Synthesis of Nanocomposite Organic/Inorganic Hybrid Materials Using Controlled/"Living" Radical Polymerization

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The preparation of hybrid organic/inorganic nanocomposites comprised of well-defined polymers was reviewed. In particular, synthetic methods using controlled/"living" radical polymerization techniques, such as stable free-radical/nitroxide-mediated polymerizations, atom transfer radical polymerization, and reversible addition−fragmentation chain-transfer polymerization were described. The various approaches taken to prepare hybrid copolymers, nanoparticles, polymer brushes, dispersed silicate nanocomposites, and nanoporous materials were discussed.

1. Introduction

The synthesis of novel materials with improved properties and performance is a continually expanding frontier at the interface of chemistry and materials science. In this pursuit, the ability to control molecular structure on atomic and macroscopic dimensions is a key parameter in designing materials with preprogrammed activity. A significant advance in this area has been the synthesis of nanocomposites where the structural order within the material can be controlled on nanometer/submicron scales. While materials possessing such structural complexity are common in nature, robust and versatile methods to prepare synthetic nanocomposites remains an exciting challenge that is being tackled by research groups around the world.[1]

One approach to prepare nanocomposites has been the incorporation of well-defined organic and inorganic components into a singular material. In particular, the inclusion of well-defined polymers to inorganic substrates is of significance, because the functionality, composition, and dimensions of these macromolecules enable the design of specific properties into the resulting hybrid.[2]

Well-defined organic polymers have been attached to inorganic (co)polymers, particles, surfaces, glassy networks and interpenetrating polymer networks to prepare organic/inorganic hybrid materials. Additionally, polymers of controlled size, composition, and architecture have been used as shape templates in the synthesis of mesoporous inorganic networks (Figure 1). Polymers, such as poly(tetramethylene oxide) and poly(oxazolines), have been used to synthesize hybrid organic/inorganic nanocomposites.[3] However, recent developments in controlled/"living" radical polymerization (CRP) have provided another valuable methodology to introduce well-defined organic (co)polymers to a variety of inorganic substrates. The scope of this review will cover hybrid organic/inorganic nanocomposites that have been
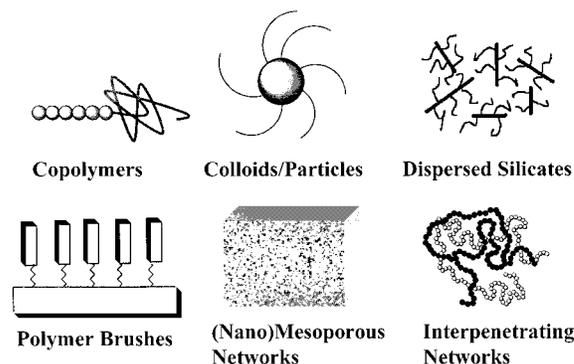
Figure 1. Examples of organic/inorganic hybrid materials.

made using CRP. For more fundamental discussions of organic/inorganic hybrid materials, the reader is directed to other reviews.[2−5]

2. Controlled Radical Polymerization

CRP has proved to be a versatile and robust method to prepare well-defined organic polymers. In the past decade, several techniques have been developed to synthesize well-defined polymers via radical polymerization. A major difference between conventional radical [i.e., azobis(isobutyronitrile)- or peroxide-initiated processes] and controlled radical polymerizations is the lifetime of the propagating radical during the course of the reaction. In conventional radical processes, radicals generated by decomposition of the initiator undergo propagation and bimolecular termination reactions within a second. In contrast, the lifetime of a growing radical can be extended to several hours in a CRP, enabling the preparation of polymers with predefined molar masses, low polydispersity, controlled compositions, and functionality.[6,7]

The mechanism invoked in CRP processes to extend the lifetime of growing radicals utilizes a dynamic equilibration between dormant and active sites with

Scheme 1. Classification and General Mechanism of CRP Methods for (1) SFRP, X = O−NR$_2$, (2) ATRP, X = Halogen, Y = M$_t^n$/L$_m$, Y^0 = X−M$_t^{n+1}$/L$_m$, (3) Degenerative Transfer, Reversible Addition−Fragmentation Chain-Transfer Polymerizations, X = I, −SC = (Z)-S−CH(R)−CH$_2$−R
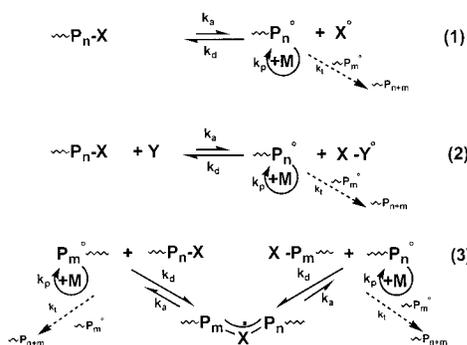
rapid exchange between the two states. Unlike conventional radical processes, CRP requires the use of persistent radical (deactivator) species, or highly active transfer agents to react with propagating radicals. These persistent radicals/transfer agents react with radicals (deactivation or transfer reactions with rate constant, k_d) to form the dormant species. Conversely, propagating radicals are generated from the dormant species by an activation reaction (with rate constant, k_a).

2.1. Classification of CRP Systems. In the past decade, the field of CRP has seen tremendous development as evidenced by the wide range of materials that have been prepared using these techniques. In particular, three methods of considerable importance are the following: stable free-radical polymerization [SFRP; e.g., nitroxide-mediated processes (NMP)], metal-catalyzed atom transfer radical polymerization (ATRP), and degenerative transfer [e.g., reversible addition−fragmentation chain transfer (RAFT)]. While these three systems possess different components, general similarities in the CRP processess can be seen in the use of initiators, radical mediators (i.e., persistent radicals or transfer agents), and in some cases catalysts (Scheme 1). It is important to note that while SFRP and ATRP are subject to the persistent radical effect (PRE),[8,9] degenerative processes, such as RAFT, do not conform to the PRE model because of the transfer-dominated nature of the reaction.

2.1.2. SFRP. In this type of CRP, alkoxyamine initiators[10] (−P$_n$X; eq 1 in Scheme 1) and nitroxide persistent radicals (X^0; eq 1 in Scheme 1) have been effectively used to polymerize styrenes and acrylates. In certain systems, alkoxyamines have also been generated in situ by the initial use of conventional radical initiators (AIBN and peroxides) and nitroxide persistent radicals, which also led to a CRP process.[11] A widely used nitroxide in the polymerization of styrene (Sty) is 2,2,6,6-tetramethylpiperidinyloxy (TEMPO), although recently developed nitroxides can also polymerize acrylates in a controlled fashion.[12,13] The current limitation in this system lies in the inability to successfully polymerize methacrylate monomers, because of β-hydrogen elimination to the nitroxide radicals. Additionally, thiuram disulfides and dithiocarbamate "iniferter"

systems have been used as agents for CRP with limited success.[14,15]

2.1.3. ATRP. In these polymerizations, radicals are generated by the redox reaction of alkyl halides (−P$_n$X; eq 2 in Scheme 1) with transition-metal complexes (Y; eq 2 in Scheme 1).[16−18] Radicals can then propagate but are rapidly deactivated by the oxidized form of the transition-metal catalyst (X−Y^0; eq 2 in Scheme 1). Initiators typically used are α-haloesters (e.g., ethyl 2-bromoisobutyrate and methyl 2-bromopropionate) or benzyl halides (e.g., 1-phenylethyl bromide and benzyl bromide). A wide range of transition-metal complexes, such as Ru-, Cu-, and Fe-based systems, have been successfully applied to ATRP. For Cu-based systems, ligands such as 2,2′-bipyridine and aliphatic amines have been employed to tune both the solubility and activity of various ATRP catalysts. ATRP has been successfully applied for the controlled polymerization of styrenes, (meth)acrylates, (meth)acrylamides, acrylonitrile, and 4-vinylpyridine. ATRP systems are currently limited to monomers that do not strongly coordinate to the catalyst.[18]

2.1.4. Degenerative Transfer. Radical polymerizations based upon a degenerative transfer system rely upon the rapid and reversible exchange of highly active transferable groups (−X; eq 3 in Scheme 1) and growing polymeric radicals (−P$_m^0$ and −P$_n^0$; eq 3 in Scheme 1). While conventional radical initiators (AIBN and peroxides) are used in this reaction, these compounds only serve as a radical source to drive reversible exchange reactions between active and dormant states. Transfer agents in this process contain moieties for both initiation and transfer which are generated in the presence of radicals. Controlled radical polymerizations from degenerative transfer reations have been done using alkyl iodides,[19] unsaturated methacrylate esters,[20] or thioesters as the transfer agents. In particular, the use of thioesters in the radical polymerization of vinyl monomers results in a RAFT polymerization.[21] The RAFT process has proven to be a versatile method to polymerize functional styrenes, (meth)acrylates, and vinyl esters.

2.2. Synthetic Methodologies To Prepare Nanocomposite Hybrids Using CRP. A variety of CRP techniques have been developed to incorporate well-defined organic polymers to inorganic substrates. A key advantage of CRP processes is the facile functionalization/deposition of initiator and polymerizable moieties onto inorganic polymers and surfaces.

2.2.1. Synthesis of Hybrid Homopolymers and Block, Graft, and Random Copolymers. In the preparation of organic/inorganic nanocomposite materials, hybrid copolymers are of particular interest because of the inherent incompatibility of the two segments. Thus, phase separation of these segments yields a variety of controlled nanostructures depending on the degree of incompatibility of the components, the composition, and the degree of polymerization in the final copolymer.

A wide range of polymeric structures have been made using different combinations of organic and inorganic components. In the simplest case, a vinyl monomer possessing an inorganic moiety (R = inorganic moiety; Scheme 2a) can be homopolymerized in the presence of initiator (R−X) to prepare a hybrid homopolymer with

Scheme 2. Synthetic Approaches To Prepare Hybrid Polymers

a) P–X Initiator → (CRP, R) → **Hybrid Homopolymer**

or

b) P–X Initiator + R$_1$ → (CRP, R) → **Random Copolymer**

or

c) ·····–X → (R, CRP) → **Block Copolymer**

or

d) Macroinitiator –X → (R$_1$) → **Block Copolymer**

e) **Inorganic Macroinitiator** + R$_1$ → (CRP) → **Graft Copolymers**

f) **Inorganic Macromonomer** + P–X Initiator + R$_1$ → (CRP) → **Graft Copolymers**

R = inorganic moiety
R$_1$ = organic moiety
X = transferrable group e.g., nitroxide, halogen, thioester

Scheme 3. Hybrid Polymers Prepared Using Inorganic Initiators

Monofunctional Inorganic Initiator –X → (CRP, R) → **End-Functional Hybrid Polymer**

Multifunctional Inorganic Initiator → **Branched/Star Hybrid Polymer**

X = CRP initiator
◯ = inorganic compound

Scheme 4. Examples of Hybrid Materials Prepared from Particles, Flat Surfaces, Layered Silicates, and Networks

a) **Functional Particles** → (CRP, R$_1$) → **Hybrid Particles**

b) **Surfaces** → (CRP, R$_1$) → **Modified Surfaces**

c) **Layered Silicate** (1.2 nm, Na$^+$) → 1) Loading of Initiator 2) CRP → **Dispersed Silicate Nanocomposite**

d) **Organic Polymer Template from CRP** → Network Formation → Template Removal → **Nanoporous Network**

X = CRP initiator, R$_1$ = organic moiety

organic main-chain and inorganic side-chain groups. Alternatively, inorganic vinyl monomers can be copolymerized in the presence of organic monomers and R–X to make random copolymers (Scheme 2b). Chain extension of an organic macroinitiator prepared by CRP with an inorganic monomer yields a block copolymer (Scheme 2c). Conversely, an inorganic macroinitiator can be used in the CRP of an organic vinyl monomer to also prepare a hybrid block copolymer (Scheme 2d). Inorganic macroinitiators can be synthesized by end-capping growing inorganic chain ends obtained from ionic or step-growth processes with coupling agents that contain CRP initiator groups. In a similar fashion, hybrid graft copolymers are prepared by chain extending a multifunctional inorganic macroinitiator with an organic vinyl monomer (Scheme 2e). Additionally, inorganic macromonomers possessing vinyl end groups can be copolymerized with organic vinyl monomers by CRP, yielding graft copolymers with organic main-chain and inorganic side-chain groups (Scheme 2f).

2.2.2. Synthesis of Hybrid Polymers from Inorganic Initiators. Another type of hybrid polymer is prepared by the use of a (multi)functional inorganic compound as an initiator for CRP. Various polymeric structures are possible depending on the functionality of the initiator. Monofunctional inorganic initiators would result in an end-functional polymer, while multifunctional initiators yield branched/star polymers (Scheme 3).

2.2.3. Synthesis of Nanocomposite Particles, Modified Surfaces, Dispersed Silicates, and Nanoporous Materials. The tethering of well-defined organic polymers to inorganic substrates such as particles (Scheme 4a) and surfaces (Scheme 4b) can be conducted using CRP. The attachment of prepared polymers was achieved by grafting to curved and flat surfaces.[22–26] However, by the use of CRP methods, grafting organic polymers from surfaces can be performed by attachment of an initiator group (–X; Scheme 4) and polymerization of a vinyl monomer. The chem-

istry required for the functionalization of CRP initiator groups on curved and flat surfaces depends on the type of inorganic substrate used. In the case of gold and silicon wafers, the incorporation of initiating moieties to surfaces requires the tethering of functional thiols, or chloro/alkoxysilanes, respectively. By the use of CRP from inorganic surfaces, ultrathin films of precise thickness and composition can be grown. Organic/inorganic nanocomposites can also be prepared by CRP from the surfaces of layered silicates (Scheme 4c). CRP of an organic vinyl monomer between the inorganic layers yields a nanocomposite of inorganic platelets dispersed in a matrix of well-defined polymer. Finally, polymers of controlled size and compositions can be prepared by CRP and used as templates in the network polymerization of inorganic resins (Scheme 4d). When the molar mass and composition of the polymer template are tuned, using CRP enables control of both the hydrodynamic volume and the compatibility of the polymer with
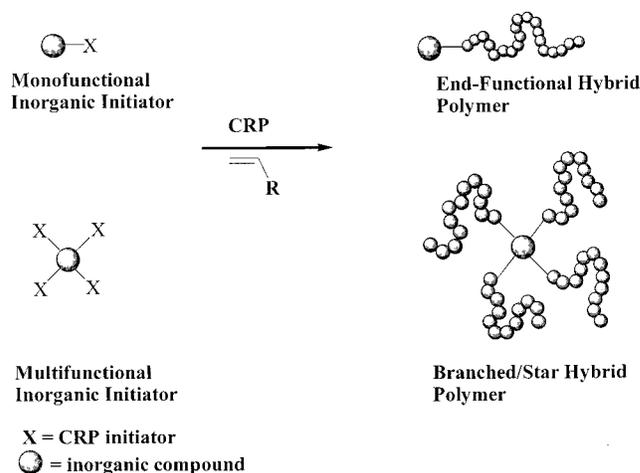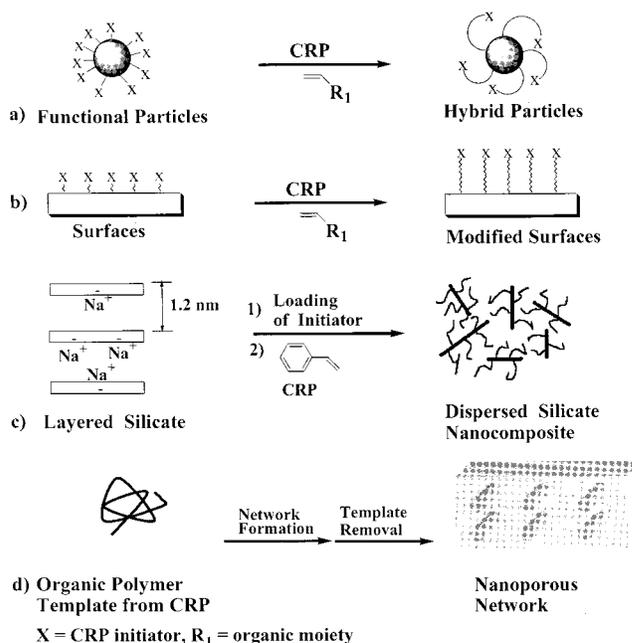
Scheme 5. Synthesis of p(Sty-*b*-DMS-*b*-Sty) via Hydrosilation and ATRP
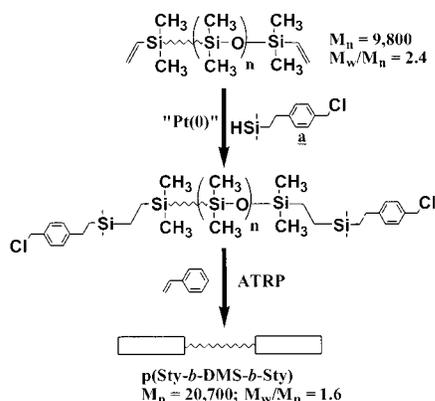
the inorganic matrix, respectively. Network formation around the polymeric templates, followed by degradation of the organic components, yields an inorganic glass with nanosized pores dispersed throughout the material.

3. Silicon-Containing Hybrid Homopolymers and Block and Graft Copolymers

3.1. Synthesis of Poly(dimethylsiloxane) (PDMS) Block and Graft Copolymers. The synthesis of copolymers containing both PDMS and polystyrene/poly-((meth)acrylates) was conducted from a variety of approaches. Copolymers containing PDMS and organic polymers are of interest, because the inherent incompatibility of the components induces phase-separated structures of nanometer dimensions. These materials have anticipated applications as thermoplastic elastomers, silicone rubbers, and surfactants for supercritical CO_2.[27] To prepare these structures, PDMS compounds prepared from both living anionic polymerization and condensation processes were functionalized with either initiator groups or polymerizable moieties for CRP.

3.1.1. Synthesis of ABA and ABC Triblock Copolymers Containing PDMS. A direct and convenient approach to preparing ABA triblock copolymers is the functionalization of telechelic PDMS with initiator end groups and application of the macroinitiator to CRP systems. Telechelic PDMS compounds with different kinds of end groups are readily prepared by condensation polymerizations and are commercially available. Difunctional PDMS with either vinyl or silane (Si−H) end groups can be reacted with various alkenes via hydrosilation to introduce functionality to the PDMS chain ends.[27] Using this general approach, PDMS macroinitiators for ATRP were made by the hydrosilation of telechelic PDMS ($M_n = 9800$; $M_w/M_n = 2.4$) possessing vinyl end groups with [2-[4-(chloromethyl)phenyl]ethyl]-dimethylsilane (**a** in Scheme 5). The ATRP of Sty from the benzyl chloride functional PDMS yielded an ABA triblock copolymer of p(Sty-*b*-DMS-*b*-Sty) ($M_n = 20\,700$; $M_w/M_n = 1.6$).[28]

Alternatively, PDMS macroinitiators bearing amine end groups were reacted with 2-bromoisobutyryl bromide to prepare difunctional PDMS macroinitiators for ATRP. These macroinitiators were then used in the ATRP of 2-(dimethylamino)ethyl methacrylate to prepare an ABA triblock copolymer, with PDMS as the middle segment.[29]
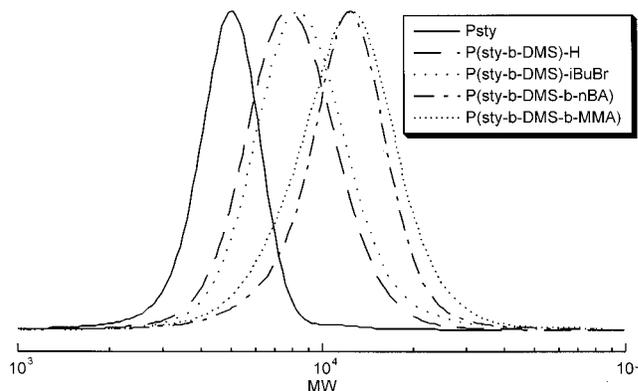
Figure 2. SEC chromatogram of ABC triblock copolymers of p(Sty-*b*-DMS-*b*-MMA) and p(Sty-*b*-DMS-*b*-*n*BA) using hydrosilation and ATRP.[30]

Scheme 6. Transformation of Living Anionic Polymerization to ATRP for the Preparation of p(Sty-*b*-DMS-*b*-MMA) and p(Sty-*b*-DMS-*b*-BA) ABC Triblock Copolymers
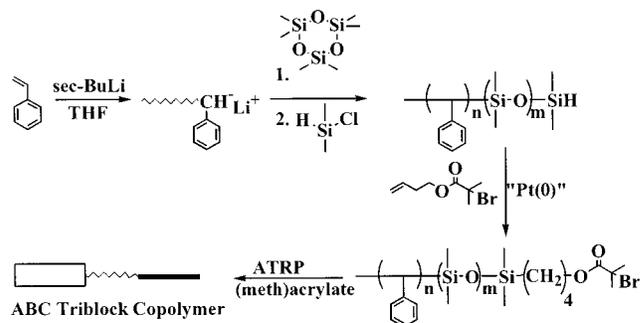
ABC triblock copolymers were synthesized by transformation of living anionic polymerization to ATRP (Scheme 6).[30] Using this methodology, the synthesis of well-defined poly[styrene-*b*-dimethylsiloxane-*b*-(*n*-butyl acrylate)] and poly[styrene-*b*-dimethylsiloxane-*b*-(methyl methacrylate)] triblock copolymers was accomplished. These types of triblock copolymers are not accessible via anionic processes because of poor cross propagation from living PDMS lithium silanoate chain ends to (meth)-acrylate monomers. In the first step of the block copolymerization, a living anionic polystyrene chain ($M_n = 4600$; $M_w/M_n = 1.09$) was used to initiate the ring-opening polymerization of hexamethylcyclotrisiloxane (D_3). Subsequent quenching of the lithium silanoate chain end of the p(Sty-*b*-DMS) block copolymer with chlorodimethylsilane yielded a silane-terminated chain end ($M_n = 7760$; $M_w/M_n = 1.15$). A macroinitiator for ATRP was then prepared by hydrosilation of the silane functional p(Sty-*b*-DMS) copolymer with 3-butenyl 2-bromoisobutyrate. ATRP with the p(Sty-*b*-DMS) macroinitiator with either *n*-butyl acrylate (BA) or methyl methacrylate (MMA) enabled the synthesis of ABC triblock copolymers. The synthesis of these triblock copolymers was confirmed by size-exclusion chromatography (SEC) analysis (Figure 2). The SEC chromatogram pointed to the synthesis of well-defined polymers at each step of the block copolymerization, starting from pSty to p(Sty-*b*-DMS) anionically, followed by addition of *n*-butyl acrylate ($M_n = 10\,200$; $M_w/M_n = 1.18$) or methyl methacrylate ($M_n = 10\,100$; $M_w/M_n = 1.21$) using ATRP.
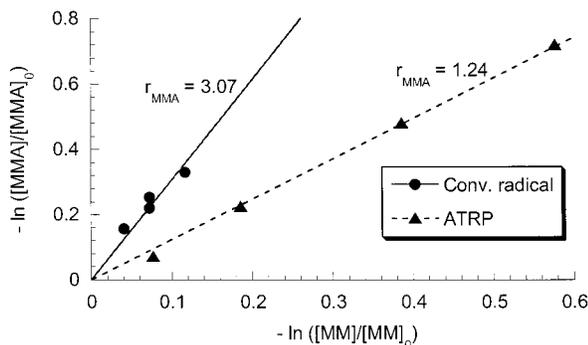
Figure 3. Jaacks plots for the copolymerizations of MMA with PDMS macromonomer ($M_n = 2200$, 5 mol % in the feed) in a xylene solution (MMA/xylene = 1/1 by weight) using the conventional radical polymerization (RP) and ATRP. Conditions: RP, $[MMA]_0/[macromonomer]_0/[AIBN]_0 = 380/20/1$, 75 °C; ATRP, $[MMA]_0/[macromonomer]_0/[initiator]_0/[CuCl]_0/[dn-Nbpy]_0 = 285/15/1/1/2$, 90 °C (dnNbpy = 4,4′-dinonyl-2,2′-bipyridine).[31]

Scheme 7. Synthesis of p(DMS-*g*-Sty) and p(MMA-*g*-DMS) Graft Copolymers Using ATRP
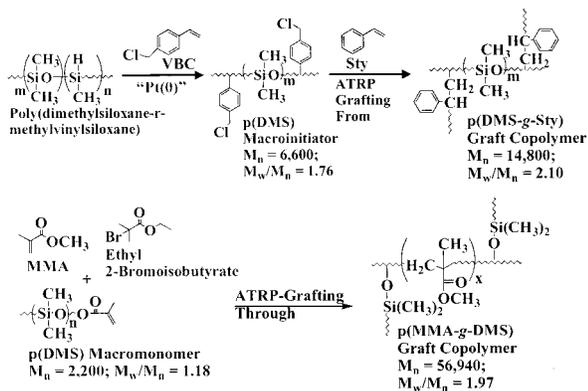
3.1.2. Synthesis of Graft Copolymers with PDMS: "Grafting from" and "Grafting through" Approaches.

The synthesis of graft copolymers possessing pSty grafts and a PDMS main chain was accomplished by a "grafting from" approach using ATRP.[28] In this method, a copolymer of poly(dimethylsiloxane-*r*-methylvinylsiloxane) was functionalized with ATRP initiator groups by hydrosilation with 4-vinylbenzyl chloride (VBC) in the presence of Karstedt's catalyst (i.e., platinum divinyltetramethyldisiloxane complex, "Pt(0)"). The multifunctional macroinitiator ($M_n = 6600$; $M_w/M_n = 1.76$) was then used in the ATRP of Sty, yielding a p(DMS-*g*-Sty) graft copolymer ($M_n = 14\ 800$; $M_w/M_n = 2.10$; Scheme 7).

Alternatively, graft copolymers with PDMS side chains were prepared by the ATRP copolymerization of a methacrylate functional PDMS macromonomer and methyl methacrylate (MMA; Scheme 7).[31] Methacrylate PDMS macromonomers were prepared by the anionic ring opening of hexamethylcyclotrisiloxane, followed by quenching of the lithium silanoate chain end with [3-(methacryloxy)propyl]chlorodimethylsilane ($M_n = 2200$; $M_w/M_n = 1.18$). ATRP of the PDMS macromonomer with MMA yielded a p(MMA-*g*-DMS) graft copolymer ($M_n = 56\ 900$; $M_w/M_n = 1.97$) with a relatively uniform distribution of grafts throughout the copolymer. Figure 3 shows the Jaacks plot for the ATRP copolymerization of MMA and the PMDS macromonomer. As shown in

Scheme 8. Synthesis of p(Sty-*b*-MPS-*b*-Sty) ABA Triblock Copolymers
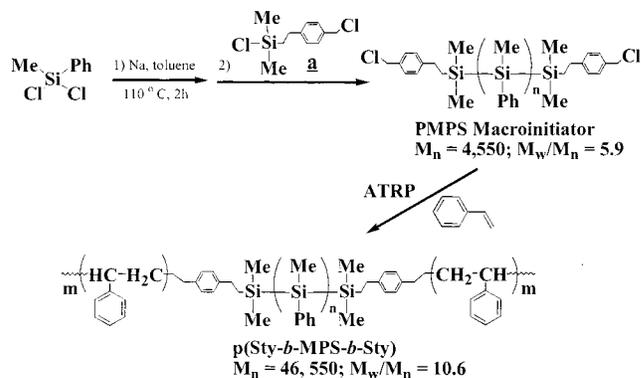
the plot, the lower reactivity ratio of MMA using ATRP ($r_{MMA} = 1.24$) revealed that a steady consumption of the PDMS macromonomer occurred throughout the reaction, unlike in the conventional radical process initiated by AIBN where MMA was preferentially consumed at a faster rate ($r_{MMA} = 3.07$).

3.2. Synthesis of ABA Triblock Copolymers Containing Polysilylenes.

Polymers containing substituted polysilylenes (polysilanes) are of interest for applications as photoresist, photoconducting, and nonlinear optical materials. The interesting electronic and optical properties of these materials arise from the delocalization of low-lying σ electrons in the Si−Si backbone of the polymer.[32] In an effort to improve the mechanical properties and processing of these materials, block copolymers with pSty segments were incorporated into polysilanes using ATRP.[33] In this approach, poly(methylphenylsilane) (PMPS) was prepared by the Wurtz-type reductive coupling of dichloromethylphenylsilane in the presence of sodium and was end-capped with **a** (Scheme 8). ATRP of Sty from the difunctional benzyl chloride macroinitiator ($M_n = 4550$; $M_w/M_n = 5.9$) yielded an ABA triblock copolymer of p(Sty-*b*-MPS-*b*-Sty) ($M_n = 46\ 550$; $M_w/M_n = 10.6$).

3.3. Hybrid Polymers Containing Polyhedral Oligomeric Silsesquioxanes (POSS).

Polymers containing side-chain groups of POSS[34] represent a novel class of hybrids that is anticipated to impart greater thermal and mechanical stability to a material.[35−38] These inorganic groups can be incorporated into polymer chains via CRP of a POSS containing monomer (e.g., methacrylate and styrene) or initiated from a POSS containing alkyl halide (e.g., benzyl chloride). Structurally, T8-POSS monomers are cubic siloxane octamers and have an outer diameter of 1.5 nm.[34] It is the inclusion of these bulky inorganic pendant groups that gives POSS polymers their unusual structure and properties. While POSS polymers and materials have been prepared from a variety of methods, the application of POSS monomers to CRP allowed for greater control of polymer molecular weight, topology, and composition.

Recently, a methacrylate-containing POSS compound, 3-(3,5,7,9,11,13,15-heptacyclopentylpentacyclo[9.5.1. 1.[3,9]1.[5,15]1[7,13]]octasiloxane-1-yl)propyl methacrylate (MA-POSS) was polymerized by ATRP to prepare homopolymers, ABA triblock and AB star diblock copolymers (Scheme 9).[39] ATRP of MA-POSS in the presence of ethyl 2-bromoisobutyrate (Scheme 9) yielded homopoly-

Scheme 9. Synthesis of POSS Containing Hybrid Polymers Using ATRP
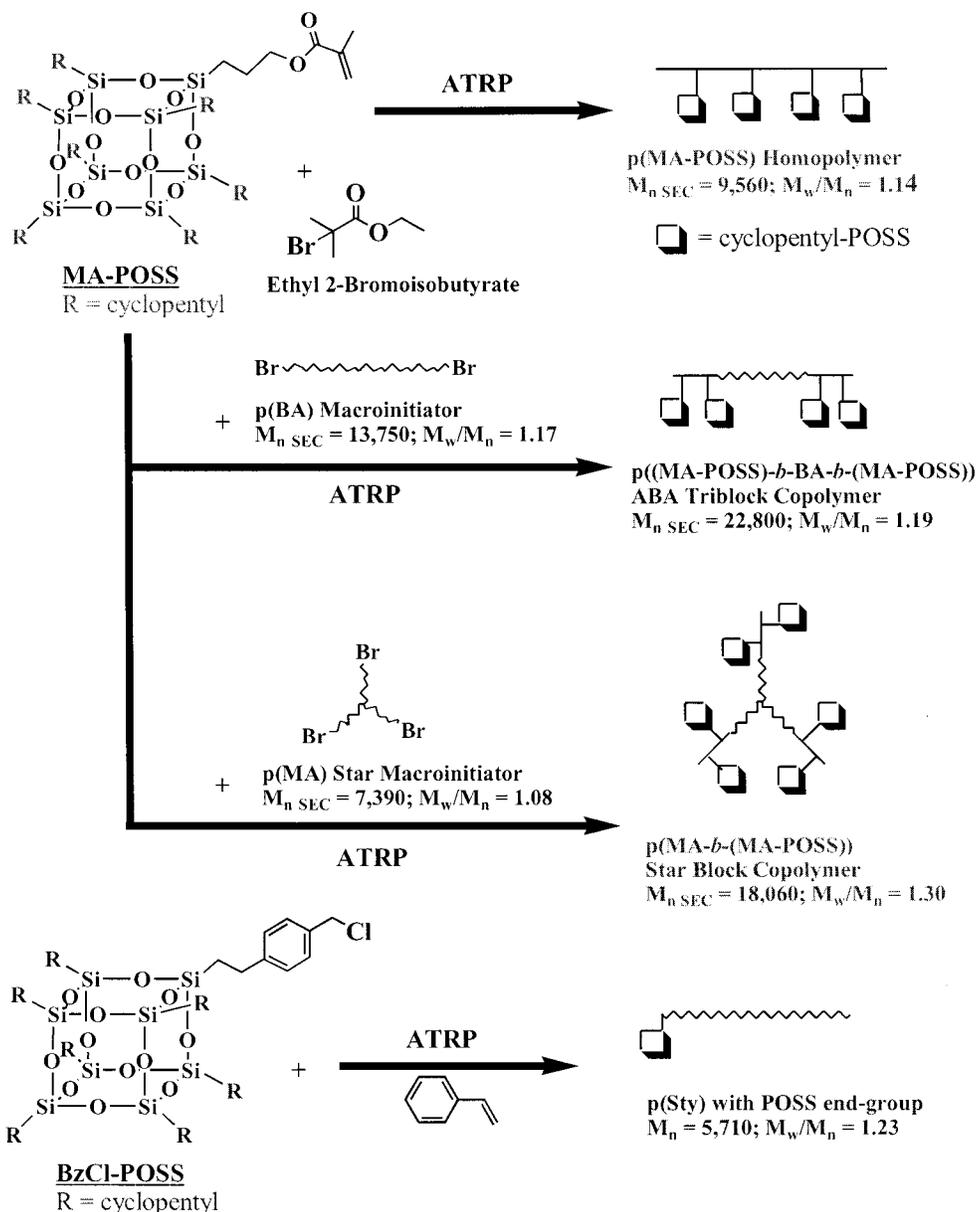
mers of p(MA-POSS). ABA triblock copolymers were synthesized by the ATRP of MA-POSS from a difunctional poly(*n*-butyl acrylate) (pBA) macroinitiator ($M_{n,SEC}$ = 13 750; M_w/M_n = 1.17). SEC of the p[(MA-POSS)-*b*-(BA)-*b*-(MA-POSS)] copolymer ($M_{n,SEC}$ = 22 800; M_w/M_n = 1.19, Figure 4) and ^{1}H NMR confirmed successful chain extension of MA-POSS from the macroinitiator. To prepare copolymers with more complex architectures, a three-armed poly(methyl acrylate) (pMA) star polymer ($M_{n,SEC}$ = 7390; M_w/M_n = 1.08) was used as a macroinitiator in the ATRP of MA-POSS, yielding a well-defined AB star diblock copolymer of p[MA-*b*-(MA-POSS)] ($M_{n,SEC}$ = 18 060; M_w/M_n = 1.30).

Hybrid polymers have also been prepared by using monofunctional POSS initiators in the ATRP of Sty (Scheme 9).[40] In the polymerization, a POSS initiator bearing one benzyl chloride and seven cyclopentyl groups at the corners of the cyclic silsesquioxane was used, yielding a well-defined pSty homopolymer with a POSS end group. Using conditions similar to those previously reported, comparison of the monomer conver-

sion and molar mass evolution with monomer conversion (Figure 5) revealed that the presence of a bulky silsesquioxane group did not affect the initiating capability of the benzyl chloride moiety. Additionally, pSty with POSS end groups made from ATRP possessed relatively low polydispersity (M_w/M_n = 1.24).

4. Hybrid Star Polymers from Inorganic Initiators

Organic star polymers with inorganic cores comprise another class of hybrid material. An advantage of using inorganic initiators to prepare stars from a "core-first" approach is the ability to make multifunctional initiators with precise functionality and reactivity. Additionally, well-defined star polymers of higher molecular weight (M_n > 500 000) have been synthesized because of the incorporation of multiple initiation sites to a single molecule.

4.1 Cyclophosphazene and Cyclotetrasiloxanes as Multifunctional Initiators for ATRP. The syn-
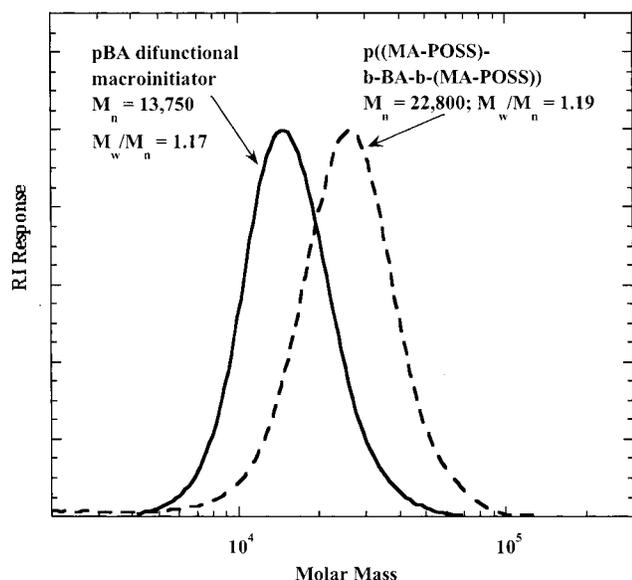
Figure 4. SEC chromatogram of p[(MA-POSS)-*b*-BA-*b*-(MA-POSS)] triblock copolymer prepared using ATRP.[39]
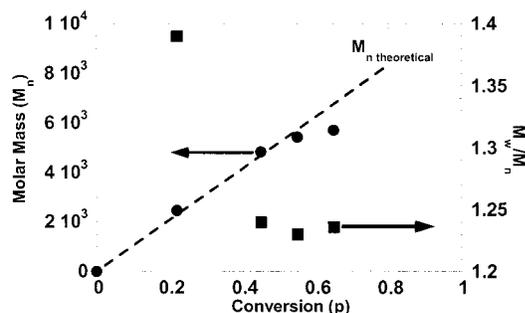
Figure 5. Plot of molar mass (filled circles) and polydispersity (squares) vs monomer conversion in the ATRP of Sty with the following conditions: [monomer]/[initiator]/[Cu^{I}Cl]/[PMDETA] = 8.6 M/0.089 M/0.045 M/0.045 M at 120 °C (PMDETA = N,N,N',N'',N''-pentamethyldiethylenetriamine).

thesis of star (co)polymers from multifunctional phosphazenes and siloxanes was conducted. The preparation of these multifunctional initiators enabled the synthesis of well-defined homopolymers and block (co)polymers using ATRP.[41] Hexafunctional inorganic initiators were synthesized by the transformation of hydroxy groups from 1,1,3,3,5,5-hexakis[4-(hydroxymethyl)phenoxy]cyclotriphosphazene to benzylic halides, or α-haloesters. From this route, hexafunctional inorganic initiators bearing benzyl bromide, 2-bromoproprionate, or 2-bromoisobutyrate groups were prepared. The use of these initiators enabled the synthesis of high molar mass/low polydispersity pMA star polymers (M_n = 557 000; M_w/M_n = 1.19) and star diblock copolymers of poly(methyl acrylate-*b*-isobornyl acrylate) (M_n = 48 000; M_w/M_n = 1.37) using ATRP. Tetrafunctional initiators for ATRP were also prepared by the hydrosilation of 1,3,5,7-tetramethylcyclotetrasiloxane and VBC. This tetrafunctional initiator was used in the synthesis of a pSty star polymer (M_n = 12 600; M_w/M_n = 1.11) using ATRP.

4.2. Metalloinitiators in the Synthesis of Hybrid Polymers. The synthesis of transition-metal-containing polymers is an area of interest for applications as sensors[42] and luminescent materials.[43] An elegant synthesis to prepare hybrid star polymers possessing a
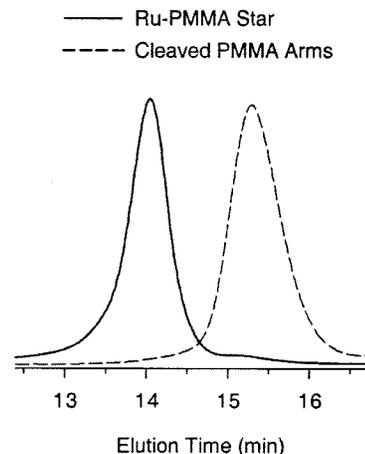
Figure 6. SEC chromatogram of a six-armed pMMA star (M_n = 54 000; M_w/M_n = 1.07) and cleaved pMMA arms (M_n = 8060; M_w/M_n = 1.13).[48]

Scheme 10. Multifunctional Metalloinitiators for ATRP from Ruthenium(II) Complexes
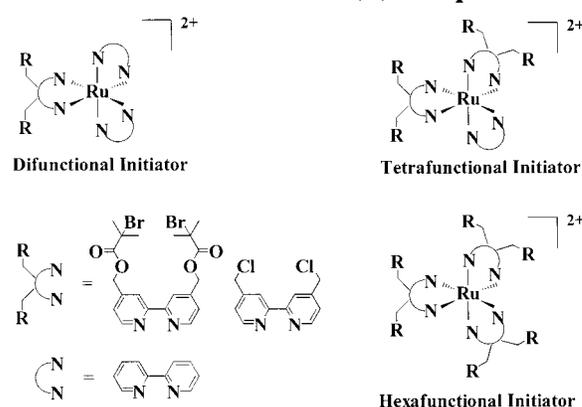
transition-metal core and organic polymer arms has been conducted using ATRP.[44−49] These metalloinitiators were comprised of transition-metal complexes possessing initiating sites for ATRP and were prepared by coordination of functional bipyridine ligands to ruthenium(II) salts. Functional bipyridine ligands possessing either benzyl chloride or 2-bromoisobutyrate groups were synthesized, enabling the efficient initiation of styrenes and (meth)acrylates (Scheme 10). In these systems, hexafunctional, tetrafunctional, and difunctional initiators were made by varying the stoichiometric ratios of functional bpy ligands to the ruthenium(II) core. Subsequent application of these metalloinitiators resulted in well-defined linear, four-armed and six-armed star polymers of pSty ($M_{n,six−armed\ star}$ = 139 000; M_w/M_n = 1.24) and pMMA ($M_{n,six−armed\ star}$ = 54 000; M_w/M_n = 1.07; Figure 6). Cleavage of pMMA chains from the six-armed pMMA star polymer revealed that well-defined polymers were obtained (M_n = 8060; M_w/M_n = 1.13; Figure 6) with molar masses in relatively good agreement with theoretical values ($M_{n,theoretical}$ = 6900).[48]

5. Organic/Inorganic Hybrid Nanoparticles

Hybrid materials composed of inorganic nanoparticles and organic surface groups possess interesting optical,[50] magnetic,[51] and blending[52] properties. These hybrids containing nanoparticles have been prepared by other synthetic routes by trapping colloids within cross-linked

Scheme 11. Synthesis of Hybrid Nanoparticles Using ATRP

Alkoxysilane
R = -CH₃, -OCH₂CH₃
R₁ = -CH₃, -CH₂CH₃

Colloid
x = 1.5, 2
R-X = functional monoalkoxysilane

Colloidal Initiator
X = benzyl chloride, 2-bromopropionate, 2-bromoisobutyrate

ATRP

Hybrid Nanoparticles with Tethered Homopolymers, Block Copolymers

Figure 7. TEM of a hybrid pSty nanoparticle with $D_{eff} = 79$ nm of a SiO_2 colloidal initiator (size bar = 100 nm).[55]
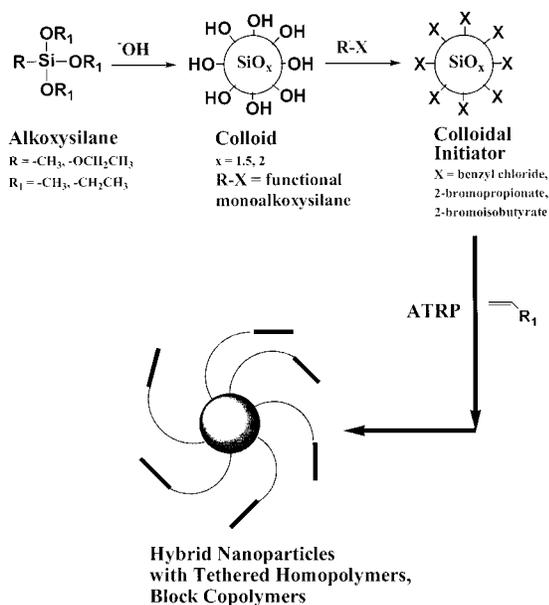
matrixes,[53] "grafting to" particles with functional molecules/polymers,[25] or "grafting from" particles using a living or controlled polymerization process.[54] Controlled radical polymerization techniques have also been introduced to colloidal materials by the attachment of ATRP initiating groups to the particle surface. Subsequent ATRP of vinyl monomers yielded core−shell particles with well-defined homopolymers and block copolymers tethered to a colloidal initiator.[55,56] The properties of hybrid nanoparticles prepared from this method can be tuned by varying the particle size of the colloidal initiator, changing the composition of the particle core, or tethering (co)polymers with novel composition/functionality. An interesting feature of hybrid nanoparticle ultrathin films has been the formation of ordered two-dimensional arrays of particles, with a spacing dependent on the radius of gyration of the tethered (co)polymer. The general methodolgy for the synthesis of hybrid nanoparticles from ATRP is presented in Scheme 11.

Siloxane-based nanoparticles have been successfully applied to ATRP systems to prepare well-defined hybrid nanoparticles. In the first step of the process, nanoparticles were synthesized via the base-catalyzed hydrolysis and condensation of tetralkoxysilanes (i.e., the Stöber process)[57,58] or by microemulsion polymerization of trialkoxysilanes.[59] Condensation reactions of surface silanol groups with functional silanes yielded colloidal initiators bearing benzyl chloride, 2-bromopropionate, or 2-bromisobutyrate groups. The synthesis of hybrid nanoparticles was then conducted by using the colloidal initiators in the ATRP of various vinyl monomers.

5.1. Hybrid Nanoparticles from Silica Colloids.
A modification of the Stöber process was developed to prepare silica (SiO_2) colloidal initiators for ATRP.[55] Dynamic light scattering (DLS) and transmission electron microscopy (TEM) revealed that functional silica particles with an average effective diameter (D_{eff}) of 70 nm were obtained. Silica colloids with benzyl chloride groups on the surface were used in the ATRP of Sty. DLS and TEM confirmed that D_{eff} of the pSty hybrid
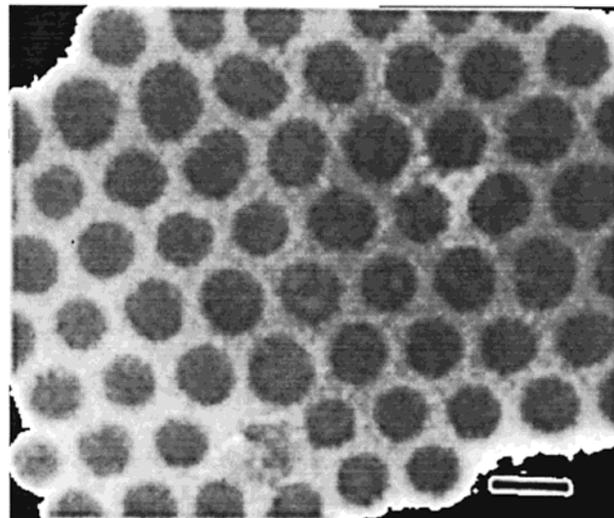
nanoparticles increased with monomer conversion. SEC of pSty chains cleaved from the particle confirmed the synthesis of well-defined polymers of low polydispersity (M_w/M_n < 1.35) and having $M_n = 26\,500$ in close agreement with $M_{n,theoretical} = 30\,600$ values. This evidence supported the controlled growth of pSty from the particle surface. TEM images of pSty nanoparticle ultrathin films revealed the presence of hexagonal packing of colloids in a polymer matrix (Figure 7). The relative uniformity of particle sizes, as well as the regularity in the interparticle spacing, also pointed to the successful synthesis of both well-defined colloids and tethered polymers.

The compositions of the colloidal initiators were also modified to encapsulate cadmium sulfide particles in a shell of silica.[60] ATRP initiating groups were introduced to the silica surface by the condensation of functional monoalkoxysilanes containing 2-bromopropionate groups. The ATRP of Sty from these core−shell colloidal initiators yielded an array of luminescent particles in a matrix of tethered pSty.

5.2. Block Copolymer Hybrid Nanoparticles from Polysilsesquioxane Nanoparticles. The synthesis of polysilsesquioxane colloidal initiators for ATRP was conducted by the microemulsion polymerization of trialkoxysilanes.[56] The resulting spherical networks were not silica (SiO_2) but were polysilsesquioxane ($SiO_{1.5}$). Surface treatment of silanol groups with functional chlorosilanes possessing 2-bromoisobutyrate groups, in addition to other silylating agents, yielded discrete colloids with ATRP initiating moieties. DLS and atomic force microscopy (AFM) both revealed that relatively uniform particles were synthesized ($D_{eff,DLS} = 27$ nm and $D_{eff,AFM} = 19$ nm). The ATRP of Sty and benzyl acrylate (BzA) was then conducted to prepare hybrid nanoparticles with tethered block copolymers. SEC of the cleaved pSty ($M_n = 5250$; $M_w/M_n = 1.22$) and p(Sty-*b*-BzA) ($M_n = 27\,280$; $M_w/M_n = 1.48$) confirmed that the successive ATRP of Sty and BzA from particles was successful. The resulting hybrid nanoparticles from polysilsesquioxane colloids possessed volume/weight fractions of tethered polymer exceeding that of the inorganic core. AFM tapping mode observations of the
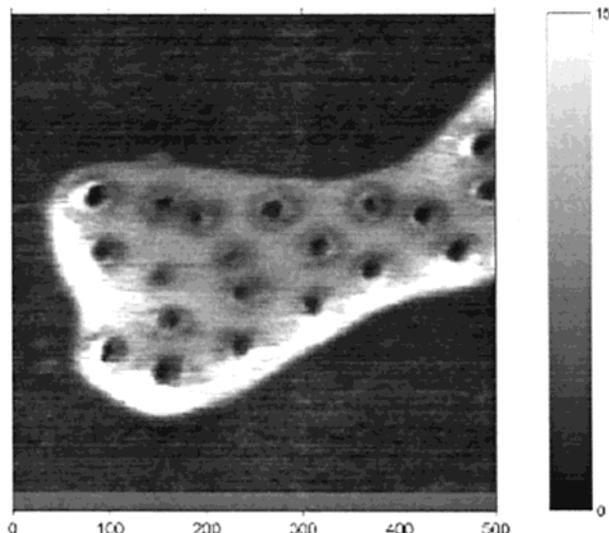
Figure 8. AFM phase image of a p(Sty-*b*-BzA) hybrid nanoparticle (sub)monolayer on mica. Assignment of domains is as follows: dark spots (polysilsesquioxane particles); dark corona around particles (tethered pSty; $M_n = 5250$; $M_w/M_n = 1.22$); light continuous matrix [tethered p(Sty-*b*-BzA); $M_n = 27,280$; $M_w/M_n = 1.48$].[56]

(sub)monolayers of the p(Sty-*b*-BzA) hybrid nanoparticles revealed the direct result of tethered copolymer composition on the morphology of the material on mica. In particular, AFM phase-contrast images showed that each component of the hybrid nanoparticle was discernible in ultrathin films cast onto mica (Figure 8). These images implied that hard cores (colloidal initiators) were surrounded by a hard corona (tethered pSty segment) and dispersed within a soft continuous matrix (tethered pBzA segment).

5.3. Organic/Inorganic Materials from Micron-Sized Inorganic Particles. The attachment of well-defined polymers to large particles ($D_{eff} > 1 \mu$m) has been conducted using CRP. Previously, surface-initiated polymerizations from micron-sized particles had been conducted using conventional radical polymerization.[61–64] However, by the use of CRP from particles, polymer coatings of controlled thickness and functionality were prepared. In particular, hybrids from larger particles were synthesized as potential chromatographic stationary phases[65–68] and templated supports.[69] In the preparation of stationary phases for liquid chromatography, thin films (~100 Å) of poly(acrylamide) were grown from benzyl chloride functional porous silica particles ($D_{eff} = 5 \mu$m and pore size$_{ave} = 860$ Å) using ATRP. The successful separation of various proteins using these poly(acrylamide) particles pointed to the successful grafting of polymers, without significant clogging of particle pores.[65] Similarly, poly(methacrylates) possessing nucleotide side-chain groups were grown from porous silica particles using ATRP. The immobilization of oligonucleotides has been demonstrated as an attractive approach for the templated synthesis of nucleic acids, with the primary goal being control of both the degree of polymerization and sequence distribution in the final product. Toward this endeavor, methacrylate derivatives of uridine and adenosine were synthesized and polymerized using a 2-bromoisobutyrate functional silica particle.[69] In a different templated system, poly-(benzyl methacrylate) was grafted to a silica surface

using ATRP and treated with hydrofluoric acid to prepare hollow polymeric colloids.[70] Hybrid particles with tethered pSty were also prepared using ATRP from 2-chloro-2-phenylacetate functional silica particles.[71]

6. Dispersed Silicate Nanocomposites

The synthesis of dispersed silicate nanocomposites was conducted by the CRP of Sty within layers of alkoxyamine-loaded montmorillonite (Scheme 12).[72] Organic/inorganic nanocomposites of intercalated and delaminated silicates containing polymers is an area of continued interest owing to the enhanced thermal and dimensional stability these materials possess. While a variety of techniques have been developed for the synthesis of polymer layered silicate nanocomposites, the preparation of dispersed silicate nanocomposites was not as extensively developed.[73] However, by the use of controlled radical polymerization, dispersions of clay particles within a matrix of well-defined pSty were formed. By the synthesis of an alkoxyamine with a pendant quaternary ammonium group, sodium cations were exchanged from the pristine clay, allowing for loading of SFRP initiators between the silicate layers. X-ray diffraction (XRD) patterns provided evidence for the loading and intercalation of alkoxyamines between silicate layers by the increase in the interlayer distance from $d = 1.26$ nm (Na$^+$ spacing) to $d = 2.35$ nm (alkoxyamine spacing; Figure 9a,b). Subsequent addition and polymerization of Sty at 125 °C in the presence of the functional montmorillonite resulted in complete delamination of the silicate layers. XRD provided further evidence for the delamination and dispersal of silicates by the disappearance of the diffraction pattern after the SFRP of Sty (Figure 9c). Ion exchange and extraction of p(Sty) ($M_n = 21\,500$; $M_w/M_n = 1.3$) from the dispersed nanocomposite revealed that well-defined polymers were made, with M_n values in close agreement with theoretical predictions.

7. Polymer Brushes and Modified Flat Surfaces

The use of CRP techniques to prepare well-defined tethered (co)polymers has been demonstrated to be an effective approach toward modifying surfaces with potential applications in microelectronics and nanoscale patterning.[74,75] While other polymerization methods have been utilized to prepare these polymer brushes,[76,77] CRP methods allow the introduction of a broader range of functionality (e.g., acid, perfluorinated) to modify surfaces in a more versatile fashion using less stringent reaction conditions. A number of CRP techniques have

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Figure 9. XRD pattern of (a) untreated montmorillonate, interlayer spacing = 1.26 nm, (b) alkoxyamine-loaded silicate, interlayer spacing = 2.35 nm, and (c) PSty-silicate-dispersed nanocomposite ($M_{n,pSty}$ = 21 500; M_w/M_n = 1.3).[72]

Scheme 13. Synthesis of Polymer Brushes from Si and Au Surfaces Using CRP

Figure 10. Linear dependence of a polymer brush with a tethered pSty brush thickness with a molar mass of untethered pSty.[78]

general approaches have been reported to prepare well-defined polymer brushes and are discussed in the following sections.

7.1.1. Addition of "Sacrificial Initiator". In this system, untethered initiator was added to a CRP reaction from a surface. The SFRP of Sty from a Si surface (Scheme 13) has been extensively investigated to demonstrate this concept.[78] The addition of untethered initiator [free alkoxyamine and 1-phenyl-1-(2′2′,6′6′-tetramethyl-1′-piperidinyloxyethane)] performed the dual purpose of increasing the rate of the polymerization, while allowing for controlled growth of tethered pSty. The external addition of untethered initiator served to generate a sufficient concentration of persistent radical (TEMPO) to establish the CRP equilibrium. Thus, by the termination of untethered radicals in solution, a higher concentration of persistent radical (TEMPO) in the system was formed, shifting the equilibrium to the dormant species. Consequently, the thickness of the tethered polymer films increased linearly with the molar mass (M_n) of the untethered polymer, indicating that controlled polymerization from the surface was successful (Figure 10). Because the polymer brush height was less than the fully extended contour length of the unbound pSty, it can be inferred that some collapse of the tethered polymer chains occurred on the surface.

7.1.2. External Addition of Persistent Radical/Deactivator. An alternative approach to controlling radical polymerizations from surfaces was the addition of persistent radical (deactivator) at the beginning of a CRP reaction. In CRP systems conforming to the PRE model, the generation of persistent radical (deactivator) is generated in situ after a sufficient buildup of terminated products.[8] However, by the external addition of persistent radical at the initial stages of the polymerization, radicals from the surface were deactivated, enabling continued exchange reactions and controlled growth of tethered polymers. External addition of deactivator was illustrated in the ATRP of styrene and acrylates from Si wafers, by the use of Cu(II) deactivating complexes at the beginning of the reaction.[82] In ATRP reactions of Sty without addition of Cu(II) at the beginning, uncontrolled growth of tethered pSty occurred with a film thickness of 106 ± 5 nm. However, by adding Cu(II), a controlled polymerization occurred, as evidenced by a linear relationship of pSty polymer

been used successfully to make polymer brushes from silicon and gold substrates, namely, SFRP,[78-80] ATRP,[78,81-93] and RAFT.[94]

The general procedure to prepare polymer brushes requires the attachment of an initiator molecule to the flat substrate followed by CRP of a vinyl monomer from the surface (Scheme 13). To functionalize Si wafers, chlorosilanes bearing alkoxyamines, α-haloesters, dithiocarbamates, or azo compounds were used to covalently bind to silanol groups arising from the thin oxidized layer of SiO_2 on the wafer. Synthesis of initiator-functionalized Au surfaces for ATRP was conducted by the self-assembly of a 11-mercaptoundecanol followed by esterification of the alcohol with an acid bromide containing an initating moiety.

7.1. Methods for Controlled Growth of Tethered Polymers from Surfaces Using CRP. CRP reactions from surfaces as depicted in Scheme 13 are complicated by the extremely low concentration of initiating sites on the surface. This problem is also compounded by the very small concentration of persistent radical (deactivator) that is generated upon activation of the initiator. Thus, rapid initiation and propagation of the growing tethered chain may occur via a redox process, resulting in an uncontrolled polymerization. The key to overcoming this problem is the generation or addition of a sufficient amount of persistent radical (deactivator) in the early stages of the polymerization to ensure controlled growth of polymers from flat substrates. Two

Figure 11. AFM image of p(Sty-*b*-MMA) polymer brushes with pSty thickness = 23 nm and pMMA thickness = 14 nm: (a) after immersion in CH$_2$Cl$_2$ for 30 min and drying under a stream of air; (b) after immersion in CH$_2$Cl$_2$ and CH$_2$Cl$_2$/cyclohexane solutions and drying under a stream of air.[86]
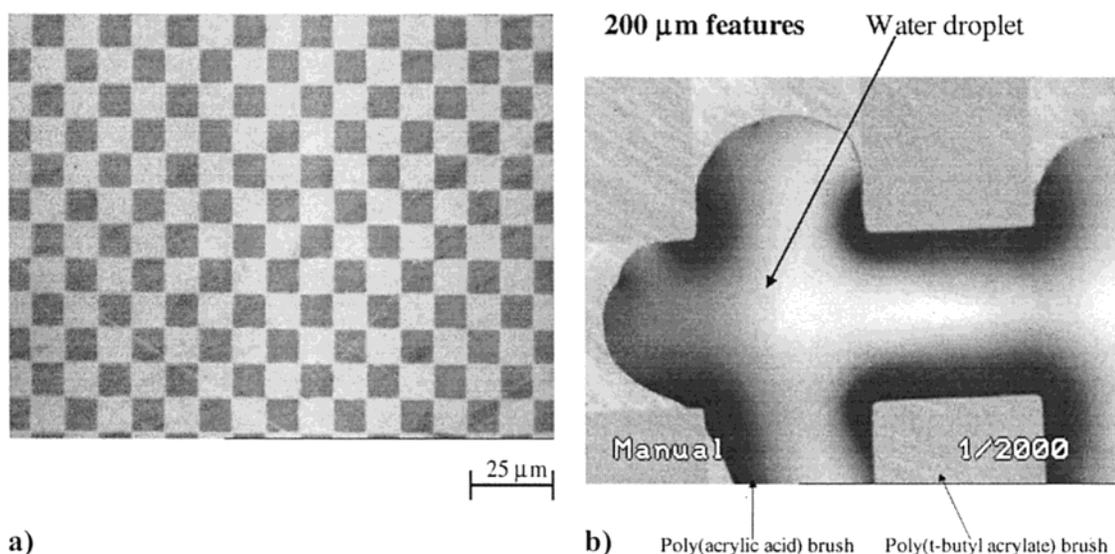
Figure 12. (a) Optical micrograph of a 10 μm patterned polymer brush with regions of poly(*t*BA) (dark) and poly(AA) (light). (b) Optical micrograph of a 200 μm pattern polymer brush with water droplet wetting poly(AA) domains.[80]

brush thickness with predicted molar mass (M_n) of tethered pSty.

7.2. Control of Surface Properties and Patterning on CRP-Prepared Polymer Brushes. Modification of tethered polymer composition has been demonstrated to effect both surface properties and wettability of various substrates. Polymer brushes with tethered random copolymers of p(Sty-*r*-MMA) and p[Sty-*r*-(hydroxyethyl methacrylate) (HEMA)] have been prepared from both "grafting to"[74] and "grafting from"[78] approaches using SFRP. In both systems, the incorporation of well-defined random copolymers had a profound effect on the wetting behavior of the polymer brushes. The surface properties of Si wafers have also been modified by the incorporation of well-defined hydrophobic and hydrophilic polymer segments using ATRP. By the homopolymerization of a perfluorinated monomer (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl acrylate), a polymer brush with a hydrophobic surface was prepared, as evidenced by water contact angle measurements (119 $\pm$ 2°). Hydrophilic Si surfaces were made by the controlled growth of a poly[styrene-

b-(*tert*-butyl acrylate)] [p(Sty-*b*-*t*BA)] followed by hydrolysis to yield the corresponding poly(styrene-*b*-acrylic acid) [p(Sty-*b*-AA)] polymer brush. Contact angle measurements from water droplets indicated a decrease in the contact angle going from p(Sty-*b*-*t*BA) (86 $\pm$ 4°) to p(Sty-*b*-AA) (18 $\pm$ 2°) surfaces.

Control of nanoscale morphology of p(Sty-*b*-MMA) polymer brushes has been demonstrated by treatment of surfaces with selective organic solvents.[86] Polymer brushes of p(Sty-*b*-MMA) were synthesized by a combination of cationic polymerizations of Sty, followed by the ATRP of MMA.[83] Immersion of the p(Sty-*b*-MMA) modified wafer in CH$_2$Cl$_2$ and drying under a stream of air yielded polymer brushes with smeared features and relatively smooth surfaces. This morphology is presumed to arise from a more extended conformation of the tethered copolymer, because CH$_2$Cl$_2$ is a good solvent for both segments (Figure 11a). Treatment of this polymer brush in cyclohexane resulted in an irregular wormlike morphology due to preferential swelling of the pSty segment. Finally, immersion of the brush with CH$_2$Cl$_2$ and mixed solvent solutions of CH$_2$Cl$_2$/

cyclohexane yielded an ellipsoidal array of tethered copolymers (Figure 11b), presumably from the collapse and encapsulation of pMMA within the tethered pSty segment.

Patterning of polymer brushes on a micron scale was achieved through the use of an acid-generating photoresist.[80] In this system, tethered polymers of p(*t*-BA) were prepared by SFRP using α-hydrogen-containing nitroxides[12] and the complementary tethered alkoxyamines. Spin coating of the photoresist mixture on the polymer brush, followed by radiation through a mask, yielded ordered patterns with 10 μm^2 domains of pSty and pAA (Figure 12a). As expected, the presence of these discrete domains had a tremendous effect on the wetting behavior of the surface. Optical micrographs of a water droplet on a 200 μm patterned surface revealed the selective wetting of the pAA regions as defined by the size of the pattern (Figure 12b).

8. Nanoporous Inorganic Networks Templated from (Co)polymers Prepared from CRP

Polymeric shape templates made from CRP were used in the preparation of nanoporous polysilsesquioxane networks. Nanoporous inorganic networks were targeted to obtain materials of lower dielectric constant relative to conventional silicate materials. Nanoporous polysilsesquioxanes were made by polymerization of methylsilsesquioxane resins in the presence of p(MMA-*r*-HEMA) star copolymers, followed by thermal degradation of the polymeric template.[95] Star copolymers of MMA and HEMA were made using ATRP from multiarmed dendritic initiators. It was found that star copolymers containing polar substituents were required to avoid macroscopic phase separation of the polymer and the inorganic network upon cure. In general, star copolymers of p(MMA-*r*-HEMA) were kept to low molar mass (M_n < 8000) and pHEMA compositions to around 20 mol %. By the use of a six-armed star of p(MMA−HEMA) (12-mol % pHEMA; $M_{n,SEC}$ = 5000; M_w/M_n = 1.27), nanoporous polysilsesquioxane networks (ϵ = 2.2) of lower dielectric constant relative to the densified network (ϵ = 2.8) were obtained.

9. Conclusion/Future Perspectives

The synthesis of hybrid organic/inorganic nanocomposites offers a route to new materials with predefined structure and performance. The use of CRP methodologies opens the door to a host of well-defined organic polymers which can be incorporated to many different inorganic substrates. The attachment of organic polymers to inorganic polymers, particles, surfaces, and networks has been conducted using CRP techniques and has demonstrated the versatility of this approach. While this seminal work has proven successful, variations and combinations of these methods will need to be explored to prepare truly advanced materials possessing a novel synergism of properties. Future developments in this field may include synthesis of novel hybrid nanocomposites, including interpenetrating polymer networks, nano-objects, and biomimetic materials. An obvious, but promising, direction in this field will also be to use CRP to prepare the polymeric components in organic/inorganic nanocomposites that previously required ionic polymerization processes.

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