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Monomer addition programs to generate constant gradient block copolymers

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Abstract

Equations are derived to calculate the monomer addition programs for semi-batch copolymerization reactions that allow to prepare gradient copolymers and block gradient copolymers containing arbitrary, pre-defined compositional gradients along the polymer chain. An analytical solution is given for the special case of ideal random copolymerizations, and numerical calculations are applied to discuss non-ideal situations. Three classes of addition programs are proposed and discussed with respect to time efficiency. Time-linear addition programs are shown to be insufficient to generate perfectly constant gradients over the whole compositional regions.

Keywords: Gradient copolymers; Gradient block copolymers; Monomer addition programs

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1. Introduction

Linear block copolymers are made from polymer chains of different chemical compositions that are covalently joined via their respective end groups [1]. The classical architecture of block copolymers implies an abrupt change in composition at the connection point of the adjacent blocks. During the last decade a new type of copolymer came to the focus of scientific interest with its chemical composition varying continuously along a certain section of the polymer chain [2,3].

It has early been predicted that the thermal properties as well as the bulk structures of such ‘‘gradient’’ copolymers should deviate from that of statistical- or diblock copolymers [4]. Gradient copolymers were calculated to undergo microphase separation like block copolymers and should form lamellar structures in the symmetric case, but the interface region between the chemically different regions will be blurred. Gradient copolymers may offer a large degree of control over the A–B interfacial profile [5] and their microphase segregation should depend on the actual shape of the gradient [5,6]. Experimental investigations showed gradient copolymers to exhibit two separate glass transitions [7,8] and very broad relaxation time distributions [7,9] indicating the presence of the expected phase segregated structures. The preparation of brush-type gradient copolymers composed of a (meth)acrylate backbone and a gradient distribution of polydimethylsiloxane side chains allowed to visualize the gradient structure by means of scanning force microscopy [10,11]. The Young’s modulus of these gradient copolymers was close to that of the random copolymer of comparable composition, however, the gradient copolymer was more tougher than the random copolymer [9].

Micelle formation is observed with block copolymers in solvents that selectively dissolve one of the blocks [12]. Up until now the number of investigations on the gradient copolymer solution structures is limited. However, ethoxymethyl vinyl ether/methoxymethyl vinyl ether gradient copolymers were shown to form micelles in water with a broad temperature region separating the micellar- and the non-micellar regions. Furthermore, a continuous transition between the molecular dispersed and the micellar state was observed on heating, where the micellar diameter decreased with ongoing

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micellization. The observation was explained by a ‘‘reel-in’’ of the gradient-corona chains caused by the diffuse interface between the micellar corona and the solution environment [13]. An overview on the physical properties of gradient copolymers can be found in Ref. [14].

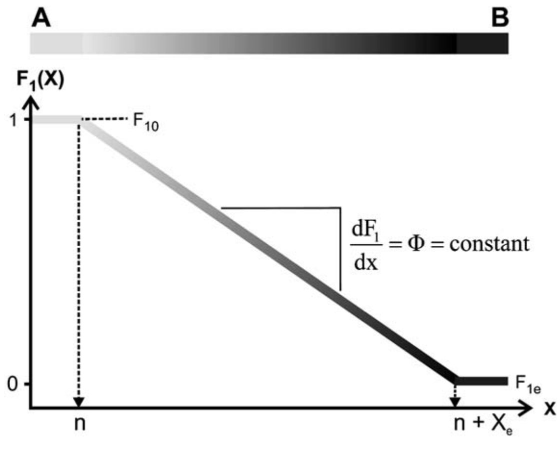
For the preparation of gradient copolymers all polymerization techniques can be applied that do not include termination reactions. It has been reported that anionic polymerizations [15], ring-opening metathesis polymerizations (ROMP) [16] and controlled radical polymerization techniques like ATRP [2,3,14] or nitroxide-initiated polymerizations [8,17] can be used to generate gradient polymers.

Two experimental approaches have been distinguished to control the compositional gradient, namely the ‘‘spontaneous’’- and the ‘‘forced’’-gradient methods. Spontaneous gradient polymerizations are batch-copolymerization reactions where a monomer mixture is polymerized to high conversions [14]. In the absence of either azeotropic points or ideal random copolymerizations the monomer composition will change gradually with the monomer conversion because of the different reactivities of the monomers. As determined by Skeist’s equation [18] a compositional gradient evolves along the polymer chain. This technique is quite simple, but suffers from three drawbacks: it is only applicable to strictly non-random copolymerization systems and will fail in close vicinity to azeotropic points; it cannot be used to cross the full compositional space from $F_1 = 0$ to $F_1 = 1$ and it is virtually impossible to generate constant compositional gradients over the full range of monomer composition.

‘‘Forced’’-gradient copolymerizations are semi-batch reactions involving the initiation of a polymerization in a pure monomer or a monomer mixture and the subsequent continuous addition of a second monomer – or a monomer mixture – during the reaction time. The addition rate as well as the composition of the added mixture may be varied to allow for full control on the composition of the generated copolymer chain. Block copolymers of the structure $\mathrm{P[M_1]}_n$-*b*-$\mathrm{P[M_1}$-*grad*-$\mathrm{M_2]}_{X_e}$-*b*-$\mathrm{P[M_2]}m$ containing constant compositional gradients with composition ranges within the gradient block from $F_1 = 1$ to $F_1 = 0$ (see Scheme 1) can only be prepared by means of forced gradient techniques.

Successful experimental attempts have been reported to create gradient copolymers by continuous addition of monomers at constant addition rate, (e.g. Refs. [3,8,19]), but no systematic presentation has been published as to how to calculate the required polymerization/monomer addition programs.

For free radical copolymerizations an extensive amount of literature dealing with the control of copolymer compositions with batch-, semi-batch or continuous reactor systems still exists (for review see Ref. [20]). Since with free radical polymerizations the life time of the polymerizing species (1–2 s) is negligible against the total time of polymerization (∼hours) any variation in monomer composition will yield physical mixtures of copolymer molecules that differ in composition. For this reason it is the main goal of free radical composition control to avoid any change of monomer- and copolymer composition during the course of the reaction. On the other hand controlled or living polymerizations lack termination reactions, hence it is possible to transform a change in monomer composition into a variation of copolymer composition along the polymer chain. This opportunity is not yet well represented in the copolymerization control literature.



Scheme 1. Schematic depiction of the composition of a $\mathrm{P[M_1]}_n$-*b*-$\mathrm{P[M_1}$-*grad*-$\mathrm{M_2]}_{X_e}$-*b*-$\mathrm{P[M_2]}m$ gradient triblock copolymer.

In the present work a systematic technique is proposed to prepare arbitrary courses of the compositional gradient along the polymer chain. Equations are derived that allow preparing gradient polymers and gradient block copolymers containing pre-defined gradient block structures.

2. Result and discussion

Consider the task to prepare a triblock copolymer of the general structure $\mathrm{P[M_1]}_{X_A}$-*b*-$\mathrm{P[M_1}$-*grad*-$\mathrm{M_2]}_{X_e}$-*b*- $\mathrm{P[M_2]}_{X_B}$, consisting of a start block of monomer 1 and an end block of monomer 2 that are connected by a gradient block $\mathrm{P[M_1}$-*grad*-$\mathrm{M_2]}_{X_e}$. The degree of polymerization of the three blocks shall be X_A, X_e and X_B, respectively. Along the gradient block the polymer composition should continuously change from $F_1 = 1$ at the start of this block down to $F_1 = 0$ at its very end. It is of particular interest that the molar fraction of monomer 1 along the gradient block decreases linearly from $F_1 = 1$ at the start of the gradient block ($X = 0$) to $F_1 = 0$ at its end ($X = X_e$). The value of the linear gradient $\Phi = \mathrm{d}F_1/\mathrm{d}X$ is then determined by the condition $\Phi = (0 - 1)/X_e = -1/X_e$.

To prepare this triblock copolymer it is necessary to apply a controlled polymerization technique to generate a start block $\mathrm{P[M_1]}_{X_a}$. Subsequently, n_I moles of this molecule are used as initiators to start the polymerization of n_{10} moles of monomer 1. During this polymerization step monomer 2 is added to the reaction mixture in such a way that the demanded copolymer compositional gradient Φ evolves, while monomer 1 is completely consumed. Subsequently, the excess of monomer 2 is allowed to grow on the gradient block to form the $\mathrm{P[M_2]}_{X_b}$ moiety.

To achieve control over the change of the copolymers’ composition F_1 along the polymer chain an expression for the value $\Phi = \mathrm{d}F_1/\mathrm{d}X$ must be derived. As expressed by Eq. (1), $\mathrm{d}F_1/\mathrm{d}X$ is related to the change of the copolymer composition with the change of the comonomer mixture composition (dF_1/df_1), the change of the comonomer composition with the change of monomer conversion (df_1/dp) as well as the change of the monomer conversion with the degree of polymerization (dp/dX).

$$\frac{dF_1}{dX} = \frac{dF_1}{df_1}\frac{df_1}{dp}\frac{dp}{dX} \tag{1}$$

F_1 = copolymer composition at the degree of polymerization X, f_1 = monomer composition at the monomer conversion p.

The term dF_1/df_1 is easily obtainable from the copolymerization equation, but to find expressions for df_1/dp and dp/dX the stoichiometry of the system under investigation must be considered (cf. Scheme 1). In the general case n_{10} moles of monomer 1, n_{20} moles of monomer 2 and n_I moles of the initiator are present at the start of the reaction. At an arbitrary value of the monomer conversion $p \in [0,1]$, n_{1p} and n_{2p} moles of the monomers have been consumed and became part of the copolymer. Up until this point the amounts n_1^{add} and n_2^{add} moles of monomers 1 and 2 were added to the reaction mixture, hence the solution contains $n_i = n_{i0} + n_i^{add} - n_{ip}$ moles of monomer i. At the end of the experiment the amount $n_e^{add} = n_{1e}^{add} + n_{2e}^{add}$ moles of monomer were added, hence the reaction vessel contains in total $n_e^{in} = n_0 + n_e^{add}$ moles of monomer units in the form of copolymer (see Scheme 2).

The monomer conversion p is defined as the number of polymerized monomer moles, n_p, divided by the total amount of monomer units introduced in the reaction system until the end of the reaction, $n_e^{in} = n_0 + n_e^{add}$ (Eq. (2)).

$$p = \frac{n_p}{n_0 + n_e^{add}} \tag{2}$$

$$X = \frac{n_p}{n_I} = \frac{n_e^{in}}{n_I}p = X_e \cdot p \tag{3}$$

n_p = number of polymerized moles of monomer ($= n_{1p} + n_{2p}$), n_0 = number of moles of monomer present at the start of the reaction ($= n_{10} + n_{20}$), n_e^{add} = total amount of monomer added to the reaction mixture from the start ($p = 0$) until the end of the reaction ($p = 1$), $n^{in} = n_0 + n^{add}$, $n_e^{in} = n_0 + n_e^{add}$.

Because of the presumed controlled nature of the polymerization process no growing polymer chain is lost during the reaction, hence the degree of polymerization X is obtained from the ratio of the polymerized moles of monomer n_p and the number of moles of initiator n_I. X is proportional to the monomer conversion p with the proportionality constant being the targeted length of the gradient block, X_e. X_e is calculated from the present amounts of monomer and initiator (see Eq. (3)); it is hence easy to see that the term dp/dX in Eq. (1) equals $1/X_e$.

	$p = 0$		$0 < p < 1$	$p = 1$	
	Solution	Polymer	Solution	Polymer	Added Monomer
Mon 1	n_{10}	n_{1p}	$n_1 = n_{10} + n_1^{add} - n_{1p}$	n_{1pe}	n_{1e}^{add}
Mon 2	n_{20}	n_{2p}	$n_2 = n_{20} + n_2^{add} - n_{2p}$	n_{2pe}	n_{2e}^{add}
Total	n_0	n_p	$n = n_0 + n^{add} - n_p$	n_{pe}	n_e^{add}

$$F_1 = \frac{n_{1p}}{n_p} \qquad f_1 = \frac{n_1}{n}$$

Scheme 2. Stoichiometric balance during copolymerization and monomer addition. n_p = Number of polymerized moles of monomer ($= n_{1p} + n_{2p}$), n_0 = number of moles of monomer present at the start of the reaction ($= n_{10} + n_{20}$), n_e^{add} = total amount of monomer added to the reaction mixture from the start ($p = 0$) until the end of the reaction ($p = 1$), $n^{in} = n_0 + n^{add}$, $n_e^{in} = n_0 + n_e^{add}$.

The composition of the comonomer mixture f_1 at an arbitrary monomer conversion p is defined as the molar fraction of monomer 1 in the solution, $f_1 = n_1/n$ (cf. Scheme 2). The drift of the monomer composition, df_1/dp is calculated by derivation of this equation with respect to p (Eq. (4)):

$$\frac{df_1}{dp} = \frac{d}{dp}\left[\frac{n_1}{n}\right] \tag{4}$$

The added amount of monomer is quantified by the parameter q, defined as the ratio of the total number of monomer moles in the system at a certain monomer conversion p ($n^{in} = n_0 + n^{add}$) and the maximum amount of monomer units present in the reaction system at the end of the reaction, n_e^{in} (Eq. (5)). At the start of the reaction $q(p = 0) = q_0 = 1/2$.

$$q = \frac{n^{in}}{n_e^{in}} \le 1 \tag{5}$$

To evaluate Eq. (4) one needs to take into account that $dn_p/dp = n_e^{in}$. For the sake of convenience, the function $\alpha_1(p)$ will be introduced, describing the instantaneous molar fraction of added monomer 1 in the added monomer mixture:

$$\alpha_1 = \frac{dn_1^{add}}{dn^{add}} = \frac{dn_1^{add}/dp}{dn^{add}/dp} \tag{6}$$

With these abbreviations one obtains Eq. (7) (cf. Appendix A), relating df_1/dp to monomer conversion p and the monomer addition functions q and α_1:

$$\frac{df_1}{dp} = \frac{1}{q-p}\left\{f_1 - F_1 + \frac{dq}{dp}(\alpha_1 - f_1)\right\} \tag{7}$$

Note that in case of no monomer addition ($q = 1$, $dq/dp = 0$, $\alpha_1 = 0$), Eq. (6) reduces to the well-known Skeist Equation [18]. Inserting Eqs. (3) and (7) in Eq. (1) allows to calculate the local copolymers' compositional gradient dF_1/dX (cf. Eq. (8)).

$$\frac{dF_1}{dX} = \frac{1}{X_e}\frac{dF_1}{df_1}\frac{1}{q-p}\left\{f_1 - F_1 + X_e\frac{dq}{dX}(\alpha_1 - f_1)\right\} \tag{8}$$

So far the relation between monomer and copolymer composition as functions of the monomer conversion p and the monomer addition q has been mentioned.

In case that no on-line analytic system is available, that allows to continuously monitor the monomer conversions, the monomer addition must follow a time-dependent scheme. For practical experiments of this kind the time dependencies of the monomer addition functions, dq/dt and $\alpha_1(t)$ are required. The conversion/time dependency is easily derived from the formal reaction kinetics of controlled copolymerizations. The rate of monomer conversion is proportional to the number of non-converted monomer moles n as well as the number of initiator molecules n_I in the solution [21,22]. Since n_I remains constant it will be included in the effective kinetic rate constant $k(f_1)=\kappa(f_1)n_\mathrm{I}$. Note that the effective rate constant $k(f_1)$ will depend on the monomer mixture composition f_1, hence the function $k(f_1)$ must be determined experimentally prior to the preparation of gradient block copolymers. The overall change of monomer in the reaction system is given by Eq. (9)

$$\frac{\mathrm{d}n}{\mathrm{d}t}=-k(f_1)n+\frac{\mathrm{d}n^\mathrm{add}}{\mathrm{d}t} \tag{9}$$

n = number of moles of non-converted monomer in the solution, n_I = number of moles of initiator, n^add = number of moles of monomer added to the solution, f_1 = molar fraction of monomer 1 in the solution, $k(f_1)=\kappa(f_1)n_\mathrm{I}$ = effective kinetic rate constant.

Taking into account that $\mathrm{d}n^\mathrm{add}/\mathrm{d}t=\mathrm{d}n^\mathrm{in}/\mathrm{d}t$ and $n=n_\mathrm{e}^\mathrm{in}(q-p)$ one obtains Eq. (10) that describes the change of the monomer conversion with time (cf. Appendix B):

$$\frac{\mathrm{d}p}{\mathrm{d}t}=k(f_1)(q-p) \tag{10}$$

p = monomer conversion – Eq. (2), t = reaction time, $k(f_1)=\kappa(f_1)n_\mathrm{I}$ = effective kinetic rate constant, f_1 = molar fraction of monomer 1 in the solution, q = monomer addition function – Eq. (5).

Since $\mathrm{d}q/\mathrm{d}p=\mathrm{d}q/\mathrm{d}t\cdot\mathrm{d}t/\mathrm{d}p$, Eqs. (7), (8) and (10) form a system of differential equations that allows to calculate the compositional gradients $[\mathrm{d}F_1/\mathrm{d}X]_{X_{(p)}}$ of the copolymer for any given monomer addition program $q(t)$ and $\alpha_1(t)$.

Note that the calculated addition program requires the kinetics of controlled or living copolymerizations to be valid. The presence of induction periods or the observation of retardation effects is indicative for deviations from the ideal kinetics. In such a case the simultaneous start as well as the simultaneous growth of all n_I0 polymer chains must be put in question and the use of this monomer addition scheme cannot be recommended to generate gradient blocks.

By investigation of the equation system it can be shown that time-linear addition programs (the "spontaneous gradient" polymerization technique can be considered as the limiting case of no monomer addition) cannot result in constant gradient copolymers. Even in the very simple case of ideal statistic copolymerization ($r_1=r_2=1$: $f_1=F_1$, $\mathrm{d}F_1/\mathrm{d}f_1=1$), addition of monomer 2 only ($\alpha_1=0$) and the idealized condition that the copolymerization rate constant $k(f_1)$ becomes independent of the monomer composition f_1 ($k(f_1)=k_0$), the targeted gradient $\Phi=-1/X_\mathrm{e}$ cannot be obtained.

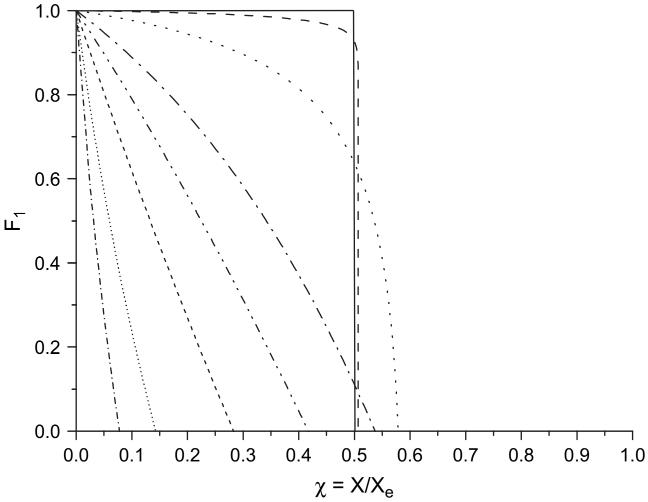


Fig. 1. Copolymer composition along the polymer chain obtained with time-linear monomer addition programs ($r_1=r_2=1$, $k(f_1)=k_0$, $j=-2(X_\mathrm{e}\Phi)/k_0$, ——: $j=0$, — — —: $j=0.01$, - - - -: $j=0.1$, —·—·: $j=0.5$, —··—··: $j=1$, - - - - -: $j=2$, ······: $j=5$, -·-·-·: $j=10$).

Fig. 1 depicts the resulting local copolymer composition $F_1(X)$ along the polymer chain depending on the reduced addition rate parameter $j=-2(X_\mathrm{e}\Phi)/k_0$ (k_0 = rate constant of copolymerization, Φ = targeted copolymer compositional gradient). Without monomer addition ($j=0$) no gradient is obtained because of the presumed ideal statistic nature of the copolymerization. At $X=1/2\cdot X_\mathrm{e}$ monomer 1 is used up and the copolymerization has to stop. With small addition rates ($j<1$) a low gradient is obtained at the start of the gradient block that strongly increases until all monomer 1 is consumed. However, although monomer 2 was added, monomer 1 is used up before X_e is reached. An almost linear gradient is obtained with $j=1$, but the average gradient is about 2.2 times larger than targeted value $\Phi=-1$. Hence, the gradient block will only reach 44% of the planned length. This effect is caused by the continuous decrease of the consumption rate of monomer 1 (since monomer 1 is used up), while the molar number of monomer 2 in the reaction mixture remains fairly constant (because monomer 2 is constantly added). At a certain point – that depends on the addition rate of monomer 2 – the remaining monomer 1 is strongly diluted by monomer 2 and the ratio of monomer 1:monomer 2 rapidly approaches to zero. At this stage the copolymerization is effectively turned into the homopolymerization of monomer 2. The faster the monomer 2 is added, the shorter the gradient block becomes.

Note that in real copolymerization experiments $k(f_1)=k_0$ = constant is not found, hence there is little chance to obtain perfectly controlled constant gradients by means of time-linear monomer addition programs.

To fix the gradient $\mathrm{d}F_1/\mathrm{d}X$ at a constant value Φ, Eq. (8) was resolved for $\mathrm{d}q/\mathrm{d}p$ after inserting $p=X/X_\mathrm{e}$ to yield:

$$\frac{\mathrm{d}q}{\mathrm{d}p}=\frac{X_\mathrm{e}\Phi}{F_1'}\,\frac{q-p}{\alpha_1-f_1}+\frac{F_1-f_1}{\alpha_1-f_1} \tag{11}$$

$\Phi=\mathrm{d}F_1/\mathrm{d}X$ = targeted copolymer compositional gradient, X_e = targeted length of the gradient block, $F_1'=\mathrm{d}F_1/\mathrm{d}f_1$, q = total monomer addition function, α_1 = molar fraction of monomer 1 in added monomer mixture, p = monomer conversion, F_1 = instantaneous molar fraction of monomer 1 in the copolymer, f_1 = instantaneous molar fraction of monomer 1 in the monomer mixture.

The differential equation system (DES) consisting of Eqs. (7), (10) and (11) allows to calculate the monomer addition functions for any arbitrary course of the gradient along the polymer chain, since the gradient Φ is allowed to become a function of the monomer conversion.

Note that in the limiting case of vanishing gradient ($\Phi = 0$), i.e. a constant copolymer composition, the differential equation system transforms into the well-known "continuous addition" equations (e.g. Ref. [23]) allowing to derive addition programs that keep constant the rate of polymerization as well as the number of monomer moles.

If the monomer conversion p can be measured online, the explicit time dependence of q is not required and Eq. (10) can be omitted from the DES. The resulting functions $q(p)$ and $\mathrm{d}q(p)/\mathrm{d}p$ can be used to set-up a feedback loop that regulates the monomer addition program accordingly. It is a large advantage of this technique that the time consuming evaluation of the effective rate constant function $k(f_1)$ can be avoided. However, the availability of the respective apparative equipment (i.e. on-line detectors coupled to a computer-controlled addition system) is required.

Since many synthetic polymer chemistry laboratories lack this equipment, the calculation of the time-dependent monomer addition functions $q(t)$ and $\mathrm{d}q(t)/\mathrm{d}t$ offers the possibility to prepare the gradient copolymers with low budget equipment. To make use of the described method, the copolymerization parameters and the effective copolymerization constant $k(f_1)$ function must be obtained. This can easily be done by performing a series of low conversion ("pilot") copolymerization experiments with different comonomer compositions f_1. For each mixture the initial rate of polymerization R_{p0} is measured and $\kappa(f_1)$ is obtained by division of R_{p0} by the molar numbers of monomers and the molar numbers of initiator [23,24]. From the low conversion copolymer composition the copolymerization parameters are obtained by means of least square fit methods [25,26].

On performing the gradient copolymerization it is, however, strongly recommended to take samples from the reaction mixture and check the reaction mixtures' composition, or the polymer composition offline. By means of this technique it is possible to prove the quality of the obtained product by constructing the composition/conversion plot *a posteriori*.

The subsequent text will be focused on constant values of the gradient, i.e. $\mathrm{d}F_1/\mathrm{d}X = \Phi$. With $\mathrm{d}F_1/\mathrm{d}X = \Phi$ as the only condition the problem is under-determined, because two monomers can be added. One of the two addition rate functions – e.g. α_1 – must remain arbitrarily. In the subsequent text three different auxiliary conditions will be mentioned, namely (i) no addition of monomer 1, (ii) adjusting a constant rate of polymerization and (iii) polymerization at a constant number of moles of monomer.

2.1. Addition of monomer 2 only

The experimental situation mentioned here resembles the semi-batch copolymerizations "Policy I" [20] in so far, that only one monomer is fed to a polymerization mixture. However, note that it is the aim of "Policy 1" to keep constant the instantaneous molar fraction of monomer 1 in the monomer mixture, while the creation of a gradient copolymer requires a deliberate monomer compositional drift. In case that only monomer 2 is added, α_1 becomes zero and the differential equation system reads:

$$\frac{\mathrm{d}q}{\mathrm{d}p} = -f_1\frac{X_{\mathrm{e}}\Phi}{F_1'}(q-p) + 1 - \frac{F_1}{f_1} \tag{12a}$$

$$\frac{\mathrm{d}f_1}{\mathrm{d}p} = \frac{1}{q-p}\left\{f_1 - F_1 - \frac{\mathrm{d}q}{\mathrm{d}p}f_1\right\} \tag{12b}$$

$$\frac{\mathrm{d}t}{\mathrm{d}p} = \frac{1}{k(f_1)}\frac{1}{q-p} \tag{12c}$$

$\Phi = \mathrm{d}F_1/\mathrm{d}X =$ targeted copolymer compositional gradient, $X_{\mathrm{e}} =$ targeted length of the gradient block, $F_1' = \mathrm{d}F_1/\mathrm{d}f_1$, $q =$ total monomer addition function, $\alpha_1 =$ molar fraction of monomer 1 in added monomer mixture, $p =$ monomer conversion, $F_1 =$ instantaneous molar fraction of monomer 1 in the copolymer, $f_1 =$ instantaneous molar fraction of monomer 1 in the monomer mixture.

An analytical solution of the differential equation system (12a)–(12c) was found for the case of an ideal statistic copolymerization ($r_1 = r_2 = 1$: $F_1' = 1$, $f_1 = F_1$) on assuming the copolymerization rate constant to depend linearly on the composition of the monomer mixture:

$$k(f_1) = k_2 + \beta f_1 \tag{13}$$

$k(f_1) =$ rate constant of copolymerization at the monomer composition f_1, $k_i =$ rate constant of homopolymerization of monomer i, $\beta = k_1 - k_2$, $f_1 =$ molar fraction of monomer 1 in the monomer mixture.

Together with the stoichiometric condition $f_1 = 1 + \Phi p$ one finds the conversion dependent monomer addition function q to equal $q = (1+p)/2$. With this result, the time dependency of the monomer conversion p as well as that of the monomer addition function q was evaluated (Eqs. (14) and (15)). To allow for a more general discussion, the dimensionless time parameter τ was introduced, relating the absolute rate of the reaction to the time scale of the homopolymerization of monomer 2 (see Eq. (16)).

$$p = \frac{(1+\beta)\exp(-\tau/2)}{\beta\exp(-\tau/2) - (1+\beta)} \tag{14}$$

$$q = \frac{1}{2}\left[1 + \frac{\exp(-\tau/2) - 1}{\dfrac{\beta}{1+\beta}\exp(-\tau/2) - 1}\right] \tag{15}$$

$$\tau = k_2 t \tag{16}$$

$p =$ monomer conversion – Eq. (2), $\beta = k_1 - k_2$, $k_i =$ rate constant of homopolymerization of monomer i, $\tau =$ dimensionless time parameter, $q =$ monomer addition function – Eq. (5).

Fig. 2 depicts the calculated results originating from the analytical solution. Because of the assumed ideal random copolymerization the monomer addition function $q(p)$ varies linearly with p (Fig. 2a). The other plots show monomer conversions, as well as the required monomer additions in dependence of the dimensionless time parameter τ for the different copolymerization rate constant/composition relations plotted in Fig. 2b. Note that the functions $q(p)$ and $dq(p)/dp$ remain of course independent of the reaction kinetics.

In all cases the monomer conversion increases linearly with time for small reaction times ($\tau/2 < 0.25$), but levels off on approaching full conversion ($p \rightarrow 1$, see Fig. 2c).

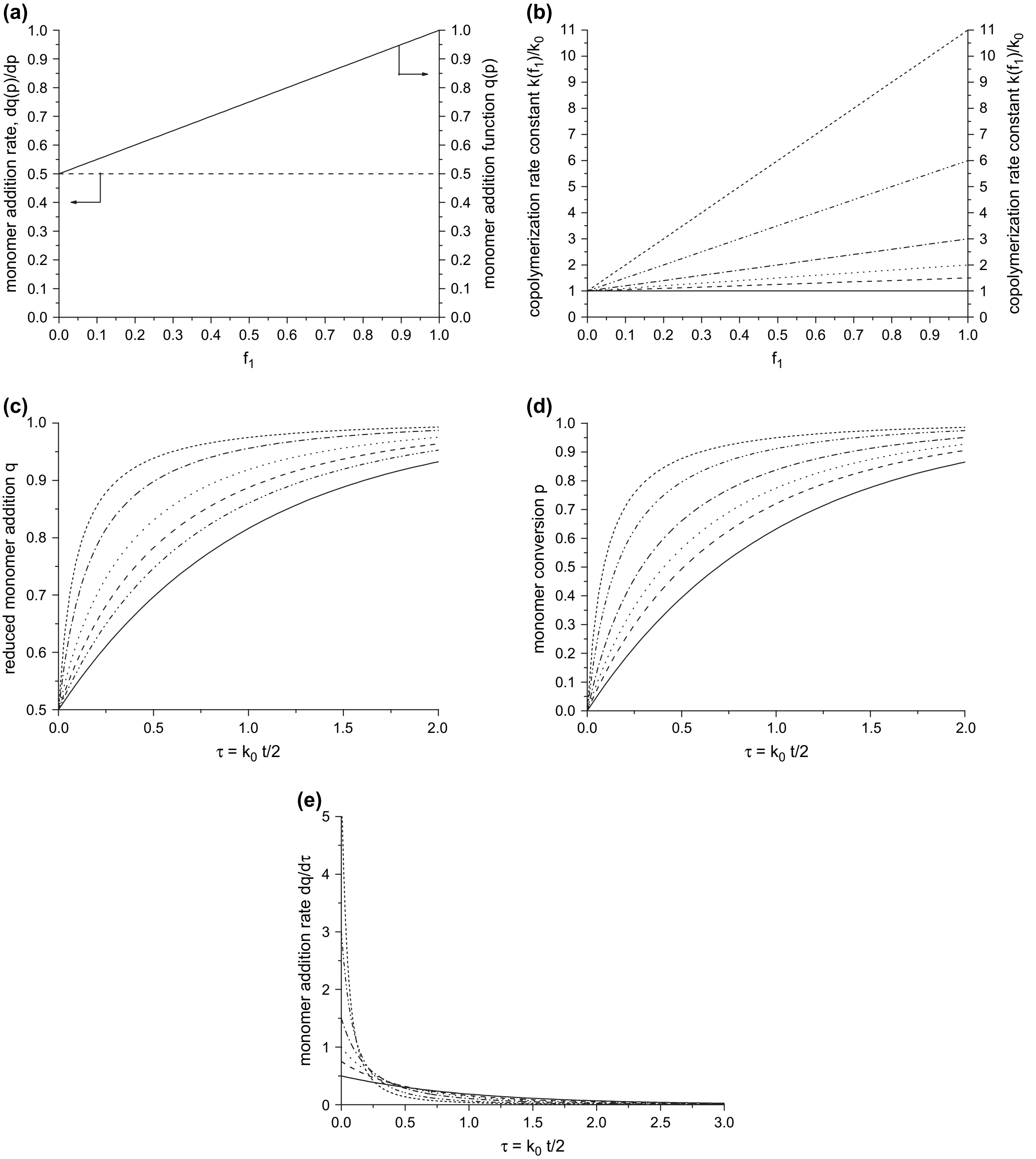


Fig. 2. (a) Monomer conversion dependence of the monomer addition function q and the addition rate $dq(p)/dp$ for ideal random copolymerizations, (b) dependence of the reduced copolymerization rate constant on the comonomer mixture composition f_1 (Eq. (14)), (c) time–conversion curve, (d) monomer addition–time curve, (e) time dependence of the monomer addition rate dq/dt according to Eqs. (14)–(16), ($r_1 = r_2 = 1$, $\alpha_1 = 0$, ——: $\beta/k_0 = 0$, − − −: $\beta/k_0 = 0.5$, ⋯⋯: $\beta/k_0 = 1$, −·−·: $\beta/k_0 = 2$, −··−··: $\beta/k_0 = 5$, ⋯⋯: $\beta/k_0 = 10$).

With increasing values of β – indicating how strongly $k(f_1)$ depends on f_1 – the monomer conversion grows faster in time, as to be expected for systems of larger effective rate constants. The same behaviour holds true for the amounts of added monomer 2.

To fix the copolymers' compositional gradient dF_1/dX at the required value Φ, monomer 2 must be added rapidly during the initial stages of the reaction, but slowly in the later stages (Fig. 2d). Fig. 2e depicts the time dependency of the monomer addition rate, dq/dt, as obtained by time differentiation of $q(t)$ (Eq. (15)).

The stronger the change of $k(f_1)$ with f_1, the more rapid dq/dt must be decreased during the first stages of the copolymerization. However, even for $\beta = 0$, assuming the rate constant to be independent of f_1, the addition rate cannot be constant in time. To obtain a constant gradient block copolymer monomer 1 must be added with decreasing addition rates.

In case of a quadratic dependence of $k(f_1)$ on f_1 (i.e. $k(f_1) = k_2 + \beta f_1 + \gamma f_1^2$), the differential equations are still integrable, however, the solution functions become impractically large and tedious. Since general analytic solutions of differential equation system (12a)–(12c) are hard to find, numeric solutions were computed for selected systems by means of a 4th order Runge–Kutta algorithm [27].

Fig. 3 depicts a more realistic system assuming $r_1 = 0.52$ and $r_2 = 0.46$, similar to the copolymerization parameter of styrene/methyl methacrylate. The monomer addition function $q(p)$ now becomes a non-linear curve and $dq(p)/dp$ cannot be kept constant (cf. Fig. 3a). Three different dependencies of the copolymerization rate constant on f_1 were considered, namely (i) a linear dependence, (ii) a quadratic dependence causing a maximum curve and (iii) an exponential behaviour simulating $k \sim$ constant for low values of f_1 and a rapid increase of k with monomer 1 – rich compositions (cf. Fig. 3b). The effect of the variation of k with f_1 is well illustrated in Fig. 3c, depicting the resulting time–conversion curves. System (iii) starts with a large rate constant at $f_1 = 1$, causing a steep increase of the time conversion curve. On exceeding a conversion of $p = 0.5$ the rate constant k becomes fairly independent of f_1 and the slope of the respective time conversion curve reduces (Fig. 3c, line:……). It is interesting to note that the rapidly growing rate constants in (i) and (ii) demand the monomer addition rates to grow until conversions of $p = 0.25$ (i: $\tau \sim 0.1$) and $p = 0.5$ (ii: $\tau \sim 0.2$) were reached.

In the later stages of the reaction, the rate increase caused by the compositional dependence of the rate constant becomes overcompensated by the reduction in available monomer concentration. Fig. 3e reveals that non-ideal copolymerization systems will require rather complex time–monomer addition programs to generate perfect linear gradient blocks. In any case, the experimental situation is finally described by a kind of "starved feed" situation. The programs will be time consuming, because of the low rate of polymerization in the later stages. However, such experiments can easily be performed with the help of modern computer-controlled HPLC pumps as well as by means of highly motivated experimentalists that manually control the feed.

2.2. Constant rate condition

A second class of monomer addition programs makes use of the possibility to add both the monomers simultaneously to the reacting system, hence resembling the "Policy II" [20] of free radical copolymerization compositional control. One interesting auxiliary condition is to add the monomers in such a way that the total rate of polymerization remains constant: $dp/dt = \pi_0$. Under such circumstances the block preparation will be ended in the finite time $t_e = 1/\pi_0$. The condition is introduced by equalling the time derivative of Eq. (10) to 0 (Eqs. (17) and (18)).

$$\frac{d}{dt}\left[\frac{dp}{dt}\right] = \frac{dk(f_1)}{dt}(q-p) + k(f_1)\left(\frac{dq}{dt} - \frac{dp}{dt}\right) = 0 \tag{17}$$

$$\frac{dq}{dt} = \pi_0 - \frac{1}{k(f_1)}\frac{dk(f_1)}{df_1}\frac{df_1}{dt}(q - \pi_0 t) \tag{18}$$

$p =$ monomer conversion, $q =$ total monomer addition function, $t =$ reaction time, $f_1 =$ instantaneous molar fraction of monomer 1 in the monomer mixture, $k(f_1) =$ rate constant of copolymerization at the monomer composition f_1, $\pi_0 =$ demanded constant rate of monomer consumption.

The change of the monomer mixture composition in time, df_1/dt, is restricted by the condition of a constant copolymer composition gradient $dF_1/dX = \Phi$:

$$\frac{df_1}{dt} = \frac{X_e \Phi}{F_1'}\pi_0 \tag{19}$$

$f_1 =$ instantaneous molar fraction of monomer 1 in the monomer mixture, $t =$ reaction time, $X_e =$ targeted length of the gradient block, $\Phi = dF_1/dX =$ targeted copolymer compositional gradient, $F_1' = dF_1/df_1$, $\pi_0 =$ demanded constant rate of monomer consumption.

The integration of Eq. (19) yields Eq. (20), demonstrating the linear change of the copolymer composition F_1 in time. This behaviour is required, since the demanded time linearity of the monomer conversion p causes a time-linear growth of the degree of polymerization X. As a consequence to obtain a constant compositional gradient Φ, F_1 has also to vary linear in time.

$$F_1 = 1 + X_e \Phi \pi_0 t \tag{20}$$

$F_1 =$ instantaneous molar fraction of monomer 1 in the copolymer, $X_e =$ targeted length of the gradient block, $\Phi = dF_1/dX =$ targeted copolymer compositional gradient, $\pi_0 =$ demanded constant rate of monomer consumption, $t =$ reaction time.

Inserting Eq. (20) in Eq. (19) and considering that a constant rate of conversion requires $q - p = \pi_0/k(f_1)$, both addition functions dq/dt and α_1 can be calculated (Eqs. (21) and (22)):

$$\frac{dq}{dt} = \pi_0\left\{1 - \frac{1}{k(f_1)^2}\frac{dk(f_1)}{df_1}\frac{X_e \Phi}{F_1'}\right\} \tag{21}$$

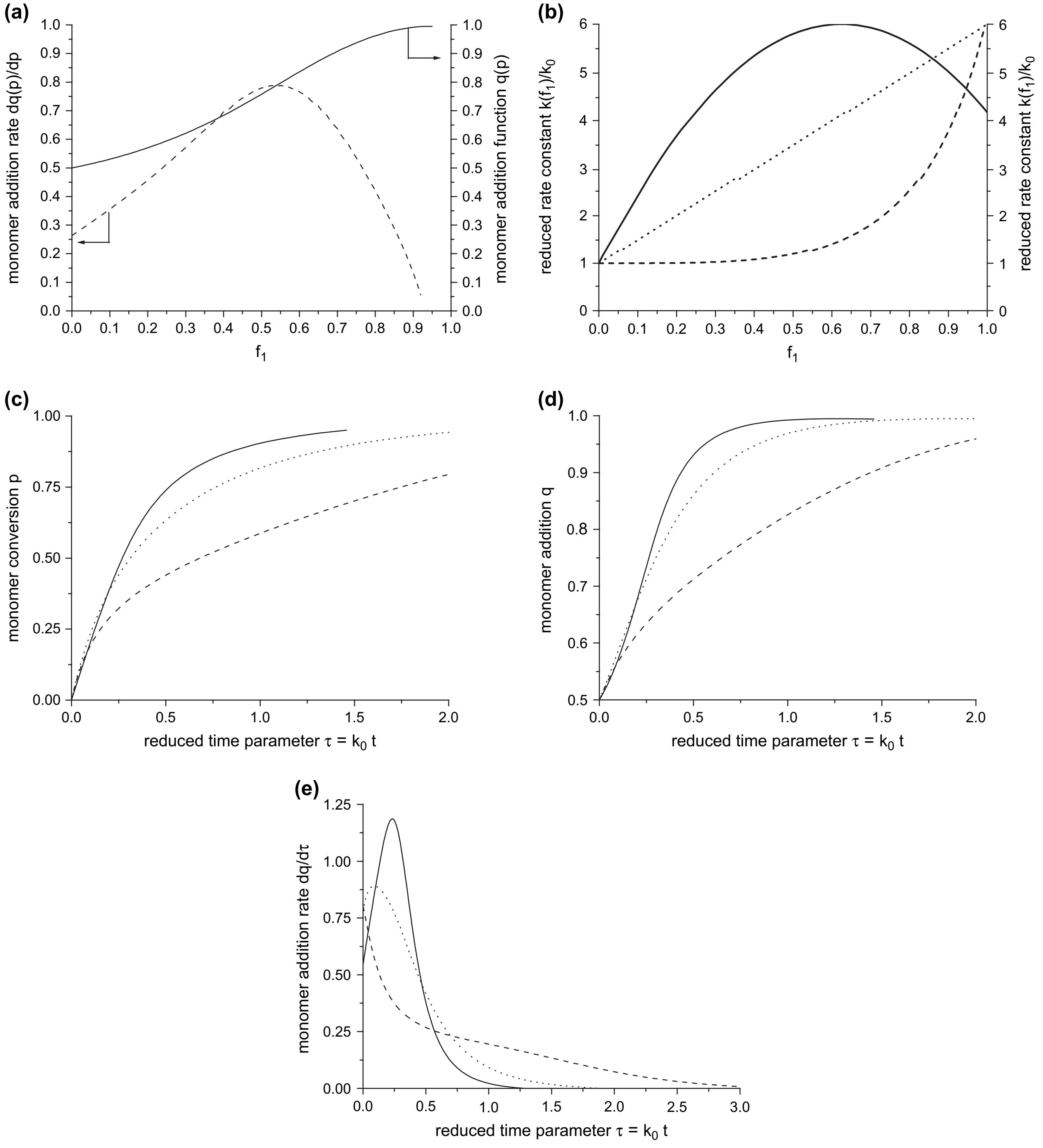


Fig. 3. (a) Monomer conversion dependence of the monomer addition function q and the addition rate d$q(p)$/dp for $r_1 = 0.52$, $r_2 = 0.46$, (b) assumed dependence of the reduced copolymerization rate constant on the comonomer mixture composition f_1, (c) time–conversion curve, (d) monomer addition–time curve, (e) time dependence of the monomer addition rate dq/dt according to DES (12a)–(12c), ($r_1 = 0.52$, $r_2 = 0.46$, $\alpha_1 = 0$, ——: $k(f_1)/k_0 = 1 + 16 \cdot f_1 - 12.8 \cdot f_1^2$, – – –: $k(f_1)/k_0 = 3\exp(f_1^4) - 2$, · · · ·: $k(f_1)/k_0 = 1 + 5f_1$).

$$\alpha_1 = f_1 + \frac{\dfrac{X_e \Phi}{F_1'} + F_1 - f_1}{\dfrac{\mathrm{d}q}{\mathrm{d}t}} \tag{22}$$

$\Phi = \mathrm{d}F_1/\mathrm{d}X$ = targeted copolymer compositional gradient, X_e = targeted length of the gradient block, $\pi = \mathrm{d}p/\mathrm{d}t$ = targeted rate of conversion, $F_1' = \mathrm{d}F_1/\mathrm{d}f_1$, q = total monomer addition function, α_1 = molar fraction of monomer 1 in added monomer mixture, p = monomer conversion, F_1 = instantaneous molar fraction of monomer 1 in the copolymer, f_1 = instantaneous molar fraction of monomer 1 in the monomer mixture, k = copolymerization rate constant.

At a given temperature the targeted rate of monomer conversion π_0 can only be adjusted by means of the initial monomer content q_0 of the reaction mixture, since at the start of the reaction $\pi_0 = q_0 \cdot k_2$ must hold true. However, this condition does not allow large conversion rates: since the copolymer compositional gradient Φ is of negative value ($\mathrm{d}F_1/\mathrm{d}X < 0$) it follows from Eq. (21) that $\mathrm{d}q/\mathrm{d}t$ must always exceed the rate of monomer conversion ($\mathrm{d}q/\mathrm{d}t > \pi_0$) as long as π_0 is not zero. Hence, at a certain time $t_e = (1 - \pi_0/k(f_{1e}))/\pi_0$ all monomer required to generate the gradient block is added, but non-converted monomer is still present in the reaction system: $p(t_e) < 1$. At this point the experimentalist loses control over the copolymer composition, because further addition of monomer is prohibited by the stoichiometric relations. Without monomer addition the non-converted monomer will polymerize "free" to generate a "spontaneous" gradient. This behaviour is illustrated in Fig. 4, depicting the time/monomer addition profiles for $q_0 = \pi_0/k_2 = 0.1$ and $q_0 = 0.01$ in the model system $r_1 = 0.52$, $r_2 = 0.46$, $k(f_1)/k_2 = 1 + 3f_1$. For $q_0 = 0.1$ the monomer addition must be stopped at a monomer conversion of ~73%. The resulting loss of control over the compositional gradient is well visible in the respective copolymer composition curve (Fig. 4b).

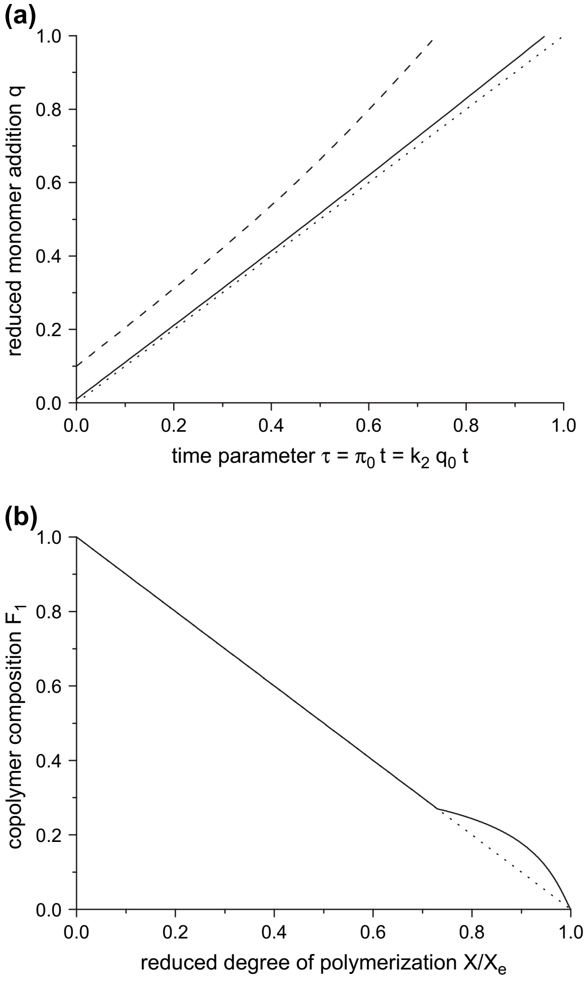


Fig. 4. (a) "Constant rate" monomer addition profiles for $q_0 = 0.1$ (– – –), $q_0 = 0.01$ (—) and $q_0 \to 0$ (····) causing the compositional gradients depicted in (b) (——: $q_0 = 0.1$, ····: $q_0 = 0.01$).

To achieve maximum control, the adjusted rate of monomer conversion π_0 must be as small as possible to minimize the difference between monomer addition rate $\mathrm{d}q/\mathrm{d}t$ and monomer consumption π_0. In the limiting case of low conversion rates ($\pi_0 \ll k(f_1)$) the monomer addition rate approaches the conversion rate ($\mathrm{d}q/\mathrm{d}t \to \pi_0$) and the composition of the added monomer mixture is identical to $\alpha_1 \to 1 - p \approx 1 - \pi_0 t$ (see Fig. 4). Experimentally, this situation supposes to add "one droplet" of a monomer mixture of the required composition to a large volume of the polymerizing mixture and to wait until this minor portion is completely consumed before the next small portion is added. Such a monomer addition program looks simple and straightforward; however, its time consumption will be prohibitively large. For each added monomer portion the experimentalist has to wait $t^* = 1/\pi_0$ for its consumption.

With n addition steps the time consumption of this addition program can be estimated to exceed the total time required for first addition program described by Eq. (13) by a factor of $n/3$. Furthermore, even with a low number of addition steps (e.g. 5–10) the required total reaction time may exceed the effective life time of the growing species.

Fig. 5 compares the time/addition rate profiles of both the addition programs for the model system: $r_1 = 0.52$, $r_2 = 0.46$, $k(f_1) = k_2(1 + 3f_1)$. The "add monomer 2 only" approach is expected to produce the gradient block ~50 times faster than the "constant rate" method.

2.3. Constant mole number condition

Also monomer addition programs were investigated that yield constant compositional gradients and simultaneously

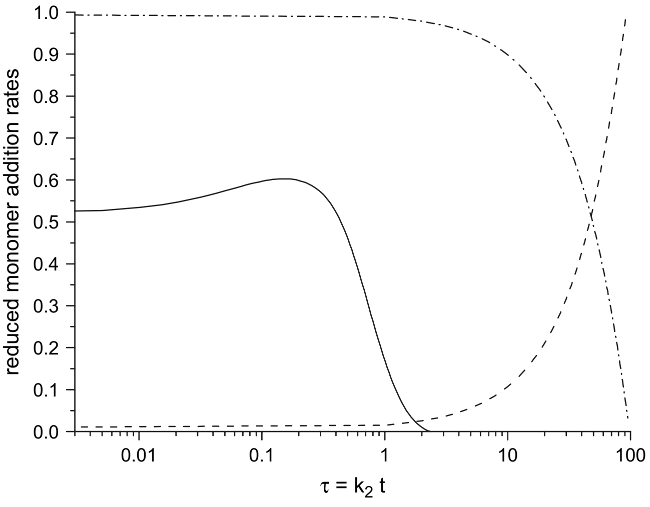


Fig. 5. Comparison of the monomer addition programs according to Eq. (13) (—: $\mathrm{d}q/\mathrm{d}\tau = \mathrm{d}q_2/\mathrm{d}\tau$, $\alpha_1 = 0$, $q_0 = q_{01} = 0.5$) and Eq. (22) (– – –: $\mathrm{d}q_1/\mathrm{d}\tau$, – · – ·: $\mathrm{d}q_2/\mathrm{d}\tau$, $q_0 = 0.01$, $\mathrm{d}p/\mathrm{d}t = \pi_0$). $r_1 = 0.52$, $r_2 = 0.46$, $k(f_1) = k_2(1 + 3f_1)$.

keep the number of moles of monomer constant during the reaction time. Such a program should also cause the polymerization to end in a finite period of time. It was, however, found that no such programs exist, because the simultaneous introduction of the conditions $dF_1/dX = \Phi$ and $dn/dp = 0$ leads to equations that either demand negative monomer addition rates or do not possess any solution (cf. Appendix C).

3. Summary

A differential equation system was derived that allows to calculate the local compositional gradient dF_1/dX along a copolymer chain obtained by controlled copolymerization of two monomers depending on the rate of monomer addition.

According to this set of equations true constant gradient blocks cannot be obtained (i) without, or (ii) with time-linear addition programs.

Two approaches were derived to adjust the compositional gradient at a selected value Φ, namely the "add monomer 2 only" and the "constant rate" approach. With the first methodology a polymerization is initiated in a mixture of n_I moles of a (macro)initiator and $n_{10} = n_I X_e/2$ moles of monomer 1, while $n_2^{add} = n_I X_e/2$ moles of monomer 2 are added during the reaction time. The rate of reaction decreases in time, hence the experimentalist has to stop the reaction on approaching a desired degree of monomer conversion (cf. "starved feed" situations).

For the second method, the start mixture is composed of n_I moles of a (macro)initiator and $n_{10} \ll n_I X_e$ moles of monomer 1. Subsequently, $n_1^{add} = n_I X_e/2 - n_{10}$ moles of monomer 1 and $n_2^{add} = n_I X_e/2$ moles of monomer 2 are added over a finite period of time t_e in such a way that the added mixture composition reflects the copolymer composition at the respective degree of conversion $p = t/t_e$ and that the rate of monomer conversion remains constant. In terms of time efficiency this approach is expected to be inferior to that of the "add monomer 2 only" technique.

Both addition programs require the knowledge of the copolymerization diagram as well as the dependence of the effective copolymerization rate constants $k(f_1)$ on the monomer mixture composition. The required information is simply obtained and the calculated time/monomer addition programs are easily realized with modern computer-controlled equipment.

Appendix A. Derivation of the general monomer drift equation

At an arbitrary monomer conversion p, n_{1p} moles of monomer 1 and n_{2p} moles of monomer 2 have reacted and became incorporated in the copolymer. The solution must then consist of:

$$n_1 = n_{10} + n_1^{add} - n_{1p} \quad \text{moles of unreacted monomer 1} \tag{A1}$$

and

$$n_2 = n_{20} + n_2^{add} - n_{2p} \quad \text{moles of unreacted monomer 2.} \tag{A2}$$

In total, $n = n_0 + \mathrm{n}^{add} - n_p$ moles of monomer are present in the solution, where $n = n_1 + n_2$, $n_0 = n_{10} + n_{20}$ and $n_p = n_{1p} + n_{2p}$. The molar fraction f_1 of monomer 1 in the solution is defined as $f_1 = n_1/(n_1 + n_2)$. The change of f_1 with the monomer conversion is given by:

$$\frac{df_1}{dp} = \frac{d}{dp}\left[\frac{n_1}{n}\right] \tag{A3a}$$

Insert Eqs. (A1) and (A2):

$$\frac{df_1}{dp} = \frac{\frac{d}{dp}\left[\left(n_{10} + n_1^{add} - n_{1p}\right)\right]\left(n_0 + n^{add} - n_p\right)}{\left(n_0 + n^{add} - n_p\right)^2} - \frac{\left(n_{10} + n_1^{add} - n_{1p}\right)}{\left(n_0 + n^{add} - n_p\right)} \frac{\frac{d}{dp}\left(n_0 + n^{add} - n_p\right)}{\left(n_0 + n^{add} - n_p\right)} \tag{A3b}$$

Take into account that $dn_{i0}/dp = 0$ and $f_1 = (n_{10} + n_1^{add} - n_{1p})/(n_1 + n^{add} - n_p)$:

$$\frac{df_1}{dp} = \frac{\frac{dn_1^{add}}{dp} - \frac{dn_{1p}}{dp}}{n_0 + n^{add} - n_p} - f_1 \frac{\frac{dn^{add}}{dp} - \frac{dn_p}{dp}}{n_0 + n^{add} - n_p} \tag{A4}$$

The number of moles of polymerized monomer n_p is related to the monomer conversion p:

$$n_p = \left(n_0 + n_e^{add}\right)p \tag{A5}$$

Hence, $dn_p/dp = n_0 + n_e^{add}$.

The change of the number of polymerized moles of monomer 1, n_{1p} with the monomer conversion is related to the instantaneous composition of the copolymer, F_1:

$$\frac{dn_{1p}}{dp} = F_1\left(n_0 + n_e^{add}\right) \tag{A6}$$

Inserting Eqs. (A5) and (A6) in (A4) yields:

$$\frac{df_1}{dp} = \frac{\frac{dn_1^{add}}{dp} - F_1\left(n_0 + n_e^{add}\right)}{n_0 + n^{add} - \left(n_0 + n_e^{add}\right)p} - f_1 \frac{\frac{dn^{add}}{dp} - n_0 + n_e^{add}}{n_0 + n^{add} - \left(n_0 + n_e^{add}\right)p} \tag{A7}$$

For the subsequent text the definition of the total amount of monomer units (polymerized and non-reacted) that are present in the system is introduced:

$$n^{in} = n_0 + n^{add} \tag{A8}$$

$$n_e^{in} = n_0 + n_e^{add} \tag{A9}$$

Here n^{in} denotes the total amount of monomer that is present in the system at a given conversion p, while n_e^{in} stands for the total amount of monomer in the system at the end of the reaction ($p = 1$).

$$q = \frac{n^{\mathrm{in}}}{n_{\mathrm{e}}^{\mathrm{in}}} \tag{A10}$$

The quotient $q \le 1$, called "monomer addition function" (Eq. (A10)) hence describes the fraction of monomer in the system with respect to the total amount of monomer that must be introduced to the system until the end of the reaction. Inserting Eqs. (A8)–(A10) in Eq. (A7) yields:

$$\frac{\mathrm{d}f_1}{\mathrm{d}p} = \frac{1}{q-p}\left\{f_1 - F_1 + \frac{1}{n_{\mathrm{e}}^{\mathrm{in}}}\left[\frac{\mathrm{d}n_1^{\mathrm{add}}}{\mathrm{d}p} - f_1\frac{\mathrm{d}n^{\mathrm{add}}}{\mathrm{d}p}\right]\right\} \tag{A11}$$

Eq. (A11) contains the total monomer addition rate $\mathrm{d}n^{\mathrm{add}}/\mathrm{d}p$ and the addition rate of monomer 1 ($\mathrm{d}n_1^{\mathrm{add}}/\mathrm{d}p$) as variables. To obtain a parameterized version of the equation, the function α_1 is introduced, describing the molar fraction of monomer 1 in the added monomer mixture:

$$\alpha_1 = \frac{\mathrm{d}n_1^{\mathrm{add}}}{\mathrm{d}p}\bigg/\frac{\mathrm{d}n^{\mathrm{add}}}{\mathrm{d}p} \tag{A12}$$

One reminds that $1/n_{\mathrm{e}}^{\mathrm{in}} \cdot \mathrm{d}n_1^{\mathrm{add}}/\mathrm{d}p = \mathrm{d}q/\mathrm{d}p$ and that $\mathrm{d}n^{\mathrm{add}}/\mathrm{d}p = \mathrm{d}n^{\mathrm{in}}/\mathrm{d}p$ (because of Eq. (A8)). Together with Eq. (A12) one finally obtains the generalized monomer drift Eq. (A13):

$$\frac{\mathrm{d}f_1}{\mathrm{d}p} = \frac{1}{q-p}\left\{f_1 - F_1 + \frac{\mathrm{d}q}{\mathrm{d}p}(\alpha_1 - f_1)\right\} \tag{A13}$$

Two limiting cases of Eq. (A13) may be of interest:
(a) No addition of monomer 1: ($\alpha_1 = 0$)

$$\frac{\mathrm{d}f_1}{\mathrm{d}p} = \frac{1}{q-p}\left\{f_1 - F_1 - \frac{\mathrm{d}q}{\mathrm{d}p}f_1\right\} \tag{A14}$$

(b) Ideal statistical copolymerization ($f_1 = F_1$) and no addition of monomer 1 ($\alpha_1 = 0$)

$$\frac{\mathrm{d}f_1}{\mathrm{d}p} = -\frac{1}{q-p}\frac{\mathrm{d}q}{\mathrm{d}p}f_1 \tag{A15}$$

Appendix B. Derivation of the time dependence of the monomer conversion, d*p*/d*t*

Consider a reaction vessel that contains n moles of monomer. The total change of n with time is described by the formal reaction kinetic Eq. (B1), where $k(f_1)$ denotes the effective reaction rate constant and $\mathrm{d}n^{\mathrm{add}}/\mathrm{d}t$ the rate of monomer addition.

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -k(f_1)n + \frac{\mathrm{d}n^{\mathrm{add}}}{\mathrm{d}t} \tag{B1}$$

Taking into account $n = n_0 + n^{\mathrm{add}} - n_{\mathrm{p}}$ (n_0 = number of monomer moles present at the start of the reaction, n^{add} = number of monomer moles added during the reaction time t and n_{p} = number of polymerized moles of monomer) yields:

$$\frac{\mathrm{d}n^{\mathrm{add}}}{\mathrm{d}t} - \frac{\mathrm{d}n_{\mathrm{p}}}{\mathrm{d}t} = -k(f_1)\left(n_0 + n^{\mathrm{add}} - n_{\mathrm{p}}\right) + \frac{\mathrm{d}n^{\mathrm{add}}}{\mathrm{d}t} \tag{B2}$$

Removing $\mathrm{d}n^{\mathrm{add}}/\mathrm{d}t$ and dividing both sides of the equation by $n_{\mathrm{e}}^{\mathrm{in}}$, being the total number of moles of monomer units present in the reaction vessel at the end of the reaction ($p = 1$), leads to:

$$-\frac{1}{n_{\mathrm{e}}^{\mathrm{in}}}\frac{\mathrm{d}n_{\mathrm{p}}}{\mathrm{d}t} = -k(f_1)\left(\frac{n_0 + n^{\mathrm{add}}}{n_{\mathrm{e}}^{\mathrm{in}}} - \frac{n_{\mathrm{p}}}{n_{\mathrm{e}}^{\mathrm{in}}}\right) \tag{B3}$$

After identifying the terms $p = n_{\mathrm{p}}/n_{\mathrm{e}}^{\mathrm{in}}$ (monomer conversion) and $q = \left(n_0 + n_{\mathrm{add}}\right)/n_{\mathrm{e}}^{\mathrm{in}}$ (monomer addition function) one obtains the required time dependence of the monomer conversion.

$$\frac{\mathrm{d}p}{\mathrm{d}t} = k(f_1)(q-p) \tag{B4}$$

Appendix C. On the existence of monomer addition programs that keep the number of monomer moles constant and yield constant gradient copolymers

A monomer addition program that generates constant gradient copolymers and keeps the number of moles of monomer in the reaction vessel constant must fulfill two conditions:

(1) $\frac{\mathrm{d}F_1}{\mathrm{d}X}X_{\mathrm{e}} = \varphi = \mathrm{const.} \Rightarrow \frac{\mathrm{d}f_1}{\mathrm{d}p} = \frac{\varphi}{F_1'} \Leftrightarrow \frac{\mathrm{d}f_1}{\mathrm{d}t} = \frac{\varphi}{F_1'}\frac{\mathrm{d}p}{\mathrm{d}t}$

$$\left(\frac{\mathrm{d}f_1}{\mathrm{d}t}\right)_{(1)} = \frac{\varphi}{F_1'}\frac{\mathrm{d}p}{\mathrm{d}t}$$

Condition (1) requires a certain time dependency of the monomer composition.

(2) $n = \mathrm{const.} = n_0$: $\frac{\mathrm{d}n}{\mathrm{d}t} = -k(f_1)n + \frac{\mathrm{d}n^{\mathrm{add}}}{\mathrm{d}t} = 0$

$$\frac{\mathrm{d}n^{\mathrm{add}}}{\mathrm{d}t} = k(f_1)n_0 \quad \Big|\text{divide by } n_{\mathrm{e}}^{\mathrm{in}},\ n^{\mathrm{add}}/n_{\mathrm{e}}^{\mathrm{in}} = q, n_0/n_{\mathrm{e}}^{\mathrm{in}} = q_0$$

$$\frac{\mathrm{d}q}{\mathrm{d}t} = k(f_1)q_0 \quad |\mathrm{d}q/\mathrm{d}p = \mathrm{d}q/\mathrm{d}t \cdot \mathrm{d}t/\mathrm{d}p,\ \mathrm{d}t/\mathrm{d}p = (q-p)/k(f_1)$$

$$\mathrm{d}q/\mathrm{d}p = q_0/(q-p)$$

Calculate $\mathrm{d}f_1/\mathrm{d}p$ according to Condition (2):

$$\frac{\mathrm{d}f_1}{\mathrm{d}p} = \frac{\mathrm{d}}{\mathrm{d}p}\left[\frac{n_1}{n_1 + n_2}\right] \quad \Big|n_0 = n_1 + n_2,\ n_1 = n_{10} + n_1^{\mathrm{add}} - n_{1\mathrm{p}}$$

$$\frac{\mathrm{d}f_1}{\mathrm{d}p} = -\frac{1}{n_0}\frac{\mathrm{d}}{\mathrm{d}p}\left[n_{10} + n_1^{\mathrm{add}} - n_{1\mathrm{p}}\right] \quad \Big|\mathrm{d}n_{10}/\mathrm{d}p = 0,\ \mathrm{d}n_1^{\mathrm{add}}/\mathrm{d}p = \mathrm{d}n_1^{\mathrm{in}}/\mathrm{d}p$$

$$\frac{\mathrm{d}f_1}{\mathrm{d}p} = \frac{1}{n_0}\frac{\mathrm{d}n_1^{\mathrm{add}}}{\mathrm{d}p} - \frac{1}{n_0}\frac{\mathrm{d}n_{1\mathrm{p}}}{\mathrm{d}p} \quad \Big|\mathrm{d}n_{1\mathrm{p}} = F_1 \cdot \mathrm{d}n_{\mathrm{p}}$$

$$\frac{\mathrm{d}f_1}{\mathrm{d}p}=\frac{1}{n_0}\frac{\mathrm{d}n_1^{\mathrm{in}}}{\mathrm{d}p}-\frac{F_1}{n_0}\frac{\mathrm{d}n_\mathrm{p}}{\mathrm{d}p}\quad |n_\mathrm{e}^{\mathrm{in}}/n_\mathrm{e}^{\mathrm{in}}$$

$$\frac{\mathrm{d}f_1}{\mathrm{d}p}=\frac{1}{q_0}\frac{\mathrm{d}q_1}{\mathrm{d}p}-\frac{F_1}{q_0}\frac{\mathrm{d}p}{\mathrm{d}p}\quad |\mathrm{d}p/\mathrm{d}p=1, \mathrm{d}q_1/\mathrm{d}p=\alpha_1\cdot \mathrm{d}q/\mathrm{d}p$$

$$\frac{\mathrm{d}f_1}{\mathrm{d}p}=\frac{\alpha_1}{q_0}\frac{\mathrm{d}q}{\mathrm{d}p}-\frac{F_1}{q_0}\quad |\mathrm{d}f_1/\mathrm{d}t=\mathrm{d}f_1/\mathrm{d}p\cdot \mathrm{d}p/\mathrm{d}t$$

$$\left(\frac{\mathrm{d}f_1}{\mathrm{d}t}\right)_{(2)}=\left\{\frac{\alpha_1}{q_0}\frac{\mathrm{d}q}{\mathrm{d}p}-\frac{F_1}{q_0}\right\}\frac{\mathrm{d}p}{\mathrm{d}t}$$

Condition (2) also requires a certain time dependence of the monomer composition. Obviously, the time dependencies $\mathrm{d}f_1/\mathrm{d}t$ arising from conditions (1) and (2) must be identical:

$$\left(\frac{\mathrm{d}f_1}{\mathrm{d}t}\right)_{(2)}=\left\{\frac{\alpha_1}{q_0}\frac{\mathrm{d}q}{\mathrm{d}p}-\frac{F_1}{q_0}\right\}\frac{\mathrm{d}p}{\mathrm{d}t}=\frac{\varphi}{F_1'}\frac{\mathrm{d}p}{\mathrm{d}t}=\left(\frac{\mathrm{d}f_1}{\mathrm{d}t}\right)_{(1)}$$

Resolve for α_1 and replace $\mathrm{d}q/\mathrm{d}p$ by $q_0/(q-p)$:

$$\alpha_1=\left\{\frac{\varphi}{F_1'}+\frac{F_1}{q_0}\right\}(q-p)\geq 0$$

Since α_1 must not become negative, investigate under what circumstances α_1 can be larger than zero:

(a) $(q-p) > 0$ for all times > 0 (the monomer conversion cannot exceed the monomer addition)

(b) $\frac{\varphi}{F_1'}+\frac{F_1}{q_0}\geq 0 \quad |q_0F_1', F_1'=\mathrm{d}F_1/\mathrm{d}X, \text{subtract}\ \varphi q_0$

$$F_1\frac{\mathrm{d}F_1}{\mathrm{d}X}\geq -\varphi q_0 \quad |\mathrm{d}X$$

$$F_1\mathrm{d}F_1\geq -\varphi q_0\cdot \mathrm{d}X \quad |\text{consider:}\quad \varphi=-1, q_0=1/2,$$

$$F_1\cdot \mathrm{d}F_1\geq \frac{1}{2}\mathrm{d}X \quad |\text{Integrate both sides, integration limits:}$$

$$F_{1,0}=1,\ F_{1,X_\mathrm{e}}=0$$

$$\int_{F_{1,X_\mathrm{e}}=1}^{F_{1,0}=0} F_1\cdot \mathrm{d}F_1\geq \frac{1}{2}\int_0^{X_\mathrm{e}}\mathrm{d}X$$

$$\frac{1}{2}\left(1^2-0^2\right)\geq \frac{1}{2}X_\mathrm{e}\Rightarrow 1\geq X_\mathrm{e}$$

This expression cannot be fulfilled for $X_\mathrm{e}>1$: the term $\{\varphi/F_1'+F_1/q_0\}$ must hence always be of negative value. The product $\{\varphi/F_1'+F_1/q_0\}(q-p)=\alpha_1$ becomes negative in all cases and so does α_1. It must be concluded that there exists no possible mixture of monomer 1 and monomer 2 that can be added to a polymerization mixture in such a way that both conditions ($n=$ constant and $\mathrm{d}F_1/\mathrm{d}X=$ constant) are valid.

The considered monomer addition program cannot be realized.

Appendix D. Source code of GRADDOS1.BAS

The program GRADDOS1.BAS allows to calculate a monomer addition program $q(t)$ and $\mathrm{d}q/\mathrm{d}t(t)$ to obtain a pre-defined course of the compositional gradient $\mathrm{d}F_1/\mathrm{d}p$ by numerical integration of the differential equation system (D1–D3) in the limits of the monomer conversion $p=p_0$ to $p=p_\mathrm{e}$:

$$\frac{\mathrm{d}q}{\mathrm{d}p}=\frac{X_\mathrm{e}\Phi}{F_1'}\frac{q-p}{\alpha_1-f_1}+\frac{F_1-f_1}{\alpha_1-f_1} \tag{D1}$$

$$\frac{\mathrm{d}f_1}{\mathrm{d}p}=\frac{1}{q-p}\left\{f_1-F_1+\frac{\mathrm{d}q}{\mathrm{d}p}(\alpha_1-f_1)\right\} \tag{D2}$$

$$\frac{\mathrm{d}t}{\mathrm{d}p}=\frac{1}{k(f_1)(q-p)} \tag{D3}$$

$\Phi=\mathrm{d}F_1/\mathrm{d}X=$ targeted copolymer compositional gradient, $X_\mathrm{e}=$ targeted length of the gradient block, $F_1'=\mathrm{d}F_1/\mathrm{d}f_1, q=$ total monomer addition function, $\alpha_1=$ molar fraction of monomer 1 in added monomer mixture, $p=$ monomer conversion, $F_1=$ instantaneous molar fraction of monomer 1 in the copolymer, $f_1=$ instantaneous molar fraction of monomer 1 in the monomer mixture.

The user has to supply (1) the copolymerization parameters r_1 and r_2, (2) the effective rate constant function $k(f_1)$, (3) the function $\alpha_1(p)$ (in case that monomer 1 should be added), (4) the desired value – or function – of the compositional gradient $\mathrm{d}F_1/\mathrm{d}p$ and (5) the initial value of monomer present in the system, q_0. The implementation in the presented source text deals with a hypothetical monomer system characterized by:

$r_1=0.52, r_2=0.46,$ (Lines 54 and 55)

$k(f_1)=1+5\cdot f_1$ (Line 154)

The standard implementation assumes that a constant gradient from $F_1(p=0)=1$ to $F_1(p=1)=0$ is required and that only monomer 2 is added:

$\alpha_1=0$ (= addition of monomer 2 only) (Line 147)

$g=\mathrm{d}F_1/\mathrm{d}p=-1$ (Line 61)

$q_0=1/2$ (Line 70)

In case where a more complex course of the gradient along the polymer chain is required, the user may implement the function $\mathrm{d}F_1/\mathrm{d}p(p)$ in FUNCTION grd(p) (Line 172) and adjust q_0 accordingly.

The instantaneous polymer composition is calculated in FUNCTION Z1(f1) (Line 219) by means of the Lewis–Mayo Equation (terminal model). More complex copolymerization equations can be implemented here if necessary. The derivation $\mathrm{d}F_1/\mathrm{d}f_1$ was deliberately implemented in FUNCTION Z1p(f1) (Line 229) in form of a numerical derivation to allow a simple exchange of the applied copolymerization equation.

The program saves the results of its calculations in an ASCII file, file name and path can be adjusted as in Line 77. The number of saved data points can be controlled by the value of the variable dps in Line 76 ($N = (p_e - p_0)$/dps). Any saving can be omitted by setting the flag sve to 0 in Line 75.

To avoid numerical problems it is recommended not to integrate to full monomer conversion, but to stop at $p \sim 0.97-0.98$. This limit can be set in Line 66, variable p_e. It is also recommended to perform the calculations in τ-space instead of the real time t. This is simply performed by dividing the effective rate constant function $k(f_1)$ by the homopolymerization constant of monomer 2, i.e. $k(f_1) = 1$ for $f_1 = 0$.

```
1    ’ Programm GRADDOS1.BAS
2    ’
3    ’ (c) Uwe Beginn, 30.11.2005
4    ’ Written in Microsoft QBasic 4.5
5    ’
6    ’ Programm to calculate the monomer addition function of
7    ’ monomer 1 to generate a gradient copolymer. Conditions:
8    ’
9    ’ - The effective rate constant of the copolymerization k(f1)
10   ’ = kp12(f1) * nI0 must be implemented in function cp(f1).
11   ’
12   ’ - The copolymerisation parameter must be known and given in
13   ’ the “system” definition part of the main program. The
14   ’ function Z1(f1) contains the copolymerisation equation
15   ’ (implemented equation: terminal model)
16   ’
17   ’ - Addition of Monomer 1: alpha1 = Function(p)
18   ’ (implemented: alpha1 = 0, i.e. dq/dt = dq2/dt)
19   ’
20   ’ - Initial amount of Monomer 1 in batch: q0 = n10/ne = 0.5
21   ’
22   ’ - Gradient Xe * dF1/dX = g = −1
23   ’ In Function grd(p) the gradient dF1/dX can be defined
24   ’ as function of the monomer conversion p: ATTENTION in
25   ’ case of g <> -1, q0 must be adapted to the stoichiome-
26   ’ try of the planned gradient block).
27   ’
28   ’ - The rate of reaction decreases down to zero, as well as
29   ’ the number of moles monomer 1 and 2.
30   ’
31   DECLARE FUNCTION DGLsyst (i!, x, Y)
32   DECLARE FUNCTION Z1 (f1)
33   DECLARE FUNCTION Z1p (f1)
34   DECLARE FUNCTION cp (f1)
35   DECLARE FUNCTION Alpha1 (p)
36   DECLARE FUNCTION grd (p)
37   ’
38   DECLARE SUB SolveDGLS (n, t0, TE, h1, h1min, h1max, eps)
39   DECLARE SUB Plot (n, xmin, xmax, ymin, ymax, Zstp, Zerr)
40   DECLARE SUB schirm (xbmin!, xbmax!, ybmin!, ybmax!, backcol!, xmin!, xmax!, ymin!, ymax!, nx!, ny!)
41   DECLARE SUB SaveIt (sve, n, p, Phi)
42   ’
43   COMMON SHARED t, n, g, r1, r2
44   COMMON SHARED xmin, xmax, ymin, ymax, sve, psve, dps
45   ’
46   n = 3: ’ number of differential equations
47   DIM SHARED Y(n), ya(n), y0(n), yf(n), f(n), f0(n)
48   DIM SHARED d(n)
49   ’ ------------------------------------
50   ’
51   ’ System definition
52   ’
53   ’ - Copolymerisation parameter
54   r1 = .52
55   r2 = .46
56   ’
57   ’ - Effective copolymerisation rate constant k(f1)
58   ’ must be defined in FUNCTION cp(f1)
59   ’
60   ’ - Desired gradient
61   g = -1: ’ g = dF1/dp
62   ’
63   ’
64   ’ - Initial conditions
65   p0 = 0: ’ Initial monomer conversion
66   pe = .98: ’ Final monomer conversion
67   ’
68   ’
69   ’
70   y0(1) = .5: ’ y1(p = 0) - q0
71   y0(2) = 1: ’ y2(p = 0) - f10
72   y0(3) = 0: ’ y3(p = 0) - t0
73   ’
74   ’
75   sve = 1 ’ 1 = save Table: tau, p, q, f1, dq/dt, F1
76   dps = .01 ’ every dps step
77   Pfad$ = “C:\COPOGRAD\GRADDOS1.DAT” ’ default save path
78   ’
```

```
79  ’
80  ’
81  ’------------------------------------
82  ’
83  ’ Integration control
84  ’
85  ep = .00000001# ’ Error - Limit
86  h1 = .00000001# ’ Start step width
87  h1min = .00000001# ’ smallest allowed step width
88  h1max = .0001 ’ largest allowed step witdh
89  ’------------------------------------
90  ’
91  ’ Programm
92  ’
93  PRINT
94  PRINT “ GRADDOS.BAS”
95  PRINT
96  PRINT
97  PRINT “ System definition:”
98  PRINT
99  PRINT “ r1 = ”; r1
100 PRINT “ r2 = ”; r2
101 PRINT
102 PRINT “ ------------ ----------------”
103 PRINT “ f1 k(f1) p dF1/dp”
104 PRINT “ ------------ ----------------”
105 FOR f1 = 0 TO 1 STEP .25
106 PRINT USING “ ###.#### ”; f1;
107 PRINT USING “ ##.####^^^^ ”; cp(f1);
108 PRINT USING “ ###.### ”; f1;
109 PRINT USING “ ##.## ”; grd(p)
110 NEXT f1
111 PRINT “ ------------ ----------------”
112 PRINT
113 PRINT “ Calculation started”
114 ’
115 ep1 = ep
116 epn = ep/n
117 IF sve = 1 THEN
118 OPEN Pfad$ FOR OUTPUT AS #1
119 psve = 0
120 END IF
121 ’
122 SolveDGLS n, p0, pe, h1, h1min, h1max, epn
123 ’
124 PRINT “ Calculation finished”
125 IF sve = 1 THEN
126 PRINT #1, “t/k2”, “p”, “f1”, “q”, “dq/dt”, “F1”
127 PRINT #1, “ ”
128 PRINT #1, “GRADDOS1.BAS”
129 PRINT #1, DATE$
130 PRINT #1, TIME$
131 PRINT #1, “r1 = ”; r1
132 PRINT #1, “r2 = ”; r2
133 PRINT #1, “kp(f1) = 3*exp(f1^4)-2”
134 PRINT #1, “dF1/dX = -1”
135 PRINT #1, “---END---”
136 CLOSE #1
137 PRINT
138 PRINT “ tau, p, f1, q, dq/dt, F1 - Table saved in:”
139 PRINT “ ”; Pfad$
140 END IF
141 END
142 ’ Define fraction of monomer 1 in
143 ’ feed solution as function of the
144 ’ monomer conversion p. Default:
145 ’ alpha1 = 0
146 FUNCTION Alpha1 (p)
147 Alpha1 = 0
148 END FUNCTION
149 ’ Define effective copolymerisation
150 ’ rate constant as function of the
151 ’ molar fraction of monomer 1 in
152 ’ the reaction mixture (f1).
153 FUNCTION cp (f1)
154 cp = 1 + 5 * f1
155 END FUNCTION
156 FUNCTION DGLsyst (i, x, Y)
157 xf = x ’x = monomer conversion p
158 yf(i) = Y
159 SELECT CASE i <= n
160 CASE i = 1
161 f(1) = -g/(yf(2) * Z1p(yf(2))) * (yf(1) - xf) + 1 - Z1(yf(2))/yf(2)
162 CASE i = 2
163 f(2) = 1/(yf(1) - xf) * (yf(2) - Z1(yf(2)) + f(1) * (Alpha1(xf) - yf(2)))
164 CASE i = 3
165 f(3) = 1/(yf(1) - xf)/cp(yf(2))
166 END SELECT
167 DGLsyst = f(i)
168 END FUNCTION
169 ’ Define the gradient Xe*dF1/dX
170 ’ = dF1/dp as function of the
171 ’ monomer conversion p. Default:
172 ’ dF1/dx = constant = g,
173 ’ default g: -1
174 FUNCTION grd (p)
175 grd = g
176 END FUNCTION
177 SUB SaveIt (sve, n, p, Phi)
178 IF sve = 1 THEN
179 IF p > = psve THEN
180 psve = psve + dps
181 PRINT #1, Y(3), p, Y(2), Y(1), f(1)/f(3), Z1(Y(2))
182 ’ t p f1 q dq/dt, F1
183 END IF
184 END IF
185 END SUB
```

```
SUB SolveDGLS (n, p0, pe, h1, h1min,
  h1max, eps)
DIM c1(n), c2(n), c3(n), c4(n)
FOR i = 1 TO n
Y(i) = y0(i)
f(i) = f0(i)
NEXT i
ep = eps * n
p = p0
DO
h2 = h1/2
dn = 0
FOR i = 1 TO n: yf(i) = Y(i): NEXT i
FOR i = 1 TO n
x = p: Y = Y(i): c1(i) = DGLsyst(i, x, Y)
x = p + h2: Y = Y(i) + h2 * c1(i): c2(i) =
  DGLsyst(i, x, Y)
x = p + h2: Y = Y(i) + h2 * c2(i): c3(i) =
  DGLsyst(i, x, Y)
x = p + h1: Y = Y(i) + h1 * c3(i): c4(i) =
  DGLsyst(i, x, Y)
ya(i) = Y(i)
Y(i) = Y(i) + h1 * (c1(i) + 2 * c2(i) + 2 *
  c3(i) + c4(i))/6
d(i) = ABS(h1 * (-c1(i) - c2(i) + 2 *
  c3(i))/3/n)
dn = dn + d(i)
NEXT i
p = p + h1
IF dn > eps THEN h1 = h1 * .9
IF dn < eps THEN h1 = h1/.9
IF h1 < h1min THEN h1 = h1min
IF h1 > h1max THEN h1 = h1max
SaveIt sve, n, p + h1, Phi
LOOP UNTIL p > pe
END SUB
' Implementation of the copolymerisation
' equation. Default: Lewis-Mayo equation
' (= terminal model)
FUNCTION Z1 (f1)
f2 = 1 - f1
f12 = f1 * f2
zz = r1 * f1 ^ 2 + f12
zn = r2 * f2 ^ 2 + f12
Z1 = zz/(zz + zn)
END FUNCTION
' Numerical calculation of the term
' F1' = dF1/df1. Can be replaced by
' an analytical expression.
FUNCTION Z1p (f1)
fa = f1 + .00005
fb = f1 - .00005
za = Z1(fa)
zb = Z1(fb)
Z1p = (za - zb)/.0001
END FUNCTION
```

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