Macromolecules

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Phenylethynyl and Phenol End-Capping Studies of Polybiphenyloxydiphenylsilanes for Cross-Linking and Enhanced Thermal Stability

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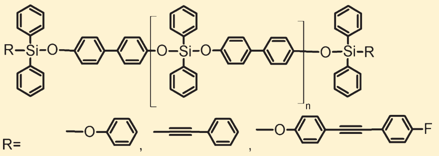
S *Supporting Information*



ABSTRACT: Polyaryloxydiphenylsilanes have been studied for decades and are known to be stable at high temperatures. Polybiphenyloxydiphenylsilane was synthesized to further study its high-temperature characteristics. However, condensation reactions between dichlorosilanes and biphenol produced polybiphenyloxydiphenylsilanes that underwent uncontrolled cross-linking through silanol end-groups, when heated to high temperatures (around 275 °C). End-capping the polymers with phenoxy groups (phenol as end-capping agent) to prevent cross-linking or with ethynyl containing end-groups to allow for controlled cross-linking resulted in improved thermal stability compared to the uncapped polymer, which was verified using rheology. Two synthetic routes were developed to end-cap the polymer with phenylethynyl containing substituents. Successful end-capping using lithiumphenylacetylide and 4[(4-fluorophenylethynyl)]phenol was verified chemically by ^{13}C NMR, FTIR, and Raman analysis. Capping was further confirmed by the cessation of growth in molecular weight after addition of the capping reagents as measured by GPC, which led to enhanced high-temperature melt stability relative to that of comparable molecular weight uncapped materials as measured by parallel plate rheometry. Exothermic peaks consistent with ethynyl curing reactions were observed by differential scanning calorimetry (DSC) analysis of ethynyl-capped polymers. This work demonstrates how end-capping can be used to control the reactivity and thermal behavior of a polymer that has high-temperature applications.

1. INTRODUCTION

Thermally stable polymers are critical for many applications. Numerous industries are pushing the limits of current organic backbone polymers.[1−3] One possible solution is to use hybrid materials, with organic−inorganic bonds in the polymer backbone, for enhanced thermal stability.[4−8] Siloxanes are one such family of materials; however, until now their ultimate thermal stabilities have been limited by degradative depolymerization which occurs at lower temperatures than anticipated based on Si−O bond strengths.[9]

Aromatically substituted polysiloxanes have been studied for decades.[10,11] The repeat unit of polydiphenylsiloxane, one of the major polymers in this category, is shown in Figure 1.

Polydiphenylsiloxane has very good short-term thermal stability. It is a polymer liquid crystal with a glass transition of 265 °C and a melting point of 540 °C. Thermogravimetric analysis (TGA) has shown a 10% weight loss temperature of 511 °C. However, processability, obtaining high molecular weights, and long-term thermal stability have been continuing issues with this material.[13]

Depolymerization via cyclization is a likely thermal degradation mechanism.[6,12] In order to inhibit this reaction, several research groups have looked at introducing aromatic spacers (biphenoxy units) into the backbone,[8,14] yielding polymers with the repeat structure shown in Figure 2.

Thermal stabilities of polyaryloxydiphenylsilanes are superior to those of polydiphenylsiloxane. TGA analysis showed a 10% weight loss of 565 °C[15] (see Supporting Information Figure S1). However, the polymer has a softening point of ∼150 °C,[11] which limits its ultimate utility as a high-temperature polymer.

Several reaction pathways are available for synthesis of this class of polymers.[16] Highest molecular weights are obtained via reaction of anilinosilanes with biphenols,[11] in which aniline is produced as a byproduct of the reaction. Attempts at cross-linking of this polymer via inclusion of vinyl moieties yielded materials of limited utility, which the authors attributed as likely due to residual aniline impurities from the synthesis (aniline is a possible free radical scavenger).[17]

In order to fully exploit the potential high-temperature properties of this polymer system, cross-linking is required, both to enable its use above its T_g and for enhanced chemical resistance in general. Ethynyl groups have been successfully used for thermal cross-linking of a family of high-temperature polyimides, PETI (phenylethynyl terminated polyimides),[18] so their use with aryloxysilanes was a logical extension of this cross-linking technology. The focus of this study, the first in our series, was to explore the feasibility of end-capping of this polymer system with phenylethynyl groups and to develop methods to verify end-capping was successful.

Received: January 14, 2011
Revised: April 15, 2011
Published: May 13, 2011

dx.doi.org/10.1021/ma200099x | *Macromolecules* 2011, 44, 4107–4115

The reaction selected for synthesis of the polymer is shown in Scheme 1. This reaction typically generates somewhat lower molecular weights than other synthetic routes, including the aforementioned anilinosilanediol route,[11] but has the advantage of utilizing commercially available reagents and also the flexibility gained from the use of relatively labile chlorosilane functional group for subsequent end-capping reactions (Figure 3). In addition, the lower molecular weights obtained by this route would yield more reactive end-groups and thus in principle more ethynyl groups per mole in the final capped polymers.

End-capping reactions that were evaluated are listed in Schemes 2 and 3. Both these reactions were selected for evaluation because the chemistries of end-capping are similar to the polymerization reaction. Both involve nucleophilic displacement of the Cl from the chlorosilane end-groups, and both end-capping reactions are feasible in the solvent systems used in this study (THF and toluene).

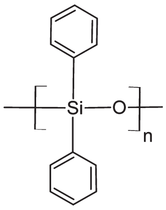


Figure 1. Polydiphenylsiloxane.

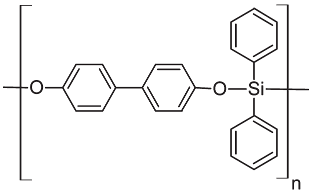


Figure 2. Repeat unit of polyaryloxydiphenylsilane.

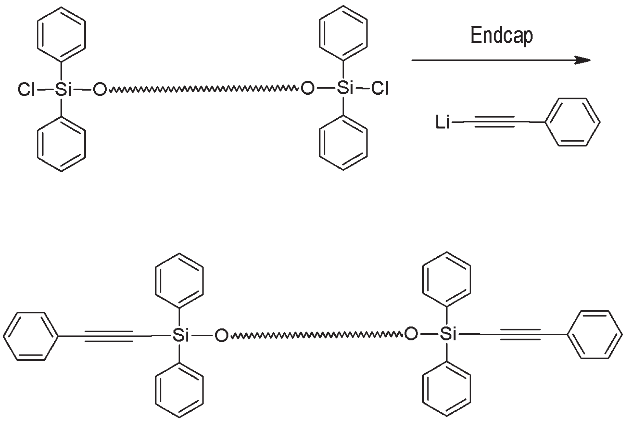
2. EXPERIMENTAL SECTION

2.1. Materials. Dichlorodiphenylsilane (DCDPS), 99%, was purchased from Gelest (catalog no. SID4510.1); 4,4′-biphenol, 99.9%, was purchased from TCI (catalog no. B0464); triethylamine (TEA), 99% (catalog no. 15791), was purchased from Acros; 4-[(4-fluorophenylethynyl)]phenol, 99%, was purchased from Wako (catalog no. 320-90143); lithium phenylacetylide 1 M solution in THF (catalog no. 340677), phenol (catalog no. P3653), and toluene (99.9% anhydrous) were purchased from Sigma-Aldrich (catalog no. 244511); anhydrous tetrahydrofuran (catalog no. 181500010) was purchased from Acros; methanol was purchased from Pharmco-Aaper. Unstabilized THF was freshly distilled in the presence of $LiAlH_4$ and used as the reaction solvent immediately after distillation.

2.2. Polymer Synthesis. Polymers were synthesized by polycondensation of DCDPS with biphenol in toluene or in THF with an inert atmosphere purge, under reflux at 60−70 °C. TEA was used as an acid scavenger to remove the condensation byproduct HCl from the system.

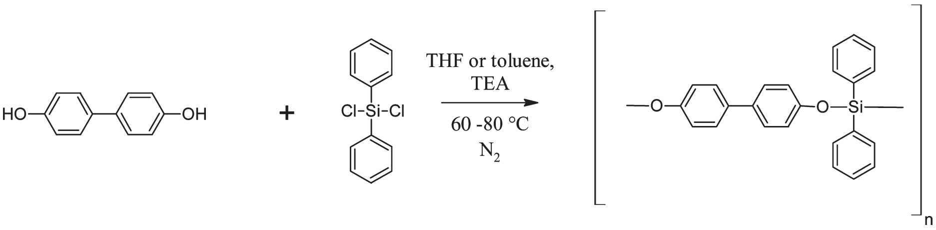
A typical synthesis in toluene was performed as follows: In a sealed 100 mL three-neck round-bottom flask equipped with a magnetic stir

Scheme 2. Lithium Phenylacetylide End-Capping Reaction



Polymer 2a

Scheme 1. Condensation Polymerization Reaction between Dichlorodiphenylsilane and Biphenol[a]



[a] Dichlorosilanes were added in 5% excess to obtain chlorosilane end-groups.

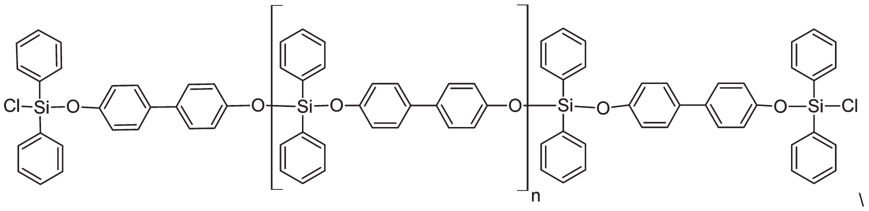
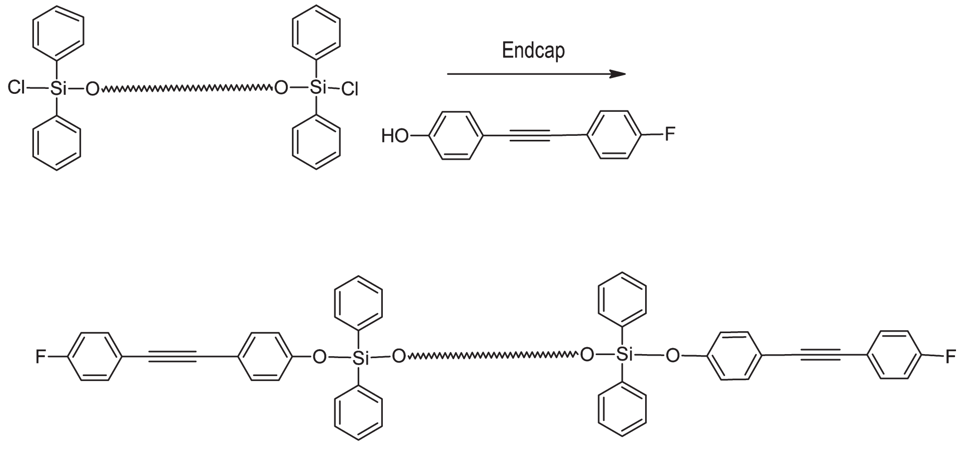


Figure 3. Polybiphenyloxydiphenylsilane polymer with chlorosilane end-groups available for end-capping reactions (general structure of samples **1a**, **1b**, **2b**, **3b**, and **4b**).

Scheme 3. 4,4′-Fluorophenyethynylphenol End-Capping Reaction



Polymer 3a

Table 1. Polymer Molecular Weight Summary (Relative to Polystyrene Standards)

sample	M_n	M_w	polydispersity index (M_w/M_n)	description
1a	6 800	12 700	1.9	low M_n uncapped polymer
1b	23 400	43 700	1.9	high M_n uncapped polymer
2a	7 700	16 200	2.1	lithium phenylacetylide capped polymer
2b	12 000	31 500	2.6	uncapped polymer (lithium phenylacetylide control)
3a	6 500	12 400	1.9	4-[(4-fluorophenylethynyl)]phenol capped polymer
3b	12 300	23 300	1.9	uncapped polymer (4,4′-fluorophenylethynyl)]phenol control)
4a	22 400	42 000	1.9	phenol capped polymer
4b	22 000	40 900	1.9	uncapped polymer, phenol control sample
				polymerization kinetics samples (toluene vs THF comparison)
5a	13 200	32 300	2.5	toluene synthesis, 12 h polymerization time
5b	16 300	37 200	2.3	toluene synthesis, 24 h polymerization time
6a	11 700	22 300	1.9	THF synthesis,1 h polymerization time
6b	22 500	42 000	1.9	THF synthesis, 2 h polymerization time

bar, a reflux condenser, and a nitrogen purge, 3.72 g (0.020 mol) of biphenol and 4.25 g (0.042 mol) of triethylamine were added to 30 mL of toluene. A thermometer was used to monitor reaction temperature by inserting into the reaction liquor through a stopper with a rubber adapter. The solution was heated to 70 °C on a hot plate with a magnetic stirrer. To this solution, 5.3 g (0.021 mol) of DCDPS and 30 mL of toluene were added via an addition funnel with an inert gas pressure equalizer. The DCDPS/toluene solution was added dropwise over ~1 h. After addition, the solution was heated under reflux overnight (13−17 h). Temperature was maintained at 65−70 °C for the remainder of the reaction. Yields after precipitation, redissolution/filtration, and reprecipitation (details in section 2.4) were in the 70% range. Synthesis in freshly distilled THF was performed following the same procedure, except times of reaction were 1−2 h.

Since the polymerization reaction is nucleophilic in nature, the use of a nonpolar aprotic solvent such as toluene would be expected to exhibit slower reaction kinetics than those obtained in a polar aprotic solvent, such as THF.[19]

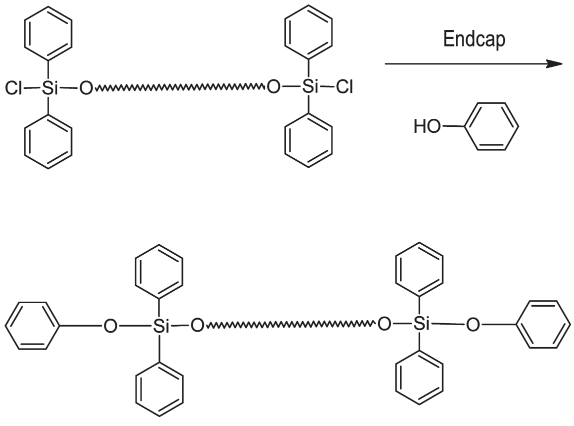
An evaluation of the effect of time on reaction extent for both systems was performed to understand reaction kinetics and determine times required to generate M_ns of ~12 000, which would yield 6 molar % of end-groups. These samples are designated as **5a**, **5b**, **6a**, and **6b**. Molecular weight data for these samples are presented in Table 1. It was found that 1 h of reaction time in THF yielded molecular weights which were equivalent to those obtained by 12 h of reaction in toluene systems.

Given the different reaction rates, direct comparison of polymerizations, and end-capping reactions performed in different solvents at equivalent times would yield misleading results. Therefore, comparison of reactions utilizing these solvent systems by extent of reaction was performed as an alternative. The sample names, molecular weight, and description of all the end-capped and uncapped polymers prepared in this work are summarized in Table 1.

2.3. End-Capping General Procedure. Prior to performing an end-capping reaction, an aliquot of the reaction liquor was removed as a control (un-end-capped sample) and allowed to continue to polymerize and build molecular weight in a separate flask. Immediately thereafter, end-capping agents were added dropwise to the remaining polymer reaction liquor through an addition funnel. End-capping reagents were added in ~4 times excess, based on nominal number-average molecular weight (M_n) of 12 000. The end-capping reactions were allowed to proceed for a time period equal to initial polymerization (an additional 1 h for THF solutions, an additional 12 h for toluene reactions).

2.3.1. Lithium Phenylacetylide End-Capping. Lithium phenylacetylide was added after 1 h of polymerization in THF or 12 h in toluene, immediately following the removal of an aliquot of uncapped sample. Both THF and toluene end-capping reactions were allowed to proceed

Scheme 4. **Phenol End-Capping Reaction**



Polymer 4a

for an equivalent time period after the addition of end-caps. In order to try to drive the end-capping reaction to the product side by removal of the condensation product, toluene reactions were also performed. LiCl, the condensation product of the end-capping reaction, is highly soluble in THF but insoluble in toluene.[20] Because of the lower polarity of toluene and slower reaction kinetics, toluene polymerizations were allowed to proceed overnight (~12−14 h); THF is a better solvent for nucleophilic reactions, so reactions were allowed to proceed ~1 h to obtain target molecular weights.

2.3.2. 4-[(4-Fluorophenylethynyl)]phenol End-Capping. 4-[(4-Fluorophenylethynyl)]phenol was added after 1 h of polymerization in THF or 12 h in toluene, immediately following the removal of an aliquot of uncapped sample. In a typical procedure, 1.06 g (0.005 mol) of 4-[(4-fluorophenylethynyl)]phenol and 10 mL of THF were transferred into an addition funnel with an inert glass pressure equalizer. The solution was then added dropwise to the polymerization reaction over 1 h. The reaction was allowed to proceed for an additional hour.

2.3.3. Phenol End-Capping. Phenol was added after 17 h of polymerization in toluene, immediately following the removal of an aliquot of uncapped sample. In a typical procedure, 0.47 g (0.005 mol) of phenol and 10 mL of toluene were transferred into an addition funnel equipped with an inert gas pressure equalizer. The solution was then added dropwise to the polymerization reaction over 1 h. The reaction was allowed to proceed for an additional 12 h.

2.4. Polymer Purification. Reaction solutions of capped polymers and uncapped controls prepared in THF were precipitated dropwise into a cold 0.1 M aqueous HCl solution to neutralize any unreacted TEA and remove the soluble TEA:HCl salt.[21] Toluene forms an emulsion in water based systems, so initial precipitations for the toluene systems were performed utilizing methanol as the nonsolvent. The insoluble polymers were then filtered, dried, and redissolved in THF. The THF solutions of the polymers were filtered to remove any residual insoluble material, mainly TEA:HCl salts, and then precipitated for a second time in methanol. The dual precipitation was performed in order to remove unreacted monomers and excess capping reagents from the final polymer prior to analysis, as both biphenol and 4-[(4-fluorophenylethynyl)]phenol (99%) are highly soluble in methanol.

2.5. Characterization. *2.5.1. Molecular Weight.* Molecular weights were determined by gel permeation chromatography using a Waters 590 LC system (Waters Corp., Milford, MA) equipped with a Phenogel 1 μ 10^3A GPC column (Phenomenex, Torrance, CA) and a Waters 410 refractive index detector. Elution rate was maintained at 1 mL/min. THF was used as the mobile phase. Polystyrene standards were used for the molecular weight calibrations.

2.5.2. Spectroscopy. Infrared spectra were collected on a Perkin-Elmer (Perkin-Elmer Co., Norwalk, CT) Spectrum One spectrometer. Spectra of polymers in solution were collected via transmission IR by dissolving small amounts of sample in THF and mounting between NaCl plates.

Raman spectra were collected on a Renishaw (Renishaw Plc., Gloucestershire, UK) RM1000 Raman microscope. Samples were dissolved in THF and mounted between two glass slides. A laser with a 513 nm wavelength was used as the excitation source.

^{13}C NMR spectra were collected using a Varian Unity Inova 300 MHz NMR (Varian Inc., Palo Alto, CA). Samples were dissolved in $CDCl_3$. Scans were collected in proton decoupled mode. Chemical shifts were calibrated using the $CDCl_3$ solvent peak as an internal reference.

2.5.3. Thermal Analysis. Differential scanning calorimetry thermograms were collected using a TA Instruments Q100 DSC (TA Instruments, New Castle, DE). Samples were analyzed in hermetic pans under a nitrogen atmosphere. Pinhole vents were introduced in the pans to allow any volatiles generated during heating to escape and also to remove residual oxygen which might otherwise be trapped in the pan and participate in undesired oxidation reactions. Pinholes were also introduced into the reference pans, for consistency. Heating rates of 20 °C/min and cooling rates of 10 °C/min were used. Thermogravimetric analyses were performed on a TA Instruments Q50 TGA. Samples were loaded onto platinum pans, and temperature was increased at a rate of 10 °C/min. Rheometric analysis was performed on a TA Instruments AR2000 rheometer with 8 mm parallel plates. Continuous oscillation testing was performed using a 1% strain and a frequency of 1 Hz. Testing was performed at 300 °C under a nitrogen purge. Approximate shear rate for these tests was 1×10^{-5} s^{-1}.

3. RESULTS AND DISCUSSION

3.1. Molecular Weight Summary. Polycondensation in THF yielded polymers with M_n in the 12 000−23 000 range, relative to polystyrene standards. This molecular weight range corresponded to roughly 32−62 repeat units; this would yield an approximate a molar concentration of 6% to 3% end-groups per mole of polymer (higher molecular weight = lower molar percentage of end-groups). Uncapped control samples had somewhat higher molecular weights than the capped samples due to the fact that the reaction was allowed to proceed for an equivalent time as the end-capped reaction. Capped and uncapped materials synthesized from the same starting polymerization reactions were compared, even though they exhibited differences in molecular weights, in order to reduce the possibility of measuring differences in thermal stabilities due solely to batch to batch variations rather than the change in thermal properties due to end-capping. This also gave further insight into the effect of molecular weight on thermal stability.

The toluene systems exhibited somewhat higher polydispersities (PDI). However, the end-capped polymers of interest, **2a** and **3a**, had comparable PDI values (1.9 vs 2.1), so direct comparisons of thermal properties should not be significantly affected by this minor difference in PDI. The most likely explanation is differences in solubilities of very low molecular weight oligomers or condensation byproducts in the final toluene/methanol solution relative to a THF/methanol solution.

High molecular weight uncapped samples were obtained by allowing the reactions to proceed for longer reaction times. 4 h in THF and 34 h in toluene were sufficient to allow molecular weights to build to the 20 000 range.

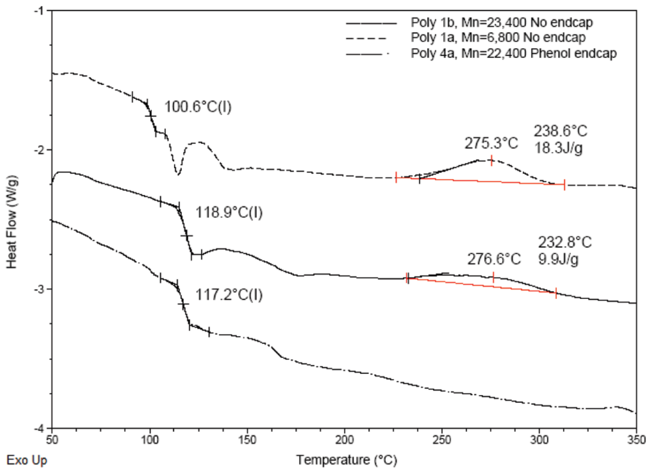


Figure 4. DSC first heat comparison of polymers **1a**, **1b**, and **4a**. Effect of M_n and end-capping on T_g and cure exotherm.

A low molecular weight (ca. 7000 M_n) uncapped polymer reference sample was also prepared by using unstabilized THF which was not freshly distilled and a polymerization time of 15 min, rather than 1 h. An M_n of 7000 corresponds to 19 repeat units. Assuming 100% conversion, this would correspond to about 10 molar % end-groups (in this case, the end-groups were not generated by controlled end-capping). Molecular weight results are summarized in Table 1.

3.2. Uncapped Polymers. Analysis of uncapped polymers as controls showed cross-linking occurred in uncapped polymers. In order to characterize this competing cross-linking reaction, thermal analysis was performed on several reference samples with different molecular weights as well as a phenol-capped control.

DSC scans were collected on two different M_n polymers and compared to the thermogram of a phenol-capped polymer (Figure 4). An exotherm peak around 275 °C was seen in both samples **1a** and **1b**, but was more pronounced in the lower molecular weight sample **1a**. This exotherm was not observed in the phenol end-capped higher M_n polymer, **4a**. In addition, the exotherm was not seen in the second heats of either uncapped sample **1a** or **1b** (Figure 5).

The T_g of heat-treated polymers, as measured from the second heat DSC scans, showed an inverse relationship with M_n. Since T_g generally increases with an increase in cross-link density,[22] this is an indication of higher cross-link density due to higher end-group content (lower M_n = more end-groups). The phenol-capped sample, which should have the lowest percentage of reactive end-groups due both to molecular weight and capping with an inactive functional group, exhibited the lowest T_g after thermal cycling, as expected. Note that **1a** had a lower T_g than **4a** and **1b** on first heat (Figure 4).

The uncapped samples were insoluble in THF after heating to 400 °C in the DSC, which was further confirmation that cross-linking reactions had occurred. The phenol end-capped polymer dissolved as expected in the absence of any significant cross-linking.

The combination of the exotherm peak at ~275 °C seen in the first heat, the T_g increase which tracked with relative end-group content, and the insolubility of uncapped polymers after heating was strong evidence that uncapped samples cross-linked via a reactive end-group mechanism, whereas the phenol end-capped polymer did not react to any appreciable extent.

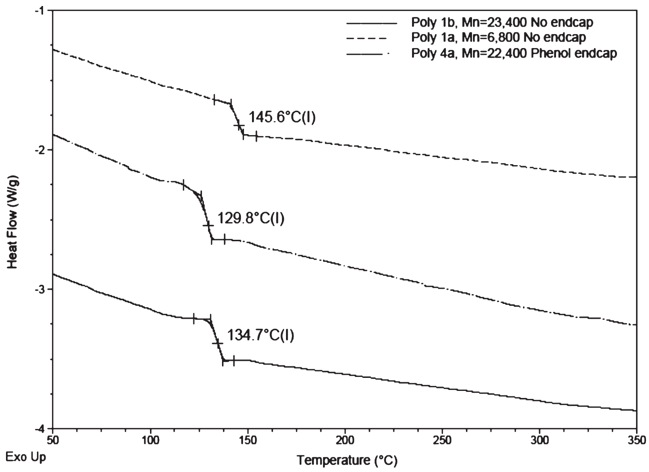


Figure 5. DSC second heat comparison of polymers **1a**, **1b**, and **4a**. Effect of heat treatment on T_g of polymers with and without end-capping (and influence of M_n).

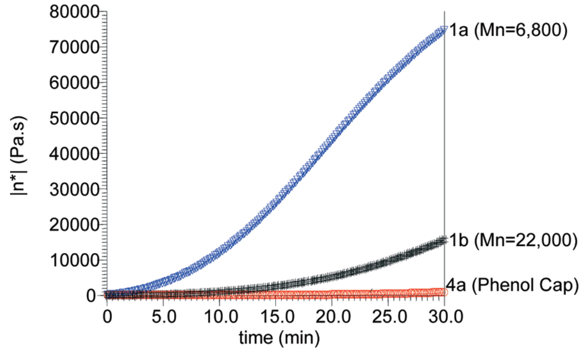
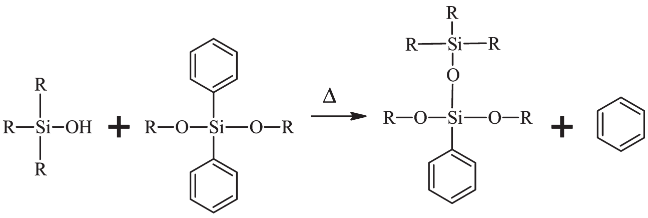


Figure 6. Rheogram of complex viscosity vs cure time at 300 °C for samples **1a**, **1b**, and **4a**. Effect of M_n and end-capping on viscosity as a function of temperature.

Samples of **1a** (6800 M_n) and **1b** (22 000 M_n) were tested via parallel plate rheometry at 300 °C under a nitrogen atmosphere. A sample of **4a** (22 000 M_n) phenol end-capped polymer was also tested for comparison. The testing temperature of 300 °C was selected to avoid cross-linking of ethynyl end-caps (section 3.3.3), which typically occurs at temperatures of 320−350 °C,[23] and focus solely on reactive end-group cross-linking, i.e., the chlorosilane ends of the polymer. Qualitative comparison of viscosity changes on heating over time is a common method of monitoring the curing of thermosets.[24] Application of this model for the study of cross-linking of end-groups is a valid extension of this methodology. Higher viscosity changes should correlate with relative concentrations of reactive end-groups and thus provide a robust probe of end-capping effectiveness.

The rate of change of the complex viscosity of the lower M_n sample **1a** was much higher than that of the high M_n sample **1b**. Again, this would be expected if more reactive end-groups were present (more reactive end-groups = faster rate of reaction). The final complex viscosity of **1a** was 4.7 times higher than that of **1b** after heating for 30 min. Note that **4b**, the higher molecular weight phenol end-capped sample, had an order of magnitude lower viscosity change than the other samples. This was a strong

Scheme 5. Silanol Thermally Induced Cross-Linking Reaction with Phenyl-Substituted Siloxane



indication that the phenol end-capping was successful and made the polymer inert to thermal cross-linking.

It has been reported by several researchers that silanol groups react with phenyl-substituted silane in a cross-linking reaction at high temperatures via Scheme 5.[13] This reaction is consistent with the cross-linking behavior observed in the uncapped polymers. Curing via this mechanism is not desired, as it is relatively uncontrollable, results in the production of benzene (boiling point ~80 °C), an undesired volatile cure byproduct, and occurs at lower temperatures than ethynyl-capped polymers.

It was also observed after testing was completed that all uncapped samples exhibited a rubbery consistency at temperatures above T_g (>150 °C). The samples stretched when removing them from the parallel plate test fixture. The stretched polymers would then contract once stress was released if $T > T_g$. This was a classical "rubbery" response, typical of a lightly cross-linked elastomer subjected to an applied stress at a temperature above T_g.[25] Once the materials cooled below T_g, they exhibited behavior more typical of glassy materials. The samples were stiff and brittle, with very limited deformation before fracturing or bending irreversibly. The phenol-capped polymer had characteristics more typical of a molten thermoplastic heated above its T_g, with irreversible deformation and viscous melt stretching seen when stress was applied to the sample. The divergent behaviors exhibited by the uncapped polymers and the phenol-capped polymer showed that phenol capping inhibited thermal cross-linking. It was also an indication of the limitations of a non-cross-linked aryloxysilane, which would have limited functional utility above T_g due to its viscous, molten state. These findings further validated the exploration of controlled cross-linking to enhance the utility of this polymer system.

3.3. Lithium Phenylacetylide End-Capping Results. *3.3.1. Molecular Weight.* GPC weight analysis showed that polymerization continued in the uncapped solution, while molecular weight building ceased in the capped solution.

3.3.2. Spectroscopic Analysis. FTIR analysis of the capped polymer showed the presence of a weak sharp ethynyl band at 2159 cm^{-1} (Figure 7). This peak was not observed in the FTIR spectrum of the uncapped polymer.

^{13}C NMR analysis revealed ethynyl peaks at 108 and 89 ppm (Figure 8).

The Si$-$C$\equiv$Cpeak has a chemical shift of 108−109 ppm, while a C$\equiv$C iso to an aromatic carbon peak has a chemical shift of 88−89 ppm. These peaks are characteristic of aromatic ethynylsilanes.[26−28]

The presence an ethynylsilane peak at 109 ppm in particular is strong evidence that the silicon ethynyl adduct had formed. Neither of these peaks was observed in the ^{13}C spectrum of the uncapped polymer.

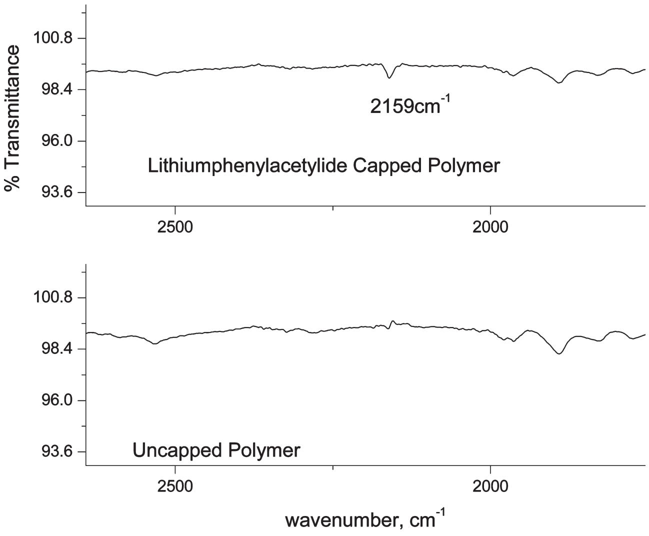


Figure 7. FTIR spectra of lithium phenylacetylide capped and uncapped polymer, showing the characteristic ethynyl peak at 2159 cm^{-1} (see Supporting Information Figure S2 for full scale IR scans).

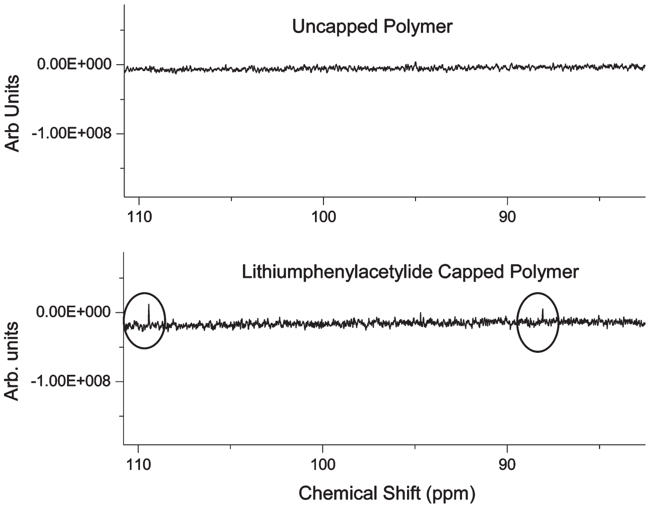


Figure 8. ^{13}C NMR spectra of lithium phenylacetylide capped and uncapped polymer, showing ethynyl peaks at 89 and 109 ppm in the capped sample (see Supporting Information Figure S3 for full scale ^{13}C NMR spectra).

3.3.3. Thermal Analysis. An exothermic peak was present at 321 °C in the first heat but was not observed in the second heat (Figure 9). Ethynl-containing compounds typically exhibit exothermic cross-linking peaks during heating at temperatures of 320−350 °C.[29,30] The presence of this peak in **3a** is further confirming evidence of the presence of ethynyl groups in the sample.

Rheological stability was determined at 300 °C under a nitrogen atmosphere. 300 °C was chosen as the test temperature so as to avoid curing the polymer via ethynyl cross-linking reactions. Thus, thermal stability at this temperature should mainly be a function of reactive end-group concentration: lower reactive end-group concentration should yield a more stable melt.

The lithium phenylacetylide-capped polymer **2a** showed a much slower change in viscosity over time relative to an uncapped

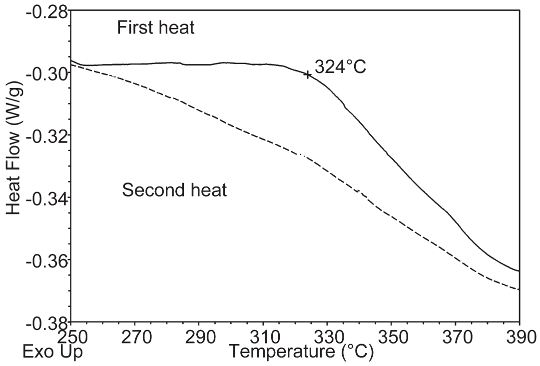


Figure 9. DSC comparison of first and second heats of **2a**, lithium phenylacetylide-capped polymer, showing the expected ethynyl cure peak at 324 °C.

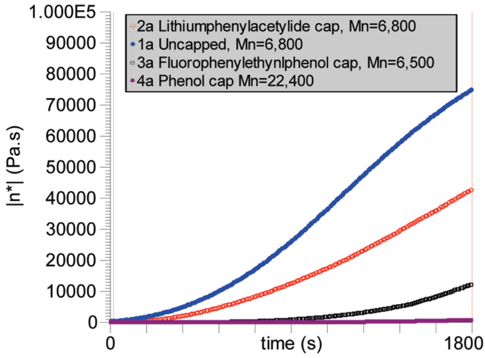


Figure 10. Comparison of viscosity change on heating of 4-[(4-fluorophenylethynyl)], lithium phenylacetylide, and phenol-capped polymers to uncapped polymer **1a** lithium phenylacetylide capped vs uncapped polymer.

polymer with comparable molecular weight, **1a** (Figure 12). This was another indication that end-capping had occurred, as the phenylethynyl cap should be more thermally stable at 300 °C than the reactive end-group of an uncapped polymer.

3.4. 4-[(4-Fluorophenylethynyl)]phenol End-Capping Results.

3.4.1. Molecular Weight. Molecular weight stopped building at M_n of 6500 in the capped system, whereas the uncapped portion of the reaction continued to build molecular weight. The uncapped system resulted in an M_n roughly double that of the 4-[(4-fluorophenylethynyl)] phenol-capped material. These results indicated that 4-[(4-fluorophenylethynyl)]phenol acted as a chain stopper to inhibit continued chain growth and did in fact end-cap the polymer as expected.

3.4.2. Spectroscopic Characterization. Since the ethynyl band in the 4-[(4-fluorophenylethynyl)] moiety is symmetric and a very weak absorber in conventional IR spectroscopy, Raman spectroscopy was used to verify the presence of the end-cap in our polymer system. The Raman spectrum of the 4-[(4-fluorophenylethynyl)]phenol end-capping reagent showed a strong absorption band at 2225 cm^{-1}, which corresponds to a stretching mode for ethynyl groups bonded to aromatic rings.[31] This peak was also observed at reduced intensity in the fluorophenylethynyl-capped polymer, but was not observed in an uncapped polymer sample (Figure 11).

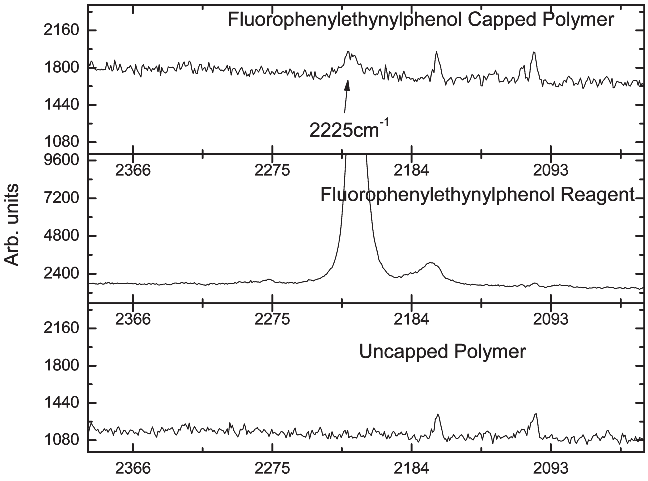


Figure 11. Raman spectrum of fluorophenylphenol-capped polymer, with spectra of 4,4′-fluorophenylphenol reagent and uncapped polymer overlaid for comparison (see Supporting Information Figure S4 for full scale Raman scans).

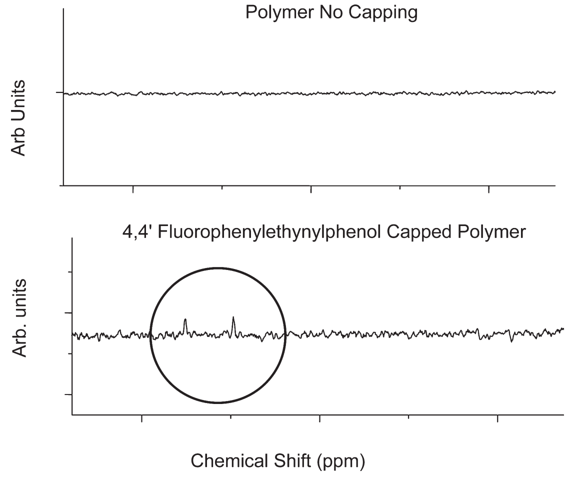


Figure 12. ^{13}C NMR spectrum of fluorophenylethynylphenol-capped polymer with an uncapped polymer spectrum overlaid for comparison, enlarged to show ethynyl carbons in capped polymer (see Supporting Information Figure S5 for full scale ^{13}C NMR spectra).

Because of the short-range symmetry of the 4-[(4-fluorophenylethynyl)]phenol molecule, C≡C ethynyl ^{13}C NMR spectra exhibit only a slight peak splitting, depending on substituents on the attached benzene rings.[32] A pure 4-[(4-fluorophenylethynyl)]phenol reagent sample showed ethynyl peaks at 88.8 and 88.3 ppm. Peaks in the 4-[(4-fluorophenylethynyl)]phenol-capped polymer were observed at 88.7 and 88.4 ppm but were not present in the uncapped polymer (Figure 12). Since 4-[(4-fluorophenylethynyl)]phenol is highly soluble in methanol, the precipitating solvent for the end-capped polymer, it is unlikely the starting reagent was present merely as component in a physical mixture.

3.4.3. Thermal Analysis. An exothermic peak was clearly seen in the first heat of this sample, but was absent in the second heat (Figure 13). Again, the presence of this peak in the 320−350 °C range is consistent with curing of an ethynyl group. After heating in the DSC test, this sample did not dissolve in THF. TGA analysis revealed that after curing at 300 °C the capped materials showed improved high temperature stability (reduced weight loss)

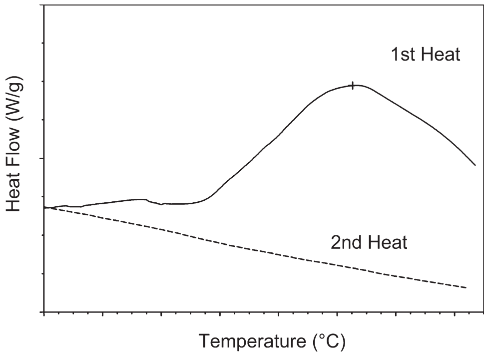


Figure 13. DSC thermogram of polymer **3c** 4-[(4-fluorophenylethynyl)]-capped polymer, enlarged to show the exothermic peak at 355 °C.

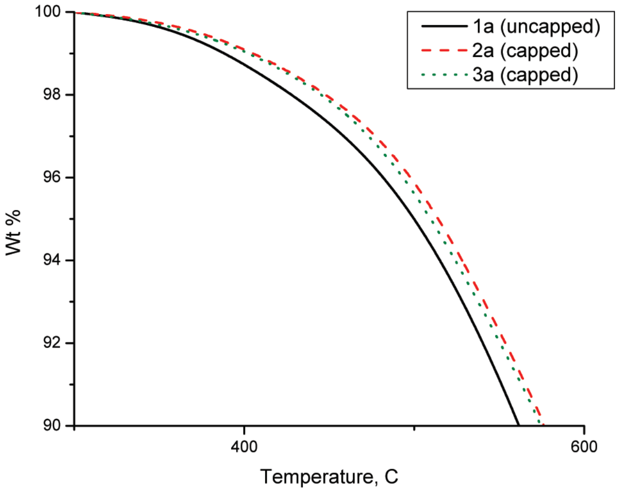


Figure 14. TGA of comparison of capped and uncapped polymer samples of comparable molecular weights, analyzed after an initial cure cycle of 300 °C for 30 min under nitrogen.

relative to an uncapped control sample of comparable molecular weight (Figure 14).

Rheological characterization showed a clear enhancement in stability during prolonged heating at 300 °C for a 4-[(4-fluorophenylethynyl)]-capped polymer, relative to a polymer with similar molecular weight that was not end-capped (Figure 12). This is further supporting evidence that end-capping was successful, as the fluorophenylethynyl end-group will not cross-link to any large degree at these temperatures and thus acts as inert capping agent. Heating above 330 °C should initiate cross-linking of ethynyl groups, as evidenced by the strong exotherm in Figure 13. TGA analysis showed this capped material also showed enhanced thermal stability, relative to comparable molecular weight uncapped polymer (Figure 10).

4. CONCLUSIONS

This work demonstrated the feasibility of end-capping to modify the thermal behavior of aryloxysilanes. Polybiphenyloxydiphenylsilanes for high-temperature applications were synthesized via condensation reactions between dichlorosilanes and biphenol utilizing a stoichiometric excess of chlorosilane for subsequent end-capping reactions. Thermal characterization of uncapped polymers showed trends in cure exotherms, viscosity changes after heating, and solubility changes that were indicative of reactive end-group chemistry and uncontrolled cross-linking. Thermally cured uncapped polymers exhibited rubber-like behavior, with pliability observed when the polymers were heated above their glass transition temperatures. These results verified the need for controlled end-capping for enhanced thermal stability in phenylsiloxane polymers obtained from chlorosilane monomers.

Successful end-capping with phenylethynyl functional groups was performed utilizing two reagents: lithium phenylacetylide and 4-[(4-fluorophenylethynyl)]phenol. End-capping was verified by several spectroscopic and thermal methods. End-capping with a nonreactive end-group (phenol) was also successfully performed and verified by thermal analysis. The end-capped polymers showed better thermal stability than uncapped polymers of comparable molecular weight at temperatures below ethynyl curing reactions. The phenylethynyl-capped reagents exhibited exothermic transitions at significantly higher temperatures than the uncapped control samples, consistent with controlled, high-temperature curing reactions.

In addition, a rheological testing method was developed for probing effectiveness of aryloxysilane end-capping reactions. The tracking of viscosity changes at temperatures above reactive end-group reaction temperatures but below the temperature of curing of ethynyl end-cap moieties was an effective screening tool to determine if an end-capping reaction was successful. Successful end-capping enhanced thermal stability of the polymer melts and results in reduced viscosity changes on heating relative to melts of uncapped aryloxysilane polymers.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Additional figures for the FTIR, NMR, and Raman analyses presented in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

We thank Greene Tweed & Co. for their financial support. We also thank Dr. Shux Li for his support and Dr. Tom Measey for assistance with Raman data collection. Y. Wei thanks the Ministry of Science and Technology of China for partial support via the National 973 Program (Grant No. 2011CB935700).

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