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New Quadricyclane-Based Cyclic Polycarbosilanes

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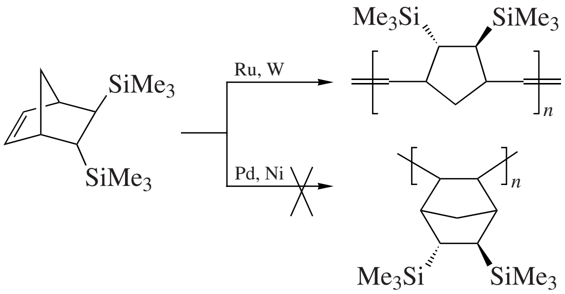
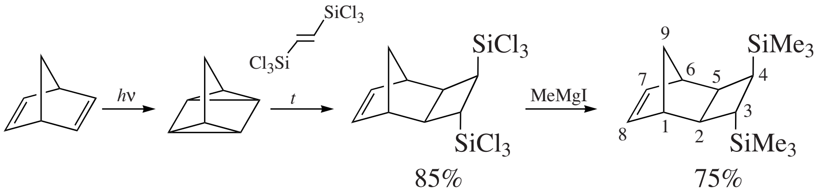
Previously, we showed that silicon-substituted norbornenes and norbornadienes can be widely used for synthesizing macromolecular structures with regularly changed substituents with the aim of revealing theoretically and practically important structure–property relationships [1]. It turned out that polynorbornenes containing trimethylsilyl side groups have good gas transport properties and can serve as efficient membrane materials [2]. We showed that it is precisely Me_3Si substituents that are responsible for the gas-separation properties and an increase in their number in the monomeric unit enhances the permeability coefficients of polymers. When studying the synthesis of polycarbosilanes of this type, we demonstrated that norbornene and norbornadiene with two $SiMe_3$ substituents, being active monomers in metathesis polymerization, are almost not polymerized by the addition (vinyl) scheme (Scheme 1). An analogous problem for fluoro-substituted norbornenes was described in [3].



Scheme 1.

In the present paper, we describe a new efficient approach to the synthesis of Me_3Si-substituted norbornenes capable of polymerizing not only by the metathesis mechanism but also by the addition one. This approach involves removal of bulky Me_3Si substituents from the double bond responsible for polymerization due to the synthesis of 3,4-bis(trimethylsilyl)tricyclo[4.2.1.0^{2,5}]non-7-ene. This compound was synthesized by a reaction that had not been described in organosilicon chemistry, namely, by the reaction of quadricyclane with the corresponding organochlorosilane, *trans*-1,2-bis(trichlorosilyl)ethylene, and subsequent methylation of the resulting chlorosilyltricyclononene (Scheme 2).



Scheme 2.

In addition to the availability of the reagents and the simplicity of the method, an important feature of the discovered reaction is its stereospecificity. The only product of heat treatment of quadricyclane with a silicon-substituted olefin is tricyclononene with the cyclobutane fragment in the *exo* position. The high reactivity of quadricyclane offers a wide spectrum of possibilities for synthesis of various otherwise unavailable norbornene derivatives from silicon-substituted olefins and acetylenes.

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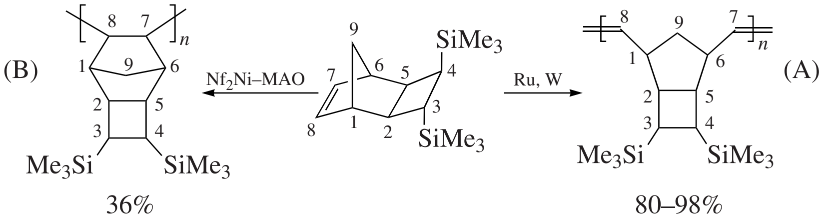
Quadricyclane was synthesized by photochemical isomerization of norbornadiene in a diethyl ether solution in the presence of a sensitizer (acetophenone) [4]. The reaction of quadricyclane with *trans*-bis(trichlorosilyl)ethylene was carried out in an inert atmosphere at 95°C and the ratio quadricyclane : olefin = 2 : 3. The conversion of quadricyclane was monitored by ^{1}H NMR. The basic side reaction is the thermal isomerization of quadricyclane into norbornadiene. Synthesized 3,4-bis(trichlorosilyl)tricyclo[4.2.1.0^{2,5}]non-7-ene and 3,4-bis(trimethylsilyl)tricyclo[4.2.1.0^{2,5}]non-7-ene (BSTN) were isolated as individual compounds and characterized by chromatography/mass spectrometry, IR spectroscopy, and NMR. The exo conformation of the cyclobutane fragment was confirmed by means of 2D NMR: the COSY spectrum lacks cross-peaks due to coupling of the protons at C-2 (C-5) with the protons at C-1 (C-6), which is typical of the exo derivatives of norbornene [5]. Two upfield signals in the ^{1}H NMR spectrum at 0.00 ppm (9H) and –0.03 ppm (9H) are evidence of the *trans* arrangement of the Me_3Si substituents.

BSTN was successfully involved in both metathesis (A) and addition (B) polymerizations (Scheme 3).



Scheme 3.

Metathesis polymerization (Scheme 3A) was carried out in different catalytic systems, including the Grubbs catalyst [6], by methods described in [2, 7]. Polymerization yielded amorphous polymers soluble in aromatics and chlorohydrocarbons. Metathesis polymers obtained from BSIN were characterized by NMR, IR spectroscopy, gel permeation chromatography (GPC), and differential scanning calorimetry (DSC). The ^{1}H NMR spectrum of the polymer shows signals due to the double bond protons (m, 5.25–5.00 ppm), the cyclopentane protons (m, 3.06, 2.78, 2.47–1.73, 1.33, 1.08 ppm), and the *exo*-$SiMe_3$ and *endo*-$SiMe_3$ protons (m, 0.01 to –0.07 ppm). Due to different stereoselectivities of the catalysts used, we were able to identify ^{1}H NMR signals due to the protons at C-1 (C-6) in the allyl position to the *cis* (3.06 ppm) and *trans* (2.77 ppm) double bonds. The characteristics of the resulting polymers are summarized in the table. As follows from the table, the $RuCl_3$–EtOH catalyst exhibits the highest stereoselectivity and WCl_6/TMSB exhibits the lowest stereoselectivity. An analogous situation was previously observed for metathesis poly(trimethylsilylnorbornene)s [7]. The synthesized silicon-substituted polytricyclononenes have a lower glass transition temperature ($T_g = 130°C$) than poly(5,6-bis(trimethylsilyl)-2-norbornene) ($T_g = 167°C$) [7].

As distinct from 5,6-bis(trimethylsilyl)-2-norbornene, BSTN is capable of addition homopolymerization (Scheme 3B) over the nickel naphthenate (Nf_2Ni)–methylalumoxane (MAO) catalyst. The polymerization was carried out as described in [2]. This polymerization is slower than metathesis polymerization and provides lower yields: at the molar ratio monomer : Ni : MAO = 400 : 1 : 100, the polymer yield is 36%, $M_w = 40\,000$, $M_w/M_n = 1.6$, and $T_g = 168°C$. Such a behavior of monomers is typical of these polymerization schemes since metathesis polymerization is considerably more favorable than addition polymerization.

Metathesis polymerization of 3,4-bis(trimethylsilyl)tricyclo[4.2.1.0$^{2.5}$]non-7-ene

Catalyst (application conditions)	BSTN/catalyst (mol/mol) ratio	Yield, %	M_w^*, g/mol	M_w/M_n	T_g, °C	*cis*/*trans* ratio of double bonds**, %
$RuCl_3$–EtOH (65°C, 15 h)	50	80	8×10^5	2.1	131	5
$Cl_2(PCy_3)_2Ru=C(H)Ph$ (20°C, 24 h)	500	98	4×10^5	1.6	123	22
	1500	98	8×10^5	1.8		
WCl_6–TMSB (20°C, 24 h)	100	98	1×10^6	1.6	129	47
	500 (30 min)	65	2×10^6	1.4		

Note: TMSB is 1,1,3,3-tetramethyl-1,3-disilacyclobutane; * determined by GPC using polystyrene standards; ** determined from ^{1}H NMR spectra.

Increasing temperature to 90°C allowed us to increase the yield of the addition polymer to 80%. Addition poly(BSTN) is soluble in aromatic solvents and chlorohydrocarbons. Its structure was proved by NMR: the lack of double bond signals in both the ^{1}H and ^{13}C NMR spectra, and the integrated intensities of the signals of the $SiMe_3$ protons (–0.01, m, 18H) and carbocycle protons (2.77–0.73, br s, 10H) correspond to the suggested structure. It is interesting that synthesized addition poly(BSTN) has a glass transition temperature of 168°C, whereas the DSC curves of unsubstituted addition polynorbornene and addition poly(5-trimethylsilyl-2-norbornene) do not show peaks corresponding to glass transition up to 350–370°C (decomposition onset). This can be associated with a less rigid packing of polymer chains in the synthesized polymer.

Thus, we discovered a new reaction for the chemistry of organosilicon compounds, namely, the condensation of quadricyclane with alkenylsilanes. This approach makes it possible to synthesize new polycarbosilanes—addition and metathesis polytricyclononenes containing more than one Me_3Si group in the monomeric unit.

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