Radical Polymerization Initiated from a Solid Substrate. 2. Study of the Grafting Layer Growth on the Silica Surface by in situ Ellipsometry

Sergiy Minko,*,†,‡,§ Alexander Sidorenko,§,|| Manfred Stamm,*,|| Galina Gafijchuk,|| Volodimir Senkovsky,|| and Stanislav Voronov⊥

Abteilung Experimentelle Physik, Universität Ulm, Albert Einstein Allee 11, D-89069 Ulm, Germany; Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D-55021 Mainz, Germany; Lviv Department of Physical Chemistry Institute, National Academy of Sciences, 3a Naukova, Lviv 290053, Ukraine; and Department of Organic Chemistry, Lviv Polytechnic State University, 12 S. Bandera, Lviv 290646, Ukraine

Received August 27, 1998; Revised Manuscript Received April 15, 1999

ABSTRACT: Kinetics of the grafting free radical polymerization of styrene from the surface of Si wafers with a top silica layer was studied by in situ ellipsometric measurements of the grafted amount (*A*). Wafers uncovered and covered by physisorbed azo- or peroxide macroinitiator or covalently bonded with the substrate azo-initiator were used. Additional initiator of the same chemical nature was added to the bath solution (bulk). It was found that the grafted amount approaches a plateau value depending on the rate of grafting polymerization. At low rates, the plateau *A* values are on the order of 1−2 mg/m^2, whereas at high rates, they are typically 10−15 mg/m^2. Two kinetic regimes were studied where (1) the surface-attached chains terminate by chain transfer to the bulk or (2) the grafted chains terminate with the bulk free radicals. The rate of polymerization for the both regimes is linearly proportional to the surface density of the initiator. Within regime 2, the rate of polymerization has inverse square root dependence on the concentration of the initiator in the bulk. Two models were applied to explain the kinetics, which provide good agreement with the experimental data.

1. Introduction

A simple evaluation on the basis of scaling theory[1] shows that there is not a principal restriction to obtain a highly dense polymer brush using grafting from the surface by the free radical polymerization mechanism.[2] In few publications, it has been shown that the possibility of reaching a high value of a grafted amount of the polymer on solid substrate exists.[3−8] The amount of grafted polystyrene on the surface reported by different authors reaches values of 15−100 mg/m^2. However, there are numerous papers[9,10] reporting that the grafting amount obtained by different methods of grafting was only about 1−5 mg/m^2 (the same initiators and monomers have been used). Two possible regimes could be responsible for these data: (1) a highly loaded substrate can be coated by a monomolecular layer of tightly stretched polymer brush at a high surface density of an initiator attached to the substrate and a very pure reaction mixture with respect to an inhibitor[6,8] or (2) the thick coatings are composed of several polymer layers.[7,11] The last regime may exist because of the following effects. (a) The Trommsdorff effect, usually observed at a grafting process, is followed by formation of partially cross-linked chains. (b) There is a difference in the rates of polymerization inside the grafting layer and of polymer diffusion from the layer into bulk when the layer grows in a “force out” regime. Ungrafted polymer chains, formed from the unattached free radicals propagating in the grafted layer, are forced out to the edge of the polymer brush, but still are retained by the layer because of very slow diffusion. In this regime, the coating propagates by the mechanism of a running front like the growth of a piece of polymer embedded in a solution of monomer.[12]

The above-mentioned problems explain the interest in the kinetics of the grafting layer formation. In this paper, we present experiments to resolve the mechanism of formation of the polystyrene (PS)-grafted layer on the surface of Si wafers. Si wafers with a top silica layer were covered by a polyperoxide macroinitiator or azo-initiator which was physisorbed or covalently attached to the substrate. The kinetics was studied by ellipsometry, which allows the measurement of the grafted layer thickness on the surface of Si wafers embedded in the reaction bath. We have chosen a relatively “soft” condition of the grafting process to avoid the Trommsdorff effect as much as it was possible. On the other hand, we have organized the grafting process to ensure two possible regimes of the surface attached free radical termination: (1) by reaction with the bulk free radicals (free radicals in the volume/solution above the substrate) and (2) by transfer to solvent or monomer. Taking into account the specific nature of the radical polymerization (high sensitivity to traces of oxygen and substances inhibiting chain propagation), we used additional initiator in the bulk because of the very small surface/volume ratio and consequently the very small amount of free radicals produced by the surface-attached initiator.

2. Experimental Section

2.1. Materials. Styrene (Merck) was distilled under reduced pressure with argon. Solvents (toluene, butyl acetate, xylene, and hexane) were distilled over sodium metal. Initiators [4,4′-azobis(4-cyanvaleric acid) (ABCPA) from Aldrich, 4,4′-azoisobutyronitrile (AIBN) from Fluka, and di-*tert*-butyl peroxide

---

[†] Present address: Centre National De La Recherche Scientifique, Institut Charles Sadron - UPR 022, 6, rue Boussingault, 67083 Strasbourg Cedex, France. Telephone: 33 03 88 41 4026. Fax: 33 03 88 41 4099. E-mail: sergey.minko@physik.uni-ulm.de.

[‡] Universität Ulm.

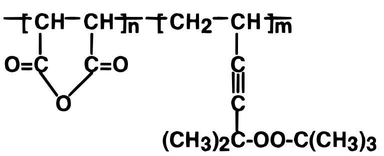
[§] National Academy of Sciences.

[||] Max-Planck-Institut für Polymerforschung.

[⊥] Lviv Polytechnic State University.

10.1021/ma9813542 CCC: $18.00

(TBP) from Merck] were used as received. The macroinitiator was a copolymer of maleic anhydride and 5-*tert*-butyl-peroxy-5-methyl-1-hexen-3-yne (mol ratio 1:1)[13]



with $M_n = 5000$ and was received from the Organic Chemistry Department of Lviv Polytechnic State University.

Silicon wafers obtained from Wacker-Chemitronics were used as substrates. They are composed of Si (index of refraction $n = 3.88-0.018i$) and a top SiO_2 layer typically 1.6 nm thick ($n = 1.462$). The SiO_2 layer thickness was determined by ellipsometric measurements for every sample. The following cleaning procedure was used to ensure the reproducibility of the results:[14] wafer pieces cut and embedded in dichloromethane were placed in an ultrasonic bath at 50 °C for 15 min, dichloromethane was removed, and the wafers were treated with an aqueous oxidizing solution (50:50 mixture of NH_3 and H_2O_2 in Millipore water) at 80 °C for 25 min, and then the wafers were rinsed in water (Millipore) and dried with dust-free nitrogen.

2.2. Attachment of the Initiators. Adsorption of the macroinitiator was carried out from toluene solution at various concentrations (0.1−1.0 mg/mL) for 2 h, as described elsewhere.[15] After this, the samples were rinsed in toluene six times. The adsorbed amount was evaluated by ellipsometry.

Adsorption (physisorption) of ABCPA was carried out from the 0.5 mg/mL butyl acetate solution for 1 h. The samples were dried with dust-free nitrogen.

Introduction of the covalently bound azo-initiator onto Si wafer surface was performed with the method described by Tsubokawa et al.[16] In the first step, a Si wafer was treated by 3-glycidoxypropyltrimethoxysilane (Aldrich) from a toluene solution. Then the Si wafer was washed by methanol. On the next step, ABCPA was introduced from dimethyl sulfoxide solution with α-picoline.

2.3. Ellipsometry Measurements and Grafting. Null ellipsometry was used to measure an adsorbed amount of the macroinitiator, as well as in situ grafting of PS from Si wafers. The ellipsometric method is based on the fact that the state of polarization of light changes upon reflection from the surface. On the basis of model calculations using Fresnel equations, it is possible to obtain the information about the thickness and refractive index of a polymer film (see below).

The measurements were carried out with a computer-controlled null ellipsometer in a vertical polarizer−compensator−sample−analyzer (PCSA) arranged as described elsewhere.[17] A He−Ne laser ($\lambda = 632.8$ nm) was used as a light source. The angle of incidence was fixed at 70.0°. This angle provides the highest sensitivity of ellipsometric measurements for our systems. The intensity of light passing through the PCSA arrangement is detected by a photomultiplier (Hamamatsu R928) and a fast integrating digital multimeter (Prema). Computer control of the analyzer allows an automated search for the null settings of the polarizer (P) and the analyzer (A). Readings on the polarizer yield the ellipsometric angle $\Delta = 2P + 90°$, and those on the analyzer yield the ellipsometric angle $\psi = A$. These angles Δ and ψ contain information about the relative phase shift and attenuation of the component waves perpendicular (s-wave) and parallel (p-wave) to the plane of incidence, respectively.

To measure the thickness of macroinitiator layers or grafted PS coating on a Si wafer, 3−6 measurements were carried out in different areas of the wafer. The polymer amount was evaluated with accuracy of 0.2 mg/m^2.

All of the in situ measurements of grafting were made in a specially built trapezoidal Teflon cell. Windows of the cell are made from glass and fixed at an angle of 70°. The cell was filled with a styrene−xylene mixture (20:80 by volume) in the argon atmosphere. The additional initiator (AIBN or TBP) was previously dissolved in the solution. The ellipsometric measurements were started approximately 5 min after the wafer was placed in the cell and fixed in the support and the cell was heated to the polymerization temperature (345 K for azo-initiators and 375 K for the macroinitiator with an accuracy of 0.1 K). Subsequently, every 30 s, a pair of ellipsometric angles, Δ and ψ, were recorded.

After 7−9 h of polymerization, the Si wafer was removed from the cell, rinsed six times in toluene, and dried with nitrogen. Then, the ellipsometric measurements of the dried polymer layer were performed. Samples of PS were extracted from the solution by precipitation in hexane, and the monomer conversion and molecular weight of the PS (by GPC) were determined.

Data Analysis. For the data interpretation, a layer model of the covering was accepted. This model considers the coating as a sandwich structure with the following layers: a Si wafer with a top silica layer, an adsorbed initiator, and grafted polystyrene layers. In this layer model, the substrate is characterized by means of ellipsometry (the thickness of SiO_2 layer was measured for every specimen). The macroinitiator refractive index was determined from ellipsometric measurements of a spin-coated film. The thickness of the adsorbed macroinitiator was measured for every sample. The refractive index of the reaction mixture at the polymerization temperature was measured using a refractometer. The change of the refractive index of the reactive mixture with conversion of monomer was determined experimentally. Two parameters of the grafted polymer layer, refractive index n_1 and thickness d_1, can be obtained from the following relationship:

$$e^{i\Delta} \tan \psi = R_p/R_s = F(n_k, d_k, \lambda, \phi)$$

where R_p and R_s represent the overall reflection coefficients for the basis p- and s-waves, respectively. They are a function of n_k and d_k, which are the refractive indices and thickness of each layer, respectively; λ is the wavelength, and ϕ is the incident angle. It is important to note that in the model a grafted layer was assumed to be homogeneous. Measurements of a pair of angles Δ and ψ allow for the evaluation of the above-mentioned two unknown parameters.[18]

The amount of grafted polymer A (mg/m^2) can be calculated from the following equation

$$A = \frac{d_1(n_1 - n_0)}{(\mathrm{d}n/\mathrm{d}c)} = d_1 c_1$$

where dn/dc is the increment of refractive index of the polymer, n_0 is the index of refraction of the solution, and c_1 is the average polymer concentration in the layer. The details of ellipsometric data computation are given elsewhere.[19]

3. Results

The typical kinetic curves of an increase of the grafting-polymer layer thickness versus time of grafting are presented in Figure 1. The curves obtained for both kinds of the initiators have a similar S-shape that is caused by the method of measurements. The ellipsometric measurements start from the moment of the heating of the cell. Changes in temperature cause changes in the rate of polymerization and other parameters in the system. The duration of the uncertainty period was not longer then 20 min. In any case, the uncertainty period was substantially less than the duration of the polymerization process and the half-life time of the initiator at the experimental conditions. Consequently, we disregard this effect on the obtained kinetic data.

In Table 1, we summarize the main characteristics of the grafting polymerization. The rate of the polym-

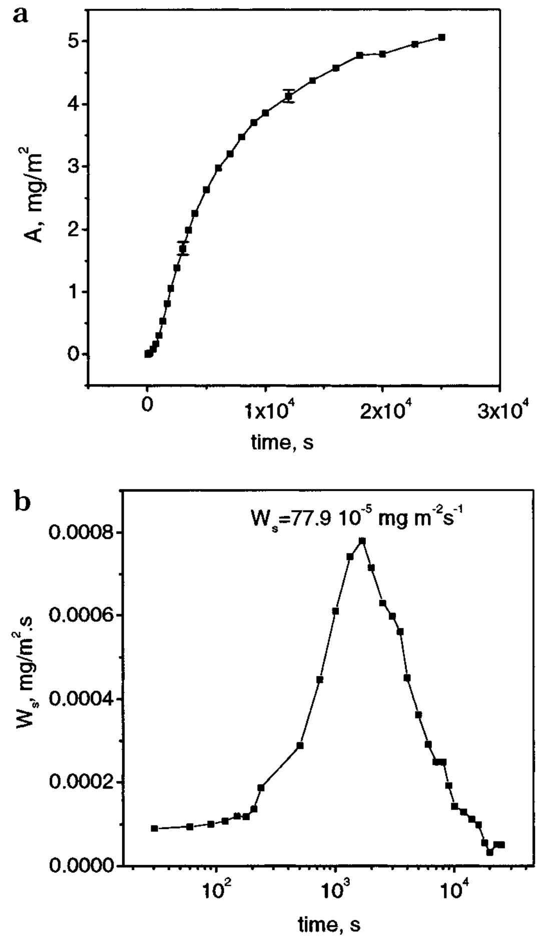


Figure 1. Dependence of the grafting amount (A) on time of grafting (t) in the (a) integral and (b) differential forms for the polymerization initiated by physisorbed macroinitiator.

erization (W_s) presented in this table was calculated at the point of inflection of the kinetic curve (Figure 1a) using the maximum of the differential curve, as indicated in Figure 1b. Molecular weights have been determined for the polymers extracted from the solution.

In Table 2, we present parameters of the grafted layers calculated from the data of Table 1. From the grafted amount A we calculate the grafting density (σ) as

$$\sigma = \frac{AN_A}{M_w}$$

where N_A is Avogadro's number, and the interchain distance $L_s = \sigma^{-1/2}$. From the gyration radius (R_g) of PS coil in toluene,[20] $R_g = 0.186N^{0.595}$, we calculate the surface density σ_o above which the PS coils are overlapping on the surface, $\sigma_o = 1/(\pi R_g^2)$, $L_s^o = \sigma_o^{-1/2}$ and the ratio L_s/L_s^o, which characterizes the degree of the PS-chain overlap on the substrate. In Table 2, we also present the initiator density (for macroinitiator, this is the density of peroxide groups) on the surface σ_i.

It is important to note that in our calculations we assume that the molecular weights of the grafted polymer and the polymer in solution are the same. This assumption is based on literature reports[5] and on the consideration of the grafting polymerization mechanism. It is clear that the process on the surface has no influence on the process in solution, because of the very high volume/interface ratio. On the other hand, the molecular weights of the grafted polymers depend on the mechanism of the termination reaction. The surface free radicals can terminate through three possible reactions by (1) termination between surface free radicals, (2) "cross" termination between surface and bulk free radicals, and (3) transfer to monomer or solvent. The first mechanism can be possible only at a very high initiation rate. However, if it has some effect in the beginning, very soon after the start, this mechanism will have very little contribution because of the fast decrease in the concentration of the surface free radicals.[8] The effect of the second and third mechanism on the termination of the surface free radicals will be the same as that of the bulk free radicals. Doubtless, the molecular weights of the surface-grafted polymer and the polymer in solution should be the same until the first monolayer is occupied and when the conditions for the surface Trommsdorff effect have not yet formed.[5] The good correlation between kinetic parameters in this paper proves the above-mentioned assumption.

It follows from the presented data that grafting layers reach a saturation in 7−9 h of polymerization. The grafting with saturation was observed for all kinds of initiators and bonds of the initiator with the substrate. The grafted amount differs for the azo-initiator and macroinitiator. In the first case, the grafted amount corresponds to the value which is usually observed for the tethered layers obtained by adsorption or "grafting to" of the end-functionalized polymers.[21] In the case of the macroinitiator, the A values are several times larger, but in both cases, A is smaller than the value predicted from scaling theory.[1] In both cases, the surface concentration of the initiator is much larger than the grafting density $\sigma_i \gg \sigma$. One can estimate from the kinetics of the initiator thermolysis that 65% of the azo-initiator and only 10% of the macroinitiator were decomposed by the end of the polymerization. This is evidence that the plateau regime is not caused by the lack of the initiator on the surface. It is noteworthy that the same grafted amounts were obtained for grafting from the physisorbed azo-initiator and for the cases when specially adsorbed initiators were not used. Below, we consider in details the kinetics of the grafting process.

3.1. Characterization of the System. The grafting process may be summarized by the following kinetic scheme

$$I_s \xrightarrow{k_d^s} R_s{*} + R_v{*} \quad \text{initiation on the surface}$$

$$I_v \xrightarrow{k_d^v} R_v{*} \quad \text{initiation in the bulk}$$

$$R_s{*} + nM \xrightarrow{k_p} R_s{*} \quad \text{propagation on the surface}$$

$$R_v{*} + nM \xrightarrow{k_p} R_v{*} \quad \text{propagation in the bulk}$$

$$R_s{*} + R_v{*} \xrightarrow{k_t} P_s \quad \text{termination on the surface}$$

$$R_v{*} + R_v{*} \xrightarrow{k_t} P_v \quad \text{termination in the bulk}$$

$$R_s{*} + X \xrightarrow{k_x} R_v{*} \quad \text{transfer on the surface}$$

$$R_v{*} + X \xrightarrow{k_x} R_v{*} \quad \text{transfer in the bulk}$$

Table 1. Data of the Kinetic Investigation of the Grafting

sample N	character of the initiator–substrate bond	initiator on the surface, I_s	$[I_s]$ (mol $m^{-2} \times 10^6$)	initiator in the bulk, I_v	$[I_v]$ (mol $L^{-1} \times 10^4$)	W_s (nm $s^{-1} \times 10^5$)	time of grafting (h)/conversion	grafted amount (mg m^{-2})	molecular weights, M_n/M_w (10^{-3} g mol^{-1})
1	physisorbed	PM-MA	3.1	DTBP	3.0	27.1	7.5/0.08	1.95	61/120
2	physisorbed	PM-MA	5.2	DTBP	2.0	77.9	7.5/0.08	5.0	69/142
3	physisorbed	PM-MA	5.3	DTBP	9.7	38.9	7.7/0.06	5.4	38/73
4	physisorbed	PM-MA	7.8	DTBP	4.9	93.4	7.5/0.08	13.4	46/89
5	physisorbed	PM-MA	8.2	DTBP	2.5	–	7.5/0.04	8.72	39/75
6	physisorbed	PM-MA	8.8	DTBP	12.3	106	7.5/0.09	9.5	41/81
7	physisorbed	PM-MA	10.7	DTBP	0.5	102	7.5	14.7	36/72
8	chem bond	ABCPA	0.3	AIBN	7.4	19	9.0	1.73	30/62
9	chem bond	ABCPA	0.3	AIBN	28.5	9.8	9.0	1.2	22/38
10	chem bond	ABCPA	0.3	AIBN	2.37	15.8	7.5	0.92	42/82
11	physisorbed	ABCPA	0.3	AIBN	7.4	21.3	8.5	1.95	33/62
12	–	–	–	DTBP	16	134	7.5/0.12	10.8	45/100
13	–	–	–	AIBN	7.4	36.3	9.5	2.8	32/65

Table 2. Characteristics of the Grafted Layers

initiator	sample N	PS grafting density, σ (nm^{-2})	initiator grafting density, σ_i (nm^{-2})	R_g (nm)	L_s^o (nm)	L_s (nm)	L_s/L_s^o	$N\sigma^{2/3}$
physisorbed macroinitiator	1	0.0098	1.9	12.3	21.9	10.1	0.46	53
physisorbed macroinitiator	2	0.021	3.1	13.6	24.2	6.9	0.28	104
physisorbed macroinitiator	3	0.045	3.2	9.2	16.3	4.7	0.29	88
physisorbed macroinitiator	4	0.091	4.7	10.3	18.3	3.3	0.18	173
physisorbed macroinitiator	5	0.070	4.9	9.3	16.5	3.8	0.23	123
physisorbed macroinitiator	6	0.071	5.3	9.8	17.3	3.8	0.22	133
physisorbed macroinitiator	7	0.12	6.4	9.1	16.1	2.9	0.18	171
chemisorbed azo-initiator	8	0.017	0.18	8.3	14.8	7.7	0.52	39
chemisorbed azo-initiator	9	0.019	0.18	6.2	11.0	7.3	0.66	26
chemisorbed azo-initiator	10	0.0068	0.18	9.8	17.4	12.2	0.70	28
physisorbed azo-initiator	11	0.019	0.18	8.3	14.8	7.3	0.49	42
no specially adsorbed initiator	12	0.065	–	11.1	19.7	3.9	0.20	155
no specially adsorbed initiator	13	0.026	–	8.57	15.2	6.2	0.41	55

In this scheme, we assume that propagation, termination, and transfer reaction constants are the same on the surface and in the bulk.[2] In this scheme, we do not consider details of the initiation reaction with respect to efficiency of the initiation or the role of cage recombination.

Macroinitiator on the Surface and TBP in the Bulk at 375 K. Kinetics of the radical polymerization is sensitive to contamination and the conditions of the experiment. The most reliable evaluation of the kinetic constant in the experiment may be done on the basis of the molecular weight of the polymer synthesized using the equation[22]

$$\frac{1}{N} = \frac{1}{N_0} + \sum c_x \frac{[X]}{[M]} = \frac{W_i^{v1/2}}{2\dfrac{k_p}{k_t^{1/2}}[M]} + \sum c_x \frac{[X]}{[M]} \qquad (1)$$

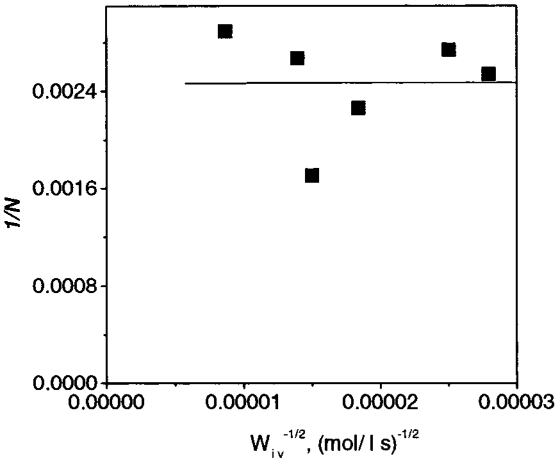


Figure 2. Dependence of $1/N$ on $W_i^{v1/2}$ for the grafting from the adsorbed macroinitiator.

where N and N_0 are the degrees of the polymerization with and without transfer reaction, respectively, $c_x = k_x/k_p$; [M] is the monomer concentration, [X] is the chain transfer reagent concentration (monomer, solvent, contamination, etc.), W_i^v is the rate of the initiation reaction in the bulk (the initiator on the surface produces too few free radicals, which has no effect on the total free radical concentration). In our case, the initiation rate in the bulk consists of two terms, $W_i^v = W_i^v(\text{term}) + W_i^v(\text{TBP})$, where $W_i^v(\text{term})$ is the rate of the thermal self-initiation of the styrene polymerization and $W_i^v(\text{TBP})$ is the initiation rate of TBP. In this case, we use from Mayo[23] $W_i^v(\text{term}) = 4.3 \times 10^{-11}$ mol L^{-1} s^{-1}. The initiation by TBP was calculated as $W_i^v(\text{TBP}) = k_i^v[I_v]$, where $k_i^v = 10^{-6}$ s^{-1} and $[I_v]$ is the concentration of TBP in solution. The dependence $1/N$ versus $W_i^{v1/2}$ is plotted in Figure 2. From the plot, it is clear that the first term on the right-hand side of the equation has a very small effect and that the molecular weight is determined by transfer reaction. Consequently, $k_x[X]/k_p[M] = 0.0024$ and for $k_p = 675$ L mol^{-1} s^{-1} and $[M] = 1.74$ mol L^{-1}, we obtain $k_x[X] = 2.8$ s^{-1}. For this experiment, we may evaluate the ratio between the rate of the surface free radical termination by two possible reactions: (a) with free radicals in the bulk and (b) by transfer with X

$$\frac{W_t}{W_x} = \frac{k_t[R_s^*][R_v^*]}{k_x[R_s^*][X]} = \frac{k_t[R_v^*]}{k_x[X]} \qquad (2)$$

Taking into account that $R_v^* = (W_i^v/k_t)^{1/2}$ and $k_t = 4 \times 10^8$ L mol^{-1} s^{-1}, we obtain from eq 2 $W_t/W_x \approx 0.1$. Consequently, in this system, the surface free radicals should be terminated mainly by chain transfer.

Azo-Initiator on the Surface and AIBN in the Bulk at 345 K. In this case, the thermal self-initiation is very

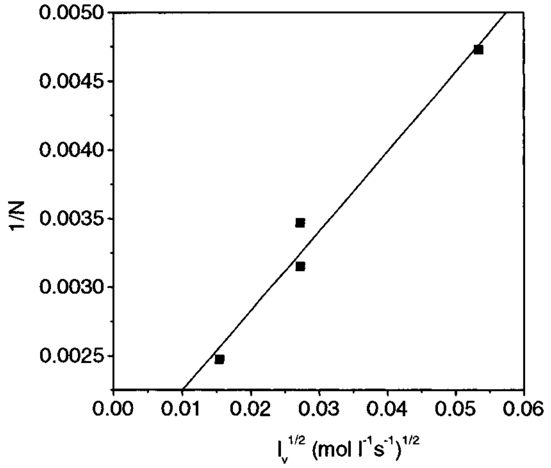


Figure 3. Dependence of $^1/_N$ on $I_v^{1/2}$ for the grafting from the azo-initiator.

small, and the relationship expressed by eq 1 may be plotted as $^1/_N$ versus $[I_v]^{1/2}$ (Figure 3). From the intercept, we can calculate $k_x[X] = 0.93$ (taking $k_p = 316$ L mol^{-1} s^{-1}) and from the slope, $k_p/k_t^{1/2} = 0.022$ L$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$ (taking $k_i^v = 2 \times 10^{-5}$ s^{-1}). All of these constants are in agreement with literature data.[24] For this case, we obtain from eq 2 $W_t/W_x \approx 4.6$. That means that in this system surface free radicals are terminated mainly by the reaction with bulk free radicals.

This kinetic analysis shows that we have two different and kinetically definite cases of the grafting process. Below, we discuss the kinetics of the polymerization on the surface for the two cases.

The kinetic model for the grafting polymerization from the solid surface, which considers the bulk free radical diffusivity (D), was described in the previous paper.[2] We denote it Model 1. A system of differential equation was suggested:

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

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

$$-D\frac{d[R_v^*]}{dx} = k_d^s[I_0^s]\exp(-k_d^s t) - k_t[R_v^*][R_s^*] + k_x[R_s^*][X] \qquad \text{Model 1}$$

with the boundary condition

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

which assumes the distribution of bulk free radicals in solution from $x = 0$ (surface) to $x = \Lambda$. In this paper, we compare the data of the numerical solution of this model with the experimental data.

On the other hand, for the two limiting kinetic cases investigated and assuming that the initiation rate in the bulk is larger than the initiation from the surface, we may suggest a more simple model that can be presented by two algebraic equations (Model 2):

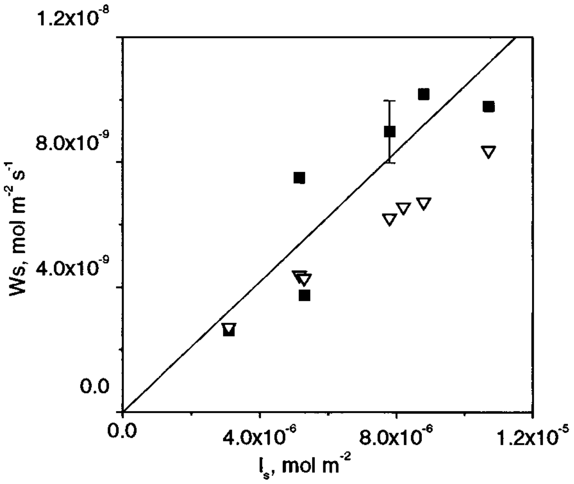


Figure 4. Dependence of W_s on I_s for the grafting from the adsorbed macroinitiator. Open triangles are the data calculated from Model 1.

$$\frac{d[R_s^*]}{dt} = k_d^s[I_s] - k_x[R_s^*][X] - k_t[R_s^*][R_v^*] = 0$$

$$\frac{d[R_v^*]}{dt} = k_d^v[I_v] - k_t[R_v^*]^2 - k_t\frac{1}{h}[R_s^*][R_v^*] + k_x\frac{1}{h}[R_s^*][X] = 0 \qquad \text{Model 2}$$

In this model, we consider the polymerization process which runs at the interface layer with the thickness h. We use these oversimplifications to show the relationships between the parameters. Solution of this equations for two limiting cases gives the following equations:

At $k_t[R_s^*][R_v^*] \ll k_x[R_s^*][X]$

$$W_s = \frac{k_p k_d^s}{k_x[X]}[I_s][M] \qquad (3)$$

At $k_t[R_s^*][R_v^*] \gg k_x[R_s^*][X]$

$$W_s = \frac{k_p}{k_t^{1/2}}\frac{k_d^s}{(k_d^v[I_v])^{1/2}}[I_s][M] \qquad (4)$$

One can see from eqs 3 and 4 that the polymerization rate is proportional to the concentration of the surface-bonded initiator in both cases but that it has inverse square root dependence on the concentration of the initiator in the bulk in the case of eq 4 or inverse dependence on the rate of transfer in the case of eq 3.

3.2. Grafting from the Macroinitiator. In Figure 4, we plot the dependence of W_s on $[I_s]$. The open triangles show data of the numerical calculation due to Model 1. Experimental data were fitted with the model using the following parameters: $k_x[X] = 2.9$ s^{-1}, $k_p = 675$ L mol^{-1} s^{-1}, $k_t = 4 \times 10^8$ L mol^{-1} s^{-1}, $k_d^s = k_d^v = 2.5 \times 10^{-6}$ s^{-1}, [M] = 1.74 mol L^{-1}. The linear relationship between W_s and $[I_s]$ is in a good agreement with Model 2, and from the slope using the above ratio $k_x[X]/k_p[M]$, we calculated $k_i^v = 2.5 \times 10^{-6}$ s^{-1}, which

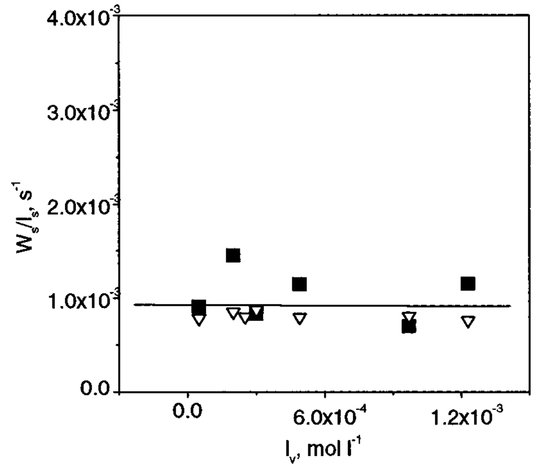


Figure 5. Dependence of W_s/I_s on I_v for the grafting from the adsorbed macroinitiator. Open triangles are the data calculated from Model 1.

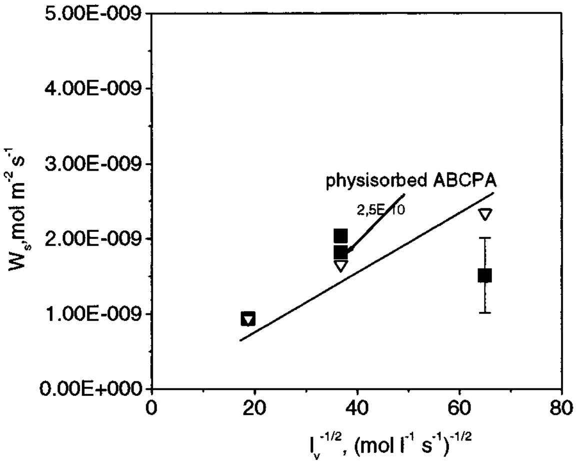


Figure 6. Dependence of W_s on $I_v^{-1/2}$ for the grafting from the azo-initiator. Open triangles are the data calculated from Model 1.

shows a good agreement between both models and the experiment.

The dependence of W_s on $[I_v]$ presented in Figure 5 is also in a good agreement with the assumption in eq 3 that termination in the system is determined by the transfer reaction. The data of the numerical solution due to Model 1 (open triangles) with the above-mentioned parameters gives the same result (Figure 5). Here and below, we do not make a difference between decomposition and initiation reaction constants. The correlation between our data proves that the efficiency of the initiation reaction does not substantially affect the kinetic calculations and is of ordinary value.

3.3. Grafting from the Chemi- and Physisorbed Azo-Initiators. In this case, the surface free radicals terminate with the bulk free radicals, and because of eq 4, W_s has an inverse square root dependence on $[I_v]$ that was also obtained from the experimental data and the numeric solution from Model 1 (Figure 6). The kinetic constants obtained from the slope are also in good agreement with the fit parameters and literature data: $k_x[X] = 1\ s^{-1}$, $k_p = 316$ L mol^{-1} s^{-1}, $k_t = 3 \times 10^8$ L mol^{-1} s^{-1}, $k_d^s = k_d^v = 2.5 \times 10^{-5}$ s^{-1}, [M] = 1.74 mol L^{-1}. It is interesting to note that the kinetics obtained for the physisorbed azo-initiator obeys the same relationship as that for the chemisorbed azo-initiator.

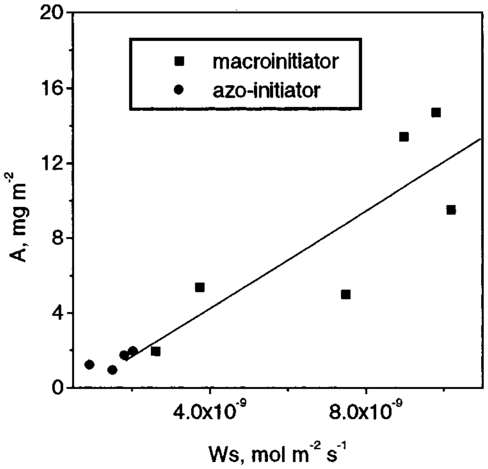


Figure 7. Dependence of A on W_s for all of the grafting experiments.

3.4. Grafting without a Specially Adsorbed Initiator. The amount of the grafted polymer and the grafting kinetics when the initiator is presented in only the solvent corresponds to the case when the initiator is attached to the substrate. This result seems to be interesting but not unexpected, despite the fact that PS is not adsorbed on a silica surface from xylene. The grafting to an uncovered inorganic surface has been reported several times in the literature.[10] Two main arguments have to be considered for this phenomena. First, most of the initiators have polar groups (in our case, e.g., AIBN) that are responsible for end-functional groups in polymer chains. Consequently, an initiator can be physisorbed from the bulk and initiate the grafting, or the synthesized polymer has end-functional groups and may be adsorbed on the surface.[19,21] From the scaling law it is clear that even the bond energy on the order of $100kT$ ensures the formation of dense polymer brush.[1] Second, one has to consider the influence of the surface on the adsorbed initiator or free radical. An inorganic surface very often can react with free radicals. For example, a very pronounced inhibition effect was found for the radical polymerization in the presence of many of the inorganic oxides, especially near those with semiconductor properties.[25] It was found that the effect can be substantially decreased when the substrate surface is capped by adsorbed polymer or other species. This effect should not significantly influence our results, as can be seen in an indirect way from our data. In Figure 4 the dependence of W_s on $[I_s]$ yields a straight line which is extrapolated to the origin. Consequently, in this case the interaction between free radicals and the substrate is decreased and has no effect on the kinetics. We may conclude the same for the case of grafting initiated from the adsorbed azo-initiator. If there was an substantial interaction of the bulk free radical with the surface, we would not obtain the inverse dependence of W_s on $[I_v]$.

4. Discussion

The kinetic analysis has shown a good correlation of the experimental data with the model assumptions. We may conclude that kinetics of grafting from a solid surface runs in accordance to the classical scheme of the radical polymerization with one important characteristic additional feature. Actually, the surface-grafted free radicals terminate in a reaction with the bulk free radicals or because of transfer reactions. We may conclude also that until the plateau-grafting value is reached there is no effect on the grafting kinetics by the type of the initiator/substrate bond.

We should consider in more detail the data with the grafted amount which is higher than 2−5 mg/m^2. From the data of Table 1, we see that the main difference in the grafted amount is caused by the difference in the polymerization rate. Similar results have been reported for grafting on a glass surface.[11] This conclusion can be very well supported by Figure 7. If we assume that A is restricted by the free energy of growth of the grafted chain, we should reach for all experiments the A value which gives the same free energy. The scaling law gives the equation for the energy of a chain in the brush as $F/kt \cong N\sigma^{2/3}$. The calculated values of $N\sigma^{2/3}$ are presented in Table 2. One can see that these values differ very much in different experiments. Consequently, the grafted amount is determined by an kinetic factor rather than by the energy of the stretched chain. Nevertheless, the energy of a chain in the brush should predetermine this situation. We may assume that the grafted chains grow in the polymer brushlike layer as long as the attachment of an additional monomer unit is not restricted by a high activation barrier due to sterical problems, as was mentioned in the Introduction. In this case, the plateau-grafted amount corresponds to the monolayer coating. We may predict that this limit increases with temperature and monomer concentration and that consequently the rate of grafting increases. The next step is a multilayer coating formation, when at a high polymerization rate due to the Trommsdorff effect in the grafting layer new chains are formed and forced out to the top of the coating. In this process, in the case of a physisorbed initiator, the already grafted chains can be involved also. With this mechanism, the grafted amount is determined by the ratio between the polymerization rate and the rate of chain diffusion from the grafted layer into the bulk. The latter causes the kinetic character of the thick layer formation. This mechanism has been discussed elsewhere.[2]

5. Conclusions

The kinetics of PS grafting from a silica surface with attached macroinitiator or azo-initiator was investigated by in situ ellipsometric measurements of the grafted amount.

The grafted amount approaches a constant value asymptotically with time of grafting. This saturation value depends on the polymerization rate.

It was found that kinetics of the grafting process can be described by the classical theory of radical polymerization, taking into account that grafted chains terminate in the reaction with the bulk free radicals or by transfer reactions. Such a specific behavior of the termination reaction results in a linear dependence of the polymerization rate on the surface concentration of the initiator and an inverse square root dependence on the initiator concentration in the bulk. The suggested models quantitatively describe the process.

The results of modeling are consistent with the assumption that the rate constants of the initiation, propagation, termination, and transfer reactions are the same for the polymerization on the surface and in the bulk in the polymerization regime that corresponds to a grafting density before grafted layer saturation.

Acknowledgment. The authors thank Dr. J. Rühe (MPIP Mainz) for fruitful discussions and Dr. V. Erb and Messrs. H. Walter and M. Bach for assistance and consultations. The financial support from Volkswagen Foundation and Grant No 4.4/60 of the Ukrainian Ministry of Science and Technology is gratefully acknowledged. S.M. thanks the Alexander von Humboldt Foundation for the support of this study. V.S. acknowledges support of Deutscher Akademischer Austausch Dienst.

References and Notes

(1) Ligoure, C.; Leibler, L. *J. Phys. France* **1990**, *51*, 1313. Milner, S. T. *Science* **1991**, *251*, 905. Szleifer, I.; Carignano, A. *Adv. Chem. Phys.* **1996**, *44*, 165.
(2) Minko, S.; Gafijchuk, G.; Sidorenko, A.; Voronov, S. *Macromolecules* **1999**, *13*, 4525.
(3) Petrik, V. N.; Kuznecova, L. L.; Livshiz, R. M. *Vysokomol. Soedin.* **1974**, *16B*, 110.
(4) Ivanchev, S. S.; Enikolopjan, N. S.; Polosov, B. V.; Dmintrenko, A. V.; Demidova, V. A.; Krupnik, A. M. *Polym. Sci. USSR* **1981**, *23*, 2248.
(5) Boven, G.; Oosterling, M. L. C. M.; Challa, G.; Schouten, A. J. *Polymer* **1990**, *31*, 2377.
(6) Rühe, J. *Nachr. Chem., Techn. Lab.* **1994**, *42*, 1237.
(7) Luzinov, I. A.; Voronov, S. A.; Minko, S. S.; Kraus, R.; Wilke, W.; Zhuk, A. *J. Appl. Polym. Sci.* **1996**, *61*, 1101.
(8) Prucker, O.; Rühe, J. *Macromolecules* **1998**, *31*, 592. Prucker, O.; Rühe, J. *Macromolecules* **1998**, *31*, 602.
(9) Dinh-Ngoc, B.; Rabe, J. G.; Schnabel, W. *Angew. Macromol. Chem.* **1975**, *46*, 23. Ivanchev, S. S.; Enikolopjan, N. S.; Polosov, B. V.; Dmintrenko, A. V.; Demidova, V. A.; Krupnik, A. M. *Polym. Sci. USSR* **1981**, *23*, 2248. Andrianov, A. K.; Olenin, L. V.; Zubov, V. P.; Kashutina, E. A.; Zhdanov, A. A.; Kabanov, V. A. *Polym. Sci. USSR* **1983**, *25*, 2314. Nagai, K.; Ohishi, Y.; Ishijama, K.; Kuramoto, N. *J. Appl. Polym. Sci.* **1989**, *38*, 2183. Fujiki, K.; Tsubokawa, N.; Sone, Y. *Polym. J.* **1990**, *22*, 661.
(10) Korshak, V. V.; Zubakova, L. B.; Kachurina, N. V.; Balashova, O. B. *Polym. Sci. USSR* **1979**, *21*, 1243. Ivanchev, S. S.; Dmitrenko, A. V.; Demidova, V. A.; Dabagova, A. K. *Polym. Sci. USSR* **1985**, *27*, 1217. Tsubokawa, N.; Naruyama, K.; Sone, J.; Shimomura, M. *Polym. J.* **1989**, *21*, 475.
(11) Luzinov, I. A.; Minko, S. S.; Senkovskiy, V. M.; Voronov, A. S.; Hild, S.; Marti, O.; Wilke, W. *Macromolecules* **1998**, *31*, 3945.
(12) Smirnov, B.; Minko, S.; Luzinov, I.; Sidorenko, A.; Stegno, E.; Ivanov, V. *Vysokomol. Soedin.* **1993**, *35B*, 161 (in Russian).
(13) Kurgansky, V. S.; Puchin, V. A.; Voronov, S. A.; Tokarev, V. S. *Polym. Sci. USSR* **1983**, *25*, 997. Voronov, S.; Tokarev, V.; Petrovska, G. *Heterofunctional Peroxides. Theoretical Basis of the Synthesis and Application*; Lviv Polytechnic State University: Lviv, Ukraine, 1994.
(14) Erb, V. Thesis, Johannes Gutenberg-Universität, Mainz, Germany, 1997.
(15) Minko, S. S.; Luzinov, I. A.; Evchuk, I. Yu.; Voronov, S. A. *Polymer* **1996**, *37*, 177.
(16) Tsubokawa, N.; Kogure, A.; Maruyama, K.; Sone, Y.; Shimomura, M. *Polym. J.* **1990**, *22*, 827.
(17) Motschmann, H.; Stamm, M.; Toprakcioglu, C. *Macromolecules* **1991**, *24*, 3681.
(18) Azzam, R. M. A.; Bashara, N. M. *Ellipsometry and Polarized Light*; North-Holland Publications: Amsterdam, The Netherlands, 1987.
(19) Siqueira, D. F.; Breiner, U.; Stadler, R.; Stamm, M. *Langmuir* **1995**, *11*, 1680.
(20) Higo, Y.; Ueno, N.; Noda, I. *Polym. J.* **1983**, *15*, 367.
(21) Pankewitsch, T.; Vanhoorne, P.; Jérôme, R.; Stamm, M. *Macromolecules* **1995**, *28*, 6986.
(22) Flory, P. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1975.
(23) Mayo, F. R. *J. Am. Chem. Soc.* **1953**, *75*, 6133. Mayo, F. R. *J. Am. Chem. Soc.* **1968**, *90*, 1289.
(24) *Polymer Handbook*, 3d ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley-Interscience: New York, 1988.
(25) Minko, S. S.; Kutcher, R. V.; Smirnov, B. R.; Luzinov, I. A. *Polym. Sci. USSR* **1991**, *33*, 85.

MA9813542