

Polyhydroxyamic Acid from 3,3'-Dihydroxybenzidine and Pyromellitic Dianhydride as a Fire-safe Polymer

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Abstract: In order to assess the potential of the hydroxy-containing polyamic acid (PHAA) synthesized from 3,3'-dihydroxybenzidine and pyromellitic dianhydride for a fire-safe polymer, the cyclization pathway of PHAA has been investigated using a model compound prepared from 2-aminophenol and phthalic anhydride. The reaction was monitored by ¹H-nuclear magnetic resonance. N-(2-hydroxyphenyl)phthalamic acid is converted to N-(2-hydroxyphenyl)phthalimide at ca. 175 °C, showing endothermic reaction. The imide structure is rearranged to the benzoxazole structure over ca. 400 °C. These results are similar with that of PHAA. According to pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) data, water and carbon dioxide are released during the cyclization and rearrangement reaction. One DMAc molecule is complexed with one carboxyl acid group in PHAA, which accelerates the imidization process to release more easily the flame retardant, water.

Keywords: Fire-safe polymer, Polyhydroxyamic acid (PHAA), Cyclization pathway, Imidization

Introduction

Polyimides (PI) and polybenzoxazoles (PBO) are well known as heterocyclic polymers with excellent thermal stability, excellent mechanical properties, and good chemical resistance [1,2]. These outstanding properties have led us to investigate their use in fibers, films, coatings, and composites. Polyamic acids (PAAs) and polyhydroxyamides (PHAs), as precursors of PI and PBO, respectively, have lower mechanical properties in comparison to PI and PBO [3-7]. It is also well known that the cyclization reaction of the precursors occurs during heating to give the resulting more stable imides and benzoxazoles. These cyclization reactions are endothermic, which provide an added advantage for fire resistance. During the cyclization reaction, these polymers and their derivatives release small molecules, such as water, phosphorus or fluorine compounds, which further assist in flame retardancy [8]. The flame retarding property of a polymer is the focus of this research and is important especially in the aircraft industry.

Our group has studied the possibility of utilizing PAA, PHA, and their derivatives containing phosphorus or fluorine compounds as fire-safe polymers. In many respects, PAA and PHA can be excellent candidates for use in fire safety. Of course, it is well known that PBO is one of the least flammable polymers, but it has not been used due to the difficulty of processing. During heating, PAA and PHA conform closely to a fire retardant process and can be cyclized to form PI and PBO, respectively. In addition, processing of these polymers is enhanced due to their good solubility in aprotic solvents such as N-methylpyrrolidone (NMP), N,N-

dimethylacetamide (DMAc), and N,N-dimethylformamide (DMF).

As a new fire-safe polymer candidate, we have prepared polyhydroxyamic acid (PHAA) from 3,3'-dihydroxybenzidine (DHB) and pyromellitic dianhydride (PMDA). The mechanical and thermal properties of the PHAA films have already reported by our group [9]. I. Ye. Karadash, D. Likhatchev, and G. L. Tullos *et al.* [10-12] supposed a cyclization pathway which involved the rearrangement of hydroxy-containing polyimides to their corresponding PBO. Since the cyclization reaction is an important consideration for fire-safe polymers especially if a heat-sink also involves release of flame quenching materials, the study of the cyclization reaction of the hydroxy-containing polyamic acid would be prior to that of the hydroxy-containing polyimide in this respect. Additionally, processibility of the hydroxy-containing polyamic acid is much better than that of the hydroxy-containing polyimide. In these respects, we have tried to investigate the cyclization reaction of PHAA for assessing the potential of the hydroxy-containing polyamic acid for a fire-safe polymer.

Experimental

Materials

3,3'-Dihydroxybenzidine (DHB) was recrystallized from water/DMAc cosolvent and dried at 60 °C under vacuum. Pyromellitic dianhydride (PMDA) was recrystallized from acetic anhydride and sublimed under reduced pressure. DMAc was distilled over phosphorus pentoxide under reduced pressure. All monomers and solvents were kept in a desiccator before use. Other reagents were used as received.

Polymerization

After DHB (0.3983 g, 1.84 mmol) was completely dissolved in 10 ml of purified DMAc under nitrogen, PMDA (0.4017 g,

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1.84 mmol) was introduced into the solution with vigorous stirring. It was kept stirring for 24 h at room temperature. The polymer concentration was adjusted to 8 % (w/v). The resulting viscous solution was poured into methanol and the precipitate was filtered, washed with excess methanol, and dried at 60 °C under vacuum.

To obtain a polymer powder, the polymer mass was pulverized under liquid nitrogen and dried at 60 °C under vacuum until no weight change was observed.

Preparation of Model Compounds

An anhydrous DMAc solution (10 ml) of 2-aminophenol (0.75 g, 6.9 mmol) was prepared under nitrogen. Phthalic anhydride (1.02 g, 6.9 mmol) was then added to the solution with stirring, which gave a light yellow color. After the reaction was carried out for 2 h, the solution was poured into an excess of water, and the white precipitate was filtered, recrystallized with ethyl ether, and dried at 60 °C under vacuum for 24 h. IR (KBr, $\nu(\text{cm}^{-1})$): 3392 (O-H str., hydroxy); 3197 (O-H str., carboxylic acid); 1727 (C=O str., carboxylic acid); 1694 (C=O, amide). $^1\text{H-NMR}$ (dms- d_6 , ppm): 13.2 (1H, carboxylic acid); 9.7 (1H, hydroxy); 9.6 (1H, amide); 6.8-8.0 (8H, aromatic).

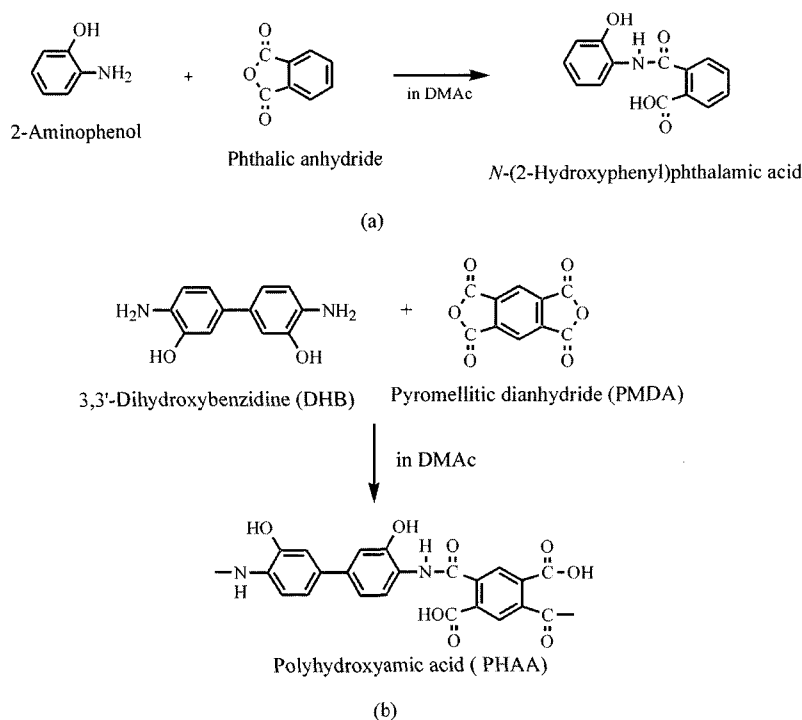
Measurements

Infrared (IR) spectra were recorded in a Bio-Rad FTS 175C FT-IR spectrometer. A Bruker 300 was used for ^1H -nuclear magnetic resonance (NMR) measurement. Dimethyl sulfoxide- d_6 was used as a solvent. The cyclization reaction

was monitored by differential scanning calorimetry (DSC) and thermogravimetry (TG) using a DuPont DSC 2910 and TGA 2950 under nitrogen at a heating rate of 10 °C/min. Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) data was obtained using a CDS Analytical Pyroprobe 2000 with a CDS 1500 Valved Interface coupled to a Hewlett-Packard 5890 Series II Plus Gas Chromatograph 5972 Series Mass Selective Detector. The sample was heated in a quartz tube at 10 °C/ms to 450 °C and then held for 15 sec. The interface temperature and the GC inlet temperature were 150 °C. The initial temperature of the GC oven was 40 °C. The temperature was ramped at 10 °C/min to 250 °C and then held. The helium flow rate was 1 ml/min. The GC column was a capillary, HP5-MS (crosslinked 5 % PH Me Siloxane; 30 m \times 0.25 mm). The inherent viscosity of PHAA was determined at 0.5 g/dl in DMAc at 23 °C using an Ubbelohde viscometer.

Results and Discussion

A model compound was prepared to study the cyclization reaction pathway of PHAA synthesized from DHB and PMDA. As shown in Scheme 1(a), *N*-(2-hydroxyphenyl)phthalamic acid was synthesized from one mole each of 2-aminophenol and phthalic anhydride in DMAc and could be precipitated in an excess of water, and recrystallized with ethyl ether to remove completely DMAc to get rid of the solvent effect on the cyclization reaction behavior. PHAA with an inherent viscosity of 0.45 dl/g was obtained as



Scheme 1. Preparation of model compound (a) and PHAA (b).

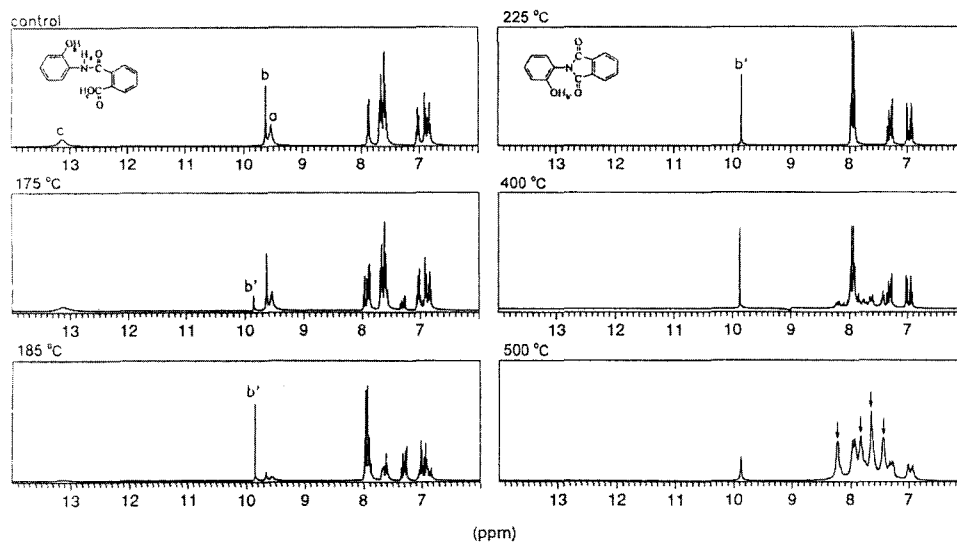


Figure 1. NMR spectra of model compound before and after heating at various temperatures.

shown in Scheme 1(b). The PHAA is soluble in DMAc and can be easily precipitated in methanol. The precipitated PHAA mass was pulverized under liquid nitrogen in order to remove completely the residual solvent.

The cyclization reaction pathway was monitored by $^1\text{H-NMR}$. The model compound had to be sealed in ampoules under vacuum when it was treated above its melting point, 225 °C. These ampoules were heated at each temperature for 30 min under nitrogen. The $^1\text{H-NMR}$ spectra of the thermally treated model sample are shown in Figure 1. The $^1\text{H-NMR}$ chemical shifts of the protons in the amide, hydroxyl, and carboxyl groups of *N*-(2-hydroxyphenyl)phthalamic acid are assigned to 9.6, 9.7, and 13.2 ppm, respectively. After heating, a new peak at 9.9 ppm appears, and the peaks at 9.6, 9.7, and 13.2 ppm decrease with increasing heat treatment. In the case of the model compound heated at 225 °C, only the new peak, b' at 9.9 ppm remains. This means that two structures, hydroxy-containing phthalamic acid and phthalimide are present below 185 °C. The new peak, b', is assigned to a proton of the hydroxyl group in *N*-(2-hydroxyphenyl) phthalimide. Above 185 °C, *N*-(2-hydroxyphenyl)phthalamic acid is completely converted to *N*-(2-hydroxyphenyl)phthalimide. Based on the area under each peak, the extent of conversion to *N*-(2-hydroxyphenyl)phthalimide at 185 °C is 71 %. The hydroxy-containing phthalimide remains stable up to 400 °C. Above this temperature, the peaks assigned to the hydroxyl group and the aromatic group in the hydroxy-containing phthalimide decrease and the new peaks (arrows) assigned to 7.4, 7.6, 7.8, and 8.2 ppm appear. This new peak pattern in the aromatic group is almost the same as for 2-phenylbenzoxazole [13]. This change suggests that hydroxy-containing phthalamic acid converts to carboxylic acid-containing 2-phenylbenzoxazole upon further heat treatment. Because the presence of a carboxylic acid is not seen by $^1\text{H-NMR}$, it can be assumed

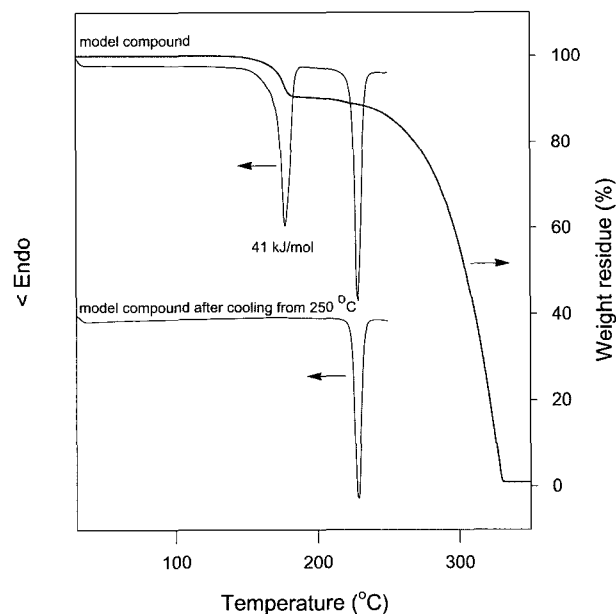


Figure 2. DSC and TGA thermograms of model compound.

that the benzoxazole ring is formed with the simultaneous decarboxylation of the acid functional group and the release of carbon dioxide [10-12].

Figure 2 shows DSC and TGA thermograms of the model compound, *N*-(2-hydroxyphenyl)phthalamic acid. It cyclizes at about 175 °C to give the related hydroxy-containing imide, *N*-(2-hydroxyphenyl)phthalimide, with a melting point of 225 °C, the same as the reference value [14]. Thus, we observe endothermic peaks at two temperatures by the DSC analysis. The heat of cyclization of the model compound is 41 kJ/mol. The endothermic reaction provides an added advantage for fire resistance. When this sample is scanned by DSC after

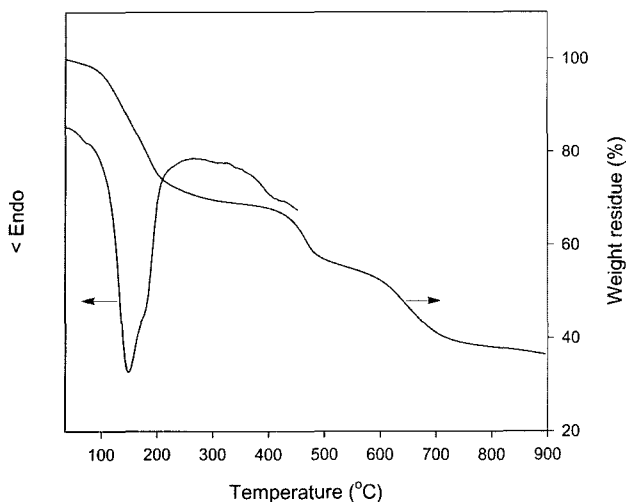


Figure 3. DSC and TGA thermograms of PHAA.

cooling, the first peak, assigned to the cyclization reaction, disappears. TGA thermogram of the model compound shows that the cyclization reaction of N-(2-hydroxyphenyl) phthalamic acid is completed by 185 °C. This result is similar to that from DSC analysis. The weight loss of the model compound is about 8.5 % at this temperature. The theoretical weight loss for cyclization, due to water loss, is about 7.0 %.

Figure 3 shows DSC and TGA thermograms of PHAA under nitrogen. Three weight loss steps occur during heating. The first step may be assigned mainly to loss of DMAc combined with imidization. The polar aprotic solvents are known to form strongly hydrogen-bonded complexes with the carboxylic acid group in PAA [15-17]. The first weight

loss of PHAA is almost 34 %, which is similar to the theoretical weight loss of 2 moles of water, 6 %, and 2 moles of DMAc, 29 %, complexed in PHAA repeating unit. Since the polymer powder was dried at 60 °C under vacuum until no weight change was observed, it has no residual DMAc except complexed one. It is likely that, in this case, loss of DMAc occurs first, followed by imidization, although it has not been possible to separate these steps. It is well known for polyamic acids that the released solvent has been shown to effectively plasticize the polymer matrix to be easily imidized even though the solvent complex hinders the imidization process [17,18]. As the results, the cyclization reaction of the hydroxy-containing polyamic acid might easily occur to release the flame quenching material, water in this case, at competitively low temperature under the complexation condition, which leads a discrete imidization step between 100 and 200 °C as shown in DSC thermogram of PHAA. The second weight loss, almost 18 %, is observed above 400 °C, and is due to loss of two moles of carbon dioxide and the conversion to PBO as previously reported. The decomposition temperature of PBO is observed to occur at approximately 600 °C to give a large residue amounting to about 80 % of its weight. It will provide limitation of heat and mass transfer across the phase boundary by creation of an insulating charred layer.

To identify the products given off during the cyclization and rearrangement reaction, a PHAA powder sample was cyclized at 450 °C at a heating rate of 10 °C /ms under a helium atmosphere using a commercially available resistively heated filament pyrolyzer. The sample was cyclized in a heated interface that was connected directly to the GC inlet. The releasing products during heating were swept directly

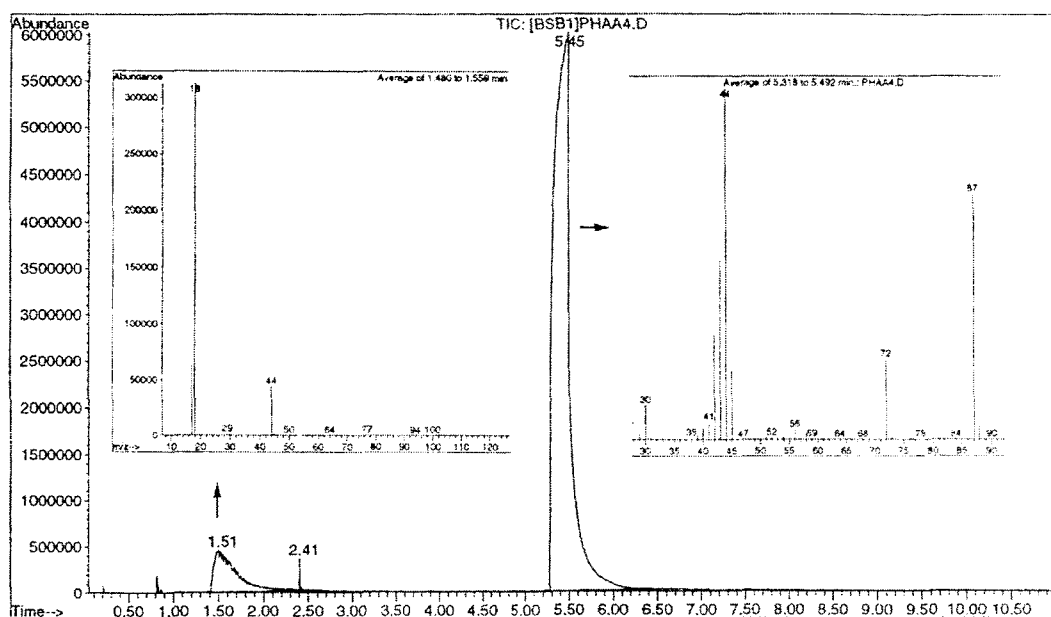
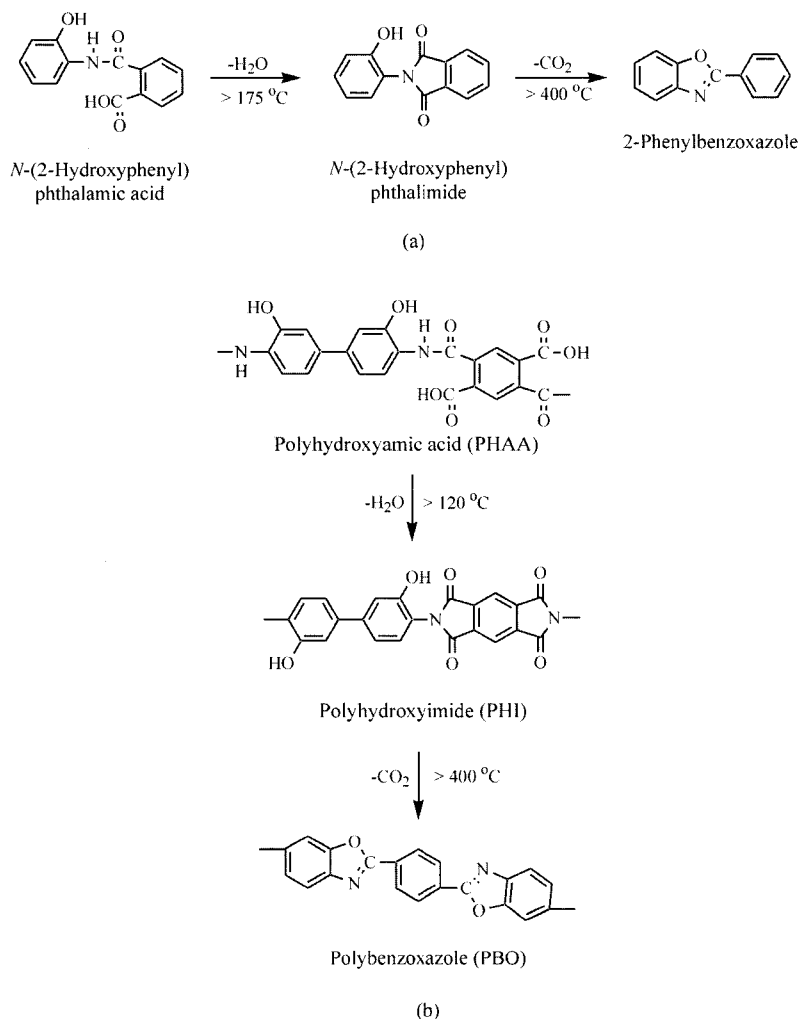


Figure 4. GC trace of products from the cyclization and rearrangement reactions of PHAA.



Scheme 2. Cyclization pathway of model compound (a) and PHAA (b).

onto the column where they were cold condensed. The GC oven was then ramped at 10 °C /min to 250 °C and the products were identified using a mass spectrometer. The GC chromatograms for the products given off during heating PHAA are shown along with the corresponding MS spectrum in Figure 4. As can be seen in the chromatograms, PHAA has a much larger amount of DMAc. Water and carbon dioxide are also detected at almost the same time. Since the decomposition temperature of PBO is over 600 °C, this carbon dioxide would not come from the decomposition of PBO. Release of water and carbon dioxide further assists in flame retardancy in our fire-safe polymer system.

The cyclization pathway of model compound and PHAA is summarized in Scheme 2. Flame retardancy can be achieved by modifying the rate of the chemical or physical process taking place in one or more of the steps of the burning process [19]. During heating, these released materials, charred layer, and endothermic reaction from PHAA will provide a great advantage for fire resistance.

Conclusion

In order to assess the potential of hydroxy-containing polyamic acid (PHAA) for a fire-safe polymer, the cyclization pathway of PHAA has been investigated. It has been known from the study of model compound synthesized from 2-aminophenol and phthalic anhydride that hydroxy-containing amic acid moieties are converted to the related imide species at ca. 175 °C. In the case of PHAA, this temperature actually decreases mainly due to the complexed solvent. The cyclization reaction is endothermic. The creation of heat-sink assists in flame retardancy. The hydroxy-containing imide structure is rearranged to the benzoxazole structure over ca. 400 °C as previously reported. During the first cyclization, water is given off, and during the second, carbon dioxide is released. PHAA creates an insulating charred layer during burning to limit heat and mass transfer across the phase boundary. PHAA is identified to be a good candidate for fire-safe polymers.

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