Copolymerization up to high conversions
IV. *Systems styrene—acrylonitrile, α-methylstyrene—acrylonitrile, and styrene—α-methylstyrene—acrylonitrile

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

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

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

The high conversion copolymerization and terpolymerization of electron-donor monomers styrene and α-methylstyrene and of electron-acceptor monomer acrylonitrile in the presence and/or absence of zinc dichloride at 60 °C was studied. The change of the copolymer and of the terpolymer composition with monomer conversion cannot be described by Mayo—Lewis and Alfrey—Goldfinger classical models of copolymerization and of terpolymerization. The presence of Lewis acid in copolymerization and terpolymerization reaction systems in comparison to the systems without Lewis acid does not practically influence the copolymer and/or terpolymer chemical composition. Addition of Lewis acid markedly influences the dependence of the fractional rate of copolymerization and of terpolymerization on conversion. In reaction systems containing Lewis acid monotonic decrease of the fractional copolymerization rate with conversion was observed. In the absence of Lewis acid the course of the fractional rate of copolymerization as a function of conversion is characterized by a pronounced maximum on the curve of fractional copolymerization rate (gel effect) in the region of 20—25 % of conversion.

Были изучены высококонверсионная сополимеризация и терполимеризация электронно-донорных мономеров, стирола и α-метилстирола и электронно-акцепторного мономера акрилонитрила в присутствии или отсутствии хлористого цинка при 60 °C. Изменение состава сополимера или терполимера в зависимости от превращения мономера

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* For Part III see Ref. [1].

нельзя описать классическими моделями сополимеризации и терполимеризации по Майо—Люису и Альфрейу—Гольдфингеру. Присутствие Люисовской кислоты в сополимеризационной или терполимеризационной реакционных системах практически не влияет на химический состав сополимера или терполимера. Добавка Люисовской кислоты существенно влияет на зависимость дифференциальной скорости сополимеризации и терполимеризации от конверсии. В реакционной системе, содержащей Люисовскую кислоту, наблюдалось монотонное понижение скорости полимеризации с конверсией. В отсутствии Люисовской кислоты кривая зависимости скорости полимеризации от конверсии проявляет выразительный максимум (гель-эффект) в области конверсии 20—25 %.

In the previous paper [1] dealing with the copolymerization of acrylonitrile and α-methylstyrene in methyl ethyl ketone up to high monomer conversion, difference between experimentally found composition of copolymer and that calculated from the integrated *Mayo—Lewis* equation [2] was observed.

In copolymerization of donor/acceptor comonomer pair the formation of an donor/acceptor comonomer complex should play an important role [3—5]. Formation of donor/acceptor comonomer complexes is enhanced in the presence of additives, *e. g.* Lewis acid, capable of complexing one of the comonomer. As a rule in such systems copolymers of nearly equimolar alternating structure are formed [6, 7]. Thus in the system acrylonitrile—α-methylstyrene the formation of donor//acceptor complexes occurs [8] and this tendency is highly increased in the presence of zinc dichloride [9].

In spite of the fact that the mechanism of alternating copolymerization including the participation of donor/acceptor comonomer complexes is still a matter of controversy [10], the donor/acceptor comonomer pair should serve as a useful model for study of the copolymerization kinetics beyond the common limit of monomer conversion used for such studies, because in alternating copolymerization system irrespective of the reaction mechanism, both monomers are equally and at relatively high rates consumed from the reaction mixture. This process continues until one of the comonomers in feed is exhausted and in further process, homopolymer of the comonomer (if the latter is capable to undergo homopolymerization) present in excess in the feed, is formed. On choosing the appropriate comonomer pair and concentrations the possibility of homopolymer formation after exhaustion of one of the comonomers can practically be reduced to zero and such reaction system is well suited for copolymerization studies up to high conversion.

In the present paper the high conversion kinetics of the acceptor monomer//donor monomer copolymerization in the presence as well as absence of zinc

dichloride was studied. Two donor monomers were chosen, namely styrene and α-methylstyrene and one acceptor monomer — acrylonitrile. Besides copolymerization also terpolymerization of the system of two donor monomers with acceptor monomer was studied.

Experimental

Monomers styrene (S), α-methylstyrene (αMS), acrylonitrile (AN) and solvents acetone and dioxan were dried with anhydrous calcium chloride and fractionally distilled under reduced pressure of nitrogen (100 Pa). 2,2'-Azoisobutyronitrile (AIBN) was recrystallized from ethanol, m.p. 103.5 °C. p-Benzoquinone (reagent grade chemical) was used without any further purification. Purification of zinc dichloride and preparation of acrylonitrile—zinc dichloride complex was described earlier [11].

Copolymerization and terpolymerization reaction mixtures were prepared by mixing the stock dioxan solutions of monomers and of azoisobutyronitrile in required molar proportions (Table 1). Aliquots of the copolymerization and of the terpolymerization reaction

Table 1

Concentration (c/(mol dm^{-3})) of copolymerization and terpolymerization mixtures; Solvent: dioxan; c(2,2'-azoisobutyronitrile) $= 1 \times 10^{-2}$ mol dm^{-3}

Series	S	αMS	AN
A	2	—	2[a]
B	2	—	2
C	—	2	2[a]
D	1	1.31	2[a]
E	1	1.31	2
F	1.5	0.5	2[a]

a) Acrylonitrile with ZnCl$_2$. [ZnCl$_2$]/[AN] $= 0.1425$ (determined by complexonometric titration [11]).

mixtures were pipetted (à 1 cm^3) into glass ampoules. The degassing of polymerization mixtures was accomplished by common freeze-thaw technique. The ampoules were then thermostatted at (60 ± 0.1) °C for a desired reaction time. Then the ampoules were cooled, opened and to the content of every ampoule the solution (4 cm^3) of c(p-benzoquinone) $= 1 \times 10^{-3}$ mol dm^{-3} in acetone was added.

Concentration of unreacted monomers in the ampoules after reaction was determined by gas chromatography (Perkin—Elmer F-11 gas chromatograph, column filled with 10 % Carbowax 1500 on 0.10—0.205 mm Chromaton (Lachema, Brno)).

Results and discussion

For evaluation of copolymerization and of terpolymerization experiments the procedure outlined in [12] was used. Details of this procedure were given in the preceding paper [13]. In calculation corrections for the volume contractions of the reaction mixtures were applied. The shrinkage factor defined as the ratio of the difference between the initial volume of the reaction mixture V_0 and volume of the reaction mixture at 100 % conversion of monomer V_{100} and of the initial volume V_0, i.e. $(V_0 - V_{100})/V_0$ was 0.26 (for Series A, B, and C) and 0.25 (for Series D, E, and F).

The dependences of the feed composition, cumulative, instantaneous and instantaneous calculated mole fractions of individual comonomer structural units in the copolymer and/or terpolymer as well as of the total monomer conversion on reaction time are given in Table 2 (Series A), in Table 3 (Series B), in Table 4 (Series C), in Table 5 (Series D), in Table 6 (Series E), and in Table 7 (Series F).

Comparing the results found for Series A and Series B, differing only by the presence (Series A) or by the absence (Series B) of zinc dichloride it may be deduced that on increasing monomer conversion the change of the feed composition is substantial only at Series A. At the same time, however, the cumulative concentration of styrene structural units in copolymer for both Series changes only

Table 2

Dependence of the styrene mole fraction (y_S) in the feed, of cumulative, instantaneous and instantaneous calculated mole fractions (y_S'', y_S', and y_{SC}') and of the total monomer conversion (x) on reaction time (t) of copolymerization of styrene and acrylonitrile in the presence of zinc dichloride (Series A); $c(2,2'\text{-azoisobutyronitrile}) = 1 \times 10^{-2}$ mol dm^{-3}; Solvent: dioxan; $[ZnCl_2]/[AN] = 0.142$; temperature 60 °C

t/h	y_S	y_S''	y_S'	y_{SC}' [a]	x
0	0.500	—	—	—	0.000
1	0.490	0.555	0.566	0.496	0.153
2	0.479	0.555	0.544	0.496	0.274
3	0.468	0.555	0.525	0.495	0.368
4	0.464	0.544	0.514	0.495	0.449
5	0.455	0.541	0.498	0.495	0.527
6	0.451	0.534	0.488	0.495	0.593
7	0.438	0.533	0.529	0.494	0.650
8	0.426	0.532	0.505	0.494	0.698
8.5	0.416	0.532	0.568	0.493	0.723
9	0.400	0.533	0.538	0.493	0.750

a) For calculation according to *Mayo—Lewis* equation [2] copolymerization ratios [7] $r_S = 0.01$ and $r_{AN} = 0.025$ were used.

Table 3

Dependence of the styrene mole fraction (y_S) in the feed, of cumulative, instantaneous and instantaneous calculated mole fractions (y_S'', y_S', and y_{SC}') and of the total monomer conversion (x) on reaction time (t) of copolymerization of styrene and acrylonitrile (Series B); $c(2,2'$-azoisobutyronitrile$) = 1 \times 10^{-2}$ mol dm^{-3}; Solvent: dioxan; temperature 60 °C

t/h	y_S	y_S''	y_S'	y_{SC}' [a]	x
0	0.500	—	—	—	0.000
1	0.496	0.553	0.561	0.593	0.070
2	0.493	0.545	0.554	0.592	0.135
3.2	0.489	0.537	0.544	0.591	0.221
4	0.487	0.533	0.537	0.590	0.285
5	0.486	0.527	0.506	0.590	0.340
6	0.484	0.526	0.502	0.589	0.388
7	0.483	0.523	0.500	0.589	0.426
8	0.480	0.524	0.556	0.588	0.460
9.2	0.474	0.526	0.479	0.586	0.496
15.4	0.481	0.511	0.448	0.588	0.637

a) For calculation according to *Mayo—Lewis* equation [2] copolymerization ratios [14] $r_S = 0.51$ and $r_{AN} = 0.030$ were used.

Table 4

Dependence of the α-methylstyrene mole fraction ($y_{\alpha MS}$) in the feed, of cumulative, instantaneous and instantaneous calculated mole fractions ($y_{\alpha MS}''$, $y_{\alpha MS}'$, and $y_{\alpha MSC}'$) and of the total monomer conversion (x) on reaction time (t) of copolymerization of α-methylstyrene and acrylonitrile in the presence of zinc dichloride (Series C); $(2,2'$-azoisobutyronitrile$) = 1 \times 10^{-2}$ mol dm^{-3}; Solvent: dioxan; $[ZnCl_2]/[AN] = 0.142$; temperature 60 °C

t/h	$y_{\alpha MS}$	$y_{\alpha MS}''$	$y_{\alpha MS}'$	$y_{\alpha MSC}'$ [a]	x
0	0.500	—	—	—	0.000
1	0.499	0.531	0.510	0.496	0.040
3	0.496	0.531	0.513	0.496	0.119
5	0.488	0.550	0.511	0.496	0.192
7	0.486	0.542	0.518	0.496	0.252
9	0.475	0.556	0.530	0.496	0.307
11	0.470	0.554	0.521	0.495	0.358
16	0.461	0.545	0.504	0.495	0.466
20	0.457	0.539	0.495	0.495	0.527
25	0.451	0.534	0.505	0.495	0.587
30	0.439	0.534	0.469	0.494	0.639

a) No literature data are available for copolymerization ratios $r_{\alpha MS}$ and r_{AN} for the system containing zinc dichloride. Therefore the data known from copolymerization of S and AN in the presence of zinc dichloride were used, *i.e.* $r_{\alpha MS} = 0.01$ nad $r_{AN} = 0.025$.

Table 5

Dependence of the styrene, α-methylstyrene, and acrylonitrile mole fractions (y_S, $y_{\alpha MS}$, y_{AN}) in the feed, of cumulative (y_S'', $y_{\alpha MS}''$, y_{AN}''), instantaneous (y_S', $y_{\alpha MS}'$, y_{AN}'), and instantaneous calculated mole fractions (y_{SC}', $y_{\alpha MSC}'$, y_{ANC}') and of the total monomer conversion (x) on reaction time (t) of terpolymerization of styrene and α-methylstyrene with acrylonitrile in the presence of zinc dichloride (Series D); $c(2,2'\text{-azoisobutyronitrile}) =$
$= 1 \times 10^{-2}$ mol dm^{-3}; Solvent: dioxan; $[\text{ZnCl}_2]/[\text{AN}] = 0.142$; temperature 60 °C

t/h	y_S''	$y_{\alpha MS}{}^a$	$y_S''{}^a$	$y_{\alpha MS}''{}^a$	$y_S'{}^a$	$y_{\alpha MS}'{}^a$	$y_{SC}'{}^{a,b}$	$y_{\alpha MSC}'{}^{a,b}$	x
0	0.232	0.304	—	—	—	—	—	—	0.000
5	0.241	0.295	0.210	0.326	0.210	0.326	0.243	0.267	0.289
10	0.242	0.290	0.220	0.321	0.238	0.321	0.245	0.265	0.450
15	0.246	0.282	0.222	0.321	0.229	0.321	0.250	0.259	0.566
20	0.255	0.277	0.219	0.319	0.195	0.319	0.257	0.253	0.646

a) The respective values for acrylonitrile are given by the expressions: $y_{AN} = 1 - (y_S + y_{MS})$; $y_{AN}'' = 1 - (y_S'' + y_{\alpha MS}'')$; $y_{AN} = 1 - (y_S + y_{\alpha MS})$; $y_{ANC}' = 1 - (y_{SC}' + y_{\alpha MSC}')$.

b) For calculation the appropriate equation of *Alfrey* and *Goldfinger* [17] and the binary copolymerization reactivity ratios were used (S – 1; αMS – 2; AN – 3): $r_{1,2} = 0.962$ [14], $r_{2,1} = 0.048$ [14], $r_{2,3} = 0.142$ [14], $r_{3,2} = 0.037$ [14], $r_{1,3} = 0.51$ [14], $r_{3,1} = 0.03$ [14], see also footnote *a*) to Table 4.

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Table 6

Dependence of the styrene, α-methylstyrene, and acrylonitrile mole fractions (y_S, y_{aMS}, y_{AN}) in the feed, of cumulative (y_S'', y_{aMS}'', y_{AN}''), instantaneous (y_S', y_{aMS}', y_{AN}'), and instantaneous calculated mole fractions (y_{SC}', y_{aMSC}', y_{ANC}') and of the total monomer conversion (x) on reaction time (t) of terpolymerization of styrene and α-methylstyrene with acrylonitrile (Series E); $c(2,2'\text{-azoisobutyronitrile}) = 1 \times 10^{-2}$ mol dm^{-3}; Solvent: dioxan; temperature 60 °C

t/h	$y_S{}^a$	$y_{aMS}{}^a$	$y_S''{}^a$	$y_{aMS}''{}^a$	$y_S'{}^a$	$y_{aMS}'{}^a$	$y_{SC}'{}^{a,b}$	$y_{aMSC}'{}^{a,b}$	x
0	0.232	0.304	—	—	—	—	—	—	0.000
3	0.236	0.305	0.166	0.290	0.167	0.305	0.384	0.267	0.065
5	0.240	0.294	0.184	0.367	0.175	0.467	0.387	0.267	0.136
7	0.243	0.271	0.196	0.418	0.243	0.503	0.391	0.248	0.226
11	0.230	0.251	0.236	0.408	0.329	0.317	0.384	0.243	0.337
15	0.217	0.241	0.255	0.400	0.368	0.301	0.375	0.243	0.396
20	0.208	0.239	0.264	0.390	0.350	0.296	0.368	0.245	0.430

a, b) See Table 5.

Table 7

Dependence of the styrene, α-methylstyrene, and acrylonitrile mole fractions (y_S, y_{aMS}, y_{AN}) in the feed, of cumulative (y_S'', y_{aMS}'', y_{AN}''), instantaneous (y_S', y_{aMS}', y_{AN}'), and instantaneous calculated mole fractions (y_{SC}', y_{aMSC}', y_{ANC}') and of the total monomer conversion (x) on reaction time (t) of terpolymerization of styrene and α-methylstyrene with acrylonitrile in the presence of zinc dichloride (Series F): $c(2,2'\text{-azoisobutyronitrile}) = = 1 \times 10^{-2}$ mol dm^{-3}; Solvent: dioxan; $[\text{ZnCl}_2]/[\text{AN}] = 0.142$; temperature 60 °C

t/h	$y_{S''}$	$y_{aMS}{}^a$	$y_S'{}^a$	$y_{aMS}''{}^a$	$y_S'{}^a$	$y_{aMS}'{}^a$	$y_{SC}'{}^{a,b}$	$y_{aMSC}'{}^{a,b}$	x
0	0.375	0.125	—	—	—	—	—	—	0.000
1	0.381	0.123	0.305	0.151	0.381	0.123	0.385	0.119	0.083
3	0.386	0.122	0.337	0.137	0.386	0.122	0.387	0.117	0.227
5	0.384	0.114	0.358	0.146	0.384	0.114	0.392	0.112	0.343
7	0.379	0.109	0.370	0.145	0.379	0.109	0.393	0.110	0.434
9	0.373	0.105	0.377	0.144	0.373	0.105	0.395	0.108	0.507
10	0.369	0.103	0.380	0.144	0.438	0.091	0.395	0.107	0.542
11.5	0.362	0.100	0.385	0.143	0.425	0.132	0.395	0.106	0.579
16	0.341	0.098	0.392	0.139	0.418	0.157	0.391	0.109	0.662
20	0.329	0.096	0.395	0.137	0.395	0.149	0.389	0.110	0.703
25.2	0.321	0.082	0.395	0.141	0.442	0.123	0.398	0.100	0.730

a, b) See Table 5.

slightly. A more pronounced change of the instantaneous copolymer composition with the reaction time of copolymerization was found at Series B.

The course of the copolymer composition in Series A and B cannot be approximated by the classical equation of *Mayo* and *Lewis* [2] (see values of the calculated instantaneous copolymer composition). The dependence of the copolymer composition on the conversion is analogical for both systems. Effect of zinc dichloride concentration on the composition of the styrene/acrylonitrile copolymer is insignificant. The presence of dioxan, *i.e.* of the solvent of complexing ability, suppresses the tendency towards alternating copolymerization, which is otherwise characteristic of the copolymerization of styrene and acrylonitrile in the presence of Lewis acid, and as a result the statistical copolymer is formed [15].

On changing styrene for α-methylstyrene for copolymerization of acrylonitrile in the presence of zinc dichloride (Series C) the qualitatively same result as for the system with styrene (Series A) was obtained. In the course of copolymerization the instantaneous copolymer composition points at the gradual enriching of copolymer by acrylonitrile structural units. Similarly as in Series A and B also here the use of *Mayo—Lewis* equation [2] for calculation of the copolymer composition did not give satisfactory agreement with the experimentally found copolymer composition. Though in the presence of zinc dichloride the copolymer composition was not markedly affected, the profound effect of zinc dichloride on the fractional rate of copolymerization was observed (Fig. 1, curves *1*, *3*, and *5*). In the presence of zinc dichloride (Series A and C) the monotonic decrease of the fractional copolymeriza-
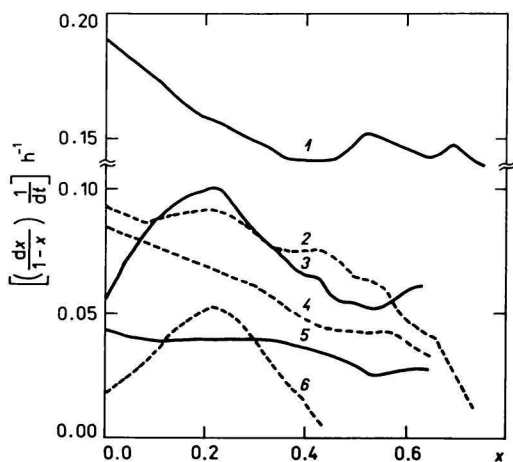

Fig. 1. Dependence of the fractional rate $(dx/dt)/(1-x)$ of copolymerization and of terpolymerization (h^{-1}) on the total monomer conversion x.

1. Series A; *2.* Series F; *3.* Series B; *4.* Series D; *5.* Series C; *6.* Series E.

tion rate with increasing conversion occurred, on the other hand in Series B remarkable maximum on the curve expressing the dependence of the fractional copolymerization rate on conversion at approximately 20 % of total monomer conversion was observed.

The initial value of the fractional copolymerization rate (extrapolated to zero conversion) in the system with zinc dichloride (Series A) is about two times higher than that for the system without zinc dichloride (Series B). The substitution of α-methylstyrene for styrene leads to decrease of the fractional copolymerization rate (at Series C ca. to one quarter of the value found for Series A) obviously due to depropagation reactions of polymer chains containing sequences of α-methylstyrene structural units [16].

For terpolymerization systems (Series D, E, and F) the presence of zinc dichloride (Series D) has a consequence that the cumulative copolymer composition remains practically constant with conversion and without substantial change is also the instantaneous copolymer composition. On the contrary, in Series F the cumulative and instantaneous concentrations of α-methylstyrene structural units in terpolymer remain unchanged, but an increase of the styrene structural units in the terpolymer on behalf of the acrylonitrile structural units in the terpolymer was found. Similar behaviour as the dependence of the cumulative terpolymer composition on conversion has the dependence of instantaneous terpolymer composition. In Series E the cumulative concentrations of styrene as well as of α-methylstyrene structural units in terpolymer increase with increasing conversion, too: i.e. terpolymer becomes gradually enriched by structural units of electron-donor monomers (styrene and α-methylstyrene). This is just reversed tendency when compared to that which was observed in copolymerization systems styrene/ /acrylonitrile and α-methylstyrene/acrylonitrile (Series A, B, and C).

The dependence of the fractional terpolymerization rate (Series D, E, and F) on conversion (Fig. 1, curves 2, 4, and 6) is similar to that found for copolymerization systems (Series A, B, and C). Monotonic decrease of the fractional rate of terpolymerization of the systems containing zinc dichloride (Series D and F) is substituted by a characteristic maximum on the curve expressing the dependence of the fractional terpolymerization rate on conversion in the system without zinc dichloride (Series E).

Application of Alfrey—Goldfinger equations for terpolymerization systems, in which one of the comonomers does not polymerize [17] gave values of the terpolymer composition (Tables 5—7), which only very roughly corresponded to the values found experimentally (Table 5, Series D), but nonconsistent results were obtained for Series E and F.

The dependence of the concentration of unreacted monomers on the terpolymerization reaction time (Series D and F) is illustrated in Fig. 2. S-shaped curves are obtained for systems without zinc dichloride (Series E), while for
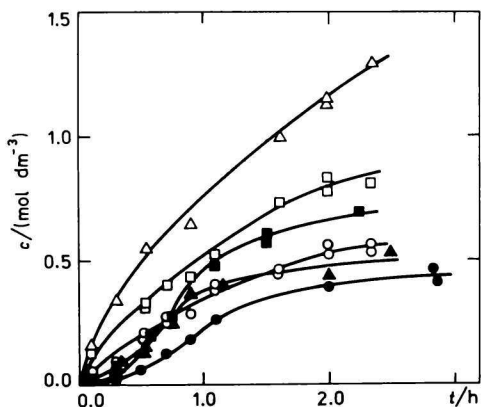
*Fig. 2.*Concentration (c/(mol dm^{-3})) dependence of reacted monomers at terpolymerization of styrene and of α-methylstyrene with acrylonitrile on the time (t/h) of terpolymerization.
○ Styrene (Series D); □ α-methylstyrene (Series D); △ acrylonitrile (Series D); ● styrene (Series F);
■ α-methylstyrene (Series F); ▲ acrylonitrile (Series F).

systems containing zinc dichloride no acceleration of the terpolymerization (gel effect) could be observed (*cf.* the dependence of the fractional rate of terpolymerization on conversion on the presence and/or absence of zinc dichloride given in Fig. 1).

On the basis of the presented results it is possible to state that the course of the propagation reactions of copolymerization is regulated significantly also by the presence of complexes (monomer complexes, complexes of monomers with solvent, complexes of monomer with Lewis acid) in the reaction system. Influencing the conditions for formation of complexes in the reaction system, *e.g.* by the change of feed composition, can result in the change of mechanism of the propagation reactions, the formal reflection of which is deviation of the course predicted by the use of the given model of copolymerization.

Influence of the change of the concentration of complexes in the dynamic copolymerizing system is not included in the present-day known models of copolymerization. Elaborating of the adequate model predicting theoretically the course of copolymerization in the wide area of monomer conversion is the matter of future for the present.

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Translated by J. Bartoň