Aqueous polymerization of vinyl monomers in the presence of surfactants

V. Copolymerization of acrylamide and acrylic acid

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Dedicated to Professor Ing. J. Beniska, DrSc., in honour of his 60th birthday

Aqueous copolymerization of acrylamide (AAm) with acrylic acid (AA) was studied at pH = 4.6 in the presence and/or in the absence of anionic emulsifier sodium dodecylphenoxybenzene disulfonate at 60 °C. It was found that the emulsifier does not affect either the kinetics of copolymerization or the composition of copolymer. The determined copolymerization parameters are $r_{\mathrm{AAm}} = 0.25$ and $r_{\mathrm{AA}} = 0.90$.

Изучалась сополимеризациа акриламида с акриловой кислотой в воде при pH = 4,6 в присутствии или отсутствии анионного эмульсификатора додецилфеноксибензолдисульфоната натрия при 60 °C. Установилось, что эмульсификатор не имеет влияние на кинетику сополимеризации и сложение сополимера. Были определены сополимеризационные параметры $r_{\mathrm{AAm}} = 0{,}25$ и $r_{\mathrm{AA}} = 0{,}90$.

Water-soluble monomers are significant components of comonomer mixtures of technical importance applied in the preparation of aqueous polymer dispersions with various physicochemical properties.

The use of monomers soluble in water or partially water-soluble in combination with monomers almost insoluble in water leads to some special features characteristic of both the process of the preparation of dispersion itself and the resulting product [1—3]. Formation of the polymeric product soluble in the aqueous phase resulting from homopolymerization or copolymerization of water-soluble monomers influences the kinetics and mechanism of emulsion polymerization [4].

On the other hand, the presence of the surface-active compound in the reaction system modifies the mechanism of homopolymerization of the water-soluble monomer; this was observed in acrylamide polymerization in the presence of sodium dodecylphenoxybenzene disulfonate [5] on the basis of the determination of the dependence of relative molecular mass of polyacrylamide on acrylamide conversion.

The micellar system formed by the surface-active compound in the aqueous phase affects the solubility of the water-soluble and oil-soluble monomer in the aqueous and oil phases and thus affects the composition of the copolymer being formed [1].

The complexity of emulsion polymerization of the water- and oil-soluble monomers requires special approaches to the study of the kinetics and mechanism of such copolymerization. One of the approaches is the investigation of the influence of various factors on the course of radical processes of polymerization in aqueous or oil phase separately [6].

In this paper we report on the copolymerization of acrylamide with acrylic acid in water in the presence of anionic emulsifier Dowfax® 2 A1 and the results obtained are compared with the copolymerization of the mentioned pair of comonomers in the absence of a surface-active compound.

Experimental

Monomers — acrylamide (AAm), product of Fluka AG Buchs and acrylic acid (AA), Chemical Works, n.e. Sokolov, Dowfax® 2 A1 (Dow Chemicals, USA, 45 mass % aqueous solution of sodium dodecylphenoxybenzene disulfonate, ammonium peroxodisulfate (Lachema, Brno) were used as supplied. To prepare a medium of pH = 4.64, we used buffer acetic acid/sodium acetate (0.1 M aqueous solutions).

Nitrogen was purified by passing through the column heated to 200 °C filled with active charcoal containing reduced copper. Distilled water was deoxygenated by heating to the boiling point and cooling while bubbling through nitrogen.

Polymerization solution was prepared by successive mixing of individual components of the polymerization system and filling up to the total volume of 100 cm^3 with acetate buffer at room temperature (*ca.* 20 °C). Polymerization solution (10 cm^3) was added into glass ampoules (30 cm^3) with a two-way cock. By freezing out the reaction mixture (at — 70 °C) and evacuating the frozen sample followed by thawing at room temperature and repeating the freeze-thawing cycles, the air was removed from the polymerization system. The ampoules were then put into a thermostat heated to 60 °C. To precipitate the formed copolymer, ethyl alcohol (technical, twice distilled) was used.

The initial rate of copolymerization expressed as a change of the degree of conversion α of both comonomers with respect to the total amount of both comonomers in a mixture (%) in time unit (s) was determined from the slope to the conversion curves at time $t = 0$ by the mirror method [7]. The composition of the copolymer was found from the determination of the nitrogen content by elemental analysis.

Results and discussion

Fig. 1 shows the dependence of the degree of conversion of acrylamide and acrylic acid on the reaction time for two different ratios between acrylamide and acrylic acid for polymerizations in the presence and/or in the absence of a surface-active compound.

The initial polymerization rate is characterized by the maximum value of the polymerization rate which smoothly decreases with conversion. With regard to

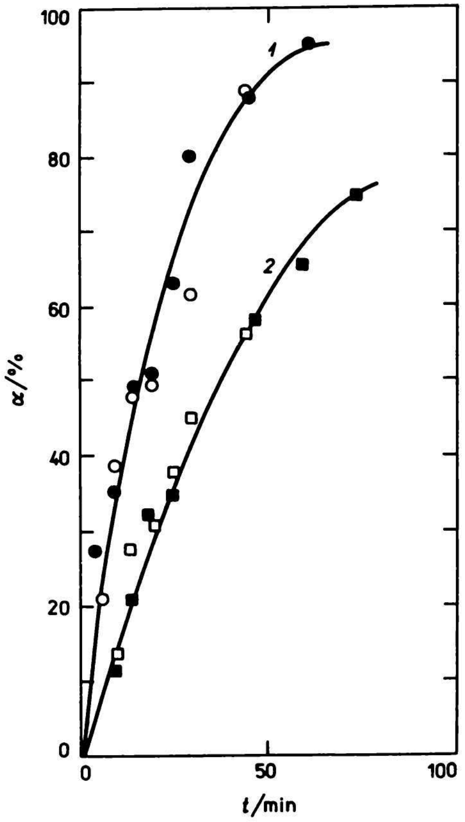

Fig. 1. A plot of the overall degree of conversion α of acrylamide and acrylic acid during aqueous polymerization at pH = 4.6 *vs.* reaction time. Concentration of ammonium peroxodisulfate: 5×10^{-4} mol dm^{-3}; $\theta = 60$ °C.

1. $[AAm]_0 = 0.4$ mol dm^{-3}; $[AA]_0 = 0.1$ mol dm^{-3} ○ Without emulsifier; ● [Dowfax 2 A1] = 1×10^{-2} mol dm^{-3}

2. $[AAm]_0 = 0.1$ mol dm^{-3}; $[AA]_0 = 0.4$ mol dm^{-3} □ Without emulsifier; ■ [Dowfax 2 A1] = 1×10^{-2} mol dm^{-3}

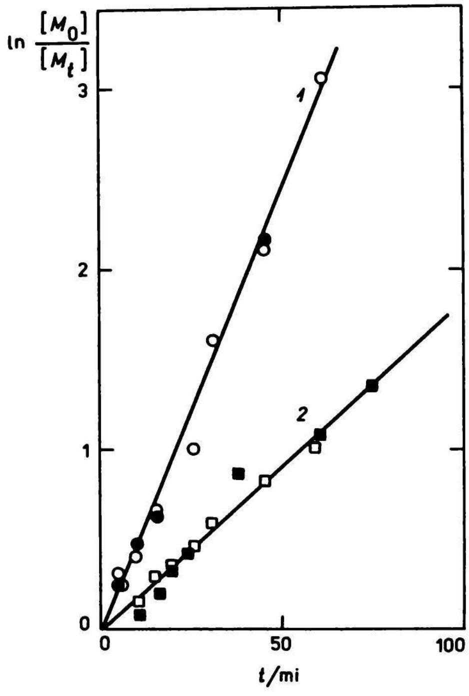

Fig. 2. A plot of the natural logarithm of the ratio of the overall concentration of acrylamide and acrylic acid at the beginning of reaction (M_0) and at time t (M_t) *vs.* reaction time during aqueous polymerization at pH = 4.6. Concentration of ammonium peroxodisulfate: 5×10^{-4} mol dm^{-3}; $\theta = 60$ °C.

1. $[AAm]_0 = 0.4$ mol dm^{-3}; $[AA]_0 = 0.1$ mol dm^{-3}. ○ [Dowfax 2 A1] = 0 mol dm^{-3}; ● Dowfax 2 A1] = 1×10^{-2} mol dm^{-3}

2. $[AAm]_0 = 0.1$ mol dm^{-3}; $[AA]_0 = 0.4$ mol dm^{-3}. □ [Dowfax 2 A1] = 0 mol dm^{-3}; ■ [Dowfax 2 A1] = 1×10^{-2} mol dm^{-3}.

a relatively low overall concentration of both comonomers ([AAm] + [AA] = = 0.5 mol dm^{-3}), no gel effect occurs. Anion-active emulsifier used in overmicellar concentration ([CMC] = 8 × 10^{-3} mol dm^{-3}) does not practically affect copolymerization rate.

The classical relation for the copolymerization rate may be expressed for viscous medium and for sufficiently high monomer conversions in a simplified form

$$\frac{-\mathrm{d}([\mathrm{M}_1] + [\mathrm{M}_2])}{\mathrm{d}t} = \mathrm{const}\,([\mathrm{M}_1] + [\mathrm{M}_2]) \qquad (1)$$

The plot shown in Fig. 2 considering Fig. 1 shows that the dependence of the copolymerization rate on conversion beyond 25—30 % reasonably satisfies eqn (*1*).

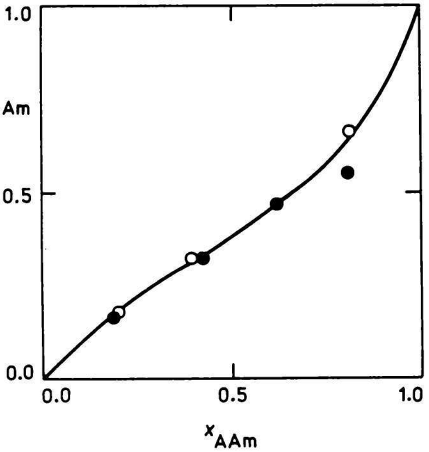

Fig. 3. A plot of the mole fraction of acrylamide structural units in copolymer y_{AAm} *vs.* mole fraction of acrylamide in feed x_{AAm}. Concentration of ammonium peroxodisulfate: 5 × 10^{-4} mol dm^{-3}; overall concentration of monomers in the system: 0.5 mol dm^{-3} Solvent: water, pH = 4.6. Copolymerization temperature: 60 °C.
○ Copolymerization system without emulsifier; ● [Dowfax 2 A1] = 1 × 10^{-2} mol dm^{-3}
Full line — dependence of the copolymer composition on feed composition calculated from copolymerization parameters $r_{\mathrm{AAm}} = 0.25$, $r_{\mathrm{AA}} = 0.90$ by the method of *Kelen* and *Tüdös* [8].

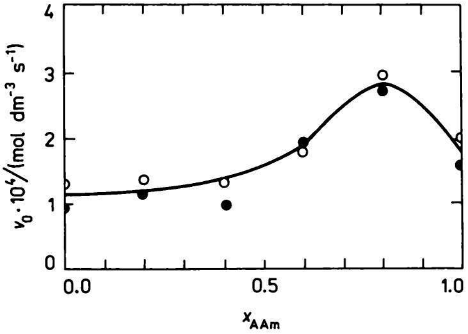

Fig. 4. A plot of the initial overall copolymerization rate

$$\left(v_0 = \frac{-\mathrm{d}([\mathrm{AAm}] + [\mathrm{AA}])}{\mathrm{d}t}\right)$$

of acrylamide with acrylic acid *vs.* mole fraction of acrylamide in feed. Solvent: water, pH = 4.6. Overall monomer concentration: 0.5 mol dm^{-3}; concentration of ammonium peroxodisulfate: 5 × 10^{-4} mol dm^{-3}; $\theta = 60$ °C.
○ Without emulsifier; ● [Dowfax 2 A1] = = 1 × 10^{-2} mol dm^{-3}

Different value of the slope of the line *1* with respect to the line *2* (see also Fig. 4) points to an increase in the value of the proportionality constant in eqn (*1*).

Fig. 3 shows the composition of copolymers as a function of the feed composition. The calculated dependence of the composition of copolymers on the feed composition is represented by a curve. Copolymerization parameters were obtained according to *Kelen* and *Tüdös* [8]. Copolymerization parameters are $r_{\mathrm{AAm}} = 0.25$ and $r_{\mathrm{AA}} = 0.90$.

The initial rate of copolymerization with the change of copolymer composition in feed in the range x_{AAm} of the mole fraction of acrylamide 0—1 shows maximum for $x_{\mathrm{AAm}} = 0.8$ (Fig. 4). The copolymerization rate is at this value of AAm concentration by about 2—2.5 times higher than the value of the copolymerization rate for the values of x_{AAm} lying between 0 and 0.6, or, than the value of the rate of the homopolymerization of acrylamide. Nor here are observed any differences in the rates of the copolymerization of the system in the presence and/or in the absence of anionic emulsifier. Reasons for anomalous rate of copolymerization at $x_{\mathrm{AAm}} = 0.8$ are not clear.

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