]). This difference in the effect of excess of the reactants on the molecular weight with the different types of polycondensation polymers is obviously associated with the nature of the reactants and with the mechanism of the formation of these high polymers.

The absence of any effect of excess of the starting materials on the molecular weight of a polyamide is due to the fact that, thanks to the high reaction velocity of the starting materials, the molecular weight is governed by kinetic factors, and in particular the rate of diffusion of monomers through the polymer film which is formed. Therefore the chain-terminating reactions constitute the main factor determining the molecular weight of the polyamide. In the preparation of polyesters, film formation does not occur, and therefore the presence of excess of one of the starting materials does have an effect on the molecular weight of the polyester, since in this case the process takes place with high degrees of conversion, so that an existing excess can block the end-groups of the polymer and terminate its growth.

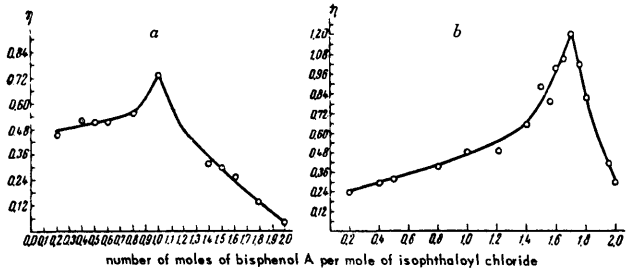


Fig. 7. Variation in the reduced viscosity of the polyester obtained by interfacial polycondensation from isophthaloyl chloride and bisphenol A: *a*) with a bisphenol A: caustic soda ratio of 0.5; *b*) with an isophthaloyl chloride: caustic soda ratio of 0.25. [38]

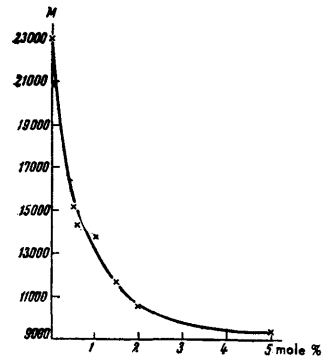


Fig. 8. Change in the molecular weight of polyhexamethyleneadipamide on addition of different amounts of butyryl chloride (abscissae). Polymer obtained by drawing out of solution. [7]

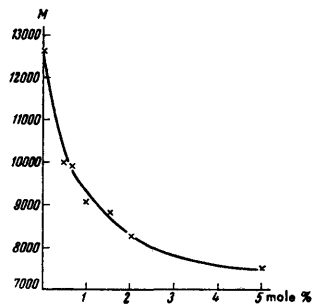


Fig. 9. Change in the molecular weight of polyhexamethyleneadipamide on addition of different amounts of butylamine (abscissae). Polymer obtained by stirring solutions of the reactants. [7]

4. Effect of Unifunctional Additives

Equilibrium polycondensation in the presence of unifunctional additives is known to yield polymers of lower molecular weight than in the absence of such additives [39-42]. This is due to degradation of the polymer under the influence of such additives, as well as to the cessation of chain growth owing to blocking of the functional end-groups of the polymer. Unifunctional compounds also cause a diminution in the molecular weight of polymers obtained by interfacial polycondensation [7,38].

Korshak *et al.* [7] showed that, in the preparation of polyamides, the molecular weight of the resulting polymer is lower if unifunctional substances of similar chemical nature to the starting materials are added to the reaction mixture. Fig. 8 shows the effect of different quantities of butyryl chloride on the molecular weight of the polyamide, and Fig. 9 shows the effect of adding various quantities of butylamine.

Addition of benzoyl chloride or phenol in the preparation of polyesters by interfacial polycondensation also leads to polyesters of lower molecular weight (Fig. 10) [38]. This effect of unifunctional additives is explained by their reacting with the end-groups of the growing macromolecule and forming end-groups which are incapable of reaction, thus causing chain termination:

$$\cdots -\mathrm{CORCOCl} + \mathrm{H_2NR'} \rightarrow -\mathrm{CORCONHR'} + \mathrm{HCl}$$

$$\cdots -\mathrm{C_6H_4ONa} + \mathrm{ClCOR} \rightarrow \cdots -\mathrm{C_6H_4OCOR} + \mathrm{NaCl}.$$

A similar state of affairs is observed in the preparation of polysulphonamides, polyureas, polyurethanes, and other polymers. It follows from this that, in order to obtain polymers of high molecular weight by interfacial polycondensation, the reactants must not contain as impurities unifunctional compounds which can react with one of the reactants. Therefore statements in the patent literature that the purity of the starting materials does not affect the properties of the resulting polymer must be regarded as incorrect.

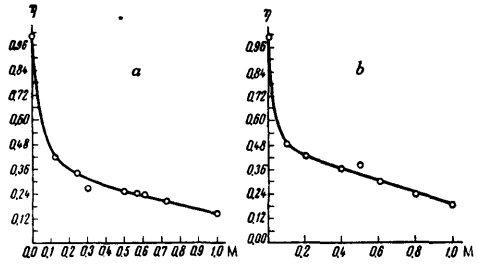


Fig. 10. Change in the reduced viscosity of the polyester obtained by interfacial polycondensation from isophthaloyl chloride and bisphenol A on addition of various amounts of: *a*) benzoyl chloride; *b*) phenol. [38]

Mikhailov *et al.*[43] have shown (see Fig. 11) that the molecular weight of polyhexamethylenesebacamide is greatly dependent on the purity of the initial sebacoyl chloride. As can be seen from Fig. 11, even 2% of impurities in the acid chloride lower the molecular weight of the polymer almost to one-third. In the preparation of polysulphonamides, too, the purity of the original disulphonyl chloride has an effect on the yield and the molecular weight of the polymer[28]. Among the impurities which diminish the molecular weight of polymers obtained from acid chlorides must be included the anhydrides of dicarboxylic acids. These are quite difficult to separate from the chlorides owing to the similarity in their boiling points. Anhydrides are harmful because, by reacting with the growing chain, they terminate it, forming unreactive end-groups:

$$\cdots -NHRNH_2 + CO(CH_2)_4CO \rightarrow \cdots -NHRNHCO(CH_2)_4COOH$$
$$\cdots -C_6H_4OH + CO(CH_2)_4CO \rightarrow \cdots -C_6H_4OCO(CH_2)_4COOH$$

Other reactive impurities are possible in the starting materials. Hence it follows that the requirement that the reactants used in equilibrium polycondensation must have maximum purity applies equally to interfacial polycondensation.

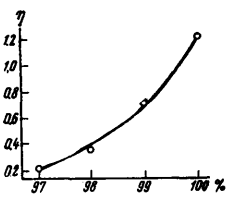


Fig. 11. Variation of the specific viscosity of polyhexamethylenesebacamide with the purity of sebacoyl chloride (abscissae). [43]

5. Effect of Reactant Concentration

The concentration of the reactants is of considerable importance.

Interfacial polycondensation can be effected even when one of the solvents is completely eliminated: *i.e.* the concentration of one of the reactants, if liquid, can be 100% [29,30,36,37]. But it is evident from several papers (see Figs. 12–15) that the preparation of each polymer has its own strictly defined relationship between molecular weight, yield of polymer, and concentration of reactants [10,18,25,26]. The accompanying diagrams show that in all cases the maximum molecular weight corresponds to a strictly defined concentration of the reactants. It is interesting that the yield of polymer depends on this concentration in the same way as the molecular weight [25]. The effect of reactant concentration on the course of the reaction was studied by Akutin and Rodivilova [31,44] and other workers [45].

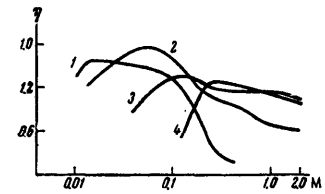


Fig. 12. Variation of the intrinsic viscosity of polyhexamethylenesebacamide with reactant concentration. Molarity of diamine solution: 1) 0.1; 2) 0.4; 3) 0.8; 4) 1.4.[18] The abscissae give the concentrations of sebacoyl chloride in carbon tetrachloride.

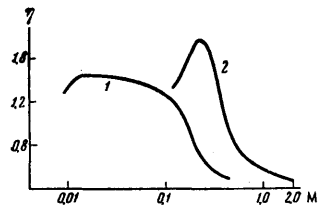


Fig. 13. Variation of the intrinsic viscosity of polyhexamethylenesebacamide with reactant concentration: 1) in the absence, 2) in the presence of an emulsifier. Concentration of diamine 0.1M. Abscissae as in Fig. 12.

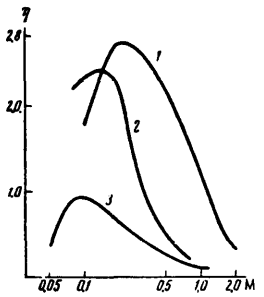


Fig. 14. Variation of the intrinsic viscosity of polyamides obtained by interfacial polycondensation with the concentration of dicarboxylic acid chlorides: 1) polyhexamethylenesebacamide; 2) polypiperazineterephthalamide; 3) polyhexamethyleneterephthalamide. Concentration of diamines 0.4M.[18] The abscissae represent concentrations of acid halide in chloroform.

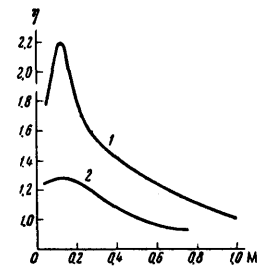


Fig. 15. Variation of the intrinsic viscosity of polyhexamethylene-*m*-benzenedisulphonamide with the concentration of the disulphonyl chloride. Effect of acid acceptor in: 1) 0.25M Na_2CO_3 + 0.13M diamine; 2) 0.25M NaOH + 1.13M diamine.[18,28] The abscissae represent concentrations of the disulphonyl chloride in dichloromethane.

6. Effect of Acid Acceptor

In order to achieve high molecular weights in ordinary equilibrium polycondensation, it is necessary to bond or to remove the products of low molecular weight (water, alcohol, ammonia, hydrogen chloride, etc.) formed during the reaction[1,4]. With polycondensation at the boundary between two phases, the reaction between the chloride of the dicarboxylic acid and the diamine or dihydric phenol leads to the evolution of hydrogen chloride, which also can cause chain termination. In most cases, therefore, a necessary condition for obtaining polymers at the interface is the presence of an acid acceptor in the aqueous phase. Several papers have shown[10,25,29,46] that we can use for this purpose various bases, oxides, hydroxides, and carbonates of the alkali and alkaline-earth metals which are particularly soluble in water, such as KOH, NaOH, $Ba(OH)_2$, or Na_2CO_3, as well as various organic bases (pyridine, triethylamine, etc.). When one of the monomers is a diamine, it itself can serve this purpose.

The quantity of the acid acceptor may vary within wide limits, from zero to a fivefold excess[30,36]. However, it is preferable not to use more than a threefold excess. Korshak *et al.*[38] have shown that the highest yields and molecular weights are obtained with polyesters by using acid acceptors in amounts approximately equivalent to the bifunctional compound. Fig. 16 shows the effect of the quantity of alkali on the molecular weight and the yield of a polyester.

Organic bases (pyridine)[25] do not give nearly such good results as do inorganic bases. Clearly, this can be explained by the fact that pyridine hydrochloride is appreciably soluble in the organic phase, causing the following equilibrium to be established:

$$C_5H_5NHCl + H_2N(CH_2)_6NH_2 \rightleftarrows C_5H_5N + H_2N(CH_2)_6NH_2 \cdot HCl$$

Sokolov and Kudim[47] point out that, in the preparation of polyamides from chlorides of aromatic dicarboxylic acids and aromatic diamines, better results are obtained in acid medium. Not only the nature and amount of the acid acceptor but also its concentration are important in determining the course of reaction, and therefore the pH of the aqueous phase has a substantial effect.

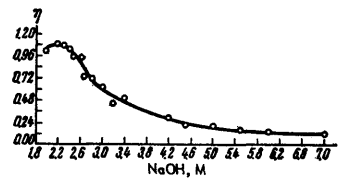


Fig. 16. Variation of the reduced viscosity of polyester from isophthaloyl chloride and bisphenol A with the quantity of caustic soda added.[38]

7. Effect of Emulsifiers

As shown above, vigorous stirring at the interface between two phases increases the reaction surface and leads to an increase in the yield and the molecular weight of the polymers[25] (see p. 256). A similar effect is exerted by emulsifiers[10,19,29,30,36,37,48], which may be either cationic, anionic, or neutral in character and can be soluble in either water or the organic solvent. The most widely used emulsifier in interfacial polycondensation is sodium lauryl sulphate.

It is evident from the results of Korshak *et al.*[48] summarised in Table 2 that the best emulsifiers with respect to the yield and molecular weight of polyesters are sodium Mersolate and Nekal.

The data in Table 3 show the effect of varying the amount of emulsifier.

The optimum concentration is ~1%. Excess of the emulsifier lowers the molecular weight of the polyester. In this case the use of an emulsifier, apart from increasing the molecular weight and the yield of polymers, makes it possible to extend the range of organic solvents which can be employed in interfacial polyesterification.

TABLE 2. Effect of the nature of emulsifier on the reduced viscosity and yield of polyester.

(Concentration of emulsifier in aqueous layer 1 wt. %)*

Emulsifier	Reduced viscosity of polyester in cresol	Yield of polyester, %
Na stearate	0.78	76
Na Mersolate	1.54	79
New product	1.06	75
OP-20	0.94	82
Trilon B [EDTA]	0.22	50
Nekal	1.44	75

* Concentration of reactant solutions: 0.125M alkaline solution of dihydric phenol, 0.5 g of emulsifier in 10 ml of water, and 0.1M solution of isophthaloyl dichloride in *p*-xylene. Stirring continued for 20 min.

TABLE 3. Effect of emulsifier concentration (Na Mersolate) on the reduced viscosity and yield of polyester.

Concn. of emulsifier in aqueous layer, wt.%	Reduced viscosity of polyester in cresol	Yield, %
0.25	1.10	78
0.50	1.24	75
0.88	1.14	77
1.00	1.54	79
1.35	1.24	83
1.75	1.10	75
2.00	1.02	82
2.50	0.76	84

8. Effect of Solvent

Interfacial polycondensation is carried out in a solvent system consisting of water and an organic solvent. The latter may belong to various classes of organic compounds which are immiscible or not very miscible with water and which do not react with the reactants. The most widely used are such solvents as benzene and its homologues, aliphatic hydrocarbons, halogenated hydrocarbons, and several other substances[25,29,30,49]. The organic solvent affects such variables in interfacial polycondensation as the distribution of the reactants between the two phases, the diffusion of the reactants, and the swelling and permeability of the polymer which is formed[50]. Wittbecker and Morgan[50], as well as Sokolov and Turetskii[51], consider that to obtain a high-molecular-weight polymer, it is necessary that the solvent should merely cause the resulting polymer to swell, whereas Eareckson[19] considers that the polymer must be dissolved. The influence of these factors has at present no theoretical explanation, and in most cases the solvents which promote the synthesis of polymers of sufficiently high molecular weight and in sufficiently high yield are selected empirically. Thus the best solvents for the preparation of polyesters, for example, prove to be chloroform, 1,1,2-trichloroethane, trichloroethylene[19], and *p*-xylene[26]. Solvents which may be successfully used for the preparation of polyamides are benzene, methylene chloride, chloroform, and carbon tetrachloride[18,25,49].

Emulsifiers can play a large part in extending the range of organic solvents which can be utilised[52]. In the preparation of polyesters, for example, Nekal increases the molecular weight of the polyester with nearly all the organic solvents used (see Table 4).

Organic solvents are used to prepare solutions of the acid halides, whereas solutions of the second reactant are usually made up with water. In the preparation of polyamides by interfacial polycondensation, water can be replaced by ethylene glycol[29]. Polycondensation can then be carried out at low temperatures (around -40°).

Inorganic salts, especially neutral salts such as sodium chloride, when added to an alkaline aqueous solution of a diamine, increase the proportion of the latter in the organic phase[18]. Furthermore, the presence of salts in the aqueous phase lowers the solubility of acid chlorides in water, and hence diminishes their hydrolysis. This considerably improves the preparation of polymers from the lower aliphatic acid dichlorides, which are more soluble in water than are the higher dichlorides. Addition of salts to the aqueous phase is especially important in the preparation of polymers of the A–B type[9,52] (see p. 263).

TABLE 4. Effect of the nature of solvent on the reduced viscosity and yield of polyester.

Solvent of isophthaloyl chloride	With emulsifier*		Without emulsifier	
	reduced viscosity of polyester in cresol	yield, %	reduced viscosity of polyester in cresol	yield, %
Xylene	1.46	80	1.02	88
Tetralin	0.64	80	0.28	86
n-Heptane	0.94	84	0.30	quantitative
Carbon tetrachloride	1.12	83	0.40	»
Chloroform	0.44	77	0.12	»
Dichloroethane	0.72	80	0.16	80
Tetrachloroethylene	1.02	82	-	-
Trichloroethylene	0.96	80	-	-
Chlorobenzene	0.72	80	0.20	83
Ethyl ether	0.58	87	0.33	77

* Concentration of emulsifier 1.5% in water.

IV. COMPARISON OF EQUILIBRIUM AND INTERFACIAL POLYCONDENSATION

The formation of polyamides and polyesterification, like other forms of equilibrium polycondensation taking place in solution or in a melt at high temperatures, are reversible reactions:

$$x\,H_2NR'NH_2 + x\,HOOCRCOOH \rightleftarrows [-NHR'NHCORCO-]_x + 2x\,H_2O$$

$$x\,HOR'OH + x\,HOOCRCOOH \rightleftarrows [-OR'OOCRCO-]_x + 2x\,H_2O$$

Therefore the extent of conversion and the molecular weight of the resulting polymers are determined by the

completeness of removal of reaction products of low molecular weight, *i.e.* of water in this case[2,32,53]. The molecular weight of the polymers then depends on the relative proportions of the starting materials, or more generally of the initial functional groups[2,3,32-35]. Polymers of high molecular weight are formed only when the starting materials are present in equivalent proportions. The presence of excess of any of the starting materials or of a product which is chemically similar leads to a diminution in the molecular weight of the polymer. Since an inverse relationship exists between the amount of this excess and the molecular weight of the polymer, the maximum value of the latter can be predetermined by adding the calculated quantity of the acid, diamine, or other compound as molecular-weight regulator[34]. Exchange reactions between the polymer molecules[4,54,55] and also between the polymer molecules and the starting materials[4,56-67] play an important role in polycondensation. These exchange reactions result in a degradation of the polymer molecules[4,57-67], which takes place more readily and more rapidly the higher the molecular weight of the polymer[68,69]. As a result, the longer molecules are first broken down under the influence of the degradative exchange reactions during polycondensation, and the polymer formed has comparatively small polydispersity, in contrast to the polymers obtained by polymerisation[69-75], as investigations of the molecular-weight distribution of the polymers have shown[1,71,75].

Unlike high-temperature equilibrium polycondensation in a melt, polycondensation at the boundary between two immiscible phases is an irreversible process[7,10,18,25,26]:

$$x\ \mathrm{ClCORCOCl} + x\ \mathrm{NH_2R'NH_2} \rightarrow [-\mathrm{NHR'NHCORCO}-]_x + 2x\ \mathrm{HCl}$$
$$x\ \mathrm{ClCORCOCl} + x\ \mathrm{HOR'OH} \rightarrow [-\mathrm{OR'OOCRCO}-]_x + 2x\ \mathrm{HCl}.$$

Since the reaction takes place at low temperatures, the products of low molecular weight which are formed do not react with the polymer, and hence do not affect its molecular weight or the extent of conversion. In the formation of polyamides by interfacial polycondensation, the molecular weight of the resulting polymer is independent of the relative proportions of the starting materials[7,10,18,36]; in polyesterification[38] the proportions of the starting materials do to some extent affect the molecular weight of the polyester (see p. 256). A peculiarity of interfacial polycondensation is the heterogeneity of the process. Another important feature which affects the preparation of polymers of high molecular weight is the occurrence of side-reactions which terminate the chains by forming end-groups which do not react under the given conditions. With equilibrium polycondensation, on the other hand, most of the terminal functional groups are retained as such, and hence the macromolecules do not lose their capacity for further chain growth.

The molecular-weight distribution[18] of polymers obtained by interfacial polycondensation may vary depending on the reaction conditions. In some cases[18] the distribution was narrower than in the case of polycondensation in a melt, and in other cases it was broader or similar.

A comparison of the properties of polymers obtained by interfacial polycondensation with those obtained at high temperatures has led several workers[10,18,76,77] to conclude that the polymers are identical in melting point, crystallinity, and also solubility. Schnell[22] points out, however, that polymers obtained by interfacial polycondensation have good mechanical properties only at relatively high molecular weights.

Table 5 gives a comparison of the two methods of polycondensation with respect to the requirements to be met by the starting materials, the conditions of polycondensation, and the properties of the resulting polymers[10,18].

Examination of these data shows that interfacial polycondensation has several advantages over polycondensation in a melt, the main advantages being as follows:

(a) The reaction is carried out at low temperatures, which permits an extension of the range of monomers which can be used, since it becomes possible to utilise thermally unstable monomers, and thus to obtain polymers which it had previously been impossible to prepare by high-temperature equilibrium polycondensation[78,79].

(b) The method of interfacial polycondensation makes it possible to obtain polymers having a high melting point, often lying above the temperature at which they decompose. It is impossible to obtain such polymers by equilibrium polycondensation in the melt, since they are decomposed.

TABLE 5. Comparison of interfacial polycondensation and polycondensation in the melt.

	Interfacial	In the melt
Starting materials		
Purity	moderate to high	high
Thermal stability	not essential	essential
Equilibrium	not essential	essential
Conditions of polycondensation		
Time	a few minutes	a few hours
Temperature	0°–40°	> 200°
Pressure	atmospheric	high or low
Equipment	simple, open	special, sealed
Products		
Yield	low to high	high
Structure	unrestricted	restricted by thermal stability and fusibility

(c) The reaction can be carried out within a very short period of time, it requires very simple apparatus, and is therefore very convenient for the laboratory preparation of polymers.

(d) Polymers of high molecular weight can often be obtained without requiring equimolecular proportions of the starting materials.

(e) The method provides an opportunity for obtaining, at the boundary between the two phases, polymer films which can be removed from the reaction zone in the form of a continuous film[80]. This enables goods made of high polymers (films, fibres) to be obtained by a continuous method directly from the reaction zone[43,46].

In this connection the production of articles from materials which are difficult or even altogether impossible to work in industry (*e.g.* cross-linked, infusible, insoluble polymers) is of particular interest. In spite of the series

of favourable aspects indicated above, interfacial polycondensation has specific disadvantages: (*a*) the process requires the presence of chlorides of dicarboxylic acids, which are less readily available than the acids themselves and require an additional stage in the synthesis of the monomers; (*b*) the yield of polymers may vary within wide limits depending on the nature of the starting materials; (*c*) the polymers contain such impurities as sodium chloride and other substances. Washing out the impurities is often a quite lengthy stage in the preparation of the polymers.

It is still too early to arrive at final conclusions concerning the future of interfacial polycondensation. The study of the process has only just begun, but it is already clear that this method has its place in the series of synthetic reactions which can be used to prepare polymers.

V. METHOD OF CARRYING OUT INTERFACIAL POLYCONDENSATION

Two procedures can be employed for polycondensation at an interface[10,30,80].

1. Preparation of Polymers with Stirring

Various macromolecular compounds can be prepared by stirring solutions of the reactants at the interface between two phases. The polymers are then obtained in the form of a powder, and can be further processed into various goods (films, fibres, etc.) in the usual way. Stirring enables the formation of the polymer to be accelerated, and the molecular weight and the yield to be increased. The preparation is carried out in an apparatus fitted with a mechanical stirrer rotating at high speed. A solution of the acid dihalide in an organic solvent immiscible with water (benzene, chloroform, hexane, etc.) is run into an alkaline aqueous solution of the multifunctional compound (diamine, dihydric phenol, etc.) with stirring, and the polymer is immediately formed as a film, a powder, or granules. The hydrogen chloride evolved during the reaction is absorbed by the alkali. The reaction is carried out at moderate temperatures, usually room temperature, in short periods of time, and is practically complete within 2–15 min.

If the multifunctional compound is insoluble in water but soluble in some organic solvent, it can be suspended in the water–organic solvent system for the purpose of polycondensation[10,29,37]. The organic solvent must not react, or may react only slightly, with the acid dihalide[29,30,37]. A water-insoluble multifunctional compound can also be introduced in the form of its water-soluble derivatives (*e.g.* the hydrochlorides of aromatic diamines)[28,30]. The calculated quantity of alkali required to liberate the free diamine and also to combine with the hydrogen chloride eliminated during the process is gradually added to a stirred solution of the reactants. The resulting polymer is most frequently obtained in solid form, and is easily separated from the reaction mixture by simple filtration. When, however, the polymer is soluble in the solvent system employed, it is isolated by distilling off the solvent or by precipitating the polymer with a suitable precipitant[49,78]. The precipitated polymer is washed successively with an aqueous solution of acetone or alcohol and warm water until chloride has been completely removed. The yield of polymer may vary within wide limits depending on the nature of the starting materials and the reaction conditions, and it is often quantitative.

The molecular weights and yields of polymers depend, as already mentioned, on several factors — intensity of stirring, concentration, temperature, presence of emulsifiers, etc.

2. Preparation of Polymers without Stirring

Polymers can also be obtained without stirring the solutions of the reactants[10,80]. When a solution of the acid dihalide is run into an alkaline aqueous solution of the diamine, a film of polymer is instantly formed at the interface, and it is often so strong that it can be removed from the reaction zone in the form of a continuous filament (Fig. 17).

The polymer obtained in this way is subjected to further treatment as described above; the yield of polymer is rather lower (25–50%) because the polymer carries a proportion of the reactants away from the zone of reaction.

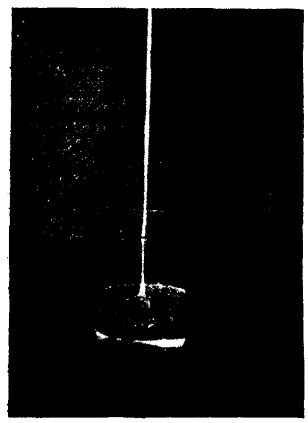


Fig. 17. Continuous preparation of polymer filament by interfacial polycondensation: first layer — alkaline aqueous solution of diamine; second layer — solution of dicarboxylic acid halide in organic solvent; third layer — polymer film formed at interface.

The molecular weights of polymers obtained without stirring are not lower than those of polymers obtained with stirring, and depend on the experimental conditions.

Interfacial polycondensation without stirring will probably find application in the direct manufacture of polymeric goods (films, fibres) from the reaction zone, using both linear and three-dimensional macromolecular compounds[10,43,46,81].

3. Design of Apparatus for Interfacial Polycondensation

Interfacial polycondensation takes place at room temperature and atmospheric pressure; therefore it can be carried out in very simple apparatus and can easily be arranged as a continuous process[36,82]. Fig. 18 illustrates

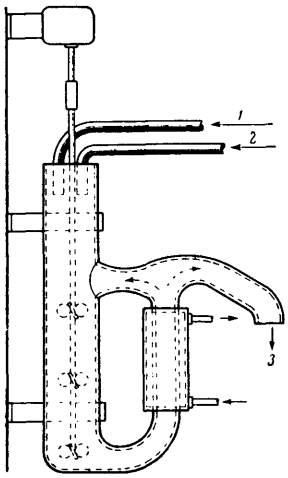


Fig. 18. Apparatus for continuous preparation of polymers by interfacial polycondensation:[10,36]
1) acid dichloride; 2) diamine; 3) polymer.

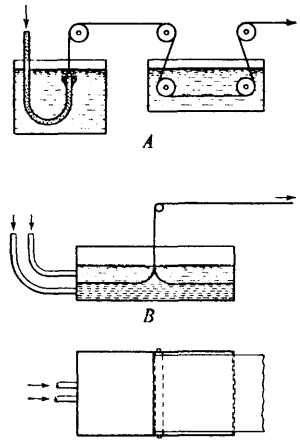


Fig. 20. Arrangement for continuous production of polyamide filament (*A*) and film (*B*) by interfacial polycondensation.[46]

an apparatus for carrying out such a process with stirring of the initial reactants and partial recirculation of the reaction mixture.

By utilising the ability of certain polymers to form a sufficiently strong film at the phase boundary, this process can be used to produce ready-made polymeric materials (films, fibres)[43,46]. Figs. 19 and 20 show arrangements for obtaining polymeric goods directly from the reaction zone.

The continuous preparation of polymers directly from the reaction zone opens up prospects for the development of a new technology for the production of polymeric materials. As a result, it becomes possible to process into fibres and films polymers which are practically insoluble and which possess melting points close to the temperatures at which they decompose.

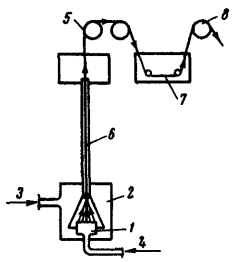


Fig. 19. Scheme for fibre production by interfacial polycondensation:
1) spinneret; 2) spinning head; 3) supply of diamine solution; 4) supply of dicarbonyl chloride solution; 5) guide roll; 6) filament after formation; 7) washing bath; 8) take-up device.[41]

VI. MACROMOLECULAR COMPOUNDS OBTAINED BY INTERFACIAL POLYCONDENSATION

1. Polyamides

Polyamides represent the class of polymers which is most readily obtained by interfacial polycondensation and is able to form films at the boundary between the immiscible phases. From the preparative viewpoint, polyamides are least sensitive to the effect of the solvents, the proportions of the reactants, and similar factors[7,10,18,25,83].

Polyamides can be prepared from substances of differing structure — aliphatic and aromatic diamines and chlorides of aliphatic and aromatic dicarboxylic acids, as well as chlorides of unsaturated acids (see Table 6).

2. Polymers of Type A–B[9,52]

Polymers of type A–B are macromolecular compounds obtained from monomers containing both interacting functional groups in a single molecule. The amino-acids form an example of such monomers. Polymers of this type are produced according to the scheme:

$$x\,\mathrm{ClCO(CH_2)_5NH_2\cdot HCl} + 2x\,\mathrm{NaOH} \rightarrow [\mathrm{—OC(CH_2)_5NH—}]_x + 2x\,\mathrm{NaCl} + 2x\,\mathrm{H_2O}\,.$$

The mechanism of the interfacial polycondensation of such monomers differs somewhat from that for two different bifunctional compounds (*e.g.* a diamine or a dihydric phenol with the dichloride of a dicarboxylic acid, etc.). The main difference is that the monomers must be used in the form of salts (to block the amino-groups).

The formation of polymers of type A–B by interfacial polycondensation takes place in the following way[52]. Since the monomer is a salt, which is only sparingly soluble in the organic solvent, it diffuses into the alkaline-aqueous phase, where the amino-group is set free. The monomer free from the salt group is readily soluble in the organic phase, where reaction takes place between the free amino-group and the acid chloride group of another molecule.

TABLE 6. Polyamides obtained by interfacial polycondensation from diamines and dichlorides of dicarboxylic acids.

Diamine	Dichloride of dicarboxylic acid	Literature references
Ethylenediamine	sebacoyl	84
	terephthaloyl	84, 85
	phthaloyl	86
N,N'-Dimethylethylene-diamine	terephthaloyl	85
N,N'-Diethylethylene-diamine	terephthaloyl	85
N,N'-Dibutylethylene-diamine	terephthaloyl	85
Trimethylenediamine		85
1,2-Diaminopropane		83
N,N'-Dimethyltri-methylenediamine		85
N,N'-Diethyltrimethylene-diamine		85
2-Hydroxytrimethylene-diamine	sebacoyl	83
Tetramethylenediamine	biphenyl-*p,p'*-dicar-bonyl	83
	terephthaloyl	85
	sebacoyl	30
N,N'-Dimethyltetra-methylenediamine	terephthaloyl	85
Pentamethylenediamine		85
Hexamethylenediamine	oxalyl	29
	fumaroyl	87, 88
	β-hydromuconoyl	83
	adipoyl	29, 30, 43, 76, 81, 83, 89, 90
	azelaoyl	76
	sebacoyl	29, 43, 76, 80, 81, 83, 89, 90
	terephthaloyl	84
	isophthaloyl	76, 83
	phthaloyl	86
	cyclohexane-1,4-dicarbonyl	83
	oxotriphenylphospho-rane-*p,p'*-dicarbonyl	91
	methylphosphonyl	78
	phenylphosphonyl	78, 79
	phosphoryl	78
2,5-Diaminohexane	terephthaloyl	29
Bis-3-amino-octyl ether	sebacoyl	29
Nonamethylenediamine	sebacoyl	90
Piperazine	adipoyl	29, 90
	azelaoyl	90
	sebacoyl	18, 90
	cyclopentane-1,3-dicarbonyl	31
	terephthaloyl	18, 89, 90
	isophthaloyl	49, 90
	phthaloyl	86, 90
	trans-hexahydrotere-phthaloyl	49
	cis-hexahydrotere-phthaloyl	49
Piperazine	biphenyl-*p,p'*-dicarbonyl	49, 83
	bibenzyl-*p,p'*-dicarbonyl	49
	2,2-diphenylpropane-*p,p'*-dicarbonyl	49
2-Methylpiperazine	terephthaloyl	49
	isophthaloyl	49
	trans-hexahydrotere-phthaloyl	49
	bibenzyl-*p,p'*-dicarbonyl	49
2-Phenylpiperazine	phthaloyl	86
	terephthaloyl	49

TABLE 6. (cont'd).

Diamine	Dichloride of dicarboxylic acid	Literature references
2,5-Dimethylpipera-zine	terephthaloyl	49
	isophthaloyl	49
	phthaloyl	86
	trans-hexahydrotere-phthaloyl	49
	cis-hexahydrotere-phthaloyl	49
	cyclopentane-1,3-dicarbonyl	49
	cis-hexahydroisophthaloyl	49
	1,4-dihydroterephthaloyl	49
	biphenyl-*p,p'*-dicarbonyl	49
	2,3,5,6-tetrachlorotere-phthaloyl	49
	2,2-diphenylpropane-*p,p'*-dicarbonyl	49
2,5-Diethylpiperazine	terephthaloyl	49
2,6-Dimethylpiperazine	terephthaloyl	49
2,3,6-Trimethyl-piperazine	*trans*-hexahydrotere-phthaloyl	49
2,3,5,6-Tetramethyl-piperazine	terephthaloyl	49
	trans-hexahydrotere-phthaloyl	49
p-Phenylenediamine	fumaroyl	88
	sebacoyl	92
	terephthaloyl	84, 92
m-Phenylenediamine	fumaroyl	88
	sebacoyl	83
m-Tolylenediamine	sebacoyl	92, 93
p-Xylylenediamine	sebacoyl	92
	terephthaloyl	92
1,4-Hexahydroxylylene-diamine	adipoyl	29, 83
Bis-(4-aminocyclohexyl) methane	terephthaloyl	83
	phthaloyl	86
Benzidine	fumaroyl	88
	sebacoyl	92
	terephthaloyl	92
4,4'-Diamino-3,3'-dimethylbiphenyl (tolidine)	sebacoyl	92
	terephthaloyl	92
Dianisidine	fumaroyl	88
1,5-Naphthylene-diamine	fumaroyl	88
Bis(4-aminophenyl) methane	sebacoyl	92
	terephthaloyl	92
Bis(4-aminophenyl) ethane	sebacoyl	92
	terephthaloyl	92
Bis(4-amino-3-methyl-phenyl)methane	sebacoyl	92
	phthaloyl	89
	terephthaloyl	92
Bis(*N*-methyl-4-amino-phenyl)methane	sebacoyl	92
	terephthaloyl	92
Bis(*N*-ethyl-4-amino-phenyl)methane	sebacoyl	92
	terephthaloyl	92
Bis(*N*-ethyl-4-amino-3-methyldiphenyl)-methane	sebacoyl	92
	terephthaloyl	92

Repetition of this reaction many times over leads to the production of a macromolecular compound. The molecular weight and the yield of polymers of type A – B depend to a considerable extent on the hydrolysability of the acid chloride groups of the monomers, since hydrolysis of these groups becomes possible when they are released in the alkaline-aqueous layer. In order to suppress this reaction, which would lead to termination of the polymer chain, high concentrations of neutral salts are introduced into the alkaline-aqueous phase, as these salt-out the "unblocked" monomer into the organic phase, thereby reducing the amount of hydrolysis.

Schaefgen *et al.*[52] used a series of salts of aminoalkyl esters of chloroformic acid for the preparation of polyurethanes and polyamides – for example, the hydrochlorides of 5-aminopentyl chloroformate and *p*-aminomethylbenzoic acid, toluenesulphonates of 4-aminobutyl chloroformate and 3(γ-piperidyl)propyl chloroformate, and similar compounds.

3. Polysulphonamides

Polymers of this class obtained by interfacial polycondensation are of practical interest, since they possess a molecular weight which is sufficient for the production of oriented films and fibres[28,36,94,95]. Attempts to obtain polysulphonamides by other methods of polycondensation yielded polymers having predominantly low molecular weights[96-99].

The most important factors in the preparation of polysulphonamides are strict concentration ratios of the reactants in both phases, a high degree of purity of the disulphonyl chlorides, a definite pH of the aqueous medium (9–10), and several other factors[28,36,94,95].

Polysulphonamides, apart from being soluble in the solvents ordinarily used for polyamides, dissolve in 10% aqueous caustic soda solution[10,28,96].

A high concentration of alkali in the aqueous phase may, apart from favouring hydrolysis of the disulphonyl chloride, promote the formation of branched chains in the polysulphonamide, as well as leading to cross-linking of the polymer chains by reaction with the hydrogen atom of the amide group[10]:

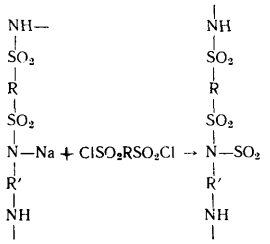


Table 7 lists a series of polysulphonamides synthesised by interfacial polycondensation.

4. Polyurethanes

Polyurethanes belong to a class of fibre-forming polymers somewhat resembling polyamides in structure. Two methods of practical interest have been worked out for preparing polyurethanes: (1) reaction between a di-isocyanate and a glycol, and (2) reaction between a bischloroformate and a diamine. Both methods have been known since 1939[96,100,101].

TABLE 7. Polysulphonamides obtained by interfacial polycondensation from aliphatic and aromatic disulphonyl chlorides.

Diamine	Disulphonyl dichloride	Literature references
Ethylenediamine	*m*-benzene-	28, 36
	p-benzene-	28
	biphenyl-4, 4′-	28, 94
	naphthalene-1, 5-	28
	phenoxybenzene-4, 4′-	28
N, *N*′-Dimethylethylenediamine	*m*-benzene-	28
	cyclohexane-1, 4-	28
Propylenediamine	biphenyl-4, 4′-	94
2-Hydroxytrimethylenediamine	*m*-benzene-	28
Trimethylenediamine	biphenyl-4, 4′-	94
1-Methyltrimethylenediamine	biphenyl-4, 4′-	94
2, 2-Dimethyltrimethylenediamine	biphenyl-4, 4′-	94
Tetramethylenediamine	biphenyl-4, 4′-	94
	pentane-1, 5-	95
Hexamethylenediamine	pentane-1, 5-	94
	m-benzene-	28, 36
	p-benzene-	28
	ethane-1, 2-	28
	hexane-1, 6-	28, 36
	cyclohexane-1, 4-	28
	naphthalene-1, 5-	28
	naphthalene-2, 7-	28
	biphenyl-4, 4′-	28, 36
	diphenylemthane-4, 4′-	35
Bis(3-aminopropyl) ether	*m*-benzene-	28
p-Xylenediamine	*m*-benzene-	28
4, 4-Dimethylheptamethylenediamine	biphenyl-4, 4′-	94
Piperazine	biphenyl-4, 4′-	94
2-Methylpiperazine	biphenyl-4, 4′-	94
trans-2, 5-Dimethylpiperazine	biphenyl-4, 4′-	94

The preparation of polyurethanes by interfacial polycondensation is a variant of the second of the above methods; the reaction is carried out using two immiscible solvents (water and an organic solvent).

The first information on the preparation of polymers of this class by the interfacial polycondensation method dates back to 1941[102], but the very broad investigation of this method began only relatively recently[103-112]. Its application allows us to obtain polyurethanes of a great variety of structures, including those containing aliphatic and aromatic groupings, as well as various copolymers[104-106].

Table 8 lists polyurethanes which have been obtained by interfacial polycondensation.

5. Polyureas

The polyureas, which are widely known representatives of polycondensation polymers, also can be obtained by interfacial polycondensation using as starting materials carbonyl chloride or thiocarbonyl chloride and a diamine,

TABLE 8. Polyurethanes obtained by interfacial polycondensation.

Diamine or diol	Bischloroformate of diol	Literature references
Ethylenediamine	butane-1,4-diol	104, 108, 111, 112
	ethane-1,2-diol	112
	2,2-dimethylpropane-1,3-diol	112
	cyclohexane-1,4-diol	112
	diglycol	112
Tetramethylenediamine	butane-1,4-diol	103–108, 111
1,3-Diaminobutane	ethane-1,2-diol	112
hexamethylenediamine	ethane-1,2-diol	112
	diglycol	112
	2,2-dimethylpropane-1,3-diol	112
	cyclohexane-1,4-diol	112
3-Methoxyhexamethylenediamine	2,2-dimethylpropane-1,3-diol	112
Bis(3-aminopropyl)ether	2,2-dimethylpropane-1,3-diol	112
Piperazine	butane-1,4-diol	112
	hexane-1,6-diol	112
	quinol	112
	ethane-1,2-diol	110, 112
	cyclohexane-*trans*-1,4-diol	112
	cyclohexane-*cis*-1,4-diol	112
	pentane-1,5-diol	110
	diphenylpropane-*p*,*p*′-diol	109, 110
	cyclohexane-1,4-diol	105, 110
trans-2,5-Dimethylpiperazine	ethane-1,2-diol	112
	quinol	112
1,4-Diaminocyclohexane	ethane-1,2-diol	112
1,3-Diaminocyclohexane	ethane-1,2-diol	112
p-Phenylenediamine	2,2-dimethylpropanediol	112
m-Tolylenediamine	2,2-dimethylpropanediol	112
Bis(4-aminophenyl)methane	2,2-dimethylpropanediol	112
Bis(4-amino-3-methylphenyl)methane	2,2-dimethylpropanediol	112
2,2-(*p*-Hydrophenyl)propane	*N*,*N*′-diphenoxycarbonylpiperazine	109
Quinol	*N*,*N*′-diphenoxycarbonylpiperazine	109
4,4′-Dihydroxybiphenyl	*N*,*N*′-diphenoxycarbonylpiperazine	109
Bis(hydroxyphenyl)propane	piperazine-1,4-dicarbonyl chloride	109

TABLE 9. Polyureas obtained by interfacial polycondensation.

Diamine	Second component	Literature references
Tetramethylenediamine	carbonyl chloride	84
Hexamethylenediamine	carbonyl chloride	84, 113
Bis(3-aminopropyl)ether	carbonyl chloride	84
Hexamethylenediamine	thiocarbonyl chloride	84
Bis(3-aminopropyl)ether	hexamethylene di-isocyanate	114
Bis(3-aminopropyl)methylamine	hexamethylene di-isocyanate	114

or a di-isocyanate and a diamine[84,113,114]. Carbonyl chloride and di-isocyanates are dissolved in an organic solvent, and diamines in an alkaline-aqueous solution. Polyureas are obtained in higher yields from a di-isocyanate and a diamine, since di-isocyanates are more resistant to the action of water than is carbonyl chloride.

6. Polyesters

Interfacial polycondensation provides one of the best methods for synthesising polyarylates, *i.e.* polyesters of dihydric phenols and dicarboxylic acids. Various polyesters obtained by this method have been described in several papers[19,21,26,38,48,88], and Table 10 lists the monomers from which these polyesters were prepared.

Polyphenyl esters are products of high molecular weight, melting at high temperatures, possessing good dielectric properties, and capable of being fabricated.

Korshak *et al.*[115] suggested using interfacial polycondensation to obtain graft and block copolymers of polyester type.

Polyesters containing carbonic acid radicals and dihydric phenols, the so-called polycarbonates, are of great practical interest. They possess good dielectric properties and high melting points. They can be obtained both by polyesterification and by "phosgenisation". The preparation of polycarbonates by the latter method represents an interfacial polycondensation reaction. Schnell[22] has described a series of polycarbonates, but his paper gives no clear indication of exactly which polymers he obtained at the phase boundary.

7. Mixed Polyamides

Korshak *et al.*[76,90,116] showed that the use of mixtures of chlorides of different dicarboxylic acids in an interfacial polycondensation reaction leads to the formation of a mixed polyamide. This is similar in composition and properties to copolymers obtained from the corresponding starting materials by the high-temperature polycondensation method, as can be seen from Figs. 21 and 22.

A limited difference in reactivity between the acid chlorides or the diamines has no material effect on the composition or properties of the copolymer[76]. The production of mixed polymers having an ordered structure requires that the reactant should differ sharply in reactivity. Otherwise it is necessary to carry out the reaction with the initial reactants introduced alternately into the zone of polycondensation. In this way Lyman and Jung[117] have synthesised mixed polyurethanes of regular and irregular structure.

Mixed polyamides have been described, obtained[2,40,86,87,90,116] by the interfacial polycondensation of the following substances: hexamethylenediamine with the following pairs of acid chlorides: adipoyl and azelaoyl, adipoyl and sebacoyl, azelaoyl and sebacoyl, adipoyl and isophthaloyl, sebacoyl and terephthaloyl, and adipoyl and fumaroyl; piperazine with adipoyl and isophthaloyl, azelaoyl and phthaloyl, chlorides; etc.

TABLE 10. Polyesters obtained by interfacial polycondensation from aromatic diols and chlorides of various dicarboxylic acids.

Diol or dithiol	Chloride of dicarboxylic acid	Literature references
Quinol	succinyl	19
	adipoyl	19, 45
	sebacoyl	19
	terephthaloyl	19, 45
	isophthaloyl	19
Resorcinol	fumaroyl	19
	terephthaloyl	19
	isophthaloyl	19
2, 2-Bis(*p*-hydroxyphenyl)propane	oxalyl	19
	fumaroyl	19, 21, 88
	adipoyl	
	sebacoyl	
	terephthaloyl	19, 21
	isophthaloyl	21, 26, 38, 48
	quinoldiglycolloyl	
	diphenylmethane-*p*, *p*'-dicarbonyl	21
	2, 2-diphenylpropane-*p*, *p*'-dicarbonyl	
	benzophenone-*p*, *p*'-dicarbonyl	21
	phenoxybenzene-*p*, *p*'-dicarbonyl	21
	diphenyldichloromethane-*p*, *p*'-dicarbonyl	21
	sulphonyl-*p*, *p*'-dibenzoyl	19, 21
p, *p*'-Dihydroxybenzophenone	sebacoyl	19
	2, 2-diphenylpropane-*p*, *p*'-dicarbonyl	21
p, *p*'-Dihydroxydiphenyl sulphone	isophthaloyl	19
	sulphonyl-*p*, *p*'-dibenzoyl	19, 21
2, 2-Bis(*p*-hydroxyphenyl)butane	isophthaloyl	21
2, 2-Bis(*p*-hydroxyphenyl)butane	phenoxybenzene-*p*, *p*'-dicarbonyl	21
	fumaroyl	21
3, 3-Bis(*p*-hydroxyphenyl)pentane	isophthaloyl	21
	terephthaloyl	21
	diphenylmethane-*p*, *p*'-dicarbonyl	21
	phenoxybenzene-*p*, *p*'-dicarbonyl	21
1, 1-Bis(*p*-hydroxyphenyl)ethane	phenoxybenzene-*p*, *p*'-dicarbonyl	21
Phenylbis(*p*-hydroxyphenyl)methane	terephthaloyl	21
	isophthaloyl	21
	phenoxybenzene-*p*, *p*'-dicarbonyl	21
1, 1-Bis(*p*-hydroxyphenyl)-1-phenylethane	isophthaloyl	21
	phenoxybenzene-*p*, *p*'-dicarbonyl	21
Bis(*p*-hydroxyphenyl) diphenylmethane	isophthaloyl	21
1, 1, 1-Tris(chloromethyl)-2, 2-bis(*p*-hydroxyphenyl)ethane	terephthaloyl	21
	isophthaloyl	21
2, 2-Bis(*p*-hydroxyphenyl)-3-methylbutane	isophthaloyl	21
Ethane-1, 2-dithiol	adipoyl	82
	sebacoyl	82
	terephthaloyl	82
	isophthaloyl	
Butane-1, 4-dithiol	adipoyl	82
Pentane-1, 5-dithiol	isophthaloyl	82

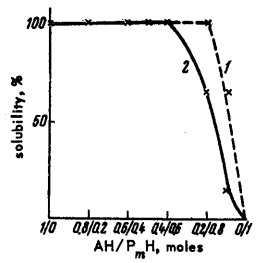


Fig. 21. Dependence of the solubility of mixed polyamides prepared from adipoyl (A) and isophthaloyl (P) chlorides and hexamethylenediamine (H) on the reactant ratio: 1) for polyamides obtained by interfacial polycondensation 2) for polyamides obtained by polycondensation in the melt. [76]

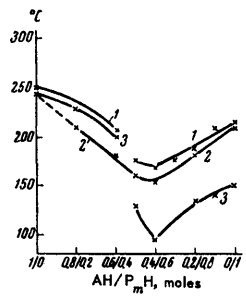


Fig. 22. Dependence of the softening temperature of mixed polyamides on the reactant ratio: 1) for polyamides obtained by polycondensation in the melt; 2) for polyamides obtained by interfacial polycondensation; 3) for polyamides obtained by polycondensation in the melt (without washing out products of low molecular weight). [76]

8. Mixed Polyesters

Eareckson [19] prepared a series of mixed polyphenyl esters whose molecular weights were greater than those of the corresponding homopolymers; this is explained by the greater solubility of the mixed polyesters in the organic phase. Examples are provided by the polyesters obtained [19,118-120] from the following substances: resorcinol plus isophthaloyl and terephthaloyl chlorides; 2,2-bis-(*p*-hydroxyphenyl)propane plus isophthaloyl and fumaroyl, isophthaloyl and oxaloyl, or isophthaloyl and terephthaloyl chlorides; 4-chlororesorcinol plus isophthaloyl and terephthaloyl chlorides; 1,5-dihydroxynaphthalene plus isophthaloyl and terephthaloyl chlorides; 4,4'-dohydroxybenzophenone plus isophthaloyl and terephthaloyl chlorides; etc.

9. Mixed Poly(amide-esters)

The interfacial polycondensation method has also been applied to the preparation of poly(amide-esters).[49] However, no detailed investigation of this class of high polymers was undertaken. The following parent compounds were used[49,121]: hexamethylenediamine + bis(hydroxyphenyl)propane + terephthaloyl chloride; hexamethylenediamine + bis(hydroxyphenyl)propane + sebacoyl chloride; piperazine + bis(hydroxyphenyl)propane + sebacoyl chloride; 2,5-dimethylpiperazine + resorcinol + terephthaloyl chloride; etc.

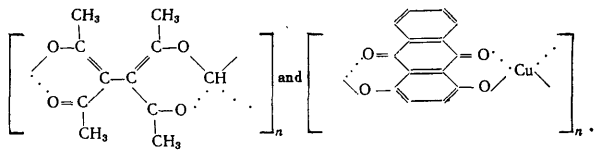
10. Mixed Poly(amide-urethanes)

Mixed poly(amide-urethanes) also can be prepared by interfacial polycondensation. Several polymers of this class have been obtained[49,86,117] by this method from the following starting compounds: piperazine + 1,2-diphenylethane-*p,p'*-dicarbonyl chloride + ethylene bischloroformate; methyl piperazine + terephthaloyl chloride + ethylene bischloroformate; 2,5-dimethylpiperazine + terephthaloyl chloride + ethylene bischloroformate; *trans*-2,5-dimethylpiperazine + terephthaloyl chloride + ethylene bischloroformate; etc.

11. Co-ordination Polymers

Recently the attention of chemists has been attracted to the preparation of co-ordination polymers[121].

Knobloch and Rauscher[123] have shown that interfacial polycondensation can be used to obtain co-ordination polymers from salts of copper and tetraketones of the type:

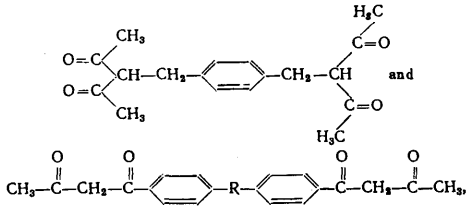


Such polymers have been obtained by mixing an aqueous solution of copper salts and a solution of the ligand in an organic solvent.

The successful preparation of co-ordination polymers requires that the copper should be present in the aqueous phase in the form of unstable ions, *e.g.* $[Cu(NH_3)_4]Cl^-$.

Solutions of tetra-acetylethane in methylene chloride and of 1,4-dihydroxyanthraquinone in benzene were taken as the initial ligands. The structure of such polymers was confirmed by chemical analysis and by their infra-red spectra.

Glukhov *et al.*[124] prepared a series of complex polymers containing Be, Mg, Ca, Cu^{II}, Fe^{II}, and Co^{II} from tetraketones having the structure:



where R = O or $>CH_2$.

VII. CONCLUSION

The distinctive feature of interfacial polycondensation is that highly reactive starting materials can be used, and hence the process can be carried out at a low temperature. Polycondensation then takes place as an irreversible process and in this respect differs fundamentally from polycondensations in solution or in a melt (*i.e.* in a homogeneous system) which have been thoroughly investigated.

This feature of interfacial polycondensation brings it close to the processes by which polymers are synthesised in the living cell, where it is possible that this type of synthesis is used. Furthermore, interfacial polycondensation has already opened up several new prospects in polymer synthesis, the most important of which is the possibility of preparing polymers having high melting points, which lie above the temperatures at which the polymers decompose. In addition, this method of synthesis enables the polymer to be obtained in the form of ready-made goods (films, fibres) and thus gives rise to the possibility of "moulding" goods from polymers at the instant they are prepared, in contrast to most known methods, which are based on the manufacture of goods from already finished polymers.

The above features explain the great interest which interfacial polycondensation has aroused among investigators in different countries, who are vigorously developing this process.

1. V.V. Korshak, "Metody Vysokomolekulyarnoi Organicheskoi Khimii, t. I. Obshchie Metody Sinteza Vysokomolekulyarnykh Soedinenii" (Methods of Macromolecular Organic Chemistry. Vol. I. General Methods for the Synthesis of Macromolecular Compounds), Izd. Akad. Nauk SSSR, Moscow, 1953, p. 431.
2. V.V. Korshak, Uspekhi Khim., 21, 121 (1952).
3. V.V. Korshak, "Khimiya Vysokomolekulyarnykh Soedinenii" (The Chemistry of High Polymers), Izd. Akad. Nauk SSSR, Moscow–Leningrad, 1950, p. 268.
4. V.V. Korshak and S.V. Vinogradova, "Geterotsepnye Poliefiry" (Heterochain Polyesters), Izd. Akad. Nauk SSSR, Moscow, 1958, p. 14.
5. V.V. Korshak, in Symposium, "Itogi Nauki. Khimicheskie Nauki. 3. Khimiya i Tekhnologiya Sinteticheskikh Vysokomolekulyarnykh Soedinenii" (Science Progress. Chemical Sciences. 3. Chemistry and Technology of Synthetic High Polymers), Izd. Akad. Nauk SSSR, Moscow, 1959, p. 116.
6. G.M. Burnett, "Mechanism of Polymer Reactions". Interscience, New York–London, 1954, p. 425.
7. V.V. Korshak, T.M. Frunze, V.V. Kurashev, and A.Yu. Alybina, Dokl. Akad. Nauk SSSR, 126, 1270 (1959).
8. V.V. Korshak, G.N. Chelnokova, and M.A. Shkolina, Vysokomol. Soed., 1, 1772 (1959).
9. Chem. Eng. News, 36, No. 37, 52 (1958).
10. P.W. Morgan, SPE J. 15, 485 (1959).
11. C. Schotten, Ber., 17, 2544 (1884); 21, 2235 (1888).
12. W. Michler and A. Zimmermann, Ber., 14, 2177 (1881).
13. A. Einhorn, Annalen, 300, 135 (1898).
14. O.A. Reutov, "Teoreticheskie Problemy Organicheskoi Khimii" (Theoretical Problems of Organic Chemistry), Izd. Moskov. Gos. Univ., Moscow, 1956, p. 299.
15. G.H. Grant and C.N. Hinshelwood, J. Chem. Soc., 1351 (1933).
16. H.K. Hall, Jnr., and P.W. Morgan, J. Org. Chem., 21, 249 (1956).
17. H.K. Hall, Jnr., J. Amer. Chem. Soc., 77, 5993 (1955).
18. P.W. Morgan and S.L. Kwolek, J. Polymer Sci., 40, 299 (1959).

19. W. M. Eareckson, J. Polymer Sci., 40, 399 (1959).
20. L. B. Sokolov and T. L. Kruglova, Vysokomol. Soed., 2, 704 (1960).
21. A. Conix, Ind. Eng. Chem., 51, 147 (1959).
22. H. Schnell, Angew. Chem., 68, 633 (1956).
23. E. Z. Fainberg and N. V. Mikhailov, Vysokomol. Soed., 2, 1039 (1960).
24. S. G. Entelis, V. Ya. Shlyapintokh, O. N. Karpukhin, and O. V. Nesterov, Vysokomol. Soed., 2, 463 (1960).
25. V. V. Korshak, T. M. Frunze, V. V. Kurashev, and P. A. Alievskii, Vysokomol. Soed., 1, 1759 (1959).
26. V. V. Korshak, S. V. Vinogradova, and A. S. Lebedeva, Vysokomol. Soed., 2, 61 (1960).
27. V. V. Korshak, T. M. Frunze, S. V. Vinogradova, V. V. Kurashev, and A. S. Lebedeva, Vysokomol. Soed., 3, 671 (1961).
28. S. A. Sundet, W. A. Murphey, and S. B. Speck, J. Polymer. Sci., 40, 389 (1959).
29. E. E. Magat, U. S. P. 2 831 834 (1958); Chem. Abs., 53, 1768 (1959).
30. Celanese Corp. of America, B. P. 737 184 (1955); Chem. Abs., 50, 8222 (1956).
31. M. S. Akutin and L. A. Rodivilova, Plast. Massy, No. 2, 14 (1960).
32. V. V. Korshak, S. R. Rafikov, and L. N. Pinkina, Zhur. Obshch. Khim., 14, 1003 (1944).
33. V. V. Korshak, S. R. Rafikov, and V. A. Zamyatina, Acta Physicochim. U. R. S. S., 21, 723 (1946).
34. V. V. Korshak and V. V. Golubev, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 185 (1946).
35. V. V. Korshak, V. V. Golubev, and G. S. Kolesnikov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 22 (1946).
36. S. B. Speck, U. S. P. 2 808 394 (1957); Chem. Abs., 52, 3356 (1958).
37. E. L. Wittbecker, U. S. P. 2 816 879 (1957); Chem. Abs., 52, 9618 (1958).
38. V. V. Korshak, S. V. Vinogradova, and A. S. Lebedeva, Vysokomol. Soed., 2, 977 (1960).
39. D. D. Coffman, G. J. Berchet, W. R. Peterson, and E. W. Spanagel, J. Polymer Sci., 2, 306 (1947).
40. V. V. Korshak and I. A. Gribova, Dokl. Akad. Nauk SSSR, 82, 397 (1952).
41. V. V. Korshak and I. A. Gribova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 550 (1954).
42. V. V. Korshak, N. N. Lebedev, and M. A. Tsipershtein, Zhur. Obshch. Khim., 19, 683 (1949).
43. N. V. Mikhailov, V. I. Maiboroda, and S. S. Nikolaeva, Vysokomol. Soed., 2, 989 (1960).
44. M. S. Akutin and L. A. Rodivilova, Plast. Massy, No. 1, 32 (1959).
45. V. V. Korshak, N. N. Lebedev, and Yu. V. Egorova, Vysokomol. Soed., 2, 1475 (1960).
46. E. E. Magat and D. R. Strachan, U. S. P. 2 708 617 (1955); Chem. Abs., 51, 4758 (1957).
47. L. B. Sokolov and T. V. Kudim, Vysokomol. Soed., 2, 698 (1960).
48. V. V. Korshak, S. V. Vinogradova, and A. S. Lebedeva, Vysokomol. Soed., 2, 1162 (1960).
49. E. I. du Pont de Nemours and Co., B. P. 785 214 (1957); Chem. Abs., 52, 7774 (1958).
50. E. L. Wittbecker and P. W. Morgan, J. Polymer Sci., 40, 289 (1959).
51. L. B. Sokolov and L. V. Turetskii, Vysokomol. Soed., 2, 710 (1960).
52. J. R. Schaefgen, F. H. Koontz, and R. F. Tietz, J. Polymer. Sci., 40, 377 (1959).
53. V. V. Korshak and S. R. Rafikov, Zhur. Obshch. Khim., 14, 983 (1944).
54. V. V. Korshak and T. M. Frunze, Dokl. Akad. Nauk SSSR, 97, 675 (1954).
55. D. N. Kursanov, V. V. Korshak, and S. V. Vinogradova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 140 (1953).
56. V. V. Korshak, G. N. Chelnokova, and G. I. Distler, Dokl. Akad. Nauk SSSR, 82, 589 (1952).
57. V. V. Korshak, T. M. Frunze, and N. G. Matveeva, Uspekhi Khim., 25, 419 (1956).
58. V. V. Korshak, "Khimiya Vysokomolekulyarnykh Soedinenii" (The Chemistry of High Polymers), Izd. Akad. Nauk SSSR, Moscow–Leningrad, 1950, p. 116.
59. V. V. Korshak and S. V. Vinogradova, Uspekhi Khim., 23, 314 (1954).
60. V. V. Korshak and V. A. Zamyatina, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 609 (1945).
61. P. J. Flory, J. Amer. Chem. Soc., 62, 2255 (1940).
62. P. J. Flory, J. Amer. Chem. Soc., 62, 2261 (1940).
63. V. V. Korshak and S. V. Vinogradova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 756 (1951).
64. V. V. Korshak and S. V. Vinogradova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 63 (1951).
65. V. V. Korshak and V. V. Golubev, in Symposium "Issledovaniya v Oblasti Vysokomolekulyarnykh Soedinenii" (Researches on High Polymers), Izd. Akad. Nauk SSSR, Moscow, 1949, p. 30.
66. V. V. Korshak and V. V. Golubev, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 379 (1949).
67. P. J. Flory, J. Amer. Chem. Soc., 64, 2205 (1942).
68. V. V. Korshak, in Symposium "Vysokomolekulyarnye Soedineniya" (Macromolecular Compounds), No. 10, Goskhimizdat, Moscow, 1950, p. 1.
69. V. V. Korshak, Uspekhi Khim., 21, 121 (1952).
70. V. V. Korshak, in Symposium "Doklady na XIII Mezhdunarodnom Kongresse Teoreticheskoi i Prikladnoi Khimii" (Papers presented at the Thirteenth International Congress of Pure and Applied Chemistry) (Translated into Russian), Izd. Akad. Nauk SSSR, Moscow, 1953, p. 263.
71. S. E. Bresler, V. V. Korshak, S. A. Pavlova, and P. A. Finogenov, Dokl. Akad. Nauk SSSR, 87, 961 (1952).
72. V. V. Korshak, Dokl. Akad. Nauk SSSR, 64, 525 (1949).
73. V. V. Korshak and V. A. Zamyatina, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 412 (1948).
74. S. E. Bresler, V. V. Korshak, S. A. Pavlova, and P. A. Finogenov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 354 (1954).
75. V. V. Korshak, Faserforsch. und Textiltechn., 6, 241 (1955).
76. V. V. Korshak, T. M. Frunze, L. V. Kozlov, and A. Yu. Alybina, Vysokomol. Soed., 2, 673 (1960).
77. N. V. Mikhailov, V. O. Gorbacheva, V. P. Kovaleva, and O. A. Klyueva, Vysokomol. Soed., 2, 1283 (1960).
78. M. S. Akutin, L. A. Rodivilova, K. P. Baibakov, and L. P. Nekrasova, Russ. P. 625 055/23 (1959).
79. D. M. Harris, R. L. Jenkins, and M. H. Neilsen, J. Polymer Sci., 35, 540 (1959).
80. P. W. Morgan and S. L. Kwolek, J. Chem. Educ., 36, 182 (1959).
81. E. E. Magat, U. S. P. 2 798 283 (1957).
82. W. A. Murphey, U. S. P. 2 870 126 (1959); Chem. Abs., 53, 6642 (1959).
83. B. G. Beaman, P. W. Morgan, C. R. Koller, E. L. Wittbecker, and E. E. Magat, J. Polymer Sci., 40, 329 (1959).
84. L. B. Sokolov and T. B. Gudakova, Russ. P. 613 835 (1958).
85. V. E. Shashoua and W. M. Eareckson, J. Polymer Sci., 40, 343 (1959).
86. M. Katz, J. Polymer Sci., 40, 337 (1959).
87. V. V. Korshak, T. M. Frunze, and V. F. Davydova, Pat. Application 672 097/23 (12th July 1960).
88. G. S. Kolesnikov and A. S. Maloshitskii, Vysokomol. Soed., 2, 1119 (1960).

89. M. S. Akutin and L. A. Rodivilova, "Materialy Mezhdunarodnogo Simpoziuma po Makromolekulyarnoi Khimii, SSSR, Moskva" (Proceedings of the International Symposium on Macromolecular Chemistry, Moscow, USSR), 1960, Section 1, p. 228.
90. V. V. Korshak, T. M. Frunze, and L. V. Kozlov, Vysokomol. Soed., 2, 838 (1960).
91. V. V. Korshak, T. M. Frunze, and V. V. Kurashev, Vysokomol. Soed., 2, 633 (1960).
92. O. Ya. Fedotova, M. L. Kerber, and I. P. Losev, Vysokomol. Soed., 2, 1020 (1960).
93. O. Ya. Fedotova, I. P. Losev, M. L. Kerber, and O. G. Fortunatov, Zhur. Vses. Khim. Obshch. Mendeleeva, 5, 111 (1960).
94. C. W. Stephens, J. Polymer Sci., 40, 359 (1959).
95. W. D. Jones and S. B. McFarlane, U. S. P. 2 667 468 (1954); Chem. Abs., 48, 5553 (1954).
96. R. Hill (Editor), "Fibres from Synthetic Polymers" (Translated into Russian), Inostr. Lit., Moscow, 1957, p. 172.
97. G. J. Berchet, U. S. P. 2 321 890 (1943); Chem. Abs., 37, 6772 (1943).
98. S. Murahashi and T. Takizawa, J. Soc. Chem. Ind. Japan, 47, 784 (1944); Chem. Abs., 43, 4856 (1949).
99. M. Raghavan, B. H. Iyer, and P. C. Guha, J. Indian Inst. Sci., 34, 87 (1952); Chem. Abs., 47, 6889 (1953).
100. O. Bayer, H. Rinke, W. Siefken, and L. Orther, German P. 728 981; Chem. Abs., 38, 381 (1944).
101. J. A. Semers, Brit. Rayon Silk J., 29, 48 (1953).
102. L. Orther, Pat. Application 1.68699 (1941); French P. 892 361.
103. Celanese Corp. of America, B. P. 683 504 (1952); Chem. Abs., 47, 5169 (1953).
104. Celanese Corp. of America, B. P. 685 729 (1953); Chem. Abs., 47, 7257 (1953).
105. Celanese Corp. of America, B. P. 743 918 (1956); Chem. Abs., 50, 12 548 (1956).
106. W. D. Jones and S. B. McFarlane, U. S. P. 2 660 574 (1953); Chem. Abs., 48, 9751 (1954).
107. W. D. Jones and S. B. McFarlane, U. S. P. 2 660 575 (1953); Chem. Abs., 48, 4255 (1954).
108. J. Swerdloff and S. B. McFarlane, U. S. P. 2 658 886 (1953); Chem. Abs., 48, 4253 (1954).
109. E. L. Wittbecker, U. S. P. 2 731 445 (1956); Chem. Abs., 50, 11 054 (1956).
110. E. L. Wittbecker, U. S. P. 2 731 446 (1956); Chem. Abs., 50, 11 054 (1956).
111. A. L. Miller and M. J. Roselle, U. S. P. 2 800 464 (1957); Chem. Abs., 51, 14 320 (1957).
112. E. L. Wittbecker amd M. Katz, J. Polymer Sci., 40, 367 (1959).
113. L. Aleksandru and L. Daskalu, "Materialy Mezhdunarodnogo Simpoziuma po Makromolekulyarnoi Khimii, 1960, SSSR, Moskva" (Proceedings of the International Symposium on Macromolecular Chemistry, 1960, Moscow, USSR), 1960, Section 1, p. 245.
114. W. Lehmann and H. Rinke, U. S. P. 2 852 494 (1958); Chem. Abs., 53, 1829 (1959).
115. V. V. Korshak, S. V. Vinogradova, and A. S. Lebedeva, Pat. Application 662 307/23 (7th April, 1960).
116. V. V. Korshak, T. M. Frunze, L. V. Kozlov, and A. Yu. Alybina, Vysokomol. Soed., 2, 845 (1960).
117. D. J. Lyman and S. L. Jung, J. Polymer Sci., 40, 407 (1959).
118. V. V. Korshak, S. V. Vinogradova, and A. S. Lebedeva, Pat. Application 661 624/23 (31st March 1960).
119. V. V. Korshak, S. V. Vinogradova, and V. S. Artemova, Russ. P. 133 222 (29th August 1959).
120. V. V. Korshak and S. V. Vinogradova, Vysokomol. Soed., 1, 1482 (1959).
121. V. V. Korshak, T. M. Frunze, S. V. Vinogradova, L. V. Kozlov, and Wu Pang-yüan, Pat. Application 675 032/23 (30th July 1960).
122. A. A. Berlin and N. G. Matveeva, Uspekhi Khim., 29, 277 (1960).
123. F. W. Knobloch and W. H. Rauscher, J. Polymer Sci., 38, 261 (1959).
124. N. A. Glukhov, M. M. Koton, and Yu. V. Mitin, Vysokomol. Soed., 2, 791 (1960).

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RESERVE GALACTOMANNANS AND GLUCOMANNANS IN SEEDS, BULBS, AND RHIZOMES†

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I. INTRODUCTION

The great majority of plants contain starch reserves, although *Compositae* and *Gramineae* contain fructose polysaccharides as their main reserve carbohydrate. Other plant reserve polysaccharides have attracted little attention[1-3], but recently heteropolysaccharides, particularly galactomannans and glucomannans, have been studied successfully. The structure of known galactomannans and glucomannans has been further elucidated, and new compounds of this type have been discovered. These polysaccharides are of interest to industry as well as in terms of organic chemistry (in relation to their structure and properties) and comparative, or evolutionary, biochemistry. Some of them are foodstuffs, especially in oriental countries; on account of their high viscosity,

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