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Polymerization of Styrene with Initiator Ionically Bound to High Surface Area Mica: Grafting via an Unexpected Mechanism

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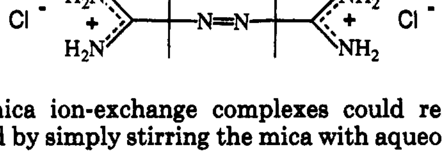
ABSTRACT: To obtain polystyrene grafted to mica, a free-radical initiator 2,2′-azobis(isobutyramidine hydrochloride) (AIBA) was attached by ion exchange to the surface of an ultrahigh specific surface area (ca. 100 m^2/g) muscovite mica powder, and the resulting material was used as an initiator to polymerize styrene. Grafted polymer was indeed obtained, in amounts up to ca. 10% by weight (ca. 30% by volume) of polymer based on mica, but it was found that grafting proceeded by an unexpected mechanism. Instead of propagation of free radicals from the surface into the bulk monomer (growth from the surface), grafting took place via attack of growing chains thermally-initiated in the monomer on disproportionation products of AIBA attached to the surface (growth to the surface). The grafted polymer consisted primarily of high molecular weight chains (*M* ca. 10^6) bound by their headgroups to a very small fraction (less than 1 per 4000) of the surface ion-exchange sites. Consistent with this mechanism, grafted polymer could also be obtained with "thermally-deactivated" AIBA–mica at rates comparable to those obtained with "fresh" AIBA–mica. Grafting was accelerated when 2,2′-azobis(isobutyronitrile) was added to the monomer as an additional initiator.

I. Introduction

Grafting of polymers to surfaces (i.e., chemically bonding the headgroups to the surface) is of potential interest in a wide variety of fields such as composite materials and adhesives,[1] chromatography,[2] protein immobilization,[3] colloid stabilization,[4] and medicine and dentistry.[5] There have been a number of such polymerizations reported, and extensive references can be found in papers by Dekking,[6,7] Laible and Hamann,[8] Tsubokawa et al.,[9] Bhattacharya et al.,[10] and Boven et al.[11] Most of this work has involved silicon dioxide aerosils, carbon black, or clays as the substrate. We have been particularly interested in the layered silicate mineral mica.[12]

Mica has a well-defined, flat, crystalline surface, and this has led to its recent widespread use as the substrate for atomic force microscopy (AFM), scanning tunneling microscopy (STM), and surface force measurement studies.[13–15] It also has surface ion-exchange sites[16] which can be used to attach initiators bearing cationic groups. A new process we have developed allows the preparation of highly delaminated mica powders with ultrahigh specific surface areas.[17] The ultrahigh specific surface areas allow accurate determination of the number of ion-exchange sites per unit of surface area and the degree of ion exchange that takes place upon treatment with cationic organic compounds.[18] These micas, therefore, seemed particularly well-suited to the study of surface-initiated polymerization.

The initiator we selected was a water-soluble bicationic azo compound previously reported for the preparation of polymer–clay composites, 2,2′-azobis(isobutyramidine hydrochloride) (AIBA):[6,7]



AIBA–mica ion-exchange complexes could readily be prepared by simply stirring the mica with aqueous AIBA solutions.[17] (For simplicity, we use the name AIBA to refer to both the compound and the cation adsorbed on the surface.)

It was, of course, expected that, using the ion-exchange complex as the initiator, graft polymerization would take place to give polymer chains bonded to the mica surface. As will be discussed, significant amounts of polymer grafted to the surface were indeed obtained, but it appears that grafting resulted via an unexpected mechanism.

II. Experimental Section

Preparation of the Mica. The starting material, a waste product (mica fines) resulting from the production of muscovite insulating papers, was supplied by Isola (Breitenbach, Switzerland) and designated by them as Mica 21. The procedure for producing ca. 15 g of highly delaminated mica is similar to that employed for very small amounts previously.[17]

A suspension of 15 g of mica fines, 260 g LiNO$_3$, and 100 mL of water was stirred at 170 °C for 7 days. The suspension was allowed to cool to nearly room temperature and then filtered. The filtrate was washed with 1 L of doubly distilled water. The LiNO$_3$ treatment was repeated with the precleaved mica. After filtration, the resulting product was washed with 0.5 L of doubly distilled water, stirred in 1 L of doubly distilled water for 1 h, filtered again, and washed with 1.5 L of doubly distilled water. The specific surface area of the resulting mica was 100–110 m^2/g (determined by methylene blue adsorption[17–19] for several runs).

Adsorption of AIBA on Mica. AIBA was obtained from Polysciences (Warrington, PA). The mica powders were dispersed in aqueous solutions of the initiator (using doubly distilled water), stirred for several hours, and left to stand overnight. The slurries were then centrifuged, and the supernatant liquid was decanted. The supernatant was retained for determination of AIBA concentration by UV absorption (see below). The solids were washed with water and again centrifuged. After the supernatant was decanted, the wet solids were slurried with a small amount of water and filtered. The wet filter cake was then slurried with isopropyl alcohol, 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 the diminuition of the UV absorption band at 368 nm in the supernatant solution (diode spectrophotometer, Model 8542 A, Hewlett-Packard, Palo Alto, CA) and was found to be ca. 210 μmol/g of mica, corresponding to 2.1 μmol/m^2 (or 4.2 μequiv/m^2), roughly that expected for complete exchange of the surface ions.[12,18,20]

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. Twenty milliliters of the freshly distilled styrene was then added under nitrogen

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to 0.4–0.5 g of the mica–AIBA complex in a polymerization tube fitted with a glass stopcock, a gas inlet side arm, and a magnetic stirrer bar. The contents were cooled and purged with nitrogen by applying several times vacuum and nitrogen alternatingly. The polymerization tube was then placed in a thermostated bath equipped with a magnetic stirrer and the tube connected to a nitrogen supply at a small superatmospheric pressure. Polymerization was carried out at 60 °C for a period of ca 0.5–5 days. Samples were removed periodically from the polymerization tube with a hypodermic syringe through the glass stopcock with nitrogen flowing out from the vessel through the stopcock.

The reaction samples were poured into methanol (volume at least 10 times that of the reaction mixture) to precipitate the polystyrene and were left standing for several hours. The mica–polymer mixture was then filtered. The solids so obtained were dried briefly under vacuum at room temperature. The mica–polymer solids were then treated by stirring for several hours in centrifuge tubes containing about 40 mL of toluene per gram of mica and centrifuged, and the supernatant was decanted into a large volume of methanol to precipitate the dissolved polymer. This treatment was repeated with fresh toluene 6–7 times. It was found that six to seven extractions, each for at least several hours, were sufficient to remove all the extractable material [additional extractions did not appear to change the amount of bound polymer, measured by thermal gravimetric analysis (TGA) (System TA 7000 thermogravimetric analyzer, Perkin-Elmer, Norwalk, CT)]. Finally, methanol was added to the centrifuge tubes instead of toluene, and following centrifugation and decantation, the remaining solids were dried under vacuum at 60 °C. The polymer obtained by precipitation of the toluene fractions into methanol was filtered and dried at 60 °C under vacuum. In this way, two products were obtained: toluene-soluble polymer and toluene-insoluble mica solids.

Further Extraction of the Toluene-Insoluble Mica Solids. Material which could not be extracted from the mica by treatment with toluene as described above (nor by treatment with tetrahydrofuran alone) could be extracted completely by stirring the mica solids for several days with a solution of 1% w/w lithium chloride in tetrahydrofuran (THF). This was shown by TGA analysis of the mica solids before and after extraction (the corresponding weight loss peaks disappeared after extraction). For NMR analysis, a solution of lithium chloride in deuterated THF was used to extract the material and spectra were obtained of this solution.

The bound polymer could also be extracted from the mica solids by treatment with lithium ethanolate in THF. The lithium ethanolate was prepared from 10.7 g of ethanol and 0.32 g of metallic lithium; the ethanolate solution was diluted with THF (0.46 g of solution in 25 mL of THF) and used to treat the polymer–mica complex for 2 h at room temperature. This appeared, from TGA, to remove the ionically bound polymer from the mica surface and the low molecular weight AIBA residues. To separate the polymer from the AIBA residues, after removal of the mica by filtration, the filtrate was shaken in a separatory funnel with 30 mL of 1 M HCl to which NaCl was added until two phases appeared: aqueous solution and organic solution I. The phases were separated, and organic phase I was extracted again twice with 1 M HCl and NaCl. Then 1 M NaOH was added to the collected aqueous phases to pH 12 and the liquid extracted 3 times with THF with NaCl added to separate the phases. The organic phases were collected and dried over sodium sulfate: to give organic phase II. The aqueous phase was discarded. The THF in organic phase I was evaporated under vacuum and the resulting polymer dissolved in a small amount of THF for GPC analysis. The THF in organic phase II was also evaporated under vacuum, and the resulting solids were dissolved in a small amount of deuterated water for NMR analysis.

Lithium ethanolate in THF was also used to extract AIBA residues from two samples of AIBA–mica complex that had been heated by themselves for 90 min at 110 °C and 1000 min at 60 °C, respectively.

III. Results

Mica with adsorbed AIBA (2.1 μmol/m^2) was treated with styrene at 60 °C. After specific intervals, the reaction was stopped and the products were analyzed. Two fractions of polystyrene were found: polystyrene that could not be removed from the mica surface by toluene extraction (polymer "bound" to mica) and toluene-soluble polymer that precipitated by addition of methanol.

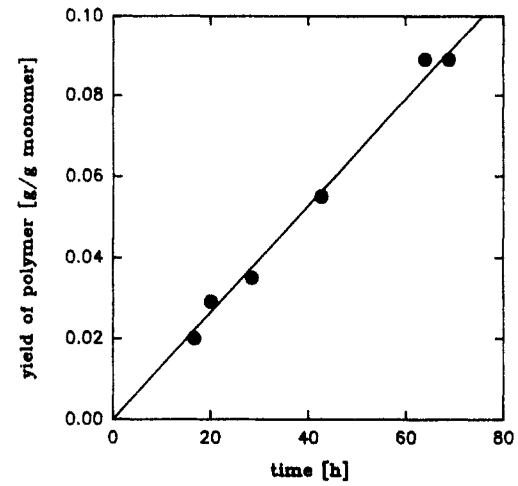


Figure 1. Yield of soluble polymer vs polymerization time.

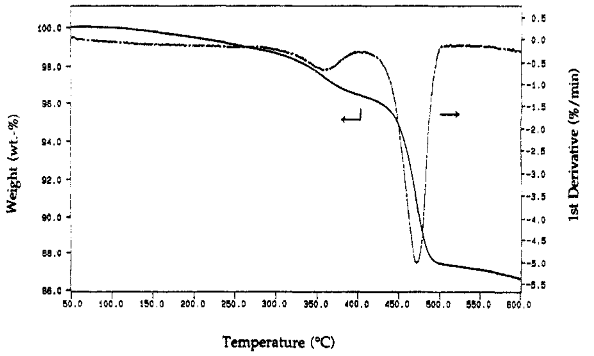


Figure 2. Weight loss (%) vs temperature for mica with toluene-insoluble polymer, in nitrogen at a heating rate of 20 °C/min.

The yield of soluble polymer (in grams of soluble polymer per gram of monomer charged) is plotted against the polymerization time for a sample run in Figure 1. The yield increases roughly linearly with time, over the observed time period. The rate of increase, about 3.1%/day, is in rough agreement with the initial rate of polymerization reported in the literature for the thermal polymerization of styrene, 2.6%/day at 60 °C.[21] ^{1}H and ^{13}C NMR spectroscopies confirmed that the product was indeed polystyrene.

The toluene-extracted mica solids were examined by TGA. Two major weight loss "peaks" were observed: one around 350 °C and one at ca. 470 °C (see Figure 2). Upon comparison of the TGA plots with those of polystyrene and AIBA residues (material remaining on mica after heating at 60 °C overnight), it was concluded that the observed weight loss at 470 °C was attributable to depolymerizing polystyrene bound to mica and that around 350 °C to AIBA residues. The maximum amount of bound polymer obtained was about 10% by weight of mica (or 30% by volume estimated from the respective densities of mica and polystyrene) depending on the reaction conditions (see below).

When untreated mica was used in place of the AIBA-treated mica in the polymerization tubes, the amount of soluble polymer formed was similar, but no bound polymer was produced. This lends support to the notion that ionic groups are responsible for the binding of polymer chains to the surface.

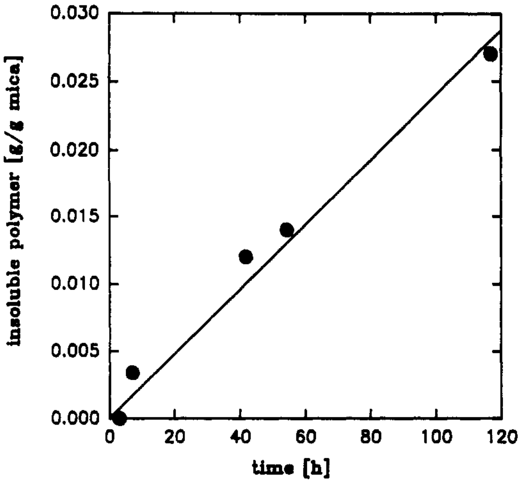


Figure 3. Yield of insoluble polymer vs polymerization time.

In contrast to untreated mica, the mica powders with bound polystyrene did not disperse in water and were clearly hydrophobic. Experiments were also performed using AIBA-treated mica sheets instead of powders in styrene polymerization. The resulting sheets, after extraction with toluene, gave contact angles with water of about 25°. This is intermediate between the 3° obtained with freshly delaminated mica and the 84° obtained with mica sheets coated with about 20 μm of polystyrene by evaporation of polystyrene solution.

The rate of formation of bound polymer varied considerably from run to run, by as much as a factor of 3, even under ostensibly identical reaction conditions. However, for samples drawn from the same tube after different periods of time, the amount of bound polymer increased linearly with polymerization time. This is shown for a sample run at 60 °C in Figure 3, where the amount of bound polymer obtained is plotted vs time.

To test the possibility that bonding of already (kinetically) terminated polystyrene chains was occurring, in some experiments preformed polystyrene was dissolved in the styrene (to 5 wt %) before heating with AIBA-mica. The amount of bound polymer which resulted was not significantly affected. In other experiments, polystyrene was dissolved in toluene (to 5 wt %) with AIBA-mica and without any styrene. When heated at 60 °C, no bound polymer was obtained. The implication is that bonding of already terminated polystyrene chains did not occur.

Infrared analysis (Nicolet 5 SXC FTIR) of the bound polymer supports the view that it is basically polystyrene. An IR spectrum of the solid mica–polymer complex is shown in Figure 4. The following assignments have been made: bands at 3600–3650 cm^{-1}, mica OH stretch; broad bands at 3000–3500 cm^{-1}, water OH stretch and amidino NH stretch; 3061 and 3028 cm^{-1}, polystyrene aromatic CH stretching vibrations; 2925 and 2852 cm^{-1}, polystyrene aliphatic CH stretch; 1696 cm^{-1}, water OH bending and amidino NH bending vibrations; 1601, 1493, and 1452 cm^{-1}, polystyrene aromatic ring skeletal vibrations. The small absorption bands at 1515, 1506, 1393, and 1372 cm^{-1} are attributed to a residue of AIBA, as they are also found in the spectra of micas treated with AIBA solutions and then heated at 60 °C for a day. A solid-state ^{13}C MAS NMR spectrum was obtained with broad signals and relatively high signal/noise; clear signals were found at ca. 40 (aliphatic carbon atoms of polystyrene), 126 (aromatic carbon atoms of polystyrene), 144 (aromatic carbon atoms of polystyrene), and 177 ppm (carbon atoms of amidinium groups).

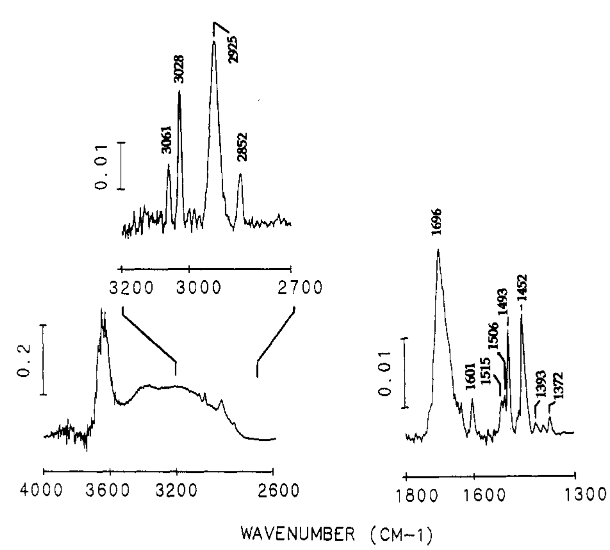


Figure 4. Infrared spectrum of toluene-insoluble polymer on mica, between KBr plates.

Table 1. NMR Analysis of AIBA Residues[a]

	δ ^{1}H, ppm	m	*n*	^3J(H,H), Hz	^4J(H,H), Hz	δ ^{13}C, ppm
		Isobutyramidinium[b]				
CH_3	1.30	d	6	7.0		22.95
CH	2.81	sep	1	7.0		35.01
		Methacrylamidinium[b]				
CH_3	2.08	d × d	3		1.0; 1.5	20.60
=CH trans	5.78	q	1		1.6	128.08
=CH cis	5.93	q	1		0.9	128.08

[a] ^{1}H and ^{13}C NMR chemical shifts, δ (in D_2O), and coupling constants, *J*, of the main products detected after desorption followed by extraction (details in the text). Indicated also are other data from ^{1}H NMR spectra, i.e., the multiplicity, m (d = doublet, q = quartet, sep = septet), and the number of hydrogen atoms represented by the integrated intensities, *n*. [b] The signals of the amidinium groups, not listed here, appear in the ^{13}C NMR spectrum at 178.69 and 180.96 ppm, respectively.

The polymer bound to mica desorbed in a LiCl/THF solution but not in THF alone (THF normally dissolves polystyrene). This is consistent with the idea that the bound polymer is attached to mica by ionic groups. The lithium ions in LiCl/THF presumably exchange with the ionic groups releasing the bound polymer and permitting its dissolution in THF. When deuterated THF containing LiCl was used, an NMR spectrum of the released substance could be obtained. The spectrum was consistent with it being polystyrene.

The bound polymer could also be dissolved in $LiOCH_2CH_3$/THF. This is again consistent with the polymer being bound to the mica by ionic chain ends. The ion exchange in this case is probably accompanied by deprotonation (aqueous NaOH deprotonates AIBA to 2,2′-azobis(isobutyramidine)[22]). The material in the THF solution could be separated into a "low molecular weight fraction" and a fraction consisting predominantly of polymer ("high molecular weight fraction") by shaking the THF solution with acidic water, followed by addition of NaOH to the aqueous phase up to a pH value of 12, and finally shaking the aqueous solutions with THF (see Experimental Section).

The low molecular weight fraction was examined by ^{1}H and ^{13}C NMR spectroscopies (Bruker, AMX 500) in D_2O. The main signals (containing ca. 85% of the total integral in the ^{1}H NMR spectrum) are presented in Table 1. The same main signals were observed in the material released from mica after AIBA-treated mica had been heated under

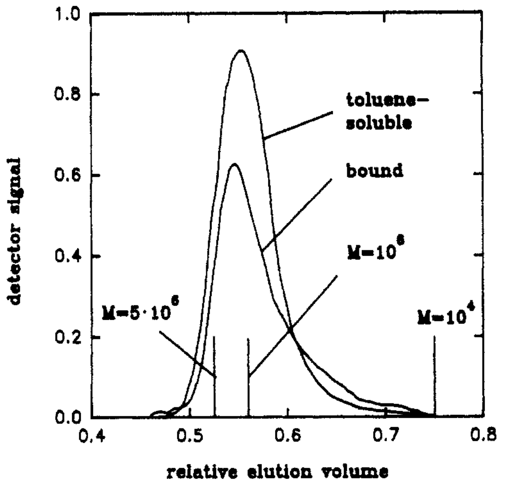
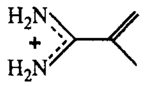
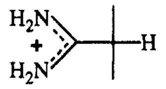


Figure 5. GPC chromatograms for toluene-soluble and bound polymers.

vacuum (ca. 100 Torr) at 110 °C for 90 min. The spectra indicate that the low molecular weight fraction consists predominantly of roughly equal amounts of methacrylamidinium (2-methylpropenamidinium) ion, hereafter MAA,



and isobutyramidinium (2-methylpropanamidinium) ion, hereafter IBA.



In the ^{1}H NMR spectrum, some small signals close to those of the main products with identical coupling patterns indicate a partial hydrolysis of the amidinium group during workup, which is confirmed by the observation of signals at 168.2 and 169.8 ppm in the ^{13}C NMR spectrum (assigned to carboxylic acid groups formed by hydrolysis of the amidinium groups). When DCl is added to the NMR solution and the solution is allowed to stand for a week, only the products attributed to the carboxylic acid species are found. No signals were detected in the aromatic region within the detection limits, i.e., the amount of phenyl groups in the low molecular weight fraction is less than 0.5% with respect to each of the two main products. The high molecular weight fraction, removed by treatment of the mica-bound polymer complex with $LiOCH_2CH_3$/THF, showed two distinct fractions in size-exclusion chromatography (GPC) (with refractometer detector, Knauer, Berlin, FRG, with a PL-Gel 5-μm mixed C 7.5- × 600-mm column, Polymer Laboratories, Shropshire, U.K.), at 45 °C in THF, one with a peak at about $M \approx 900$ (the lower limit of resolution) or lower and one with a peak at $M \approx 1.5 \times 10^6$. The low molecular weight material may contain AIBA residues, oligomers, or residual lithium ethanolate. The toluene-soluble polymer was also examined by GPC and found to display a peak at $M \approx 1.4 \times 10^6$.

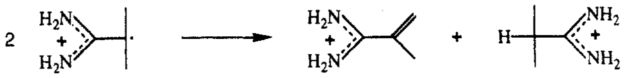
GPC with a known concentration of polystyrene showed that the amount of bound polymer (per weight of mica) measured by TGA at ca. 470 °C and that found in the GPC peak ($M > 2000$) are essentially the same.

The high molecular weight GPC peaks, for the toluene-soluble polymer and the bound polymer, are shown for comparison in Figure 5. Also shown is the relative elution volume corresponding to $M = 10^6$ (calibrated with a polystyrene of narrow molecular weight distribution). This is the value of $\langle M_n \rangle$ expected for the thermal polymerization of styrene.[23] It can be seen that the chromatograms for the toluene-soluble and the bound polymer are similar, with similar peak positions, although the bound polymer has more low molecular weight material present.

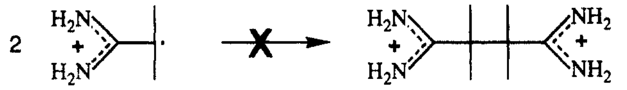
IV. Discussion

Crystalline AIBA is quite stable at 60 °C and only decomposes upon melting at about 170 °C.[24] In contrast, AIBA in solution or adsorbed on mica is much less stable. We found, for AIBA in dry AIBA-mica complex, half-life ($\tau_{1/2}$) of about 1 h at 60 °C using mass spectrometry to determine the rate of nitrogen evolution. That the stability of the AIBA complex is so different from that of neat solid AIBA suggests that the adsorbed AIBA is indeed molecularly dispersed on the surface. For AIBA dissolved in water, the $\tau_{1/2}$ is quite different from either that of adsorbed AIBA or that of the pure solid: we found it to be about 5 h at 60 °C, in good agreement with the values measured in the literature.[6,25] That $\tau_{1/2}$ is different, in this case shorter, for the compound complexed to a surface than for the compound in solution is not without precedent. For example, the $\tau_{1/2}$ of AIBA adsorbed on kaolin is about 3 h.[6] It has also been reported for similar azo initiators that binding to a silica surface destabilizes the initiator and that destabilization is greater when the initiator is bound at both ends than at just one end; this latter effect was attributed to "ring tension",[11,26,27] with "ring" referring to the structure formed by surface and initiator bound at both ends. It is therefore quite plausible that a $\tau_{1/2}$ of AIBA depends not only on whether it is adsorbed but also on the chemical and steric characteristics of the surface ion-exchange sites with which it is complexed.

The main products produced by AIBA decomposition on mica, MAA and IBA, appear to form by disproportionation of the free radicals generated by loss of nitrogen in AIBA

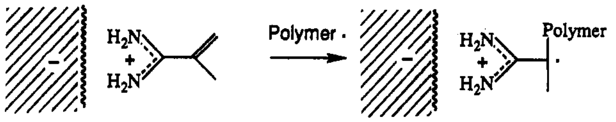


rather than by coupling of the free radicals

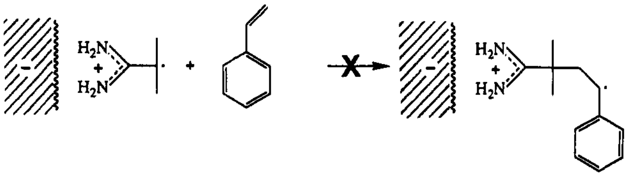


In free-radical polymerization, initiation, growth, and termination of individual chains is normally complete in a few seconds or less.[28,29] For surface-initiated polymerization, one would expect that the rate of formation of bound polymer would parallel the rate of decomposition of the bound initiator. With a $\tau_{1/2}$ for AIBA adsorbed on mica of about 1 h at 60 °C, the initiator should substantially lose its activity after a few hours, and the amount of bound polymer would be expected, for initiation by surface-bound free radicals, to parallel the rate of decomposition of AIBA adsorbed on mica. The rate of growth would be highest at the outset and decrease steadily toward zero with a rate of decrease reflecting the $\tau_{1/2}$ of the initiator. Such behavior was indeed observed for the growth of bound polymer in the polymerization of styrene using azo compounds bound to silicon dioxide surfaces.[30] Yet Figure 3 shows that bound polymer formed at a roughly constant rate over a period of several days; i.e., the rate of polymerization for the bound polymer and in particular its constancy with time is not consistent with surface-

Scheme 1



Scheme 2



initiated polymerization. In contrast, in the present work, growth of bound polymer continued at a fairly steady rate over periods of time far in excess of the half-life of the AIBA on the surface.

Our explanation for these observations is that bound polymer forms predominantly from the addition of growing, thermally-initiated polystyrene chains, R•, to the MAA ion on the surface (Scheme 1) and not from the addition of monomer to surface free radicals generated by AIBA decomposition (Scheme 2). The fate of the free radical resulting from Scheme 1 is not known, but its subsequent elimination by a chain-transfer step, to monomer for example, is one of several possibilities.

That AIBA, bound to the surface, is ineffective in initiating chains is probably due to spacial juxtaposition of the two intermediate radicals determined by the binding of the AIBA to the mica exchange sites. It has been found that many compounds having the azo group in a ring structure are unsuitable as polymerization initiators, because the diradicals formed upon azo decomposition couple to form cycloalkanes or disproportionate to form olefins, instead of initiating chains.[31] The same appears to occur in the present case, with disproportionation as the predominant reaction. However, the possibility that some chains are initiated by surface free radicals and then terminated by coupling after the addition of only a few styrene units (formation of bound oligomer) cannot be ruled out at this point.

For Scheme 1, it is to be expected that (1) the amount of soluble polymer and the amount of bound polymer both increase roughly proportional to the time of polymerization over a period of several days and (2) the molecular weight of the soluble polymer is about the same as that of the bound polymer. This was actually observed.

As previously noted, preheated AIBA–mica complex yields predominantly the disproportionation products MAA and IBA. If addition of thermally-initiated chains to MAA on the surface is indeed the main mechanism for formation of bound polymer, then "deactivated" AIBA–mica in styrene should also give bound polymer. Complex which had been preheated overnight at 80 °C and was then kept at 60 °C in neat styrene did indeed yield bound polymer at a rate comparable to that obtained with fresh complex.

Polymerizations were also carried out with 0.23 wt % (relative to styrene) AIBN added to the styrene. Growing chains initiated by AIBN would be expected to bind to the surface in the same way as growing chains which are thermally initiated. However, as the rate of initiation by AIBN is higher than that of thermal initiation, the amount of bound polymer should increase more rapidly in this case. The amount of bound polymer would also in this case, after an initial period, be expected to increase linearly with time. The data in Figure 6 show that this behavior was indeed observed.

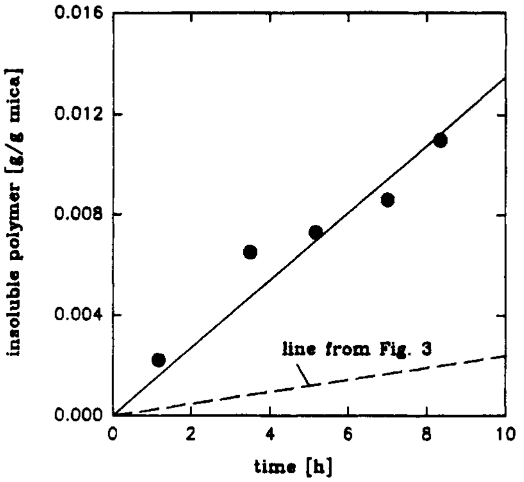


Figure 6. Yield of insoluble polymer vs time with 0.23 wt % AIBN added.

There are a number of possible alternatives to Scheme 1 that, however, seem less likely. One is chain transfer of thermally-initiated chains to MAA on the surface. This would initiate a growing free radical on the surface. Another alternative is Scheme 2, modifed by the hypothesis of retarded growth and termination, giving a type of "living" polymerization. Both could explain the steady growth of bound polymer over several days, but neither can in a satisfying way account for the strong similarity in molecular weight between bound polymer and thermal polymer. This variant of Scheme 2 is also incompatible with the observed effectiveness of thermally-inactivated AIBA–mica in forming bound polymer and also the effectiveness of added AIBN.

It is evident that the bound high polymer chain ends are very sparcely distributed on the mica surface. Considering that there are about 4 μmol/m^2 of ion-exchange sites on the mica with a specific surface area of about 100 m^2/g, about 400 g of polymer/g of mica could be expected if each site had a chain attached with $M \approx 10^6$. In none of the runs was the amount of bound polymer more than ca. 10 wt % mica, however, and it follows that only a very small fraction of initiator sites (less than 1 in 4000) had high molecular weight polymer attached. Nevertheless, on a weight basis and even more on a volume basis, a significant amount of polystyrene is grafted to the mica. As the density of mica is about 3 g/cm^3 and the density of (amorphous) polystyrene about 1 g/cm^3, a bound polymer content of 10 wt % corresponds to about 30 vol %.

These results indicate that grafting of polymer to surfaces can be induced by attaching a disproportionating free-radical initiator to the surface and adding an unbound free-radical initiator to the bulk liquid.

V. Conclusions

When AIBA–mica complex is heated in the presence of styrene at 60 °C, surface free radicals are formed which predominantly disproportionate. As a result, initiation from the surface plays a minor role in the formation of polymer. Instead, growing chains of polymer in solution, created by thermal initiation (or by addition of AIBN), react with the AIBA decomposition products on the surface to yield polymer bound by the headgroups to the surface. The bound polymer consists predominantly of high molecular weight chains bound to a very small fraction of the surface ion-exchange sites. Because of the high molecular weight of the polymer and the high surface area of the mica, a significant amount (by weight and volume fraction) of grafted polymer is formed.

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