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Nontraditional methods of synthesising metal-containing polymers

A D Pomogailo, V S Savost'yanov
Branch Institute of Chemical Physics, USSR Academy of Sciences
Associated Institute of Energy Problems of Chemical Physics, USSR Academy of Sciences

ABSTRACT. Complexes of metals with (meth)acrylates and acrylamides are used as examples for examining the application of nontraditional methods for initiating polymerisation of metal-containing monomers: graft, low-temperature, electrochemical, matrix, solid-state (under high pressure with shear deformation), frontal and spontaneous. Such approaches are demonstrated to be very effective for preparing metal-containing polymers with a wide sprectrum of relative molecular masses and with different solubility and stereotacticity. A bibliography containing 39 citations is included.

Contents

I. Introduction 762
II. Graft polymerisation of metal-containing monomers 762
III. Low-temperature radical polymerisation 764
IV. Solid-state polymerisation under high pressure with shear deformation 765
V. Electrochemical polymerisation 766
VI. Matrix polymerisation 766
VII. Frontal polymerisation in the melt 767
VIII. Spontaneous polymerisation 769
IX. Photopolymerisation with an applied magnetic field 771
X. Conclusion 771

I. Introduction

The synthesis and polymerisation of metal-containing monomers (MCM) has recently advanced at such a rapid pace owing to the efforts of scientists in many countries that a new scientific discipline has formed. It is characterised by novel compositions, methods for their polymerisation, and new approaches to studying the structure of the metal-containing polymers formed.[1-3] The ever increasing interest in such polymers is due to their unusual properties, which are determined not only by the metals in them but also the nature of the polymer matrix. The products of MCM polymerisation are composites with new physicomechanical and operating properties, catalytically and biologically active macromolecules, etc.

Furthermore, considerable attention has been given to polymerisation of MCM by traditional methods (primarily polymerisation in solutions with an initiator, usually a radical, at elevated temperatures). Besides difficulties in choosing a suitable solvent and initiator (which might react with the MCM), problems arise with separating the polymer and removing from it residues from the reaction mixture.

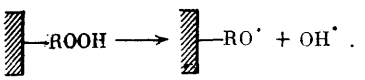
This has led to numerous investigations on nontraditional methods of MCM polymerisation. It was expected that the structures and properties of MCM would facilitate successful application of these methods. Indeed analysis of the data obtained indicates that nontraditional methods of polymerisation have to a large extent been used with nontraditional monomers (MCM are undoubtedly in this class).

Let us recall that MCM are compounds containing an organic moiety with a reactive multiple bond capable of undergoing addition and a metal-containing group chemically bonded to it.[1-3] All MCM can be divided into four groups: monomers with covalent, ionic, donor–acceptor, and π-bonds between the metal and organic part. However, the principal achievements in application of nontraditional methods have involved two groups of MCM: ionic, e.g. metal (meth)acrylates $M(OCOCR=CH_2)_n$ (R = H or CH_3, n is the metal valence), and donor-acceptor, e.g. metal complexes of acrylamides (AAm) $M(H_2NCOCH=CH_2)X_n(H_2O)_p$ (p = 0 or 2).

Let us examine the principal nontraditional methods of initiating polymerisation of such MCM.

II. Graft polymerisation of MCM

Graft polymerisation is an effective method for preparing metal-containing polymers that combine properties of the starting polymeric support (film, fibre, powder, etc.) and the grafted polymer. Radiation grafting of MCM, in which the polymer–support is previously irradiated in the presence of oxygen from air, is the most effective approach. This forms hydroperoxide (HP) groups on the surface of the polymer. These can then initiate grafting under the appropriate conditions:



Thus, boiling a suspension of irradiated polyethylene (PE) powder in an alcoholic solution of MCM produces graft polymerisation of acrylates containing the transition metals Cr^{III}, Fe^{III}, Co^{II}, Ni^{II}, and Cu^{II}.[4,5] A distinguishing feature of the grafting of these MCM is the almost complete absence of the homopolymer. Graft polymerisation of potassium acrylate gave 30% homopolymer. A redox-active metal clearly hinders initiation of polymerisation. The kinetic dependences of the process are the same for all acrylates studied. In the first 0.5 h the rate is maximal. It then rapidly drops (Fig. 1). It is interesting that acrylates of divalent metals graft at higher rates than those of trivalent ones. The activity of the acrylates changes in the following order: $Co^{II} > Cu^{II} > Ni^{II} > Cr^{III} > Fe^{III}$. Grafting of Cu^{II} acrylate is characteristically rather effective, in contrast with polymerisation of this MCM in solution. This is obviously due to adsorption of the metal acrylate on the surface of the hydrophobic polymeric support.

The initial rate of graft polymerisation w_0 for all acrylates studied is practically constant for 0.04–0.40 *M* MCM in alcohol. The existence of a limiting rate is probably due to the attainment of a limiting [MCM] on the PE-powder surface. The adsorption isotherm of Co^{II} acrylate confirms this hypothesis (Fig. 2). The amount of adsorbed monomer increases with increasing [acrylate] in solution and reaches the limiting value corresponding to coverage by a monolayer.

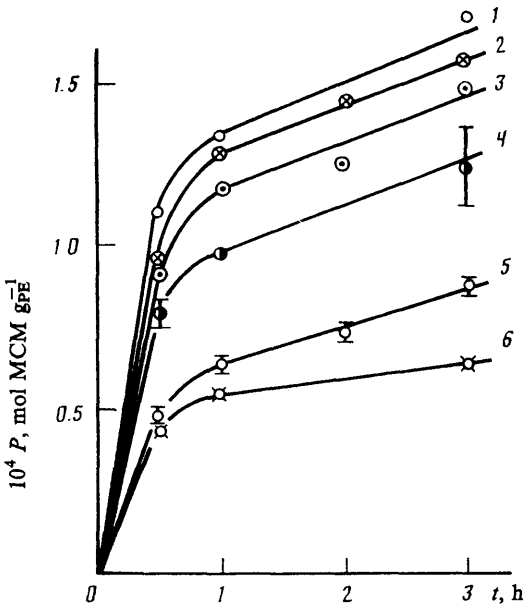


Figure 1. Kinetic curves for yield (*P*) of grafted metal acrylate polymer: *1,3*, Co^{II}; *2*, Ni^{II}; *4*, Cu^{II}; *5*, Cr^{III}, Fe^{III}. The solvent is alcohol. [MCM] = 0.04 mol dm^{-3}, *T* = 79 °C. *1,2,5,6*, *D* = 200 kJ kg^{-1}; *3,4*, *D* = 100 kJ kg^{-1}; *1,3,4*, *I* = 2.8 J kg^{-1} sec^{-1}; *2,5,6*, *I* = 1.4 J kg^{-1} sec^{-1}.

The nature of the transition metal has a substantial influence on the grafting of acrylates. The dependence of the initial rate of grafting on [HP] in irradiated PE can be represented as follows: $w_0 \sim [HP]^{\alpha}$ with α = 0.7, 0.6, 0.5, 1.1 and 1.1 for grafting of Co^{II}, Ni^{II}, Cr^{III}, Cu^{II} and Fe^{III} acrylates, respectively. Such values for α are consistent with predominantly bimolecular termination of the growing chains for Co^{II}, Ni^{II} and Cr^{III} and monomolecular for Cu^{II} and Fe^{III}. The special behaviour of various types of MCM based on Cu^{II} and Fe^{III} has been noted in many other instances[3] and was explained by the increased probability of monomolecular chain termination involving Cu^{II} and Fe^{III}.

Grafting of metal acrylates is characterised by low activation energy E_a from 42 to 55 kJ mol^{-1}. The rate of polymerisation also depends weakly on the presence of radical inhibitors.

The observed dependences are probably general in nature and can be used to examine graft polymerisation of other MCM. Indeed it has been demonstrated that the kinetic curves for grafting of metal chelates of monomers, complexes of metal acrylates with 2,2′-bipyridyl and 1,10-phenanthroline, are analogous.[6] The order of activity for the metals is the same as found in graft polymerisation.

Graft polymerisation after irradiation has been investigated for AAm complexes of metal chlorides and nitrates under conditions analogous to those for acrylates.[5,7] Like for the acrylates, the amount of homopolymer of these MCM in the polymeric products was insignificant. It was 4–8 times less than for grafting of the metal-free analogue, AAm. The only exception was $MnCl_2$, the rate of thermal homopolymerisation of which surpasses that of grafting.

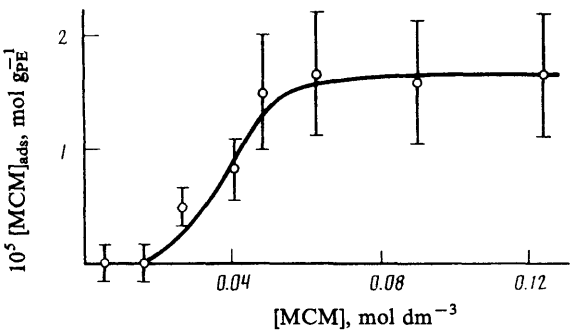


Figure 2. Adsorption isotherm of Co^{II} acrylate on PE powder: MCM in alcohol (15 dm^3), 5 g PE, *D* = 200 kJ kg^{-1}, *I* = 2.8 J kg^{-1} sec^{-1}, *T* = 22 °C.

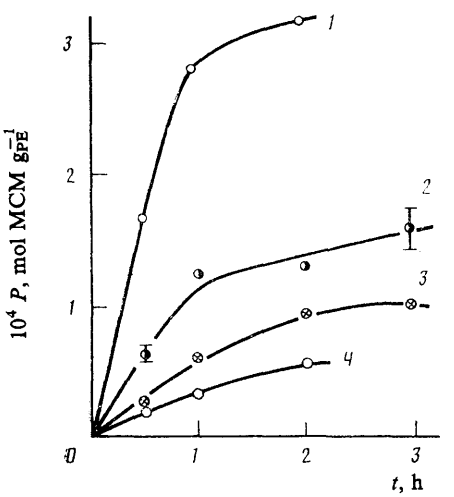


Figure 3. Kinetic curves of yield of grafted polymers of AAm complexes: *1*, $Cr(AAm)_4Cl_3$; *2*, $Co(AAm)_4Cl_2$; *3*, $Ni(AAm)_4Cl_2$; *4*, $Co(AAm)_4(H_2O)_2(NO_3)_2$. In alcohol, [MCM] = 0.1 mol dm^{-3}, *T* = 80 °C, *D* = 200 kJ kg^{-1}, *I* = 1.4 J kg^{-1} sec^{-1}.

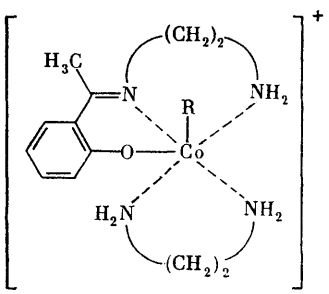
In contrast with graft polymerisation of metal acrylates, the rate of grafting of AAm complexes of metal chlorides varies as follows: Cr^{III} > Co^{II} > Ni^{II} (Fig. 3). This order is opposite that of the metal ion electronegativities. The nature of the anion of the complexant also has a significant effect. Graft polymerisation of

$Co(AAm)_4(H_2O)_2(NO_3)_2$ proceeds with a rate almost three times less than that of $Co(AAm)Cl_2$. Complexes of Cu^{II} with AAm are typically inactive in graft polymerisation.

The rate of grafting of AAm complexes of metals is proportional to [MCM] in solution whereas for grafting of uncoordinated AAm $w_0 \sim [AAm]^{1.7}$. Graft polymerisation of AAm and its complexes is characterised by monomolecular chain termination. The E_a for the complexes $Co(AAm)_4Cl_2$ and $Ni(AAm)_4Cl_2$ are 51 and 60 kJ mol^{-1}, respectively. As in graft polymerisation of acrylates, radical inhibitors had little effect on the reaction of AAm complexes. This is probably due to formation of complexes of the inhibitors with MCM.

III. Low-temperature radical polymerisation

It is difficult to choose an initiator for free-radical polymerisation of MCM at low temperatures. As a rule, traditional initiators are used at elevated temperatures and the redox systems used at low temperatures can lead to side reactions. Therefore, organometallic compounds capable of acting as low-temperature radical initiators are of great interest. For instance, cationic Co^{III} complexes such as



$R = CH_3$, C_2H_5, C_3H_7.

can undergo homolytic cleavage of the Co–R bond.[8] This was used to initiate low-temperature polymerisation of $M[OCOCH=CH_2]_2$, where M = Zn^{II}, Mg^{II}, Pb^{II} and Ba^{II} in methanol.[9] The overall scheme taking into account partial dissociation of the monomer and participation of $[MOCOCH=CH_2]^+$ in the decomposition of the complex can be represented as follows:

$$RCo \xrightarrow{[M(OCOCH=CH_2)]^+} R^{\cdot},$$

$$CH_2=CH + R^{\cdot} \longrightarrow {\sim}CH_2{-}\underset{\displaystyle COOM(OCOCH=CH_2)}{\underset{|}{CH}}{\sim}$$

$$\underset{\displaystyle COOM(OCOCH=CH_2)}{\underset{|}{CH_2=CH}}$$

The kinetics of polymerisation, in addition to the complete inhibition by radical traps, confirm that the process is radical in nature. Such initiators enable polymerisation to be carried out at comparatively low temperatures (from –20 to 10 °C) at sufficiently high rates. The products produced under such conditions are expected to have high relative molecular masses (stereotactic structures may also form).

Another possible method for initiating low-temperature radical polymerisation is irradiation. The post-irradiation polymerisation method has become widespread. The matrix is vitrified, transforming the system from a glass to a supercooled liquid.[10] In a number of instances the process occurs at high rates and the yield of polymers is quantitative. This is due to the sharp change of molecular mobility during phase transitions.

On cooling to –196 °C, Co^{II}, Ni^{II}, Cr^{III}, Mn^{II} and Cu^{II} acrylates in 10% alcohol are completely vitrified. On warming up they devitrify and, with the exception of Ni^{II} acrylate, crystallise and melt (Table 1).[11] On warming up Ni^{II} acrylate that had been vitrified and irradiated at –196 °C in a calorimeter, an exotherm associated with MCM polymerisation is observed immediately after the devitrification step (Fig. 4). The polymer forms a separate phase. As a result, the concentration of monomer decreases. This produces on the calorimetric heating curve an exotherm for crystallisation and an endotherm for melting in addition to the exotherm for polymerisation.

Table 1. Phase-transition temperatures of 10% acrylate salt solutions in ethanol.[11]

Metal acrylate	T_v, °C	T_{cr}, °C	T_m, °C
Ni(II)	–173	–	–
Co(II)	–173	–138	–118
Cu(II)	–171	–143	–118
Mn(II)	–171	–138	–118
Cr(II)	–171	–138	–118

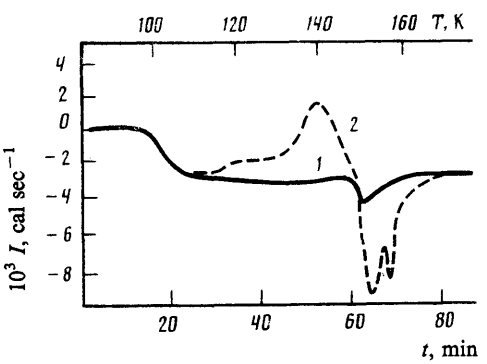


Figure 4. Calorimetric heating curve of 10% Ni^{II} acrylate in alcohol before (*1*) and after (*2*) irradiation. D = 100 kJ kg^{-1}, T = –196 °C.

Post-irradiation polymerisation of AAm complexes of Co^{II} and Ni^{II} chlorides and nitrates proceeds analogously (Fig. 5). It is noteworthy that the calorimetric heating curves of unirradiated MCM differ from the classical curves for the vitreous state. This may be due to the formation and rearrangement of different complexes of the MCM with ethanol. The yield of polymer in this instance reaches 45%. The relative molecular mass was low, $\overline{M}_\eta$ = 5600 (for comparison, $\overline{M}_\eta$ = 8700 for polyacrylamide prepared by polymerisation of AAm under analogous conditions).

Investigation of polymers formed by devitrification of irradiated alcohol matrices revealed that syndiotactic structures are primarily formed. For example, polyacrylic acid prepared by hydrolysis of the product of polymerisation of Co^{II} acrylate contains up to 60% of

the syndiotactic fraction (Table 2). However, the corresponding fraction obtained by polymerisation of acrylic acid under the same conditions gave ony 25–30%.

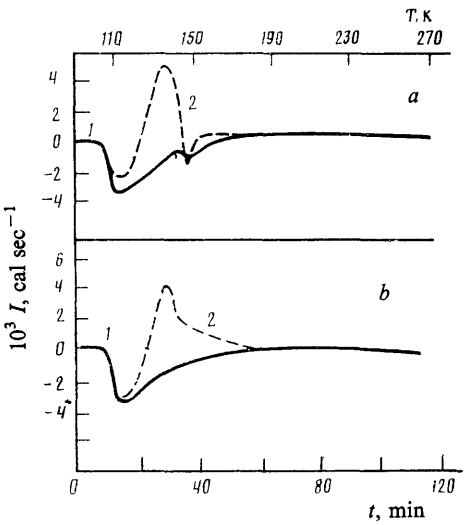


Figure 5. Calorimetric heating curves of 10% $Ni(AAm)_4Cl_2$ (*a*) and $Co(AAm)_4(H_2O)_2(NO_3)_2$ (*b*) in alcohol before (*1*) and after (*2*) irradiation. D = 100 kJ kg^{-1}, I = 100 kJ kg^{-1} h^{-1}, T = –196 °C.

Table 2. Fractional composition of PPA prepared by polymerisation of acrylic acid and isolated from the polymerisation product of Co^{II} acrylate.[11]

Fraction	Selective solvent	Fraction, %	
		PAA	PAA(Co)
Syndiotactic	Dioxane–water (80:20 vol.%)	25–30	45–60
Atactic	Dioxane	60–65	10–20
Insoluble gel	—	10–15	20–30

IV. Solid-state polymerisation under high pressure with shear deformation

Polymerisation under high pressure with shear deformation is performed in a Bridgman anvil cell. It is very effective for converting solid monomers,[12] among which MCM are one of the most interesting. Metal acrylates are so reactive in this process that high degrees of conversion are attained even at pressures from 500 to 1000 MPa and anvil rotation angles from 100 to 200° (Fig. 6).[13,14]

The participation of metal ions in this process was suggested by investigations of the polymerisation of transition metal acrylates under analogous conditions. Thus, the Mössbauer spectrum of Fe^{III} acrylate treated at 2 GPa exhibits two doublets with (shift relative to SnO_2) δ = 1.35 mm sec^{-1} and Δ = 2.22 mm sec^{-1} and δ = 1.44 mm sec^{-1} and Δ = 2.62 mm sec^{-1} (Fig. 7, curves *3* and *4*) in addition to the doublet from starting Fe^{3+} with δ = 0.76 mm sec^{-1} and Δ = 0.65 mm sec^{-1} (Fig. 7, curve *1*).[15] Comparison of Mössbauer spectra of Fe^{3+} and Fe^{2+} demonstrated that the new lines in the spectra of Fe^{III} acrylate that appear after treatment under pressure correspond to Fe^{II} acrylate.

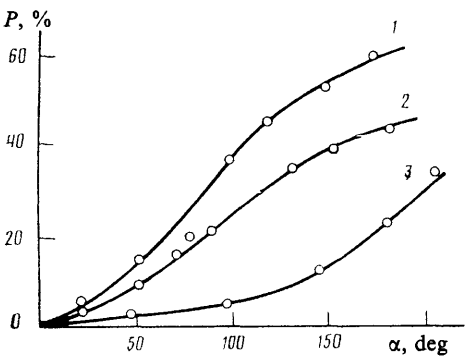


Figure 6. Polymer yield as a function of anvil rotation angle α under high pressure with shear deformation. Pressure, 160 MPa. Metal acrylate monomers: *1*, Ba^{II}; *2*, Pb^{II}; *3*, Zn^{II}.

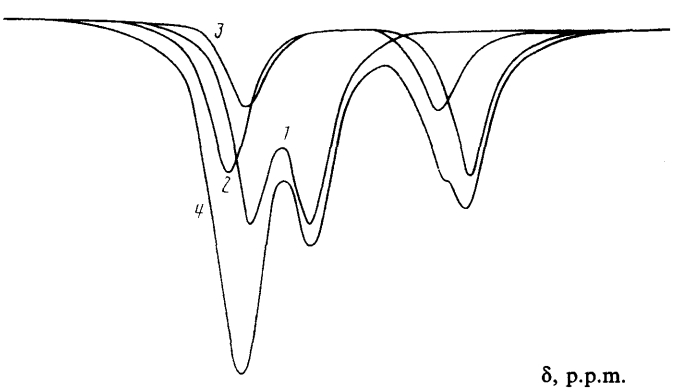


Figure 7. Mössbauer spectra of Fe^{III} acrylate: *1*, before treatment; *2,3*, doublet arising after treatment; *4*, summed spectrum after treatment. Pressure, 2 GPa; anvil rotation angle, 100–200 °C.

As vinyl monomers polymerise during plastic flow under pressure, the flow resistance increases as polymer accumulates.[12] This effect can be used for direct evaluation of the reactivity of monotypic monomers. The flow resistance (σ) as a function of deformation (anvil rotation angle α) for several AAm complexes is plotted in Fig. 8.[16] The data show that the greatest change occurs for $Co(AAm)_4Cl_2$; the least, for $Cu(AAm)_4(NO_3)_2$. The unusual nature of the function for $Fe(AAm)_4(NO_3)_3$ is noteworthy. The AAm complexes can be placed in the following order of

reactivity on the basis of the functions obtained: $Co(AAm)_4Cl_2$ > $Co(AAm)_4(H_2O)_2(NO_3)_2$ > $Ni(AAm)_4(H_2O)_2(NO_3)_2$ > $Mn(AAm)_4$. $.(H_2O)_2(NO_3)_2$ > $Cu(AAm)_4(NO_3)_2$.

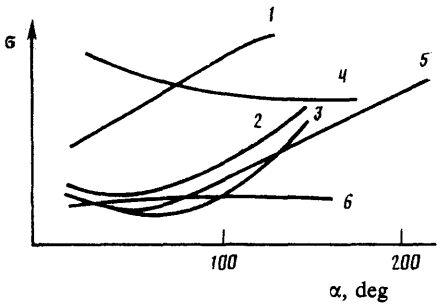


Figure 8. Dependence of flow resistance on deformation for AAm complexes: *1*, $CoCl_2$; *2*, $Co(NO_3)_2$; *3*, $Ni(NO_3)_2$; *4*, $Fe(NO_3)_3$; *5*, $Mn(NO_3)_2$; *6*, $Cu(NO_3)_2$.

This method can also be applied to copolymerisation of MCM. Thus, copolymerisation of acrylates and of AAm complexes of Y^{III}, Ba^{II} and Cu^{II} nitrates is effective.[17] It is noteworthy that high pressure with shear deformation is the only method for introducing into the copolymer MCM based on Cu^{II}, which are usually unreactive in polymerisation. The synthesised ternary copolymers were used as polymeric starting materials for preparing high-temperature superconducting ceramics with good properties.

V. Electrochemical polymerisation

Electrochemical polymerisation of MCM is a unique method for preparing films containing redox centres in each repeating unit. The redox conductivity enables the film to grow continuously since its exterior is active in electron transfer at the film–solution interface.

Electrochemical polymerisation can be examined in more detail using the rather numerous mixed-ligand complexes of Ru^{II}, Os^{II} and Fe^{II} perchlorates and hexafluorophosphates as examples.[18–21] The ligands used were 4-vinylpyridine, other more complicated monomers containing pyridine, derivatives of cinnamates, stilbazole, etc., in addition to unsubstituted polypyridyl ligands (2,2′-bipyridyl, 2,2′,2″-terpyridyl, 1,10-phenanthroline, etc.).

The polymerisation was carried out in 0.1 M tetraethylammonium perchlorate in CH_3CN by repeated cycling of a Pt electrode near the reduction potential of the ligand. Homogeneous even polymer films were formed. For the majority of investigated MCM, the first step of electrochemical polymerisation is formation of the anion–radical by electron transfer into the π^*-orbital of the unsubstituted ligand.

$$[Ru(bipy)_2L_2]^{2+} \overset{+e^-}{\rightleftharpoons} [Ru(bipy)(bipy)^{\cdot-})L_2]^{+} \overset{+e^-}{\rightleftharpoons} [Ru(bipy)^{\cdot-})_2L_2]^{0}.$$

An electron then transfers onto the substituted ligand either by an intramolecular mechanism or by disproportionation. Repetition of these reactions produces the polymer.

Electrochemical polymerisation of complexed AAm is of great interest. However, the majority of studies have been performed using transition metal chlorides such as $ZnCl_2$ and $AlCl_3$.[22–24] Therefore, polymerisation of AAm in aqueous solutions using nitrates, perchlorates and sulphates is impossible. However, effective electrochemical polymerisation of AAm in nonaqueous media in the presence of Co^{II} nitrate and perchlorate was recently reported.[25] The reaction was carried out in DMF, from which the polymer precipitated, and DMSO, in which the reaction mixture remained homogeneous. The rate in DMSO was an order of magnitude greater than that in DMF. The kinetic equation has the following form:

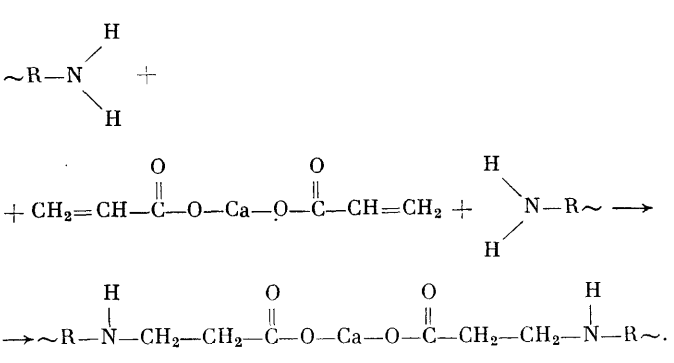
$$w_p = K[AAm]^{1.5}[Co(NO_3)_2]I^{0.5}.$$

This dependence was explained by assuming that two types of monomers, free AAm and that complexed to Co^{II} nitrate, simultaneously participate in chain growth. This was confirmed by the comparatively small amount of $Co(NO_3)_2$ in the polymer, 6–10 mass%. The process can produce polyacrylamide of very high relative molecular mass, greater than 2 500 000. The reaction is inhibited by *p*-benzoquinone, indicative of the radical nature of the process. It is interesting that polymerisation does not occur in the presence of Co^{II}. Most likely this suggests that participation of nitrate in initiation of the process has not been considered.[25]

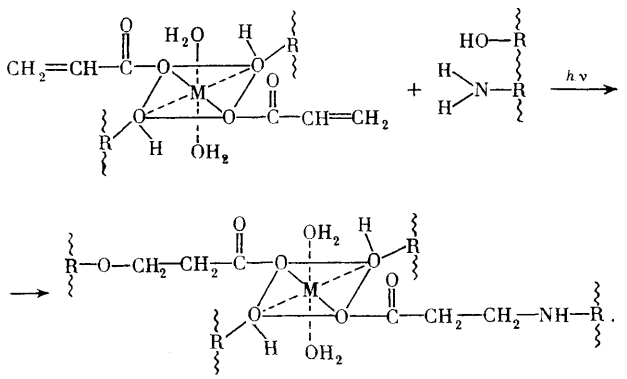
VI. Matrix polymerisation

Polymerisation of MCM in the matrix of a different polymer or compound can lead to dramatic modification of the properties of various materials. Various methods are possible. Among these, polymerisation in the polymer melt is one of the most effective. Thus, polymerisation of acrylates and AAm complexes of Zn^{II} and Ni^{II} nitrates in a high-density PE melt was investigated.[26] The MCM were added to the polymer as a solution in methanol. The mixture was polymerised in a press-form for 5 min at 190 °C and 15 MPa. It was found that adding even 0.5 mass% Zn^{II} acrylate to the PE completely stops the flow at 190 °C. However, adding 10 mass% MCM increases the melting point from 131 to only 135 °C. The crystallinity of the polymer does not change. This is consistent with crosslinking of the amorphous PE during polymerisation of the acrylate. Crosslinking of a polymer is characterised by a sharp drop of the relative expansion (for 0, 2, 5 and 10 mass% Zn^{II} acrylate, its value is 790, 20, 10 and 2%, respectively). The tensile strength of the modified polymer is maximal for 2–5 mass% MCM (Fig. 9).

Interesting results were obtained during investigations of laser-induced polymerisation of Ca^{II}, Co^{II}, Ni^{II} and Cu^{II} acrylates in a gelatin matrix.[27–29] Holographic information can be recorded using laser radiation by adding a metal acrylate to the gelatin matrix. The holograms produced in this manner diffract more efficiently and have better resolution than ordinary holograms. Crosslinking of gelatin by Ca^{II} acrylate can be represented as follows:



The analogous process involving transition metal acrylates is more complicated and includes preliminary formation of macrocomplexes of MCM and gelatin. This is confirmed by IR and electronic spectroscopy. The photochemically induced formation of structures from such complexes is represented by the following scheme:



The sensitivity to absorption of radiation by the macrocomplexes and the degree of crosslinking (number of double bonds reacted) depends on the nature of the transition metal: $Cu^{II} > Ni^{II} > Co^{II}$.

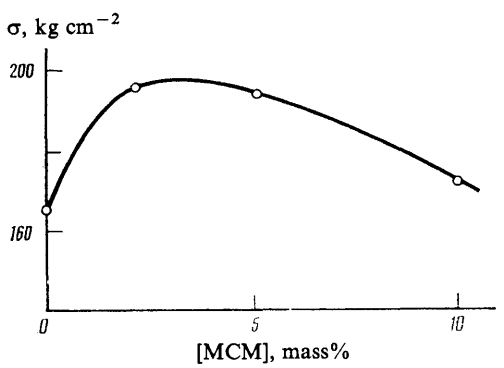
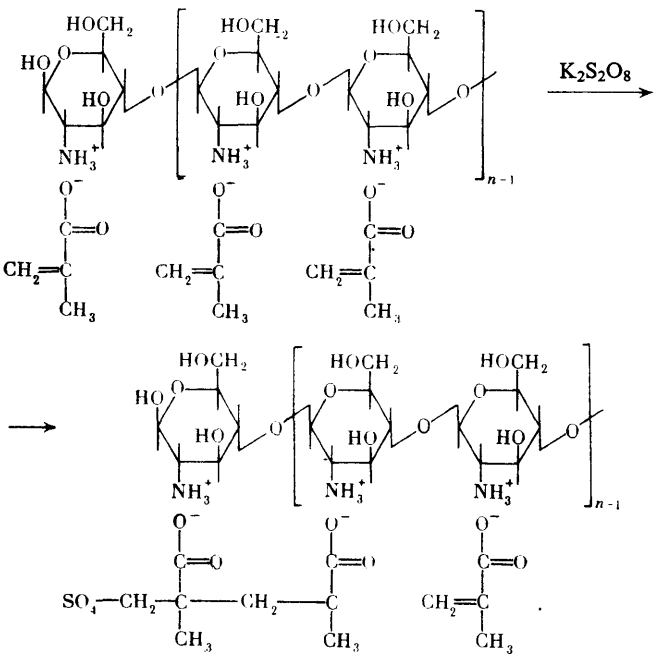


Figure 9. Dependence of tensile strength (σ) of the Zn^{II} polymerisation product in high density PE melt on MCM content.

Matrix effects were detected during an investigation of the polymerisation of aqueous sodium methacrylate in the presence of chitosan acetate (mole ratio chitosan : MCM = 1 : 1) initiated by $K_2S_2O_8$.[30] The rate is described by: $w_p = K[M]^{0.8}[K_2S_2O_8]^0$ up to $[K_2S_2O_8] < 3.5 \times 10^{-3}$ mol dm^{-3} and $w_p = K[M]^{0.8}[K_2S_2O_8]^{1.8}$ for $[K_2S_2O_8] > 3.5 \times 10^{-3}$ mol dm^{-3}. However, w_p changes linearly with initiator concentration in the presence of a chitosan analogue with a low relative molecular mass, glucosamine hydrochloride. The relative molecular mass of the sodium polymethacrylate increases linearly with conversion. The polymerisation is distinguished by a rapid initiation and continuous nature. The polymer contains only one SO_4 group per chain. These data are consistent with the following scheme for matrix polymerisation of MCM owing to inclusion of acrylate bound through ionic and hydrophobic bonds to the polymeric chain of chitosan residues:



VII. Frontal polymerisation in the melt

During an investigation of the properties of $M(AAm)_4 \cdot (H_2O)_2(NO_3)_2$, where M = Mn^{II}, Co^{II}, Ni^{II} and Zn^{II}, it was unexpectedly discovered that these monomers readily undergo polymerisation in a self-propagating (frontal) regime without addition of any initiators or activators.[31] In the frontal polymerisation method, the bottom of the vessel containing the MCM is briefly heated. After the "ignition" is stopped, the boundary where the substance changes colour, the polymerisation front, continues to advance of itself. This effect is the first documented instance of thermally initiated frontal polymerisation. The reaction proceeds under the most mild conditions of any known for such processes: monomer powders pressed at low pressures, the lack of specially added initiator or activator, comparatively low ignition temperature temperatures (120 – 180 °C), and a reaction at normal pressure. The dependences of the front advance rate during polymerisation of $Co(AAm)_4(H_2O)_2(NO_3)_2$ on time from the moment of ignition for various ignition temperatures are plotted in Fig. 10. It is clear that the kinetic functions consist of two parts corresponding to the nonequilibrium and steady-stage regimes of polymerisation front advance. Depending on the ignition temperature, the rate before equilibrium is reached can be higher or lower than the steady-state rate w_{fr}.

Addition of radical inhibitors has a significant influence on frontal polymerisation. Addition of 2,2,4,4-tetramethylpiperidine-1-oxyl to the polymerising system practically linearly decreases w_{fr}. At inhibitor concentrations $\geqslant$ 0.1 mass%, the frontal process is completely stopped. The effective inhibition is consistent with a radical mechanism for thermally initiated frontal polymerisation. An estimate of the number of active centres gives a value less than 3.0×10^{-3} mol per mol of MCM.

A study of the influence of the nature of the metal on the rate of frontal polymerisation of $M(AAm)_4(H_2O)_2(NO_3)_2$ demonstrated that w_{fr} decreases in the order $Co^{II} > Ni^{II} > Mn^{II} > Zn^{II}$.

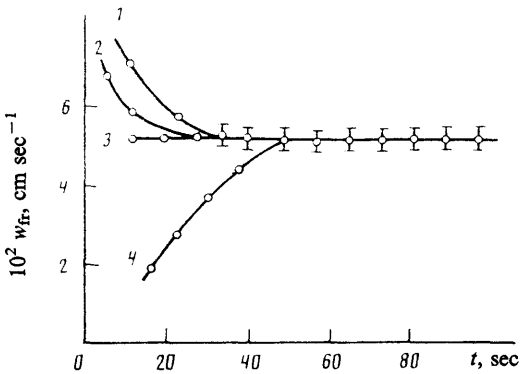


Figure 10. Dependence of front advance rate during polymerisation of $Co(AAm)_4(H_2O)_2(NO_3)_2$ on ignition temperature and process time. Diameter of sample container d = 4 mm, p = 1.02 g cm^{-3}. Ignition temperature, °C: *1*, 300; *2*, 250; *3*, 180; *4*, 120.

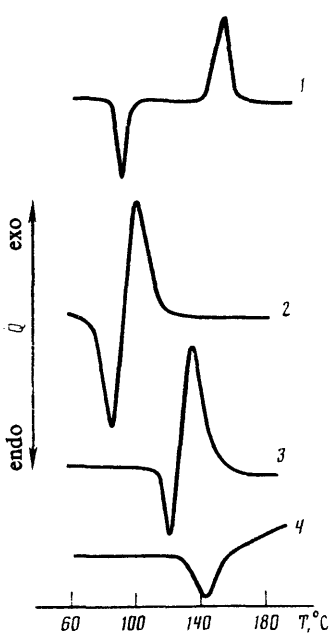


Figure 11. DSC curves of acrylamide and its complexes: *1*, AAm; *2*, $Co(AAm)_4(H_2O)_2(NO_3)_2$; *3*, $Cu(AAm)_4(NO_3)_2$; *4*, $Ni(AAm)_4Cl_2$.

It should be emphasised that frontal polymerisation has been detected only for AAm complexes of Mn^{II}, Co^{II}, Ni^{II} and Zn^{II}. Uncoordinated AAm, AAm complexes of Cu^{II} and Fe^{III} nitrates and transition metal chlorides, bromides and perchlorates, and the complex of 4-vinylpyridine with Co^{II} under analogous conditions do not polymerise in spite of a wide variation of the process parameters. Therefore, this is a unique property of the AAm complexes of Mn^{II}, Co^{II}, Ni^{II} and Zn^{II} nitrates, analogues of which have not yet been found.

Thermal polymerisation of these MCM was investigated by differential scanning calorimetry (DSC). The process was demonstrated to proceed at a high rate with participation of all four unsaturated AAm ligands. The yield of polymer reaches 100%.[32] The reaction occurs at unexpectedly low temperatures (80–100 °C). It characteristically occurs close to the melting point of the complex (Fig. 11, curve *2*). However, heating $Cu(AAm)_4(NO_3)_2$ and $Fe(AAm)_4(NO_3)_3$ effectively oxidises the organic part of the AAm complex. This is apparently initiated by nitrate decomposition (Fig. 11, curve *3*).

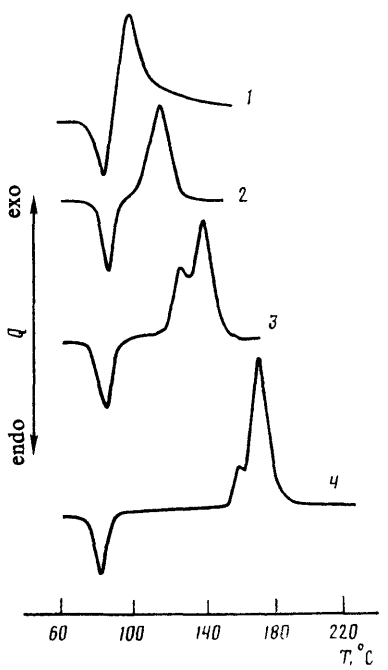


Figure 12. DSC curves of $Ni(AAm)_4(H_2O)_2(NO_3)_2$ with various amounts of 2,2,4,4-tetramethylpiperidine-1-oxyl, mass%: *1*, 0 (no inhibitor); *2*, 0.35; *3*, 0.9; *4*, 8.5.

Addition of radical inhibitors to $Ni(AAm)_4(H_2O)_2(NO_3)_2$ prevents polymerisation close to the melting point of the MCM (Fig. 12). However, extensive nitrate decomposition occurs at certain inhibitor concentrations ($\geqslant$0.9 mass%) with oxidation of the organic part of the complex. The two exotherms (Fig. 12, curves *3* and *4*) can probably be explained by two processes, partial polymerisation (the low-temperature peak) and nitrate decomposition with oxidation of the organic part of the complex (high-temperature peak).

It was concluded that Mn^{II}, Co^{II}, Ni^{II}, Zn^{II}, Cu^{II} and Fe^{III} nitrates in monomeric AAm complexes are thermally unstable at

temperatures above 130 °C. However, these complexes, which are incorporated into the polymer matrix during polymerisation, remain stable up to 200 °C, i.e. the polymer matrix to a large extent prevents their decomposition.

It is interesting that AAm complexes of Mn^{II}, Co^{II}, Ni^{II} and Zn^{II} nitrates can undergo thermal copolymerisation with other monomers. Thus, AAm complexes effectively copolymerise with uncoordinated AAm (Fig. 13). At ratios [AAm]:[MCM] < 4, thermal copolymerisation is seen in the thermogram as a single peak (Fig. 13, curve *2*), like for the starting complex (Fig. 13, curve *1*). At [AAm]:[MCM] > 4, the polymerisation region in the thermograms appears as a high-temperature shoulder apparently owing to polymerisation of uncoordinated AAm (Fig. 13, curve *4*).

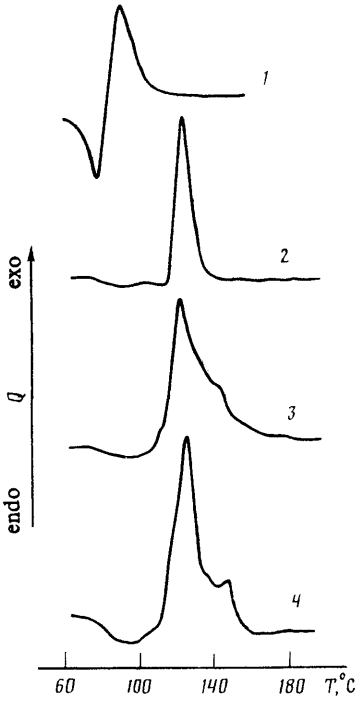


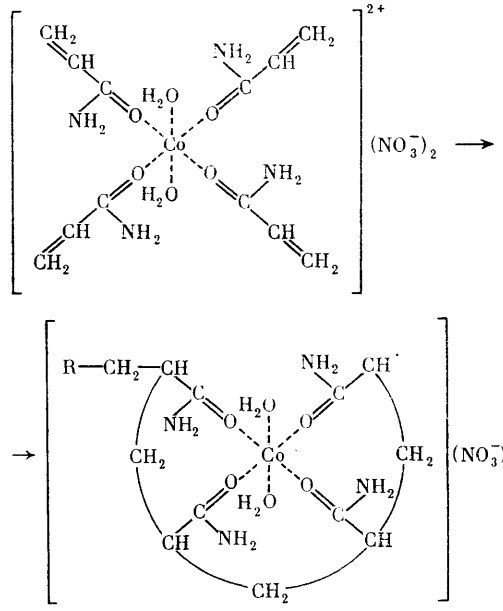
Figure 13. DSC curves of $Ni(AAm)_4(H_2O)_2(NO_3)_2$ and AAm mixtures. [AAm]:[MCM] ratio: *1*, 0; *2*, 2.0; *3*, 4.0; *4*, 7.1.

Elemental analysis of the frontal polymerisation products showed that the polymers produced were practically identical to the starting MCM. The average relative molecular mass of the polyacrylamide isolated from polymeric AAm complexes of Co^{II} and Ni^{II} nitrates after removal of metal compounds was 9.88×10^5 and 4.14×10^5, respectively. This is 100 and 200 times greater than the relative molecular mass of the polymer obtained by radical-initiated polymerisation of $Co(AAm)_4(H_2O)_2(NO_3)_2$ in water.

The following scheme involving nitrate decomposition products was proposed for initiation of the process:

$$Co^{2+}(AAm)_4(H_2O)_2(NO_3^-)_2 \rightleftharpoons$$
$$\rightleftharpoons Co^{3+}O(AAm)_4(H_2O)_2(NO_3^-) \ldots (NO_2).$$

The high rate constant for polymerisation of AAm complexes of these metal nitrates is probably attained owing to a favourable steric position of the AAm molecules in the metal complex. Growth of the polymeric chain can be represented as follows:[33]



The polymeric chain seemingly twists around the four AAm groups of the complex. The chain is then apparently transferred to the next precursor.

VIII. Spontaneous polymerisation

The properties of AAm complexes of metal nitrates are not limited to the ability to undergo thermal polymerisation. Complexes of AAm with such metal nitrates as Cr^{III}, Bi^{III}, Pb^{II}, Ca^{II}, Er^{III} and Nd^{III} spontaneously polymerise in concentrated aqueous solutions even at room temperature during synthesis and cannot be isolated as monomers.[34,35] The water in the starting mixture is retained in the polymer formed. This enables the polymerisation process to be investigated using measurements of the relative permittivity of the system. As seen in Fig. 14, the relative permittivity of reaction mixtures based on AAm and Cr^{III} and Bi^{III} nitrates sharply decreases in the first 10–30 min after complex formation. After this both ε' (real part of the relative permittivity) and ε'' (imaginary part) change slowly.

The kinetics of spontaneous polymerisation were investigated by calorimetry.[36] The composition of the reaction mixture was found to have a substantial influence on the reaction. The kinetic curves plotted in Fig. 15 describe polymerisation of AAm in the presence of $Cr(NO_3)_3.9H_2O$ at various ratios [AAm]:[$Cr(NO_3)_3.9H_2O$]. In the majority of instances, they are analogous, with the exception of 5:1. Here the process occurs at a significantly higher initial rate and a more rapid decrease. A similar path of the curves (although less clearly evident) is observed on addition of a small amount of water (Fig. 15*b*). It can be proposed that the composition of the polymerising complex in this instance has the ratio [AAm]:[$Cr(NO_3)_3.9H_2O$] = 5:1.

It is interesting that the amount of heat released by polymerisation at 20 °C for 3–6 h after the start is only 20–25% of

the calculated value. This may indicate that a comparatively small fraction of the AAm molecules are activated at the start of the reaction. The process is finally finished only after 1–2 days at room temperature. The mixture is already solid. Therefore, its second step cannot be recorded but does become detectable at elevated temperatures where the rate of the process increases (Fig. 16). Thus, the reaction is practically completely finished after 2 h at 60 °C. Increasing the temperature further to 70 °C causes the nitrate to decompose with subsequent oxidation of the organic part of the complex.

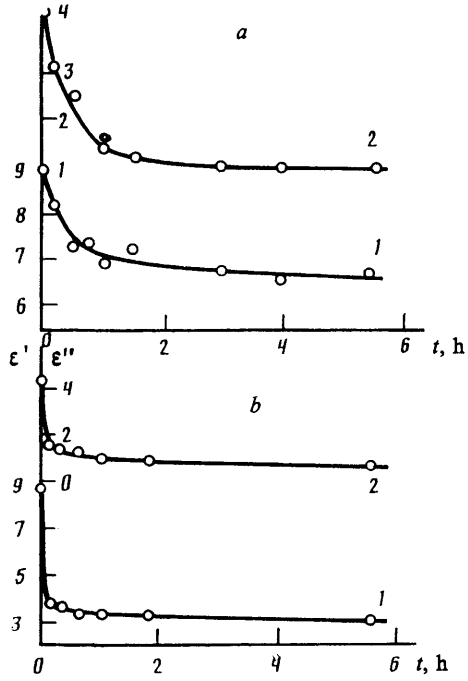


Figure 14. Dependence of change of relative permittivity ε′ (curve *1*) and ε″ (curve *2*) on time during spontaneous polymerisation in the systems [AAm]–[$Cr(NO_3)_3.9H_2O$] (*a*) and [AAm]–[$Bi(NO_3)_3.5H_2O$] (*b*). T = 20 °C. Mole ratio [AAm]:[$M(NO_3)_3.nH_2O$] = 5:1.

Investigation of the spontaneous polymerisation of AAm complexes of Cr^{III} nitrate in the presence of 2,2,4,4-tetramethylpiperidine-1-oxyl demonstrated that this process is radical in nature. The data were used to estimate the rate of initiation of the reaction, equal to 4×10^{-9} mol sec^{-1}. The dependence of the rate on the amount of water added to the system is rather unexpected. Practically the same effects are observed as adding an inhibitor to the system. The start of the reaction shifts. Its initial rate falls. The steric proximity of the polymerising complexes obviously is important for occurrence of spontaneous polymerisation.

Investigation of the properties of the product formed during spontaneous polymerisation of AAm–$Cr(NO_3)_3.9H_2O$ revealed that it contains two fractions. One of these dissolves in water at room temperature, the other does not. The insoluble part is practically pure (without metal compounds) polyacrylamide. It can be assumed that a gigantic molecular polymer forms during spontaneous polymerisation.

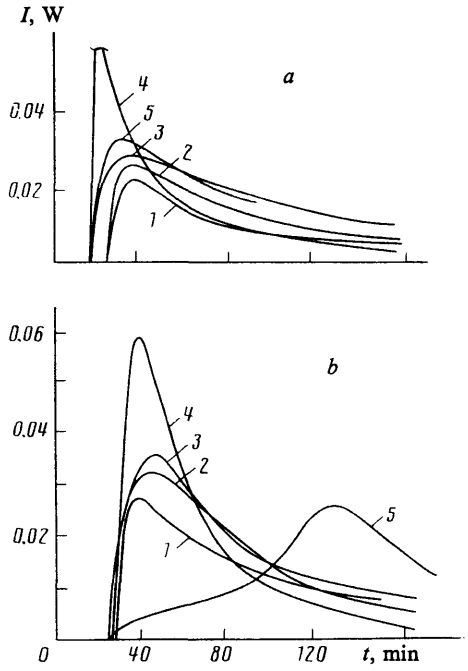


Figure 15. Dependence of rate of heat release on time of spontaneous polymerisation of AAm in the presence of $Cr(NO_3)_3.9H_2O$ with reaction mixtures of various composition: *a*) 20 °C, 0.516 g AAm; [AAm]:[$Cr(NO_3)_3.9H_2O$] ratio: *1*, 2.0; *2*, 3.0; *3*, 4.0; *4*, 5.0; *5*, 6.0. *b*) 20 °C, 0.516 g AAm, 0.10 dm^3 H_2O; [AAm]:[$Cr(NO_3)_3.9H_2O$] ratio: *1*, 3.0; *2*, 4.0; *3*, 5.0; *4*, 6.0; *5*, 8.0.

Addition of other comonomers opens broad possibilities for regulating the properties of the product formed during spontaneous polymerisation of coordinated AAm. This ability was demonstrated using AAm–$Cr(NO_3)_3.9H_2O$–CH_2=CH–CO_2H as an example. Spontaneous polymerisation is slower than homopolymerisation. The reaction is finished only after 5–7 days. However, the product is stronger. The ability to prepare copolymers of the AAm complex of metal nitrates with *N,N*-methylene-*bis*-acrylamide, methacrylic acid and *N*-vinylpyrrolidone has also been demonstrated.

The mechanism of spontaneous polymerisation of AAm complexed with metal nitrates is still largely unclear. However, the fact that the reaction occurs only using the nitrate salts suggests that nitrate is involved in the initiation.

In contrast with the example examined above, spontaneous polymerisation in DMF of vinylazoles complexed with $MnCl_2$, Mn(vinylbenzimidazole)$_2Cl_2$ and Mn(vinylbenztriazole)$_2Cl_2$, stopped after 15% conversion of MCM.[37] The reaction was inhibited by *p*-benzoquinone. Its occurrence depended strongly on the presence in the system of oxygen from air. The reaction rate increased significantly on saturation of the reaction mixture with oxygen. In

the absence of oxygen spontaneous polymerisation was not observed. It was proposed that the reaction is initiated by Mn^{3+} formed by partial oxidation of Mn^{2+}. Manganese(III) coordianted to DMF can probably be reduced by vinylazole to generate radicals that initiate spontaneous polymerisation.

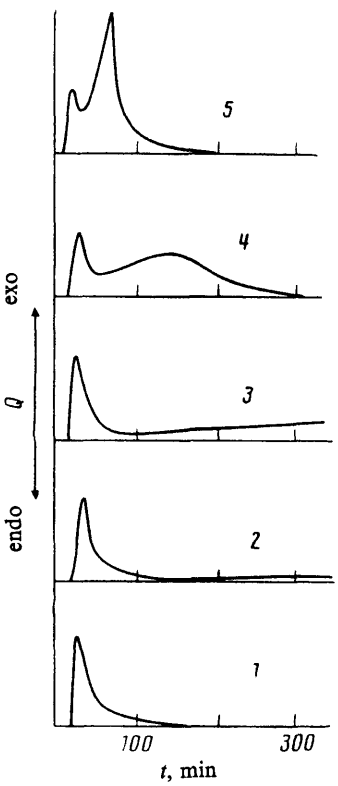


Figure 16. Dependence of rate of heat release on time of spontaneous polymerisation of AAm in the presence of $Cr(NO_3)_3.9H_2O$ at various reaction temperatures, °C: *1*, 20; *2*, 30; *3*, 40; *4*, 50; *5*, 60. m_{AAm} = 0.516 g, $m_{Cr(NO_3)_3.9H_2O}$ = 0.574, [AAm]:[$Cr(NO_3)_3.9H_2O$] = 5:1.

IX. Photopolymerisation with an applied magnetic field

A recent patent[38] claiming photopolymerisation of uranyl acrylate in alcohol with simultaneous application of a high-intensity magnetic field (10 kG) is extremely interesting. As it turned out, the process occurred at a disproportionately greater rate for ^{235}U than for ^{238}U. The insoluble polymer obtained in this way contained up to 50% of the former isotope (natural abundance ^{238}U, 99.3%; ^{235}U, 0.7%). Photopolymerisation typically did not occur without the magnetic field. This was related to the magnetic properties of the U isotopes, including the magnetic dipole of ^{235}U. Therefore, polymerisation of uranyl acrylate can be used to separate U isotopes. It should be noted that this is still the only example where the isotopic composition of the metal in the monomer affects the polymerisation properties of the MCM.

X. Conclusion

A large variety of nontraditional methods have been used to polymerise ionic and donor–acceptor MCM. It is noteworthy that the polymerisation properties of metal (meth)acrylates have been studied rather well. Nevertheless, involvement of such monomers in polymerisation by nontraditional methods enables their polymerisation properties to be more fully described. With respect to acrylamide complexes of metal nitrates, they have been practically ignored until recently. A recent surge of interest in polymerisation of complexes of traditional vinyl monomers with metal nitrates has been noted. This class of MCM is very interesting since the metal cation, the nitrate anion and the reactive double bond coexist in one molecule. Such symbiosis can lead to very unexpected effects, as evident from the material presented above. Hence, MCM based exclusively on metal nitrates participate in frontal and spontaneous polymerisation. It should also be noted that $M(NO_3)_3L_3$, where M = Fe^{III}, Cr^{III} and Co^{III} and L = vinylsulphoxide, can spontaneously explode during synthesis, storage or polymerisation to form oxides of N, S and metals and carbon-containing products.[39] The thermal explosion is caused by spontaneous polymerisation of spatially organised monomeric precursors formed by self-association of MCM through van der Waals and coordinative interactions.

Non-traditional approaches to synthesising metal-containing polymers recently have been extensively developed. This is due primarily to the desire to reduce the influence of extraneous factors that occur with traditional initiation. However, it should be remembered that a differentiated approach to the choice of MCM polymerisation method must be taken in order to account for the specific structures and properties.

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