Polycarbosiloxane Networks

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Polycarbosiloxane networks were obtained by the crosslinking reaction of bis(triethoxysilylethylene) cyclocarbosiloxanes. For this purpose 2,5-dimethyl-2,5-dihydro-3,4-diphenyl-1-oxa-2,5-disilacyclopentane and 2,7-dimethyl-2,7-dihydro-3,3,6,6-tetraphenyl-1-oxa-2,7-disilacycloheptane were modified with triethoxy-vinylsilyl groups via catalytic hydrosilylation. These monomers were characterized through spectral analysis by ^{1}H-NMR, ^{13}C-NMR and FT-IR. The crosslinking process of the cyclocarbosiloxane precursors was studied in various reaction conditions of temperatures and catalyst concentration. Using swelling measurements of the polymers in gelation state, the specific development of the polycyclocarbosiloxane network systems toward the final hyper-crosslinked state was investigated. Through this approach details concerning the influence of the precursor chemical structure over the characteristic evolution of the crosslinking process were revealed.

Keywords: Polymer, Sol-gel, Polycarbosiloxane, Carbosiloxanes, Polycyclic

The synthesis of inorganic polymers with predetermined physico-chemical properties could be made through enclosing of organic segments with specific chemical structure within inorganic networks. This procedure allows tuning of the material morphology by control of the phase domain dimensionality down to the nanometer level [1, 2]. For the synthesis of these nano-composites, both the organic and inorganic fragments are coupled in the same polymerizable molecular structure and the specific morphology of the material is obtained directly from the organic/inorganic ratio [3]. This procedure could be used for synthesis of organic-inorganic hyper-crosslinked materials starting from cycles or linear blocks that contain an organic fragment attached to tri-functional silyl groups through non-hydrolysable silicon-carbon bonds.

A known example is the sol-gel polymerization of poly(trialcoxysilyl)- which leads to polysilsesquioxane type networks where the inorganic component dimension is very small compared with the organic segment [4]. In this case, improvement of the control over the material morphology could be achieved by using in the building process of the tris(alcoxysilyl)- network of molecular blocks coupled through rigid spatiators [5-11].

The carbosiloxane cycles have the advantage of providing the requested hybrid blocks designed according to the application demands and allow engineering of the silicon based molecular structures with the purpose to control their properties. The hyper-crosslinked networks obtained by this way could be used in formation of nano-particles for nanoclusters synthesis [12] for enclosing of organic functions within catalysts [13] or for preparing of highly transparent films with special optical or non-linear optical properties [14].

This work presents an alternate method to obtain hyper-crosslinked polycyclic structures of poly-silsesquioxane type. The presence of the cyclocarbosiloxane fragments induces a controlled porosity within the material in its hyper-crosslinked state and, on the other side, the cyclic core could participate further to dimensional or chemical interactions with reactive environmental species.

The liquid cyclocarbosiloxane precursor allows processing as thin films which, by exposure to the ambient humidity, could be transformed in highly crosslinked material. The dimension of these films could reach the nanometer level trough collapsing of the network due to elimination of important amounts of material (6 alcoxy groups) [15].

The evolution of the crosslinking process was studied through swelling experiments in an adequate solvent.

Experimental part

Reagents

Methyldichlorosilane (purity 98.5%) and vinyl-triethoxysilane (purity >98%) were supplied by Merk and freshly distilled before using. The hexachloroplatinic acid, $H_2PtCl_6.6H_2O$ solution in isopropanol (HCPA) and dibutyltindilaurate (DBTL, purity >97%) were from Fluka Ag.

Cyclocarbosiloxanes were synthesized according to earlier published works [16, 17].

2,5-dimethyl-3,4-diphenyl-1-oxa-2,5-disilacyclopentane (**HDFE**) (fig.1).

$Si_2C_{16}H_{18}O$ (390/ 405.2$_{exp}$): 14.35/ 14.28$_{exp}$ (Si%); 49.23/ 49.41$_{exp}$ (C%); 4.61/ 4.42$_{exp}$ (H%). Mp= 120.5-122.3 °C.

^{1}H-NMR (CDCl$_3$, δ ppm): 0.14, s, 6H (Si-CH$_3$); 3.2, d, 2H, (-CH-); 4.50, s, 2H (Si-H); 7.08-7.21, m, 10Har, (-C$_6$H$_5$).

^{13}C-NMR (CDCl$_3$, δ ppm):- 4.5 (-Si-CH$_3$); 25.8 (-CH-); 126.0-128.7 (-Si-C$_6$H$_5$).

2,7-dimethyl-3,3,6,6-tetraphenyl-1-oxa-2,7-disilacycloheptane (**HTFB**) (fig. 1).

$Si_2C_{30}H_{32}O$ (464/ 473$_{exp}$): 12.06/ 11.89$_{exp}$ (Si%); 77.58/ 77.41$_{exp}$ (C%); 6.89/ 6.77$_{exp}$ (H%). Mp= 98.6 °C.

^{1}H-NMR (CDCl$_3$, δ ppm): 0.14, s, 6H (Si-CH$_3$) ; 1.90, d, 4H, (-CH$_2$-); 4.50, s, 2H Si-H; 7.08-7.21, s, 20H, (-C$_6$H$_5$).

^{13}C-NMR (CDCl$_3$, δ ppm):- 6.8 (-Si-CH$_3$); 24.8 (-C-); 33.8 (-CH-); 126.3-129.3 (-Si-C$_6$H$_5$).

Measurements

The ^{13}C- and ^{1}H-NMR spectra were obtained on a JEOL 80 MHz spectrometer in CDCl$_3$ without TMS internal standard. The IR spectra were registered on a Perkin-Elmer spectrophotometer within 400-4000 cm^{-1} range on KBr pellets.

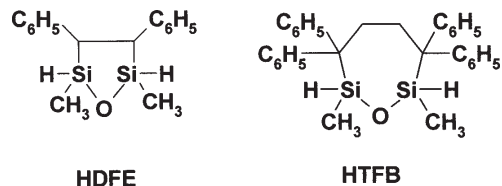** email: livius@icmpp.ro; Tel: +40232217454*

HDFE   HTFB

Fig. 1. Si-H functional carbosiloxane cycles

Bis(triethoxysilylethylene)cyclocarbosiloxane synthesis

A mixture of 0.024 mole Si-H functional cyclocarbosiloxane and 0.05 mole vinyltriethoxysilane in 50 ml anhydrous n-heptane was poured under dry nitrogen atmosphere in a round bottomed three necked reaction flask provided with dropping funnel, reflux condenser and mechanical stirrer. This mixture was gently heated until reflux and then HCPA, 0.01 N solution in isopropanol (5.10^{-6} g H_2PtCl_6/ mole compound with vinyl groups), was added. The reaction proceeds smoothly in about 30-60 min. The process could be considered finished when the Si-H bond IR absorption band at 2150 cm^{-1} disappeared from the IR spectrum. The final product is obtained after solvent and excess vinyltriethoxysilane distillation under vacuum (1).

Through this approach were synthesized:

2,5-dimethyl-3,4-diphenyl-2,5-bis[2-(triethoxysilyl)ethyl]-1-oxa-2,5-disilacyclopentane, (**EDFE**), brown, liquid product; 10 g, yield: 80%.

2,7-dimethyl-3,3,4,4-tetraphenyl-2,5-bis[2-(triethoxysilyl)ethyl]-1-oxa-2,5-disilacycloheptane, (**ETFB**), brown, liquid product; 9.5 g, yield: 70%.

Study of swelling behavior

To study the swelling behavior of the material and to evaluate the crosslinking conditions, the cyclo-carbosiloxane precursor was exposed to the ambient humidity in predetermined conditions of temperature and catalyst dibutyltindilaurate (DBTL). For this purpose an installation was built using two communicating sealed chambers. One of the chambers is charged with a specific amount of water and the second one, containing the precursor samples, is equipped with a programmable heating system. The samples are maintained in the prescribed experimental conditions observing the gel formation. Further on, constant amounts of this gel are extracted at measured intervals of time, maintained in solvent for 24 h then weighted (m_1).Then, the resulted samples are centrifugated at 5000 rpm for 1 h to separate the solid, dried under vacuum for 24 h at room temperature and weighted again (m_2). The swelling degree (S) is calculated according to the expression:

$$S = \frac{m_1 - m_2}{m_2} \qquad (1)$$

Results and discussions

A special class of hyper-crosslinked polycarbosiloxane structures obtained through hydrolytic condensation of the bis(triethoxysilylethylene)cyclocarbosiloxanes monomers derivatives of HDFE and HTFB was studied (fig.2).

These monomers were synthesized through the Si-H functional cyclocarbosiloxanes addition to vinyltriethoxysilane in the presence of hexachloroplatinic acid (scheme 1) [18].

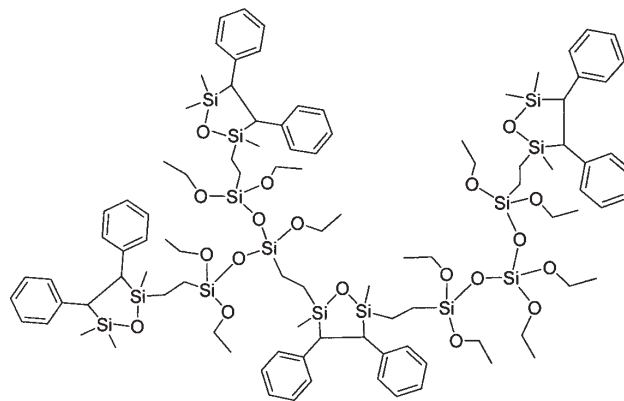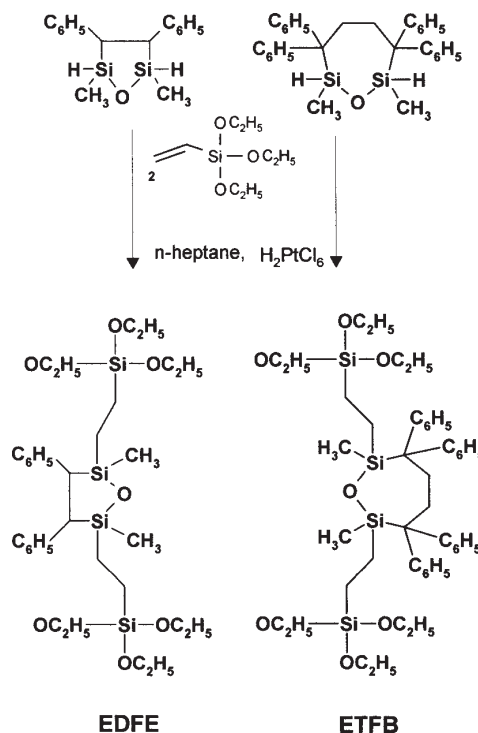The spectral analyses of EDFE and ETFB confirm their chemical structure [19].

Fig. 2. EDFE network

Scheme 1

The ^{1}H-NMR spectrum of EDFE shows the following specific chemical shifts (CDCl$_3$, δ ppm): 0.08, 6H (Si-CH$_3$); 0.60, 8H (-Si-CH$_2$-CH$_2$-Si-); 1.23, 18H (CH$_3$-); 3.2, 2H (-CH-); 3.83, 12H (-CH$_2$-); 7.08-7.21, 10Har (-C$_6$H$_5$).

IR absorption bands specific for EDFE (λ, cm^{-1}): 700-850 (-CH-); 1080 - 1100 (Si-O-); 1100-1170 (Si-CH$_2$-) ; 1250 (Si-CH$_3$); 2900-3000 (CH arom) (fig.4).

^{1}H-NMR spectrum of ETFB shows the following chemical shifts (CDCl$_3$, δ ppm): 0.08, 6H (Si-CH$_3$); 0.60, 8H (Si-CH$_2$-CH$_2$-Si); 1.22, 18H (-CH$_3$); 1.90, 2H (CH-); 3.83, 12H (-CH$_2$-); 7.08–7.21 m, 20Har, (-C$_6$H$_5$).

The IR spectrum of ETFB presents the following absorption bands (λ, cm^{-1}): 700-900 (-CH-); 1070 - 1090 (Si-O-); 1100-1160 (Si-CH$_2$-); 1260 (Si-CH$_3$); 2950-3100 (CH arom).

The spectral analyses confirm the addition reaction products by the presence of the ethylene bridge specific signals. Therefore, the ^{1}H-NMR spectra show at 0.60 ppm the specific chemical shift of the –CH$_2$- protons. In the IR spectrum the ethylene bridge formation could be deduced from the characteristic dental shape of the peak at 1070-1170 cm^{-1}, due to overlapping of the (Si-CH$_2$-CH$_2$-Si) and (Si-O-C$_2$H$_5$) absorptions bands (fig.4).
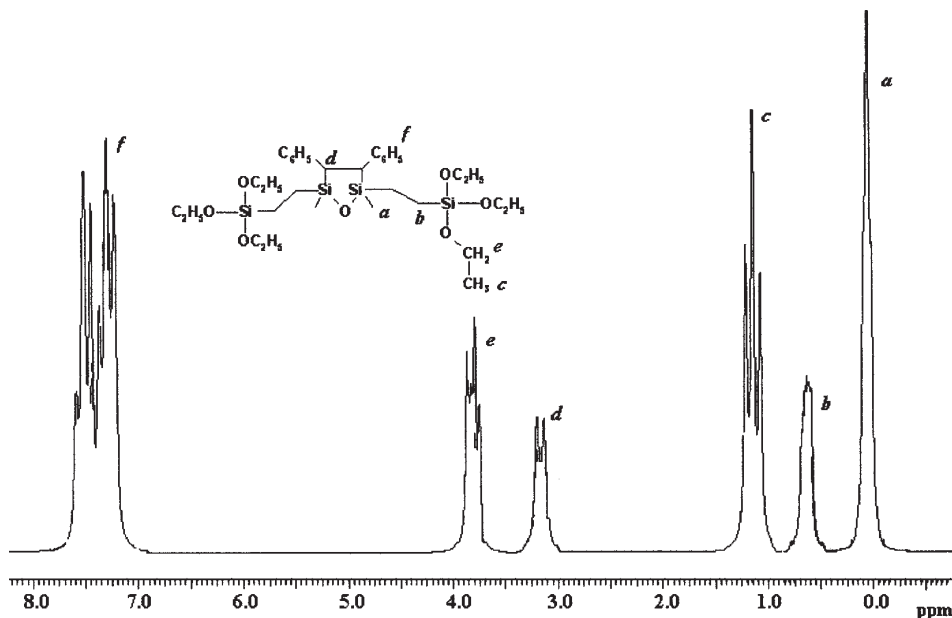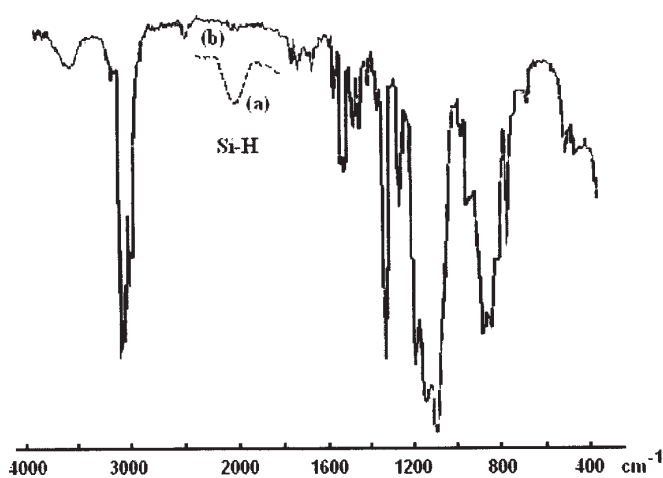
Fig. 3. ¹H-NMR spectrum of EDFE

Fig. 4. IR spectrum of EDFE. Si-H absorption intensity:
(a) initially; (b) finally

The hyper-crosslinked structures formation mechanism is based on the ethoxysilane groups' hydrolysis reaction followed by the silanols condensation. The properties of the resulted polymers depend strongly onto specific reaction parameters such as reaction time, catalyst, temperature and humidity. A possible method to estimate the optimal values of these parameters is based on the swelling degree measurement.

Method Principle

The exposure of the triethoxysilyl modified cyclcocarbosiloxanes to humidity leads through hydrolysis and polycondensation processes to the appearance of the crosslinking phenomenon. The first step of this process usually provides materials as gels. This specific moment could be visualized due to the fact that the polymer does not flow anymore. The corresponding reaction time should be noted as gelation time. In this particular state the polymer network encloses important amounts of unreacted or partially reacted precursor. If the material is maintained further in the experimental conditions, the hyper-crosslinked product formation is observed and the chemical processes responsible for the network formation gradually stop. This final moment could be established by swelling degree measurements and should be registered as the crosslinking time. The swelling phenomenon appears when the polymer, partially or totally crosslinked, absorbs a specific amount of solvent dislocating the unreacted precursor. Therefore, by this approach it is possible to obtain a quantitative evaluation of the crosslinking process evolution.

Influence of the crosslinking temperature

The exposure of the precursor to the ambient humidity starts the crosslinking process. Its development is conditioned by the water vapors diffusion through the liquid layer and then, through the solid layer of the continuously forming network. The crosslinking experiments in the absence of catalyst were performed at temperatures of 25, 50 and 70°C using the described installation. It was observed that in the specified temperature and humidity conditions the crosslinking process is very slow so that in both cases the gelation time is in the range of days. The temperature has a specific influence on the process due both to the diffusion and to the chemical structure of the cyclic segment and attains a maximum threshold from which the crosslinking process acceleration could be not observed. In the case of ETFB polymer a temperature value above 50 °C does not produce any visible effects on the gelation time which remains almost constant.

Table 1
GELATION TIME VERSUS TEMPERATURE

Monomer	Temperature (°C)	Time (days)
EDFE	20	4
	50	3
	70	2
ETFB	20	7
	50	5
	70	5

Attempts to reduce the gelation time by adding small quantities of water (~2 % vol.) under stirring, directly in the liquid samples, did not produce reproducible results leading to inhomogeneous mixtures of oligomers with low crosslinking degrees. It was assumed that the presence of water in the liquid sample initiates an important number of incomplete hydrolysis processes which proceed simultaneously and increase the polymer chains polydispersity.

The influence of the catalyst concentration

Experiments concerning the study of the crosslinking process in the presence of catalyst dibutyltindilaurate (DBTL), which is currently used for alcoxysilane condensation, were performed. Because it was observed that the process acceleration usually appears at DBTL concentrations lower than 2%, the crosslinking reaction was investigated using catalytic amounts of 0.5, 1 and 1.5%. Simultaneously the exposure temperature was varied at 25°C, 50°C and 70°C. The presence of DBTL in the reaction system leads to a strong acceleration of the crosslinking process, decreasing the gelation time to hours (tabelul 2).

Table 2
GELATION TIME VERSUS DBTL CONCENTRATION AND TEMPERATURE

Monomer	Temperature, °C	DBTL conc., (%)		
		0.5	1	1.5
EDFE	20	22 h	16 h	15 h
	50	18 h	14 h	13 h
	70	17 h	13 h	13 h
ETFB	20	28 h	24 h	22 h
	50	21 h	20 h	20 h
	70	19 h	19 h	19 h

The study of the crosslinking process through measuring of the swelling degree shows some characteristic aspects (fig.5).
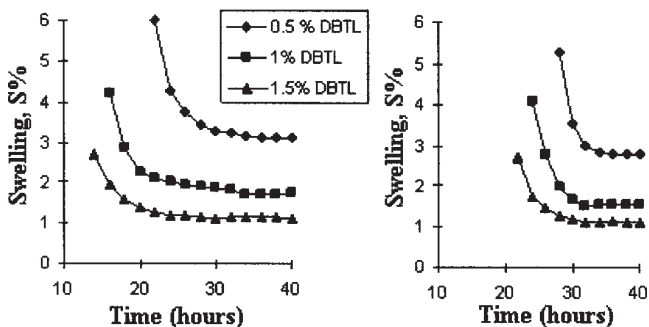

Fig. 5. Swelling versus crosslinking time for EDFE (left) and ETFB (right) copolymers at room temperature and various DBTL concentrations

The swelling degree decreases depending on the catalyst concentration. Therefore, at 0.5% DBTL and 20°C the crosslinking process produces a rarefied network which is capable of embedding important amounts of unreacted precursor. In this case the swelling degree should decrease rapidly through involving of the increased amount of reactive centers as unreacted monomers, in the consolidation process of the polymeric network. Increasing of the crosslinked fragments density attenuates the swelling degree decreasing which finally tends to an equilibrium value depending on the network elasticity and dimension of the pores. On the other hand the structural influence observed in the variation of the swelling degree versus crosslinking time should be assigned to the carbosiloxane cycle's different dimensions.

Increasing of the catalyst concentration leads to the attenuation of the swelling degree-crosslinking time variation and to diminishing of the structural influences. This phenomenon is the result of an increased rate due to the higher DBTL concentration and leads finally to formation of the polymeric networks in a relatively shorter time. This is the reason why for a catalyst concentration of 1.5%, significant variations of the swelling degree during the crosslinking process could not be observed. The polymeric network reaches the maximum degree of density and the pores dimension corresponds merely to the carbosiloxane cycle dimension.

In the next step the swelling experiments were performed using materials crosslinked at the gel point, various temperatures, 20, 50, 70°C, and a constant catalyst concentration of 0.5 %.

At precise intervals of time the swelling degree was measured (fig. 6,7). It was observed that the variation of the swelling degree versus the crosslinking time keeps the same profile no matter the temperature and chemical structure of the network. This fact is related to the kinetic model of the process and fallows the variation curve of the unconsumed $Si-OC_2H_5/Si$ ratio versus time [20]. Increasing of the temperature has a different effect from the point of view of the gelation time-polycyclocarbosiloxane network structure relationship. Therefore, the EDFE type of precursors generates networks which attain more rapidly the gel point then the ETFB monomers. Above the gel point, the crosslinking process continues. This is confirmed by a rapid decreasing of the swelling degree within a relatively short interval of time of few hours.
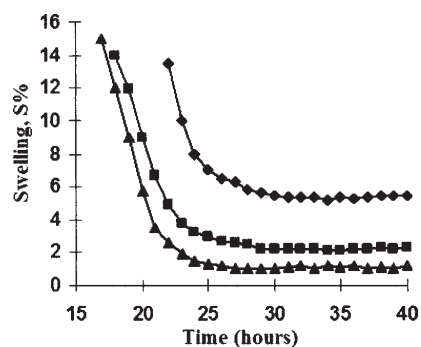

Fig. 6. Swelling versus crosslinking time of EDFE copolymer at 0.5 % DBTL and temperatures of (♦) 20 °C; (■) 50 °C; (▲) 70 °C
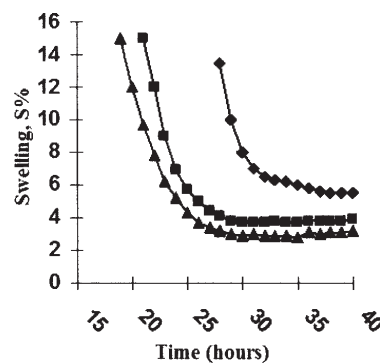

Fig. 7. Swelling versus crosslinking time of ETFB copolymer at 0.5 % DBTL and temperatures of (♦) 20 °C; (■) 50 °C; (▲) 70 °C

As expected, the crosslinking process becomes more intense when the temperature is raised from 20°C to 50°C. This tendency is limited and a new modification of the temperature to 70 °C has no effect on the process development. The swelling degree tends to a constant value which in fact marks the ending of the hyper-crosslinked networks formation process. In the EDFE case this moment is reached in 24 h and for ETFB in 30 h considering the same experimental conditions (70°C and 0.5% DBTL).

Conclusions

Carbosiloxane precursors with polycyclic structure were synthesized through the addition of triethoxyvinylsilane to Si-H functional cyclocarbosiloxanes. The process concerning the hyper-crosslinked networks formation using 2,5-dimethyl-3,4-diphenyl-2,5-bis[2-(triethoxysilyl)ethyl]-1-oxa-2,5-disilacyclopentane, **(EDFE)** and 2,7-dimethyl-3,3,4,4-tetraphenyl-2,5-bis[2-(triethoxysilyl)ethyl]-1-oxa-2,5-disila-cycloheptane, **(ETFB)**, precursors was also presented. The study of the temperature and catalyst influences in the gelation and hyper-crosslinking steps of the process showed some specific features determined by the peculiar structure of the precursors. Therefore, it was observed that the EDFE monomer has a higher reactivity both in the non-catalytic and catalytic processes. Through the correlation of the swelling degree with temperature and catalyst concentration details concerning the consolidation of the polycarbosiloxane network above the gel point were revealed together with the estimation of the requested time to obtain the hyper-crosslinked polymer.

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