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Metal-Free Synthesis of Poly(silyl ether)s under Ambient Conditions

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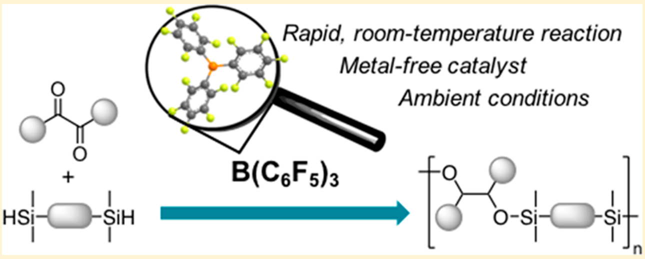
Supporting Information

ABSTRACT: Metal-free hydrosilylation using tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) as a catalyst enables the rapid polymerization of α-diketone and bis(silane) monomers under ambient conditions to give high molecular weight poly(silyl ether)s (PSEs). A wide selection of commercially available monomers bearing different backbone and side-chain functional groups are shown to be compatible with these metal-free conditions. Significantly, the thermal properties of these poly(silyl ether)s are highly tunable, with novel semicrystalline materials being obtained in a variety of cases. These poly(silyl ether) materials serve as a versatile platform for materials with designed degradation profiles and crystallinity.

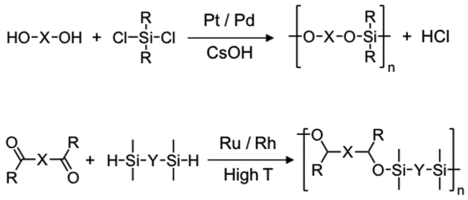


■ INTRODUCTION

Poly(silyl ether)s (PSEs) are high-performance materials that, similar to poly(siloxane)s, exhibit exceptional low-temperature flexibility coupled with enhanced thermal stability. These features have led to their broad implementation as elastomers, gas-permeable membranes, and biocompatible coatings.[1−3] In addition, the labile silyl ether (Si−O−C) linkages of PSEs provide susceptibility to acid-catalyzed hydrolysis, suggesting a new design motif for triggered degradation in biomedical or environmental applications[4,5] that is particularly appealing due to increased interest in degradable materials for commodity applications.[6]

During the past decades, several strategies have been developed for the synthesis of PSEs.[4,7,8] One commonly used approach is the condensation polymerization of diols with dihydrosilanes, dialkoxysilanes, diaminosilanes, or dihalosilanes (Scheme 1).[9] While high molecular weight materials are obtained, the poor atom economy[10] and production of hydrogen gas, alcohols, amines, or HX as byproducts are undesirable. Addition polymerization of cyclic ethers with dichlorosilanes or dimethyldiphenoxysilane monomers has also been demonstrated; however, the range of readily available starting materials is limited, leading to a lack of viable synthetic strategies.[11−13]

Scheme 1. Traditional Synthetic Strategies for Poly(silyl ether)s (PSEs), Including the Polycondensation of Diols and Difunctional Silanes or Transition-Metal-Catalyzed Hydrosilylation



In addressing these challenges, our attention was directed toward hydrosilylation reactions involving the addition of silicon hydrides across unsaturated bonds as an attractive approach toward novel poly(silyl ether)s.[14−17] Pioneering work by Weber illustrated that poly(silyl ether)s can be prepared by hydrosilylation coupling catalyzed by transition metal complexes, including ruthenium and rhodium;[18−23] however, the reported processes suffer from harsh reaction conditions and side reactions as well as the high cost/low abundance of Ru/Rh catalysts (Scheme 1). Because of these drawbacks and an increasing interest in mild, metal-free methods for the synthesis of functional polymers,[24] we examined the hydrosilylation of carbonyl groups catalyzed by tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) in detail. Seminal work by Piers and co-workers[25−32] has shown that $B(C_6F_5)_3$ is a water-tolerant catalyst that can be widely used in a variety of hydrosilylation coupling reactions under mild conditions.[28−32] Unlike transition-metal catalysts

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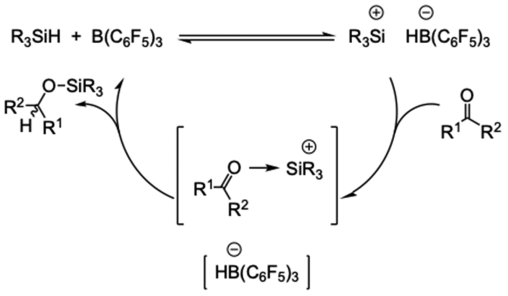
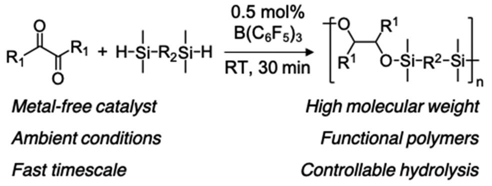
that trigger the reaction by an oxidative insertion into the Si−H bond, the electron-deficient $B(C_6F_5)_3$ Lewis acid activates the Si−H bond via η-coordination, leading to its addition across unsaturated groups (Scheme 2). Importantly, the hydrosilylation of the C═O unit in ketones, aldehydes, and esters[33−36] occurs in high yields with low catalyst loadings. This allows for $B(C_6F_5)_3$ to be used in the synthesis of complex structures such as functionalized carbon nanotubes[37] as well as for the polycondensation of dihydrosilanes with dialkoxysilanes to form polycarbosiloxanes.[38]

Scheme 2. Mechanism of the $B(C_6F_5)_3$-Catalyzed Hydrosilylation of Ketones



Inspired by the efficiency and functional group tolerance of $B(C_6F_5)_3$, we report the synthesis of a tunable library of poly(silyl ether)s from readily available starting materials. Specifically, we demonstrate a highly efficient, scalable, and metal-free hydrosilylation polymerization using α-diketone and bis(silane) monomers (Scheme 3). These polymers are conveniently prepared in a single step under ambient reaction conditions using low $B(C_6F_5)_3$ loadings and short reaction times. The resultant functional polymers exhibit high structural regularity and novel thermal and semicrystalline behavior.

Scheme 3. Synthetic Strategy for Poly(silyl ether)s (PSEs) Using Borane-Catalyzed Metal-Free Hydrosilylation Addition Polymerization



EXPERIMENTAL SECTION

Materials. Benzil (98%), 4,4′-difluorobenzil (98%), 4,4′-dibromobenzil (98%), 4,4′-dimethylbenzil (97%), dimethylphenylsilane (>98%), 1,1,3,3-tetramethyldisiloxane (97%), 1,1,3,3,5,5-hexamethyltrisiloxane (95%), 1,2-bis(dimethylsilyl)ethane (>97%), tris(pentafluorophenyl)borane (95%), chloroform (99% anhydrous), tetrahydrofuran (>99%), and *N*-methyl-2-pyrrolidinone (>98.5%) were used as received from Sigma-Aldrich. 2,3-Butanedione (97%, Sigma), 3,4-hexanedione (95%, Sigma), and 1,4-bis(dimethylsilyl)benzene (97%, Gelest) were dried over CaH_2 and distilled before use. Toluene was distilled from sodium benzophenone prior to use.

Methods. Nuclear magnetic resonance (NMR) measurements were performed using Varian Unity Inova 500 and 600 MHz instruments. All samples were dissolved in $CDCl_3$ or DMSO-d_6, and chemical shifts (δ) are reported in ppm relative to the residual proton signal of the deuterated solvent as appropriate. Mass spectrometry was performed on a Micromass QTOF2 quadrupole/time-of-flight tandem mass spectrometer (ESI) or a Waters GCT Premier time-of-flight mass spectrometer (EI and FD). Infrared (IR) spectra were recorded on a Thermo Nicolet iS10 Fourier-transform infrared (FTIR) spectrometer with a Smart Diamond attenuated total reflectance (ATR) sampling accessory. Size exclusion chromatography (SEC) was performed on a Waters 2695 separation module equipped with a Waters 2414 refractive index detector and a Waters 2996 photodiode array detector eluting with 0.25% triethylamine in chloroform. Molar masses were estimated relative to polystyrene standards. Differential scanning calorimetry (DSC) was performed on a TA Instruments Q2000 DSC system at a heating rate of 10 °C/min under a nitrogen atmosphere. Thermal stability was evaluated using a TA Discovery thermogravimetric analyzer with a heating rate of 10 °C/min under a nitrogen or air atmosphere. Single-crystal X-ray diffraction (XRD) data acquisition was performed on a Bruker Kappa APEX II CCD diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.7107 Å) at T = 100(2) K. Data were collected using an ω scan width of 0.588° and three axes with exposure times of 15 s and a fixed sample-to-detector distance of 60 mm. X-ray data collection was monitored by the APEX2 program. Data were corrected for Lorentz, polarization, and absorption effects using SAINT and SADABS. SHELXTL was used for structure solution and full matrix least-squares refinement on F2. All the H atoms were placed in geometrically idealized position and constrained to ride on their parent atoms.

Synthesis. *Model Small-Molecule Reaction.* In a 20 mL glass vial equipped with a Teflon coated stir bar, dimethylphenylsilane (2.78 g, 20.0 mmol) was added to a solution of $B(C_6F_5)_3$ (25.6 mg, 0.05 mmol) in chloroform (5.0 mL), and the resulting solution was stirred briefly. Benzil (2.10 g, 10.0 mmol) was then added slowly. The reaction mixture was stirred at room temperature for 30 min. The obtained solution of diastereomers was investigated by ^{1}H NMR, and the chloroform allowed to evaporate at room temperature to generate suitable crystals for single-crystal X-ray diffraction. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45−7.00 (m, Ar), 4.70 (s, *dl*-OC*H*Ph), 4.50 (s, *meso*-OC*H*Ph), 0.16 and −0.04 (d, J = 16.0, $-Si(CH_3)_2-$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.5, 141.2, 139.5, 137.5, 133.6, 133.5, 129.3, 129.2, 127.6, 127.5, 127.3, 127. 2, 127.0, 79.8, −1.0, −1.4, −1.5, −1.8. ^{29}Si NMR (79.5 MHz, $CDCl_3$): δ 7.9, 7.6. MS (ESI+) calcd for $C_{30}H_{34}O_2Si_2^+$ [M + H$^+$] 483.21; found 483.21. FTIR ν_{max} (cm^{-1}): 2950. 2850, 1750, 1620, 1550, 1275, 1110.

Representative Polymer Synthesis. In a 10 mL glass tube equipped with a Teflon-coated stir bar, 1,4-bis(dimethylsilyl)benzene (194 mg, 1.00 mmol) was added to a solution of $B(C_6F_5)_3$ (2.56 mg, 0.005 mmol) in toluene (1.0 mL), and the resulting solution was stirred briefly. Benzil (210 mg, 1.00 mmol) was then added. The reaction mixture was stirred at room temperature for 30 min. The resulting mixture was diluted with 2.0 mL of chloroform, passed through a neutral alumina filter, and precipitated into cold hexanes. The final precipitate was isolated and dried in a vacuum oven to give the poly(silyl ether), **2a**. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37−6.95 (m, Ar), 4.73 (d, J = 5.1 Hz, *dl*-OC*H*Ph), 4.56 (s, *meso*-OC*H*Ph), 0.41 and −0.16 (m, $-Si(CH_3)_2-$). ^{13}C NMR (151 MHz, $CDCl_3$): δ 142.66, 142.63, 141.28, 138.80, 132.83, 132.74, 132.69, 132.60, 132.57, 127.84, 127.71, 127.61, 127.41, 127.33, 127.14, 79.98, 1.08, −1.08, −1.33, −1.35, −1.37, −1.57. ^{29}Si NMR (119 MHz, $CDCl_3$): δ 7.80 (d, J = 4.1 Hz), 7.69 (d, J = 5.1 Hz). FTIR ν_{max} (cm^{-1}): 3065, 3034, 2957, 1493, 1452, 1380, 1251, 1200, 1136, 1100, 1069, 1027, 891, 844, 822, 778, 699, 664, 588, 560, 545. SEC: M_n = 55 kg/mol, M_w = 98 kg/mol, M_w/M_n = 1.8. TGA: $T_{d5,N2}$ = 415 °C. DSC: T_g = 40 °C, T_c = 135 °C, T_m = 175 °C.

RESULTS AND DISCUSSION

Model Small-Molecule Reaction. The elegant studies of Rosenberg et al. on borane-catalyzed hydrosilylation of both carbonyl and thiocarbonyl compounds coupled with our own investigations on $B(C_6F_5)_3$-catalyzed side-chain functionalization reactions[39,40] prompted a series of small molecule studies to define the reaction scope and optimized conditions. The reaction of benzil (α-diketone) and dimethylphenylsilane (bis(silane)) was identified as a model small molecule system with initial studies under ambient conditions showing that quantitative and highly efficient hydrosilylation of the α-diketone could be achieved within 30 min using only 1 mol % of the $B(C_6F_5)_3$ catalyst (Scheme 4). Significantly, this allows the stable silyl ether, **1**, to be produced on a gram scale from readily available starting materials with ^{1}H NMR spectroscopy indicating the presence of *meso*- and *dl*-diastereomers, discernible by the distinct resonances located at 4.55 and 4.71 ppm, as well as 0.07 and 0.19 ppm, attributed to the CH–Si–O and the CH_3 groups of the respective bis-silyl ether isomers (Figure 1). The major isomer, (4*R*,5*S*)-2,7-dimethyl-2,4,5,7-tetraphenyl-3,6-dioxa-2,7-disilaoctane (ca. 80 mol %), was shown to be the *meso*-diastereomer by single-crystal X-ray diffraction with clear melting and crystallization transitions (T_m = 90 °C, T_c = 30 °C) being observed by DSC.

Scheme 4. Model Reaction of Benzil and Dimethylphenylsilane

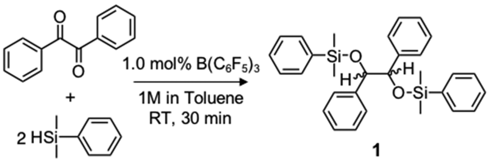
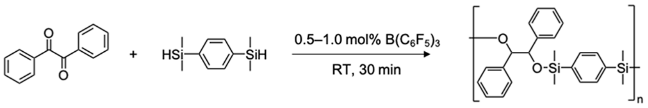


Table 1. Optimization of the $B(C_6F_5)_3$-Catalyzed Hydrosilylation Polymerization



entry[a]	BDMSB[b] [equiv]	solvent	cat. [mol %]	isolated yield (%)	M_n[c]	M_w[c]	Đ[c]
1a	1.0	$CHCl_3$	0.5	80	26	47	1.8
1b	1.0	toluene	0.5	80	55	98	1.8
1c	1.0	THF	0.5	0			
1d	1.0	NMP	0.5	0			
1e	1.0	toluene	0.1	60	3	6	1.8
1f	1.0	toluene	0.25	80	14	28	2.1
1g	1.0	toluene	1.0	80	46	84	1.8
1h	0.9	toluene	0.5	80	15	31	1.8
1i	1.1	toluene	0.5	80	14	29	2.0

[a] Polymerization conditions: benzil (1.00 mmol), 1,4-bis-(dimethylsilyl)benzene, and $B(C_6F_5)_3$ in 1.0 mL of solvent. [b] 1,4-Bis(dimethylsilyl)benzene. [c] Determined by size exclusion chromatography (SEC) calibrated with polystyrene standards in chloroform. Molar masses are reported in kg mol^{-1}.

Polymerization Conditions. On the basis of the efficiency of this metal-free hydrosilylation, we subsequently studied the reaction between benzil and 1,4-bis(dimethylsilyl)benzene as a model step-growth polymerization system with benzil acting as an A_2 monomer (Table 1). Significantly, low $B(C_6F_5)_3$ catalyst loading (0.5 mol %) and equimolar conditions in toluene gave the desired poly(silyl ether) as a high molecular weight product (M_n = 55 kDa; Đ, M_w/M_n = 1.8, entry 1b) in >80% yield. Varying the solvent from toluene to chloroform resulted in similar reactivity; however, no polymerization was observed in either THF or NMP, presumably due to deactivation of the catalyst. Decreasing the catalyst loading to 0.25 and 0.1 mol % results in lower molecular weights as did off-stoichiometric loading of the monomers, fully consistent with a step-growth polymerization. Interestingly, in all polymerizations a well-defined, low molecular weight component (~15% yield) was observed by GPC which could be easily purified by selective precipitation of the polymer in cold hexanes or methanol. In agreement with the step-growth process, this was identified as the cyclic dimer, which was fully characterized by NMR and mass spectrometry with the macrocyclic structure being confirmed by single crystal XRD (Figure 2). The formation of this cyclic byproduct could possibly be suppressed by increasing the concentration of the reaction mixture to favor intermolecular polymerization over cyclization.

Characterization of the poly(silyl ether) derived from benzil and 1,4-bis(dimethylsilyl)benzene reveals a number of interest-

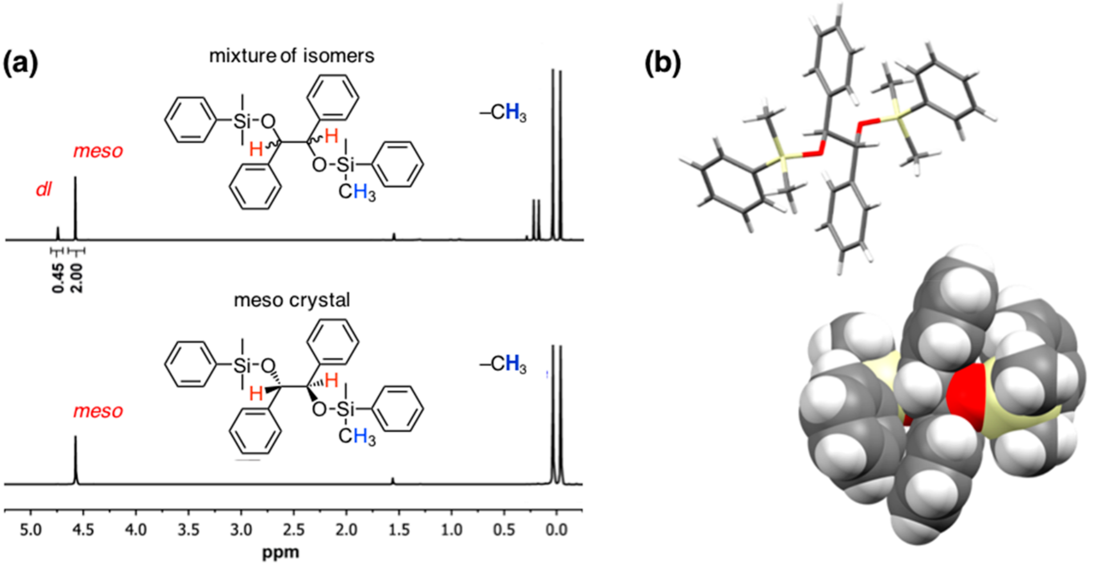


Figure 1. (a) ^{1}H NMR spectra of the diastereomer mixture of **1** (top) and the crystallized *meso*-product ((4*R*,5*S*)-2,7-dimethyl-2,4,5,7-tetraphenyl-3,6-dioxa-2,7-disilaoctane) (bottom) obtained from the model hydrosilylation reaction between benzil and dimethylphenylsilane. (b) Crystal structure of *meso*-product; the methyl and phenyl groups provide steric protection for the labile Si–O bonds.

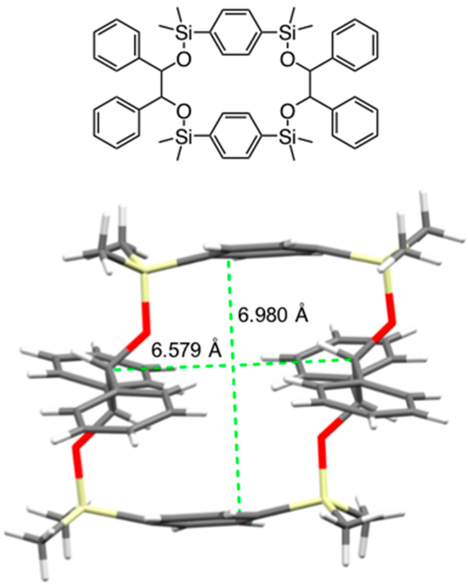


Figure 2. Structure and single crystal diffraction of the [2 + 2] cyclic product.

ing features. As anticipated from the small molecule model studies, hydrosilylation proceeds in a stereoselective manner, resulting in a chiral backbone with ∼70% *meso*- and ∼30% *dl*-configuration, which is clearly shown in the relative integration of the ^{1}H NMR resonances at 4.55 and 4.71 ppm (Table 1, entry 1b, M_n = 55 kDa; Figure 3a). In addition, the structural regularity of the polymer is supported by well-resolved and sharp peaks in the ^{13}C and ^{29}Si NMR spectra; again an ∼7:3 ratio is observed for the carbon signals of the Si(CH$_3$)$_2$ units, and the backbone silicon atom displayed a set of two narrow ($\Delta\nu_{1/2}$ < 10 Hz) resonances at 7.7 ppm (Figure 3b,c). As will be discussed in detail below, the thermal properties of this aromatic poly(silyl ether) are of particular interest and suggest that borane-catalyzed hydrosilylation of diketones and bis(silanes) is a viable platform for stereochemically enriched backbone polymers based on readily available starting materials, opening up new application areas for poly(silyl ether)s.

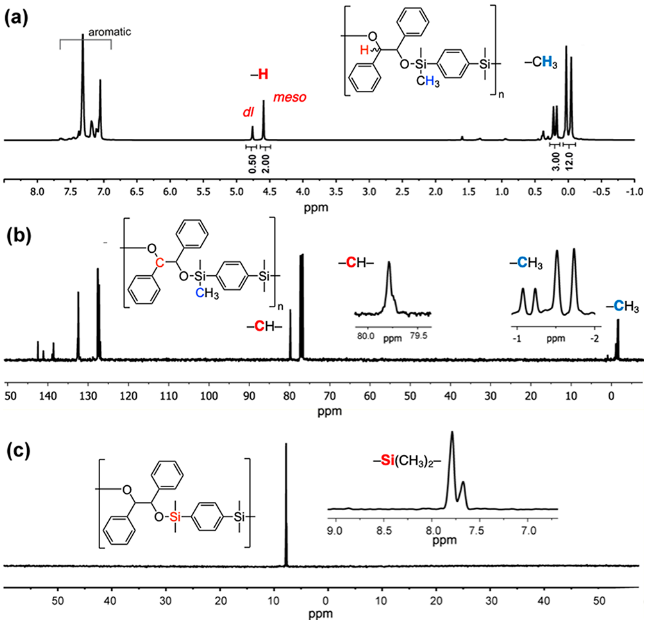


Figure 3. (a) ^{1}H, (b) ^{13}C, and (c) ^{29}Si NMR spectra of model poly(silyl ether) in CDCl$_3$. The sharp and well-resolved peaks in (a)−(c) indicate high structural regularity of this novel PSE.

Expansion of Monomer Scope. The scope and functional group tolerance of this metal-free polymerization process were then investigated using a series of readily available α-diketone and bis(silane) derivatives under standard conditions (Table 1, entry 1b). Variation in the α-diketone structure was explored by employing 1,4-bis(dimethylsilyl)benzene as a common comonomer with substitution on the benzil unit as well as exchange of the aromatic units for aliphatic groups (Table 2, polymers **2a**−**2h**). Changing the substituents from hydrogen to halogen at the benzil *para*-position did not impact polymerization efficiency, with high degrees of polymerization being produced in all cases (polymers **2a**−**2c**). Polymerization was also successful with cyclic, “tied-back” analogues of benzil, notably 9,10-phenanthrenequinone and acenapthenequinone. The high reactivity of these systems shows that conjugation and steric rigidity in the monomer units do not inhibit the polyhydrosilylation reaction, although the poor solubility of the latter reduces the efficacy of the polymerization. One of the attractive features of this polymerization process is the ready availability of diketones, as exemplified by the aliphatic systems that are widely used as flavoring and fragrance agents. For example, butane-2,3-dione is added to food to impart a buttery flavor, while hexane-3,4-dione is found in a variety of foods. Exchange of benzil with either butane-2,3-dione or hexane-3,4-dione was shown to also lead to the generation of high molecular weight polymers, with the aliphatic repeat units imparting increased solubility when compared to the benzil-derived materials.

Substitutions of the bis(silane) monomer were then examined using benzil as a common comonomer. In these systems, high conversions were observed, but the resulting molecular weights were lower when compared to the phenylene-bridged bis(silane) monomer. For the ethylene-bridged and oxo-bis(silane) derivatives, polystyrene-equivalent molecular weights were less than 10000 g/mol with hydrogen-terminated polydimethylsiloxane macromonomers affording oligomers (Table 2, polymers **2i**−**k**). If the mechanism of the B(C$_6$F$_5$)$_3$-mediated α-diketone hydrosilylation reaction is considered (see Scheme 2), it is postulated that stabilization of the β-silylium intermediate is critical for attaining high degrees of polymerization with aryl-bridged silanes offering higher reactivity as well as improved sterics for formation of the silylium cation, therefore resulting in higher molar mass materials.

Physical and Thermal Properties. The synthetic versatility inherent in these metal-free systems allows structure-property relationships to be developed based on a poly(silyl ether) backbone. As expected, thermal stability for these materials is high as exemplified by aromatic systems based on benzil and 1,4-bis(dimethylsilyl)benzene where increased thermal decomposition temperatures are observed when compared to traditional siloxanes (**2a**−**c**, $T_{d5,N2}$ > 380 °C). Similarly, the glass transition temperature could be varied from ≈−30 to ≈80 °C by selecting the appropriate side chain groups (derived from the diketone) and the backbone linker unit (derived from the bis(silane)). Surprisingly, a wide range of these materials proved to be semicrystalline in analogy with engineering plastics such as high-density polyethylene and polylactide leading to a rich array of melting/crystallization temperatures and thermal behavior being observed (Figure 4). Moreover, cold crystallization on heating is apparent for

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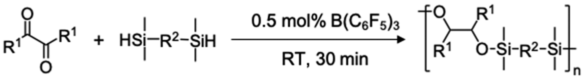
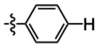
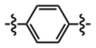
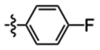
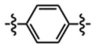
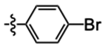
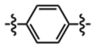
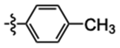
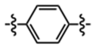
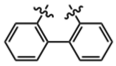
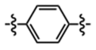
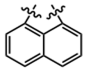
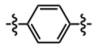
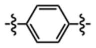
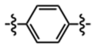
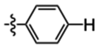
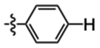
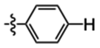
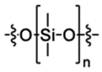
Table 2. Preparation of PSEs from α-Diketones and Bis(silane)s



Polymer[a]	R^1	R^2	M_n[b]	Đ[b]	[*meso*]:[*dl*][c]	T_g[d] (°C)	T_{d5}[e] (°C)
2a			55.0	1.8	70:30	40 (T_m 175)	415
2b			40.0	2.0	70:30	50 (T_m 160)	380
2c			48.2	1.8	70:30	80 (T_m 120)	380
2d			14.1	2.1	60:40	-2	195
2e			20.7	1.7	50:50	70	335
2f[f]			8.0	1.5	–	30	285
2g	CH_3		30.3	1.7	70:30	-30	250
2h	C_2H_5		27.3	2.7	70:30	-25 (T_m 120)	310
2i		C_2H_4	2.6	1.2	–	-20 (T_m 65)	310
2j		O	7.0	1.5	–	-15 (T_m 95)	330
2k[g]			12.3	2.2	85:14	–	340

[a]Polymerization conditions: 1 M of each monomer with 0.5 mol % $B(C_6F_5)_3$ in toluene. [b]M_n determined by size exclusion chromatography (SEC) calibrated with polystyrene standards in chloroform. Molar masses are in kg mol^{-1}. [c]Ratio of [*meso*]:[*dl*] determined by ^{1}H NMR. [d]Melting and glass transition temperatures (T_m and T_g, respectively) were measured via differential scanning calorimetry (DSC). [e]Thermal decomposition temperatures (T_{d5}) were measured by thermogravimetric analysis (TGA) and indicate the temperature at 5% mass loss under nitrogen. [f]Polymerization run in chloroform instead of toluene due to poor solubility of acenaphthenequinone. [g]Molar mass of siloxane linker, M_n = 500 g mol^{-1}.

phenylene-bridged poly(silyl ether)s with the benzil-based system, **2a**, showing a T_c of 135 °C and a T_m of 175 °C. Replacement of the freely rotating phenyl rings in **2a** with a rigid phenanthrene unit leads to an increase in the glass transition temperature but no observable T_c or T_m in the measurement window. This absence of crystallinity may be due to the stereochemically random nature of the backbone for **2e**. In contrast, the alkyl-substituted hexane-3,4-dione derivative, **2h**, was observed to have sharp transitions with the T_c being 30 °C and the T_m being 120 °C. For the benzil-based polymer with ethylene linker unit, **2i**, crystallization was observed on cooling with multiple melting transitions. It should be noted that all semicrystalline behavior was further supported by sharp, well-defined maxima observed by XRD (see the Supporting Information) which illustrates the utility of this polymerization strategy for producing libraries of semicrystalline thermoplastics based on readily available poly(silyl ether) building blocks.

Hydrolysis. PSEs are known for their potential to undergo hydrolysis due to the nucleophilically labile Si−O−C bonds in the backbone. In investigating the degradability of the polymers presented here, we selected four representative examples: the bis(silyl)phenylene-based polymers **2a** (−H substituted), **2c** (−Br), and **2d** (−CH_3) as well as the siloxane polymer **2j**. After dissolving these polymers in $CHCl_3$ solutions containing either methanol (80/20 (v/v)), TEA (20 mM), or HCl (1 mM), we monitored alcoholysis and hydrolysis as a function of time via changes in the relative molar mass by SEC analysis. The silphenylene-containing polymers **2a**, **2c**, and **2d** proved very stable against alcoholysis, showing no change in molecular weight after an extended period (Figure 5). In contrast, the siloxane-based copolymer **2j** underwent methanolysis under the same reaction conditions, as indicated by a 2-fold molecular weight decrease after 15 days. Significantly, in the presence of triethylamine (TEA), both the silphenylene copolymer **2a** and siloxane copolymer **2j** are stable, with no apparent change in molar mass over the same time period. As expected, these materials did prove to be susceptible to acid-catalyzed hydrolysis, exhibiting complete degradation for the poly(siloxane) derivative, **2j**, within 12 h and for the phenylene derivative over 5+ days. This tunable degradation of **2j** relative to the silphenylene polymer **2a** is attributed to decreased steric hindrance and electronic nature of the Si−O bonds. In all cases, the degradation products were isolated and characterized by ^{1}H NMR and gas chromatography−mass spectrometry (GC-MS) measurements and for **2a** shown to be consistent with hydrolysis of the silyl ether backbone, yielding hydrobenzoin and phenylsilanediol (Figure 5a). The results demonstrate the further tunability of the properties of these PSEs with the

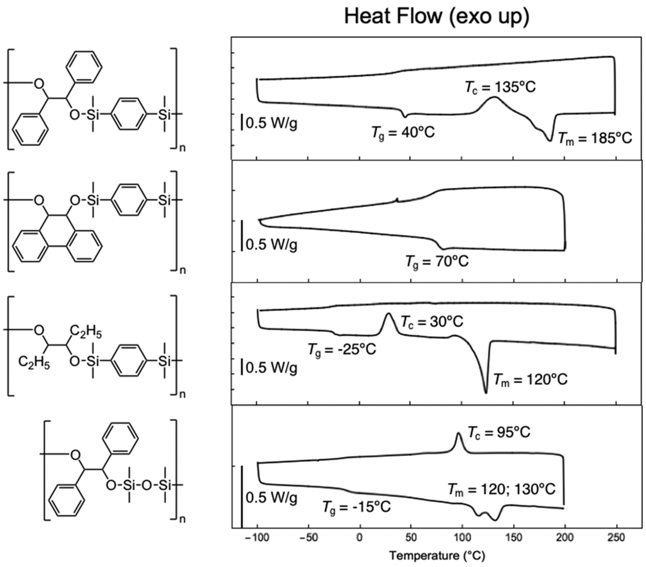


Figure 4. DSC chromatograms of selected PSEs **2a**, **2e**, **2h**, and **2j** on the second heat and cool cycle at a rate of 10 °C min^{-1}. The phenylene bridged **2a** and **2h** exhibit cold crystallization peaks during heating (T_c = 135 and 30 °C, respectively), while **2j** displays exothermic crystallization on cooling (T_c = 95 °C). The phenanthrene-based **2e** shows no crystallization in the temperature window examined.

observed acid-promoted degradation providing a new platform for the construction of responsive polymeric Si-based materials.

■ CONCLUSION

In conclusion, the step-growth polymerization of α-diketone and bis(silane) monomers was successfully demonstrated using the Lewis acid catalyst $B(C_6F_5)_3$. A wide variety of commercially available monomers, including benzil and other aryl-substituted α-diketones, could be coupled with bis-silanes to produce a library of functionalized semicrystalline polymers with high molar mass, tunable thermal properties, and degradable Si−O−C backbones. Further development of this facile metal-free polyhydrosilylation chemistry and expansion to other Lewis acids, copolymers, and PSE-based thermosets are underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.8b02741.

Crystallographic data, polymer XRD, hydrolysis analysis, and synthetic characterization details (PDF)

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Notes

The authors declare no competing financial interest.

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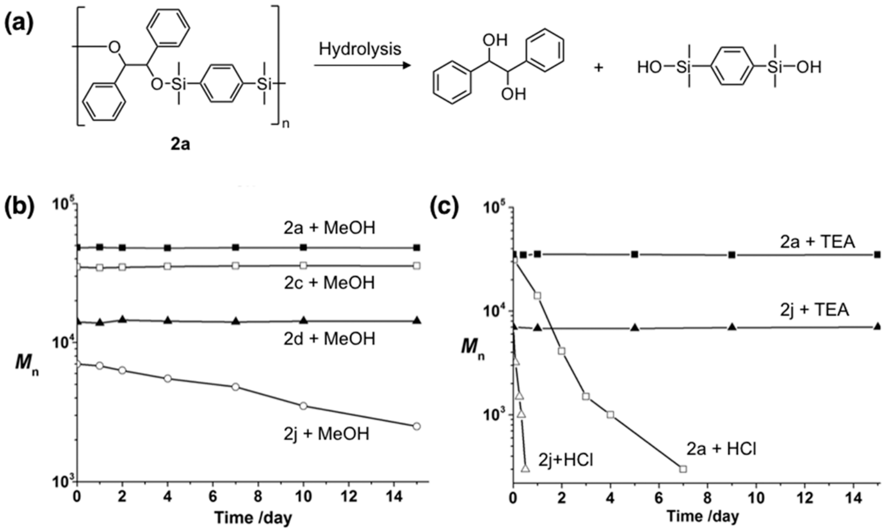

Figure 5. (a) Representative degradation behavior of PSE **2a**. Number-average molar mass of PSE samples estimated via SEC as a function of time after exposure to (b) $CHCl_3$/MeOH mixture (80/20, v/v) or (c) $CHCl_3$/TEA (20 mM) or $CHCl_3$/HCl (1 mM).

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