Thermal polymerization of acrylamide during the formation of the structures of acrylamide complexes with metal nitrates

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The effects of the composition of Mn^{II}, Co^{II} or Ni^{II} nitrate hydrate — acrylamide (AAM) mixtures and of the duration of their aging at ambient temperature on the structurization of acrylamide complexes and on the character of their thermal polymerization have been studied by scanning and isothermic differential calorimetry. Structurization is a rather prolonged step in the synthesis of acrylamide complexes. The peculiarities and rate of this step are determined by the composition of the mixture and by the nature of the complex-forming compound; it yields several structural modifications of the AAM complexes. The thermal polymerization of those structural forms of acrylamide complexes that polymerize at low temperatures may be formally described as polymerization in an acrylamide—nitrate—water mixture. The effective activation energy of the polymerization of acrylamide mixed with Mn^{II} nitrate hydrate is 45 kJ mol^{-1}.

Key words: acrylamide, complexes; polymerization; differential scanning calorimetry.

In previous works we have found that the kinetics of thermal polymerization (TP) of acrylamide (AAM) bound in a complex with Co^{II} nitrate changes essentially as the conditions under which the specimen is synthesized vary.[1,2] Based on the data obtained we concluded that depending on the conditions of the synthesis and the preparation of specimens, several different hydrate forms of AAM complexes are formed, whose structures and compositions have a substantial effect on the course of TP.

It was also found that when the synthesis of AAM complexes of Co^{II} nitrate consists of the trituration of the starting AAM—metal nitrate hydrate mixture to its maximum "liquefaction", the TP in these liquid-like mixtures is recorded at a temperature 30—50 °C lower than that for the solid complexes.[2] When the "liquefied" mixture is kept at ambient temperature, it hardens with time (apparently, involving no polymerization of the monomer), which indicates the formation of crystal solvate structures incorporating AAM molecules, the metal nitrate, and, possibly, water. In the present paper, this phenomenon is referred to as structurization.

The purpose of this work has been to elucidate the effect of structurization occurring during the synthesis of AAM complexes of Mn^{II}, Co^{II}, and Ni^{II} nitrates on the kinetic characteristics of TP of complex-bonded AAM by investigating the effects of the composition of the starting mixture and the duration of structurization on the character of heat evolution during heating of the starting complexes: the number of peaks on the heat evolution curve, the integral thermal effect, the rate of TP, and the positions of regions where efficient polymerization occurs.

Experimental

The kinetics of thermal polymerization was studied by differential scanning and isothermic calorimetry. The measurements were carried out on a DSM-3 microcalorimeter ("Biopribor" special design office).

The samples for the study were prepared as follows. Fine powders of AAM and the corresponding hydrate of metal nitrate in a desired molar ratio x (x = [AAM]:[nitrate hydrate], mol mol^{-1}) were placed in a porcelain bowl and triturated for 1—2 min till its maximum "liquefaction"; then the resulting mass was stored in a closed vessel, and samples of weight 5—10 mg were withdrawn at intervals and placed into the aluminum cells of a calorimeter and sealed by a hand-operated press.

Thermograms (TG) obtained on a calorimeter operating in the scanning mode recorded the rate of heat evolution R in the samples as they were heated from 30 to 130 °C. The calorimetric procedure used allows one to go from the scanning mode to the isothermic mode and to record R over the course of time at a constant temperature. The time required to change the operation mode is no more than 0.5 min.

Results and Discussion

Monitoring the synthesis of the AAM complexes of Mn^{II}, Co^{II}, and Ni^{II} nitrates showed that the trituration of dry powders of AAM and the corresponding crystal hydrates (x = 4 : 1) initially yields a rather liquid mass, which gradually solidifies when stored in a bowl with a

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glass cover (or when further triturated). Since this storage does not completely rule out the possibility of evaporation of water, check weighings were carried out, which showed that the decrease in the weight during storage was no more than 3—5 %. This value converted to the possible evaporation of water corresponds to about 20 % of its initial content in the mixture. Therefore, we may consider that the hardening of the mixture observed during the storage is due to structurization. We may assume that a relatively substantial portion of the water evolved in the initial stage of trituration is again incorporated in the complexes, thus building them and creating various structural forms.

The change in the consistency of the samples observed as the starting composition of the mixture, x, varied was unexpected. If one assumes that the consistency of the product resulting from the trituration of a mixture is determined by the amount of water that is liberated when it is replaced by AAM molecules in the crystal hydrate, then the products obtained by the replacement of 4—6 water molecules, *i.e.*, at $x = 5 : 1$, should be the most "liquid". In the case of an excess ($x = 8 : 1$) or a deficiency ($x = 1 : 1$) of AAM, one might expect that the product would be more "sticky". Practically the opposite picture is observed in the experiments. In fact, the mixtures of compositions 1 : 1 and 2 : 1 obtained are quite liquid, and their consistency practically does not change over a period of several hours. Mixtures with a composition of 8 : 1 are rather liquid, but they gradually solidify on storage. Mixtures of composition 4 : 1 are the thickest, but they solidify on storage rather rapidly.

In our opinion, the phenomena observed could be explained by assuming that "liquefaction" of a mixture is due to the amorphization of the crystal hydrate structures of nitrate salts resulting from their contact with even small quantities of AAM (1—2 AAM molecules per mol of the hydrate salt), rather than to the chemical liberation of water from these structures. The interaction of the remaining AAM molecules with water molecules and metal ions (complex formation) most likely occurs in the already amorphized mixture. In the absence of active stirring, these processes may proceed rather slowly.

The considerable acceleration of the structurization when x increases to 4 : 1 apparently indicates that the formation of new crystal structures from the resulting amorphized liquid-like mixture requires that at least 4—6 AAM molecules be present near the metal ion. The mixtures containing 1—3 AAM molecules per metal ion remain amorphized. The decrease in the rate of structurization in 8 : 1 mixtures may be explained by the formation of structures that differ noticeably from those formed at $x = 4 : 1$.

In view of the explanation suggested one may assume that the solid structures formed from the mixture that amorphized during synthesis, probably contain no less than 4 AAM molecules, and the liquid phase probably includes complexes with 1—2 molecules of AAM. When the liquid-like mixture is kept at ambient temperature, the composition of the complexes and also the compositions of the liquid and solid phases may substantially change.

Figure 1 presents thermograms (TG) of a mixture of AAM and Ni^{II} nitrate hydrate ($x = 4 : 1$) 2 min (*1*), 20 min (*2*), 60 min (*3*), and 50 h (*4*) after stirring of the mixture was stopped. The exothermic effects observed on the TG indicate that in the samples studied, polymerization of AAM occurs. TP of the AAM complexes exhibits several peaks of heat evolution. This indicates that the specimens contain several forms of the AAM complexes of Ni^{II} nitrate have different temperature ranges in which polymerization of each of them is the most efficient. At least three regions can be distinguished: the region where the maximum rate of heat evolution is at 60 °C (region I), the region where the maximum rate is at 75 °C (region II), and the region where the maximum rate is at 105 °C (region III). The modifications of the AAM complex that polymerize in these temperature ranges have been denoted as modification I, II, and III, respectively.

The overall thermal effects measured in the thermograms (see Fig. 1, curves *1*—*4*) and the heats of polymerization calculated from them practically coincide with one another and correspond to a degree of polymerization of AAM of 80—90 %. This suggests that the

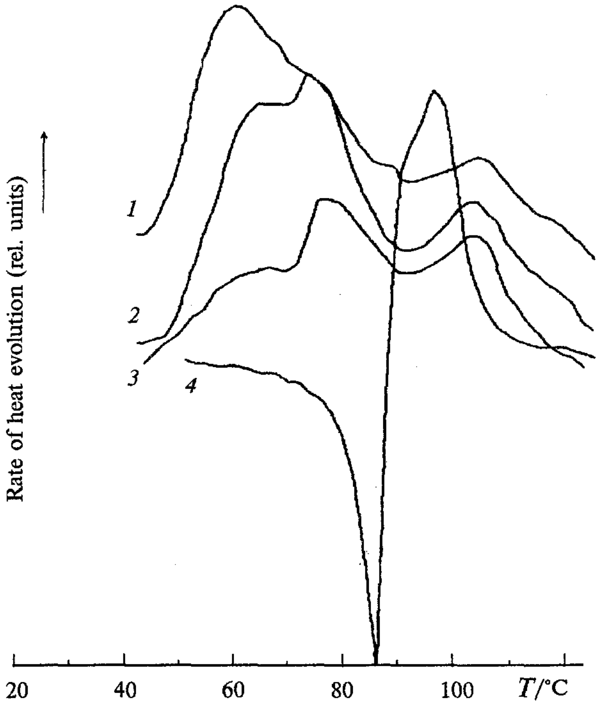

Fig. 1. Thermograms of heating for specimens of a mixture of AAM with the hydrate of Ni^{II} nitrate recorded after 2 (*1*), 20 (*2*), and 60 (*3*) min and 50 h (*4*) of aging of the mixture after its preparation. The rate of scanning was 4 deg min^{-1}.

ratios between the heat evolution in the three above-mentioned temperature regions observed on TG *1—4* correspond to the relative proportions of the I, II, and III forms of the AAM complexes of Ni^{II} nitrate in each of the specimens studied. As one can see, the proportions of these complexes in the starting specimens noticeably change with time after stirring is stopped.

In the initial minutes after the completion of stirring form I predominates (*1*); when the specimen is kept at ambient temperature for 20 min, the proportion of form I appreciably decreases (*2*), and after 1 h, form II becomes the prevailing form. After the mixture is aged at ambient temperature for 50 h, it polymerizes efficiently in the region attributed to modification III (*4*). This specimen mostly consisting of modification III undergoes an endothermic transformation at 80—85 °C, which should apparently be assigned to the melting of the completely formed solid AAM complex of Ni^{II} nitrate (see Refs. 1 and 5).

From the data presented, one may conclude that structural forms I and II that arise during TP are unstable at ambient temperature and are gradually transformed into III, which remains practically unchanged after a period of several months. (Obviously it was modification III of the AAM complex of Ni^{II} nitrate that we have studied previously.[1,3]) The synthesis of the AAM complexes of Ni^{II} nitrate involves the formation of structural form III from the liquid-like mixture; it forms rather slowly, probably passing through forms I and II. The structural organization of the mixture and of the hydrated AAM complexes of Ni^{II} nitrate is an important factor in the TP, similarly to the TP of the previously studied[2] AAM complexes of Co^{II} nitrate. The displacement of the temperature region of the active polymerization of AAM in different forms of this mixture is 30—50 °C. Since during the first minutes after stirring is terminated (see Fig. 1, curve *1*), intense polymerization of the specimen that has a more liquid consistency occurs at the lowest temperature, the increase in the temperature of the polymerization of AAM in modifications II and III may be due to either "bonding" of AAM molecules into complexes, which persists after the termination of stirring, or structurization of the amorphized part of the mixture.

Figure 2 shows the TG of mixtures of AAM with hydrates of Ni^{II} nitrates (*1—3*) or Mn^{II} nitrates (*4—7*) 1 h after they are prepared at compositions of the mixture of 1 : 1 (*1, 4*), 2 : 1 (*2, 5*), 4 : 1 (*6*), and 8 : 1 (*3, 7*). The most important conclusion from the data presented in Fig. 2 is that the thermal polymerization of AAM occurs efficiently in mixtures of various compositions at substantially different consistencies of the samples. Calculations of the thermal effects show that the degree of polymerization of AAM at 50—120 °C is ~80—90 % in all of the systems studied. This means that in the presence of nitrates, the AAM molecule is efficiently involved in polymerization, irrespective of the composition of the complex incorporating it. However, the temperatures at which TP is observed and the shapes and numbers of the heat evolution peaks on the TG corresponding to the mixtures differing in compositions and complex-forming compounds are substantially different. Polymerization of AAM mixed with Ni^{II} nitrates in liquid samples with a composition of 2 : 1 is efficient at 50 °C (see Fig. 2, curve *2*), while that in mixtures with Mn^{II} nitrate is efficient at 70 °C (see Fig. 2, curve *5*); in samples with a composition of 8 : 1, polymerization of AAM mixed with Ni^{II} nitrate occurs at 60 °C, and that for Mn^{II} nitrate is observed at 100 °C. In 4 : 1 mixtures of AAM with Mn^{II} nitrate (see Fig. 2, curve *6*), relatively rigid structures, which apparently melt in the 75—80 °C region, are formed after 1 h. In AAM mixtures with Ni^{II} nitrate of the same composition (see Fig. 1, curve *3*) structurization is not completed in the same period.

Despite the diversity of the structural forms produced and their essential effect on TP, we could elucidate the following general tendency: the more liquid the consistency of the specimen under study, the lower the temperature at which its polymerization occurs; higher temperature regions of polymerization are characteristic of more structurized specimens. It is reasonable to assume that a decrease in the viscosity of the reaction medium is a significant condition for the occurrence of

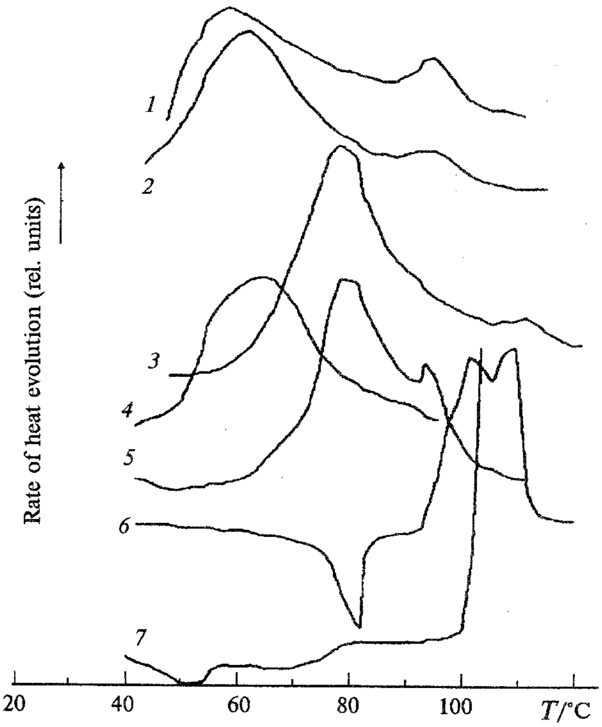

Fig. 2. Thermograms of heating for mixtures of AAM with hydrates of Ni^{II} nitrate (*1—3*) and Mn^{II} nitrate (*4—7*) 1 h after their preparation. Compositions of the mixtures: 1 : 1 (*1, 4*), 2 : 1 (*2, 5*), 4 : 1 (*6*), 8 : 1 (*3, 7*). The rate of scanning was 4 deg min^{-1}.

TP; the fact that no polymerization of structurized specimens is observed at low temperatures is probably due to the fact that their viscosities noticeably decrease only at elevated temperatures. The temperature of the amorphization of structurized specimens is obviously determined by the nature of the metal and the chemical and phase composition of the mixture. The presence of several structural modifications of AAM complexes in a specimen can manifest itself as their successive softening at different temperatures.

The above-stated suggestion that the specimens must be softened before their TP occurs is also supported by the following. When the cells were opened after TP, the polymeric products always looked like transparent uniformly colored films irrespective of the initial concistency of the corresponding monomeric specimens, which indicates that the TP occurs in a homogeneous and, possibly, relatively liquid mass. The data presented allow one to formally regard the thermal polymerization of AAM complexes as polymerization of AAM in solutions. In this case, polymerization of AAM is most likely initiated by nitrogen dioxide resulting from the hydrolysis of metal nitrates in aqueous solutions, as has been shown[4] for the spontaneous polymerization of AAM mixed with Ca^{II} nitrate. This assumption makes it possible to compare the polymerization properties of AAM in mixtures with different complex-forming compounds having various compositions and consistencies by comparing the measured rates of polymerization normalized to the concentrations of the nitrate and AAM, R_{red}.

Figure 3 shows the correlation between the values of R_{red} for mixtures of AAM with hydrates of Mn^{II}, Co^{II}, and Ni^{II} nitrates of various compositions (1 : 1 to 8 : 1) and the temperature in the coordinates of the Arrhenius equation. The maximum rates observed in the isothermic operation mode of the calorimeter are taken as R_{red}. The temperatures at which the R_{red} values given in Fig. 3 were determined correspond to the initial section of the lowest temperature region of polymerization for each of the mixtures studied.

As the data presented imply, the R_{red} values determined by this method obey the Arrhenius dependence. The greatest interval of the variation of temperature can be observed for mixtures of AAM with Mn^{II} nitrate hydrate (see Fig. 3, curve *1*). Thermal polymerization of AAM in these mixtures, whose composition varies from 1 : 1 to 8 : 1, can be described by the Arrhenius equation (the straight line in Fig. 3) with an effective activation energy of ~45 kJ mol^{-1}.

The E_{eff} values for AAM mixtures with Ni^{II} hydrates (see Fig. 3, curve *3*) and Co^{II} hydrates (see Fig. 3, curve *2*) determined in a similar way were 28 and 21 kJ mol^{-1}, respectively. The accuracy of the determination of these values, especially in the case of Co^{II} hydrate, is substantially lower, and the resulting values are only approximate estimates. It should be noted that in these systems, the points shown in Fig. 3 are characteristic of the TP of mixtures whose composition varies over wide limits. The TP of AAM observed in the lowest temperature region for all of the systems studied exhibits virtually no selectivity with respect to any particular optimal composition of the mixtures. This fact, together with the data presented previously, confirms that within the above-specified limits, polymerization of the AAM incorporated in complexes with metal nitrates may be regarded as polymerization in a solution.

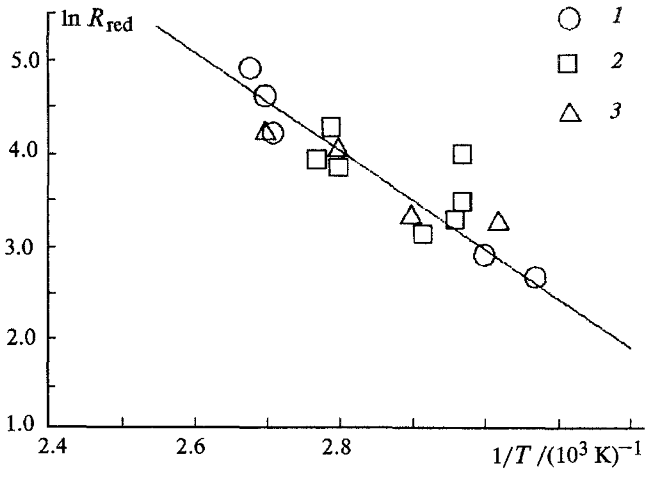

Fig. 3 The temperature dependence of the reduced rates of the TP of AAM (R_{red}) for modifications of AAM complexes of Mn^{II} (*1*), Co^{II} (*2*), and Ni^{II} (*3*) nitrate polymerizing at low temperatures. The composition of the initial mixtures varied from 1 : 1 to 8 : 1.

Considering the data shown in Fig. 3, we should note that in this case, we compare the rates of polymerization of AAM in the structural forms that polymerize at the lowest temperatures, and the E_{eff} values obtained characterize the TP in all of the systems (with different compositions and different concentrations of components) at low degrees of conversion. The other regions of polymerization observed at higher scanning temperatures may be characterized by different activation energies. The mechanism of the initiation and growth of the polymer chain in higher temperature regions may differ essentially from that discussed in the present paper. In fact, the value of E_{eff} calculated by us previously[1] for the TP of AAM bound in complexes with Ni^{II} nitrate having structural modification III amounted to 151 kJ mol^{-1}, which is much larger than the value determined in this work for the structural form that polymerizes at lower temperatures.

We introduced the concept of structural forms or modifications of AAM complexes[1,2] in order to account for the existence of several temperature regions of the polymerization of complex-bonded AAM on heating. The data presented in Figs. 1 and 2 indicate that even after prolonged aging at ambient temperature the specimens synthesized are mixtures of modifications that behave rather independently during TP. The differences may result from dissimilar chemical compositions of the complexes. However, the results of this work make it possible to suggest that the effect of the structural modifications of the complexes on the polymerization properties of systems can be practically reduced to the difference in the temperature at which the viscosity necessary for the efficient polymerization of AAM in amorphized mixtures is achieved. This can be said with confidence for, at least, the lowest temperature region of polymerization of AAM in the formation of the structures of the AAM complexes with Mn^{II}, Co^{II}, and Ni^{II} nitrates.

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References

1. D. A. Kritskaya, V. S. Savost'yanov, and A. N. Ponomarev, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1410 [*Russ. Chem. Bull.*, 1993, **42**, 1344 (Engl. Transl.)].
2. D. A. Kritskaya, V. S. Savost'yanov, and A. N. Ponomarev, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1414 [*Russ. Chem. Bull.*, 1993, **42**, 1348 (Engl. Transl.)].
3. V. S. Savost'yanov, A. D. Pomogailo, G. P. Belov, D. A. Kritskaya, and A. N. Ponomarev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 1015 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 905 (Engl. Transl.)].
4. N. P. Piven', V. S. Savost'yanov, S. D. Babenko, and A. N. Ponomarev, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 534 [*Russ. Chem. Bull.*, 1994, **43**, 494 (Engl.Transl.)].

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