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Kinetics of the Copolymerization of the Donor–Acceptor Monomers

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ABSTRACT: A general equation for the copolymerization rate at low monomer conversion has been proposed on the basis of theoretical considerations concerning the monomers' capability of forming intermolecular complexes. Modifications for the case of linear or quadratic termination and for the case of the bifunctional allyl monomers have also been proposed. An algorithm for the solution of these equations has been prepared, and the values of the rate constants of elementary reactions of chain growth for the two systems have been determined. These values (L/mol·s) are as follows for the system styrene (1)–acrylonitrile (2): $K_{11} = 247$, $K_{12} = 393$, $K_{21} = 27\ 027$, $K_{22} = 1405$, $K_{1c1} = 1057$, $K_{1c2} = 706$, $K_{2c1} = 18\ 811$, $K_{2c2} = 21\ 370$, and for the system diethylene glycol bis(allyl carbonate) (3)–maleic anhydride (4): $K_{33} = 65$, $K_{34} = 155$, $K_{43} = 173$, $K_{44} = 0$, $K_{3c3} = 72$, $K_{3c4} = 3155$, $K_{4c3} = 9356$, $K_{4c4} = 0$.

Introduction

The general contribution of the molecular complexes to the chain-growth reactions at copolymerization of different monomers has been widely discussed.[1-4] But the approaches for determination of separate contribution of each elementary reaction of chain growth in the total rate of process have not been proposed. The well-known equations of the copolymerization rate and copolymer composition do not allow for the solution of this problem without the additional experiments of the homopolymerization of the separate monomers. But even in this case, the values of the rate constants only for four elementary reactions of binding of the free monomers to the growth radicals (K_{ii}, K_{ij}, K_{ji}, K_{jj}) can be determined. The contribution of the monomer complexation into the chain growth reactions can be estimated only as rate constant ratios: K_{ici}/K_{ij}, K_{icj}/K_{ij}, etc.[5,6]

In the present work, the general equation of the copolymerization rate for the donor–acceptor systems of vinyl and allyl monomers has been proposed as well as its modifications for the case of linear or quadratic termination and for the case of bifunctional allyl monomers. The solution of this equation allows us to determine the values of the eight rate constants of the elementary chain growth reactions for two systems: styrene (1)–acrylonitrile (2) and diethylene glycol bis(allyl carbonate) (3)–maleic anhydride (4). This makes it possible to estimate the contribution of each elementary chain-growth reaction in the total rate of the process.

Materials and Methods

The monomers styrene (1), acrylonitrile (2), diethylene glycol bis(allyl carbonate) (3), and maleic anhydride (4) were purified until the grade of 99.97% by well-known methods.[7] Benzoyl peroxide (BP) with an analytical grade of 99.98% was used as the radical initiator of the polymerization at a concentration of 1–5 mM. All other commercial reagents and chemicals were chromatographic grade and were used without additional purification.

The complexation between comonomers was investigated by NMR spectroscopy with mathematical processing of the obtained data according to the equation[4]

$$\frac{1}{\Delta} = \frac{1}{K_k\Delta_k}\frac{1}{[M_{i(j)}]_0} + \frac{1}{\Delta_k} \qquad (1)$$

where Δ is the difference between the chemical shifts of donor protons in a mixture with the acceptor and in neutral solvent like cyclohexane (M_1–M_2) or acetonitrile (M_3–M_4); Δ_k is the chemical shift of a complex; $[M]_0$ is the initial monomer concentration; M_i is donor 1 or 3; M_j is acceptor 2 or 4; and K_k is the constant of a complex formation.

The measurements were performed at constant temperatures of 273–333 K. NMR spectra were recorded on a "Tesla" spectrophotometer (Czechoslovakia) at 80 MHz. The initial acceptor concentration changed in the interval 1.7–6.0 M (for system M_1–M_2) or 1.2–3.7 M (for system M_3–M_4) under a constant concentration of a donor of 0.5 or 0.1 M, respectively. The treatment of experimental data was performed by usual statistical methods. The complex concentration (C) was calculated according to a well-known equation[3] on the basis of experimentally measured value of constant K_k.

The copolymerization was performed in bulk and in dioxane solution at 333 K until 1–5% conversion, which was determined by dilatometry, gas–liquid chromatography (GLC), and gravimetry. The obtained copolymers were purified by sedimentation (two times) from a 1% chloroform solution into methanol (system M_1–M_2) or from a 1% acetone solution into diethyl ester (system M_3–M_4). The copolymer compositions were determined by IR and NMR spectroscopy; molecular weights, by gel-permeable chromatography (GPC) and termoelectrical methods.

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The initiation rate was measured using 2,2,6,6-tetramethylpiperidine-1-oxyl as an inhibitor. The effective rate constants of the chain termination reactions (K_t^{ef}) were measured by rotating sector method.[5]

Results and Discussion

The traditional kinetic scheme of chain growth reactions for a two-component donor–acceptor system[2] taking into account donor–acceptor complex formation can be written as follows:[3]

$$\sim M_i^* + M_i \xrightarrow{K_{ii}} \sim M_iM_i^* \tag{2}$$

$$\sim M_i^* + M_j \xrightarrow{K_{ij}} \sim M_iM_j^* \tag{3}$$

$$\sim M_j^* + M_i \xrightarrow{K_{ji}} \sim M_jM_i^* \tag{4}$$

$$\sim M_j^* + M_j \xrightarrow{K_{jj}} \sim M_jM_j^* \tag{5}$$

$$\sim M_i^* + M_i \cdots M_j \xrightarrow{K_{ici}} \sim M_iM_iM_j^* \tag{6}$$

$$\sim M_i^* + M_j \cdots M_i \xrightarrow{K_{icj}} \sim M_iM_jM_i^* \tag{7}$$

$$\sim M_j^* + M_i \cdots M_j \xrightarrow{K_{jci}} \sim M_jM_iM_j^* \tag{8}$$

$$\sim M_j^* + M_j \cdots M_i \xrightarrow{K_{jcj}} \sim M_jM_jM_i^* \tag{9}$$

$$M_i + M_j \overset{K_k}{\leftrightarrow} M_i \cdots M_j \text{ (or } M_j \cdots M_i) \tag{10}$$

The total rate of monomer expenditure during reactions 2–9 can be expressed by the following equation:

$$\begin{aligned} d([M_i] + [M_j])/dt = K_{ii}[\sim M_i^*][M_i] + \\ K_{ij}[\sim M_i^*][M_j] + K_{ji}[\sim M_j^*][M_i] + K_{jj}[\sim M_j^*][M_j] + \\ K_{ici}[\sim M_i^*][M_i \cdots M_j] + K_{icj}[\sim M_i^*][M_j \cdots M_i] + \\ K_{jci}[\sim M_j^*][M_i \cdots M_j] + K_{jcj}[\sim M_j^*][M_j \cdots M_i] \end{aligned} \tag{11}$$

The concentration of free radicals in the stationary state at diffusion control of chain termination can be written as follows for quadratic termination:

$$[\sim M_i^*] = \left(\frac{V_{in}}{K_0}\right)^{1/2} \times \frac{K_{ji}[M_i] + K_{jcj}[M_j \cdots M_i]}{K_{ji}[M_i] + K_{jcj}[M_j \cdots M_i] + K_{ij}[M_j] + K_{ici}[M_i \cdots M_j]} \tag{12}$$

$$[\sim M_j^*] = \left(\frac{V_{in}}{K_0}\right)^{1/2} \times \frac{K_{ij}[M_j] + K_{ici}[M_i \cdots M_j]}{K_{ji}[M_i] + K_{jcj}[M_j \cdots M_i] + K_{ij}[M_j] + K_{ici}[M_i \cdots M_j]} \tag{13}$$

where V_{in} is the initiation reaction rate.

It is assumed that composition of donor–acceptor complexes is equal to a 1:1 ratio ($[M_1 \cdots M_2] = [M_2 \cdots M_1] = [C]$). In this case the substitution of eqs 12 and 13 into eq 11 leads to the general equation of the copolymerization rate:

$$\begin{aligned} V = \left(\frac{V_{in}}{K_0}\right)^{1/2} \Bigg([M_i]^2 + \frac{K_{jcj}}{K_{ji}}[M_i][C] + 2\frac{K_{ij}}{K_{ii}}[M_i][M_j] + \\ \frac{K_{ij}K_{jcj}}{K_{ii}K_{ji}}[M_j][C] + 2\frac{K_{ici}}{K_{ii}}[M_i][C] + \frac{K_{jj}K_{ij}}{K_{ji}K_{ii}}[M_j]^2 + \\ \frac{K_{jj}K_{ici}}{K_{ji}K_{ii}}[M_j][C] + 2\frac{K_{ici}K_{jcj}}{K_{ii}K_{ji}}[C]^2 + \frac{K_{icj}}{K_{ii}}[M_i][C] + \\ \frac{K_{icj}K_{jcj}}{K_{ii}K_{ji}}[C]^2 + \frac{K_{jci}K_{ij}}{K_{ji}K_{ii}}[M_j][C] + \frac{K_{jci}K_{ici}}{K_{ji}K_{ii}}[C]^2 + \\ \frac{K_{jcj}K_{ij}}{K_{ji}K_{ii}}[M_j][C] \Bigg) \Bigg/ \Bigg(\frac{1}{K_{ii}}[M_i] + \frac{K_{jcj}}{K_{ii}K_{ji}}[C] + \\ \frac{K_{ij}}{K_{ii}K_{ji}}[M_j] + \frac{K_{ici}}{K_{ji}K_{ii}}[C] \Bigg) \end{aligned} \tag{14}$$

It is convenient, as was proposed for the same scheme,[3] to mark the definite ratios of the rate constants of elementary reactions as follows:

$$K_{ii}/K_{ij} = r_{ij};\ K_{ici}/K_{ij} = \alpha_{ii};\ K_{icj}/K_{ij} = \alpha_{ij};\ K_{jj}/K_{ji} = r_{ji};\ K_{jcj}/K_{ji} = \alpha_{jj};\ K_{jci}/K_{ji} = \alpha_{ji} \tag{15}$$

Then substituting such ratios in eq 14, one can obtain the following:

$$\begin{aligned} \frac{1}{K_{ii}} + \frac{1}{K_{ji}}\left(\frac{[M_j] + \alpha_{ii}[C]}{r_{ij}([M_i] + \alpha_{jj}[C])}\right) = \\ \left(\frac{V_{in}^{1/2}}{VK_0^{1/2}([M_i] + \alpha_{jj}[C])}\right)\Bigg\{[M_i]^2 + \frac{2}{r_{ij}}[M_i][M_j] + \\ \frac{r_{ji}}{r_{ij}}[M_j]^2 + \left(\alpha_{jj} + \frac{2\alpha_{ii}}{r_{ij}} + \frac{\alpha_{ij}}{r_{ij}}\right)[M_i][C] + \\ \left(\frac{2\alpha_{jj} + r_{ji}\alpha_{ii} + \alpha_{ji}}{r_{ij}}\right)[M_j][C] + \\ \left(\frac{2\alpha_{ii}\alpha_{jj} + \alpha_{ij}\alpha_{jj} + \alpha_{ji}\alpha_{ii}}{r_{ij}}\right)[C]^2\Bigg\} \end{aligned} \tag{16}$$

The whole right part of this equation can be marked by symbol D, and the expression in the brackets at the left part, by symbol A. Then eq 16 will be as follows:

$$D = 1/K_{ii} + (1/K_{ji})A \tag{16'}$$

The obtained general equation of the copolymerization rate (16 or 16′) is linear. The V, V_{in}, K_t^{ef} and equilibrium $[M_i]$, $[M_j]$, $[C]$ values can be determined experimentally. Then it is possible to obtain the values K_{ii} directly by using the graphical method (Figure 1) for solution of linear eq 16′. By extrapolation of the linear dependence D vs A on Figure 1, the value of the intercept on ordinate (ΔD) was obtained, which is equal to $1/K_{ii}$. So, $K_{ii} = 1/\Delta D$. The value of the K_{ji} can be determined from the tangent of the angle slope of this linear dependence: $\mathrm{tg}\,\alpha = 1/K_{ji}$ (Figure 1). Therefore, $K_{ji} = 1/\mathrm{tg}\,\alpha$, without additional experiments on homopolymerization of separate monomers. After this, all the other constants of elementary reactions of chain growth can be easily determined, as will be shown below.

For systems like styrene–maleic anhydride, where one monomer cannot be homopolymerized ($K_{jj} = 0$, $\alpha_{jj} = 0$), eq 16 will be as follows:

$$\frac{1}{K_{ii}} + \frac{1}{K_{ji}}\left(\frac{[\mathrm{M}_j] + \alpha_{ii}[\mathrm{C}]}{r_{ij}[\mathrm{M}_i]}\right) = \frac{V_{\mathrm{in}}{}^{1/2}}{VK_0{}^{1/2}[\mathrm{M}_i]}\left([\mathrm{M}_i]^2 + \frac{2}{r_{ij}}[\mathrm{M}_i][\mathrm{M}_j] + \frac{2\alpha_{ii}\alpha_{ij}}{r_{ij}}[\mathrm{M}_i][\mathrm{C}] + \frac{\alpha_{ji}}{r_{ij}}[\mathrm{M}_j][\mathrm{C}] + \frac{\alpha_{ji}\alpha_{ii}}{r_{ij}}[\mathrm{C}]^2\right) \quad (17)$$

If M_i is a monoallyl monomer, for which the reaction of intramolecular cyclization is negligable and the predominant termination reaction is a reaction of degradation chain transfer, then, according to work,[1] the following equation can be written:

$$[\sim\mathrm{M}_i{}^*] + [\sim\mathrm{M}_j{}^*] = V_{\mathrm{in}}/K_{\mathrm{M}}[\mathrm{M}_i]_0 \quad (18)$$

where K_M is the rate constant of chain transfer reaction on allyl monomer. In this case eq 16 can be shown as follows:

$$\frac{K_{\mathrm{M}}}{K_{ij}} + \frac{K_{\mathrm{M}}}{K_{ji}}\left(\frac{[\mathrm{M}_j] + \alpha_{ii}[\mathrm{C}]}{r_{ij}([\mathrm{M}_i] + \alpha_{jj}[\mathrm{C}])}\right) = \frac{V_{\mathrm{in}}}{V[\mathrm{M}_i]_0([\mathrm{M}_i] + \alpha_{jj}[\mathrm{C}])}\left\{[\mathrm{M}_i]^2 + \frac{2}{r_{ij}}[\mathrm{M}_i][\mathrm{M}_j] + \frac{r_{ji}}{r_{ij}}[\mathrm{M}_j]^2 + \left(\alpha_{jj} + \frac{2\alpha_{ii}}{r_{ij}} + \frac{\alpha_{ij}}{r_{ij}}\right)[\mathrm{M}_i][\mathrm{C}] + \left(\frac{2\alpha_{jj} + r_{ji}\alpha_{ii} + \alpha_{ji}}{r_{ij}}\right)[\mathrm{M}_j][\mathrm{C}] + \left(\frac{2\alpha_{ii}\alpha_{jj} + \alpha_{ij}\alpha_{jj} + \alpha_{ji}\alpha_{ii}}{r_{ij}}\right)[\mathrm{C}]^2\right\} \quad (19)$$

If M_i is a bifunctional allyl monomer, capable to complexation ($M_i\cdots M_j$), then reaction equations 2, 4, 6, and 9 and the rates of each reaction can be shown as follows:

$$\sim\mathrm{M}_i{}^* + \mathrm{M}_i \xrightarrow{K_{ii}} \sim\mathrm{M}_i\mathrm{M}_i{}^* \qquad V_{ii} = 2K_{ii}[\sim\mathrm{M}_i{}^*][\mathrm{M}_i] \quad (2')$$

$$\sim\mathrm{M}_j{}^* + \mathrm{M}_i \xrightarrow{K_{ji}} \sim\mathrm{M}_j\mathrm{M}_i{}^* \qquad V_{ji} = 2K_{ji}[\sim\mathrm{M}_j{}^*][\mathrm{M}_i] \quad (4')$$

$$\sim\mathrm{M}_i{}^* + \mathrm{M}_i\cdots\mathrm{M}_j \xrightarrow{K_{ici}} \sim\mathrm{M}_i\mathrm{M}_i\mathrm{M}_j{}^* \qquad V_{ici} = (K_{ici} + K_{ii}) \times [\sim\mathrm{M}_i{}^*][\mathrm{C}] \quad (6')$$

$$\sim\mathrm{M}_j{}^* + \mathrm{M}_i\cdots\mathrm{M}_j \xrightarrow{K_{jci}} \sim\mathrm{M}_j\mathrm{M}_i\mathrm{M}_j{}^* \qquad V_{jci} = (K_{jci} + K_{ji}) \times [\sim\mathrm{M}_j{}^*][\mathrm{C}] \quad (8')$$

The equation of copolymerization in this case will be as follows:

$$\frac{K_{\mathrm{M}}}{K_{ij}} + \frac{K_{\mathrm{M}}}{K_{ji}}\left(\frac{[\mathrm{M}_j] + \alpha_{ii}[\mathrm{C}]}{2[\mathrm{M}_i] + [\mathrm{C}]}\right) = \frac{V_{\mathrm{in}}}{V[\mathrm{M}_i]_0(2[\mathrm{M}_i] + [\mathrm{C}])} \times \left\{2r_{ij}[\mathrm{M}_i]^2 + 2[\mathrm{M}_i][\mathrm{M}_j] + (2r_{ij} + 2\alpha_{ii} + \alpha_{ij})[\mathrm{M}_i][\mathrm{C}] + (1 + \alpha_{ji}/2)[\mathrm{M}_j][\mathrm{C}] + \left(\alpha_{ii} + \frac{r_{ij}}{2} + \frac{\alpha_{ij}}{2} + \frac{\alpha_{ii}\alpha_{ji}}{2}\right)[\mathrm{C}]^2\right\} \quad (20)$$

or

$$D' = K_{\mathrm{M}}/K_{ij} + (K_{\mathrm{M}}/K_{ji})A' \quad (20')$$

For the determination of all eight rate constants of elementary reactions of chain growth, using eq 20, it is necessary first to obtain in a separate experiment the K_M value.[6] Then other constants can be determined by using the graphical method for solution of linear eq 20′, shown in Figure 1.

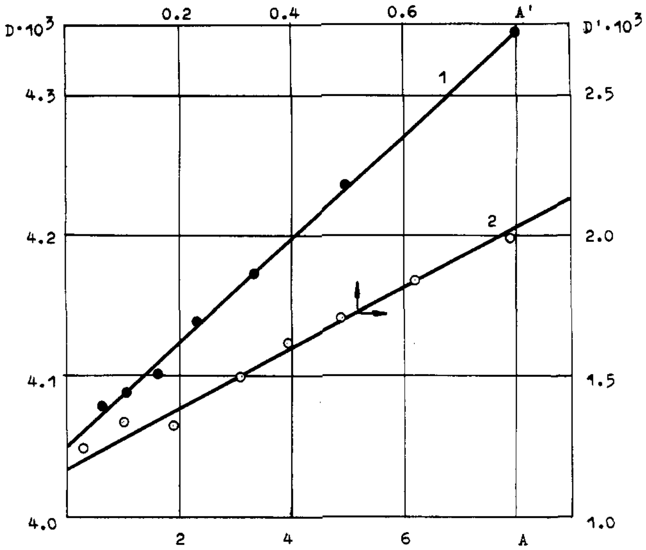

Figure 1. The dependences in the coordinates of eqs (16′) and (20′) for the systems M_1–M_2 (1) and M_3–M_4 (2), respectively.

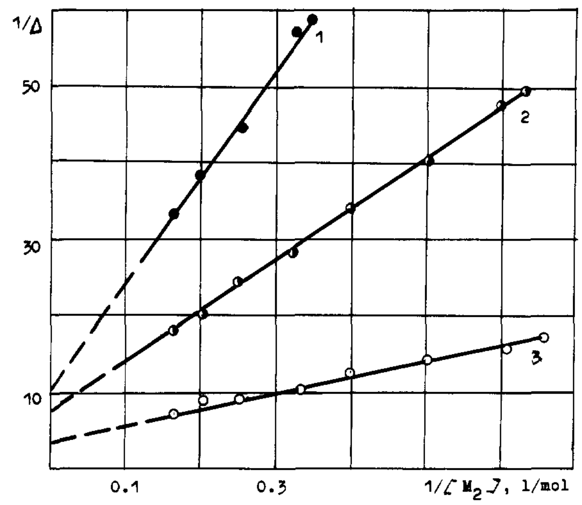

Figure 2. The dependences of the chemical shift changes (Δ) of donor protons in NMR spectra vs the acceptor concentration [M_2] for the system M_1–M_2 at the temperatures 333 (1), 315 (2), and 298 K (3).

Two systems, styrene (1)–acrylonitrile (2) and diethylene glycol bis(allyl carbonate) (3)–maleic anhydride (4), were carefully investigated as examples of applicability of the obtained equations. First, the change of chemical shifts of donor M_1 or acceptor M_4 protons dependent on concentrations of acceptor M_2 or donor M_3, respectively (Figures 2 and 3), were measured for calculation of concentrations of monomers binding in complex. The obtained equilibrium constants decreased from 0.18 to 0.07 ± 0.04 L/mol for system M_1–M_2 or from 0.18 to 0.14 ± 0.04 L/mol for system M_3–M_4 when the temperature increased from 298 or from 273 to 333 K, respectively. Using the K_k values at 333 K (temperature of copolymerization), the equilibrium complex concentrations were calculated in dependence of monomers mixture compositions (Table I). It was shown that such values were continuously decreasing as [M_j] decreased. The complexes M_1–M_2 and M_3–M_4 belong to the π–π and n–π types. Their maximal concentrations were at 40% of donor monomer for system M_1–M_2 and at 50% for M_3–M_4.

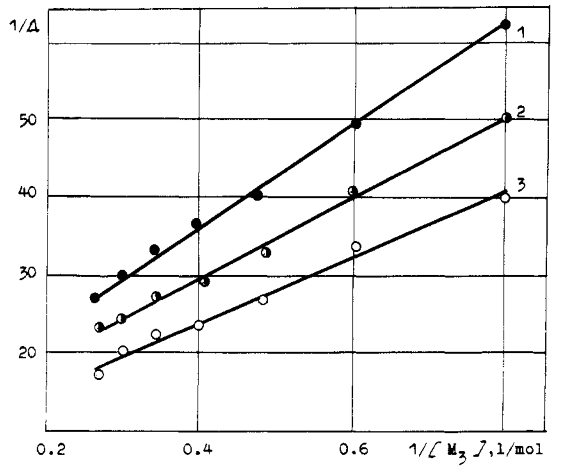

Figure 3. The dependences of the chemical shift changes (Δ) of acceptor protons in NMR spectra vs the donor concentration [M_3] for the system M_3–M_4 at the temperatures 333 (1), 303 (2), and 273 K (3).

The analysis of logarithmic dependence of copolymerization rate vs benzoyl peroxide concentration shows that the degree of initiator concentration is 0.5 for the first system and increases up to 1.0 for the second with increases of [M_4] in the initial mixture. Therefore the quadratic termination is characteristic for the M_1–M_2 system. For the M_3–M_4 system, some of the primary radicals can "perish" as a result of high-active "allyl" hydrogen coming off or can recombine with low-active "allyl" radicals, which form in the chain-transfer reaction on monomer M_3. In this case, the copolymerization rate must be decreased with the increase of M_3 concentration, as shown in Table II, and the maximal value is observed at equimolar monomers ratio.

The copolymerization rate in the M_1–M_2 system decreases with a decrease of acrylonitrile concentration in the initial monomer mixture (Table II). In contrast, for this system copolymerized without benzoyl peroxide, the maximum of the dependence of polymerization rate vs concentration of comonomers was found at a ratio close to equimolar. This is the additional evidence of the complex formation in the styrene–acrylonitrile system. The other behavior of the total polymerization rate in the presence of benzoyl peroxide can be due to strong complex formation between acrylonitrile and benzoyl peroxide (K_k = 0.20 L/mol at 293 K and 0.07 L/mol at 333 K). It is obvious that the presence of such complexes at the initial stage of the reaction (the constant of the decomposition of benzoyl peroxide in acrylonitrile is in 43 times higher than in styrene) has a strong influence on the total rate of polymerization, especially at high acrylonitrile concentrations in the initial mixture. The other reason may be the essential influence of homo- and cross-chain growth of free monomers on the total rate of the process. This must be characteristic for all donor–acceptor systems if the reaction abilities of their growth radicals differ by more than 1 order of magnitude. In this case, one can expect the dependence of V_{in} and K_t^{ef} from the initial monomers ratio, which was also observed experimentally (Table II). Apparently, such dependence does not exactly reflect reality because the participance of binding in complex monomers for the chain termination and initiation reactions is not taken into account in the kinetic scheme and equations.

For both systems it seems to be fruitful to include in the general kinetic scheme of the reaction of initiation with peroxide binding in the complex with acrylonitrile or maleic anhydride, which can be the limiting stage of peroxide disintegration. So at the equal conditions V_{in} in the system $M_1\cdots M_2$ is more than 1 order of magnitude higher compared to the system $M_3\cdots M_4$. This experimental fact cannot be explained by the mechanism of radicals "going out" of the cell. Obviously, a more correct explanation seems to be in the existence of interaction reactions between the primary radical and monomer (M_3) or monomers' complex $M_3\cdots M_4$ by the side of M_3:

$$R^* + M_3 \longrightarrow RH + M_3^* \qquad (21)$$

$$R^* + M_3\cdots M_4 \longrightarrow RH + M_3^* + M_4 \qquad (22)$$

$$R^* + M_3\cdots M_4 \longrightarrow RH + M_3M_4^* \qquad (23)$$

The additional evidence is the character of experimentally obtained dependence of $1/P_n$ vs $([M_3] + [M_4])^2$ (Figure 4). The tangent of the angle of the slope of the dependence is near zero, which excludes the bimolecular chain termination. The obtained values of the effective rate constant of chain transfer on the monomer (C_M^{ef}) change from 0.025 to 0.018 under a [M_4] decrease from 65 to 30% in the initial mixture. The correlation between the C_M^{ef} values, obtained under copolymerization and homopolymerization of M_3 (0.014), shows that complex formation between monomers accelerate not only the chain-growth reaction but also the the chain transfer-reaction due to reactions 21–23 and due to the interaction between growth radical and complex:

$$\sim M_i^* + C \xrightarrow{K_M^*} \sim M_iH + R^* \qquad (24)$$

where K_M^* is the rate constant of the chain-transfer reaction on binding in complex allyl monomer; R*, binding in complex allyl radical.

The obtained copolymer composition, diethylene glycol bis(allyl carbonate)–maleic anhydride, determined by NMR spectroscopy, deviates from equimolar under an [M_3] increase in the initial mixture (Table I). This effect can be caused by the binding of the growth radical (ending on M_3^* unit) to the M_3 side of the complex. The analysis of the obtained copolymer composition shows that the complex formation in the systems of allyl–vinyl monomers activates the double allyl groups in the chain-growth reaction.

The r_{ij} and r_{ji} values were determined from the obtained values of copolymer composition. Then the equation of copolymerization was solved using a special computing program and taking into account the equilibrium monomers and complex concentrations (Table I). The following values of the ratios of rate constants of elementary chain-growth reactions were obtained from system $M_1\cdots M_2$:

$$\alpha_{11} = 2.69 \pm 0.34;\ \alpha_{22} = 0.79 \pm 0.04;$$
$$\alpha_{12} = 1.80 \pm 0.09;\ \alpha_{21} = 0.70 \pm 0.12;$$
$$r_{12} = 0.63 \pm 0.22;\ r_{21} = 0.05 \pm 0.005 \qquad (25)$$

and for system M_3–M_4:

$$\alpha_{33} = 0.46 \pm 0.14;\ \alpha_{44} = 0;\ \alpha_{34} = 20 \pm 1.5;$$
$$\alpha_{43} = 53.97 \pm 2.88;\ r_{34} = 0.42 \pm 0.11;\ r_{43} = 0 \qquad (26)$$

Then these parameters (25–26), K_{33} = 65 L/mol·s,[7] and data collected in Table II (V, V_{in}, K_t^{ef}) were inserted into eqs 16′ and 20′. The values of the elementary rate constants were determined from dependences shown on Figure 1. These values (in L/mol·s) are as follows for the

Table I
Values of Copolymer Compositions (m_1 and m_4, mol parts), Equilibrium Complex Concentrations (C, mol/L), and Monomer Concentrations (M_1, M_2, M_3, and M_4, mol/L) vs Initial Donor Concentration (M_i) (333 K, Benzoyl Peroxide, 5% Conversion)

	system, M_1–M_2					system M_3–M_4			
$[M_i]$, mol parts	m_1	$m_1{}^a$	C	$[M_1]$	$[M_2]$	m_4	C	$[M_3]$	$[M_4]$
0.02	0.23	0.24	0.14	0.15	13.51				
0.04	0.27	0.28	0.32	0.36	12.66				
0.08	0.35	0.36	0.61	0.76	11.20				
0.20	0.47	0.47	0.98	1.52	8.95				
0.30	0.49	0.50	1.16	2.34	7.00				
0.35	0.52	0.53	1.19	2.72	6.21	0.50	1.01	1.74	4.10
0.40	0.54	0.54	1.22	3.18	5.39	0.50	0.96	1.98	3.45
0.45	0.55	0.55	1.20	3.61	4.75	0.51	0.90	2.21	2.90
0.50	0.57	0.58	1.16	4.05	4.05	0.51	0.83	2.43	2.43
0.55	0.59	0.59	1.11	4.99	3.46	0.52	0.75	2.64	2.02
0.60	0.60	0.61	1.03	4.92	2.94	0.52	0.67	2.84	1.67
0.65	0.63	0.62	0.95	5.35	2.44	0.53	0.58	3.04	1.37
0.70	0.64	0.65	0.82	5.78	2.01	0.54	0.50	3.22	1.09
0.75	0.68		0.73	6.24	1.62		0.41	3.40	0.86
0.80	0.70	0.69	0.58	6.63	1.23	0.59	0.33	3.56	0.64
0.85	0.75	0.75	0.45	7.10	0.89		0.24	3.72	0.46
0.90	0.79	0.79	0.30	7.46	0.56	0.63	0.16	3.88	0.30

[a] Calculated taking into account complex formation.

Table II
Kinetic Data of Copolymerization: V_{in} (mol/L·s), $K_0{}^{ef}$ (L/mol·s), V (mol/L·s) (333 K, Benzoyl Peroxide, 2% Conversion)

	system M_1–M_2			system M_3–M_4	
$[M_i]$, mol parts	10^7V_{in}	$10^{-8}K_0{}^{ef}$	10^4V	10^8V_{in}	10^4V
0.20	2.75 ± 0.33	10.10 ± 0.31	1.81 ± 0.11		
0.30	2.41 ± 0.28	9.30 ± 0.32	1.66 ± 0.10		
0.35	2.05 ± 0.19	8.20 ± 0.22	1.61 ± 0.11	1.25 ± 0.15	0.88 ± 0.05
0.40	1.84 ± 0.22	6.40 ± 0.11	1.54 ± 0.08	1.64 ± 0.16	0.98 ± 0.06
0.45	1.69 ± 0.21		1.47 ± 0.08	2.15 ± 0.26	1.08 ± 0.06
0.50	1.52 ± 0.19	5.20 ± 0.11	1.34 ± 0.07	2.60 ± 0.31	1.10 ± 0.07
0.60	1.40 ± 0.17	4.30 ± 0.11	1.20 ± 0.06	3.20 ± 0.38	0.95 ± 0.06
0.70	1.24 ± 0.15	3.60 ± 0.10	1.01 ± 0.05	3.23 ± 0.39	0.65 ± 0.04
0.80	1.16 ± 0.11	3.10 ± 0.10	0.82 ± 0.06	2.84 ± 0.38	0.37 ± 0.04
0.90	1.08 ± 0.08	2.80 ± 0.10	0.62 ± 0.05		

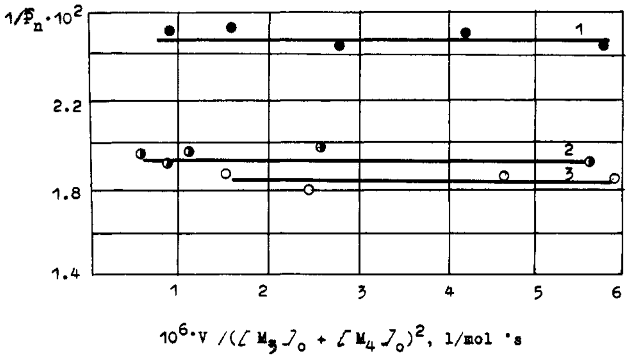

Figure 4. The dependences of the polymerization degree (P_n) vs the normalized rate of process at various monomers ratios (mol parts): 0.35:0.65 (1), 0.50:0.50 (2), 0.70:0.30 (3).

system M_1···M_2:

$$K_{11} = 247, K_{22} = 1405, K_{12} = 393, K_{21} = 27027, K_{1c1} = 1057, K_{1c2} = 706, K_{2c1} = 18811, K_{2c2} = 21370$$

and for system M_3–M_4:

$$K_{33} = 65, K_{34} = 155, K_{43} = 173, K_{44} = 0, K_{3c3} = 72, K_{3c4} = 3155, K_{4c3} = 9356, K_{4c4} = 0$$

Using these data and values of V_{in} (Table II), the concentrations of the growth macroradicals were calculated according to eqs 12 and 13. The obtained results are shown on Figure 5. Now, having adduced the above experimental data, it is possible to determine the rate of each elementary act of chain growth (Table III). Analysis of these data shows that for the system M_1–M_2 the main contribution to the total rate is the cross reactions of free monomers. The rates of elementary reactions of complex-binding monomers decrease in the row $V_{2c2} < V_{2c1} < V_{1c1} < V_{1c2}$ under styrene excess in the initial mixture. At an equimolar monomer ratio the rates of the same reactions change in the following row: $V_{1c1} > V_{1c2} > V_{2c2} > V_{2c1}$. If acrylonitrile is in excess in the initial mixture, then the rates decrease in the same manner as in the case of equimolar monomer ratios. The binding of the growth radicals $\sim M_i{}^*$ and $\sim M_j{}^*$ to the same sides of the complexes is a reason for enrichment of obtained copolymer composition with styrene units even at a styrene concentration in the initial mixture lower than 50%.

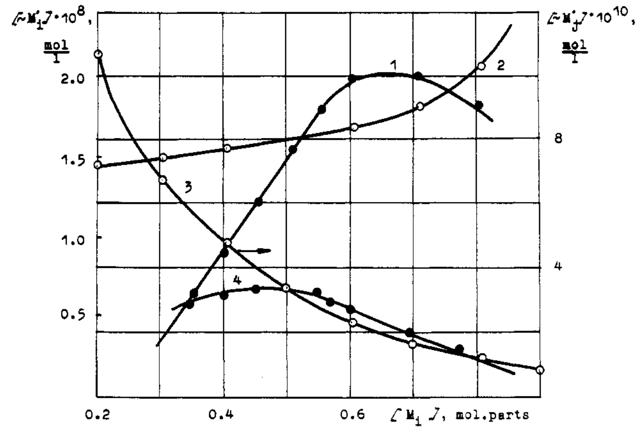

Figure 5. The dependences of the growth radical concentrations [$\sim M_i{}^*$], [$\sim M_j{}^*$] vs the initial donor concentration [M_i] for the systems M_1–M_2 (1, 2) and M_3–M_4 (3, 4), respectively.

Table III
The Influence of Initial Monomer Mixture Composition on the Rates of Elementary Reactions of Chain Growth (V_{ij}, mol/L·s) in Copolymerization for the Systems M_1–M_2 and M_3–M_4 (333 K, Benzoyl Peroxide, 2% Conversion)

[M_i], mol parts	$10^5 V_{xy}$, mol/L·s								$10^5 V_{total}$
	V_{ii}	V_{jj}	V_{ij}	V_{ji}	V_{ici}	V_{icj}	V_{jci}	V_{jcj}	
System M_1–M_2									
0.20	0.54	1.35	5.10	4.38	1.48	0.99	1.94	2.20	17.98
0.30	0.87	0.67	4.14	4.35	1.85	1.24	1.49	1.69	16.25
0.40	1.24	0.36	3.34	4.13	2.03	1.36	1.10	1.25	14.81
0.50	1.67	0.20	2.62	3.78	2.03	1.36	0.76	0.86	13.28
0.60	2.03	0.10	1.92	3.21	1.81	1.21	0.46	0.53	11.27
0.70	2.60	0.05	1.43	2.71	1.58	1.06	0.27	0.31	10.01
0.80	3.43	0.02	1.01	2.14	1.28	0.85	0.13	0.15	9.01
0.90	4.91	0.01	0.59	1.38	0.84	0.56	0.04	0.04	8.37
System M_3–M_4									
0.35	0.15		0.41	0.36	0.09	2.07	5.69		8.77
0.40	0.23		0.48	0.43	0.12	2.71	5.79		8.76
0.45	0.35		0.55	0.52	0.15	3.45	5.81		10.83
0.50	0.48		0.57	0.56	0.17	3.97	5.30		11.05
0.55	0.62		0.56	0.58	0.19	4.27	4.52		10.74
0.60	0.72		0.51	0.54	0.18	4.11	3.46		9.52
0.70	0.85		0.34	0.39	0.14	3.18	1.63		6.53
0.80	0.84		0.18	0.22	0.08	1.87	0.54		3.73

For the system M_3–M_4 the main contribution to the total rate of the process is the reaction of binding of the growth radical $\sim M_j{*}$ to the complex by the side of $M_i \cdots M_j$ (8) and radical $\sim M_i{*}$ to the $M_j \cdots M_i$ (7). But the contribution of other elementary reactions to the chain growth changes significantly with the dependence of the initial monomers' mixture composition.

Conclusions

Thus the general equation for copolymerization rate determination in the binary donor–acceptor systems of vinyl and allyl monomers, as well as some its modifications, were proposed. As an example, the results of copolymerization in the systems styrene–acrylonitrile (quadratic termination) and diethylene glycol bis(allyl carbonate)–maleic anhydride (linear termination) were described. The reasonable applicability of the proposed rate equations for determination of the rate constants of elementary reactions of chain growth was shown, using the complete kinetic scheme and taking into account the equilibrium concentrations of molecular complexes and free monomers. The knowledge of these values makes it possible to quantitatively describe the binary copolymerization in the donor–acceptor systems.

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