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Silicon Functionalized Styrene Polymers[1]

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Materials that have the ability to undergo controlled homogeneous or heterogeneous cross-linking are inherently interesting. This is due in particular to the ability to manipulate the properties of the final material by controlling the cross-link density and, in the latter case, the nature of the two different polymeric species. Intriguing compounds of this type include polymers containing functional silanes that can undergo cross-linking by moisture cure. Much of silicon rubber technology (RTV cure) is based upon this idea;[5] many examples of both grafted and copolymerized silane functionalized polyolefins, including commercial examples,[6] are known.[7]

Recently,[8] we reported that the cationic oligomerization of β-(trichlorosilyl)styrene 1 (Scheme IA) led to materials which possess a high degree of functionality. Two challenges remained before materials of this type could be considered for practical application: to increase the length of the functionalized chain and to disperse the silicon functionality along a longer polymeric chain. To solve the latter synthetic problem, we have examined the cationic copolymerization of 1 with styrene (Scheme IB). The polymerization of 1,2-difunctional olefins is generally not a facile process. It was, therefore, of additional interest to see whether functionalized 1,2-disubstituted monomers could be efficiently incorporated into higher molecular weight polymers.

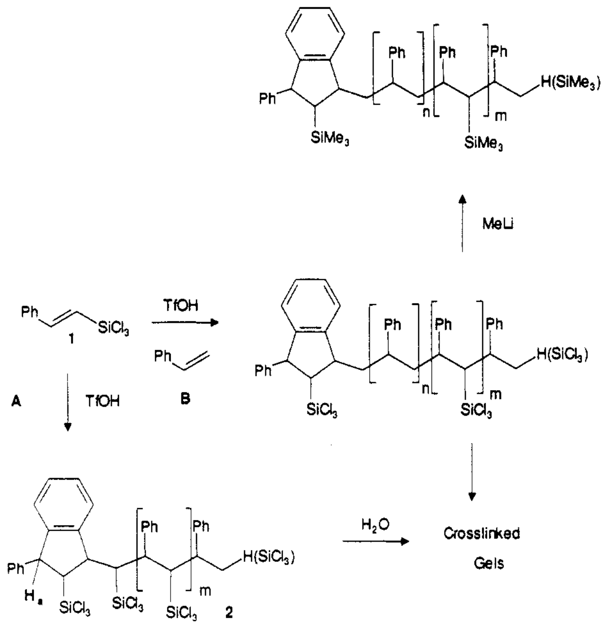
The reaction was performed neat at −78 °C (1 h and then at 0 °C over 2 h) under a nitrogen atmosphere with triflic acid (CF_3SO_3H, 5 mol %)[9] as the initiator and led to homogeneous solutions of the functional copolymers: these solutions varied in color from light brown to dark red, reflecting, we believe, the presence of benzylic cationic species in solution. Quenching any of these solutions even with nearly impotent nucleophiles such as trifluoroacetic acid led to an immediate decrease in the color intensity and a color change from red to pale yellow/brown.

Functional silanes are known to spontaneously form disiloxanes in the presence of moisture; the rate of this reaction depends, among other things, on the type of functional group and the nature of any catalysts present. Precipitation of the products in methanol or methanol–water led to off-white materials, presumably by way of slow cross-linking of the first-formed methoxysilane (i.e., $2R_2R'SiCl \rightarrow 2R_2R'SiOMe \rightarrow R_2R'SiOSiR_2R'$). If allowed to cross-link with atmospheric moisture, hard, amorphous polymers were similarly obtained but were red/brown. We believe the concomitant production of HCl, which in the latter case is much more concentrated, is associated with this color difference.

In order to examine the structure of the materials produced in the polymerization, following the reaction they were immediately converted to the corresponding trimethylsilyl derivatives by reaction with MeLi in THF (N_2 atmosphere). These light yellow oils were characterized principally by NMR and GPC.

As we had observed previously[8] and in contrast to β-(trimethylsilyl)styrene which undergoes loss of the silyl group under acidic conditions,[10] the trichlorosilyl group is a poor leaving group and remains bound to the polymer backbone. After methylation, comparison of the integration of the $SiMe_3$ peaks (δ 0–1) with that of the aromatic peaks (δ 6.5–8) in the ^1H NMR of the trimethylsilyl derivatives clearly showed that the initial and final ratios of 1/styrene were constant in all the reactions examined.

Scheme I



Our initial concern was that the styrene was rapidly undergoing homopolymerization and, subsequently, that the less reactive silylstyrene[11-13] was forming a separate homopolymer or a functionalized terminating block. However, the evidence from GPC and NMR supports a random copolymer as the structure. The GPC traces (refractive index detector, Figure 1A) always show a typical broad distribution at quite a low molecular weight (1–27 000, Table I) which increases with increasing styrene content.[9] The silicon-selective GPC trace (Figure 1B) demonstrates that the silicon is evenly spread throughout the molecular weight range; the traces from the two detectors could be superimposed, demonstrating that the materials are true copolymers, not a mixture of homopolymers of styrene and β-(trichlorosilyl)styrene, respectively.

We used NMR to characterize the structural nature of the copolymers. In the ^{13}C NMR, new peaks were observed that are related to, but not identical with, those from cationically initiated polystyrene (Figure 2). The signals in the copolymers originating from 1 also underwent chemical shift changes. The copolymer spectra could not be superimposed with that of either the poly(silylstyrene) 1 or polystyrene homopolymers. If the copolymers were block polymers terminated with the silylstyrene oligomer, the NMR spectra should have been similar to the sum of the homopolymer spectra. Given the spectral differences between the homo- and copolymers, we believe that the copolymers are random in nature.

The homopolymerization of 1 leads to a very distinctive ^1H NMR signal due to the benzylic hydrogen H_a in 2 and its coupling to other protons on the indan 5-membered ring.[14] No characteristic changes, helpful in assigning structural features of the polymers, were observed with this signal as the proportion of styrene in the mixture was increased. One feature, however, was characteristic. In the $SiMe_3$ region (δ 0.0–0.7), the ratio of two multiplets centered at δ 0.15 and 0.5 changes with increasing styrene

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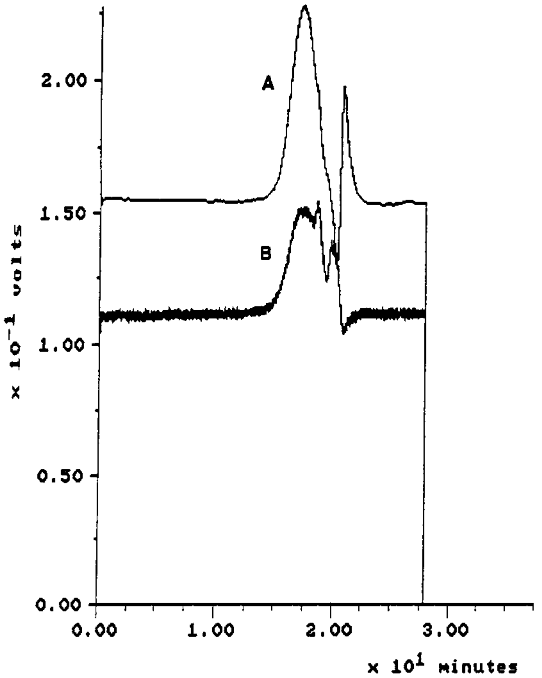


Figure 1. Typical GPC trace of methylated derivatives shown for entry 6, Table I: (A) refractive index trace; (B) infrared trace (1090 cm^{-1}).

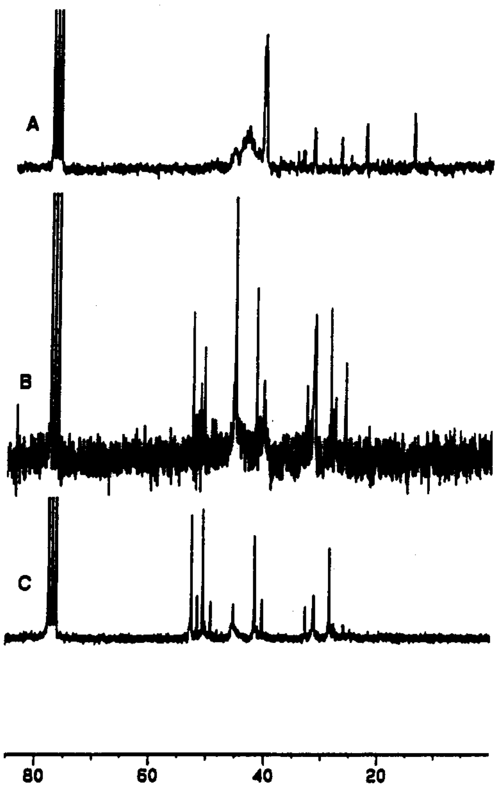
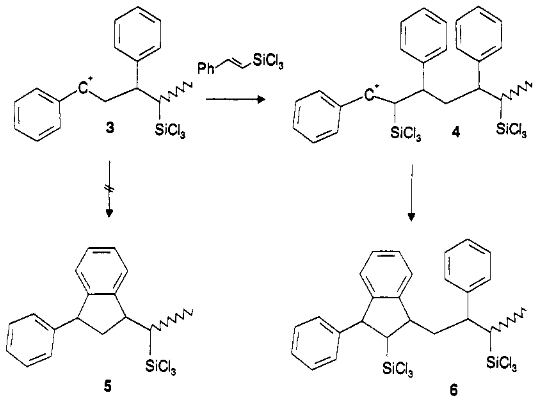


Figure 2. Superposition of the ^{13}C NMR spectra of chlorinated derivatives δ 0–80 ppm: (A) polystyrene (initiated with triflic acid); (B) entries 1 and 4, Table I; (C) polymer of pure 1.

content; the intensity of the lower field peak decreases to a final ratio of approximately 1:3 (intensity δ 0.15:0.5). Similarly, in the ^{29}Si NMR, two peaks of approximately equal intensity give way to a single peak as the styrene content in the copolymer is increased. We believe that this reflects an increase in the amount of polymer initiated by proton addition to styrene rather than to a monomer of 1 as the styrene content is increased.

The propagation of styrene homopolymerization under acidic conditions is much more efficient than that with 1.

Scheme II



We believe this reflects the lower relative stability of the cation derived from 1 (4, Scheme II) than that derived from styrene (3, Scheme II);[11] unless the monomer concentration is sufficiently high with 4, termination leading to 6 via a Friedel–Crafts reaction occurs. We have never observed termination by way of proton loss and double-bond regeneration in the homopolymerization of 1. Although Friedel–Crafts termination can also occur with styrene under strongly acidic conditions,[15] via 3 to give 5, we have observed no evidence of this and conclude that the materials are terminated with an indan structure of type 6.

Experimental Section

^{1}H and ^{13}C NMR spectra were obtained on Bruker AC-200 (200-MHz) and WM-500 (500-MHz) spectrometers. For preliminary quality checks a Varian EM-390 (90 MHz) was used. Spectra were referenced by an $SiMe_4$ signal, residual solvent signal in $CDCl_3$, or the internal reference signal of CH_2Cl_2 at 5.3 ppm. ^{29}Si NMR spectra were obtained on a Bruker WR-250 (250-MHz) spectrometer using the signal of Me_4Si as an external reference (0 ppm).

Infrared spectra were run on a Perkin-Elmer 283 or a Bio-Rad FTS-40 (Fourier transform IR) spectrometer as a film on an NaCl disk.

The copolymers were analyzed for the molecular weight distribution using a Waters gel permeation chromatograph equipped with a Waters 410 differential refractive index detector and a Foxboro Miran 1A variable-wavelength IR detector to monitor silicon distribution in copolymers. Narrow molecular weight polystyrene standards from Polymer Laboratories were used for calibration of the chromatographic system. The IR detector was set at 1090 cm^{-1}; at this wavelength only bands involving Si were observed, while bands involving polystyrene alone give no signal.

Tetrahydrofuran (THF), diethyl ether, and benzene were freshly distilled under a nitrogen atmosphere from benzophenone/potassium. Dichloromethane (CH_2Cl_2) was freshly distilled under a nitrogen atmosphere from calcium hydride (CaH_2) or phosphorus pentoxide (P_2O_5).

Phenylacetylene and MeLi were obtained from Aldrich and were used without purification. Styrene was obtained from Dow Chemical (Canada) and was distilled prior to use. β-(Trichlorosilyl)styrene (1) was prepared according to reported procedures by the H_2PtCl_6-catalyzed hydrosilation of phenylacetylene with $HSiCl_3$ in THF.[16]

Due to the instability of the reagents toward hydrolysis, all syntheses were performed with dry glassware, under a nitrogen atmosphere, using syringe techniques or in a glovebag that was dried with anhydrous phosphorus pentoxide (P_2O_5) and continuously purged with dry nitrogen.

Synthesis of Silicon Functionalized Styrene Copolymers. Typical Polymerization Procedure Given for a 5:1 1/Styrene Ratio (Entry 2, Table I). In a flame-dried two-necked round-bottom flask equipped with a rubber septum, a nitrogen inlet, and a magnetic stirrer was placed a mixture of β-(trichlorosilyl)-

Table I. Characteristics of the Copolymers of Styrene and 1[a]

entry	1 (mmol)	styrene (mmol)	styrene (equiv)	M_w[b]	M_w/M_n
1	10.6	0	0	850	1.22
2	10.6	2.1	0.2	2800	2.19
3	10.6	4.2	0.4	3700	2.64
4	10.6	6.4	0.6	3400	2.12
5	10.6	8.5	0.8	2700	2.95
6	10.6	10.6	1	4500	2.29
7	10.6	12.7	1.2	6000	4.47
8	10.6	14.8	1.4	27000	14.6

[a] The results are based on GPC of methylated derivatives (after methylation of the crude chlorosilyl derivatives with MeLi) using μ-Styragel columns and chloroform as solvent. In all cases, yields of the $SiCl_3$-containing polymer exceeded 95%. [b] Determined using a refractive index detector.

styrene (1; 2.5 g, 10.6 mmol) and styrene (0.22 g, 2.1 mmol). This mixture was stirred continuously (before and after it froze) and cooled to −78 °C by means of an acetone/dry ice bath. To the frozen mixture was added 5 mol % of triflic acid (based on 1) using an air-tight syringe. The acetone/dry ice bath was removed, and the reaction mixture was allowed to warm to room temperature slowly over 2 h. The copolymer thus obtained was stored under nitrogen for further reaction. Using a similar procedure, six additional copolymers were synthesized by varying only the amount of styrene monomer. In the control experiment no styrene monomer was added to 1. The molecular weight data are shown in Table I.

None of the polymers were shown to contain starting material by NMR, and the yields of the $SiCl_3$-containing polymer were >95%; the yields of the $SiMe_3$ derivatives (see below) were slightly lower but still >90% after aqueous workup.

Permethylation of TCSS Copolymers. The copolymers were dissolved in dry ether and treated with an excess of MeLi (1.5 M in Et_2O, 3.3 equiv of MeLi based on the amount of 1 in the copolymer), at 0 °C. The reaction mixture was warmed up to room temperature over 2 h and quenched with water. The product was isolated by washing with distilled water. The combined ether extracts were dried over $MgSO_4$ and the solvents removed under vacuum to give light yellow, viscous oils. The stable copolymers thus obtained were characterized using GPC, NMR, and IR spectroscopy.

The proton NMR's appear to be a composite of the spectra of polystyrene and the homopolymer of 1 and are reported as such below. The ratios of the two multiplets in the ^{1}H NMR centered at δ 0.15 and 0.5 and of the two peaks in the ^{29}Si NMR are given. The IR spectra of all the compounds are virtually identical, and thus the data are only provided once (under entry 8).

Polystyrene Prepared under the Conditions Described above. ^{13}C NMR ($CDCl_3$): δ 14.12, 22.46, 22.64, 26.96, 31.58, 31.81, 40.40, 43.22, 45.84, 125.65, 127.68, 127.99, 145.33, 145.68.

Table Entry 1; Homopolymer of 1. ^{1}H NMR ($CDCl_3$): δ 0.0–0.3 (m, $^{1}/_{2}$ 9 H, $SiMe_3$), 0.3–0.5 (m, $^{1}/_{2}$ 9 H, $SiMe_3$), 1.1–1.7 (m, 2 H), 7.1–7.8 (m, 5 H_{arom}). ^{13}C NMR ($CDCl_3$): δ 26.1, 27.74, 28.57, 31.31, 32.79, 40.39, 41.69, 45.33, 49.20, 50.23, 50.60, 51.56, 52.61, 114.38, 123.95, 124.43, 125.11, 125.59, 126.47, 126.86, 127.18, 127.49, 127.60, 127.81, 127.90, 128.03, 128.20, 128.79, 140.93, 142.08, 142.44, 143.04, 143.68, 144.1, 144.86, 146.1, 146.61.

Table Entry 2; 1/Styrene (5:1). ^{1}H NMR ($CDCl_3$): styrene derived, δ 1.2–1.4, 1.4–2.3 (m, 3 H), 7.2–7.8 (m, 5 H_{arom}); 1 derived, 0.0–0.3 (m, $^{2}/_{3}$ 9 H, $SiMe_3$), 0.3–0.5 (m, $^{1}/_{3}$ 9 H, $SiMe_3$), 1.3–1.7 (m, 2 H), 7.2–7.8 (m, 5 H_{arom}). ^{13}C NMR ($CDCl_3$): δ 27.78, 28.61, 31.33, 32.86, 41.69, 45.33, 50.64, 52.61, 116.48, 123.95, 124.43, 125.12, 126.86, 127.59, 127.82, 128.00, 128.12, 128.78, 140.96, 141.1. ^{29}Si NMR ($CDCl_3$): δ 0.59 ($^{1}/_{2}$), 6.56 ($^{1}/_{2}$).

Table Entry 3; 1/Styrene (5:2). ^{1}H NMR ($CDCl_3$): styrene derived, δ 1.2–1.4, 1.4–2.3 (m, 3 H), 7.2–7.8 (m, 5 H_{arom}); 1 derived, 0.0–0.3 (m, $^{7}/_{10}$ 9 H, $SiMe_3$), 0.4–0.6 (m, $^{3}/_{10}$ 9 H, $SiMe_3$), 1.3–1.7 (m, 2 H), 7.2–7.8 (m, 5 H_{arom}). ^{13}C NMR ($CDCl_3$): δ 26.1, 27.79, 28.62, 31.36, 40.42, 41.69, 45.34, 50.64, 51.60, 52.62, 101.44, 114.70, 116.48, 124.42, 125.12, 126.86, 127.49, 127.83, 128.19, 140.99, 144.1. ^{29}Si NMR ($CDCl_3$): δ 0.56 ($^{1}/_{2}$), 6.56 ($^{1}/_{2}$).

Table Entry 4; 1/Styrene (5:3). ^{1}H NMR ($CDCl_3$): styrene derived, δ 1.2–1.4, 1.4–2.3 (m, 3 H), 7.2–7.8 (m, 5 H_{arom}); 1 derived, 0.0–0.3 (m, $^{3}/_{4}$ 9 H, $SiMe_3$), 0.4–0.6 (m, $^{1}/_{4}$ 9 H, $SiMe_3$), 1.3–1.7 (m, 2 H), 7.2–7.8 (m, 5 H_{arom}). ^{13}C NMR ($CDCl_3$): δ 25.97, 27.75, 28.61, 31.32, 32.84, 40.39, 41.66, 45.34, 50.63, 51.27, 52.62, 114.31, 116.42, 123.94, 124.49, 125.1, 125.58, 126.44, 127.44, 127.82, 128.18, 128.64, 128.77, 140.94, 144.1, 145.99; ^{29}Si NMR ($CDCl_3$): δ 0.57 ($^{1}/_{4}$), 6.56 ($^{3}/_{4}$).

Table Entry 5; 1/Styrene (5:4). ^{1}H NMR ($CDCl_3$): styrene derived, δ 1.2–1.4, 1.4–2.3 (m, 3 H), 7.2–7.8 (m, 5 H_{arom}); 1 derived, 0.0–0.3 (m, $^{2}/_{3}$ 9 H, $SiMe_3$), 0.4–0.6 (m, $^{1}/_{3}$ 9 H, $SiMe_3$), 1.3–1.7 (m, 2 H), 7.2–7.8 (m, 5 H_{arom}). ^{13}C NMR ($CDCl_3$): δ 26.1, 27.75, 28.20, 28.61, 31.53, 40.41, 41.66, 45.33, 50.61, 52.60, 114.37, 124.40, 125.1, 125.58, 126.44, 126.84, 127.44, 127.94, 128.0, 128.18, 128.29, 128.64, 128.75, 140.97, 144.1, 146.0. ^{29}Si NMR ($CDCl_3$): δ 0.58 ($^{1}/_{5}$), 6.70 ($^{4}/_{5}$).

Table Entry 6; 1/Styrene (1:1). ^{1}H NMR ($CDCl_3$): styrene derived, δ 1.2–1.4, 1.4–2.3 (m, 3 H), 7.2–7.8 (m, 5 H_{arom}); 1 derived, 0.0–0.3 (m, $^{4}/_{5}$ 9 H, $SiMe_3$), 0.4–0.6 (m, $^{1}/_{5}$ 9 H, $SiMe_3$), 1.3–1.7 (m, 2 H), 7.2–7.8 (m, 5 H_{arom}). ^{13}C NMR ($CDCl_3$): δ 25.92, 27.68, 28.13, 31.39, 40.31, 45.27, 114.0, 114.81, 116.29, 121.17, 123.85, 125.86, 126.41, 126.75, 127.42, 127.78, 128.26, 128.59, 140.83, 141.1, 141.96, 142.37, 143.97, 144.11, 145.92. ^{29}Si NMR ($CDCl_3$): δ 0.56 ($^{1}/_{10}$), 6.52 ($^{9}/_{10}$).

Table Entry 7; 1/Styrene (5:6). ^{1}H NMR ($CDCl_3$): styrene derived, δ 1.2–1.4, 1.4–2.3 (m, 3 H), 7.2–7.8 (m, 5 H_{arom}); 1 derived, 0.0–0.3 (m, $^{5}/_{8}$ 9 H, $SiMe_3$), 0.4–0.6 (m, $^{3}/_{8}$ 9 H, $SiMe_3$), 1.3–1.7 (m, 2 H), 7.2–7.8 (m, 5 H_{arom}). ^{13}C NMR ($CDCl_3$): δ 25.92, 27.68, 28.13, 31.39, 40.31, 45.27, 114.0, 114.81, 116.29, 121.17, 123.85, 125.86, 126.41, 126.75, 127.42, 127.78, 128.26, 128.59, 140.83, 141.1, 141.96, 142.37, 143.97, 144.11, 145.92. ^{29}Si NMR ($CDCl_3$): δ 6.55.

Table Entry 8; 1/Styrene (5:7). ^{1}H NMR ($CDCl_3$): styrene derived, δ 1.2–1.4, 1.4–2.3 (m, 3 H), 7.2–7.8 (m, 5 H_{arom}); 1 derived, 0.0–0.3 (m, $^{5}/_{7}$ 9 H, $SiMe_3$), 0.4–0.6 (m, $^{2}/_{7}$ 9 H, $SiMe_3$), 1.3–1.7 (m, 2 H, 1 backbone), 7.2–7.8 (m, 5 H_{arom}). ^{13}C NMR ($CDCl_3$): δ 25.92, 27.68, 28.13, 31.39, 40.31, 45.27, 114.0, 114.81, 116.29, 121.17, 123.85, 125.86, 126.41, 126.75, 127.42, 127.78, 128.26, 128.59, 140.83, 141.1, 141.96, 142.37, 143.97, 144.11, 145.92. ^{29}Si NMR ($CDCl_3$): δ 6.88. IR (ν): 612, 700, 757, 843, 908, 1053, 1118, 1176, 1252, 1375, 1416, 1452, 1508, 1601, 1803, 1874, 1944, 2871, 2924, 2956, 3026, 3061, 3083, 3162 cm^{-1}.

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(9) With the homopolymer of 1, a large amount of catalyst is needed because catalyst is bled off by the exchange reaction of triflate for Cl at silicon: HCl will not induce the polymerization. As the amount of styrene in the mixture is increased, it is almost certainly true that less catalyst will be needed to take the reaction to completion. Nonetheless, we used 5 mol % throughout to facilitate the comparison of the different copolymers. It is expected that this large amount of initiator results in similar molecular weights for all the copolymers. From the evidence above, judiciously balancing the amount of initiating acid and styrene content should lead to much higher molecular weight copolymers if desired.

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