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Radical Polymerization Initiated from a Solid Substrate. 1. Theoretical Background

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ABSTRACT: From a survey of the literature on grafting free radical polymerization from solid surfaces we suggest kinetic schemes for the process. The system of differential equations in partial derivatives including the diffusion equation based on the classical theory of free radical polymerization and the assumption that surface-bonded free radicals terminate by (1) reactions with bulk free radicals and (2) chain transfer to solvent or monomer are introduced. Computer simulations performed using the equations have shown good agreement with the characteristic features of the grafting process. The rate of grafting is linearly proportional to the surface concentration of the initiator and decreases as the initiation rate in the bulk increases. It follows from the concentration profiles of the bulk free radicals that free radical concentration in the vicinity of the surface can be several times larger than that in the bulk. The concentration profile depends on the distance between two surfaces. For distances less than a critical distance of about 2 μm, the concentration profile of the bulk free radicals is homogeneous.

1. Introduction

Radical polymerization initiated from a solid surface has been the subject of great interest for the past two decades as a method of solid substrate modification by a polymer for numerous applications, such as colloidal stabilization of ultra fine particles, control of wetting and adhesion, corrosion resistance, encapsulation, microelectronics, and so on, Tsubokawa,[1] Bouen et al.,[2] and Espiard and Guyot[3] (see, for example and references therein). Other common methods of preparation of ultrathin coverings, such as spin-coating (in the case of a flat surface) and polymer adsorption, are available. However, it is not clear whether the adsorption of a block copolymer or a functional-terminated polymer, grafting of previously prepared polymer onto the solid surface, or grafting from the solid surface is preferable for some of the above-mentioned applications. Obviously, the main reason for the uncertainty is the problem of investigating the morphology of ultrathin polymer coverings and their effect on the properties of a specific system. Recently the situation improved initially because of the availability of surface force measurement techniques and scanning probe microscopy which make the study of polymer layers on the nanometer scale possible. At the same time great success has been achieved in the field of polymer interface theory. The aim of the present and companion papers is to clarify the mechanism of free radical graft polymerization from solid substrates, the morphology of synthesized coverings, and consequently, the advantages and disadvantages of the grafting method.

Most published papers in this field concentrate on the attachment to the solid substrate of the reactive species which are responsible for the subsequent initiation of grafting polymerization. The discussion of the characteristics of the grafting process is restricted to the grafting amount versus time relationships. Only a few papers consider details of the kinetics of the process.[2−6] Detailed analysis of the mechanism of the grafting polymerization of adsorbed monomers from the gas phase was presented in the book by Bruk and Pavlov.[7] Although the most accessible grafting process is polymerization when the solid substrate is immersed in monomer solution, very few papers offer a detailed analysis of the mechanism of this process. In this paper, we present the mechanism of grafting using mathematical models. The companion papers deal with the experimental results and investigation of the morphology of the synthesized coverings.

Radical polymerization at the solid−liquid interface is classified as a heterogeneous chemical process that, in contrast to the polymerization in the bulk (solution), is caused by such phenomena as adsorption of reagents. Effects of the latter are pronounced and include (a) localization of the individual reactions and differences of the reagent concentrations from those in the bulk, (b) change of reactivity of the adsorbed reagents and macroradicals, (c) change in the kinetics of the reactions controlled by diffusion. In this paper, we do not consider any specific organization of reactive centers on the surface. We assume that adsorption sites and reactive centers are distributed statistically.

It is worth noting that after some specific time of grafting polymerization the grafting layer becomes completely occupied by polymer coils and the subsequent grafting of new chains requires stretching of the coils. This process continues until the maximum possible

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surface grafting is reached. If there is still initiator on the solid substrate, it produces new free radicals. One may assume two possible ways of a subsequent evolution of the process: (1) the chain transfer reaction to the bulk ingredients and (2) the force out regime, when new chains are forced out into the bulk. For both cases grafting can either stop or yield a multilayer covering.[8,9] Consequently, the kinetics of grafting in the saturated grafted-layer regime is more complicated and the process should be divided into two steps: (1) grafting when the chains grow in the diluted grafting layer and (2) grafting in the brush layer. Below, we refer to these regimes as regime 1 and regime 2, respectively.

The objective of this paper is to summarize the data about the free radical polymerization initiated from the solid surface obtained for different systems and provide understanding of the process in terms of simple mathematical models.

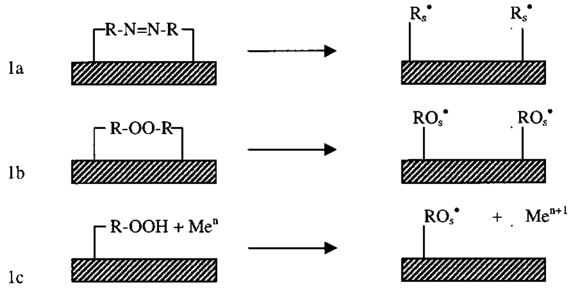
2. Brief Review of the Literature Data

A common picture of the grafting polymerization on the solid surface emerges from the literature. Its features are the following: (a) At a relatively short time after the start of the process, the grafting amount approaches a plateau value;[8,10] however, especially for methacrylates, the acceleration of grafting (like the Trommsdorff effect) has been observed.[2,6,8,9,11] (b) A pronounced dependence on monomer concentration occurs.[2,4−6] (the grafting rate order in monomer concentration is very often larger than 1). (c) A low efficiency (0.01−0.45) of the initiation reaction is noted.[4,5,12] (d) The polymerization rate order on the initiator concentration is 0.5−1 (often it is higher than 0.5).[5−7,11,13,14] (e) Very often, the grafted polymer layer is composed of partially cross-linked polymer.[9] (f) Both a decrease and an increase of the grafting amount with an increase of the molecular weight of the grafted chains has been observed.[2,15] (g) Free radicals can react with a solid substrate, and in some cases, this causes the inhibition effect.[16] For the most part, the above features represent the differences between the grafting process and ordinary free radical polymerization.

2.1. Individual Steps. *2.1.1. Initiation.* The characteristic features of the kinetics of the initiation from the solid surface are not discussed in this paper. We note, however, that this question has been discussed intensively and should be the subject of a separate consideration from the viewpoint of a reactivity in the adsorbed layer.[2,4−6] It is also worth noting that in regime 2 at very high grafted density we may assume a decrease of the efficiency of the initiation reaction, because of the high local viscosity.

In this work, it is important to distinguish between free radicals provided by the initiator which are attached and those which are nonattached to the solid surface. Considering all possible initiation mechanisms, we extract the most important variants (see Schemes 1−3): (1) An initiator (I_s) produces the surface-bonded free radicals (R_s*) attached to the solid substrate, e.g., symmetric peroxide or azo-initiators bonded with the substrate by two sites or red-ox initiation (Scheme 1a−c); (2) an initiator produces two sorts of free radicals, one which is surface-bonded (R_s*) and one which is able to diffuse into the bulk (R_v*), e.g., peroxide or azo initiators bonded with the substrate by one site (Scheme 2a,b); (3) there are two initiators in the reaction mixture, one produces two sorts of free radicals as in case 2 above. The second, denoted I_v, is dissolved in the bulk and produces R_v* free radicals. It is necessary to note why we consider the second initiator in the bulk. The amount of the attached initiator is very small. Consequently, even a small amount of oxygen in the system can affect the polymerization. The same can be said about the other impurities in solution. These impurities can accelerate (peroxides) or inhibit (oxygen and other inhibitors) the polymerization with a very small amount of an initiator in the reaction vessel. Consequently, addition of the second initiator is necessary to stabilize the polymerization process and obtain reproducible data. Only in the case of concentrated suspension of ultrafine particles with the initiator introduced onto the surface is the total amount of the initiator enough to avoid the effects of impurities. On the other hand, at temperatures as high as 373 K, the thermal self-initiated polymerization of styrene has a large influence

Scheme 1. Kinetic Scheme for the Grafting Free Radical Polymerization Initiated from the Solid Substrate for the Case of Azo (1a), Peroxide (1b), and Hydroperoxide + Metal Salt (1c) Initiators Which Yield Only Attached Free Radicals



$I_s \xrightarrow{k_d^s} R_s^*$ initiation $\frac{d[R_s^*]}{dt} = k_d^s[I_o^s]\exp(-k_d^s t) - k_t[R_v^*][R_s^*] - k_x[R_s^*][X]$

$R_s^* + nM \xrightarrow{k_p} R_s^*$ propagation $\frac{\partial[R_v^*]}{\partial t} = D\frac{\partial^2[R_v^*]}{\partial x^2} - k_t[R_v^{*2}]$

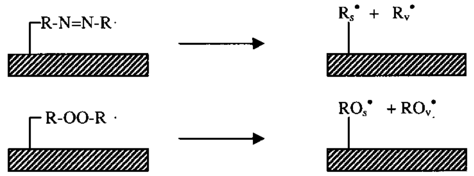
$R_v^* + nM \xrightarrow{k_p} R_v^*$ $-D\frac{d[R_v^*]}{dx} = -k_t[R_v^*][R_s^*] + k_x[R_s^*][X]$

$R_s^* + X \xrightarrow{k_x} R_v^*$ transfer

$R_s^* + R_v^* \xrightarrow{k_t} P_s$ termination

$R_v^* + R_v^* \xrightarrow{k_t} P_v$

Scheme 2. Kinetic Scheme for the Grafting Free Radical Polymerization Initiated from the Solid Substrate for the Case of Azo and Peroxide Initiators Which Yield Attached and Nonattached Free Radicals



$I_s \xrightarrow{k_d^s} R_s^* + R_v^*$ initiation $\frac{d[R_s^*]}{dt} = k_d^s[I_o^s]\exp(-k_d^s t) - k_t[R_v^*][R_s^*] - k_x[R_s^*][X]$

$R_s^* + nM \xrightarrow{k_p} R_s^*$ propagation $\frac{\partial[R_v^*]}{\partial t} = D\frac{\partial^2[R_v^*]}{\partial x^2} - k_t[R_v^{*2}]$

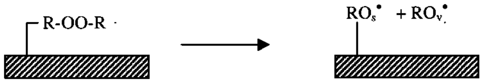
$R_v^* + nM \xrightarrow{k_p} R_v^*$ $-D\frac{d[R_v^*]}{dx} = k_d^s[I_o^s]\exp(-k_d^s t) - k_t[R_v^*][R_s^*] + k_x[R_s^*][X]$

$R_s^* + X \xrightarrow{k_x} R_v^*$ transfer

$R_s^* + R_v^* \xrightarrow{k_t} P_s$ termination

$R_v^* + R_v^* \xrightarrow{k_t} P_v$

Scheme 3. Kinetic Scheme for the Grafting Free Radical Polymerization Initiated from the Solid Substrate for the Case of Initiators Attached to the Substrate and Additional Initiator in the Bulk



$$\text{R-OO-R} \longrightarrow 2\ RO_v^{\bullet}$$

$$I_s \xrightarrow{k_d^s} R_s^* + R_v^* \quad \text{initiation} \quad \frac{d[R_s^*]}{dt} = k_d^s[I_o^s]\exp(-k_d^s t) - k_t[R_v^*][R_s^*] - k_x[R_s^*][X]$$

$$I_v \xrightarrow{k_d^v} R_v^*$$

$$R_s^* + nM \xrightarrow{k_p} R_s^* \quad \text{propagation} \quad \frac{\partial[R_v^*]}{\partial t} = D\frac{\partial^2[R_v^*]}{\partial x^2} - k_t[R_v^{*2}] + k_d^v[I_o^v]\exp(-k_d^v t)$$

$$R_v^* + nM \xrightarrow{k_p} R_v^* \qquad -D\frac{d[R_v^*]}{dx} = k_d^s[I_o^s]\exp(-k_d^s t) - k_t[R_v^*][R_s^*] + k_x[R_s^*][X]$$

$$R_s^* + X \xrightarrow{k_x} R_v^* \quad \text{transfer}$$

$$R_s^* + R_v^* \xrightarrow{k_t} P_s \quad \text{termination}$$

$$R_v^* + R_v^* \xrightarrow{k_t} P_v$$

on polymerization in the bulk. In this case, we cannot avoid the "additional initiation" in the reaction mixture.

2.1.2. Propagation. In the adsorbed monomer layer, the rate constant (k_p) of the chain propagation reaction strongly depends on the degree of occupancy of the surface with the adsorbed monomer[7,17] (Θ). On the surface, k_p is much lower than it is in the bulk and increases as Θ increases. Incorporation within the vinyl acetate adsorbed layer of solvent (ethyl acetate), which competes in adsorption with the monomer, results in a 4 times increase of k_p.[18] A sharp increase of k_p at $\Theta = 0.5$ has been observed, which coincides with the sharp change of the heat of adsorption. Evaluations of the effect of monomer diffusion for methyl methacrylate and vinyl acetate adsorbed on silica show that the propagation reaction is not limited by diffusion in the case of a nonspecific monomer−substrate interaction. Therefore, the adsorption of the monomer affects its reactivity, and this effect depends on the degree of occupancy of the surface, which in turn is explained by heterogeneity of the surface and lateral interactions. Obviously, we may presume that in the case of polymerization at the solid−liquid interface if the monomer is present in excess, the nonadsorbed monomer molecules preferably participate in the chain growth and the propagation rate constant is close to the magnitude in the bulk. This assumption allows us to use ordinary k_p magnitudes for vinyl monomers and is valid for the polymerization of the monomers that have no strong specific interaction with the substrate. If this were not the case, the chain propagation will be limited by a decrease in reactivity of the adsorbed macroradical. The above-mentioned data refer to regime 1. The situation becomes more complicated in the case of the regime 2. The chain growth can be confined when the energy of the stretched polymer chain is higher than the energy of the covalent bond or the monomer concentration is decreased at high density of grafting ("dry" brush regime). We may evaluate the above-mentioned effects using scaling equations for the polymer brush:[19]

$$F/kT \cong N\sigma^{2/3}$$

$$h \cong aN\sigma^{1/3}$$

where F is the free energy per grafted chain, h is the height of the brush, N is the degree of polymerization, and σ is the dimensionless grafting density $\sigma = na^2/S = a^2/L_s^2$ (where n is the number of chains per surface S, a is the size of the monomer, and L_s is the interchain distance on the surface). Consequently, a chain in the brush can grow if $E > F$, where E is the energy of the bond between monomer units in the chain or the chain-substrate bond. For a very weak bond between an anchor group and a substrate with an energy of $E = 10kT$, $N = 1000$, $a = 0.6$ nm we obtain $\sigma/a^2 < 0.0027$ nm^{-2} or $L_s = 19$ nm, which corresponds to about 0.45 mg/m^2 of grafted polymer. If E is larger, for instance, for a hydrogen ($E = 100kT$) or chemical bond ($E = 700 \div 1000kT$), we obtain the substantially denser brush in which the interchain distance is close to the value of a and the grafting amount is about 15 and 250−400 mg/m^2, respectively. The fraction of monomer or solvent (φ_m) in a brush may be evaluated as follows. Let us consider the area occupied by the brush like polymer layer of the size x^2 and height of the brush h. The volume of the layer will be x^2h. The volume occupied by segments will be $(\sigma/a^2)x^2N\pi a^3/6$. Consequently, the fraction of brush like layer available for monomer or solvent is

$$\varphi_m \approx 1 - \frac{Nx^2\sigma\pi a^3}{6x^2a^2h} \approx 1 - \frac{\sigma^{2/3}}{2}$$

For the same parameters and the $\sigma/a^2 = 1$ nm^{-2}, we obtain $\varphi_m = 0.75$. Consequently, quantitative evaluation suggests that the neither factor restricts the chain growth up to a very dense brush.

It is known from the published data[2,7−10,20] that in most cases the grafted amount reaches a plateau value which is on the order of the polymer adsorption value (1−2 mg/m^2). However, in some cases, it was found that the grafting amount could be on the order of 50−100 mg/m^2. The latter data were obtained at high monomer concentrations and initiation rates. It was assumed that the Trommsdorff effect caused the high grafted amount of the polymer and that the covering had a multilayer structure.[2,9,14] Consequently, the monolayer obtained in the graft polymerization in most cases is of approximately the same density as that obtained with polymer adsorption or grafting of end-functionalized polymers to the surface. This unexpected behavior may be explained by such possible effects as the following. (1) When a chain grows in the brush layer, the attachment of a new monomer costs an increase of the chain free energy and requires stretching of the growing and all neighbor chains of the brush. Such reconformation should be correlated in time with the monomer attachment, which means an increase in the activation entropy of the propagation reaction and decrease of the k_p value. Obviously, in this case, the value of the rate constant of the chain transfer reaction to monomer, solvent, and polymer should not be changed. (2) The grafted layer is swollen by ungrafted polymer, which is synthesized in the layer from the bulk free radicals. The growth of the nonattached chain in the brush layer costs less stretching energy. Besides, the free chain can occupy an edge part of the brush, which is less busy (the brush has a parabolic concentration profile[19]). It was shown that the constant of the propagation reaction in a swollen polymer net is the same as in solution when the constant of the termination decreases substantially.[21] (3) The Trommsdorff effect in the grafted layer speeds up the polymerization inside the layer. The following development of the process depends on the ratio between the rates of chain diffusion and chain propagation.[9] If the diffusion into the bulk is slower than the polymerization in the layer, the grafting layer becomes a "reactor", which produces polymer, at a high rate and forces them outside the grafted layer. (4) The bond between surface sites and initiator is not always well-defined. The same can be said of the surface concentration of the initiator. We may assume that because of the surface impurities the energy of the bond and surface concentration of the initiator could be overestimated. Recently, it was reported by Prucker and Rühe[6] that at a high density of the chemisorbed initiator and in a well-purified reaction mixture one can approach a high grafting density.

2.1.3. Termination. The reaction of the chain termination may proceed according to three possible mechanisms:[6,9] first, by interaction between two surface-bonded macroradicals upon their migration on the surface (in the case of a physisorbed initiator); second, by "growing through" two surface-bonded free radicals toward each other by a type of "reactive diffusion";[7] third, by chain transfer to monomer, solvent or reactive sites on the substrate, followed by the formation of macroradicals in the bulk and the following "cross" interaction between the surface-bonded macroradicals and the macroradicals in the bulk. Comparative analysis elsewhere[6] suggests that the termination rate constant between two adsorbed macroradicals diffusing along the surface is larger than in the reactive diffusion. Very soon after the start of grafting, the layer becomes occupied by polymer, which slows the surface diffusion. The reactive diffusion is also unlikely, unless the initiation rate is extremely high. Consequently, we assume that the third mechanism is the most likely termination reaction. This assumption is based on experimental data which give a high reaction order in the surface initiator concentration. Surface free radical termination with the bulk free radicals is equivalent to linear termination (the polymerization rate is directly proportional to the initiator concentration).

3. Mathematical Models

We consider regime 1 in this paper. We assumed that termination of the surface-bonded chains proceeds mostly by the reaction with the free radicals from the bulk and the chain transfer to monomer or solvent (*X*). According to this assumption and the above-mentioned mechanisms of the initiation reaction (Schemes 1−3), we suggest three variants of the polymerization schemes for the development of the mathematical models. The relative systems of differential equations in partial derivatives are presented alongside the schemes.

In the case represented by the Scheme 3 (the most general case), the concentration of the surface free radicals (R_s*) is described by the following equation for the local balance for R_s*.

$$\frac{d[R_s^*]}{dt} = k_d^{\,s}[I_0^{\,s}]\exp(-k_d^{\,s}t) - k_t[R_v^*][R_s^*] - k_x[R_s^*][X] \quad (1)$$

where k_d^s is the rate constant of the decomposition reaction of the initiator on the surface, k_x is the rate constant of the transfer reaction, k_t is the rate constant of the termination reaction, $[I_0^s]$ is the initial concentration of the initiator on the surface. Here, the first term on the right-hand side corresponds to the rate of the initiation on the surface, the second corresponds to the termination reaction of the surface free radicals with the bulk free radicals, and the third corresponds to the chain transfer reaction from the surface free radicals to a bulk component *X*. We suppose for simplicity that the distribution of the volume free radicals R_v* obeys the diffusion as follows:

$$\frac{\partial[R_v^*]}{\partial t} = D\frac{\partial^2[R_v^*]}{\partial x^2} - k_t[R_v^{*2}] + k_d^{\,v}[I_0^{\,v}]\exp(-k_d^{\,v}t) \quad (2)$$

where k_d^v is the rate constant of the decomposition reaction of the initiator in the bulk, $[I_0^v]$ is the initial concentration of the initiator in the bulk, and *D* is the diffusion coefficient of the bulk free radicals. In this equation, the second term on the right-hand side corresponds to the recombination reaction between two free radicals in the bulk. Because of the termination and chain transfer on the surface, we accept the following boundary condition at $x = 0$:

$$-D\frac{d[R_v^*]}{dx} = k_d^{\,s}[I_0^{\,s}]\exp(-k_d^{\,s}t) - k_t[R_v^*][R_s^*] + k_x[R_s^*][X] \quad (3)$$

We set the average length between two surfaces to 2Λ. In this case we consider the distribution of the bulk free radicals in the space *x* from $x = 0$ to $x = \Lambda$ with the boundary condition,

$$\left.\frac{d[R_v^*]}{dx}\right|_{x=\Lambda} = 0 \quad (4)$$

This follows from the fact that the concentration distribution is symmetrical with respect to the point $x = \Lambda$.

For the calculation, eqs 1−4 were transformed into dimensionless forms.

$$\frac{dS}{d\tau} = \alpha\exp(-\alpha\tau) - RS - \mu S \quad (5)$$

$$\frac{\partial R}{\partial \tau} = \frac{\partial^2 R}{\partial \zeta^2} - R^2 + qI\exp(-q\tau) \quad (6)$$

with the boundary condition at $x = 0$ as

$$-\frac{d}{d\zeta}R = \delta[\alpha\exp(-\alpha\tau) - RS + \mu S] \quad (7)$$

and the boundary condition at $x = \Lambda$:

$$\left.\frac{dR}{dx}\right|_{x=\Lambda} = 0 \quad (8)$$

using the following relationships:

$$R = [R_v^*]/R_0,\quad L^2 = D/(R_0k_t),\quad \zeta = x/L,\quad \tau = tk_tR_0,\quad S = [R_s^*]/[I_0^{\,s}],\quad \alpha = k_d^{\,s}/(k_tR_0),\quad \mu = k_x[X]/(k_tR_0),\quad \delta = k_t[I_0^{\,s}]L/D,\quad q = k_d^{\,v}/(k_tR_0),\quad I = [I_0^{\,v}]/R_0,\quad l = \Lambda/L$$

where R_0 is a normalization constant (the initial con-

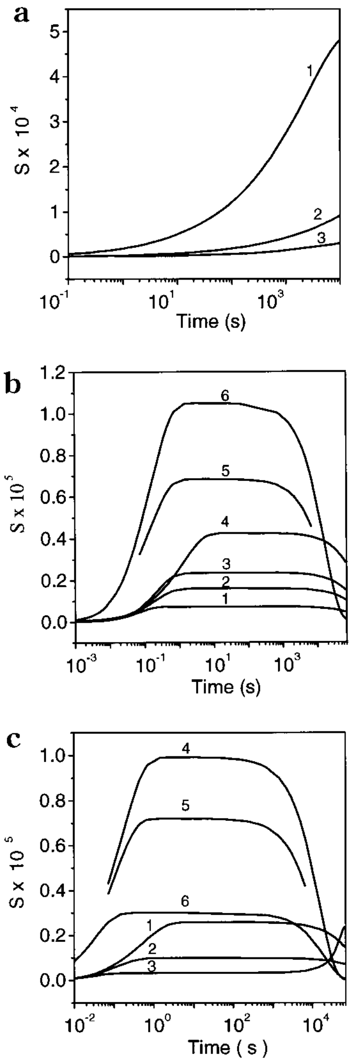


Figure 1. (a) Current concentration of the surface free radicals (S) for the model of Scheme 1. For $D = 10^{-11}$ m^2 s^{-1}, $[I_0^s] = 10^{-4}$ mol m^{-2}, $k_x[X] = 0$ s^{-1}, and k_d^s = (curve 1) 10^{-4}, (curve 2) 10^{-5}, and (curve 3) 10^{-6} s^{-1}. (b) Current concentration of the surface free radicals (S) for the model of Scheme 2. For $k_d^s = 10^{-5}$ s^{-1}, $D = 10^{-11}$ m^2 s^{-1}, and $I_0^s = 10^{-4}$ mol m^{-2}, $k_x[X]$ (curve 1) 5, (curve 2) 1, and (curve 4) 0.1 s^{-1}. For $k_d^s = 10^{-4}$ s^{-1}, $I_0^s = 10^{-4}$ mol m^{-2}, $k_x[X] = 1$ s^{-1}, D = (curve 6) 10^{-10} and (curve 5) 10^{-11} m^2 s^{-1}. For $k_d^s = 10^{-6}$ s^{-1}, $D = 10^{-11}$ m^2 s^{-1}, and $I_0^s = 10^{-4}$ mol m^{-2}, $k_x[X]$ = (curve 3) 1 s^{-1}. (c) Current concentration of the surface free radicals (S) for the model of Scheme 3. For $k_d^s = 10^{-5}$ s^{-1}, $D = 10^{-11}$ m^2 s^{-1}, $[I_0^s] = 10^{-4}$ mol m^{-2}, and $[I_0^v] = 0.1$ mol L^{-1}, k_d^v = (curve 1) 10^{-6}, (curve 2) 10^{-5}, and (curve 3) 10^{-4} s^{-1}. For $k_d^s = 10^{-4}$ s^{-1}, $D = 10^{-10}$ m^2 s^{-1}, $[I_0^s] = 10^{-4}$ mol m^{-2}, $[I_0^v] = 0.1$ mol L^{-1}, k_d^v = (curve 4) 10^{-6}, (curve 5) 10^{-5}, (curve 6) 10^{-4} s^{-1}.

centration of free radicals in the bulk; we used in our calculation the typical value 10^{-8} mol/L).

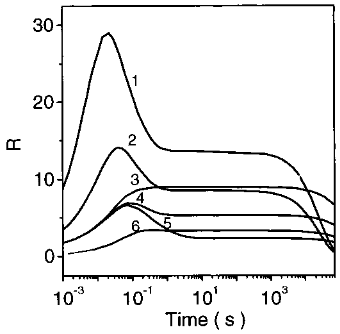


Figure 2. Current concentration of the bulk free radicals (R) for the model of Scheme 2. For $k_d^s = 10^{-5}$ s^{-1}, $D = 10^{-11}$ m^2 s^{-1}, and $[I_0^s] = 10^{-4}$ mol m^{-2}, $k_x[X]$ (curve 5) 0.1, (curve 4) 1, (curve 3) 5 s^{-1}. For $k_d^s = 10^{-4}$ s^{-1}, $[I_0^s] = 10^{-4}$ mol m^{-2}, $k_x[X] = 1$ s^{-1}, D = (curve 1) 10^{-10}, (curve 2) 10^{-11}, (curve 6) 10^{-12} m^2 s^{-1}.

In the models, we use the commonly accepted assumption for the initial stage of the free radical polymerization: reactivity of free radicals is independent of chain length. We also assume that reactivity of the surface-bonded propagating free radical and free radical in the bulk is the same. We assume that only bulk free radicals can diffuse. In calculations, we use an average coefficient of diffusion which is assumed to be the same for the free bulk radicals of different sizes. These models do not consider any steric restrictions for the growth of the surface-bonded chains and consequently are valid for the grafting process when the monolayer of grafted chains is not saturated. In the equations for Schemes 1 and 2 we removed additional terms responsible for the R_v* free radicals and I_v, respectively.

4. Results and Discussion

The systems of the differential equations rearranged into the dimensionless form were solved numerically. The current concentrations of surface-bonded free radicals and free radicals in the bulk expressed by the S and R dimensionless parameters typical for the different models are shown in Figures 1 and 2. The polymerization is accompanied by a steady-state period for all of the models. The exception is Scheme 1 at $k_x[X] = 0$ (Figure 1a). The concentration of R_s* free radicals decreases in all cases as the rate of chain transfer increases (compare curves 1, 2, and 4 in Figure 1b). For Scheme 2 (no additional initiation in the bulk), the increase in the diffusivity of bulk free radicals causes an increase in the concentration of R_s* free radicals (compare curves 5 and 6 in Figure 1b). As the rate of the additional initiation in the bulk increases (Scheme 3), the concentration of R_s* free radicals decreases (compare curves 1–3 and 4–6 in Figure 1c).

The concentration of the bulk free radicals R_v* increases as the chain transfer component increases (Figure 2, curves 3–5). Larger diffusivity of the bulk free radicals causes a decrease of their concentration as in the case of the surface free radicals (Figure 2, curves 1, 2, and 6).

The concentration profiles of the free radicals in the bulk are shown in Figure 3a,b. The calculated profiles show the sharp decrease of the free radical concentration as the distance to the wall increases (in some cases, a 5 times decrease is observed). For Scheme 3 (Figure 3b), the profile becomes smoother. With a large additional amount of initiator in the bulk, only small changes of the bulk free radical concentration as a function of the distance from the surface are observed (Figure 3b, curve 1). The profile depends on the value of the l parameter, which expresses the distance between two surfaces (Figure 4). At $l = 0.1$ the bulk concentration of free radicals becomes independent of distance from the surface (curve 3). Therefore, in this region, the free radical polymerization can be considered as a quasihomogeneous process with respect to the polymerization in the bulk. This regime is interesting for the experimental investigation of the kinetics because one can use macroscopic kinetic measurements to study the kinetics of the bulk polymerization caused by the polymerization from the surface using the simple

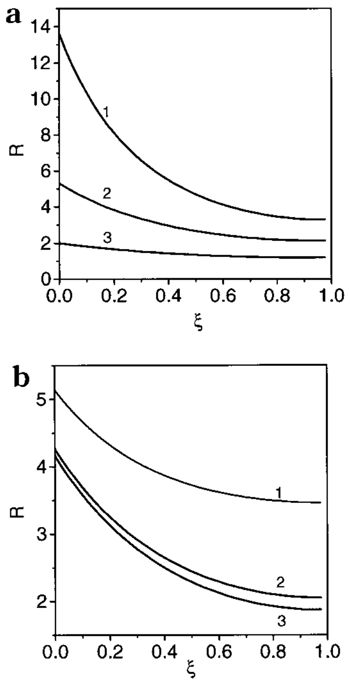


Figure 3. (a) Concentration profile of the bulk free radicals (R) for the model of Scheme 2. For $t = 10$ s from the start of the process, $D = 10^{-11}$ m^2 s^{-1}, $k_x[\mathrm{X}] = 1$ s^{-1}, and $k_d{}^s$ = (curve 1) 10^{-4}, (curve 2) 10^{-5}, and (curve 3) 10^{-6} s^{-1}. (b) Concentration profile of the bulk free radicals (R) for the model of Scheme 3. For $t = 10$ s, $D = 10^{-11}$ m^2 s^{-1}, $[I_0{}^s] = 0.000\,1$ mol m^{-2}, $k_x[\mathrm{X}] = 0.5$ s^{-1}, $[I_0{}^v] = 0.001$ mol L^{-1}, and $k_d{}^v$ = (curve 1) 10^{-4}, (curve 2) 10^{-5}, and (curve 3) 10^{-6} s^{-1}.

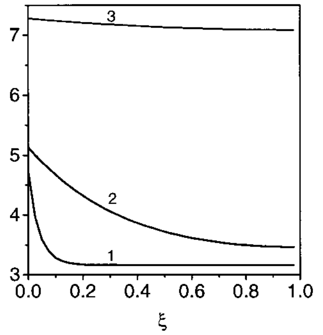


Figure 4. Concentration profile of the bulk free radicals (R) for the model of Scheme 3. For $t = 10$ s, $D = 10^{-11}$ m^2 s^{-1}, $[I_0{}^v] = 0.000\,1$ mol L^{-1}, $k_x[\mathrm{X}] = 0.5$ s^{-1}, and $[I_0{}^v] = 0.001$ mol L^{-1}, $k_d{}^v = 10^{-4}$ s^{-1} for the different distances between surfaces l = (curve 1) 10, (curve 2) 1, and (curve 3) 0.1.

model without a diffusion component. One can evaluate the distance between two surfaces for the condition $l < 0.1$ as

$$2\Lambda \le 2/L = 2l\sqrt{D(R_0k_t)^{-1}} = 2 \times 0.1\sqrt{10^{-10}\,(10^{-8} \times 10^{8})^{-1}} = 0.2 \times 10^{-5}\ \mathrm{m\ or\ } 2\Lambda \le 2\ \mu\mathrm{m}$$

To investigate the kinetics of polymerization from the solid surface, one can use two limiting cases: (1) the surface/volume ratio is very small and the grafting process has no effect on the polymerization in the bulk, e.g., polymerization on the plate embedded in a monomer solution, and (2) a very high surface/volume ratio when the distance between two surfaces is lower as 2 μm; e.g., it is possible to reach this condition in suspensions of ultrafine particles. These two cases have been studied experimentally and will be reported in future papers. Here, we perform computer experiments to study the influence of the initiation rate in the bulk and from the surface on the grafting polymerization process. The polymerization rate on the surface can be presented as $W_s = k_p[R_s{}^*][\mathrm{M}]$. Consequently, we may use the S value as a measure of the W_s. The polymerization rate in the bulk is

$$W_v = \frac{k_p}{\Lambda}\int_{x=0}^{x=\Lambda} [R_v{}^*][\mathrm{M}]\,\mathrm{d}x$$

Therefore, we use in our computations the value

$$R_{\mathrm{int}} = \frac{1}{l}\int_{x=0}^{x=l} R\,\mathrm{d}x$$

as a measure of the polymerization in the bulk.

The results of the calculations are presented in Figures 5 and 6. The effect of the initiation from the surface on both polymerization on the surface and in the bulk is very pronounced at $l = 0.1$ (curves 1 and 2 in Figure 5). At high initiation rates, the rate of the polymerization from the surface increases linearly with the initiation rate on the surface for both l depicted in the figures. Polymerization in the bulk is affected by the initiation from the surface only at $l = 0.1$. An increase of the initiation in the bulk causes a decrease of the polymerization from the surface. It is clear that this phenomenon is observed for both l values (Figure 6). This effect is explained by an increase of the

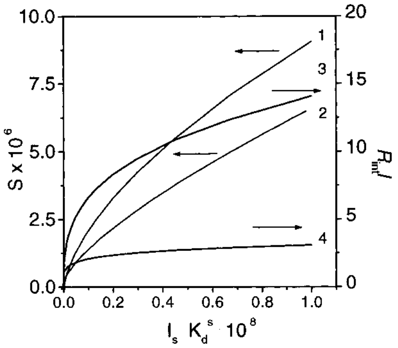


Figure 5. Dependence of the normalized surface and bulk polymerization rates from the initiation rate from the surface for the model of Scheme 3. For $k_d{}^s = 10^{-5}$ s^{-1}, $D = 10^{-11}$ m^2 s^{-1}, $t = 10$ s, $[I_0{}^v] = 0.001$ mol L^{-1}, and $k_x[\mathrm{X}] = 0.5$ s^{-1}, l = (curves 1 and 3) 1 and (curves 2 and 4) 0.1.

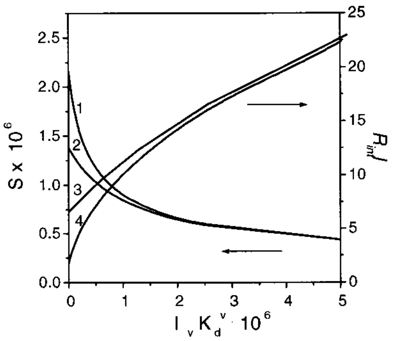


Figure 6. Dependence of the normalized surface and bulk polymerization rates from the initiation rate in the bulk for the model of Scheme 3. For $[I_0{}^s] = 0.000\,1$ mol m^{-2}, l = (curves 1 and 3) 1 and (curves 2 and 4) 0.1. Other parameters are the same as those for the data of Figure 5.

termination reaction rate of the surface-bonded free radicals. The same conclusion for the termination reaction of the surface free radicals was made on the basis of the inverse effect, observed in the real experiment.[22] When particles with inhibiting properties were added to the reaction mixture, an increase of the grafting rate was observed, because the addition of the inhibitor decreased the bulk free radical concentration. In this case, the inhibitor was on the surface of the solid particles and was not able to react with the surface-bonded free radicals on the surface of another particle.

The above-mentioned results explain characteristic features of the polymerization, including the order of the polymerization rate as a function of the surface initiator concentration. This order can approach the value of 1 because the surface-bonded free radicals terminate mainly by reaction with the bulk free radicals or by means of the chain transfer reaction. The concentration profile of the bulk free radicals shows that the free radical concentration near the surface can be very high. The latter could be the reason for the experimentally observed Trommsdorff effect and cross-linking of the grafted polymer. These data also show an interesting way to control the molecular weight of the grafted polymer by changing the initiation rate in the bulk using additional initiator.

5. Conclusions

We propose several kinetic schemes of the free radical polymerization initiated from the solid−liquid interface. We suggest that the termination reaction for the surface-bonded free radicals is possible only by means of reaction with the bulk free radicals or the chain transfer reaction to solvent or monomer. The kinetic models allow one to couple the system of differential equations in partial derivatives with the diffusion equation. The computer simulations based on the numerical solution of the kinetic equations show a good agreement with the characteristic features of the grafting polymerization usually observed in experiments. The conditions for and duration of the steady-state regime of the polymerization, the bulk free radicals concentration profile, and the polymerization rate orders in the surface-bonded initiator and the initiator in the bulk at different parameters of the process were obtained.

The concentration profile of the bulk free radicals shows a sharp decrease of free radical concentration as distance to the surface increases. At a very close distance between two surfaces (less than 2 μm), the regime with homogeneous distribution of the free radicals in the bulk was found. The rate of grafting linearly increases as the surface initiator concentration increases and decreases as the concentration of an additional initiator in the bulk increases.

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