Synthesis and Study of New Radial Organic/Inorganic Hybrid Epoxides

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ABSTRACT: A new approach to the synthesis of reactive organic/inorganic hybrid molecules was developed. Alternating hydrocarbon and siloxane segments were introduced into the arms of radial oligomers using hydrosilation chemistry. Cycloaliphatic and glycidyl epoxy-terminal systems with bisphenol A-based aromatic hydrocarbon cores and siloxane units derived from 1,1,3,3-tetramethyl-disiloxane were synthesized and fully characterized (molecules **7** and **6**, respectively). The cationic UV and thermal curing behavior of these two new radial hybrid epoxies was investigated using photo- and thermal- differential scanning calorimetry. Hybrid cycloaliphatic epoxy **7** exhibited good UV curing kinetics and photopolymerized to high conversion. The glycidyl analog **6** exhibited poor UV curing kinetics, but was readily cured using 2-ethyl-4-methylimidazole as a nucleophilic curing agent. Both hybrid epoxysiloxanes exhibited extensive thermal cationic cure. The physical properties of cured films of the two new radial epoxysiloxanes were studied and compared with various commercially available hydrocarbon and siloxane benchmark materials. The cured systems exhibited lower moisture uptake and better thermal stability than most hydrocarbon epoxies examined. Several visually compatible blends of the new hybrid molecules with common hydrocarbon resins were identified, and in general organic compatibility was found to be intermediate among selected siloxane-containing benchmarks. Molecules **6** and **7** represent progress towards the goal of synthesizing highly functional organic/inorganic hybrid molecules which combine the best attributes of both hydrocarbon epoxides and siloxane materials. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 3244–3257, 2008

Key words: epoxysiloxane; organic/inorganic hybrid; radial oligomer

INTRODUCTION

As epoxy technology has matured over the last four decades, much effort has been placed on improving the high temperature/high humidity performance of cured materials and in tailoring their toughness and flexibility.[1–3] One important approach to such ends has been to incorporate siloxane functionality into the cured epoxy matrix either through blending or through the synthesis of organic/inorganic hybrid epoxy molecules. In general, such studies have endeavored to combine the high reactivity, adhesion, and excellent mechanical properties of hydrocarbon epoxies with the flexibility, hydrophobicity, chemical resistance, and thermal stability of siloxane-based materials. Within this class of hybrid materials many different synthetic approaches and molecular architectures have been investigated. The utility of epoxy-functional siloxane oligomers and polymers is exemplified by their commercial use in UV curable release coatings.[4–7] The most common synthetic approach for producing epoxysiloxanes has been the hydrosilation of unsaturated epoxies onto SiH-functional backbones.[8–11] This methodology has proven to be quite versatile and scaleable.

Within our group, we have a particular interest in radiation and thermally curable adhesives, coatings, and sealants. For such applications, control of cured properties may be achieved by blending hybrid epoxies with more traditional hydrocarbon-based materials, and in doing so the organic compatibility and mechanical properties of the epoxysiloxane resins becomes quite important. Because it is often desirable to achieve high crosslink density in the cured products, there is interest in utilizing highly functional hybrid resins. As an approach to obtaining good organic compatibility and mechanical properties, we selected a synthetic route that utilized an aromatic hydrocarbon ''core.'' To achieve the high targeted levels of epoxy functionality, we chose to synthesize reactive oligomers with radial geometries. The aromatic core was extended radially with ''arms'' containing siloxane units and epoxy

endgroups using a "grafted from" synthetic approach. Less symmetrical multifunctional epoxysiloxanes derived from polybutadiene and synthesized via a "grafted to" approach have been described by Malik and Crivello.[12] This group also similarly used a "grafting to" approach to synthesize a trifunctional radial epoxysiloxane derived from trivinyl cyclohexene, and in some ways our architectures expand upon that example.[13] Radial propenyl ethers with aromatic cores, but no siloxane segments, have also been synthesized.[14] Interesting dendrimeric and hyperbranched siloxane/silane-containing polymers and copolymers have also been described in the literature,[15–25] as have radial hybrid epoxies synthesized via the hydrosilation of unsaturated epoxies onto siloxane cores (such as the silsequioxane and cyclotetra(methylhydrosiloxane) (D'_4) structures).[9,26–29] We chose to utilize hydrocarbon cores in our radial architectures to capitalize on the structural diversity and low cost of such core materials, as well as to potentially achieve high organic compatibility. The "grafting from" synthetic approach was chosen to facilitate the production of multiple target molecules (**6** and **7**) from a common intermediate, and can be extended to produce longer arms with multiple organic/inorganic repeat units. The basic physical and mechanical properties of two new hybrid epoxies **6** and **7** were examined in detail and compared with relevant benchmark materials to assess their potential utility for use in application areas such as high performance adhesives, sealants, and coatings.

EXPERIMENTAL SECTION

Characterization

Infrared spectra were obtained on a Midac M2200 spectrometer. ^{1}H, ^{13}C, and ^{29}Si-NMR spectra were obtained on either a Bruker Avance DPX400 400 MHz spectrometer or a Bruker AC-250 250 MHz instrument using CDCl$_3$ as the solvent, referenced to residual CHCl$_3$ at δ = 7.26 ppm for proton spectra and δ = 77.0 ppm for carbon data unless otherwise noted. ^{29}Si{H} data was collected using a DEPT (Distortionless Enhancement by Polarization Transfer) pulse sequence optimized for long range H—C—Si coupling, using a relaxation delay of >10 s.[30] This provided excellent ^{29}Si sensitivity enhancement and qualitative abundance data for peaks having similar chemical environments. For peaks with significant chemical shift differences (e.g., >10 ppm), relative abundance comparisons are not considered accurate based on data collected for several siloxane reference compounds. Internal standards were not used for most experiments to avoid potential overlap with sample peaks. The chemical shift of tetramethylsilane (TMS) using this pulse sequence is zero, and as

such reported chemical shifts are indirectly referenced to TMS. UV-Visible spectra were collected on a Perkin-Elmer Lamda 20 UV/Vis spectrometer. Gas chromatography was performed on a Perkin–Elmer GC using either an FID or MS detector. Gel permeation chromatography was performed isocratically in THF at 35°C and 1-mL flow rate using a Waters 515 pumping system, Waters 717 Plus Injector, PLGel 5 μm guard and Mixed C, 500A, and 100A columns. Calibration curves were created using polystyrene standards. A Waters 410 differential refractometer (RI) and UV detectors were utilized in series, and data from the RI detector is reported in this document. GPC M_n values are the average of two reproducible runs. Thermal curing properties were measured using a Q100 heat flux differential scanning calorimeter from TA Instruments. Experiments were performed from 30 to 300°C using a thermal ramp rate of 10°C/min. UV curing behavior was measured isothermally at 30°C using a Perkin–Elmer Diamond DSC differential scanning calorimeter equipped with an Exfo OmniCure 2000 spot curing light source. Irradiance values were ~ 50 mW/cm^2 as measured using graphite disk absorbers in the sample and reference cells. A bifurcated quartz light guide which transmitted wavelengths above ~ 160 nm was used to irradiate the samples. Sample size was maintained between 1.0 and 1.5 mg. Data was obtained under an ultra-high purity dry nitrogen environment, and samples were equilibrated/purged 1 min prior to each experimental run. Data reported is an average of at least three typical runs. A Surface Measurement Systems Dynamic Vapor Sorption-2000 was used to measure saturation moisture uptake. Dynamic mechanical analyses were performed on cured films using a TA RSA 3 solids analyzer at a frequency of 1 Hz. A Scientific Instruments Vortex Genie-2 mixer was used to blend resin mixtures. Epoxide titrations were performed using excess tetrabutyl ammonium bromide, perchloric acid, and crystal violet indicator according to Shell Analytical Method HC-427E-91. SiH titrations were performed using HgCl$_2$/MeOH to oxidize the silane, followed by potentiometric titration of the HCl by-product using methanolic potassium hydroxide titrant. Olefin titrations were performed using iodine monochloride in glacial acetic acid (Wijs solution), 0.100N sodium thiosulfate titrant, and starch indicator solution. Spectral and other analytical data for new compounds **3**, **6**, and **7**, as well as selected reference data for compounds **1** and **2**, are available in the supporting information for this article.

Materials

Tetra(allyl) bisphenol A was supplied by Bimax, USA (Cockeysville, MD). The siloxane

1,1,3,3-tetramethyldisiloxane (TMDS) was purchased from Clariant Corp. (Charlotte, NC). The silane bis (dimethylsilyl)ethane was purchased from Gelest (Tullytown, PA). Tris(triphenylphosphine)rhodium[I], allyl glycidyl ether, and vinylcyclohexene oxide were purchased from Aldrich (Milwaukee, WI). The photoinitiator (p-isopropylphenyl)(p-methylphenyl) iodonium tetrakis(pentafluorophenyl)borate was purchased from Gelest or sampled from Rhodia under the tradename Rhodorsil 2074. The photoinitiator UV9380C (a mixture consisting essentially of 45 wt % bis(dodecylphenyl)iodonium hexafluoroantimonate and 2.5 wt % isopropylthioxanthone in a C_{12}-C_{14} alkyl glycidyl ether reactive solvent) was sampled from GE Silicones. Epon 862 (bisphenol F diglycidyl ether chain with low levels of bisphenol F chain extension) and Epon 828 (bisphenol A diglycidyl ether with low levels of bisphenol A chain extension), also known as Epikote 862 and Epikote 828 respectively, were obtained as samples from Resolution Performance Products. ERL 4221 was obtained as a sample from Dow Chemical. CHVE was obtained as a sample from International Specialty Products. The ECMS 924 and PC 1000 epoxoysiloxanes were purchased from Gelest. Toluene was ACS grade, purchased from EMD Chemicals (Darmstadt, Germany). All reagents were utilized as received unless otherwise noted.

General experimental

Mixtures for compatibility studies

Mixtures of various resins with hybrid epoxies **6** and **7** were formed by manually mixing resins with a lab spatula in 20-mL glass lab vials until visibly uniform blends were obtained. Each vial was then subsequently mixed for 60 s using a Scientific Instruments Vortex Genie-2 vortex mixer. Vials were then allowed to sit undisturbed for a specified amount of time, at which point visual observations of compatibility were recorded.

Analysis of 1,1,3,3-tetramethyldisiloxane (''TMDS,'' 2)

Commercial grades of TMDS typically contain low levels of the 1,1,3,3,5,5-hexmethyltrisiloxane (HMTS). This impurity can readily be detected by GC/MS analysis and $^{29}Si\{H\}$ NMR. Representative spectral data is included in the supporting information. Within the context of this work, HMTS reacts similarly to TMDS and the small impurity peaks associated with the presence of HMTS can be traced through to the reaction products as noted for individual compounds hereafter. The HTMS impurity does not appear to affect the physical properties of

the radial hybrid epoxy compounds. The TMDS used for these studies typically contained less than 1 wt % HMTS impurity as determined by GC analysis (FID detector). Pure TMDS can be fractionally distilled from the HMTS contaminant as well if desired.

Analysis of tetra(allyl) bisphenol A (''TABPA,'' 1)

Structure **1** is an idealized structure in several ways. The all-para regioisomer of the bisphenol A starting material is one of several geometrical isomers produced during its synthesis, and several trace ortho-connected isomers can also be detected through detailed analyses of typical commercial bisphenol A. The all para representation is used hereafter for simplicity. More importantly, the sequence of allylation/Claisen rearrangement/allylation used to synthesize tetra(allyl) bisphenol A[31] from bisphenol A typically produces a mixture of primarily tetrafunctional and trifunctional allylated products. This has an impact on the nature of the products described herein related to their true level of functionality and in the interpretation of their analytical data. GC-MS, ^{1}H-NMR, and GPC analysis analyses of commercial tetra(allyl) bisphenol A showed it was ~ 90 wt % tetrafunctional material, with ~ 8 wt % trifunctional material (two primary isomers) and lower levels of unidentified impurities. GPC analysis produced a primary peak at 440 amu with a PDI of 1.1, and a small peak at 783 amu. Spectra and analytical data are provided in the supporting information. Titrated olefin values of 8.48.8 mequiv allyl/g resin were typically obtained for TABPA (82–85% of theory for the ideal structure). Tetrafunctional representations for TABPA and the hybrid epoxies derived from it (structures **6** and **7**) are used in the text for simplicity with the recognition that they are idealized. Some of the polydispersity reported for these new compounds is likely derived from the slight polydispersity measured for TABPA.

Tetra(allyl)bisphenol A/TMDS Adduct 3

A 1000-mL four-necked round bottom flask was equipped with a reflux condenser, addition funnel, internal temperature probe and magnetic stirrer and placed under light nitrogen flow. The flask was charged with 1,1,3,3-tetramethyldisiloxane (861.1 mL, 4.87 mol; ''TMDS''). The addition funnel was charged with a mixture of TMDS (50.0 mL, 0.28 mol) and tetra(allyl)bisphenol A (50.0 g, 0.129 mol; ''TABPA''). Approximately 7 mL of this solution was added to the stirred TMDS of the main reaction vessel. The pot temperature was raised to 50°C, at which point chlorotris(triphenylphosphine) rhodium (''Wilkinson's catalyst,'' 22.7 mg, 50 ppm Rh based

on mass of TABPA) was added to the reactor. The internal reaction temperature was then raised to 70°C. The TABPA/TMDS solution was added dropwise to the reactor over a period of ∼ 40 min, maintaining an internal temperature between 68 and 72°C during the addition. A steady reaction exotherm was observed during the addition. The reaction was stirred at ∼ 70°C for 15 min after the addition was complete. FTIR analysis indicated essentially complete consumption of the allyl double bonds as judged by the disappearance of the C=C stretching bands centered at 1638 and 1606 cm^{-1}. The reaction was allowed to cool to below 40°C, at which point two scoops (∼ 2 g) of activated carbon was added to the reactor. The resulting slurry was stirred for 1 h under ambient conditions and light nitrogen purge. The slurry was filtered, and excess TMDS was removed under vacuum. This recovered TMDS is pure (as determined by GC, ^{1}H-NMR and ^{29}Si analysis), and can be recycled. A pale yellow product was isolated (111.2 g, 93% based on ideal product structure, 102% based on ene value for TABPA of 8.8 mequiv ene/g resin): ^{1}H-NMR: δ 7.10–6.60 (m, 6H), 4.68 (m, 4H), 3.86 (t, 4H), 2.55 (t, 4H), 2.90–1.40 (m, 14H), 0.65 (t, 4H), 0.55 (t, 4H), 0.15 (s, 24H), 0.05 (s, 24H). ^{13}C{H} NMR (primary peaks): δ 155.0, 142.5, 130.0, 128.2, 125.7, 110.0, 70.2, 41.8, 34.5, 31.3, 24.0, 23.5, 18.2, 14.2, 9.2, 1.0, 0.0. ^{29}Si{H} NMR (primary peaks): δ 10.2, −6.0, −6.7. FTIR (KBr): 2957 (s), 2869 (m), 2119 (s), 1606 (w), 1499 (s), 1469 (m), 1411 (w), 1382 (w), 1253 (vs.), 1181 (w), 1060 (vs.), 908 (vs.), 838 (vs.), 769 (s), 705 (w), 626 (w). GC-MS (ei MS probe) M.+ calc. 924.5, found 924.5 (100), 925.5 (89), 926.5 (66), 927.5 (34) a small higher MW molecular ion at 998.5 is often observed, which is attributed to a small amount of hexamethyltrisiloxane present in the tetramethyldisiloxane starting material and the associated additional 74 amu. GPC analysis produced a single peak with M_n = 1444 and a polydispersity of 1.2. SiH titration: 4.0 mequiv SiH/g resin, 100% theoretical value (theoretical SiH value = 4.0 mequiv SiH/g resin; calculated from the typical titrated olefin content of the TABPA starting material of 8.8 mequiv olefin/g resin).

Radial cycloaliphatic epoxysiloxane 7; ''TSiCHO.''

Siloxane **3** (40.0 g, 160 mmol SiH based on a titrated SiH value of 4.0 mequiv SiH/g) was solvated in heptane (40 mL) in a 1-L four-necked flask equipped with magnetic stirring, an internal temperature probe, reflux condenser, and addition funnel. The reactor was placed under a gentle dry nitrogen purge. Vinylcyclohexene oxide (''VCHO,'' 22.9 mL, 175 mmol) was charged to the addition funnel. Approximately 1 mL of this epoxy was dripped into the

reaction pot, and the contents of the pot was raised to 50°C. Chlorotris(triphenylphosphine)rhodium (18 mg, 50 ppm based on siloxane mass) was added to the pot. The internal temperature of the reaction was then raised to 70°C, and the dropwise addition of VCHO was commenced. An exotherm was observed during the addition, which was complete after ∼ 40 min. The internal temperature of the reaction was maintained below 76°C during the addition process. This temperature was easily controlled via the VCHO addition rate and the application/removal of heat to the reaction vessel. The reaction was stirred at 70°C for 5 min after the addition was complete. FTIR analysis indicated the reaction was complete, as judged by the absence of a SiH band (2119 cm^{-1}) in the IR spectrum (occasionally, slightly longer postaddition stirring times are needed to achieve complete SiH conversion). The reaction was allowed to cool to room temperature, at which point activated carbon (∼ 1 g) was slurried with the solution for 30 min. The solution was filtered, and solvent was removed from the filtrate under vacuum to yield a pale yellow oil in essentially quantitative yield (60.0 g, 100% theoretical yield calculated based upon the SiH value of the starting silane **3**): ^{1}H-NMR: δ 7.10–6.80 (m, 4H), 6.60–6.75 (m, 2H), 3.90 (t, 4H), 3.10 (m, 8H), 2.55 (t, 4H), 2.25–0.75 (m, 42H), 0.65–0.56 (m, 4H), 0.44–0.55 (m, 4H), 0.45–0.35 (m, 8H), 0.1–$^-$0.1 (m, 48H). ^{13}C{H} NMR (primary peaks): δ 154.8, 142.3, 130.0, 128.6, 124.8, 110.0, 70.0, 53.0, 52.6, 51.5, 41.5, 35.2, 34.3, 32.0, 31.5, 31.0, 30.2, 30.0, 29.7, 26.9, 25.0, 24.0, 23.9, 23.6, 23.5, 18.5, 15.0, 14.9, 14.4, 9.5, 0.0. ^{29}Si{H} NMR (primary peaks): δ 8.5, 8.0, 7.9. FTIR (KBr): 2954 (s), 2916 (s), 1607 (w), 1501 (s), 1470 (m), 1453 (m), 1434 (m), 1411 (m), 1383 (w), 1360 (w), 1338 (w), 1312 (w), 1252 (vs.), 1184 (m), 1155 (m), 1057 (vs.), 973 (w), 886 (m), 840 (vs.), 795 (vs.), 706 (m), 683 (w), 543 (w), 474 (w). MS (ei probe) M.+ calc. 1421.8, found 1420.8 (81), 1421.8 (100), 1422.8 (84), 1424.8 (52), 1425.8 (25), a small higher MW molecular ion at 1497.7 was observed, which is attributed to the presence of a small amount of hexamethyltrisiloxane present in the tetramethyldisiloxane starting material. GPC analysis produced a main peak (M_n = 1330, 82.3 area %, PDI = 1.0) and a secondary peak (M_n = 2795, 17.7 area %, PDI = 1.2). Titrated epoxy equivalent weight (EEW): 370 g/mol epoxide (EEW for ideal chemical structure: 355 g/mol epoxide; EEW calculated from the SiH value of 4.0 mequiv/g for adduct **6**:374 g/mol epoxide).

Radial glycidyl epoxysiloxane 6; ''TSiGE.''

Siloxane **3** (50.0 g, 216 mmol SiH based on a titrated SiH value of 4.0 mequiv SiH/g) was solvated in

heptane (50 mL) in a 500-mL four-necked flask equipped with magnetic stirring, an internal temperature probe, reflux condenser, and addition funnel. The reactor was placed under a gentle dry nitrogen purge. Allyl glycidyl ether ("AGE," 25.6 mL, 216 mmol) and heptane (10 mL) were charged to the addition funnel. Approximately 1 mL of this epoxy solution was dripped into the reaction pot, and the contents of the pot were raised to 55°C. Chlorotris (triphenylphosphine)rhodium ("Wilkinson's catalyst," 22.7 mg, 50 ppm based on siloxane mass) was added to the pot. Trace amounts of undissolved catalyst were often observed, but the majority of the catalyst dissolved quickly. The internal temperature of the reaction was raised to 70°C, and the dropwise addition of the AGE solution was commenced. An exotherm was observed during the addition, which was complete after ~ 40 min. The internal temperature of the reaction was maintained below 75°C during the addition process. This temperature was easily controlled via the AGE addition rate and the application/removal of heat to the reaction vessel. The reaction was stirred at 70°C for 10 min after the addition was complete. FTIR analysis indicated trace levels of residual SiH (2119 cm^{-1}), so an additional 2 mL of AGE were added and the reaction was stirred an additional 10 min at 70°C. FTIR analysis then indicated complete SiH conversion. The reaction was allowed to cool to room temperature, at which point activated carbon (~ 1 g) was slurried with the solution for 30 min. The solution was filtered, and solvent was removed from the filtrate under vacuum to yield a pale yellow oil (70.4 g, 94% theoretical yield calculated based upon the SiH value of the starting silane **3**): ^{1}H-NMR: δ 7.20–6.80 (m, 4H), 6.60–6.75 (m, 2H), 3.85 (t, 4H), 3.75–3.60 (m, 4H), 3.55–3.25 (m, 12H), 3.10 (m, 4H), 2.75 (t, 4H), 2.55 (m, 8H), 1.75 (m, 4H), 1.60 (m, 18H), 0.55 (m, 16H), 0.02 (m, 48H). ^{13}C{H} NMR (primary peaks): δ 154.4, 142.1, 129.8, 128.3, 124.4, 110.0, 73.8, 73.7, 71.1, 71.0, 69.8, 50.4, 43.7, 43.6, 41.2, 34.0, 31.5, 30.9, 28.6, 23.5, 23.2, 22.3, 18.1, 14.2, 14.0, 13.8, 11.3, 0.1, 0.0. ^{29}Si{H} NMR (primary peaks): δ 7.7, 7.6, 7.5, 7.2. FTIR (KBr): 3048 (m), 2955 (versus), 2931 (versus), 2870 (s), 1740 (w), 1664 (w), 1654 (w), 1607 (m), 1560 (w), 1500 (s), 1471 (m), 1438 (m), 1384 (m), 1360 (m), 1340 (m), 1253 (versus), 1183 (m), 1156 (m), 1133 (m), 1106 (s), 1058 (versus), 952 (m), 909 (m), 840 (versus), 797 (versus), 705 (m), 684 (m), 668 (w). MS (ei probe) M.+ calc. 1381.7, found 1380.7 (87), 1381.7 (100), 1382.7 (82), 1383.7 (49), 1384.7 (25), a small higher MW molecular ion at 1455.2 is usually observed, which is attributed to the presence of a small amount of hexamethyltrisiloxane present in the tetramethyldisiloxane starting material. GPC analysis produced a primary peak ($M_n = 1437$, 73.2 area %, PDI = 1.0) and a second smaller peak ($M_n = 3159$, 26.8 area %, PDI = 1.2). Titrated epoxy equivalent

weight (EEW): 382 g/mol epoxide (EEW for ideal chemical structure: 345 g/mol epoxide; EEW calculated from the SiH value of 4.0 mequiv/g for adduct **3**:373 g/mol epoxide).

RESULTS AND DISCUSSION

Synthesis and characterization

Selective hydrosilation was chosen as the basic synthetic methodology for the organic/inorganic hybrid target molecules of this study because of its versatility and the fact that in many cases very high yield and by-product free processes can be developed, even on manufacturing scales. We sought to extend the work of previous studies into new architectures containing hydrocarbon cores and higher levels of functionality through the use of sequential hydrosilation reactions, which alternately introduced organic and inorganic segments into the molecular structure in a "grafting from" type process. The arms were then endcapped with reactive epoxy groups to form crosslinkable liquid products. The basic synthetic approach, as applied to target molecules **6** and **7**, is shown in Scheme 1. Generally, a multifunctional olefin is utilized as the "core," which is extended with siloxane units via hydrosilation in the presence of excess bis(SiH)-functional siloxane. The use of an acceptably volatile siloxane is essential, as the excess reagent is vacuum distilled from the reaction product and recycled (see Experimental section). The resulting tetra(SiH)-functional intermediate is then endcapped with an unsaturated epoxy in a second hydrosilation reaction to produce the hybrid epoxy product.

As shown in Scheme 1, for much of our work we utilized tetra(allyl) bisphenol A ("TABPA," **1**) as the multifunctional olefinic core, 1,1,3,3-tetramethyldisiloxane ("TMDS," **2**) as the inorganic siloxane unit, and vinylcyclohexene oxide ("VCHO," **4**) as the epoxy endcapping agent. The initial hydrosilation of TABPA with a large excess (20 equiv, $\sim$ fivefold excess) of TMDS yielded tetra(SiH)-functional compound **3**. It is notable that the excess siloxane used for this step functions both as a reagent and solvent for the process. After the investigation of a number of Pt and Rh catalysts for use in this conversion, it was found that chlorotris(triphenylphosphonium)Rh (ClRh(PPh$_3$)) provided an optimal balance of reaction rate, selectivity, and product stability. Certain Pt^{II} catalysts were also successfully employed, but due to the potential incompatibility of SiH and epoxy functionality (especially cycloaliphatic epoxy) in the presence of Pt,[11,32–34] the use of Wilkinson's catalyst was preferred given subsequent reaction steps involving epoxy endcapping groups. After vacuum removal and recovery of excess TMDS, endcapping
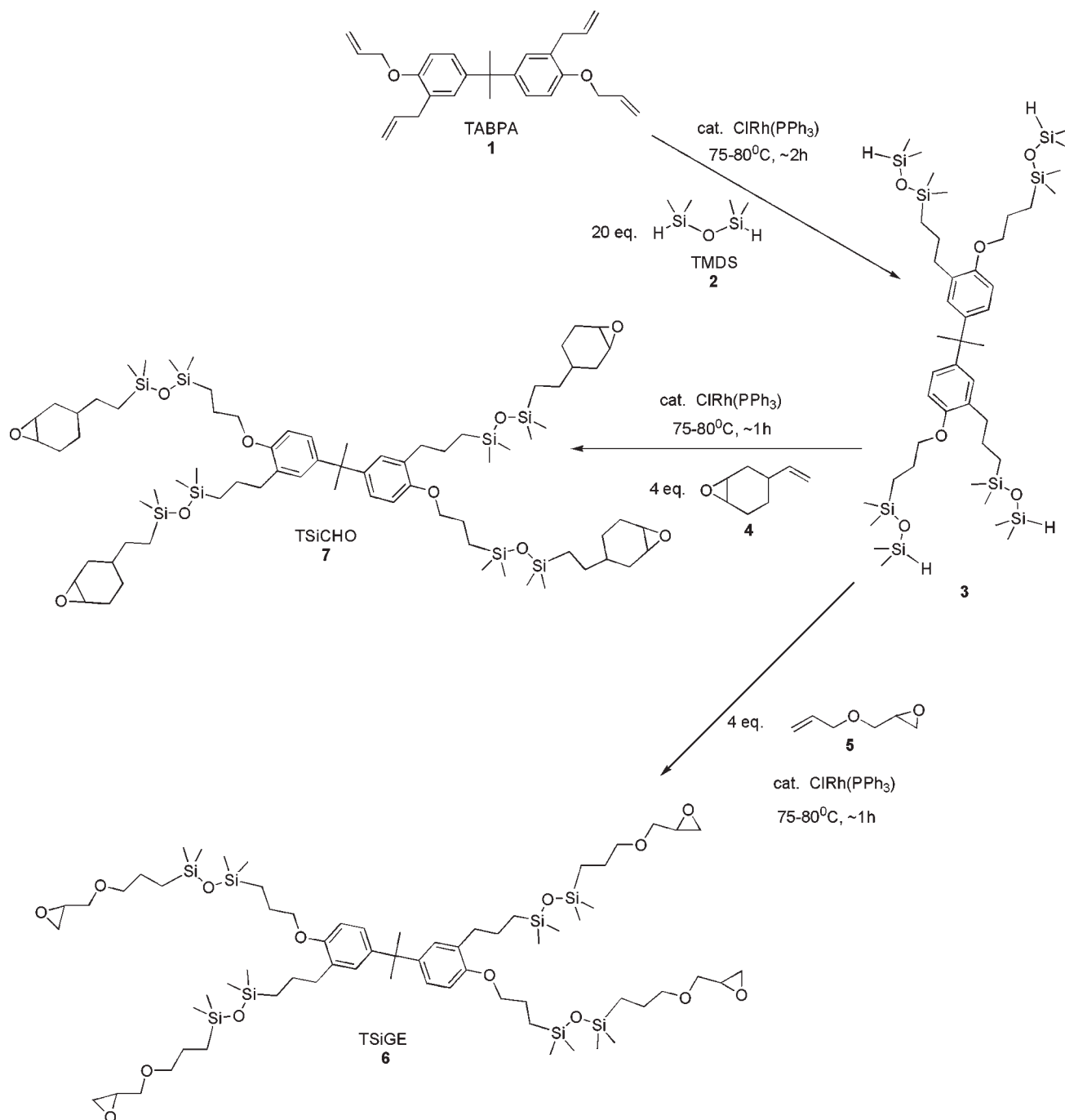
Scheme 1 Synthesis of radial hybrid epoxysiloxanes **7** (''TSiCHO'') and **6** (''TSiGE'').

of intermediate **3** with stoichiometric unsaturated epoxy, VCHO, provided radial hybrid epoxysiloxane **7** (''TSiCHO''). Although solvent can be utilized to control the exotherm of this step, it was found that excellent thermal control could be maintained simply by monitoring the internal reaction temperature and varying the rate of addition of the VCHO endcapping molecule so as to hold the internal temperature close to 80°C. The progress of the reaction was readily monitored by following the disappearance of the

SiH IR absorbance at 2119 cm^{-1}. By endcapping SiH-functional intermediate **3** with allyl glycidyl ether (AGE), the radial glycidyl epoxysiloxane **6** (''TSiGE'') was similarly obtained. As detailed in the Experimental section, procedures were similar, but not identical, when using AGE in place of VCHO as the endcapping agent.

There are several aspects of this synthetic approach that warrant additional comment. First, several authors have previously reported that certain

SiH-terminal siloxanes and silanes can selectively undergo hydrosilation at only one of the two available reactive SiH groups when appropriate mild hydrosilation catalysts and conditions are determined and utilized. It appears that once the first end of the molecule reacts, the second SiH group is deactivated to some extent (at least for short chain siloxanes and silanes).[13,35,36] This basic premise has been verified in our own labs for several bis(SiH)-functional siloxanes, but in our hands selectivity (i.e., reaction of only one end of the siloxane on essentially all of the molecules) was sometimes difficult to completely control. For our multifunctional radial systems, any significant amount of reaction at both ends of the siloxane will result in rapid molecular weight increase and fairly quickly to gelation of the system. We have found that, as long as the excess siloxane used for the hydrosilation of olefin groups is easily removed via vacuum distillation and recovered for recycling, the use of such excess siloxane to statistically favor reaction of only one end of the bis(SiH) unit is the most practical and reliable methodology. Overall, the approach exploits both the differential reactivity of the SiH groups during the reaction and the statistical aspects of using excess reagent. Crivello and Bi et al.[13] have described the hydrosilation of VCHO and other unsaturated epoxies onto only one SiH group of low–molecular-weight silane-terminal siloxanes such as TMDS to produce SiH-functional epoxy molecules. These intermediates were subsequently grafted onto cer-

tain olefins. In our hands, this alternative ''grafting to'' synthetic approach was successfully utilized to produce both linear and radial molecules (such as 6, 7, and related linear analogs), however, the potential chemical incompatibility of SiH, epoxy, and trace metal catalyst[37–39] was considered a potential synthetic and storage issue when large scale processes are undertaken. We have determined that the utilization of a large excess of TMDS or similar low-molecular-weight siloxane component in our current approach results in a robust synthesis on larger (kg) scales and is quite economically and environmentally desirable given the fact that the TMDS can be recovered and reused. This allows for a very controllable, ''solvent-free'' synthesis with minimal waste or by-products. One limitation of this synthetic approach is that the siloxane component (or any diene component used for arm extension) must be recoverable via vacuum distillation under practical conditions. We have successfully utilized 1,1,3,3-tetramethyldisiloxane (TMDS), 1,1,3,3,5,5-hexamethyltrisiloxane, and bis(dimethylsilylethane) in this synthetic process. Our discussions hereafter are limited to molecules 3, 6, and 7, derived from TMDS inorganic units.

^{29}Si{H} NMR was very useful for following the conversion of tetrasilane 3 to epoxysiloxane derivatives 6 and 7. The DEPT ^{29}Si{H} spectrum and chemical structure of hybrid tetrasilane 3 are shown in Figure 1. Two primary sets of peaks are observed in
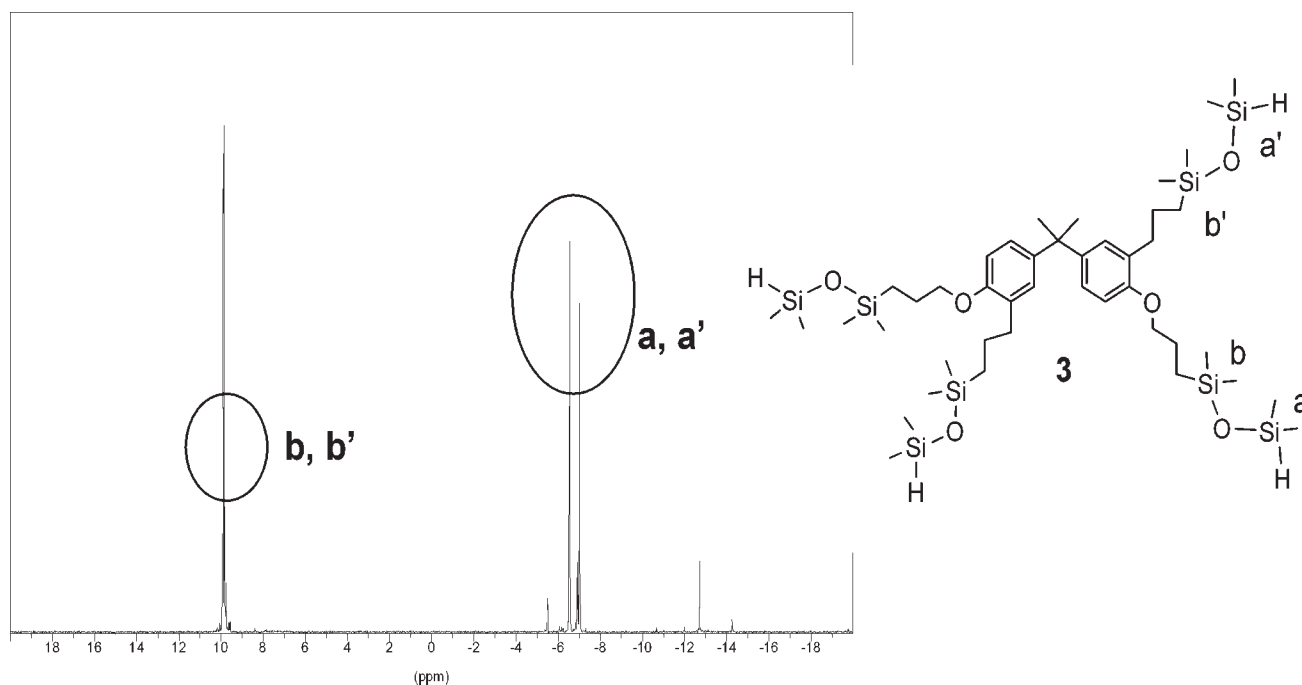

Figure 1 ^{29}Si-NMR of tetrasilane **3**.

the $\delta = -7$ and $\delta = 10$ ppm regions. These peaks are assigned to the terminal —OSiMe$_2$H (labeled a, a') and internal —RSiMe$_2$O— (labeled b, b') silicon atoms, respectively, based on reference spectra. As expected, both groups of resonances exhibited two primary peaks reflecting the chemical nonequivalence of the Si atoms on arms attached to the phenoxy oxygens and those attached directly to aromatic carbons of the bisphenol A core. On the basis of reference spectra, the impurities in the −13 ppm region are believed to originate from siloxane oligomers formed as a result of trace moisture being present in the reaction vessel, solvents, and raw materials. The third smaller peak in the −7 ppm region ($\delta = -5.5$) is tentatively assigned to be the —OSiMe$_2$H Si atoms of molecules with only three arms which are derived from analogous three-armed impurities in the TABPA starting material.

The conversion of tetrasilane **3** to tetraepoxide **7** is easily observed by ^{29}Si{H} NMR, shown in Figure 2. Hydrosilation of the terminal silane SiH moieties (Si atoms a and a') with vinylcyclohexene oxide resulted in the disappearance of peaks in the −7 ppm region and the appearance of new peaks in the 5–10 ppm region. This is consistent with the conversion of terminal —OSiMe$_2$H groups to —OSiMe$_2$R groups. As can be seen in the expansion inset, the peak cluster in the 7 ppm region consists of six main singlets. One singlet is downfield at 7.7 ppm, with five relatively shielded singlets grouped closely in the 7.3–7.5 ppm region. Four of these peaks are expected for Si atoms c, c', d, and d' of the idealized structure **7** shown. The other two peaks may relate

back to trifunctional impurities in the starting material TABPA and/or various diastereomers resulting from the chiral centers of VCHO. The previously noted impurity around −15 ppm is carried through into the final product. The analogous conversion of silane **3** to the hybrid glycidyl epoxy **6**, using allyl glycidyl ether in place of vinylcyclohexene oxide, has been followed in the same way using ^{29}Si{H} NMR.

As detailed in the Experimental Section, the structures of compounds **6** and **7** were also confirmed by ^{13}C and ^{1}H-NMR, FTIR, EI-MS, GPC, and epoxy titration.

Thermal and radiation curing studies

Thermal cure

The basic thermal curing behavior of hybrid epoxysiloxanes **6** and **7**, along with several reference epoxy resins, was measured using differential scanning calorimetry (DSC). The commercial resins used as benchmarks are shown in Figure 3, and were selected to represent typical hydrocarbon and siloxane-based epoxies. Samples were heated from 30 to 300°C at a rate of 10°C/min under a nitrogen atmosphere. Thermal curing was examined using both a cationic curing agent (Rhodorsil 2074) and a nucleophilic/anionic curing agent (2-ethyl-4-methylimidazole, 2E4MZ). In all cases visually uniform mixtures were obtained prior to DSC analysis. The enthalpy of polymerization (ΔH_p), peak temperature (temperature of maximum heat flow, T_p), and calculated functional group conversion
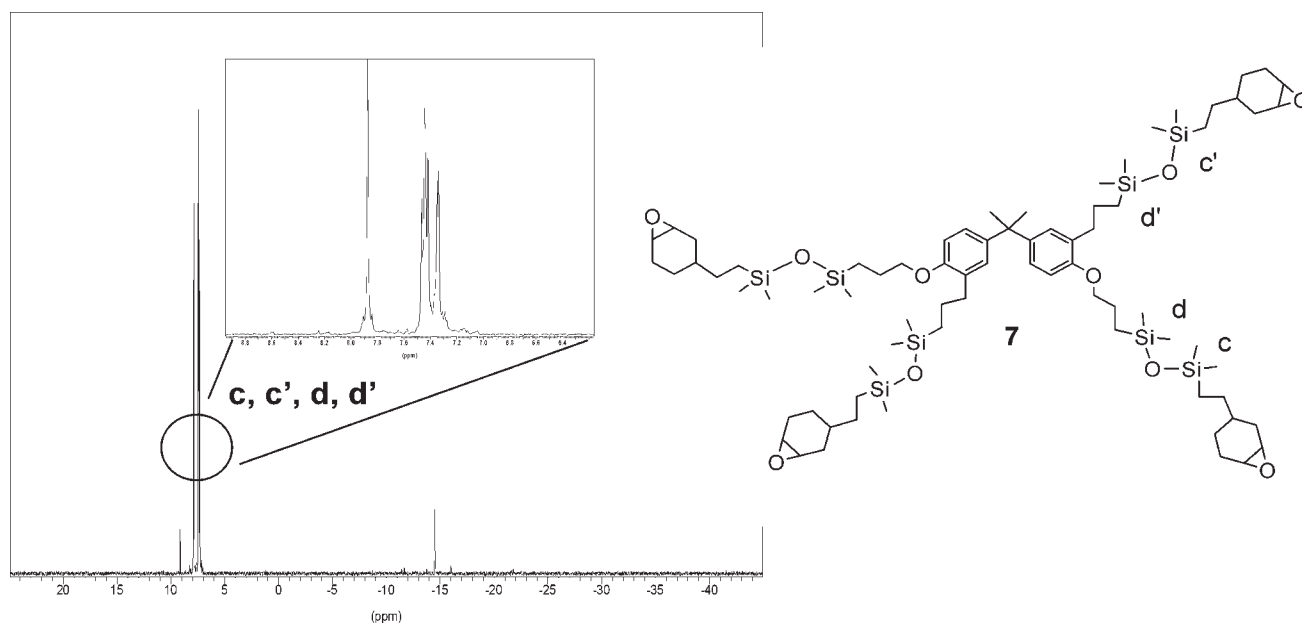

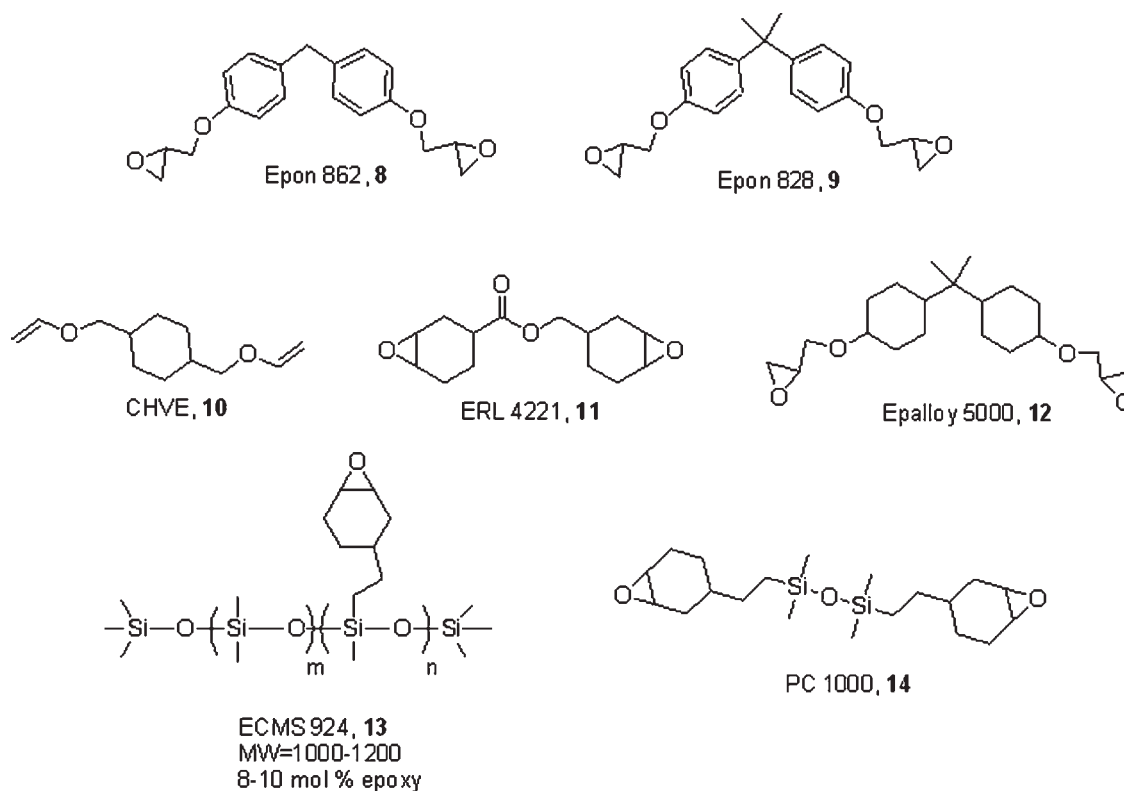**Figure 2** ^{29}Si-NMR of hybrid epoxy **7**.

Figure 3 Commercial epoxy resins used for comparative studies.

were recorded for each experiment. Conversions were calculated using theoretical reaction enthalpy values of −97 kJ/mol (that of cyclohexene oxide) for cycloaliphatic epoxy molecules and −94.5 kJ/mol (that of propylene oxide) for glycidyl epoxy molecules.[40] Conversion calculations are based on an epoxy hompolymerization mechanism, although curing with 2E4MZ also introduces a low level of an epoxy-amine curing mechanism as well. Theoretical epoxy equivalent weights were used for all approximate conversion calculations. Results are summarized in Table I.

In general, all siloxane and hydrocarbon epoxy molecules cured efficiently using the Rhodorsil 2074 iodonium salt to initiate thermal cationic cure. Although not represented in the data shown, thermal cure kinetics were good (fairly sharp DSC exotherm peaks) for both cycloaliphatic and glycidyl epoxy resins. Calculated conversions for the resins examined were between 66 and 94%. Conversion was high for both new tetrafunctional epoxysiloxanes **6** and **7**, perhaps facilitated by the segmental mobility of the siloxane units and the relatively high equivalent weight of these compounds. As anticipated, only the glycidyl-functional materials reacted efficiently when cured with the imidazole 2E4MZ. Among the glycidyl resins tested, the TSiGE epoxysiloxane **6** exhibited the highest conversion.

Radiation cure

The UV curing reactivity of hybrid epoxies **6** and **7** were compared with several of the reference epoxies using differential photocalorimetry. All systems were photoinitiated using 4 wt % of the UV9380C diaryliodonium antimonate salt solution (∼ 2 wt %

TABLE I
Thermal Curing Data for Representative Epoxy Resins

Resin	Curing Agent	$-\Delta H_p$ (J/g)	T_p (°C)	Conversion (%)
TSiCHO, **7**	0.5 wt % R2074[a]	230	169	84
	5.0 wt% 2E4MZ[b]	74	237	27
TSiGE, **6**	0.5 wt % R2074	248	152	90
	5.0 wt% 2E4MZ	252	146	92
Epon 828, **9**	0.5 wt % R2074	494	191	89
	5.0 wt% 2E4MZ	470	125	84
ERL 4221, **11**	0.5 wt % R2074	724	166	94
	5.0 wt% 2E4MZ	43[c]	221	6
Epalloy 5000, **12**	0.5 wt % R2074	355	122	66
	5.0 wt% 2E4MZ	63	126	12
PC 1000, **14**	0.5 wt % R2074	351	138	69
	5.0 wt% 2E4MZ	37	234	7

[a] R2074, Rhodorsil 2074 (tolylcumyl)iodonium tetrakis (pentafluorophenyl) borate.
[b] 2E4MZ, 2-ethyl-4-methylimidazole.
[c] Still reacting at $T > 300$°C, accurate enthalpy baseline difficult to discern.

TABLE II
Photopolymerization Enthalpic and Kinetic Data

Resin	$-\Delta H_p$ (J/g)	time$_{\text{o-p}}$ (min)	Conversion (%)
TSiCHO, **7**	164	0.14	63
TSiGE, **6**	84	0.22	34
Epon 828, **9**	169	0.13	30
ERL 4221, **11**	90	0.12	12
Epalloy 5000, **12**	177	0.17	33
PC 1000, **14**	350	0.04	69

active diaryliodonium salt). The enthalpy of polymerization (ΔH_p), time to peak exotherm once the lamp shutter was opened ($t_{\text{o-p}}$), and calculated functional group conversion were measured for each experiment. The samples were irradiated at 30°C through a bifurcated quartz light guide using an Omnicure 2000 Hg arc lamp spectral output at a light intensity of $\sim$ 50 mW/cm^2. Other data collection parameters are detailed in the experimental section.

The photopolymerization data is summarized in Table II, and selected data is shown in Figure 4. PC1000 clearly exhibited the fastest polymerization kinetics, as evidenced by its onset-to-peak time of only 0.04 min. TSiCHO, ERL 4221, and Epon 828 all had similar calculated onset-to-peak times (0.12–0.14 min), and from Figure 4 it can be seen that TSiCHO exhibited the best photopolymerization kinetics of these three resins, followed by Epon 828. It should be noted that the PC1000 data is not plotted in Figure 4 to compress the Y scale of the graph, and that this resin was observed to photopolymerize significantly faster than the others shown on the plot. The two cycloaliphatic epoxysiloxanes TSiCHO and PC1000 exhibited, by far, the most extensive chemical conversion in these photoDSC experiments. This is attributed to the unique combination of the typical cationic reactivity of cycloaliphatic epoxies and the high segmental mobility imparted to these
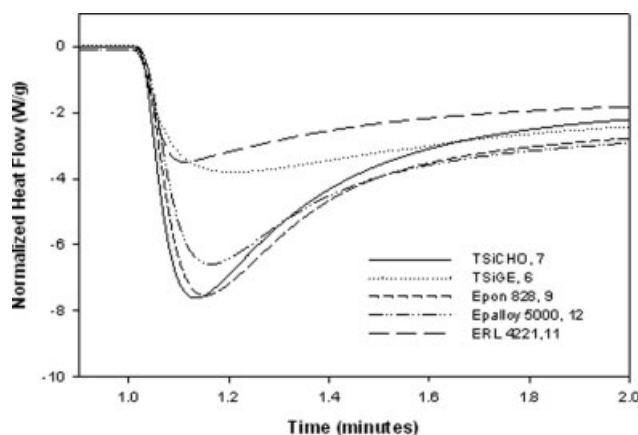

Figure 4 PhotoDSC overlay of selected epoxies.

two materials by their siloxane segments. The unusually high photopolymerization conversion and good UV curing kinetics exhibited by TSiCHO and PC1000 certainly represent potential utility in application areas involving radiation curing. Although the aromatic core of compound **7** overlaps with some of the photoinitiator absorbance, for thin film samples this did not adversely affect UV curing. The TSiGE glycidyl-type epoxysiloxane exhibited generally poor photopolymerization kinetics and conversion, consistent with other data collected for UV cured samples of this material to be detailed hereafter. It appears that in this resin the mobility imparted by the siloxane units is offset by the lower reactivity of the glycidyl epoxy endgroups, although why this material photopolymerizes even slower than other glycidyl epoxy benchmarks such as Epon 828 and Epalloy 5000 is currently not clear.

The photopolymerization kinetics, conversion, and mechanical properties exhibited by any of these epoxies can be varied widely through formulation with various cationically reactive materials such as polyols, vinyl ethers, and oxetanes. This lead us to examine the hydrocarbon compatibility and physical properties of the materials as described in the following sections.

Material properties

Hydrocarbon compatibility

Because applications such as adhesives, sealants, and coatings will often involve blended resin systems, we investigated the organic compatibility of epoxysiloxanes **6** and **7** with several representative hydrocarbon resins. The structures of the resins used for this compatibility study are shown in Figure 3. We included two common aromatic glycidyl ethers, Epon 828 (**9**) and Epon 862 (**8**), and aliphatic resins such as ERL 4221 (**11**) Epalloy 5000 (**12**), and CHVE (**10**). For comparison, hydrocarbon/epoxysiloxane blends were also made with two commercial epoxysiloxanes ECMS 924 (**13**) and PC 1000 (**14**). We examined blends of 5, 10, and 20 wt % of the various hybrid epoxies in each hydrocarbon resin. As described in the Experimental section, mixtures were manually blended and subsequently agitated for 60 s in a vortex mixer. Compatibility observations were made visually at time = 0 (just after mixing), t = 16 h, and time = 168 h. Results are summarized below, and tables of compatibility data are available for all mixtures through the supporting information for this article.

In the blends containing 20 wt % of the hybrid epoxies **6**, **7**, **13** and **14**, phase separation was observed for TSiCHO (**7**) and TSiGE (**6**) within 16 h

in both aromatic epoxy resins (**8** and **9**). Blends of hybrids **6** and **7** with all of the aliphatic hydrocarbon resins (**10**, **11**, and **12**) were observed to be homogenous, clear solutions at the end of the 1 week maximum observation time. In comparison, the ECMS-924 epoxysiloxane (**13**) was found to be incompatible with all hydrocarbon resins (aromatic and aliphatic) save CHVE (**10**). PC 1000 (**14**) formed clear solutions with all aliphatic resins, and formed apparently stable translucent/hazy blends with the aromatic epoxies for the entire 1 week period. Similar overall results were observed for the mixtures containing 10 wt % of the hybrid materials. For the mixtures containing 5 wt % of the hybrid resins, hybrid epoxy **7** eventually still phase separated from both aromatic epoxies, whereas epoxy **6** remained a hazy mixture with the aromatic epoxies out to 1 week. Apparently, the glycidyl endgroups of **6** render it slightly more compatible with glycidyl hydrocarbon epoxies relative to the hybrid cycloaliphatic epoxy resin **7**. The ECMS-924 hybrid did not macroscopically phase separate from any of the hydrocarbon resins at the 5 wt % level, but the mixtures with both aromatic epoxies and ERL 4221 remained a milky-white suspension for the 1 week period. It is likely that this turbid suspension would phase separate given sufficient time, but that kinetics were slow because of the relatively higher molecular weight/polymeric structure of ECMS-924 and the high viscosity of the blended system.

In summary, PC 1000 was clearly the most organic-compatible epoxysiloxane studied. Experimental resins **6** and **7** exhibited intermediate organic compatibility. These resins were quite miscible with aliphatic materials, but less so with aromatic epoxy resins. ECMS-924 exhibited the most limited hydrocarbon compatibility of the epoxysiloxanes studied.

Hydrophobicity

An important design principle for this study was that the siloxane segments of compounds **6** and **7** would impart improved hydrophobicity relative to typical hydrocarbon epoxy materials. Saturation moisture uptake at 85°C/85% relative humidity was used to examine this expectation. The various epoxy resins tested were formulated with 0.5 wt % Rhodorsil 2074 cationic photo/thermal iodonium salt initiator (unless otherwise noted), and $\sim$ 100 μm films were formed using a drawdown bar. The films were first UV cured (unfiltered 100 W Hg arc lamp) using a UV dose of $\sim$ 5.3 J/cm^2 ($\sim$ 3.0 J/cm^2 UVA, 2.1 J/cm^2 UVB, 0.2 J/cm^2 UVC, 2.1 J/cm^2 UVV), followed by a thermal cure for 1 h at 175°C unless otherwise noted in Table III below. This rigorous dual UV/thermal cure profile was chosen to achieve maximum chemical conversion to best evaluate funda-

TABLE III
Saturation Moisture Uptake Comparison

No.	Resin	% mass gain	Comments
1	TSiCHO, 7	0.6	Flexible, tough
2	TSiGE, 6 (0.5 % cationic initiator)	1.4	Rubbery, weak
3	TSiGE, 6 (1.0 % cationic initiator/200°C)	1.6	Rubbery, weak
4	ERL 4221, 11	5.0	Rigid, brittle
5	Epon 828, 9 (cationically cured/200°C)	1.8	Rigid, tough
6	Epon 828, 9 (imidazole cured)	1.9	Rigid, tough
7	Epalloy 5000, 12	2.0	Rigid, tough
8	PC1000, 14	0.3	Flexible, tough
9	ECMS-924, 13	0.2	Rubbery, weak
10	Sycar® siloxane thermoset	0.1	Rigid, brittle

mental molecular/matrix characteristics by minimizing extent of cure variability among the different resins. Epon 828 was also thermally cured using 5 wt % 2-ethyl-4-methylimidazole (175°C, 1.5 h) as an example of an imidazole cured glycidyl epoxy system. The Sycar® siloxane thermoset reference was cured using 100 ppm Pt^0-D$_4^v$ complex (200°C/1 h). Cured films were allowed to equilibrate for at least 24 h under ambient conditions, and were then placed in the test chamber of a dynamic vapor sorption (DVS) apparatus, predried for 2 h at 100°C/0% relative humidity, and subsequently exposed to 85°C/85% RH conditioning until moisture uptake ceased and total mass equilibrated. Moisture pickup (mass increase) was reported as a percentage of the original sample mass. Results are summarized in Table III.

Cationically cured epoxysiloxane **7** was significantly more hydrophobic than the benchmark hydrocarbon materials ERL 4221, Epon 828 (cured either cationically or anionically with 2E4MZ) and Epalloy 5000. It is notable that the common UV curable epoxy ERL 4221 is the most hydrophilic, (presumably due to the large number of polar ester groups present in this cured matrix), and that epoxysiloxane **7** exhibits nearly an order of magnitude lower moisture uptake. Somewhat unexpectedly, glycidyl epoxysiloxane **6** exhibited higher moisture uptake than compound **7**, on the order of that measured for Epon 828. Experiment no. 3 verified this was not due to insufficient initiator level or cure temperature. PC 1000 and ECMS-924 represent commercial organic/inorganic hybrid materials. PC 1000 is structurally somewhat similar to epoxysiloxanes **6** and **7**, whereas ECMS-924 is a more silicone-like resin. Both of these resins have higher siloxane content than **7**, and their slightly lower saturation moisture uptake

TABLE IV
TGA Weight Loss Analysis of Various Homopolymerized Epoxies

No.	Epoxy	temperature of 1% wt. loss (°C)	wt. loss at 300°C (%)	wt. loss at 400°C (%)
1	TSiCHO, 7	239	6	17
2	TSiGE, 6[a,b]	148	19	30
3	Epon 828, 9[b]	279	1	8
4	Epalloy 5000, 12	125	57	85
5	ERL 4221, 11	198	17	62
6	PC 1000, 14	236	15	58
7	ECMS 924, 13	215	6	8

[a] 1 wt % Rhodorsil 2074 used as initiator to maximize cure.
[b] Thermal cure of 200°C/1 h used based on DSC experimental data

reflected this compositional feature. The highly crosslinked, high silicone content Sycar siloxane thermoset provided an example of the extremely low moisture uptake typical of materials with predominantly silicone character. Overall, the data of Table III shows that radial cycloaliphatic epoxysiloxane **7**, and to a lesser extent glycidyl epoxysiloxane **6**, exhibited hydrophobicity intermediate between hydrocarbon materials and siloxane materials as was anticipated.

Additionally, upon aging at 85°C/85% RH for ~ 1000 min, the acid cured epoxysiloxane materials exhibited varying degrees of mass loss after initial saturation with moisture. This mass loss after saturation ranged from significant for ECMS-924 **13** (~ 15 wt %) to minimal for TSiCHO **7** (~ 0.2 wt %) and PC1000 **14** (~ 0.1 wt %). An intermediate value was observed for TSiGE **6** (~ 0.6 wt %). Similar mass losses upon extended aging at 85°C/85% RH were not observed for the various acid cured hydrocarbon epoxy resins or the Pt cured Sycar siloxane resin. The origin of this observation is under continued investigation, but may be the result of acid catalyzed hydrolysis of the siloxane segments of the cationically cured materials at elevated temperature and humidity levels.

Thermal stability

The thermal stability of hybrid epoxies **6** and **7** was compared with hydrocarbon and siloxane-containing benchmarks using TGA weight loss analysis. Results are summarized in Table IV. Samples were analyzed under nitrogen from 30 to 400°C using a temperature ramp rate of 10°C/min. As in the DVS experiments discussed earlier, the attempt was made to test a ''fully cured'' cationically homopolymerized sample of each epoxy, and samples were cured as described in that section.

Hybrid epoxy **7**, Epon 828, PC 1000, and ECMS 924 all exhibited temperatures of 1% weight loss over 200°C. Of these, hybrid epoxy **7**, Epon 828, and ECMS 924 also exhibited relatively low weight loss at 300 and 400°C. Such low weight loss is expected of the siloxane-containing materials, and the thermal stability of cured Epon 828 reflects the stability of its aromatic backbone. The thermal stability of PC1000 began to degrade rapidly above 300°C. Hybrid epoxy **6** showed higher weight loss than expected in all three categories despite exhibiting extensive thermal cationic cure by DSC as detailed in the thermal curing section earlier. The reasons for the significant differences in weight loss and thermal stability between cationically cured epoxysiloxanes **6** and **7** is under further investigation. The low weight loss of TSiCHO **7** indicates progress has been made toward reducing weight loss via the incorporation of siloxane segments, although molecules designed with higher siloxane levels are expected to show even better thermal stability by analogy to those containing siloxane cores.[26]

Dynamic mechanical analysis

The bulk mechanical properties of selected cured film samples were compared using dynamic mechanical analysis. Films of several samples were formed and cured using procedures identical to those described in the Thermal Stability and Hydrophobicity Sections. Analyses were performed in the tensile rectangle geometry at a frequency of 1 Hz using small strains well within the linear region of the cured materials as determined by separate strain sweep experiments. The T_g (taken as the peak in the loss factor/tan δ curve) as well as the elastic modulus (E') 50°C above and below T_g are summarized in Table V.

The TSiGE sample exhibited a lower T_g and rubbery modulus relative to the TSiCHO material. As noted in the Thermal Cure section and summarized

TABLE V
Dynamic Mechanical Analysis of Hybrid and Hydrocarbon Epoxy Films

No.	Resin	T_g (°C)	Glassy elastic modulus (E'; Pa)	Rubbery elastic modulus (E'; Pa)
1	TSiCHO, 7	79	6.57×10^8	3.77×10^7
2	TSiGE, 6[a,b]	0	1.17×10^9	9.96×10^6
3	Epon 828, 9[b]	168	1.04×10^9	7.31×10^7
4	Epalloy 5000, 12	78	2.00×10^9	2.07×10^7

[a] 1 wt % Rhodorsil 2074 used as initiator to maximize cure.
[b] Thermal cure of 200°C/1 h used based on DSC experimental data.

in Table I, DSC data indicated that this effect does not seem to be due to incomplete cure. The use of a higher level of iodonium catalyst and higher cure temperature for the TSiGE test sample was an additional attempt to maximize chemical conversion for the DMA analysis. The reproducible differences in T_g and modulus measured here are somewhat surprising given the identical nature of the core and siloxane segments for both **6** and **7**. It is possible that the slightly longer, ether-containing glycidyl segments of TSiGE are responsible for the differences in mechanical properties observed relative to TSiCHO, which contains shorter cycloaliphatic hydrocarbon segments between crosslinks. The future synthesis of structural analogs of compounds **6** and **7** may help to clarify such differences.

All four of the epoxies tested exhibited reasonably high rubbery moduli, with Epon 828 maintaining the highest elastic modulus at temperatures greater than T_g. In general, the moduli observed indicate the materials maintain useful mechanical strength even above their T_g. The TSiCHO sample exhibited a slightly lower glassy modulus and, along with Epon 828, a relatively small overall change in modulus it was heated through T_g. This effect is potentially useful in applications which require a low stress/flexible material in the glassy region in addition to useful strength in the rubbery region.

CONCLUSIONS

Practical synthetic methodology for cleanly introducing alternating siloxane and hydrocarbon segments into multifunctional/radial epoxysiloxane molecules was developed. The prototype radial epoxysiloxanes TSiCHO (**7**) and TSiGE (**6**), which possess an aromatic core and that incorporate siloxane segments derived from 1,1,3,3-tetramethyldisiloxane, represent the synthetic viability and flexibility of the process. Of the several analytical techniques used to characterize the new molecules, ^{29}Si-NMR proved to be the most useful and interesting.

Both compounds **6** and **7** exhibited high conversions when thermally cured cationically using an iodonium salt initiator. As expected, only the glycidyl epoxy **6** exhibited efficient curing when an imidazole catalyst was used. Differential photocalorimetric analysis demonstrated that the cycloaliphatic hybrid epoxy **7** UV cures efficiently, whereas the glycidyl epoxy analog **6** exhibits generally poor UV cure kinetics and conversion relative to **7** and other common light curable epoxies.

Comparisons of the material properties of hybrid epoxies **6** and **7** to several common hydrocarbon and siloxane-containing benchmarks indicated that their properties were intermediate between those of siloxane and hydrocarbon resins, as anticipated. The hydrocarbon compatibility of compounds **6** and **7** was generally good, although slightly lower than the PC1000 epoxysiloxane. In moisture uptake experiments of cationically cured films, cycloaliphatic epoxy **7** exhibited siloxane-like levels of moisture uptake, whereas the glycidyl analog **6** was best classified as being similar to a hydrophobic hydrocarbon. The thermal stability of thermal cationically cured films was examined, and hybrid epoxy **7** was among the best materials tested. Thermomechanical analysis indicated that the new materials exhibit useful basic mechanical properties above and below T_g. In general, radial hybrid epoxies **6** and **7** exhibited many of the properties targeted during their molecular design, such as good hydrocarbon compatibility, hydrophobicity, flexibility, and thermal stability. It is likely that structural variations such as the siloxane/hydrocarbon ratio and the specific composition of both the siloxane and hydrocarbon segments in such hybrid materials has not been optimized. It is possible that the synthetic methodology developed here might be further exploited to continue to tailor and control such parameters and eventually yield even better materials.

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