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The Influence of the Solvent on the Rates of Chain Propagation and Termination Reactions in Radical Polymerisation

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The influence of the solvent on the rate of radical polymerisation and copolymerisation, observed and investigated in the last ten years and caused mainly by a change in the rate of the elementary chain propagation reaction, is discussed. The published data on the polymerisation and copolymerisation of a number of monomers in solvents of different types are surveyed. Attention is drawn to the fact that the greatest effects are observed for polar monomers, particularly for water-soluble monomers in an aqueous medium. The causes of the change in the overall rate of reaction, the constants k_p, and the copolymerisation constants for different monomers are examined.
The bibliography includes 104 references.

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I. INTRODUCTION

Various aspects of solvent effects on the kinetics and mechanisms of chemical and particularly chain reactions have been investigated in many studies whose results have been surveyed[1-3]. However, the influence of the solvent on the rate of the chain propagation reaction in polymerisation proceeding via a radical mechanism has been scarcely discussed until recently. It has usually been assumed that the chain propagation and termination rate constants in the initial stages of homogeneous radical polymerisation are independent of the nature of the medium†. The influence of solvents on radical copolymerisation was tested experimentally as early as 1950s. It was established that, in the homogeneous copolymerisation of styrene and methyl methacrylate in benzene and acetonitrile (with dielectric constants of 2.28 and 38.8), the copolymerisation constants are similar. The same result was obtained for the copolymerisation of styrene and 2,5-dichlorostyrene in a number of solvents with markedly different dielectric constants[7]. Significant differences between the reactivities of reacting species as a function of the nature of the medium have been found only in the polymerisation and copolymerisation of certain polar, particularly ionising, monomers[8].

During the last 15–20 years, studies of the influence of the nature of the medium on homogeneous radical polymerisation and copolymerisation have developed extensively in various directions[8-23], including studies on the influence of the solvent on the kinetics and on the structure and properties of polymers. Appreciable effects have been observed in many instances. Furthermore, it has been found that inorganic complex-forming agents (coordination-unsaturated metal compounds) can alter significantly the rates of the elementary reactions and the molecular weights and structures of the polymers. This phenomenon was discovered and investigated in detail by a number of workers[24-27].

Thus the possibility arose of influencing appreciably the rate of chain propagation reactions under the conditions of radical polymerisation. In radical copolymerisation procedures were developed for the regulation and composition and distribution of units in the macromolecule and also of the structure of polymer chains. New ways for the regulation of the properties of the products were devised. Previously no such possibilities were available in radical polymerisation; it was assumed that, in contrast to ionic and ionic-coordination polymerisation, the constants k_p are determined solely by the nature of the monomer—namely by the reactivities of the monomers and the radicals, which are independent of the nature of the medium.

The influences of the solvent on the rates of chain propagation and termination reactions are different, in terms of the magnitude of the effect and frequently its mechanism, for weakly polar and polar monomers.

II. WEAKLY POLAR MONOMERS

Individual observations showing that the influence of solvents on the initial rate of homogeneous radical polymerisation cannot be reduced solely to their involvement in the initiation and chain transfer reactions, were published in several studies as early as the 1950s–1960s.[28-32] It was suggested that polymerisation in solutions involves the formation of complexes between the polymeric radicals and the monomer or solvent molecules. Thus, apart from the interaction with polymeric radicals via a chain transfer

† This review does not deal in detail with the widely known influence of the viscosity of this system on the rate constant for the termination of polymer chains (k_t), which is manifested most significantly at advanced stages of the process. At these stages an increase of the viscosity of the polymerisation system also induces a decrease of the chain propagation rate constant[4] (k_p). The influence of the viscosity of solvents on k_t at the beginning of the reaction has also been demonstrated. Little attention has been devoted to the above problems in the literature (see, for example, Bagdasar'yan[5] and Gladyshev and Popov[6]). The dependence of the rate of initiation on the viscosity of the medium has also been demonstrated[6].

mechanism, in the polymerisation of styrene in bromobenzene the molecules of the latter are probably involved in complex formation[31]. The extremely low rates of polymerisation of vinyl benzoate in bulk could be caused by the formation of a complex of the growing radical with the aromatic ring of the monomer[29]. The appreciable decrease of the rate of polymerisation of vinyl acetate in benzene could also be caused by the formation of a complex between the polymeric radicals and benzene molecules, which leads to the formation of species which are relatively inactive in the chain propagation reaction.

The influence of the nature of the solvent on the overall rate of radical polymerisation of styrene was probably first clearly established experimentally by Henrici Olive and Olive[11-13] A little later the constant k_p and k_t were determined for the polymerisation of methyl methacrylate in a number of solvents[16]. However, the influence of the medium on the rate of radical polymerisation of weakly polar monomers is low: the overall reaction rate changes at the most by a factor of 1.5–2.

The polymerisation of styrene has been investigated in a large number of organic substances of different classes (aromatic and carbonyl compounds, ethers, and alkyl halides) and the dependence of the overall rate of reaction on the nature of the solvent has been demonstrated[11-13]. The observed effect has been examined taking into account the intermolecular interaction between the polymer radicals and the monomer and solvent molecules.

Table 1. The influence of the "τ-ratio" in the polymerisation of styrene in solvents of different classes at 50°C.[13]

Solvent	τ_S/τ_M	Solvent	τ_S/τ_M
Mesitylene	1.62	Tetrahydropyrene	1.01
Methyl isobutyrate	1.53	Anisole	0.97
Dimethoxyethane	1.52	Bromobenzene	0.93
Ethyl acetate	1.44	Dimethylformamide	0.91
Ethylbenzene	1.28	Chloroform	0.90
Toluene	1.28	Pyridine	0.87
Butanone	1.22	Dioxan	0.87
Tetrahydrofuran	1.09	1,2-Dichloroethane	0.85
Benzene	1.04	Methylene chloride	0.83

The electron affinities of typical polymer radicals hardly differ from that characteristic of, for example, tetracyanoethylene and chloranil, which form charge-transfer complexes with the solvents usually employed in vinyl polymerisation. It is therefore assumed that donor–acceptor complexes of polymer radicals with both monomer and solvent molecules arise in polymerisation in solution. The concentration of complex species in the reaction system is proportional to the product of the monomer and solvent concentrations and to the lifetime of the corresponding complexes, which depends on the electronic structure of the species. The influence of the solvent on the rate of polymerisation can be expressed with the aid of a single parameter, namely the "τ-ratio"—the ratio of the lifetime of the donor–acceptor complex between the polymer radical and the solvent molecule (τ_S) to that of the complex between the polymer radical and the monomer molecule (τ_M). The values of the "τ-ratio" for 18 solvents of different classes have been determined from experimental data (Table 1).

The solvent is inert for $\tau_M = \tau_S$. If $\tau_M > \tau_S$, then the rate of polymerisation is higher than in an inert diluent; correspondingly, for $\tau_M < \tau_S$, it is lower. For polymerisation in bulk the "τ-ratio" is unity. Depending on the nature of the solvent, the "τ-ratio" and hence the overall rate of polymerisation of styrene vary at most by a factor of two.

The constants k_p and k_t for the polymerisation of styrene in several solvents have been determined[33] by the usual methods (k_p^2/k_t was obtained from the measured rate of polymerisation and the molecular weights of the polymers, and k_p/k_t was found by the rotating sector method). Table 2 shows that these quantities are somewhat smaller than in the polymerisation of styrene in bulk and decrease with increase of solvent concentration. It has been shown experimentally[33] that k_t is inversely proportional to the viscosity of the solution. The influence of the nature of the solvent on k_p has been explained by the formation of complexes of the growing radicals with the solvent. The stability and reactivity of these complexes determines the difference between the quantity k_p in solution and that of polymerisation in bulk.

Table 2. Photopolymerisation of styrene in solutions at 25°C in the presence of azobisisobutyronitrile[33].

Solvent	$\eta_{mixt.}$, cP	k_p, litre mole^{-1} s^{-1}	$10^{-7}k_t$, litre mole^{-1} s^{-1}
—	11.1	35±7	1.9±0.4
Bromobenzene (50%)	10.5	29±8	1.6±0.3
Bromobenzene (20%)	10.8	35±5	1.9±0.3
Diethyl malonate (20%)	12.1	29±7	1.5±0.4
Diethyl phthalate (50%)	26.1	20±5	0.8±0.2
Diethyl phthalate (20%)	15.2	23±8	1.1±0.2
Dinonyl phthalate (60%)	58.2	27±4	0.31±0.04

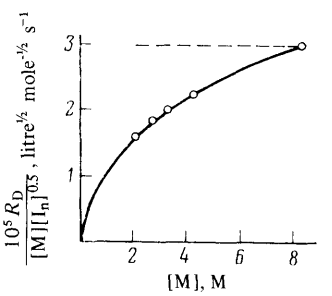


Figure 1. Dependence of the specific rate of polymerisation of styrene $R_p/[M][In]^{0.5}$ on the monomer concentration in the reaction mixture; $[In]/[M] = 0.71 \times 10^{-2}$; dashed line—ideal behaviour.

The influence of the solvent concentration in the reaction system on the overall rate of reaction has also been observed in the polymerisation of styrene in acetone under homogeneous conditions[34]. Here the rate of reaction (R_p) is proportional to the concentration of the initiator (In)

raised to a power of 0.45; however, the dependence of R_p on the monomer concentration differs sharply from linearity (Fig. 1). As in the studies of Henrici-Olive and Olive [11-13], the observed effect is explained by postulating the formation of a complex between the growing polymer radicals and acetone molecules. The formation of complexes between free radicals and various organic compounds has been established experimentally [35]. The stability constants of complexes of the t-butylmesitylnitroxy-radical with various organic substrates (monomers and solvents) as well as their free energies of formation have been determined by gas–liquid chromatography and spectrophotometry. It has been established that solvents forming the most stable complexes exert the greatest influence on k_p in the polymerisation of methyl methacrylate (Fig. 2). The formation of complexes between a stable radical (2,2,6,6-tetramethylpiperidinyl-1-oxy-radical) and methacrylate esters has also been established [36] by NMR and EPR.

The hypothesis put forward by Henrici-Olive and Olive [11-13] was confirmed in a study [16] of the photopolymerisation of methyl methacrylate in fluoro-, chloro-, and bromo-benzenes, anisole, and benzonitrile. The rate of polymerisation is somewhat higher in all these solvents than in benzene. Although all the values of k_p lie within the limits of the accuracy of the determination, nevertheless according to the authors [16] they increase steadily in the sequence benzene < fluorobenzene < chlorobenzene < anisole < bromobenzene < benzonitrile. The values of k_t vary in inverse proportion to the viscosity of the solvent.

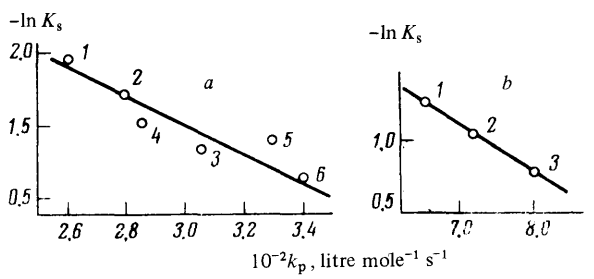


Figure 2. Dependence of k_p for the polymerisation of methyl methacrylate in different solvents at 25° (*a*) and 60°C (*b*) on the stability constants of the complexes of the t-butylmesitylnitroxy-radical with the solvents: *a*) [1) benzene; 2) chlorobenzene; 3) bromobenzene; 4) anisole; 5) benzonitrile; 6) methyl benzoate]; *b*) [1) 1-fluoronaphthalene; 2) 1-chloronaphthalene; 3) 1-bromonaphthalene].

The polymerisation of methyl methacrylate in solutions in halogeno-derivatives of benzene and naphthalene has been investigated in a series of studies [37-40]. The rate of polymerisation in monosubstituted aromatic hydrocarbons is higher than that in benzene and varies with the nature of the halogen in the sequence fluorobenzene < chlorobenzene < bromobenzene < iodobenzene, i.e. increases with decrease of the electronegativity of the substituent. Under identical conditions, the overall rate of reaction is 0.19 wt. % min^{-1} in benzene and 0.35 wt.% min^{-1} in iodobenzene. Dihalogenobenzenes increase the overall rate of polymerisation of methyl methacrylate to a somewhat greater extent than the monosubstituted derivatives and the 1,2-isomer is more effective than the 1,3- or 3,4-isomers. The nature of the substituent has the same influence in this case as for monosubstituted benzene derivatives. Di- and tetrabromobenzenes do not affect the rate of polymerisation.

It has been suggested [37-39] that the main cause of the influence of the solvent is a change in the rate of initiation. However, determination of the absolute rate constants for the elementary chain propagation and termination reactions as well as the rates of initiation in the polymerisation of methyl methacrylate in solution and halogenonaphthalenes [40] showed that the rate of initiation remains almost constant and the effect is due to a slight change in k_p and k_t. The constant k_t varies inversely with the viscosity of the solution; on the other hand, the variation of k_p is probably due to the formation of a complex with the solvent. As in the study of Bamford and Brumby [16], it was found that [37-40] the overall effect of the solvent on k_p is extremely small. On the basis of the results obtained in the polymerisation of methyl methacrylate in halogenated aromatic solvents in the presence of an inhibitor, it has been concluded [41] that the solvent affects mainly the constant k_t.

A slight increase of the overall rate of polymerisation, due to the increase of the ratio $k_p/k_t^{1/2}$, is also observed in the polymerisation of methyl methacrylate in aromatic solvents [42]. The rate of reaction increases in the sequence toluene < *p*-chlorotoluene < benzene < bromobenzene.

In the polymerisation of methyl methacrylate in ethereal solvents [43] a change in the overall rate of reaction as a function of the nature of the solvent is also observed. Here too, the change in k_t, associated with the different viscosities of the solution, exerts the main influence; however, the change in k_p, reaching 20–25%, also has some effect. Analogous results were obtained in the study of the polymerisation of benzyl methacrylate in ethereal solvents differing in viscosity [44] and also in the polymerisation of tetrahydrofurfuryl methacrylate [45] and phenyl methacrylate [46] in various media. The constant k_p for benzyl methacrylate increases somewhat with increasing viscosity of the solution (by 30–35%).

Table 3. Polymerisation of vinyl benzoate in different solvents at 30°C. [46]

Solvent	k_p, litre mole^{-1} s^{-1}	$10^{-8}k_t$, litre mole^{-1} s^{-1}
Anisole	106	2.53
Benzene	185	4.02
Fluorobenzene	245	5 22
Chlorobenzene	168	3.83
Ethyl benzoate	69	2.57
Benzonitrile	33	2.99
Ethyl acetate	267	4.51

Much greater effects are observed in the polymerisation of vinyl benzoate [46] in various aromatic solvents (Table 3). The change in the constant k_p in this system is probably due to the formation of π-complexes between solvent molecules and the growing radical, which leads to a significant alteration in the reactivity of the radicals. The constants k_t are inversely proportional to the viscosity of the reaction system.

The overall rate of homogeneous polymerisation of cyclohexyl and cyclododecyl acrylates increases in the following sequence of solvents: benzene < tetrahydrofuran < dioxan[47]. Thus at 60°C (azobisisobutyronitrile concentration 0.01 M, monomer concentration 0.8 M), the overall rates of polymerisation ($10^5 R_p$, mole litre^{-1} s^{-1}) of cyclododecyl acrylate are 15.1 in benzene, 21.3 in tetrahydrofuran, and 60.0 in dioxan. Under analogous conditions, the overall rates of polymerisation of cyclohexyl acrylate are 9.87, 11.6, and 22.1 respectively. The change in the overall rate of the process is caused, according to the authors[47], by the different degrees of polarisation of the carbonyl group in the acrylate monomer in the solvents investigated. It had been found earlier[48] that the polarisation of the carbonyl group ($\rangle C^+=O^-$) of methyl methacrylate increases the reactivity of this monomer in its copolymerisation with styrene. It has been established by infrared spectroscopy[47] that (the carbonyl groups of) cyclohexyl and cyclododecyl acrylates are polarised to a greater extent in solutions in dioxan and tetrahydrofuran than in benzene solutions. The change in the overall rate of polymerisation is therefore probably associated in this case with the change in k_p.

The influence of the solvent on the rate of polymerisation has also been demonstrated for the homogeneous polymerisation of vinyl chloride[49]. The ratio $k_p/k_t^{1/2}$ for the polymerisation is 0.68 in dichloroethane (50°C) and 0.19 in benzene.

III. POLAR MONOMERS

The influence of the nature of the medium has been found to be much greater in the polymerisation of vinyl polymers containing heteroatoms with a lone electron pair and capable of involvement in the formation of hydrogen bonds‡.

At the beginning of the 1960s it was already shown[50-53] that the rate of polymerisation of a number of monomers in bulk is related to the presence or absence of intermolecular hydrogen bonds in these substances. Thus the rates of polymerisation of the *o*-isomers of ethoxy- and methoxy-phenylmethacrylamides, ethoxy-phenylacrylamide, chlorophenylmethacrylamide, biphenylylmethacrylamide, and carboxyphenylmethacrylamide exceed the rates of polymerisation of the *m*- and particularly *p*-isomers. This is because the *o*-isomers of these compounds exist in the form of unassociated molecules, while the *m*- and *p*-isomers form associated species via hydrogen bonding. The presence of associated structures in the *m*- and *p*-compounds has been established[50-53] by infrared spectroscopy. One should note that in the case of tolylmethacrylamide, where all the isomers are capable of forming associated species via hydrogen bonding, the rates of polymerisation of the isomers do not differ from one another[51].

‡ The results of certain studies concerning the influence of the solvent on the radical polymerisation of polar monomers (acrylic acids, vinylpyridines, and *N*-vinylpyrrolidinone) and also on their copolymerisation with other vinyl monomers have been described in a recently published monograph[8] and are therefore not considered in detail in the present review.

Presumably the addition of certain solvents, capable of dissociating intermolecular hydrogen bonds and thus preventing the association of monomer molecules, to the monomer present in the associated form leads to an alteration of the rate of its polymerisation.

A very appreciable influence of the solvent on the overall rate of polymerisation and the chain propagation rate constant has been established for acrylamide and methacrylamide[21,54]. The polymerisation was studied in water, dimethyl sulphoxide (DMSO), and tetrahydrofuran (THF) under the influence of azobisisobutyronitrile. In water and DMSO acrylamide polymerises under homogeneous conditions, while the polymerisation of acrylamide in THF and also that of methacrylamide in all the solvents investigated takes place heterogeneously. However, in all cases the reaction in dilute solutions takes place at the beginning of the process at a constant rate which is proportional to the monomer concentration and the square root of the initiator concentration. The overall rate of polymerisation of acrylamide and methacrylamide decreases significantly in the sequence water > DMSO > THF. The average molecular weights of the acrylamide polymers decrease in the same sequence. The ratio $k_p/k_t^{1/2}$ measured for acrylamide decreases to an even greater extent, since the rate of initiation varies in the opposite sequence. Thus at 40°C the ratio $k_p/k_t^{1/2}$ is 3.3 in water, 0.35 in DMSO, and only 0.05 in THF.

An appreciable increase of the overall rate of reaction and of the molecular weight of the polymer with increasing water content in the solvent has been observed in the polymerisation of acrylamide in water–methanol mixtures[55,56]. A similar influence of water has been observed also for the polymerisation of acrylamide in water–DMSO mixtures[57].

Table 4. Polymerisation of acrylamide in various solvents[22,54].

Solvent	$k_p/k_t^{1/2}$, litre$^{1/2}$ mole$^{-1/2}$ s$^{-1/2}$ (40°C)	E_p, kcal mole^{-1}	$10^{-7}A_p$, litre mole^{-1} s^{-1}	E_t, kcal mole^{-1}	$10^{-8}A_t$, litre mole^{-1} s^{-1}
Water (pH 7)	4.1	2.7	1.0	2.7	780
Water (pH 13)	3.6	3.6	2.2	1.0	9.7
Formamide	1.0	5.0	4.4	0.8	7.2
DMSO	0.32	5.4	3.0	0	2.5
Tetrahydrofuran	0.05				

The photopolymerisation of acrylamide (sensitised by azobisisobutyronitrile) has been studied in greater detail in water at pH 7 and 13, formamide, and DMSO[21,22,58]. The constants k_p and k_t and the corresponding activation energies were determined separately (Table 4). It was established that, compared with k_p for the polymerisation in water at pH 7, the constant k_p at 20°C is smaller by a factor of 2 in water at pH 13, by a factor of 12 in formamide, and by a factor of 35 in DMSO. The decrease of k_p is caused by the increased activation energy for this reaction: the pre-exponential factors are almost the same or change only slightly in the opposite sequence. The values of k_t, activation energies, and pre-exponential factors for this reaction (A_0) are the same in all the solvents investigated with the exception of water at pH 7. In the latter case higher values were obtained for E_0 and A_0. The

latter quantity is higher than for other solvents by two orders of magnitude, so that ultimately k_t is somewhat higher despite the greater activation energy (2.7 kcal mole^{-1} compared with 0–1 kcal mole^{-1}).

The observed influence of the solvent on the kinetic parameters of the polymerisation process can probably be explained by the intermolecular interaction of the acrylamide molecules with one another (in the monomeric and polymeric forms) and also with solvent molecules. The different extents of this interaction are indicated by the heats of solution and polymerisation of acrylamide in certain solvents [22,59] (Table 5) and also by the results of cryoscopic measurements, which showed that the degree of association of acrylamide molecules is 1.30 in DMSO and 1.15 in formamide; in aqueous solution (at pH 7 and 13) acrylamide is almost non-associated. The heat of polymerisation of acrylamide also depends on the nature of the solvent. The polymerisation in aqueous solution has the highest heat, the latter being significantly smaller in organic media. The dependence of the heat of polarisation on the nature of the solvent shows that monomer molecules are associated to a greater extent than the polymer radicals and polymer molecules [59].

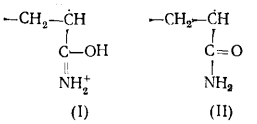
Table 5. Heats of solution and polymerisation of acrylamide and methacrylamide in various solvents [22,59].

Solvent	ΔH, kcal mole^{-1}			Solvent	ΔH, kcal mole^{-1}		
	of soln.	of polymerisation	of polymerisation		of soln.	of polymerisation	of polymerisation
	acrylamide		methacrylamide		acrylamide		methacrylamide
Water (pH 7)	−2.9	19.5	13.4	Chloroform	—	—	10.2
Water (pH 13)	−2.75	—	—	Acetone	—	16.9	9.4
Formaide	−2.5	—	—	Benzene	—	14.4	8.4
DMSO	−1.1	—	—	n-Hexane	—	13.8	—

Such intermolecular interaction makes the energy levels of the initial and final states in the polymer chain propagation reaction dependent on the nature of the solvent. For polymerisation in aqueous solutions the activation energy for the chain propagation reaction is therefore lowest and the heat of reaction highest. In formamide and DMSO, where the monomer molecules interact via hydrogen bonds, the activation energy for the propagation reaction is significantly higher, since it includes the energy necessary for the dissociation of the intermolecular hydrogen bonds.

Since the heat of polymerisation of methacrylamide in various solvents changes in the same way as for acrylamide [59], the decrease in the rate of polymerisation of this monomer in the sequence water > DMSO > THF is apparently due to the same causes.

The most intense solvation of acrylamide by solvent molecules is observed in aqueous solution. In the limiting case there is a possibility of a chemical reaction between acrylamide and the protons formed in the dissociation of water, because acrylamide has weakly basic properties. This reaction takes place with acrylamide radical to a greater extent, because the presence of an unpaired electron probably leads to an increase of the basicity of the radical compared with the neutral molecule, increasing thereby the equilibrium constant of the protonation reaction. The addition of a proton to the oxygen atom [60] of the acrylamide radical (I) and the consequent appearance of a positive charge at the nitrogen atom lead to the localisation of the unpaired electron and to an increase in the reactivity of the radical:



(I) (II)

In the non-protonated radical (II) there is a possibility of the conjugation of the unpaired electron with the C=O double bond; in radical (I) there is no such conjugation. The positive charge of the nitrogen atom draws the π electrons of the C=N double bond towards itself, which prevents the conjugation of the unpaired electron with this double bond.

The idea of the higher reactivity of the acrylamide radical in water as a result of the addition of a proton and of the involvement of this radical to some extent in the chain propagation and termination reactions is confirmed by the following experimental data: (1) the increase of the chain propagation and termination rate constants in the polymerisation of acrylamide in aqueous solution with decrease of the pH of the medium from 13 to 1 (Currie et al. [61]); (2) the increase of k_t for the reactions in water at pH 7 compared with the value of k_t for the polymerisation in water at pH 13, formamide, and DMSO. The activation energy for the termination of polymer chains in water at pH 7 is 1.7–2.7 kcal mole^{-1} higher than in other solvents. The difference is probably due to the energy expended on overcoming the repulsion of the charged polymer radicals.

The higher rates of chain propagation in the polymerisation of acrylamide in aqueous solution compared with the polymerisation in formamide and DMSO are caused both by more favourable solvation conditions in water and by a definite role of the hydrogen ion formed by the dissociation of water in interacting with the amide group of the growing chain. The two factors are interrelated and undoubtedly exert a parallel influence on the rate of polymerisation of acrylamide. The role of the second factor naturally increases with increase of the concentration of H^+.

The formation of insoluble polyacrylamide in neutral and particularly in acid concentrated aqueous solutions is associated with the presence of hydrogen ions and probably protonated acrylamide radicals (I). [62] This hypothesis is supported by the following facts: (1) polymerisation in alkaline concentrated aqueous solutions yields a fully soluble polymer; (2) the polymerisation of acrylamide in neutral and acid concentrated aqueous solutions in the presence of β,β',β'', nitrilotripropionamide, which is a stronger proton acceptor than acrylamide, is not accompanied by the cross-linking of the polymer chains; (3) in concentrated solutions in an aprotic solvent (DMSO) soluble polymers are formed at advanced stages of the reaction.

A fairly large number of studies [63–67] have been devoted to the investigation of the influence of the nature of the solvent on the polymerisation of acrylic and methacrylic acids§. Acrylic acid polymerises in bulk under the influence of γ-radiation at a very high rate with formation of

§The polymerisation of ionogenic monomers, particularly acrylic and methacrylic acids at different pH values as well as dioxan in the presence of complex-forming agents, has been examined in detail in a monograph [8].

high-molecular weight stereoregular polymers (with a molecular weight up to 3×10^7). The activation energy for this process in the temperature range from 20° to 70°C is only 2.7 kcal mole^{-1}. Solvents capable of forming hydrogen bonds with the monomer (water, methanol, acetic acid, and dioxan) do not alter significantly the rate of polymerisation of acrylic acid when they are added in an amount of 20–25%. None of these solvents (with the exception of water) influences the syndiotacticity of polyacrylic acid. On the other hand, small amounts of chloroform (5–10%) and hydrocarbon solvents (n-hexane and toluene) reduce appreciably the overall rate of polymerisation and the syndiotacticity of the polymer.

In order to account for these results, it has been suggested[63-67] that, apart from dimeric cyclic aggregates (characteristic of carboxylic acids), acrylic acid gives rise to a linear high-molecular weight aggregate structure, where the distribution of vinyl groups favours a very rapid chain propagation and the formation of a syndiotactic polymer. The addition of water, methanol, and dioxan leads to the binding of the linear acrylic acid aggregates to one another. In contrast to this, benzene, toluene, n-hexane, and chloroform disrupt the linear aggregates. Such changes in the structure of the aggregates of polymeric molecules in the solvents investigated are in fact responsible for the different kinetic characteristics of the polymerisation of acrylic acid in these solvents. The observed[65] sharp increase in the rate of polymerisation of acrylic acid in n-hexane when the temperature is raised from 20° to 40°C has also been explained by the equilibrium transition from cyclic dimers to linear associated species as the temperature is increased.

However, there is apparently no need to resort to ideas about the formation of high-molecular weight aggregates in acrylic acid solutions in order to account for the results obtained[63-67], particularly since according to some data[23,68], obtained by the cryoscopic method, acrylic acid exists in the form of individual molecules in water and formamide, while in solution in DMSO it is associated only to the extent of approximately 10%. It has been shown[69] that the reactivity of the dimerised acrylic acid is lower than that of the non-dimerised acid. The difference between rates of polymerisation of this monomer, observed in different solvents, can therefore be caused by the fact that acrylic acid in bulk exists in the form of dimers, which dissociate to some extent into individual molecules as a result of the formation of hydrogen bonds with solvent molecules in solutions in water and other polar solvents but are little altered in hydrocarbon media. In non-polar solvents, particularly in n-hexane, an increase of temperature favours the dissociation of the acid dimers, which leads to a marked temperature dependence of the rate of polymerisation in n-hexane.

In examining the results of the above studies[63-67], one must therefore take into account the phase state of the reaction system, which depends on the nature and amount of the solvent. Indeed, whereas in the polymerisation of acrylic acid in dilute solutions in water, methanol, and dioxan, the reaction proceeds in a homogeneous system, when acetic acid, toluene, n-hexane, and chloroform are used as solvents and also in polymerisation in bulk the resulting polymer is produced in the form of a new phase, which greatly complicates the kinetic picture of the process.

The influence of the nature of the solvent on the polymerisation of acrylic acid and its derivatives, (methacrylic and α-fluoroacrylic acids) has been investigated in greater detail in other investigations[23,68,70-72]. The homogeneous polymerisation has been studied in water, formamide, and DMSO. The overall rate of polymerisation is a maximum in water and diminishes on passing to formamide and then to DMSO. The reaction proceeds in all cases at a rate proportional to the concentration of the monomer and to the square root of the concentration of the initiator. The data in Table 6 show that the increase of the overall rate of the process is accompanied by the increase of k_p owing to the decrease of the activation energy for this reaction. At the same time the results indicate a significant difference in the behaviour of acrylic acid and its α-derivatives. Whereas in the polymerisation of acrylic acid a sharp dependence of the overall rate of reaction and of k_p on the nature of the solvent is observed, for methacrylic and particularly fluoroacrylic acids, the influence of the medium is much less. Thus k_p decreases by a factor of 50 on passing from water to DMSO for acrylic acid, by a factor of 25 for methacrylic acid, and only by a factor of 3 for fluoroacrylic acid.

Table 6. Parameters characterising the chain propagation and termination reactions in the polymerisation of acrylic (AA), fluoroacrylic (FAA), and methacrylic (MAA) acids in various solvents[71,72].

Monomer	k_p, litre mole^{-1} s^{-1} (20°C)	E_p, kcal mole^{-1}	$10^{-7}A_p$, litre mole^{-1} s^{-1}	$10^{-8}k_t$, litre mole^{-1} s^{-1} (20°C)	E_t, kcal mole^{-1}	$10^{-8}A_t$, litre mole^{-1} s^{-1}
			Water			
AA	27 200	3.1	0.60	1.8	0	1.8
MAA	4 100	4.3	0.67	0.12	0.2	0.16
FAA	2 600	4.5	0.60	0.87	0.6	2.0
			Formamide			
AA	4200	5.6	6.2	1.0	0	1.0
FAA	2200	4.9	0.75	0.74	0.4	1.5
			DMSO			
AA	500	8.0	47	0.2	0	0.2
MAA	150	7.3	4.1	0.09	1.0	0.48
FAA	850	5.2	0.66	0.49	0.4	1.0

It follows from cryoscopic data[68] that the observed influence of the solvent on the rate of the chain propagation reactions involving acrylic acids cannot be associated solely with the different degrees of association of the monomeric molecules in the solvents, as has been suggested for acrylamide[22]. Indeed, although acrylic acid is in fact partly dimerised in solution in DMSO, the concentration of dimers does not exceed 10%, so that their contribution cannot probably be decisive. Acrylic acid in aqueous solution and fluoroacrylic acid in solutions in water and in DMSO are present in the form of individual molecules.

As for acrylamide, the heats of solution and polymerisation of acrylic and fluoroacrylic acids vary with the nature of the medium (Table 7). However, the heats of solution of acrylic and fluoroacrylic acids in DMSO and formamide change in the same way for both monomers: the dissolution in water is accompanied by the absorption of heat; on passing to formamide and DMSO, the heat of solution increases. However, the heats of polymerisation of these monomers vary in different ways as a function of the nature of the solvent. Whereas the heat of polymerisation of acrylic acid in water is significantly greater than in DMSO

(18.5 and 14.1 kcal mole^{-1} respectively), the heat of polymerisation of fluoroacrylic acid in these solvents is virtually the same (~ 13 kcal mole^{-1}).

Table 7. Heats of solution and polymerisation of acrylic (AA) and fluoroacrylic (FAA) acids in various solvents[72].

Monomer	ΔH, kcal mole^{-1} of soln.	ΔH, kcal mole^{-1} of polymerisation	Monomer	ΔH, kcal mole^{-1} of soln.	ΔH, kcal mole^{-1} of polymerisation	Monomer	ΔH, kcal mole^{-1} of soln.	ΔH, kcal mole^{-1} of polymerisation
	Water			Formamide			DMSO	
AA	−0.2	18.5	AA	0.6	—	AA	3.0	14.1
FAA	−2.3	13.3	FAA	−1.1	—	FAA	0.3	13.0

The observed difference between the heats of polymerisation of acrylic acid in the solvents investigated can be due to the different conformational states of the polymer molecules in these media. Water is a better solvent for polyacrylic acid than DMSO. The polymer chain therefore exists in water in the form of looser coils than in DMSO, which promotes a more effective penetration of the solvent into the polymer coil in aqueous solution. This difference between the states of the polymer molecules in water and in DMSO leads to an appreciably higher energy of solvation of polyacrylic acid molecules in aqueous solution compared with the solution in DMSO which is the reason for the difference between the heats of polymerisation [because the solvation energies (heats of solvation) of the monomer and its saturated analogue are virtually the same[73,74]].

The greater density of the polymer coil of polyacrylic acid in DMSO compared with aqueous solutions leads to a lower rate of bimolecular polymer chain termination in DMSO compared with water (Table 6). The introduction of a fluorine atom into the polymer chain increases the rigidity of the chains, as a result of which the influence of the solvent on the conformational state of the macromolecules and hence also on the heat of polymerisation is much smaller for fluoroacrylic acid than for acrylic acid.

As for acrylamide[22], the decrease of the activation energy for chain propagation in the polymerisation of acrylic and fluoroacrylic acids is accompanied by an increase in the heat of polymerisation, i.e. the Polanyi–Semenov rule holds qualitatively. For isotypical reactions the following equality is valid[75]: $\Delta E = -\alpha\Delta(\Delta H)$, where $\alpha \simeq 0.25$ for the usual radical reactions. It follows from a comparison of the values of ΔH and E_p for the polymerisation of acrylic and fluoroacrylic acids in water that $\alpha = 0.26$. However, α for the polymerisation of acrylic and fluoroacrylic acids in DMSO exceeds 1.0. The value $\alpha > 1.0$ is also obtained on comparing the results for acrylic acid in water and in DMSO.

The failure of the Polanyi–Semenov rule can indicate a different nature of the reacting species in the solvents investigated. This is also suggested by data for the compensation effect observed in the polymerisation of acrylic acid in different solvents (see Table 6). The presence of the compensation effect in liquid-phase radical reactions can be due[2] to the specific interaction of the radicals with the medium (particularly the formation of π-complexes).

It has been suggested[11-13] that free radicals are capable of forming π-complexes with solvents exhibiting electron-donating properties. The formation of complexes of this kind has been shown[76] to lead to decreased unpaired electron density in the radical, which decreases the reactivity of the latter. The solvents employed[68,70-72] are electron donors under the conditions investigated, the electron-donating capacity increasing in the sequence water < formamide < DMSO. The complex between the polymer radical and the solvent is therefore most probably formed in solution in DMSO, which leads to the maximum reactivity of the polymer radical in this solvent. The probability of the radical forming of a complex with formamide and particularly with water is lower; consequently, the reactivity of the radical in these media diminishes to a smaller extent than in DMSO; this leads to the experimentally observed dependence of k_p on the nature of the solvent.

The formation of complexes between solvent molecules and polymer radicals should be reflected also in the energetics of the chain propagation reaction. In the transition state a complex between the radical and the solvent probably has to be decomposed in order to achieve the chain propagation reaction; this requires an additional energy, which is part of the activation energy for the chain propagation process. Since the formation of a radical–solvent complex takes place to the greatest extent in DMSO, the energy E_p for polymerisation should also be a maximum in this case.

The probability of the formation of complexes between the solvent and the polymer radical apparently decreases with decreased reactivity of the radical. In the polymerisation of methacrylic and especially fluoroacrylic acids, whose polymer radicals are less reactive than the radicals of polyacrylic acids, the influence of the nature of the medium is therefore less pronounced than for acrylic acid.

Thus the different effects of the nature of the solvent on the polymerisation of acrylic, methacrylic, and fluoroacrylic acids reduce the reactivity of the initially more reactive radical, formed from acrylic acid (the reactivity of this radical is characterised by the constant k_p in water, where the probability of the formation of a complex with the solvent is low), compared with the fluoroacrylic and methacrylic acid radicals in DMSO—a solvent capable of forming a complex with this radical.

Table 8. Polymerisation of methacrylic acid in various solvents at 10°C.[77]

Solvent	k_p, litre mole^{-1} s^{-1}	$10^{-7}k_t$, litre mole^{-1} s^{-1}
Methanol	517	3.7
Pyridine	527	2.3
Dimethylformamide	28	0.44

The polymerisation of methacrylic acid in different solvents has also been investigated by Shryver et al.[57] The reaction was carried out under the influence of azobisisobutyronitrile at 60°C. The authors showed that the addition of water to organic solvents (ethanol, ethanol–dioxan, and DMSO) increases significantly the overall rate of polymerisation and the molecular weight of the polymers. One should note particularly that the rate of reaction is almost independent of the dielectric constant of the reaction mixture and is determined by its water content. In this case the observed effect can probably be accounted for by the different degrees of complex formation between the polymer radicals and solvent molecules.

The polymerisation of methacrylic acid in methanol and pyridine is characterised by identical constant k_p and k_t (Table 8); in the polymerisation in dimethylformamide the above constants are significantly lower[77]. The observed change in the rate constants for the chain propagation and termination reactions has been attributed[77] to the polar effect, which changes as a function of the solvent. However, in this case the different degrees of association of the acid molecules in the solvents is also presumed to have a significant influence. Owing to the formation of hydrogen bonds between the acid and solvent molecules, in methanol and pyridine the degree of dimerisation of methacrylic acid is appreciably lower than in dimethylformamide, which is indicated by spectroscopic data[77]. The reactivity of dimerised methacrylic acid is lower, as with acrylic acid[68], than that of the non-dimerised acid.

A change in the degree of ionisation of the acid can also exert a definite influence on the polymerisation of acrylic acids in solvents of different polarity. Kabanov and coworkers[8] showed quite definitely that the reactivity of the ionised acid is much lower than that of the unionised acid.

Taking into account the different degrees of dimerisation and ionisation, it is possible to explain the results obtained in the polymerisation of butadiene-1-carboxylic acid in different electron-donating solvents[78]. The rate of polymerisation of this monomer under the influence of azobisisobutyronitrile increases in the sequence dimethylformamide < tetrahydrofuran < ethyl methyl ketone < acetonitrile < benzene.

Among the polar monomers for which the rate constants for the elementary chain propagation and termination reactions have been determined in different solvents, mention should be made also of *N*-vinylpyrrolidinone. It has been shown in an early study[79] that the rate of its radiation-induced polymerisation depends significantly on the nature of the solvent. The overall rate of reaction increases appreciably on passing from methanol to ethanol, isopropyl alcohol, and t-butyl alcohol. An even greater increase in the rate of the radiation-induced polymerisation was observed after the addition of water to methanol. Thus, following the addition of 25, 50, and 75% of water, the overall rate of reaction increased from 0.5–0.8 wt.% min^{-1} to 1.7, 3.5, and 5.75 wt.% min^{-1} respectively. Whereas the increase of the reaction rate in different alcohols can be accounted for by the increased rate of initiation owing to the change in the radiation-chemical yield of the initiation process (G_{in}), for aqueous methanol solutions the change in G_{in}, even if it is observed, cannot explain the sharp change in the overall rate of polymerisation.

Table 9. Polymerisation of *N*-vinylpyrrolidinone in various solvents at 26°C.[70]

Solvent	$k_p/k_t^{1/2}$, litre$^{1/2}$ mole$^{-1/2}$ s$^{-1/2}$	k_p, litre mole^{-1} s^{-1}
Tetrahydrofuran	0.08	400
Dichloroethane	0.08	400
Methanol	0.17	870
N-Vinylpyrrolidinone	0.15	1200
Water	1.40	>3500

In the study of the homogeneous polymerisation of *N*-vinylpyrrolidinone in different solvents it was established that the reaction under the influence of azobisisobutyronitrile can proceed in solution in methanol at a higher rate than in tetrahydrofuran or dichloroethane[80]. It follows from Table 9 that an increase of the overall rate of the process in methanol is almost fully due to the higher constant k_p. The change in k_p is in its turn related to the change in E_p: for virtually identical pre-exponential factors A_p (3.16×10^8 and 3.4×10^8 litre $mole^{-1}$ s^{-1} in methanol and tetrahydrofuran respectively), E_p for the polymerisation in methanol is smaller by 0.5 kcal $mole^{-1}$ than in tetrahydrofuran (7.6 and 8.1 kcal $mole^{-1}$ respectively).

The homogeneous polymerisation of *N*-vinylpyrrolidinone in bulk[81] and particularly in aqueous solution[70] is characterised by an even greater increase of the overall rate of the process (of the ratio $k_p/k_t^{1/2}$) than in methanol, compared with polymerisation in tetrahydrofuran and dichloroethane (Table 9). Here too, the change in the overall rate of polymerisation is accompanied by a change in k_p. In terms of their influence on k_p in the polymerisation of *N*-vinylpyrrolidinone the solvents can be arranged in the following sequence: tetrahydrofuran, dichloroethane < methanol < *N*-vinylpyrrolidinone < water. Evidently the increase in solvent polarity leads to an increase of k_p, which can be attributed to the influence of the solvent on the distribution of electron density in the pyrrolidinone ring and hence on the reactivity of the monomer and the radical formed from it. Neither can one rule out the influence of complex formation between the polymer radicals and the solvent, which varies as a function of the nature of the solvent.

IV. COPOLYMERISATION

The different reactivities of the monomers in different solvents can lead to the variation of the rate of copolymerisation and the composition of the copolymers. The results of studies on the influence of the medium on copolymerisation involving acrylic and methacrylic acids as well as their amides are examined below, because the influence of the nature of the solvent on the reactivities of these monomers is most significant.

Many studies have been devoted to the copolymerisation of methacrylic and acrylic acids with certain vinyl monomers in solvents of different types. Both acrylic and methacrylic acids are known to exist in bulk phase as dimers, whose reactivity differs from that of the non-dimerised monomer molecules[69]. However, in many solvents the dimers decompose owing to the specific interactions between the acid and solvent molecules. In addition, one should bear in mind that the degree of ionisation of acid molecules can change with the polarity of the solvent, which should also be reflected in the reactivity of the acids. The composition of the copolymers of these acids with other monomers therefore usually depends on the nature of the solvent.

In the copolymerisation of methacrylic acid with methyl methacrylate or styrene the addition of dimethyl formamide or ethanol to the mixture of monomers reduces the content of the acid units in the copolymer[82] and dimethylformamide influences the composition of the copolymer to a much greater extent than does ethanol (Fig. 3). The decreased reactivity of methacrylic acid is caused by the formation of a complex with the solvent via –H...O–C hydrogen bonds, which is indicated by the appearance of a sharp maximum on the curve describing the variation of the viscosity of solutions of the acid in dimethylformamide or ethanol, as well as spectroscopic data. For mixtures of methyl methacrylate with dimethyl formamide, a linear

relation between the viscosity and mixture composition has been observed. The addition of water to the methyl methacrylate–methacrylic acid system also reduces the number of acid units in the copolymer[83].

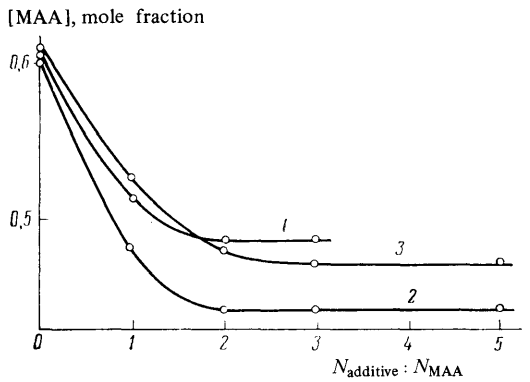
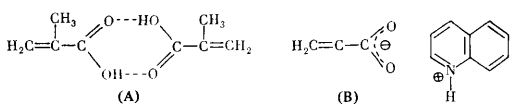


Figure 3. Variation of the content of methacrylic acid (MAA) in the copolymers formed in equimolar mixtures of methyl methacrylate (curves *1* and *2*) with methacrylic acid as the content of ethanol (curve *1*) and dimethylformamide (curve *2*) is increased and also in equimolar mixtures of styrene (curve *3*) with MAA as the content of dimethylformamide in the reaction mixture is increased.

The addition of Lewis bases (tetrahydrofuran, quinoline, pyridine, and DMSO) to the methacrylic acid–styrene system reduces the reactivity of methacrylic acid[84], pyridine and DMSO having the greatest effect. The reactivity of methacrylic acid decreases in their presence and the resulting copolymers are depleted in methacrylic acid compared with the copolymers synthesised in the absence of a solvent. It has been suggested[84] that in the presence of electron-donating solvents, for example quinoline, methacrylic acid can exist in two forms:



The reactivity of methacrylic acid in copolymerisation depends on the quantitative ratio between forms (A) and (B), which is determined in its turn by the nature of the solvent. The greater the amount of acid in form (B), the electropositive properties of the double bond of which are less marked than in (A), the lower the reactivity of the monomer in copolymerisation with styrene.

An appreciable variation of the constants for the copolymerisation of acrylic acid with styrene and methyl methacrylate as a function of the nature of the solvent has been observed[69,85,86]. Whereas for the reaction in bulk the constants for the copolymerisation of styrene with acrylic acid at 50°C are 0.25 (styrene) and 0.15 (acrylic acid), in solvents capable of forming hydrogen bonds with acrylic acid the relative reactivity of this monomer diminishes. In ethyl methyl ketone, dioxan, tetrahydrofuran, and dimethylformamide the copolymerisation constant is virtually invariant for the acid (0.13–0.15), but that for styrene changes from 0.70 (in ethyl methyl ketone) to 1.03 (in dimethylformamide), which indicates a decrease of the reactivity of acrylic acid. Analogous results were obtained for the copolymerisation of acrylic acid with methyl methacrylate[85,86]. A correlation has been established between the copolymerisation constants (for styrene and methyl methacrylate) and the stability constants of the complexes between acrylic acid and the solvent. One should note that the observed changes in the copolymerisation constants in the solvents investigated are not related to the different reactivities of the dissociated and undissociated acrylic acid, since a correspondence between the copolymerisation constants and the dielectric constants of the solvents has not been observed.

A more complete survey on studies of the influence of the medium on the copolymerisation of methacrylic and acrylic acids as well as vinylpyridines with other monomers, published up to 1973, has been carried out by Kabanov and Topchiev[8].

The different reactivities of the radicals formed from acrylic and fluoroacrylic acids in different solvents, established in a number of investigations[23,68,70-72], lead to a significant dependence of the rate of copolymerisation and the composition of the copolymers of these acids on the nature of the reaction medium[87]. Whereas in aqueous solution the addition of even small amounts of fluoroacrylic acid to acrylic acid entails a sharp decrease in the rate of the process, a different behaviour is observed in solution in DMSO (Fig. 4), where the rate of reaction passes through a small maximum as a function of the composition of the initial monomer mixture at low fluoroacrylic acid concentrations (20 mole%) and then gradually diminishes, reaching values characteristic of the rates of the separate polymerisation of acrylic and fluoroacrylic acids.

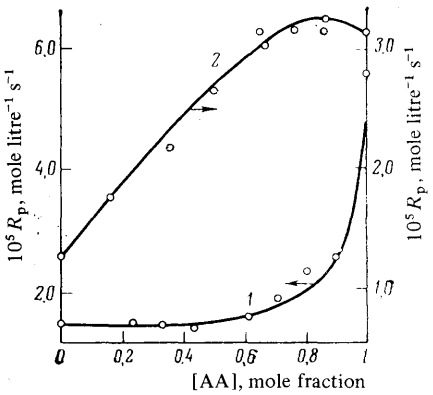


Figure 4. Dependence of the rate of copolymerisation of acrylic and α-fluoroacrylic acids on the composition of the mixture of monomers in copolymerisation in water (1) (initiator concentration 5×10^{-4} M) and in DMSO (2) (initiator concentration 4×10^{-3} M); $[M_1] + [M_2] = 1$ M.

The copolymerisation constants for the given pair of monomers are r_1(AC) = 0.5 and r_2 = 1.5 for copolymerisation in water, and r_1 = 0.5 and r_2 = 0.7 in DMSO. The rate constants for the addition of the radical to a "foreign" monomer (Table 10) have been calculated from the copolymerisation constants and rates of separate chain propagation[68]

(Table 10). These results show that, in the copolymerisation in water, the reactivities of the monomers and radicals differ strongly: the more reactive radical is that of acrylic acid and the more reactive monomer is fluoroacrylic acid. In polymerisation in DMSO the reactivities of the radicals and the monomers are similar. This is apparently associated with the formation of complexes between the polymer radicals and DMSO molecules, as suggested by Gal'perina et al.[72]

Table 10. The rate constants for chain propagation in the copolymerisation of acrylic (M_1) and fluoroacrylic (M_2) acids at 50°C.

Constant	Water	DMSO
r_1	0.5	0.5
r_2	1.5	0.7
k_{11}, litre mole^{-1} s^{-1}	47 600	1790
k_{22}, litre mole^{-1} s^{-1}	5 350	1950
k_{12}, litre mole^{-1} s^{-1}	95 200	3580
k_{21}, litre mole^{-1} s^{-1}	3 570	2790

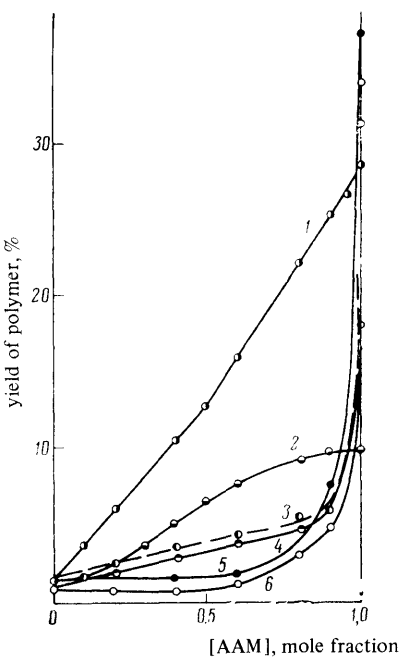


Figure 5. The influence of the composition of the initial mixture of monomers on the yield of copolymers of acrylamide and acrylonitrile in their radiation-induced copolymerisation in different solvents at 20°C; $[M_1] + [M_2] = 2.5$ M: 1) dioxan; 2) acetonitrile; 3) methanol; 4) dimethylformamide; 5) water; 6) acetic acid.

In the copolymerisation of methacrylic acid with acrylate and methacrylate esters (methyl acrylate, methyl methacrylate, and butyl methacrylate) in dioxan–water mixtures[88] an increase of the water content in the solvent leads to a decrease of the copolymerisation constant for the acid and an increase of that for the ester comonomer. The above data indicate a higher reactivity of the acid radical in water and are in good agreement with the ideas developed by Gal'perina et al.[72]

The formation of hydrogen bonds with the solvent also influences the reaction kinetics and the composition of the acrylamide–acrylonitrile copolymers[89]. In solutions in acetic acid, dimethylformamide, water, and methanol, i.e. solvents forming hydrogen bonds with acrylamide the addition of small amounts (up to 10%) of acrylonitrile to this monomer reduces the rate of the process significantly. In dioxan and acetonitrile the decrease of the rate of polymerisation following the addition of acrylonitrile is much smaller (Fig. 5). The greatest number of acrylamide units in the copolymer has been found in polymerisation in dioxan and acetonitrile. The copolymerisation constant for acrylamide depends little on the nature of the solvent (0.21–0.50), whereas for acrylonitrile the constant changes from 0.08–0.10 in acetonitrile and dioxan to 0.50 in acetic acid, 1.13 in methanol, and 1.9 in water and dimethylformamide. The observed effects are probably due to the different degrees of association of acrylamide molecules in the above solvents.

Table 11. Copolymerisation of acrylamide (M_1) with styrene in various solvents[90] ($\Delta\nu$, cm^{-1}, is the shift of the absorption bands).

Solvent	r_1	r_2	$\Delta\nu_{CO}$	$\Delta\nu_{NH^I}$	$\Delta\nu_{NH^{II}}$	$\Delta\nu_{NH,\,av}$
Benzene	12.5	0.25	1	15	10	12.5
o-Dichlorobenzene	12.5	0.25	3	5	5	5
Benzene–benzonitrile	4.4	1.5	8	46	45	45.5
Chloroform	—	—	13	47	55	51
Benzonitrile	2.4	1.35	12	70	55	62.5
Dioxan	1.38	1.27	10	205	170	187.5
Diglyme	1.09	1.40	10	190	206	198
Ethanol	0.30	1.44	13	205	230	217.5
Methoxyethoxyethanol	0.27	1.66	22	205	230	217.5
Water–t-butyl alcohol	0.78	2.93	28	205	230	217.5
DMSO	0.16	2.01	17	245	235	240
DMSO	0.43*	2.0*	—	—	—	—
Methanol	0.20	1.05	13	205	230	217.5
Pyridine *N*-oxide	—	—	9	65	90	77.5
Tetrahydrofuran*	0.62	1.1	—	—	—	—

*Gromov's data[21].

The copolymerisation of acrylamide with styrene in a large number of solvents of different types has been investigated[90]. The solvents selected were compounds which influence the acrylamide structure by the formation of hydrogen bonds, by dipole–dipole interaction, or by both factors. The change in the structure of acrylamide was inferred from the shift of the infrared absorption bands characterising the NH_2 or C=O groups. Thus the formation of hydrogen bonds between the monomer and the solvents as well as the polar interaction between them induce a change in the electron density around the double bond of acrylamide and hence alter its reactivity. The relatively low dipole moment as well as the inertness of styrene molecules with respect to the formation of hydrogen bonds entail a virtual constancy of the reactivity of this monomer as well as its radical in different solvents. The data presented in Table 11 show that the copolymerisation constant for acrylamide changes significantly in different solvents as $\Delta\nu_{NH}$ is altered. In solvents where neither dipole–dipole

interactions nor the formation of hydrogen bonds with acrylamide are observed (benzene, dichlorobenzene) the resulting copolymer is enriched in the acrylamide component. In those cases where the acrylamide molecules form strong hydrogen bonds with the solvent or are actively involved in a dipole–dipole interaction the copolymers are enriched in styrene.

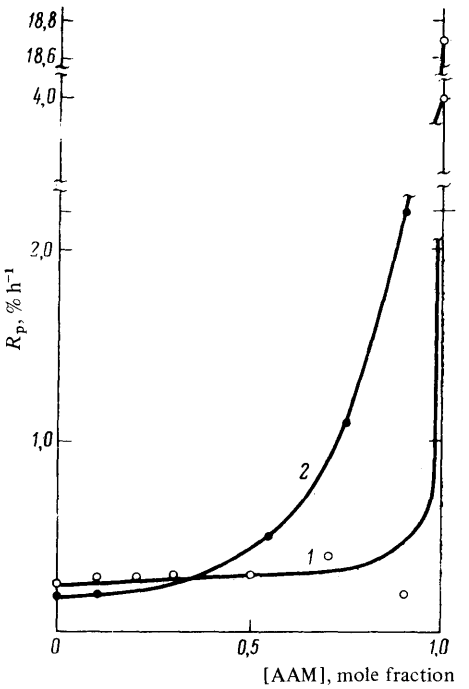


Figure 6. Dependence of the rate of copolymerisation of acrylamide with styrene on the composition of the initial mixture in DMSO (curve *1*) and THF (curve *2*); $[M_1]+[M_2] = 2.0 - 2.7$ M; initiator concentration $(5.3-6.5) \times 10^{-3}$ M; 40°C.

The nature of the solvent also influences the kinetics of the copolymerisation of acrylamide with styrene[22]. Fig. 6 shows that the addition of 10 mole % of styrene decreases the initial rate of reaction relative to the rate of the separate polymerisation of acrylamide, by a factor of approximately two in solution in tetrahydrofuran and by a factor of 50–60 in solution in DMSO. An even greater change in the rate of polymerisation is observed when the reaction is carried out in water. Thus the addition of even 0.01 mole % of styrene reduces the rate of reaction by a factor of 1.5–2.5, while the rate of polymerisation of a mixture of monomers containing 6 mole % of styrene is smaller by a factor of approximately 100 than the rate of homopolymerisation of acrylamide. The copolymers are in all cases enriched in styrene, the degree of enrichment being greater in DMSO and formamide than in tetrahydrofuran. The copolymer formed in water on copolymerisation of 94 mole % of acrylamide (AAM) and 6 mole % of styrene is virtually pure polystyrene. The copolymerisation constants for this pair of monomers are r_1(AAM) = 0.43 and $r_2 = 2.0$ in DMSO and $r_1 = 0.62$ and $r_2 = 1.1$ in tetrahydrofuran.

In conformity with the known characteristics of radical copolymerisation, the results obtained[22] indicate different reactivities of the acrylamide radical in the solvents investigated: the reactivity is highest in water and lowest in tetrahydrofuran, which agrees with the rates of separate polymerisation of acrylamide in the above solvents[54]. These results can be accounted for, as in Gal'perina's study[23], by the formation of complexes between the solvent and the polymer radical.

The different degrees of dimerisation of acrylamide and acrylic acid molecules as a result of hydrogen bonding with the solvent are responsible for the difference between the copolymerisation constants for the above monomers in water and acetone. r_1(AAM) = 1.38 and $r_2 = 0.36$ for the copolymerisation in acetone, while in aqueous solution $r_1 = 0.60$ and $r_2 = 0.43$.[91,92] These values indicate that the formation of hydrogen bonds between the monomeric molecules has a greater effect on the reactivity of acrylamide than on that of acrylic acid, since the transition from the associated form of acrylamide (in acetone) to the non-associated form (in water) is accompanied by a greater increase of the reactivity of the acrylamide radical compared with that of acrylic acid. Data[93] for the copolymerisation of acrylamide with acrylic and methacrylic acids in solvents of different polarity (dioxan, dioxan–ethylene glycol, and chloroform–ethanol), according to which an increase of solvent polarity entails a decrease of the copolymerisation constant for acrylamide, lead to the same conclusion.

Table 12. Copolymerisation of acrylamide and its derivatives (M_1) with styrene (St) and methyl methacrylate (MMA) in various solvents[95–99].

Solvent	St		MMA		Solvent	St		MMA	
	r_1	r_2	r_1	r_2		r_1	r_2	r_1	r_2
Acrylamide					**Dimethylacrylamide**				
Dioxan	1.38	1.27	2.45	2.55	Dioxan	0.44	1.28	0.51	2.04
Dioxan + ethanol (70:30 by volume)	0.59	1.13	0.82	2.53	Ethanol	0.42	1.33	0.42	2.30
Ethanol	0.30	1.44	0.44	2.60	Toluene	0.23	1.23	0.45	1.80
Diacetoneacrylamide					**Methacrylamide**				
Dioxan	0.47	1.85	0.50	1.80	Dioxan	1.29	1.46	1.27	1.55
Ethanol	0.30	1.80	0.31	2.00	Ethanol	0.54	1.27	0.43	1.68
Benzene	0.49	1.77	0.57	1.68					
Ethyl acetate	0.49	1.70	0.46	1.70					
					***N*-Methylacrylamide**				
					Dioxan	0.64	2.10	1.03	3.50
					Ethanol	0.20	2.20	0.28	3.30

These results conflict with data for the copolymerisation of acrylamide with methyl methacrylate published by Jacob et al.,[94] who showed that the addition of water to DMSO or chloroform increases significantly the content of acrylamide units in the copolymer and correspondingly the copolymerisation constant for acrylamide:

Solvent	DMSO	DMSO + H_2O (9:1)	Chloroform	Chloroform + 1% H_2O
r_{AMM}	0.2	1.0	1.0	3.5

The addition of water has virtually no influence on the copolymerisation constant for methyl methacrylate in both cases. Unfortunately no data are presented in the above communication[94] concerning the phase state of the reaction system and also the yields of the copolymers, so that it is difficult to account for the observed inconsistency with data obtained elsewhere[22,89,90].

The influence of hydrogen bonds between monomers and solvents on the reactivity of the former has been demonstrated particularly clearly in a series of studies[95–99]. The

copolymerisation constants for acrylamide, methacrylamide, *N*-methylacrylamide, and *N*-(1,1-dimethyl-3-oxobutyl)acrylamide (diacetoneacrylamide) with methyl methacrylate or styrene depend on the nature of the solvent (dioxan, ethanol, and their mixtures), the effect being most pronounced for acrylamide and methacrylamide (Table 12). In the copolymerisation of *N*,*N*-dimethylacrylamide with styrene or methyl methacrylate the quantities r_1 and r_2 are virtually the same in different solvents (dioxan, toluene, ethanol, dimethylformamide, and ethyl acetate). The difference between the behaviour of these monomers is apparently associated with the fact that, whereas acrylamide, methacrylamide, *N*-methylacrylamide, and diacetoneacrylamide can exist in the form of dimers (which are partly or fully decomposed as a result of the formation of hydrogen bonds with solvent molecules, which alters their reactivity and hence influences the copolymerisation constants), *N*,*N*-dimethylacrylamide molecules do not dimerise. The data presented also show that the hydrogen bonds between the solvent and the carbonyl group of amides have almost no influence on the reactivity of the amides.

The influence of the solvent on the intermolecular association of monomer molecules evidently explains the results obtained in the copolymerisation of methacrylamide with styrene in different solvents. The addition of ethanol, dimethylformamide, and pyridine to the mixture of monomers lowers the proportion of methacrylamide units in the copolymer [100]. The copolymerisation constant for methacrylamide changes little in the copolymerisation in acetic acid, ethanol, dimethylformamide, and pyridine (0.30–0.50), while the copolymerisation constant for styrene increases on passing from acetic acid (0.65) to other solvents (1.4–1.8). It has been assumed [100] that, in copolymerisation in acetic acid, methacrylamide reacts in the form of dimers, since the stereochemistry and size of the amide group of the monomer and those of the carboxy-group of the acid differ appreciably.

Indeed, the compositions of the methacrylamide–styrene copolymers obtained in acetic acid (in the region of homogeneous copolymerisation) and in benzene, which does not form hydrogen bonds with methacrylamide and does not therefore decompose its dimers, are the same. As for acrylamide and acrylic and methacrylic acids, the formation of hydrogen bonds between methacrylamide and solvent molecules in other solvents causes the dimeric methacrylamide aggregates to dissociate; this alters the electron density at the double bond of the monomer and decreases the reactivity of the latter.

The influence of the solvent on the copolymerisation of monomers of low polarity is much less marked, as in their separate polymerisation. Thus, in the copolymerisation of styrene (M_1) with methyl methacrylate at 60 °C in benzene solution [48], the values of r_i are as follows: $r_1 = 0.57$ and $r_2 = 0.46$, whereas in phenol $r_1 = r_2 = 1.35$. A slight change in the reactivity of polymer radicals, which alters r_1 and r_2, has also been observed in the copolymerisation of cyclododecyl or cyclohexyl acrylate with acrylonitrile in solution in benzene, dioxan, and tetrahydrofuran. When styrene instead of acrylonitrile is used as the second comonomer, the solvent has no influence [101].

V. CONCLUSION

The above discussion shows that a definite influence of the nature of the solvent on the rates of polymer chain propagation and termination reactions under the conditions of radical polymerisation has now been established. Whereas in the case of weakly polar monomers the role of the solvent is largely manifested to only a slight extent, for polar monomers (acrylamide, acrylic acids, and *N*-vinylpyrrolidinone) an appreciable variation in the constant k_p is observed in solvents of different types.

The observed variation of k_p due to the different reactivities of the polymer radicals in different solvents is associated with different kinds of specific interactions between the reacting species and solvent molecules (donor–acceptor interaction, the formation of π-complexes, and hydrogen bonding). In the few studies dealing with the temperature dependence of the rates of the elementary chain propagation reactions it was shown that the variation of k_p is caused by the change in the activation energy for this reaction.

In the polymerisation of weakly polar monomers (particularly styrene) the relatively weak donor–acceptor interaction between the components of the reaction system apparently plays the main role. The solvent effect is therefore comparatively slight in this instance. The particularly marked differences observed in the polymerisation of water-soluble monomers in water, on the one hand, and in organic solvents, on the other, are probably associated both with the presence of hydrogen bonds between the reacting species and solvent molecules and with the formation of π-complexes between the solvent and the growing radicals.

Unfortunately, there are not yet any direct experimental literature data permitting the determination in each specific case of the type of interaction between the reacting species and solvent molecules, which determines the observed influence of the solvent. The claim that different kinds of complexes are formed between the components of the reaction mixture is merely tentative. The formation of such complexes has been demonstrated in only a few instances. Evidently further study should be directed towards the experimental determination of the constants k_p and k_t and the corresponding activation energies for other monomers in different solvents and their mixtures as well as towards the elucidation of the detailed mechanism of the influence of solvents.

Furthermore, it is quite likely that the influence of the solvent on k_p and k_t in radical polymerisation is also caused by a change in the conformation of the polymer radicals as a function of the nature of the medium. A clear relation has been established between the rates of polymerisation of monomeric electrolytes (acrylic acids, β-betaine) and the conformational state of the macromolecules. The rates of polymerisation and viscosities of polymer solutions vary in parallel as a function of the pH of the medium and the salt concentration in solution [8].

The polymerisation of acrylamide in the DMSO–water binary solvent has been investigated recently and an increase of the overall rate of reaction and of the molecular weight of the polymers with increasing water content in the solvent has been demonstrated. It has also been shown (on the basis of viscosity data) that the effective size of the macromolecular coils increases with increasing water content in the solvent. It is suggested that the influence of solvent composition on the rate of reaction is caused by a change in the local concentration of monomer molecules in the coils containing polymer radicals [102].

The recently published studies [103,104], where the constants k_p and k_t have been determined for the first time for the polymerisation of acrylamide in binary solvents, are significant. In DMSO–water mixtures the overall rate of reaction ($k_p/k_t^{1/2}$) and the constant k_p change sharply following the addition of even small amounts of DMSO and

then decrease more smoothly (Fig. 7). The constant k_t passes through a minimum as a function of solvent composition, corresponding to the maximum solvent viscosity (Fig. 7). In mixtures of water with dioxan and tetrahydrofuran having the same composition the quantities $k_p/k_t^{1/2}$ and k_p give rise to the sequence DMSO < dioxan < tetrahydrofuran, i.e. the same as in the polymerisation of acrylamide in one-component solvents [22,54,58].

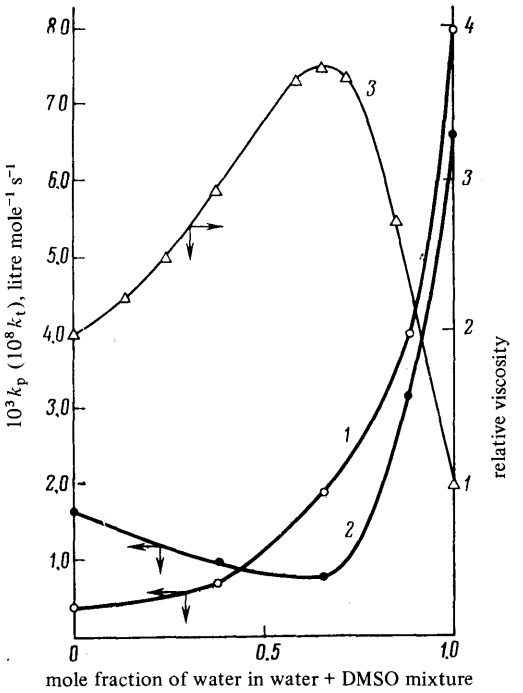


Figure 7. Dependence of k_p (curve *1*) and k_t (curve *2*) for the polymerisation of acrylamide in a water–DMSO mixture at 30°C and of solvent viscosity (curve *3*) on solvent composition.

The results [103,104] have been examined on the basis of the idea of complex formation between the growing radicals and solvent molecules. Furthermore, a correspondence has been demonstrated between the constants k_p and the intrinsic viscosities of the polymers in the solvents investigated; it is suggested that the influence of the solvent may be due to the different dimensions of the growing macroradical coils [104].

Thus, when the causes responsible for the influence of the solvent on k_p and k_t in radical polymerisation are examined, account must be taken of at least two factors:

1. The formation of complexes of different kinds by the reacting species with one another and with solvent molecules.

2. The state of the polymer coils (their dimensions) containing macroradicals and the dependence of this state on the nature of the reaction medium (solvent). Here the results of more detailed studies, for example, of the determination of the concentration of the monomer in the coil near the growing end of the polymer chain, are significant.

The contribution of each of these factors to the overall effect is at present obscure. It is probably different for different monomers and solvents.

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