

# Copolymerization up to high conversions

## III. Kinetic measurements of the copolymerization of acrylonitrile and $\alpha$ -methylstyrene

I. CAPEK, V. JURANIČOVÁ, and J. BARTOŇ

*Polymer Institute, Centre of Chemical Research,  
Slovak Academy of Sciences, CS-842 36 Bratislava*

Received 4 November 1982

*Dedicated to Professor RNDr. J. Gašperík, founder of the Department of Organic Technology and of the Department of Chemical Technology of Plastics and Fibres of the Slovak Technical University on the occasion of the 40th anniversary of their foundation*

Conversion—time curves for the free-radical copolymerization of acrylonitrile (AN) and  $\alpha$ -methylstyrene ( $\alpha$ MS) in methyl ethyl ketone ( $[\alpha\text{MS}]/[\text{AN}] = 0.1$  and  $0.5$ ; total comonomer concentrations in methyl ethyl ketone:  $10 \text{ mol dm}^{-3}$  and  $3 \text{ mol dm}^{-3}$ ) at temperatures close to ceiling temperature of  $\alpha$ -methylstyrene are linear up to approximately 60 % of conversion. The gel effect is observed in the range 60—80 % of conversion. The initial copolymerization rates are functions of  $\alpha$ -methylstyrene concentration in the feed; with increasing  $\alpha$ -methylstyrene concentration the copolymerization rate decreases. The copolymer composition cannot be predicted on the basis of the Mayo—Lewis equation of copolymerization.

Кривые конверсии для радикальной сополимеризации акрилонитрила и  $\alpha$ -метилстирола в метилэтилкетоне ( $[\alpha\text{MS}]/[\text{AN}] = 0,1$  и  $0,5$ ; общая концентрация сомономера в метилэтилкетоне:  $10 \text{ моль дм}^{-3}$  и  $3 \text{ моль дм}^{-3}$ ) при температурах близких к температуре покрытия  $\alpha$ -метилстирола линейны до приблизительно 60 %-ной конверсии. Гель-эффект наблюдается в области конверсии 60—80 %. Начальные скорости сополимеризации являются функцией концентрации  $\alpha$ -метилстирола в реакционной смеси и скорость понижается при увеличении концентрации  $\alpha$ -метилстирола. Состав сополимера невозможно определить на основании уравнения сополимеризации Майо—Льюиса.

Free-radical copolymerization of vinyl monomers is a common reaction carried out by man. The nature of the low conversion copolymerization is understood relatively well and this led many to believe that the subject was no more interesting.

However, the research of the copolymerization kinetics continues in the area of high monomer conversion because the complexity of the latter has anyone so far prevented from giving a simple kinetic model of the high conversion copolymerization.

The preliminary studies on the copolymerization of acrylonitrile (AN) and  $\alpha$ -methylstyrene ( $\alpha$ MS) have shown the strong dependence of the copolymer composition not only on the feed composition but also on the degree of conversion and reaction temperature.

It is known that  $\alpha$ -methylstyrene has a ceiling temperature (61 °C) in the temperature range used normally for free-radical polymerizations. When conducting the copolymerization at ceiling temperature or at temperatures lying above the ceiling temperature, the copolymerization of  $\alpha$ -methylstyrene with vinyl monomers is characterized by depropagation reaction. This circumstance should be considered and appropriate corrections for copolymerization equation are necessary [1, 2].

In this paper the results of the copolymerization of acrylonitrile and  $\alpha$ -methylstyrene at temperature below the ceiling temperature of  $\alpha$ -methylstyrene are reported to show how the copolymer composition as well as the shape of the conversion curves are influenced by the feed composition and the degree of conversion.

## Experimental

### Chemicals

The initiator 2,2'-azoisobutyronitrile (AIBN) was recrystallized from absolute ethanol. Acrylonitrile (AN) and  $\alpha$ -methylstyrene ( $\alpha$ MS) were dried over anhydrous calcium dichloride and distilled twice at reduced pressure (100 Pa) of nitrogen before use. Methyl ethyl ketone (MEK) was dried by anhydrous calcium dichloride and distilled.

### Procedures

Copolymerizations of acrylonitrile and  $\alpha$ -methylstyrene were carried out in methyl ethyl ketone at 50 and 60 °C. In all runs the initiator concentration  $2 \times 10^{-2}$  mol dm<sup>-3</sup> was used. A copolymerization solution was prepared by mixing the initiator, methyl ethyl ketone, and monomers in a vessel. Ampoules were then filled with known volumes of the copolymerization solution. The content of ampoules was degassed by repeated successive freezing, pumping, and melting. The copolymerization technique and g.l.c. analyses were similar to those described elsewhere [3].

## Results

The conversion—time curves for acrylonitrile/ $\alpha$ -methylstyrene copolymerization in methyl ethyl ketone for a given reaction temperature and feed composition are given in Fig. 1. The conversion curves for all samples investigated are linear

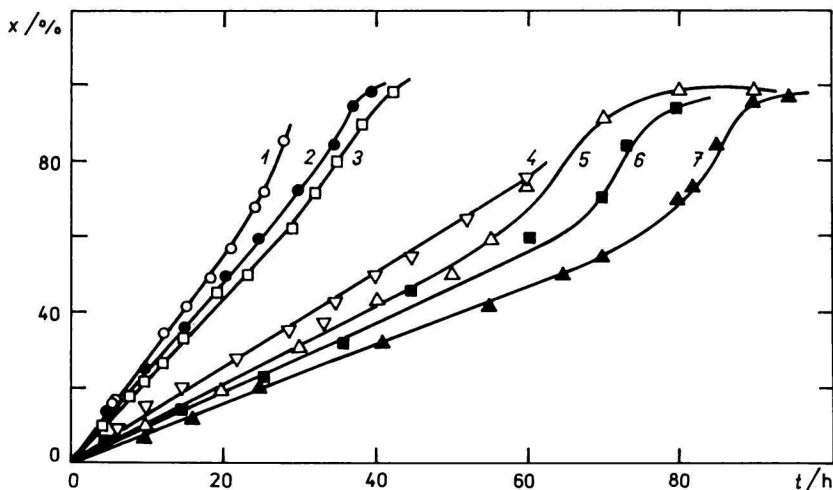


Fig. 1. Variation of the total monomer conversion ( $x$ ) in free-radical copolymerization of acrylonitrile and  $\alpha$ -methylstyrene with reaction time and monomer feed composition. Solvent: methyl ethyl ketone;

$$[\text{AIBN}] = 2 \times 10^{-2} \text{ mol dm}^{-3}.$$

1.  $\circ$   $[\alpha\text{MS}]/[\text{AN}] = 0.1$ ; 2.  $\bullet$   $[\alpha\text{MS}]/[\text{AN}] = 0.3$ ; 3.  $\square$   $[\alpha\text{MS}]/[\text{AN}] = 0.5$ .

(Temperature  $60^\circ\text{C}$ ;  $[\text{AN}] + [\alpha\text{MS}] = 10 \text{ mol dm}^{-3}$ .)

4.  $\nabla$   $[\alpha\text{MS}]/[\text{AN}] = 0.1$ ; 6.  $\blacksquare$   $[\alpha\text{MS}]/[\text{AN}] = 0.5$ .

(Temperature  $50^\circ\text{C}$ ;  $[\text{AN}] + [\alpha\text{MS}] = 10 \text{ mol dm}^{-3}$ .)

5.  $\triangle$   $[\alpha\text{MS}]/[\text{AN}] = 0.1$ ; 7.  $\blacktriangle$   $[\alpha\text{MS}]/[\text{AN}] = 0.5$ .

(Temperature  $60^\circ\text{C}$ ;  $[\text{AN}] + [\alpha\text{MS}] = 3 \text{ mol dm}^{-3}$ .)

(phase I) up to relatively high degree of conversion, *i.e.* ca. 60%. The autoacceleration of the copolymerization is observed beyond this level of conversion, approximately in the region of 60—80% of conversion (phase II). At conversions higher than 80—90% the conversion curves level off (phase III). The initial rate of copolymerization in phase I, as expected [4], decreases with increasing content of  $\alpha$ -methylstyrene in the feed (*cf.* curves 1, 2, and 3; 4 and 6; 5 and 7 in Fig. 1) and with decreasing temperature (*cf.* curves 1 and 4; 3 and 6 in Fig. 1). From the data of the copolymerization rates for 50 and  $60^\circ\text{C}$  the activation energy of  $65 \text{ kJ mol}^{-1}$  can roughly be estimated.

The conversion—time data of Fig. 1 (curves 3, 6, and 7) were graphically differentiated to yield the fractional rate of copolymerization  $(dx/dt)/(1-x)$  as a function of conversion  $x$  (Fig. 2). The value  $x$  was calculated from the relation

$$x = 1 - n_t/n_0 \quad (1)$$

where  $n_0$  and  $n_t$  represent the total amount of the monomer (moles) in feed at time zero and time  $t$  of the copolymerization. One can note (cf. with the course of the curves 3, 6, and 7 in Fig. 1) that the fractional rates of copolymerization exhibit the maxima at conversions 85—95 %.

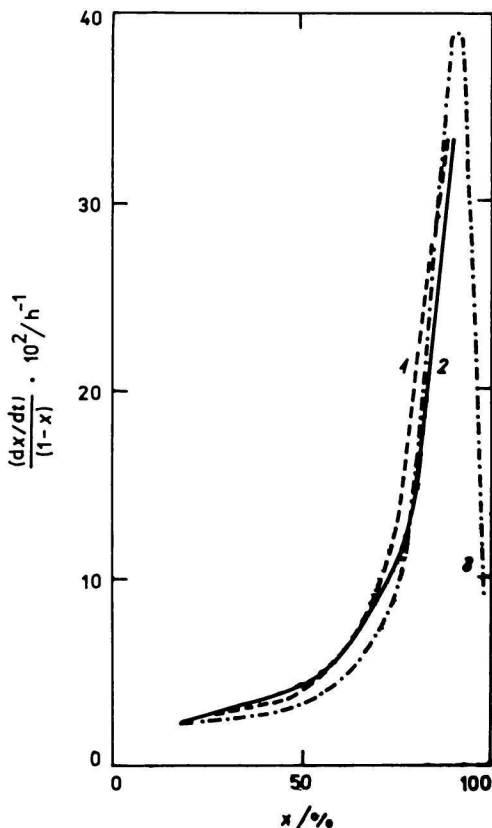


Fig. 2. Variation of the fractional rate of copolymerization with conversion ( $x$ ). Solvent: methyl ethyl ketone;  $[AIBN] = 2 \times 10^{-2} \text{ mol dm}^{-3}$ .

1.  $[AN] + [\alpha MS] = 10 \text{ mol dm}^{-3}$ ,  $[\alpha MS]/[AN] = 0.5$ , temperature  $50^\circ\text{C}$ ; 2.  $[AN] + [\alpha MS] = 10 \text{ mol dm}^{-3}$ ,  $[\alpha MS]/[AN] = 0.5$ , temperature  $60^\circ\text{C}$ ; 3.  $[AN] + [\alpha MS] = 3 \text{ mol dm}^{-3}$ ,  $[\alpha MS]/[AN] = 0.5$ , temperature  $60^\circ\text{C}$ .

The variation of the instantaneous feed composition with conversion is plotted in Fig. 3.

Using the equation [5]

$$y'_{AN} = y_{AN} - \frac{dy_{AN}}{dx} (1 - x) \quad (2)$$

where  $y'_{AN}$  is the instantaneous mole fraction of the acrylonitrile structural units in the copolymer,  $y_{AN}$  is the mole fraction of acrylonitrile in the feed at conversion  $x$ ,

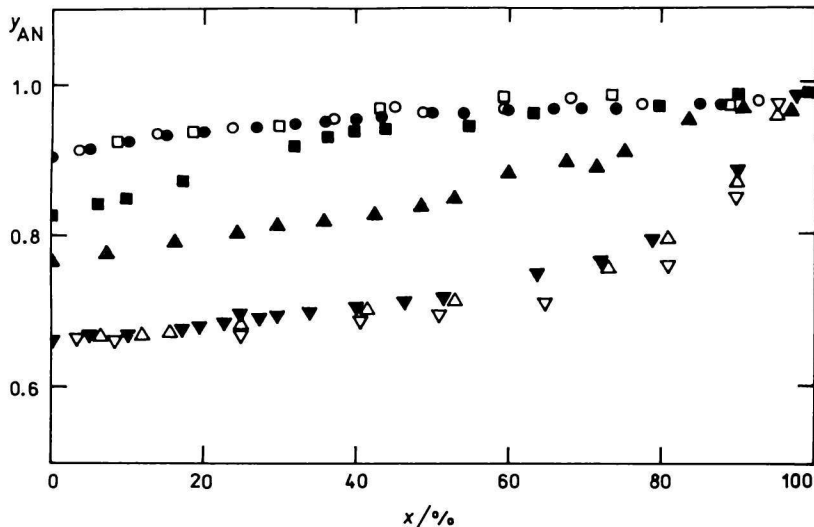


Fig. 3. Variation of the monomer feed (mole fraction of acrylonitrile ( $y_{AN}$ )) with conversion ( $x$ ).

Solvent: methyl ethyl ketone;  $[AN] + [\alpha MS] = 10 \text{ mol dm}^{-3}$ ;

○  $[\alpha MS]/[AN] = 0.1$ , temperature  $50^\circ\text{C}$ ; ●  $[\alpha MS]/[AN] = 0.1$ , temperature  $60^\circ\text{C}$ ; ■  $[\alpha MS]/[AN] = 0.2$ , temperature  $60^\circ\text{C}$ ; ▲  $[\alpha MS]/[AN] = 0.3$ , temperature  $60^\circ\text{C}$ ; △  $[\alpha MS]/[AN] = 0.5$ , temperature  $50^\circ\text{C}$ ; ▼  $[\alpha MS]/[AN] = 0.5$ , temperature  $60^\circ\text{C}$ .

$[AN] + [\alpha MS] = 3 \text{ mol dm}^{-3}$ ;

□  $[\alpha MS]/[AN] = 0.1$ , temperature  $60^\circ\text{C}$ ; △  $[\alpha MS]/[AN] = 0.5$ , temperature  $60^\circ\text{C}$ .

the instantaneous composition of copolymer was calculated and the results were presented in Figs. 4 and 5. The cumulative copolymer composition  $y''_{AN}$  (mole fraction of acrylonitrile structural units in the copolymer), calculated from the mass balance, as a function of conversion  $x$  is also given in Figs. 4 and 5. The course of the  $y'_{AN}$  and  $y''_{AN}$  functions with conversion was compared with that (curve 3 in Figs. 4 and 5) of instantaneous calculated copolymer composition  $y''_{ANC}$  (mole fraction of the acrylonitrile structural units in copolymer). To obtain  $y'_{ANC}$  the Mayo—Lewis

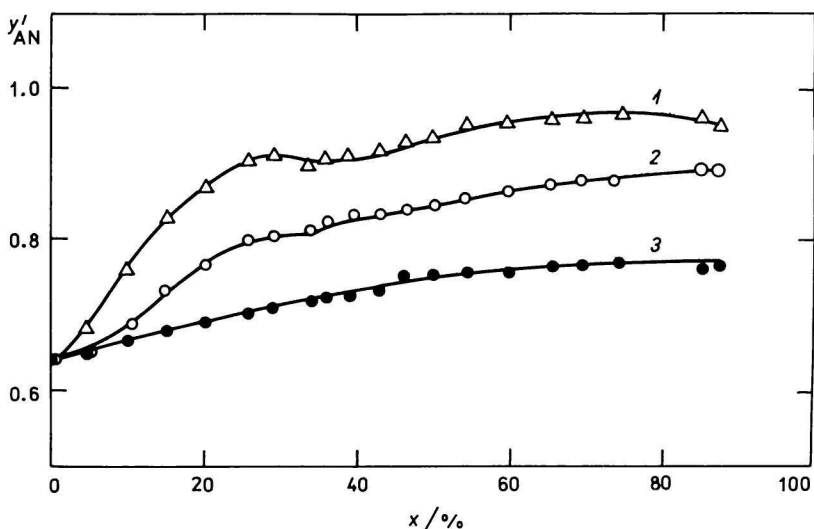


Fig. 4. Variation of the 1. instantaneous copolymer composition (mole fraction of acrylonitrile structural units ( $y'_{AN}$ )), 2. cumulative copolymer composition (mole fraction of acrylonitrile structural units ( $y''_{AN}$ )), 3. calculated instantaneous copolymer composition (mole fraction of acrylonitrile structural units ( $y'_{ANC}$ )) with conversion ( $x$ ). Solvent: methyl ethyl ketone;  $[AN] + [\alpha MS] = 10 \text{ mol dm}^{-3}$ ;  $[\alpha MS]/[AN] = 0.1$ , temperature  $60^\circ\text{C}$ .

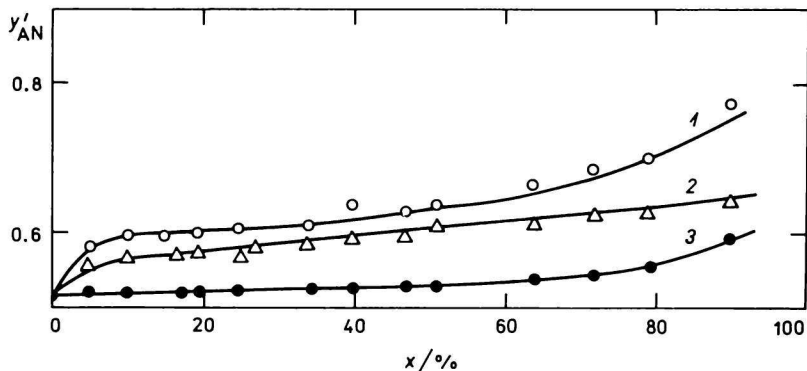


Fig. 5. Variation of the 1. instantaneous copolymer composition (mole fraction of acrylonitrile structural units ( $y'_{AN}$ )), 2. cumulative copolymer composition (mole fraction of acrylonitrile structural units ( $y''_{AN}$ )), 3. calculated instantaneous copolymer composition (mole fraction of acrylonitrile structural units ( $y'_{ANC}$ )) with conversion ( $x$ ). Solvent: methyl ethyl ketone;  $[AN] + [\alpha MS] = 10 \text{ mol dm}^{-3}$ ;  $[\alpha MS]/[AN] = 0.5$ , temperature  $60^\circ\text{C}$ .

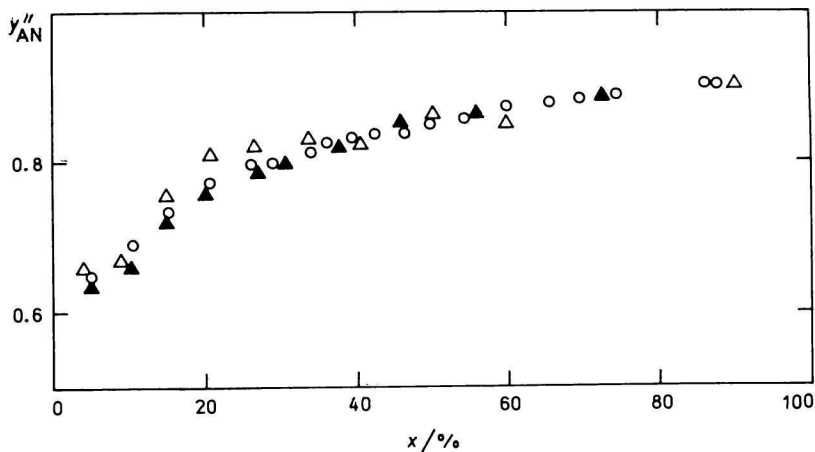


Fig. 6. Variation of the cumulative copolymer composition (mole fraction of acrylonitrile structural units ( $y''_{AN}$ )) with conversion ( $x$ ) for various initial monomer concentrations. Solvent: methyl ethyl ketone;  $[\alpha MS]/[AN] = 0.1$ :

○  $[AN] + [\alpha MS] = 10 \text{ mol dm}^{-3}$ , temperature  $60^\circ\text{C}$ ; ▲  $[AN] + [\alpha MS] = 10 \text{ mol dm}^{-3}$ , temperature  $50^\circ\text{C}$ ; △  $[AN] + [\alpha MS] = 3 \text{ mol dm}^{-3}$ , temperature  $60^\circ\text{C}$ .

equation [6] and reference data [7] for reactivity ratios  $r_{AN} = 0.07$ ,  $r_{\alpha MS} = 0.08$  together with the experimental (Fig. 3) values of the instantaneous feed composition were used. The effect of the reaction temperature on the course of cumulative copolymer composition  $y''_{AN}$  for mole ratio  $[\alpha MS]/[AN] = 0.1$  in the feed and for various total comonomer concentrations is presented in Fig. 6.

## Discussion

It is now widely accepted that the autoacceleration (gel effect) in the free-radical polymerization results from the restricted mobility of the growing polymer chains [8–12]. The low mobility of the chains leads to a decrease of the rate of termination reaction of macroradicals and thus to the increase of the polymerization rate. The termination rate constant for a given monomer is a function of polymer radical size (relative molecular mass), viscosity of the reaction medium, and dimensions of the polymer coil [13]. In the present work the experimental conditions of the copolymerization with respect to the initial viscosity of the reaction system and/or to the polymer coil dimensions are nearly the same for all systems studied. The last statement should fairly hold because the differences of the copolymer composition arising from feed composition and/or degree of monomer

conversion are not so great to influence substantially the value of the polymer—solvent interaction parameter of the said reaction systems. In other words, the copolymer coil of a given relative molecular mass should have the same size, irrespective of the monomer feed composition, because the copolymer composition is nearly the same for a given degree of conversion (*cf.* cumulative copolymer composition given in Fig. 6).

The observed broad region of linear dependence of the copolymerization rate on the reaction time (in phase I) points at the unhindered mobility of the active copolymer chains even at relatively high conversions. The mobility of the active copolymer chains in the system of a given value of the polymer—solvent interaction parameter depends mainly on the relative molecular mass and degree of branching of the copolymer and on the concentration of the copolymer in the system. The latter is responsible for the enormous increase of the viscosity of the reaction system. Though the systems of various initial concentrations of monomers were used ( $10 \text{ mol dm}^{-3}$  and  $3 \text{ mol dm}^{-3}$ ), the incipient gel effect was observed at about 60 % conversion. One can therefore believe that relative molecular masses of the copolymers prepared from monomer feed concentration  $3 \text{ mol dm}^{-3}$  should be higher (because the total concentration of copolymer at 60 % monomer conversion is *ca.* 3.3 times smaller than for the system with initial comonomer concentration  $10 \text{ mol dm}^{-3}$ ) and the equal value of the viscosity can be reached (see above) only by an increase of copolymer relative molecular mass. Such situation is possible in reaction systems, where high transfer to monomer can be expected. This is the case of  $\alpha$ -methylstyrene. Lowering of the  $\alpha$ -methylstyrene concentration in the feed decreases the extent of the transfer reaction of macroradical to  $\alpha$ -methylstyrene and consequently the relative molecular mass of the copolymer increases. On the other hand, decreasing the  $\alpha$ -methylstyrene concentration in the feed simultaneously lowers the probability of depropagation reactions of sequences formed from  $\alpha$ -methylstyrene structural units, but this effect on the autoacceleration of the copolymerization is not so great in comparison to comonomer concentration effect, as can be seen from Fig. 1 (curves 1 and 3; 5 and 6). Larger differences on the time scale are observed (Fig. 1, curves 1 and 5; 3 and 7) if systems with different total monomer concentrations in the feed are considered.

With advancing copolymerization reaction the copolymer becomes enriched with acrylonitrile structural units. Classical Mayo—Lewis equation cannot adequately describe the course of the copolymer composition with conversion. The deviation from the theory may be also due to a steric effect in the case of  $\alpha$ -methylstyrene monomer restricting its mobility especially in medium and high conversions and reactivity of  $\alpha$ -methylstyryl radical due to extensive delocalization of unpaired electron, steric hindrance to addition and low segmental mobility. The restricted mobility of  $\alpha$ -methylstyrene monomer and low reactivity of active  $\alpha$ -methylstyrene chain in moderately concentrated solution can lead to a decrease in  $r_{\alpha\text{MS}}$  with an



increase in  $r_{AN}$ . It is supposed that the observed fluctuations in the copolymer composition—conversion data are the results of the variations in the reactivity ratios  $r_{\alpha MS}$  and  $r_{AN}$  during the copolymerization [14]. It is interesting to note that for systems where  $[\alpha MS]/[AN] = 0.1$  the cumulative concentration of acrylonitrile structural units increase quickly up to 30 % of conversion and this increase represents ca. 20 % of the initial feed concentration. In further reaction interval the increase of acrylonitrile content in the copolymer is much slower. Such behaviour can be explained on the basis of rapid  $\alpha$ -methylstyrene exhaustion at the beginning of the copolymerization. Indeed, for the ratio  $[\alpha MS]/[AN] = 0.5$  the increase of acrylonitrile content in copolymer in the first 10 % of conversion represents only 10 % of the initial acrylonitrile concentration in the feed. Conforming with the foregoing discussion is the course of the acrylonitrile cumulative concentration in copolymer dependent on the total monomer conversion. Experimental points lie practically on the same curve, irrespective of the initial feed concentration and temperature. This points to the weak sensitivity of the copolymer microstructure towards the reaction conditions used in this work.

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Translated by I. Capek