Synthesis and Characterization of Well-Defined Star Polymers via a Controlled Sol-Gel Process

Introduction. Living anionic polymerizations are especially suited for the preparation of oligomers and macromolecules with well-defined end-group functionality, predictable molecular weight, and narrow molecular weight distribution. Due to the living nature of the propagating chain end, an appropriate reactant can be added to the stable polymeric carbanion in order to place a specific functionality at the chain end. Reagents such as carbon dioxide,[1] chlorosilanes,[2] alkylene oxides,[3] and benzyl chlorides[4] have been added to living carbanions to generate a terminal functional group. For example, the addition of CO_2 to polystyryllithium leads to a lithium carboxylate anion and upon acidification generates a terminal carboxylic acid. Morton has recently assembled a review of suitable additives and the corresponding functionalities formed.[5]

Most efforts in end-group functionalization have been directed toward the preparation of difunctional oligomers for subsequent cocondensation to form a high molecular weight linear polymer or cross-linking with a multifunctional cross-linking agent to form an insoluble network.[6,7] However, monofunctional living chain ends have also served as key intermediates for radial star copolymer syntheses.[8,9] In addition, macromonomers are prepared by adding a molecule that contains both a site for the attack of a monofunctional polymeric carbanion and a site for subsequent free-radical copolymerization. Many novel graft copolymers have been prepared by utilizing the macromonomer technique.[10-12] Consequently, the ability to control the functionality ($f = 1$ or 2) allows for the preparation of a wide variety of well-defined macromolecular architectures.

This work uses the direct reaction of living polymeric carbanions to form well-defined phenyltrialkoxysilyl functional organic polymers. The macromonomers ($f = 1$) were subsequently hydrolyzed and condensed to yield narrow molecular weight distribution star polymers. Although telechelic ($f = 2$) phenyltrialkoxysilyl functional oligomers have also been prepared and studied in detail, the product after hydrolysis and condensation is an insoluble network not a soluble, star polymer. These cross-linked condensation products are not amenable to structural characterization in solution and will be described in a future report.

Experimental Section. Materials. Styrene (Aldrich) was stirred over finely ground calcium hydride for 1–2 days and vacuum distilled. Distilled monomer was stored at −25 °C under nitrogen in a brown bottle until further use. Immediately prior to polymerization, the monomer was vacuum distilled from dibutylmagnesium (DBM). DBM (Lithco) was obtained as a 25% solution in heptane and was transferred by using syring techniques. This reagent has been shown[13] to efficiently remove air and water from various hydrocarbon monomers. DBM was added dropwise to the monomer at room temperature until a stable, pale, yellow color persisted.

sec-Butyllithium (sBLi) was obtained from the Lithco Division of FMC as a 1.3 M solution in cyclohexane. The initiator was used as received and was stored at −25 °C for several months without significant degradation.

Tetrahydrofuran (Baker, HPLC grade), the polymerization solvent, was distilled from a purple sodium benzophenone ketyl under argon immediately prior to polymerization. [*p*-(Chloromethyl)phenyl]trimethoxysilane (CMPTMS) (Petrarch) was vacuum distilled immediately prior to use.

Polymerization and Functionalization. All glassware was rigorously cleaned and dried in an oven at 120 °C for 24 h. For small-scale polymerizations, the reactor consisted of a 250-mL, one-neck, round-bottomed flask equipped with a magnetic stirrer and rubber septum. The septum was secured in place with copper wire to maintain a positive pressure of ultrapure nitrogen. The reactor was assembled while hot and subsequently flamed under a nitrogen purge. After the flask had cooled, the polymerization solvent (THF) was added to the reactor via a double-ended needle (cannula). The reactor was submerged into a −78 °C bath and allowed to reach thermal equilibrium. Purified styrene monomer was charged into the reactor with a syringe. The calculated amount of initiator was quickly syringed into the reactor, and immediately the formation of orange polystyryllithium anion was observed. Polymerization was allowed to proceed for 20 min to ensure complete conversion.

Upon completion of polymerization, end-capping reagent (50% molar excess compared to lithium) was added quickly via a syringe. Complete disappearance of the orange color was indicative of total deactivation of the polymeric carbanion.

Hydrolysis and Condensation. Polymers were dissolved in tetrahydrofuran (15–18% solids), and excess water compared to silicon (4:1 water–silicon based on polymer repeat unit molecular weight) was added as a 0.15 N solution of HCl. The solutions were allowed to evaporate slowly at room temperature for 4 days. Resulting films were dried in vacuo at various conditions.

Size-Exclusion Chromatography. The functionalized oligomers and corresponding hydrolyzed/condensed products were analyzed by using differential viscosity (DV), low-angle laser light scattering (LALLS), and differential refractive index (DRI) detectors. This system has been described in detail elsewhere.[14] The LALLS and DV detectors were connected in parallel after three 5-μm PL gel mixed-bed columns (Polymer Laboratories, Amherst, MA). The DRI was connected in series after the LALLS detector. Samples were injected at a concentration of 1.5 mg/mL or less in a volume of 100 μL. The nominal flow rate was 1.00 mL/min.

Results and Discussion. Two criteria must be met for the selection of a suitable functionalization reagent. First, an electrophilic site for direct deactivation of the polymeric carbanion must be present in the molecule. The extent of the functionalization reaction must be characterizable by a variety of complimentary techniques, e.g., spectroscopic and chemical. This is not a trivial task since the concentration of the end group is generally quite low. Second, if the molecule contains the ultimate end-group functionality, then this group must be inert to a polymeric carbanion at appropriate conditions for attack at the electrophilic site. CMPTMS met both structural prerequisites and was commercially available.

The end-capping of living polystyryllithium with CMPTMS is depicted in Scheme I. The orange color that is associated with the polystyryllithium carbanion disappears immediately upon addition of end-capping reagent. ^1H NMR analysis indicates the presence of the phenyltrimethoxysilyl group (3.6 ppm). Presence of the initiator fragment residing at the other end of the polymer chain is verified by resonances between 0.6 and 1.2 ppm. Either the initiator fragment or the trialkoxysilyl group integration was compared to the repeat unit methylene and methine integration to determine functional molec-

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Scheme I
Synthesis of Phenyltrimethoxysilyl-Terminated Polystyrene via Living Anionic Polymerization in Tetrahydrofuran at −78 °C with *sec*-Butyllithium (1.3 M in Cyclohexane) as Initiator

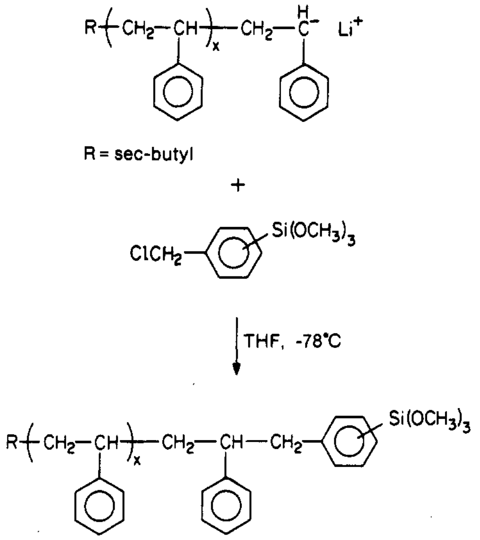


Table I
Molecular Weight Determinations for *p*-(Chloromethylphenyl)trimethoxysilane-Terminated Polystyrene Oligomers[a]

M_n(GPC)[b]	M_n(NMR)[c]	M_n(NMR)[d]	M_w/M_n
3900	3000	3100	1.19
3100	2700	2700	1.13
3900	3500	3500	1.22

[a] Polymerization conditions: THF, −78 °C, *sec*-butyllithium. [b] Polystyrene standards, THF, 25 °C, DRI detector. [c] Ratio repeat unit resonance to initiator fragment (*sec*-butyl). [d] Ratio repeat unit resonance to $Si(OR)_3$.

ular weights. Table I shows functional molecular weights for various end-capped polystyrene samples. Excellent agreement exists between functional molecular weights based on the initiator fragment and functional molecular weights based on the trialkoxysilyl end group. In addition, functional molecular weights compare favorably with number-average molecular weights determined by size-exclusion chromatography (SEC). These observations support an efficient and quantitative end-capping reaction. Molecular weight distributions are also narrow (1.10–1.20), which indicates a well-defined polymerization and efficient functionalization reaction. The preparation of low molecular weight oligomers with a narrow molecular weight distribution (~1.05) is difficult in polar solvents due to rapid rates of initiation and propagation.

Neutron activation analysis (NAA) also was used to verify the presence of both silicon and oxygen in the polymer and to calculate functional molecular weights. Functional molecular weights were obtained by comparing the percent silicon or oxygen to the percent carbon. These values agree within 5% of the M_f values determined by ^{1}H NMR spectroscopy.

^{29}Si NMR is the most discriminatory technique for characterization of these end-capped oligomers. A typical spectrum for a 3100 g/mol functionalized polystyrene oligomer is shown in Figure 1. In most cases, only a resonance that is associated with a phenyltrimethoxysilyl group is observed at approximately −54 ppm. However, often hydrolysis and condensation of the end groups during either precipitation or exposure to air leads to a small amount (2–10%) of dimer formation. The dimer SiOSi resonance appears at approximately −60 ppm. ^{29}Si NMR also confirms that the displacement of the methoxy group with a second living carbanion during functionalization does not occur. A side reaction of this nature would lead to formation of a $CSi(OR)_2C$ resonance with a substantially different chemical shift. It should be noted that the splitting (8–10 Hz separation) in the trialkoxysilyl resonance is reproducible and is currently being investigated. Preliminary explanations attribute this observation to polymer tacticity at the functionalized chain end.

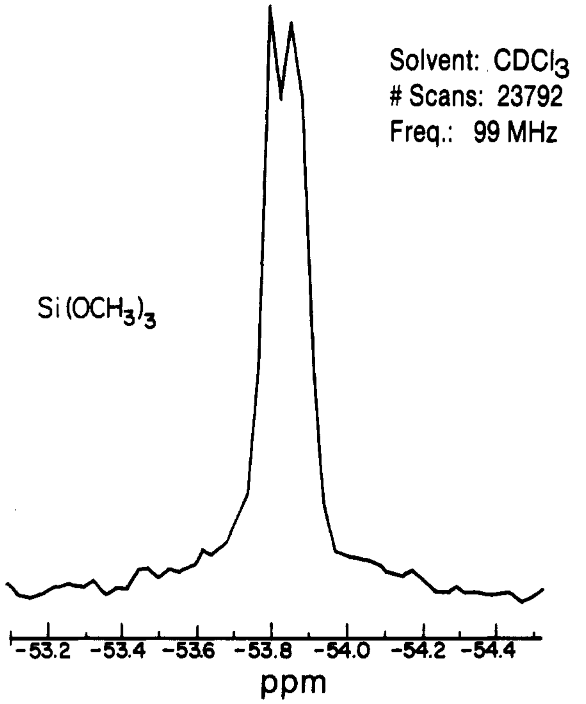


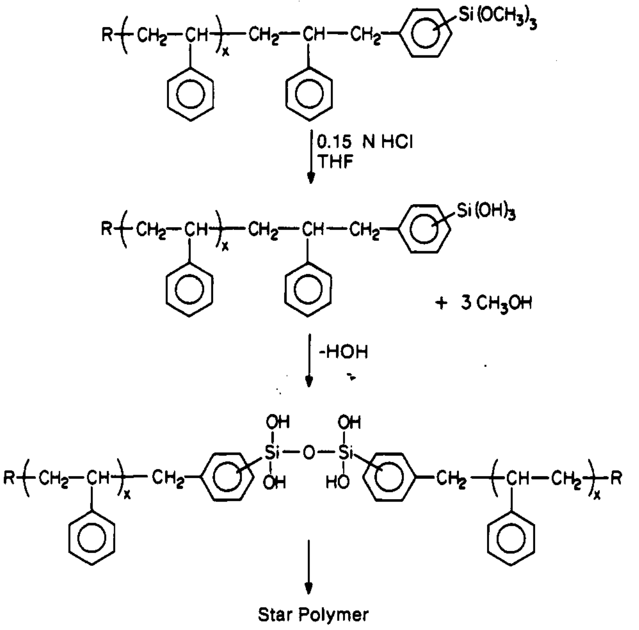
Figure 1. ^{29}Si NMR spectrum (99 MHz, TMS = 0.0 ppm, 0.15 M $Cr(AcAc)_3$, $CDCl_3$) of phenyltrimethoxysilyl-terminated polystyrene, M_n = 3100 g/mol.

Thin-layer chromatography (TLC) is a useful technique for the qualitative characterization of functional oligomers. Polymers ascend conventional TLC plates in a fashion similar to low molecular weight, organic compounds. The nature of the end group alters the interaction characteristics of the macromolecule with the silica gel plate. TLC demonstrates the absence of homopolystyrene in the functionalized oligomers. Quirk has shown[15] that this technique is capable of detecting 1% unfunctionalized oligomer. In fact, unfunctionalized oligomer was added to the functionalized oligomer in order to demonstrate the effectiveness of this technique.

Hydrolysis and Condensation. The functionalized polymers were readily soluble in tetrahydrofuran with an excess of water (compared to silicon) added. Hydrolysis and condensation were catalyzed by addition of 0.15 N HCl. After allowing the solutions to dry to a film in air, the samples were heated in vacuo at various conditions. Scheme II depicts the hydrolysis and condensation to form dimer for a trialkoxysilyl-functionalized polystyrene macromonomer. Variables such as trialkoxysilyl group, molecular weight, functionality, and subsequent heat treatment have been addressed.

The solubility characteristics of hydrolyzed/condensed phenyltrimethoxysilyl-terminated polystyrene oligomers were particularly interesting. After hydrolysis and condensation of the monofunctionally terminated oligomers, their films remained soluble in tetrahydrofuran. This

Scheme II
Acid-Catalyzed (0.15 N HCl) Hydrolysis and Condensation in THF (15 wt %) of Phenyltrimethoxysilyl-Terminated Polystyrene



characteristic facilitates the characterization of the reaction product by spectroscopic and gel permeation chromatographic techniques. Difunctional oligomers were rendered insoluble after hydrolysis and condensation and their films would only swell in tetrahydrofuran. Consequently, characterization of difunctional condensates was more difficult.

Solubility of the monofunctional condensates permits the facile characterization of hydrolysis and condensation reactions. A size-exclusion chromatograph equipped with viscometric and light scattering detectors was used to determine absolute molecular weight changes after hydrolysis and condensation. Figure 2 depicts the chromatograms of unreacted, phenyltrimethoxysilyl-terminated precursor (solid line) and the hydrolysis/condensation product after heating at 70 °C for 3 h (dashed line). The most striking feature is the narrow molecular weight distribution of the condensate. The weight-average molecular weight of the condensate is approximately 4 times the molecular weight of the precursor (M_w = 5000 g/mol). This implies a macromolecule with four branches was formed under these conditions; however, processing conditions and precursor molecular weight define the size of the condensate and will be discussed later.[16] Absence of appreciable uncondensed precursor in the chromatogram of the condensate implies that the end-capping reaction was quite efficient. SEC evidence for quantitative functionalization was reproducibly observed for various phenyltrimethoxysilyl-terminated precursors with different molecular weights. The small shoulder on the low molecular weight side of the distribution may imply either the presence of a minor amount of unfunctionalized oligomer or functionalized oligomer (T^0, uncondensed end groups) below the ^{29}Si NMR detection limit (<5 mol %).

Monofunctional condensates were analyzed by ^{29}Si NMR in solution. The spectrum in Figure 3 implies that at least two different types of silicon are present in the branched molecule (precursor M_w = 5000 g/mol, condensate M_w = 20 200 g/mol). The chemical shifts are consistent with 60% T^2 and 40% T^1. T^2 represents a silicon atom that has undergone two condensation reactions (i.e., SiO*Si*OSi), and T^1 has one such linkage. This interpretation is consistent with assignments previously published for other sol–gel systems.[17-19] In addition, we have recently disclosed preliminary ^{29}Si NMR assignments on a phenyltrimethoxysilane model system.[20]

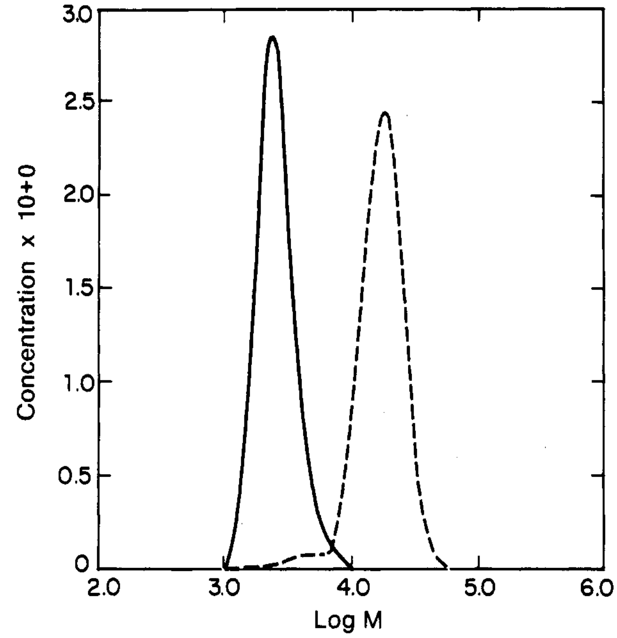


Figure 2. Absolute molecular weight distributions obtained by size-exclusion chromatography (SEC) of unreacted, phenyltrimethoxysilyl-terminated polystyrene precursor (solid line, M_w = 5000 g/mol) and the hydrolysis/condensation product after heating at 70 °C for 3 h.

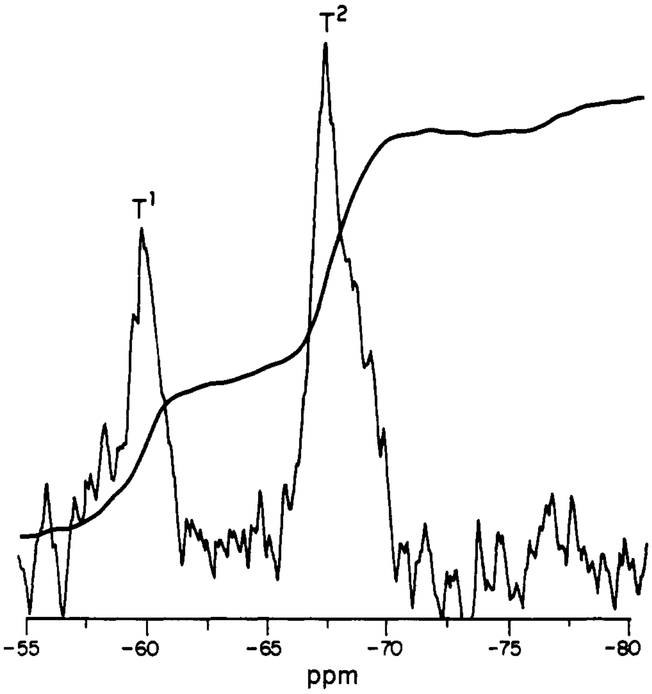


Figure 3. ^{29}Si NMR spectrum (99 MHz, TMS = 0.0 ppm, 0.15 M Cr(AcAc)$_3$, CDCl$_3$) of a polystyrene (precursor M_w = 5000 g/mol) hydrolysis/condensation product after heating at 70 °C for 3 h. T^1 represents one SiOSi linkage, and T^2 represents two SiOSi linkages.

The presence of T^1 and T^2 implies that the condensate is not a single cyclic species but may, for example, be a 20:80 mixture of cyclic–linear tetramers (cyclic T^2 and linear T^2 cannot be separated due to the broad T^2 resonance, approximately 5 ppm). Although the star molecule has a narrow molecular weight distribution, it is probable that the distribution consists of different size species (e.g., trimer or pentamer) with different core structures. The condensate may simply consist of a linear silicon–oxygen backbone with pendant polystyrene branches. In addition, since the core contains both T^1 and T^2 silicon atoms, the exclusive formation of a silica-like tetrahedral structure (only T^3) or a cyclic (only T^2) structure in the core is impossible. In fact, the formation of T^3 is relatively difficult and only forms at the expense of T^1 and T^2.

Conclusions. Phenyltrimethoxysilyl-terminated oligomers were successfully prepared by conventional anionic techniques. The oligomers possessed narrow molecular weight distributions, predictable molecular weights, and high functionality. Monofunctional oligomers remained soluble after condensation and were amenable to SEC and ^{29}Si NMR analysis. On the other hand, difunctional condensates were insoluble in common organic solvents. The monofunctionalized oligomers exhibited extraordinary condensation behavior. The narrow molecular weight distribution of the precursors was preserved after condensation. Thus, monofunctionalized oligomer serve as stable precursors for the preparation of soluble star-shaped polymers.

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