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SYNTHESIS OF ORGANOSILICON POLYMERS—I. SILICONE AND SILICON CARBIDE COPOLYMERS: SYNTHESIS AND PHYSICAL PROPERTIES

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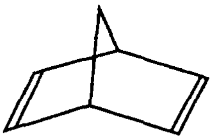
Abstract—This work relates to a novel silicone and silicon carbide copolymer prepared by copolymerizing a cyclic or polycyclic non-conjugated diene with polysiloxane or dihydrosilyl hydrocarbon through the so-called hydrosilation. Norbornadiene, 5-vinyl-[2,2,1]bicyclohept-2 ene and 4-vinylcyclohexene have been copolymerized with 1,1,3,3-tetramethyldisiloxane and 1,4-bis(dimethylsilyl)benzene. The polymers are stable thermally up to 440°.

INTRODUCTION

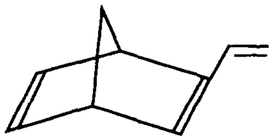
This work relates to a novel silicone copolymer [1] and silicon carbide copolymer [2] prepared by copolymerizing a cyclic or polycyclic nonconjugated diene with polysiloxane or dihydrosilylhydrocarbon through the so-called hydrosilation.

Very few attempts to obtain organosilicon polymers by hydrosilation have been made up to now. Silicon-containing resins such as silicone polymers are however produced on an industrial scale because of their excellent physical properties such as thermal stability. In addition it is anticipated that polymers having cyclic structures in the main chain have improved thermostability. It is therefore the primary object of the present work to provide a novel thermally stable linear polymer prepared by hydrosilation of a cyclic nonconjugated diene with telechelic dihydropolysiloxane or telechelic dihydrosilylhydrocarbon.

[2,2,1]-Bicyclohepta-2,5-diene or norbornadiene (NBD) and 5-vinyl [2,2,1]-bicyclo hept-2-ene or vinylbicycloheptene (VBH) have been chosen as dienes.

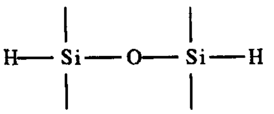


(NBD)



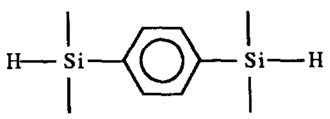
(VBH)

They are copolymerized with 1,1,3,3,-tetramethyldisiloxane (M'_2) and 1,4-bis(dimethylsilyl)benzene (DMSB).



$H—Si—O—Si—H$

(M'_2)



(DMSB)

Part I of this communication describes the synthesis of the various polymers and examination of their physical properties (glass transition temperature and thermal stability) in relation to molecular weight and structure. Part II deals with the isolation of a catalytic species: the norbornadiene/Pt^{II} complex and its use in step "hydrosilation-polymerization".

EXPERIMENTAL PROCEDURES

Polycondensation

In a typical run 1.843 g (0.02 mol) of NBD were mixed with 3.889 g (0.02 mol) of DMSB and 0.08 ml of the catalyst solution in isopropanol ($1.7 \cdot 10^{-6}$ mol of hexachloroplatinic acid) without any reaction solvent. The mixture was heated at 68° for 3 hr to obtain a polymer at a yield of 100%. After cooling to ambient temperature, the polymers were fractionated and purified by precipitation from THF solution with methanol and dried under vacuum at 60°.

Polymer characterization

The molecular weight distribution was found by gel permeation chromatography using a Waters apparatus and THF as eluent. The number-molecular weight was measured by tonometry in toluene (Knauer apparatus). The DSC analysis was performed with a DSC 2 Perkin–Elmer apparatus. The thermogravimetric measurements were made with a Mettler thermobalance using a temperature programme of 10°/min from 35° to 750°.

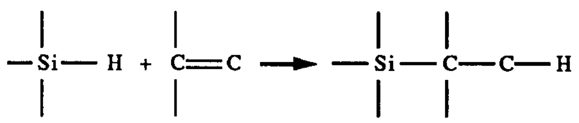
Monomers

NBD and VBH were supplied by Nippon Petrochemicals. M'_2 was a Wacker Chemie product. DMSB was provided from Petrarch. They were used without further purification.

RESULTS AND DISCUSSION

I. Synthesis of polymers

It is well known, that hydrosilanes having hydrosilyl groups can be added to olefins in the presence of a catalyst. This reaction proceeds according to the following scheme:



$$-\overset{|}{\underset{|}{Si}}-H + \overset{|}{\underset{|}{C}}{=}C \longrightarrow -\overset{|}{\underset{|}{Si}}-\overset{|}{\underset{|}{C}}-C-H$$

The hydrosilation takes place in the presence of several catalysts such as peroxides [3], platinum derivatives [4] or azo-compounds [5].

The polymers obtained in this work by "hydrosilation-polymerization" have relatively low molecular weights ranging from 1500 to 25,000 g · mol^{-1}. They have the following structures:

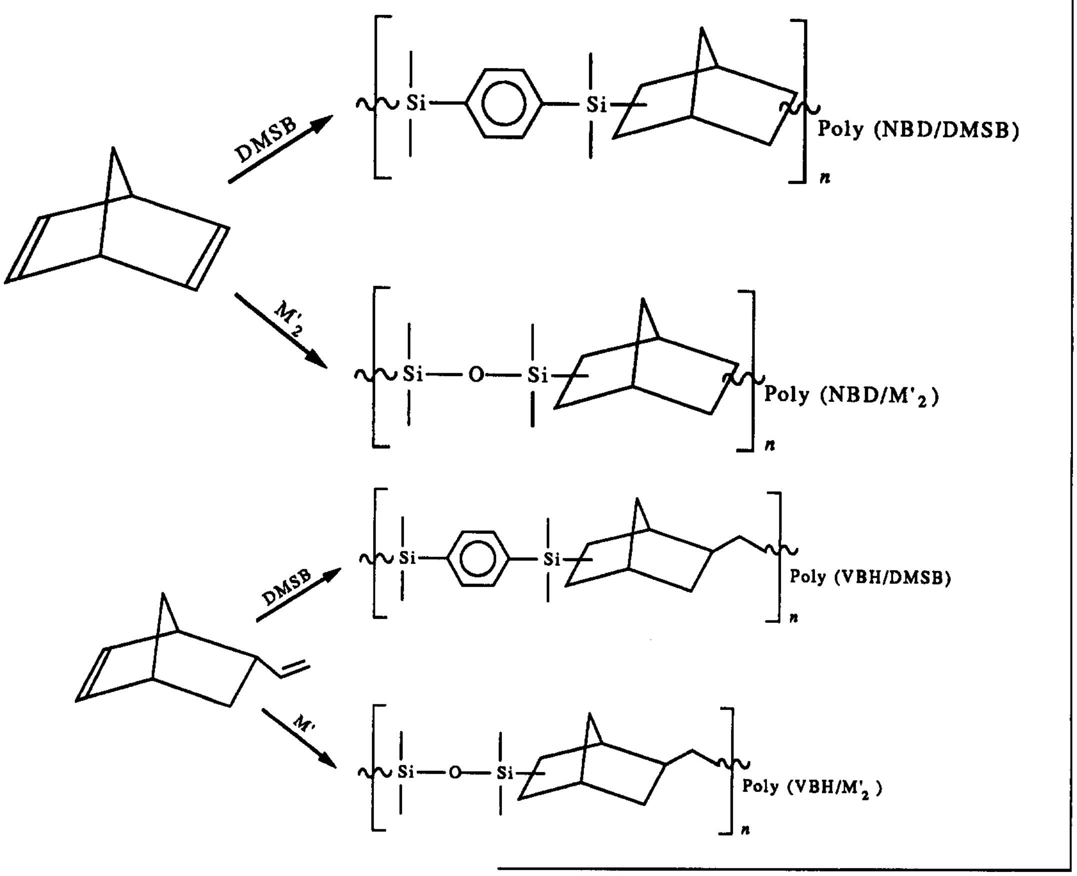


Table 1 shows the results for various experimental conditions.

It is surprising to note that the number-average molecular weight of poly(NBD/DMSB) does not change significantly on modifying the experimental conditions. Even catalyst concentration, temperature and duration of the reaction do not greatly affect $\bar{M}_n$ which ranges from 1200 to 3300 g · mol^{-1}.

On the other hand, the polycondensation of VBH is more affected as shown by the variation of $\bar{M}_n$. In some cases it is possible to reach molecular weights of the order of 25,000 g · mol^{-1} after fractionation by precipitation in methanol. But if one compares the crude product before separation of the high molecular weight fraction, the molecular weights of the two types of polycondensates remain low ($\leqslant$ 5500 g · mol^{-1}).

This fact may be explained because the polycondensation is conducted in the bulk state. In the presence of DMSB, the reaction mixture turns from liquid to solid after 20–30 min according to the catalyst concentration: the macromolecular active species would be trapped and the rate becomes very low. This phenomenon may be explained by considering cyclization reactions or side reactions of the Si—H group as mentioned in the literature [6, 7]. In order to increase the rate and therefore to obtain higher molecular weights, we attempted polycondensation with DMSB in the molten state (Table 2).

In the first step, the reaction mixture was heated at 68° for 1.5 to 6 hr. The initial reactants in the liquid state solidified. In the second step, the solid reaction mixture was heated to 200° for 6 hr to obtain a solid polymer at a yield of 100%. Table 2 shows that these drastic new experimental conditions do not affect greatly the molecular weights which are of the same magnitude as those mentioned above or those reported

Table 1. Polycondensation of NBD and VBH with DMSB and M'_2 P_{SiH}, extent of reaction; $\overline{M_{n_i}}$, number molecular weight before fractionation; $\overline{M_{n_2}}$, number molecular weight after fractionation by precipitation with methanol; $\overline{DP_n}$, polymerization degree of the fractionated polymer

Monomer	[Monomer] (mol/l)	[Pt] (mol/l)	T(°C)	Time (hr)	Yield (%)	P_{SiH}	$\overline{M_{n_i}}$	$\overline{M_{n_2}}$	$\overline{DP_n}$
NBD/DMSB	3.02	10^{-4}	65	66	100	0.95	1500	—	—
NBD/DMSB	3.02	$2.56 \cdot 10^{-4}$	65	66	100	0.94	1800	2700	19
NBD/DMSB	3.02	$3.00 \cdot 10^{-4}$	65	66	100	0.97	1700	—	—
NBD/DMSB	3.02	$5.00 \cdot 10^{-4}$	65	66	100	0.98	2800	—	—
NBD/DMSB	3.02	$2.56 \cdot 10^{-4}$	58	66	100	0.98	1200	—	—
NBD/DMSB	3.02	$2.56 \cdot 10^{-4}$	65	66	100	0.95	1800	2700	19
NBD/DMSB	3.02	$2.56 \cdot 10^{-4}$	78	66	100	0.97	1400	—	—
NBD/DMSB	3.02	$2.56 \cdot 10^{-4}$	65	42	100	0.94	1600	—	—
NBD/DMSB	3.02	$2.56 \cdot 10^{-4}$	65	66	100	0.95	1800	2700	19
NBD/DMSB	3.02	$2.56 \cdot 10^{-4}$	65	90	100	0.95	3300	—	—
NBD/M'_2	3.50	$2.56 \cdot 10^{-4}$	65	24	100	0.96	2700	6000	53
VBH/DMSB	2.73	$2.88 \cdot 10^{-5}$	65	24	100	0.95	3100	3500	22
VBH/DMSB	2.73	$5.78 \cdot 10^{-5}$	65	24	100	0.95	2500	3100	20
VBH/DMSB	2.73	$1.16 \cdot 10^{-4}$	65	24	100	0.97	3000	5100	32
VBH/DMSB	2.73	$2.56 \cdot 10^{-4}$	65	24	100	0.99	2800	5700	36
VBH/DMSB	2.73	$3.18 \cdot 10^{-4}$	65	24	100	0.99	4800	7800	50
VBH/DMSB	2.73	$2.56 \cdot 10^{-4}$	65	24	100	0.99	2800	5700	36
VBH/DMSB	2.73	$2.56 \cdot 10^{-4}$	80	24	100	0.99	2500	6900	44
VBH/DMSB	2.73	$2.56 \cdot 10^{-4}$	100	24	100	0.98	3200	25,300	161
VBH/DMSB	2.73	$2.56 \cdot 10^{-4}$	65	6	100	0.98	2500	3700	24
VBH/DMSB	2.73	$2.56 \cdot 10^{-4}$	65	24	100	0.99	2800	5700	36
VBH/DMSB	2.73	$2.56 \cdot 10^{-4}$	65	43	100	0.99	2200	5600	36
VBH/DMSB	2.73	$2.56 \cdot 10^{-4}$	65	72	100	0.99	2400	6100	39
				120	100	0.99	2300	6600	42
VBH/M'_2	3.12	$2.56 \cdot 10^{-4}$	65	24	100	0.99	1900	5000	39

Table 2. Polycondensation in the molten state of NBD/DMSB

Step 1		Step 2					
T(°C)	Time (hr)	T(°C)	Time (hr)	P_{SiH}	$\overline{M_{n_i}}$	$\overline{M_{n_2}}$	$\overline{DP_n}$
68	1.5	200	6	0.98	3000	4200	29
68	3	200	6	0.98	2500	7000	49
68	6	200	6	0.97	3500	4300	29

[NBD], 3.02 mol/l.
[Pt], $2.56 \cdot 10^{-4}$ mol/l.

Table 4. Thermal stability data.

Sample	$\overline{M_n}$	T_0(°C)	T_{max}(°C)
Poly(NBD/DMSB)	1500	430	516
Poly(NBD/DMSB)	2500	430	517
Poly(NBD/DMSB)	7000	440	520
Poly(VBH/DMSB)	3000	430	505
Poly(VBH/M'_2)	1900	350	500

T_0, initial degradation temperature.
T_{max}, total degradation temperature.

in the literature [3, 8]. Nevertheless the GPC curves show a narrower molecular weight distribution when the reaction is done in the molten state, with a shift to higher molecular weights.

The polymers obtained with DMSB are solid and semi-crystalline and those obtained with M'_2 are highly viscous liquids.

II. Physical properties

(a) Variation of glass transition temperature with $\overline{M}_n$. T_g increases with molecular weight as predicted by the Fox and Loshaek theory [9]. This effect is illustrated in Table 3.

If we compare poly(NBD/DMSB) and poly(VBH/DMSB), T_g decreases sharply for the second species: it drops from 56° to 37° for $\overline{M}_n = 3300\ g \cdot mol^{-1}$ and $3000\ g \cdot mol^{-1}$, respectively. This result is in good agreement with the structure of the VBH/DMSB polycondensate: in that case the polymer backbone is less rigid because of the presence of the CH_2—CH_2 structural group. This effect is markedly increased if DMSB is replaced by M'_2 in which case T_g drops to −34°.

Table 3. Variation of T_g with $\overline{M}_n$ and structure

Monomer	$\overline{M_n}$	T_g (°C)
NBD/DMSB	1200	35
NBD/DMSB	1300	42
NBD/DMSB	1600	49
NBD/DMSB	1800	52
NBD/DMSB	3300	56
VBH/DMSB	3000	37
VBH/M'_2	2500	−34

(b) Thermal stability. Table 4 shows that no change in weight was observed up to 430–440° for the silicon carbide polymer when heated in nitrogen. Nevertheless it seems that the polysiloxane type polymers (polyVBH/M'_2) are less stable ($\leqslant$ 350°) than the polysilylcarbide polymers. The stability is not dependent on the molecular weight.

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