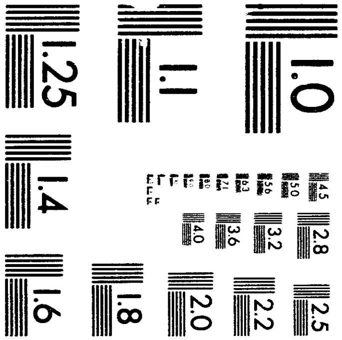
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Synthesis and Characterization of Novel Spiro Penta- and Hexacoordinate Anionic Polysiliconate and Polygermylate Ionomers Derived from the Condensation of (±) 5,5',6,6'-Tetrahydroxy-1,1'-Spiro-Bis(Indane) with trialkoxysilanes, tetraalkoxysilanes, and trialkoxygermanes.

James H. Small and Kenneth J. Shea*
Department of Chemistry
University of California at Irvine
Irvine, California 92717

and

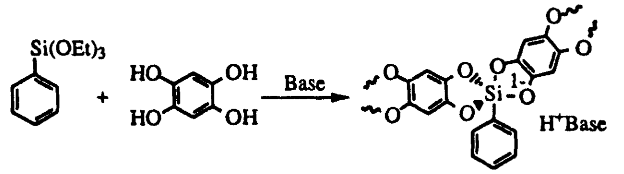
Douglas A. Loy and Gregory M. Jamison
Organization 1812, Properties of Organic Materials Department
Sandia National Laboratories
Albuquerque, New Mexico 87185

Introduction

There has been a tremendous amount of research focused on the synthesis and application of ion-containing polymers.[1] Although a wide variety of ion-containing polymers have been prepared to date, relatively few examples of backbone containing ionomers exist in the literature.[2] Another area enjoying an explosion of interest is the synthesis of hybrid organic-inorganic materials.[3] Manipulation of the building block monomer units at the molecular level has been shown to have a pronounced effect on the bulk properties of these materials Recent research conducted in our lab has been focused on combining these two important areas by developing a facile route for the synthesis of hybrid organic-inorganic backbone containing ionomeric materials. These materials may find applications as both solid and solution polymer electrolytes[4], ion-exchange resins[5], or as preceramic materials[6].

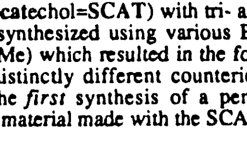
We have previously reported the first synthesis and characterization of penta- and hexacoordinate anionic polysiliconate ionomeric materials.[7] The synthesis of these materials was achieved by the condensation of tetrahydroxybenzene (THB) with phenyl triethoxysilane (PTES), a bis(trialkoxysilyl) alkane, or tetraethoxysilane to yield a pentacoordinate ladder ionomer, a pentacoordinate network ionomer, and a hexacoordinate network ionomer, respectively. An example of this synthetic strategy applied to the formation of a pentacoordinate ladder ionomer (PTES-THB-H$^+$Base) is shown in Scheme I.

Scheme I. Synthesis of an anionic pentacoordinate ladder ionomer.



PTES THB PTES-THB-H$^+$Base

We wish to report here the synthesis and characterization of a new family of air stable anionic penta- and hexacoordinate polysiliconate materials derived from the condensation of (±)-5,5',6,6'-tetrahydroxy-1,1'-spiro-bis(indane) (spirocatechol=SCAT) with tri- and tetraalkoxysilanes. These materials were synthesized using various Bronsted-Lowry bases (Et_3N, Me_4NOH, NaOMe) which resulted in the formation of ionomeric materials containing distinctly different counterions. In addition, we would like to report the *first* synthesis of a pentacoordinate anionic polygermylate network material made with the SCAT condensing reagent.



(Spirocatechol=SCAT)

Experimental

General:

^{13}C and ^{29}Si solid state NMR were obtained on a Chemagnetics CMX-200 spectrometer at 50.29 MHz and 39.73 MHz respectively. Both CP MAS and Bloch Decay MAS measurements were conducted on all materials. Infra-red spectra were obtained using a Perkin-Elmer 1600 series FTIR spectrophotometer. Surface area measurements were made on a Micromeritics ASAP 2000 porosimeter using high purity N_2 as adsorbate at 77K and calculated using the BET equation ($0.01 < p/p_0$, 0.30).[8] Thermal analysis measurements (DSC and TGA) were recorded on a Dupont Thermal Analyst 2000 with 910 DSC and 951 TGA modules with a 10°C/min heating rate under N_2. All solvents used were purified using standard purification methods. All reactions were conducted under an N_2 atmosphere.

Synthesis of 5,5',6,6'-Tetrahydroxy-1,1'-Spiro-Bis(Indane) (SCAT):

SCAT was synthesized following published procedures.[9] To a solution of catechol (60.02 g, 545.1 mmol), reagent grade acetone (200.1 mL, 2.73 mol), and reagent grade acetic acid (336.0 mL, 5.44 mol) was added 48% HBr (442.0 mL, 5.45 mol) and the solution brought to reflux. The solution was refluxed at 110°C for 6 h to afford a dark brownish solution. The solution was worked-up following standard organic extraction-aqueous washing purification techniques to give a dark brown solid. The solid was recrystallized from 1:1 Hex/EtOAc (2X) to yield a tan powder (20.39 g, 22%). ^1H NMR (300 MHz, DMSO-d_6) δ 8.52 (s, 4H, Ar-O*H*), 6.49 (s, 2H, Ar-*H*), 6.06 (s, 2H, Ar-*H*), 2.16 (d, 2H, J=12.84 MHz, CH_2), 1.99 (d, 2H, J=12.83 MHz, CH_2), 1.25 (s, 6H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ 144.6 (Ar), 142.1 (Ar), 140.6 (Ar), 110.1 (Ar-H), 108.3 (Ar-H), 59.6 (CH_2), 55.3 (Q), 42.4 (Q), 31.6 (CH_3), 30.5 (CH_3); FTIR (KBr) υ 3429, 3236, 2966, 2924, 1616, 1508, 1450, 1300, 864, 814 cm^{-1}; HRMS (CI, isobut) calcd. for $C_{21}H_{24}O_4$: 340.1670, found: 340.1670.

Monomer Syntheses:

Tetraethoxysilane (TEOS) and phenyl triethoxysilane (PTES) were purchased from Aldrich Chemical Co. and distilled from CaH_2. 1,2-Bis(trimethoxysilyl) ethane (BMSE) and 1,6-bis(trimethoxysilyl) hexane (BMSH) were purchased from Huls America and used as received. 1,4-Bis(triethoxysilyl) benzene (BESP) and 4,4'-bis(triethoxysilyl) biphenyl (BESB) were synthesized using previously published procedures obtained in our lab.[10] 1,2-Bis(triethoxygermyl) ethane (BEGE), 1,6-bis(triethoxygermyl) hexane (BEGH), and 1,10-bis(triethoxygermyl) decane (BEGD) were sythesized by hydrogermylation of the appropriate unsaturated compound using trichlorogermane followed by basic ethanolysis to yield the bis(trialkoxygermyl) alkane.[11] Monomer purity was verified by solution ^1H, ^{13}C, and ^{29}Si NMR, IR, MS, and gas chromatography.

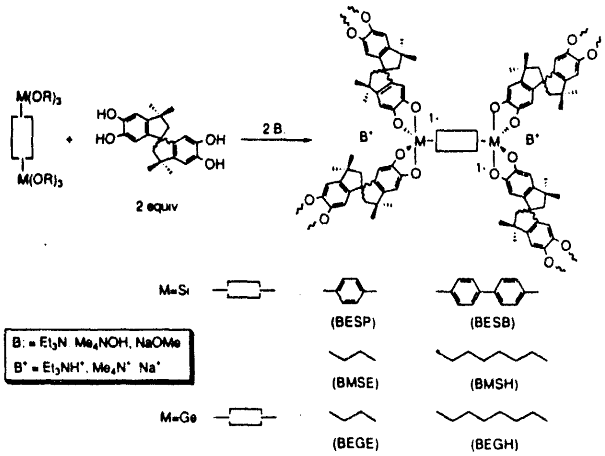
Polymer Syntheses:

A typical preparation for the synthesis of an anionic polysiliconate or polygermylate material is given below for the synthesis of a phenylene-bridged pentacoordinate anionic polysiliconate (BESP-SCAT-Et_3NH^+, Scheme II). To a refluxing solution of BESP (0.895 g, 2.22 mmol) and SCAT (1.50 g, 4.41 mmol) in THF (9.0 mL) was added Et_3N (2.00 mL, 14.4 mmol). After 16 h a white solid formed. The solution was refluxed for an additional 4 h and then cooled slowly to room temperature. The solids were filtered, washed with THF (3 X 25 mL) and dried under dynamic vacuum (< 1mTorr, 6 h) at room temperature to afford a tan powder (1.84 g, 83%). ^1H NMR (300 MHz, DMSO-d_6) δ 8.7-8.5 (br d, NH^+), 7.7-7.1 (br m, Ph-*H*), 6.6-6.2 (br s, SCAT), 6.0-5.7 (br s, SCAT), 3.8-3.7 (br s, OCH_2CH_3), 3.7-3.5 (br s, THF), 3.0-2.8 (br s, N(CH_2CH_3)$_3$), 2.3-1.8 (br m, CH_2), 1.8-1.65 (br s, THF), 1.5-1.1 (br m, CH_3), 1.1-0.7 (br m, N(CH_2CH_3)); ^{13}C Solid State NMR (50.29 MHz, CP MAS) δ 149.0 (SCAT), 141.9 (SCAT), 133.5 (Ph), 104.9 (SCAT), 68.0 (THF), 60.4 (CH_2), 57.8 (OCH_2CH_3), 47.2 (NCH_2CH_3), 43.6 (Q), 31.6 (CH_3), 25.8 (THF), 18.5 (OCH_2CH_3), 8.8 (NCH_2CH_3); ^{29}Si Solid State NMR (39.73 MHz, CP MAS) δ -57.6, -87.1; ^{29}Si Solid State NMR (39.73 MHz, Bloch Decay) δ -87.0; FTIR (KBr) υ 3446, 3037, 2951, 2860, 1637, 1485, 1360, 1279, 1220, 1141, 878, 695, 600 cm^{-1}; Elemental analysis calcd. for $C_{60}H_{76}N_2O_8Si_2$: C 71.39, H 7.59, Si 5.56, found: C 69.77, H 7.49, Si 5.62.

Results and Discussion

The presence of the hypervalent siliconate functionality within the polysiliconate materials was verified by ^{29}Si solid state NMR. ^{29}Si NMR has been utilized as the primary analytical method in the evaluation of the valence at silicon.[12] Figure I shows the ^{29}Si CP MAS spectra of the phenyl substituted ladder polysiliconate with Et_3NH^+ as the counterion

Scheme II. Synthsis of Pentacoordinate Bridging Polysiliconates and Polygermylates.



(PTES-SCAT-Et_3NH^+, similar to Scheme I). The resonance centered at -87 ppm is indicative of a pentacoordinate siliconate and corresponds with literature values.[13] Lack of an absorbance at -57 ppm implies the absence of residual monomeric units (tetracoordinate silicon) indicating complete condensation during polymerization. The ^{29}Si CP MAS spectra for a hexacoordinate polysiliconate with Me_4N^+ as the counterion (TEOS-SCAT-Me_4N^+) is shown in Figure II. Two resonances were observed at -98 and -139 ppm which correspond to the tetra- and hexacoordinate siliconate functionality. The resonance at -98 ppm can be explained by incomplete condensation during the polymerization leaving a tetracoordinate silicon functionality in the ionomeric framework.

^1H NMR was used to verify the presence of the pentacoordinate germylate functionality within the polygermylate ionomer (BEGE-SCAT-Et_3NH^+, Scheme II). We have previously seen an upfield chemical shift for the aromatic protons in the model compounds (catecholates) when the hypervalent siliconate functionality is present.[14] This charcteristic upfield shift is seen in the ^1H NMR of the polygermylate materials verifying the presence of the penatcoordinate germylate functionality.

Due to the network formation of the bridging polysiliconates it was thought that the materials may possess significant surface areas. However, N_2 adsorption porosimetry indicated that these materials were non-porous with surface areas between 0.2-8.5 m^2g^{-1}. Thermal analysis (DSC and TGA) indicates that there is an onset of decomposition ranging from 265-338°C (DSC) corresponding to a 62-76% weight loss by 900°C (TGA). The TGA of SCAT reveals an onset of decomposition at 325°C and complete weight loss by 600°C. A correlation between the onset of decomposition for SCAT and the materials is likely. This would imply that the hypervalent siliconate functionality in the materials is thermally stable to temperatures greater than 350°C. An example of the TGA of a bridging polysiliconate is shown in Figure III for the phenylene-bridged material (BESP-SCAT-Et_3NH^+, Scheme II).

Conclusion

The synthesis of hybrid organic-inorganic materials with ionic functionality within the polymer backbone has been achieved. A new family of hypervalent spiro anionic polysiliconates and polygermylates has been prepared. These materials were shown to be thermally stable to moderate temperatures and are completely air and moisture stable. Analysis of the materials by solution and solid state NMR verified the presence of the hypervalent functionality. We are currently examining the effect that alteration of the condensing reagent and/or the counterion may have on the bulk properties of the ionomeric material.

Acknowledgements

We would like to acknowledge the Division of Materials Research of the National Science Foundation and the Air Force Office of Scientific Research for financial support. The research conducted at Sandia National Laboratories was supported by the U.S. Dept. of Energy, Contract Number DE-AC04-94AL85000.

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Figure I. ^{29}Si Solid State NMR Spectra of PTES-SCAT-Et_3NH^+.

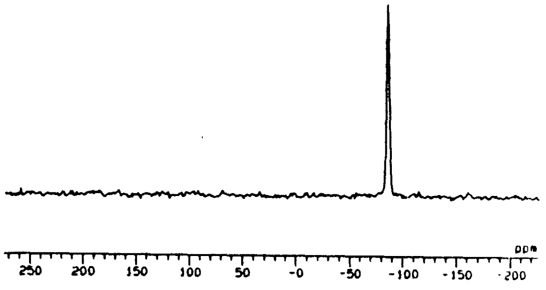


Figure II. ^{29}Si Solid State NMR Spectra of TEOS-SCAT-Me_4N^+.

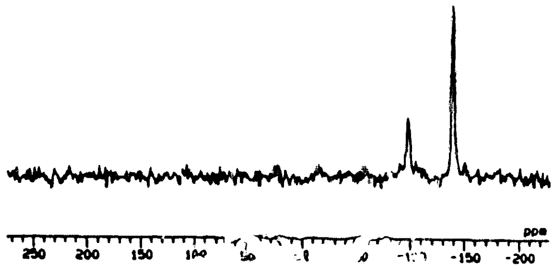
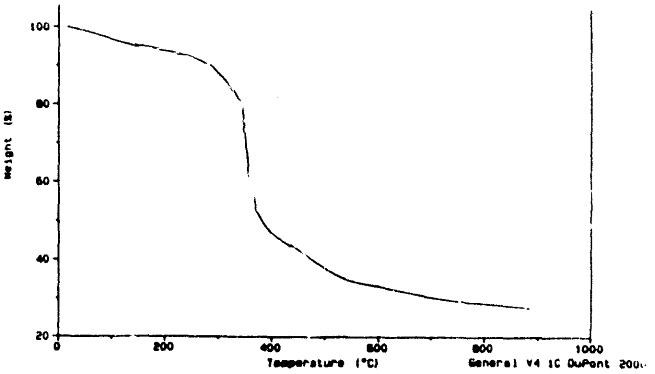


Figure III. Thermogravimetric Analysis (TGA) of BESP-SCAT-Et_3NH^+.



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