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POLYCYCLOCARBOSILOXANE NETWORKS

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ABSTRACT

A new class of hybrid organic-inorganic materials was synthesized and characterized. These compounds were obtained through the hydrosilylation reaction of a vinyl-containing polydimethylsiloxane with two kinds of Si-H functional cyclic carbosiloxanes: 1) bis-[1,4-bis(methylhydrosiloxanyl)-dihydronaphthalene],- (MHCDHNF); 2) 2,5-dimethyl-2,5-dihydro-3, 3-diphenyl-1,4-di-oxa -2,5-disil-a-cyclopentane, (MHCDFMO).

The different reactivities of the Si-H groups resulted in a two-stage crosslinking process (in the presence of the hexachloroplatinic acid as catalyst) with onset of crosslinking occurring at 100˚C and 150˚C. The components of the final reaction mixture were analyzed by IR, ^{1}H-NMR and gel-permeation chromatography (GPC) to establish their formal structure and infer a reaction pathway.

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INTRODUCTION

The silicon-containing materials represent an important part of inorganic chemistry. These materials can range from physical mixtures of inorganic oxides and organic macromolecules to compounds with silicon covalently bonded to organic fragments. A method to improve physical properties of these silicon-containing compounds is the reduction of the heterogeneous components domain size to the molecular level via incorporation of inorganic and organic constituents in the same molecule [1, 2]. Using specially designed organic segments will permit the engineering of silicon-containing molecular structures with novel chemical and physical properties. Of particular interest is the porous structure of specially designed macromolecular networks. These networks can be exploited for growing nano-scale particles in nanocluster synthesis [3]; for the incorporation of useful organic functionalities into catalysts [4]; or for the preparation of transparent films with special optical properties and nonlinearities [5]. Until now, bridged polysilsequioxanes were one of the main sources for these materials. The present study shows how cyclocarbosiloxanes may be used as an alternate route to obtain crosslinked organic-siloxane materials. The porous structure of these materials will be the result of cyclic segments inclusion as well as bridging processes, leading to better control of the final architecture of the network. The synthesis of the hybrid cyclic compounds and some successful attempts to obtain cyclolinear oligomers were presented by the current authors in previous works [6-8, 9, 10].

EXPERIMENTAL

Materials

Octamethylcyclotetrasiloxane (D_4) - supplied from Fluka Ag.

M = 296.62; purity (GC) = 99%; b.p. = 176˚C.n_D^{20}= 1.3962; d_4^{20}= 0.955 g/cm^3.

Tetramethyltetravinylcyclotetrasiloxane (V_4) was synthesized as presented in [11]. M = 344.66; purity: 99% (GC); M.p.= -43.5˚C; b.p.= 111˚C/10mmHg;n_D^{20}= 1.4343. d_4^{20}= 0.9862. Hexamethyldisiloxane (HMDS) - supplied from Petrarch ABCR.

M= 162.38; purity: 99% (GC). B.p.= 90˚C; n_D^{20}= 1.3774; d_4^{20}= 0.7619. VIONIT, catione exchanger. Hexachloroplatinic acid, $H_2PtCl_6.6H_2O$ solution in isopropyl alcohol (HCPA) - supplied from Fluka Ag.

Apparatus

IR spectra were recorded on a Specord M80 spectrophotometer using KBr pellets.

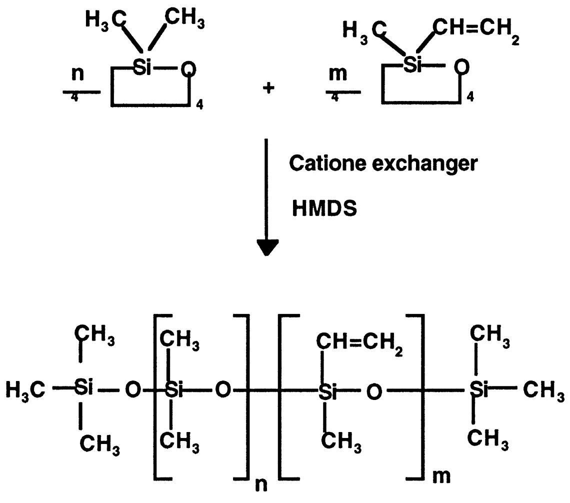
^{1}H-NMR Spectra were registered using a Bruker AC-80 HL spectrophotometer with TMS as an internal standard.

The relative and kinematic viscosities measurements were made in toluene at 20˚C using a Canon-Ubbelohde viscometer.

Molecular weights were obtained through GPC analysis using a modular Gilson HPLC system equipped with Zorbax PSM-S columns. An UV116 spectrophotometer and a R132 differential refractometer were used as detectors. Molecular weight was calibrated with 13 polystyrene etalons, each with narrow molecular weight distribution. To obtain the mean molecular weight values all the chromatograms were processed on an ICERP computer.

Synthesis of Poly(dimethylsiloxane-co-methylvinylsiloxane) (Mn= 5000 g/mole)

The poly(dimethylsiloxane-co-methylvinylsiloxane) oligomer was obtained through a cationic heterogeneous polymerization reaction of octamethylcyclotetrasiloxane (D_4) and methylvinylcyclotetrasiloxane (D_V) using VIONIT as catalyst [11] (reaction Scheme 1). To maintain the final products sol-



Reaction Scheme 1

ubility for subsequent reaction steps, the D_4/D_V mole ratio was adjusted to higher values to obtain a low degree of cross-linking. The prescribed molecular weight (5000 g/mole) was achieved by adding hexamethyldisiloxane (end groups capping agent). The experimental procedure was as follows: into a reaction flask (equipped with mechanical stirrer, reflux condenser and gas inlet), were charged: 0.08 moles of D_4, 0.008 moles of V_4 and 0.005 moles of HMDS. Previously the reactor was carefully purged with dry argon. This mixture was heated to 70˚C and then 0.625 g of catalyst were introduced.

After 25 hours, the reaction was stopped and the catalyst was removed through filtration.The final product (transparent oil) was distilled at 150˚C and 8 Torr. The ^{1}H-NMR spectrum of the resulting copolymer shows a dimethylsiloxi/methylvinylsiloxi groups ratio of 19:1 (11.6% vinyl groups).

Functional Cyclocarbosiloxanes Synthesis

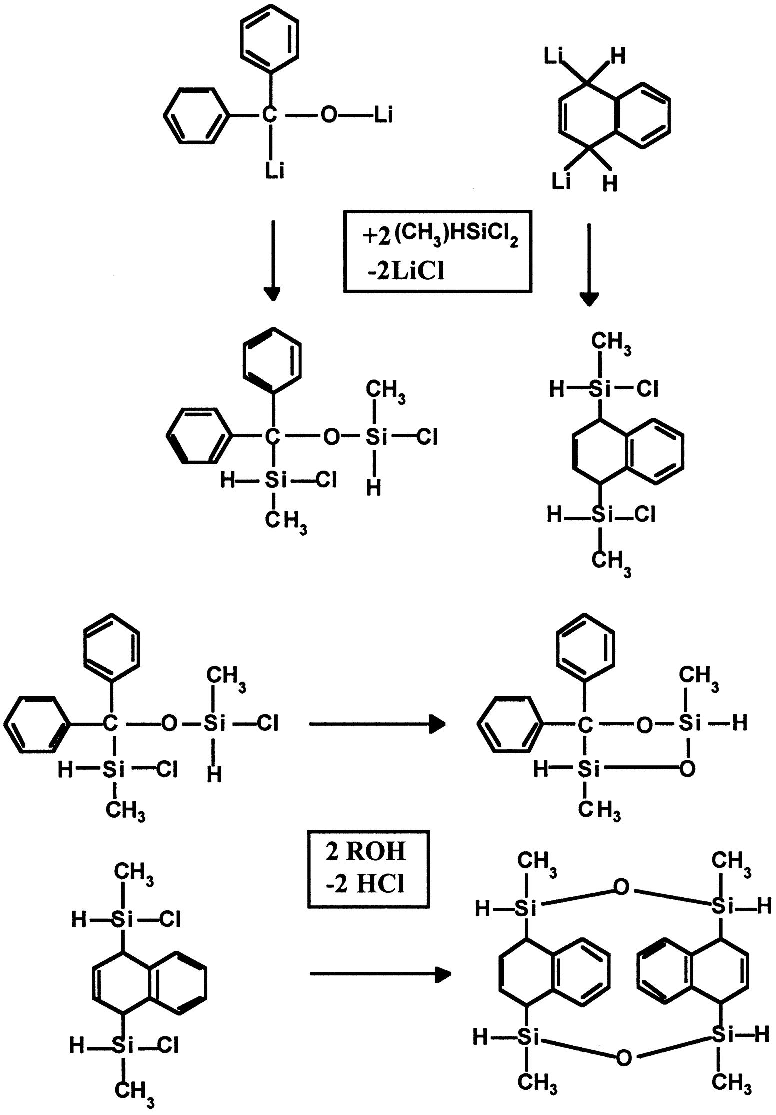
Cyclocarbosiloxane from the dihydronaphthalene and diphenylmethoxi series were prepared according to a previously described method [6, 10] using the condensation reaction of methyl(H)dichlorosilane with dilithium derivatives of naphthalene and diphenylketone respectively. The alcholysis reaction of both Si-Cl groups leads to cyclic organosilicon compounds with reactive hydrosilyl functional groups (reaction Scheme 2).

Synthesis of the Three-Dimensional Polycyclocarbosiloxanes Architectures

Polycyclocarbosiloxanes were synthesized through the hydrosilylation reaction of the vinyl siloxane oligomer with the Si-H reactive groups of the cyclic carbosiloxane structures (reaction Schemes 3 and 4).

Both reactants, 5 g (0.001 moles) of linear copolysiloxane and 0.001 moles of functional cyclocarbosiloxane (molar ratio 1:1), were charged under dry inert atmosphere into freshly dried toluene (50-60% by volume) in a reaction vessel equipped with reflux condenser and mechanical stirrer. Then 0.01N solution of hexachloroplatinic acid in isopropyl alcohol (5.10^{-6} g H_2PtCl_6/ mole compound with vinyl groups) was added. The reaction mixture was heated to 100°C and maintained at this temperature until constant viscosity was achieved.

In the second stage, the solvent (toluene) was eliminated through distillation and then, the reaction temperature was raised to 150°C under continuous stirring. When the reaction was complete (40 hours for the DHNF series and 21 hours for the DFMO series), the mixture was cooled to room temperature giving



Reaction Scheme 2

a brownish-yellow viscous liquid. This product was washed with isopropyl alcohol to remove the unreacted cyclocarbosiloxane (yield 60-70%) and then analyzed using GPC (1% solution in chloroform) to determine the molecular weight distribution.

The same procedure was used for both series of cyclocarbosiloxanes.

RESULTS AND DISCUSSION

The hydrosilylation reaction [12] was used to obtain three-dimensional structures from a parent vinyl containing polysiloxane and Si-H functional cyclocarbosiloxanes derived from either dihydronaphthalene series or diphenylmethoxy series.

The common Speier catalyst (HCPA) [13] leads to a small degree of conversion (especially in the cyclodihydronaphthalene case), as a consequence of the steric hindrance.

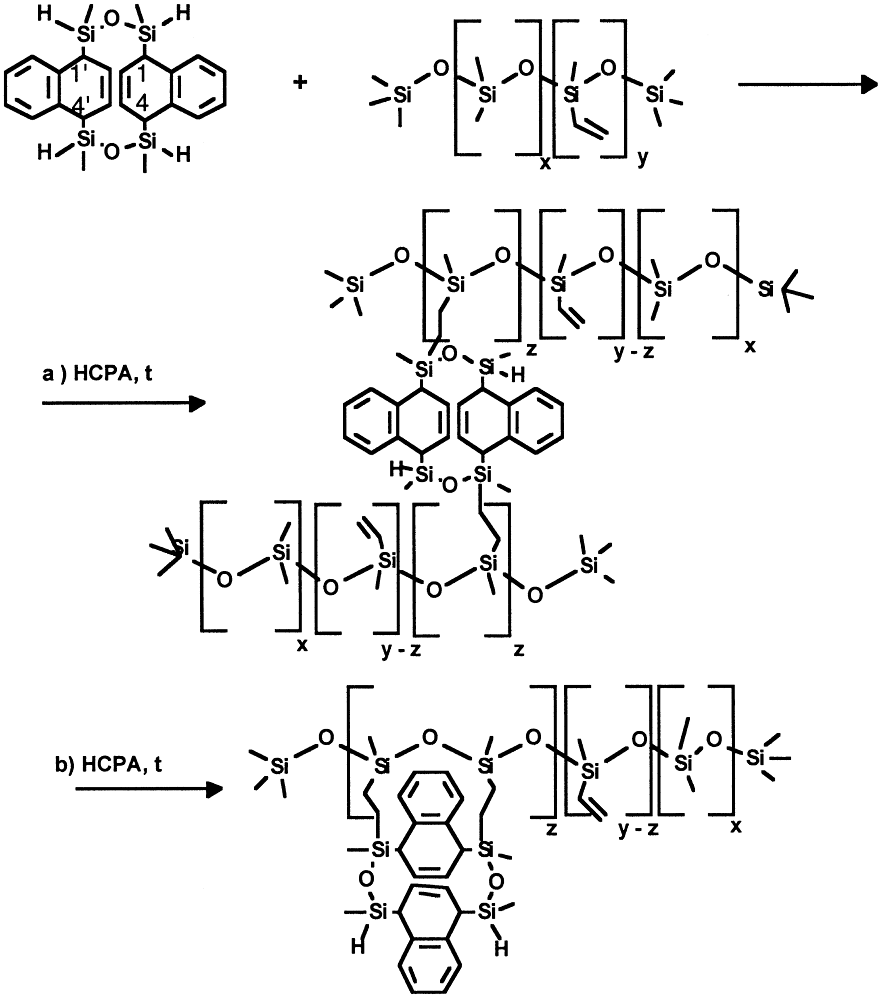
In the cyclic structures the reactivity of the functional groups was influenced by the reaction temperature and the relative position of these functional groups [14]: the reaction was thermally dependent if both functional groups belonged to silicon atoms engaged in the same siloxanic bond. Below 100°C only one of the functional Si-H groups reacted, while over 150°C the second Si-H group became reactive; if the two functional groups were separated and positioned at longer distances, then both participated in the hydrosilylation process at temperatures below 100°C.

For this reason, cyclocarbosiloxanes of the dihydronaphthalene series were bifunctional compounds even below 100°C, resulting in the presence of crosslinked products at the onset of reaction.

As illustrated in reaction Scheme 3, there are two possible reaction mechanisms: the addition reaction is intramolecular, resulting in small values of the oligomer molecular weight; the addition reaction is intermolecular and leads to considerably increased molecular weight values.

Because the GPC analysis of the reaction product yielded a molecular weight close to the apriori estimated value for an intermolecular crosslinked product (Table 1), it was concluded that the second mechanism (intermolecular crosslinking), was the principal pathway for the reaction. The presence of the three different peaks suggests that the reaction mixture contains unreacted polysiloxane, partially reacted chains and polycyclocarbosiloxane product (Figure 1).

Finally, we can conclude that in the first stage of the reaction only two of the four Si-H groups of the cyclic structure were involved in the crosslinking process (position 1, 4). The basic element of the structure encloses two siloxane linear chains bridged through a cyclic carbosiloxane (path a). The molecular weight values show that only a portion of the reactive groups participated in the addition reaction. Therefore, the final product in this reaction stage is a mixture of siloxane oligomer chains with pendant cyclic units (as a result of a single Si-



(For clarity methyl groups are not illustrated)
Reaction Scheme 3 (DHNF series)

TABLE 1. Kinematic Viscosity and Molecular Weight of the Synthesized Products at 100°C and 150°C, Respectively (DHNF Series)

T °C	n cSt	Mw_o g. mole^{-1}	M_W (a) g. mole^{-1}	M_W (b) g. mole^{-1}
25	54	5000		
100	124.5		8200	5500
150	381		14100	10500

Mw_o = gravimetric mean molecular weight of the siloxane oligomer with pendant vinyl groups.
M_W (a)= gravimetric mean molecular weight of the carbosiloxane network on reaction path (a) (GPC).
M_W (b) = estimated gravimetric mean molecular weight of the carbosiloxane network on the reaction path (b).

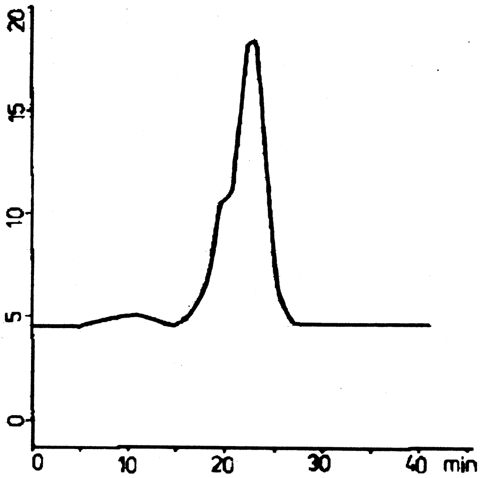


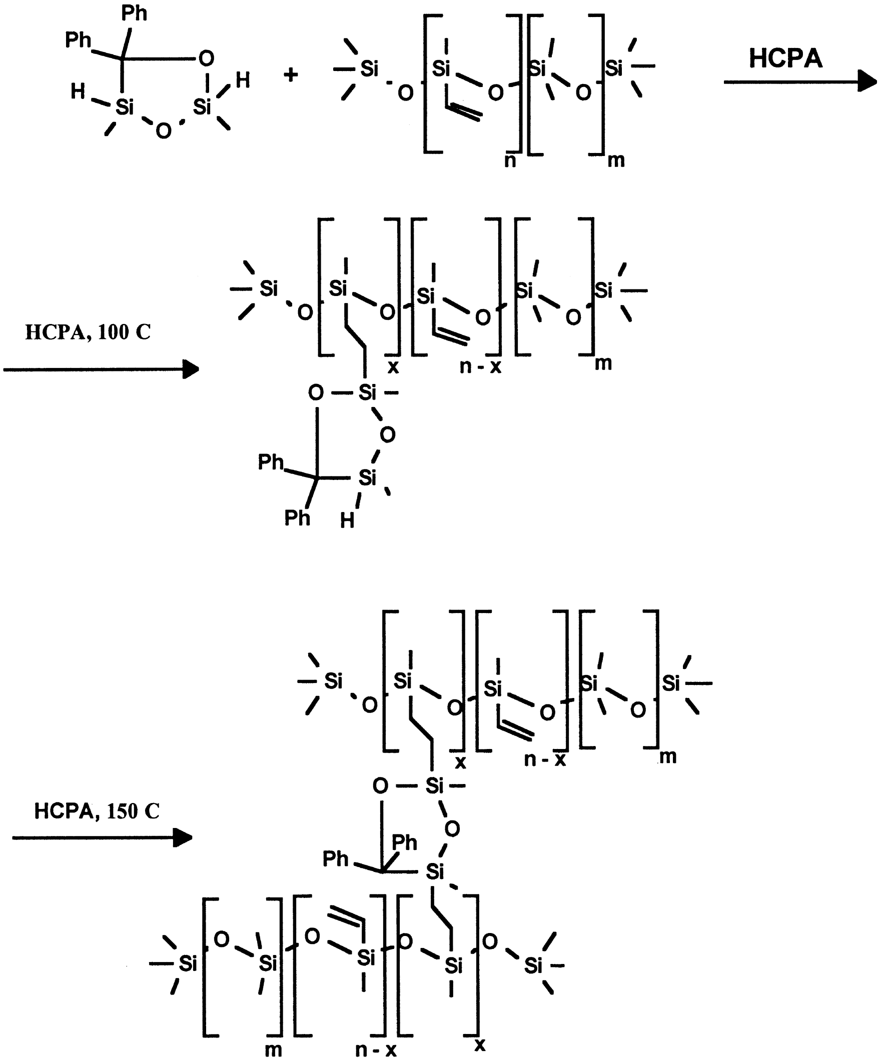
Figure 1. GPC elution chromatogram of the final mixture (DHNF series).

H group reaction) and macromolecular chains crosslinked through cyclic units (as a result of the two Si-H reactive groups both reacting). In the second stage, increasing the reaction temperature leads to an activation of the two remaining Si-H groups on the cyclic structure. The random presence of neighbouring vinyl groups will make the hydrosilylation process proceed. The molecular weight values suggest the conclusion that: the initiated crosslinking process through the reactive Si-H groups (position 1,4 or 1,4') continued, and a new similar addition reaction have started as a result of the activation of the other groups (position 1,1' or 4,4'), leading to significantly increased values of the relative viscosity (path a).

In the diphenylmethoxy series (DFMO), there was only one reactive Si-H group for the first stage of the reaction and therefore, higher molecular weight products appeared only in the second phase of the process (reaction Scheme 4).

To obtain information about the formal architecture of this polymer, molecular weight analysis and viscosity measurements were also made. The results are presented in Table 2.

In conclusion, in the first reaction stage (up to 100°C) the slight variation of the molecular weight values and viscosities (Table 2) suggest that the hydrosilylation reaction proceeds through only one of the Si-H groups of the cyclic



Reaction Scheme 4 (DFMO series)

MHCDFMO compound. In this case, the basic structure encloses the siloxane chain and one or two pendant cyclic segments.

In the second stage of the reaction, above 150°C, the viscosity shows significantly higher values (Table 2). For this reason the final product was considered to be the result of the addition reaction of the second Si-H group of the cyclic structure with vinyl groups from a neighbor polymethylvinylsiloxane

TABLE 2. Molecular Weight (GPC, 1% in Chloroform) and Kinematic Viscosity for the Cyclocarbosiloxane Mixture (DFMO Series)

Temperature °C	n cSt	M_W* g.mol^{-1}	M_W g. mole^{-1}
100	58.6	4600	5300
150	123.8	5300	7150

M_W*-gravimetric mean of the molecular weight before the reaction started.

chain. The molecular weight analysis shows that the final product is a mixture of macromolecular chains with pendant cyclic segments and crosslinked chains formed through the participation of both Si-H groups (Figure 2).

^{1}H-NMR and IR analyses were performed to monitor the appearance of the characteristic signals of the ethylene bridge which confirmed the addition process (Table 3).

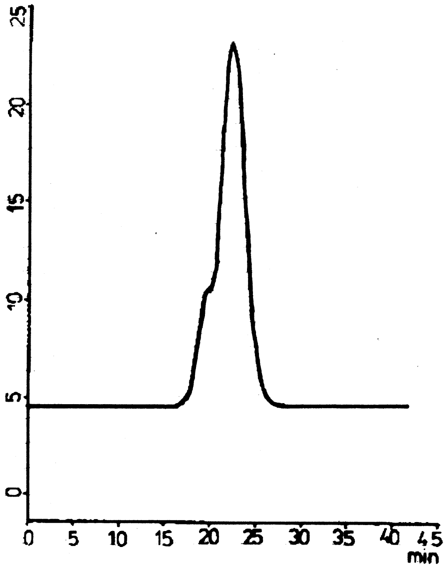
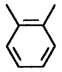
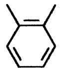


Figure 2. GPC elution chromatogram of the final mixture (DFMO series).

TABLE 3. IR and ^{1}H NMR Analysis of the Synthesized Products

T ^{0}C	Assignment	^{1}H RMN d ppm, $CDCl_3$ DHNF	DFMO	IR cm^{-1} DHNF	DFMO
100		7.02-7.81		3000	
	$C(C_6H_5)_2$		7.21-7.25		3010
	C-H (alkyl)			2900	2900
	Si-H			2150	2160
	Si-Vi	6.01	5.98	1600, 1405	1600,1400
	$Si-CH_2-CH_2-$	0.37	0.38	2910, 1165	1162
	$Si-CH_3$	0.3	0.28	1250, 800	1200,800
150		7.00-7.62		3000	
	$C(C_6H_5)_2$		7.21-7.25		3000
	C-H (alkyl)				2910
	Si-Vi			1600, 1405	
	Si-H			2150	
	$Si-CH_2-CH_2-$	0.36	0.40	2900, 1180	1170
	$Si-CH_3$	0.3	0.30	1200, 800	1200,800

In the ^{1}H-NMR spectrum these signals appeared in the 0.36-0.38 ppm region. Other spectral data correspond to both cyclic and siloxane oligomer. The ^{1}H-NMR analysis shows in the 7.02-7.81 ppm region a complex multiplet which was assigned to the aromatic protons of the cyclic structures. The 5.98-6.01 ppm multiplet, (CH_2=CH-Si-) and the 0.28-0.30 ppm singlet (-Si-CH_3) came merely from the siloxane oligomer as a consequence of it's major ponderal contribution.

IR spectral data show a characteristic fan shaped peak in the 1165 cm^{-1} region (Si-CH_2-CH_2-Si) and a 2900-2950 cm^{-1} absorption band (C-H) which were assigned to ethylene bridge formation.

CONCLUSION

Using Si-H functional cyclic carbosiloxanes, a new class of copolysiloxanes with three-dimensional cyclolinear architectures was developed. The thermal control inherent in the process suggests the possibility of obtaining thermosetting porous materials by increasing the vinyl content of the polysiloxane oligomer.

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