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Characteristic features of the radical polymerisation of water-soluble monomers

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Abstract. The results of studies on the influence of the nature of the solvent on the kinetics of the radical polymerisation of water-soluble monomers are surveyed. It is noted that the rate of the process and the chain propagation rate constant in the polymerisation of monomers of this kind change sharply on passing from organic solvents to aqueous solutions. Comparative analysis of the kinetic data and the results of spectroscopic and viscometric studies made it possible to put forward a mechanism for the polymerisation of water-soluble monomers in various solvents. A distinctive feature of the polymerisation of water-soluble monomers is the hydrophobic interactions arising in aqueous solutions of the polymers and leading to a sharp difference between the kinetic parameters of the polymerisation of monomers of this class in water and organic solvents. The bibliography includes 76 references.

I. Introduction

The development of the classical theory of the radical polymerisation of vinyl monomers was completed towards the end of the 1950s. It was formulated in final form in the monographs of Bamford et al.[1] and Bagdasar'yan,[2] which appeared almost simultaneously. The theory is based mainly on the results of studies of the polymerisation of weakly polar hydrocarbon monomers (for example, styrene). The principal postulate of this theory is that the reactivity of the monomers and of the polymeric radicals formed from them, and hence the rate constant for the propagation of polymer chains (k_p), are determined solely by the chemical structure of the compounds and do not depend on the nature of the solvent in which the polymerisation takes place.

However, by the beginning of the 1960s studies had already been carried out in which it was established that the nature of the solvent affects not only the chain termination rate constant (k_t), as a consequence of a change in the viscosity of the reaction system, but also the propagation constant k_p in the polymerisation of monomers such as styrene, methyl methacrylate, and certain others.

Subsequently studies on the influence of the solvent and of various added compounds on the polymerisation of vinyl monomers were developed in a number of investigations (see, for example, Refs 3 – 15). They led to the establishment of new aspects of the field of radical polymerisation, in particular complex-radical polymerisation.[16] Studies on the influence of the nature of the solvent on the radical polymerisation of vinyl monomers published up to 1978 were examined in an earlier review.[17] The results of these investigations demonstrate that the influence of the solvent on the polymerisation of weakly polar monomers is associated with the formation of a donor – acceptor complex between the polymeric radicals and the solvent molecules, which alters the reactivity of the polymeric radicals. It is noteworthy, however, that the change in the overall rate of polymerisation and of the constant k_p for nonpolar monomers such as styrene is small (it does not usually exceed 30% – 50%). A more significant influence of the nature of the solvent is observed in the polymerisation of monomers containing functional groups capable of participating in a specific interaction with the solvent molecules. Such compounds include the esters of acrylic and methacrylic acids, vinyl acetate, and others. According to a series of data,[13–15] the overall rate of polymerisation of such monomers and the constant k_p may vary severalfold depending on the nature of the solvent.

The solvent exerts a much greater influence in the polymerisation of monomers containing atoms with a lone pair and functional groups capable of being involved in the formation of stronger complexes, in particular in the formation of hydrogen bonds. Such monomers include primarily water-soluble monomers incorporating amide, carboxy-, and carbonyl groups. In the polymerisation of these monomers, the replacement of the solvent may be accompanied by a change in the overall rate of polymerisation by a factor of several tens, an especially sharp change being observed on passing from an organic solvent to an aqueous solution.

The study of the influence of the nature of the solvent on the radical polymerisation of water-soluble monomers was initiated in the 1960s. Since then, numerous investigations of this problem have been published. The objects of study have been usually acrylamide, acrylic acid, *N*-vinylpyrrolidone, and the salts of the aminoesters of methacrylic and acrylic acids.

Apart from the elucidation of purely theoretical problems concerning the mechanism of the polymerisation of water-soluble

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monomers, the interest in this problem is also due to the fact that water-soluble anionic and cationic polymers, primarily acrylamide polymers and copolymers, have found extensive application in various branches of the economy as flocculants, for the purification of drinking and waste waters, in increasing the extraction of petroleum, in reducing the hydrodynamic resistance to friction, etc.

The fact that, for the monomers investigated above, the influence of the nature of the solvent not only on the overall rate of the process but also on the rate constants for the elementary polymer chain propagation and termination has been determined is especially important for the determination of the mechanism by which the nature of the solvent influences radical polymerisation. Studies on these lines, carried out up to 1980, were devoted mainly to the investigation of polymerisation in various individual solvents.[16–20] In the present review, we shall deal only briefly with the results of these studies, attention being concentrated on later studies, and an attempt will be made to formulate the principal characteristic features of the radical polymerisation of water-soluble monomers and the causes responsible for these features.

II. Kinetics of the polymerisation of water-soluble monomers in various solvents

According to the nature of the solvent, the overall rate of polymerisation of water-soluble monomers varies by 1.5–2 orders of magnitude. These effects were first observed and then studied in detail for acrylamide, acrylic acid, and their derivatives, as well as for the salts of the aminoesters of methacrylic and acrylic acids.[17,19]

In terms of the influence on the overall rate of polymerisation of acrylamide, the above solvents can be arranged in the sequence water > formamide > dimethylsulfoxide(DMSO) > tetrahydrofuran (THF). In the polymerisation of acrylamide in aqueous solution at 40 °C, the quantity $k_p/k_t^{1/2}$ is 12 times greater than in DMSO and 50 times greater than in THF. The decrease in the rate of polymerisation on passing from water to DMSO and THF is accompanied by a decrease in the molecular mass of the polymers.

A similar effect of the nature of the solvent has been established also in the polymerisation of methacrylamide.[17]

In order to elucidate the causes responsible for the observed kinetic effect, the absolute values of k_p and k_t were determined for the polymerisation of acrylamide under homogeneous conditions.[17] These data show that the change in the overall rate of polymerisation of acrylamide on passing from an aqueous solution to a solution in an organic solvent is caused mainly by the change in k_p. The chain termination constant changes in the same direction (albeit to a much lesser extent) and thus diminishes the influence of k_p on the overall rate.

An appreciable influence of the nature of the solvent on the overall rate of reaction and the constant k_p has also been established in the polymerisation of *N*-vinylpyrrolidinone. The solvents investigated can be arranged in the following sequence: tetrahydrofuran ≈ dichloroethane < methanol < *N*-vinylpyrrolidinone < water, the change from polymerisation in THF to polymerisation in an aqueous solution entailing a change in k_p by a factor of ~50.[21–23]

Qualitatively the same results have been obtained in the study of the homogeneous polymerisation of acrylic acid and its derivatives in various solvents (Table 1). In this case too, the polymerisation is fastest in aqueous solution, the overall rates as well as the constant k_p decreasing significantly on passing to polymerisation in formamide and DMSO. However, the data in Table 1 indicate a significant difference between the behaviour of the acids investigated in the polymerisation in different solvent. Whereas in the case of acrylic acid the sharp dependence of the overall rate of polymerisation and of the constant k_p on the nature of the solvent is observed, in the case of methacrylic and especially fluoroacrylic acid this dependence is much less pronounced. Nevertheless, in all the systems investigated the overall rate of polymerisation increases in the series of solvents DMSO < formamide < water. The increase in the rate of polymerisation in the above sequence is almost wholly determined, as in the case of acrylamide, by the increase in k_p, which is in its turn associated with the decrease in the activation energy for the chain propagation reaction.

According to the classical theory of radical polymerisation,[1,2] the rate of chain propagation is determined by the reactivity of the polymeric radical. Comparison of the data presented in Table 1 shows that the change in the nature of the solvent in the polymerisation of the acids investigated makes the reactive radical formed in the polymerisation of acrylic acid in water (the reactivity of this radical is characterised by the constant k_p) less reactive than the radicals derived from fluoroacrylic and methacrylic acids in DMSO. The different degrees of dissociation of these acids in water and DMSO as well as the ability of the acid polymeric radicals to participate in the formation of complexes with DMSO (which has basic properties) probably play a definite role in such alteration of the reactivity of polymeric radicals.

The homogeneous polymerisation of the aminoesters of acrylic or methacrylic acid and of their tertiary and quaternary salts is also much faster in water than in organic solvents (Table 2). As in the radical polymerisation of other water-soluble polymers, the increase in the overall rate of polymerisation in water is also caused by the increase in the chain propagation rate constant. Thus the constant k_p in the polymerisation of acetate salts of diethylaminoethyl methacrylate in water (72 000 litre mol^{-1} s^{-1}) is 240 times greater than k_p in the polymerisation of dioxane.[26] Furthermore, a very considerable change in k_t was established in this system on passing from an organic solvent to an aqueous solution: the constants k_t in water and dioxane are 65×10^7 and 0.1×10^7 litre mol^{-1} s^{-1} respectively.

There is no doubt that the polymerisation of ionogenic monomers such as acrylic and methacrylic acids and their salts or the salts of their aminoesters is influenced significantly by the degree of ionisation, which depends on the nature of the solvent.[18] Nevertheless, the principal features of the polymerisation of water-soluble ionogenic anionic and cationic monomers do not

Table 1. Polymerisation of acrylic (AA), methacrylic (MAA), and α-fluoroacrylic (FAA) acids in different solvents.[17]

Monomer	k_p (20 °C)/litre mol^{-1} s^{-1}	E_p/kcal mol^{-1}	$10^{-7} A_p$	$10^{-8} k_t$/litre mol^{-1} s^{-1}	E_t/kcal mol^{-1}	$10^{-8} A_t$
In water						
AA	27200	3.1	0.60	1.8	0	1.8
MAA	4100	4.3	0.67	0.12	1.0	0.16
FAA	2600	4.5	0.60	0.87	0.6	2.0
In formamide						
AA	4200	5.6	6.2	1.0	0	1.0
FAA	2200	4.9	0.75	0.74	0.4	1.5
In dimethyl sulfoxide						
AA	500	8.0	47	0.20	0	0.20

Table 2. The rates of polymerisation ($10^5 v_0$/mol litre^{-1} s^{-1}) of dialkylaminoethyl methacrylates and their salts in water and different organic solvents.[24–26]

Monomer	H_2O	DMSO	DMF	C_2H_5OH
DM	1.3	0.30	0.20	0.40
DE	1.5	0.25	0.20	0.30
DM.C_2H_5Br	7.0	2.7	–	2.0
DE.C_2H_5Br	9.6	6.2	–	3.6
DE.HBr	5.0	3.4	2.4	1.7
DE.CH_3I	4.0	–	1.1	–

Note. The following notation has been adopted: DM = dimethylaminoethyl methacrylate, DE = diethylaminoethyl methacrylate, and DMF = dimethylformamide. In all cases, the reaction was initiated by azobisisobutyronitrile at 60 °C; monomer concentration 0.25 M; initiator concentration 1 × 10^{-3} M.

differ from those of the radical polymerisation of nonionogenic water-soluble monomers of the type of acrylamide or *N*-vinylpyrrolidinone and are determined mainly by the same factors.

Analysis of the results obtained in the study of the polymerisation of water-soluble monomers in solvent mixtures of different composition is very important in elucidating the causes of the influence of the nature of the solvent on the polymerisation of such monomers. In our view, the study of the reaction in mixtures of water with organic solvents is especially important. Such investigations have been carried out in greatest detail for acrylamide.

The addition of even small amounts of an organic solvent in the homogeneous polymerisation of acrylamide in water–DMSO mixtures diminishes k_p significantly. A similar effect is exerted by the addition of dioxane or THF.[27,28] The addition of small amounts of benzene to a DMSO–H_2O mixture, which do not alter the homogeneity of the process, is also accompanied by a decrease in the overall rate of the process and in the constant k_p (Table 3).

Fig. 1 presents the dependence of the constants k_p and k_t and also of the relative viscosity of the reaction mixture on the water content in the solvent in the polymerisation of acrylamide in water–DMSO mixtures. Evidently there is no relation of any kind

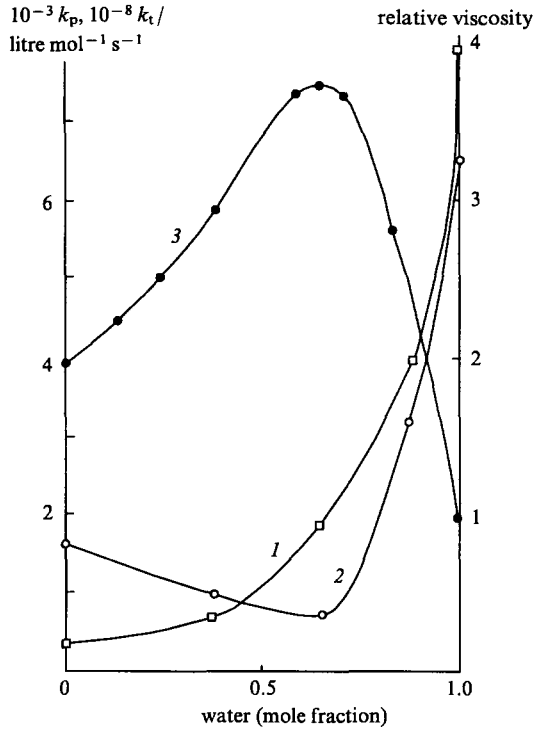


Figure 1. Dependence of k_p (curve *1*), k_t (curve *2*), and the viscosity of the initial reaction mixture (curve *3*) on the water content in the polymerisation of acrylamide in water–DMSO mixtures.[31] Monomer concentration 0.38 M.

between k_p and the viscosity of the reaction system: while k_p diminishes continuously on passing from water to DMSO, the viscosity of the reaction mixture passes through a maximum. The constant k_t also decreases with increase in the DMSO content in the solvent mixture, reaches a minimum for the water : DMSO = 65 : 35 molar ratio corresponding to the maximum viscosity of the reaction mixture, and then again increases somewhat. However, comparison of the data obtained in the polymerisation of acrylamide in individual and mixed solvents (Fig. 2) demonstrates the absence of a linear relation

Table 3. Polymerisation of acrylamide in different solvents.[27,28]

Solvent	$10^{-4} k_p$ (30 °C)/ litre mol^{-1} s^{-1}	E_p/ kcal mol^{-1}	$10^{-7} A_p$	$10^{-8} k_t$ (30 °C)/ litre mol^{-1} s^{-1}	E_t/ kcal mol^{-1}	$10^{-10} A_t$
Water (pH 7)	7.9	2.8	0.8	6.6	2.8	6.8
Formamide	1.2	5.0	4.4	2.3	0.8	0.072
Water–DMSO						
90 : 10	4.3	3.8	2.4	3.5	2.6	2.9
88 : 12	4.0	3.8	2.6	3.2	2.6	2.3
65 : 35	1.9	4.5	3.3	0.80	2.6	0.57
38 : 62	0.70	4.9	2.4	1.0	1.9	0.23
Water–DMSO–benzene						
64.4 : 34.7 : 0.9	1.4			0.70		
36.8 : 59.9 : 3.3	0.48			0.72		
DMSO	0.37	6.0	7.8	1.7	0	0.017
Water–dioxane						
95 : 5	5.7	3.5	1.9	4.5	2.6	3.4
90 : 10	3.3	4.2	3.4	2.3	2.5	1.5
Water–THF						
96 : 4	4.1	3.8	2.4	3.2	2.7	2.9
92 : 8	2.3	4.6	5.0	1.6	2.6	1.2
90 : 10	1.9	4.6	5.0	1.4	2.6	1.2

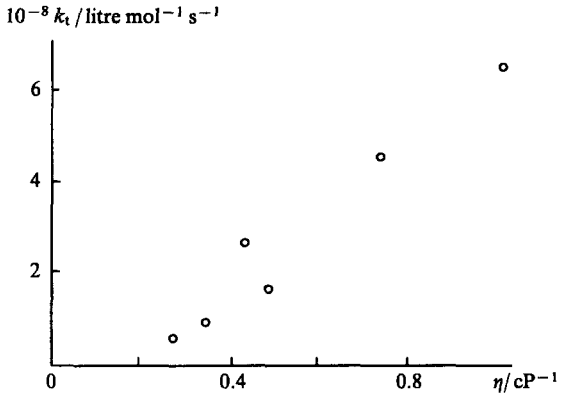


Figure 2. Dependence of k_t for the polymerisation of acrylamide in different solvents on the fluidity of the reaction mixture.[27]

between k_t and the fluidity of the initial polymerisation solution. Such a relation is characteristic of a diffusion-controlled chain termination reaction, for example, in the polymerisation of styrene and methyl methacrylate in various solvents.[1] The deviation from linearity shows that k_t for the polymerisation of acrylamide in the solvents investigated is not determined solely by diffusion. A similar relation has also been observed[29,30] in the polymerisation of vinyl benzoate and vinyl acetate in various solvents.

In the polymerisation of acrylamide in individual and mixed solvents, there is no definite relation between k_p and the relative permittivity of the solvent (ε). In particular, there is no linear correlation between the logarithm of k_p and the polarity parameter $(\varepsilon - 1)/(2\varepsilon + 1)$. This result shows that the solvent polarity is not in this case a factor which determines the reactivity of the reacting species.[31]

The addition of water to individual and mixed organic solvents (ethanol, ethanol–dioxane, DMSO) also increases significantly the overall rate of polymerisation of methacrylic acid and of the molecular masses of the polymers.[32] In this case too, the rate of reaction is almost independent of the relative permittivity of the reaction mixture and is determined by the amount of water present in it. The same pattern has been observed also in the polymerisation of diethylaminoethyl methacrylate and its salts. The addition of even 5 mol.% of water to methanol or dioxane is accompanied by an appreciable increase in the overall rate of polymerisation and also in the rate constant k_p both for the aminoester itself and for its acetate and chloride salts (Table 4).

Table 4. The influence of the nature of the solvent on the chain propagation and termination rate constants in the radical polymerisation of diethylaminoethyl methacrylate (DE) and its acetate (DE.HAc) and chloride (DE.HCl) salts.[26,33]

Monomer	Solvent	$10^{-3}k_p$/ litre mol^{-1} s^{-1}	$10^{-7}k_t$/ litre mol^{-1} s^{-1}
DE	dioxane	0.09	0.06
	dioxane–water	0.36	0.33
	methanol	0.70	1.3
DE.HAc	dioxane	0.30	0.10
	dioxane–water	1.8	1.2
	water	72	65
DE.HCl	methanol	3.3	0.90
	methanol–water	10.8	6.0

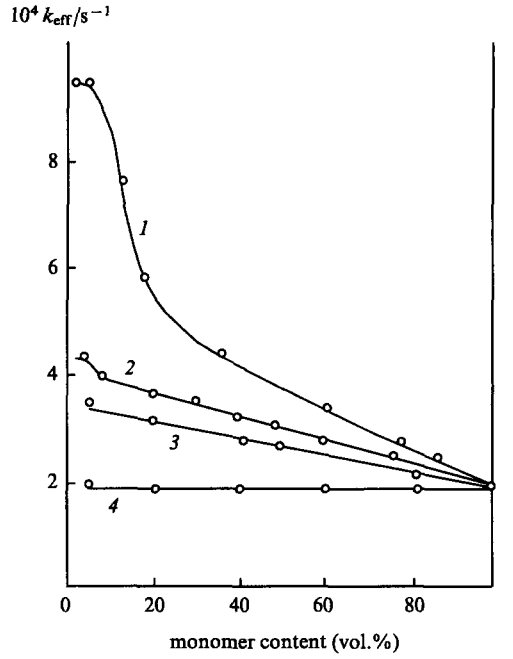


Figure 3. Dependence of k_{eff} on the *N*-vinylpyrrolidinone concentration in polymerisation in water (curve *1*), ethanol (curve *2*), 2-pyrrolidinone (curve *3*), and 2-methylpyrrolidinone (curve *4*) at 60 °C; concentration of azobisisobutyronitrile 1×10^{-3} M (data of Kirsh et al.[35]).

The influence of the composition of the reaction mixture on the effective overall rate of polymerisation constant $k_{eff} = V_o/[M]$, where V_o is the overall rate of polymerisation and [M] the monomer concentration, was established also in the polymerisation of *N*-vinylpyrrolidinone.[23,34,35] In the homogeneous polymerisation of this monomer in protic solvents such as water, ethanol, and 2-pyrrolidinone, the effective reaction rate constant decreases with decrease in the monomer concentration in solution. This effect is manifested to the greatest extent for aqueous solutions (Fig. 3). When the polymerisation is carried out in 2-methylpyrrolidinone, which is, as it were, a saturated analogue of the monomer, the constant k_{eff} remains unchanged over a wide range of monomer concentrations.

It is possible to distinguish three *N*-vinylpyrrolidinone concentration ranges depending on their influence on the rate of polymerisation in water: (1) the range from 100 to 30 vol.% of the monomer, where k_{eff} increases only slightly; (2) the range from 30 to 10 vol.% of *N*-vinylpyrrolidinone (in this range, a sharp rise in k_{eff} is observed with increase in the concentration of the monomer); (3) the range from 10 to 2 vol.% of the monomer, where the rate constant hardly changes.

Thus a sharp increase in k_{eff} in the polymerisation of *N*-vinylpyrrolidinone in aqueous solution is observed in the range of monomer mole fractions in the solution from 0.1 to 0.018, i.e. in the range where the number of water molecules per monomer molecule increases from 10 to ~60. For a higher water content in the reaction mixture, k_{eff} does not change. The ratio 60:1, established as a result of a kinetic study of the polymerisation, corresponds to the maximum number (55) of water molecules in the hydration shell of *N*-vinylpyrrolidinone in a dilute aqueous solution, i.e. to the maximum degree of solvation of the monomer by water molecules.[35] It is noteworthy that the maximum effective rate of polymerisation is observed in a medium with a minimal viscosity, which rules out the possible influence of the rate of the chain termination reaction on the overall rate of the process. The change in k_{eff} on passing from polymerisation in bulk to polymerisation in aqueous solution containing 10 vol.% of the monomer (~1 M) is wholly determined, as in the polymerisation of acrylamide, by the change in the constant k_p.

Thus k_p = 1200 litre mol^{-1} s^{-1} for the polymerisation of *N*-vinylpyrrolidinone in bulk,[22] while in the polymerisation in 10% aqueous solution $k_p = 2.2 \times 10^4$ litre mol^{-1} s^{-1}.[23]

The addition of small amounts of water to a solution of 1-vinyl-1,2,4-triazole in dimethylformamide or dimethylacetamide is accompanied by an appreciable increase in the molecular mass of the polymer obtained under the influence of radical initiators.[36]

Thus a distinctive feature of the polymerisation of water-soluble monomers is the marked dependence of the overall rate of polymerisation and also of the chain propagation rate constant and the molecular mass of the polymer on the nature of the solvent. The reaction proceeds at the highest rate and with formation of polymers having the maximum molecular mass in aqueous solution. The addition of even small amounts of an organic solvent to an aqueous solution of the monomer diminishes appreciably both the rate of polymerisation and the molecular mass of the polymers.

III. The role of solvation effects in the radical polymerisation of water-soluble monomers

The change in the kinetic parameters of the polymerisation of water-soluble monomers in various solvents may be influenced, as in the case of weakly polar monomers, by complex formation between the growing radicals and the solvent and also by the solvation of the monomers and radicals by the solvent. The role of the second factor is much more pronounced. This is associated with the fact that the water-soluble monomers, and especially amides and carboxylic acids, can exist in a self-associated form as a result of the formation of intermolecular hydrogen bonds even in dilute solutions,[37] the degree of association depending on the ability of the solvents to form hydrogen bonds. Cryoscopic studies have shown[27,28] that, at an acrylamide concentration of 1.0 M in water, acrylamide exists in the monomeric form, whereas in formamide and DMSO it is 15% or 30% dimerised respectively. The degree of dimerisation of acrylic acid in DMSO is ~10%, while fluoroacrylic acid exists exclusively in the monomeric form in both water and in solution in DMSO.[38] Different degrees of interaction with the solvent are also indicated by the heats of solution of acrylamide and acrylic acids in different solvents and by ^{1}H NMR spectroscopic data.[28] The difference between the degrees of self-association of the monomer molecules may be the cause of the observed difference between the activation energies for the chain propagation reaction and between the heats of polymerisation of water-soluble monomers.[38]

The formation of complexes between the polymeric radicals and solvent molecules can exert only an insignificant influence, as in the case of nonpolar vinyl monomers, on the kinetic parameters in the polymerisation of water-soluble monomers. Firstly, the energy of such interaction in not very great (thus it amounts to ~1 kcal mol^{-1} in the interaction of aromatic solvents with radicals). Secondly, the formation of a complex with an active centre is accompanied by the appearance of a compensation effect,[39] which should diminish the overall effect of the solvent on the overall rate of the process. Therefore, even when a complex is formed between the solvent and the unpaired electron of the radical via a hydrogen bond, the energy of which is higher than the energy of the donor–acceptor bond, the overall influence of the solvent should not be very great, particularly if one takes into account the fact that only a certain proportion of polymeric radicals are involved in the formation of the complex.

The solvation of the monomer by solvent molecules and especially the formation of hydrogen bonds between the monomer and the solvent can alter the electronic structure of the monomers and hence their reactivity. A distinctive feature of water-soluble monomers such as acrylamide, acrylic acids, and the salts of the aminoesters of methacrylic acid is conjugation between the C=C and C=O groups, which has been established experimentally for a series of water-soluble monomers by various spectroscopic methods.[26,40–43] Therefore the change in electron density at the carbon atom of the carbonyl group as a consequence of the formation of a hydrogen bond between the C=O group and the proton-donating solvents should naturally be accompanied by a change in electron density in the C=C double bond and hence by a change in the reactivity of the monomer.

According to IR spectroscopic data, the frequency $\nu_{C=O}$ in the spectra of the acetate salt of diethylaminoethyl methacrylate increases on passing from dioxane and acetonitrile to the dioxane–water mixed solvent and further to water, a linear relation being observed between the rates of polymerisation of this monomer and the frequency $\nu_{C=O}$ in the corresponding solvent.[26] A linear correlation between $k_p/k_t^{1/2}$ and $\nu_{C=O}$ for the monomer is observed in the polymerisation of certain other salts of the aminoesters of methacrylic acid, acrylamide, and *N*-vinylpyrrolidinone in various solvents.[26] The formation of a hydrogen bond between the monomer and the solvent diminishes the electron density on the protons and carbon nuclei of the CH_2 group of the monomer. This is indicated by the increase in the chemical shift of the proton and the carbon atom in the given group on passing from solutions of the monomers in an aprotic solvent (dioxane) to aqueous solutions. The decrease in electron density on the CH_2 group of the salt of the aminoester of methacrylic acid and hence the increase in the polarisation of the double bond of the monomer increases the rate of interaction between the monomer and the radical. As a consequence of the nucleophilic properties of alkyl radicals,[44] this leads to an increase in the rate of polymerisation on passing from a solution in dioxane to aqueous solutions, i.e. on formation of a hydrogen bond between the C=O group of the monomer and the solvent.

It is noteworthy that the formation of a hydrogen bond with the proton-donating solvent leads to some increase in the overall rate of polymerisation and in the constant k_p in the homogeneous polymerisation of a series of monomers which do not dissolve in water but contain the carbonyl group. Thus k_p for the polymerisation of methyl methacrylate in acetic acid is somewhat higher than in the polymerisation of the monomer in bulk.[45]

In the case of ionogenic monomers, a change in the nature of the solvent exerts a significant influence also on the degree of ionisation of the monomers and the polymeric radicals in the reaction system. The different degrees of ionisation as well as the presence of monomers in solution in the form of free ions or ion pairs lead in their turn to a change in the kinetic parameters of polymerisation of monomers such as methacrylic and acrylic acids or the salts of their aminoesters. The influence of ionisation on the polymerisation of ionogenic monomers has been examined in detail by Kabanov and Topchiev[18] and Bune et al.[19]

Valuable information for the determination of the mechanism of the polymerisation of water-soluble monomers in water–organic solvent mixtures of different composition has been obtained by comparing kinetic and spectroscopic data. A detailed study of the influence of the composition of the water–DMSO mixed solvent on the NMR spectra of acrylamide has been carried out[46] and it has been established that an increase in the concentration of water in the solvent mixture leads to an appreciable downfield displacement of the ^{13}C chemical shift of the C=O group of acrylamide ($\delta_{C=O}$). The comparatively slight alteration of the chemical shifts of the protons of the NH_2 group observed under these conditions shows that the strength of the intermolecular hydrogen bond between the NH_2 group of acrylamide and the solvent does not change very greatly on passing from DMSO to water and cannot be the cause of such a significant alteration of $\delta_{C=O}$. The change in $\delta_{C=O}$ is apparently caused mainly by the formation of a hydrogen bond between the carbonyl group of acrylamide and water molecules. An increase in the concentration of water in the acrylamide–DMSO system is not only accompanied by a change in $\delta_{C=O}$

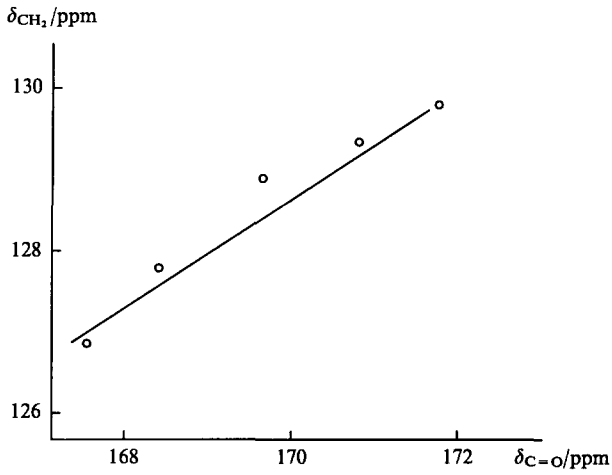


Figure 4. Relation between the ^{13}C chemical shifts of the CH_2 and C=O groups of acrylamide.[46] The measurements were performed in water–DMSO mixtures of different composition.

but also leads to an alteration of the chemical shifts of the hydrogen and carbon atoms involved in the double bond of acrylamide. There is a linear relation between the chemical shifts δ_{CH_2} and $\delta_{C=O}$ (Fig. 4), showing that the change in the electronic state of the C=O group as a consequence of the formation of a hydrogen bond between the groups and water alters the electronic state of the C=C group.

Indeed the formation of the C=O...H hydrogen bond between acrylamide and water is responsible for the enhancement of the electron-accepting properties of the amide group, the conjugation of which with the C=C double bond diminishes the electron density on the carbon atom of the CH_2 group. This conclusion follows from the correlation established[47–49] between the chemical shifts of the carbon atoms of the double bond and the elecron density in this bond. The change in the electron density in the C=C bond of the monomer should naturally alter its reactivity.

Assuming that both free acrylamide molecules and such molecules bound in a complex are present in the water–DMSO mixture and are characterised by different chain propagation rate constants, it was shown[46] that the effective chain propagation rate constant k_p^{eff} in the polymerisation of acrylamide in the water–DMSO mixture should vary linearly with $\delta_{C=O}$ or δ_{CH_2}. However, as can be seen from Fig. 5, this relation has a sharp break in the region of high concentrations of water in the mixed solvent. This type of curve indicates the existence of additional factors determining the reactivity of acrylamide in its polymerisation in the presence of water. The dependence of k_{eff} in the polymerisation of *N*-vinylpyrrolidinone in an aqueous solution on the ^{13}C chemical shift of the CH_2 group of this monomer is similar.

The relative contribution of the change in the electronic structure of the monomer as a consequence of its solvation by the solvent to the alteration of the reactivity of vinyl monomers and their radicals in radical polymerisation can be estimated approximately from the data of Sutyagin et al.[50] According to these data, a linear correlation is observed between the activation energy for chain propagation E_p in the polymerisation of vinyl monomers and the chemical shift of the β-carbon atom of the monomer in the ^{13}C NMR spectrum. The change in δ_{C_β} by ~25 ppm (transition from styrene to acrylonitrile) is accompanied by a change in E_p by 2.4 kcal mol^{-1} (Table 5). The maximum change in δ_{C_β} for acrylamide when the water content in the mixture with DMSO varies from 0% to 100% is 4.4 ppm.[46] Therefore, if account is taken only of the difference between the conditions in the solvation of acrylamide in water and DMSO, one may expect that E_p for the polymerisation of acrylamide in water should be lower by ~0.5 kcal mol^{-1} than in DMSO. On the other hand, the real difference between the values of E_p in these systems is more than 3 kcal mol^{-1}.[51] A similar situation is observed in the polymerisation of acrylic acid (the experimental change in E_p on passing from water to DMSO is ~5 kcal mol^{-1} [51]) and *N*-vinylpyrrolidinone in different solvents.[34,35]

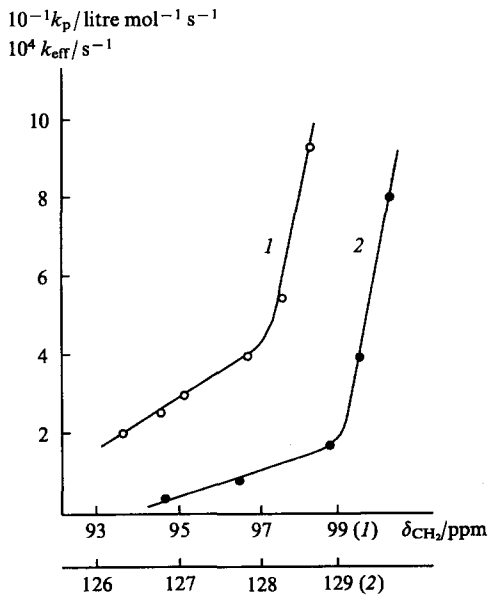


Figure 5. Dependence of k_p for the polymerisation of acrylamide (curve *1*) and k_{eff} for the polymerisation of *N*-vinylpyrrolidinone (curve *2*) on the ^{13}C chemical shift of the CH_2 group of the monomer.[55,56] Acrylamide was polymerised in water–DMSO mixtures of different composition; *N*-vinylpyrrolidinone was polymerised in aqueous solution at different monomer concentrations.

Table 5. Chemical shifts of the C_β atoms in the ^{13}C NMR spectra of vinyl monomers and certain parameters characterising their reactivity in radical polymerisation.[50]

Monomer	δ_{C_β}/ppm	Relative localisation energy of		E_p/kcal mol^{-1}
		monomer	radical	
Vinyl acetate	96.30	2.037	0.320	9.5
Vinylcarbazole	–	–	–	6.9
α-Methylstyrene	112.13	1.703	0.729	–
Styrene	113.20	1.704	0.720	6.3
Vinyl chloride	117.30	1.877	0.635	3.9
Methyl methacrylate	121.80	1.740	0.770	4.7
Ethylene	123.30	2.000	–	–
Methyl acrylate	132.30	1.704	0.645	4.1
Acrylonitrile	137.90	1.696	0.834	3.9

Thus the solvation of the monomer and the resulting change in its reactivity have a much greater influence on the overall rate of polymerisation and k_p than the formation of donor–acceptor complexes between the polymeric radical and the solvent. Nevertheless, this factor cannot fully explain the observed influence of the solvent on the radical polymerisation of water-soluble monomers.

IV. The influence of the solvent on the conformational characteristics of water-soluble polymers

The data presented above show that the hypotheses postulating different solvation conditions in water and organic solvents as well as the formation of complexes between polymeric radicals and the solvent cannot fully explain the results obtained in polymerisation in the presence of small amounts of added organic solvent. Indeed, it is difficult to postulate that such small amounts of the additive (up to 10 mol. %) can lower significantly the degree of dimerisation of acrylamide in solution. Nevertheless, as can be seen from Table 3, they appreciably diminish k_p. One can postulate that the change in the rate of chain propagation in such systems is partly caused by the change in the conformation of the polymer chains. This hypothesis is based on a comparison of the size of the polymer coil with the constant k_p for the polymerisation of acrylamide in various solvents.[52] It is seen from the data presented in Table 6 that the intrinsic viscosity of the same polymer and hence the size of the polymer coil in solution diminishes on passing from water to its mixtures with DMSO, dioxane, and THF containing 10 mol. % of the organic solvent.

Table 6. The influence of the solvent on the intrinsic viscosity of the polyacrylamide.[52]

Solvent in which polymerisation was carried out	Solvent in which the viscosity was measured	$[\eta]$/dl g^{-1}	
		25 °C	50 °C
Water	water	16.9	–
	water–DMSO (90 : 10)	10.0	–
	water–dioxane (90 : 10)	9.4	–
	water–THF (90 : 10)	9.2	–
Water–DMSO = 90 : 10	water	4.5	4.5
	water–DMSO (90 : 10)	3.4	3.6
	water–dioxane (90 : 10)	3.0	3.2
	water–THF (90 : 10)	2.9	3.5
Water–dioxane = 90 : 10	water	2.9	–
	water–DMSO (90 : 10)	2.2	–
	water–dioxane (90 : 10)	1.9	–
	water–THF (90 : 10)	1.8	–
Water–THF = 90 : 10	water	0.60	–
	water–DMSO (90 : 10)	0.46	–
	water–THF (90 : 10)	0.39	–
Water–DMSO = 65 : 35	water	2.5	–
	water–DMSO (65 : 35)	1.8	–
	water–DMSO (65 : 35) + + 0.25 M benzene	1.2	–
Water–DMSO = 38 : 62	water	1.6	–
	water–DMSO (38 : 62)	1.0	–
DMSO	water	0.88	–
	DMSO	0.65	–

It was found that the nature of the change in the size of the polymer coil as a function of the solvent is the same as for k_p (Fig. 6). An increase in temperature from 25 to 50 °C hardly affects the intrinsic viscosity of the polymer in aqueous solution (Table 6). On the other hand, in mixtures of water with organic solvents the viscosity $[\eta]$ increases somewhat as the temperature is raised. Consequently the size of the polymer coil formed in mixed solvents increases with increase in temperature relative to the size of the macromolecular coil formed on polymerisation in aqueous solution. Such a change in the morphology of the polymer coil as the temperature is altered may be one of the factors responsible for the marked temperature dependence of the overall rate of reaction and of the rate of chain propagation in mixtures of water with an organic solvent compared with the polymerisation of acrylamide in aqueous solution (Table 3).

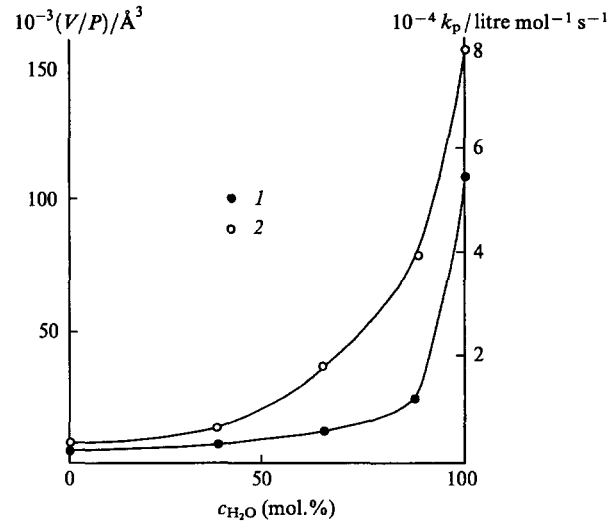


Figure 6. Dependence of the relative size of the polymer coil (curve *1*) and of the constant k_p (curve *2*) on the water content in the polymerisation of acrylamide in water–DMSO mixtures.[56] V = volume of polymer coil; P = degree of polymerisation.

An increase in the size of the polymer coil on passing from an organic solvent to water has also been observed for polymers of the tertiary salts of the aminoesters of methacrylic acid.[26,53] It is striking that in this case there is a sharp decrease in the size of the coil following the addition to water of even small amounts of an organic solvent. Thus the intrinsic viscosity of the solution of the acetate salt of poly(diethylaminoethyl methacrylate) (and hence also the volume of the polymer coil) diminishes from 1.3 in aqueous solution to 1.1 in the water–dioxane mixture containing 20 mol. % of dioxane and to 1.05 in dioxane.[33]

Calculations have shown that the density of the polyacrylamide coil synthesised in an organic solvent or in an aqueous organic medium exceeds by a factor of 30–40 the density of the polymer coil formed in aqueous solution.[27] A similar result has been obtained in a study[54] where it was shown that the addition of even small amounts of precipitants such as acetone or methanol to dilute aqueous solutions of high-molecular-mass polyacrylamide [$M_W = (2 - 3) \times 10^7$] diminishes the volume of the polymer coil by a factor greater than 100. The change in the density of the polyacrylamide coil on impairment of the quality of the solvent (the same picture has been observed also for other water-soluble polymers, in particular the polymers of the salts of dimethylaminoethyl methacrylate) indicates a possible conformational transition of the coil–globule type and may lead to the appearance of steric hindrance in the interaction between macroradicals and monomers.

The change in the conformation of polymer coils depends on the rigidity of the polymer chain. The introduction of a fluorine atom into the acrylic acid molecule increases the rigidity of polyfluoroacrylic acid compared with polyacrylic acid. Therefore the influence of the nature of the solvent on the conformational characteristics of the polymer and the kinetic parameters of the polymerisation of fluoroacrylic acid is much more pronounced than in the case of acrylic acid.

It is noteworthy that some influence by the conformational characteristics of the polymers on the constant k_p and k_t has been observed also in the polymerisation of butyl acrylate in different solvents.[14]

Thus the change in the overall rate of polymerisation of water-soluble monomers and of the rates of the elementary polymer chain propagation and termination reactions on passing from aqueous solutions to solutions in aqueous organic mixtures and organic solvents is caused both by a complex formation reaction of the solvent with the monomer molecules and growing

radicals as well as a number of physical factors, including the solvation of the monomeric and polymeric molecules, the change in the conformational characteristics of the macromolecules, etc. Ultimately all these factors lead to a change in the effective rates of chain propagation and termination.

V. Ideas concerning the mechanism of the influence of the solvent on the radical polymerisation of water-soluble monomers

Analysis of the kinetics of the polymerisation of acrylamide in water–DMSO mixtures, NMR spectroscopic data characterising the state of the monomer in these mixtures, as well as data on the conformational state of the polymer in solution permits a more accurate estimation of the role of various factors in the polymerisation of water-soluble monomers in different solvents.

It follows from the results in a number of investigations [27, 55, 56] that, on the one hand, a sharp increase in the overall rate of polymerisation of acrylamide, in the constant k_p, and in the volume of the polymer coil was observed after the addition of a large amount of water to DMSO (the water content in the solvent mixture was ~80–85 mol. %). On the other hand, the chemical shift δ_{CH_2} increased almost linearly with increase in the amount of water in the water–DMSO mixture up to 100%. In order to elucidate the causes of such discrepancy, the solvation of a number of water-soluble monomers and polymers in water, organic solvents, and water–organic solvent mixtures was investigated by NMR spectroscopy. [43, 56] It follows from the data presented in Tables 7 and 8 that the signals due to the carbon atoms of the C=O and CH_2 groups of the monomers are displaced downfield on passing from solutions in organic solvents to water–organic solvent mixtures and aqueous solutions, which is due to the formation of a hydrogen bond between the C=O group and water. Qualitatively the same picture has been observed also for $\delta_{C=O}$ for the polymers. However, whereas for acrylamide and *N*-vinylpyrrolidinone the change in $\delta_{C=O}$ is 4.4 and 5.0 ppm respectively on passing from a solution of the monomers in DMSO, which does not form a hydrogen bond with the carbonyl group, to an aqueous solution, for the polymers the replacement of DMSO by water is accompanied by a change in $\delta_{C=O}$ by only 2.3 and 3.6 ppm respectively. In the case of acrylic and polyacrylic acids, $\delta_{C=O}$ changes to almost the same extent on passing from DMSO to water (2.9 and 3.1 ppm respectively).

Analysis of the NMR spectroscopic data for a large number of low-molecular-mass compounds of the type RCOX (where X = OR', OH, NH_2) in solvents of different nature made it possible to establish [43, 57] that, regardless of the nature of the substituent R, the formation of a hydrogen bond between the carbonyl group and the solvent leads to a downfield displacement of the chemical shift $\delta_{C=O}$, which is rigorously defined for each type of compound. For different carboxylic acids, as well as their esters and amides, such displacements are 4.0, 4.0, and 5.0 ppm respectively. The results presented in Tables 7 and 8 show that the carbonyl groups of acrylamide, *N*-vinylpyrrolidinone, and dimethylaminoethyl methacrylate are almost fully linked by hydrogen bonds to water molecules, but in the case of the corresponding polymers only some of the carbonyl groups are involved in the formation of bonds of this kind.

A similar conclusion was reached for acrylic acid and its polymer. It is noteworthy that in this case analysis of the NMR spectroscopic data took into account the influence of the degree of ionisation of the ionogenic monomers and polymers on $\delta_{C=O}$. [43, 58] An estimate showed that, regardless of the nature of the polymer, ~70% of the carbonyl groups of the water-soluble polymers are involved in the formation of hydrogen bonds with water molecules in the aqueous solution. This difference between the numbers of carbonyl groups participating in the formation of hydrogen bonds with water molecules is due to the fact that the interactions of the monomer and polymer molecules with water are determined not only by the ability to form hydrogen bonds but also by the accessibility of the carbonyl groups for such interaction. Water-soluble monomers form a homogeneous solution in water, which is the reason for the ready accessibility of water for interaction with all the carbonyl groups of the monomer.

Another situation probably arises in the case of polymer solutions, where hydrophobic interactions begin to play a significant role. The unique properties of water-soluble polymers (in particular, polyacrylamide), which permit the use of these polymers as agents modifying the viscous and rheological properties of aqueous solutions, are apparently actually determined by the hydrophobic interactions, which lead to the formation of organised hydrophobic microdomains in the system. [59–63]

Table 7. The ^{13}C chemical shifts ($\delta_{C=O}$) of the monomers and polymers in different solvents and the increments in the influence of the hydrogen bond (Δ_{hb}). [43, 57]

Compound	Solvent	$\delta_{C=O}$	Δ_{hb}
MMA	dioxane	167.5	
	water	171.5	4.0
PMMA	dioxane	178.0	
DM	–	166.6	
	water	170.3	3.7
DE.HCl	acetone	167.0	
	water	169.1	2.1
AA	DMSO	168.3	
	water	171.2	2.9
PAA	DMSO	177.0	
	water	180.1	3.1
AM	DMSO	167.5	
	water	171.9	4.4
PAM	DMSO	178.3	
	water	180.6	2.3
VP	–	172.9	
	water	177.9	5.0
PVP	DMSO	175.2	
	water	178.8	

Note. The following notation has been adopted: MMA = methyl methacrylate; PMMA = poly(methyl methacrylate): PAA = polyacrylic acid; AM = acrylamide; PAM = polyacrylamide; VP = *N*-vinylpyrrolidinone; PVP = poly-*N*-vinylpyrrolidinone; $\Delta_{hb} = \delta_{H_2O} - \delta_{Solv.}$.

Table 8. The ^{31}C chemical shifts (ppm) of acrylamide, *N*-vinylpyrrolidinone, and their polymers in different solvents. [55]

Solvent	Monomer		Polymer	
	δ_{CH_2}	δ_{CH_2}	$\delta_{C=O}$	$\delta_{C=O}$
	Acrylamide			
DMSO : water				
100 : 0	126.8	133.2	167.5	178.3
62 : 38	127.7	132.5	168.4	178.6
35 : 65	128.9	131.9	169.7	179.4
12 : 88	129.3	131.3	170.9	180.2
0 : 100	129.7	130.4	171.9	180.6
Acetic acid	129.1	130.8	171.6	–
Dioxane	126.1	132.2	167.5	–
Methanol	127.2	131.7	170.2	–
	N-Vinylpyrrolidinone			
DMSO	93.4	130.5	172.9	175.2
Water	98.2	129.6	177.9	178.8
Dioxane	92.9	130.6	172.9	–
Chloroform	94.3	129.5	173.8	–
Methanol	95.5	129.9	175.5	–
VP	93.3	129.8	172.9	–

Water-soluble polymers containing a long main hydrocarbon chain and short hydrophilic side groups of the type of COX (where X = OH, NH_2, etc.) may be regarded to some extent as compounds exhibiting surface activity. In view of this, in aqueous solution they should tend to form microaggregates of the type of micelles containing the hydrophobic hydrocarbon chain of the polymer in their interior, while the hydrophilic groups are located on the outside as far as possible. The entry of water into the interior regions of these microaggregates is difficult because of their hydrophobic properties, so that only the carbonyl groups located in the aqueous phase participate in the formation of hydrogen bonds with water molecules. The appearance of aggregates of this kind in aqueous solutions has been established experimentally in the study of the fluorescence spectra of acrylamide polymers containing very small amounts of added (<0.5 mol. %) hydrophobically modified units, in particular acrylamide units with long alkyl substituents (C_8 and longer) or other hydrophobic substituents at the nitrogen atom of the amide group.[64-69]

The formation of micelle-like clusters has also been observed in aqueous solutions of hydrophobically modified poly(ethylene oxide).[70] The hydrophobic microaggregates are present in solution even at very low polymer concentrations. An attempt has been made[66] to determine experimentally the concentration of the polymers below which they do not aggregate but form monomolecular polymer solutions. Although the exact values of this 'critical concentration for aggregation' have not been determined for different hydrophobically modified acrylamide polymers, it has been established that hydrophobic microdomains exist in these systems at a very high dilution of the polymer solutions. Thus, in the case of the hydrophobically modified polyisopropylacrylamide, the presence of hydrophobic microdomains in aqueous solution has been observed at a polymer concentration of 10^{-3}%. The formation of interchain associated species of this kind depends on the extent to which the polymers are hydrophobic. Presumably in the case of unmodified water-soluble polymers the same situation occurs, while in aqueous solutions of these polymers different microaggregates of the type of micelles arise (albeit to a lesser extent). For example, the fact that only four polymer chains are sufficient for the formation of interchain associated species may serve as a basis for such a hypothesis.[71] Associated species of this kind can catalyse the reactions occurring within them and in particular the chain propagation reaction, i.e. a kind of micellar catalysis, capable of increasing the rates of various processes to a consider-able extent, may be observed.[72]

The associated species formed as a result of hydrophobic interactions solubilise the molecules of organic compounds, in particular those of the monomer, which may alter its local concentration in the vicinity of active centres — the growing polymeric radicals within the associated species. The preferential sorption of organic compounds by polymer chains is indicated by the results obtained in a study of the dissolution of polyisopropylacrylamide in water–methanol mixtures.[73] The favourable spatial disposition of the groups participating in the chain propagation reaction within their associated species evidently decreases the activation energy for this reaction in polymerisation in water. At the same time, association as a result of hydrophobic interactions should diminish the entropy of the system. Indeed the pre-exponential factor in the Arrhenius equation for the chain propagation reaction in the polymerisation of acrylamide and acrylic acid in aqueous solution is smaller than in other solvents investigated (Table 3).

The addition of even small amounts of an organic solvent to water should apparently lead to a decrease and then to a complete disappearance of the hydrophobic effect and hence to a decrease in the rate of chain propagation and in the overall rate of polymerisation. Precisely such a situation is observed in the polymerisation of acrylamide in mixtures of water with DMSO, dioxane, and THF, in the polymerisation of *N*-vinylpyrrolidinone in water at different monomer concentrations, and also in the polymerisation of salts of diethylaminothiomethacrylate [diethylaminoethyl methacrylate?] in mixtures of water with methanol or other organic solvents.

The ideas described above concerning the hydrophobic interaction in aqueous solutions of polymers combined with kinetic data, as well as the results of spectroscopic and viscometric studies, made it possible to put forward the following mechanism for the influence of the nature of the solvent on the radical polymerisation of water-soluble monomers.[52,56]

In the polymerisation of water-soluble monomers in various organic solvents and also in water–organic solvent mixtures containing up to ~70%–80% of water, the change in the overall rate of polymerisation and its k_p is caused mainly by the change in the reactivity of the monomer as a consequence of the alteration of the electron density in the C=C bond on formation of a hydrogen bond between the carbonyl group of the monomer and the solvent. This is confirmed by the linear dependence of the rate of polymerisation on δ_{CH_2} for many of the systems investigated.

The influence of the solvent on the kinetic parameters of the polymerisation of water-soluble monomers in such systems does not differ quantitatively from that in the polymerisation of acrylic acid esters, which, for example k_p, may vary by a factor of 3–4 depending on the nature of the solvent.[13-15,29,30] Approximately the same change in the rate of the process has been observed in the polymerisation of acrylamide in water–DMSO mixtures, where the water content increases to 60–70 mol. %[52,56] and also in the polymerisation of *N*-vinylpyrrolidinone, where the concentration of water in the reaction mixture does not exceed 70 mol. %.[34,35] A further increase in the amount of water in the reaction mixture leads, not withstanding the linear relation between the water content and δ_{CH_2}, to a sharp increase in the rate of polymerisation and in k_p, which is due to the hydrophobic interactions. The increase in the rate of copolymerisation of the hydrophobically modified salts of dimethylaminoethyl methacrylate with methyl methacrylate or styrene on passing from dimethylformamide to an aqueous solution has been explained[74] by the influence of the hydrophobic interaction in the aqueous systems.

Even at high water concentrations in the organic solvent–water mixture the organic solvent enters preferentially the microaggregates and the composition of the solvent within these microaggregates, i.e. in the vicinity of the active centres, remains almost constant. Therefore the solvation of the polymer, even at a relatively high concentration of water in the reaction mixture, and also the constant k_t (adjusted to the same viscosity of the reaction mixture) should remain unchanged. Indeed $\delta_{C=O}$ for polyacrylamide, characterising the formation of hydrogen bonds between the carbonyl group and water, as well as the constant k_t remain virtually unchanged when the water content in the mixture with DMSO is altered from 0 to 50 mol. % (Fig. 7). For a higher content of water in the mixture, the latter begins to penetrate into the polymer coil; the composition of the solvent in the coil, where the chain termination reaction takes place, begins to change, which is the reason for the experimentally observed change in the quantities $\delta_{C=O}$ and k_t.[55,56]

The characteristic features of the copolymerisation of water-soluble monomers which have been established comparatively recently are apparently also determined by the hydrophobic interactions in aqueous solutions of polymers. The study of the copolymerisation of acrylamide with water-soluble anionic and cationic monomers (ethylenesulfonic acid and the sulfate salts of dimethylaminoethyl methacrylate) in water established that the composition of the copolymers formed remains almost constant as the conversion increases up to a 70%–80% yield of the polymer.[75,76] Such behaviour can be explained by assuming that the compositions of the copolymerising monomer mixture within the active polymerisation zone (in the polymer coil) and outside it are different and that a constant ratio of the concentrations of the comonomers is maintained in the active zone.

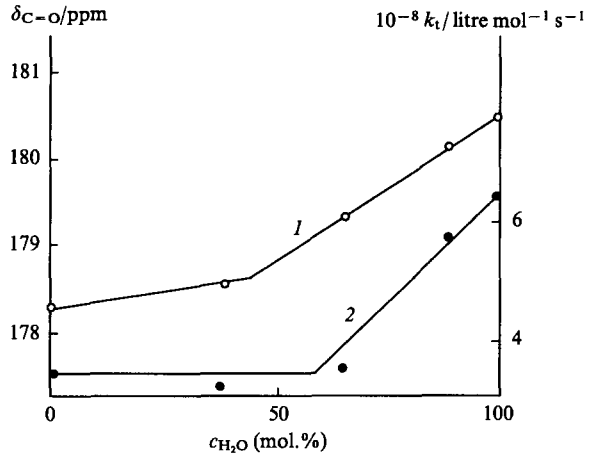


Figure 7. Dependence of the ^{13}C chemical shift of the C=O group of polyacrylamide (curve *1*) and of the constant k_t (curve *2*), adjusted to the same viscosity of the reaction system, on the water content in the polymerisation of acrylamide in a water–DMSO mixture.[55]

Such behaviour is probably a specific feature of the copolymerisation of water-soluble monomers in aqueous solutions and is associated with the formation of different interchain associated species resembling micelles, which solubilise preferentially the hydrophobic groups. A difference between the average composition of the initial monomer mixture and its composition in the active zone has been demonstrated in the emulsion copolymerisation of styrene and methyl methacrylate with long-chain alkyl salts of dimethylaminoethyl methacrylate,[74] which confirms the important role of the micellar structures in water in determining the distribution of the monomers in the reaction system.

Depending on the nature of the ionogenic comonomers, their copolymers with acrylamide are enriched either in the acrylamide units or in the units of the second comonomer. In the acrylamide–sulfate salt of dimethylaminoethyl methacrylate system, the copolymer is enriched in the cationic comonomer units, while in the copolymerisation of acrylamide with sodium ethylenesulfonate the enrichment of the copolymer in acrylamide units is observed. The rate of copolymerisation diminishes with increase in the content of the ionogenic comonomer in the initial monomer mixture regardless of the nature of the ionogenic monomer. This difference can be accounted for as follows. In the copolymerisation in an aqueous solution of monomers having different hydrophobic properties, a particular type of hydrophobic associated species is formed, depending on the composition of the copolymer, and determines the incorporation into the latter of definite amounts of the comonomers. Evidently the more hydrophobic (compared with acrylamide) cationic comonomer (the sulfate salt of dimethylaminoethyl methacrylate) enters the hydrophobic associated species more readily than acrylamide. Its local concentration in the vicinity of the active centre is therefore higher than in the initial monomer mixture. With increase in the amount of the polymer in solution, the role of the hydrophobic associated species should increase, which in fact probably leads to the observed constancy of the composition of the copolymer as the conversion is varied.

A somewhat different situation occurs in the acrylamide–sodium ethylenesulfonate system.[76] Since the hydrophilic properties of these comonomers are similar, one can postulate that, in contrast to the first system with a cationic comonomer, in this case the composition of the monomer mixture in the polymer coil differs little from the average composition of the mixture. Here one should bear in mind that sodium ethylenesulfonate was fully ionised under the copolymerisation conditions in the above study[76] and was present in the form of free ions solvated by water molecules. This factor probably hinders the incorporation of charged ethylenesulfonate anions in the hydrophobic associated species, so that the monomer mixture in these species is enriched in acrylamide compared with the average composition of the initial monomer mixture.

The independence of the composition of the copolymer of the conversion has also been established in the emulsion copolymerisation of the hydrophobically modified salt of an aminoester of methacrylic acid with styrene or methyl methacrylate. The idea that the compositions of the monomer mixture within and outside the active zone are different as a consequence of the sorption of the more hydrophobic comonomers by the polymer coil was also invoked to account for this finding.[74]

VI. Conclusion

The results presented above demonstrate convincingly that the nature of the solvent is an important factor determining the course of the radical polymerisation of water-soluble monomers. The influence of the solvent is significantly greater in the case of water-soluble monomers than in the case of the radical polymerisation of weakly polar monomers such as, for example, styrene. An especially large change in the overall rate of the reaction and in the constant k_p is observed on passing from polymerisation in organic solvents to polymerisation in an aqueous solution.

The influence of the nature of the solvent may be attributed to a number of causes, among which the following should be noted primariliy:

(1) The formation of donor–acceptor complexes between the polymeric radicals and the solvent molecules, which decreases the reactivity of the radicals.

(2) The solvation of the monomer molecules and the polymeric radicals or the specific interaction of these species with solvent molecules, in particular via the formation of hydrogen bonds, which alter the electron density in the C=C bond of the monomer or the unpaired electron density in the radical and hence alter the reactivity of the reacting species.

(3) The changes in the conformational characteristics of the polymer molecules in solvents possessing different solvent powers in relation to the polymer.

However, in our view, a distinctive feature of the polymerisation of water-soluble monomers is the hydrophobic interaction arising in aqueous solutions of the polymers. It leads to a sharp difference between the kinetic parameters of the polymerisation of monomers of this class in water and in solutions in organic solvents. The hydrophobic interaction is also responsible for the appreciable decrease in the rate of polymerisation and in the constant k_p following the addition of even small amounts of an organic solvent to water as a consequence of the preferential sorption of the organic solvent by the polymer coil.

Naturally, the formation of interchain associated species as a result of the hydrophobic interactions and hence their "catalytic" effect must depend on the hydrophobic properties of the monomers employed.

A fairly large number of studies devoted to the rheological properties of aqueous solutions of hydrophobically modified polymers have been published recently. However, there are virtually no data on the kinetics of the polymerisation of water-soluble monomers containing hydrophobic groups. At the same time, we believe that, in order to confirm the influence of the hydrophobic effect on the radical polymerisation of water-soluble monomers, it is necessary to expand the range of systems investigated, especially water-soluble monomers containing hydrophobic groups. The study of the polymerisation of monomers of this kind in water, organic solvents, and water–organic solvent mixtures of different composition will yield additional information about the role of hydrophobic interactions in radical polymerisation in aqueous solutions.

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