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Physical Chemistry of the Polycondensation of Polyfunctional Nucleophilic Compounds with Polycarboxylic Acid Derivatives

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The literature data on the kinetic and thermodynamic characteristics of the polycondensation of aromatic diols, diamines, tetramines, and their derivatives with tetracarboxylic acid dianhydrides and dicarboxylic acid dihalides in amide solvents are surveyed. Attention is concentrated on the analysis of the dependence of the physicochemical parameters of the polycondensation on the nature of the nucleophile and electrophile.
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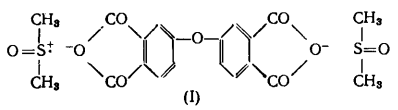
I. INTRODUCTION

Polycondensation in solution is nowadays widely used in industrial practice; as regards the industrial application of various polycondensation processes, this procedure is inferior only to polycondensation in the melt[1] (p.130). Aromatic polyamides, polyarylates, and other thermostable polymers are synthesised in solution by low-temperature polycondensation methods. This type of polycondensation began to be widely employed also in connection with the development of a two-stage method for the synthesis of polyheteroarylenes. In this synthesis, intermediate or so-called prepolymers are obtained in the first stage by the polycondensation of aromatic diamines and their derivatives with carboxylic acid dianhydrides or dihalides and are then converted into the final heterocyclochain polymers in the second stage of the process by solid-phase cyclodehydration at elevated temperatures.

Numerous studies of the low-temperature polycondensation processes in solution have been described in the literature: in the present review an attempt is made to give a systematic account and a survey of the results of these investigations.

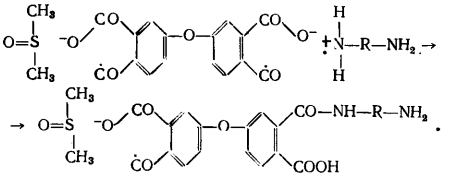
II. THE INFLUENCE OF SOLVENTS ON LOW-TEMPERATURE POLYCONDENSATION PROCESSES

In considering the mechanism of polycondensation in solution, many workers have suggested the formation of complexes between the polycarboxylic acid dianhydrides, and particularly dicarboxylic acid dihalides, with polar solvents.[2-8] For example, in a study of the reactions of benzidine, di(4-aminophenyl)methane, and di(4-aminophenyl)-ether with the dianhydride of oxydi(3,4-dicarboxybenzene) in solution in dimethylsulphoxide (DMSO), Kolesnikov et al.[8] suggested the formation of an anhydride–solvent adduct having the structure



(I)

The higher the nucleophilicity of the solvent, the more stable is the complex of this kind and the higher its concentration in solution. This can apparently explain the difference between the molecular weights of the polyamidoacids obtained in different solvents other conditions being equal, which has been observed in two investigations.[2,7] The above complex reacts with a diamine to form a new adduct:

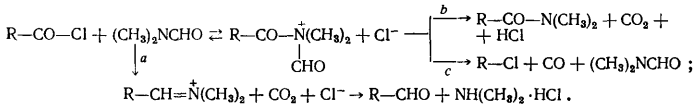


The transfer of one of the protons is responsible for the appearance of the amide bond and the formation of the polyamidoacid molecule.[5]

Boiko and Zhubanov[9] and Efimova et al.[10] pointed out the possibility of isolating such complexes, and presented the results of comparative studies of the rates of their interaction with diamines in polar solvents. Complexes of the dianhydrides of pyromellitic acid (PMDA) and 3,6-endoethene-9-bicyclo-2,4-octane-1,2,9,10-tetracarboxylicacid {3,6-(9-endoethene)bicyclo[2.4]octane-1,2,9,10-tetracarboxylic acid?} (AB) with DMSO, *NN*-dimethylformamide (DMF), and *NN*-dimethylacetamide (DMA) were chosen as the objects of study. The amine components selected were *m*-phenylenediamine (*m*-PDA), di(4-aminophenyl)ether (DAPE), and di(4-aminophenyl)methane (DAPM). Both in the case of AB and PMDA (Fig.1), the rate of the process is higher than the rate of interaction of the corresponding complexes. The polarity of the solvent forming part of the complex exerts an appreciable influence under these conditions on the reactivity of the complex. Analogous conclusions have been reached in other studies[10-12] where it was shown by infrared spectroscopy that polyamide–solvent complexes, whose nature influences greatly the molecular weight of the polymer formed, arise in solution in DMSO.

The studies of the reactions involving the synthesis of aromatic polyamides with carboxylic acid dichlorides in solvents of the amide type have shown that DMF is entirely unsuitable for such purposes. The impossibility of obtaining

high-molecular-weight compounds in this solvent[13,14] and the sharp decrease of the viscosity of the reaction solution following the preliminary dissolution of the dihalides in other amide solvents indicates the occurrence of side reactions, the main one being the interaction of the acid dihalide with the amide solvent.[4,15-17] This problem has been examined in fair detail in a number of investigations[16-18] in relation to the interaction of a series of acid dihalides with DMF. Thus it has been established[18] that two types of salts can be formed simultaneously in solution of the carboxylic acid chloride in DMF as a consequence of the attack by the electrophilic centre of the chloride on the oxygen or nitrogen atom in DMF:



If the acid chloride in which the R–C bond is weakened by structural features participates in the reaction of DMF, the corresponding salts of the acid chloride with DMF undergo decarboxylation (pathway *a*) or decarbonylation (pathway *c*), which lead to the formation of an aldehyde or a chloralkane. On the other hand, when the chloride of an acid incapable of decarboxylation is made to react with DMF, then transamidation takes place under more severe conditions and leads to the formation of the dimethylamide of the corresponding acid (pathway *b*).

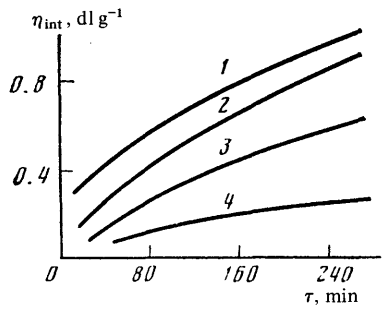
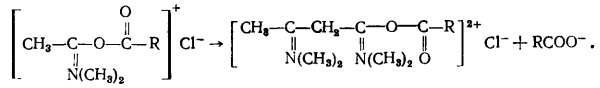


Figure 1. Dependence of the intrinsic viscosities of 0.5% DMF solutions of polyamidoacids obtained at T = 303 K via different reactions: 1) DAPE + AB; 2) DAPE + AB.DMSO; 3) DAPE + AB.DMA; 4) DAPE + AB.DMF (for the significance of the abbreviations, see text).[9]

It has been shown[19] in relation to the reaction of aniline with acid halides of different structure in DMF and DMA that at room temperature the acylation of aniline in DMF leads to the formation not only of the corresponding anilides but also of considerable amounts (up to 50%) of *NN*-dimethyl-*N'*-phenylformamidine, which means that, when the reaction was carried out in DMF, it proceeds via the formation of the intermediate adducts (I) (Scheme 1) of the acid halides with DMF and the adduct formation reaction is reversible. When aniline is added to the system, the equilibrium is displaced towards the formation of an adduct the rate constant for the interaction of which with aniline is much higher than that for the acylation of aniline by the acid halide.

The sharp decrease in the molecular weight of the polymer following the preliminary dissolution of the acid halides in DMF and other polar solvents has been explained[20] by the occurrence of side reactions other than those provided for by Scheme (1). For example, such a reaction may be the self-condensation of the adduct of DMA with the acid halide in accordance with the scheme[10]



It has been demonstrated convincingly[16] in relation to the acylation of aniline by the dichloride of isophthalic acid in solution in DMA that the amount of aniline which has not reacted increases the longer the acid dichloride has been kept in DMA and also with increase in the concentration of the salt in the same solvent. Analogous results have been obtained likewise in the analysis of the conditions governing the synthesis of polyterephthalamide based on di(4-aminophenyl)ether.

It is believed[21] that oligoanhydrides can be formed in amide–salt solvents together with other reactions.[14,15] In this case the presence of metal chlorides in solution in the synthesis of aromatic polyamides induces, together with an increase in the solubility of the polymers, an increase in the chemical reactivity of the solvent towards the initial monomers. This diminishes the molecular weight of the polymer formed.[16] In order to obtain polymers with a high molecular weight, it is therefore necessary to seek ways of diminishing the contribution of the reactions involving the formation of complexes between the monomers and the solvent. Thus the possibility of employing reactive solvents has been demonstrated.[1] It has been proposed[22] that the difluorides be used instead of the more reactive dichlorides. In order to diminish the extent of complex formation, it is recommended that preliminary dissolution of the acid dihalides in the amide solvent be avoided.[4]

The conditions in the polycondensation process in the synthesis of aromatic polyamides in amide solvents have been analysed by Ivanov et al,[23] who showed, in particular, that an increase of the rate at which the measured amount of the dichloride is introduced and especially the use of a solid dichloride leads to the formation of a polyamide with a higher molecular weight. Analogous results have been obtained by other workers,[24-26] who found that the polymer with the maximum molecular weight is obtained when the dry dianhydride is added to the solution of the diamine in small portions. Changing the order in which the reactants are added does not make it possible to obtain solutions with a sufficiently high viscosity. Similar conclusions were reached by other investigators[27-29] in relation to the polycondensation reaction of phenolphthalein with terephthalic acid dichloride in various solvents and also by Krongauz et al,[4] who investigated the reaction of the dihydrazide and dichloride of di(4-carboxyphenyl) ether in solution in hexamethylphosphoramide.

Thus, as already mentioned by Sokolov[1] (p.144), a quantitative estimate of the reactivity of the solvent in relation to the initial monomers is very important. Several methods for such estimations have been proposed in the literature. For example, in the study of the characteristics of the low-temperature polyesterification in a series of solvents[30-33] and also in the study of the reaction of 2,2-di(3-chloro-4-hydroxyphenyl)propane with terephthalic acid dichloride in the presence of triethylamine,[34] a tendency towards a decrease of the molecular weight of the polyarylates with increase of the dielectric constant of the solvent was established. Another method for estimations

of this kind involves the study of the reactions with participation of model compounds in various solvents. This problem has been examined in detail in a monograph,[1] where the results of studies of the condensation reactions of aniline with the dichlorides of isophthalic and terephthalic acids are analysed.

According to Sokolov,[1] the thermochemical method is very convenient for the quantitative estimation of the relative reactivities of solvents in complex formation reactions with the starting materials. As an example, Table 1 presents the enthalpies of solution ΔH^0_{solv} of isophthalic acid dichloride in organic solvents obtained in a number of studies.[22,35,36] The markedly different values of ΔH^0_{solv} at 298 K indicate comparatively strong interactions of isophthalic acid dichloride with amide solvents and conversely weak interaction with all others. The latter is indicated also by the results of a study of the viscosity (density)—composition diagrams[35] for the isophthalic acid dichloride–tetrahydrofuran (THF) system at 323 K. Both these relations are linear over the entire composition range, which indicates the absence of a specific interaction between the components. The intrinsic viscosities of solutions of polyisophthalamide obtained in DMA and DMF are 1.5 and 0.07 dl g^{-1} respectively (c = 0.5 wt.%, T = 293 K). These results agree with data[14] obtained in the study of the reaction of aniline with isophthalic acid dichloride in DMF and DMA. It has been shown[14] that, when the reaction is carried out in DMF, up to 70% of the monoanilide is formed, while in DMA the content of the monoanilide does not exceed 2–5% under the same conditions.

Table 1. The enthalpies of solution ΔH^0_{solv} of isophthalic dichloride in organic solvents at 298 K.[35]

Solvent	$-\Delta H^0_{solv}$, kJ mol^{-1}	Solvent	$-\Delta H^0_{solv}$, kJ mol^{-1}
Carbon tetrachloride	27.6	Tetramethylurea	18.0
Nitrobenzene	22.6	*N*-Methylpyrrolidinone	43.9
Methylene chloride	21.3	Dimethylacetamide	57.3
Toluene	20.9	Pyrrolidinone	157.7
Tetrachloroethane	18.4	Dimethylformamide	204.6
Tetrahydrofuran	16.7		

The interaction of acid chlorides with solvents of the amide type depends not only on the nature of the latter but also on the chemical structure of the initial dichloride.[35] The results of Sokolova and Sokolov[36] demonstrate, firstly, the higher reactivity of aromatic carboxylic acid dichlorides compared with those of aliphatic acids and, secondly, that the reactivity of aromatic acid halides in relation to amide solvents decreases in the sequence bromides > chlorides > fluorides. These results are satisfactorily correlated with data concerning the synthesis of polymers: the higher the enthalpy of reaction of the acid halide with the solvent, the lower the molecular weight of the polymer formed[1] (p.148).

It has been shown[37] that aromatic diamines are also capable of interacting with solvents to form side products. Thus, when a solution of di(3-amino-4-dydroxyphenyl) sulphone in DMA is heated, 87.5% of dimethylaniline relative to the theoretical amount is evolved. However, in solutions of benzidine, 3,3'-dihydroxybenzidine, and 2,2-di(3-amino-4-hydroxyphenyl)propane in DMA, dimethylamine in amounts of only 1.9, 2.15, and 5.4% respectively was detected after standing for 2 h at 298 K.[37] However, when DMA is capable of acylating the amino-group of the monomer, then this type of reaction should occur also in later stages of the polycondensation. This conclusion has been confirmed[37] in relation to the synthesis of poly[4,4'-dihydroxy-3,3'-(isophthalamido)diphenyl sulphone] in which not only chain termination but degradation of the polymer takes place.

As an illustration of the foregoing, one may also quote a study of the stability of the intrinsic viscosity of solutions of polyamidoacids based on pyromellitic anhydride and di(4-aminophenyl) ether[3] or bis(4-aminodiphenyl ether) of hydroquinone.[38] It was observed that the stability of the polyaminoacid in solution in DMF and DMSO is approximately the same and is significantly lower than in *N*-methylpyrrolidinone (MP). Comparison of the activation energies for the degradation of the polymers in various solvents (50 kJ mol^{-1} in DMF, 63 kJ mol^{-1} in DMSO, and 83 kJ mol^{-1} in MP) with data for the hydrolysis of the amide bond (75–85 kJ mol^{-1}) permits the conclusion[3,38] that the decomposition of polyamidoacids in amide solvents takes place preferentially as a result of the dissociation of the amide bond.

It follows from the foregoing that the choice of a solvent for the polycondensation of tetracarboxylic acid dianhydride or dicarboxylic acid dihalides with aromatic diamines and diols plays an extremely important role in the synthesis of the corresponding high-molecular-weight compounds. The presence of moisture in the reaction system must be very carefully monitored for such purposes. A detailed study[39] of the kinetics of the hydrolysis of isophthalic and terephthalic acid dichlorides has shown that in the temperature range 283–323 K they interact with water, which leads to the loss of the functional acid chloride groups. The presence of a definite amount of water in the solvent can therefore result in the cessation of polycondensation. Analogous effects of the hydrolysis of tetracarboxylic acid anhydrides have been observed also in the synthesis of polyamidoacids in amide solvents.[40]

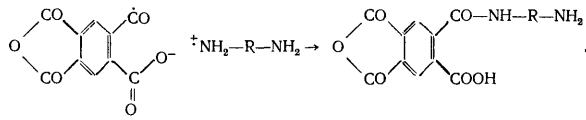
At the same time a number of workers[26,41–45] found in analysing various processes leading to the synthesis of polyamidoacids that the dependence of the molecular weight of the polymer formed on the concentration of water in the solvent always passes through an extremum. In other words, a small water content in the solvent (from 0.5 to 1.5 wt.%) not only does not lead to the hydrolysis of the initial dianhydride but also promotes an increase of the molecular weight of the polymer. The fact that, in conformity with the change in the equivalent conductance of aqueous solutions of aromatic acid dianhydrides on their interaction with the diamine, the rate of polycondensation is many times greater than the rate of hydrolysis agrees with this finding. The positive influence of the presence of water on the polycondensation has been explained[47] by the increased degree of swelling of the polymers in the presence of water, but no rigorous evidence for this is yet available.

III. CHARGE-TRANSFER COMPLEXES IN POLYCONDENSATION REACTIONS

Numerous studies[48–54] dealing with the synthesis and the interpretation of the electronic and infrared spectra of the solid reactants at 77–90 K and their solutions in non-polar

and highly polar solvents have been devoted to the donor-acceptor interaction in the systems carboxylic acid anhydrides–tertiary and primary amines. Analogous data have been obtained by other investigators[55–58] for the systems aromatic acid halides–tertiary and primary amines.

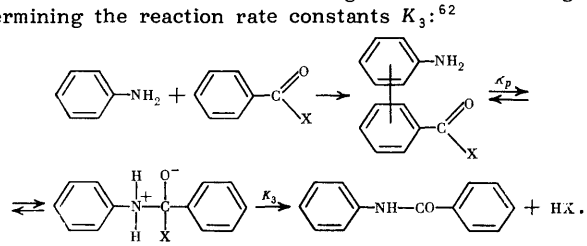
The results of these studies yield the conclusion that the reactions involved in the synthesis of polyamides, polyamidoacids, and their derivatives entail the formation of charge-transfer complexes (CTC) between the reactants. However, under the real conditions of low-temperature polycondensation (253–313 K) such complexes are unstable because their formation is followed by the rapid transfer of a proton from the amine to the anhydride group and the formation of an amide bond:



For a quantitative estimate of the electron-accepting and electron-donating properties of the reactants in acylation reactions, calculations have been made,[54,60–63] of the electron affinities and ionisation potentials of a series of carboxylic acid halides and anhydrides and aromatic diamines. The results of these investigations have been discussed in detail in a review[62] and we shall therefore quote here only the most important conclusions reached on their basis.

In the first place, the energy of charge transfer for the CTC of acid derivatives with the same electron donor increases linearly with their electron affinity. An analogous relation has been observed also for the CTC with the same electron acceptor, for example, with pyromellitic dianhydride for which the charge transfer energy varies in parallel with the variation of the ionisation potential of the aromatic amine.[62] The donor–acceptor interaction of amines with carboxylic acid derivatives, leading to the formation of CTC, is determined both by the electron-donating and electron-accepting properties of the reactants and by the polarity of the reaction medium. For example, bands of the *p*-phenylenediamine radical-cation and the chloranil radical-anion (total electron transfer) have been observed[64,65] in the study of the absorption spectra of this system in methanol.

It is believed[62] that the formation of the CTC of acid anhydrides with aromatic diamines is due mainly to the interaction of the aromatic rings (π-interaction). On the other hand, in the acylation of diamines by acid halides it was possible to detect the formation, together with the π-complex, of an adduct with a zwitter-ionic structure (a σ-complex) which is particularly stable in the case of tertiary amines. A mechanism has been proposed[62] for the acylation reaction including a CTC formation stage and the subsequent total electron transfer, which involves the appearance of a σ-complex in the system; the donor–acceptor properties of the reactant then determine the equilibrium constants K_p of the corresponding reactions. When the σ-complex is converted into the final products, the dissociation of the carbon–halogen bond is the stage determining the reaction rate constants K_3:[62]



Studies in which the energetics of the CTC formation reactions have been determined are therefore extremely interesting. Thus the thermodynamic functions of the CTC of dimethylaniline with phthalic, tetrachlorophthalic, and benzoic acids as well as the chlorides of benzoic, isophthalic, and phthalic acids in solution in acetonitrile have been calculated[66,67] (Table 2). In the CTC formation reactions involving acid chlorides the equilibrium constant is greater than for the formation of the complexes of the corresponding anhydrides. Since the enthalpies of both reactions are almost identical, the difference between the equilibrium constants is caused by the difference between the entropies of the above processes.[66]

Table 2. The energy characteristics of certain CTC formation reactions with participation of dimethylaniline.[66]

Acceptor	λ_{max}, μm	E_t, kJ mol^{-1}	$-\Delta H^0$ (298), kJ mol^{-1}	$-\Delta G^0$ (298), kJ mol^{-1}
TCPA	460	260.7	15.1±7.5	5.94
PA	375	318.8	8.4±6.3	3.51
BA	339	353.5	5.0±0.4	3.14
IPC	360	332.6	7.5±1.3	4.73
BC	338	354.0	4.6±0.8	5.65
PC	330	362.3	8.4±1.3	2.76

Notation. TCPA = tetrachlorophthalic acid anhydride; PA = phthalic anhydride; BA = benzoic acid anhydride; IPC = isophthalic acid dichloride; BC = benzoyl chloride, PC = phthalic acid chloride; E_t = electron transfer energy.

It is noteworthy that the calculated resonance energies and the contribution of the ionic structure of the complex in its ground state (which are 0.25 and 0.41% respectively in the case of benzoic acid anhydride and chloride, for example) did not confirm the conclusion[62] that there is a high contribution by the ionic structure. At the same time one of the principal postulates put forward by the above workers,[62] namely that the kinetics as well as the energetics of the CTC formation reactions and the electron affinity of the electron acceptor vary in parallel, has been confirmed,[66] because it has been found that in a series of anhydrides the decrease of the electron affinity of the acceptor is accompanied also by a decrease of the equilibrium constant for the CTC formation reaction.

Extensive information about the CTC of aromatic diamines with chloranil, which is similar to pyromellitic dianhydride as regards the character of its interaction with π-donors,[68] has been obtained.[57,69] It was found that the complex formation equilibrium constant diminishes with decrease of the basicity of the amine. In addition, a correlation has been observed between the thermodynamic characteristics of the CTC investigated and the rate constant for the reaction of the same diamine with pyromellitic dianhydride. The above workers[71] carried out a spectroscopic-kinetic study of the reaction of *m*-phenylenediamine with pyromellitic dianhydride and dichloropyromellitic dianhydride. The electron phototransfer and thermotransfer in model systems containing primary and substituted aromatic diamines and electron acceptors have been investigated. A mechanism for the elementary stage in the polycondensation reaction, which consists of successive electron and proton transfer from the amino-group to the partially positive centre of the dianhydride, has been proposed on the basis of the results.

Thus analysis of the literature data has shown that interaction involving the formation of CTC is an essential stage in polycondensation reactions with participation of aromatic diamines and carboxylic acid derivatives.

IV. KINETIC CHARACTERISTICS OF THE REACTIONS OF AROMATIC DIOLS, DIAMINES, AND THEIR DERIVATIVES WITH CARBOXYLIC ACID DIANHYDRIDES AND DIHALIDES

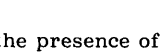
The first studies of the polycondensation reactions of aromatic diamines with tetracarboxylic acid dianhydrides already made it possible to establish the series of the relative reactivities of the corresponding nucleophiles[72,73] and electrophiles[72] on the basis of the results of measurements of the viscosities of the solutions of the polymers formed. The same method has been used[74-77] for the analysis of the reactivities of the bisphenols and aromatic acid dichlorides in polyesterification reactions. In particular, it has been shown[76] that the decrease in the reactivity of the dichloride not only diminishes the molecular weight of the polyarylate but also abolishes its temperature dependence.

The influence of the chemical structure of diamines and acid dianhydrides on the molecular weights of the polymers formed has also been examined by other investigators.[78,79] The reactivity of tetracarboxylic acid dianhydrides has been estimated[80] from measurements of the electron conductivities of their aqueous solutions. It has been suggested[81] that the comparative rates of dissolution of the monomers in organic solvents be used for the estimation of their reactivities. For the same purpose, the copolycondensation constants have been compared in a number of studies, in particular by Zhubanov et al,[82] which have been used to determine the relative reactivities of alicyclic tetracarboxylic acid dianhydrides. The reactivities of aromatic diamines have been estimated quantitatively[83-86] from the rate constants for the polycondensation with 1,6-hexamethylene diisocyanate in various solvents. It has been shown that the introduction of electron-accepting substituents into the diamine molecule lowers its reactivity and in many cases the reaction hardly proceeds.[84] As regards dianhydrides, particularly alicyclic acid dianhydrides, their reactivity is significantly influenced by steric factors.[73,87]

In view of the complexity of polycondensation processes, particularly as a consequence of the changed reactivity of the second reaction centre in bifunctional monomers after the first has reacted, many studies have examined the reactivity of the starting materials by using the reactions of model compounds. In one investigation[88] this has been done in relation to the reactions of aromatic amines with *p*-nitrobenzoyl chloride (or picryl chloride) while in another investigation[1] (p. 90) reactions of *p*-anisidine with acyl halides were used.

The reactivities of aromatic acid dichlorides in *p*-nitroaniline acylation reactions have been investigated[89] in solution in DMA at 298 K. It has been shown that the separation of the acid chloride groups by two benzene rings lowers appreciably the reaction rate constant compared with the amination of terephthalic acid dichloride. However, the introduction of powerful electron-accepting groups (for example, SO_2) between the benzene rings increases the rate constant for the above reaction. It is noteworthy that the reactivity of dinuclear acid dichlorides depends much less on the nature of the bridging group in a molecule than the reactivity of diamines with an analogous structure.[60,81,83,84]

The rate constants k_1 and k_2 for the reactions involving the successive addition of aniline derivatives to isophthalic and terephthalic acid dichlorides in various solvents have been determined[90] [see also Sokolov[1] (p. 24)]. It was found that in all cases $k_1 > k_2$. The reduced reactivity of the second COCl group is manifested to a greater extent by terephthalic acid dichloride. For the same acid dichlorides, k_1/k_2 increases with increase of the basicity of the amine and is independent of the nature of the solvent. At the same time in individual instances there is a possibility also of the opposite relation between k_1 and k_2 (Table 3).

Table 3. The rate constants for the reactions of terephthalic acid dichloride with the phenols 

in the presence of triethylamine (dioxan, 303 K).[91]

R	k_1, litre mol^{-1} s^{-1}	k_2, litre mol^{-1} s^{-1}	k_1/k_2	pK_a^*
CH_3	11.5±1.0	4.7±0.3	2.45	14.4
H	10.0±1.0	6.8±0.9	1.47	13.7
Cl	17±1	15±1	1.13	12.7
NO_2	48±2	62±3	0.77	10.1

*The ionisation constant of the phenol.

The acylation[92] of *o*-phenylenediamine by an equimolar amount of *m*-carbaboranedicarboxylic acid monochloride has been investigated[92] in solution in THF at 263 K in the presence of tertiary amines and the quantity $\alpha = k_2/k_1$, characterising the relative reactivities of the amino-groups in the *o*-phenylenediamine molecule, has been calculated from the equation quoted by Emanuel' and Knorre[93] (p. 194). It was found that in all cases $\alpha < 1$ and depends on the nature of the tertiary amine (for example, $\alpha = 0.15$ and 0.018 for reactions involving pyridine and trioctylamine respectively). The marked difference between the reactivities of the amino-groups in the presence of trioctylamine consists also in aromatic tetra-amines, which leads to the formation of linear polyaminoamides (PAA). In the presence of pyridine and quinoline the difference between the reactivities of the amino-groups diminishes ($\alpha = 0.11-0.15$), which results in the formation of soluble PAA with a branched structure. In the presence of triethylamine and dimethylaniline ($\alpha = 0.39$ to 0.47), insoluble cross-linked polymers are formed.[94]

Thus the synthesis of polybenzimidazoles involves difficulties associated primarily with the high probability of the cross-linking of the growing macrochains owing to the low reactivities of all four amino-groups in the tetra-amine molecule. It has been shown[95-97] that this phenomenon can be avoided by using for the reaction with acid dichlorides, aromatic bis(*N*-phenyl-*o*-phenylenediamines) or tetramines in which two amino-groups have been replaced by acetamido-groups.[98]

The possibility of employing indirect methods for the estimation of the reactivities of polycondensation monomers, for example, using the ionisation constants, the stretching vibration frequencies of the reacting bonds, and other properties, has been noted.[7] This postulate has been confirmed for the condensation of benzoyl chloride with aromatic amines[1] (p. 27).

The calculation of molecular diagrams by the LCAO-MO method in terms of the Hückel π-electron approximation has proved extremely useful for such purposes. Calculations of this kind have been carried out for aromatic diamines,[99]

tetramines,[100] dicarboxylic acid bisamidrazones,[101] bisphenols,[102] and carboxylic acid dianhydrides[103] and dichlorides.[104] The calculations showed that the charges on the oxygen atoms in bisphenols and on the carbon atoms in acid dichlorides are linearly related to the Hammett substituent constants. In the case of amines, the electron densities at the nitrogen atom vary in parallel with the basicity of the amines. For example, the data of Bochvar et al[100] have been used to interpret the formation of linear polyaminoamidoacids;[105] the same data[100] agree with the ionisation constants of the tetramines quoted by Balyatinskaya et al.[106] The calculated energies of the lowest valence orbital of acid dianhydrides and their derivatives and the frontier electron densities of the carbonyl carbon atoms[103] made it possible to elucidate the detailed mechanism of acylation reactions, i.e. they determine the direction of nucleophilic attack.

Sokolov and co-workers[1] (pp. 28, 107, 147) were among the first groups of investigators who proposed a method for the estimation of the reactivities of diamines and acid dihalides from the enthalpies of their reactions with organic solvents (DMF, DMA, etc.) or an aqueous hydrochloric acid solution. The quantitative information obtained by this procedure makes it possible to select the reactants for the synthesis of polymers, since the higher the enthalpy of reaction of the acid dichloride with the solvent the lower the molecular weight of the polyamide formed in the corresponding reaction.

The reactivities of monomers depend to a large extent on the nature of the solvent chosen for polycondensation. This has been demonstrated convincingly in relation to the synthesis of poly-*m*-phenyleneisophthalamide[1] (p. 88) and also in the analysis of the kinetics of the acylation of *p*-nitroaniline by terephthaloyl chloride[89] in the following solvents: acetonitrile ($pK_a = 10.13$; $k = 0.03$ litre mol^{-1} s^{-1}); *N*-methylpyrrolidinone ($pK_a = 0.92$; $k = 1.80$ litre mol^{-1} s^{-1}); dimethylacetamide ($pK_a = 0.19$; $k = 2.90$ litre mol^{-1} s^{-1}).[89] Evidently the basicity of the solvent is a significant factor, which influences the rate of polycondensation reactions.

However, one must note that, whilst giving preference to monomers with a higher reactivity in polycondensation reactions, one must rigorously take into account the role of side reactions. Since the more reactive monomer is more actively involved in such reactions, in many instances this can lead to a decrease of the molecular weight of the polymer formed[1] (p. 89).

The most thoroughly investigated branch of the polycondensation kinetics is that of the high-temperature (423–483 K) polyesterification of dicarboxylic acid dichlorides with bisphenols in solution. For a comparatively large number of reactions, the rate constants and activation energies for the synthesis of polyarylates have been determined. The results of these studies are presented and discussed in the monograph of Korshak and Vinogradova[108] (chapter III). The problems of the kinetics and mechanism of the low-temperature condensation of the same reactant in the presence of tertiary amines (acceptor–catalytic polycondensation) have already been examined in detail in reviews.[109–111] In this review we shall only mention that fact that the mechanism of the acceptor-catalytic polyesterification can be represented by two "catalytic fluxes": nucleophilic [the formation of complex (II)] and general basic [the formation of complex (III)]:

$$R'COCl + R''OH + R_3N \left\{ \begin{array}{l} \rightleftarrows R'-C(=O)-\overset{+}{N}R_3\ Cl^- + R''OH \\ \qquad\qquad\qquad\qquad\qquad\qquad (II) \\ \rightleftarrows R''OH \ldots NR_3 + R'COCl \\ \qquad\qquad\qquad\qquad\qquad\qquad (III) \end{array} \right\} \rightarrow R'COOR'' + R_3N \cdot HCl.$$

The relative contributions of the above mechanism are determined mainly by the basicity of the tertiary amine employed and the acidity of the phenol. Increase in the acidity of the phenol and in the basicity of the tertiary amine creates conditions for reaction via the general base catalytic mechanism. Questions concerning the choice of the catalyst and of its influence on the side reactions in polycondensation processes and the properties of the polymers formed have been examined in very great detail in a review.[112] The kinetic aspects of the reactions in the low-temperature polycondensation of aromatic diamines with tetracarboxylic acid dianhydrides have been analysed in a number of investigations. The kinetics of the formation of polyamidoacid (PAAC) based on pyromellitic dianhydride (PMDA) and *m*-phenylenediamine in solution in DMF have been investigated.[113,114] The kinetics of the polycondensation of PMDA with dinuclear aromatic diamines in the same solvent have been discussed.[115] Quantitative information about the kinetics of the reactions of 9,9-di(4-aminophenyl)fluorene with a series of tetracarboxylic acid dianhydrides in solution in *N*-methylpyrrolidinone has been obtained.[116] The systematic investigations of the kinetics of the formation of DAAC based on the dianhydrides of tricyclodecenetetracarboxylic acids in solution in DMF have been carried out.[117–120] Certain postulates concerning the mechanisms of the above reactions have been published in other communications.[117,118,120,121] Analysis of the experimental results of the above studies permits the following conclusions.

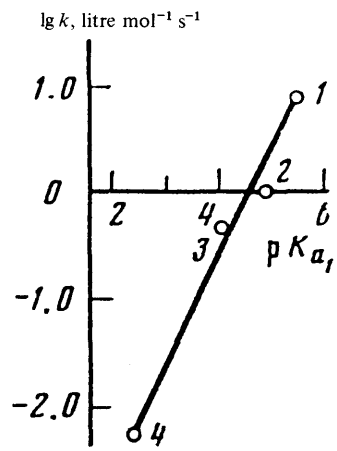


Figure 2. Dependence of the logarithms of the rate constants for the reactions of PMDA with amines on the logarithms of the first ionisation constants of the amines: 1) reaction with di(4-aminophenyl) ether; 2) reaction with *m*-phenylenediamine; 3) reaction with di(4-aminophenyl) sulphide; 4) reaction with di(4-aminophenyl) sulphone; 5) solvent—DMF; 298 K.[70]

Firstly, the rate constants for the polycondensation reactions of the same acid dianhydrides with different aromatic amines increases with increasing basicity of the amine (Fig. 2). In the reactions of the same diamine with different carboxylic acid dianhydrides the rate increases with increasing electrophilic character of the carbon atoms in the anhydride molecule. For example, according to

Vygodskii et al,[116] the rate constants for the polycondensation of 9,9-di(4-aminophenyl)fluorene at 298 K in solution in *N*-methylpyrrolidinone with dinuclear dianhydrides are 0.079, 0.49, and 1.70 litre mol^{-1} s^{-1} for the dianhydrides of tetracarboxylic acids derived from diphenyl ether, benzophenone, and diphenyl sulphone respectively.

Secondly, the reactivities of the dianhydrides of aliphatic and alicyclic acids are lower than those of the dianhydrides of aromatic acids, other conditions in the polycondensation reaction being equal. For example, the rate of reaction of di(4-aminophenyl)ether in solution in DMF with PMDA is 1000 times higher than the rate of polycondensation of the same diamine with the dianhydride of tricyclo[4,2,2,$0^{2,6}$]dec-7-ene-3,4,9,10-tetracarboxylic acid AB[70] and approximately 100 and 50 times greater than the rates of acylation of di(4-aminophenyl)ether by the dianhydrides of mesobutane-1,2,3,4-tetracarboxylic acid (MBTCA) and cyclopentane-1-*cis*, 2-*cis*, 3-*cis*-tetracarboxylic acid (CPTCA) in the same solvent.[121] On the other hand, the activation energies for the last two reactions[121] exceed by factors of 6 and 4.5 respectively the activation energy for the polycondensation of di(4-aminophenyl)ether with PMDA.[122]

Thirdly, the formation of polyamidoacids from aromatic diamines and acid dianhydrides consists of rapid (I) and slow (II) stages (Table 4). Whereas Koton[121] attributes this to the formation of monoacyl derivatives with a reduced basicity of the amino-groups in the first stage, Zhubanov et al[118] explain the above finding by the different reactivities of the dianhydride groups in asymmetric alicyclic acid dianhydrides relative to the reactions of diamines. For example, this can be caused by the different electron-donating properties of the cyclobutane and cyclohexane fragments and also by the shielding of one of the anhydride groups.[123]

Table 4. Kinetic parameters of the interaction of di(4-aminophenol) ether with AB[118] MBTCA, and CPTCA[121] (solvent—DMF; 298 K).

Dianhydride	Rate constant, litre mol^{-1} s^{-1}		E_a, kJ mol^{-1}	
	section I	section II	E_I	E_{II}
AB	$4.15 \cdot 10^{12}$	$4.18 \cdot 10^{-3}$	40.0±2.0	30.5±2.0
MBTCA	$(0.8 \pm 0.3) \cdot 10^{-1}$	$(3.1 \pm 0.5) \cdot 10^{-3}$	—	—
CPTCA	$(1.6 \pm 0.4) \cdot 10^{-1}$	$(3.6 \pm 0.5) \cdot 10^{-3}$	—	—

For the significance of the abbreviations, see text.

Nevertheless, one can agree with the view[121] that the onset of the growth of the macrochain in the synthesis of PAAC is associated with the formation of monoacyl derivatives of diamines and that the chain growth is caused by the preferential reactions of their functional groups. It has also been noted that the kinetics of the reactions involved in the synthesis of polyamidoacids can be successfully described taking into account their autocatalytic and equilibrium character.[120]

The kinetic features of the reactions involved in the single-stage polycondensation of diamines with tetracarboxylic acid dianhydrides have been elucidated in relation to the synthesis of polyimides. The molecular weights of the polymers obtained in solution are higher than those of the same polyimides synthesised by the two-stage method. The factors influencing the rate constants for the reactions involving the single-stage synthesis of polyimides are mainly the same as for the processes in the synthesis of polyamidoacids: the structure of the starting materials,[128,129] the nature of the solvent,[130] and the conditions in the polycondensation process.[113,124]

V. THERMODYNAMICS OF THE REACTIONS

The principal relations between the number-averaged degree of polycondensation $\bar{P}_n$ and the degree of reaction p, between $\bar{P}_n$ and the polycondensation equilibrium constants K_p, and between $\bar{P}_n$ and the molecular weight distribution of the linear polycondensation polymer have been obtained by Flory.[132] Later these postulates were analysed in detail in a number of investigations,[1,133-141] which showed that the study of the polycondensation thermodynamics is important because the equilibrium states in these processes determine the average degree of polycondensation, the molecular weight, and the molecular weight distribution of the polymer formed.

In connection with the development of the two-stage method for the synthesis of polyheteroarylenes, special attention is devoted in the literature to the low-temperature polycondensation processes in solution. Much quantitative information about the thermodynamics of the reactions of phthalic anhydride (PA) with aniline, which models the formation of polyamidoacids, has been published.[142]

The results permit the conclusion that the equilibrium constants for the acylation reaction depend on the structure of the starting materials: whereas the reactions of phthalic anhydride with *p*-nitroaniline and of PMDA with di(4-aminotetrafluorophenyl) ether hardly occured at 313 K, the equilibrium in the phthalic anhydride–aniline and PMDA–*p*-phenylenediamine systems is markedly displaced towards the formation of *o*-carboxyamides under the same conditions. The introduction of the electron-donating substituents CH_3, CH_3O, $(CH_3)_2N$ in the *para*-position in the aniline molecule entails an even greater increase of the equilibrium constants, i.e. its parallel variation with the basicity of the amine employed is observed.

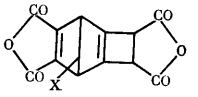
Comparison the equilibrium constants for the same reaction in different solvents has shown that the equilibrium shifts to the right with increasing basicity of the solvent. Thus, on passing from acetonitrile to THF, K_p increases almost by a factor of 10, while in dimethylsulphoxide and diemthylacetamide this constant exceeds 1×10^5. The influence of the basicity of the medium is reflected also in the enthalpy of the process, which amounts to −48.0 kJ mol^{-1} in acetonitrile and −54.5 kJ mol^{-1} in THF. This is believed[142] to be related to the association of the carboxy-groups of the products with the solvent molecules, which has been confirmed by the infrared spectroscopic data for a series of model compounds.

Analogous data concerning the influence of the solvent on the enthalpy of the reaction of phthalic anhydride with 4-aminodiphenyl ether, which models the synthesis of PAAC, were obtained later.[143]

Zhubanov and co-workers[119,144-147] used infrared spectroscopy to investigate the polycondensation reactions of aromatic diamines with the dianhydrides of tricyclodecenetetracarboxylic acid at 298 K in DMF; the results are compiled in Tables 5 and 6. The reactivity series of the dianhydrides has been proposed on the basis of the decreasing absolute Gibbs energy of the reaction (ΔG_r^0, Table 5). The aromatic

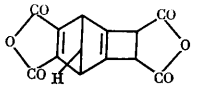
diamines investigated can be arranged in a series, based on the absolute values of ΔG_r^0 (298) for the polycondensation reaction with a specific dianhydride (Table 6), which agrees with the series based on their first ionisation constants.

Table 5. Thermodynamic parameters of the reactions of di(4-aminophenyl)ether with the dianhydrides.[146]



X	$-\Delta H_r^0$, kJ mol^{-1}	$-\Delta G_r^0$, kJ mol^{-1}	$-\Delta S_r^0$, kJ mol^{-1} K^{-1}	K_c, litre mol^{-1}
F—	114.5	22.7	308	9700
Cl—	109.1	21.8	293	6600
H—	122.4	16.6	356	807
H_3C H_3C CH—	122.7	13.7	365	274
$H_3C-C(CH_3)-CH_3$	136.3	12.2	417	139
H_3C H_3C CH—CH_2—	117.7	11.8	356	121

Table 6. Thermodynamic parameters of the reactions of aromatic diamines with the dianhydride.[146]



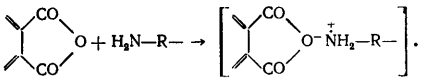
Diamine	$-\Delta H_r^0$, kJ mol^{-1}	$-\Delta G_r^0$, kJ mol^{-1}	$-\Delta S_r^0$, J mol^{-1} K^{-1}	K_c, litre mol^{-1}
p-Phenylenediamine	128.2	18.9	367	2075
m-Phenylenediamine	99.0	16.4	277	746
Di(4-aminophenyl)methane	114.4	16.5	329	790
Di(4-aminophenyl)sulphide	79.8	14.1	221	302
Di(4-aminophenyl)sulphone	—	2.7	—	3

We shall next consider the results of the study of the thermodynamics of the polycondensation reactions of tetracarboxylic acids dianhydrides with aromatic diamines, tetraamines, and their derivatives in solution.[148-157]

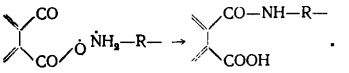
1. Thermodyamics of the Polycondensation Reactions of Tetracarboxylic Acid Dianhydrides with Aromatic Diamines

Tables 7–9 present the results of the determination of the enthalpies of the reactions of the dianhydrides of oxybis-(benzene-3,4-dicarboxylic) acid (OBBDA) and PMDA with mononuclear and dinuclear diamines and also with aromatic diamines containing benzimidazole and triazole groups.

The synthesis of poly(o-carboxy)amides proceeds via a bimolecular reaction involving the acylation of amines whose mechanism includes the nucleophilic attack on the amino-group, leading to the opening of the anhydride ring with formation of the amide bond. The attack by the nucleophile on the partially positive centre of the dianhdyride terminates in electron transfer (complete or partial depending on the dielectric constant of the medium) to the acceptor (the dianhydride):



However, this system is unstable, because its formation is followed by the rapid proton transfer from the amine to the anhydride group and by the formation of the amide bond:



This process is accompanied by the dissociation of the N–H and C–O bonds in the diamine and dianhydride molecules respectively and by the formation of new bonds (O–H, C = O, and C–N) in the polymer macromolecule. The fact that interaction of various diamines with the same dianhydrides results in the evolution of unequal amounts of heat is due primarily to the different nucleophilicites of the initial nucleophiles. On the other hand, the nucleophilicities of the amines investigated, determined by the presence of the unshared electron pair at the nitrogen atom of the amino-group, depend on the basicity of these substances.

The present authors[150,151] have attempted to relate the enthalpies of the synthesis of poly(*o*-carboxy)amides to the basicities of the initial diamines. Indeed, the higher the basicity of the amine, i.e. the higher the electron density at the nitrogen atom of the amino-group, the easier the electron transfer to the partially positive centre of the anhydride. This leads in its turn to a relatively greater deficiency of electron density at the nitrogen atom of the amino-group, i.e. promotes the appearance of an excess positive charge. The latter promotes the polarisation of the N–H bond in the amine and facilitates the abstraction of a proton from the amino-group.

Thus an increase of the basicity of the amine diminishes the dissociation energy of the N–H bond in the amine. Since the enthalpy of the chemical reaction is determined by the algebraic sum of the energies of the bonds which have been ruptured and formed, the above fact should diminish the enthalpy with increasing basicity of the amine, bearing in mind that the energies of the other bonds indicated above vary to a lesser extent with the chemical nature of the amine in reactions with the same dianhydride. Indeed, linear relations between the enthalpies and the logarithms of the first ionisation constants of aromatic diamines have been observed for their reactions with OBBDA and PMDA.[151-153,156]

$$\Delta H_r^0(298) = A + B \cdot pK_{b_1}.$$

For the reactions of OBBDA with mononuclear diamines, the quantities ($-A$) and B are 203.0 ± 0.8 and 10.5 ± 0.3 respectively; for the reactions of OBBDA with dinuclear diamines the corresponding quantities are 969.0 ± 1.0 and 89.1 ± 0.8. Finally, the same parameters for the reactions of dinuclear diamines with PMDA are 934.0 ± 1.0 and 87.7 ± 0.7.

The above conclusions agree with the results quoted in Fig. 3, where the dependence of the enthalpies of the polycondensation of four dinuclear diamines with OBBDA and PMDA on the stretching vibration frequency of the amino-groups is presented.[153] On this basis, we suggest that an increase of the stretching vibration frequency indicates an increase of the N–H bond energy in the sequence di(4-aminophenyl) ether < 4,4′-diaminobiphenyl < di(4-aminophenyl) disulphide < di(4-aminophenyl)sulphone. The enthalpies of the corresponding polycondensation reactions vary in the

same direction. For example, the introduction of an electronegative substituent between the benzene rings in the amine molecules (oxygen bridge) diminishes the enthalpy of reaction in solution by 8.0 ± 1.5 kJ mol^{-1} (Tables 8 and 14). The introduction of the electron-accepting CO or SO_2 groups between the benzene rings increases the enthalpy of reaction in solution in DMF by 15 ± 5 and 23 ± 2 kJ mol^{-1} respectively (Tables 8 and 14).

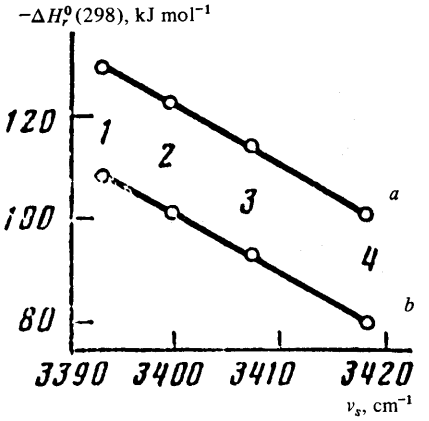
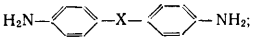


Figure 3. Dependence of the enthalpies of polycondensation of aromatic diamines with OBBDA (*a*) and PMDA (*b*) on the stretching vibration frequency ν_S of the NH_2 groups of the diamines[153]



X = *1*) -O-; 2) -S-S-; 3) $-SO_2-$.

Table 7. The enthalpies of polycondensation reactions of OBBDA with monocuclear aromatic diamines (solvent—DMF; 298 K).[157]

Diamine	pK_{b_1} (H_2O)	$-\Delta H_r^0$, kJ mol^{-1}
1,4-Diaminoxylene	7.35	125.9±4.2
p-Phenylenediamine	7.96	119.7±0.4
m-Phenylenediamine	9.12	108.0±1.3
o-Phenylenediamine	9.48	103.3±2.1

In the case of the *para*- and *meta*-derivatives of amines, the lower enthalpy of the polycondensation of the latter with OBBDA refers respectively to *p*-phenylenediamine (−119.7 and −108.0 kJ mol^{-1}, Table 7), bis(*o*-aminophenyl)-*p*-benzoylene-2,2-bistriazole (−83.7 and −95.4 kJ mol^{-1}, Table 9), and the bisamidrazone of terephthalic acid (−116.3 and −128.0 kJ mol^{-1}, Table 9); the corresponding enthalpy difference is 11.7 kJ mol^{-1} in all cases under these conditions.

A linear relation has been established between the enthalpies of polycondensation of aromatic diamines with PMDA in solution in DMF and the logarithms of the rate constants for the same processes:[153]

$$\Delta H_r^0(298),\ (\text{kJ mol}^{-1}) = (-102.0 - 8.45 \lg K) \pm 1{,}0,$$

where K are the rate constants for the corresponding polycondensation reactions expressed in litre mol^{-1} s^{-1}. From this it follows that the variation of the enthalpy of the above reaction with the nature of the amine is correlated with the variation of the activation energy for the reaction.

Table 8. The enthalpies (kJ mol^{-1}) of the reactions of OBBDA, PMDA, and phthalic anhydride (PA) with the diamines $H_2N-C_6H_4-X-C_6H_4-NH_2$ (solvent—DMF; 298 K).[150]

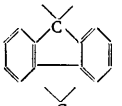
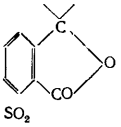
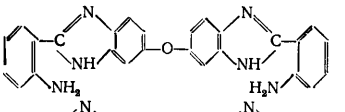
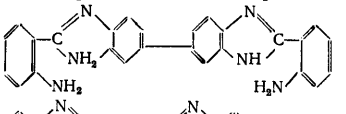
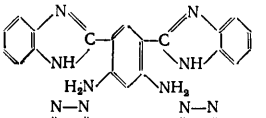
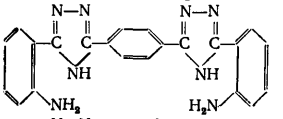
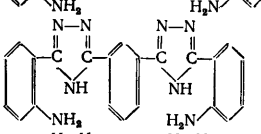
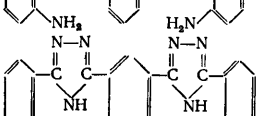
X	pK_{b_1}	pK_{b_2}	$-\Delta H_r^0$		PA		$\Delta H_1^0/\Delta H_2^0$
			OBBDA	PMDA	$-\Delta H_1^0$	$-\Delta H_2^0$	
CH_2	9.42	11.65	130.1±1.7	108.9±3.2	68.6	62.3	1.10
O	9.42	11.70	128.9±1.3	108.0±0.8	69.9	62.8	1.11
O	9.45	11.90	127.6±1.3	105.9±0.8	68.2	60.7	1.12
—	9.52	12.12	123.0±1.3	100.8±1.3	67.4	57.7	1.17
S	9.53	—	120.8±2.5	99.6±1.3	—	—	—
S—S	9.58	—	115.2±2.5	94.1±1.3	—	—	—
CO	9.69	13.42	105.4±1.7	85.0±0.8	61.9	31.4	1.97
	—	—	102.5±1.3	81.5±2.5	—	—	—
	—	—	101.5±1.3	80.5±2.5	—	—	—
SO_2	9.75	13.57	88.0±2.1	79.5±2.1	60.3	28.5	2.12

Table 9. The enthalpies of the polycondensation reactions of OBBDA with aromatic diamines containing benzimidazole and triazole rings (solvent—DMF; 298 K).[149,150]

Diamine	$-\Delta H_r^0$, kJ mol^{-1}
	147.3±4.2
	109.6±1.3
	92.1±2.9
	95.4±1.3
	83.7±2.1
	83.7±2.1

On the basis of the kinetic studies of the reactions of di(4-aminophenyl) ether with carboxylic dianhydrides, it has been suggested[121] that the synthesis of poly-(*o*-carboxy)-amides in solution in polar solvents proceeds via a stage involving the formation of monoacyl derivatives. It is therefore of interest to compare the enthalpies of the reactions for the successive addition of two moles of phthalic anhydride (PA) to one mole of the corresponding diamine. It follows from Table 8 that, for the reactions involving the addition of the second mole of PA to the diamine, $\Delta H_r^0(298)$ is in all cases smaller in absolute magnitude than the analogous values for the reactions of the first mole of PA with the initial diamine: $\Delta H_1^0 > \Delta H_2^0$. It has also been established[154] that ΔH_1^0 and ΔH_2^0 vary in parallel with the variation of the ionisation constants of the amines pK_b, namely for the first and second anhydride addition reactions the following relations have been obtained respectively:

$$\Delta H_1^0, \text{ (kJ mol}^{-1}) = (-338.4 + 28.5 \cdot pK_{b_1}) \pm 1.0 ;$$
$$\Delta H_2^0, \text{ (kJ mol}^{-1}) = (-286.2 + 18.9 \cdot pK_{b_2}) \pm 2.5.$$

Since in practice polyamidoacids are synthesised by adding the solid dianhydride to a solution of the diamine, we shall consider the thermodynamic characteristics of the dissolution of a series of dianhydrides in DMF. These results, which are presented in Table 10, show that the affinity of tetracarboxylic acid dianhydrides for DMF diminishes in the sequence PMDA > TBBDA > OBBDA.

Table 10. Thermodynamic parameters of the dissolution of dianhydrides in DMF at 298 K.[150]

Dianhydride	ΔH^0_{solv}, kJ mol^{-1}	$-\Delta G^0_{solv}$, kJ mol^{-1}	ΔS^0_{solv}, J mol^{-1} K^{-1}
PMDA	—12.96	100.5	288.7
TBBDA	—5.02	96.0	299.2
OBBDA	12.55	92.0	351.5

By adding together the enthalpies of solution of PMDA and OBBTA in DMF to the enthalpies of mixing of the solutions of the dianhydride and a diamine (Table 8), we obtain the enthalpy of reaction of the crystalline dianhydride with the solution of the diamine. Linear relations obtained from calorimetric data for the reactions of mononuclear diamines with crystalline OBBDA are presented below for the calculation of the enthalpies of such reactions of PMDA or OBBTA with other diamines from the enthalpies of reaction of the same anhydrides with the amines which we have investigated:[151–153,156]

$$\Delta H_r^0(298), \text{ (kJ mol}^{-1}) = (-182.1 + 9.48 \cdot pK_{b_1}) \pm 2.0.$$

For the reactions of dinuclear aromatic diamines with a crystalline OBBDA, we have

$$\Delta H_r^0(298), \text{ (kJ mol}^{-1}) = (-953.4 + 88.74 \cdot pK_{b_1}) \pm 2.5.$$

For reactions of dinuclear aromatic diamines with crystalline PMDA, we have

$$\Delta H_r^0(298), \text{ (kJ mol}^{-1}) = (-956.5 + 87.67 \cdot pK_{b_1}) \pm 1.0.$$

Analysis of the enthalpies presented in Table 8 for reactions carried out by mixing solutions of the starting materials established a linear relation between the enthalpies of polycondensation of OBBDA and PMDA with the same amine in DMF:

$$\Delta H_r^0(298, \text{OBBDA}) \text{ (kJ mol}^{-1}) = [-20.2 + 1.0 \Delta H_r^0(298, \text{PMDA}) \pm 1.5.$$

The relation obtained makes it possible to estimate reliably the enthalpy of reaction of a specific amine with one dianhydride from the known enthalpy of polycondensation of the same diamine with another dianhydride. An analogous relation has been obtained also for the enthalpies of polycondensation of the same amines with OBBDA and PMDA by adding the solid dianhydrides to a solution of the diamine in DMF:

$$\Delta H_r^0(298, \text{OBBDA}) \text{ (kJ mol}^{-1}) = [5.4 + 1.0 \times \Delta H_r^0(298, \text{PMDA}) \pm 1.5.$$

The entropies and Gibbs free energies of two processes of the type discussed have been determined calorimetrically for the reactions of OBBDA with di(4-aminophenyl)ether (DAPE) and di(4-aminophenyl) sulphone (DAPS) in DMF.[152] The above polycondensation reactions have been chosen because they are characterised by the maximum and minimum enthalpies respectively for the series of diamines investigated, which have been used to synthesise polyamidoacids. The results presented are listed in Table 11. It follows from these data that the entropies of the reactions investigated are negative and increase in absolute magnitude with increasing temperature. In contrast to ΔH_r^0, ΔS_r^0 is virtually the same for both processes. Consequently the enthalpies of the above processes are the factor which determines the differences between the Gibbs free energies of the acylation of the diamines by the same dianhydride.

Table 11. Thermodynamic parameters and equilibrium constants of the reactions of OBBDA with DAPE and DAPS (solvent—DMF; 101.325 kPa).[152]

T, K	$-\Delta H_r^0$, kJ mol^{-1}		$-\Delta S_r^0$, J mol^{-1} K^{-1}		$-\Delta G_r^0$, kJ mol^{-1}		K_c	
	DAPE	DAPS	DAPE	DAPS	DAPE	DAPS	DAPE	DAPS
240	114.0	69.0	114.0	95.0	87.5	46.5	$1 \cdot 10^{19}$	$1 \cdot 10^{10}$
260	122.0	80.0	145.0	139.0	84.5	44.5	$1 \cdot 10^{17}$	$8 \cdot 10^{8}$
280	129.5	88.0	175.0	169.0	80.5	41.5	$1 \cdot 10^{15}$	$4 \cdot 10^{7}$
300	129.0	88.0	191.5	190.5	72.0	31.0	$4 \cdot 10^{12}$	$3 \cdot 10^{5}$

It follows from the analysis of the dependence of ΔG_r^0 on T that the reactions of DAPE and DAPS with OBBDA in DMF are thermodynamically allowed over the entire temperature range and are characterised by high equilibrium constants. Presumably the equilibrium constants for other diamines at 298 K are also in the range 10^5–10^{12}. Thus the equilibria in the syntheses of poly(*o*-carboxyl)amides are almost completely displaced towards the formation of the polymers. With increase of temperature, their equilibrium constants diminish in conformity with the principle of the displacement of chemical equilibrium.

2. Thermodynamics of the Reactions of the Dianhydrides of Tetracarboxylic Acids with Aromatic Tetramines and Their Derivatives

Table 12 presents the enthalpies of polycondensation of OBBDA with certain bisamidrazones of dicarboxylic acids in dimethyl sulphoxide (DMSO) at 298 K. The enthalpies of the reactions involving the successive addition of two moles of PA to one mole of the corresponding bisamidrazone (Table 12) have also been determined. As in the reactions of PA with aromatic diamines (Table 8), the $\Delta H_r^0(298)$ values for the addition of the second mole of PA to the bisamidrazone are in all cases smaller in absolute magnitude than the analogous value for the reactions of the first mole of PA with the initial bisamidrazone. The difference between the enthalpies of addition at different stages of the process is greater for the bisamidrazone of terephthalic acid than for the bisamidrazone of isophthalic acid.

Table 12. The overall enthalpies of polycondensation of OBBDA with acid bisamidrazones in DMSO and the enthalpies (ΔH_1^0 and ΔH_2^0) of the subsequent addition of two moles of PA to one mole of the bisamidrazone.[150]

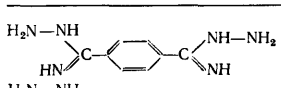
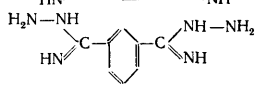
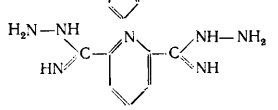
Bisamidrazone	$-\Delta H_r^0$ (298), kJ mol^{-1}	$-\Delta H_1^0$, kJ mol^{-1}	$-\Delta H_2^0$, kJ mol^{-1}	$\Delta H_1^0/\Delta H_2^0$
	128.0±1.7	75.7	46.4	1.63
	116.3±2.1	72.0	49.4	1.46
	111.3±2.1	69.5	50.2	1.38

Table 13 lists the values of ΔH_r^0 (298) for the reactions of OBBDA with tetramines. The introduction of electron-accepting substituents, for example, phenyl groups, into the tetramine molecule increases ΔH_r^0 (298 K), which agrees with the above hypothesis concerning the relation between the enthalpies of reaction of the dianhydrides with amines and the basicity of the latter. In particular, such a relation has been established in the following form for the tetramines which we have investigated:

$$\Delta H_r^0(298),\ (\text{kJ mol}^{-1}) = (-302.7 + 13.8 \cdot pK_{b_1}) \pm 2.5.$$

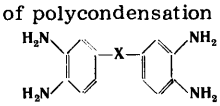
The ΔH_r^0 (298) for the reactions of tetra-aminobiphenyl and its phenyl-substituted analogue with OBBDA and also the ΔH_r^0 (298) for the polycondensation of bis(diaminophenyl) sulphone and its phenyl-substituted derivative with OBBDA differ by ~27 kJ mol^{-1}. The enthalpies of polycondensation of the phenyl-substituted tetramines with OBBDA in solution in DMF then vary in parallel with the variation of the ionisation constants of the amines in the same solvent:[151]

$$\Delta H_r^0(298),\ (\text{kJ mol}^{-1}) = (-354.2 + 19.5 \cdot pK_{b_1}) \pm 3.5.$$

An analogous relation has been obtained also for the reactions of phenyl-substituted tetramines with one mole of PA in DMF:

$$\Delta H_1^0(298),\ (\text{kJ mol}^{-1}) = (-127.9 + 5.2 \cdot pK_{b_1}) \pm 1.0,$$

where the experimental ΔH_1^0 (298) are −76.1, −62.8, and −56.5 kJ mol^{-1} for the phenyl-substituted derivatives of tetra-aminobenzene, tetra-aminobiphenyl, and bis(diaminophenyl) sulphone respectively.[151]

Table 13. The enthalpies (kJ mol^{-1}) of polycondensation of OBBDA with the aromatic tetramines  (solvent—DMF; 298 K; p = 101.325 kPa).[150]

X	pK*	$-\Delta H_r^0$ (298)	X	pK	$-\Delta H_r^0$ (298)
O	11.31	145.6±1.7	—	11.80	136.4±2.1
CH_2	11.58	142.3±0.4	CO	12.87	124.7±0.4
O—Ph—O	11.75	141.0±0.4	SO_2	13.66	115.4±0.4

*The ionisation constants of the tetramines in DMF have been determined by Balyatinskaya et al.[106]

Table 14. The entropies and Gibbs free energies of the polycondensation reactions of BDAPE with acid dianhydrides (solvent—DMF).[151]

T, K	$-\Delta S_r^0$, J mol^{-1} K^{-1}				$-\Delta G_r^0$, kJ mol^{-1}			
	TBBDA	OBBDA	BPDA	PMDA	TBBDA	OBBDA	BPDA	PMDA
240	28.0	73.0	31.5	10.5	171.5	131.8	131.8	106.7
260	33.5	75.5	33.5	17.0	169.5	131.8	129.7	106.7
280	42.0	75.5	42.0	23.0	167.4	129.7	127.6	104.6
300	52.0	77.5	48.0	33.5	165.3	127.6	125.5	102.5

It follows from the above conclusions concerning the thermodynamics of the polycondensation reactions of tetracarboxylic acid dianhydrides with aromatic diamines and their derivatives that a change in the nature of the electron acceptor in the reactions of the same nucleophile with different dianhydrides should exert a significant influence on the enthalpies of formation of the polymers. The determination of ΔH_r^0 (298) for the reactions of bis(3,4-diaminophenyl) ether (BDAPE) with various tetracarboxylic acid dianhydrides in solution in DMF established that in such cases an increase of the strength of the corresponding acid entails an increase of the absolute enthalpy of polycondensation of the dianhydrides with the same tetramine. The fact that the absolute value of ΔH_r^0(298) for the reaction of BDAPE with OBBDA is greater than the corresponding value for the reaction of BDAPE with the dianhydride of benzophenone-3,3′-4,4′-tetracarboxylic acid (BPDA) (−145.6 and −139.3 kJ mol^{-1} [157]) is associated with the fact that the addition of the first anhydride group in the case of BPTA results in a more marked decrease of the enthalpy of addition of the second

anhydride group than for OBBDA:[157]

	$-\Delta H_1^0$, kJ mole^{-1}	$-\Delta H_2^0$, kJ mol^{-1}	$\Delta H_1^0/\Delta H_2^0$
BPDA	60.2	33.1	1.8
OBBDA	57.7	40.2	1.4

The entropies and Gibbs free energies of reaction of a number of dianhdyrides with BDAPE in solution in DMF have been determined (Table 14). As for the polycondensation of dianhydrides with aromatic diamines (Table 11), the entropies of reaction of BDAPE with various dianhydrides are negative at all temperatures. On the other hand, the absolute value of ΔS_r^0 is comparatively small and the entropy component ΔS_r^0 in the expression for the Gibbs free energy is 10–15% of the enthalpy component.[151] The results obtained make it possible to set up the following reactivity series for the dianhydrides in their reactions with aromatic amines: TBBDA > OBBDA > BPDA > PMDA.

The equilibrium constants for the reactions investigated permit the conclusion that the equilibrium is in all cases almost fully shifted towards the formation of the corresponding polymer.

VI. CONCLUSION

Examination of the data described makes it possible to note the following points. The reactions of aromatic diamines, diols, and their derivatives with carboxylic acid dianhydrides and halides in amide solvents proceed in two stages. The first functional groups of these substances interact in the first stage and the activation energy is 30–40 kJ mol^{-1}. The second functional groups of the initial monomers react in the second stage and the rate constant for their interaction is lower by two–three orders of magnitude than the analogous value for the first stage, while the activation energy for the second stage is 20–30 kJ mol^{-1}.

The introduction of electrophiles into the solvent before adding the nucleophile leads to a significant decrease of the molecular weight of the polymer formed compared with that obtained when the reactants are added to the solvent in tbe opposite order or simultaneously.

The transition state in the polycondensation reactions is a charge-transfer complex whose formation can be detected, for example, from the infrared spectra of the solutions at low temperatures (~180 K). The processes involving the formation of such complexes are exothermic and their enthalpies amount to several tens of kJ mol^{-1}; their entropies are negative and amount to tens of J mol^{-1} K^{-1}, which leads to Gibbs free energies ranging from −2 to −10 kJ mol^{-1}.

The enthalpies of the polycondensation reactions with formation of aromatic polyesters, polyamides, or their *ortho*-derivatives in solution are negative and are linearly related to the logarithms of the ionisation constants of the nucelophiles. The entropies of the polycondensation reactions in solution are negative and depend only slightly on the nature of the reactants or are comaratively small in the given reaction series. The variation of the Gibbs free energies of the polycondensation processes with the chemical nature of the amine or the dianhydride is therefore determined mainly by the simultaneous variation of the enthalpy of the process, whose magnitude is significantly influenced by the variation of the dissociation energy of the N–H chemical bond (or the C–O or C–Cl bonds) in the starting materials of the above reactions. In conformity with the equation for the reaction isobar, the equilibrium constants of the polycondensation processes in solution diminish with increasing temperature. From the thermodynamic point of view, it is therefore more convenient to carry them out at a lower temperature, particularly when a weakly basic nucleophile has been selected for their synthesis. The lower limit of the temperature of these reactions is virtually determined by the freezing points of the solutions, which are close to the freezing point of the pure solvent because of the low concentrations of the reactants.

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