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The radical polymerisation of acrylamide and its derivatives in the presence of complexing salts

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Abstract. The results of studies of the radical polymerisation of acrylamide and of its derivatives in the presence of inorganic salts (Lewis acids) in various solvents are correlated. It is shown that the effect of inorganic salts on the polymerisation of acrylamide depends to a large extent on the nature of the solvent. During polymerisation in water the addition of Lewis acids has no effect on the rate of the process. The effect of Lewis acids is most marked when the reaction is carried out in organic solvents of relatively low polarity. It is shown that the change in the overall rate of the process in the presence of Lewis acids is due to a change in the rate constants of the chain growth and chain breaking reactions, induced by the formation of a complex between the amide group of the propagating radicals and/or monomers and the inorganic salt. The introduction of substituents into the acrylamide suppresses the formation of a complex with the salt, and therefore the effect of the salt on the polymerisation of substituted acrylamides is less marked than in the polymerisation of acrylamide itself. The bibliography includes 52 references.

I. Introduction

Studies reported during the past 15–20 years have convincingly established that in the radical polymerisation of vinyl monomers the nature of the reaction medium has a strong influence on the overall rate of the process, on the rate constants of the elementary propagation and termination reactions of the polymer chains, and on the molecular characteristics of the resulting polymers. Changing the nature of the solvent or introducing various complexing additives into the reaction mixture can significantly affect the kinetic parameters of the homogeneous radical polymerisation reaction.

Solvent effects are especially marked in the polymerisation of water-soluble monomers. Thus, in the polymerisation of monomers such as acrylamide, acrylic acids, *N*-vinylpyrrolidone, and the tertiary salts of the aminoesters of (meth)acrylic acid the chain propagation rate constant (k_p) is increased 50–100-fold[1–6] when the homogeneous polymerisation in organic solvents is replaced by polymerisation in an aqueous solution. The nature of the solvent has a smaller effect on the polymerisation of nonpolar and moderately polar vinyl monomers such as styrene and methyl methacrylate. But even in this case the overall rate of the reaction can be varied by a substantial factor by changing the nature of the solvent, and the k_p value for the homogeneous polymerisation of styrene varies by 50%–70% depending on the nature of the solvent. These effects have been discussed in depth in several monographs and reviews (see, for example, Refs 1 and 7–14). An analysis of published data suggests that the principal causes of the influence of the nature of the solvent on the kinetic parameters of the homogeneous radical polymerisation of vinyl monomers are the formation of specific complexes between the reacting species (the monomer, and the polymeric radicals) and the solvent molecules, the hydrophobic interactions stimulated by the polymerisation of water-soluble monomers in aqueous solutions, and also the change in the quality of the solvent as compared with the growing polymer. In the case of low-polarity hydrocarbon monomers of the styrene type the factor which mainly determines the effect of the solvent on k_p is the formation of donor–acceptor complexes between the solvent molecules and the growing polymer radicals, leading to a decrease in the activity of these radicals.

The formation of donor–acceptor complexes between the vinyl monomers and/or their radicals (on the one hand) and inorganic salts acting as Lewis acids (on the other) can also affect the radical polymerisation of the vinyl monomers. Detailed analyses of the reported studies of polymerisation in the presence of Lewis acids can be found in several publications.[15–22] Their results, correlated in those reviews, show that the addition to the reaction system of Lewis acids such as zinc chloride, aluminium bromide and chloride, stannic chloride, lithium chloride, and also various organoaluminium compounds leads to marked changes in the kinetics of the homopolymerisation of vinyl monomers (acrylonitrile, methacrylonitrile, methyl acrylate, methyl methacrylate, etc.) and of the copolymerisation of these monomers. Under these conditions substantial changes in the molecular masses of the polymers also take place. Most of the authors explain the observed kinetic effects in terms of complex formation between the components of the reaction mixture and of the influence of these complexes on the rate constants of the elementary propagation and termination reactions of the polymer chains. The formation of complexes in systems containing vinyl monomers and various Lewis acids has been established experimentally by spectroscopic methods: in many cases the complexes between the monomer and the Lewis acids were isolated in a pure state. A study of the effect of the complexing

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agent on the radical polymerisation of (meth)acrylonitrile and methyl(meth)acrylate [23] showed that (depending on the strength of the Lewis acid, its concentration, and the donor–acceptor properties of the monomer) the complex-forming salts can both accelerate and inhibit this process.

Thus we have very extensive and convincing evidence of the effect of the nature of the solvent and of added complexing salts on the radical polymerisation of a large number of vinyl monomers. One of the sources of the observed effect is the formation of various types of complex between the components of the reaction system. Furthermore, the nature of the resulting complexes and their influence on the polymerisation kinetics may be different if the polymerisation is carried out in different solvents or in the presence of Lewis acids. Therefore information on the effect of the nature of the solvent on the radical polymerisation in the presence of complexing salts could be useful in establishing the mechanism by which the composition of the reaction medium affects the kinetic parameters of the polymerisation. The aim of the present review is to generalise the results of studies of this problem.

Studies of the influence of the nature of the solvent on the polymerisation in the presence of complex-forming salts were carried out mainly on acrylamide and on some of its derivatives. The polymers of acrylamide offer a wide range of important properties for practical applications. [24–26] They are used as efficient flocculants in the purification of potable water and of effluents from metallurgical, mining, and other industrial plants, to improve the performance of petrol engines, to decrease the hydrodynamic resistance to the motion of water along pipelines and to the motion of various objects in water, in the textile and the food industry, etc. Therefore studies of the polymerisation mechanism of acrylamide and its derivatives in the presence of salt additives are of great interest not only in establishing the fundamental rules governing the radical polymerisation process but also for practical purposes.

II. Polymerisation of acrylamide and its derivatives in the presence of Lewis acids

We know that the amide group has a planar configuration, the *trans* form being the most favourable: [27,28]



In the absence of metal ions the amide group is almost neutral; in an acid medium it can add on a proton, the protonation taking place mainly at the oxygen atom. [28,29]

Complex formation with metal ions lengthens the C = O bond and shortens the C–N bond. Experimental and theoretical studies have identified an increase in the double-bond character of the carbon to nitrogen bond, due both to metallisation and to the protonation of the amide group in an acid medium. [27]

These results suggest that in the polymerisation of amide monomers a specific interaction should exist between the amide group of the monomer (and/or the polymeric radical) and the metal atoms of the Lewis acid, leading to a change in the reactivity of the reacting species and therefore also of the kinetic parameters of the polymerisation of these monomers. A partial confirmation of these changes is provided by data on the copolymerisation of acrylamide with other vinyl monomers in the presence of Lewis acids. Thus, in the copolymerisation of acrylamide with acrylic acid the addition of zinc chloride strongly influences both the copolymerisation constant and the overall rate of the process. [30] Whereas in the absence of the salt the copolymerisation of these monomers in benzene produces a random copolymer, and the system is characterised by the copolymerisation constants $r_1 = 1.38$ and $r_2 = 0.36$, the addition of zinc chloride (at all concentrations of the initial mixture of monomers) produces an alternating copolymer of equimolar composition. The changes in the copolymerisation constants of acrylamide with vinyl acetate and methacrylic acid in the presence of a Lewis acid are also confirmed by independent results. [31]

Several studies of the complex formation of acrylamide and some of its derivatives with the halides of various metals (in particular, with zinc chloride and bromide) in the solid state and of the polymerisation of these solid complexes were reported in the early 1980s. [32–35] The polymerisation of several *N-tert*-alkylacrylamides in solution under the influence of zinc chloride was also studied. The formation of solid complexes of acrylamide, methacrylamide, and their *N*-substituted analogues with zinc, cadmium, and mercury halides has been investigated. [32] The ability of these systems to form complexes depends both on the structure of the amide and on the nature of the salt. The presence of bulky *tert*-alkyl substituents near the nitrogen atom of the amide group strongly suppresses the complex-forming properties of the monomer. Furthermore methacrylamide is less effective in complex formation than acrylamide. A study of the structure of the *N-tert*-butyl- and *N-tert*-amylacrylamide complexes with zinc chloride in dioxan showed that in this case the electrophilic attack of zinc chloride takes place at the oxygen atom of the carbonyl group in the amide. [33]

The complex formation of *N-tert*-butyl- and *N-tert*-hexylacrylamide with zinc chloride increases the rate of radical polymerisation of these amides in the solid state. In most cases the formation of complexes of these amides with zinc bromide is accompanied by a decrease in the reactivity of the monomers. [34] At a given polymerisation temperature an increase in the size of the alkyl substituent on the nitrogen atom increases the rate of solid-phase polymerisation of the complexed monomer. However, at a given reduced temperature (i.e. for a fixed $T:T_m$ ratio) we observe the opposite activity sequence of the complexed monomers. It is important to note that the activation energy for the polymerisation of the complexed monomers is higher than the value for the free amide monomers.

In the presence of zinc chloride *N-tert*-alkylacrylamides (*N-tert*-butyl- and *N-tert*-amyl-) are polymerised at 60 °C even without a radical initiator if the reaction is carried out in solvents of low polarity (benzene, dioxan). [35] The yield of the polymers depends on the strength of the interaction between the salt and the solvent (Table 1). When this interaction is very strong (with polar solvents like pyridine, ethyl acetate, and especially water) the influence of the Lewis acid on the reactivity of the monomer is slight, and the rate of polymerisation is low. Adding water to a solution of the monomer in dioxan breaks the bond between the monomer and the salt and thus lowers the yield of polymer.

Table 1. Polymerisation of *N-tert*-butylacrylamide (I) and *N-tert*-amylacrylamide (II) under the influence of zinc chloride. [35]

Solvent	Yield of polymer (%)	
	I	II
Water	—	0.85
Pyridine	0.81	1.80
Dioxan	45.80	23.57
Ethyl acetate	0.81	2.52
Benzene[a]	60.00	40.00
Methanol	0	0
Acetone	0	0

Note. Reaction conditions: concentration of amide 0.2866 M, of salt 0.1433 M; temperature 60 °C; polymerisation time 1 h.
[a]During the polymerisation in benzene the polymer is partially precipitated as a separate phase.

The effect of Lewis acids on the polymerisation of acrylamide has been examined in much greater depth. The polymerisation of this monomer was studied in detail in various solvents and in the presence of inorganic salts of different types, thus allowing a well founded mechanism of the process to be developed.

1. Effect of the nature of the solvent on the polymerisation of acrylamide in the presence of Lewis acids

The radical polymerisation of acrylamide in water and in various organic solvents and water–organic mixtures in the presence of Lewis acids has been studied in our laboratory.[36–40] In every case the reaction was carried out under UV radiation in the presence of the dinitrile of azoisobutyric acid (DAA) as a photosensitiser. The polymerisation of acrylamide (AA) in an aqueous solution in the presence of lithium bromide has also been discussed.[36,39] It can be seen from the results in Fig. 1 that at relatively low rates of initiation the addition of the salt (lithium bromide) produces a marked decrease in the overall rate of the reaction. However, at higher rates of initiation the effect of the salt becomes less marked and the reaction no longer depends on the additions of salt. An analysis of these results (and in particular the study of the effect of the salt on the order of the polymerisation reaction with respect to the initiator, which varies from 1 to 0.5 as the salt concentration is increased) leads to the conclusion that the lithium bromide additive has no effect on the rate constants of the chain propagation and chain termination reactions in the polymerisation of acrylamide in aqueous solution.[36,39] On the other hand the decrease in rate observed at low rates of initiation is entirely due to the presence of additives in the system. The conclusion that additions of Lewis acids have no effect on the rates of the propagation and termination reactions of the chains during the polymerisation of amide monomers (and also of acrylonitrile) in aqueous solutions is also consistent with other results.[35,41]

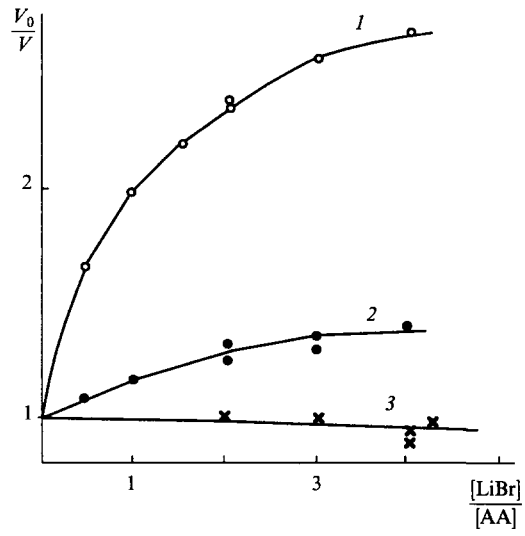


Figure 1. Dependence of the relative rate of polymerisation of acrylamide in water on the concentration of lithium bromide. Concentration of acrylamide 0.5 M; $T = 20$ °C; V_0 and V are the reaction rates in the absence and in the presence of the salt respectively. Concentration of DAA, M: 0.5×10^{-4} (*1*), 0.8×10^{-3} (*2, 3*); intensity of incident UV light, arbitrary units: 1 (*1, 2*), 2.5 and 4.0 (*3*).

It should be noted that some studies have revealed a change in the rate of polymerisation of acrylamide under the influence of several oxidation–reduction initiating systems after the addition of sodium, potassium, iron, manganese, and other salts (see, for example, the monograph by Finch[26]). However, this effect is fully explained by the influence of those salts on the rate of the oxidation–reduction initiation, and is not dependent on any interaction of the salts with the monomer and/or the growing radicals.

A different state of affairs is found in the polymerisation of acrylamide in less polar solvents. The addition of lithium bromide to a solution of acrylamide in dimethyl sulfoxide (DMSO) leads to an increase in the total rate of polymerisation, which reaches a maximum at a molar ratio of [salt] : [monomer] = 1.5, followed by a slight decrease when the salt concentration is increased beyond this value (Fig. 2). The order of the reaction with respect to the initiator is 0.5, both in the absence of salt and in the presence of a [salt] : [monomer] ratio of 1.5. When the concentration ratio of salt to monomer is kept constant the order of the reaction with respect to the monomer increases from 1.0 (in the absence of the salt) to 1.96 (at a ratio of 1.5). Increasing this ratio to 2.0 produces a decrease in the order of the reaction with respect to monomer.[37,39]

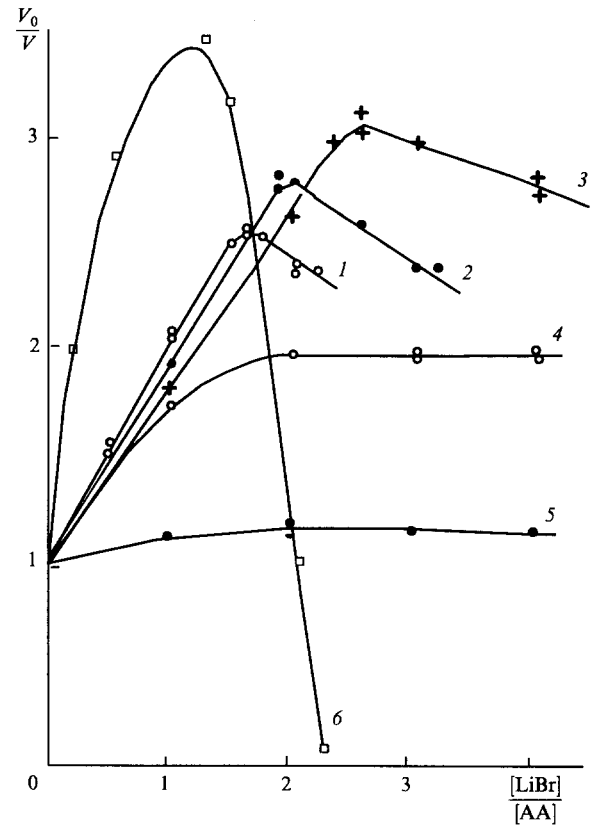


Figure 2. Dependence of the relative rate of polymerisation of acrylamide in DMSO (*1*), in a water–DMSO mixture (*2–5*), and in tetrahydrofuran (THF) (*6*) on the concentration of lithium bromide. Concentration of acrylamide 0.5, concentration of DAA 3×10^{-3} M; $T = 30$ °C; concentration of water in the mixture with DMSO mol %: (*2*) 8.4, (*3*) 20, (*4*) 65, (*5*) 85.

Adding water to the DMSO produces a gradual decrease in the effect of the salt on the rate of polymerisation of acrylamide. For small additions of water (8.4 and 20 mol% of the DMSO) the plots of the overall rate of polymerisation (V) against the concentration of the salt show a maximum at higher concentrations than in the polymerisation in the absence of water (Fig. 2, curves *2* and *3*). Under these conditions the effect of the salt on the rate of polymerisation (i.e. the ratio V/V_0, where V_0 is the rate of polymerisation in the absence of water) is greater in the presence of water than when the polymerisation takes place in dry DMSO. For higher water concentrations in the mixed solvents (65 and 85 mol%) the maximum effect of the salt is less marked than in pure DMSO (Fig. 2, curves *4* and *5*). Furthermore at high

water contents there is practically no decrease in the reaction rate beyond the lithium bromide concentration at which the maximum value is reached.

The effect of lithium bromide on the polymerisation of acrylamide is strongest in THF. In this solvent the reaction takes place with precipitation of the polymer from solution, and therefore the rate of photopolymerisation was determined in the earliest stages of the process, when the loss of transparency of the reaction system produced by the precipitation of the polymer was not too serious, i.e. the rate of photoinitiation was practically constant. The results in Fig. 2 show that, as in DMSO, in the polymerisation in THF (curve *6*) the reaction rate reaches a maximum at a well defined concentration of the salt, and that in this case the maximum V/V_0 ratio is much higher than in the polymerisation in DMSO and the maximum is observed at a lower concentration ratio of the salt and the monomer. However, at higher concentrations of lithium bromide the rate of polymerisation of acrylamide falls off steeply.

The addition of saturated acetamide to a reaction system containing lithium bromide and acrylamide lowers the rate of polymerisation in DMSO, and this effect increases with the concentration of acetamide.[39, 40] In the absence of the salt, adding acetamide has no effect on the rate of polymerisation of acrylamide. When acrylamide is polymerised in DMSO in the presence of acetamide, salt additions increase the rate of the reaction but in this case the accelerating effect of lithium bromide is less marked than in the absence of acetamide (Fig. 3).

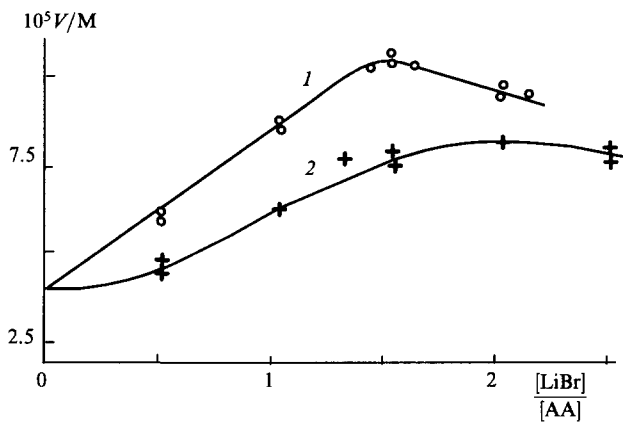


Figure 3. Effect of the concentration of lithium bromide on the rate of polymerisation of acrylamide in DMSO in the presence (*1*) and in the absence of 1.0 M of acetamide (*2*). Concentration of acrylamide 0.5, of DAA 3 × 10^{-3} M, $T = 30$ °C.

2. Effect of the nature of the inorganic salt on the polymerisation of acrylamide

The effect of the nature of the Lewis acid on the polymerisation of acrylamide has been studied for the reaction in DMSO.[38-40]

Lithium, calcium, and zinc chlorides were used as the Lewis acids. The reaction was carried out under the conditions used in the presence of lithium bromide. In every case the reaction proceeds (without a period of induction) with a constant initial rate. The polymerisation in the presence of lithium and calcium salts produces a maximum in the plot of the overall rate of the process against the concentration of the salt (Fig. 4). However, the position of the maximum varies with the nature of the salt. With respect to their influence on the overall rate of polymerisation of acrylamide the salts can be arranged in the following series: LiBr < LiCl < $CaCl_2$. The rate of polymerisation of monomers such as acrylonitrile and methyl methacrylate,[42] and also *N*-alkylacrylamides,[35] increases markedly in the presence of zinc chloride, but the addition of this salt has

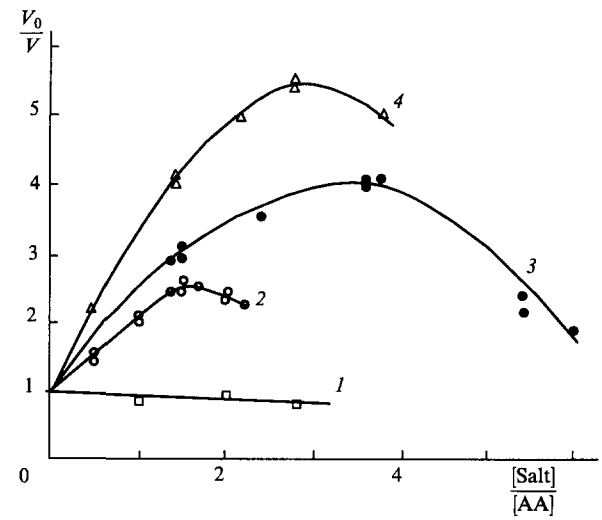


Figure 4. Dependence of the relative rate of polymerisation of acrylamide in DMSO on the salt concentration. Concentration of acrylamide 0.5, concentration of DAA 3 × 10^{-3} M; $T = 30$ °C; salt (*1*) $ZnCl_2$, (*2*) LiBr, (*3*) LiCl, (*4*) $CaCl_2$.

almost no effect on the rate of homogeneous polymerisation of acrylamide under the conditions of these experiments.

The rate of polymerisation of acrylamide in the presence of lithium bromide or calcium chloride depends on the nature of the solvent in which the reaction is carried out: the accelerating effect of small additions of salt on the polymerisation process increases as the polarity of the solvent decreases (Fig. 5).[40] It should be noted that (as in the polymerisation of *N-tert*-alkyl substituted acrylamides in a low-polarity medium[35]) the polymerisation of acrylamide in *N*-methylpyrrolidone (the least polar of the solvents used in that work[40]) with [salt]:[monomer] ratios between 0.35 and 0.40 takes place even in the absence of radical initiators. The spontaneous polymerisation of acrylamide (in the

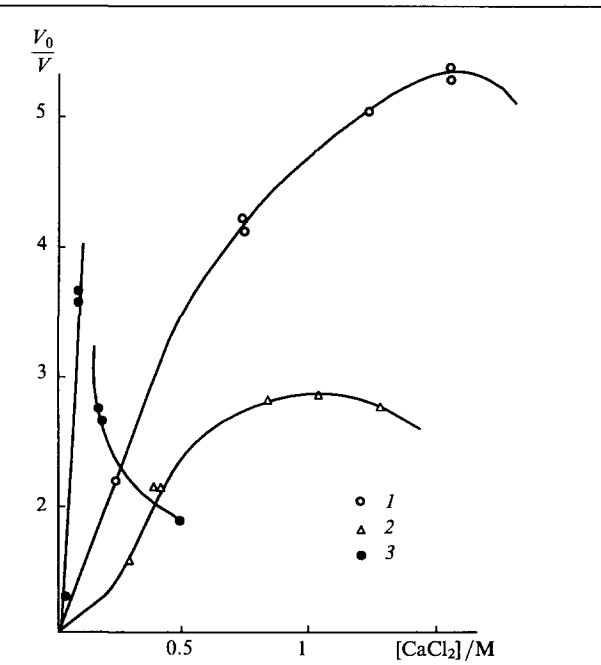


Figure 5. Dependence of the relative rate of polymerisation of acrylamide in DMSO (*1*), formamide (*2*), and *N*-methylpyrrolidone (*3*) at 30 °C (*1*) and 20 °C (*2, 3*) on the concentration of calcium chloride. Concentration of acrylamide 0.5, concentration of DAA 3 × 10^{-4} M.

Table 2. Order of the reaction with respect to the monomer in the polymerisation of acrylamide in DMSO for different concentration ratios of salt to monomer.[38,39]

Salt	[Salt]:[Monomer]	n	Relative viscosity of salt solution in DMSO	n' (see [a])
LiBr	0.5	1.3	1.4	1.3
	1.0	1.6	1.6	1.3
	1.5	1.9	2.0	1.7
LiCl	0.5	1.4	1.4	1.2
	1.5	2.2	2.0	1.9
$CaCl_2$	1.5	2.8	4.0	2.2
	3.0	3.6	19	2.5

Notes. Reaction conditions: concentration of acrylamide 0.5, of DAA 3×10^{-3} M; $T = 30$ °C.
[a] n' was calculated from the rates of polymerisation reduced to a fixed viscosity of the reaction system equal to the viscosity of DMSO.

absence of UV radiation) was not observed at other salt concentrations in *N*-methylpyrrolidone.

The kinetic order with respect to the initiator in the polymerisation of acrylamide in DMSO is 0.5 in the presence of lithium and calcium chlorides (as it is in the presence of lithium bromide). On the other hand the order of the reaction with respect to the monomer (n) at a constant ratio between the salt and the monomer varies with this ratio between 1.3 and 3.6 (Table 2). The addition of salts to a solution of acrylamide in DMSO produces a large increase in the viscosity of the reacting solution. Thus, at a salt concentration of 0.75 M the viscosity of the solution increases 2-fold with lithium chloride and bromide and 4-fold when calcium chloride is added. As was pointed out,[43] an increase in the viscosity of the reaction medium should be accompanied by an increase in the overall rate of polymerisation. Therefore the reaction rates were recalculated for a fixed viscosity of the reaction solution, equal to the viscosity of DMSO, and the order of the reaction with respect to the monomer was then redetermined (n'). It was assumed that the rate of the reaction was proportional to the viscosity of the reaction system to the power 0.5. The results (see Table 2) show that the order of the reaction with respect to the monomer was greater than 2.0 in the presence of calcium chloride at high [salt]:[monomer] ratios, whereas it approached this value during polymerisation in solutions containing lithium chloride or bromide.

Additions of inorganic salts (Lewis acids) affect not only the overall rate of polymerisation but also the molecular mass of the polymers, which is much greater than the molecular mass of the polyacrylamide synthesised in the absence of salts.[38-40] Thus, the intrinsic viscosity of the polymer produced in DMSO at a monomer concentration of 0.5 M is 0.88 dL g^{-1}, whereas the polymers synthesised in the presence of 1.0 M of lithium bromide or chloride or of calcium chloride have an intrinsic viscosity of 2.9, 3.5, and 4.1 dL g^{-1} respectively.

The change in reactivity of acrylamide and/or its radical in the presence of Lewis acids also results in changes in the overall rate of the process and in the copolymerisation constants of acrylamide with styrene in DMSO. It has been shown[40] that the rate of polymerisation of acrylamide decreases rapidly with small additions of styrene, the effect depending on the presence of a Lewis acid in the reaction system. Thus, adding 5 mol% of styrene lowers the rate of polymerisation in the absence of the salt by a factor of 17, whereas in a system containing lithium bromide ([salt]:[acrylamide] = 1.5) the rate falls by a factor of 32, and in the copolymerisation under similar conditions but in the presence of lithium chloride it falls by a factor of 40. The copolymerisation constants of acrylamide with styrene in DMSO are $r_1 = 0.21$ and $r_2 = 2.35$ in the presence of lithium chloride and $r_1 = 0.40$ and $r_2 = 2.0$ in the absence of the salt.[44]

3. Mechanism of the effect of salts on the polymerisation of acrylamide

The results discussed above denote a specific interaction between the reacting species and the salts (Lewis acids) in the polymerisation of acrylamide. The IR and PMR spectra of acrylamide–salt systems in DMSO were analysed in order to confirm the presence of this interaction.[38-40] In the IR spectra the absorption band which characterises the NH group of the monomer is shifted towards lower frequencies in the presence of lithium bromide (Fig. 6). The PMR spectrum also reveals a small shift of the signal due to the protons of the NH_2 group towards lower energies.[36,40] A more substantial shift is observed when lithium chloride is added to a solution of acrylamide in DMSO, and an even stronger shift when calcium chloride is added. On the other hand the addition of zinc chloride to the acrylamide–DMSO system does not produce a significant shift of this signal. Thus the spectroscopic results point to the formation of a complex between the amide group of acrylamide and the inorganic salts (except zinc chloride). The C=C vinyl group does not take part in complex formation. A similar result was obtained in a study[45] of the interaction between methyl methacrylate and Lewis acids. The formation of complexes between the amide group of acrylamide and the salt is confirmed by kinetic data on the effect of acetamide on the polymerisation of acrylamide in DMSO in the presence of lithium bromide. If the vinyl group had contributed to the formation of a complex between acrylamide and the salt, the rate of polymerisation of the acrylamide would not have been affected by the addition of acetamide. Evidently acetamide (like acrylamide) forms a complex with lithium bromide, and the addition of a saturated amide to the reacting system creates a competition between the acrylamide and the acetamide for the formation of a complex, which lowers the rate of polymerisation. The fact that even small additions of acetamide (as compared with the acrylamide) produce a marked decrease in the rate of polymerisation is evidence that the formation of a complex between the salt and a saturated amide has a higher probability than the same reaction with the unsaturated acrylamide. PMR spectroscopy results[36,40] lead to the same conclusion: under otherwise identical conditions the signal which characterises the protons of the amide group is shifted by the addition of lithium bromide by 0.30 and 0.23 ppm for acetamide and acrylamide respectively.

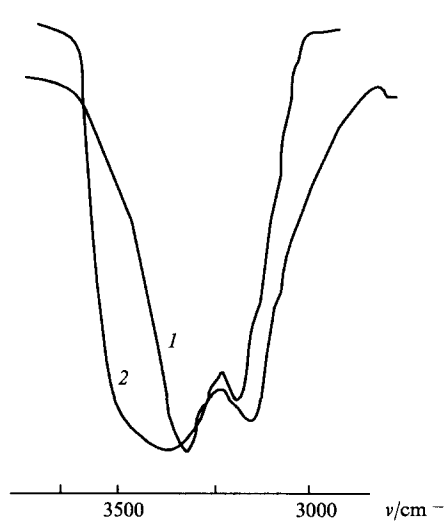


Figure 6. IR spectra of solutions in DMSO (*1*) and in DMSO + LiBr (*2*). Concentration of acrylamide 0.5 M, of salt 0.75 M.

The PMR spectroscopy data indicate an increase in the double-bond character of the C–N bond in acrylamide after the addition of the Lewis acid. It may be assumed that the presence of a C=C double bond undergoing conjugation with the C=O bond of the amide lowers the probability of complex formation between the acrylamide and the salt as compared with acetamide.

According to the IR and PMR spectroscopy data the amount of monomer complexed in the reaction mixture is small. Therefore we may assume that the complexed radicals (which have a high activity) and not the complexed acrylamide play the key role in the change in the rate of polymerisation of acrylamide in the presence of Lewis acids.

The stability constants of the complexes formed by acrylamide with salts (K) in various solvents have been calculated[36,38–40] from PMR data. The K values for 27 °C calculated by the Hildebrand–Benes method[46] from the dependence of the shift of the PMR signal at 7.50 ppm on the concentration of acrylamide at constant salt concentration are shown below:

Solvent	DMSO	DMSO	THF	Water
Salt	LiBr	$CaCl_2$	$CaCl_2$	LiBr
K/L mol^{-1}	0.066	0.14	0.23	0

As in the case of lithium bromide, in systems containing lithium chloride or calcium chloride the complexed radicals play the main part in the polymerisation process. However, at high salt concentrations the contribution from the complexed monomer cannot be ignored. This is specially true of polymerisation in a DMSO solution of calcium chloride, since the power to form complexes with acrylamide is highest in this salt.[36–40]

The following kinetic scheme for the formation of a complex between the reacting species (monomer and radical) and the salt and also for the polymerisation of acrylamide in the presence of Lewis acids was derived[36–40] from the reported kinetic and spectroscopic data.

If $R_c^{\cdot}$ radicals bound in a complex take part in the polymerisation process their concentration in the reaction system is determined by the reaction

$$\text{Salt} + R^{\cdot} \xrightarrow{K} R_c^{\cdot}.$$

If the concentration of the salt is much greater than the concentration of the radicals we have

$$[R_c^{\cdot}] = K[\text{Salt}]([R^{\cdot}]_0 - [R_c^{\cdot}]).$$

and

$$[R_c^{\cdot}] = \frac{K[\text{Salt}][R]_0}{1 + K[\text{Salt}]}.$$

On the assumption that the chain propagation reaction is characterised by the constant k_p when the participating radicals are not complexed and by the constant k'_p in the case of complex-bound radicals we can write the following equation for the overall rate of polymerisation in the presence of a complex-forming salt:

$$V = [M]\{k_p([R^{\cdot}]_0 - [R_c^{\cdot}]) + k'_p[R_c^{\cdot}]\}. \quad (1)$$

After substituting for $R_c^{\cdot}$ we find

$$V = [M][R^{\cdot}]_0\left(\frac{k_p}{1 + K[\text{Salt}]} + \frac{k'_p K[\text{Salt}]}{1 + K[\text{Salt}]}\right). \quad (2)$$

If $K[\text{Salt}] \ll 1$ the overall rate of polymerisation is

$$V = [M][R_0^{\cdot}](k_p + k'_p K[\text{Salt}]). \quad (3)$$

For a polymerisation process involving not only radicals bound in a complex but also complexed monomer molecules the following rate equation for the polymerisation has been obtained:

$$V = [M][R^{\cdot}]_0(k_p + k_1[\text{Salt}] + k_2[\text{Salt}]^2). \quad (4)$$

Here k_1 and k_2 are constants which characterise the rate of the chain propagation reaction of the corresponding complexed species and the stability constant of the complex. The term $k_2[\text{Salt}]^2$, which does not appear in Eqn (3), results from allowing for the interaction of complexed radicals with the monomer.

It follows from Eqn (4) that the overall rate of polymerisation should increase linearly with the concentration of the monomer, and that the order of the reaction with respect to the salt as a function of the relative values of k_p, $k_1[\text{Salt}]$, and $k_2[\text{Salt}]^2$ should vary from 0 to 1 if only complexed radicals contribute to the polymerisation [see Eqn (3)], or from 0 to 2 if both complexed radicals and the monomer bound in a complex are involved. Therefore the overall order of the polymerisation reaction with respect to the monomer and the salt (i.e. when the concentrations of the salt and of the monomer are both changing, but the ratio of these components of the reaction mixture is held constant) should increase from 1 to 2 or from 1 to 3 respectively with the salt concentration. The experimental data shown in Table 3 agree satisfactorily with these predictions. They also confirm the participation of the complexed monomer in the polymerisation of acrylamide in a DMSO solution containing calcium chloride. This is not surprising, since the concentration of complexed acrylamide in this system is approximately 15%–20% of the total concentration of monomer under the conditions corresponding to the maximum rate in curve *4* of Fig. 4.

In order to explain the mechanism of the effect of inorganic salts on the radical polymerisation of acrylamide the absolute values of the rate constants of the elementary reactions for the propagation and termination of the polymer chains were determined for the reaction in DMSO in the presence of various salts.[38–40] It was found that the changes in the rate of polymerisation of acrylamide can be attributed almost entirely to changes in the rate constants for the propagation (k_p) and termination (k_t) of the chains, and are not dependent on changes in the rate of initiation produced by the addition of salts (see Table 3 and Fig. 7). A similar state of affairs was observed in the polymerisation of acrylonitrile in the presence of Lewis acids.[42]

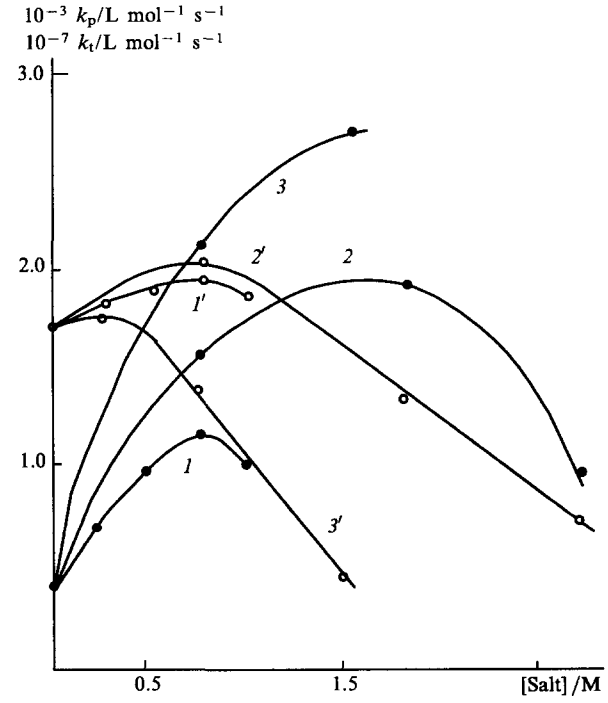


Figure 7. Dependence of the rate constants for the propagation (*1*–*3*) and for the termination of the chains (*1'*–*3'*) on the salt concentration during the polymerisation of acrylamide in DMSO at 30 °C. Salt: (*1*) LiBr, (*2*) LiCl, (*3*) $CaCl_2$.

Table 3. Rate constants of the chain propagation (k_p) and termination reactions (k_t) in the homogeneous polymerisation of acrylamide in DMSO in the presence of complexing salts (acrylamide concentration 0.5 M).[36]

[LiBr] / M	T/ °C	10^{-3} k_p/ L mol^{-1} s^{-1}	E_p/ kcal mol^{-1}	10^{-7} A_p/ L mol^{-1} s^{-1}	10^{-7} k_t/ L mol^{-1} s^{-1}	E_t/ kcal mol^{-1}	10^{-8} A_t/ L mol^{-1} s^{-1}
0	20	2.5	6.0	7.8	16.7	0.3	2.8
	30	3.7			16.9		
	40	5.0			17.3		
0.25	20	4.6	5.4	5.3	17.7	0.3	3.0
	30	6.8			18.1		
	40	9.0			18.4		
0.50	20	7.0	4.7	2.5	18.7	0.3	3.1
	30	9.7			19.0		
	40	12.5			19.3		
0.75	20	8.5	4.3	1.5	19.0	0.4	3.8
	30	11.6			19.4		
	40	14.5			19.8		
1.0	20	7.0	4.8	2.8	18.2	0.6	5.1
	30	10.0			18.8		
	40	12.9			19.4		

The changes in the overall rate of polymerisation observed after the addition of lithium bromide to a solution of acrylamide in DMSO are due mainly to changes in k_p (since the changes in k_t are only slight). Additions of this salt lower the activation energy of the chain propagation reaction, and this effect is associated with a decrease in the complex formation constant with temperature. Thus an increase in temperature is accompanied by a decrease in the stability constant of the complex, and therefore also in the concentration of complexed radicals, and this leads to a less steep temperature dependence of the rate of chain propagation.

The complex formation constant decreases as the polarity of the solvent increases. This accounts for the influence of the nature of the solvent on the polymerisation of acrylamide in the presence of lithium bromide or calcium chloride. The effect of the salt on the polymerisation is greatest in tetrahydrofuran ($K = 0.23$ L mol^{-1}), whereas in an aqueous solution no acceleration is produced by the salt (the stability constant of the complex in water is zero).

In the presence of complexing salts the constant k_p varies in the same sense as the change in the overall rate of polymerisation (see Table 3). The experimentally observed dependence of the chain termination rate constant on the salt concentration is due to the diffusion control of the polymer chain propagation reaction. We know[43] that the chain termination rate constant is directly proportional to the fluidity of the reaction system. Therefore we used the formula[40]

$$k_t' = \eta k_0$$

(where k_t' is the experimental value, and η is the viscosity of the initial reaction mixture relative to DMSO) to calculate the k_t' values for a viscosity equal to that of pure DMSO. It was shown that the k_t' values are directly proportional to the salt concentration (Fig. 8), which suggests an increase in the reactivity of the polymeric radicals with increasing salt concentration and confirms the concept of complex formation by polymeric radicals.[36-40]

The difference in the chain propagation rate constants observed in the homogeneous polymerisation of acrylamide in DMSO containing various salts can be attributed to different degrees of complex formation between the active centres and the salt. It should not be forgotten that free radicals both bound and not bound in a complex contribute to the polymerisation. An increase in the complex formation constant results (not surprisingly) in an increased number of complexed active centres and therefore in an increase in the effective rate coefficient of the chain propagation reaction. Since the complex formation constant for potassium chloride with acrylamide in DMSO is higher than for lithium bromide we may suggest that the complex formation constants of these salts with polymeric radicals vary in the same sequence. Therefore the propagation of chains should have its highest specific rate in the presence of calcium chloride and its lowest in the presence of lithium bromide, as is indeed observed experimentally. It follows from PMR spectroscopy data that zinc chloride does not form a complex with acrylamide in a DMSO solution. Therefore the addition of this salt to a solution of acrylamide in DMSO does not affect the overall rate of polymerisation.

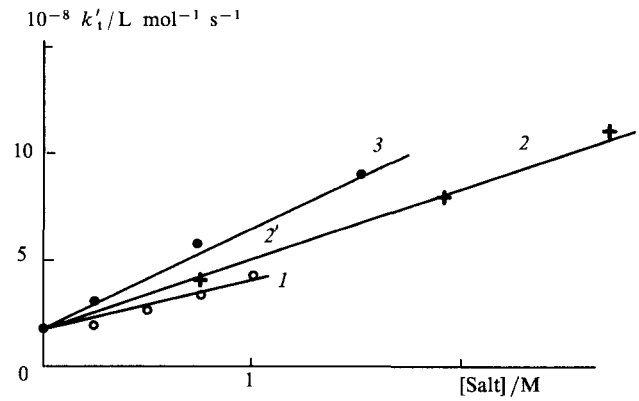
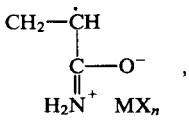


Figure 8. Plots of the rate constant of the chain termination reaction reduced to a single viscosity for the polymerisation of acrylamide in DMSO at 30 °C against the salt concentration. Salt: (*1*) LiBr, (*2*) LiCl, (*3*) $CaCl_2$.

The formation of a complex between the acrylamide molecules and the salts is accompanied by an increase in the distance between the signals in the PMR spectra which characterise the protons of the amide group in the monomer. Whereas the signal at 7.0 ppm is almost unaffected by the addition of salts the signal at 7.5 ppm is shifted towards lower

energies, indicating an increase in the double-bond character of the C–N bond in acrylamide as a result of the formation of a complex with the salt.[36,38]

The higher reactivity of the complexed acrylamide radical, which produces an increased rate of polymerisation of acrylamide in the presence of Lewis acids, can be attributed to the formation of the structure



whose most important feature is the localisation of an unpaired electron on the carbon atom.

In the PMR spectrum the distance between the signals which characterise the protons of the amide group in acrylamide decreases at higher temperatures, and both signals (at 7.0 and 7.5 ppm) become broader. At a well defined temperature the two signals merge together. This temperature is determined by the energy of the rotation round the C–N bond, and depends on the degree of double-bond character between these two atoms. The merging temperature of the singlets is strongly dependent on the nature of the complexing salt, and increases on changing from lithium bromide (80 °C) to lithium chloride (92 °C) and to calcium chloride (106 °C) (Fig. 9). This sequence shows that the double-bond character of the C–N bond is more marked in acrylamide complexed with calcium chloride than in acrylamide complexed with lithium salts.

The presence of a single signal in the PMR spectrum of acrylamide denotes free rotation round the C–N bond. In this case the presence of a Lewis acid in the system does not affect the reactivity of the acrylamide radical, and therefore also the rate of polymerisation of acrylamide. Thus, in the polymerisation of acrylamide in the presence of lithium bromide in DMSO at 80 °C, i.e. under conditions which produce only one signal from the protons of the amide group in the PMR spectrum of acrylamide, the addition of salt (in the region of the maximum in curve *1* of Fig. 2) does not affect the rate of polymerisation as compared with the polymerisation of acrylamide without the salt.

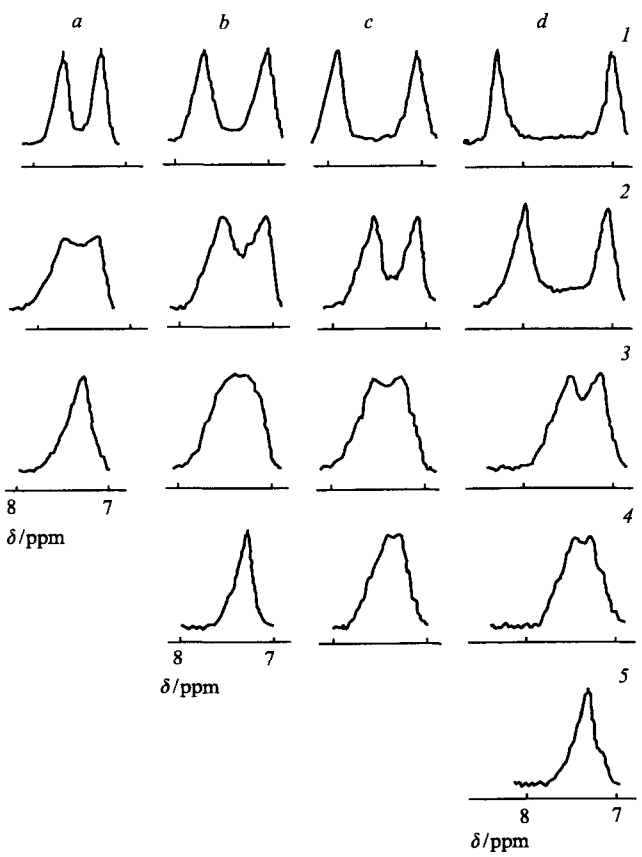


Figure 9. Effect of temperature on the shape of the PMR spectrum of acrylamide in DMSO in the presence of various salts. Salt: (*a*) none, (*b*) LiBr, (*c*) LiCl, (*d*) $CaCl_2$; *T*, °C: (*1*) 27, (*2*) 50, (*3*) 70, (*4*) 90, (*5*) 106.

The decrease in the overall rate of polymerisation and in the rate constants of the chain propagation and termination reactions beyond their maxima may be due to a change in the conformational characteristics of the macromolecules in the solution at high salt concentrations. The addition of a large quantity of salt probably degrades the thermodynamic quality of the solvent, and therefore it lowers the rate coefficients of the propagation and growth of the chains (as is found in the homogeneous radical polymerisation of acrylamide in the absence of salts[6,47,48]). Therefore the maximum in the plots of the overall rate of polymerisation and of the rate coefficient for the growth of the chains against the concentration of the salt is probably due to the competing effects of complex formation (leading to an enhanced rate of polymerisation and to an increased rate coefficient for the propagation) and of the conformation of the macromolecules (i.e. of the salting-out effect of the salts). The greater complex-forming capacity in lithium chloride and in calcium chloride (as compared with lithium bromide) produces a shift in the maximum rate towards higher salt concentrations (see Fig. 4).

We know that in the radical polymerisation of hydrocarbon monomers the reactivity of the radicals and that of the monomers change in opposite directions.[23] Therefore the decrease in the rate of polymerisation in the presence of high concentrations of salt could also be due to the participation in the polymerisation reaction of monomer molecules bound in a complex, whose activity may be lower than the activity of noncomplexed acrylamide molecules. This approach was proposed earlier to account for the maxima on the plots of the overall rate of the process against the salt concentration in the polymerisation of methyl methacrylate.[23] The participation of complexed monomer molecules in the reaction can make a substantial contribution, since at high salt concentrations (and in spite of a relatively low complex formation constant) the number of complexed monomers should be appreciable. Thus, at 30 °C and a molar ratio of 4.0 between the calcium chloride and the acrylamide the fraction of complexed monomer should be ~30%. However, if allowance is made only for the change in reactivity of the complexed monomer and for its relative concentration the maximum in the dependence of the overall rate of polymerisation on the salt concentration should be found at lower concentrations for calcium chloride than for lithium bromide, since the complex formation constant of acrylamide is lower for the lithium salt than for calcium chloride.

III. Polymerisation of *N*-substituted acrylamides in the presence of calcium chloride

These ideas on the effect of the complex formation by the amide group of the monomer with the complexing Lewis acids on the polymerisation kinetics were confirmed by studies of the polymerisation of derivatives of acrylamide (methacrylamide and *N-tert*-butylacrylamide) in various solvents in the presence of calcium chloride. The photopolymerisation of *N-tert*-butylacrylamide in *N*-methylpyrrolidone and that of methacrylamide in formamide have been studied.[49] The polymerisation of these monomers takes place under homogeneous conditions both in the absence of a salt and in the presence of calcium chloride. In every case the initial rate of the polymerisation becomes constant immediately after the application of UV light. The dependence of the overall rate of the polymerisation on the salt concentration is shown in Fig. 10. For comparison the figure also shows data for

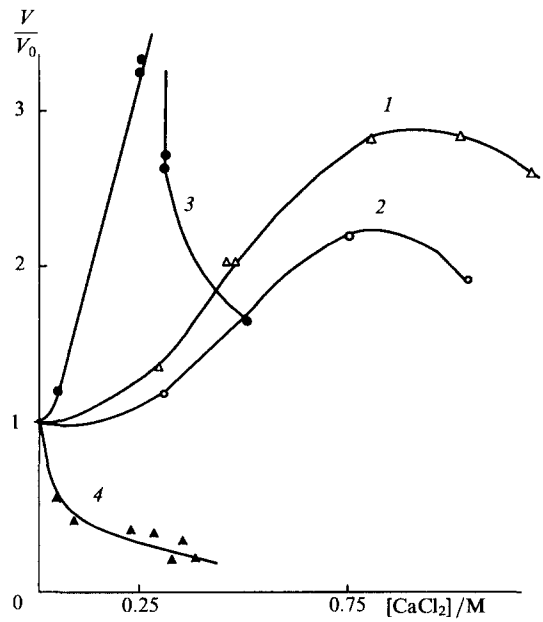


Figure 10. Dependence of the relative rate of polymerisation of acrylamide and its derivatives in various solvents on the concentration of calcium chloride at 20 °C. Concentration of monomer 0.5, concentration of DAA 3×10^{-3} M. System: (*1*) acrylamide in formamide, (*2*) methacrylamide in formamide, (*3*) acrylamide in *N*-methylpyrrolidone, (*4*) *N-tert*-butylacrylamide in *N*-methylpyrrolidone.

the polymerisation of acrylamide in formamide and in *N*-methylpyrrolidone. It follows from these results that in the polymerisation of acrylamide in both these solvents and in the polymerisation of methacrylamide in formamide additions of calcium chloride initially produce a large increase in the reaction rate, which goes through a maximum at a definite concentration of the salt before falling off again. The initial rate of polymerisation in these systems is proportional to the square root of the rate of initiation; the order of the reaction with respect to the monomer is close to unity. The $k_p/k_t^{1/2}$ ratios were calculated from the overall rate of polymerisation and from the rate of initiation, determined by measurements in the presence of an efficient radical polymerisation inhibitor (2,2,6,6-tetramethyl-4-oxopiperidine-*N*-oxyl). In the polymerisation of acrylamide this ratio increases from 0.61 in the absence of the salt to 2.0 when calcium chloride is added ([$CaCl_2$]:[acrylamide] = 1.8). In the case of methacrylamide the parameter $k_p/k_t^{1/2}$ increases from 0.06 to 0.14 when the same amount of salt is added. Comparing the overall rates and the $k_p/k_t^{1/2}$ values for these systems shows that the changes in the rate of polymerisation produced by the addition of calcium chloride are almost wholly due to changes in the rate of the chain propagation and termination reactions.

The effect of calcium chloride on the polymerisation of methacrylamide in formamide is less marked than in the case of acrylamide. This difference is due partly to a decrease in the complex formation constant between methacrylamide and its radical, and partly to a decrease in the same parameter for calcium chloride. PMR spectroscopy data also confirm that the complex formation of methacrylamide with lithium bromide is weaker than the corresponding reaction of acrylamide. The addition of lithium bromide (0.75 M) to a solution of acrylamide in DMSO (0.5 M) increases by 0.30 ppm the spacing of the signals which characterise the protons of the amide group. On the other hand with methacrylamide the increase in the spacing of the signals from the protons of the amide groups is 0.20 ppm under similar conditions. Other results[32] also confirm that methacrylamide is less reactive towards the formation of complexes with Lewis acids.

In contrast to acrylamide and methacrylamide no increase in the rate of the process is observed when calcium chloride is added to *N-tert*-butylacrylamide. Conversely, the addition of even small amounts of this salt (0.04 M at a monomer concentration of 0.5 M) markedly lowers the rate of homogeneous polymerisation of this monomer in *N*-methylpyrrolidone. An increase in the salt concentration produces a further decrease in the rate of polymerisation of *N-tert*-butylacrylamide (see Fig. 10). Most probably, the formation of a complex between the amide group and the salt is seriously hindered (if not completely suppressed) by the presence of a bulky *tert*-butyl substituent on the nitrogen atom of *N-tert*-butylacrylamide. As a result the addition of calcium chloride to a solution of *N-tert*-butylacrylamide does not increase the rate of polymerisation but only produces a 'salting-out' effect which degrades the thermodynamic quality of the solvent and is accompanied by a decrease in the overall rate of polymerisation. It should be noted that the results published from our laboratory[49] are consistent with the report[35] that in polar solvents the spontaneous polymerisation of *N-tert*-butylacrylamide in the presence of Lewis acids takes place slowly or not at all.

IV. Complex-radical polymerisation of acrylamide in the presence of zinc chloride

It is of interest to examine the causes of the difference in behaviour of salts such as lithium chloride and bromide, and calcium chloride (on the one hand) and zinc chloride (on the other) in the homogeneous polymerisation of acrylamide in DMSO. Zinc chloride is a Lewis acid of moderate strength, and it effectively accelerates the polymerisation of several other vinyl monomers such as acrylonitrile, methyl methacrylate, and other esters of acrylic and methacrylic acid. Since metal ions are involved[27,28] in complex formation between inorganic salts and amides it could be suggested that the different effects of salts on the polymerisation of acrylamide in DMSO are related to differences in their degree of dissociation in the relatively basic solvent DMSO.[36-40]

In order to test this hypothesis the dissociation of various salts in DMSO was measured, and the polymerisation of acrylamide in the presence of zinc chloride was also studied in another solvent.[50] The dissociation of the salts was determined by studying the dependence of the electric conductivity of their solutions in DMSO on the salt concentration, and the equivalent conductivity at infinite dilution (λ_∞) was obtained. To simplify the calculation all the salts were treated as 1:1 electrolytes. The λ_∞ values found in this way for lithium chloride and bromide and for calcium chloride lie in the range of 33–39 Ω^{-1} cm^2 (g-equiv)$^{-1}$, in good agreement with published data.[51] The degree of dissociation of the salts (α) was calculated as in the case of weak electrolytes: from the ratio of the specific to the equivalent conductivity. The results thus obtained showed that at concentrations of lithium salts and of calcium chloride between 0.2 and 0.3 M their dissociation is not less than 30%.

The conductivity of zinc chloride solutions in DMSO was almost constant at salt concentrations between 0.01 and 0.32 M, and did not exceed 1.0 Ω^{-1} cm^2 (g-equiv)$^{-1}$. Therefore the dissociation of this salt in the concentration range examined is ~1%–2%. It appears that the interaction of DMSO with zinc chloride produces an adduct which suppresses the dissociation of this salt in a solution of DMSO.

We know[52] that zinc chloride is partially dissociated in a mixed solution of water and tetrahydrofuran containing 77.5 mol% of water. The dissociation of the salt in that solution at concentrations of 0.1–0.5 M is 30%–12%, i.e. it is close to the dissociation of lithium salts and of calcium chloride in DMSO. The photopolymerisation of acrylamide in a mixture of THF and water was therefore studied in the presence of various concentrations of zinc chloride.[50] As can be seen from the results in Fig. 11 these polymerisation conditions produce a

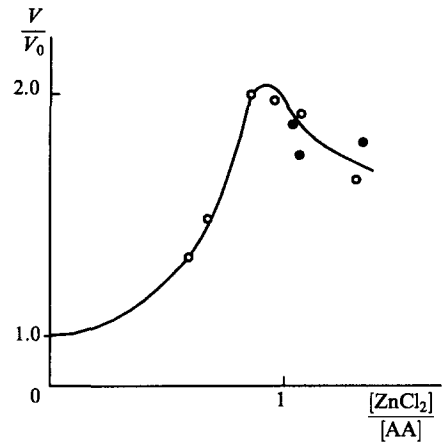


Figure 11. Dependence of the relative rate of polymerisation of acrylamide in a mixture of tetrahydrofuran and water containing 77.5 mol% of water on the concentration of zinc chloride at 20 °C. Concentration of acrylamide 0.5 M.

dependence of the overall rate of polymerisation on the concentration of the salt similar to the dependences observed in the polymerisation of acrylamide in DMSO in the presence of lithium salts or of calcium chloride (see Figs 2 and 4).

As in the case of the other salts, the changes in the kinetic parameters of the polymerisation of acrylamide in the presence of zinc chloride are due to complex formation between the reacting species and the salt. The formation of a complex between the monomer and zinc chloride in a mixture of water and tetrahydrofuran is confirmed by IR spectroscopy results: the 1695 cm^{-1} absorption band, characteristic of the C=O group in acrylamide, is shifted by 10 cm^{-1} towards lower frequencies by the addition of the salt.

The largest change in the overall rate of polymerisation of acrylamide in the presence of zinc chloride is somewhat smaller than for the polymerisation in DMSO in the presence of the other salts which have been studied. The lower effect of the salt during polymerisation in a mixture of water and tetrahydrofuran may be due (at least partially) to the influence of the water on the complex formation between the salt and the acrylamide, and/or its growing radical. Thus the addition of water should markedly lower the formation constant of the complex between the amide group and the salt.

Further evidence of the participation of the salt in an ionised state in the complex formation process was obtained during the study of the acrylamide–tetrahydrofuran–zinc chloride system. Additions of zinc chloride to a solution in tetrahydrofuran do not affect the IR spectrum of acrylamide, showing that in this solvent no complexes are formed between zinc chloride and the monomer.

The participation of lithium chloride (in an ionised form) in the complex formation with acrylonitrile radicals, leading to an increase in their reactivity and therefore also to an increase in the overall rate of polymerisation of acrylonitrile in the presence of lithium chloride, was first suggested by Bamford.[19] We may therefore assume that the influence of the nature of the solvent on the complex-radical polymerisation of vinyl monomers in the presence of inorganic Lewis acids is determined by the effect of the solvent on the dissociation of the Lewis acid, and also on the constant which defines the formation of a complex between the metal ions and the reacting species (the monomer and the polymeric radicals).

V. Conclusion

Available data show that (as in the polymerisation of vinyl monomers) inorganic Lewis acids have a substantial influence on the polymerisation of acrylamide and its derivatives. In every case the effect of inorganic salts such as metal halides is the result of their formation of a complex in the ionic form with the monomer, and also with the growing polymeric radicals, and of the change in the reactivity of the reacting species produced by this complex formation. The formation of complexes between the salts (Lewis acids) and the functional groups of the monomers and/or the growing polymeric radicals is strongly dependent on the polarity of the solvent in which the reaction is carried out. The acid–base characteristics of the solvent also have a definite effect. For this reason the Lewis acids show their strongest kinetic effect in polymerisations carried out in solvents having a relatively low polarity and no basic properties. In the radical polymerisation of acrylamide in aqueous solutions the addition of Lewis acids does not affect the kinetic parameters of the process or the molecular characteristics of the resulting polyacrylamide.

The results discussed in this review show that (as in the radical polymerisation of vinyl monomers such as acrylonitrile, methyl methacrylate, and the vinylpyridines) the addition of various Lewis acids to the reaction system can be used to control the radical polymerisation of acrylamide and its derivatives. In this way a change in the composition of the reaction medium can be used to carry out the polymerisation of acrylamide at different rates and to obtain polymers having different molecular masses and the required operational properties.

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