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Progress and problems in activated polycondensation

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ABSTRACT. New polycondensation methods for the synthesis of polymers based on non-traditional ways of activating monomers are classified. For the sake of convenience and as a contrast to traditional low-temperature polycondensation, it has been proposed to combine the new methods under the general title of "activated polycondensation". It is shown that the most versatile method in terms of synthesis is that based on the activation of the "leaving" part of the biselectrophile—the "activated amide and ester method". The considerable future potential of the latter is demonstrated. Questions relating to the synthesis, structure, and reactivity of different classes of activated diesters are examined. The possibility of synthesising various heterochain polymers by reaction of activated diesters with di- and poly-functional nucleophiles is demonstrated. The advantages of this method for the synthesis of polymers are established.

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I. Introduction

It is widely known that two methods are principally used to synthesise large chains of macromolecules—polymerisation and polycondensation.

Each of these methods has its distinct features. Without analysing them in detail, we shall merely note that in terms of synthesis the polycondensation method has advantages which are reflected in particular by the fact that it can be used to obtain a higher proportion of novel polymers.[1]

In turn, it is usual to subdivide polycondensation processes into two types—high-temperature and low-temperature.

With high-temperature polycondensation[2] (carried out at 200–300 °C in a molten state or in a high-boiling organic solvent) it is possible to use monomers (mainly biselectrophiles) with low reactivity either in an "inactive" state or as their low-activity derivatives (for example, dicarboxylic acids and their alkyl esters for the synthesis of polyamides, polyesters, etc.). High-temperature polycondensation, however, occurs in many cases at a low rate and is accompanied by numerous side reactions which lead to decomposition of the functional groups (and hence to disruption of their equimolarity) as well as to the formation of anomalous chain units ("unit heterogeneity").[3] In a number of cases such as when aromatic diamines are used, high-molecular-weight polyamides are not formed at all.[4]

In such cases low-temperature polycondensation methods (most frequently carried out over a temperature range from –30 to +50 °C in an organic solvent or by phase transfer) are more effective. These are based on the use of activated monomers—acid dichlorides, cyclic dianhydrides, bischloroformates, diisocyanates, and others.[5–8]

These methods have contributed to the further development of macromolecular chemistry and to the solution of many practical problems, but they are characterised by a number of disadvantages, the main ones being:

1) numerous side reactions (namely, the "multi-channelling" of the process),[3,5–8] leading to a restriction in chain growth and also to "unit heterogeneity";[3]

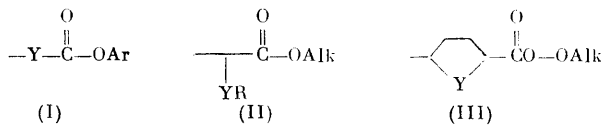
2) the need to synthesise individual activated monomers (acid dichloride, dichloroformate, or diisocyanate) that are not possible to obtain in a number of specific cases;

3) limited synthetic opportunities, for example, in the development of novel macromolecular systems, particularly of functional polymers.

These factors have in many respects determined during the last 10–15 years the development of new polycondensation methods of polymer synthesis based on nontraditional ways of activating monomers, the so-called "activated polycondensation".

Five main variants of activated polycondensation can be distinguished in relation to the method of activating the monomers.

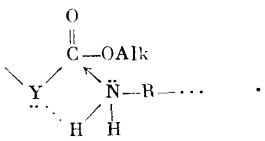
1) "Activated alkyl esters" method. This may also be called the "skeletal activation" method, and it is based on the introduction of heteroatoms (O, S, N) into the skeleton of a dicarboxylic acid at the α- or β-position relative to the carbonyl group of the ester;[9–21] the heteroatom can form part of the main molecular chain [compound (I)], of side groups (II), or a heterocycle (III).



(I) (II) (III)

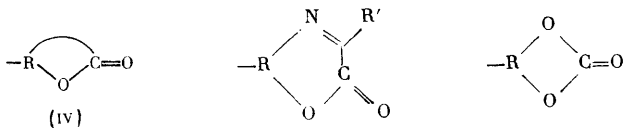
Y = O, S, NR_2, where R = H or a univalent radical.

The reactivity of alkyl diesters of the type (I)–(III) increases approximately by a factor of 10^1-10^4 compared to the unsubstituted analogues,[22] and they react with aliphatic diamines under quite mild conditions. The acceleration in these cases is mainly achieved through the so-called "anchor effect":



The inductive effect of heteroatom Y may also play a decisive role, particularly if it is situated at the α-position.

2) "Active rings" method. Many bifunctional monomers which contain different heterocycles—lactones (IV),[23–27] azalactones (V),[28–40] cyclic carbonates (VI),[41–44] and others—as functional groups exhibit a higher activity than their linear analogues as a result of intramolecular electronic effects or ring strain, and they react with nucleophiles (mainly with highly basic aliphatic diamines) under mild conditions to give high-molecular-weight polyamides, including those with different functional groups.



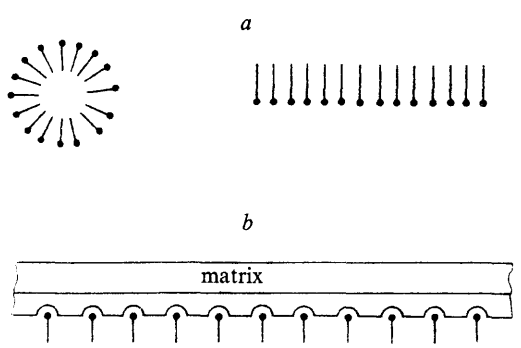
(IV) (V) (VI)

3) "Direct polycondensation" method (or "activation *in situ*"). The reaction between dicarboxylic acids or carbon dioxide and bisnucleophiles (mainly aromatic amines and bisphenols) occurs under mild conditions in the presence of various condensation agents (B).

$$n\text{HOOCRCOOH} + n\text{HY} - \text{Ar} - \text{YH} \xrightarrow{B} -(-\text{CORCOYArY}-)_n-,$$

Y = NH, O.

This modification of polycondensation as well as the condensation agents used have been reviewed by Katsarava.[45]



where | – is a molecule of monomer

Figure 1. Polycondensation of "organised molecular masses". Possible molecular orientation: *a*, in micellar and liquid-crystalline forms; *b*, in matrix forms.

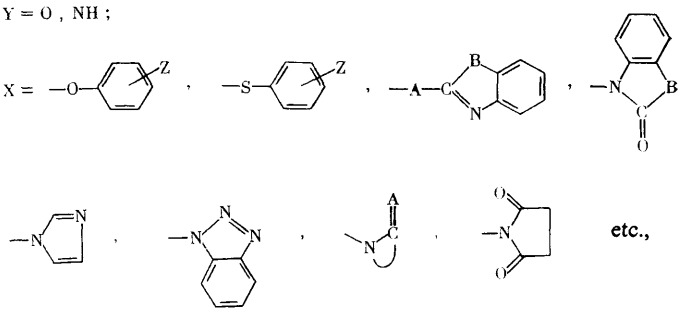
4) "Organised molecular masses" method. It has been shown that a considerable acceleration of the reaction that forms the basis of many polycondensation processes can be achieved by the formation of organised molecular masses (according to Oakenfull[46] this acceleration in a number of cases reaches a factor of 10^6, which corresponds to the level of enzyme processes) of a micellar or liquid-crystalline phase[45–47] (Fig. 1*a*) or by the introduction of various matrices, more often those that are polymeric in nature, into the reaction medium[58–67] (Fig. 1*b*).

In these systems the acceleration is achieved either through the favourable relative configuration of the monomers in space or through the increase in their local concentration. We should note that the formation of organised molecular masses not only accelerates the reaction but also alters its course. For example, when α-amino acid derivatives are used, high-molecular-weight polypeptides are formed instead of cyclic diketopiperazines.[47–49] A change in the course of the reaction was also detected in the polycondensation of urea with formaldehyde in the presence of a polyacidic matrix.[68,69]

5) "Activated esters and amides" method. In contrast to the "activated alkyl esters" method, this method is based on activation of the leaving groups, i.e. that part of the monomer which is eliminated as a low-molecular-weight by-product of polycondensation.

$$n\text{XOC—R—COX} + n\text{HY—R}'\text{—YH} \xrightarrow[-2n\text{HX}]{} \longrightarrow -[-\text{CO—R—CO—Y—R}'\text{—Y—}]_n-,$$

Y = O, NH;



(A, B = O, S); Z = electron-withdrawing substituent.

Attempts to use activated dicarboxylic acid derivatives other than acid chlorides in polycondensation (polyamidation) were made as early as the 1950s. Thus, for example, mixed anhydrides of dicarboxylic acids and diesters of orthophosphoric acid[70] or monoesters of carbonic acid[71] as well as dinitrodiamides[72] and diimidazole derivatives of dicarboxylic acids ("activated amides")[73] have been used. However, the majority of these compounds, frequently obtained in a fairly complex manner, on reaction with diamines only gave low-molecular-weight polyamides that were of little use for practical application. This circumstance would appear to have played not an inconsiderable role in causing this promising method to have remained without propert attention being given to it until the beginning of the 1970s.

At the end of the 1960s it was shown that activated esters[74] and "cyclic activated amides" such as benzoylenebenzimidazoles[75] could be used for the synthesis of heterochain polymers. Systematic studies of this modification of activated polycondensation, however, were only started in the 1970s.[76]

Formally the "leaving group" method is similar to traditional low-temperature polycondensation based on the use of acid dichlorides, but it has wider synthetic possibilities because of the use of "leaving groups" of varied nature and structure as well as "single-channelling", namely, the absence (or minimal contribution) of side reactions.

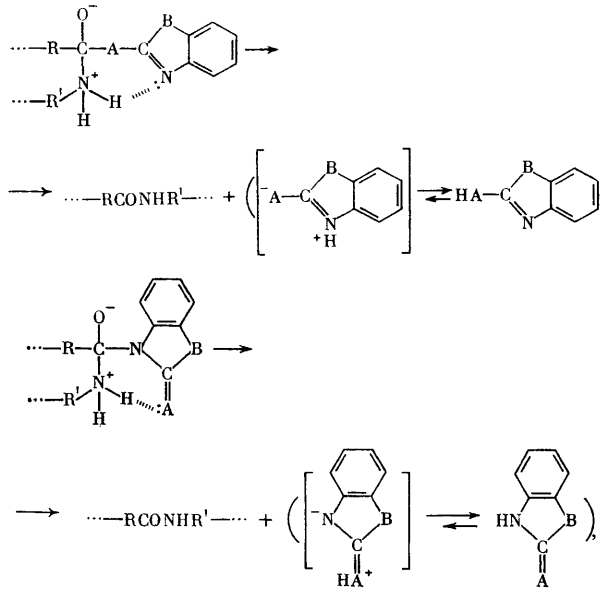
The activation of the monomers (biselectrophiles) in the "leaving group" method is achieved as follows:

1) by introduction of electron-withdrawing substituents into the leaving group or by the use of sulphur-containing leaving groups (thioesters), which are more active than those containing oxygen because of the lower basicity (better stabilisation of the negative

charge in the leaving anion X^-)† resulting from the larger radius of the sulphur atom;

2) by using nitrogen-containing leaving groups (activated amides), which when having the same pK_a values are approximately 10^4 times more reactive than oxygen-containing leaving groups;[77]

3) by making use of anchimerically assisting leaving groups



A, B = 0.5.

Anchimeric assistance

Thus, activated diamides of dicarboxylic acids, in particular those with anchimerically assisting leaving groups, have high acylating potential and are used for the synthesis of high-molecular-weight polyamides under mild conditions (see the study of Katsarava[76] and the references in it). However, they are characterised by a number of disadvantages, which can be mainly classified as: 1) the relatively high cost and complexity of obtaining the activating agents—various benzazoles and other nitrogen-containing heterocycles; 2) the synthesis of activated diamides, mainly via the corresponding acid dichlorides, which imposes certain synthetic restrictions on the method (the synthesis of only activated diamides of dicarboxylic acids and hence a single class of heterochain polymers—polyamides—is described in the literature).

In relation to the above, activated diesters have greater potential as monomers, displaying the following advantages: 1) availability and economical price of the activating agents XH (substituted phenols, etc.);[76] 2) simple "direct" syntheses of activated diesters that achieve complete independence of the method of activated polycondensation; 3) the possibility of controlling the reactivity of activated diesters and hence the polycondensation processes over a wide range by varying the leaving groups together with the low tendency of diesters to undergo side reactions; and, what is particularly important, 4) the ready availability of activated esters of different classes and hence the possibility of synthesising various heterochain polymers (Scheme 1) using activated polycondensation.

It is appropriate to mention here that, starting in the middle of the 1950s, the "activated ester" method has been successfully used in peptide chemistry for obtaining both pure peptides[78–81] and poly(amino acids)[82,83] and regularly alternating polypeptides.[84–87]

In drawing a parallel between peptide chemistry and activated polycondensation, the considerable differences between them should be pointed out. In peptide synthesis the problem of the retention of optical purity is central. Of course, single-channelling of the reaction is of considerable importance in multistage peptide synthesis, but the small contribution from side reactions (1–5%) is not so significant. In polycondensation single-channelling of the reaction acquires particular significance—activated monomers (or low-molecular-weight reaction products) should not undergo side reactions with monomers of an opposite kind, solvents, or products being formed. At the concluding stages of polycondensation the rate of reaction (fundamental act) is of crucial significance—it must be high so as to achieve chain propagation with the vanishingly small concentrations of terminal functional groups.

Scheme 1

Activated diesters of dicarboxylic acids XCORCOX	→	Polyamides Polyesters Polybenzazoles
Activated biscarbonates of diols XCOOROCOX	→	Polyurethanes
Activated carbonates XCOX Activated biscarbamates XCONHRNHCOX	→	Polyureas

Therefore the questions relating to the synthesis, structure, and reactivity of activated diesters, as well as their tendency to undergo side reactions, are key ones in activated polycondensation and in the present review considerable attention is given to them.

II. Synthesis, structure, and reactivity of monomers. Model reactions

1. Synthesis of activated diesters

The reactions which form the basis of the synthesis of different classes of activated diesters are shown in Scheme 2. These monomers can, of course, be readily obtained via the corresponding traditional forms of activated monomers—acid dichlorides, bischloroformates, and diisocyanates—a genetic link being retained between activated polycondensation and traditional low-temperature polycondensation. This approach is justified in a number of cases. It can be used to change to monomers of a "milder" nature, leading to better results in the synthesis of polymers (see below). However, for a number of reasons, as mentioned above, direct methods of synthesising activated diesters have greater future potential.

Activated diesters of dicarboxylic acids are synthesised using free dicarboxylic acids and condensing agents according to reaction (1*b*) or transesterification agents according to reaction (1*c*)[76,88–91] (see Scheme 2).

Activated biscarbonates of diols can be obtained by the reaction of diols with suitable chloroformates [reactions (2*b*) and (2*c*)] or carbonates [reaction (2*d*), and the former, depending on the synthetic requirement, can be carried out even in the absence of an acceptor of HCl (B_N).[76,92]

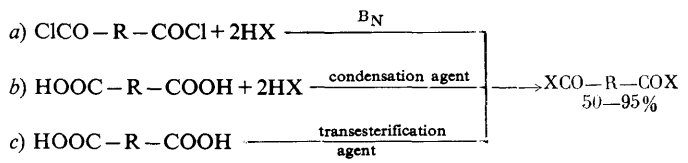
† For the reaction mechanisms, see below.

The "direct" method of synthesising activated biscarbamates involves the treatment of free diamines with a chloroformate or carbonate [reactions (3*b*) and (3*c*), Y = H]. Bis(trimethylsilyl) derivatives of the diamines (Y = $SiMe_3$) can be used successfully in these reactions. In this case there is no need for an acceptor of HCl (B_N), which would cause the dissociation of the resulting carbamate to a diisocyanate (see below).

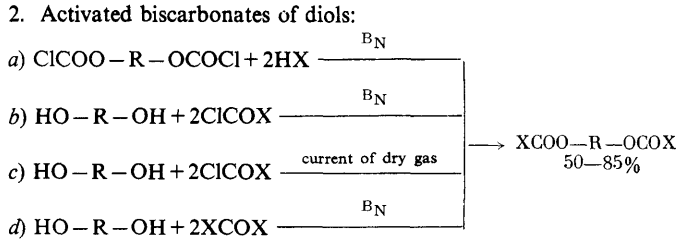
Scheme 2

Syntheses of different classes of activated diesters

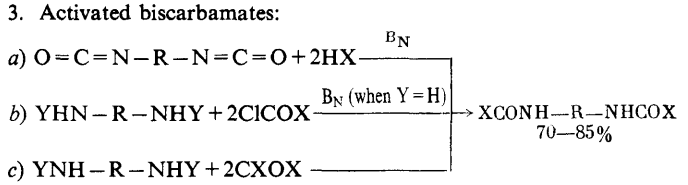
1. Activated diesters of dicarboxylic acids:



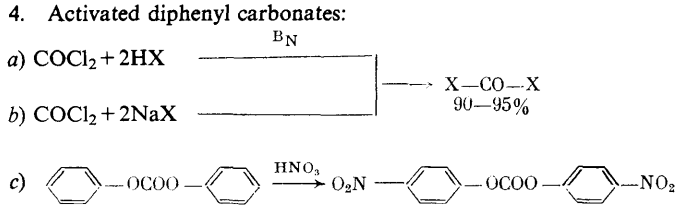
2. Activated biscarbonates of diols:



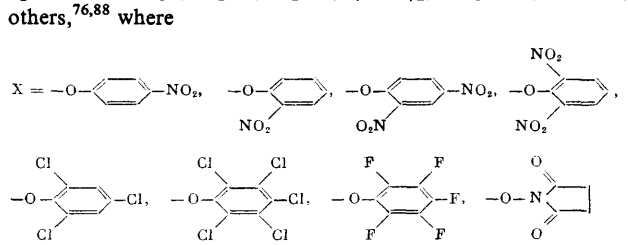
3. Activated biscarbamates:



4. Activated diphenyl carbonates:



Note. Condensation agents are: dicyclohexylcarbodiimide, PCl_3, $SOCl_2$, TsCl, $COCl_2$ $(CF_3CO)_2O$, and others.[45,76] Transesterification agents are: X_3P, X_2SO, X_2CO, $(XCO)_2$, CF_3COX, ClCOX, and others,[76,88] where

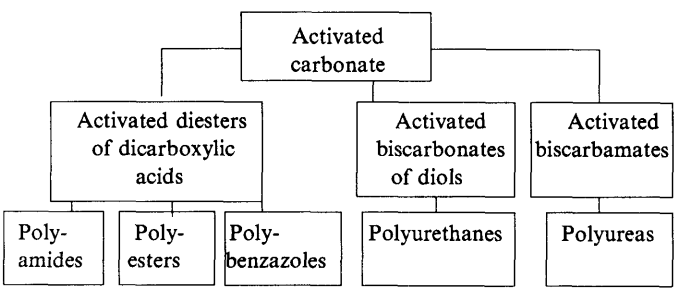


and others (Ref.76). Y = H, $SiMe_3$, B_N = tertiary amine.

Activated diphenyl carbonates (which are also of interest as transesterification agents) are obtained by reaction of phosgene (diphosgene and triphosgene, which are more convenient to handle, can also be used) with a suitable phenol in the presence of B_N [reaction (4*a*)] or a phenoxide [reaction (4*b*)] (Scheme 2). Activated diphenyl carbonates can also be synthesised by nitration of diphenyl carbonate.[93] The latter, in turn, is obtained by a phosgene-free method using CO_2 and phenol as the starting materials.[94] This opens up a route to a new phosgene-free scheme for the synthesis of polyurethanes and polyureas.

Many of the methods that have been developed lead to activated diesters in high yield and it is possible to standardise their syntheses. For example, by using a single transesterification agent it is possible to synthesise an almost unlimited number of diesters of dicarboxylic acids. Similarly, a variety of activated biscarbonates of diols and biscarbamates can be obtained from a single activated phenyl chloroformate. When starting from an activated carbonate X_2CO, it is possible to standardise the syntheses of virtually all classes of monomers and their corresponding polymers (Scheme 3).

Scheme 3

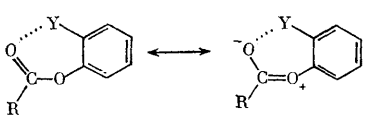


At the same time because of the wide choice of esterification and condensation agents it is possible to vary flexibly the strategy and tactics of designing macromolecular systems, in particular the so-called functional polymers, taking into account both economic and ecological requirements.

2. Structure and reactivity of activated phenyl esters

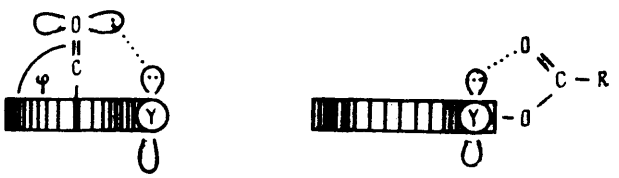
From IR and ^{13}C NMR spectroscopic studies of *ortho*-, *para*-, and poly-substituted phenyl esters in solution[95–98] it was possible to assign a *trans*-conformation to them, with the torsion angle (φ) of the plane of the ester group relative to the plane of the benzene ring of the phenol residue close to 90° (Fig. 2*a*). The literature data on the conformation of esters also attest to this.[99–102]

With such a conformation of the ester there is no through conjugation between the substituents of the phenyl residue and the carbonyl group, although an interaction occurs through space (in the case of *ortho* substituents), which gives rise to a reduction in contribution from the canonical structure (*K*2).



This, in turn, leads to an increase in the double-bond character of $\diagdown C{=}O$ and a reduction in polarity of the π-bond, which manifests itself (especially strong when halogen atoms are present in *ortho*-positions) in an increase in frequency of the carbonyl stretching vibration and in an upfield displacement of the chemical shift of the $^{13}C{=}O$ group.[98] The "ortho effect" which occurs on reaction of activated esters with nucleophiles, as will be demonstrated below, leads to a reduction in the apparent rate constant of reaction.

The dependence of the reactivity of esters on the nature of the leaving groups has been studied in the case of the anilinolysis of activated adipates in hexamethylphosphoramide (HMPA).[103] The leaving groups can be arranged in the series given in Table 1 in accordance with the values of the second-order rate constants of reaction (k_2^{app}) (with decreasing activity of the respective esters).



a *b*

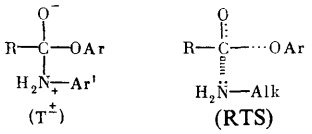
Figure 2. Conformation of *ortho*-substituted phenyl esters of carboxylic acids in solution: *a*, front view; *b*, side view.

On the basis of these results the following conclusions can be made:

1. By changing the nature of the leaving groups it is possible to vary the activity of the diesters over a wide range (in this case by a factor of 10^6). This factor—one of the most important advantages of the activated ester method—clearly suggests the possibilities for controlling the reactivity of electrophilic monomers and hence polycondensation processes without external influences (changes in properties of the medium, temperature, use of a catalyst, etc.).

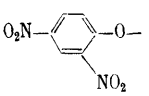
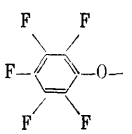
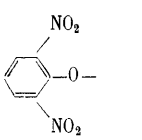
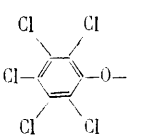
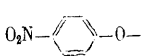
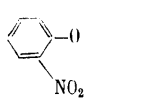
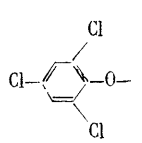
2. The most active esters are 2,4-dinitrophenyl esters, and they are superior to their pentafluorophenyl analogues in every case regardless of the nature of the acyl residue, reacting amine, and reaction medium,[98] which is inconsistent with the results of Covacs et al.,[111] obtained for α-amino acid derivatives.

3. There is no correlation between the apparent rate constants (k_2^{app}) and the pK_a values of the leaving groups (phenols—conjugate acids to the base); the magnitude of the pK_a characterises the stability of the leaving phenoxide anion and correlates with the Hammett σ-constants.[109] Consequently, there is a lack of that kind of correlation between the activity of the esters and the Hammett σ-constants which usually occurs for esters substituted only at the *para* position[112] and which suggests that the leaving groups become detached at the rate-determining stage. It is known that if pre-barrier processes—the formation of intermediate complexes—are rate-determining (see below), the rate constant must correlate with the Taft σ^0-constants because of the virtually orthogonal structure of the esters and the absence of "through resonance". The frequencies of the carbonyl stretching vibrations of esters correlate well with the σ^0-constants.[98-100] If decomposition of the intermediate complexes is rate-determining, the rate constant correlates with the Hammett σ-constants.[99,112] It is appropriate to note that according to Oleinik et al.,[113] a zwitterionic tetrahedral intermediate $T^{\pm}$ is formed in the reaction between esters and arylamines: with alkylamines the reaction occurs via a reactant-like transition state (RTS), which is shifted to the left on the reaction coordinate as the electrophilicity of the ester increases (i.e. with an increase in electrophilicity of the ester the barrier decreases).



$(T^{\pm})$ (RTS)

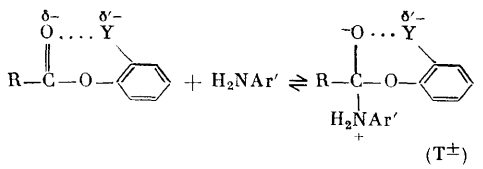
Table 1. Kinetics of the reaction of $ArOOC(CH_2)_4COOAr + H_2NPh$ (molar ratio of 1 : 2) in HMPA at 30 °C.[103]

ArO–	k_2^{app}, litre mol^{-1} s^{-1}	pK_a in water	σ (or Σσ)	σ^0 (or $\Sigma\sigma^0$)
	>1.05	4.0 [104] 4.1 [105–107] 4.39 *	2.48	2.00
	$1.3 \cdot 10^{-2}$	5.3 [106] 5.5 [104] 5.86 *	1.82	2.09
	$6.9 \cdot 10^{-3}$	3.7 [105] 4.39 *	2.48	2.54
	$5.4 \cdot 10^{-4}$	4.5 [108] 5.3 [104. 106] 4.72 *	2.33	2.33
	$2.6 \cdot 10^{-4}$	7.16 [104] 7.15 [109]	1.24	0.73
	$3.9 \cdot 10^{-5}$	7.21 [104]	1.24	1.27
	$3.6 \cdot 10^{-6}$	6.42 [108] 7.59 [104] 6.37 *	1.59	1.57

* The pK_a values calculated according to the study of Barlin and Perrin[109] are given because of discrepancies in the experimental pK_a values (H_2O). According to Bykova and Petrov,[110] the acidity series in water for acids of a single group (phenols in this case) is also retained in organic solvents.

An analysis of the results of Table 1 using the Taft equation indicates[98] that the apparent steric constants have lower values (calculated using Hammett σ-constants) than those reported in the literature (given in brackets): $E_{S\,app}^{F} = 0.22$ (0.46); $E_{S\,app}^{Cl} < -1$

(0.18); $E_{S\,app}^{NO_2}$ = −1.56 (−0.75) [calculated for bis(2,4-dinitrophenyl) adipate] [a value of −0.75 has also been adopted for bis-(*o*-nitrophenyl) adipate in calculations]. The reduction in $E_{S\,app}$, which is particularly noticeable when there are two *ortho* chlorine atoms,‡ may be related to the above-mentioned "ortho effect", which creates additional difficulties in the formation of $T^{\pm}$ and shifts this equilibrium to the left, increasing the apparent shielding effect of the *ortho* substituents.



($T^{\pm}$)

Table 2. Apparent constants k_2 for alcoholysis reactions of activated esters at 30 °C.

Ester	Alcohol	Reaction medium	$k \times 10^4$, litre mol^{-1} s^{-1}
p-Nitrophenyl acetate	phenol	chlorobenzene	4.7±0.3
o-Nitrophenyl acetate	»	»	1.6±0.2
Pentafluorophenyl acetate	»	»	5.5±0.4
Pentachlorophenyl acetate	»	»	(1.2±0.1)·10^{-1}
2,4,5-Trichlorophenyl acetate	»	»	1.8±0.2
2,4,6-Trichlorophenyl acetate	»	»	(4.8±0.2)·10^{-2}
2,4-Dinitrophenyl acetate	»	1,2-dichloroethane	(3.2±0.7)·10
	n-butanol	»	3.8±0.5

Note. Catalyst—triethylamine (TEA); initial ratio (mol litre^{-1}) of ester : alcohol : TEA = 0.6 : 0.6 : 0.6

Results obtained on the alcoholysis and phenolysis of model acetates (Table 2) may also provide an indication of the reality of the "ortho effect". In these reactions an RO^- anion is the nucleophile, so the intermediate has an anionic character (T^-) without intramolecular balance of charge. This enhances the role of this interaction and leads to a substantial change in the relative reactivity of the esters compared to aminolysis reactions. The difference in activity of *p*-nitro- and pentafluoro-phenyl esters is levelled out, the *p*-nitrophenyl ester is more reactive than its *o*-nitro-substituted analogue (in the reaction with aniline in the same medium the opposite occurs, see below) and 2,4,5-trichloro-substituted analogue (according to the literature data the latter is more active in aminolysis)[114] and pentachlorophenyl acetate is less active than *p*-nitrophenyl acetate by a factor of approximately 40 (in the reaction with aniline in chlorobenzene the former is 13 times more active, see Table 3).

‡ While the reduction in $E_{S\,app}$ (increase in steric hindrance) by a factor of 2 in the case of 2,6-dinitro- and pentafluoro-phenyl esters can be attributed to the presence of two *ortho* substituents, the large reduction in $E_{S\,app}^{Cl}$ is difficult to explain solely on the basis of two *ortho* atoms.

However, depending on the properties of the medium, *ortho* substituents can have the opposite effect—a catalytic action on aminolysis processes. Thus, for example, in the reaction with aniline in a weakly polar, proton-inert medium, *o*-nitrophenyl esters are 2–4 times more active than their *para*-substituted analogues,[98] which may be related to the formation of an intramolecular hydrogen bond which stabilises $T^{\pm}$.

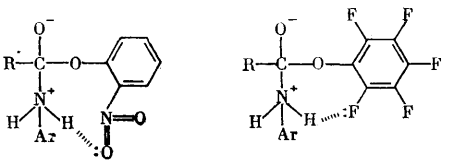


Table 3. Relative reactivity of activated diesters (C_0 = initial concentration of reactants in mol litre^{-1}).

Ester pair (A + B) (C_0)	E_{LUMO}^{*}, eV	Amine (C_0)	Reaction medium (T, °C)	k_1, s^{-1}	k_1^A/k_1^B
A. *p*-Nitrophenyl acetate (0.1)	−0.04	aniline	C_6H_5Cl	1.3·10^{-6}	3.1
B. Methyl *p*-nitrophenyl carbonate (0.1)	−0.95	(4.0)	(30)	0.4·10^{-6}	
A. *p*-Nitrophenyl acetate (0.1)		»		6.5·10^{-4}	3.2
B. Methyl *p*-nitrophenyl carbonate (0.1)			HMPA (30)	2.0·10^{-4}	
A. *p*-Nitrophenyl acetate (10^{-4})		n-butyl amine	C_6H_6 (28)	1.2·10^{-3}	0.3
B. Methyl *p*-nitrophenyl carbonate (10^{-4})		(0.2)		3.7·10^{-3}	
A. 2,4-Dinitrophenyl acetate (10^{-4})	−0.62	t-butyl amine	C_6H_6	3.5·10^{-3}	0.7
B. Methyl 2,4-dinitrophenyl carbonate (10^{-4})	−1.35	(0.2)	(28)	5.1·10^{-3}	
A. *p*-Nitrophenyl acetate (0.05)	−0.04	aniline	HMPA	5.5·10^{-4}	15
B. *p*-Nitrophenyl benzoate (0.05)	−0.07	(2.0)	(30)	3.6·10^{-5}	
A. *p*-Nitrophenyl acetate (0.5)		»	C_6H_5Cl	0.5·10^{-6}	13
B. Pentachlorophenyl acetate (0.5)			(30)	6.3·10^{-6}	

* Energy of the lowest unoccupied molecular orbital calculated by the MINDO/3 method.

In a proton-active medium such as HMPA, where the formation of strong hydrogen bonds is possible, the catalytic effect from an *ortho*-nitro group is absent (only an inhibiting "ortho effect" seems to occur), and in this case *para*-substituted esters are more active (by a factor of approximately 8).[98] We should note that an intramolecular catalytic effect can be exhibited by *ortho*-fluorine atoms, which may partly explain the high activity of pentafluorophenyl esters in aminolysis reactions (in contrast to reactions with ROH, Table 2).

The nature of the acyl residue has a considerable effect on the relative activity of esters (Table 3). According to the data obtained, esters make up the following series of decreasing activity (other

conditions being equal):

a) Reaction with an arylamine: acetate > methyl phenyl carbonate > benzoate;

b) Reaction with an alkylamine: methyl phenyl carbonate > acetate > benzoate.

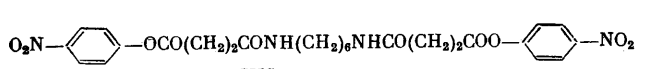
The experimental data obtained can be interpreted on the basis of the above-mentioned mechanism.[113] In a reaction with an arylamine that occurs via the intermediate formation of $T^{\pm}$, carbonates are less active since they correspond to a lower ground state energy (because of the mesomeric interaction between the methoxyl oxygen and the carbonyl group),[115] which results in an increase in the energy barrier. In reactions with alkylamines the transition state is reactant-like and in the case of carbonate (which according to the E_{LUMO} value is more electrophilic than acetate, Table 3) is shifted more to the left along the reaction coordinate, thus reducing the barrier. It follows from the results obtained that the difference in rates of aminolysis on changing from an alkylamine to an arylamine is greater for carbonates.

The medium has a considerable effect on the rate of aminolysis, and it was found that the most important of the properties of solvents is their ability to form strong hydrogen bonds (characterised by the value of pK_{HB}, Table 4). Thus, for example, the rate of reaction of *p*-nitrophenyl acetate with aniline is higher by a factor of about 10^3 in DMSO and HMPA than in the proton-inert chlorobenzene and even acetonitrile, which is comparable to the former in terms of polarity and dielectric constant but has a considerably lower pK_{HB}.

Table 4. Effect of medium on apparent pseudo-first-order rate constants (k_1) of reaction between *p*-nitrophenyl acetate (C_0 = 0.05 mol litre^{-1}) and aniline (C_0 = 2.0 mol litre mol^{-1}) and rate constants of imidisation (k_{im}) of the bis(*p*-nitrophenyl) ester of *N,N'*-hexamethylenedisuccinamide (VII) at 30 °C.

Medium	Properties of medium			k_1, s^{-1} (Ref.103)	k_{im}, s^{-1} (Ref.91)
	μ	ε	pK_{HB} (Ref.116)		
C_6H_5Cl	1.69	5.62	–	$4.7\cdot10^{-7}$	does not cyclise
CH_3CN	3.92	36.2	1.05	$5.2\cdot10^{-7}$	»
HMPA	5.37	30.0	3.56	$5.5\cdot10^{-4}$	$4.0\cdot10^{-6}$
DMSO	3.96	49.0	2.53	$1.4\cdot10^{-4}$	$1.6\cdot10^{-6}$

Similarly, the bis(*p*-nitrophenyl) ester of *N,N'*-hexamethylenedisuccinamide (VII)



(VII)

undergoes cyclisation (imidisation) at an appreciable rate only in a medium with a high pK_{HB} value (Table 4). The experimental data obtained can be accounted for by the considerable catalytic effect of these solvents on the aminolysis of esters. We have established that a single molecule of HMPA and three molecules of DMSO participate in catalysis. The reason for the unusual behaviour of DMSO is apparently related to the formation of a solvent-separated ion pair (the formation of which is supported by UV spectroscopy) involving an acyloxysulphonium ion:

$$R{-}COOAr + O{\leftarrow}SMe_2 \longrightarrow R{-}CO{-}O{\leftarrow}\overset{+}{S}Me_2 \ldots O{\leftarrow}SMe_2 \ldots ArO^-.$$

The third DMSO molecule, as with HMPA, participates in proton transfer in $T^{\pm}$.

In proton-inert organic solvents the reaction is catalysed by the amide that is formed[117] (amides have high values of $pK_a \approx 2$)[116] and the initial amine. Under pseudo-first-order reaction conditions (excess amine) the apparent rate constant is given by the familiar equation $k_1 = \sum k_{i+1}[A]^i$, where $i = 1, 2$.[112,113] However, in *n*-heptane the high order term $k_4[A]^3$, with $i = 3$ (Table 5) was first found, which suggests associated (trimeric) forms of the amine take part in the reaction. This result confirms the mechanism according to which catalysis by amine is no different from the action of a specific solvent[117,118] that is capable of forming a strong hydrogen bond, and is given by:

$$R'NH_2 + B \rightleftharpoons R'NH_2 \ldots B,$$

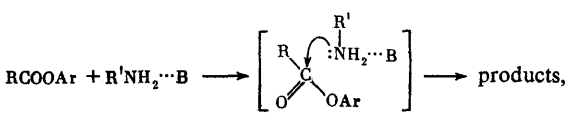


Table 5. Kinetics of the aminolysis of activated *p*-nitrophenyl esters *p*-RCOO–C_6H_4–NO_2 in proton-inert media.

R	(A)	Variation in [A], mol litre^{-1}	Reaction medium	$k_2\times10^2$ litre mol^{-1} s^{-1}	$k_3\times10^2$ litre^2 mol^{-2} s^{-1}	$k_4\times10^2$ litre^3 mol^{-3} s^{-1}
CH_3	BA	0.02–0.35	n-heptane	–	1.3	22.2
	BA	0.04–0.40	benzene	–	3.1	–
	BA	0.01–0.50	1,2-dichloroethane	0.2	9.8	–
	AN	1.5–4.0	chlorobenzene	$1.6\cdot10^{-5}$	$0.4\cdot10^{-5}$	–
CH_3O	BA	0.01–0.42	n-heptane	–	4.6	81.8
	BA	0.04–0.34	benzene	–	9.4	–
	BA	0.04–0.48	1,2-dichloroethane	0.5	22.5	–
	AN	2.0–4.0	chlorobenzene	$0.3\cdot10^{-5}$	$0.2\cdot10^{-5}$	–
CH_3NH	BA	0.05–0.67	n-heptane	–	0.4	2.6
	BA	0.07–0.50	benzene	–	0.16	0.7
	BA	0.04–0.54	1,2-dichlorobenzene	–	1.4	3.7

Note. The reaction with aniline (AN) was carried out at 30 °C, that with *n*-butylamine (BA) at 28 °C. Initial concentrations of esters were 0.05 mol litre^{-1} (reaction with AN) and 10^{-4} mol litre^{-1} (reaction with BA).

where B is a molecule of proton-active solvent or the amine itself.

It was established that activated alkyl aryl carbonates react with amines with removal exclusively of a phenoxide ion ArO^- and

formation of the required urethane [route (*a*)]; the alternative route (*b*) does not occur:

$$ROCOOAr + H_2NR' \begin{cases} \xrightarrow[-ArOH]{(a)} ROCONHR' \\ \xrightarrow[-ROH]{(b)} R'NHCOOAr \rightleftharpoons R'-NCO + ArOH \text{ etc.} \end{cases}$$

In other words, aminolysis of activated esters of carboxylic acids and alkyl aryl carbonates occurs by the same "direct" mechanism—either via the formation of $T^{\pm}$ or via a RTS.

In contrast to activated esters, activated carbamates react with amines by a more complicated mechanism, forming an intermediate isocyanate:

$$RNHCOOAr + (H_2NR')_{i-1} \xrightarrow[-ArOH]{} R-NCO \xrightarrow{H_2NR'} RNHCONHR'$$

An indication of this is provided in particular by the constantly occurring term $k_4[A]^3$, regardless of the properties of the medium (see Table 5).

The mechanism of aminolysis of activated diphenyl carbonates consists of a unique combination of both mechanisms

$$ArOCOOAr \xrightarrow{H_2NR} \begin{bmatrix} T^{\pm} \text{ or} \\ RTS \end{bmatrix} \rightarrow ArOCONHR \xrightarrow[-ArOH]{(H_2NR)_{i-1}}$$

$$\rightarrow RNCO \xrightarrow{H_2NR} (RNH)_2CO\ .$$

Thus, aminolysis of activated esters is a complex process and is susceptible to various intra- and inter-molecular influences, which have a considerable effect on the formation of macrochains in activated polycondensation.

3. Possible side reactions

Studies have been conducted on the tendency of activated esters to undergo various side reactions in which traditional activated forms of the monomers are fairly readily involved and which constitute the reason for the restriction on chain propagation and the unit heterogeneity.

It has been established that the majority of activated diesters do not react with alcohols (methanol, ethanol) even on boiling. In the absence of an amine only the most active 2,4-dinitrophenyl esters undergo appreciable alcoholysis.[119,120]

Activated esters are also stable towards amide solvents. Only 2,4-dinitrophenyl esters exhibit relatively low stability; in HMPA at 30 °C about 10% of the ester groups have decomposed after 6 h (when their initial concentration is 0.1 mol litre^{-1}).

Activated esters also exhibit high hydrolytic stability in these weakly basic solvents even in the presence of considerable quantities of water (up to 9%) (see Table 6), with pentafluoro- and *p*-nitrophenyl esters considerably surpassing their 2,4-dinitro-substituted analogues in this respect. It is worth noting that when triethylamine (TEA) is introduced into solution, the pentafluorophenyl ester is the least susceptible to its catalytic action, which may be attributed to the above-mentioned inhibitory effect from two *ortho*-fluorine atoms in attack on an ester by OH^- ions. Alkyl aryl carbonates have similar hydrolytic stability to that of their ester analogues (Table 6).

In contrast to the "conventional" esters (adipates) examined above, the catalytic effect of TEA is absent in the hydrolysis of diester (VII) and only an acceleration of imidisation occurs (see Table 6). This may be related to structural features of diester (VII).

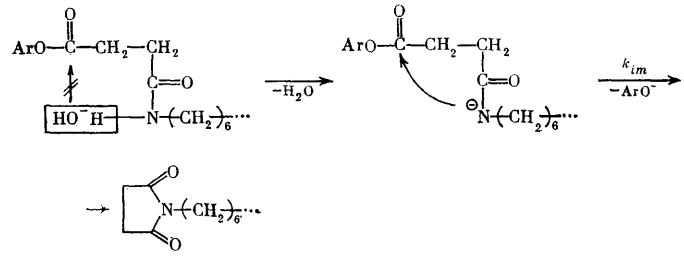


Table 6. Apparent pseudo-first-order rate constants ($k_1^{H_2O}$) of the hydrolysis of activated diesters at 30 °C (not catalysed and catalysed by TEA).

Ester	Solvent	$k_1^{H_2O}$, s^{-1} noncatalytic	$k_1^{H_2O}$, s^{-1} catalytic	$\frac{k_1^{H_2O}(cat)}{k_1^{H_2O}(noncat)}$	$\frac{k_1(aminolysis)^*}{k_1^{H_2O}(noncat)} \cdot 10^{-3}$
$ArOCO(CH_2)_4COOAr$, $ArO = 2,4\text{-}(NO_2)_2C_6H_3O$	HMPA	$1.3 \cdot 10^{-4}$	$4.5 \cdot 10^{-3}$	36	16
$ArO = C_6F_5O$	HMPA	$8.5 \cdot 10^{-6}$	$2.7 \cdot 10^{-5}$	3	3
$ArO = 4\text{-}NO_2C_6H_4O$	HMPA	$3.5 \cdot 10^{-7}$	$3.2 \cdot 10^{-6}$	9	0.6
	DMSO	$5.2 \cdot 10^{-7}$	$1.6 \cdot 10^{-6}$	3	–
Diester (VII)	DMSO	$1.2 \cdot 10^{-6}$ ($k_{im} = 1.6 \cdot 10^{-6}$) **	$1.2 \cdot 10^{-6}$ ($k_{im} = 5.8 \cdot 10^{-6}$) **	1 –	– –
$CH_3OCOO\text{-}4\text{-}NO_2C_6H_4$	HMPA	$3.8 \cdot 10^{-7}$	$5.3 \cdot 10^{-6}$	14	0.5

Note. Initial concentration of ester groups = 0.1 mol litre^{-1}; molar ratio of [COOR]:[TEA]:[H_2O] = 1:1:50.

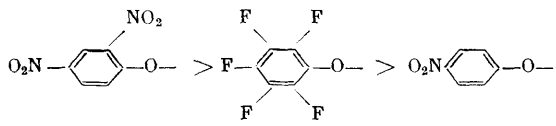
*For k_1 values (aminolysis), see Tables 1 and 3.

**k_{im} = apparent rate constant for imidisation of ester (VII).

In inert organic solvents activated esters hardly react at all with TEA (molar ratio of ester:TEA = 1:2) at 30 °C over a period of more than 24 h. The stability of activated esters towards highly basic tertiary amines is of considerable significance in terms of the synthesis of high-molecular-weight linear heterochain polymers and makes it possible to carry out a number of new polycondensation schemes using a highly basic proton acceptor (see below).

On the whole it may be concluded from the combined results obtained from studying reactions catalysed by TEA that of the possible mechanisms of catalysis—1) nucleophilic catalysis, 2) formation of an intermediate ketene, and 3) general-base catalysis—the latter is the most probable.

We should note that the hydrolysis of $ArOCO(CH_2)_4COOAr$ occurs at a considerably slower rate than even the slowest of its aminolysis reactions—the reaction with aniline. The ratio of constants k_1 (aminolysis)/$k_1^{H_2O}$ is as high as the order of $10^3-10^4:1$ (see Table 6) and decreases as ArO varies in the series



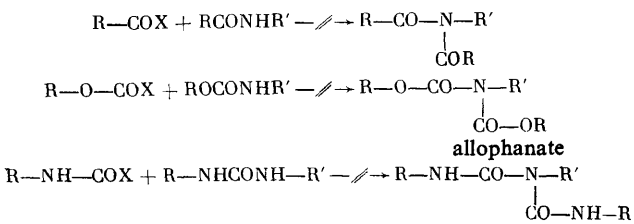
In other words, an increase in activity of the ester helps to suppress hydrolysis. This is consistent with the results of Menger and Smith,[112] according to which aminolysis is more sensitive to the nature of the leaving group than is hydrolysis. An increase in basicity of the amine has a similar effect; the rate of aminolysis increases by a factor of 10^3-10^5 (see Tables 3 and 5) while side reactions (catalysed by amine) are only accelerated by a factor of 10^1 (see Table 6).

Acid-base processes are of considerable importance in relation to polycondensation in an organic medium. It has been established that the phenols used in weakly polar aprotic media mainly form with amines either molecular complexes $ArOH\cdots H_2NR$ without significant charge separation or hydrogen-bonded ion pairs (in the case of the most acidic phenols) in equilibrium with molecular complexes $ArO^-\cdots H_3N^+R \rightleftarrows ArOH\cdots H_2NR$.[121,122] In weakly basic aprotic media with a high value of pK_{HB} (HMPA, DMF, DMSO) the ion pairs are in equilibrium with strong $ArOH\cdots$solvent complexes.[123,124] All of this makes it possible to carry out the aminolysis of activated esters in any organic medium freely and quantitatively without the use of a proton acceptor.

In contrast to phenols, *N*-hydroxysuccinimide forms with primary and secondary amines strong complexes that are insoluble in organic solvents, including polar aprotic ones.[125] However, the amino groups in these complexes are readily acylated by highly active esters. *N*-Hydroxysuccinimide does not form an insoluble complex with tertiary amines.

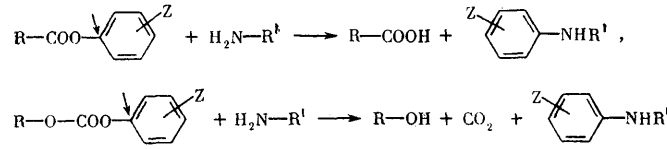
In addition to what has been mentioned, the absence of a reaction between these esters and their aminolysis products should also be considered as an advantage of activated esters (Scheme 4):

Scheme 4



Thus, activated esters differ favourably from the traditional forms of activated polycondensation monomers because of their low tendency to undergo side reactions, which are typical for the latter and lead to a restriction on chain propagation and to unit heterogeneity in the polymers.

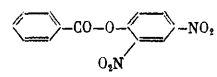
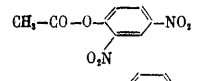
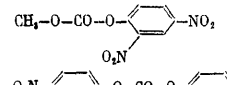
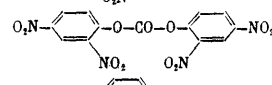
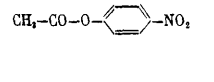
It was found by Katsarava et al.[126] that nucleophilic substitution resulting in the loss of ester groups and a restriction on chain propagation, is of considerable significance in the aminolysis of activated phenyl esters



where Z is an electron-withdrawing substituent.

This reaction occurs to the greatest extent when two nitro groups are present in the phenol residue, the yield of product being dependent on the nature of the acyl residue and the amine (Table 7). It was established that a reduction in temperature, dielectric constant and pK_{HB} of the medium helps to suppress nucleophilic substitution.[127]

Table 7. Yield of product obtained from nucleophilic substitution in the aminolysis of activated esters in HMPA.

Ester	Amine	Temperature, °C	Yield of product, mol%
	benzylamine	30	1.29
	aniline	80	0.44
	benzylamine	30	0.28
	aniline	80	0.08
	benzylamine	30	1.50
	aniline	30	2.60
	benzylamine	30	0.14
	aniline	30	0.28
	benzylamine	30	trace amounts
	aniline	80	not detected

Note. Initial concentration of ester = 0.6 mol litre^{-1}; molar ratio of ester : amine = 1 : 1.2.

As has been mentioned, the activating groups considered above (see Table 1) make it is possible to control the reactivity of esters over a wide range. A further increase in reactivity of phenyl esters through the introduction of additional electron-withdrawing substituents, in our view, is inappropriate because of the sharp increase in the contribution from nucleophilic substitution.

III. Polycondensation

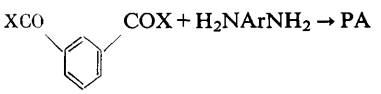
1. Synthesis of polyamides and polybenzazoles

Bifunctional monomers can be divided into four groups according to their nature and reactivity (see Section II). The effect of the nature of the leaving group of an ester on the molecular weight of

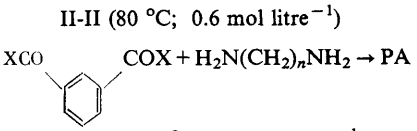
required polyamide (PA) during polycondensation in HMPA has been studied (the conditions of synthesis are given in brackets):[128]

$$XCO(CH_2)_4COX + H_2NArNH_2 \rightarrow PA$$

II-I (80 °C; 0.6 mol litre^{-1})



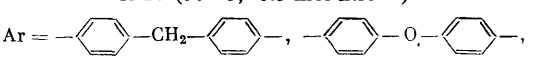
II-II (80 °C; 0.6 mol litre^{-1})



II-III (30 °C; 0.6 mol litre^{-1})

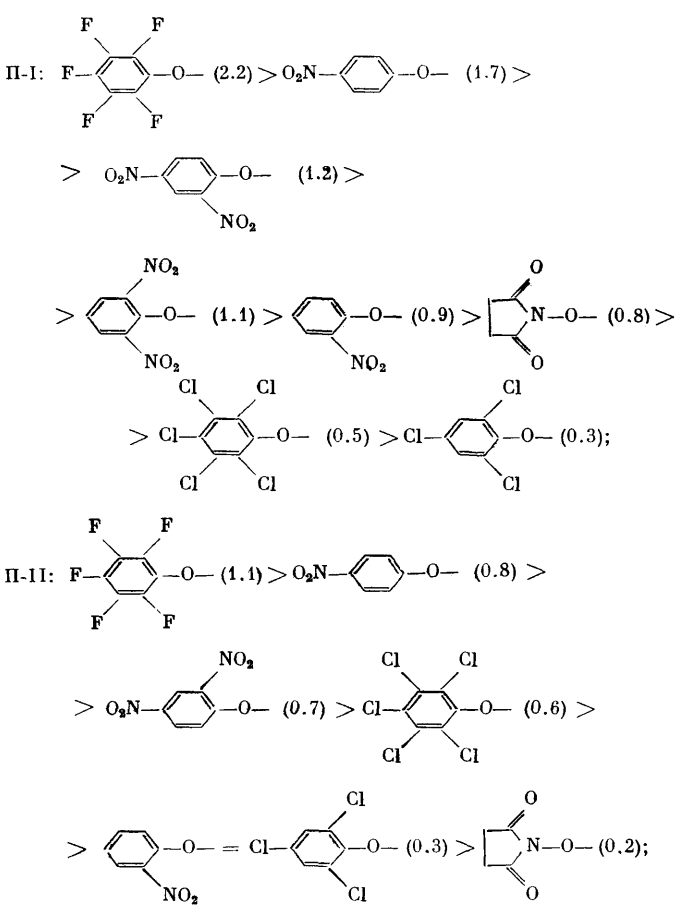
$$XCO(CH_2)_4COX + H_2N(CH_2)_nNH_2 \rightarrow PA$$

II-IV (30 °C; 0.3 mol litre^{-1})



$n = 6, 12$; PA – polyamide .

Polycondensation of pairs II-I to II-III occurs homogeneously, while that of pair II-IV is heterogeneous (polyamide separates out). According to the data obtained, the leaving groups (X) make up the following series with respect to their tendency to form high-molecular-weight polyamides (values of intrinsic viscosity η_{int} at 25 °C and a concentration of polymer solution of 0.5 g dl^{-1} are given in brackets):



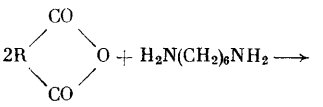
The series obtained do not correlate with the reactivity of the diesters. Under these conditions the pentafluorophenoxide leaving group proved to be more effective in the synthesis of polyamides starting from aromatic diamines (pairs I-II, and II-II), although 2,4-dinitrophenol derivatives lead to good results. When aliphatic diamines are used, one of the best leaving groups is *p*-nitrophenoxide, while in the synthesis of completely aliphatic polyamides the *N*-oxysuccinimide group is one of the best.

A study of the kinetics of polycondensation of pairs II-I to II-III (homogeneous reactions) showed[103] that on the whole its rate is consistent with the reactivity of the monomers [bis(pentachlorophenyl) adipate constitutes an exception, see below]. At the same time the polycondensation of diesters with aliphatic diamines is virtually complete after 1–2 h (at 30 °C), while with aromatic diamines polycondensation lasts from 4 to 40 h depending on the activity of the diester (at 80 °C). The lack of correlation between reactivity of the monomers and the η_{int} value of the resulting polyamides is mainly due to the occurrence of nucleophilic substitution as a side reaction (see Section II.3), resulting in chain termination.

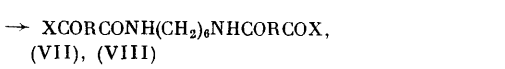
Polycondensation of the monomer pair II-IV, which takes place heterogeneously, is also complete after 1–2 h. The resulting polymers are readily soluble in organic solvents (trifluoroethanol, *m*-cresol), which suggests the absence of intermolecular imide cross-linking which arises when the corresponding acid dichlorides are used.[129]

On the basis of the high stability of intermediate activated amidoesters of the type (VII), which are not very susceptible to imidisation (see Tables 4 and 6), high-molecular-weight polysuccinamides were obtained by reaction of activated succinates with hexamethylenediamine (HMDA) and dodecamethylenediamine (DMDA).[91] The best leaving group for the pair, like II-IV, proved

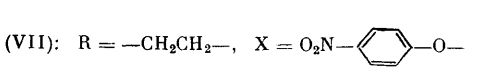
to be *N*-oxysuccinimide. Polysuccinamides were also obtained by a different route using the pure activated bisamidoester (VII):



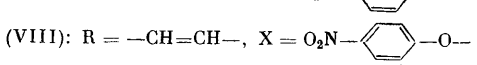




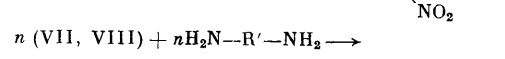
(VII), (VIII)

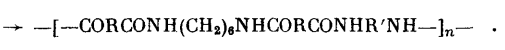


(VII): R = —CH_2CH_2—, X = O_2N—C$_6$H$_3$(NO$_2$)—O—



(VIII): R = —CH=CH—, X = O_2N—C$_6$H$_3$(NO$_2$)—O—

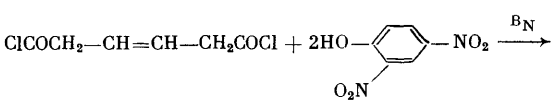


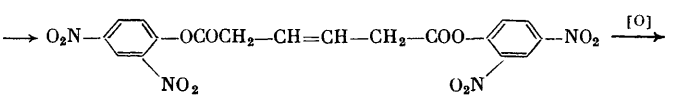


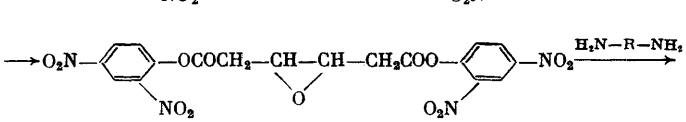
Polyamides with a strict alternation of two diamine residues can be synthesised by this route, and it can be used to prepare polyamides based on "cyclising" dicarboxylic acids (for example, maleic acid) whose activated diesters are difficult to obtain. Thus, polycondensation of diester (VIII) with hexamethylenediamine in HMPA gave polyhexamethylenemaleimide with η_{int} = 0.67 dl g^{-1}).

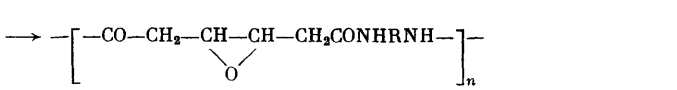
The use of activated diesters proved fruitful in the synthesis of polyamides starting from indole-containing dicarboxylic acids,[130,131] whose dichlorides in the presence of an acceptor (triethylamine) undergo intermolecular cyclisation to form diketopyrazinoindole residues.[132]

The synthesis of high-molecular-weight epoxypolyamides via an activated diester has been achieved:[19]







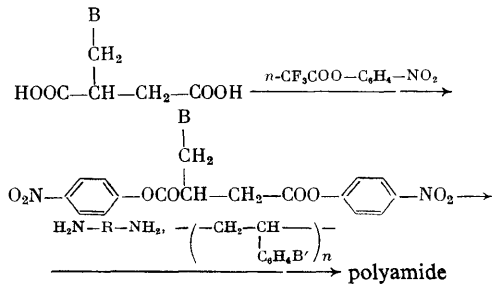


η_{int} = 0.42 – 0.48 (R = Alk) and 0.73 – 3.62 (R = Ar) dl g^{-1}.

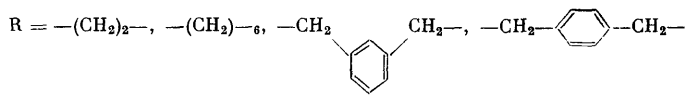
Lower molecular-weight polyamides ($\eta_{int} \leqslant$ 0.15 dl g^{-1}) are formed using the corresponding acid dichloride.

The latter two examples provide support for the view expressed above (see Section II.1) that in a number of specific cases the synthesis of activated diesters is worthwhile even if carried out via the corresponding acid dichlorides.

Activated diesters containing nuclei bases have been used in matrix polycondensation reactions:[59]



where



B = adenine, theophylline, thymine/uracil

B′ = adenine/theophylline.

It was established that in the presence of a polystyrene matrix containing a complementary base B′, polyamidation is accelerated by a factor of more than ten.

We should note that the development of activated polycondensation methods opens up a means of studying matrix polycondensation—a relatively new and little-studied process compared to matrix polymerisation.[133]

We have successfully utilised the highly selective acylating capacity of activated diesters to synthesise soluble polybenzimidazoles. Polycondensation of activated isophthalates with aromatic tetraamines in *N*-methylpyrrolidone gave high-molecular-weight polybenzimidazoles, the best results being achieved when 2,4-dinitrophenyl (η_{int} = 2.2 – 2.4 dl g^{-1}) and 2-mercaptobenzthiazole (η_{int} = 1.1 dl g^{-1}) esters were used. The synthesis of polybenzimidazoles occurs under mild conditions (70 – 100 °C), the polymers obtained form golden-brown coloured films with a tensile strength σ_f = (10 – 12) × 10^7 Pa. The corresponding polybenzoxazoles and polybenzthiazoles (η_{int} = 1.1 – 1.2 dl g^{-1}) were obtained under similar conditions by reaction of bis(2,4-dinitrophenyl) isophthalate and aromatic dihydroxy- and dimercaptodiamines.

2. Synthesis of polyesters

"Activated polyesterification" processes have been carried out in dichloroethane at 25 – 60 °C using trimethylamine as a catalyst (4 moles [Sic. Ed. of Translation) per mole of diol).[134,135] It was established that high-molecular-weight, film-forming polyesters ($\eta_{int} \leqslant$ 0.9 dl g^{-1}) are only formed by the polycondensation of activated esters of aliphatic dicarboxylic acids with bisphenols. We should note that it is this class of polyesters that is the most difficult to obtain by means of traditional polycondensation methods using the corresponding aliphatic acid dichlorides, which actively undergo various side reactions, including that with the acceptor (tertiary amine).[5] The best leaving group in the synthesis of the polyesters proved to 2,4-dinitrophenoxide. It was concluded from the results of studying polycondensation and model reactions that "activated polyesterification" occurs by a mechanism involving general base catalysis.

Thus, on the one hand, "activated polyesterification" extends the synthetic opportunities of the polycondensation method for

synthesising polyesters, while on the other hand, it opens up interesting prospects for studying acceptor-catalytic polyesterification processes (usually occurring by two catalytic channels—nucleophilic and general-basic),[136] since it makes it possible to distinguish the general-basic channel in a "pure form".

3. Synthesis of polyurethanes and polyureas

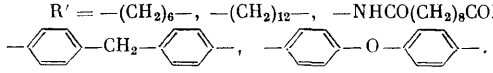
The polycondensation of activated biscarbonates of diols with diamines was carried out according to the scheme:[92]

$$n\ \mathrm{ArOCOO{-}R{-}OCOOAr} + n\ \mathrm{H_2N{-}R'{-}NH_2} \longrightarrow$$

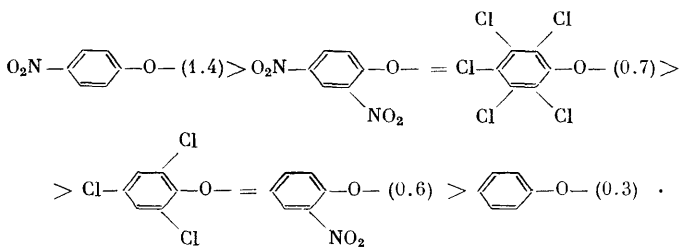
$$\longrightarrow\ \mathrm{{-}[{-}COO{-}R{-}OCONHR'NH{-}]_n{-}}\ ,$$

where

$$\mathrm{R' = {-}(CH_2)_6{-},\ {-}(CH_2)_{12}{-},\ {-}NHCO(CH_2)_8CONH{-},}$$



The effect of the nature of the leaving groups has been studied in the case of the reaction of activated biscarbonates of propane-1,3-diol with hexamethylenediamine in DMF (the best solvent for this monomer pair) at 110 °C and a monomer concentration of 0.6 mol litre^{-1}. According to the results obtained the ArO^- leaving groups make up the following series with respect to their tendency to form high-molecular-weight polyurethanes (the η_{int} values in *m*-xylene, dl g^{-1}, are given in brackets):



Branched butane-1,3-diol derivatives proved more sensitive to the nature of the leaving groups. Thus, for example, while activated carbonates of propane-1,3-diol form high-molecular-weight polyurethanes with virtually all leaving groups, in the case of butane-1,3-diol high-molecular-weight polyurethanes ($\eta_{int} \leqslant 3.8$ dl g^{-1}) are only obtained when the *p*-nitrophenol derivative is used.

Polycondensation of bis(*p*-nitrophenyloxycarbonyl)butane-1,3-diol with hexamethylenediamine in amide solvents (DMF, *N*-methylpyrrolidone) occurs homogeneously at 30 °C, and a high-molecular-weight polyurethane is formed after only 1–2 h, but subsequently the process slows down slightly and the increase in viscosity ceases within 12–24 h depending on the concentration of the initial monomers (1.2–0.3 mol litre^{-1}). The occurrence of a "slow stage" in this case may be related to the reduced activity of the carbonate group formed by the secondary hydroxyl as a result of the shielding effect of the methyl group. The "slow stage" virtually disappears when the temperature is increased to 70 °C.

It is appropriate to note that this example [like the increase in molecular weight of a polyamide that continues for several hours at the fairly high temperature of 80 °C (see Section III.1)] additionally and clearly suggests that activated esters have high stability in an amide solvent (see Section II.3).

The nature of the diamine has a considerable effect on "activated polyurethane formation". Polyurethanes with $\eta_{int} \leqslant 0.5$ dl g^{-1} are obtained with aromatic diamines (at the same time polyamides are formed equally effectively with diamines of both classes, see Section III.1). This may be due to a greater reduction in rate of aminolysis on changing from an aliphatic amine to an aromatic one (see Section II.2).

Activated polyurethane formation occurs by "direct" aminolysis (via $T^{\pm}$ or RTS) without the formation of an intermediate isocyanate (see Section II.2), which excludes the formation of anomalous urea residues, allophanate and biuret branches, and intermolecular cross-linking. It was also established that this reaction is irreversible (like the "activated polyamidation" examined above), and the urethane bond does not react with terminal carbonate groups (see Scheme 4). All this assists the formation of linear polyurethanes. An additional advantage of this method is the lack of necessity for using a proton acceptor or catalyst.

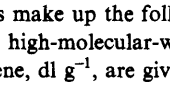
In contrast to urethane formation, the aminolysis of activated carbonates (see Section II.2) occurs via the formation of an intermediate isocyanate:

$$n\ \mathrm{ArOCOOAr} + n\ \mathrm{H_2N{-}R{-}NH_2} \xrightarrow[-\mathrm{HOAr}]{} [\mathrm{ArOCONH{-}R{-}NH_2}] \underset{+\mathrm{HOAr}}{\overset{-\mathrm{HOAr}}{\rightleftharpoons}}$$

$$\rightleftharpoons [\mathrm{O{=}C{=}N{-}R{-}NH_2}] \longrightarrow \mathrm{{-}[{-}CONH{-}R{-}NH{-}]_n{-}}, \qquad (1)$$

where

$$\mathrm{R = {-}(CH_2)_6{-},}$$



$$\mathrm{ArO =}$$

Of the two leaving groups—2,4-dinitro- and *p*-nitrophenoxide—the latter proved more effective in the synthesis of polyureas according to the above Scheme.[137] In the polycondensation of bis(*p*-nitrophenyl) carbonate with hexamethylenediamine in dimethylacetamide (DMAA) (containing 15% LiCl) at 90–100 °C, a polyurea with $\eta_{int} = 0.75$ dl g^{-1} was obtained. Under these conditions a high-molecular-weight polyurea is formed even when an aromatic diamine is used ($\eta_{int} = 1.34$ dl g^{-1}). The use of bis(2,4-dinitrophenyl) carbonate in these reactions leads to poorer results (a polymer with $\eta_{int} = 0.2-0.4$ dl g^{-1} is formed), which may be due to its tendency to undergo nucleophilic substitution as a side reaction (see Table 7).

The synthesis of polyureas is also carried out by another method, using the "intermediate" of the aminolysis of a carbonate—the activated carbamate (IX)—as a monomer:[138]

$$n\mathrm{O_2N{-}}\underset{\text{(IX)}}{\langle\bigcirc\rangle}\mathrm{{-}OCONHRNHCOO{-}}\langle\bigcirc\rangle\mathrm{{-}NO_2} + n\mathrm{H_2NR'NH_2} \longrightarrow$$

$$\longrightarrow \mathrm{{-}[CONHRNHCONHR'NH{-}]_n{-}}$$

$$\mathrm{R, R' = {-}(CH_2)_2{-},\ {-}(CH_2)_4{-},\ {-}(CH_2)_6{-},\ {-}(CH_2)_{12}{-}}\ \textit{etc.} \qquad (2)$$

Polycondensation of (IX) with diamines occurs under the same conditions as the synthesis of polyureas according to Eqn. (1), giving polymers with $\eta_{int} = 0.5-0.7$ dl g^{-1}.

We should note that the formation of the intermediate isocyanate in the synthesis of polyureas according to Eqns. (1) and (2) does not hinder the preparation of linear soluble polymers. Cross-linked polymers are not formed in this case apparently because of the equilibrium nature of the reaction at the stage involving regeneration of isocyanate. The *p*-nitrophenol that separates out in an amide solvent vigorously reacts with the isocyanate [the equilibrium constants of the dissociation of (IX) with R = $-(CH_2)_6-$ and the

reaction of hexamethylenediisocyanate with *p*-nitrophenol in DMAA are very close to each other and at 30 °C are equal to $(4.5 \pm 0.5) \times 10^{-3}$. This does not prevent the latter reacting with an amino group but it suppresses the formation of biuret.

Thus, the use of the activated polycondensation method considerably simplifies the processes involving formation of linear polyurethanes and polyureas. In terms of synthetic possibilities they are also superior to traditional methods and can be used to obtain polymers in solution under mild conditions without resorting to the synthesis of the corresponding diisocyanates or bischloroformates, which are often difficult or completely impossible to obtain. This circumstance is of particular importance for the preparation of polymers with special properties from those diamines and diols for which the traditional polycondensation methods cannot be used.

4. Some general characteristics of activated polycondensation

We have established in the case of the reaction of activated diesters of dicarboxylic acids and activated biscarbonates of diols with diamines that, in activated polycondensation, polymers with a maximum molecular weight are obtained when there is a strictly equimolar ratio of monomers, regardless of whether the process is homogeneous or heterogeneous.

The dependence of the molecular weight of the polymer in the synthesis of polyamides and polyurethanes on the concentration of monomers for homogeneous processes at 25–30 °C is extremal in nature with a maximum at monomer concentrations of 0.6 and 0.8–1.0 mol litre^{-1} respectively. At higher temperatures (100–120 °C) the results of polycondensation over the concentration range studied (0.2–1.2 mol litre^{-1}) are virtually independent of the initial concentration of the monomers. In heterogeneous polycondensation (the synthesis of aliphatic polyamides in HMPA) the maximum molecular weights are achieved when the reaction solution is diluted to 0.15 mol litre^{-1}, regardless of the nature of the dicarboxylic acid (succinic, adipic) or diamine (hexamethylenediamine, dodecamethylenediamine). The reason for this dependence should be sought in the improved swelling of the polymers when they are diluted, since the polymer grain size decreases on dilution, assisting chain propagation in the heterophase.

The use of amide solvents and DMSO, in which reactions involving both aromatic and aliphatic diamines can occur successfully, as the reaction medium proved the most fruitful. In the case of the latter, other organic solvents such as acetone, dioxan, THF, dichloroethane, etc., in which high-molecular-weight polyamides (regardless of the heterogeneous nature of the process) were obtained at 25–30 °C, are also suitable. Under these temperature conditions in HMPA, diesters with 2,4-dinitro-, 2,6-dinitro-, and pentafluoro-phenoxide leaving groups readily react with aromatic diamines. For esters with other leaving groups the optimum temperature is 80 °C. On comparing these results with the data in Table 1, it may be assumed that for activated polycondensation to be effective the apparent rate of reaction (fundamental stage) must be of the order of $\sim 10^{-2}$ litre mol^{-1} s^{-1}.

While the synthesis of polyamides and polyurethanes from aliphatic diamines occurs successfully at 25–30 °C, for the preparation of high-molecular-weight polyureas it is necessary to increase the temperature to 90–100 °C in order to change the reaction to homophase conditions. This is due to the equilibrium nature of the process at the stage involving dissociation of the intermediate carbamate to isocyanate. In the swollen precipitate the equilibrium is shifted towards unreactive carbamate, which inhibits chain propagation. After homogenisation of the solution the viscosity of the polyureas increases considerably (from 0.5 to 0.75 dl g^{-1}).

In the synthesis of polyamides and polyurethanes, where equilibrium stages do not occur, separation of the polymer out of solution apparently assists chain propagation through a local increase in concentration of the functional groups and their favourable relative position in space (resembling "liquid-crystalline polycondensation"). If the process occurs in a weakly polar proton-inert solvent, catalysis by an amide (see Section II.2) assumes considerable significance. In the condensed state this catalysis should only have a slight effect because of the high local concentration of the amide groups. The polyamide chain may also fulfil the role of an acceptor of HX (strong hydrogen complexes are formed), although in weakly polar solvents this problem is not so important since salt-like complexes (inactive ammonium cations) are hardly formed at all (see Secton II.3).

Thus, in certain specific cases of activated polycondensation the separation of the polymer out of solution may constitute one of the reasons for a restriction on chain propagation. In other cases, such as in the polycondensation of diamines with pentachlorophenyl diesters of adipic and isophthalic acids in HMPA, the poor solubility of the diesters results in considerable inhibition of the process at the initial stages.[103] After homogenisation of the solution the rate of polycondensation of bis(pentachlorophenyl) adipate with 4,4′-diaminodiphenylmethane is still low and considerably slower than the rate of polycondensation involving bis(*p*-nitrophenyl) adipate, which does not correspond to the expected reactivity of the diesters (see Table 1). The reason for this discrepancy should be sought either in the "immuring" of the terminal ester groups inside the macromolecular coil because of their low affinity for HMPA ("lyophobic effect") or in an increase in the inhibitory "ortho effect" through a reduction in the local dielectric constant of the medium.

Of the other causes of a restriction on chain propagation in the aminolysis of activated diesters, we can single out nucleophilic substitution. The results of model reactions (see Section II.3) are supported by the presence of terminal 2,4-dinitroaniline groups in the corresponding polymers (a characteristic absorption occurs in the region 355–365 nm) at a level of 0.6–1.8 mol%.[126] The contribution of nucleophilic substitution in the reaction between 2,4-dinitrophenyl esters of carboxylic acids, in particular aliphatic acids, and an aromatic amine is comparatively low (see Table 7). The successful synthesis of high-molecular-weight polyamides in the reaction between dinitrophenyl diesters and aromatic amines is considerably dependent on this (see series II-I and II-II). The same diesters actively undergo a nucleophilic substitution reaction with aliphatic diamines and form polyamides that are considerably inferior in terms of viscosity to the samples synthesised via other diesters (series II-III and II-IV). 2,4-Dinitrophenyl diesters have improved behaviour in the synthesis of polyesters and polybenzazoles, which is also an indication of the low contribution of nucleophilic substitution in these processes. In the reaction between 2,4-dinitrophenyl carbonates and an aromatic amine, on the other hand, the yield of the product obtained from nucleophilic substitution is higher than in the reaction with an alkylamine (see Table 7), which inhibits the formation of high-molecular-weight polyurethanes and polyureas based on aromatic diamines ($\eta_{int} \leqslant 0.2–0.4$ dl g^{-1}).

Protonation of the amino groups by low-molecular-weight products of an acidic nature which separate out is known to result in chain termination during low-temperature polycondensation. However, as was demonstrated in Section II.3, in the case of the

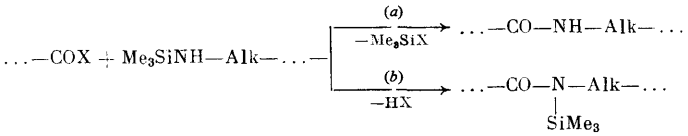
weak acids which we have used as phenols, this reaction is not critical. An indication of this is provided by the results given above on polycondensation involving aliphatic diamines without using a proton acceptor in different media—both proton-active and proton-inert.

Polycondensation involving *N*-oxysuccinimide esters occurs in a distinctive manner.[139] The ability of *N*-hydroxysuccinimide to bind with primary aliphatic amines, giving strong insoluble complexes (see Section II.3) has a considerable effect on polycondensation; it inhibits, for example, the reaction between the corresponding isophthalate and hexamethylenediamine. Polycondensation of hexamethylenediamine with a more active adipate readily occurs with the formation of a high-molecular-weight polyamide (series II-IV). In this case triethylamine cannot deprotonate the primary amino group and has no significant effect on the course of the reaction. An increase in temperature to 80–120 °C leads to a marked acceleration of the reaction, but at the same time the side reaction between *N*-hydroxysuccinimide itself and the aliphatic diamine is intensified.[125]

Thus, the various processes for restricting chain propagation are primarily responsible for the lack of a clear relationship between the reactivity of activated diesters and the viscosity properties of the resulting polymers. The role of these processes may be reduced through a choice of suitable reaction conditions or leaving groups.

5. Syntheses using trimethylsilylated derivatives and diamine salts

As an alternative to free aliphatic diamines, their *N,N'*-bis-(trimethylsilyl) derivatives have been used successfully in polycondensation with activated diesters.[90,91,125,137,138,140,141]

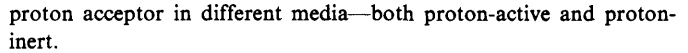


Despite the lower nucleophilicity of trimethylsilylated amino groups,[142,143] polycondensation of these derivatives with various activated diesters occurs at sufficiently high rates, resulting in the formation of heterochain polymers that are comparable in terms of molecular weight to the corresponding polymers obtained via the free bases.

Polycondensation of activated diesters with trimethylsilylated diamines mainly takes place with the formation of a "normal" amide [route (*a*)][141] (the eliminated phenol HX acts as a desilylating agent). Even if route (*b*) does occur in this reaction, the number of trimethylsilylated amide groups are either insufficient for formation of cross-linked polymers or the rate of their acylation by activated esters is much lower than the rate of desilylation.[142] Activated diesters differ in this respect favourably from acid dichlorides, which on reacting with trimethylsilylated diamines give cross-linked polymers in a number of cases.[141]

The stability of trimethylsilylated amino groups towards alkyl esters of carboxylic acids (which is important when diamines containing ester groups are used, see below) and also the elimination of the low-molecular-weight silylated reaction product Me_3SiX, which is incapable of protonating an amino group, should be included amongst the advantages of nucleophiles of this class. This is an important factor in the case of polycondensation systems for which a powerful inhibitory reaction between acidic by-products and diamines is typical, such as when bis(*N*-oxysuccinimide) esters of dicarboxylic acids are used as monomers (see Section III.4).[125]

Because of the high stability of the activated diesters towards triethylamine, we were able to use stable diamine salts as monomers in polycondensation.



Y = Cl, CH_3COO.

The reactions examined in this Section are especially useful for the design of macromolecular systems based on diamines that are unstable as free bases. In particular, they have been used successfully for the synthesis of functional heterochain polymers of different classes—polyamides, polyurethanes, and polyureas—from alkyl esters of the natural diaminocarboxylic acids—lysine and cystine—which are of practical interest for medical and biological applications.[144,145]

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In summarising the above material we may conclude that during the last 10–15 years another versatile method for the synthesis of heterochain polymers has been developed. With this method a standardised approach can be made towards the synthesis of heterochain polymers of different classes and to design novel, functional macromolecular systems that were previously unobtainable, including biomedical polymers. This makes the new method particularly promising and attractive for the "fine chemistry" of polymers with special properties. With regard to large-scale production, problems of a practical nature may arise in the future, stimulating the development of new technologies based on the reactions examined above, including efficient methods of regenerating the low-molecular-weight polycondensation products, and corresponding to economic and ecological requirements.

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