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SYNTHESIS AND PROCESSING OF POLYMERIC COMPOSITES

THE INFLUNCE OF TEMPERATURE MODE ON KINETICS OF SODIUM METHACRYLATE AND METHACRYLIC ACID AMIDE COPOLYMERIZATION

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Experimental studies of sodium methacrylate and methacrylamide copolymerization in aqueous solutions with a total monomer content of 34–50% were accomplished. Potassium persulfate was used as the initiator. Three variants of the process operation conditions were investigated: isothermal, quasi-isothermal and adiabatic. The effect of temperature, initial concentration of monomers and initiator on the rate of copolymerization, the extent of monomers conversion, the duration of the process, the reaction mass viscosity were studied under isothermal conditions. The copolymerization takes place at a constant rate at all temperatures in the range of 55– 80°C until conversion is less than 70%. This behavior is typical for the polymerization system with initial total concentration of monomers of about 4.4 mol·L^{-1} and above. It is found that the reaction rate is directly proportional to the initial concentration of the reaction system. Increasing temperature reduces the viscosity of a 1% aqueous solution of the product, thus reducing the average molecular weight of the copolymer. By means of studying the copolymerization under adiabatic conditions the dependences of the monomers conversion degree, the viscosity of a 1% aqueous solution of the product and the reaction mass temperature upon copolymerization time were obtained. In the adiabatic mode the monomers conversion is less than 70%, the viscosity of a 1% solution of the reaction mass is approximately 13·10^{-6} m^2/s, and the temperature rises to ~ 120°C. The product is a polymer gel, water-swellable and soluble in an aqueous alkaline medium. The quasi-isothermal mode of copolymerization with the same duration allows obtaining the degree of conversion of about 94% and a viscosity of the reaction mass of about 400·10^{-6} m^2/s. An important advantage of the copolymer obtained in the quasi-isothermal mode as compared to that obtained in the adiabatic conditions is complete water solubility. Based on experimental results, the recommended conditions for the sodium methacrylate and methacrylamide copolymerization are as follows: the monomers concentration in the reaction mass is 5.55–6.75 mol·L^{-1}; initiator concentration is 2·10^{-3} – 6·10^{-3} mol·L^{-1}; copolymerization temperature is 55–65°C.

Keywords: *water-soluble polymers, acrylic polymers, sodium methacrylate, methacrylamide, copolymerization.*

Introduction

Water-soluble polymers and copolymers based on acrylic and metacrylic acid derivatives have a vast complex of useful consumer properties. They are widely used in various areas of technology as thickeners of solutions, glues, paints and varnishes, surfactants, coagulants, sizing agents, etc. The copolymerization of sodium methacrylate (SMA) with methacrylamide (MAA) in aqueous solutions gives a water-soluble copolymer important in practice, an effective stabilizer of drill fluids [1, 2]. Besides, it found application as an effective absorber of hydrophilic metal complexes, such as $CdCl_2$, $ZnCl_2$ and NaH_2AsO_4 metalloid, from water [3]. When obtaining a firm commercial form of the polymer, the final stage is drying. In order to reduce power consumption for moisture removal it is expedient to carry out the synthesis in concentrated solutions of the initial monomers.

The kinetics of SMA copolymerization with MAA has already been a subject of research. The authors of publications [4, 5] studied the initial stage of the process in dilute solutions. The relative activities of the monomers for the copolymerization in concentrated solutions were determined in [6]. Article [7] suggests a mathematical model of the process, and article [8] presents a method for calculating the composition of this polymerization system. However, the results of the experiments carried out in the classical form by no means can always be applied to conditions of real technology, where the process is carried out in concentrated solutions up to high conversion degrees of the initial monomer.

Previously, we have carried out research on the kinetics of polymerization of water-soluble polymers in concentrated aqueous solutions with polyacrylamide as an example [9, 10]. In order to find out general regularities of the polymerization of various water-soluble polymers in concentrated aqueous solutions, the kinetics of SMA copolymerization with MAA was studied in this work. One of the research problems was to bring to light the effect of the temperature mode on the copolymerization kinetics.

Experimental

Potassium persulphate (PPS) was used as an initiator. Sodium methacrylate was obtained immediately before the copolymerization by the interaction of methacrylic acid with an aqueous solution of sodium hydroxide. Then a mixture of monomers of the predetermined molar ratio was prepared. A solution of the initiator was added to the mixture. The obtained reaction mixture was placed into aluminum ampoules, and the latter were located in a liquid thermostat. Water circulation in the thermostat provided intensive heat exchange. The low thermal resistance of the ampoule wall and of the polymerization mixture provides sufficiently exact temperature maintenance. The ampoules were removed from the thermostat one-by-one at predetermined timepoints and quickly cooled to stop the reaction. Then their content was analyzed. The total concentration of the monomers was determined by the bromide-bromate method [11], and the change in the system rheological properties was estimated by the flow time of a 1% aqueous solution of the reaction mass in a capillary viscosimeter.

At the first stage the study of kinetics of SMA copolymerization with MAA was carried out in isothermal conditions in the temperature range of 55–80°C at total concentration of the monomers in the aqueous medium of 3.8–6.75 mol·l^{-1}. The concentration of the initiator (PPS) was varied in the range of $3\cdot10^{-3}$–$12\cdot10^{-3}$ mol·l^{-1}. The molar ratio of the monomers was 1:1.

In practice it is rather difficult to remove the reaction heat completely and to provide the isothermal mode. So, we checked the possibility of obtaining the SMA–MAA copolymer in adiabatic conditions and upon partial removal of the reaction heat. In these experiments the reaction mass was a 50% aqueous solution of the monomers (5.55 mol·l–1). PPS was used as an initiator in the amount of 0.3% of the monomers mass. The reaction mass was prepared at 55°C.

Results and Discussion

Figure 1 presents the results of experimental studies characterizing the effect of temperature on the kinetics of SMA copolymerization with MAA at the same initial total concentration of the monomers.

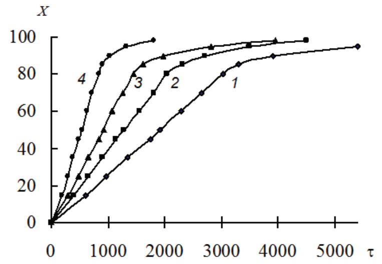

Fig. 1. Dependence of the monomers conversion degree X (%) on the copolymerization time τ (s). Temperature t (°C): 1 – 55, 2 – 60, 3 – 65, 4 – 80. Initial concentration of the monomers C_0 = 5.55 mol·l^{-1}. Initiator concentration I = 5.95·10–3 mol·l^{-1}.

The copolymerization proceeds practically at a constant rate at all temperatures in the studied range up to a conversion degree of about 70%. When the concentration of the monomers decreases, this is possible if the rate of chain termination continuously decreases due to the increase in the reaction mass viscosity. When the conversion of the monomers is higher than 80%, the process rate starts decreasing rapidly.

The curves in Fig. 2 characterize the dependence of polymerization rate on the current concentration of the monomers in the reaction mass at various initial concentrations of the monomers. The curves have regions of constant process rate beginning from the initial concentration of monomers ~ 4.4 mol·l^{-1} and higher. It is obvious that the diffusive control of the reactions with the participation of macromolecules, particularly, of chain termination reactions, takes place even at the initial stage of the copolymerization.

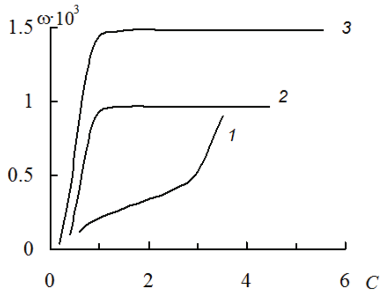

Fig. 2. Dependence of polymerization rate ω (mol·(l·s)$^{-1}$) on the monomers concentration in the reaction mass C (mol·l^{-1}). Initial concentration of the monomers C_0 (mol·l^{-1}): 1 – 3.81, 2 – 4.4, 3 – 5.55. Temperature t = 65°C. Initiator concentration I = $5.95\cdot10^{-3}$ mol·l^{-1}.

It follows from the graphs in Figure 3 that the increase in the initial concentration of the initiator in the reaction system allows to considerably reduce the process time. The increase in PPS concentration from $3 \cdot 10^{-3}$ to $6 \cdot 10^{-3}$ mol·l^{-1} leads to a decrease in polymerization time by a factor of 2.2. Further additional 2-fold increase in PPS concentration (to $12 \cdot 10^{-3}$ mol·l^{-1}) reduces the process time by a factor of 1.7. At the same time it should be considered that increasing the initiator concentration leads to a decrease in polymerization degree.

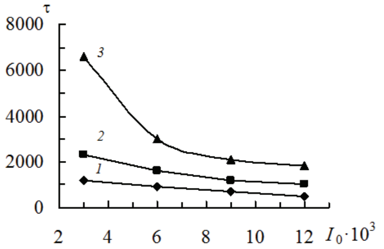

Fig. 3. Dependence of the process time τ (s) on the initial concentration of the initiator I0 (mol·l^{-1}). Conversion X (%): 1 – 45, 2 – 80, 3 – 95. t = 65°C.

Figure 4 presents curves characterizing the change in the viscosity of a 1% aqueous solution of the obtained product depending on the copolymerization time and on its temperature. It follows from the curves that the temperature increase leads to a decrease in the viscosity of the 1% aqueous solution of the product, i.e., to a decrease in the average molecular weight of the obtained copolymer. This should be considered when determining the optimum process conditions.

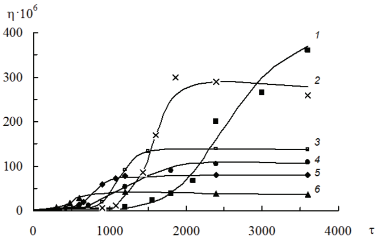

Fig. 4. Dependence of the viscosity $\eta \cdot 10^6$ (m^2·s^{-1}) of a 1% aqueous solution of the reaction mass on the copolymerization time τ (s). Temperature, ºC: 1 – 55, 2 – 60, 3 – 65, 4 – 70, 5 – 75, 6 – 80. C_0 = 5.55 mol·l^{-1}, $I_0 = 5.95 \cdot 10^{-3}$ mol·l^{-1}, M_1:M_2 = 1.

The above pertains to the results of experiments under isothermal conditions.

Figure 5a presents dependences of conversion degree (1), viscosity of a 1% aqueous solution (2) and temperature (3) of the reaction mass on copolymerization time in adiabatic conditions. The reaction proceeds at a high rate, which is caused by the fast increase of temperature in the reaction volume. When a conversion degree of ~ 50% is attained, the reaction mass temperature increases to ~ 100 °C, and the viscosity of a 1% aqueous solution becomes equal to ~ $20 \cdot 10^{-6}$ m^2·s^{-1}.

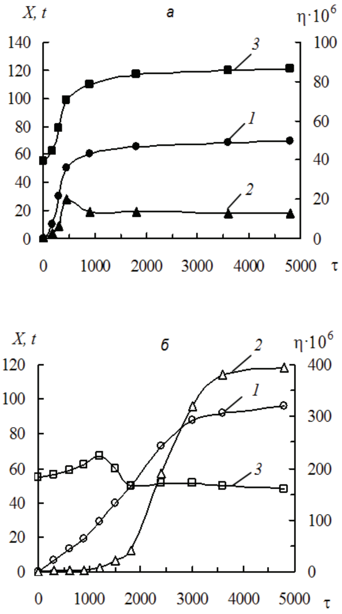

Fig. 5. Dependence of conversion degree X (%) (1), viscosity of a 1% solution η (m^2·s^{-1}) (2) and temperature t (°C) (3) of the reaction mixture on copolymerization time τ (s): a) adiabatic mode; b) quasi-isothermal mode.

At later stages the reaction rate decreases. After 80 minutes conversion degree ranges up to ~ 70%, the viscosity of a 1% water-alkaline solution of the reaction mass becomes ~ $13 \cdot 10^{-6}$ m^2·s^{-1}, and temperature is ~ 120°C. It should be noted that the final product is a polymeric gel swelling in water and soluble in water-alkaline media. The reaction delay at relatively low conversion degrees is caused by the fast consumption («burning out») of the initiator at elevated temperatures. The experiment results showed that carrying out the SMA copolymerization with MAA in the adiabatic mode does not allow obtaining a product of the required quality. The observed temperature increase to 120°C results in side transformations. It is known [12] that the intra- and intermolecular condensation of amide groups of a polymer takes place in the course of the synthesis of acrylamide and methacrylamide (co)polymers at elevated temperatures. This leads to irregularity of the polymer linear structure and, as a result, to solubility deterioration. However, polymer cross-linking by secondary amide groups is not irreversible, because they are easily broken when treating the polymer with a weakly alkaline solution.

Figure 5b shows for comparison curves characterizing the change of conversion degree (1), viscosity of a 1% aqueous solution (2) and reaction mass temperature (3) in the course of the copolymerization with partial removal of heat. In these experiments we used reaction vessels of larger diameter than the aluminum ampoules mentioned above. As the reaction vessel diameter increases, heat removal is to a greater degree determined by internal transfer by means of heat conductivity than by external conditions. Internal thermal resistance increases, which leads to reduction of the heat flow into the environment (thermostatic liquid). Respectively, a part of the evolved reaction heat goes into the increase of internal energy of the system, which shows itself as a rise of the reaction mass temperature.

During the first 1200 s the reaction vessel was in a medium with a temperature of 55°C. In this period, a conversion degree of ~ 30% and a viscosity of a 1% solution of the reaction mass of $\sim 30 \cdot 10^{-6}$ $m^2 \cdot s^{-1}$ are attained. The reaction mass temperature monotonously increases to ~ 67°C, because the evolved heat is not removed completely. Then the reaction vessel was transferred to a thermostat with a temperature of 34°C. The heat removal was intensified; the reaction mass temperature decreased and remained subsequently at the level of 50°C. This is accounted for by the fact that, as the temperature difference of the reaction mass and the vessel wall increases (the wall temperature is close to the thermostatic liquid temperature), the driving force of heat conductivity (temperature gradient) increases. Thermal equilibrium is established at a lower temperature of the reaction mass.

The copolymerization rate remained constant up to a conversion degree of ~ 80% due to the gel effect. The viscosity of a reaction mass solution increases to $250 \cdot 10^{-6}$ $m^2 \cdot s^{-1}$.

The reaction rate decreases at conversion degrees higher than 80%. At the end of the process (the overall time of 80 minutes) a conversion degree of 94% and viscosity of a 1% aqueous solution of the reaction mass of $\sim 400 \cdot 10^{-6}$ $m^2 \cdot s^{-1}$ are attained, which conforms to the requirements specified for the product. An important difference of the copolymer obtained in the quasi-isothermal conditions from the samples obtained in the adiabatic conditions is ideal water solubility.

Conclusions

Having carried out the analysis of the obtained experimental results we can recommend the quasi-isothermal mode of sodium methacrylate copolymerization with methacrylamide. It is expedient to prepare the reaction mass and to start the process at 55°C and to maintain further the temperature of the reaction volume in the range of t = 50–65°C. The recommended initial concentration of the monomers in the reaction mass $C_0 = 5.55–6.75$ $mol \cdot l^{-1}$; the initiator (PPS) concentration $I = 2 \cdot 10^{-3}–6 \cdot 10^{-3}$ $mol \cdot l^{-1}$. Such a mode of copolymerization allows obtaining a water-soluble copolymer with a high conversion degree and viscosity conforming to the required quality indicators of the product.

In the adiabatic mode the reaction medium temperature increases to 120°C, which leads to side transformations causing irregularity of the polymer linear structure and, as a result, solubility deterioration.

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Aclenowlegements

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References:

1. Bolívar G., Mas M., Ramírez M., Tortolero M.,; Cañizales E. // Revista Latinoamericana de Metalurgia y Materiales. 2011-12. V. 31. № 2. P. 150–160.

2. Sadeghalvaad M., Sabbaghi S. // Powder Technology. 2015. V. 272. P. 113–119.

3. Ashraf S., Cluley A., Mercado C., Mueller A. // Water Science and Technology. 2011. V. 64. № 6. P. 1325–1332.

4. Basova T.G., Zilberman E.N., Shvareva G.N., Chernych V.N. // Polymer science. 1975. V. 17 B. № 5. P. 379–380.

5. Basova T.G. // Izvestiya Vysshikh Uchebnykh Zavedenii, Khimiya i Khimicheskaya Tekhnologiya [Proceedings of the higher educational institutions. Chemistry and chemical technology]. 1975. № 8. P. 1827–1829.

6. Shubin A.A., Kiselnikov V.N., Vyalkov V.V., Shvareva G.N. // Izvestiya Vysshikh Uchebnykh Zavedenii, Khimiya i Khimicheskaya Tekhnologiya [Proceedings of the higher educational institutions. Chemistry and chemical technology]. 1983. V. 26. № 10. P. 1249–1253.

7. Lipin A.G., Bubnov V.B., Shubin A.A., Lebedev V. Ya. // Izvestiya Vysshikh Uchebnykh Zavedenii, Khimiya i Khimicheskaya Tekhnologiya [Proceedings of the higher educational institutions. Chemistry and chemical technology]. 1999. V. 42. № 4. P. 71–73.

8. Kuo Jen-Feng, Chen Chuh-Yung, Luo Shieh-Huang, Pan Ting-Chung // J. Applied Polymer Science. 1989. V. 38. № 3. P. 529–537.

9. Lipin A.A., Shibashov A.V., Lipin A.G. // Russian J. Applied Chemistry. 2015. V. 88. № 1. P. 97−102.

10. Lipin A.A., Shibashov A.V., Lipin A.G. // Izvestiya Vysshikh Uchebnykh Zavedenii, Khimiya i Khimicheskaya Tekhnologiya [Proceedings of the higher educational institutions. Chemistry and chemical technology]. 2014. V. 57. № 12. P. 85–87.

11. Averko-Antonovich I.Yu., Bikmullin R.T. Metody issledovaniya struktury i svoistv polimerov [Methods of polymers structure and properties investigation]. Kazan’: KSTU, 2002. 604 p.

12. Abramova L.I., Baiburdov T.A., Grigoryan E.P., Zilberman E.N., Kurenkov V.F., Myagchenkov V.A. Poliakrilamid [Polyacrylamide]. Moscow: Khimiya, 1992. 192 p.