

# Synthesis and Characterization of Bis-Triethoxysilane Endcapped Polyurethane/Urea

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**ABSTRACT:** A type of bistriethoxysilane endcapped polyurethane/ureas (SPU) with well-defined structure was synthesized from bis(triethoxysilylpropyl) amine and purified prepolymers, which were obtained from the reaction of 2,4-toluene diisocyanate (TDI) and polyoxyethylene glycol (PEG) with different molecular weight. Then, fourier transform infrared spectroscopy (FTIR), hydrogen nuclearmagnetic resonance (<sup>1</sup>H-NMR) and standard dibutylamine back-titration method were used to confirm the structures of prepolymers and SPUs. Moreover, the properties of SPU were investigated by wide angle X-ray diffraction (WAXD), differential scan-

ning calorimetry (DSC), thermogravimetric analyses (TGA), and percentage of water uptake. Results indicated that these polyurethanes were amorphous, and the percentage of water uptake and thermal stability of these polyurethanes went up with the increase of  $\bar{M}_n$  of SPU, accompanying with the glass transition temperature ( $T_g$ ) values decreased with the increase of  $\bar{M}_n$ . This study provides us with a method to synthesize well-defined end-functionalized polyurethane. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 798–803, 2011

**Key words:** polyurethanes; synthesis; structure

## INTRODUCTION

Polyurethane is widely used in agriculture, industry, and military areas as plastics, elastomers, protective coatings, lacquers, and adhesives biomaterials, etc., due to its excellent properties.<sup>1–10</sup> Over the past decades, extensive investigations have been carried out in polyurethane field and its wide applications have brought about higher requirements for the structure and performance.<sup>4–10</sup> Therefore, the design and synthesis of polyurethane with desired structure have become one of the most important aspects both in laboratories and industries. However, the preparation of polyurethane with well-defined structure is always much more difficult.

Generally, polyurethanes are usually synthesized by the following methods: prepolymers (generated from the reaction between diisocyanate and polyol groups where their mole ratio is approximately 2 : 1) or quasipolymer<sup>11</sup> (generated from the reaction between diisocyanate and polyol groups where their mole ratio is more than 2 : 1). Unfortunately, polyurethane obtained by these methods always produces ill-defined structure because of the step-by-step

polymerization process and the high reactivity between isocyanates and polyols. Moreover, if the diisocyanates are not completely reacted, the residual groups are not only hazardous to human health but also ill-defined when they are used as materials.<sup>9,12,13</sup> To obtain polyurethane with well-defined structure, purified quasiprepolymers were also used to synthesize this class of polymers.<sup>14,15</sup> However, the side reaction resulted from the high temperatures,<sup>9</sup> will confuse the molecular structure that restricts the desired performance of polyurethanes. Therefore, the polyurethane with well-defined structure cannot be obtained through the conventional methods. Thus, removing excess diisocyanates from quasiprepolymers under mild conditions to avoid side reaction is the key to obtain prepolymer and polyurethane with well-defined structure.

The primary purpose of this study was to synthesize a type of bistriethoxysilane endcapped polyurethane/urea with well-defined structure using bis(triethoxysilylpropyl) amine, 2,4-toluene diisocyanate (TDI) and polyoxyethylene glycol (PEG) with different molecular weight and investigate its property. With this method, various end-functionalized polyurethanes with well-defined structure can be obtained, which was significant both in theory and practice. Furthermore, the components of this polyurethane have been widely used in biomaterials and environmental protection owing to their superior biocompatibility, low toxicity, etc.,<sup>16–19</sup> which also

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made whole molecule of SPU that can be applied in these areas. Finally, the structure of SPU was novel and the correlative work has not been reported.

## EXPERIMENTAL

### Materials

TDI, PEG with  $\overline{M}_n = 400, 600, 800,$  and  $1000$  g/mol, benzoyl chloride, hexane, ethyl acetate and various reagents were purchased from Sinopharm Chemical Reagent Co., (Ltd, Shanghai, China). Bis-(triethoxysilylpropyl) amine (DB-520) (>98%) was provided by Diamond New Material of Chemical Inc., (Ying Cheng, HuBei, China). PEG was dried under vacuum (266 Pa/110°C) for 2 h before use, and hexane, ethyl acetate and various reagents were purified in standard method before use.

### Preparation of SPU

Synthesis of polyurethane prepolymers

In flask purged with dry nitrogen, 1 mol PEG with molecular weights 400, 600, 800, and 1000 g/mol reacted with diisocyanates containing 0.3 wt % benzoyl chloride (the stoichiometric ratio of NCO : OH = 3 : 1), respectively. The reaction was kept under a temperature of 40°C for 3 h till the concentration of NCO reached the theoretical value (the percentage of residual-NCO groups was determined by typical dibutylamine chemical titration). The resulting products were first washed by the mixture of *n*-hexane and ethyl acetate<sup>20</sup> for several times and then evaporated under vacuum. The concentration of NCO groups of purified prepolymers was reported in Table I.

Synthesis of SPU

In flask purged with dry nitrogen, bis(triethoxysilylpropyl) amine reacted with different prepolymers (the stoichiometric ratio of NH : NCO = 1 : 1) at room temperature for 1 h, respectively. And the different SPUs were subsequently obtained. The synthetic routes and the structure of prepolymer and SPU are shown in Figure 1.

### Preparation of SPU membranes

SPUs were casted into a polytetrafluoroethylene mold and solidified at 80°C for 72 h, and then the membranes of SPUs were obtained.

### Characterization

FTIR spectroscopic measurements in KBr pellets were carried out using a NICOLET 370DTGS FT-IR spectrometer. <sup>1</sup>H-NMR spectrum was recorded on

**TABLE I**  
The Theoretical and Experimental NCO Group Value in Prepolymer with Different Molecular Weight PEG

Prepolymers	400	600	800	1000
Theoretical NCO value (%)	11.23	8.86	7.32	6.23
Experimental NCO value (%)	11.1	8.7	7.2	6.2

an INOVA-600 spectrometer using CDCl<sub>3</sub> as solvent. Wide angle X-ray diffraction (WAXD) analysis was performed with thin film samples of 0.5–1.0 mm thick using a Rigaku D/max-rA X-ray diffractometer (Rigaku Co., Japan) operated at 35 kv and 25 mA with Cu ( $\lambda = 10,154$ ) irradiation at the rate of 2°/min in the range 2–80°. The thermogravimetric analysis (TGA) was carried out with a TGA Perkin-Elmer thermogravimetric apparatus at a heating rate of 10°C/min in nitrogen. The flow rate of nitrogen was 50 cm<sup>3</sup>/min and the scanning temperature ranged from ambient temperature to 700°C. Glass transition temperatures ( $T_g$ ) of SPUs were measured after the curing process using a differential scanning calorimeter TA, model Q100. The heating rate was 20°C/min over a temperature ranged of –70 to 100°C. After the first scan, the samples were quickly cooled to –70°C at the rate of 20°C/min and the  $T_g$  were determined as the onset of the transition of the second scan at the rate of 10°C/min. The water uptakes of SPU were measured by square specimens (20 mm × 20 mm). The SPUs were weighed and immersed in water at 25°C and then weighed after 24 H again. Percent of water swelling/percent of water uptake ( $P_s$ ) was calculated by the formula shown as below:

$$P_s = \frac{\text{Weight of swollen hydrogen} - \text{weight of dry hydrogen}}{\text{weight of dry hydrogen}} \times 100\%$$

## RESULTS AND DISCUSSION

### Confirmation of structure

FTIR analysis

The preparation of SPUs proceeded in two steps and was investigated by FTIR spectra. Figure 2 shows both the FT-IR spectra of purified prepolymer and SPU. In the first step, the hydroxyl groups of the PEG reacted with the isocyanate groups of TDI. The absorption of NCO groups at 2270 cm<sup>-1</sup> and the appearance of C=O adsorption in urethane groups at 1721 cm<sup>-1</sup> indicated the reaction between NCO and OH had happened and the NCO groups existed in prepolymer. In the second step, the NCO groups of prepolymers were further reacted with secondary

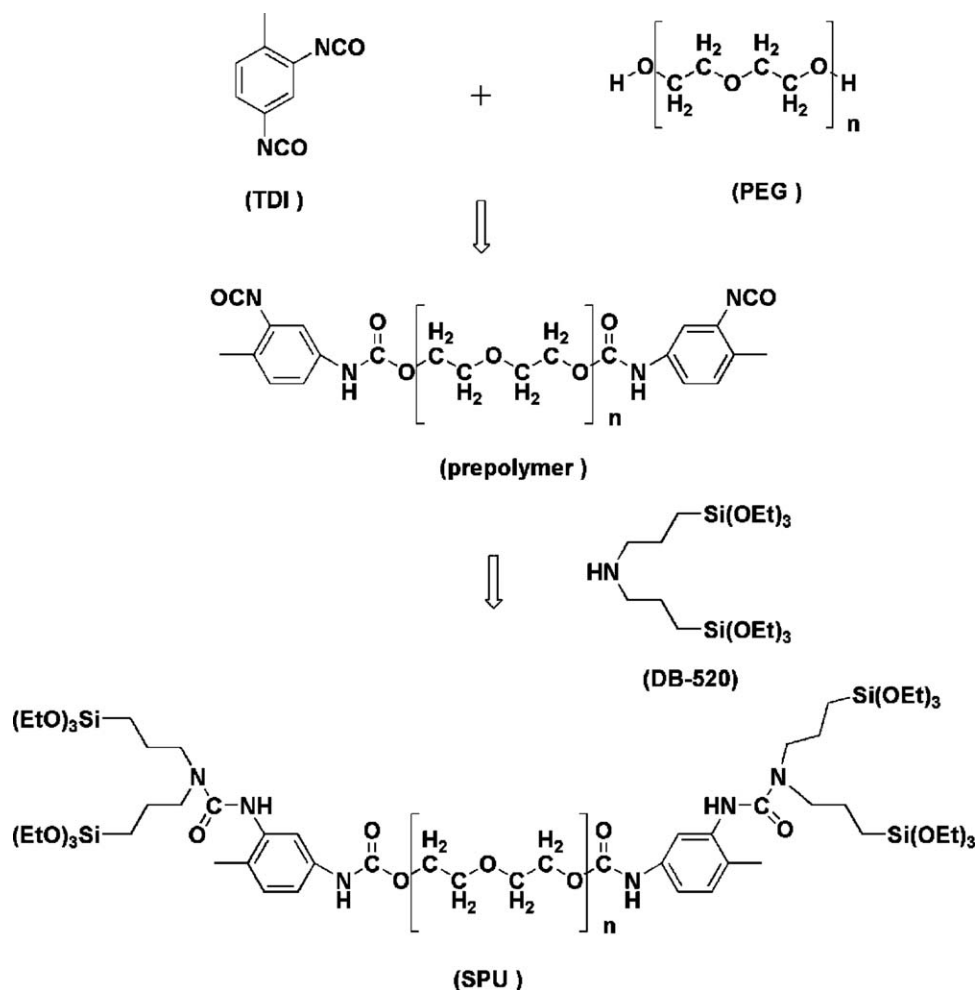


Figure 1 The synthetic routes of SPU.

amine of DB-520. The disappearance of NCO peak at  $2270\text{ cm}^{-1}$  accompanying with the appearance of C=O peak of urea groups at  $1640\text{ cm}^{-1}$  confirmed that the reaction between DB-520 and prepolymers was completed.

#### $^1\text{H-NMR}$ analysis

To further confirm the chemical structure of prepolymer and SPU, the  $^1\text{H-NMR}$  spectra of prepolymer and SPU based on PEG1000 were shown in Figure 3(a,b), respectively. In the spectrum of prepolymer, the proton signals of Ar- $\text{CH}_3$ ,  $-\text{CH}_2-\text{O}-\text{CH}_2-$ ,  $-\text{CH}_2-\text{OCOONH}-$  and Ar- $\text{H}$  separately gave its singlet or multiplet at  $\delta = 2.19\text{ ppm}$ ,  $\delta = 3.64\text{--}3.75\text{ ppm}$ ,  $\delta = 4.28\text{ ppm}$ , and  $\delta = 6.7\text{--}7.7\text{ ppm}$ . However, in the spectrum of SPU, compared with that of prepolymer, several new chemical shifts at  $\delta = 0.629\text{ ppm}$ ,  $\delta = 1.21\text{ ppm}$ ,  $\delta = 1.75\text{ ppm}$ ,  $\delta = 3.3\text{ ppm}$ ,  $\delta = 3.8\text{ ppm}$ , and  $\delta = 6.4\text{ ppm}$  appeared, which was attributed to the absorption of protons of  $-\text{CH}_2\text{Si}-$ ,  $-\text{SiOCH}_2\text{CH}_3$ ,  $-\text{CH}_2\text{CH}_2\text{CH}_2-$ ,  $-\text{CH}_2\text{CH}_2\text{CH}_2-$ ,  $-\text{SiOCH}_2\text{CH}_3$  and Ar- $\text{NHCON}-$ , respectively.<sup>21,22</sup>

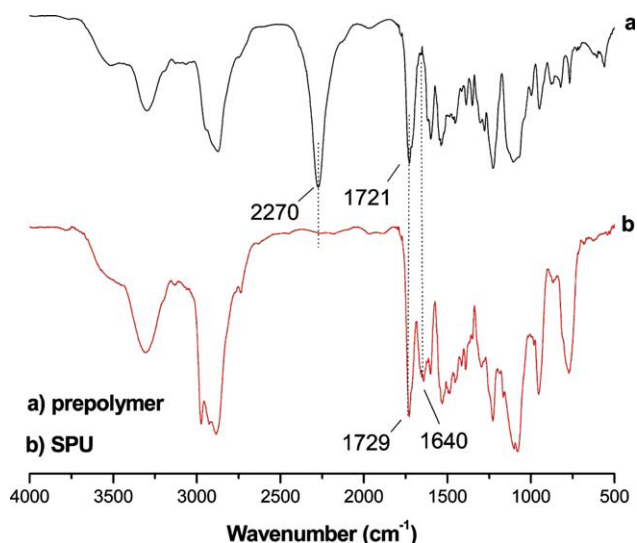
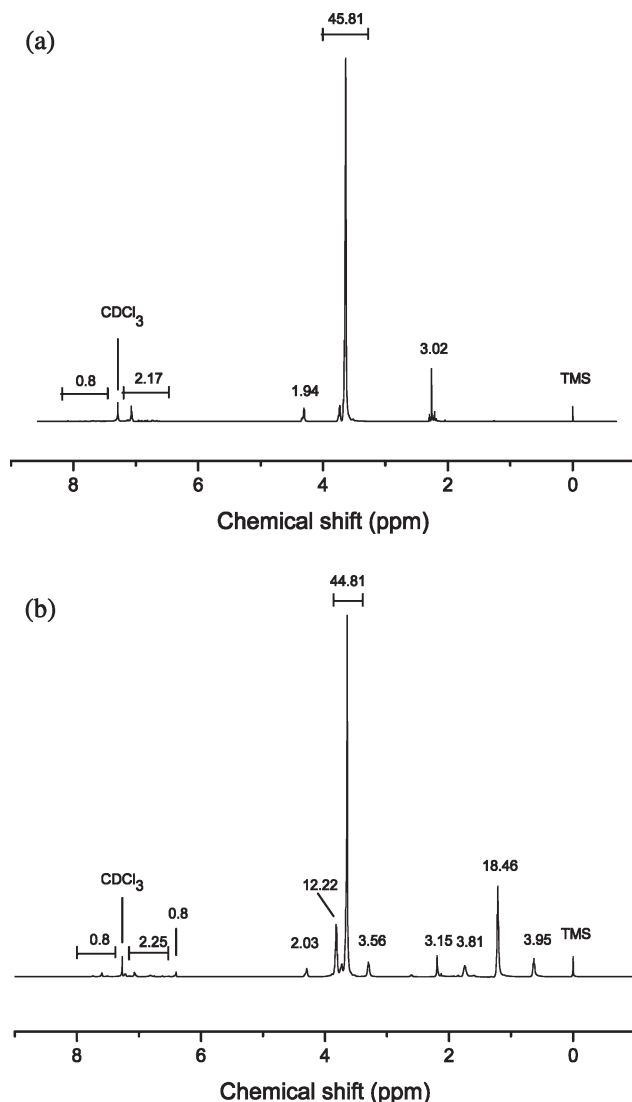


Figure 2 FTIR spectra of prepolymer and SPU based on PEG400. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

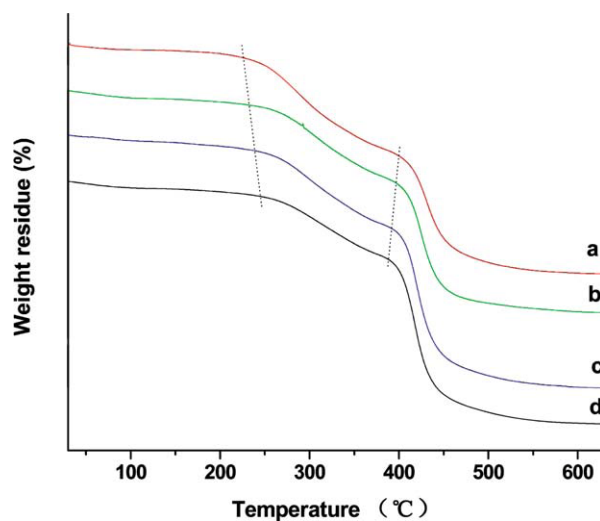


**Figure 3**  $^1\text{H-NMR}$  spectra of prepolymer and SPU based on PEG1000 in  $\text{CDCl}_3$  [(a) prepolymer; (b) SPU.]

Furthermore, both the integral areas of the proton peaks were proportional and in accordance with the theoretical value of prepolymer and SPU. Hence, the structure of prepolymer and SPU can be confirmed as PEG chains endcapped with NCO groups and prepolymer endcapped with DB-520, respectively, through the data analyze of FTIR,  $^1\text{H-NMR}$  and method of dibutylamine chemical titration. The  $^1\text{H-NMR}$  spectra of prepolymers and SPUs synthesized based on other PEGs were similar to that based on PEG1000 and will not be discussed repeatedly.

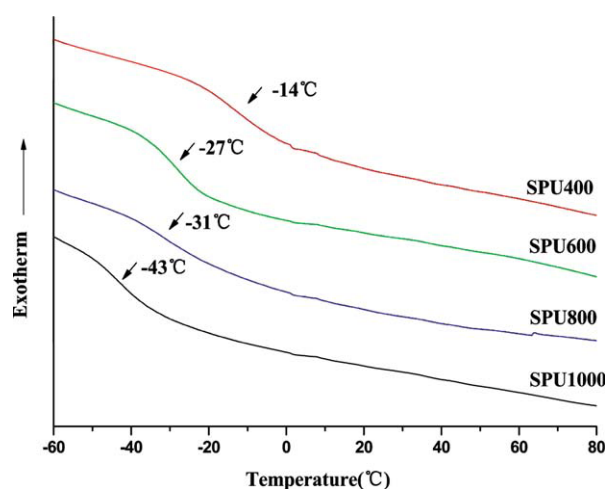
### Thermogravimetric analysis

Figure 4 depicts TGA thermograms of the SPUs. There were two distinct regions of weight losses, including the degradation of the first stage (stage I) and the second stage (stage II) around 208–229°C

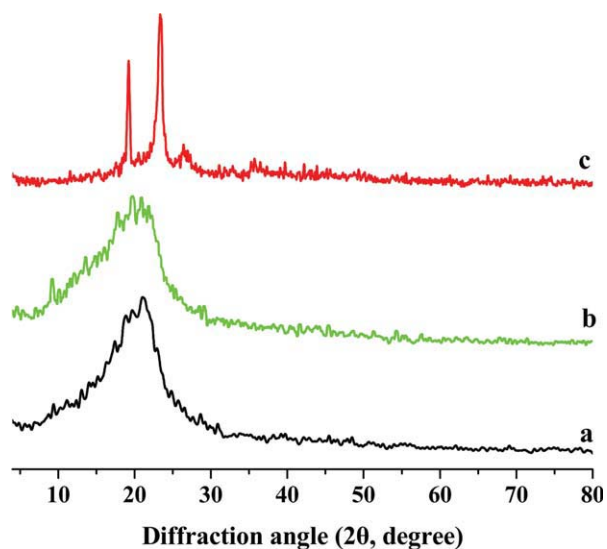


**Figure 4** TGA thermograms for SPU [(a) SPU400; (b) SPU600; (c) SPU800; (d) SPU1000]. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

and 366–397°C, respectively. Stage I and stage II separately signified the decomposition of urethane/urea groups and ether groups.<sup>23</sup> Comparing the different TG curves, it should be noted that the thermal stabilities of SPUs went up with the increase of  $\overline{M}_n$  of SPUs in stage I, but went down in stage II. It was because this series of SPUs had the same structure and Si, urethane, and urea content which reduced with the increase of  $\overline{M}_n$  of SPU. Less content of urethane, urea groups, and higher organic silicone content led to higher thermal stabilities of SPUs in stage I and stage II, respectively. However, the thermal properties of polyurethane were always determined by its first stage, thus the TG curves indicated that



**Figure 5** DSC curves of SPUs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 6** WAXD measurements for SPU and PEG1000 [(a) SPU400; (b) SPU1000; (c) PEG1000]. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

the thermal stabilities of this series of cured SPUs went up with the increase of  $\bar{M}_n$  of SPUs.

#### DSC analysis of SPU

From Figure 5, as we can see, SPU with a higher molecular weight had a lower  $T_g$  value. In this system, the ethoxysilane groups formed into siloxane networks after SPUs curing. Therefore, the cured SPU with lower molecular weight contains higher density of siloxane networks and the chains connecting these siloxane networks are shorter than that in high molecular weight SPUs. The siloxane network can hinder the mobility of PEG chains, thus the  $T_g$  value of the SPUs decreased with the increase of the molecular weight of SPUs.

#### Wide angle X-ray diffraction

To investigate the underlying microstructure of SPUs, wide angle X-ray diffraction (WAXD) was employed. The X-ray diffraction patterns of PEG1000 and SPUs based on PEG were shown in Figure 6. From the Figure, we can see that PEG1000 had two prominent peaks at Bragg's angles  $19.36^\circ$  and  $23.44^\circ$ , but SPUs had one broad peak around  $20^\circ$ , which were typical for amorphous polymeric materials.<sup>24</sup> The absence of obvious crystalline reflected in the WAXD pattern of SPUs was ascribed to the condensation of ethoxysilane groups that disturbed the orientation of polyurethane molecular chains. In our work, the chain length of PEG is not long enough for crystallization orientation. Thus, the cured SPUs existed in the form of amorphous state.

#### Water uptake studies

For many applications, the investigation of the water absorption properties is of great importance. For a long time, to determine application areas of materials, tremendous efforts have been taken to understand the relationship between the polymer structures and their uptakes.

The percentage of water uptake of SPU's membranes are 8.50%, 20.47%, 30.11%, and 44.5%, respectively, with the  $\bar{M}_n$  of PEG increased from 400 to 1000 in this system. PEGs have the ether structure which is hydrophilic, while the organic silicone components are always hydrophobic. When the  $\bar{M}_n$  of SPU was increased, the content of PEG increased and organic silicone accordingly decreased, thus leading to an increase of water uptake of SPU. The percentage of water uptake of this type of polyurethane can be tuned by changing  $\bar{M}_n$  to satisfy the application.

#### CONCLUSIONS

A series of bistrifluoromethylsilyl endcapped polyurethane/ureas (SPU) with well-defined structure were synthesized from PEG, TDI, and DB-520. The structure of prepolymer and SPU were confirmed by FTIR,  $^1\text{H-NMR}$ , and standard dibutylamine back-titration method. Moreover, the properties of SPUs were characterized by WAXD, DSC, TGA, and percentage of water uptake. Results showed that these SPUs were amorphous and the percentage of water uptake and thermal stability of SPUs went up with the increase of  $\bar{M}_n$  of SPU, while the  $T_g$  values accordingly decreased. The synthesized method offered us an access to preparing various end-functionalized polyurethanes with well-defined structure.

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