

Copolymerization up to high conversions

V. Effect of temperature on the copolymerization of acrylonitrile and α -methylstyrene

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Dedicated to Professor Ing. A. Hrivík, CSc., in honour of his 60th birthday

The high conversion copolymerizations of acrylonitrile and α -methylstyrene at 50 °C, 90 °C, and 120 °C, respectively, have been studied in bulk. Conversion—time curves for the copolymerization of acrylonitrile and α -methylstyrene at temperatures 50 °C and 90 °C are linear up to 60 % of conversion (approx.). The gel effect is observed between 60 % and 80 % of conversion (approx.).

The variation of copolymer composition with conversion and temperature up to the high conversion was investigated. Differences are observed between the experimentally obtained copolymer composition and those predicted by an integrated form of the Mayo—Lewis copolymer equation above the ceiling temperature for poly(α -methylstyrene).

The ceiling temperature for the polymerization of α -methylstyrene is 61 °C and therefore the depropagation effects can be important at polymerization temperatures 90 °C and 120 °C even if the average sequence lengths of α -methylstyrene in the copolymer are supposed to be very short.

Изучены процессы сополимеризации в массе с высокой степенью конверсии акрилонитрила и α -метилстирола при 50 °C, 90 °C и 120 °C. Кривые зависимости степени конверсии от времени сополимеризации акрилонитрила и α -метилстирола при температурах 50 °C и 90 °C имеют вид линейной зависимости до приблизительно 60 % степени конверсии. Гелевый эффект наблюдается между 60 % и 80 % степенью конверсии (приблизительно).

Исследована зависимость состава сополимера от степени конверсии и температуры вплоть до высоких степеней конверсии. Обнаружены различия между составом экспериментально полученного сополимера и предсказываемым на основании интегрированной формы сополимеризационного уравнения Майо—Льюиса для температур, превышающих предельную для поли(α -метилстирола).

Предельная температура для полимеризации α -метилстирола равна 61 °C и, по-этому, приобретают значение депропагационные эффекты при температурах полимеризации 90 °C и 120 °C даже в случае, если средняя длина цепочек α -метилстирола в сополимере предполагается очень короткой.

Much attention has been devoted to the copolymerization of α -methylstyrene with large number of vinyl monomers. α -Methylstyrene copolymers are interesting from both the practical and theoretical point of view.

Little experimental work has been done at high conversion, hence the classical model proposed previously [1—3] describing free radical copolymerization has not been tested at high conversions.

It was proposed [1—3] that for a given pair of monomers the copolymer composition is a function of the reactivity ratio and the monomer feed composition only. During the last decades it has been shown that the copolymer composition depends also on the reaction medium, in particular being affected by solvent, catalyst, pH, pressure, and temperature [4—8]. The classical model of copolymerization has been considered to be inadequate in these cases and other models have been proposed on penultimate [9, 10] and antepenultimate [11] effects, depropagation reaction [12], and charge-transfer complex [13, 14].

The authors [15, 16] have recently showed some discrepancies between the experimental and predicted values of the copolymer composition if the copolymerization of styrene with methyl methacrylate was carried out in bulk at both low and high conversions.

The analysis of vinyl polymerization at high conversion is complicated by the influence of the gel effect on the kinetic parameters that control the polymerization behaviour. The gel effect is a well known phenomenon that is accompanied by an increase in both rate and degree of polymerization.

It is common to relate phenomenon "the gel effect" to the formation of a fluctuation network of macromolecules in the polymerizing system which causes reduction of the macroradical mutual diffusion rate resulting in their termination [17, 18]. This phenomenon has also been evaluated by the macromolecular close packing model [19].

We have performed the copolymerization of α -methylstyrene and acrylonitrile at the initial feed composition of 50 mole % α -methylstyrene in bulk above and below ceiling temperature for the polymerization of α -methylstyrene (61 °C) [20]. It is the purpose of this paper to show how the polymerization temperature and the depropagation reaction can influence the onset of the gel effect.

Experimental

Reagents

The initiator 2,2'-azoisobutyronitrile (AIBN) was crystallized twice from absolute ethanol. The initiators *t*-butylperoxybenzoate (TBPB) and di-*t*-butyl peroxide (TBP) were used without any purification as received.

Acrylonitrile (AN) and α -methylstyrene (AMS) were dried over anhydrous calcium dichloride and distilled twice at reduced pressure (100 Pa) of nitrogen used. Acetone and 1,4-dioxan were dried by anhydrous calcium dichloride and distilled.

Procedures

Copolymerizations of acrylonitrile and α -methylstyrene were carried out in bulk at 50 °C, 90 °C, and 120 °C, respectively. In all runs the initiator concentration $5 \times 10^{-2} \text{ mol dm}^{-3}$ was used. The initiators were used at different temperatures: AIBN at 50 °C, TBPB at 90 °C and TBP at 120 °C.

A polymerization solution was prepared by mixing the initiator and monomers in a vessel. Ampoules were then filled with known volumes of the polymerization solution. The copolymerization mixtures in glass ampoules were frozen with a dry ice/ethanol mixture and then evacuated (to 0.01 Pa) during 10 min. After disconnecting the vacuum they were de-frozen and after repeated freezing again evacuated. This cycle was repeated three times. The polymerization technique was similar to that described elsewhere [21, 22]. The composition of copolymers was determined by GLC (here doubled by C, H, N analyses) [23].

Results and discussion

Fig. 1 shows the conversion—time dependences for acrylonitrile/ α -methylstyrene copolymerization in bulk for the given reaction temperatures and feed compositions. The conversion curves for all runs are linear up to relatively high conversion, i.e. ca. 60 %. The autoacceleration of the copolymerization is observed beyond this conversion at 50 °C and 90 °C (cf. curves 1 and 2 in Fig. 1). When the

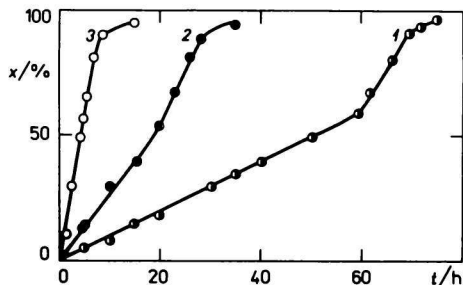


Fig. 1. Variation of the total monomer conversion (x) in free-radical copolymerization of acrylonitrile and α -methylstyrene in bulk with the reaction time and temperature. $[\text{AIBN}] = [\text{TBPB}] = [\text{TBP}] = 5 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{AN}] = [\text{AMS}] = 5.1 \text{ mol dm}^{-3}$.
1. 50 °C; 2. 90 °C; 3. 120 °C.

copolymerization was carried out at 120 °C no visible gel effect was observed (cf. curve 3 in Fig. 1). The initial rate of copolymerization increases with the increasing temperature even though the copolymerizations were carried out at comparable rates of initiation (see later).

Conversion—time data in Fig. 1 (curves 1, 2, and 3) 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 monomer (mol) in feed at time zero and time t of the polymerization. It is seen that the fractional rate increases abruptly beyond 60 % conversion and exhibits the maximum at conversions 80—85 %. The free radical copolymerization of acrylonitrile and α -methylstyrene produces number-average molar masses $\bar{M}_N = 20.000 \text{ g mol}^{-1}$ at 50 °C and $\bar{M}_N = 30.000 \text{ g mol}^{-1}$ at 90 °C. It means that the active polymer chains even in high concentrated solution are too small to be regarded as entangled and thus of unrestricted mobility. These polymer chains are regarded as having the same value of k_t as in more dilute solution.

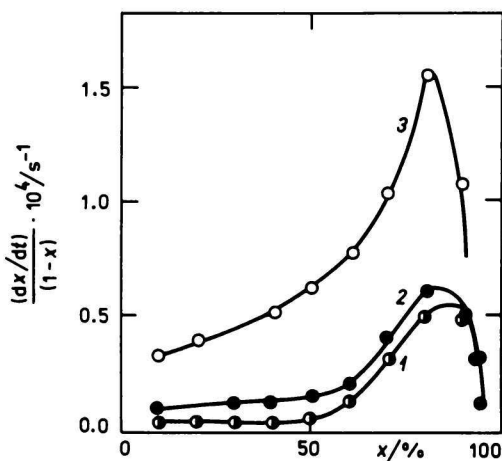


Fig. 2. Variation of the fractional rate of copolymerization $(dx/dt)/(1-x)$ with the conversion and reaction time. 1. 50 °C; 2. 90 °C; 3. 120 °C. Other conditions as given in the legend to Fig. 1.

In copolymerization of acrylonitrile and α -methylstyrene “semiheterogeneous” process was observed above conversions of 80 % or 90 %. Up to this conversion copolymers were transparent. Beyond this conversion copolymer solutions were translucent.

Despite of the high initiation rate the rate of bulk copolymerization of acrylonitrile and α -methylstyrene is very slow, probably in connection with the low degree of polymerization. The report of the authors [24] is consistent with our assumption that the kinetic factors are responsible for the low copolymer molecular masses, *i.e.* the propagation rate is very slow due to the steric factors and the termination rate is high. The high value of termination rate constant for α -methylstyryl radicals was obtained in the copolymerization of styrene and α -methylstyrene [25].

The increase in the copolymer molecular mass with higher reaction temperature at approximately equal rates of initiation indicates that the propagation reaction rate increases faster than the termination rate due to the lower activation energy of the latter. It is expected that the retarding effect of α -methylstyrene will somewhat

decrease with increasing temperature. The chain transfer to initiator will slightly decrease the molecular mass of copolymer formed at 90 °C (TBPB used as initiator) but not at 50 °C (AIBN used as initiator, $c_1 \approx 0$). It is clear that the chain transfer to initiators cannot be responsible for the observed trend in the values of polymer molecular masses.

The influence of the temperature on the copolymerization behaviour of acrylonitrile and α -methylstyrene is also shown in Fig. 3. This dependence comes from the following equation

$$\ln ([M]_0/[M]_t) = k_p/k_t^{0.5} (2fk_d [I])^{0.5} t \quad (2)$$

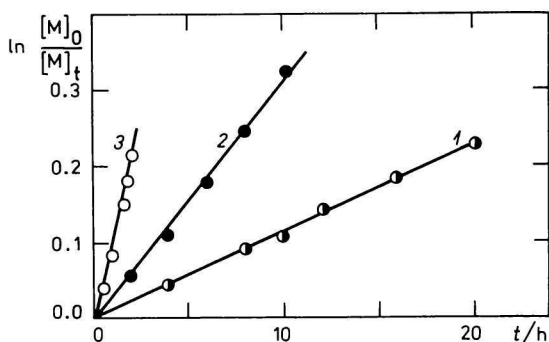


Fig. 3. First-order plots for the copolymerization of acrylonitrile and α -methylstyrene. $[AIBN] = [TBPB] = [TBP] = 5 \times 10^{-2} \text{ mol dm}^{-3}$, $[AN] = [AMS] = 5.1 \text{ mol dm}^{-3}$.
1. 50 °C; 2. 90 °C; 3. 120 °C.

where $[M]_0$ is the initial concentration of monomer, k_p denotes the propagation rate constant, k_t is the rate constant for termination reaction, k_d is the rate constant for the decomposition of the initiator, f is the initiator efficiency, $[I]$ is the concentration of the initiator, and t is the polymerization time. From this simplified procedure the known rate of initiation expressed by $2fk_d [I]$ allows evaluation of the ratio $k_p/k_t^{0.5}$.

The ratio of mean rate constants $k_p/k_t^{0.5}$ of the copolymerization of acrylonitrile and α -methylstyrene was determined by eqn (2) using values of R_i and slopes of the straight lines in Fig. 3. Kinetic constants obtained from such plots are together with other parameters listed in Table 1. This behaviour corresponds to a difference in apparent energies of activations of propagation and termination steps. From the data of the copolymerization rates for the temperature range 50–60 °C the overall activation energy of 65 kJ mol⁻¹ was estimated [29]. From the data of the $k_p/k_t^{0.5}$ ratios for the temperature range 50–60 °C a difference in apparent energies of activations, $E_p - (E_t/2)$, ca. 17.5 kJ mol⁻¹ was estimated. From these data the activation energy of initiation ca. 95 kJ mol⁻¹ was estimated, which is physically

Table 1

Kinetic parameters of α -methylstyrene and acrylonitrile copolymerization

θ	50 °C	50 °C	60 °C	90 °C	120 °C
Initiator	AIBN	AIBN	AIBN	TBPB	TBP
$c/(\text{mol dm}^{-3})$	0.05	0.02	0.02	0.05	0.05
$k_d \cdot 10^6 \text{ s}^{-1}$	2.77	2.77	8.5	1.0	7.5
f	0.5	0.5	0.5	0.7	0.7
$\frac{R_i \cdot 10^7}{\text{mol dm}^{-3} \text{ s}^{-1}}$	1.38	0.554	1.7	0.7	5.25
$\frac{k_p/k_t^{0.5} \cdot 10^2}{(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})^{0.5}}$	0.85	684*	85*	3.25	4.02

The values of k_d and f are taken from Ref. [26–28].

* The values of polymerization rates are taken from Ref. [29] to calculate the values of $k_p/k_t^{0.5}$.

quite reasonable. From the data of the ratios of the rate constants for propagation and termination ($k_p/k_t^{0.5}$) for the temperature range 90–120 °C a difference in apparent energies of activations, $E_p - E_d - (E_t/2)$, ca. 8.5 kJ mol⁻¹ was estimated.

The variations of the cumulative copolymer composition (the mole fraction of acrylonitrile structural units in the copolymer) with conversion and temperature are plotted in Fig. 4. The copolymer composition was simply calculated from a mass balance. It is seen that the content of acrylonitrile in the copolymer increases with the increasing polymerization temperature.

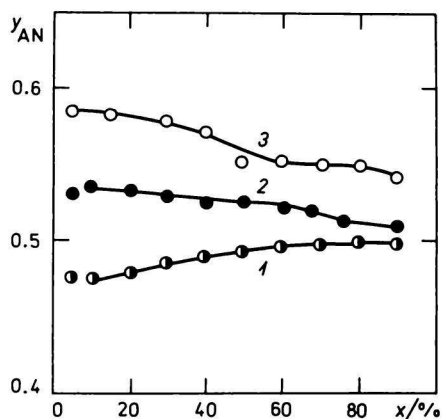


Fig. 4. Variation of the cumulative average mole fraction of acrylonitrile in the copolymer, y_{AN} , with the conversion and reaction temperature. 1. 50 °C; 2. 90 °C; 3. 120 °C. Other conditions as given in the legend to Fig. 3.

The instantaneous copolymer composition (the mole fraction of acrylonitrile) calculated from the single integrated copolymer composition equation [3] and reference data [30] for reactivity ratios $r_{AN}=0.06$ and $r_{AMS}=0.1$ together with the initial monomer feed composition $[AN]/[AMS]=1.0$ ($[AN]+[AMS]=$

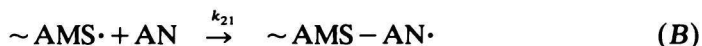
= 10.2 mol dm⁻³) is 0.49. Reactivity ratios are assumed to be independent of reaction temperature [31] and therefore the predicted copolymer composition is 0.49 (for a given monomer feed composition) for different polymerization temperatures. The observed copolymer composition at 90 °C and 120 °C differs, however, from the predicted one.

The values of copolymer composition and the shape of copolymer conversion curves show that the system deviates from simple kinetics of copolymerization. The observed fluctuations in the copolymer composition data point out as if they were the results of variations in the values of reactivity ratios r_{AN} and r_{AMS} as the polymerization advances. This approach implies, however, a variation of the propagation rate constants with conversion. In the range of high conversions the propagation rate constants vary with conversion. In the range of high conversions the variation of the propagation rate constants should be associated with the onset of gel effect. On the other hand, this explanation cannot explain the change of propagation rate constants at conversions as moderate as 20 %.

Due to the fact that the simple kinetic model was not applicable, other models were also considered for an explanation of the kinetic anomalies of the present copolymerization, e.g. the penultimate unit effects and the charge transfer complex formation but both were rejected.

The increase of acrylonitrile structural units in copolymer with increasing temperature indicates that the depropagation of α -methylstyrene sequences should take place, i.e. some decrease in the value of the equilibrium constant K (the ratio of the propagation and depropagation rate constants) should be observed. However the relative reactivities of acrylonitrile and α -methylstyrene are such that α -methylstyrene sequences should not be very long. The experimental results show that the copolymerization behaviour of α -methylstyrene is strongly temperature-dependent.

In free radical copolymerization of α -methylstyrene and acrylonitrile there are several steps involved in the formation of a chain and one or two are reversible



Below the ceiling temperature for the polymerization of α -methylstyrene the polymer chain is formed only by irreversible propagation steps. The relative

reactivities of acrylonitrile and α -methylstyrene indicate that the cross propagation reaction (eqn (B)) should be dominant in the propagation mechanism at temperatures below 60 °C. Above the ceiling temperature of 61 °C the polymerization kinetics is supposed to be effected by depropagation reactions (eqn (D) — reversible step).

These results can be explained on the grounds that short sequence lengths of α -methylstyrene in the copolymer have greater enthalpies of polymerization and correspondingly higher ceiling temperatures than 61 °C [32]. Thus the copolymer with higher α -methylstyrene sequence lengths is characterized by lower ceiling temperature and reversely. Our results show that the polymerization temperature of 90 °C is high enough to initiate the depropagation of certain α -methylstyrene sequence lengths or to change the equilibrium constant K . It seems that with increasing the polymerization temperature the depropagation of shorter sequences of α -methylstyrene proceeds.

Results of turbidimetric titrations and extractions of the polymer product indicate that it contains only the acrylonitrile/ α -methylstyrene copolymer. The formation of polyacrylonitrile was not detected.

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