

Research Article

Effect of Oxygen and Initiator Solubility on Admicellar Polymerization of Styrene on Silica Surfaces

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Although admicellar polymerization has been termed the surface analog of emulsion polymerization, previous reports utilizing free radical-initiated admicellar polymerization relied on high levels of the free radical initiator when compared to emulsion polymerization, likely due to the presence of oxygen in the reported admicellar polymerization systems. Admicellar polymerizations of styrene on the surface of precipitated silica initiated by either a water-soluble or a water-insoluble initiator were studied to determine the effect of dissolved oxygen and free radical initiator solubility on the kinetics, yield, and molecular weight of the polymer formed. Results show that the presence of oxygen reduces the polymer yield and limits molecular weight. The solubility of the initiator also affected the polymer formed in the admicellar polymerization of styrene. While monomer conversions and polymer yield were similar, the molecular weights of polymerizations initiated by a water-soluble initiator were higher than comparable polymerizations initiated by a water-insoluble initiator.

1. Introduction

Since initial reports in the mid-1980s [1, 2], the admicellar polymerization technique has proven to be an effective way to modify the surface characteristics of solid substrates for rubber reinforcement [3–5], corrosion control [6, 7], the formation of conducting films [8–12], the modification of cotton fibers [13–19], and composite fillers [20, 21]. Admicellar polymerization has been summarized as a four-step process: formation of adsorbed surfactant aggregates (admicelles), monomer solubilization into the admicelle (adsolubilization), polymerization, and partial removal of surfactant. Admicellar polymerization systems typically utilize surfactant concentrations just below the critical micelle concentration (CMC). Sparingly soluble monomers preferentially partition from the bulk into the interior of the admicelle prior to and during polymerization. Following polymerization, the adsorbed surfactant can be partially removed by repeated washings with negligible loss of the formed polymer [22].

Although admicellar polymerization has been called the surface analog of emulsion polymerization [1, 2], there are major differences between the two. One major difference is the molar ratios of monomer to initiator (M/I) that are

typically used in emulsion and admicellar polymerization. In an emulsion polymerization system, this ratio is typically greater than 500 and may exceed 1000 [23, 24]. Previous admicellar polymerization studies demonstrated that low M/I values (below 15) were needed in order to achieve significant conversion of monomer into polymer [4, 16–18, 25–30]. Pongprayoon et al. studied the effect of M/I values ranging from 1 to 4 for the synthesis of a polystyrene-coated cotton fabric via admicellar polymerization and found that cotton fibers with the highest surface hydrophobicity were formed at M/I values of 1 [31, 32]. The authors hypothesized that polymerization at higher initiator concentrations (lower M/I values) formed more polystyrene, resulting in increased hydrophobicity despite the polymer thin films having a low weight-averaged molecular weight (M_w) of 6×10^3 g/mol [32]. This study also demonstrated that emulsion and admicellar polymerization performed under similar conditions (same surfactant-to-monomer concentration of 1 : 10 and M/I value of 1 : 1, without deoxygenation) were able to achieve similar polymer molecular weights of approximately 2×10^5 g/mol. However, polymer obtained via admicellar polymerization contained a substantial fraction of lower molecular weight polymer [32].

Admicellar polymerization has usually been carried out in the presence of oxygen, both in the headspace and dissolved in the solution. Oxygen is a well-known radical inhibitor, forming peroxide radicals that compete with chain propagation [33–36]. Sparging admicellar polymerization systems with an inert gas would cause foaming of the surfactant solution and significant loss of volatile monomers; however limited studies have explored admicellar polymerization in an inert environment achieved by purging the headspace of the reaction vessel [37–39]. Lai et al. performed admicellar polymerization of tetrafluoroethylene in perfluorocarbon admicelles on alumina in a nitrogen-purged reactor [38]. The authors reported a fivefold increase in monomer conversion (from 7% to 35%) when the initiator concentration increased by a factor of 100. However, the authors noted that the supernatant turned cloudy at the highest initiator concentration and hypothesized that solution-phase polymerization occurred at the highest initiator concentration despite having the system below the CMC. A subsequent study by Seul et al. examined the effect of initiator concentration on the admicellar polymerization of methyl methacrylate on calcium carbonate in a nitrogen-purged reactor, finding an optimal M/I value of ~225 to achieve 100% monomer conversion in five hours [39]. The authors reported incomplete conversion of monomer at lower initiator concentrations (higher M/I values) and coagulation of the calcium carbonate particles at higher initiator concentrations. Karlsson et al. utilized admicellar polymerization of methyl methacrylate (MMA) to coat aluminum pigments in a nitrogen-purged environment utilizing M/I values range from 114 to 9 to achieve organic weight losses of up to 24% after 24 hours of polymerization [37]. Despite these examples, the impact of removing oxygen from the system on the molecular weight of the polymer formed by admicellar polymerization has not been systematically studied and compared to polymerization in the presence of oxygen. A better understanding of the effect of oxygen in free radical admicellar polymerization may allow applications of the method to significantly lower initiator amount, improving their profitability.

Herein, we report the admicellar polymerization of styrene in the absence of oxygen using hexadecyltrimethylammonium bromide (CTAB) to form admicelles on porous silica particles and compare the results to control polymerizations performed in the presence of oxygen. We examine M/I values varying from 15 (high values for admicellar polymerization) to 1000 (typical of emulsion polymerizations). We also investigate the effect of initiator solubility on the conversion and molecular weight formed via the admicellar polymerization of styrene.

2. Materials and Methods

2.1. Materials. Precipitated silica Hi-Sil 233 (N_2 BET surface area of $135 \text{ m}^2/\text{g}$) was obtained from PPG Industries (Pittsburgh, PA). CTAB, AIBN, and V-501 were purchased from Sigma Aldrich (St Louis, MO). Styrene was obtained from Acros Organics (New Jersey) and was passed through a bed of aluminum oxide to remove the inhibitor. Ultrapure water was dispensed from a Millipore Direct-Q 3UV dispenser

system (resistivity $18.2 \text{ M}\Omega\text{-cm}$, 25°C). All other chemicals were purchased from Fisher Scientific (New Jersey) and used as received.

2.2. Admicellar Polymerization of Styrene. Adsorption and adsolubilization studies were performed according to a modified literature procedure [40]. Silica, CTAB, initiator, and distilled water in appropriate ratios determined from adsorption and adsolubilization studies were added to a 250 mL flask. In a typical experiment, silica (10 g) and CTAB (0.99 g, 2.7 mmol) were added to water (150 mL) to form admicelles on the silica surface and equilibrate at a bulk concentration of CTAB of ~90% of the CMC (CMC ~ $950 \mu\text{M}$) [41]. The initiator (V-501 or AIBN) was then added to give M/I values of 1000, 150, or 15. The headspace of the deoxygenated samples was purged with nitrogen for 30 minutes. Styrene (0.54 g, 5.2 mmol) was then added before removing the nitrogen purge, yielding a styrene to adsorbed CTAB molar ratio of 2:1. After the addition of the styrene, samples were mixed for 3 hours to allow for the adsolubilization of styrene prior to immersion in a water bath at 70°C . Polymerization was terminated after a predetermined time by immersion in a cold water bath and by introduction of air into the samples. Subsequently, the supernatant of the sample was decanted and the surface-modified silica sample was washed with 1 L of 1:1 (v/v) methanol and water mixture followed by 3 L of water. The modified silica samples were collected and dried at $\sim 100^\circ\text{C}$ for at least 6 hours before analysis. Polymer was recovered from the modified silica via Soxhlet extraction with refluxing THF for 48 hours followed by precipitation in water. The polymer was rinsed thoroughly with water and dried prior to analysis. Control polymerizations samples followed the same procedure without purging the headspace with nitrogen. All polymerizations were performed in triplicate.

2.3. Characterization. The modified silica samples were analyzed with an Agilent Technologies Cary 630 Fourier transform infrared (FTIR) spectrometer from 4000 to 650 cm^{-1} to confirm the presence of polystyrene on the surface of the modified silica samples. The amount of polymer formed for each of the modified samples was determined using TA Instruments Q500 thermogravimetric analyzer heating from room temperature to 650°C at $20^\circ\text{C}/\text{min}$ under a nitrogen atmosphere to determine. Weight loss above 300°C was attributed to the degradation of the polystyrene formed on the silica surface. Based on the amount of silica (10 g) and styrene (0.54 g) added to each sample, if all of the styrene formed polymer on the surface of the modified silica, the maximum weight loss observed in TGA would be 5.1%. Therefore, the apparent conversion for a sample can be calculated by

$$\rho_{\text{app}} = \frac{\text{Percent Weight Loss above } 300^\circ\text{C}}{5.1\%} \quad (1)$$

M_w and polydispersity index (PDI) of the extracted polymer samples were measured by size exclusion chromatography (SEC) utilizing THF as the mobile phase at a flowrate of 1 mL/min, a Thermo Scientific Dionex UltiMate 3000 pump

and autosampler, a Water Styragel guard column (4.6 mm \times 30 mm), two Waters Styragel HR 5E columns (7.8 mm \times 300 mm), a Wyatt miniDAWN TREOS light scattering detector ($\lambda = 690$ nm), and a Wyatt Optilab t-REX differential refractive index (dRI) detector ($\lambda = 690$ nm). The dn/dc of polystyrene was measured using a Wyatt Optilab t-REX, and the measured dn/dc values were used for absolute molecular weight determination with the Wyatt Technology ASTRA software.

3. Results and Discussion

3.1. Effects of Oxygen on Admicellar Polymerization. Polymer-modified silica samples were prepared by the free radical admicellar polymerization of styrene in CTAB admicelles on Hi-Sil 233 precipitated silica. FTIR analysis was used to confirm the presence of polystyrene on the surface of the modified silica samples. FTIR spectra for a polystyrene standard, extracted polystyrene, untreated silica, silica modified by AIBN-initiated deoxygenated admicellar polymerization (M/I of 1000, polymerization time of 6 hours), and silica modified by the control admicellar polymerization (M/I of 1000, polymerization time of 6 hours) are presented in Figure 1. The spectra of the extracted polystyrene (Figure 1, curve (b)) and modified silica (Figure 1, curve (d)) synthesized under an inert atmosphere demonstrate the characteristic phenyl group absorbance at ~ 700 cm^{-1} , confirming the presence of a polystyrene thin film on the surface. In contrast, the FTIR spectra of the control samples synthesized at an M/I of 1000 (Figure 1, curve (e)) exhibit minimal, if any, polystyrene formed on the silica surface. TGA was performed to quantify the polymer formed on the surface of the silica. The TGA profile of modified silica samples at an M/I value of 1000 is shown in Figure 2. Weight loss below $\sim 150^\circ\text{C}$ and between 200 and 300°C was attributed to water loss and CTAB decomposition (decomposition temperature of CTAB is 230°C), respectively. Meanwhile, weight lost above 300°C was attributed to the decomposition of polystyrene and is representative of the amount of polymer formed on the silica surface. All modified silica samples except the control samples at an M/I value of 1000 exhibited measureable weight loss above 300°C , attributed to polystyrene decomposition. Figure 2 compares the TGA profiles of silica modified by deoxygenated admicellar polymerization and by the control admicellar polymerization. After a polymerization time of six hours at an M/I value of 1000, the deoxygenated sample exhibits a weight loss attributed to polystyrene of 4.1% (Figure 2, curve (b)), corresponding to an apparent conversion of $\sim 80\%$. In contrast, the control sample only showed a 0.54% weight loss (Figure 2, curve (c)), corresponding to an apparent conversion of $\sim 11\%$.

3.2. Effects of Oxygen on the Kinetics of Admicellar Polymerization. In order to investigate the effects of oxygen on the kinetics of the admicellar polymerization, the apparent conversion was compared for deoxygenated and control (nondeoxygenated) polymerization samples at M/I values of 15, 150, and 1000 at varying polymerization times as shown in Figure 1. The kinetics of the deoxygenated polymerizations

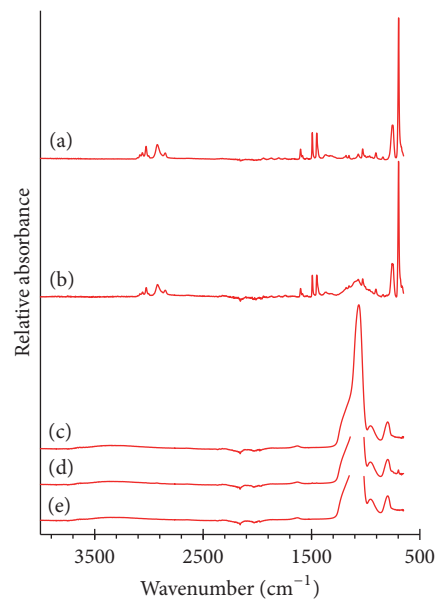


FIGURE 1: FTIR spectra for (a) polystyrene standard (M_w 6×10^5 g/mol), (b) extracted polystyrene (M/I of 1000, polymerization time of 6 hours), (c) untreated silica, (d) silica modified by deoxygenated admicellar polymerization of styrene (M/I of 1000, polymerization time of 6 hours), and (e) silica modified by the control admicellar polymerization of styrene (M/I of 1000, polymerization time of 6 hours).

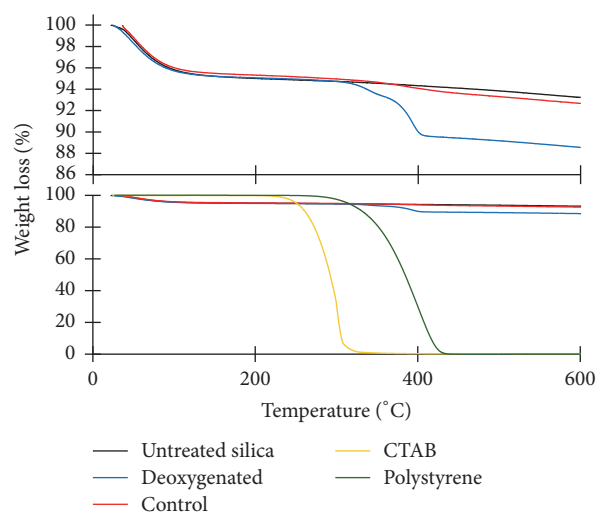


FIGURE 2: TGA profile for (black line) untreated silica, (blue line) deoxygenated admicellar polymerization on silica (M/I of 1000, 6 hours of polymerization), and (red line) control admicellar polymerization on silica (M/I of 1000, 6 hours of polymerization).

followed the expected trend of the rate of polymerization being slower for polymerizations with higher M/I values (less initiator). This is consistent with both free radical polymerization and emulsion polymerization with higher initiator concentrations leading to faster polymerization kinetics. An interesting observation is made by comparing the deoxygenated samples to the control samples at the three

TABLE 1: Polymer weight loss of modified silica (in terms of apparent monomer conversion %) and weight-averaged molecular weight (M_w , g/mol) and polydispersity (PDI) of extracted polymer for deoxygenated and control admicellar polymerizations initiated by AIBN.

M/I molar ratios	Deoxygenated			Control		
	Apparent conversion (%)	M_w (g/mol)	PDI	Apparent conversion (%)	M_w (g/mol)	PDI
15	91	3.7×10^5	2.1	94	1.7×10^5	2.1
150	88	8.5×10^5	1.6	57	7.1×10^5	1.7
1000	80	1.8×10^6	1.2	11	N/A	N/A

M/I values investigated. At an M/I value of 15, there is little, if any, difference in the kinetics of the deoxygenated polymerization versus the control, with both reaching an apparent conversion of $\sim 90\%$ in one hour and an ultimate conversion of $\sim 97\%$. At this M/I value, there was enough initiator in the system to overcome the inhibition of the oxygen dissolved in solution and in the headspace. In contrast, at an M/I value of 150, the deoxygenated sample reached a conversion of 78% while the control sample achieved only 12% after one hour. The presence of oxygen either retarded the polymerization rate or inhibited the polymerization until all the oxygen was consumed by free radicals derived from the initiator. Additionally, the conversion of the control polymerization at M/I of 150 plateaus was $\sim 57\%$ after 6 hours, compared to an ultimate conversion of $\sim 95\%$ for the deoxygenated polymerization at M/I of 150. This suppression of the achievable conversion is exacerbated when the M/I value is increased to 1000. The deoxygenated polymerization achieves 94% conversion after 24 hours with the control sample plateaus at $\sim 11\%$ after 1 hour. This is in stark contrast to the results reported by Cunningham et al. on the effects of oxygen on the emulsion polymerization of styrene [42]. The authors observed that the presence of oxygen leads to concentration-dependent induction periods between 10 and 150 minutes with increasing oxygen concentrations leading to greater induction times but found that all of the emulsion polymerization systems ultimately reached greater than 90% conversion.

Experiments were also conducted to ascertain the effect of oxygen on the molecular weight of the polystyrene synthesized by admicellar polymerization. Figure 4 and Table 1 summarize M_w , polydispersity indices (PDI), and apparent conversions of the polystyrene formed on the surface of the silica after six hours of polymerization at varying M/I values. As can be seen, the experimentally determined M_w increases with larger M/I values (lower initiator concentrations) in both deoxygenated and control samples. This trend agrees with the behavior of both free radical and emulsion polymerizations where the molecular weight (neglecting the effects of chain transfer) is inversely proportional to the initiator concentration [36]. As can be seen in Figure 4, the deoxygenated polymerization samples, in general, have higher apparent monomer conversions (as discussed above) and higher M_w 's than the control samples. This effect can best be observed

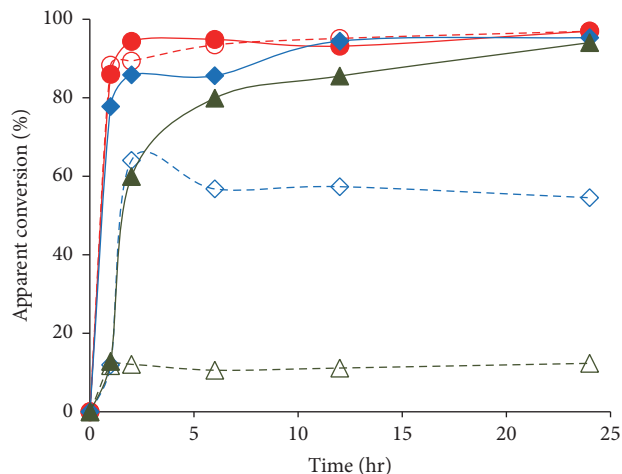


FIGURE 3: Apparent conversion versus polymerization time in AIBN-initiated, deoxygenated admicellar polymerization (“solid red circle” M/I of 15; “solid blue diamond” M/I of 150; “solid green triangle” M/I of 1000) and control admicellar polymerization (“vacant red circle” M/I of 15; “vacant blue diamond” M/I of 150; “vacant green triangle” M/I of 1000). Lines are drawn solely to guide the eye.

in the samples at an M/I value of 1000. The deoxygenated admicellar polymerization initiated by AIBN achieved an apparent conversion of 80% as determined by TGA and an M_w of 1.8×10^6 as measured by SEC. The control sample had an apparent conversion of 11% and resulted in insufficient polymer recovery for SEC analysis. While the presence of oxygen has less of an effect on the apparent conversion of the polystyrene formed at an M/I value of 15 (Figure 4), likely due to excess initiator available to compensate for the loss of active radicals to oxygen, there is a significant difference in M_w measured by SEC (3.7×10^5 for the deoxygenated samples versus 1.7×10^5 for the control samples). A previous study by Cunningham et al. demonstrated that the presence of oxygen in emulsion polymerizations leads to lower molecular weights due to premature termination of the growing polymer chains by oxygen [42]. Interestingly, the authors reported that the polymer molecular weights increased after the consumption of the dissolved oxygen to achieve a final M_w similar to the oxygen-free system at the end of the reaction. In the present study, however, the molecular weights of the samples polymerized for 6 hours in the presence of oxygen are lower than the deoxygenated samples (Figure 3). It is important to note that there is a dramatic difference between the ratios of initiator to oxygen present in the emulsion polymerization study by Cunningham et al. (between 1 and 2) and the admicellar system examined in the present study (1.125 at M/I of 15, 0.113 at M/I of 150, and 0.017 at M/I of 1000). Additionally, there is ~ 400 times more monomer in the emulsion study reported by Cunningham et al. than in the present admicellar system, leading to a greater likelihood of polymerization occurring after the oxygen is consumed in the system studied by Cunningham et al.

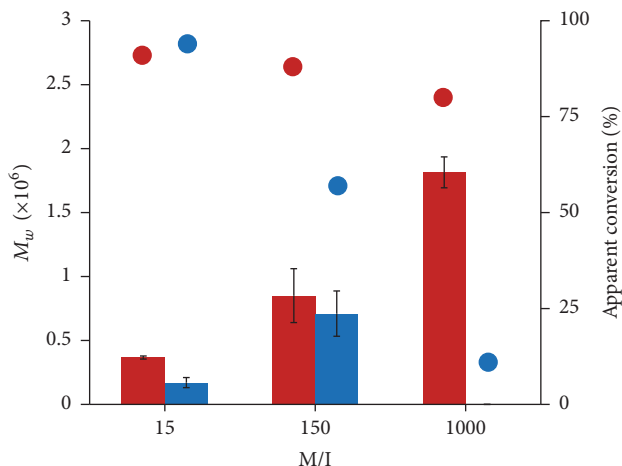


FIGURE 4: Weight-averaged molecular weight (bars) and apparent conversion (circles) for the AIBN-initiated (red color) deoxygenated and (blue color) control admicellar polymerizations of styrene at M/I values of 15, 150, and 1000. Control samples at M/I = 1000 did not generate enough polymer for SEC analysis.

3.3. Effect of Initiator Solubility on Admicellar Polymerization.

The effect of the initiator location (predominantly in the admicelle versus predominantly in solution) on the conversion and molecular weight of polystyrene synthesized by admicellar polymerization was examined by preparing samples utilizing either a water-soluble (V-501) or a water-insoluble (AIBN) initiator (Table 2). Karlsson et al. reported that the utilization of a hydrophobic initiator at an M/I value of ~ 9 for the 24-hour deoxygenated admicellar polymerization of methyl methacrylate on aluminum pigments resulted in a fourfold increase in weight loss compared to a system using a hydrophilic initiator under the same conditions [37]. However, it is important to note that the study by Karlsson et al. used a higher initial concentration of monomer (280 mM) compared to the present study (4.6 mM), which may have led to the formation of monomer droplets, either in solution or phase separated in the admicelle [43]. Interestingly, in our studies, the apparent conversion was similar for comparable M/I values regardless of the initiator solubility (Figure 5) and followed the expected trend of conversion decreasing at six hours as the M/I value increases. This data leads us to the conclusion that the initial location of the initiator does not affect the conversion of admicellar polymerization.

Utilizing size exclusion chromatography, we also measured the molecular weights of the extracted polystyrene samples generated by the AIBN- and V-501-initiated admicellar polymerizations. Interestingly, at M/I values of 15 and 150, the AIBN-initiated polymerization of styrene exhibited smaller M_w 's (3.7×10^5 at M/I = 15 and 8.5×10^5 at M/I = 150) compared to that of the V-501-initiated polymerization (8.0×10^5 at M/I = 15 and 1.2×10^6 at M/I = 150). This is attributed to a greater fraction of the hydrophobic initiator (AIBN) partitioning to the admicelle core, thereby increasing the number of polymerization sites in the admicelle and lowering molecular weight of the polymer. This finding is consistent with the report of Karlsson et al. [37]. While they did not

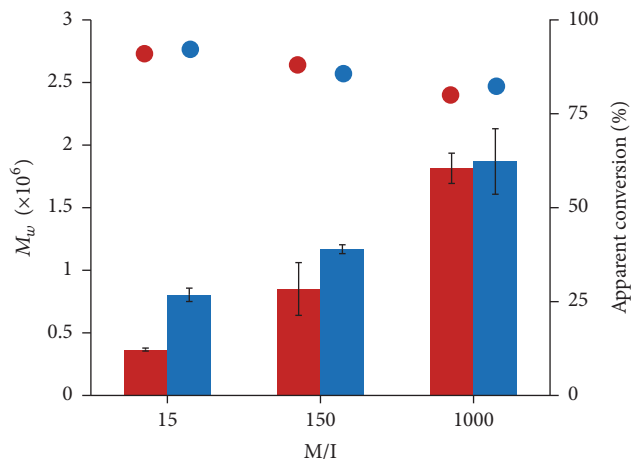


FIGURE 5: Weight-averaged molecular weight (bars) and apparent conversion (circles) for the deoxygenated admicellar polymerizations of styrene initiated by (red color) AIBN and (blue color) V-501 at M/I values of 15, 150, and 1000.

TABLE 2: Polymer weight loss of modified silica (in terms of apparent monomer conversion %) and weight-averaged molecular weight (M_w , g/mol) and polydispersibility (PDI) of extracted polymer for deoxygenated admicellar polymerizations initiated by AIBN and V-501.

M/I molar ratios	AIBN			V-501		
	Apparent conversion (%)	M_w (g/mol)	PDI	Apparent conversion (%)	M_w (g/mol)	PDI
15	91	3.7×10^5	2.1	92	8.0×10^5	1.5
150	88	8.5×10^5	1.6	86	1.2×10^6	1.4
1000	80	1.8×10^6	1.2	82	1.9×10^6	1.2

determine polymer molecular weights via SEC, the TGA results showed thermal decomposition at lower temperatures for polymer samples synthesized using a hydrophobic initiator, and the authors attributed this to the formation of lower molecular weight polymer. In the present study, the effect of initiator solubility on the molecular weight is found to be negligible at an M/I of 1000. We hypothesize that, at this M/I value, the molecular weight of the admicellar polymerizations initiated by either initiator are now controlled by the diffusion of monomer to the active radical in the admicelle as opposed to polymerizations at lower M/I values where the number of active sites is great enough that monomer does not have to diffuse a great distance to encounter a growing radical chain. This hypothesis is also supported by the decreasing conversion as the M/I increases.

4. Conclusions

Previous reports utilizing free radical-initiated admicellar polymerization relied on high concentration of initiator (M/I values between 1 and 15) for the surface modification of substrates by formation of polymer thin films. We hypothesized that is due to the presence of oxygen in the polymerization

system, consuming active radicals and forming the peroxide radicals, resulting in low molecular weight chains and limited monomer conversion. Herein, we examined deoxygenated admicellar polymerizations of styrene at three M/I values, 15, 150, and 1000. Our results show that while there is little difference between conversions in deoxygenated and control admicellar polymerizations at an M/I value of 15, as the M/I values increase the conversion in the deoxygenated sample remains high while the control samples exhibit significantly lower conversions. We believe this is due to there being enough initiator at an M/I of 15 to overcome the presence of oxygen, while at higher M/I values the presence of oxygen dramatically limits the number of initiator fragments that initiate polymerization. The presence of oxygen also has a dramatic effect on the molecular weight of polymer formed in admicellar polymerizations, limiting the molecular weight obtained. The effect of initiator location was also examined and found to have a profound effect on the resulting polymer formed in the admicellar polymerization of styrene. In AIBN-initiated polymerizations, when the initiator will predominantly partition into the admicelle, the molecular weight of the polymer formed at M/I values of 15 and 150 was significantly lower than polymerizations initiated by V-501, with the initiator predominantly in the aqueous phase as in emulsion polymerization.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

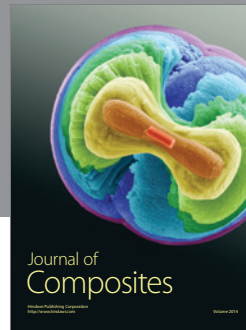
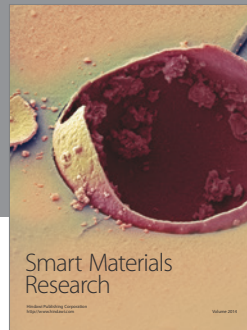
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