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Hyperbranched polycyclocarbosiloxane

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Abstract

A new cross-linkable naphthalene-cyclocarbosiloxane was synthesised starting from bis[1,4-bis(methylhydrosiloxanyl)-dihydronaphthalene] via catalytic addition of the Si–H reactive groups to the unsaturated bond of triethoxyvinylsilane. Hyperbranched polycyclocarbosiloxane networks were formed by condensation of the alcoxyl groups in the presence of dibutyltin dilaurate as catalyst. The cross-linking process was studied in order to obtain information concerning the values of the reaction parameters and to determine the position of the gelation point relative to conversion.

GPC analysis, IR, and ^{1}H-NMR spectral analysis techniques were used to investigate the chemical structures of the intermediates and of the product. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Siloxane; Carbosiloxane; Hydrosilylation; Carbosiloxane network; Polycyclic architectures

1. Introduction

Over the last twenty years, hyperbranched macromolecular structures with unusual chemical and physical properties and intrinsic "geometrical beauty" have been developed. These structures could be obtained through the development of branched compounds, process that starts at a core and builds outward. The hyperbranched polymers have numerous applications in many areas, such as medicine and biology [1], analytical chemistry [2], catalysis [3], as host molecule for metal ions [5] or molecules [4].

The hyperbranched carbosiloxanes were obtained previously mainly via hydrosilation reactions. The monomers used in these preparations ranged from allyl- or vinylsilanes to specific aliphatic or aromatic analogues [6]. The combination of molecular properties like symmetry, branch content, backbone flexibility, radial distribution, with functional group content and reactivity allowed the development of new materials [7].

Another approach to obtaining three-dimensional networks involves bridged polysilsesquioxanes which are characterised by incorporation of an organic fragment as an integral component of a merely inorganic network [8–10]. Generally these are porous materials with properties determined by the chemical structure of the organic fragment.

This paper describes the synthesis of an ethoxy-functionalised cyclocarbosiloxane, which could be used as a molecular building block to obtain new hyperbranched polycyclic architectures. The rigid dihydronaphthalene cycle could induce a specific pore size and pore distribution in the resulting cross-linked material similar with those characteristic for the bridged polysilsesquioxanes networks.

2. Experimental section

2.1. Materials

Methyldichlorosilane (98.5%) and vinyltriethoxysilane (>98%) were supplied by Merck. Hexachloroplatinic acid, $H_2PtCl_6 \cdot 6H_2O$ solution in isopropyl alcohol

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(HCPA), naphthalene (98.5%) and dibutyltin dilaurate (>97%) were purchased from Fluka Ag.

All monomers were freshly distilled before use.

2.2. Apparatus

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

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

GPC experiments were carried out in toluene solution at 30 °C, at a flow rate 1 cm^3/min using a Spectra Physics 8800 gel permeation chromatograph with two PL-gel packed columns (10^3 and 500 Å). Polystyrene standards with low polydispersity (PL-Lab.) were used to generate a calibration curve.

2.3. Synthesis of bis[1,4-bis(methylhydrosiloxanyl)-dihydronaphthalene]

The synthesis and properties of similar compounds were described in previous works [11,12]. The general procedure is based on the coupling reaction of a specific organodilithium intermediate with functional dichlorosilanes from the $R_1R_2SiCl_2$ series, where $R_1 = –CH_3$ and $R_2 = –CH_3$, $–C_6H_5$, –H, $–CH{=}CH_2$, etc., followed by the hydrolysis reaction of the resulted intermediate (Reaction Scheme 1).

2.4. Synthesis of 1,4-dilithium-1,4-dihydronaphthalene

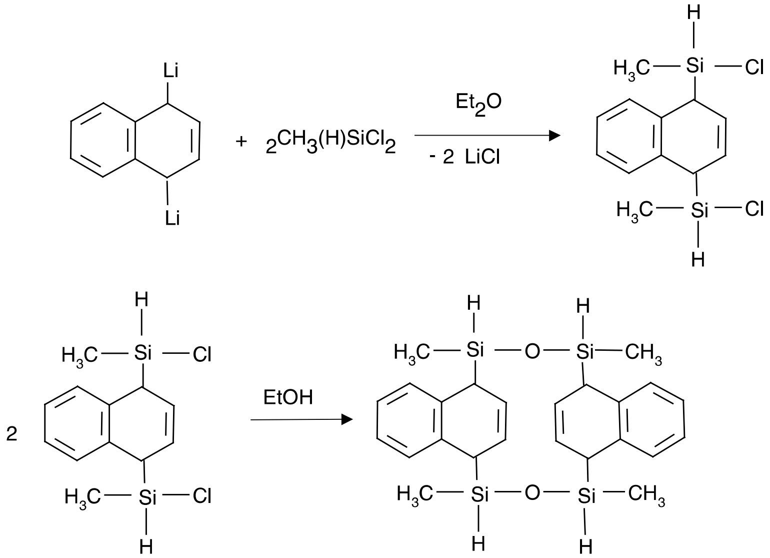
A 250-ml, three-necked, flat-bottomed reaction flask, was carefully dried, and equipped with a magnetic stirrer. 10 g (0.07 mol) of pure naphthalene, 50 ml diethyl ether previously dried over Na wire and 2 g (0.28 mol) of lithium in small grains were added and the reaction vessel was sealed. The mixture was stirred at ambient temperature for 90 h. The dark red ethereal solution of 1,4-dilithium-1,4-dihydronaphthalene (DLDHN) was for immediate use.

2.5. Synthesis of 1,4-(methylhydrochlorosilyl)naphthalene

An identical reaction flask equipped with a stirring bar, a reflux condenser, an argon inlet and a dropping funnel was carefully dried and 0.20 mol methyldichlorosilane dissolved in 50 ml anhydrous diethyl ether were added. The DLDHN solution in diethyl ether was added dropwise with vigorous stirring to avoid overheating due to the exothermic effect of the reaction. After separation of the white LiCl precipitate stirring was continued for one hour. Finally the mixture was refluxed for another 60 min in order to ensure the completion of the reaction and then the reaction mixture was cooled to room temperature. The unreacted lithium grains and LiCl were filtered under positive argon pressure and the excess of methyldichlorosilane and the solvent were stripped off. An amount of 8 g dark yellow liquid product was obtained. Yield: 35%.

2.6. Bis[1,4-bis(methylhydrosiloxanyl)-dihydronaphthalene]

Bis[1,4-bis(methylhydrosiloxanyl)-dihydronaphthalene] (MHDHN) was prepared through the hydrolysis reaction of 1,4-(methylhydrochlorosilyl)naphthalene



Scheme 1. Synthesis of bis[1,4-bis(methylhydrosiloxanyl)-dihydronaphthalene].

(MHCSN) in ethanol. For this purpose, 5 g of MHCSN was added dropwise over 800 ml of ethanol at 5–10 °C under vigorous stirring. The white precipitate was purified by recrystallisation from an (1:1) acetone/isopropyl alcohol mixture. The final product was obtained as a white, solid powder with m.p. = 140.2 °C [11].

2.7. *Synthesis of bis[1,4-bis(triethoxysilylethylenemethylsiloxanyl)-dihydronaphthalene*

This product was obtained via addition of vinyltriethoxysilane to the MHDHN "core" in the presence of a platinum catalyst at 70–80 °C. 3 g (6 m mol) of MHDHN ($M = 464$ g mol^{-1}) in 50 ml dried toluene and hexachloroplatinic acid catalyst solution in isopropyl alcohol (5–8 ppm metal/total weight of the reaction mixture) were mixed in a reaction flask equipped with addition funnel and reflux condenser and heated to 80 °C. Vinyltriethoxysilane, 5 g (31 m mol) was added dropwise, while maintaining the temperature constant. The reaction mixture was refluxed for 36 h, under stirring. IR spectral analysis was used to observe the disappearance of the Si–H bonds. Finally the reaction mixture was cooled to room temperature and the unreacted vinyltriethoxysilane and solvent were distilled under vacuum. The final product was obtained as a viscous oil, 5.2 g, yield = 51% (Fig. 1).

2.8. *Cross-linking reaction*

Cross-linking of the bis[1,4-bis(triethoxysilylethylenemethylsiloxanyl)-dihydronaphthalene (TEDN) was performed using catalytic amounts of dibutyltin dilaurate at various temperatures and exposure to the atmospheric moisture. For this purpose a set of TEDN samples carefully cured under controlled conditions has been prepared. The samples were extracted with toluene and separated into toluene-soluble and toluene-insoluble fractions. The process was considered finished when the insoluble fractions reached a constant weight. The results of the cross-linking process are summarised in Table 1.

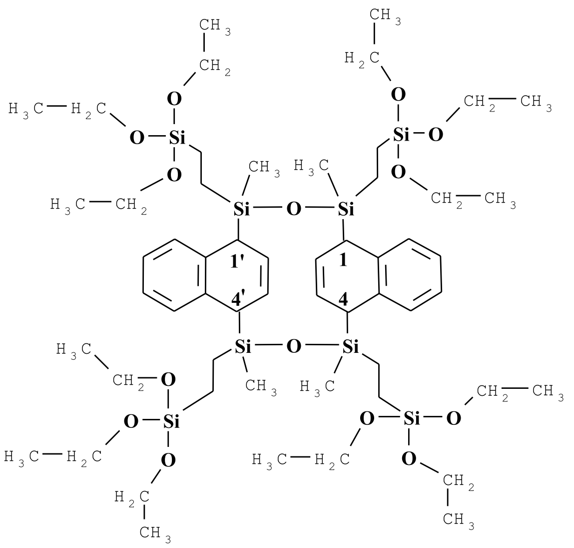


Fig. 1. TEDN branched structure.

Table 1
Cross-linking experimental data: time versus concentration of dibutyltin dilaurate and temperature

	Catalyst concentration wt.%		
	0.5	1	1.5
Room temperature	22 h	16 h	15 h
50 °C	18 h	14 h	13 h
70 °C	17 h	13 h	13 h

Further processing of the samples was performed using the same procedure in order to obtain information concerning the evolution of the cross-linking process. For this purpose six curing times varying from 2 to 13 h have been used at 25, 50 and 70 °C respectively. Under these experimental conditions, gelation occurred after 8–10 h. The toluene soluble fractions were extracted, weighed and analysed for conversion by ^{1}H-NMR. The results of the analysis are summarised in Table 2.

Table 2
Experimental data resulted from cross-linking of TEDN using 1.5% DBTL

Sample	Cure time (h)	Toluene soluble (%)			Conversion[a] (%)		
		70 °C	50 °C	25 °C	70 °C	50 °C	25 °C
1	2	90.5	90	88	30.5	35.5	36
2	4	88.3	89	89	35.2	40.1	41.2
3	6	90.0	88	87	48.5	56.8	51.8
4	8	30.2	45	74	53.2	62.1	54.1
5	10	18.5	41	35	56.8	62.4	59.8
6	13	10.6	39	29	58.4	67.7	63.7

[a] Resulted from ^{1}H-NMR analysis.

3. Results

A new cross-linkable tetra(triethoxysilyl)-dihydronaphthalenecyclocarbosiloxane was synthesised via addition of vinyltriethoxysilane to MHDHN, in the presence of hexachloroplatinic acid as catalyst.

Spectral analyses sustained the proposed structures.

IR spectral analysis of MHDHN shows characteristic absorption bands at: 3050–3085 cm^{-1}, CH aromatic; 2940–2960 cm^{-1}, C–H; 2150 cm^{-1}, Si–H; 1460–1600 cm^{-1}, C–C aromatic; 1260 cm^{-1}, Si–CH$_3$; 1050–1100 cm^{-1}, Si–O; 850–900 cm^{-1}, Si–CH–.

The ^{1}H-NMR analysis of MHDHN (δ ppm, CDCl$_3$): 0.30, s, 12H, Si–$\mathbf{CH}_3$; 4.53, s, Si–**H**; 2.8, s, 4H, Si–**CH**–; 6.05, d, 4H, –**CH**=**CH**–; 7.22, m, 16H aromatic. The presence of the Si–CH$_3$ characteristic peak at $\delta = 0.30$ ppm confirmed the cyclic structure of the product, linear oligomers having for the same group of protons chemical shifts located below 0.15 ppm.

IR spectrum of TEDN (Fig. 2) shows characteristic absorption bands at 700–850 cm^{-1}, –CH– naphthalene; 1080–1100 cm^{-1} Si–O– and Si–O–C$_2$H$_5$ (overlapping); 1100–1170 cm^{-1} (Si–CH$_2$–CH$_2$–Si); 1250 cm^{-1} (Si–CH$_3$); 2900–3000 cm^{-1} (CH aromatic).

The ^{1}H-NMR spectrum of TEDN (Fig. 3) shows characteristic chemical shifts (δ ppm, CDCl$_3$): 0.2, s, Si–$\mathbf{CH}_3$; 0.37, s, Si–$\mathbf{CH}_2$–$\mathbf{CH}_2$–Si; $\delta = 1.41$ and 3.72, m, Si–O–$\mathbf{CH}_2$–$\mathbf{CH}_3$; 2.50, s, Si–**CH**–; 5.80, d, –**CH**=**CH**–; 7.02–7.51, m, –C$_6\mathbf{H}_4$–.

The GPC trace of TEDN showed a peak with higher molecular weight (1560) which was assigned to the four-branched product, another peak corresponding to a lower molecular weight (1015) assigned to a two-branched structure and finally, in the low molecular region, by-products (unreacted cyclic carbosiloxane) (Fig. 4). The formation of the two categories of branched compounds results from the different reactivities of the Si–H groups relative to their position inside the cyclocarbosiloxane ring [12].

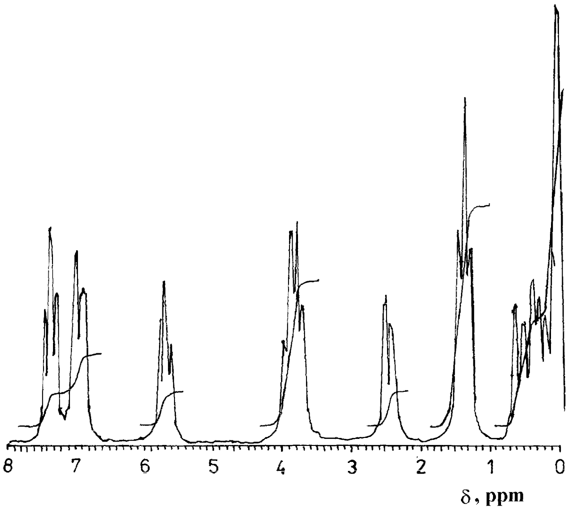


Fig. 3. ^{1}H-NMR spectrum of TEDN.

The curing process of TEDN was studied by varying the cross-linking reaction conditions.

As shown in Table 1 and Fig. 5 a strong influence of the temperature on the cross-linking time could be noticed mainly below 50 °C. At higher temperatures (70 °C) a constant cross-linking time was reached. Further increase of temperature or DBTL concentration did not result in the modification of the cross-linking time.

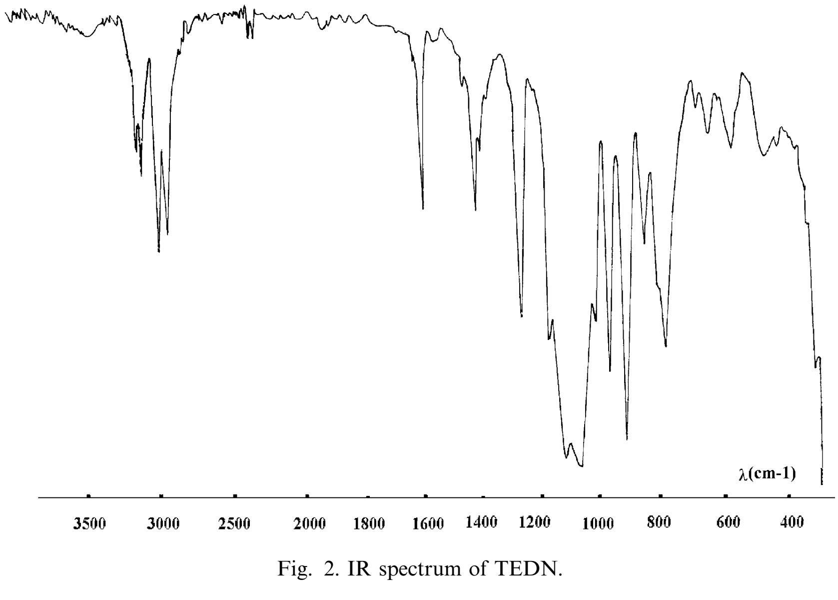


Fig. 2. IR spectrum of TEDN.

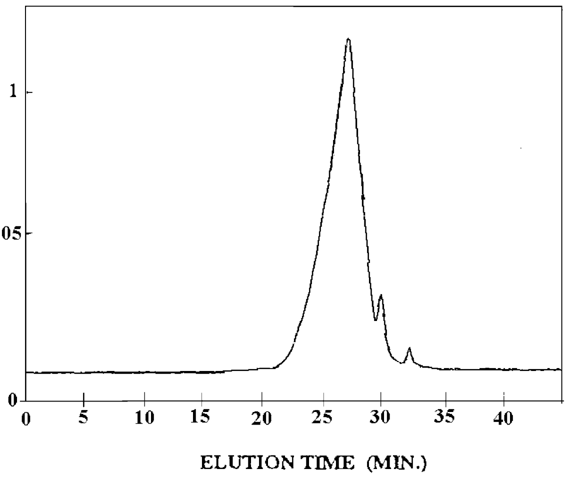


Fig. 4. GPC trace of TEDN.

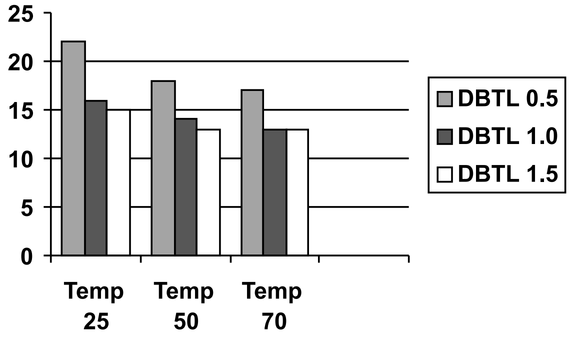


Fig. 5. Cross-linking time versus DBTL concentration and temperature.

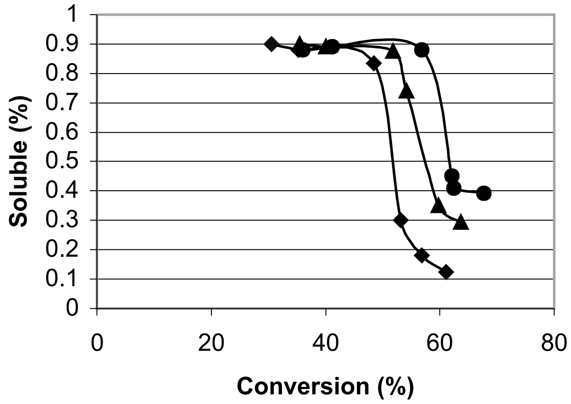


Fig. 6. Gelation plot: soluble fraction versus conversion. Experiments made at: (■) 70 °C, 1.5% DBTL; (▲) 50 °C, 1.5% DBTL; (●) 25 °C, 1.5% DBTL.

Further processing of the experimental data presented in Table 2 shows that the sol content decreases rather sharply after the gel point (Fig. 6). This observation was useful for determining the relative position of the gel point as a function of conversion and temperature at 48.5% (70 °C), 51.8% (50 °C) and 56.8% (25 °C).

The presence of the percolation threshold (the part of the plot with the greatest slope) suggests a different behaviour of the reaction system near the gelation point (Fig. 6). Therefore, before the gelation point the cross-linking reaction occurs mostly in the liquid state and allows all reactive functional groups to react until gelation is reached. This means that the reactive groups have a greater mobility and a moderate diffusion constraint. After the gelation point the reaction system can be considered as a solid lattice which becomes more constrained and leads to formation of "pockets" of less reactive oligomers. As presented in Fig. 6, the increase in temperature has a relaxing effect on the rigidity of this lattice and the gelation point shifts to lower conversions.

4. Conclusion

Starting from dihydronaphthalene cyclocarbosiloxane, a new cross-linkable ethoxy-functionalised compound was obtained.

Experimental data concerning the synthetic procedure and characterisation of the new product together with estimations of the cross-linking reaction parameters were presented and discussed.

The novel hyperbranched polycyclocarbosiloxane obtained is expected to present practical applications as protective layers or as a precursor for materials with increased porosity.

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