4690 *Macromolecules* **2006,** *39,* 4690−4695

Feasibility Analysis of Surface Mediation in Supported Atom Transfer Radical Polymerization

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Received March 8, 2006; Revised Manuscript Received May 5, 2006

ABSTRACT: Supported catalysts are used in atom transfer radical polymerization (ATRP) to facilitate catalyst recovery and recycling. These catalysts consist of catalytic sites that are covalently tethered to larger supporting particles. It is generally believed that supported ATRP is a surface-mediated polymerization process; that is, both activation and deactivation reactions take place at the surface of the particles. However, recent experiments show that this may not be the case. This paper provides a theoretical analysis to test the concept of surface-mediated ATRP. It is found that deactivation at the surface is unlikely. The *geographic isolation* of catalytic sites, rather than *polymer diffusivity limitation*, is primarily responsible for this infeasibility. A trace amount of free catalyst in solution that minimizes the geographic isolation is essential for mediating supported ATRP.

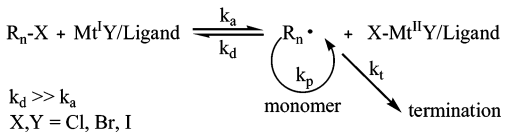
Introduction

Atom transfer radical polymerization (ATRP) is a type of controlled/living radical polymerization.[1,2] It allows for the synthesis of polymers with controlled molecular weight and narrow molecular weight distribution, block copolymers, polymers with complex architecture, and polymer-modified surfaces. ATRP relies on a fast equilibrium between dormant and live radical species to control the polymerization. In ATRP, this process is catalytic as shown in Scheme 1.[1,3,4] A ligated metal salt ($Mt^{+}-Y/L$) abstracts a halide from the initiator or dormant polymer chain and thus activates polymerization. The catalyst is thereby oxidized ($X-Mt^{2+}-Y/L$), and a radical ($R^{\bullet}$) is formed. This radical can propagate by addition of a monomer (M), terminate with other radicals/impurities, or be deactivated by the oxidized catalyst. The deactivated polymer ($R-X$) can be reversibly reactivated and deactivated following the same cycle. Radical−radical termination is minimized by an equilibrium that favors the dormant alkyl halide. The minimization of termination results in a quasi-living polymerization that allows for the macromolecular tailoring.

Although ATRP is widely used in laboratories, its industrial applications are limited. The primary reason for this is the catalyst's low activity (mass of polymer produced/mass of catalyst used), which makes high catalyst loadings necessary to run polymerizations at reasonable rates. This high catalyst loading contaminates the final product, making product purification necessary. While purification in a laboratory is manageable, purification at an industrial scale is taxing. One approach developed to facilitate purification is to support the catalyst onto micron-sized particles that allow in situ catalyst separation postreaction.[5−27]

Several solid supported ATRP catalysts have been devised and are successfully used. The polymers produced from supported catalyst generally have molecular weights and polydispersities which are less controlled than those produced by soluble catalysts. This depreciated control is attributed to the low mobility of supported catalyst and polymer radicals.[5−13] It is hypothesized that the deactivation rate is limited by the diffusivity of polymer radicals and that this diffusion limitation causes the deteriorated control.[5−12] Activation is a relatively slow process, as compared to deactivation, and thus is less affected by the diffusivity of polymer radicals. Several strategies have been developed to overcome this hypothesized limitation (i.e., low polymer diffusivity) in supported ATRP.[6−15]

Scheme 1. Atom Transfer Radical Polymerization Mechanism



Matyjaszewski et al. developed a novel hybrid catalyst system consisting of mainly surface-bound catalyst and a relatively small concentration of soluble deactivating catalyst.[6−8] The soluble catalyst ($Cu^{II}Br$/tris(2-(dimethylamino)ethyl)amine) acts as a deactivator. In the absence of this deactivator, polymerizations were generally poorly controlled.[5−8] Zhu et al. grafted CuBr/tetraethyldiethylenetriamine to silica gel surfaces via poly(ethylene oxide) spacers to increase the mobility of the grafted catalyst sites.[9] Optimum control was obtained with a three ethylene glycol unit spacer but deteriorated with longer spacers. Shen et al. designed a reversibly supported catalyst on silica using self-assembly.[10,11] The catalyst was designed to detach from the support during polymerization, thereby increasing its mobility. At the end of polymerization, cooling allows a fraction of the catalyst to reattach to the support, permitting catalyst recovery and recycling. Kröll et al. used extended attachments synthesized via ring-opening metathesis polymerization to facilitate reactions at interfaces.[14] The surface-supported catalyst performed similarly to a corresponding homogeneous catalyst in terms of polymerization rate; however, polymer yields for both homogeneous and supported catalysts were low (<20%), and polymer molecular weight distributions were broad ($M_w/M_n > 1.5$). Honigfort et al. used a more flexible support (JandaJel) to increase catalyst mobility, and low polydispersities were achieved.[12] Duquesne et al. employed a supported nickel bromide catalyst on cross-linked polystyrene resins and added a soluble ligand for ATRP of various monomers.[13,15] In the absence of the free ligand, polymerization was not controlled.

No measures to improve the control of polymerization are taken for many supported catalyst systems, however.[5,16−27] Some of these systems generate polymers with polydispersities higher than 1.5.[5,14,27] Others yield acceptable molecular weight control

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10.1021/ma060515w CCC: $33.50

and relatively narrow polydispersities, generally with $M_w/M_n < 1.5$.[16−25] Polydispersities as low as 1.1 are achieved with physically adsorbed and recyclable catalysts.[18,25] It is however recognized now that these low polydispersities are a result of leached (soluble) catalyst species.[28−30] Polydispersities as low as 1.2−1.3 are also achieved for catalysts chemically grafted to the supports.[9,12,21−24]

Thus, in summary, it is a widely held view that catalytic sites tethered to a particle surface are capable of mediating the ATRP equilibrium shown in Scheme 1; that is, both activation and deactivation take place at the surface. It is now being recognized however that this surface-mediated process is challenging, which is attributed to low diffusivities of the polymer radicals. However, the extent of this challenge and its hypothesized cause (i.e., low polymer diffusivity) are unclear and have not been investigated. Thus, surface-mediated deactivation is still widely believed to be feasible, although hypothesized to be made difficult by low polymer diffusivities. We provide here a simple picture of molecular processes involved in surface-mediated ATRP that sheds light on these important notions.

Surface-Mediated Deactivation

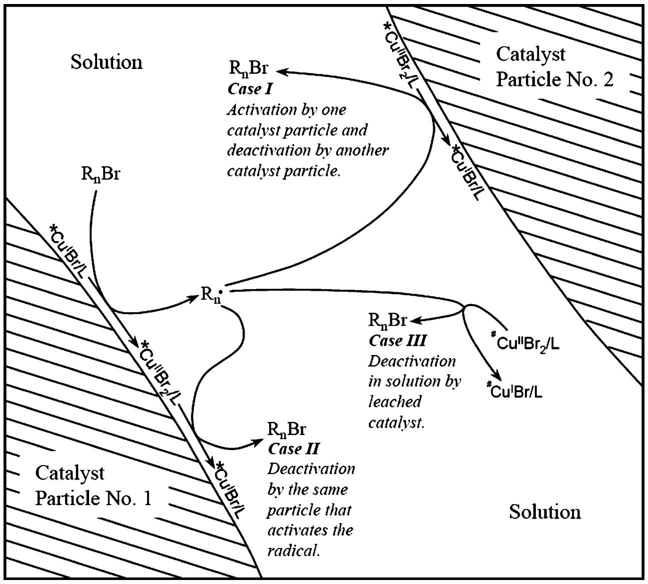
We begin by visualizing the processes that take place in supported ATRP for activation of a dormant polymer chain and deactivation of the resulting living radical chain. The activation process requires that a dormant polymer chain end and catalyst surface come together to within a distance of a few angstroms. This process can be visualized to occur in three steps. First, the polymer and catalyst particle must come together via translational diffusion. It is useful here to imagine the polymer and particle as two entities differing only in their sizes, the particle being much larger than the polymer coil. Second, the dormant chain end must diffuse to an activating catalyst site (MtX/L/support) on the support's surface via segmental diffusion (through conformational changes in its backbone orientation). Third, the energy barrier for chemical reaction must be overcome, resulting in formation of a radical and oxidation of the activating catalyst site. The deactivation sequence is similar: translational diffusion of polymer and catalyst particle together, segmental diffusion of radical end to surface deactivating site (MtX_2/L/support), and chemical reaction deactivation.

Loci of Deactivation. Once activated, a radical may be deactivated by a second catalyst particle with tethered catalyst sites (case I), by the same catalyst particle with tethered catalyst sites (case II), or possibly by a leached/free soluble catalyst species if these are present (case III). Which scenario dominates depends on the catalyst particle concentration, radical lifetime, diffusivity of reacting species, and presence or absence of leached/free catalyst species. Scheme 2 shows these three cases.

Distances Traveled. Cases I and II represent two geographic extremes in the location of deactivation for a polymer radical. The diameters of the supporting particles are on the order of 100 μm, and their diffusion is therefore neglected because of the faster diffusion rates of polymer coils. These particles, rich in surface-tethered catalyst sites (MtX/L and MtX_2/L), are thus considered stationary relative to the polymer species. A radical must then travel sufficiently far to reach the next catalyst particle (case I) or stay relatively close to the activating particle (case II) during its lifetime to be deactivated.

For case I, the distance traveled by a radical is related to the cubic root of reciprocal particle concentration. The particle concentration is calculated from typical porous particle characterization data, as outlined in Table 1. For a typical supported catalyst, particles have diameters of ~100 μm.[6,7,10,13−21] Based on this, the particle concentration in the reaction is on the order of 10^8 particles/L. The calculated particle-to-particle center-line distance is 130 μm. Discounting for the particle diameter itself, the surface-to-surface distance between particles averages 30 μm. Thus, for deactivation by a second catalyst particle (case I), the polymer radical must travel this distance during its lifetime.

Scheme 2. Possible Loci of Deactivation in Supported ATRP[a]



[a] Two catalyst particles are shown in cross section. Catalyst sites ($*Cu^{I}Br/L$ and $*Cu^{II}Br_2/L$) are covalently tethered to the particles. Between the particles, reaction fluid is present where dormant polymer chains (R_nBr) and radical polymer chains ($R_n^\bullet$) exist. Shown are the activation of a dormant polymer chain and the three possible deactivation cases considered. Leached/soluble catalyst sites are represented by $^{\#}Cu^{I}Br/L$ and $^{\#}Cu^{II}Br_2/L$. Propagation is not shown for clarity.

Table 1. Typical Silica Gel Support Characteristics and Resulting Average Particle-to-Particle Surface Distance

characteristic (symbol, units)	value[a]
average particle diameter[9] (d_{pt}, μm)	100
surface area[9] (A_s, m^2/g)	500
average pore size[9] (d_p, Å)	60
density of silica[31] (ρ, g/mL)	2.64
porosity of particles (ξ, −)	*0.66*
no. of particles (β, # particles/g)	*2.2×10^6*
mass of silica gel used[9] (m, g)	1
reaction volume[9] (V, mL)	5
volume per particle (V_p, m^3/particle)	*2.3×10^{-12}*
av particle−particle CL distance (λ_{CL}, μm)	*130*
av particle−particle surface distance (X, μm)	*30*

[a] Values in italics are calculated based on d_{pt}, A_s, d_p, ρ, m, and V.[32] CL stands for center line.

Kinetic Lifetimes. The dormant ($\tau_{D,k}$) and radical ($\tau_{R,k}$) polymer lifetimes are defined by ATRP equilibrium kinetic rate constants. It is expected, given comparable reaction rates and polymer molecular weight control observed in supported and homogeneous ATRP systems, that these lifetimes differ marginally between homogeneous and supported ATRP. To estimate their lifetimes, we use the activation rate constant (k_a) on the order of 10^0 L/(mol s) and the deactivation constant (k_d) on the order of 10^7 L/(mol s) as measured for homogeneous ATRP systems.[33]

For deactivation, the number of polymer radicals deactivated per second is defined by eq 1. Thus, the rate of deactivation per radical is $R_d/[R^\bullet]$, and its reciprocal is the polymer radical lifetime (eq 2). Equations 3 and 4 provide the corresponding activation rate equation and dormant polymer lifetime, respectively. For a typical ATRP, deactivating and activating catalyst concentrations are on the order of 10^{-3} and 10^{-2} mol/L, respectively.[3] Thus, radical ($\tau_{R,k}$) and dormant ($\tau_{D,k}$) lifetimes are 10^{-4} s and 10^{2} s per eqs 2 and 4. These are the time scales over which radical and dormant polymers are free to diffuse before they must encounter a particle surface to react. Given discussions in the literature of diffusion-controlled deactivation in supported ATRP with resulting rate constants (k_d') on the order of 10^5 L/(mol s),[6] another potential radical lifetime ($\tau_{R,k}'$) is considered and calculated to be 10^{-2} s. These two deactivation rate constants (k_d and k_d') provide a range of radical lifetimes (10^{-4}–10^{-2} s).

$$R_d = k_d[\mathrm{R}^\bullet][\mathrm{MtX}_2] \tag{1}$$

$$\tau_{R,k} = [\mathrm{R}^\bullet]/R_d = 1/k_d[\mathrm{MtX}_2] \tag{2}$$

$$R_a = k_a[\mathrm{RX}][\mathrm{MtX}] \tag{3}$$

$$\tau_{D,k} = [\mathrm{RX}]/R_a = 1/k_a[\mathrm{MtX}] \tag{4}$$

Diffusion Times. The time taken for a polymer radical to travel away from the particle surface depends on its diffusion rate. The diffusion considered is that of Brownian motion described by random walk statistics. While stirring is present in supported ATRP systems to suspend the catalyst particles, the increase in mass transfer rate obtained over that of Brownian diffusion is negligible on account of the small particle size and its low relative density.[34] For a one-dimensional random walk, the time taken (t) for a diffusing entity to travel an average root-mean-square displacement (i.e., total distance traveled, X) is described by eq 5.[35] This relationship, derived by Einstein, allows us to relate diffused path lengths (X) to diffusion time scales (t) where D (diffusivity) is the proportionality constant.

$$t = \frac{\bar{X}^2}{2D} \tag{5}$$

Diffusivity. To estimate the diffusion time scale, the diffusivity of the polymer radical in the reaction media must be known. Polymer diffusivities vary depending on polymer size, concentration, solvency, and other environmental factors. At a given monomer conversion, these conditions are known for a typical ATRP system. A typical supported ATRP recipe uses monomer-to-initiator ratios in the range of 100:1. Monomer concentrations are ∼30 wt % with the remainder being a solvent (e.g., toluene). Assuming high initiator efficiency, polymer molecular weight is estimated from the mathematical product of monomer-to-initiator ratio, monomer molecular weight, and conversion. Thus, for a monomer conversion of 50%, i.e., midway through polymerization, polymer size is ∼5000 g/mol (assuming polymerization of methyl methacrylate or styrene with molecular weights of about 100 g/mol). The concentration of polymer is ∼15 wt % (30 wt % of solution × 50% of conversion). In a dilute solution, diffusivities of poly(methyl methacrylate) and poly(styrene) with molecular weights between 10^3 and 10^4 g/mol are on the order of 10^{-10} m^2/s.[36] This diffusivity is applicable to the calculation of diffusion time scales since the polymerization system described here is also dilute as shown below.

In a dilute solution, polymers behave independently, and their diffusivities are a function of polymer size. This diffusion behavior is modeled using the Stokes–Einstein relation for independent spherical diffusers:

$$D = \frac{k_B T}{f} \tag{6}$$

where k_B is Boltzmann's constant, T is temperature, and f is the friction factor, a function of sphere size and thus polymer size.[37,38] At higher concentrations, polymer chains overlap and their dynamic behavior becomes dependent.[37–39] Diffusion in this overlapped regime is described using de Gennes' reptation-scaling model.[37] The concentration at which overlap begins (c^*) is defined by the polymer's radius of gyration (R_g) since overlap occurs when the distance between polymer coils is less than $2R_g$.[38,39] Overlap concentration (c^*, wt % polymer in solution) is calculated by

$$c^* = \frac{M_w}{\rho_{soln}\frac{4}{3}\pi R_g{}^3 N_A} \times 100\% \tag{7}$$

where M_w, ρ_{soln}, R_g, and N_A are the polymer weight-average molecular weight, solution density (ca. 0.90 g/mL), polymer radius of gyration, and Avogadro's number, respectively.[39] For polystyrene in toluene, the radius of gyration as a function of M_w is fitted to

$$R_g{}^2 = 1.38 \times 10^{-4} M_w{}^{1.19} \quad \mathrm{nm}^2 \tag{8}$$

based on light scattering data.[39,40] Thus, for a M_w of 5000 g/mol, R_g equals 1.9 nm. The corresponding overlap concentration (c^*) is 30 wt % (via eq 7). Since this overlap concentration (30 wt %) is higher than the polymer concentration (15 wt %) at 50% conversion, the system is dilute and the diffusion coefficient of 10^{-10} m^2/s applies.

Case I. Equation 5 provides the diffusion time as a function of diffusivity and root-mean-square (rms) displacement. This rms displacement is the average distance traveled by the polymer between its starting position at time zero and its position after a specified time (t). For deactivation by a second catalyst particle to occur, the polymer radical must travel an interparticle distance of 30 μm as calculated previously. We use this distance (30 μm) as the rms displacement in eq 5. Thus, with a diffusivity of 10^{-10} m^2/s, it takes the polymer ∼5 s to travel between particles (30 μm). This time is 4 orders of magnitude higher than the radical's lifetime ($\tau_{R,k} = 10^{-4}$ s). Even a small molecule in solution with a diffusivity of 10^{-9} m^2/s cannot travel this distance quickly enough. In order for the radical to cover this distance in the radical's lifetime (10^{-4} s), a diffusivity of 10^{-6} m^2/s is required. This diffusivity is comparable to those measured for gases and thus cannot be achieved by polymer chains or any other molecules in solution. Therefore, activation by one particle and deactivation by another (case I) is impossible for a typical supported ATRP system. The same conclusion is reached if we consider the alternate radical lifetime ($\tau_{R,k}'$) of 10^{-2} s derived from $k_d' = 10^{-5}$ L/(mol s): the diffusion time (5 s) is 2 orders of magnitude higher than this longer radical lifetime (10^{-2} s). From this analysis, we conclude that surface-mediated deactivation of a radical by a particle different from the one that activates it is impossible (case I).

A better understanding of why case I is unachievable is attained when homogeneous ATRP is considered. In a homogeneous system, catalysts are well distributed throughout the reaction media, resulting in an average distance between deactivation site and polymer radical of 6 nm.[41] Such a distance is well within the diffusion range of a polymer radical during its lifetime. It takes a polymer 10^{-7} s to travel 6 nm (eq 5). Although a more accurate scenario considers the catalyst as the diffusing species ($D_{\mathrm{catalyst}} \approx 10^{-9}$ m^2/s > $D_{\mathrm{polymer}} \approx 10^{-10}$ m^2/s), polymer diffusivity alone is sufficiently high to yield a favorable diffusion (10^{-7} s) to kinetic time scale (10^{-4} s).

It is apparent from this analysis that we cannot attribute the failure of case I to the polymer's limited diffusivity. The difference between the diffusivities of a homogeneous catalyst and polymer are not sufficiently different to account for the failure of case I. Even with a diffusivity comparable to that of a small molecule ($D \approx 10^{-9}$ m^2/s), the polymer is unable to reach another deactivating particle in sufficient time. The large distance between catalyst sites is the cause of the failure of case I. This in turn is caused by the tethering of all catalyst sites to supporting particles and the low concentration of these particles in the reaction space (in terms of the number of particles per liter of solution, compared to the number of catalytic sites per liter of solution in a homogeneous system). By concentrating catalyst sites onto supporting particles, much of the reaction space is left void of catalyst. This *geographic isolation of catalytic sites* is the primary distinguishing feature of supported vs homogeneous ATRP. This isolation, rather than the hypothesized *low* polymer diffusivity, explains why surface-mediated ATRP is challenged.

Reducing the size of supporting particles (for the same total mass of support) increases particle concentration and decreases interparticle distance. Conceptually, catalyst size reduction homogenizes the system. Based on the same calculation approach outlined above, case I becomes feasible only when the supporting particle size is less than 0.45 μm.[42] This is a 2 orders of magnitude reduction in particle size from those generally used for ATRP. At this scale, however, particle–solution separation postpolymerization becomes more difficult.

Jones did support catalyst onto fumed silica particles (Cab-O-Sil) with an aggregate size of 0.2–0.3 μm with good results.[22–24] The actual sizes of the supporting particles in the reaction conditions were not however reported. The manufacturer reports the formation of larger agglomerates with sizes inferior to 44 μm, which are formed from the smaller 0.2 μm aggregates. It is unknown whether these agglomerates persist in the polymerization system and therefore what is the true particle size when using Cab-O-Sil as a support. Matyjaszewski also used small supporting catalyst particles (fumed silica, 0.012 μm) for ATRP.[5] In this system, the fumed silica formed larger agglomerates which made stirring difficult and greatly reduced the particles mobility.[5] The authors did not report the particle size as a function of stirring strength, and therefore the actual particle (agglomerate) size during the polymerization is not known.

Alternate Locals for Deactivation. The infeasible scenario of two-particle surface-mediated ATRP (case I) leaves two options to account for radical deactivation (cases II and III). If activation–deactivation occurs on the same particle (case II), a radical must remain within a short distance (a few angstroms) of this surface during its lifetime.[43] In this scenario, all radicals formed exist exclusively at the particle surfaces and none are in solution. This picture is unreasonable given the path lengths traveled by the radical (at the 10^2 nm level)[44] during its lifetime. This path length is 3 orders of magnitude higher than the distance within which the formed radical must remain from the surface for deactivation. Thus, we must imagine mechanisms by which the radical is retained at the surface for this to be valid. If polymer adsorption accounts for this retention, we must then reconsider the viability of activation by surface supported sites. If polymer adsorbs, particles are wrapped with polymer materials and accesses to catalyst sites by the polymer coils in solution will be limited. Since good solvents are used to solvate the polymer during ATRP, adsorbed polymer will repulse incoming polymer coils via osmotic forces and steric interactions.[35] Furthermore, once adsorbed, it is improbable that a polymer would leave the surface since it retains many trains of contact with it.

Deactivation via Leached Catalyst (Case III)

As described above, the probability of surface-mediated deactivation is improved when interparticle distances are reduced. This is achieved by decreasing the supporting particle size, as described previously, or by introducing a small quantity of free/soluble catalyst in addition to the supported catalyst. Such doping of reaction solutions can be deliberate or achieved unintentionally via supported catalyst leaching. Free metal concentrations in the parts-per-billion range are sufficient to make kinetic and diffusion time scales competitive.[45] Copper concentrations within the polymer in the parts-per-million range are reported in the literature following supported catalyst separation.[46,47] This copper is evidence of leached catalyst species since copper halides are insoluble in organic solutions in their uncomplexed form.[48]

Split-filtering tests have been used to demonstrate more directly the presence of leached catalyst species. For CuBr/HMTETA physically adsorbed to silica gel, catalyst activity has been attributed primarily to species found in solution.[28] These species are essential to the deactivation process; in their absence, polymerization is uncontrolled.[30] Nguyen and Jones investigated catalyst leaching for a physically adsorbed catalyst (Cab-O-Sil-(CuBr/dMBpy)) and reported increases in monomer conversion from 16 to 26% and polymer molecular weight from 4900 to 5200 following removal of the supported catalyst from the polymerizing system.[24] Similarly, for a catalyst chemically tethered to the support (Cab-O-Sil–CuBr/SdMBpy), monomer conversions increased from 16 to 26% and polymer molecular weights increased from 3100 to 4200 g/mol following removal of the supported catalyst.[24] We conclude from these data that leached catalyst species are present in these systems. Duquesne et al. demonstrated by removing the supported catalyst (Ni(II)-Br/diphenylphosphinopolystryrene resin) during ATRP that purposely added free ligand (triphenylphosphine) acquired a metal center from supported catalyst and became a catalyst of high activity in solution.[15]

Purposeful catalyst doping in supported ATRP provides further evidence that soluble catalyst species are necessary for controlled polymerization. In absence of free ligand (and therefore catalyst in solution), Duquesne et al. reported uncontrolled polymerizations with their supported nickel-based catalyst.[15] We found that adding free ligand regenerates an otherwise depleted supported catalyst in continuous ATRP and was essential for mediating ATRP equilibria.[30] Matyjaszewski et al. showed that free catalyst species were necessary for controlling supported ATRPs using catalyst tethered to polystyrene beads.[6–8] In their absence, polymerizations were uncontrolled. The lack of control, in the absence of free catalyst, has been attributed to the low diffusivity of the polymer radical.[6,7] By adding a free catalyst in solution (the "shuttle bus" concept), it is proposed that this diffusivity limitation is overcome because free catalyst diffusivities are higher. While the shuttle bus strategy remains an excellent approach to improving control in supported ATRP, its success is attributed to filling of reaction space by free deactivating catalyst that overcomes the *geographic isolation of catalyst sites*. Adding free deactivating catalyst in solution at ppm levels is sufficient to reduce distances between deactivation sites, making mediation feasible.

The infeasible scenario of two-particle activation−deactivation (case I) leaves us two options to explain the success of some supported ATRP systems (cases II and III). For reasons outlined previously, however, case II is unreasonable. The presence and role of leached or purposely added free catalyst species provide a valid explanation for the observed success of some supported ATRP systems. It is obvious that leached species do exist on the basis of the above-cited work. What is made clear here is that these sites are essential for mediating an ATRP equilibrium (case III). Their presence in solution, even at low concentrations, fills the reaction space with necessary deactivation sites, making diffusion and kinetic time scales comparable. In their absence, the diffusion time scale (for any molecules in solution, polymeric or not) is much larger (4 orders of magnitude) than the kinetic time scale, making surface mediation impossible.

It must be pointed that our analysis assumes the catalyst supports to be nonporous vis-à-vis the growing polymer chains. In reality, the support's pores may be accessed by small polymer chains at the start of polymerization. For example, catalyst supports consisting of polystyrene cross-linked with divinylbenzene have been used.[6,7,13,15] These supports, prepared by suspension polymerization in the absence of porogens, are porous to macromolecules with molecular weights up to 3500 g/mol for 1% cross-linking and 1700 g/mol for 4% cross-linking.[49] Supported ATRP systems using these polystyrene particles produce polymers with molecular weights in the range of 25 000−46 000 g/mol (M_w).[6,7,13,15] Therefore, while the polymer can access particle pores at the start of the polymerization, it is later excluded from entering the pores. It is over this latter and predominant period of time that our nonporous analysis applies. Silica gel particles, with 53−60 Å pores, have also been used as catalyst supports.[5,7,9,10,14,16−21] On the basis of knowledge of exclusion limits observed in size exclusion chromatography columns, we estimate that for 60 Å pores polymers with molecular weights of 5000 g/mol will be excluded from the pores. For column packings with pore sizes of 50 and 100 Å, molecular weight cutoffs (MWCO) are approximately 4000 and 6000 g/mol, respectively. If we base our analysis on the radius of gyration calculated by eq 8, the molecular weight cutoff for 60 Å pores would be 11 000 g/mol. Therefore, the MWCO for silica gels with 60 Å pores will be in the range of 5000−11 000 g/mol. In contrast, catalysts supported on silica gel particles produce polymers with molecular weights (M_w) ranging from 10 000 to 240 000 g/mol (typically around 20 000).[5,7,9,10,14,16−21] The polymer will be excluded from entering the silica gel pores for a large fraction of the polymerization time in these systems. Our nonporous model therefore also applies to silica gel supported catalysts. Nonporous supports such as Cab-o-Sil, fumed silica, and silica powder have been used as catalyst supports.[5,22−24] In these systems, the nonporous model applies to the entire polymerization period.

While our analysis does not address the use of larger porous structures as ATRP catalyst supports, it does reflect the present particle supports used and reported on. Larger porous particles could conceivably provide a fourth case, not considered here, where activation and deactivation would occur within the same pore. Such a system would be challenged by the slow diffusion of polymer chains within the nanopores (similar to Knudsen diffusion) and by the low pore volume as compared to the total reaction volume. The low pore volume (<10% of the total reaction volume) would limit the total rate of polymerization. For this not to be the case, a fast renewal of the solution in the pores would be required, ensuring that all polymers grow at the same rate. These challenges along with the high probability of polymer adsorption on the supporting particles indicate that the feasibility of deactivation by this fourth mechanism is also unlikely. Our analysis does not however rule it out.

Conclusion

For a typical supported catalyst using particles in the range of 100 μm, surface-mediated ATRP is not feasible. It is the *geographic isolation of catalytic sites*, rather than *polymer diffusivity limitation,* that causes this infeasibility. The distances between deactivating particles are too large, making it impossible for a polymer radical (and even a faster diffusing small molecule) to reach a mediating surface in its lifetime. Similarly, polymer radicals travel too far from their activating surface to be deactivated by this same surface. The cause of this deficiency is not the diffusivity of polymer radicals. Their diffusivity is only an order of magnitude lower than that of small molecules ($D_{\text{small molecule}} \approx 10^{-9}$ m^2/s vs $D_{\text{polymer}} \approx 10^{-10}$ m^2/s), which provide the maximum attainable rate of travel in solution. Even at these higher diffusivities, surface-mediated ATRP is still not feasible. Surface-mediated ATRP is not viable because the particles, to which the catalyst is tethered, are in low concentration in terms of the number of particles per liter of solution in the reaction space (as compared to the number of catalytic sites per liter in homogeneous ATRP), which causes the geographic isolation of catalytic sites. For ATRP, deactivating catalyst sites must be well distributed throughout the reaction space. This can be accomplished by reducing supporting particle size (to nanoscales) or by using soluble catalyst species at ppb to ppm levels in addition to supported catalyst. Even at these low concentrations, soluble catalyst fills the empty reaction space with necessary deactivating sites for ATRP. Soluble catalyst species are found in supported ATRP systems and have been shown in certain cases to be crucial for controlled ATRP. The analysis presented here demonstrates theoretically this essential role and clarifies why surface-mediated ATRP is challenged: a lack of deactivation sites in the majority of the reaction space.

Acknowledgment. We thank the Natural Science and Engineering Research Council of Canada (NSERC) for supporting this research and the Canada Foundation of Innovation, who support our research facilities. We also thank Dr. Cecile Fradin, Professor and Canada Research Chair in Molecular Biophysics, Department of Physics and Astronomy, McMaster University, for helpful discussions.

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(41) Typical deactivator concentrations are in the range of 10^{-3} mol/L. Multiplying this concentration by Avogadro's number and then taking the cubic root of the inverse of this product gives a deactivator-to-deactivator distance of 12 nm. The average distance between the polymer and a deactivation site is half this distance: 6 nm.

(42) This is an iterative calculation and therefore more easily verified using the result (0.45 μm) in the following calculation (described in more detail in ref 32). Particle porosity remains unchanged ($\xi = 0.664$). Number of particles per gram ($\beta = [1/[[\pi \times d_{pt}{}^3/6][1 - \xi] \times \rho]]$) equals 2.37×10^{13} for a particle diameter (d_{pt}) of 0.45 μm. The distance between particle center lines (λ_{CL}) for a system where 1 g (m) of particles is placed in 5 mL (V) of solution is calculated from $[V/(\beta \times m)]^{1/3.}$ This distance (λ_{CL}) is 0.6 μm. Therefore, the particle-to-particle surface distance is 0.15 μm ($\lambda_{CL} - d_{pt}$, 0.6−0.45 μm). The time taken by the polymer to diffuse this distance is 1×10^{-4} s ($t = X^2/2D = [0.15 \times 10^{-6}\ \text{m}]^2/[2 \times 10^{-10}]$), which is equal to the polymer radical lifetime.

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(44) The distance traveled by the radical away from the catalyst particle is of the order of 10^2 nm; this is calculated as follows: $X = [2Dt]^{1/2} = [2 \times 10^{-10} \times 10^{-4}]^{1/2} = 140\ \text{nm} \approx 10^2\ \text{nm}$.

(45) The average distance traveled by a catalyst in the radical's lifetime is 4.47×10^{-7} m ($X = [2Dt]^{1/2} = [2 \times 10^{-9} \times 10^{-4}]^{1/2}$). Therefore, the concentration of this deactivating catalyst in that volume is 1.86×10^{-5} mol/m^3 ($C_d = 1/[X^3 \times N_A]$); N_A is Avogadro's number. From this, we calculate the concentration of copper (deactivator metal center) to be ∼1 ppb ($C_d \times MW_{Cu}/\rho_{soln} \times 10^9$), where $\mathrm{MW_{Cu}}$ (63.546 g/mol) is the molecular weight of copper and ρ_{soln} (900 kg/m^3) is the density of the reaction solution.

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MA060515W