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Inorganic Block Copolymers

Block Copolymers with Functional Inorganic Blocks: Living Addition Polymerization of Inorganic Monomers

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Block copolymers, macromolecules that contain two or more separate homopolymer segments that are joined together, are currently attracting intense attention. Interest in block copolymers is a consequence of the general immiscibility of the blocks, which leads to spontaneous self-assembly in thin films to yield phase-separated nanometer-size domains with a variety of morphologies such as spheres and cylinders as well as gyroid and lamellar phases. In addition, in selective solvents block copolymers afford micelles with core-shell structures.[1] Impressive fundamental advances in the organic block copolymer field have led to a wealth of promising applications, including their use as templates for nanopatterning surfaces (Figure 1), as templates for nanostructuring silicon gates in flash-memory devices, and as hollow vesicles with tunable permeation for drug delivery.[2,3]

To access well-defined block copolymers, polymerization protocols that allow exquisite control are necessary. These processes, termed living polymerizations, allow the creation of polymer chains by chain-growth methods without the loss of architectural control that takes place when there are significant irreversible chain-transfer or chain-termination reactions.[4] The lack of chain transfer and chain termination allows the sequential polymerization of monomers and, if the initiation steps are fast, well-defined block copolymers can be prepared with narrow molecular-weight distributions. Although the living polymerization concept was first realized for anionic polymerizations in the 1950s,[5] many key recent advances have been made in the organic polymer field, notably in the areas of radical polymerization of olefins, group-transfer polymerization of methacrylates and acrylates, ring-opening metathesis polymerization of cyclic olefins, and metal-catalyzed ring-opening polymerization of cyclic α-amino acid *N*-carboxyanhydrides to yield polypeptide block copolymers.[4] Living polymerizations are now widely used in organic polymer synthesis to access well-defined carbon-based macromolecular materials with controlled architectures such as end-functionalized polymers and block and star copolymers.

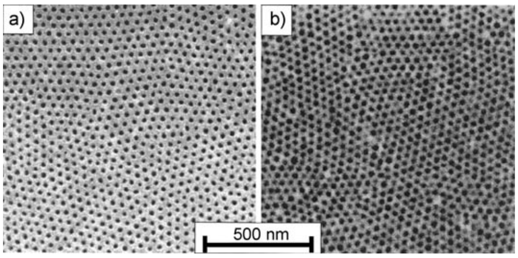

Figure 1. Nanopatterning using block copolymer templates. Scanning electron micrographs (SEMs) derived from a self-assembled thin film of a polystyrene-*b*-polyisoprene (PS-*b*-PI) block copolymer which forms spheres of PI in a matrix of PS. a) SEM of a monolayer film after etching of the PI spheres with ozone: the empty PI domains are exposed as holes and appear darker in the micrograph. b) SEM showing hexagonally ordered arrays of holes in silicon nitride on a thick silicon wafer. This pattern was transferred from a copolymer film such as that in (a) by reactive-ion etching. The darker regions are approximately 20-nm-deep holes in silicon nitride, which have been etched out through the holes in the film in (b). Similar approaches can be used to nanopattern magnetic materials for high-density data storage and other applications. Reproduced from reference [3b] with permission.

In contrast to the advances in the living polymerization of organic monomers, until recently such processes were virtually unknown for inorganic species. The introduction of inorganic elements is of broad current interest as a means to impart additional functionalities which can complement those available with organic blocks.[6] This field has developed slowly because of the synthetic challenge of preparing inorganic macromolecules. Despite many recent advances, the presently available methods for the preparation of inorganic polymers generally do not usually allow molecular-weight control and yield materials with broad molecular-weight distributions; living polymerization methods, which allow access to precisely designed structures such as block copolymers are, unfortunately, still very rare.

The first examples of successful living polymerizations of inorganic monomers were provided by polysiloxanes by using anionic ring-opening polymerization (ROP) methods, which have provided routes to diblock copolymers such as the polystyrene-*b*-polydimethylsiloxane (PS-*b*-PDMS) described by

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Saam in 1970 (Figure 2).[7] Recently devised routes to polysilane and polyphosphazene block copolymers (for example, polysilane-*b*-poly(methacrylic acid) (PSi-*b*-PMAA) and poly(ethylene oxide)-*b*-polyphosphazene (PEO-*b*-PP)) have further expanded the range of functional inorganic blocks.[8,9] Block copolymers with polyferrocenylsilane (PFS) and polyferrocenylphosphine (PFP) blocks such as PS-*b*-PFS and PFP-*b*-PDMS, respectively, have also been prepared by living anionic ROP methods.[10,11]

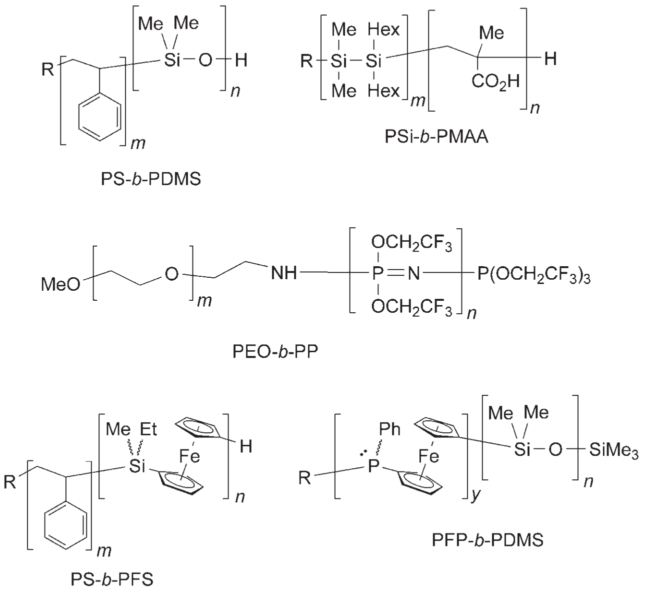


Figure 2. Block copolymers with main-chain inorganic blocks.

Block copolymers with labile metallosupramolecular linkers at the block junction (for example, **1**) or at the core of star structures (for example, **2**) have also been recently accessed through creative living polymerization techniques by the groups of Schubert and Fraser (Figure 3).[12,13]

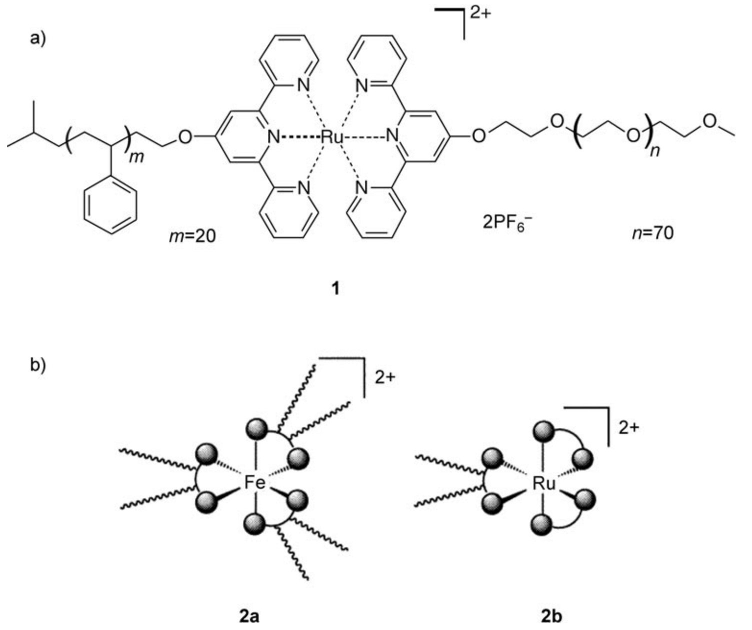
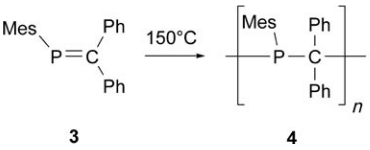


Figure 3. Block and star copolymers with transition metals at the a) block junction (in **1**) or b) in the core (**2a** and **2b**, which contain bipyridine-based ligands with or without polyoxaline chains).

Living polymerizations which lead to block polymers with inorganic elements in the side-group structure have also been subject to major advances. For example, the groups of Schrock, Weck, Chan, Sleiman, and Grubbs have created block copolymers containing side-chain coordination complexes,[14–18] and Jaekle has developed structures with Lewis acidic borane blocks.[19] In all of these cases, the key motivation is the generation of additional functionality by the presence of inorganic blocks or main-chain junction or pendent main-group or transition elements (Table 1).

Despite the recent progress, the most versatile and important method for making organic polymers, addition polymerization of olefins, was until recently unknown as a productive route for species with inorganic multiple bonds. The first well-characterized example of such a process was reported by the group of Gates at the University of British Columbia, Canada in 2003 [Eq. (1)].[20] The phosphaalkene **3** was shown to slowly thermally polymerize at 150 °C over 24 hours to yield poly(methylenephosphine) materials **4** with molecular weights in the 30000 range with broad molecular-weight distributions.



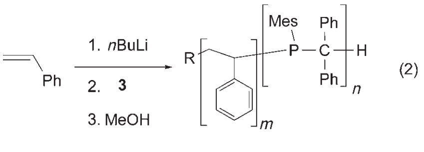
(1)

In a recent key breakthrough, Noonan and Gates have demonstrated that phosphaalkenes successfully undergo living anionic polymerization at ambient temperature in the presence of organolithium initiators in a reaction reminiscent of that for olefins such as styrene.[21] This allowed access to poly(methylenephosphine) materials with controlled molecular weights (based on the chosen monomer/initiator ratio) and narrow molecular-weight distributions. Moreover, use of living polystyrene anions as initiators led to poly(methylenephosphine) block copolymers **5** for the first time [Eq. (2)].

Table 1: Functionality imparted to self-assembled block copolymers by the presence of inorganic elements.

Inorganic component	Functionality introduced	Ref.
Main-chain inorganic block		
polysiloxane $(SiR_2O)_n$	low T_g,[a] thermooxidative and UV stability, hydrophobicity, resistance to radiation and plasmas	[6, 7]
polyphosphazene $(PR_2{=}N)_n$	low or high T_g, structure tunability (hydrophilic or hydrophobic), flame retardant, controllable stability toward hydrolytic degradation, ionic conductor	[6, 8]
polysilane $(SiR_2)_n$	conductivity due to delocalized σ electrons, photoconductor, photosensitive toward near-UV light for applications in nanopatterning, precursor to SiC ceramic nanodomains	[6, 9]
polyferrocenylsilane $[(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_4)SiR_2]_n$	redox-active, precursor to ceramic domains with Fe nanoparticles, etch-resistant for plasmas and electron beams for surface nanopatterning, semiconductor due to hole hopping, high refractive index	[10]
polyferrocenylphosphine $[(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_4)PR]_n$	coordination of catalytically active transition-metal species, high refractive index	[11]
Inorganic elements at block junction or star polymer core		
-RuL$_x$- linker	redox-controlled block dissociation for nanopatterning applications	[12]
-FeL$_x$- or -EuL$_x$- core	Fe: facile degradation to form magnetic Fe nanoparticles; Eu: photoluminescent	[13]
Inorganic elements in the side chain of a block		
-ZnX$_2$ or -PdL$_x$	precursor to quantum dots (for example, ZnS) and Pd nanoparticles	[14]
-PdL$_y$	site for noncovalent crosslinking	[15]
-ReL$_x$	photoluminescent material	[16]
-RuL$_x$	photoluminescent material	[17]
-Co$_2$(CO)$_x$	precursor to Co nanoparticles	[18]
-BR$_2$	potential luminescent sensor for Lewis bases (R = dithiophenyl), electroluminescent for light-emissive devices (R = quinolate)	[19]

[a] T_g = glass transition temperature.



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There are a number of noteworthy features of the living polymerization of phosphalkene **3**. Firstly, the polymerization is successful despite the presence of bulky Mes and Ph substituents (Mes = 2,4,6-$Me_3C_6H_2$) as a result of the presence of the second-row element phosphorus in the main chain, which has a substantially (ca. 40%) larger covalent radius than carbon. The larger size of phosphorus helps to relieve steric interactions which would otherwise disfavor polymerization. As an example for comparision, even diphenylethylene, $CH_2{=}CPh_2$, an analogue which lacks a very bulky Mes substituent, does not homopolymerize because of an unfavorable chain-propagation step. The presence of bulky substituents in **3** does however lead to extremely slow chain propagation with a rate constant approximately 10^6–10^7 slower than that for styrene. As a second feature, the route provides access to methylenephosphine segments, which represent a new type of unit in block copolymers. Dialkylarylphosphine sites are of interest owing to easy functionalization and also their intrinsic ability to strongly bind transition metals. Already, applications of poly(methylenephosphine) random copolymers have been demonstrated in Suzuki coupling chemistry where the polymer functions as a support and allows facile product–catalyst separation.[22] The possibility for creating self-assembled structures such as catalytically active micelles is certainly highly attractive. As a final point, the demonstration of the controlled polymerization of inorganic monomers by living anionic polymerization should help stimulate interest in the successful polymerization of other monomers that contain multiple bonds involving inorganic elements. The field of inorganic multiple bonds is now extensive and well-established with examples now known for most elements in the p and d blocks.[23] The generalization of addition polymerization protocols for such species will require the selection of side groups which allow sufficient kinetic monomer stability for ready isolation and purification but also for thermodynamically favorable polymerization.

This is an exciting future challenge at the interface of inorganic chemistry and macromolecular science.

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