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Estimation of the aluminum salt effect on homopolymerization of acrylamide and its copolymerization with acrylic acid by DSC

RAPID COMMUNICATION

Summary — The estimation of thermal effects occurring during the homopolymerization of acrylamide (AAm) and acrylic acid (AA) and their copolymerization in aqueous solutions at 40 °C in the presence of aluminum salt has been performed on the basis of DSC measurements. The presence of AA in the reaction system reduces the total heat effect of the copolymerization and indicates the reduction of the final conversion. The influence of the aluminum sulfate added in two concentrations (0.04 and 0.33 mol %) and changes in positions of polymerization peak maxima in comparison to the polymerization peaks of the neat monomers were registered. Aluminum sulfate causes retardation of AAm homopolymerization by shifting the position of exothermal peaks to longer polymerization times as compared to the neat homopolymerization reaction. On the other hand the aluminum salt seems to have a beneficial effect on the AA homopolymerization under the experimental conditions. The exothermal peaks of the monomer mixture copolymerizing in the presence of aluminum sulfate were found to be significantly shifted in comparison to those for AAm homopolymerization peaks in neat as well as in AAm/Al salt system.

Key words: acrylamide, acrylic acid, aluminum sulfate, thin-layer polymerization, differential scanning calorimetry.

ZASTOSOWANIE DSC DO OCENY WPŁYWU SOLI GLINU NA HOMOPOLIMERYZACJĘ AKRYLOAMIDU I JEGO KOPOLIMERYZACJĘ Z KWASEM AKRYLOWYM

Streszczenie — Metodą DSC przeprowadzono ocenę efektów cieplnych towarzyszących reakcji wolnorodnikowej homopolimeryzacji akryloamidu (AAm) oraz kwasu akrylowego (AA), a także ich kopolimeryzacji w wodnych roztworach w temperaturze 40 °C, w obecności soli glinu (rys. 1—3). Stwierdzono, że obecność AA w układach reakcyjnych zmniejsza całkowity efekt cieplny (ko)polimeryzacji, co wskazuje na mniejszą konwersję monomerów. Zbadano wpływ dwóch stężeń siarczanu glinu: 0,04 oraz 0,33 % mol; zaobserwowano przesunięcia w kierunku wyższych wartości czasu maksimów egzotermicznych pików odpowiadających kopolimeryzacji, w stosunku do położeń pików reakcji homopolimeryzacji AAm (tabela 1 i 3). Siarczan glinu wykazywał działanie opóźniające przebieg reakcji homopolimeryzacji AAm (tabela 1). Natomiast jego obecność (szczególnie przy wyższym stężeniu) wydaje się sprzyjać reakcji homopolimeryzacji AA (tabela 2), bowiem w warunkach testów DSC (40 °C) wodny roztwór tego monomeru (niezawierający soli) praktycznie nie ulega konwersji do polimeru.

Słowa kluczowe: akryloamid, kwas akrylowy, siarczan glinu, polimeryzacja w cienkiej warstwie, różnicowa kalorymetria skaningowa.

Water soluble acrylamide polymers find applications in a number of fields *e.g.* as flocculants and water treatment agents in waste-water disposal, thickening and binding agents in paint and lacquer industry, adhesives and lubricants reducing friction in aqueous systems and in paper and extractive industries (components of drilling fluids) [1—6].

Acrylamide (AAm) polymerization reactions are usually carried out in aqueous solution. The major technological problems associated with the polymerization reaction of the monomer in the aqueous environment are:

— highly exothermic character of the reaction and difficulties associated with the process control during solution polymerization at higher monomer concentrations,

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— carcinogenic character of AAm monomer forcing to minimize its residue in the raw polymer product,

— hydrophilic character of the polymer which hinders the water removal.

Besides the traditional methods of AAm polymerization reaction in the aqueous systems *i.e.* in solution, suspension, emulsion or a modification of the latter methods [7—9] — polyacrylamide can be also synthesized by unconventional methods, without or with a minimized amount of solvent.

An example of AAm polymerization reaction without the solvent is frontal polymerization. In such type of the reaction, a high exothermic character of this polymerization is used for the formation of self-sustaining front of the reaction. After the initiation with a source of heat at high temperature (about 200 °C) the polymerization process spontaneously runs on. Research on the frontal acrylamide polymerization, including the acrylamide monomers in the form of the metal cation complexes was performed among others by: Savostyanov *et al.* [10], Pojman *et al.* [11] and Davtyan *et al.* [12]. This mode of polymerization should significantly influence the cost reduction by elimination of solvent removal step. On the other hand, high temperatures used in the polymerizing system cause the changes in the polymer chain structure, thus disadvantageously affecting the hydrophilicity of the polymer [13]. Technological solutions of AAm frontal polymerization process are not known yet.

Other variant of AAm polymerization in which the conventional reactors are not required, includes the processes carried out in a thin-layer. These reactions are initiated by persulfates, redox systems and UV or γ radiation [14, 15]. The final heat effect of the polymerization under given experimental conditions is a key factor of such process.

Acrylamide polymers serve as very efficient synthetic flocculants for water treatment. The reason why such monomer(s)/inorganic salt system has been investigated is based on earlier findings that acrylic acid polymers form complexes with some multivalent metal cations and these complexes show promising flocculation features [16].

The aim of the work was to investigate, using DSC, the heat effects during a thin-layer acrylamide homopolymerization and its copolymerization with acrylic acid in the presence of aluminum salt. Recently this technique was employed to study a similar polymerization reaction *i.e.* the synthesis of hydrophilic acrylic acid polymers [17].

EXPERIMENTAL

Materials

Acrylamide (AAm, ~99 %, Fluka), acrylic acid (AA, ~98 %, Aldrich) and ammonium persulfate [$(NH_4)_2S_2O_8$, ~98 %, POCh, Gliwice] as an initiator were used. Aluminum sulfate [$Al_2(SO_4)_3 \cdot 18\ H_2O$, purchased from POCh Gliwice (~98 %)], was used as received.

Polymerization

The homopolymerization reactions were carried out in an aluminum DSC pan. The heat effects accompanied the polymerization were registered using differential scanning calorimeter (DSC Q 100, TA Instruments, USA). Aqueous solution (50 wt. %) of the AAm or AA monomer containing 1 wt. % of radical initiator and aluminum sulfate (0.04 or 0.33 mol % based on the monomer) were placed in open DSC pan. The sample weight was about 5 mg and the average thickness of the layer was about 300 µm. Thus, the polymer was obtained in the form of a thin film. The isothermal reaction at temp. 40 °C was run for 20 min under nitrogen flow 50 cm^3/min. The "stand by" temperature of DSC apparatus was 35 °C. Registration of the polymerization heat begun when the DSC cell has been closed. The care was taken to keep the same time lag between the mixing of the reagents and placing the sample pan with the weighted sample into the chamber. The copolymerization of AAm with AA (70/30 mol/mol) was carried out in the same way.

In order to obtain reliable data each experiment was repeated five times.

RESULTS AND DISCUSSION

A thin-layer AAm homopolymerization begins after about 6—7 minutes of the reaction at temp. 40 °C, which can be seen in exemplary thermograms shown in Fig. 1. The addition of aluminum salt to acrylamide aqueous

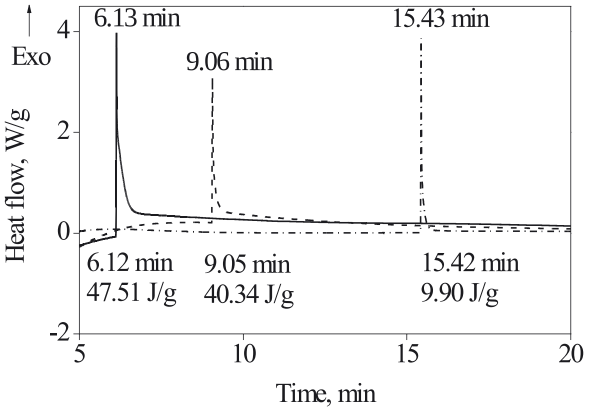

Fig. 1. DSC thermograms of selected acrylamide homopolymerizations (Table 1); solid line — AAm homopolymerization without $Al_2(SO_4)_3 \cdot 18H_2O$ (series 5), dashed line — AAm homopolymerization in the presence of 0.04 mol % of $Al_2(SO_4)_3 \cdot 18H_2O$ (series 3), dashed-dotted line — AAm homopolymerization in the presence of 0.33 mol % of $Al_2(SO_4)_3 \cdot 18H_2O$ (series 4)

solution retards the homopolymerization reaction. The exothermal peaks appear after *ca.* 9 min on the curve corresponding to lower aluminum salt concentration or even above 15 min in one case of higher aluminum sulfate content.

Table 1. Position of exothermal peak maximum of AAm homopolymerization

Series	Time, min		
	AAm homopolymerization	AAm homopolymerization in the presence of 0.04 mol % of $Al_2(SO_4)_3 \cdot 18H_2O$	AAm homopolymerization in the presence of 0.33 mol % of $Al_2(SO_4)_3 \cdot 18H_2O$
1	5.44	7.42	12.46
2	8.53	9.46	7.34
3	7.59	9.06	8.59
4	6.64	9.15	15.43
5	6.13	10.96	8.61
Mean	6.9 ± 23 %	9.2 ± 19 %	10.5 ± 47 %

In Table 1 the data of the positions of the exothermal peaks for AAm homopolymerization and reactions carried out in the presence of two aluminum sulfate concentrations are presented for the five experiment repetitions. It can be seen that the addition of 0.04 mol % of aluminum sulfate shifts the maximum of the exothermal peak approximately from 6.9 to *ca.* 9.2 min. A subsequent increase in the salt content in the reaction system (up to 0.33 mol %) shifts the maximum of the thermal effect in a similar way; however, the scatter of the position of the peak maximum is twice as high as that for AAm homopolymerization without or with a low amount of the salt.

Table 2. Position of exothermal peak maximum of AA homopolymerization

Series	Time, min		
	AA homopolymerization	AA homopolymerization in the presence of 0.04 mol % of $Al_2(SO_4)_3 \cdot 18H_2O$	AA homopolymerization in the presence of 0.33 mol % of $Al_2(SO_4)_3 \cdot 18H_2O$
1	absence of maximum	absence of maximum	7.32
2			4.48
3			absence of maximum
4			
5			7.51
Mean	—	—	6.44 ± 30 %

Independent tests of the AAm homopolymerization by a thin-layer method which were performed on a larger scale (on the belt) at the same temperature showed a high monomer conversion (>90 %) to the polymer [18].

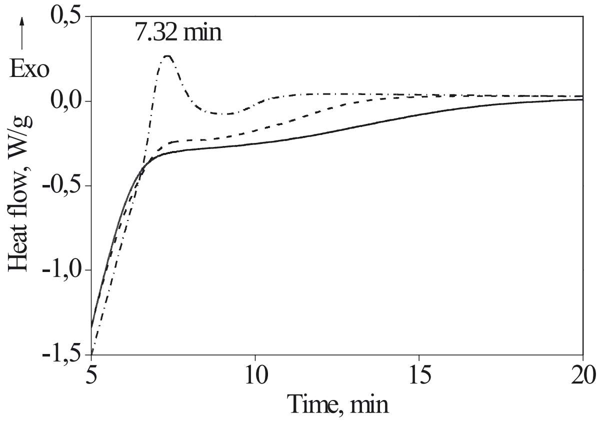

Fig. 2. DSC thermograms of selected acrylic acid homopolymerizations (Table 2, series 1); solid line — AA homopolymerization without $Al_2(SO_4)_3 \cdot 18H_2O$, dashed line — AA homopolymerization in the presence of 0.04 mol % of $Al_2(SO_4)_3 \cdot 18H_2O$, dashed-dotted line — AA homopolymerization in the presence of 0.33 mol % of $Al_2(SO_4)_3 \cdot 18H_2O$

On the other hand AA homopolymerization under DSC test conditions practically does not occur both of neat AA as well as in the presence of lower salt concentration *i.e.* 0.04 mol % (Tab. 2). However, at higher aluminum salt content (0.33 mol %) the appearance of exothermal peaks after *ca.* 4.5—7.5 min (Tab. 2 and Fig. 2) can be observed.

Customarily the polymerization of aqueous AA solutions is performed at higher temperatures and distinct exothermic peaks can be observed during DSC measurements (see data in ref. [17] for the processes performed in the temperature range of 70—95 °C).

Table 3. Position of exothermal peak maximum of AAm/AA (0.7/0.3 mol/mol) copolymerization

Series	Time, min		
	AAm/AA (0.7/0.3 mol/mol) copolymerization	AAm/ AA copolymerization in the presence of 0.04 mol % of $Al_2(SO_4)_3 \cdot 18H_2O$	AAm/ AA copolymerization in the presence of 0.33 mol % of $Al_2(SO_4)_3 \cdot 18H_2O$
1	5.82	absence of maximum	absence of maximum
2	absence of maximum	17.07	16.69
3		19.60	absence of maximum
4		23.44	
5		10.75	13.44
Mean	—	17.71 ± 61 %	15.06 ± 12 %

Figure 3 and Table 3 presents DSC results of the copolymerization of AAm with AA without and in the presence of aluminum sulfate. The thermograms of AAm/AA copolymerization (70/30 mol/mol) without a salt exhibit no exothermal peaks (with exception of series 1, see Table 3) within the range of the reaction times observed for AAm homopolymerization. On the other hand, from independent thin-layer tests performed in larger scale it was found that the copolymerization of AAm/AA mixture occurs, but the reaction time (4 h 30

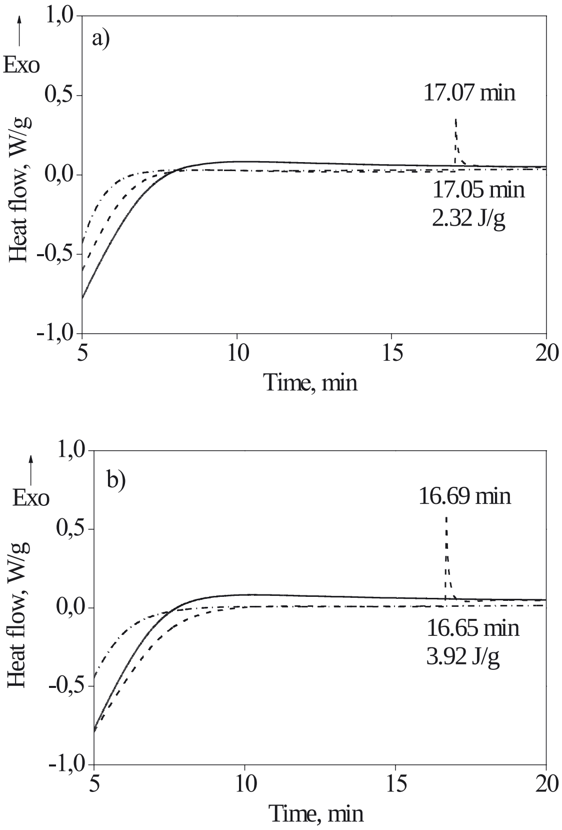

Fig. 3. DSC thermograms of selected AAm/AA copolymerizations (Table 3) in the presence of $Al_2(SO_4)_3 \cdot 18H_2O$: a) 0.04 mol % and b) 0.33 mol % in comparison with AAm/AA copolymerization without $Al_2(SO_4)_3 \cdot 18H_2O$ (series 2, solid line); dashed line — AAm/AA copolymerization in the presence of $Al_2(SO_4)_3 \cdot 18H_2O$ (series 2), dashed-dotted line — AAm/AA copolymerization in the presence of $Al_2(SO_4)_3 \cdot 18H_2O$ [a) — series 1 and b) — series 4]

min) is much longer than of the AAm homopolymerization (20 min) [18].

However, in the presence of 0.04 mol % of aluminum sulfate slight exothermal peaks appear in the range of 17—23 minutes (average 17.7 minutes based on four of five experiments) (Fig. 3, Tab. 3). The results obtained in the presence of the higher aluminum salt concentration (0.33 mol %) are not consistent (Table 3). Despite the absence of polymerization exotherm for the three experiments, in the rest of cases the time needed to reach the peak maximum was shorter than in the presence of 0.04 mol % of the aluminum salt, which may suggest that also the higher amount of the salt added can be beneficial for the copolymerization.

Concluding, it was found that the addition of the aluminum sulfate salt to the aqueous solution of AAm retards its polymerization. On the other hand, both AA and its mixture with AAm, which do not (co)polymerize in aqueous solution under conditions used in this work, begin polymerize in the presence of the aluminum salt.

It is known that reactivity ratios depend on the pH [19]. For solution polymerization, with pH increasing from 2 to 6, the reactivity ratio of acrylamide increases from 0.48 to 1.32, whereas that of acrylic acid decreases from 1.73 to 0.35 [19]. From the independent research it is also known that Al^{3+} and water interact following the equation described by Zhao *et al.* [20]:

$$[(H_2O)_5Al(OH_2)]^{3+} \rightarrow [(H_2O)_5Al(OH)]^{2+} + H^+$$

causing the changes of pH of the (co)polymerizing mixture. That could be an explanation for registered results in our experimental conditions.

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