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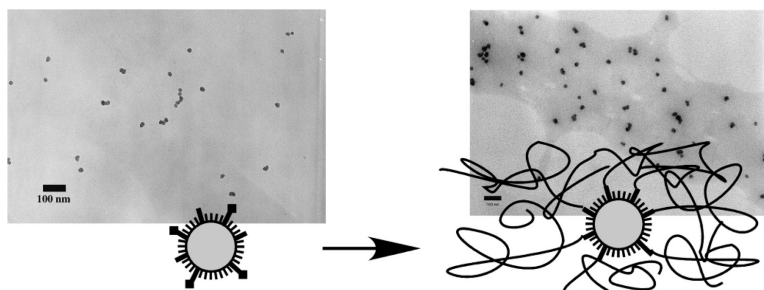
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Quantitative Determination of the Chemical Composition of Silica−Poly(norbornene) Nanocomposites

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Abstract: Nanoparticle hybrid materials consisting of a silica core surrounded by a poly(norbornene) brush have been prepared by ring opening metathesis polymerization (ROMP). A quantitative determination of each stage of composite formation has been accomplished, including a determination of the density of surface-bound functional groups, catalyst molecules, and polymer chains. This analysis has enabled the determination of the reaction efficiency between the catalyst and the surface-bound functional groups as well as the determination of the fraction of metal-mediating species that initiate a polymer chain. Control of the chain density was demonstrated by two methods: the use of controlled reaction times between the catalyst and the surface, and the variation of the surface functional group density. Polymer chain densities resulting from composites prepared with different tether structures will also be reported. The resulting brush densities were found to span a wide range, including those previously reported for polymer layers formed by adsorption, grafting of preformed polymer chains, and surface-initiated polymerization (SIP).

Introduction

The formation of nanocomposites consisting of an inorganic nanoparticle core surrounded by a polymer layer has received increasing attention in recent years.[1−10] Inorganic−organic hybrids often preserve the optical and magnetic properties of inorganic nanoparticles, but also exhibit improved mechanical and thermal properties, such as storage modulus, stability, hardness, and abrasion resistance, when applied as inorganic fillers.[2,6] These materials have potential applications in diffractive optics, sensors, electro-optical devices, information storage, and composites.[11,12] Inorganic−organic nanocomposites are also useful as model systems for testing theoretical models of polymer brushes due to the large surface area provided by nanoparticle supports. The synthesis of macroscopic amounts of polymer from high surface area supports allows the use of conventional techniques, such as GPC and NMR, in the analysis of brush layers.[2] This can be contrasted with work on flat surfaces where these techniques are not readily applied.[13−15]

This article focuses on using this advantage for the quantitative analysis of the structure of silica−poly(norbornene) nanocomposites.

To completely control the structure of inorganic−organic nanocomposites, it is necessary to control all aspects of composite architecture, including the nanoparticle core size, tether structure, polymer chemistry, polymer molecular weight and its polydispersity, and the polymer chain density. The polymer chain density is one of the least studied of these parameters, although chain density is directly related to important material properties, such as hydrolytic stability, and fundamental dimensions, such as brush height. The inherent difficulty in determining the number of polymer chains attached to flat surfaces is a result of the small sample sizes.

Two studies have been reported in which the chain density was varied for brushes grown from a flat surface. In one, Yamamoto and co-workers varied initiator densities by controlled photodecomposition of 2-(4-chlorosulfonylphenyl)ethyltrichlorosilane to polymerize poly(methyl methacrylate) using atom transfer radical polymerization (ATRP) in the presence of excess free initiator.[16] Direct determination of brush molecular weight was not possible due to the small sample size; therefore, Yamamoto et al. assumed that chains formed in solution were similar to those in the brush. Calculated values for the area per chain ranged from 1.4 to 14 nm² and were determined based on the layer thickness and the molecular weight, assuming the

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density of the polymer brush was equal to that of the bulk. The stiffness of the brushes as well as the layer thickness for a single molecular weight increased with increasing brush density.

A second study by Jones et al. used mixed monolayers of thiols on flat gold substrates.[12] The resulting area per chain varied from 5 to 32 nm[2]. These values were calculated as in Yamamoto's study except that brush molecular weights were determined by GPC by cleaving the polymer from the surface after demonstrating the absence of solution-grown polymers. The large variation (20−30%) that was observed for repeat analyses of a single sample was attributed to the small sample sizes. It was necessary to form dense layers on the substrate in order to provide sufficient material for the analysis. Therefore, this approach is unsuitable for dilute brushes of lower molecular weight. A comparison of the initiator concentration with the chain density suggested that not all initiators resulted in a polymer chain, but the margin of error was large. Their results supported the previous assertion that the layer thickness increased more rapidly for brushes formed with a higher chain density.

We have previously reported the synthesis of silica−poly-(norbornene) nanocomposites using ring opening metathesis polymerization.[17] In this report, we will detail the quantitative structure of these nanocomposites with a focus on features that affect the chain density. We have determined the density of norbornene groups on the particle surface, the number of catalyst molecules per unit area, and the number of polymer chains per unit area. The large surface area of the nanoparticle substrates provides an advantage over previous studies on silicon oxide-coated wafers in that we directly determine the chain density with greater accuracy. We have used this advantage to vary the polymer chain density by several synthetic methods. Comparisons between the chain densities observed for nanoparticles coated with a monolayer, multilayer, or mixed monolayer of initiators clarify the effect of tether structure on chain density. This effort has effectively determined the yield for each step in the construction of our nanocomposites.

Results and Discussion

Nanocomposite Synthesis: The synthetic procedure used to form silica−poly(norbornene) nanocomposites has been previously reported.[17] It consists of four steps, including the preparation of the silica nanoparticles, functionalization of the particle surfaces with norbornenyl initiator ligands using silane coupling agents, reaction to form a ruthenium alkylidene moiety, and chain growth polymerization from the surface. A generalized reaction scheme and detailed experimental protocols can be found in the Supporting Information. In the first step, Stöber silica nanoparticles were prepared with diameters ranging from 15 to 30 nm. Most particles in this study were ∼20 nm. In the second step, two reagents, 5-norbornen-2-yl(ethyl)ethoxydimethylsilane (NEEDS) and 5-(bicycloheptenyl)triethoxysilane (BCH), shown in Figure 1, were used to coat the particles and serve as ROMP initiators. Trimethylethoxysilane was used with NEEDS for the formation of mixed monolayers. Pyrolysis gas chromatography mass spectrometry (PY-GCMS) confirmed the presence of the coupling agent on the particles. Transmission
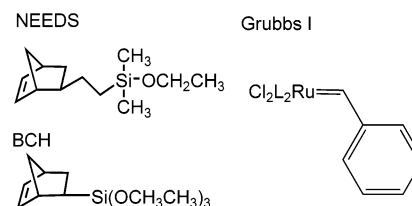
Figure 1. Coupling agents used to form mono- and multilayer surface coatings and the 1st generation Grubbs catalyst (Grubbs I) used in this study. The ligand, L, is tricyclohexylphosphine.

electron microscopy (TEM) and dynamic light scattering (DLS) were used to confirm that the particles had not aggregated during each coating step. Thermogravimetric analysis (TGA) was performed on several samples to determine the composition of coated particles, but there was no significant difference between the uncoated and coated particles. This is the result of uncondensed alkoxy groups in the nanoparticles and a variation in surface hydration. This phenomenon has been reported previously.[17,18] Our use of TGA was, therefore, restricted to determinations of composition in fully polymerized materials as discussed below.

In step three, nanoparticle surfaces bearing tethered norbornene initiators were reacted with a stoichiometric amount of Grubbs 1st generation catalyst, also shown in Figure 1.[19,20] Unreacted catalyst was removed by centrifugation and resuspension under nitrogen. The particles were then redispersed into THF that contained tricyclohexylphosphine (TCP) to slow the polymerization rate and to prevent decomposition of the surface-bound catalyst. DLS and TEM again demonstrated that the aggregation state was essentially unchanged. In step four, we combined a TCP-spiked, THF solution of catalyst bearing nanoparticles with a norbornene monomer solution to initiate polymerization. This was followed by termination with ethyl vinyl ether (EVE). Then, the samples were precipitated into methanol. Catalyst bearing particles in THF without added TCP polymerized norbornene too rapidly for analysis. In the absence of TCP and monomer, THF solutions of the catalyst bearing nanoparticles would change color, indicating catalyst decomposition. Purified samples were then analyzed by DLS and TEM to determine the size and structure of the resulting nanocomposites. FTIR, ^{1}H NMR, and TGA were used to analyze the chemical composition, purity (i.e., absence of residual monomer), and mass fraction of organic material in the composite. Weight fractions of organic material for the resulting composites were found to range from 30 to 80%.

Determination of Brush Molecular Weight Distributions: To evaluate the polymers grown from these surfaces, we cleaved the brush layers from particle surfaces by stirring the samples in a 24% solution of hydrofluoric acid for 24 h. The cleaved polymer was washed and dried and then analyzed by FTIR, TGA, and TEM to establish that all the silica had been removed. We used FTIR and ^{1}H NMR to establish that the product was pure poly(norbornene) and GPC to determine the polymer molecular weight and polydispersity. This same acid treatment was applied to poly(norbornene) prepared in homogeneous

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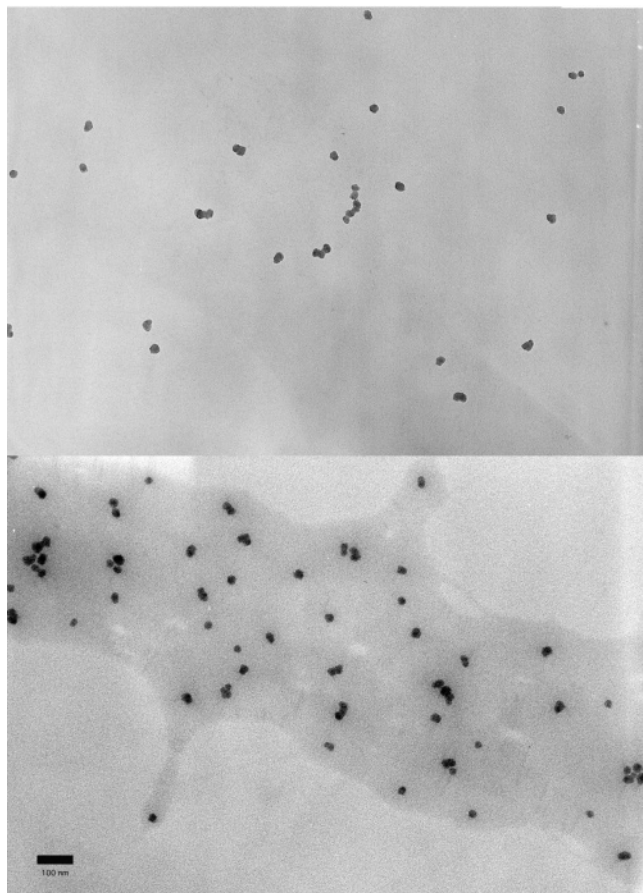
Figure 2. TEM images of poly(norbornene)−silica nanocomposite before (top) and after (bottom) polymerization from the surface. Both images are the same magnification, and the scale bar in the lower figure is 100 nm.

solution using Grubbs I. No degradation was detected in six trials (vide infra, Figure 4, for example). GPC analyses were conducted in THF since, in this solvent, the hydrodynamic size of poly(styrene) and poly(norbornene) of equal molecular weight is the same.[21] Nanocomposite-derived polymers had molecular weights ranging from 42 000 to 307 000. A TEM image of the nanocomposite before and after surface-initiated polymerization can be seen in Figure 2. We conducted several control experiments to ensure that the polymer layer was bound to the surface and that the composite did not contain free polymer chains. For example, we confirmed that norbornene did not spontaneously polymerize in the presence of silica nanoparticles, and we observed that mixtures of poly(norbornene) and coated silica particles phase separated under the same conditions used to prepare the sample in Figure 2b.

Quantitating Initiator Densities: Following these procedures, we prepared a series of poly(norbornene)−silica nanocomposites with the goal of determining the density of norbornene groups, catalyst molecules, and polymer chains on the particle surface. As the first step in determining the densities, we calculated the number concentration and surface area of our nanoparticles following methods used elsewhere for spherical nanoparticle systems.[1,2,22−24] We used the density of silica

reported by van Blaaderen and co-workers of 2.0 g/mL. This is a consensus value from the range cited in the literature (1.6− 2.1 g/mL).[18,24−29] The mass concentration of nanoparticles was determined from multiple trials of drying and weighing. PY-GCMS confirmed the absence of contaminants in dried, purified samples. To account for loss of particles during successive manipulations, the number concentration of nanocomposites was also determined using TGA in conjunction with the dried mass of nanocomposite. The nanoparticles' volumes and masses were calculated from their radii and the density of silica, assuming spherical geometry. Nanoparticle number concentrations (1.3×10^{15} particles/mL) were then calculated from the total weight of silica and the average mass of particles.

The surface area per particle was calculated from the DLS radius, assuming a smooth spherical geometry, as done elsewhere.[1,2,18,22,25,26,30−33] TEM and DLS were used to confirm single spherical particles and the absence of aggregates. Surface area measurements in the literature are obtained with mercury porosimetry and nitrogen absorption. The measured values exceed the surface area of a sphere by as much as 30% for a given radius. The increase in surface area was attributed to surface roughness or porosity of the nanoparticles. Differences between the surface areas and those calculated by geometric considerations should be constant for Stöber silica of a single size. However, the majority of authors have assumed spherical geometry when determining grafting density so that comparisons between our data and the literature will be valid for similar-sized particles.[1−3,18]

The surface area per nanoparticle determines the maximum number of norbornene initiators available. Surface-bound norbornene could not be observed with enough precision to directly determine the yield for initiator functionalization. It was possible to demonstrate the presence or absence of the coupling agent through PY-GCMS from the characteristic cyclopentadiene fragment from surface-bound NEEDS versus the later eluting peak of the unbound NEEDS, as shown in Figure 3. However, this method was not quantitative because in the PY-GCMS technique, the sample is burned to obtain recognizable fragments of the starting molecules and the efficiency of that fragmentation process is unknown. A ceiling for the amount of norbornene initiator could be established from the difference between the amount of NEEDS or BCH used in the surface functionalization step and the amount left unreacted. After the initiator grafting reaction was complete, excess coupling agent was collected by repeated centrifugation and resuspension of the nanoparticles in fresh solvent. The quantity of unreacted coupling agent in these washings was determined using calibrated GC−MS. The absence of residual unbound coupling agent in dried samples of the washed nanoparticles was confirmed using PY-GCMS. An example chromatogram of the dried nanoparticle sample

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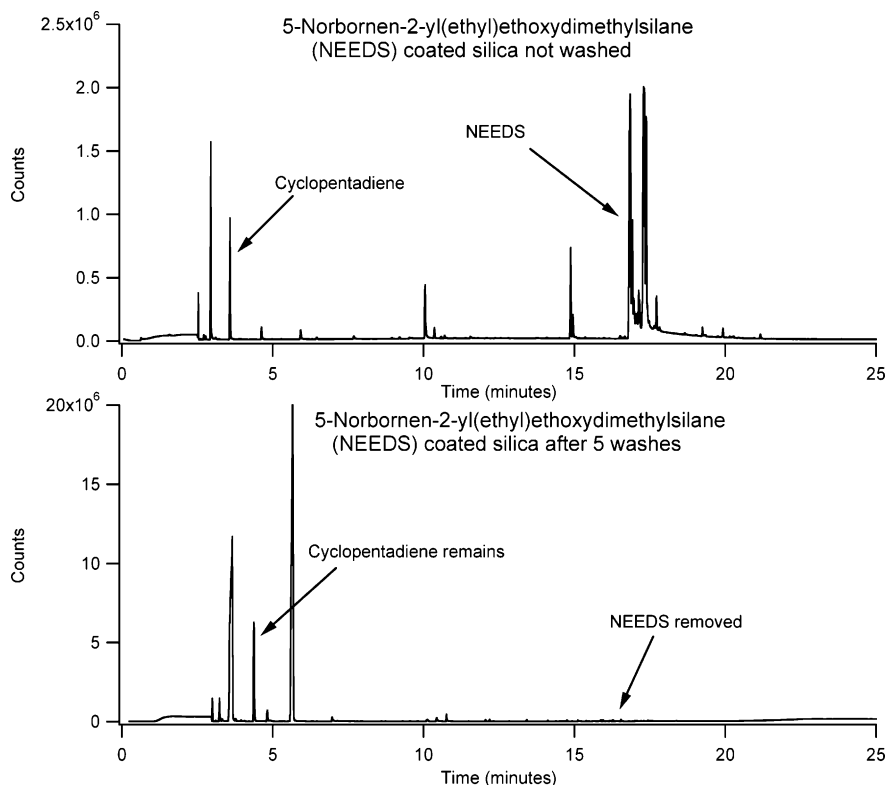
Figure 3. PY-GCMS chromatograms of NEEDS-coated nanoparticles before (top) and after (bottom) washing. Cyclopentadiene peaks are characteristic of bound silanes, while the unbound NEEDS elutes later as a double peak from the *exo*- and *endo*-norbornenyl silanes. All peaks are identified by MS as absolute elution times, and unlabeled peaks derive from other degradation products.
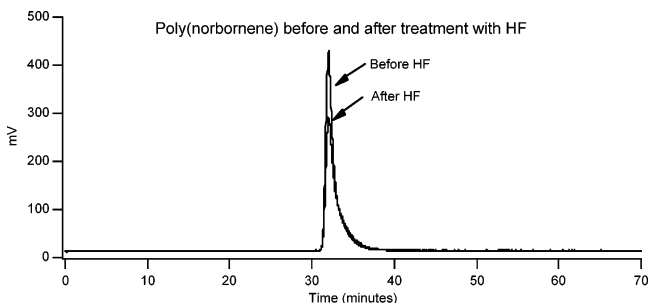
Figure 4. GPC overlay for composite before and after treatment with HF where the nanocomposite is fully excluded from the column, while the cleaved polymer can be analyzed after the HF treatment.

Table 1. Coupling Agent Density for NEEDS- and BCH-Coated Nanoparticles (in units of initiators/nm^2) for Multiple Trials (1–3) of One Particle Sample, Different Diameter Particles with the Same Initiator, and Different Initiator (BCH) at Similar Particle Size

sample number	initiator density (initiators/nm^2)	diameter (nm)
Initiator Density for NEEDS-Coated Nanoparticles		
1	2.1	19.2
2	1.9 ± 0.2	19.2
3	1.7 ± 0.1	19.2
4	1.9 ± 0.2	28.4
Initiator Density for BCH-Coated Nanoparticles		
1	2.6 ± 0.4	16.6

before and after washing can be seen in Figure 3, where the peaks are identified by their associated mass spectra (retention times vary substantially from day to day). The bottom chromatogram clearly demonstrates the removal of all unbound silane.

This method provides a maximum value for initiator on the nanoparticle surfaces. The loss of additional initiator groups through bonding to the reaction flasks is negligible. It was possible to rule out losses due to the dimerization of silanes, as these products were detectable by GC–MS. Excluding these possibilities, we assume that all coupling agents not recovered in the washing procedures are on the nanoparticle surfaces. As summarized in Table 1, the average coupling agent density determined for NEEDS was 1.8 ± 0.2 molecules/nm^2 or 2264 ± 225 norbornene groups on a particle with a 20.0 nm diameter. This corresponds to an organic weight fraction of 6.7%. The coupling agent density was unchanged over 10 trials of four independently prepared nanoparticle samples using the

same nanoparticle concentration of 10 g/L. This surface density indicates that nearly one-third of the available silanol groups react and represents the maximum reactivity for this coupling agent on a silica surface. This is likely a result of its steric bulk being significantly larger than the area per silanol.[2] A similar analysis for BCH, a triethoxysilane that is capable of forming multilayers, found that there were 2.6 ± 0.4 BCH molecules/ nm^2 or 3270 ± 449 norbornene groups per 20.0 nm particle. This corresponds to a weight fraction of 7.1%. The increased coupling agent density for BCH as compared to that for NEEDS suggests that a bilayer may have been formed. Literature results for monofunctional silanes similar to NEEDS yielded values ranging from 0.8 to 5 groups/nm^2, while multifunctional silanes comparable to BCH formed coatings with densities ranging from 3.06 to 20 groups/nm^2.[1–3,11,23,24,26,34]

Ruthenium Analysis: The concentration of ruthenium on the particle surface was obtained using neutron activation analysis

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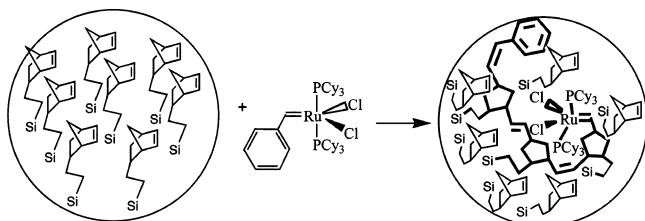
Figure 5. Schematic of polymerization across a section of the surface. Ethyl norbornene groups of the NEEDS coupling agents are shown forming a trimer of poly(norbornene) (in bold) with unreacted groups (in gray).
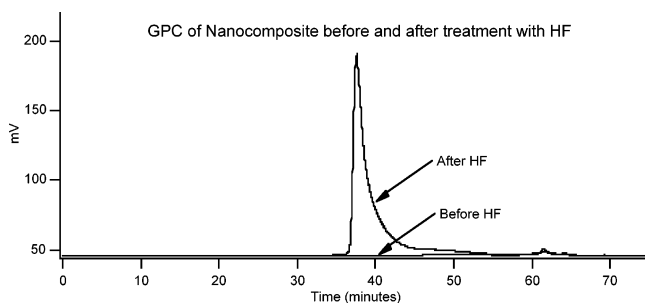
Figure 6. GPC overlay of poly(norbornene) before and after treatment with HF, demonstrating that this treatment does not affect the molecular weight distribution.

(NAA) in order to determine the yield of the reaction between the functional nanoparticles and the ruthenium alkylidene.[35,36] The number of ruthenium atoms per unit surface area was calculated from the sample weight and the ruthenium concentration. The resulting catalyst density of 0.031 ± 0.001 catalyst molecule/nm^2 can be compared with the density of norbornene groups for these particles (1.8 groups/nm^2). These results can be more easily understood by noting that a 20 nm particle would contain nearly 2250 norbornene groups to which only 39 catalyst molecules would be bonded, approximately 2%. Mayr and Buchmeiser suggested that each catalyst molecule reacts with more than one norbornene group, effectively polymerizing a layer parallel to the surface, as shown in the schematic in Figure 5.[37] The steric factors influencing polymerization across the surface and the rate of initiation versus propagation would then determine the extent of catalyst loading.

Determination of Initiation Efficiency: The number of chains produced per particle should provide a measure of the initiation efficiency. The weight of organic material in a composite is derived from TGA in combination with the silica core mass that was calculated using the core's hydrodynamic radius. The ratio of the mass of polymer per particle and the molecular weight of cleaved polymer as determined by GPC yields the number of chains per particle. GPC curves of solutions of nanocomposites before and after treatment with HF (Figure 6) show that the guard column in our GPC captures nanocomposites. Simple mixtures of independently prepared polymer and particles resulted in a peak at the molecular weight expected for the polymer. Thus, the absence of a peak in the curve for the nanocomposite indicated that all chains were attached to the particle surface. Nanocomposites synthesized under conditions where significant backbiting and cross metathesis occurred (vide infra) showed substantial quantities of free chains. HF-
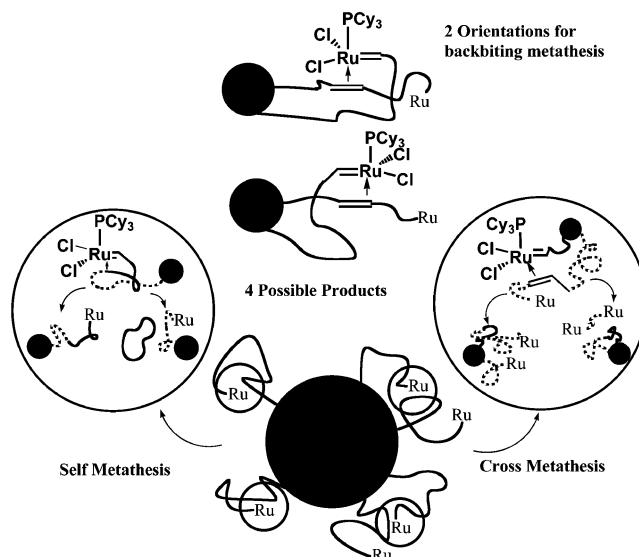
Figure 7. Schematic of the backbiting and cross metathesis reaction pathways. Backbiting (left) either regenerates the growing chain or produces an inert cyclic fragment and a shorter growing chain. Cross metathesis (right) either "swaps" the terminal chain ends or produces a chain with two growing ends, leaving a loop on the surface. Dashed and solid lines are intended to distinguish chain segments, and organometallic fragments in products are abbreviated with "Ru", indicating the metal center. Two of the four possibilities produce fragments that will tend to increase polydispersity.

treated nanocomposite samples provided GPC traces of free polymer. The number of chains in a nanocomposite is calculated from these data independently from the determinations of catalyst or initiator density. A total of 23 different nanocomposites were analyzed, including those from nanoparticles coated with mono- and multifunctional coupling agents, as well as those with reduced initiator densities.

Implications of Chain Transfer: An initial calculation of the chain density for nanoparticles fully coated with NEEDS yielded a value of 10 chains/nm^2. This corresponds to nearly 12 500 chains per 20 nm particle, or 320 times the amount of catalyst present. This fact and the increase in polydispersity with polymerization time led to the conclusion that chain backbiting and or cross metathesis was occurring. Lynn, Kanaoka, and Grubbs reported that cross metathesis and backbiting can compete with propagation when the monomer concentration is sufficiently low.[38] They also noted that low molecular weight fragments (which increase the polydispersity) result from this process. In our case, backbiting releases a cyclic fragment leaving the growing chain on the particle, while cross metathesis will leave a loop on the surface and release a chain with two growing ends. A schematic diagram of these mechanistic outcomes can be seen in Figure 7. Subsequent experiments were conducted using short polymerization times (5 min) and sufficiently high monomer concentrations (2.1−4.3 M) to minimize these processes. Under these conditions, a series of reproducible results were obtained, which agreed well with the data for the number of catalyst molecules. It was found that for NEEDS-coated nanoparticles, there was an average of 29.9 nm^2/chain, as opposed to 32.0 nm^2/catalyst. Table 2 shows the values for the area per norbornene group, catalyst molecule, and polymer chain for 20 nm particles coated with monofunctional

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Table 2. Measured Values for the Density of the Initiator, Catalyst, and Polymer for Surfaces Coated with NEEDS: Features Per Particle Are Calculated for 20 nm Particles after a 5 min Polymerization in 4.3 M Monomer

surface feature	features/particle	nm^2/feature
norbornene groups	2300 ± 300	0.56 ± 0.06
catalyst	39 ± 1.6	32.0 ± 1.3
polymer	42 ± 0.4	29.9 ± 0.3

Table 3. Apparent Chain Density as a Function of Polymerization Time using 2.1 M Monomer for 28 nm Diameter Particles

time (min)	chains/particle	MW ($\times 10^3$ g mol^{-1})	PDI	nm^2/chain[a]
5	87	134	1.06	29
10	99	233	1.14	26
15	141	254	1.33	18

[a] Decreasing area per chain reflects influence of backbiting reactions.

Table 4. Chain Density for 20 nm Nanoparticles Reacted for Different Lengths of Time with Catalyst[a]

reaction time (min)	sample	chains/particle	MW ($\times 10^3$ g mol^{-1})	PDI	nm^2/chain
5	1	31	126	1.24	38
10	1	43	118	1.29	27
15	1	62	96.6	1.47	19
3	2	43	266	1.11	30
30	2	58	268	1.19	22
60	2	75	217	1.35	17
420	2	42	274	1.13	31

[a] Polymerizations were run for 5 min in 2.1 M monomer solution.

increase the catalyst loading by increasing the reaction time between the catalyst and the surface. If the surface norbornene groups were polymerized, then the increased time would allow the remaining free catalyst to perform backbiting reactions with the polymerized surface layer. In this way, a reaction that had limited catalyst densities might, under different circumstances, be used to increase them. Two experiments were conducted in which the catalyst was added to a larger nanoparticle sample, and it subsequently split into fractions. Each sample was reacted with the catalyst for a different time ranging from 3 to 7 h. The results were then compared only among particles from the same starting batch to exclude the small variations due to changes in the initiating surface. Polymerization times were limited to 5 min in 2.1 M monomer solution in order to minimize backbiting. The calculated chain densities observed for the resulting nanocomposites can be seen in Table 4. The highest calculated chain density resulted in an area of 17 nm^2 per chain or 73 chains per 20 nm particle. This can be compared with our earlier result that indicated that there were 39 initiator sites per particle for standard reaction times. A corresponding increase in the polydispersity of the polymer chains from 1.2 to a maximum of 1.5 was also observed. An increase in polydispersity has been used throughout this study as a marker for chain backbiting; conversely, a narrow polydispersity is an indicator that each ruthenium center generates a single polymer chain. Therefore, because the polydispersity increased for samples with longer catalyst reaction times, it cannot be conclusively shown that the chain density did increase for these samples. The decreased chain density and polydispersity observed for the sample reacted with catalyst for 7 h indicate that deactivation of the catalyst at longer reaction times may also be a factor.

Controlling Chain Density: There are several interesting features of the observed chain densities following increased catalyst reaction times. The polymerizations from these surfaces were conducted using conditions similar to those for the earlier analyses. However, in all the above cases, the chain densities were higher. This is, despite our earlier results, very reproducible. The control polymerizations (i.e., polymerizations carried out on the same batch of nanoparticles using our standard monomer concentrations and catalyst loading conditions) used in this study were also similar to previous results and yielded values of 30 and 38 nm^2/chain as compared to the value of 30 nm^2/chain obtained in our earlier work. They also did not display an increase in the polydispersity of the chains. No samples that were reacted with catalyst for the standard 3 min ever displayed an area per chain lower than 29 nm^2. It is also probable that an increase in polymer chain density would increase the rate of chain backbiting due to the increased proximity of the polymer chain segments. Thus, an increase in chain density would be

silanes. The slightly higher chain density (lower area per feature) as compared to that of the catalyst may be a result of a small degree of backbiting but is within the experimental errors. The polydispersities of the cleaved polymer layers were consistently below 1.2, further suggesting that backbiting was largely eliminated under these conditions. Surfaces prepared with BCH were also analyzed and resulted in an area per chain of 26 nm^2. Therefore, the use of the monofunctional or trifunctional silane did not have a strong effect on the resulting chain density. This corresponds well with our analyses of the coupling agent density that found that only a slightly thicker surface layer was prepared with BCH as compared to NEEDS.

We then examined the chain density as a function of polymerization time for a single composite to determine if it remained constant in the presence of a high monomer concentration. Polymerization was initiated from a single large sample of nanoparticles (28 nm diameter) and then subsequently split into three equal portions. Each polymerization was terminated using ethyl vinyl ether at different times while holding all other factors constant. Nanocomposites were then analyzed individually to determine the chain density. The monomer concentration used was 2.1 M, and relatively short polymerization times of 5, 10, and 15 min were chosen. The rate of the polymerization was still very high under these conditions, resulting in polymer molecular weights as large as 250 000. The resulting number of chains per particle for each sample is shown in Table 3. It was found that the number of chains per particle increased from 87 to 141 throughout the course of the polymerization. This implies that a small number of free chains are being formed throughout the polymerization, even in the presence of high monomer concentrations. The 5 min polymerization showed catalyst densities on par with the previous values. This indicates that significant backbiting does not occur over 5 min. The onset of chain backbiting is indicated by the increased number of chains per particle and broadened PDI for polymerization times as low as 10 min. This may be a sign of local monomer depletion if the rate of polymerization exceeds the rate of monomer diffusion, or it may simply be a result of the close proximity of the surface-bound chains.

Controlling Initiator Concentration: A comparison of the catalyst density to the chain density, as reported above, indicated that the reaction between the surface norbornene groups and the catalyst was not stoichiometric. An attempt was made to

Table 5. Chain Density for Partially Functionalized Surfaces and for Nanoparticles Reacted with Catalyst in the Presence of TCP[a]

Chain Density after Diluting Norbornene Surface Groups

coupling agent reaction mix	chains/particle	MW (×10³ g mol⁻¹)	PDI	nm²/chain
25% TMS:75% NB	11	273	1.17	118

Chain Density vs TCP to Ruthenium Alkylidene Molar Ratio

TCP ratio	chains/particle	MW (×10³ g mol⁻¹)	PDI	nm²/chain
150:1	6	303	1.26	214
7:1	23	273	1.41	54
2:1	40	240	1.12	30

[a] Polymerizations were run for 5 min in 4.3 M monomer solution.

consistent with all of the observations made in these systems. Work in our labs is currently being directed toward confirming these results using monomers that are less susceptible to backbiting reactions.

Reducing the chain density was accomplished using two methods. The first was the reduction of the concentration of norbornene initiator groups through the use of mixed monolayers. Nanoparticles were first reacted with a less than stoichiometric amount of trimethylethoxysilane (25 mol % relative to surface silanols) to form a partially coated surface. The particles were then reacted using NEEDS (75 mol % relative to the surface silanols) to coat the remaining surface with norbornene groups. Only 25−50% of the surface silanols are reported to be accessible to reaction with alkyl dimethylsilanes. Our previous results indicate that about 33% react. This should result in a surface that is primarily passivated with TMS and a dilution of norbornene initiators by a factor of 4. These nanoparticles were then used to initiate polymerization after functionalization with ruthenium alkylidenes. The second method was to increase the additional tricyclohexylphosphine (TCP) in the reaction between the ruthenium alkylidene and the nanoparticle surface. It has been reported previously that the reactivity of Grubbs 1st generation catalyst is reduced in the presence of excess tricyclohexylphosphine (TCP).[39] We reasoned that the amount of catalyst that reacted with the nanoparticle surface could be varied using different concentrations of TCP along with controlled reaction times. The TCP concentrations during polymerizations were the same as for previous studies, while the polymerization times (5 min) and monomer concentrations (4.3 M) were chosen to minimize backbiting and chain transfer.

The results for the calculated chain densities for surfaces prepared using varying amounts of TCP, along with the results for a sample prepared using mixed monolayers, can be seen in Table 5. The calculated values vary from 30 to 214 nm²/chain and demonstrate that these methods allow access to a wide range of polymer brush densities. Polydispersities were narrow for nearly all samples. Initial synthetic attempts revealed that, depending on brush density, a large volume of particle initiators was necessary to obtain a characterizable quantity of polymer.

The area per chain calculated for the sample prepared using a mixed monolayer was 118 nm², which indicates that reduction of the concentration of norbornene groups on the surface was effective for lowering the chain density. It was originally speculated that a decrease in the concentration of norbornene groups on the surface might actually result in an increased chain density due to the inability of a single catalyst molecule to polymerize multiple norbornene groups on the surface. However, this was not observed. The application of TCP for controlling the chain density was the most easily applied method and resulted in the broadest range of chain densities. Polymer densities obtained in this study ranged from 17 to 214 nm²/chain and spanned a large portion of the reported literature values of 1.7−1000 nm² that include both adsorbed block−copolymer systems as well as SIP.[12,16]

Conclusions

The synthetic methods described in this paper provide the basis for the systematic study of material properties as a function of polymer chain density in these systems. This work also demonstrates the challenges inherent in applying homogeneous polymerization chemistries to surface-initiated systems. The structure of silica−poly(norbornene) nanocomposites has been fully characterized. The calculated values for the density of norbornene groups on the surface were found to range from 1.8 to 2.6 group/nm², depending on the nature of the silane coupling agent applied. These results were shown to fit well with literature values for similar silanes. The reaction of the catalyst with the surface is believed to be nonstoichiometric, with nearly 57 norbornene groups being consumed per catalyst molecule. Chain densities have been calculated from nanoparticle surfaces coated with both mono- and trifunctional silanes. It was determined that the chain densities were similar for both systems, with only a slight increase for surfaces prepared with a multifunctional silane. A comparison of the catalyst loading with the chain density for monolayer coatings has revealed that, within experimental error, all catalyst molecules initiate polymer chains. This initiation efficiency compares well with the quantitative initiation efficiency seen in the homogeneous polymerization systems. The results of our attempt to increase the polymer chain density were inconclusive but suggested it had been accomplished. Work is currently in progress which will remove the ambiguity of these results. The ability to decrease the chain density has also been demonstrated by two methods allowing the formation of a broad range of brush densities. The values for the area per chain reported in this study ranged from 17 to 214 nm²/chain. These results cover a broad range of the reported literature values, including brushes formed by adsorption as well as those formed by SIP.

Supporting Information Available: Generalized reaction scheme and detailed experimental protocols. This material is available free of charge via the Internet at http://pubs.acs.org.

(39) Bielawski, C.; Grubbs, R. *Macromolecules* **2001**, *34*, 8838−8840.

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