# Mechanism of Radical Chain Polymerizations Initiated by Azo Compounds Covalently Bound to the Surface of Spherical Particles

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ABSTRACT: The kinetics and mechanism of a radical chain polymerization reaction initiated from a self-assembled monolayer of an azo initiator attached to the surfaces of silica particles are investigated. The rate of the decomposition of the surface-attached initiator is followed by differential scanning calorimetry and volumetry. The kinetics of formation of the terminally attached polymer is studied by dilatometry. After polymerization the polymer is removed from the surfaces and the molecular weight averages and molecular weight distribution of the degrafted polymer are studied as a function of reaction parameters during polymerization. From the molecular weight, the mass of the attached polymer, and the specific surface area, the number of polymer molecules per area (or the distance between the anchoring sites) can be calculated and compared to the corresponding values of the initiator monolayers. The mechanism of a polymerization with surface-attached radicals is compared to that of conventional radical chain polymerization in solution.

## Introduction

Most systems in which a polymer is covalently linked to a solid surface have been obtained by a "grafting to" technique, in which a functional group of the (preformed) polymer is reacted with a corresponding site on the surface of the substrate.[1] However, the growth of such layers from solution is hampered by several limitations, e.g., an intrinsic limitation of the graft density and accordingly layer thickness due to a strong kinetic hindrance for the attachment of polymer molecules occurring once the surface is significantly covered.[2] Recently, we have described a strategy that circumvents such limitations. In this concept the polymerization reaction is started from a self-assembled monolayer of an initiator and the polymer is formed directly at the surface of the substrate.[3] We could show that, with this technique, very reproducible layers with high graft density and high molecular weight of the tethered chains can be formed.[4]

Although several studies have been performed in recent years, where initiators have been attached to surfaces of solid substrates,[5] the mechanism of such a polymerization reaction is not well understood. In most cases only the amount of polymer deposited under the given reaction conditions is known and very little or even no information on the kinetics of the initiation process and the influence of the immobilization on the growth and termination of the growing polymer chains has been published. This is partly due to the fact that the exact composition of the initiator layers is not known because in all cases reported so far the initiator layer is formed during several surface reaction steps and side reactions can occur. The products of these side reactions are, however, difficult to characterize and quantify due to the small amount of the grafted material. Another major problem is the fact that the systems known up to now are based exclusively on initiators with multifunctional (mostly trifunctional) "anchoring" groups connecting the initiator molecules to the surfaces. These multifunctional groups can react not only with appropriate reactive sites at the surfaces of the substrates but also with each other to form three-dimensional surface-attached networks of the initiator molecules. The consequence of this network formation is that the exact graft density of the initiating species is difficult to control. For a detailed understanding of the surface polymerization process, however, a well-defined initiator layer is one of the basic requirements.

The attachment of polymers to surfaces has been intensely investigated from a theoretical point of view.[6] In particular, surface layers with high graft density ("polymer brushes") have been studied in a large number of publications. However, the theoretical treatment of the surface attachment of polymer chains has been mostly directed toward the immobilization of preformed polymer molecules at the surface (grafting to). The growth of polymer chains away from a surface has not been covered by theoretical calculations so far, and knowledge about the formation of polymers at surfaces *in situ* is very limited.

As one of the few exceptions, Wittmer et al. recently studied the growth of polymers at surfaces from a theoretical point of view.[7] They predict strong differences between polymer molecules grown at surfaces and polymer generated in solution. For example, they have shown that it can be expected that in some scenarios polymer formed in situ at the surface has a much higher polydispersity compared to the same reaction occurring in solution. The reason for this predicted increase is the calculated result that long chains are more efficient at adding additional monomer than short chains, which are consequently growing much more slowly. It should be noted, however, that the situation discussed by Wittmer et al. is not generally applicable for all systems. One of the basic assumptions of the theoretical treatment was that many simultaneously growing (essentially living) chains compete for a small influx of monomers to the surface.[7] In a typical radical chain polymerization, however, the number of monomer molecules present in the surface layer is several orders of magnitude higher than that of the growing chains,

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which requires a completely different theoretical approach.

To achieve control of the polymerization with surface-attached initiators, it is essential to know to what extent the mechanism of polymer growth is affected by the immobilization of the growing chains at the solid surface. For example it is conceivable that the surface attachment and the close packing of the initiator molecules at the surfaces leads to a strong reduction of the radical efficiency, thus decreasing the number of growing polymer chains and limiting the graft density that can be obtained by this method. Furthermore, it is difficult to judge, *a priori*, how the confinement of the growing polymer radicals to a thin surface layer influences the molecular weight and molecular weight distribution as the rate constants of propagation and termination could be influenced by the attachment. In contrast to a conventional solution polymerization where all chains are evenly distributed throughout the solution, the covalent bond between the growing chains and the surface of the substrate prevents free diffusion and restricts all (active and already terminated) polymer chains to a small volume in close proximity to the surface.

In this paper we describe studies on the kinetics and mechanism of radical chain polymerization with an initiator that has been immobilized to the surface of a highly dispersed silica substrate. The kinetics of the growth of the polymer chains immobilized at the surface was investigated by dilatometry experiments. The mechanism of the surface polymerization is studied through a systematic variation of the reaction parameters during polymerization. The molecular weight averages and molecular weight distributions of the attached materials are analyzed after cleaving the attached polymer. The mechanism of the polymerization in the molecularly thin surface layer is compared to that of formation of unbound polymer in a conventional solution polymerization.

## Experimental Section

**Materials.** The silica gel (Aerosil A300, Degussa) used in this study had a specific surface area of 285 ± 15 $m^2\ g^{-1}$ according to nitrogen adsorption measurements (BET technique). Toluene was refluxed under a nitrogen atmosphere over sodium/potassium alloy and benzophenone until a dark blue color was obtained and then distilled. The stabilizer was removed from the styrene monomer through chromatography over aluminum oxide (ALOX B). The styrene was then distilled under vacuum from copper(I) chloride and stored under nitrogen at −30 °C. All reaction mixtures were carefully degassed during repeated freeze−thaw cycles. Removal of oxygen traces before polymerization is especially important for the experiments described here because the total number of growing chains is rather small (typically between 5 and 500 $\mu$mol). The structure of the surface-attached initiator is shown in Figure 1. A detailed description of the synthesis and characterization of the monolayers has been published elsewhere.[4] Briefly, the azo compound with the chlorosilane moiety **1** is self-assembled at the surface of the silica gel in a base-catalyzed reaction. By adjusting the silane concentration in solution, silica gels with the immobilized initiator **2** (in the following termed $SiO_2$-AMCS) with surface concentrations between 550 $\mu$mol/g (1.9 $\mu mol/m^2$) and 50 $\mu$mol/g (0.2 $\mu mol/m^2$) were obtained. Graft densities of the surface-attached initiators were determined by elemental analysis and DSC.

The polymerization reactions were carried out in a thermostat (accuracy ±0.1 °C) at temperatures between 50 and 90 °C. After the polymerizations were stopped, the polymer-modified silica gel was removed by centrifugation (>10 000 rpm). The solid material obtained was repeatedly redispersed in toluene and separated again by centrifugation. The supernatant solutions were dropwise added to a 10−15 times excess of methanol. The washing procedure was continued until no more precipitate could be detected, indicating that no more free polymer could be removed. Additionally, to check whether the washing procedure is sufficient, the graft density $\delta$ of some samples of the surface-attached polymer (mass of polymer per mass of silica gel) was determined after the individual washing steps by elemental analysis. Washing was continued until the amount of polymer in the isolated material remained constant, indicating that no more nonattached polymer could be removed. Both methods gave the same results within experimental error.

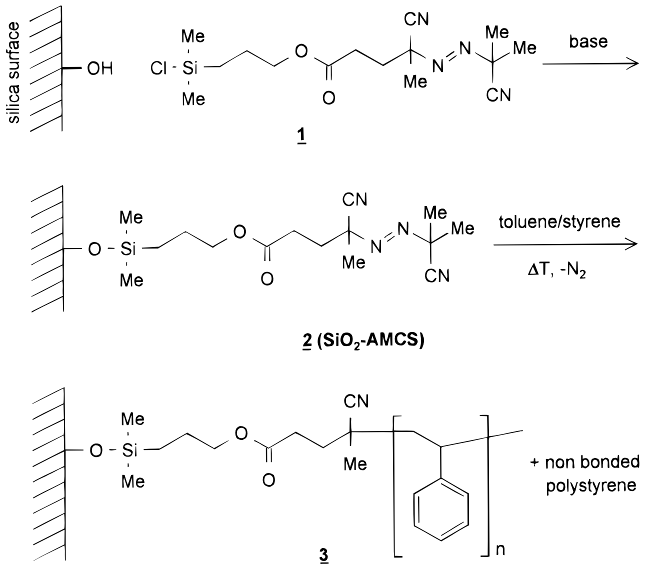

**Figure 1.** Reaction scheme for the synthesis of covalently attached polystyrene monolayers on silica surfaces using immobilized AIBN-type azo initiators.

Both the $SiO_2$-PS **3** and nonattached polymer were separately precipitated into methanol and freeze-dried from benzene. In all cases 1.5−6 times more surface-attached than nonattached polymer could be isolated. The grafted polymer could be removed from the silica gel upon refluxing a dispersion of the $SiO_2$-PS in toluene/methanol (9:1) with *p*-toluenesulfonic acid as a transesterification catalyst.[4] The degrafted polymer was also precipitated in methanol and freeze-dried from benzene.

**Methods.** Differential scanning calorimetry (DSC) traces were recorded on a Perkin-Elmer DSC 2 at a scan rate of 10 K/min. The experiments were carried out under nitrogen in a temperature range between 25 and 190 °C. Except for thorough drying at room temperature under high vacuum conditions, no pretreatment of the samples was performed.

For volumetric experiments, 2 g of the surface-attached azo initiator was weighed into a 10 mL flask equipped with a capillary tube attached to a mercury pressure gauge. The flask was evacuated to $10^{-3}$ mbar at 25.0 °C, separated from the vacuum, immersed in a thermostat, heated to the desired temperature for a chosen period of time, and cooled back to the starting temperature. The amount of nitrogen formed during the decomposition of the initiator was calculated from the measured pressure in the flask.

Dilatometric measurements were performed using a flask equipped with a calibrated capillary tube (accuracy: 0.001 mL). The total volume of the setup was approximately 39 mL. After weighing in about 400 mg of the silica gel with the attached initiator and filling in the monomer, the solutions were repeatedly degassed. The experiments were performed in a thermostat at 60.0 ± 0.1 °C. The dispersions were stirred during polymerization by a magnetic stirrer in order to avoid sedimentation, as this would lead to an inhomogeneous distribution of the particles and therefore varying concentrations of the growing chains.

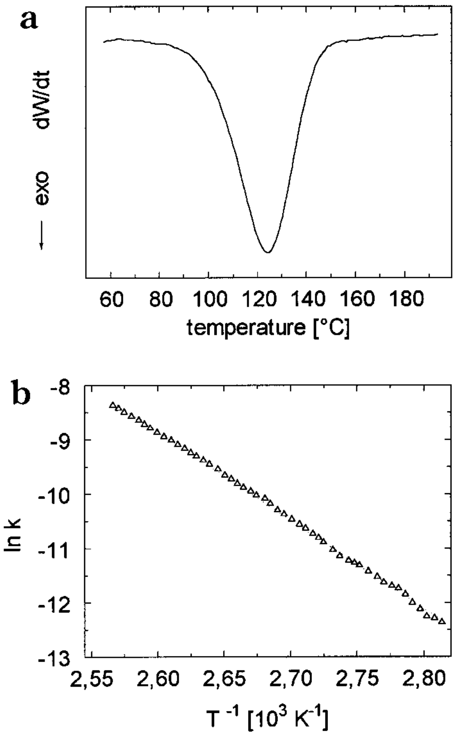

**Figure 2.** (a) DSC trace of $SiO_2$-AMCS; heating rate 10 K/min. (b) Arrhenius plot calculated from the DSC curve depicted in (a) according to eq 3.

The molar masses of the cleaved polymers were determined by size exclusion chromatography on a Waters 150C using Ultrastyragel columns and $CHCl_3$ (HPLC grade quality; room temperature) as eluent. The equipment was calibrated with narrow molecular weight distribution polystyrene standards.

## Results

To obtain monolayers with a controlled thickness and graft density, it is important to know how the attachment of the initiators and the growing polymer chains influences the different elementary steps of the polymerization reaction (initiation, growth, termination). A basic requirement for the understanding of the kinetics and mechanism of the polymerization with immobilized initiators is the knowledge of the decomposition behavior of the surface-attached azo initiator. This is of special importance considering that in some systems published in the literature it is found that the thermal behavior of a surface-attached initiator is quite different from that in solution or bulk polymerization reactions.[8]

**Kinetics of Azo Decomposition.** The decomposition kinetics of the nonattached azo initiator (AMCS **1**) and the immobilized initiator ($SiO_2$-AMCS **2**) were investigated by differential scanning calorimetry (DSC). In Figure 2a, the DSC trace of the decomposition of $SiO_2$-AMCS is depicted. From the DSC experiments, the activation energy of the decomposition of the azo compound was calculated according to a method developed by Nuyken and co-workers.[9] They and others have shown that, under suitable conditions, the complete Arrhenius plot of the thermal decomposition of a thermally labile compound can be obtained from one single DSC experiment.[9−11]

If the thermal decomposition is assumed to be a first-order reaction, the rate of the reaction ($dn/dt$) is given by:

$$-\frac{dn}{dt} = k_d n_t \tag{1}$$

where $k_d$ is the rate constant of the decomposition reaction and $n$ is the number of molecules still present at time $t$. Furthermore, the rate of the thermal-induced reaction is proportional to the heat flow $dH_d/dt$ at time $t$:[10]

$$-\frac{dn}{dt} = \frac{n_0}{\Delta H_d}\frac{dH_d}{dt} \tag{2}$$

$n_0$ is the number of initially present initiator molecules, $n$ is the number of molecules present at time $t$, $\Delta H_d$ is the enthalpy of decomposition, and $dH_d/dt$ is the heat flow. Accordingly, the rate constant of the decomposition reaction $k_d$ can be expressed as

$$k_d = \frac{n_0}{n\Delta H_d}\frac{dH_d}{dt} \tag{3}$$

The last factor can be directly read from the DSC trace for any given time $t$. The number of azo molecules $n$ still not decomposed at time $t$ can be calculated from the integral of the DSC curve. For this the signal has to be integrated from the beginning of the reaction until time $t$ is reached and subtracted from the total amount of heat released during complete decomposition. For a detailed description of the technique, the reader is referred to refs 9 and 10.

Figure 2b shows the Arrhenius plot derived from the DSC trace of $SiO_2$-AMCS via the method described above. Only the linear part of the data, which is obtained for temperatures between 80 and 120 °C, is presented. At both lower and higher temperatures, deviations from a linear slope are observed. At lower temperatures the DSC signal is too small for reliable analysis; for example, at a temperature of 60 °C the half-life time of the initiator is about 20 h, which is orders of magnitude smaller than the time scale of the DSC experiment. Deviations at higher temperatures (which also means higher conversion of the initiator in this context) are most likely due to the accumulation of the decomposition products, which can undergo further thermal reactions. Ketenimines and methacrylonitriles are known thermally labile compounds generated in the decomposition of AIBN-like azo compounds.[12] Accordingly, only data obtained up to 50% conversion were used for the analysis. From the slopes of the Arrhenius plots the activation energies of the free and the immobilized initiator were calculated to be ca. 130 kJ $mol^{-1}$. This value is in close agreement to the reported $E_A$ of AIBN (124−130 kJ $mol^{-1}$).[13] It can therefore be concluded that neither the modification of AIBN with the ester and chlorosilane function nor the immobilization of the compound to silica gel has a significant influence on the thermal behavior of the azo moiety.

In order to check the reliability of this result, volumetric measurements on the decomposition of AIBN and $SiO_2$-AMCS were performed. In these measurements the amount of nitrogen that evolves during the decomposition of the azo compound was determined. This method measures the amount of decomposed initiator directly and is not influenced by side reactions that will influence the analysis by calorimetric methods. As shown in Table 1, the results of the volumetric experi-

**Table 1. Rates of Dissociation of AIBN and Surface-Attached Azo Compounds $SiO_2$-AMCS at 59 °C**

| initiator | method | $10^6k_{dec}$ ($s^{-1}$) |
|---|---|---|
| AIBN | diverse[13] | 7.8[a] |
| AIBN | volumetry | 7.7 |
| $SiO_2$-AMCS | volumetry | 7.4 |
| $SiO_2$-AMCS | DSC | 7.5 |

[a] Calculated from the kinetic data[13] for the reaction temperature of 59 °C

ments are in close agreement with the results of the DSC experiments.

The fact that the decomposition kinetics of the azo compounds are not affected by the tethering to the surface of the silica gel is not surprising, as many azo initiators, which are structurally close to AIBN, show identical thermal behavior. Differences occur only if functional groups or special steric situations influence the stability of the azo moiety or the radical obtained after thermal activation.[14] In the case of the initiators described here, the functional groups, which allow the attachment to the surface, are decoupled from the azo group by several methylene units, thus minimizing their influence on the decomposition behavior.

**Dilatometry.** In order to study the kinetics of the graft polymerization process, we first performed dilatometric measurements, as this method is a well-established technique for the investigation of solution polymerizations. Many studies have been performed on the polymerization of styrene using AIBN as an initiator and a large set of data is available for comparison.[15]

The rate of polymerization $\nu_P$ defined as the decrease of the monomer concentration [M] with time $t$, is given according to conventional kinetics of radical chain polymerization[16] by

$$\nu_P = -\frac{d[M]}{dt} = k[M][I]^{0.5} \quad \text{with} \quad k = k_p\left(\frac{2fk_d}{k_t}\right)0.5 \qquad (4)$$

In this equation $k_p$, $k_d$, and $k_t$ are the rate constants of propagation, azo decomposition, and termination respectively. [I] stands for the initiator concentration, and $f$ represents the radical efficiency factor.

The dilatometric method uses the volume contraction that occurs during polymerization to determine the amount of monomer converted to the polymer because the density of a polymer is usually larger than that of its monomer. In the case of polystyrene this contraction amounts to about 14.1% at quantitative conversion.[17] From the total volume of the reaction mixture at a specific time, the actual monomer concentration can be calculated according to

$$M(t) = \frac{V_t - V_\infty}{V_0}\,\frac{10^3}{[\rho^{-1}{}_M - \rho^{-1}{}_P]M_M}\ (\text{mol/L}) \qquad (5)$$

$V_t$ represents the volume at the time $t$, $V_0$ is the volume at $t = 0$, $V_\infty$ is the volume at 100% conversion, $\rho_{M,P}$ are the densities of monomer and polymer, respectively, and $M_M$ is the molecular weight of the monomer. To study the polymerization at the surface, several different experiments were performed. In one set of experiments the surface concentration of the initiator was varied by using azo-modified silica gels with different graft densities. For every run the same amount of silica gel was used so that changes in the total amount of initiator are only due to changes in the surface concentration of the initiator. The polymerizations were carried out in neat styrene at 60 °C. The different initiator concentrations are summarized in Table 2. The monomer concentration $[M]_t$ at a selected time $t$ was calculated from the volume changes according to eq 5. It is plotted as a function of time in Figure 3a for every run. From the slopes of the linear regression curves, $\nu_P$ was determined and listed in Table 2. It should be noted that the observed initial rates of polymerization are in close agreement with those of the polymerization of bulk styrene with AIBN if the same total concentrations are used. This is again an indication that the immobilization of the initiator does not influence the initiation step of the polymerization reaction significantly.

**Table 2. Rate of the Polymerization of Styrene Initiated with the Surface-Attached Azo Compound $SiO_2$-AMCS As Measured by Dilatometry**

| $\delta$ (azo) ($\mu$mol/g) | $\Gamma$ (azo) ($\mu$mol/$m^2$) | [M] (mol/L) | $10^3\nu_{Br}$ (mol/L) |
|---|---|---|---|
| 112 | 0.39 | 8.47 | 1.62 |
| 140 | 0.49 | 8.47 | 1.75 |
| 223 | 0.78 | 8.47 | 2.50 |
| 324 | 1.14 | 8.47 | 2.97 |
| 422 | 1.48 | 8.47 | 3.69 |
| 498 | 1.75 | 8.47 | 4.05 |
| 525 | 1.82 | 8.47 | 4.67 |
| 525 | 1.82 | 4.35 | 2.48 |
| 525 | 1.82 | 2.90 | 1.55 |
| 525 | 1.82 | 1.74 | 0.82 |
| 525 | 1.82 | 1.08 | 0.49 |

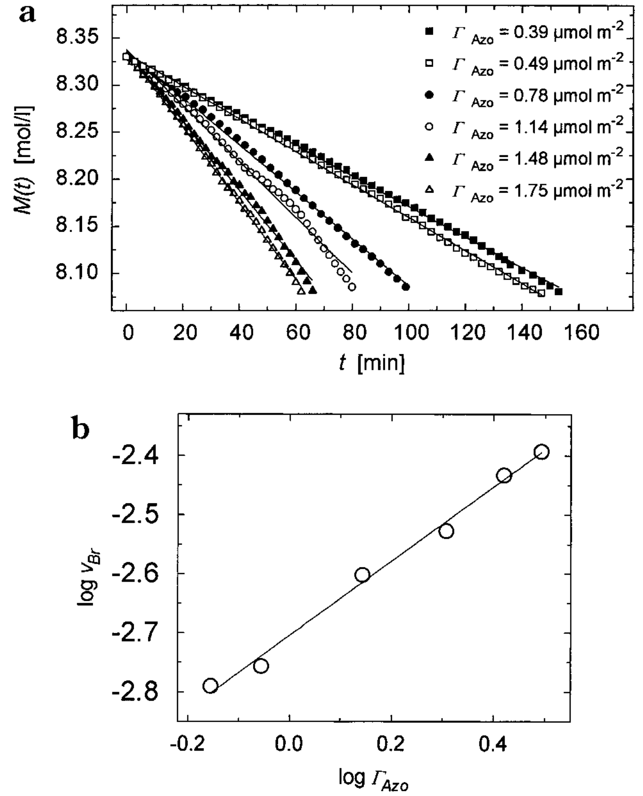

**Figure 3.** (a) Monomer concentration $M(t)$ as a function of polymerization time as derived from the volume contraction during polymerization; the area densities Γ(azo) of the initiators are given in the inset; bulk polymerization ($[M_0]$ = 8.47 mol $L^{-1}$), $T$ = 60 °C. (b) Plot of the logarithm of the rate of polymerization $\nu_{Br}$ versus the logarithm of the area densities Γ(azo).

It can be seen that at high initiator concentrations and longer polymerization times the relation between

$M(t)$ and $t$ is not strictly linear, but the rate of polymerization increases stronger than proportional with increasing reaction time. Increasing the reaction time, however, is equivalent to an increased conversion of the initiator and accordingly to a higher density of the attached chains. It should be noted that this increase in the rate of polymerization with increasing conversion can even be seen when the conversion of the initiator is well below 5% and conversion of the monomer is below 1%.

The dependence of the obtained rate constants $\nu_P$ on the initial surface concentration of initiator $\Gamma$ (Figure 3b) can be described according to

$$\nu_P = c\Gamma^{0.62\pm0.03} \qquad (6)$$

with $c$ being a combination of the rate constants of all reactions involved and the dependence of $\nu_P$ on the monomer concentration [M]. The increase in the rate of polymerization with increasing density of the attached chains is reflected in an increase of the exponent in eq 6 compared to a solution polymerization where a value of 0.5 is observed (eq 4).

A second set of dilatometry experiments was carried out at a fixed initiator concentration of 525 $\mu$mol/g of $SiO_2$ (1.8 $\mu$mol/m$^2$), but different monomer concentrations (1.08−8.47 mol L$^{-1}$) were used (Table 2). The total initiator concentration was 6.7 mmol L$^{-1}$, and the solvent was toluene in all cases. Again the monomer conversions were calculated from the volume contraction during polymerization using eq 5 and the values of $\nu_P$ were determined from the slopes of these curves (Figure 4a). In Figure 4b the logarithm of the overall rate of polymerization $\nu_P$ is plotted as a function of the initial monomer concentration [$M_0$]. From these values the following relationship was evaluated:

$$\nu_P = c'[M]^{1.11\pm0.03} \qquad (7)$$

$c'$ contains all rate constants and the dependence of $\nu_P$ on the initiator concentration. Also, here the exponent is significantly higher than the one observed for a solution polymerization (eq 4). The error margins for the exponents given in eqs 6 and 7 are the standard deviations. In control experiments using nongrafted initiators it was proven that the obtained differences between the surface polymerization and the solution polymerization are well outside the experimental error of the dilatometry experiments.

It can be seen from the results of the dilatometric measurements that the kinetics of the polymerization in ultrathin films is in some sense similar to that of polymerization reactions in solution but the measured rates of polymerization in the $SiO_2$-PS system are dependent on the number of the already formed, attached chains. A quantitative picture of how the surface polymerization proceeds cannot be evaluated from dilatometry measurements alone for several reasons. Firstly, in dilatometry experiments, only the total polymerization reaction combining the one at the surface and the one in solution, is monitored. The chains growing in solution are started by the second, nonattached radical, by thermally induced polymerization of the monomer or by transfer of a surface-attached radical to monomer and solvent. Secondly, for a quantitative analysis and evaluation of the molecular weights of the products, it is problematic that the dilatometry experiments were always carried out until the same volume change was reached; i.e., the same conversion of the monomer was obtained. Consequently, the graft densities and the molecular weights of the attached chains differ in all experiments, which makes a detailed understanding of the process difficult. Therefore, in another series of experiments, polymerization reactions were carried out during which the reaction parameters were systematically varied.

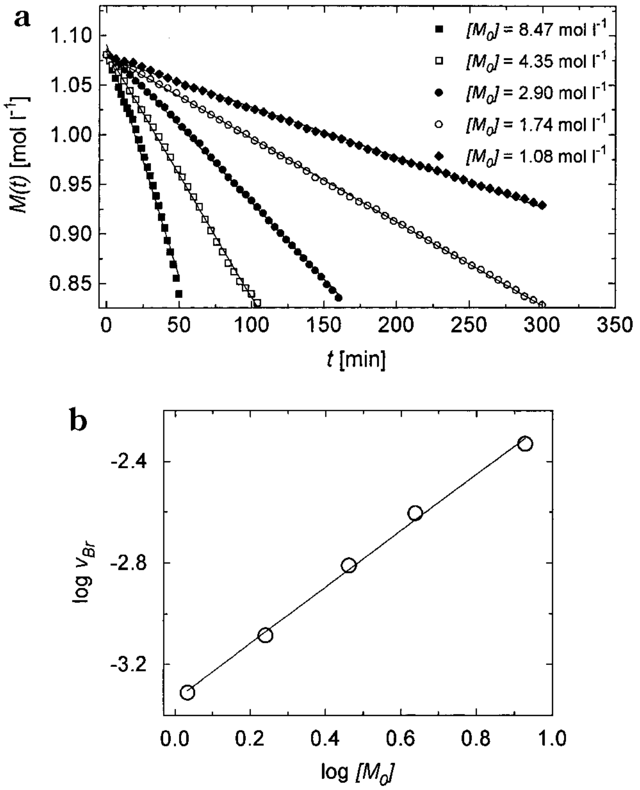

**Figure 4.** (a) Monomer concentration $M(t)$ calculated from the volume contraction during polymerization as a function of polymerization time. The starting monomer concentrations are given in the inset; for clarity the data for the higher monomer concentrations have been shifted vertically by subtraction so that all curves start at the same [$M_t$] value: i.e., −7.25 for □, −3.09 for ●, −1.70 for ○, and −0.59 for ◆; $\Gamma$(azo) = 1.82 mol/m$^2$, $T$ = 60 °C. (b) Plot of the logarithm of the rate of polymerization $\nu_{Br}$ versus the logarithm of starting monomer concentration [$M_0$].

**Variation of Polymerization Temperature.** With increasing temperature the rate of decomposition of the initiator increases strongly. Thus more polymer radicals grow simultaneously, leading to a higher concentration of growing radicals in the film. This increases the probability that two of them are generated and grow in such close vicinity that the active centers meet and terminate each other by recombination or disproportionation. Thus the degree of polymerization is strongly reduced with increasing temperature. The total mass of the attached polymer immobilized to the silica surface is therefore expected to be strongly influenced by the temperature during polymerization.

Several polymerization reactions were performed, each of them being identical in all parameters except for the reaction temperature. On the basis of the kinetics of azo decomposition, each run was stopped after a polymerization time had passed, which corresponded to an initiator conversion of 50%. The temperatures applied in these experiments ranged from

**Table 3. Mass Density $\delta$ and Average Molecular Weight $M_n$ of SiO$_2$-PS as a Function of the Temperature during Polymerization (Initiator: SiO$_2$-AMCS (Graft Density 525 $\mu$mol/g = 1.82 $\mu$mol/m$^2$)**

| $T$ (°C) | $t$ (h) | $\delta$ (g of PS/g of SiO$_2$)[b] | $10^{-3}M_n$ (SiO$_2$-PS)[c] | $10^5 n$ (mol)[d] |
|---|---|---|---|---|
| 50 | 96 | 9.8 | 274 | 3.5 |
| 60 | 21.5 | 7.3 | 177 | 4.1 |
| 65 | 10 | 4.9 | 108 | 4.5 |
| 70 | 4 | 2.2 | 42 | 5.2 |
| 80 | 1 | 1.1 | 12 | 9.2 |
| 90 | 0.4 | 1.0 | 10 | 10 |

[a] Initiator: 0.5 g SiO$_2$-AMCS (graft density 525 $\mu$mol/g); $[M_0] = 1.74$ mol/L. [b] Calculated from elemental analysis. [c] According to GPC analysis after degrafting. [d] Moles of grafted polymer; calculated from graft density $\delta$ and molecular weight of the surface attached polymer $M_n$ (SiO$_2$-PS).

50 to 90 °C. The polymerization times varied accordingly from 0.4 to 96 h. Table 3 summarizes the conditions and results of these measurements. The values of the molecular weights of the attached polystyrene chains were determined by GPC after degrafting.

Assuming that the efficiency for the initiation step is not strongly affected by the temperature variation, each sample should consist of the same number of immobilized polystyrene chains. Indeed, as can be seen from Table 3, the total number of moles of polymers $n$ formed on the SiO$_2$ surfaces is roughly identical for all samples except for those generated at very high temperatures. The reason for the observed deviations could be an increase of the radical efficiency at higher temperatures due to a lower viscosity of the solutions or they could be simply due to the fact that at the short polymerization times in the high-temperature experiments the time required for thermal equilibration of the reaction medium became close to the total reaction time. Additionally, it has to be considered that the reaction time was calculated from the decomposition kinetics of the initiator and a small experimental error in the determined activation energy would give significant deviations in the rate constants.

In Figure 5a,b it can be seen that both the mass of the attached polymer $\delta$ and the molecular weight $M_n$ of the immobilized polymers decrease strongly with increasing temperature. Since in all cases the polymerizations were carried out until the same number of polymer molecules had formed, the decrease in the graft density should be only due to a decrease in the chain length of the immobilized macromolecules. This is shown in Figure 6 directly where the mass density of the attached chains $\delta$ is shown as a function of the molecular weight of the attached chains. From the linear relationship it can be concluded that the temperature decrease of the mass of the attached polymer at higher temperatures is indeed due only to changes in the molecular weight of the surface-bound material.

The temperature dependence of the number average degree of polymerization $P_n$ and the overall activation energy $E_{A,P}$ can be calculated according to[16]

$$\ln P_n = A - \frac{E_{A,P}}{RT} \tag{8}$$

In this equation the constant $A$ contains the preexponential factors of the Arrhenius expressions for the different processes (initiation, propagation, and termination) and other constants (i.e., the different concentrations). The total activation energy $E_{A,P}$ is the summation of the energies of all elementary reaction steps of the radical chain polymerization.[17] According to eq 8, a plot of ln $P_n$ against $T^{-1}$ should give a linear relationship and $E_{A,P}$ can be calculated from the slope of the regression curve. This dependence can indeed be observed roughly for the data of our experiments, as shown in Figure 7. From this plot a value of $E_{A,P} = 92 \pm 15$ kJ mol$^{-1}$ can be calculated. This result is in agreement with the values reported in the literature for the AIBN-initiated styrene polymerization that range from 85 to 95 kJ mol$^{-1}$.[18]

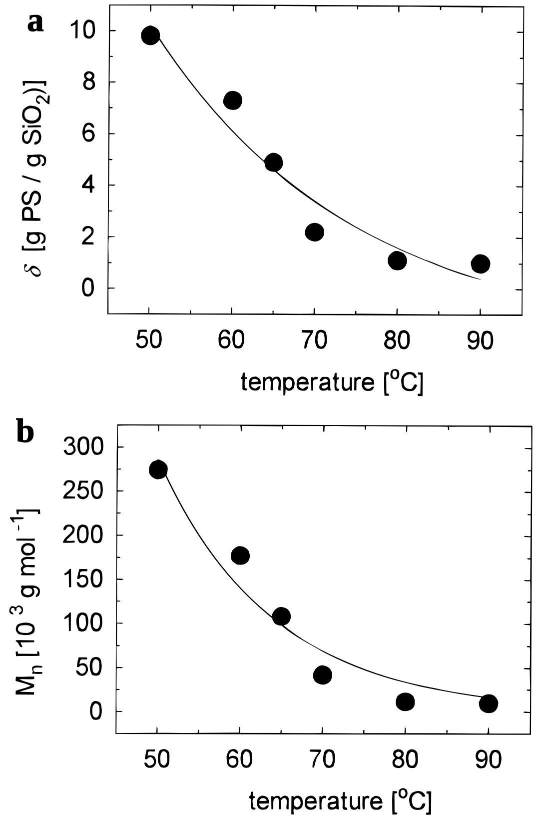

**Figure 5.** (a) Graft density $\delta$ and (b) average molecular weight $M_n$ of the covalently attached polymers as a function of temperature during the polymerization reaction; $\Gamma$(azo) = 1.82 mol m$^2$, $[M_0] = 1.74$ mol L$^{-1}$.

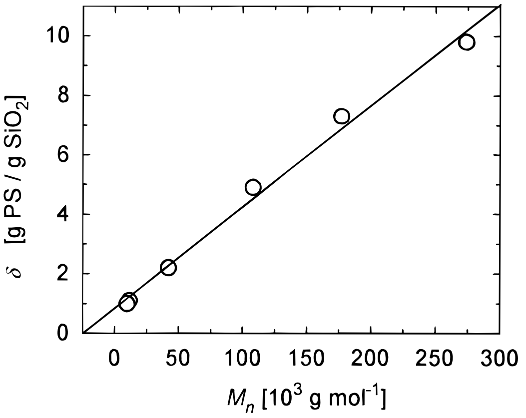

**Figure 6.** Plot of the graft density $\delta$ versus average molecular weight $M_n$ of the covalently attached polymers from the polymerization reactions described in Figure 5.

**Variation of Polymerization Time.** The polymerization with surface-attached initiators is different from solution polymerizations in so far as all formed

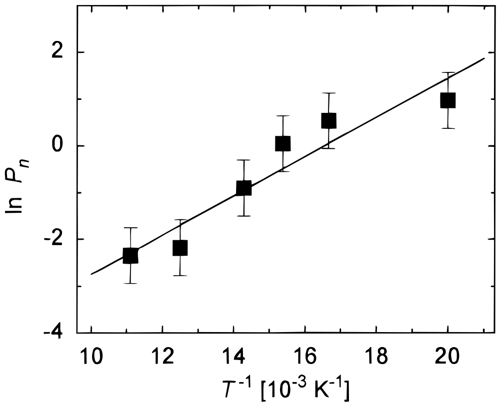

**Figure 7.** Arrhenius plot of the relationship between the degree of polymerization $P_n$ and the temperature $T$ applied during radical graft polymerization of styrene using immobilized initiators.

polymer chains are located in a small zone at the surface of the substrate. An important factor for this reaction is therefore the conversion of the initiator, which can be controlled by changing the polymerization time. To study the influence of the graft density of the already attached polymer chains on the formation of new polymer molecules, we performed several nearly identical polymerization reactions, during which samples were withdrawn after different periods of time.

The initiator used in the experiments had a graft density of $\delta$(azo) = 525 $\mu$mol $g^{-1}$; the total initiator concentration was 3.2 mmol $L^{-1}$. The starting styrene concentration was 2.9 mol $L^{-1}$ (i.e., styrene/toluene 1/2 v/v). Samples were withdrawn after 1.5, 3, 4.5, 6, 8, and 10 h. All samples were extracted until no more nonbonded polymer could be separated. The products were analyzed by gravimetric measurements, elemental analysis, and GPC. For GPC investigations the covalently bonded polymer material was detached from the surface by treatment of the $SiO_2$-polystyrene samples with *p*-TsOH/MeOH in toluene, as described above. From the results of combustion analysis the graft density $\delta$ (in g of PS/g of $SiO_2$) of each sample was calculated. In Figure 8a the amount of the attached material is shown as a function of the polymerization time. It can be seen that the graft density $\delta$ increases steadily from about 0.6 g of PS/g of $SiO_2$ (or 30 wt %) after 1.5 h up to 10 g of PS/g of $SiO_2$ (91 wt %) after 14 h of polymerization. It should be noted that this is not the maximum amount of polystyrene that can be covalently bonded to silica gel. If different conditions are employed, even higher graft densities can be obtained, as will be discussed in more detail further below.

The results of the GPC measurements on the degrafted PS are depicted in Figure 8b. It can be seen clearly that the molecular weights of the grafted polystyrene molecules are not constant but increase with increasing polymerization time. After short polymerization times (1.5 h) molecular weights of 75 000 ($M_n$) are measured. The molecular weights increase steadily with polymerization time and after 14 h, for example, a value of 175 000 is obtained. In contrast to that, the molecular weight of the nonbonded polymers stays constant at about 130 000. This value is close to the predicted molecular weight as calculated from the Mayo equation using the respective concentrations of all reactants and the rate constants as described in the literature.[13] It should be specifically emphasized that the two polymers have different molecular weight averages and molecular weight distributions, although they have been prepared in the same solution, though in different locations, one in the surface film and the other in solution.

This increase of the average degree of polymerization with increasing polymerization time should be also reflected in the polydispersity of the grafted polymer. In Figure 8c the polydispersity $M_w/M_n$ of the samples described above is depicted. The polydispersities range between $M_w/M_n = 1.5$ and 2. Samples, which were polymerized using still longer polymerization times had slightly higher dispersities. However,it should be noted that the polydispersities of all PS samples measured in this study were between $M_w/M_n = 1.5$ and 3 and therefore remain very close to values observed in a typical radical chain polymerization in solution: Therefore it can be concluded that the surface attachment does not cause an excessive broadening of the distribution. In fact at very short reaction times polydispersities are obtained that are close to theoretical values for a radical chain process. At longer reaction times, however, the polydispersity increases steadily. This increase in the polydispersity is caused by the fact that with increasing reaction time increasingly longer chains are generated, thus increasing the average molecular weight and the width of the distribution function.

Using the graft density $\delta$, the molecular weight $M_n$, and the specific surface area of the initiator, the area density of the attached chains as a function of polymerization time can be calculated. Since the kinetics of the azo decomposition is known, the number of initiator molecules which have decomposed up to a specific time can be calculated and compared to the number of polymer chains that have actually formed. From this comparison the radical efficiency factor $f$ can be derived. The obtained values of the radical efficiency are depicted in Figure 8d. They show that the overall efficiency $f$ is quite high despite the fact that the initiators are bound to the surface and all radicals are generated in close vicinity to each other. Additionally, it can be seen that the efficiency decreases slightly from 0.4 at the beginning to 0.3 at the end of the polymerization reaction.

However, it should be noted that the graft density of the $SiO_2$-PS derivatives did not level off after 14 h at 60 °C as then only 40% of the initiator molecules initially present have decomposed. Several other experiments were performed and samples were withdrawn after chosen periods of time and handled as described above and characterized by elemental analysis and GPC (after cleavage). For all polymerizations $SiO_2$-AMCS initiator with the same graft density ($\delta$(AMCS) = 525 $\mu$mol $L^{-1}$) was used. However, different monomer concentrations were employed. Especially when the polymerizations reactions were driven to high conversion, large amounts of bound and free polymer are formed and therefore more diluted solutions were required to keep the viscosity at a practicable level. As the monomer concentration influences the molecular weights of the attached polymer chains, different mass densities were obtained when samples were polymerized up to the same conversion (i.e., polymerization time). These differences can be eliminated if the number of immobilized macromolecules per surface area, i.e., the area density $\Gamma$, or the corresponding distance between the anchoring sites is calculated. The graft density $\Gamma$ as a function of the polymerization time for a large

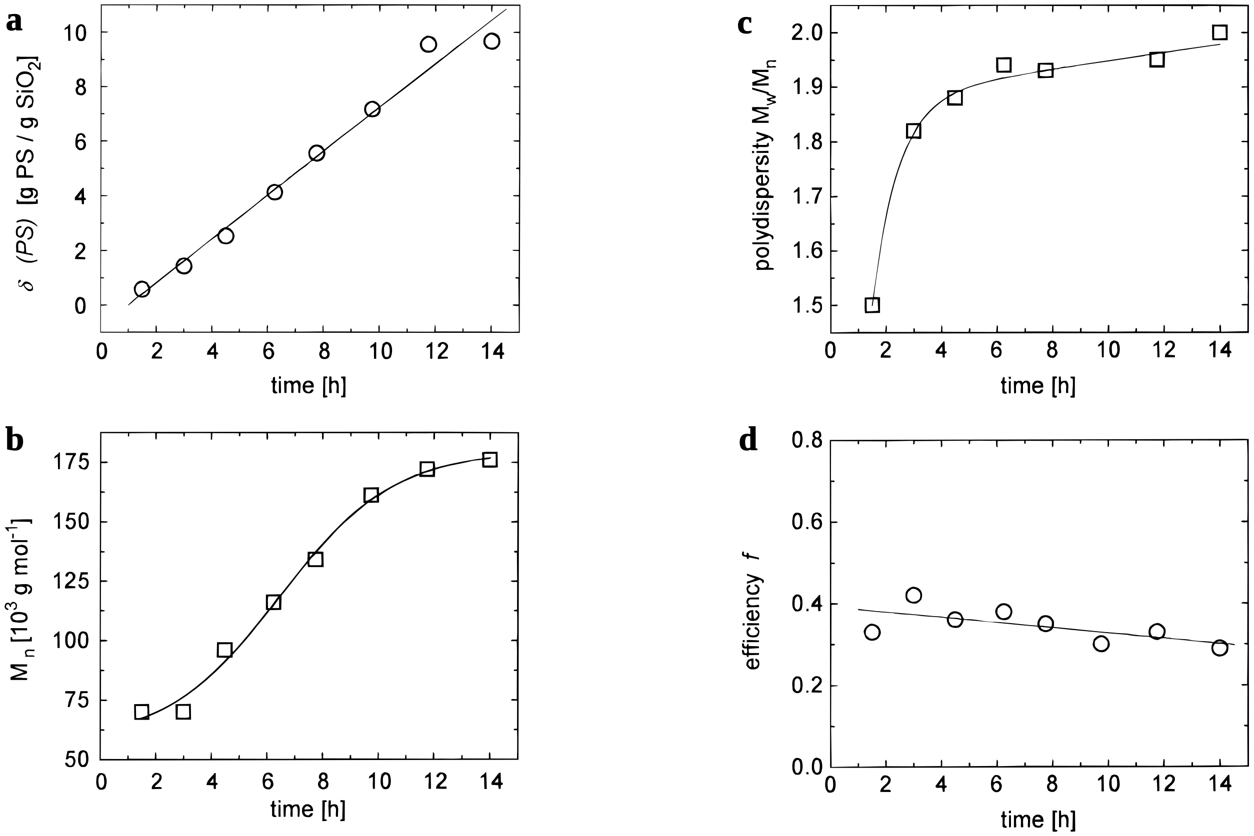

**Figure 8.** Results of the variation of azo conversion (i.e., polymerization time) during polymerization of styrene with $SiO_2$-AMCS: (a) graft densities $\delta$(PS); (b) molecular weights $M_n$; (c) polydispersity of the covalently attached polymers; (d) radical efficiency (calculated from $\delta$(azo), $\delta$(PS), and $M_n$ using the decomposition kinetics of the initiator). $M_n$ and the polydispersity were determined by GPC after degrafting by cleavage of the ester break seal. $\delta(\text{azo}) = 525\ \mu\text{mol g}^{-1}$, $[M_0] = 2.9$ mol $L^{-1}$, T = 60 °C.

number of experiments is shown in Figure 9a. It can be seen from this plot that the amount of immobilized polystyrene can be controlled up to very high grafting densities using this "grafting from" method. In the experiments carried out for 60 h about 25 g of PS/g of $SiO_2$ (which is roughly equal to 100 mg of polymer/m$^2$) could be attached to the surface of the silica gel. It should be noted that such a material consists of about 95 wt % of a surface-bound monolayer in the original sense of the definition, i.e., a single layer of surface-attached (polymer) molecules.

Furthermore, it can be seen that all experimental values fall very closely onto a single (master) curve describing the kinetics of the growth of the attached layer of polymer molecules. In fact these kinetics could be calculated from the initial graft density of the attached azo molecules at the beginning of the polymerization reaction, the kinetics of the azo decomposition from the DSC experiments, and the radical chain efficiency factor. The solid line in Figure 9a shows the result of such a calculation of the number of attached chains per surface area in which the radical chain efficiency factors (and their conversion dependence) from Figure 8d were used. The good agreement between the calculated and the measured values shows that the surface polymerization with the surface-attached initiators can be well controlled.

A more intuitive picture about the steric situation at the surface is given when not the number of moles per area but the average distance $d$ between two anchoring sites is used. These values can be calculated from the area density Γ according to

$$d = \sqrt{\frac{N_A}{\Gamma}} \tag{9}$$

$N_A$ is here the Avogadro number. The values for the distances between the anchoring sites as a function of polymerization time (and accordingly azo conversion) are shown in Figure 9b. Even after short polymerization times the distance between the anchor points of two tethered chains is less than 8 nm. At that time only ca. 10% of the initiator molecules have decomposed. Consequently, the distance $d$ decreases further to 3−2 nm if the conversion is increased. As the molecular weights of the grafted polymers are known, the radii of gyration of corresponding polymer molecules in solution can be calculated according to

$$\langle R_G \rangle = K_\alpha {M_w}^\alpha \tag{10}$$

with $K_\alpha = 1.27 \times 10^{-2}$ and $\alpha = 0.59$.[19]

The values are summarized and compared to the distances $d$ in Table 4. According to these calculations, the distance $d$ is smaller than the diameter of a coil of the same molecular weight in solution already at low initiator conversion. The distance of the anchoring points of the chains on the surface are much closer than the dimensions of the projection of the corresponding polymer molecule in solution ($2\langle R_G \rangle$).

**Control of the Molecular Weight.** A very notable difference between a radical chain polymerization in solution and the corresponding reaction at surfaces concerns transfer reactions. While with polymerization in solution the active center is only transferred and a new polymer chain is started, with polymerizations of

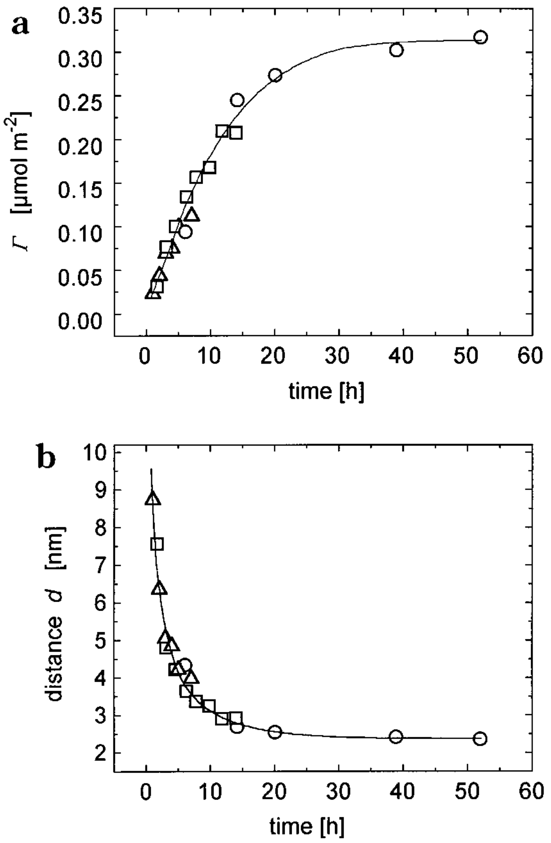

**Figure 9.** (a) Area densities of and (b) averaged distances between the covalently attached polystyrene molecules as a function of polymerization time. The data for three different runs are plotted using different symbols; for experimental details, see the text. The solid line in (a) is a function composed of the initiator decomposition kinetic and a function describing the time dependence of the radical efficiency during polymerization (cf. text).

**Table 4. Comparison of the Average Distance $d$ between Anchor Points of the Grafted Polymer Chains with the Dimensions of Polymer Molecules of the Same Molecular Weight in Solution (2⟨$R_G$⟩)**

| time (h) | $10^{-3}M_w$ | 2⟨$R_G$⟩[a] (nm) | $d$ (nm) |
|---|---|---|---|
| 1.5 | 100 | 22.6 | 5.7 |
| 3 | 127 | 26.1 | 3.6 |
| 4.5 | 180 | 32.0 | 3.2 |
| 6 | 227 | 36.7 | 2.7 |
| 8 | 259 | 39.7 | 2.5 |
| 10 | 290 | 42.4 | 2.4 |
| 12 | 337 | 47.6 | 2.2 |
| 14 | 352 | 46.4 | 2.2 |

[a] ⟨$R_G$⟩ was calculated according to eq 10.

surface-attached species the transfer to monomer, solvent, or transfer agents causes a complete stop of the graft polymerization. Although also in this case a new polymer chain is started, this new chain leads only to the formation of additional free polymer in solution and no more segments are added to the film. As the nonattached polymer is removed after completion of the reaction, the effect of chain transfer is identical to that of a termination reaction.

To study the effect of transfer agents on the surface polymerization, dodecanethiol was added to the reaction mixture. Already during workup of the reaction mixture it was observed that much more nonattached polymer was isolated from the solution, while in all polymerization reactions without transfer agent more graft polymer than free polymer was obtained as described above. Upon addition of small amounts of the thiol the situation thus completely reverses and 2–4 times more free polymer than graft polymer is obtained. This reflects the fact that now almost all chains that have been started cause the growth of polymer in solution.

**Table 5. Influence of Addition of 1-Dodecanthiol on the Radical Chain Polymerization of Styrene with the Surface-Attached Azo Compound[a] $SiO_2$-AMC**

| mol of added thiol (µmol) | mass density $\delta$ (g of polymer/g of $SiO_2$) | $M_w$(graft polymer) |
|---|---|---|
| 0.90 | 0.11 | 13 000 |
| 0.42 | 0.12 | 19 000 |
| 0.22 | 0.22 | 37 000 |
| 0.10 | 0.37 | 72 000 |
| 0.00 | 3.3 | 356 000 |

[a] Reaction conditions: 1 g of $SiO_2$-azo (graft density 500 µmol/g); 200 mL of toluene, 100 mL of styrene; temperature 60 °C; polymerization time 10 h; degrafting as described in the text.

In Table 5 it is shown that upon addition of only $2 \times 10^{-4}$ mol % thiol the mass of the attached polymer is reduced by 1 order of magnitude due to a reduction in the molecular weight of the attached chains.

## General Discussion

From the data described above a model for the mechanism of the radical chain polymerization in restricted geometry can be developed. A discussion and comparison to the situation for solution polymerizations will follow the elementary processes involved.

**Initiator Decomposition and Start of the Polymerization.** From the dilatometry experiments it can be concluded that initiation and start of the polymerization reaction with the surface-attached radicals proceed in a way very similar to that of a solution polymerization. The only difference is perhaps a decrease of the radical efficiency caused by the surface attachment. While for the solution polymerization of styrene with AIBN a radical efficiency factor of 0.5–0.7 (at low conversion) is reported,[19,21] in the experiments described here the efficiency with which decomposed azo molecules actually start a polymer chain is between only 0.3 and 0.4. One trivial explanation for this observation could be that attached low molecular weight polymer is lost during the degrafting reaction and the subsequent workup. It should be noted that the efficiency reported in this paper is based on the number of polymer molecules isolated and the number of initiator molecules decomposed according to the measured rate constants. However, the solutions into which the polymer was precipitated have been checked and a significant loss of polymer due to the experimental procedure can be excluded.

Furthermore, it can be seen that in the experiments with the surface-attached initiator the total radical efficiency is decreasing strongly with increasing conversion of the initiator, even though the conversion of monomer is still quite small under the chosen conditions (i.e., only a few percent). This behavior contrasts strongly to that of a conventional AIBN/styrene polymerization, where a strong reduction of the radical efficiency factor is observed only at high conversion of monomer where the viscosity of the polymerization medium is strongly increased.[21]

To explain this stronger influence of the conversion of the initiator on the radical efficiency, the specific situation at the $SiO_2$ surface must be considered.

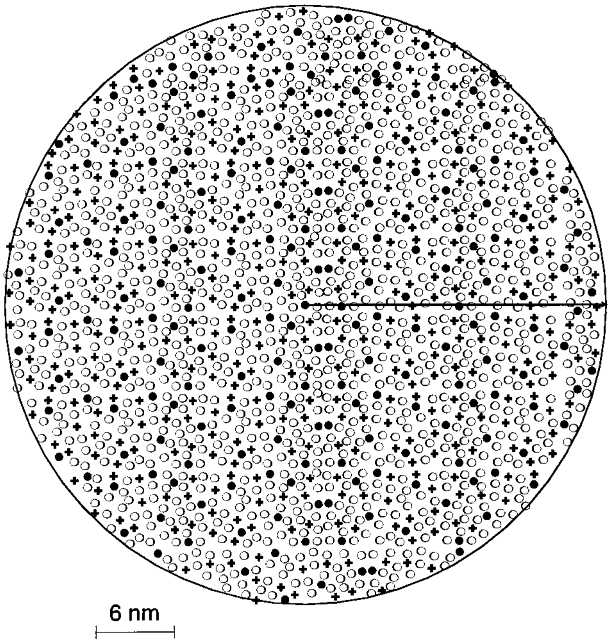

**Figure 10.** Schematic illustration of the surface coverage of the silica surface (to scale) after 10 h of polymerization at 60 °C: ○ = still intact initiator molecules, + = decomposed, but initiator molecules, which did not start a polymer chain, ● = grafted polystyrene chains. The symbols only mark the anchoring sites of the molecules and do not describe their size. The circle depicts the size of the projection of one polymer molecule $\langle R_G \rangle$ in solution with $M_w = 290\,000$.

Although the radical center of the covalently attached part of the initiator is connected to the surface by a long, flexible alkyl chain, the diffusion constant might still be lowered and the rate of diffusion of the radical out of the cage of solvent and monomer molecules might be decreased. This situation would enhance the probability of direct deactivation of the primary radicals, lowering the value of $f$. Secondly, the decrease of the radical efficiency might be the consequence of the high polymer concentration near the surface of the substrate. Consequently, the viscosity of the medium can be expected to be higher at close proximity to the surface, favoring the recombination of the primary radicals.

Despite the observed differences between a polymerization reaction at a surface and in solution, however, it can be stated that the efficiency of the initiation process of the surface polymerization is high enough to allow the formation of a layer of polymer molecules with a high graft density.

**Propagation.** Once the primary radicals leave the solvent and monomer cage they start a polymerization reaction and two macroradicals—one in solution and the second tethered to the surface—grow to form the polymer. In both cases high molecular weight polymer is formed. The degrees of polymerization obtained in the different reactions are in rough agreement with values calculated according to conventional theory for radical chain polymerization when the values for the rate constants of the solution polymerization, the monomer and initiator concentrations, and transfer reactions are considered.

The analysis of grafting density and molecular weights of the $SiO_2$-PS derivatives shows that over the whole period of time studied the distance between two anchoring sites is smaller than the solution dimensions of the macromolecules. This situation is described schematically in Figure 10. In the drawing, which is prepared according to scale, the situation on the $SiO_2$ surface after polymerization for 10 h at 60 °C is shown. The different symbols depict the anchoring sites of the different species immobilized to the substrate (note that the size of the spots is not related to the dimensions of the molecules). At this point in time, about 30% of the azo molecules have been thermally decomposed and the other 70% are still intact. Most of the generated radicals were caught in the solvent cage and were not able to start a polymerization reaction. About 30−40% of the decomposed initiator molecules, however, successfully started a polymerization reaction. The polymer molecules generated under these conditions have a molecular weight (weight average $M_w$) of about 290 000. With eq 10 the radius of gyration of a polymer coil in solution with such a molecular weight is calculated to be about 21.5 nm. In Figure 10 a projection of one single PS molecule in solution with such a radius of gyration is depicted. Already at this low conversion roughly 170 other polymer molecules compete for the same space at the surface of the substrate. At higher conversion and/or with higher molecular weights of the attached chains, even more polymer chains compete for the available space.

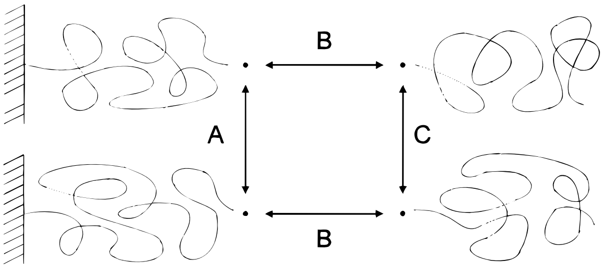

**Figure 11.** Schematic illustration for possible termination reactions between two simultaneously growing chains during a radical graft polymerization.

**Termination.** Probably the most significant difference between polymerization in solution and polymer formation in the thin film at the surface is given by the steady increase of the molecular weight of the grafted polystyrene chains with increasing conversion of the initiator. In contrast to that the molecular weight of the nonbonded material remains constant.

To explain this behavior, the different possibilities for bimolecular termination of the growing chains have to be considered. They are schematically depicted in Figure 11. In this drawing no distinction is made whether the termination occurs by recombination or disproportionation. The reaction of two radicals growing on different particles is very unlikely as the concentration of particles is low and such a termination would require the interpenetration of the two polymer films surrounding the growing particles. Therefore this pathway is not considered in the following.

One possibility for a termination reaction is the spontaneous deactivation of two simultaneously growing polymer radicals on the surface. If the polymerization is carried out at low temperatures, the average distance between two radicals is very large as the average lifetime of the radicals is several orders of magnitude smaller than the half-life of the initiator. However, with increasing temperature the average distance between two active radicals decreases and the molecular weight of the growing, attached chains is decreased, as shown above.

A second possibility is given by the reaction between a grafted and a freely growing chain. Freely growing chains can originate from the second, nonattached radical generated during homolysis of the initiator, from transfer reactions or from a thermally initiated polymerization. As the concentration of growing chains in solution is not negligible, this pathway for deactivation may be even the predominant one under the given reaction conditions. Indeed, the concentration of chains growing in solution is of the same order of magnitude as in a conventional radical chain polymerization reaction. The importance of this pathway for deactivation of surface-attached chains becomes apparent when it is considered that always 1.5−6 times more grafted than free polymer can be isolated. The reason for this, at first sight, unexpected behavior is that all combination reactions between free chains and surface-attached chains reduce the amount of free polymer and increase the amount of attached material. An additional indication for the importance of this pathway for the deactivation of the growing surface-attached chains is that, under conditions under which the concentration of radicals in solution is strongly reduced (i.e., if low surface area substrates, such as planar substrates, are employed and thus only a small number of initiator molecules is involved), graft polymer is obtained with an order of magnitude higher molecular weight ($M_n$ of more than $10^6$), although the reaction conditions are otherwise exactly the same.[5] The reason for this difference is that when planar substrates are employed, the total number of surface-attached initiator molecules and accordingly the number of chains started by the second, nonattached initiator fragment are in a typical experiment several orders of magnitude lower than in the experiments with the high surface area silica gels described here. The low concentration of growing chains in solution, however, makes a deactivation of a growing surface-attached chain by a chain growing in solution highly improbable and other reaction pathways will determine the length of the attached polymer molecules.

For deactivation of a surface-attached chain by a chain growing in solution it is necessary that the nonbonded chain diffuses into the polymer film to reach the surface-attached reaction partner. This diffusion process, however, becomes more and more difficult with increasing graft density, as the polymer has to diffuse against the concentration gradient into the film. Therefore, the termination reaction is slowing down with increasing graft density of the polymer molecules due to the confinement of the molecules to a thin surface layer. This effect could be termed a “two-dimensional Trommsdorff (gel) effect”. In contrast to a solution polymerization, this slowing down of the termination reaction is only dependent on the graft density of the attached chains and can already be observed when the monomer conversion is very low, i.e., only a few percent. During a solution polymerization of styrene, a significant increase of the rate of polymerization due to a decrease in the rate of termination is only observed if the conversion of the monomer is almost quantitative and is not observed at all if the polymerization solutions are sufficiently dilute.[16,20] When the polymerization reactions described here are carried out at high monomer concentrations and high conversion, a conventional Trommsdorff effect can be observed in addition to the 2D-gel effect observed during early stages of reaction.

However, it should be noted, that the 2D-gel effect occurs only if termination of surface-attached radicals by chains growing in solution is an important pathway of termination. If the reaction conditions are chosen in such a way that this reaction path becomes less important (e.g., if the major portion of the chains growing at the surfaces is terminated through radical transfer, or if the polymerization reaction is carried out in such a way that the radical concentration in solution is very small, e.g., by using planar, low surface area substrates), this effect cannot be observed.

## Conclusions

The mechanism of the polymerization reaction induced by a self-assembled monolayer of initiators attached to a solid surface shows many similarities and some differences to polymerization reactions in solution. Initiation and growth of the polymer at low conversion of a surface-attached initiator are very comparable to polymerization in solution. Differences in the polymerization mechanism between surface and solution polymerization are mostly due to differences in the termination reactions. If the termination of surface-attached chains by free chains growing in solution becomes a significant pathway of termination, the rate of termination decreases with increasing graft density of the attached chains. This is due to the fact that the free chains have to diffuse against the concentration gradient into the film in order to allow a termination reaction to occur. Consequently, the molecular weight of the newly growing chains becomes a function of the number of already attached chains. Another difference between solution polymerization and surface polymerization is that in the latter one all transfer reactions to either solvent or monomer or transfer agent lead to a termination of the growth of the surface-attached chains and the film growth is completely stopped.

Although the surface attachment leads to a slight decrease in the radical efficiency of the initiator, it still allows the formation of high molecular weight polymer with a high graft density. During the polymerization process a low molecular weight compound is replaced by a high molecular weight polymer, a very high density of the attached chains can be achieved, and large quantities of polymer can be covalently linked to the substrate. The mass density of the attached chains and therefore the thickness of the surface bound layer can be readily controlled, by controlling either the graft density or the molecular weight of the attached chains.

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## References and Notes

(1) (a) Krenkler, K. P.; Laible, R.; Hamann, K. *Angew. Makromol. Chem.* **1953**, *53*, 101. (b) Tsubokawa, N.; Hosoya, M.; Yanadori, K.; Sone, Y. *J. Macromol. Sci. Chem.* **1990**, *A27*, 445. (c) Tsubokawa, N.; Kuroda, A.; Sone, Y. *J. Polym. Sci.* **1989**, *27*, 1701. (d) Ben Ouada, H.; Hommel, H.; Legrand, A. P.; Balard, H.; Papirer, E. *J. Colloid Interface Sci.* **1988**, *122*, 441. (e) Bridger, K.; Vincent, B. *Eur. Polym. J.* **1980**, *16*, 1017.

(2) Zajac, R.; Chakrabarti, A. *Phys. Rev. E* **1995**, *52*, 6536.

(3) Rühe, J. Thesis (Habilitationsschrift), University of Bayreuth, 1995.

(4) Prucker, O.; Rühe, J. Submitted for publication.

(5) (a) Tsubokawa, N.; Hayashi, S. *J. Macromol. Sci., Chem.* **1995**, *A32*, 525. (b) Tsubokawa, N.; Ishida, H.; Hashimoto, K. *Polym. Bull.* **1993**, *31*, 457. (c) Boven, G.; Folkersma, R.; Challa, G.; Schouten, A. J. *Polymer* **1991**, *32*, 50. (d) Laible, R.; Hamann, K. *Angew. Makromol. Chem.* **1975**, *48*, 97.

(6) (a) Halperin, A.; Tirrell, M.; Lodge, T. P. *Adv. Polym. Sci.* **1992**, *100*, 31. (b) Special issue: *Macromol. Rep.* **1992**, *A29* (Suppl.2). (c) Szleifer, O.; Carignano, A. *Adv. Chem. Phys.* **1996**, *94*, 165.

(7) Wittmer, J. P.; Cates, M. E.; Johner, A.; Turner, M. S. *Europhys. Lett.* **1996**, *33*, 397.

(8) Meier, L. P.; Shelden, R. A.; Caseri, W. R.; Suter, U. W. *Macromolecules* **1994**, *27*, 1637.

(9) Nuyken, O.; Gerum, J.; Steinhausen, R. *Makromol. Chem.* **1979**, *180*, 1497.

(10) Torfs, J. C. M.; Deij, L.; Dorrepaal, A. J.; Heijens, J. C. *Anal. Chem.* **1984**, *56*, 2863.

(11) Starnes, W. H.; Plitz, I. M.; Schilling, F. C.; Villacoprta, G. M.; Park, G. S.; Saremi, A. H. *Macromolecules* **1984**, *17*, 2507.

(12) (a) Jaffe, A. B.; Sinner, K. J.; McBride, J. M. *J. Am.Chem. Soc.* **1972**, *94*, 8510. (b) Hammond, G. S.; Trapp, O. D.; Keys, R. T.; Neff, D. L. *J. Am. Chem. Soc.* **1959**, *81*, 4878. (c) Bevington, J. C.; Troth, H. G. *Trans. Faraday Soc.* **1962**, *58*, 186.

(13) Masson, J. C. In *Polymer Handbook*, 2nd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley& Sons: New York, 1989; p II/2.

(14) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99.

(15) Braun, D.; Cherdron, H.; Kern, W. *Praktikum der makromolekularen organischen Chemie*, 3rd ed.; Hüthig: Heidelberg, 1979; p 166.

(16) See, e.g.: Odian, G. *Principles of Polymerisation*, 3rd ed.; Wiley: New York, 1991, Chapter 3.

(17) (a) Rudd, J. In *Polymer Handbook*, 2nd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley& Sons: New York, 1989; p V/82. (b) Fleischer, D. *Ibid*, p III/9.

(18) (a) Henrice-Olive, G.; Olive, S. *Makromol. Chem.* **1960**, *37*, 71. (b) Mahabadi, H. K.; O'Driscoll, K. F. *J. Macrol. Sci., Chem.* **1977**, *A11*, 967. (c) Soh, S. K.; Sundberg, D. C. *J. Polym. Sci., Chem. Ed.* **1982**, *20*, 1345.

(19) Wintermantel, M.; Antonitti, M.; Schmidt, M. *J. Appl. Polym. Sci., Appl. Polym. Symp.* **1993**, *52*, 91.

(20) *Comprehensive Polymer Science*; Allen, G., Bevington, C., Eds.; Pergamon Press: Oxford, U.K., 1989; Vol. 3.

(21) (a) Moad, G.; Rizzardo, E.; Solomon, D. H.; Johns, S. R.; Willing, R. I. *Makromol. Chem. Rapid Commun.* **1984**, *5*, 793. (b) Ayrey, G. *Chem. Rev.* **1963**, *63*, 645. (c) Fink, J. K. *J. Polym. Sci.* **1983**, *21*, 1445.

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