Hyperbranched Polyhedral Oligomeric Silsesquioxane (HB-POSS) Nanomaterials for High Transmission and Radiation-Resistant Space and Solar Applications

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Hyperbranched Polyhedral Oligomeric Silsesquioxane (HB-POSS) Nanomaterials for High Transmission and Radiation-Resistant Space and Solar Applications

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ABSTRACT: Hyperbranched polycarbosiloxanes and polysiloxanes with octafunctional polyhedral oligomeric silsesquioxane (POSS) branchpoints and curable alkoxysilane or silanol end-groups were formulated with linear polysiloxanes to fabricate transparent and robust nanostructured POSS-containing materials for use in a range of high performance space and solar applications. The effect of methyl vs. phenyl content, architecture and linear polysiloxane mass on transmission, thermal, physical, and proton, electron and UV radiation resistance properties was determined, and the physical properties of the nanomaterials were tailored to produce adhesives, or rigid or flexible coatings as desired. The methyl formulations showed superior electron resistance relative to a commercial space control material and to a POSS-free HB polymer control material, even when directly exposed to radiation in coating form, whereas the phenyl formulations were shown to have inferior electron and UV resistance. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 3849–3861, 2013

INTRODUCTION

Much of the early research and development work on polyhedral oligomeric silsesquioxanes (POSS) was driven by the need for materials that could withstand the aggressive environment encountered by objects in space, and that required excellent resistance to extremes of temperature ($-175°C$ to $120°C$ in Earth orbit and up to $250°C$ on other missions), out-gassing and atomic oxygen, proton, electron, and UV radiation over a 15-year service life.[1–4] POSS, as a close relative of quartz and other forms of silica, has excellent transmission at visible and UV wavelengths, and thus POSS materials have great potential in space solar cell or telescope applications where transparent adhesives or coatings are required, and also in terrestrial solar applications where transparent and UV-resistant materials are required. To date, hybrid siloxane-POSS resin compositions, POSS-modified methacrylates, POSS-modified polyimides, and POSS-modified epoxy resins have been evaluated in these applications.[5–9] Hybrid siloxane-POSS resin compositions show increasing proton resistance with increasing phenyl content, and good transmittance, but have the disadvantages of poor long-term stability in the presence of UV and VUV radiations, and a tendency to delaminate and crack at $-15°C$.[67] The POSS-

modified methacrylates, polyimides, and epoxys show better resistance than the corresponding materials without POSS,[7] although both the POSS-modified methacrylate and the POSS-modified polyimide resins have absorption cutoff wavelengths above 400 nm, which limits their use in future multi-junction solar cell applications, wherever wider wavelength ranges are required.

The current generation of rigid space solar cells carries a protective cover glass bound to the solar cell with a space adhesive.[1] As the space adhesive is prone to UV-induced darkening, it is necessary to dope the cover glass with a UV-absorbing cerium compound to maintain the transmittance required for the solar cell to function. In addition, the cover glass must carry an antireflective (AR) coating such as aluminum oxide-tin oxide (Al_2O/TiO_x) and a conductive electrostatic discharge coating such as indium-tin oxide (ITO) to prevent high voltage discharge. The various layers must also have matching refractive indices, e.g., the adhesive and the cover glass both have RIs of 1.5. Future generations of space solar cells are expected to be thinner and more flexible, and to carry protective coatings in place of cover glasses and multiple other layers. Flexible systems can be rolled and easily transported, and can be deployed in an almost unlimited range
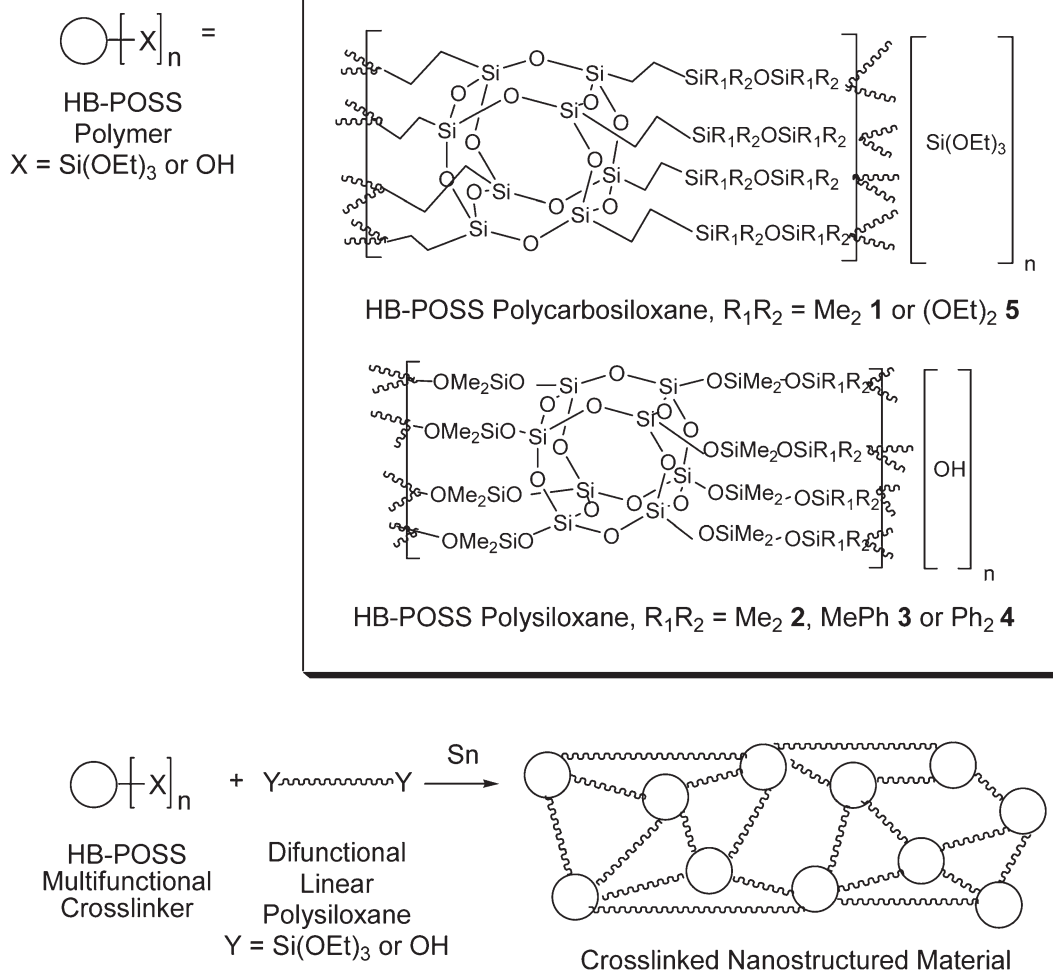
Figure 1. HB-PCSOX carrying curable terminal $Si(OEt)_3$ groups (top, box, where $R_1R_2 = Me_2$ for HBP **1** or $(OEt)_2$ for HBP **5**), HB-PSOX carrying curable SiOH terminal groups (bottom, box where $R_1R_2 = Me_2$ for HBP **2**, MePh for HBP **3** and Ph_2 for HBP **4**) and scheme for fabrication of a crosslinked nanostructured coating or adhesive.

of configurations and designs. They are lighter in weight and lower in volume, meaning that higher specific powers (W/kg), higher stowed volume efficiencies (kW/m^3), and higher packing densities of solar arrays can be achieved. In space applications lower weight immediately translates into reduced costs. Advanced multijunction solar cells, e.g., gallium indium phosphide on gallium arsenide on indium gallium arsenide (GaInP$_2$/GaAs/InGaAs, efficiency 34%), will also operate over an increasingly wide range of UV–visible–IR wavelengths extending from 1700 nm (above which photons lack sufficient energy to be useful) down into the region below 300 nm. Hence there is a need for advanced materials with excellent transmission properties, and with physical properties that can be tailored to perform as adhesives, rigid coatings or flexible coatings as required.

The first examples of hyperbranched polyhedral oligomeric silsesquioxane (HB-POSS), polycarbosiloxanes (HB-PCSOX), and polysiloxanes (HB-PSOX) with octafunctional POSS branching units,[10,11] were recently reported, and the feasibility of fabricating transparent and robust nanostructured coatings from formulations containing HB-POSS polymers, silanol-terminated linear polysiloxanes, bis(2-ethylhexanoate) tin(II) catalyst and

hexane at various hyperbranched polymer (HBP)/linear w/w compositions was briefly demonstrated. This is the first structure-property study of these novel HB-POSS nanostructured materials (Figure 1) covering the properties of key importance in space and solar cell applications, (i.e., optical transmission, and resistance to extreme temperature cycling, out gassing, ultraviolet, proton and electron radiation), and the effect of phenyl vs. methyl content, architecture (pendant dimethyl, diphenyl, or methylphenyl in polysiloxanes, or backbone phenyl in polysilarylene siloxanes[12]) and molecular mass upon these properties are measured (Figure 2). The tailoring of the physical properties of a coating by varying the HB-POSS polymer to linear siloxane polymer ratio in the formulation is also demonstrated, and adhesives and both rigid and flexible coatings are fabricated and characterized for hardness, coefficient of thermal expansion (CTE), and permeability.

EXPERIMENTAL

Materials

POSS® reagents were purchased from Hybrid Plastics (Hattiesburg, MS) and other reagents and solvents were purchased
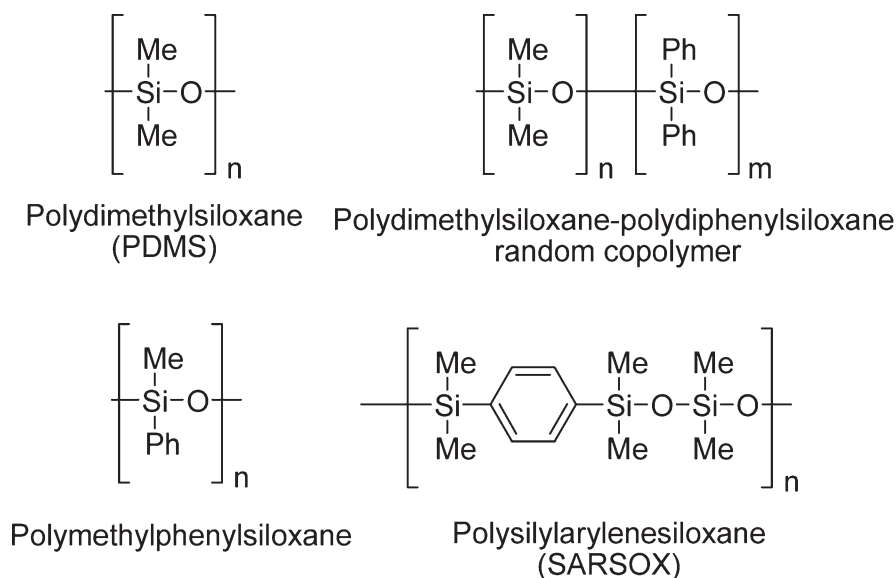
Figure 2. Linear polysiloxanes of various phenyl architectures, phenyl contents, and molecular masses.

from Sigma-Aldrich (Milwaukee, WI) or Gelest (Tullytown, PA). HBPs with octafunctional POSS (T_8) branch points were synthesized and characterized as described in an earlier study.[10] The following silanol-terminated linear polysiloxanes were purchased from Gelest (Tullytown, PA): DMS-S31 (PDMS, M_w 26,000) linear **1**, DMS-S15 (PDMS, M_w 2000) linear **2**, DMS-S12 (PDMS, M_w 400) linear **3**, and PDS-1615 (PDMS-polydiphenylsiloxane random copolymer, 14% $SiPh_2$ content, M_w 1000) linear **4**. Linears **5**, **6**, and **7** were prepared by triethoxysilyl end-capping of the following telechelic vinyl-terminated polysiloxanes: Gelest PDV-1641(vinyl-terminated PDMS-polydiphenylsiloxane random copolymer, 15% $SiPh_2$ content, M_w 55,000), Gelest PDV-2335 (vinyl-terminated PDMS-polydiphenylsiloxane random copolymer, 22% $SiPh_2$ content, M_w 23,000) and Gelest PMV-9925 (vinyl-terminated polymethylphenylsiloxane, 100% SiMePh content, M_w 2000). A representative example for linear **5** is given below. Polysilylarylene siloxane (SARSOX) linear **8** was synthesized from monomers[12] and is also described below. Dow Corning DC-93-500 space grade adhesive was used as a control material (a two-part system composed of base and curing agent, cast from hexane, and cured at 140°C for 15 min). A HB-PCSOX with no POSS content was used as a second control material (Figure 3) and its preparation has been described elsewhere.[13–16]
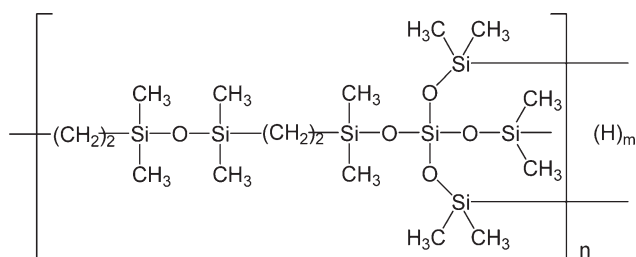
Characterization

IR spectra were recorded on a Nicolet 20DXB FTIR spectrometer and samples were prepared for analysis by solution casting onto potassium bromide discs. ^{1}H and ^{29}Si NMR spectra were recorded on a Varian Unity 400-MHz NMR spectrometer equipped with a 5-mm four nuclei probe. Solvent signals were used as internal standards, and chemical shifts are reported relative to tetramethylsilane. Size exclusion chromatography (SEC) was carried out using a Waters 510 pump, a Waters 717 auto-injector, a Waters CHM column heater, two Polymer Laboratory PLgel columns, and a Polymer Laboratory PL-ELS 1000 evaporative light scattering detector. Detector conditions appropriate to the eluting solvent were used, and the column was calibrated with Dow 1683 polystyrene standards. The transparent or hazy appearance of samples was determined by visual inspection. Quantitative transmission spectra were measured for the qualitatively transparent samples using a Cary 5000 spectrometer. The 90% transmission cutoff was defined as the wavelength at which the transmission dropped below 90% with decreasing wavelength (see for example Figure 5). A Bausch and Lomb ABBE-3L refractometer was used to make refractive index measurements at 23°C. Elemental analysis for ppm platinum (μg/g) was performed by Huffman Laboratories (Golden, CO). CTE was measured by TMA from −120°C to 160°C at 2°C/min.

Circular 75 mm diameter quartz coupons (Quartz Unlimited, Boca Raton, FL) or fused silica cover glasses (JDSU 7980 FS, 2 × 2 cm, 6 mil) were used when transmission testing of samples was required. Both of these substrates have transmission >90%, 250–2500 nm. Samples where transmission testing was not required were applied to glass microscope slides or to flexible
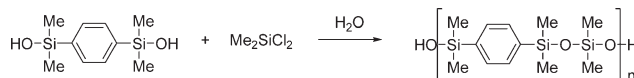

Figure 3. POSS-free hyperbranched control polymer.

Figure 4. Preparation of linear silylarylene siloxane (SARSOX) polymer **8**.
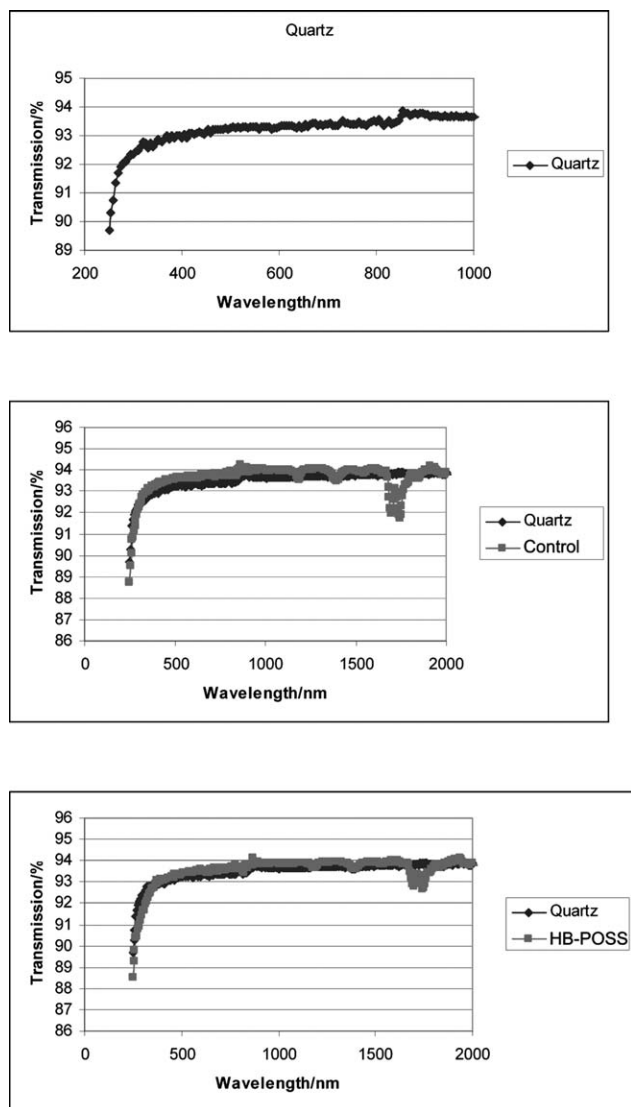
Figure 5. Transmission spectra for quartz (top), a transparent industry standard silicone space adhesive (DC-93-500, center) and a 25% HBP **3**/75% PDS-1615 formulation (bottom).

titania-coated PET substrates. Conformability in tests on flexible substrates was defined as an absence of cracking, crazing, or delamination after rolling into a 1″ diameter circle in both directions (i.e., with either the PET side of the flexible substrate on the outside of the roll, or with the PET side on the inside of the roll).

Polysiloxane Linear 5

A 50-mL round-bottomed flask equipped with a vertical cooling condenser was charged with Gelest PDV 1641 (vinyl-terminated PDMS-polydiphenylsiloxane random copolymer, 15% SiPh$_2$ content, M_w 55,000, 5.0 g) and anhydrous THF (5 mL) followed by triethoxysilane (0.3 mL). It was flushed with N$_2$ and stirred for 5 min. Karstedt's catalyst (0.01 g, ~2% platinum-divinylte-tramethyl-disiloxane complex in xylene) was added to the mixture. It was stirred at room temperature for 1 h and then heated in an oil bath at 50°C for 16 h. The clear viscous oil was washed with anhydrous acetonitrile (5 × 15 mL) and dried in a

rotary evaporator. The product was further dried under vacuum for 16 h. The yield was 4.9 g. IR showed the disappearance of vinyl and SiH groups.

Polysilylarylenesiloxane (SARSOX) Linear 8

1,4-Bisdimethylhydroxysilylbenzene (5 g, 22 mmol) was weighed into a triple-necked 250-mL flask equipped with stirrer bar, condenser, septum, and dropping funnel with septum. The system was dried with a heat gun and flushed with nitrogen several times. Anhydrous THF (75 mL) was added followed by redistilled pyridine (3.48 g, 3.55 mL, 44 mmol). The solution was cooled to −78°C in a dry ice/acetone bath. Dimethyldichlorosilane (2.84 g, 2.65 mL, 22 mmol) was added dropwise. The reaction was allowed to warm up to room temperature and stirred for 2 days. The white pyridinium chloride precipitate was filtered out. Water (1 mL) was added and the solution was stirred for 1 day. The solvent was evaporated to give a white wax-like product. The product was dissolved in 20 mL hexanes to give a cloudy solution. This was filtered to give a clear solution and dried over anhydrous sodium sulfate, and volatiles were removed in vacuo to give the product as a white sticky solid. IR (thin film): v (cm^{-1}) 3309 (SiOH), 3048 (ArCH), 2998, 2959, 2901 (CH$_3$ sym and asym), 1408, 1380, 1357, 1258 (SiCH$_3$), 1139 (SiOSi), 1070, 1020 (SiOSi), 825, 793, 736. ^{1}H NMR (THF-d$_8$): δ (ppm) 0.12 (s; O$_2$SiCH$_3$), 0.38 (s; OArSiCH$_3$), 7.58 (s; ArH). ^{29}Si NMR (30 wt % in THF-d$_8$) −17.1 (O$_2$Si(CH$_3$)$_2$), 2.7 (OSiAr(CH$_3$)$_2$). SEC (Toluene): M_w = 3200, M_n = 2500, polydispersity = 1.3.

Standard Preparation of Formulations

A small vial was charged with a freshly prepared solution of 10% bis(2-ethylhexanoate)tin in hexanes (20 mg, 2 wt % catalyst to polymer ratio), HBP (100 mg), linear polymer, and hexanes (100 mg). The solutions were mixed at room temperature and the homogenous solution was cast onto the substrate. In cases where SARSOX linear **8** was used, a few drops of THF were added to hexane to achieve solubility. Formulations were either cast as coatings onto a single substrate, or cast as adhesives sandwiched between two substrates, where the solution was pipetted onto the center of a coupon, and then another coupon was placed on the top of the solution. The solution was spread to cover the whole area. The films were allowed to dry at room temperature for up to 6 h, warmed to 50°C for 1 h, then cured at 120°C for 24 h. Film thicknesses were measured using a digital micrometer, calculated by difference relative to the thickness of the uncoated substrate(s) and were in the order of 50 μm. In some cases the same procedure was carried out using a slower dibutyl tin dilaurate catalyst (DBTDL, a tin(IV) compound) or with an acid catalyst at the desired wt %. Heat screening tests, liquid nitrogen screening tests, hardness tests, and outgassing tests were carried out in coating configuration. Unless otherwise stated, all radiation tests and thermal cycling tests, and associated transmission spectroscopy, were carried out in adhesive configuration.

Partial Precure Preparation of Formulations

The HBP and linear components in appropriate ratios were mixed in hexane. Dibutyl tin dilaurate (Gelest, in 1% w/w

hexane solution, 1 wt % catalyst to polymer ratio) was added at 1%. The mixtures were stirred at room temperature for several days until the casts after evaporation turned clear. The formulations were cast and cured at 120°C for 24 h.

Heat Screening Test
Formulations coated onto glass microscope slides were put in an oven at 250°C for 24 h, removed and then allowed to cool to room temperature. The appearance (transparency, texture, cracking) of the coatings was observed.

Liquid Nitrogen Screening Test
Formulations coated onto glass microscope slides were immersed in liquid nitrogen (−196°C) for 2 min, removed and allowed to warm up to room temperature. The appearance (transparency, texture, cracking) of the coatings was observed.

Thermal Cycling Test
Samples were tested for 2000 cycles at temperatures of +120°C to −180°C at ∼52.6 cycles per day under a nitrogen atmosphere. Transmittance from 200 to 1800 nm was measured before and after exposure.

Hardness Test
The scratch hardness of cured coatings was determined using a Paul-Gardner Scratch Tester (Model #3363). The hardness measurements were conducted in accordance with the protocol established by the American Society for Testing and Materials, ASTM D 3363-74.

Permeability Test
A formulation was cast on a PTFE filter membrane (47 mm, 0.22 μm, purchased from Grace Davison Discovery Science) and cured at 120°C for 24 h. Duplicate experiments were performed, and formulations were tested for both water and oxygen permeability (MOCON, Minneapolis, MN).

Out-gassing Test
Samples were heated at 125°C under high vacuum ($< 7 \times 10^{-3}$ Pa) for 24 h, and weight losses were measured, according to ASTM test E595-93 (Standard Test Method for Total Mass Loss and Collected Volatile Condensable Materials from Out-gassing in a Vacuum Environment, 1999). The masses of the samples before and after vacuum exposure were recorded, and percent mass loss was calculated using the mass of material lost and the initial sample mass. Duplicate experiments were run for each sample.

Proton and Electron Tests
Adhesives samples sandwiched between two fused silica coupons (or coatings on single coupons) were tested against 2 MeV protons (fluence 1E13 p/cm^2, flux 1.8E8 p/s/cm^2, equivalent to 15 years in geostationary orbit, GEO, Auburn University Space Research Institute) or 1 MeV electrons (fluence of 3E15 e/cm^2, NIST, Gaithersburg, MD) via EMCORE Photovoltaics (Albuquerque, NM). Transmission from 200 to 1800 nm was measured before and after exposure.

UV Test
Adhesives samples sandwiched between two fused silica coupons (or coatings on single coupons) were subjected to combined vacuum UV spectra wavelengths for an equivalent of 500 sun

hours (4.5 days). The light source was a 1600 W xenon lamp, where the xenon lines dominate between 750 and 1000 nm, but the spectrum shows little variation across the UV and visible wavelengths. Transmission from 200 to 1800 nm was measured before and after exposure.

RESULTS AND DISCUSSION

Preparation of HB-POSS Nanostructured Materials
Nanomaterials were formulated from HB-PCSOX or HB-PSOX with octafunctional branchpoints (the synthesis of which has been described elsewhere[10]) and various linear polysiloxanes of varying phenyl contents and phenyl architectures (Figures 1 and 2). In earlier work two linear silanol-terminated polysiloxanes of similar molecular mass (M_w = 1000 to 2000) but varying pendant phenyl content were briefly evaluated: one polydimethylsiloxane (linear **2**) and one polydimethylsiloxane-polydiphenylsiloxane random copolymer (14% diphenyl repeat units, linear **4**). In the current study the range of linear polysiloxane components with curable silanol (SiOH) or ethoxysilane (SiOEt) end-groups is greatly extended (Figure 2 and Table I), and polysiloxanes were either purchased (linears **1–4**), prepared by hydrosilylation of vinyl-terminated polysiloxanes with triethoxysilane (linears **5–7**) or prepared from precursor monomers (SARSOX linear **8**, Figure 4). Hydrosilylation products **5–7** were characterized by IR spectroscopy, and the disappearance of the SiH band at 2100–2250 cm^{-1} was observed. A scale of 5–10 g preparations of linear silylarylene-siloxane (SARSOX) polymer[12] were carried out by reacting a 1:1 molar ratio of 1,4-bisdimethylhydroxysilylbenzene and dimethyldichlorosilane (Figure 4) in the presence of pyridine to scavenge the hydrogen chloride by-product. Water was added at the end of the reaction to generate a product with reactive SiOH end-groups necessary for the cure of the formulations. This material was characterized by IR, ^{1}H NMR and ^{29}Si NMR, and shown by SEC to have a molecular mass of 3000. The ^{29}Si NMR spectrum showed two peaks corresponding to the OSiMe$_2$Ar silicon atoms at 2 ppm and the O$_2$SiMe$_2$ silicon atoms at −17 ppm, respectively.

Formulations were prepared by direct casting from hexane solutions carrying a HB-POSS polymer component, a linear polysiloxane component (**1–8**, Table I) and a tin catalyst such as bis-2-ethylhexanoate tin(II) or dibutyl tin (IV) dilaurate (Figure 1). For each HB-linear combination, samples were prepared at x/y mass ratios (x% HB polymer/y% linear polysiloxane) of 10/90, 25/75, 50/50, 75/25, and 90/10. Casting solutions were composed of a 1:1 w/w polymer–solvent ratio, and catalyst was present at 1–2 wt % relative to the total mass of polymer (HB and linear). Samples were compared with a Dow Corning 93–500 space adhesive control sample and also with a HB-PCSOX control sample with no POSS content (Figure 3).[13–16]

Tin compounds are known poisons of platinum catalysts[17]; hence when tin catalysts are used to cure systems containing residual platinum (i.e., catalyst remaining from earlier hydrosilylation preparations of HBPs or linear formulation components **5–7**), a tin-platinum reaction may generate a highly colored product unsuitable for applications requiring high-transmission materials. Color was eliminated by purifying to remove platinum residues, and by minimizing the levels of platinum used in

Table I. Qualitative Transparent vs. Hazy Appearance, Cracking Behavior, and Transmission Cutoff Data for Selected Tin-Cured Formulations

HB → Linear ↓	HB-POSS-free control	HB-PCSOX Me **1**	HB-PSOX Me **2**	HB-PSOX- MePh **3**	HB-PSOX- Ph **4**
DMS-S31 SiOH **1** M_w 26,000 PDMS	–	10/90 25/75 Transparent 90/10 cracks	25/75 Transparent Hot cracks	25/75 Transparent 75/25 hazy	Hazy
DMS-S15 SiOH **2** M_w 2000 PDMS	25/75 327 nm	**25/75** 329 nm	25/75 351nm	25/75 Transparent	25/75 Hazy
DMS-S12 SiOH **3** M_w 400 PDMS	–	**10/90 25/75** 323 nm	25/75 360 nm	10/90 25/75 351 nm	25/75 360 nm
PDS-1615 SiOH **4** M_w 1000 14% SiPh$_2$	25/75 330 nm	25/75 Transparent	Hazy	25/75 Transparent	25/75 50/50 354 nm
PDV-1641 Si(OEt)$_3$ **5** M_w 55,000 15% SiPh$_2$	–	25/75 292 nm	Hazy	Hazy	Hazy
PDV-2335 Si(OEt)$_3$ **6** M_w 23,000 22% SiPh$_2$	–	25/75 Transparent Cold cracks	Hazy	Hazy	Hazy
PMV-9925 Si(OEt)$_3$ **7** M_w 2000 100% MePh	–	25/75 Transparent Hot cracks	Hazy	Hazy	–
SARSOX **8** M_w 3000	–	25/75 Transparent Hot cracks	Hazy	Hazy	25/75 Hazy 75/25 309 nm

Cutoff wavelength (nm) is the value at which the transmission of a qualitatively transparent sample dropped below 90% with decreasing wavelength. DC-93-500 control adhesive showed a 90% cutoff wavelength of ∼250 nm. The following HBP-linear mass ratios were studied: 90/10, 75/25, 50/50, 25/75, and 10/90. Best performing formulations shown in **bold**.

the syntheses of HB and linear formulation components.[10] Purification was attempted using either activated carbon and or a flash silica column.[18] In a sample of HB-PCSOX **1** SiH-terminated precursor with a platinum content of 54 ppm, carbon treatment had little impact on the platinum level, reducing it to 40 ppm, but silica treatment was successful, and reduced the platinum level to 2.6 ppm as measured by elemental analysis. It was found that formulation components with platinum levels below 4 ppm were necessary to achieve colorless formulations after tin cure. The HBP **1**, **2** and **3** series of formulations were prepared using the Sn(II) catalyst bis-2-ethylhexanoate tin, and the HBP **4** series of formulations was prepared using the slower Sn(IV) catalyst dibutyl tin dilaurate (Table I). HBP **5** (Figure 1) formulations for the fabrication of nano-reinforced coatings are discussed in a later section. Various acids at 5–20 wt % were also evaluated as catalysts in place of the two tin compounds above. A 5-wt % propionic acid system resulted in a transparent and physically robust cured material, but hydrochloric acid and benzoic acid gave cloudy materials, and acetic acid only cured formulations with very high HBP contents (90–100%). All data in Tables I–IV was measured for tin-cured systems.

Formulations which were hazy or which cracked upon cure were eliminated from further studies. Transparent formulations were screened by dipping in liquid nitrogen (−196°C) and also by heating to 250°C, and those which cracked were also eliminated. All formulations were prepared using the standard casting method with the exception of the linear **1** series (first row,

Table I), where standard casting gave hazy formulations, but transparent formulations were obtained using a method where the HB and linear components were stirred in hexane with dibutyl tin dilaurate for several days at room temperature to achieve a partial precure in solution before casting and completion of the cure process.

Transparency and Texture
A lack of transparency before cure may be caused by the presence of incompatible casting solvent, or by the ethanol or water by-product of the cure chemistry (prior to removal by heating). A lack of transparency after cure (Table I) implies a lack of compatibility between the HBP and the linear component. Thus the HBP **1** (no phenyl)/linear **5** (15% phenyl) formulation had the lowest 90% transmission cutoff value in Table I (292 nm), and better transparency than the HBP **1** (no phenyl)/linear **6** formulation (22% phenyl) (Table I). HBPs **1–3** (zero or low phenyl content)/PDMS linear formulations (10/90 and 25/75) were all transparent independent of PDMS linear chain length, but HBP **4** (high phenyl content)/PDMS linear formulations were hazy. HBP **1**/linear PDMS-diphenylsiloxane copolymer formulations were generally transparent irrespective of chain length, percent SiPh$_2$ content and linear end-group (SiOH or Si(OEt)$_3$). The transmission properties of HB polysiloxane–linear PDMS–diphenylsiloxane formulations were not affected by percent SiPh$_2$ content, but did depend on linear end-groups, where SiOH-terminated linears gave transparent formulations, whereas Si(OEt)$_3$-terminated linears gave more hazy

formulations. SARSOX appears to have good compatibility with the methyl-HBP **1** and poor compatibility with the phenyl-containing HBPs **3** and **4**. The exception to this is the transparent 75% HBP **4**/25% SARSOX **8** formulation, where the HBP would form the continuous phase. It is notable that SARSOX is capable of forming transparent cured formulations despite being an opaque waxy solid. All HBP **1**/SARSOX **8** formulations were clear except for 10/90 that was hazy. All HBP polysiloxane (**2–4**)/SARSOX **8** formulations were hazy with the exception of 75/25 HBP **4**/SARSOX linear **8** that was transparent. The high phenyl content of the clear formulation (HBP with highest Ph content at highest percent HBP) further confirms that the haziness is caused by incompatibility between SARSOX phenyl groups and HBPs with lower phenyl content than HBP **4**.

Cracking at extreme temperatures (heating to 250°C or liquid nitrogen immersion at −196°C) increased as the HBP content of the formulations increased (e.g., HBP **1**/linear **1**). 100% HBP/0% linear formulations take the idea of maximum cross-link density to its extreme, and all of these formulations (HBPs **1–4**) cracked (note 100% HBP data does not appear in Table I). Cracking was greater when HBPs with $Si(OEt)_3$ end-groups (HBP **1**) were used rather than HBPs with SiOH end-groups (HBPs **2–4**). Both of these observations may be rationalized in terms of increasing cross-link density resulting in increased cracking. Extra HBP content generates additional cross-links, and HBP **1** is terminated with sets of three SiOEt groups, whereas the HBP siloxanes **2-4** are terminated with single SiOH groups.

The HBP **1**/linear **5** formulation had better crack resistance than the HBP **1**/linear **6** formulation (Table I). The longer chain length of linear **5** (55,000) may result in lower cross-link density and less cracking. The lower glass transition temperature (T_g) associated with a lower phenyl content, may also explain less cracking at extremes of low temperature. Note PDMS has a T_g of −123°C, whereas polymethylphenylsiloxane has a T_g of −28°C and polydiphenylsiloxane has a T_g of +40°C.[12] 100% HBP/0% linear formulations take the idea of maximum cross-link density to its extreme, and all of these formulations (HBPs **1–4**) cracked. The space control adhesive was clear and crack-resistant after liquid nitrogen exposure and after heating to 250°C. Selected formulations were further tested by taking a single sample and alternately exposing it to liquid nitrogen and heating (a simple laboratory approximation to a thermal cycling regime performed in a thermal test chamber). In all cases where samples were crack-resistant in individual liquid nitrogen or heating tests, they were also crack-resistant when exposed to liquid nitrogen/250°C extreme temperature cycling.

Transmission and Refractive Index

All adhesives samples were sandwiched between two coupons with the exception of the linear **8** (SARSOX) formulation (final row, Table I). This became hazy when the second coupon was applied, but remained clear in a coating on a single coupon. Hence the transmission spectrum was measured for a single coated coupon. Transmission spectroscopy experiments were carried out for formulations coated onto fused silica or quartz substrates having a transmission cutoff at ∼250 nm (in contrast

to products such as the Qioptiq CMG 100 AR cover glass carrying cerium for UV protection, and thus having a much higher transmission cutoff at ∼400 nm). Transmission cutoff values for the wavelength at which transmission drops below 90% are given in Table I and examples of the transmission performances of an HB-POSS nanostructured material and a space adhesive control against an uncoated quartz coupon control are shown in Figure 5. For the silicone control space adhesive and for HB-POSS materials with no phenyl content, the transmission cutoff was comparable with that of quartz (Figure 5), but as phenyl content increased, cutoff occurred at higher wavelengths (Table I). In addition, the use of Sn(II) catalyst resulted in a higher cutoff than Sn(IV) catalyst for the same 25% HBP **3**/75% linear **4** combination. The space adhesive control transmission dropped below 90% at 230 nm, whereas the transmission of the HB-POSS materials dropped below 90% at higher wavelengths (290–360 nm). The 90% transmission cutoff values were a function of the type the HBP used in the formulation, i.e., the POSS-free HBP polycarbosiloxane control formulations cutoff at ∼330 nm, the HBP **1** formulations cutoff at 290–330 nm, the HBP **2-4**/linear siloxane formulations cutoff at 350–360 nm and the HBP **2-4**/linear **8** formulation cutoff at 309 nm. Since ∼3% of the possible current of a current-generation space solar cell is obtained between 300 and 350 nm, good transmission down to 300 nm is of paramount importance.

Generally propionic acid cured systems showed pre-exposure 90% transmission cutoffs comparable to those of tin cured systems. In the specific case of the 25% HBP **1**/75% linear **2** formulation, changing from tin (Table I) to 5% propionic acid did not affect the transmission, and cutoff remained at 329 nm.

The refractive indices of the HB-POSS materials were a function of phenyl content. The silicone space adhesive control and the HB-POSS formulations with no phenyl content (i.e., HBP **1** with the various PDMS linears) had refractive indices of 1.41, whereas the 25% HBP **1**/75% linear **8** formulation had a refractive index of 1.49.

Transmission spectra were measured before and after thermal cycling testing at 2000 cycles from +120°C to −180°C (52.6 cycles per day under nitrogen). In all cases the transmission was unaffected by exposure to the thermal cycling regime, and the pre- and postexposure spectra were identical. Excellent performance, with no cracking or delamination, was seen for all adhesives (sandwiched between two substrates) and for all coatings samples except for 75% HBP **4**/25% linear **8**, which cracked and flaked off the substrate.

Physical Properties

All the formulations that were clear and were crack-resistant at extreme temperatures were tested for hardness and found to have values of less than 3B, showing that the formulations were comparatively soft (where 4B and 5B values are softer, whereas 2B, 1B, 1H, 2H values are harder). The space control adhesive also had a pencil hardness of less than 3B.

CTE was measured for a 25% HBP **1**/75% linear **1** formulation and a value of 466 ppm/°C was obtained, comparable to the

Table II. Outgassing Data for Selected Formulations

HB → Linear ↓	HB-POSS-free control	HB-PCSOX Me **1**	HB-PSOX Me **2**	HB-PSOX-MePh **3**	HB-PSOX- Ph **4**
DMS-S31 SiOH **1** M_w 26,000 PDMS	–	10/90, 1.3%	25/75 Transparent	25/75, 1.3%	Hazy
DMS-S15 SiOH **2** M_w 2000 PDMS	25/75, 0.9%	**25/75**, 1.0%	25/75, 0.9%	25/75, 0.3%	25/75, Hazy
DMS-S12 SiOH **3** M_w 400 PDMS	–	**10/90**, 0.1%	25/75, 1.4%	10/90, 1.1%	25/75, 1.8%
PDS-1615 SiOH **4** M_w 1000 14% $SiPh_2$	25/75, 1.3%	25/75, 4.1%	Hazy	25/75, 3.1%	25/75, 3.9%
PDV-1641 Si(OEt)$_3$ **5** M_w 55,000 15% $SiPh_2$	–	25/75, 1.6%	Hazy	Hazy	Hazy
SARSOX **8** M_w 3000	–	25/75 Transparent	Hazy	Hazy	75/25, 2.6%

x/y denotes formulations comprised of x% HBP and y% linear by weight. 125°C under high vacuum ($<7 \times 10^{-3}$ Pa). Best performing formulations shown in **bold**.

values of typical rubbers and elastomers. The CTE of the control space adhesive was measured as 300 ppm/°C.

Solution-cast coatings have a greater tendency to crack with increasing coating thickness. In order to determine the threshold at which cracking occurred, a series of 25% HBP **1**/75% linear **2** coatings of increasing thickness was prepared. Thickness was varied by varying the weight percent solids content in the casting solution. It was found that cracking did not occur until the thickness reached 300 μm (0.3 mm). In the current generation of space solar cells, the adhesive layer is typically 2–5 mil

(0.05–0.13 mm, 50–130 μm) in thickness; hence these results show that HB-POSS formulations do not crack in the desired 2–5 mil thickness range.

The oxygen and water permeability of a typical adhesive formulation was measured under industry standard conditions and was found to be typical of a siloxane-based material. A coating of 25% HBP **1**/75% linear **2** had a mean oxygen permeability value of 6545 cc/(100 in^2 day) or 101,448 cc/(m^2 day) (at 23°C/0% RH) and a mean water permeability value of 8.65 g/(100 in^2 day) or 134 g/(m^2 day) (at 23°C/100% RH). For comparison,

Table III. Electron (E) and UV Resistance Data for Samples in Adhesive Configuration

HB → Linear ↓	HB-POSS-free control	HB-PCSOX Me **1**	HB-PSOX Me **2**	HB-PSOX-MePh **3**	HB-PSOX-Ph **4**
DMS-S31 SiOH **1** M_w 26,000 PDMS	–	25/75* Slight E	25/75 Transparent	25/75 Some E 532 nm UV	Hazy
DMS-S15 SiOH **2** M_w 2000 PDMS	25/75 Slight E 344 nm UV	**25/75*** Slight E	25/75* No E	25/75 Transparent	Hazy
DMS-S12 SiOH **3** M_w 400 PDMS	–	**10/90*** Slight E	25/75* No E	10/90 25/75 Slight E	25/75 Some E 576 nm UV
PDS-1615 SiOH **4** M_w 1000 14% $SiPh_2$	25/75 Some E 664 nm UV	25/75 Slight E 670 nm UV	Hazy	25/75 Some E	25/75 Slight E 678 nm UV
PDV-1641 Si(OEt)$_3$ **5** M_w 55,000 15% $SiPh_2$	–	25/75 Some E 660 nm UV	Hazy	Hazy	Hazy
SARSOX **8** M_w 3000	–	25/75 Transparent	Hazy	Hazy	75/25* Severe E 798 nm UV

Post-UV exposure transmission cutoff data for selected formulations (nm) is the value at which the transmission of the sample dropped below 90% with decreasing wavelength. Samples marked with an asterisk (*) were also tested in coating configuration. DC-93-500 control adhesive showed some electron damage and some UV damage (with a 90% post-UV transmission cutoff at 260 nm). Best performing formulations shown in **bold**.
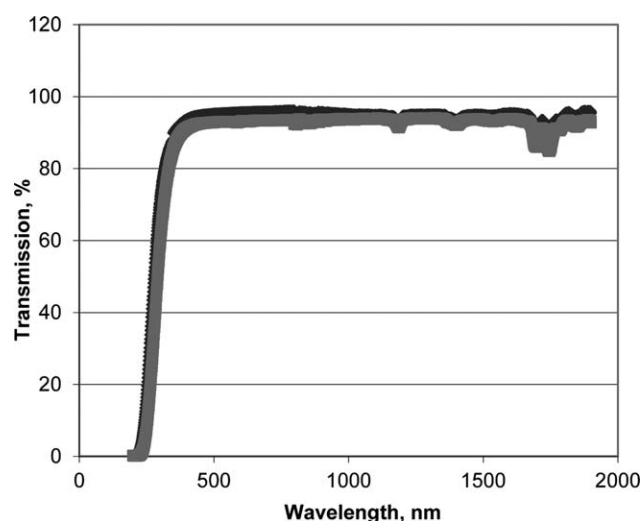
Figure 6. Transmission spectra of 10% HBP **1**/90% linear **3** (PDMS, M_w 400) coating (tin cure) before (gray) and after (black) 2 MeV proton exposure.

Figure 7. Transmission spectra of 10% HBP **1**/90% linear **3** (PDMS, M_w 400) coating (tin cure) before (gray) and after (black) 1 MeV electron exposure.

typical oxygen barrier packaging has an oxygen permeability of 1 cc/(100 in^2 day).

Outgassing

Formulations that were transparent and crack-resistant at extreme temperatures were tested for out-gassing using ASTM test procedure E595-93 (125°C under high vacuum $< 7 \times 10^{-3}$ Pa, Table II) and compared with the space adhesive control that had an outgassing value of 0.58%. The formulations with PDMS linears (**1**–**3**) had better or comparable outgassing performance to the control (0.1–1.4%), whereas the formulations with phenyl-containing linears (**4**, **5**, and **8**) outgassed more than the control (1.6–4.1%). Linear **2** gave low outgassing values when used with four different HBPs (0.3–1.0%). Outgassing decreased with increasing linear mass for both PDMS and phenyl linears when other variables were held constant, i.e., linear **5** (M_w 55,000) outgassed less than linear **4** (M_w 1000), and linear **2** (M_w 2000) outgassed less than linear **3** (M_w 400). The best outgassing performances were associated with PDMS linear **2** (0.3–1.0%). Varying the HBP (while other formulation variables were held constant) had no discernible effect on outgassing performance. In a second series of experiments, percent mass loss from fully cured samples after exposure to vacuum for 24 h at room temperature was measured, and in all cases mass changes of 0.3% or less were measured for duplicate samples. The space adhesive control sample also showed a mass change of 0.3% or less.

Proton, Electron, and UV Radiation Resistance

A range of transparent and crack resistant formulations were tested for proton, electron, and UV resistance (Table III). Samples were exposed to either 2 MeV protons (fluence 1E13 p/cm^2, flux 1.8E8 p/s cm^2, equivalent to 15 years in geostationary Earth orbit), 1 MeV electrons (fluence of 3E15 e/cm^2) or 500 sun hours of UV radiation (1600 W xenon source), Figures 6–9 and their transmission was measured before and after exposure.

All samples including the commercial space adhesive control and the POSS-free HBP control had excellent proton resistance
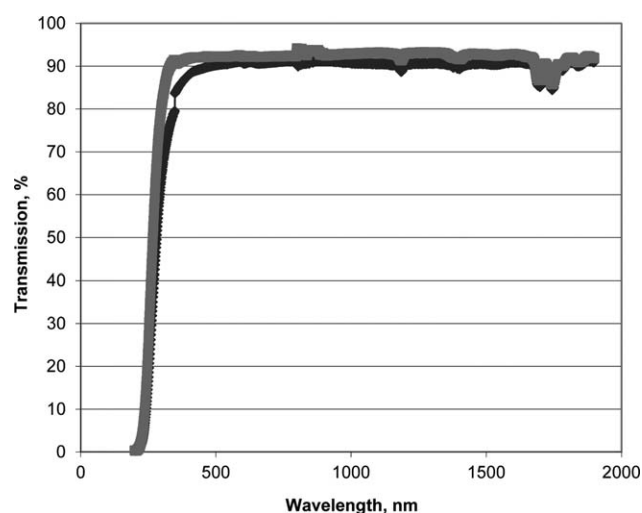
from 200 to 1800 nm as assessed by transmission spectroscopy, and no differences were observed in the transmission spectra before and after exposure Figure 6. All samples including the space adhesive control and the POSS-free HBP controls also had good electron resistance from 300 to 1800 nm, Figure 7 with the exception of the SARSOX sample. When electron damage was observed, it generally occurred in the low wavelength 200–300 nm region, and the damage was qualitatively classified as either slight, moderate, or severe (Table III). The SARSOX sample was so severely damaged that transmission dropped below 90% at visible wavelengths as high as 600 nm.

The best-performing samples were based on phenyl-free HB polysiloxane **2** and short-chain linear PDMS **2** or **3** and showed no electron damage from 200 to 300 nm. HB-PCSOX (control or HBP **1**) with short-chain linear PDMS **2** or **3** showed slight damage. In addition, an all-phenyl sample composed of 25% HBP **4**/75% linear **4** and a lightly phenylated sample composed of 25% HBP **3**/75% linear **3** showed slight damage. All of these samples performed better than the DC-93-500 space control adhesive, which showed significant electron damage in the 200–300 nm region. Significant 200–300 nm electron damage appeared to be most associated with formulations based either on a phenyl HBP with a nonphenyl linear (e.g., 25% HBP **4**/75% linear **3**), or a nonphenyl HBP with a phenyl linear (e.g., 25% HBP **1**/75% linear **4** and 25% HBP **1**/75% linear **5**). This could be associated with reduced compatibility between the HB and linear formulation components. For HBP polysiloxane/linear PDMS **3** formulations, 200–300 nm electron damage increased with increasing phenyl content in the order HBP **2** < HBP **3** < HBP **4** (i.e., most damage was observed for the phenyl-HBP **4** and the nonphenyl linear **3** pair).

Samples were tested either in an adhesive configuration sandwiched between two quartz coupons (i.e., adhering the two coupons together), or in a coating configuration, where a single quartz coupon was coated with a formulation, and the coated
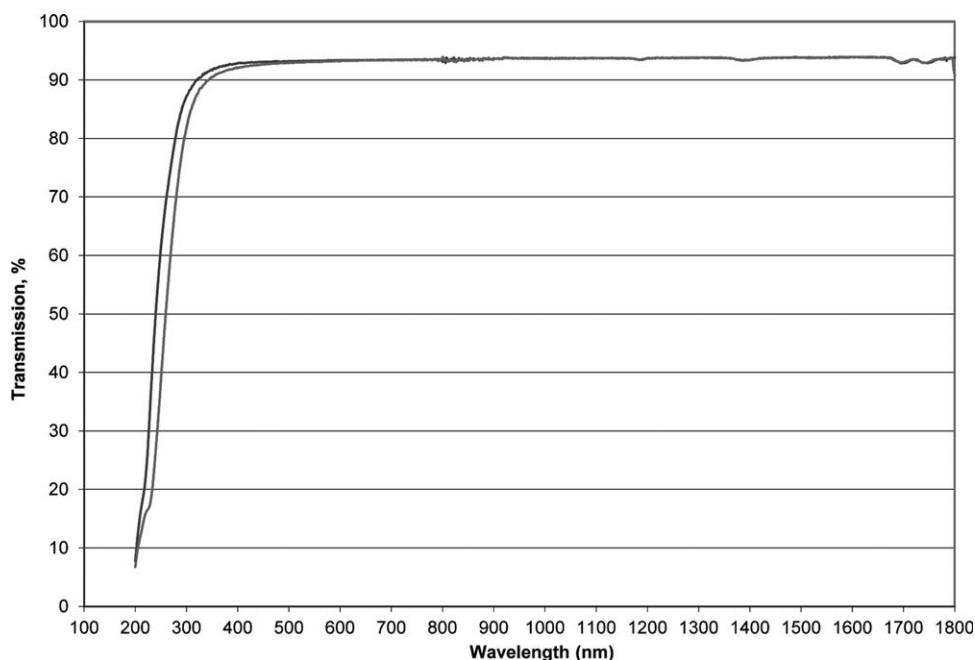
Figure 8. Transmission spectra for 25% HBP **1**/75% linear **2** adhesive (tin cure) before (black) and after (gray) UV exposure (500 sun hours).

side was exposed to radiation. The coating test experiment is more aggressive because the formulation was exposed directly to radiation, whereas the adhesive was only exposed to radiation via a cover glass. The space adhesive control sample was damaged by protons and electrons in coating form, whereas in adhesive form it had showed no proton damage. In contrast, when HB-POSS formulations were tested as coatings, they were far more robust; none were damaged by protons, and of those that were damaged by electrons, the damage was comparable for coatings and adhesives configurations. Two formulations had superior performance to the space adhesive control, showing no electron damage (10% HBP **1**/90% linear **3** and 25%

HBP **2**/75% linear **2**). The 90% transmission cutoff values for the coatings samples before they were exposed to radiation were generally comparable to those for the same materials in adhesive configuration, as expected.

Generally propionic acid cured systems showed greater proton and electron damage relative to both the tin-cured 25% HBP **1**/ 75% linear **2** coating and the tin-cured 25% HBP **1**/75% linear **2** adhesive. No tin-cured adhesives or coatings showed any proton damage, whereas propionic acid cured coatings were damaged by protons. Whereas a number of tin-cured adhesives and coatings had shown zero or slight electron damage (Table III),
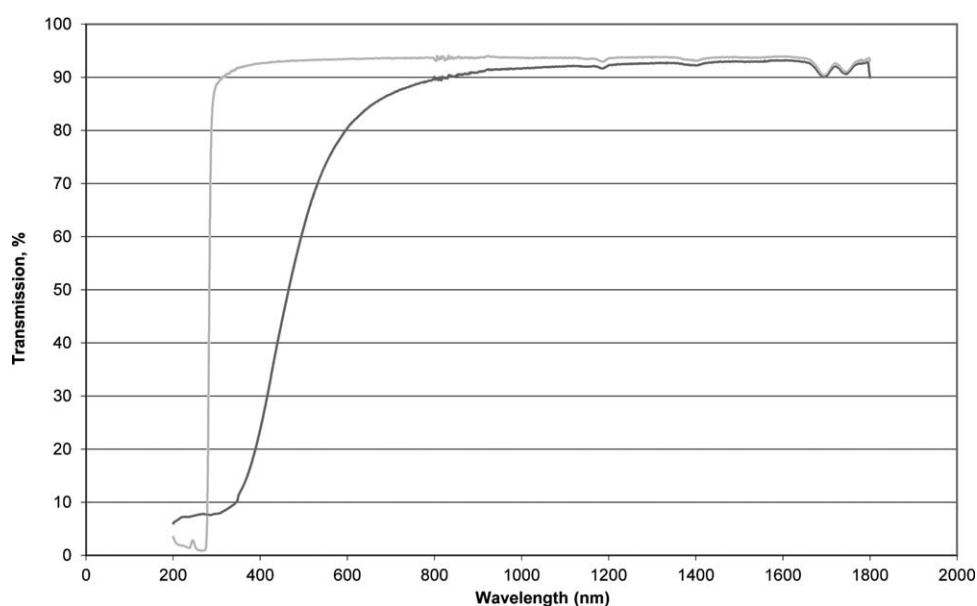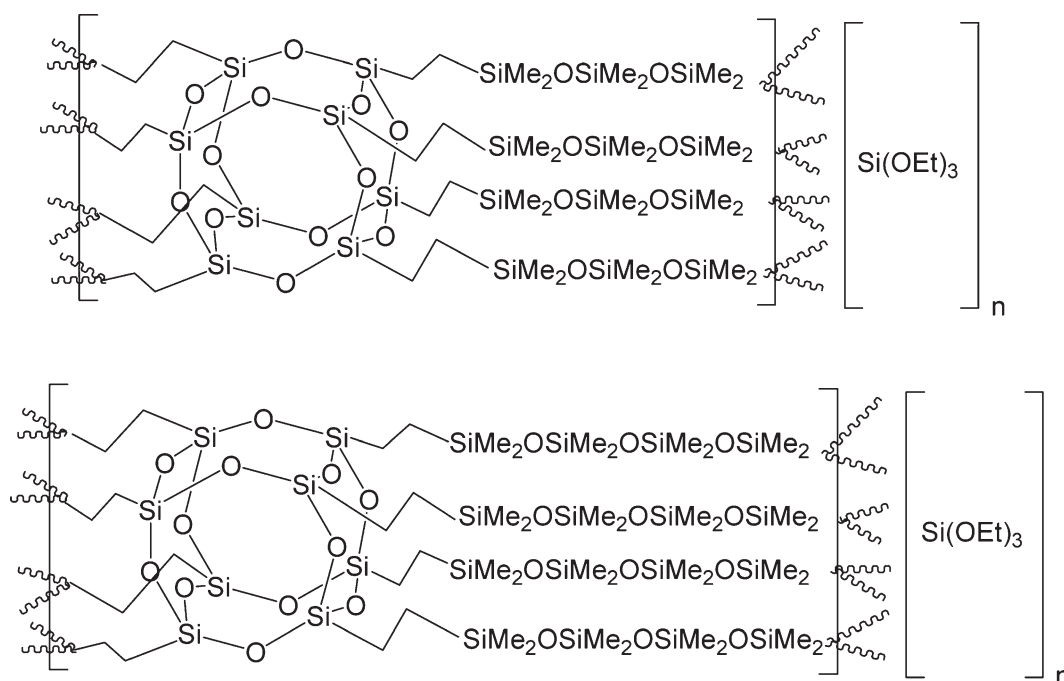

Figure 9. Transmission spectra for 75% HBP **4**/25% linear **8** coating (tin cure) before (gray) and after (black) UV exposure (500 sun hours).

HBP **6** and HBP **7**

Figure 10. Two "long arm" HBP variants with three and four SiMe$_2$O spacer units between branchpoints.

the propionic acid cured coatings showed significant electron damage.

UV radiation exposure results are summarized in Table III, where the 90% transmission cutoff wavelength is defined as the wavelength at which transmission drops below 90%. The degree of damage was classified as follows: none (cutoff below 350 nm) Figure 8, damage (cutoff 350–600 nm), severe damage (cutoff 600–700 nm) Figure 9, and extremely severe damage (cutoff above 700 nm). In addition, the damaged samples were characteristically brown in appearance. All the samples were crack free at the end of the 500 sun hour UV experiment except for the 75% HBP **4**/25% linear **8** formulation. The degree of damage appears primarily to correlate with the phenyl content in the linear component, where the linear is the largest mass contributor of the formulation. Thus the 75% HBP **4**/25% linear **8** formulation suffered the worst damage, and transmission was compromised across the entire visible spectrum (cutoff 798 nm). Formulations containing phenylated linears **4** or **5** (both polysiloxanes having 14–15% SiPh$_2$ content) suffered severe damage (cutoff 600–700 nm), and the degree of damage was independent of the molecular mass of the linear (M_w 1000 for linear **4** and M_w 55,000 for linear **5**). The HBP phenyl content in these formulations had little effect upon the degree of damage (phenyl-free HBP **1** vs. phenylated HBP **4**). Formulations based on nonphenylated PDMS linears **1**–**3** suffered the least damage. Some damage was seen for formulations with phenylated HBPs **3** and **4** and nonphenylated linears **1** and **3**, but no damage was seen for phenyl-free HBPs and nonphenylated linears (linear **1**, **3** or control space adhesive). The presence of POSS in the formulation does not appear to be detrimental to UV stability; a

pair of analogous formulations with and without POSS content both suffered a similar degree of damage (POSS-free HBP control or HBP **1** with linear **4**).

In adhesive form (between two cover glasses) the space control adhesive had been undamaged, but in coating form it was damaged and its 90% cutoff increased from 296 to 496 nm. In contrast, HB-POSS formulations had good UV resistance in both adhesive and coating form and some samples showed no damage at all. The 25% HBP **1**/75% linear **2** formulation was undamaged in adhesive form (cutoff 344 nm) and slightly damaged in coating form (415 nm cutoff).

For the acid-cured systems, use of propionic acid as a cure catalyst was associated with UV damage. A tin-cured 25% HBP **1**/75% linear **2** adhesive was undamaged, a tin-cured 25% HBP **1**/75% linear **2** coating was only slightly damaged, but a 5% propionic acid cured 25% HBP **1**/75% linear **2** coating was significantly damaged.

Hard Nano-Reinforced Coatings

In order to increase the modulus of a formulation and obtain a material with suitable protective coating properties, its crosslink density must be increased. Crosslink density is a function of the number of multifunctional branch points in the formulation. These branch points are provided by the HBP component. Crosslink density can be increased by increasing the percent HBP content (increasing the number of crosslinks), and also by decreasing the length of the linear component in the formulation (i.e., decreasing the distance between crosslinks). Coatings may also be reinforced by introducing curable groups within the hyperbranched component (e.g., SiOEt in HBP **5**, Figure 1).[10] When

Table IV. Various x% **HBP**/y% Linear Coating Formulations (x/y) that were Transparent, Flexible and Conformable from −196°C to 200°C

HB → Linear ↓	HB-PCSOX Me **1**	HB-PSOX Me **2**	HB-PCSOX Me **6**	HB-PCSOX Me **7**
DMS-S31 SiOH **1** M_w 26,000 PDMS	7/93*	18/82	12/88	17/83
DMS-S15 SiOH **2** M_w 2000 PDMS	**49/51*** E P	25/75, 50/50	65/35	Cold cracks
DMS-S12 SiOH **3** M_w 400 PDMS	**10/90** E P	**25/75** E P	–	–
PDS-1615 SiOH **4** M_w 1000 14% SiPh$_2$	–	25/75, 50/50	–	–
PDV-1641 Si(OEt)$_3$ **5** M_w 55,000 15% SiPh$_2$	25/75*	–	–	–

An asterisk (*) denotes coatings observed to have high friction anti-slip surfaces.

these groups cure, the HBP domain is able to function as a reinforcing nanofiller. The challenge in this situation is to keep the domain size small enough to maintain the optical transparency of the coating.

HBP **5** was prepared in a hydrosilylation polymerization reaction between octasilane POSS and divinyltetraethoxydisiloxane followed by triethoxysily-end-capping.[10] Because of the presence of the internal SiOEt groups, both HBP **5** and its vinyl-terminated precursor (denoted HBP **5**-vinyl, M_w 130,000) are capable of cure. A 100% HBP **5**-vinyl formulation gave a hard transparent coating, either when Sn(II)-cured or when cured slowly by exposure to ambient air and moisture. HBP **5**-vinyl was evaluated in 25% HBP/75% linear **2** coatings formulations, hard transparent coatings of at least 3H were successfully obtained when the formulations were Sn(II)-cured or Sn(IV)-cured. In another series of experiments, coatings based on 25% HBP **5**/75% linear **2** or **3** were evaluated with Sn(II) or Sn(IV) cure, and hard transparent coatings of high quality were obtained. These four hard coatings (i.e., 25% HBP **5**-vinyl 75% linear **2**, 25% HBP **5**-vinyl/75% linear **3**, 25% HBP **5**/75% linear **2**, and 25% HBP **5**/75% linear **3**) were characterized for transmission, radiation resistance, and thermal cycling performance. They were found to have undesirably high transmission cutoffs (350–478 nm, i.e. well into the visible region) relative to space adhesive control, the HBP control and to the other HBP formulations (Table I). In some cases 90% transmission was not achieved at any wavelength. However, the coatings had good proton and electron resistance and one coating (25% HBP **5**-vinyl/75% linear **2**) was undamaged by protons or electrons. Proton and electron resistance were independent of the molecular mass of the linear (**2** or **3**) and of Sn(II) or Sn(IV) catalyst. UV resistance was independent of linear siloxane mass, but was dependent upon catalyst; when Sn(II) was used no damage was observed, but when Sn(IV) was used, severe damage was observed. Upon thermal cycling exposure, Sn(IV)-cured coatings delaminated, but the Sn(II)-cured analogs showed better performance, with either no discernible change, or a slightly bubbled texture. As Sn(II) is a faster catalyst than Sn(IV), the coatings that delaminated could have had a lower degree of cure, degree of bonding to quartz surface, and crosslink density.

Flexible and Conformal Coatings

Two strategies were employed to obtain flexible but robust coatings. The first strategy was the optimization of the x/y values in x% HBP/y% linear formulations for maximum toughness (or other physical parameters) of interest,[19] and the second strategy was to produce HBPs **6** and **7** with longer spacer units between branch points (Figure 10), and with greater flexibility.[10] HBP **6** and **7** are variants of HBP **1** (Figure 1) having spacers three or four SiO units in length (Figure 10) instead of two (as in HBP **1**). Coatings were screened for transparency, cracking, and general appearance using glass slides as substrates and screened for conformability using a flexible PET substrate. The coated PET substrate was folded sharply in half, and also rolled up into a cylinder with a diameter of one inch, and the coating was assessed for cracking or delamination. The coatings that passed the tests at room temperature then underwent the same conformability tests at −196°C (i.e., the coated PET substrate was manipulated in liquid nitrogen) and at 200°C (i.e., the coated PET substrate was manipulated in an oven). Table IV summarizes the data for the most promising flexible coating formulations.

Three coatings (in **bold**, Table IV) and the space adhesive control material were tested for electron, proton, UV, and thermal cycling resistance, enabling the comparison of different HBP contents (10/90, 25/75, and 49/51), different POSS contents (none in control *versus* some in HBP formulations), different linear chain lengths (linear **2** or **3**), and to make direct comparisons between the same formulation as a coating (direct radiation exposure) and previous results (Table III) where it was used as an adhesive (indirect radiation exposure via a cover glass on top of it). The selected formulations were phenyl-free, as the best UV resistance (after 500 equivalent sun hours) had been obtained with zero phenyl content formulations made from HBPs with ultra-low platinum levels (see earlier discussion). None of the HBP coatings showed any changes in color or texture, or any cracking or delamination.

After proton exposure, the transmission of the DC-93-500 control and 49% HBP **1**/51% linear **2** dropped below 90% at wavelengths above 1000 nm, whereas 10% HBP **1**/90% linear **3** and 25% HBP **2**/75% linear **3** both showed superior proton

resistance above 1000 nm. In the important visible region below 1000 nm, the control, 10% HBP **1**/90% linear **3** and 49% HBP **1**/51% linear **2** all showed transmissions above 90%, but 25% HBP **2**/75% linear **3** was slightly lower, at 90%. After electron exposure, all samples maintained transmissions of 90% and above across the entire wavelength range (300–1500 nm) except for 10% HBP **1**/90% linear **3** that dropped below 90% above 1000 nm. After electron exposure 49% HBP **1**/51% linear **2** had superior transmission to DC-93-500 at the key wavelengths below 1000 nm. After thermal cycling, the three HBP coatings had transmissions of 90% or higher below 1000 nm. Above 1000 nm, all samples also had transmissions of 90% or higher, except for 10% HBP **1**/90% linear **3** that dropped below 90%. Ten percent HBP **1**/90% linear **3** had the lowest HBP content, and also had the poorest transmission above 1000 nm after both electron and thermal cycling exposures. Hence higher HBP contents might be beneficial when designing future coatings formulations.

ACKNOWLEDGMENTS

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