Polymerization of Styrene with Peroxide Initiator Ionically Bound to High Surface Area Mica

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ABSTRACT: Mica powders with ultrahigh specific surface areas (ca. 100 m^2/g) were treated with aqueous solutions of peroxide radical initiators bearing a single cationic group to exchange the mica surface ions with initiator cations. The stability of the initiators, the adsorption isotherms on the mica, and the adsorption equilibrium constants were measured. The resulting materials initiate the polymerization of styrene at various conditions, forming bound polymer chains in amounts up to ca. 30 wt % polymer (ca. 55 vol %) with respect to the mica. The bound chains could be removed from the surface by extraction with good solvents for poly(styrene) only when the solvent contained ions for ion exchange. On the basis of kinetic evidence, the mechanism of grafting appears to be propagation of free radicals from the surface into the monomer solution, i.e., “growth from the surface”. The results differ strongly from those previously obtained with a dicationic surface-bound azo initiator, where grafting was shown to occur by “growth to the surface”.

I. Introduction

Mica is an important commercial filler for composite polymer materials as well as a popular model substrate for surface studies. For example, mica “paper” renders excellent electrical properties to polymer composites for high-voltage insulators,[1] mica powders are used as “fillers” to increase the stiffness of thermoplastic polymers, especially polypropylene,[2] and mica platelets show promise for permeation barriers in polymer composites.[3] Mica sheets, with their well-defined, molecularly flat surfaces and specific interactions with surface ions, are also a popular substrate for surface studies such as atomic force microscopy (AFM)[4−8] and surface force measurements.[9−11] Hence, possibilities for modifying mica’s surface properties are of potentially wide interest. As mica has ion-exchangeable surface ions, a variety of organic moieties bearing cationic groups can readily be attached to the surface via ion exchange at very high surface densities (ca. 1 per 50 A^2). In the present study, we wished to investigate the grafting of polymers to mica surfaces using surface-bound free radical initiators, in particular, cation-bearing peroxides attached to the surface by ion exchange.

Ion exchange processes on commercially available muscovite mica are often difficult to follow experimentally because the specific surface areas of these materials are relatively low, in contrast to other layered minerals such as montmorillonite, vermiculite, hectorite, or bentonite. To overcome this disadvantage, a procedure for the delamination of muscovite was developed.[12,13] As the delamination procedure takes place in hot lithium nitrate solution, the resulting high surface area mica contains lithium surface ions that readily exchange with inorganic and organic ions.[14−16]

While free radical polymerization in bulk (neat) and in solution has been intensively investigated, polymerization with free radical initiators attached to inorganic surfaces has been much less studied. The latter is, however, receiving increased attention as a potentially flexible and convenient method for modifying inorganic surfaces and creating hybrid organic−inorganic materials.[17−38] Previous studies demonstrated that poly(styrene) chains attached to a muscovite mica surface by polymerization with a dicationic azo initiator, 2,2′-azobis(isobutyramidine) hydrochloride (AIBA), adsorbed by ion exchange on the mica surface.[13,14] However, it could be demonstrated from kinetic measurements and investigation of the surface products after reaction that growth did not proceed as expected by the propagation of surface free radicals into the liquid monomer phase (growth “from the surface”) but rather by attack of growing thermally initiated poly(styrene) chains on unsaturated initiator residues on the surface, resulting from the disproportionation of initiator radicals (i.e., growth “to the surface”).[13] It has been suggested that this effect originates as a consequence of the proximity of the bound free radicals in the pair formed on the surface by the decomposition of the dicationic initiator.[13] To eliminate this factor, it seemed reasonable to use an initiator with only one cationic group. In this case only one of the free radicals in the pair formed by decomposition of the initiator is bound to the surface; the other can escape into the solution. A disproportionation reaction of the two simultaneously formed radicals in this case seems less likely. The goal of the present study was to apply this concept with a monocationic peroxide in order to bind polymers to mica by growth from the surface. A number of peroxides bearing a single cationic group have been prepared, adsorbed on mica, and examined as surface-bound free radical initiators.

II. Experimental Section

Preparation of the Peroxides. The initiators [4-(*tert*-butyldioxy)butyl]trimethylammonium bromide (in the following designated as **I-4**), [4-(*tert*-butyldioxy)hexyl]trimethylammonium bromide (**I-6**), and [4-*tert*- butyldioxy)decyl]trimethylammonium bromide (**I-10**) (Figure 1) were prepared

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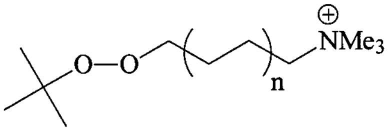

n = 1: **I-4**
n = 2: **I-6**
n = 4: **I-10**

Figure 1. Initiator structures.

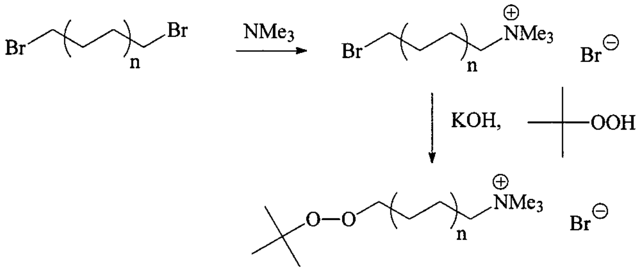

Figure 2. Reaction scheme.

following the procedure reported in the literature.[39] The reaction scheme is shown in Figure 2. In the first step, monocationic precursors [4-brombutyl]trimethylammonium bromide (**P-4**), [6-bromohexyl] trimethylammonium bromide (**P-6**), and [10-bromodecyl]trimethylammonium bromide **(P-10)** were synthesized. In the second step, the precursor was reacted to form the peroxide.

For example, 1,6-dibromohexane (43.19 g, 200 mmol) was dissolved in 500 mL of dry diethyl ether. After cooling to 0 °C, trimethylamine (33% in ethanol, 4.2 M, 10 mL, 40 mmol) was added, and the solution was stored for 3 days in the dark at room temperature. The product, [6-bromohexyl]trimethylammonium bromide (**P-6**), precipitated as white crystals. For workup, the crystals were filtered, washed with diethyl ether, and recrystallized from a mixture of ethanol and diethyl ether.[39] The procedure was repeated with the filtrate, so that a total yield of at least 90 wt % could be obtained.

NMR spectra of the products (in ppm):

P-4: *^{1}H NMR (D_2O):* $\delta = 3.42$ (t, 2H, $R-CH_2-Br$); 3.23 (m, 2H, $R-CH_2-N^+(CH_3)_3$); 2.99 (s, 9H, $R-CH_2-N^+(CH_3)_3$); 1.82 (m, 4H, $-CH_2-$).

^{13}C NMR (D_2O): $\delta = 64.25$ ($R\text{-}CH_2-N^+(CH_3)_3$); 51.56 ($R-CH_2-N^+(CH_3)_3$); 31.94 ($R-CH_2-Br$); 27.16, 19.92 (2 $\text{-}CH_2-$).

P-6: *^{1}H NMR (D_2O):* $\delta = 3.42$ (t, 2H, $R-CH_2-Br$); 3.29 (m, 2H, $R-CH_2-N^+(CH_3)_3$); 3.07 (s, 9H, $R-CH_2-N^+(CH_3)_3$); 1.80 (2m, 8H, $-CH_2-$).

^{13}C NMR (D_2O): $\delta = 66.64$ ($R-CH_2-N^+(CH_3)_3$); 52.92 ($R-CH_2-N^+(CH_3)_3$); 35.02 ($R-CH_2-Br$); 31.77, 26.85, 24.65, 22.21 (4 $-CH_2-$).

P-10: *^{1}H NMR (D_2O):* $\delta = 3.37$ (t, 2H, $R-CH_2-Br$); 3.16 (m, 2H, $R-CH_2-N^+(CH_3)_3$); 2.96 (s, 9H, $R-CH_2-N^+(CH_3)_3$); 1.70, 1.24 (2m, 16H, $-CH_2-$).

^{13}C NMR (D_2O): $\delta = 68.27$ ($R-CH_2-N^+(CH_3)_3$); 54.62 ($R-CH_2-N^+(CH_3)_3$); 36.78 ($R-CH_2-Br$); 34.31, 30.73, 30.68, 30.37, 30.12, 29.57, 27.50, 24.26 (8 $-CH_2-$).

To obtain the peroxide initiators, e.g. **I-6**, potassium hydroxide (259.2 mg, 4.62 mmol) was dissolved in 20 mL of *tert*-butyl hydroperoxide (80%). The solution was cooled to 0 °C and **P-6** (1.0 g, 3.30 mmol) added. The solution was stirred for 20 h while the temperature was allowed to rise to room temperature. For workup the solvent was evaporated under reduced pressure while the temperature was kept below 35 °C. The residue was treated with a large amount of dry diethyl ether to obtain a white solid. After decantation of the diethyl ether, the residue was extracted with chloroform to separate the product from inorganic materials. After filtration, evaporation of the solvent and drying at room temperature, 0.77 g (75%) of **I-6** was obtained.

NMR spectra of the products (in ppm):

I-4: *^{1}H NMR (D_2O):* $\delta = 3.95$ (t, 2H, $R-CH_2-OOC(CH_3)_3$); 3.22 (m, 2H, $R-CH_2-N^+(CH_3)_3$); 2.99 (s, 9H, $R-CH_2-N^+(CH_3)_3$); 1.76, 1.57 (2m, 4H, $-CH_2-$); 1.14 (s, 9H, $-OOC(CH_3)_3$).

^{13}C NMR (D_2O): $\delta = 82.32$ ($-OOC(CH_3)_3$); 74.65 ($R\text{-}CH_2-OOC(CH_3)_3$); 66.29 ($R-CH_2-N^+(CH_3)_3$); 52.90 ($R-CH_2-N^+(CH_3)_3$); 25.49 ($-OOC(CH_3)_3$); 24.16, 19.50 ($-CH_2-$).

I-6: *^{1}H NMR (D_2O):* $\delta = 3.99$ (t, 2H, $R-CH_2-OOC(CH_3)_3$); 3.28 (m, 2H, $R-CH_2-N^+(CH_3)_3$); 3.07 (s, 9H, $R-CH_2-N^+(CH_3)_3$); 1.74, 1.59, 1.39 (3m, 8H, $-CH_2\text{-}$); 1.22 (s, 9H, $-OOC(CH_3)_3$).

^{13}C NMR (D_2O): $\delta = 82.22$ ($-OOC(CH_3)_3$); 75.68 ($R-CH_2-OOC(CH_3)_3$); 66.65 ($R-CH_2-N^+(CH_3)_3$); 52.94 ($tR-CH_2-N^+(CH_3)_3$); 25.61 ($-OOC(CH_3)_3$); 26.92, 25.36, 25.00, 22.26 (4 $-CH_2-$).

I-10: *^{1}H NMR (D_2O):* $\delta = 3.88$ (t, 2H, $R-CH_2-OOC(CH_3)_3$); 3.15 (m, 2H, $R-CH_2-N^+(CH_3)_3$); 2.95 (s, 9H, $R-CH_2-N^+(CH_3)_3$); 1.63, 1.45, 1.19 (3m, 16H, $-CH_2\text{-}$); 1.11 (s, 9H, $-OOC(CH_3)_3$).

^{13}C NMR (D_2O): $\delta = 79.85$ ($-OOC(CH_3)_3$); 74.59 ($R-CH_2-OOC(CH_3)_3$); 66.05 ($R\text{-}CH_2-N^+(CH_3)_3$); 52.44 ($R-CH_2-N^+(CH_3)_3$); 25.50 ($-OOC(CH_3)_3$); 28.67, 28.62, 28.67, 28.23, 27.08, 25.42, 25.34, 22.09 (8 $-CH_2-$).

Adsorption of Peroxides on Mica. Delaminated mica was prepared according to the literature,[12,13] using muscovite fines supplied by Von Roll Isola, Breitenbach, Switzerland. This process involves treatment with lithium nitrate and leaves lithium ions as the exchangeable cations on the surface. A material with a specific surface area of 105 m^2/g, as determined by methylene blue adsorption,[12] was employed. Typically, 130 mg of the mica powder was dispersed in 25 g of water and 25 g of ca. 0.01 mol/L aqueous solution of initiator added. In both cases doubly distilled water was used. The resulting suspensions were then stirred for several hours and left to stand overnight.

In the case of **I-10**, the ion exchange was accompanied by visible changes: upon pouring an aqueous solution of **I-10** into a mica dispersion, the mica flocculated, presumably because the surfaces became hydrophobic after the adsorption. With **I-4** and **I-6,** the mica particles remained finely dispersed. The suspensions were finally centrifuged, and the supernatant liquid was decanted. The solids were washed five times with water, 50 mL each time, and again centrifuged. After decanting the supernatant, the wet solids were slurried with methanol, filtered, and dried under vacuum, yielding a mica powder instead of the mica "paper" which otherwise results.

The amount of adsorbed initiator was determined by two methods: (1) in solution, by measuring the amount of lithium ions released into solution using inductively coupled plasma−atomic emission spectroscopy (ICP-AES) (Plasmaquant 110, Carl Zeiss Jena, Jena, Germany), and (2) in the solid state, after washing and drying the mica solids, by measuring the amount of heat released by the decomposition of the peroxide groups on the surface using differential scanning calorimetry (DSC). Thermogravimetric analysis (TGA) was found to be insufficiently accurate for this purpose.

Polymerization. Styrene (Fluka Chemie, Buchs, Switzerland) was shaken several times in a separatory funnel, first with aqueous (10 wt %) NaOH and then with water, and finally dried with sodium sulfate and distilled under vacuum (about 15 mbar). For the bulk polymerizations, 4 mL of the freshly distilled styrene was used. For the solution polymerizations, 3 mL of styrene and 3 mL of dry toluene were used. These were added under nitrogen to 0.1 g of the mica−peroxide complex in a polymerization tube fitted with a gas inlet sidearm and a magnetic stirrer bar. The contents were then frozen with liquid nitrogen and purged with nitrogen gas by applying vacuum and nitrogen gas alternatingly several times. The polymerization tubes were then placed in a thermostated bath equipped with a magnetic stirrer, and the tube was connected to a nitrogen supply at a pressure slightly greater (about 2 kPa) than atmospheric. Polymerizations were carried out at either 100 or 120 °C for varying periods from 0.5 to 24 h and under vigorous stirring to maintain the mica powder well dispersed in the styrene. It was found that the mica with **I-10** adsorbed dispersed very readily in styrene to give a very finely distributed powder, while the mica with **I-4** and **I-6** adsorbed had to be stirred for ca. 1 h in styrene to obtain such a dispersion.

The reaction samples were poured into methanol (volume at least 10 times that of the reaction mixture) and left standing for several hours to precipitate the poly(styrene). Where the reaction samples were too viscous to be poured, toluene was first added to dilute or dissolve the polymer, before pouring into methanol. The mica−polymer mixture was then filtered. The solids were dried under vacuum at 60 °C and then treated by stirring in centrifuge tubes with about 50 mL of toluene per 100 mg of mica, followed by centrifugation and decantation of the supernatant. This treatment was repeated with fresh toluene seven to eight times. It was found that this was sufficient to remove all the extractable material; additional extractions did not change the amount of bound polymer determined by TGA (system TA 7000 thermogravimetric analyzer, Perkin-Elmer, Norwalk, CT). Finally, methanol was added to the centrifuge tubes instead of toluene, and following filtration, the solids were dried under vacuum at 60 °C. The supernatant solutions (decanted from the centrifuge tubes), containing toluene-soluble polymer, were combined and distilled to remove most of the toluene; the polymer was then precipitated by pouring into methanol, filtered, and dried at 60 °C under vacuum (about 50 mbar).

The molecular weight of the poly(styrene) fractions was analyzed by size exclusion chromatography (SEC) (PL-Gel 5 μm mixed C 7.5 × 600 mm column, Polymer Laboratories, Shropshire, U.K.). The bound polymer was removed by extraction of the mica solids with 1% LiCl solutions in tetrahydrofuran.

III. Results and Discussion

Synthesis of the Initiators. The initiators were prepared according to the literature[39] (see Figure 2). In the first step, the cationic intermediates **P-4, P-6**, and **P-10**, each bearing a cationic trimethylammonium group and a terminal bromine atom, could be readily synthesized by reacting an excess of the corresponding dibromoalkane with trimethylamine. The competitive reaction of a double nucleophilic attack at both bromo functions could be suppressed by using dry diethyl ether, which is a good solvent for the reactants but a poor solvent for the cationic intermediates. The latter precipitated as solids, on which no further attack could be observed. Using potassium hydroxide as base and *tert*-butyl hydroperoxide as reactant and solvent, the desired products **I-4, I-6,** and **I-10** could readily be obtained. Under these conditions, no elimination of the acid hydrogen in the β-position of the cationic headgroup could be observed.

Thermal Behavior of the Peroxide Initiators. The stability and reactivity of the peroxides upon heating were assessed to determine their ability to survive the adsorption process, which lasts several hours at room temperature, and to determine the temperature conditions most suitable for the initiation of polymerization. The peroxides were examined both in bulk (neat) and ion exchanged onto the mica surface, using TGA with a heating rate of 20 K/min and DSC with a heating rate of 10 K/min. The behavior of all three peroxides was similar.

Taking **I-10** for illustration, in bulk, TGA showed that decomposition occurs in two steps: there was a weight loss peak of about 20 wt % at ca. 180 °C followed by another of about 70 wt % at ca. 260 °C. The first peak was attributed to cleavage of the O−O bond and the second to decomposition of the aliphatic residue. DSC confirmed the exothermic nature of the first peak. No endothermic peak (from melting) was detected at a lower temperature than this exothermic peak. The overall enthalpy change for the exothermic peak was −206 kJ/mol for **I-4**, −210 kJ/mol for **I-6**, and −218 kJ/mol for **I-10**.

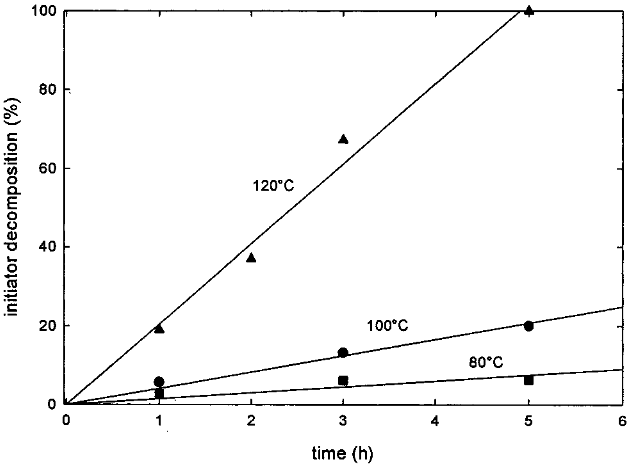

Figure 3. Decomposition of bulk **I-10** at 80, 100, and 120 °C.

The thermal behavior of the compounds ion-exchanged onto mica (discussed in the Experimental Section and also below) and that of the pure bulk compounds was not identical. For example, on fully exchanged mica, **I-6** and **I-10** cations decomposed at respectively ca. 130 and 140 °C, compared with respectively ca. 170 and 180 °C in bulk. (As discussed below, **I-4** was substantially removed from the surface in the washing procedure.) Decomposition at lower temperatures on the mica surface than in bulk was previously observed with AIBA on mica[13] and suggests that the adsorbed peroxide is indeed dispersed on the surface. A relatively high decomposition temperature for the peroxides, such as 130 or 140 °C, is not unexpected, given the absence of chemical groups providing resonance stabilization of the resulting free radicals.

Some variation in the decomposition temperature of the peroxide was also observed with the degree of exchange on the surface. At a low peroxide surface coverage, the exothermic peak for **I-6** and **I-10** appeared at ca. 180 °C (accompanied by an endothermic peak at ca. 150 °C). With essentially complete exchange, a second exothermic peak appeared at 130 °C for **I-6** and 140 °C for **I-10**, and the endothermic peak disappeared. This thermal behavior could be explained by an interaction of the peroxide group with aluminum ions or with hydroxyl groups at the mica surface. As long as there is sufficient space, i.e., at low surface coverage, the peroxide ions can “bend back” and interact with these surface moieties, but this is not possible when the surface coverage is high and the peroxide ions are tightly packed together. The endothermic signal at 150 °C would, in this view, result from the detachment of the peroxide group from the surface at this temperature.

The rate of decomposition of bulk initiator at 80, 100, and 120 °C was investigated by TGA. It was found that a significant amount decomposed during 6 h at 100−120 °C, with a constant rate at a given temperature. The data for **I-10** are shown in Figure 3. This was the temperature range used for the polymerizations. At these relatively high temperatures for the polymerization of styrene, the rate of thermal polymerization, i.e., polymerization that takes place spontaneously in pure styrene upon heating without added initiator,[40] is high and the resulting degree of polymerization low.

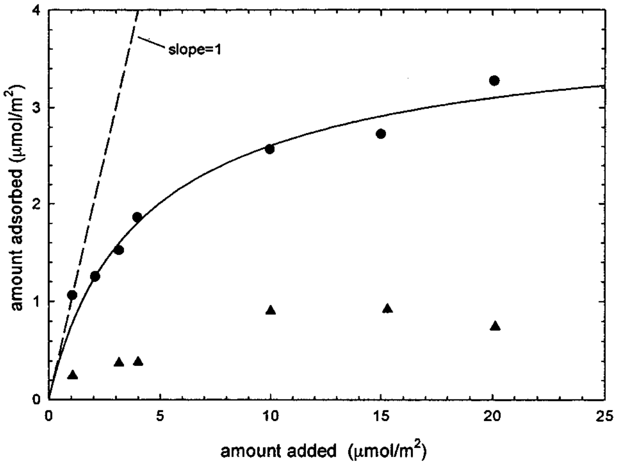

Figure 4. **I-4** adsorbed, as measured from lithium release, filled circles. **I-4** remaining on surface as measured with DSC, filled triangles. The curve is a plot of eq 1 with fitted parameters.

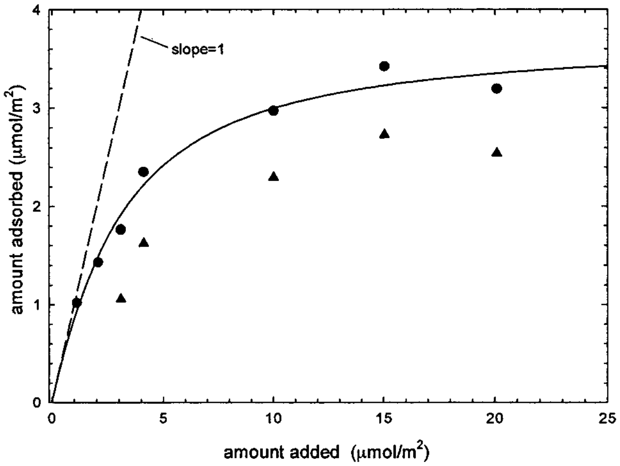

Figure 5. **I-6** adsorbed, as measured from lithium release, filled circles. **I-6** remaining on surface as measured with DSC, filled triangles. The curve is a plot of eq 1 with fitted parameters.

Adsorption Isotherms. The adsorption isotherms of the peroxide initiators were determined directly in solution by measuring the amount of lithium ions released into the solution, assuming one lithium ion released per peroxide ion adsorbed, as found in previous studies.[14] The isotherms for the three peroxide initiators plotted as Γ_A, the amount of cation adsorbed, versus a, the amount of cation added, both in amount of substance per unit surface area (Figures 4−6), were similar to those observed previously for other organic cations.[14] Γ_A increases with increasing a, approaching a "plateau" at a value $\Gamma_A = S$, which represents the ion exchange capacity of the surface for that ion.

The ion exchange equilibrium can be described quantitatively by eq 1:[14]

$$K = \frac{{\Gamma_A}^2}{(S - \Gamma_A)(a - \Gamma_A)} \tag{1}$$

where K is the equilibrium constant.

The curves in Figures 4-6 are plots of eq 1 with K and S fitted to the data by nonlinear regression using a Marquardt−Levenberg algorithm. A line through the origin with slope equal to unity, i.e., $\Gamma_A = a$, corresponding to quantitative adsorption, is also shown for comparison. The fitted values of K and S are summarized in Table 1.

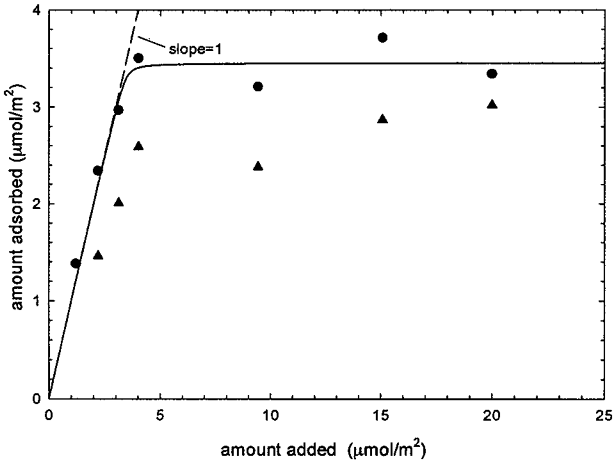

Figure 6. **I-10** adsorbed, as measured from lithium release, filled circles. **I-10** remaining on surface as measured with DSC, filled triangles. The curve is a plot of eq 1 with fitted parameters.

Table 1. Values of *S* and *K* for Ion Exchange on Mica, with Standard Error

peroxide	S (μmol/m^2)	K (μmol/m^2)
I-4	3.9 ± 0.5	0.7 ± 0.3
I-6	3.7 ± 0.2	1.7 ± 0.5
I-10	3.5 ± 0.1	400 ± 1300

The values of S for the three peroxides are all similar, and roughly equal, within experimental error, to that expected from the mica crystal structure, 3.5 μmol/m^2, and that found in previous studies on adsorption of small ions on muscovite, ca. 3.8−4.3 μmol/m^2.[14] It therefore appears that, for the higher a values, the peroxide cations completely exchange the surface lithium ions and form relatively compact monolayers on the surface. The measured K values increase with the length of the alkyl groups; the value for **I-6**, 1.7, is about 2.5 times that for **I-4**, 0.7, while the value for **I-10** is much higher. (Adsorption of **I-10** is virtually quantitative up to the ion exchange capacity, and the K value is too high to be measured accurately.) That K increases with alkyl chain length is not surprising, as alkyl cations were found previously to adsorb on mica more strongly than lithium ions[14] and long alkyl groups might well be expected to adsorb more strongly than short ones. This would reflect a lower free energy for the system with the inorganic ions in solution and the organic ions in an oleophilic layer on the surface, compared with the organic ions in a highly polar aqueous medium and the lithium ions on the surface. The longer the hydrocarbon chain, the more pronounced this effect would be. Similar effects have been reported in a number of papers on surface monolayer adsorption as discussed by Bain et al.[41]

As noted in the Experimental Section, the mica−peroxide solids used in the polymerizations were prepared by adsorption of the peroxide from aqueous solution—after which the solids were repeatedly washed with water to remove unbound peroxide and then dried. In the adsorption step, a values of about 20 μmol/m^2 were used to prepare mica samples for the experiments aimed at initiation of polymerization from the surface. Judging from the isotherms, these samples were at least ca. 80% peroxide-exchanged during the adsorption step. The amount of peroxide remaining on the mica after washing and drying was also estimated using DSC by measuring the exothermic peaks for the peroxide on the surface and comparing these with the heat of reaction of the pure peroxides. This method has been described in the literature[37] for determining the amount of bound azo initiator on silica surfaces. Our measurements suggest that some of the adsorbed peroxide is removed by the washing or reacts on the mica surface. The amounts remaining on the surface, as estimated by DSC, are shown in Figures 4−6 plotted against the a values used in the adsorption experiments. For the samples with $a \approx 20$ μmol/m^2 used in the polymerizations, the DSC measurements indicate that about 3 μmol/m^2 remained after workup for **I-10**, about 2.5 μmol/m^2 for **I-6**, but only about 0.5−0.8 μmol/m^2 for **I-4**. The removal of peroxide ions in washing might for example occur by ion exchange with adventitious trace ions in the wash water. That **I-4** is more readily removed than **I-6** and **I-10** is consistent with its being less strongly bound, as indicated by the lower K value for **I-4** in Table 1.

It should be noted that the DSC method used to measure the amount of peroxide remaining on the surface may have a systematic error, if there is a significant difference between the enthalpy of reaction on the surface and that measured in bulk, e.g., due to a difference in the respective enthalpies of fusion. However, a study reported in the literature on graft polymerization by azo compounds immobilized on silica[37] reported good agreement, i.e., similar values, for the enthalpies of decomposition of azo compounds in bulk (about 180 kJ/mol) and the same compounds immobilized on silica. We incline to the view that the same applies in the present case and that the estimated amounts of peroxides on the surface are substantially correct.

Polymerization. Mica with initiator adsorbed on the surface was heated in a series of experiments with neat styrene or equivolume solutions of styrene and toluene, at temperatures of either 100 or 120 °C, for periods of 0.5, 1, 3, 6, and 24 h. When the reaction mixture was poured into methanol, a mixture precipitated of mica, polymer soluble in toluene, and polymer insoluble in toluene, i.e., bound to the surface. The soluble polymer resulted presumably from the radicals released into solution by the cleavage of the surface-bound peroxide groups and also free radicals formed by thermal polymerization processes. The insoluble polymer chains were presumably attached to the mica surface via the residues of the surface-bound peroxide cations which initiated polymerization from the surface.

The polymer, which could not be removed from the mica by treatment with toluene as described above, could also not be removed with tetrahydrofuran (THF) alone, although toluene and THF are both normally solvents for poly(styrene). The polymer could, however, be completely extracted by stirring the mica solids for several days with a solution of 1 wt % lithium chloride in THF. This was shown by TGA analysis of the mica solids before and after extraction (the weight loss peaks for the polymer disappeared after extraction). The extraction of this polymer by LiCl−THF is most likely due to ion exchange of the lithium ions in solution with the polymer cations on the surface, releasing the polymer into the solution. Thus, two polymer fractions are ultimately obtained: toluene-soluble polymer and LiCl−THF-soluble polymer, which had presumably been bound to the mica solids by ionic bonds.

The mica solids after toluene extraction were examined under air by TGA using a heating rate of 20 °C/min. The major weight loss "peaks" were in the range 350−500 °C depending on how much poly(styrene) was attached to the surface. This corresponds to the peak observed for bulk poly(styrene), which depolymerizes under the same conditions at ca. 400 °C.

Mica with adsorbed initiator heated with styrene at low temperatures (ca. 60 °C) or at 100 and 120 °C for short times (ca. 20 min.) showed an additional weight loss "peak" at ca. 180 °C. This peak is attributed to the cleavage of the O−O bond of unreacted peroxide initiator on the surface. After 6 h at 100 or 120 °C there are only poly(styrene) peaks left because the O−O bonds are completely cleaved after this time. The alkyl chain residues of those peroxide cations that reacted but did not initiate polymerization could not readily be detected due to the much larger amount of attached poly(styrene).

The maximum amount of bound polymer obtained in these experiments as measured by TGA was generally about 30 wt % based on the weight of mica (i.e., ca. 0.30 g of polymer/g of mica), depending on the reaction conditions (see below). For comparison, a sample with only initiator attached to the mica shows, in the case of **I-10,** a weight loss peak with TGA of only about 3 wt %. For **I-4** and **I-6,** the weight loss peak is even smaller, because of the shorter alkyl chains.

The reaction mixtures of the polymerization experiments performed with initiator-treated mica in neat styrene at 120 °C became highly viscous after 3 h and already solid after 6 h. After 24 h, almost all the styrene had reacted. After removing the soluble poly(styrene), TGA measurements on the remaining mica solids showed that poly(styrene) was attached to the surface in amounts that increased with reaction time, up to ca. 15−20 wt %. However, the amount of bound polymer formed was small compared with the amount of soluble polymer formed. It seemed desirable to reduce the amount of soluble polymer to facilitate separation of the polymer fractions and the study of the kinetics. Under the assumption that part of the soluble polymer was due to thermal polymerization, some experiments were performed at 100 °C. At this temperature, the mixture became highly viscous after 6 h and solidified after 24 h. Although thermal polymerization was presumably slower, after 24 h most of the styrene had still reacted. After removal of the soluble poly(styrene), TGA measurements showed ca. 10−15 wt % poly(styrene) attached to the mica.

To keep the reaction mixture stirrable throughout the experiment and to further reduce the amount of thermal polymerization, toluene was used as an inert solvent for the polymerization. This improved the reaction conditions and reduced the amount of thermal polymerization. Performing the polymerization at 120 °C in toluene gave, overall, the best and most reproducible results.

Bound Polymer. For polymerization in toluene at 120 °C, the amount of bound polymer P, in g of polymer per g of mica, is shown plotted against time t in Figure 7. Also shown is the fit for each peroxide to eq 2, which is based on first-order kinetics for the decomposition of

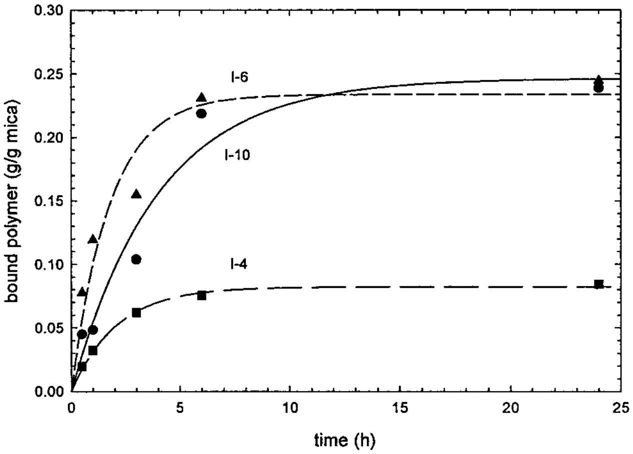

Figure 7. Bound polymer, obtained by reaction in toluene at 120 °C. **I-4**: filled squares, long dotted line. **I-6**: filled triangles, short dotted line. **I-10**: filled circles, full line. Curves are plots of eq 2 with fitted parameters.

Table 2. Values of P_∞, k_d, and $\tau_{1/2}$, with Standard Error[a]

peroxide	P_∞ (g/g of mica)	k_d (h^{-1})	$\tau_{1/2}$ (h)
I-4	0.082 ± 0.002	0.48 ± 0.03	1.4 ± 0.1
I-6	0.23 ± 0.02	0.56 ± 0.20	1.2 ± 0.3
I-10	0.25 ± 0.02	0.25 ± 0.06	2.8 ± 0.6

[a] Polymerization in toluene at 120 °C.

the initiator (see Appendix):

$$P = P_\infty(1 - e^{-k_d t}) \qquad (2)$$

Here k_d is the rate constant for the decomposition of initiator, and P_∞ is the value of P as $t \rightarrow \infty$. The fit was done by nonlinear regression using a Marquardt–Levenberg algorithm. The data appear to be consistent with eq 2. The constants P_∞ and k_d so obtained and the values of $\tau_{1/2}$ calculated from k_d (see Appendix) are displayed in Table 2. It can be seen from Figure 7 that P increased in each case with time over a period of several hours, but at a rate that decreased with time. These first-order kinetics are in sharp contrast with the zero-order kinetics (constant reaction rate) previously found for bound poly(styrene) in experiments with AIBA on mica as the initiator. This lends support to the hypothesis that growth in the present case is due to propagation into solution of the surface-bound free radicals in contrast to the growth "to the surface" found with AIBA.[13]

The fitted values of P_∞ for **I-6** and **I-10** are equal, within the estimated experimental error of about 10%. The value for **I-4** is substantially lower. However, this is probably due to the substantially smaller amount of **I-4** remaining on the surface, after washing and drying, compared with **I-6** and **I-10**. Indeed, the ratio of P_∞ to $\Gamma_{RX,0}$ is about the same for all three peroxides. Thus, they appear to be roughly equivalent in their efficiency of initiation. Varying the "spacer" length between the peroxide group and the cation end on the surface therefore did not appear to have a significant effect on the initiator efficiency for the peroxides studied.

The bound polymer samples, after removal from the surface, were examined by SEC. Because the amounts of polymer were quite small and low molecular weight impurities were present, the polymer peak maxima could be determined with much greater precision than the number- and weight-average molecular weights. Therefore, for comparison of the molecular weights of bound and soluble polymer, we refer to the peak maxima. The data were most reproducible, as previously noted, for polymerization at 120 °C in toluene. Here, the molecular weight peaks (as determined with a viscometric detector) were mostly in the range 90 000–250 000. For the soluble polymer, prepared under the same conditions, the molecular weights peaks were generally higher, ranging from about 420 000–600 000.

Initiator Efficiency. It is possible to estimate the efficiency of initiation f using eq 2 (see Appendix for further details). For **I-10**, with ca. 3 μmol/m^2 peroxide on the surface, 105 m^2/g mica, and a mean chain molecular weight of, say, 100 000, there would be about 30 g of bound polymer/g of mica if every surface peroxide cation generated one chain. Since for $t \geq 6$ h, i.e., for reaction times long enough for most of the peroxide to react, there is experimentally found about 0.3 g/g of mica, f is on the order of 0.01 chains per bound peroxide cation. Thus, only a small fraction of the peroxide cations on the surface appear to initiate polymerization. Of course, because of the high specific surface area of the mica and the high molecular weight of the chains, a nevertheless substantial amount of polymer by weight (about 30%) and even more by volume (about 50%) can be bound to the surface. The reason for the low efficiency is not known. Some preliminary polymerization experiments, varying the amounts of peroxide on the mica surface and determining the amount of soluble polymer formed, indicated that most of the soluble polymer resulted from thermal polymerization and that the X$^\bullet$ free radicals released into solution have a low efficiency of initiation, similar in magnitude to that of the R$^\bullet$ free radicals bound to the surface. This would suggest that annihilation reactions between R$^\bullet$ radicals and X$^\bullet$ radicals play an important and perhaps the predominant role here.

While only a small fraction of the peroxide cations appear to initiate polymerization, the fraction that do so is far higher than was observed with the dicationic azo compound AIBA.[13] With AIBA, substantially less than 1 per 10 000 surface-bound free radicals initiated polymerization. This follows from the fact that with AIBA only about 1 in 10 000 cationic sites had chains attached, and most of these resulted from growth to the surface rather than growth from the surface. The improvement with the monocationic peroxides, i.e., the higher efficiency of initiation, is presumably due to the fact that with the peroxides only one of the pair of free radicals formed by decomposition of the initiator is bound to the surface rather than both. This allows a greater fraction of the bound free radicals formed to escape disproportionation reactions and initiate polymerization.

The initiator efficiencies found in other grafting studies reported in the literature appear to vary over a very wide range. For example, Prucker and Ruhe[37,38] report the radical grafting of poly(styrene) to high surface area (ca. 300 m^2/g) silica by surface-bound azo initiator. Their kinetic data suggest growth from the surface, and they report up to 25 g of grafted polymer per gram of silica. In contrast, Tsubokawa et al.[25] also report the radical grafting of poly(styrene) to high surface area (ca. 200 m^2/g) silica by surface-bound azo initiator. Their kinetic data also suggest growth from the surface, and they report about 0.3 g of grafted

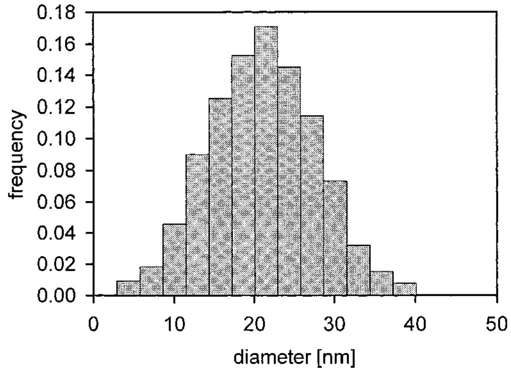

Figure 8. Droplet size distribution obtained in the polymerization of styrene in toluene with **I-6** treated mica at 100 °C for 30 min.

polymer per gram of silica, which is similar to what we obtained here with 100 m^2/g mica.

Molecular Droplets. In previous work on the polymerization of styrene with dicationic AIBA bound to the mica surface, it was found that the individual bound chains on the surface could be imaged with scanning electron microscopy (SEM) in the form of isolated "molecular droplets".[42,43] Here, similar features were observed with SEM in a number of cases. For example, an **I-6** treated mica used as initiator in the polymerization of styrene in toluene solution at 100 °C gave, after 30 min polymerization, droplets with diameters ranging from about 4 to 40 nm. The frequency distribution of droplet diameters is shown in Figure 8. The distribution is roughly symmetric, with a maximum frequency in the range 20−24 nm. The mean diameter is about 21 nm. This is reasonably consistent with that expected for single chain molecules bound to the surface. Assuming a mean molecular weight of about 200 000, a density for amorphous poly(styrene) of 1.05 g/cm^3, and a hemispherical structure for the droplets, a mean diameter of about 11 nm would be calculated. This is somewhat smaller than the mean diameter of 21 nm determined from Figure 8, but of the correct order of magnitude. The difference might be due to in part to (1) the tungsten coating used to image the droplets (which is ca. 2 nm in thickness), (2) under representation of difficult-to-discern very small droplets in the droplet count, (3) the droplets being spherical segments with contact angles less than 90 °C rather than hemispheres, and (4) uncertainty in the estimated mean molecular weight. It seems likely that here, as in the previous studies, the droplets observed are individual chain molecules.

At longer polymerization times the droplets began to overlap and eventually form films. These samples, with roughly 20−30 wt % bound polymer, are calculated to have film thicknesses of 2−3 nm.

IV. Conclusions

The cationic peroxide initiators **I-4**, **I-6**, and **I-10** adsorb by ion exchange from aqueous solutions onto the surface of ultrahigh specific surface area delaminated mica. The affinity of the initiators for the surface increases with increasing number of methylene groups, corresponding to the increasing hydrophobicity of the molecules. This is also reflected in the resistance to removal upon washing. For **I-4**, a large part of the initiator was removed from the surface upon washing, while for **I-6** and **I-10** most of the adsorbed initiator remained on the surface. The fraction of the surface covered with initiator could readily be varied by changing the *a* value in the adsorption step, as determined from the adsorption isotherm.

Poly(styrene) grafted to mica surfaces is obtained when cation-bearing peroxide initiators are attached to mica powders by ion exchange and used to polymerize styrene. The formation of bound polymer follows first-order reaction kinetics, in agreement with the assumption of a grafting process from the surface. In addition to bound polymer, soluble polymer also results. The bound polymer originates in surface bound free radicals, the soluble polymer in both thermal initiation and free radicals released into solution by the peroxide cleavage. The grafting results are in marked contrast to those observed in the polymerization of styrene with the dicationic azo initiator AIBA on mica. There, grafting followed zero-order kinetics, and the poly(styrene) was attached by a process of growth to the surface.[13]

It appears that only a small fraction of the peroxide ions (perhaps 1 per 100) initiate polymerization of bound chains. Nevertheless, because of the high specific surface area of the micas, substantial amounts of grafted polymer, up to ca. 30 wt % or ca. 55 vol % related to the mica, could be obtained. In some cases, the individual bound chains could be imaged by SEM in the form of "molecular droplets". The droplet dimensions are in reasonable agreement with those expected from the molecular weight of the bound poly(styrene) chains.

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Appendix

It is assumed that the peroxide cations, RX, attached to the surface by ion exchange, each decomposes to give two free radicals: $R^\bullet$ attached to the surface and $X^\bullet$ released into the solution. The decomposition is assumed to be kinetically first-order with respect to the concentration of initiator on the surface:

$$\frac{d\Gamma_{RX}}{dt} = -k_d\Gamma_{RX} \tag{A-1}$$

where Γ_{RX} is the surface concentration of RX at time t and k_d is the rate constant. Integrating gives

$$\Gamma_{RX} = \Gamma_{RX,0}e^{-k_dt} \tag{A-2}$$

where $\Gamma_{RX,0}$ is the initial concentration.

Let f be the efficiency of initiation, the fraction of peroxide cations that, upon decomposition, initiate chains. If M, the number-average molecular weight of the bound chains, is constant, then bound polymer P, in mass/mass mica, will form at a rate

$$\frac{dP}{dt} = fk_d\Gamma_{RX}MA_s \tag{A-3}$$

where A_s is the specific surface area of the mica.

Substituting eq A-2 in eq A-3 and integrating gives

$$P = P_{\infty}(1 - \mathrm{e}^{-k_{\mathrm{d}}t}) \tag{A-4}$$

where $P_{\infty} = f\Gamma_{\mathrm{RX},0}MA_{\mathrm{s}}$. This is eq 2 in the text. P increases with time, asymptotically approaching P_{∞} as a limiting value.

The half-life of the initiator on the surface $\tau_{1/2}$ is given by

$$\tau_{1/2} = -\frac{\ln 0.5}{k_{\mathrm{d}}} \tag{A-5}$$

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