Polym. Bull. (2011) 66:571–581
DOI 10.1007/s00289-010-0427-2

ORIGINAL PAPER

Kinetics of formation of unitary three-dimensional structural elements: numerical experiment

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Received: 1 July 2010 / Revised: 14 October 2010 / Accepted: 28 December 2010 /

Abstract For the first time the results of numerical experiments (by the Monte Carlo method) on the kinetics of three-dimensional free radical polymerization of tetrafunctional monomers within the framework of the formation of a unitary three-dimensional structural element on the cubic lattice 50 × 50 × 50 have been presented.

Keywords Polymerization kinetics · Monte Carlo method · Simulation · Tetrafunctional monomer

Introduction

The problem of studying the kinetics of free radical polymerization of three-dimensional multi-functional monomers and oligomers (MFM) to form the final product—a three-dimensional polymer, can be divided into two subproblems: (1) the study of the kinetics of the gross process throughout the reaction volume (the case of multiple initiating of polymerization of MFM in different microvolumes of the reaction mass); (2) the identification of the kinetics of the process in the framework of formation of a unitary three-dimensional structural element (UTSE). The (1) subproblem has been the subject of research for at least 65–70 years, advances in this field of investigation have been represented in many publications [1–27]. In scientific literature there are the results of the kinetic studies of the three-dimensional free radical polymerization of these classes of polymerizationable compounds (PSO) like oligoesteracrylates [1–3], multiallyl derivatives [4–6] and

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others, with the polymerization being carried out in PSO multiple initiation of polymerization PSO, let alone separate UTSE. To solve the (1) subproblem the simulating models of three-dimensional MFM polymerization by the Monte Carlo method (MC method) and a number of other methods were developed.

For example, the authors of [7] proposed a kinetic model for the simulation of MFM polymerization and its copolymerization with vinyl monomers the critical behavior near the gel point being found, and others parameters. By the MC method the influence of the MFM fraction on the number of trapped radicals, the position of the gel point, etc., was discovered [8]. The authors of [9] described the simulation model of MFM polymerization by the MC method, which allowed to monitor the decay of the initiator and certain mechanisms of the mobility of the active centers establishing the kinetic dependence of the degree of the monomer conversion, etc. The developed [10–20] kinetic models [10–20] allow to describe the formation of polymers identifying the features of the cycloformation, the role of the solvent, the kinetic chain length, and the architecture of branched polymers, the distribution of topological structures, sticking together polymer particles, density of the distribution of crosslink, molecular weight distribution, trapping radicals, and others. In the works [21–23] the formation of microscopically inhomogeneous structure in the three-dimensional MFM polymerization process was confirmed. The reviews [24–27] provide much information on a large number of works performed on study of the kinetics of the three-dimensional of polymerization and copolymerization of MFM by different methods, but all studies were undertaken within the (1) subproblem solution, that is in the regime of the multi-initiation of the process MFM polymerization in the reaction volume with the formation of macrobody of the three-dimensional polymer.

There are no scientific articles on the (2) subproblem, except our works [28–31]. It is next to impossible to solve the (2) subproblem experimentally using up-to-date methods, because it means operating the quantity of the substance under study at a level of 10^{-19} to 10^{-22} mol. We have developed a model based on the statistical Monte Carlo method, allowing to make a numerical experiment on a free radical polymerization of tetrafunctional monomers (TFM) within the frame of the UTSE formation [31].

The investigation of the physical structure of three-dimensional polymers TFM by electron microscopy and X-ray diffraction methods showed that for macrobody the three-dimensional polymers microinhomogeneous globular structure with a diameter of the structural elements of 15–60 nm is typical, besides the identified structural formations are secondary formations of smaller globules with an average diameter of 5–10 nm [1, 2]. A primary globule (nanogel) like the structure we call a unitary three-dimensional structural element (UTSE); the study of the kinetics of generation UTSE and the structure of formation UTSE is assigned to the solution of subproblem (2).

The solution of the above mentioned problem is important for various practical issues, including the creation of nanotechnology to obtain nanomaterials, or to answer the question—Is it possible to obtain nanomaterials (we do not mean the materials at a level of nanoscale, but we mean the nanomaterials having a set of required properties), or impossible to obtain them based on TFM?

Setting up the problem

To establish the peculiarities of the formation of UTSE, namely the multitude of UTSE forms the macrobody a three-dimensional polymer, we developed a model of the GSU-UTSE (model of Gysin F.R.–Sivergin Y.M.–Usmanov S.M.–UTSE) [28, 31]. The simulation of TFM polymerization in this study was performed on a simple cubic lattice of 50 × 50 × 50 dimensionality (for this lattice the share of intravolume nodes with a degree of freedom 6 is 88.5%). If we take the density of TFM equal to 1.05 g/cm^3 and the molecular mass equal to 200 g/mol, the simulated volume for the lattice (assuming that the molecule of TFM is three nodes (and two ribs)) amount to 13179 nm^3. This corresponds to the structural formation with a radius of 14.6 nm.

Randomly on the lattice we placed one molecule TFM and initiated one of the double bonds TFM (R_o—initiating radicals and molecules TFM are found in the internodes). The rate of the chain initiation is:

$$v_i = k_i[R_o][M] \tag{1a}$$

where k_i—the rate constant for the initiation of the chain, [M]—the monomer concentration. Within the frame of the UTSE formation the reaction initiation (1) of the monomer is implemented only once—during the beginning initiation of the chain. In the next stages of the process by pendant double bonds PG which is found on to macrochains (the share of these groups PG is denoted by D) is initiated; besides, the reactivity of the double bond in the M and PG is assumed to be similar [32, 33]:

$$v_i = k_i[R_o][PG] \tag{1b}$$

After the initiation stage of the chain the reactions of chain propagation takes place

$$v_p = k_p[R][M] \tag{2}$$

$$v'_p = k'_p[R'][M] \tag{3}$$

as well as the chain termination

$$v_t = k_t[R]^2 \tag{4}$$

$$v'_t = k_t[R][R'] \tag{5}$$

$$v''_t = k_t[R']^2 \tag{6}$$

where R—radical in the form of the pendant group (it is connected with one macrochain of the i-generation), R′—less active radical (it is connected with two macrochains or with the cycle and is characterized by more sterically hindered radical than R, so for R′ it was assumed that $k'_p = 0.1k_p$); k_p, k'_p, k_t are reaction rate constant of propagation and termination of chain. In subsequent stages of the process at random (stochastic process) one of the possible reactions (1–6) was selected. The values of k_t for the radicals R and R′ are taken to be equal. The initiating radical R_o is used only in the initiation reaction chain. Obviously, if R_o is allowed to participate in the reactions of chain termination, the polymerization will not take place because of the loss of the radicals R and R′ with R_o and the model will not work.

In the case of three-dimensional polymerization TFM reactions of crosslinking (7–11) and cycloformation (12–16) take place on the mechanisms of R–PG, R′–PG, R–R, R–R′, and R′–R′:

$$v_{cr} = k_{cr}[R][PG] \tag{7}$$

$$v'_{cr} = k'_{cr}[R'][PG] \tag{8}$$

$$v_{tcr} = k_{tcr}[R]^2 \tag{9}$$

$$v'_{tcr} = k_{tcr}[R][R'] \tag{10}$$

$$v''_{tcr} = k_{tcr}[R']^2 \tag{11}$$

$$v_{cy} = k_{cy}[R][PG] \tag{12}$$

$$v'_{cy} = k'_{cy}[R'][PG] \tag{13}$$

$$v_{tcy} = k_{tcy}[R]^2 \tag{14}$$

$$v'_{tcy} = k_{tcy}[R][R'] \tag{15}$$

$$v''_{tcy} = k_{tcy}[R']^2 \tag{16}$$

where v_{cr}, v'_{cr}, v_{tcr}, v'_{tcr}, v''_{tcr}, v_{cy}, v'_{cy}, v_{tcy}, v'_{tcy}, v''_{tcy}—the reaction rates of crosslinking and cycloformation; k_{cr}, k'_{cr}, k_{tcr}, k'_{tcr}, k''_{tcr}, k_{cy}, k'_{cy}, k_{tcy}, k'_{tcy}, k''_{tcy}—the rate constants of the same reactions. Since the reactivity of double bonds in the M and PG is accepted to be equal and the equality of the rate constants $k_{cr} = k_{cy} = k_p$, $k'_{cr} = k'_{cy} = k'_p$ then the reactions (7, 8, 12, 13) are included in the reactions (2, 3); because the equal reactivity of radicals R and R′ in the reactions (4–6) and (9–11, 14–16) and the equality of the reaction rate constants $k_{tcr} = k_{tcy} = k_t$ therefore the reactions (9–11, 14–16) are included in the reactions (4–6). The possibility of an elementary reaction of the above mentioned reactions will be determined by the probability of in pairs meetings (contacts) of the reactive centers.

For the foregoing reasons, at the calculation of the reaction probability p_i we take into account only six elementary stages $j = 1\ldots 6$ (where p_i is the statistical weight of the i-th reaction). At each stage of simulation it is necessary to identify which one of these six reactions is realized. The number of the stage j is found from the condition:

$$\sum_{i=1}^{j-1} p_i < \xi_1 < \sum_{i=1}^{i=j} p_i \tag{17}$$

where p_i is the probability of the i-th elementary stage; denoting by V_i the speed of i-th reaction, we obtain $V = \sum V_i = v_i + v_p + v'_p + v_t + v'_t + v''_t$; $P = \sum p_i = 1$.

If for the reaction number is i then there are several options (for example, more active or less active radicals, etc.), the choice of one of them is made with an equal probability out of all possible. In the case of the MC method, this situation is demonstrated by stochastic way in the increase of the number of attempts to achieve the possibility of the reaction.

In the simulation of the TFM polymerization process by the MC method simulation at each stage of the simulation a random selection of the elementary reaction is revealed (random selection of a state in which the reaction system will pass), its direction, the location of the molecule TFM, the waiting time of transition [28, 31]. The waiting time of specific elementary stages of polymerization is found from the relation:

$$\tau_k = \frac{-\ln \xi_2}{\sum_{i=1}^{6} V_i} \tag{18}$$

here ξ_1 and ξ_2 is random numbers uniformly distributed in the interval (0, 1). In the product tk_p parameter k_p is the reaction rate constant of pseudo first-order. The total time of polymerization (T_pol) was determined by the sum of waiting times at all stages

$$T_\mathrm{pol} = \sum \tau_k \tag{19}$$

As mentioned above, if the initial stages of a three-dimensional PSO polymerization are a purely stochastic process, then beginning with a certain degree of conversion an element of determinism appears and its contribution increases with growth of the conversion and with a transition of a three-dimensional polymerization mostly in a deterministic regime in the final stages.

In addition to the quadratic termination reactions of radicals R–R, R–R′, and R′–R′, in the reaction system there is a linear radical break with their immobilization (these radicals are automatically taken into account as the residual radicals R and R′, for example, at the end of the process):

$$\mathrm{R} + \mathrm{Y} \rightarrow \mathrm{RY} v_\mathrm{tl} = k_\mathrm{tl}[\mathrm{R}][\mathrm{Y}] \tag{20}$$

$$\mathrm{R}' + \mathrm{Y} \rightarrow \mathrm{R}'\mathrm{Y} v'_\mathrm{tl} = k'_\mathrm{tl}[\mathrm{R}'][\mathrm{Y}] \tag{21}$$

where v_tl, v'_tl—rates and k_tl, k'_tl—rate constants of the linear termination of radicals.

From the reaction schemes, it is clear that the increase in molecular mass of the skeleton UTSE occurs only on the reactions of the chain propagation (2, 3). The crosslinking and cycloformation reactions do not lead to an increase in molecular mass UTSE, but only determine the topological changes in the skeleton UTSE—crosslinking of macrochains with each other and generation of cyclic structures of different sizes take place. The process of three-dimensional radical TFM polymerization was led up to the maximum degree of conversion of double bonds and it was finished in the cases when all of the available three-dimensional lattice nodes were occupied, when in the chain propagation there are no free ribs on the lattice for the placement of a new monomer molecule, when there are no available radicals R and R′. The following values for reaction rate constants were taken: $k_\mathrm{i} = (0.0001 \div 100)k_\mathrm{p}$, $k_\mathrm{p} = 400$ L/mol s, $k'_\mathrm{p} = 40$ L/mol s, $k_\mathrm{t} = 10^6$ L/mol s. Chain transfer reactions were not take into account, the walls of the reactor were believed to be inert towards reactive groups.

It is common knowledge [34] that, depending on the nature of the initiating radical R_o and the monomer and the external conditions, the value of k_i varies within very wide limits. We have taken a range of $k_i = 0.04 \div 40000$ L/mol s which completely covers a usual practical variation of k_i. Details of the model GSU-UTSE are given in the works [28, 31]. The averaging of the results of the experiment was carried out on 5000 realizations of the simulation (5000 runs) and this averaging may be accomplished along the maximum values of the parameters or along the values of the parameters achieved at a specific moment of time (up to $k_i/k_p < 0.01$ average magnitude of the parameters found along the maximum value is somewhat higher than the magnitude of the parameters found at a specific moment of time; with a higher ratio k_i/k_p there occurs their inversion); in the given investigation magnitude of the parameters averaged over the time was used.

Each experiment is an event independent of other experiments, but the check showed that the average values of one series of experiments, found in 5000 runs differ from the average values of another series (also 5000 runs) not more than $0.5 \div 2\%$. In the course of the experiment, the decrease in the number of parallel runs from 5000 to 70–2000 (depending on the ratio k_i/k_p) runs was observed at the end of the experiment due to the formation of low molecular UTSE (as a result of the cycloformation reactions, the loss of radicals by different mechanisms, as well as immobilization of double bonds and radicals).

Results and discussion

In the work [28] the results of simulation the kinetics of formation UTSE on some low-dimensional lattices (from 3^3 to 7^3) were described and we revealed kinetic peculiarities of free radical polymerization of TFM in small volumes. Continuing to study the (2) subproblem, in this work we have performed a numerical experiment on the kinetics of the formation UTSE on a cubic lattice of dimension 50^3. A simple cubic lattice, in contrast to a real reactor, introduces restrictions on the mobility of reacting molecules. But the lattice nodes have some degrees of freedom (from 3 to 6), which to some extent imitate the mobility of molecules at their construction and in choosing the direction of the reaction. In reality, reaction environment of the molecules of monomers and oligomers also have restrictions on mobility due to the formation of associates (in view of the polar nature of the monomer molecules) from a few molecules and a definite period of their life time in the occupied nanovolumes. In the course of polymerization process the role of these factors in the polymerization system increases, approaching the version of the lattice by the mobility (the fall of the mobility). The above mentioned causes make us think that the results obtained in the implementation of the numerical experiments on a cubic lattice, adequately describe the formation of UTSE in real conditions.

From the relationship of P_n degree of polymerization (hereafter expressed in units) versus time (Fig. 1a–f) it is clearly seen that with the increase of values k_i curves $P_n(t)$ vary significantly: for $k_i = 0.0001k_p$ dependence of $P_n(t)$ has the form of a monotonically changing slope of the curve with the lowest slope compared with other curves of $P_n(t)$, but with $k_i = 0.001k_p$ dependence of $P_n(t)$ is a curve with a

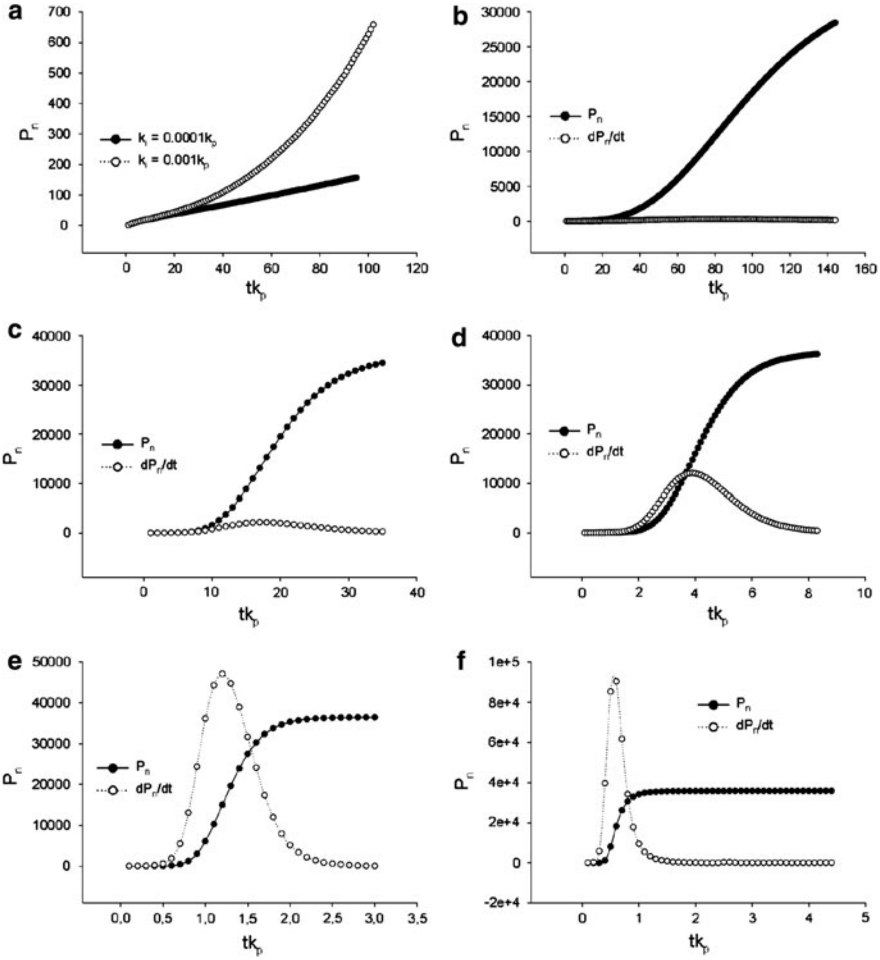

Fig. 1 The dependence of the degree of polymerization P_n UTSE (**a**–**e**) and the rate of polymerization $\mathrm{d}P_n/\mathrm{d}t$ (**b**–**e**) on time with the ratio $k_i/k_p = 0.0001$ and 0.001 (**a**), 0.01 (**b**), 0.1 (**c**), 1 (**d**), 10 (**e**), and 100 (**f**)

marked self-acceleration, starting with the relationship $k_i \geq 0.01k_p$ curves of $P_n(t)$ become a sigmoid shape of curves characteristic of the degree of conversion from t in a real experiment (for example, for the class oligoesteracrylate) [1–3].

A limiting degree of polymerization $P_{n\lim}$ increases from 156 (at $k_i = 0.0001k_p$) to 36460 ($k_i = 10k_p$) and then decreased to 35860 ($k_i = 100k_p$) (see Table 1). The growth of $P_{n\lim}$ is conditioned by the rise of the number of radicals, and the fall is conditioned by an increased loss of radicals in the reactions cycloformation and their immobilization in physical traps (linear termination). The reaction of chain propagation is responsible for increasing of the degree of polymerization P_n.

The curves of the velocity change of P_n have the form of asymmetric curves $\mathrm{d}P_n/\mathrm{d}t$ on t (Fig. 1b–e), which clearly identify two fields of TFM polymerization—

Table 1 The limiting of values the kinetic of parameters at different ratios k_i/k_p

k_i/k_p	$P_n \times 10^{-2}$	N_R	$N_{R'}$	$N_R + N_{R'}$
0.0001	1.56	1.13	0.37	1.5
0.001	6.58	6.9	2.4	9.3
0.01	284.6	2551	584	3135
0.1	344.0	5359	907	6266
1	362.3	7002	895	7897
10	364.6	7487	647	8134
100	358.6	7669	327	7996

autoacceleration (up to the maximum on the curve) and autoinhibition. A noticeable autoacceleration of the three-dimensional polymerization process is due to the phenomenon of TFM nanogel formation, and autoinhibition (after the maximum on the curve dP_n/dt)—the phenomenon of nanovitrous state. Earlier [1–3] the autoacceleration and autoinhibition of TFM polymerization were interpreted by the role of the diffusion factor and by the change in the rate constants of chain propagation and of chain termination. There is no reason to reject the action of these factors for the case of the UTSE formation as well. Obviously, UTSE, in essence, is a micro-reactor, in which the reactions (1–16) take place. The experimental kinetic curves of TFM polymerization given in [1–3] are average values for the TFM polymerization in the multitude of UTSE in any practical reaction system.

Our model allows us to obtain some information on the kinetics of radical changes (we have identified two types of radicals—R and R′) in the reaction system. The generation of radicals R is carried out by the reactions (1b, 2, 3), and the radicals R′ is carried out by the reactions (7, 8, 12, 13). The number of radicals N_R and $N_{R'}$ (Fig. 2a–f) in the reaction system increases with the growth of k_i (e.g., from the thresholds 1–2 radicals, at $k_i = 0.0001k_p$ to 8134 when $k_i = 10k_p$ and 7996 with $k_i = 100k_p$; Table 1). The shape of the curves $N_R(t)$, $N_{R'}(t)$, $(N_R + N_{R'})(t)$ with the increase of k_i gradually acquires S-shape. The rate $dR/dt \neq 0$ (Fig. 2d–f, unsteady state conditions on (R + R′) almost to the end of the process remains) up to the moment when this curve comes to its limit at the end of the process (e.g., Fig. 2e, f). The number N_R steadily increases with k_i, but $N_{R'}$ with $k_i > k_p$ decreases (see Table 1). From these data, the question arises about the correctness of the kinetic parameters obtained in [3, etc.] in the processing of experimental kinetic curves on the principle of steady state of radicals for the case of the three-dimensional TFM polymerization.

For the first time in the world practice the above described kinetic results of the simulation by the MC method (model GSU-UTSE) of three-dimensional free radical TFM polymerization within the frame of the formation of UTSE were obtained. They allowed to significantly deepen the understanding of the mechanism of the process: at low rates the initiation of the chains of low molecular mass of UTSE is formed and UTSE are weakly cross-linked and strongly cyclized structures (it is known that in practice for preparing similar structures inhibitory method, for example, is used; an alternative method can be arbitrary, it follows from the results of this work, which suggests the lowering of the rate of initiation to the required

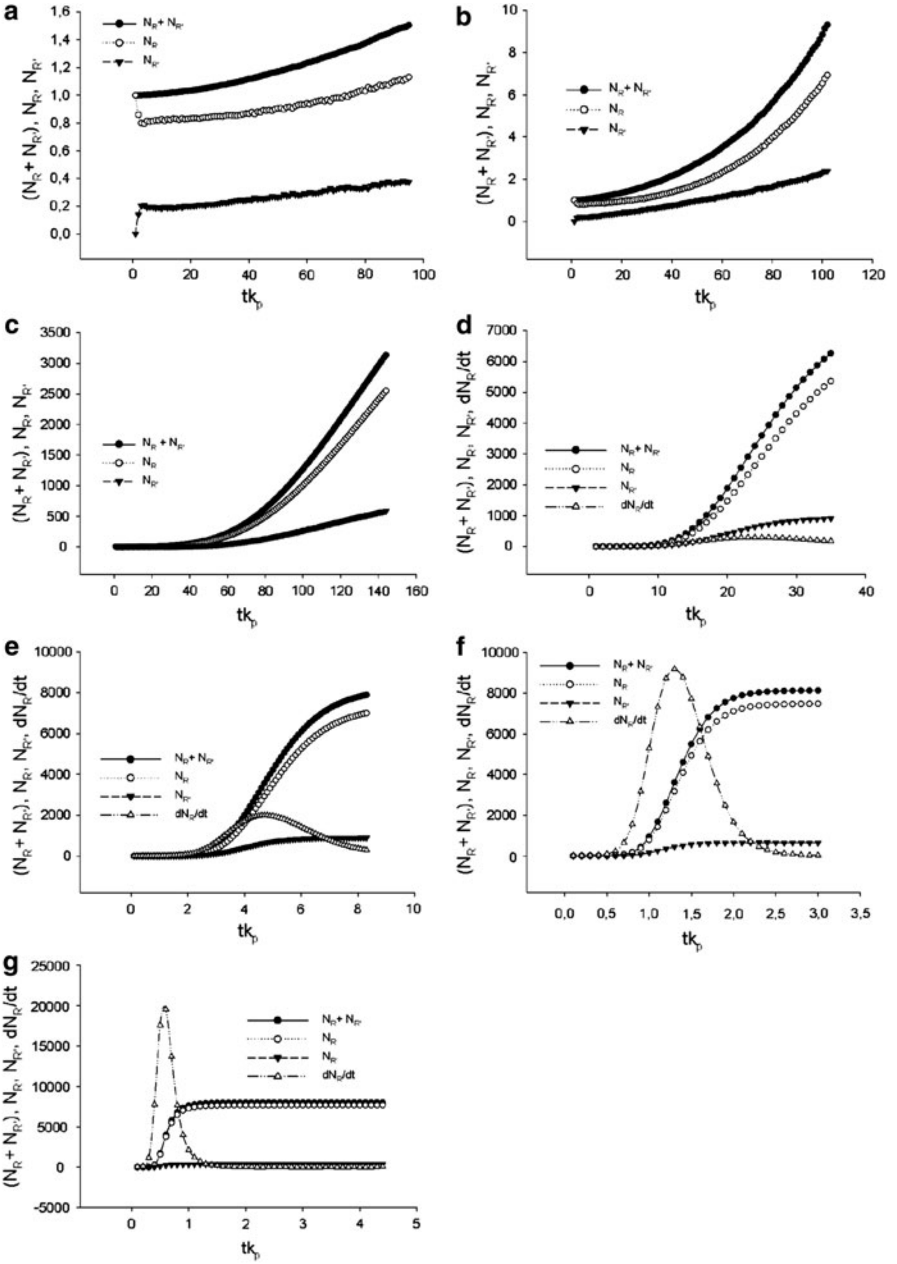

Fig. 2 Changing of the number of radicals N_R, $N_{R'}$, and the amount $(N_R + N_{R'})$, dN_R/dt (**d**–**g**) on the time when the ratio is $k_i/k_p = 0.0001$ (**a**), 0.001 (**b**), 0.01 (**c**), 0.1 (**d**), 1 (**e**), 10 (**f**), and 100 (**g**)

values); if there is a practical problem of obtaining more cross-linked structures, as it follows from the results of our study, it is necessary to increase the rate of initiation; for the first time the kinetics behavior of the radicals in the process of a three-dimensional TFM polymerization has been discovered and the unsteady state of the process on the radicals has been proven; the functions of UTSE have been looked upon as micro-reactors process; the immobilization in a matrix UTSE of the radicals has been demonstrated (as it is known, their prolonged existence in the glassy matrix of the three-dimensional polymer is proved by the EPR method); the transition of the process of TFM polymerization at certain stages of the conversion of TFM from purely stochastic in the deterministic regime has suggested.

Thus, during the three-dimensional TFM polymerization, first a reactive skeleton of branched macromolecules is formed from singly linked macrochains and it is framed by radicals, PG, cycles. After the formation of crosslinks between the chains, macrochains become *q*-fold connected and branched macromolecules pass into another state—a three-dimensional structural element UTSE. The UTSE skeleton includes a number of *i*-th macrochains with various degrees of polymerization, the number of crosslink N_{cr}, and bordered by the number of cycles N_{cy}, radicals N_{R} and $N_{\text{R}'}$, the number of pendant double bonds N_{PG}. The UTSE has a molecular mass distribution and it is a defective reactive structural formation (nanogel) which changes its characteristics depending on the rate of initiation.

When put into practice the results of our study allow:

(a) to choose the optimal regime of the TFM polymerization when an initiating system is being chosen (at low-rate regimes, at high-rate regimes, etc.);
(b) to be properly oriented during the synthesis of nanogels at the low-rate regime of the initiation of TFM polymerization;
(c) to vividly represent the peculiarities of the mechanism of the structure formation during the process of forming the macrobody of three-dimensional polymers;
(d) to give a chance to comprehend that where widely spread regimes and methods of TFM polymerization are used it is improper to account on the creation of highly durable polymers (i.e., tensile strength > 200–300 MPa), therefore, it is necessary to direct your efforts to create radically new principles, for example, the polymerization in the fields of force which orient TFM molecules.

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