Synthesis of Bi- and Trifunctional Cyclic Carbonates Based on Trimethylolpropane and Their Application to Networked Polyhydroxyurethanes

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Abstract

The reaction of trimethylolpropane (TMP) and diphenyl carbonate gives three types of TMP-based six-membered cyclic carbonates (TMPCs) via phosgene-free route. TMPC having one hydroxyl group (TMPC-OH) reacted with terephthaloyl chloride or trimesoyl chloride to give bifunctional (Ph-TMPC$_2$) or trifunctional cyclic carbonate monomers (Ph-TMPC$_3$), respectively. The ring-opening polyaddition of Ph-TMPC$_2$ and conventional diamines efficiently proceeded without the cleavage of ester bonds to afford linear polyhydroxyurethanes (PHUs) with well-controlled molecular weights and polydispersities via isocyanate-free route. Moreover, the polyaddition of Ph-TMPC$_2$ and diamine at TMPC$_2$/diamine feed ratio of 1.1 afforded PHUs having cyclic carbonate terminals, the hydroxyl side chains of which were easily reacted with acetic anhydride to give acetylated PHUs with cyclic carbonate terminals. On the other hand, the polyaddition at Ph-TMPC$_2$/diamine feed ratio of 0.91 gave PHUs with amine terminals. The copolymerization of Ph-TMPC$_2$, Ph-TMPC$_3$ and diamine gives PHUs comprising covalently-bridged networked structures. After DMF solutions of Ph-TMPC$_2$, Ph-TMPC$_3$ and diamines were simply kept at 60 °C overnight, networked PHU films with well transparency were successfully fabricated. The PHU films prepared at different diamines showed similar transparency and thermal stability, while the mechanical properties were significantly affected by the methylene spacers of diamines.

Keywords: trimethylolpropane, diphenyl carbonate, networked polyhydroxyurethane, polyhydroxyurethane film

1. Introduction

Poly(hydroxyurethane)s (PHUs) have been attracting great interest as the promising alternatives of widely-used polyurethanes because PHUs can be synthesized by ring-opening polyaddition of bifunctional cyclic carbonates and diamines without using toxic isocyanates (Nohra, 2013; Kathalewar, 2013). In particular, five-membered cyclic carbonates (5-CCs) can be derived from epoxides and CO$_2$ under mild conditions (Fleischer, 2013; Sheng, 2015) and therefore, numerous 5-CCs-derived PHUs have been synthesized using bisphenol A (Ochiai, 2014; Lambeth, 2013; Ochiai, 2007; Ochiai, 2005; Kihara, 1996) and bio-based polyols (Kathalewar, 2015; Maisonneuve, 2014; Annunziata, 2014; Guillaume, 2013; Guillaume, 2011) as starting materials. PHUs can be functionalized by the use of functional diamines or by chemical modifications via their hydroxyl side chains. Nowadays it has been reported that silicone-conjugated PHUs show lower glass transition temperatures and well water repelling properties (Ochiai, 2014) and networked PHU gels are obtainable by the reaction with metal alkoxides (Kihara, 1996) or by the free-radical polymerization of methacryl groups modified in their side chains (Ochiai, 2007). In addition, urethane linkages of PHUs can be degraded at alkaline conditions and further shows biodegradability, thus, PHUs are one of promising candidates for versatile materials based on biocompatibility and biodegradability. Meanwhile, PHUs from six-membered cyclic carbonates (6-CCs) are hardly reported except for a few case (He, 2011; Maisonneuve, 2014; Tomita, 2001). The ring-opening reaction of 6-CCs with amines requires the lower energy compared to 5-CCs because of the larger ring strain energy of 6-CCs (Tomita, 2001). This implies that PHUs can be synthesized at milder conditions. Besides, β-substituted 6-CCs generate only primary alcohols (hydroxymethyl groups) after the ring-opening reaction with amines, therefore, simple structured PHUs are obtainable. However, 6-CCs are generally synthesized using toxic phosgene or its derivatives (He, 2011; Maisonneuve, 2014; Tomita, 2001), which hinders the practical usage of 6-CCs and their application to PHU materials.

The development of synthetic route to 6-CCs without toxic phosgene and its derivatives is one of important issues in polycarbonate and polyurethane chemistry. It has been reported that the synthesis of mono- and bifunctional 6-CCs using diphenyl carbonate (DPC) and their application to networked polycarbonate and PHU films via their copolymerization (Matsukizono, 2015, 2016). Without phosgene and its derivatives, DPC can be synthesized from ethylene carbonates through the reaction with methanol and phenol (Nishihara, 2010; Okuyama, 2003) or from CO and phenol (Kanega, 2013; Murayama, 2012). Furthermore, Matsukizono and Endo (2016) have recently reported that the reaction of trimethylolpropane (TMP) with an excess amount of DPC gives three types of different structured TMP-based cyclic carbonates (TMPCs) shown in Scheme 1: TMPC bearing a hydroxyl group (TMPC-OH), TMPC bearing a phenoxycarbonylated hydroxyl group (TMPC-OCOPh) and TMPC dimers bridged by an acyclic carbonate bond (TMPC-dimer). In addition, they have reacted TMPC-dimer with conventional diamine to form poly(carbonate-hydroxyurethane)s and characterized their hydrolytic properties in basic aqueous media. Meanwhile, TMPC-OH contains one hydroxyl group, which can be reacted with multifunctional acyl chloride to synthesize multifunctional 6-CCs bridged by ester linkages. This approach lets us expect that networked PHU materials such as gels and films can be easily fabricated by the simple reaction of multifunctional 6-CCs with diamines.
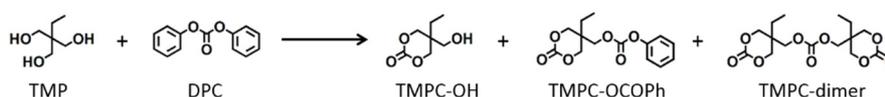

Scheme 1. Three types of different structured cyclic carbonates synthesized by the reaction of TMP and DPC
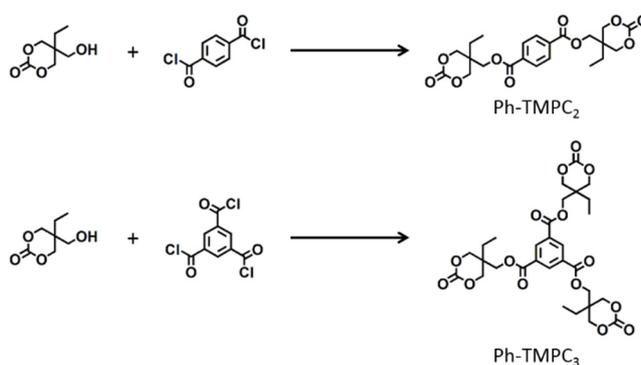
Scheme 2. Synthesis of bifunctional 6-CCs (Ph-TMPC$_2$) or trifunctional 6-CCs (Ph-TMPC$_3$) from TMPC-OH.

Here in, we describe the facile fabrication route to networked PHU material. At first, we synthesized bi- and trifunctional 6-CCs from TMPC-OH (Ph-TMPC$_2$ and Ph-TMPC$_3$) (See Scheme 2). Next, we performed the ring-opening polyaddition of Ph-TMPC$_2$ and conventional diamines to yield linear PHUs (Scheme 3a). Finally, we reacted Ph-TMPC$_2$, Ph-TMPC$_3$ and diamines at different feed ratios to build networked PHU films and characterized their transparency, thermal stability and mechanical properties (Scheme 3b). Monomers and polymers were analyzed by ^{1}H and ^{13}C nuclear magnetic resonance (NMR), Fourier translation infra-red (FT-IR) spectroscopy, size exclusion chromatography (SEC), thermogravimetric analysis (TGA), UV/Vis.-near infra-red (NIR) absorption spectroscopy and tensile tests.
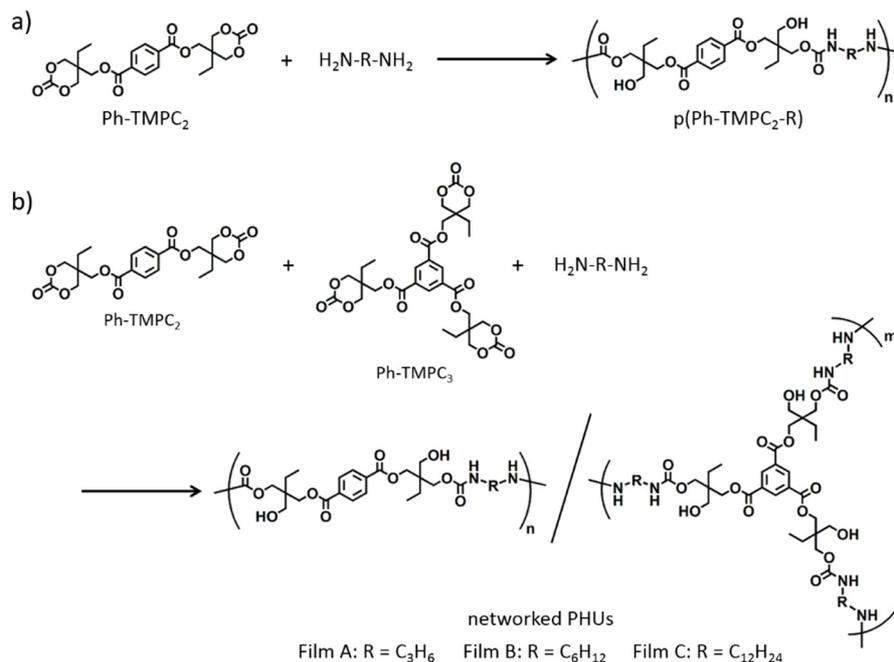
Scheme 3. a) Synthesis of linear PHUs (p(Ph-TMPC$_2$-R)) by ring-opening polyaddition of Ph-TMPC$_2$ with conventional diamines (R = C$_3$H$_6$, C$_6$H$_{12}$, C$_{12}$H$_{24}$). b) Fabrication of networked PHUs by the copolymerization of Ph-TMPC$_2$, Ph-TMPC$_3$ and diamines

2. Method

2.1 Reagents

TMP, terephthaloyl chloride, dehydrated pyridine, trimethylamine and acetic anhydride were purchased from Wako Pure Chemical Co., Ltd. DPC, trimesoyl chloride, 1,3-diaminopropane (C$_3$), 1,6-diaminehexane (C$_6$) and 1,12-diaminododecane (C$_{12}$) were obtained from Tokyo Chemical Industry Co., Ltd. Other reagents and solvents were commercially obtained and used without any purification.

2.2 Synthesis of TMPC-OH

TMPC-OH was synthesized by the same procedure reported previously (Matsukizono, 2016). TMP 13.4 g (100 mmol) was added slowly to DPC 85.7 g (400 mmol) melted by heating at 140 °C. After the mixture was stirred at 140 °C for 1-2 days, the mixture was cooled to ambient temperature and then dissolved in EtOAc (120 mL) and hexane (40 mL). TMPC-OH was isolated by silica gel column chromatograph (eluent: n-hexane/EtOAc volume ratio of 1/3). The crude product was used for the following reactions without further purification. Yield: 56.6%. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 4.26 (dxd, 4H, J = 70, 11 Hz, - CH$_2$-OCOO- of cyclic carbonate), 3.67 (d, 2H, J = 4.8 Hz, HO-CH_2-), 2.77 (t, 1H, J = 5.4 Hz, HO-), 1.51 (q, 2H, J = 7.6 Hz, CH$_3$-CH_2-), 0.93 (t, 3H, J = 7.6 Hz, CH$_3$-). ^{13}C NMR (400 MHz, DMSO-d$_6$, δ): 148.6 (C=O), 72.8 (-CH$_2$-OCO-), 59.8 (HO-CH$_2$-), 35.8 (C-(CH$_2$O)$_3$), 22.5 (CH$_3$-CH$_2$-), 7.6 (CH$_3$). IR (ATR): ν = 3408 (m; ν(O-H)), 2968-2883 (w; ν(CH$_2$)), 1714 (s; ν(C=O)), 1472-1409 (m; δ(CH$_2$)), 1180-1110 cm^{-1} (s; ν(C-O) of carbonate and alcohol).

2.3 Synthesis of Ph-TMPC$_2$

TMPC-OH 3.37 g (21.0 mmol) and terephthaloyl chloride 2.04 g (10.0 mmol) were individually dissolved in dehydrated THF (15 mL). To the TMPC-OH solution at 0 °C, triethylamine 2.13 g (21.0 mmol) and the terephthaloyl chloride solution were slowly added and the mixture were stirred at ambient temperature for 14 h. Resulting precipitates were collected by suction filtration and washed with THF. After dried, the precipitates were dissolved in CH$_2$Cl$_2$ (100 mL) and then washed three times with distilled water (100 mL). The organic layer were dried over with anhydrous Na$_2$SO$_4$ and then concentrated. After drying under reduced pressure, Ph-TMPC$_2$ was obtained as a white solid. Yield: 3.09 g (68.5%). ^{1}H NMR (400 MHz, CDCl$_3$, δ): 8.10 (s, 4.0H, phenyl), 4.43-4.30 (m, 12.0H, -CH$_2$-OC(=O)-), 1.64 (q, 4.0H, J = 7.6 Hz, CH$_3$-CH_2-), 1.02 (t, 6.0H, J = 7.8 Hz, CH$_3$-). ^{13}C NMR (400 MHz, CDCl$_3$, δ): 165.1 (C=O of ester), 148.1 (C=O of carbonate), 133.5 (C1 of phenyl), 129.9 (C2 of phenyl), 72.7

(CH$_2$-O of carbonate), 64.1 (CH$_2$-O of ester), 35.0 (C-(CH$_2$O)$_3$), 23.9 (CH$_3$-CH$_2$), 7.5 (CH$_3$). IR (ATR): ν = 2966-2885 (w; ν(CH$_2$)), 1756 (s; ν(C=O of ester)), 1721 cm^{-1} (s; ν(C=O of carbonate))

2.4 Synthesis of Ph-TMPC$_3$

TMPC-OH 5.29 g (33.0 mmol) and dehydrated pyridine 2.61 g (33.0 mmol) were dissolved in dehydrated THF (50 mL) and the solution was cooled to 0 °C in ice bath. To the solution was added slowly a dehydrated THF (30 mL) containing trimesoyl chloride 2.67 g (10.1 mmol) and the mixture was stirred at ambient temperature for 21 h. Resulting precipitates were collected by suction filtration and washed with THF. After dried, the precipitates were dissolved in CH$_2$Cl$_2$ (100 mL) and washed three times with distilled water (100 mL). After dried over with anhydrous Na$_2$SO$_4$, the organic layer was concentrated. The residues were purified by reprecipitation from acetone/methanol to give Ph-TMPC$_3$ as a white solid. Yield: 3.73 g (58.6%). ^{1}H NMR (400 MHz, CDCl$_3$, δ): 8.81 (s, 3.0H, phenyl), 4.52-4.31 (m, 18.0H, -CH$_2$-OC(=O)-), 1.64 (q, 6.0H, J = 7.6 Hz, CH$_3$-CH$_2$-), 1.02 (t, 9.0H, J = 7.6 Hz, CH$_3$-). ^{13}C NMR (400 MHz, CDCl$_3$, δ): 164.3 (C=O of ester), 148.2 (C=O of carbonate), 135.2 (C1 of phenyl), 130.8 (C2 of phenyl), 72.9 (CH$_2$-O of carbonate), 65.3 (CH$_2$-O of ester), 34.9 (C-(CH$_2$O)$_3$), 24.0 (CH$_3$-CH$_2$), 7.5 (CH$_3$). IR (ATR): ν = 2973-2882 (w; ν(CH$_2$)), 1728 cm^{-1} (s; ν(C=O of carbonate and ester)).

2.5 Synthesis of linear PHUs

2.5.1 Synthesis of p(Ph-TMPC$_2$-C$_3$)

To DMF (1.5 mL) containing Ph-TMPC$_2$ 212 mg (0.47 mmol) was added a DMF (1.5 mL) of C$_3$ 32 mg (0.43 mmol) at ambient temperature. The mixture was stirred at ambient temperature for 24 h and the fraction was analyzed by ^{1}H NMR spectroscopy and SEC measurements. After that, the mixture was added in distilled water (100 mL) and then the resulting precipitates were washed thoroughly with distilled water. The precipitates were collected by dissolving in acetone and drying under reduced pressure to obtain p(Ph-TMPC$_2$-C$_3$) having TMPC terminals as colorless liquids. Yield: 109 mg (44.7%). ^{1}H NMR (400 MHz, CDCl$_3$, δ): 8.11-8.05 (m, 4.3H, phenyl), 7.05 (br, 1.9H, NH), 4.68 (br, 2.0H, OH), 4.42-4.31 (m, 1.4H, -CH$_2$-OC(=O)- of terminal cyclic carbonates), 4.12 (s, 4.0H, -CH$_2$-OC(=O)-Ph), 3.92 (s, 3.8H, -CH$_2$-OC(=O)-NH), 3.37 (s, 3.9H, -CH_2-OH), 3.03-2.87 (m, 4.4H, NH-CH_2-CH$_2$-), 1.54-1.37 (m, 6.4H, CH$_3$-CH_2- and NH–CH$_2$-CH_2-), 0.87-0.81 (m, 6.6H, CH$_3$-). IR (ATR): ν = 3360 (w; ν(OH)), 2963-2883 (w; ν(CH$_2$)), 1713 (s; ν(C=O of carbonate and ester)), 1268 cm^{-1} (s; ν(C-O)).

2.5.2 Synthesis of p(Ph-TMPC$_2$-C$_6$)

p(Ph-TMPC$_2$-C$_6$) was synthesized by the same procedure of p(Ph-TMPC$_2$-C$_3$) and obtained as white solids. Yield: 91.8%. ^{1}H NMR (400 MHz, DMSO-d$_6$, δ): 8.09-8.05 (m, 4.5H, phenyl), 7.04 (br, 1.8H, NH), 4.73-4.68 (br, 1.9H, OH), 4.42-4.31 (m, 1.5H, -CH$_2$-OC(=O)- of terminal cyclic carbonates), 4.12 (s, 4.0H, -CH$_2$-OC(=O)-Ph), 3.92 (s, 3.7H, -CH$_2$-OC(=O)-NH), 3.37 (s, 3.9H, -CH_2-OH), 3.00-2.85 (m, 4.0H, NH-CH_2-CH$_2$-), 1.51-1.11 (m, 12.4H, CH$_3$-CH_2- and NH–CH$_2$-(CH_2)$_4$-), 0.87-0.81 (m, 6.6H, CH$_3$-). IR (ATR): ν = 3339 (w; ν(OH)), 2962-2881 (w; ν(CH$_2$)), 1700 (s; ν(C=O of carbonate and ester)), 1246 cm^{-1} (s; ν(C-O)).

2.5.3 Synthesis of p(Ph-TMPC$_2$-C$_{12}$)

p(Ph-TMPC$_2$-C$_{12}$) was synthesized by the same procedure of p(Ph-TMPC$_2$-C$_3$) and obtained as white solids. Yield: 69.3%. ^{1}H NMR (400 MHz, DMSO-d$_6$, δ): 8.09-8.05 (m, 4.4H, phenyl), 7.03 (br, 1.8H, NH), 4.73-4.67 (br, 1.9H, OH), 4.42-4.31 (m, 1.5H, -CH$_2$-OC(=O)- of terminal cyclic carbonates), 4.12 (s, 4.0H, -CH$_2$-OC(=O)-Ph), 3.92 (s, 3.8H, -CH$_2$-OC(=O)-NH), 3.37 (s, 3.9H, -CH_2-OH), 3.01-2.85 (m, 4.0H, NH-CH_2-CH$_2$-), 1.51-1.27 (m, 8.6H, CH$_3$-CH_2- and NH–CH$_2$-CH_2-), 1.13 (s, 16.0H, NH-(CH$_2$)$_2$-(CH_2)$_8$-), 0.87-0.80 (m, 6.6H, CH$_3$-). IR (ATR): ν = 3345 (w; ν(OH)), 2964-2881 (w; ν(CH$_2$)), 1698 (s; ν(C=O of carbonate and ester)), 1243 cm^{-1} (s; ν(C-O)).

2.5.4 Synthesis of p(Ph-TMPC$_2$-C$_3$-OAc)

p(Ph-TMPC$_2$-C$_3$) was synthesized by the reaction of Ph-TMPC$_2$ 202 mg (0.45 mmol, 1.1 equiv.) and C$_3$ 30 mg (0.41 mmol, 1.0 equiv.) in DMF (2.0 mL). Without purification, p(Ph-TMPC$_2$-C$_3$-OAc) was synthesized. To the DMF solution of p(Ph-TMPC$_2$-C$_3$), acetic anhydride 315 mg (3.09 mmol) and pyridine 245 mg (3.10 mmol) were added at ambient temperature and the mixture was stirred at 40 °C for 41 h. After DMF was removed, the yellow residues were dissolved in CH$_2$Cl$_2$ (100 mL) and then washed three times with distilled water (100 mL). After drying with anhydrous Na$_2$SO$_4$, CH$_2$Cl$_2$ was evaporated. After the yellow residues were dried under reduced pressure, p(Ph-TMPC$_2$-C$_3$-OAc) was obtained as pale yellow solids. Yield: 253 mg (95.0%). ^{1}H NMR (400 MHz, CDCl$_3$, δ): 8.08 (m, 4.4H, phenyl), 5.23 (br, 2.1H, NH), 4.44-4.41 (m, 1.2H, -CH$_2$-OC(=O)- of terminal cyclic carbonates), 4.32-4.11 (m, 11.6H, -CH$_2$-OC(=O)-), 3.27-3.12 (s, 4.0H , NH-CH_2-CH$_2$-), 2.06 (s, 5.8H, CH$_3$-(C=O)), 1.67-1.57 (m, 6.4H, CH$_3$-CH_2- and NH–CH$_2$-CH_2-), 1.04-0.93 (m, 6.6H, CH_3-CH$_2$-). IR (ATR): ν = 3367 (w; ν(OH of residual hydroxyl group or adsorbed water)), 2965-2880 (w; ν(CH$_2$)), 1720 (s; ν(C=O of carbonate and ester)), 1241 cm^{-1} (s; ν(C-O)).

2.5.5 Synthesis of p(Ph-TMPC$_2$-C$_3$)'

A DMF solution (1.0 mL) of C$_3$ 163 mg (2.2 mmol, 1.1 equiv.) was added to a DMF solution (2.0 mL) of Ph-TMPC$_2$ 901 mg (2.0 mmol) at 70 °C. At the temperature, the mixture was stirred for 17 h and then cooled to ambient temperature. After concentrated, the mixture was added to distilled water (200 mL) and the precipitates were washed with distilled water. After the precipitates were dissolved in acetone, the solution was concentrated and then dried under reduced pressure to give p(Ph-TMPC$_2$-C$_3$)' as white solids. Yield: 95.2%. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 8.05 (s, 4.1H, phenyl), 7.05-6.72 (m, 2.0H, NH), 4.68 (br, 1.9H, OH), 4.12 (s, 4.0H, -CH$_2$-OC(=O)-Ph), 3.92 (s, 4.0H, -CH$_2$-OC(=O)-NH), 3.37 (s, 4.0H, -CH$_2$-OH), 3.01-2.85 (m, 4.3H, NH-CH$_2$-CH$_2$-), 1.55-1.37 (m, 6.2H, CH$_3$-CH$_2$- and NH–CH$_2$-CH$_2$-), 0.81 (t, 6.1H, J = 7.2 Hz, CH$_3$-). IR (ATR): ν = 3364 (w; ν(OH and NH$_2$)), 2964-2881 (w; ν(CH$_2$)), 1698 (s; ν(C=O of carbonate and ester)), 1243 cm^{-1} (s; ν(C-O)).

2.6 Fabrication of Networked PHU Films

Ph-TMPC$_2$ and Ph-TMPC$_3$ were dissolved in DMF (1 mL) at 70 °C to prepare the Ph-TMPC$_2$/Ph-TMPC$_3$ solution at different molar ratios (5-20 mol% of Ph-TMPC$_3$ with respect to the total carbonate monomers (Ph-TMPC$_2$ + Ph-TMPC$_3$), [TMPC] = 0.5 M). To the solutions, C$_3$ dissolved in DMF (0.5 mL, [C$_3$] = 0.25 M) was added and then the mixed solutions (TMPC/NH$_2$ = 1.0) were stirred at 70 °C for within 5 min. After that, the solutions were poured in glass petri-dishes with 6.0 cm in diameter and allowed to stand at 60 °C overnight. The resulting films were carefully removed and immersed in distilled water for purification. After drying, the networked PHU films (Film A) were obtained. Similarly, Film B and Film C were prepared using 20 mol% Ph-TMPC$_3$ and C$_6$ or C$_{12}$, respectively.

2.7 Measurements

^{1}H and ^{13}C NMR spectra were recorded with a JEOL ECS-400 NMR spectrometer operating at 400 MHz using a tetramethylsilane (TMS) as an internal reference. FT-IR spectroscopy was conducted with a Thermo Fisher Scientific Nicolet iS10 equipped with an ATR instrument. SEC were performed with a Tosoh HLC-8320GPC using DMF as eluents operating at a flow rate of 0.5 mL min^{-1}. Number averaged molecular weight (M_n), Weight averaged molecular weight (M_w) and polydispersity (M_w/M_n) were determined from SCE traces using polystyrene standards. PHU films were fabricated by gradual drying of monomer solutions under ambient atmosphere using a Sanso Vacuum Drying Oven SVD10P (width, 20 cm; depth, 25 cm; height, 20 cm). TGA was carried out with a TG/DTA 6200 (Seiko Instrument Inc.) at a heating rate of 10 °C min^{-1} under nitrogen gas at a flow rate of 200 mL min^{-1}. UV/Vis.-NIR spectra were recorded on a Jasco V570 UV/VIS/NIR spectrophotometer equipped with Pbs power supply instruments. Stress-strain curves were measured with a Shimazu EZ Test EZ-LX with an operation rate of 50 mm min^{-1}. Young's modulus (E), stress at yield point ($σ_{yield}$), stress at break point ($σ_{break}$) and strain at break point ($ε_{break}$) of the films were analyzed with a TRAPEZIUM X software. The tensile tests were performed 1-3 times and then mechanical parameters were averaged.

3. Results and Discussion

3.1 Synthesis of bi- and Trifunctional 6-CCs Based on TMPC

The reaction of TMP and DPC gives mainly three types of different structured TMPCs (Matsukizono, 2016). These TMPCs can be to some extent individually produced by the modulation of synthetic conditions. Longer reaction time leads to the formation of TMPC-OCOPh and TMPC-dimer, while shorter reaction periods afford dominantly TMPC-OH. In this case, TMP was reacted with 4 equiv. of DPC at 140 °C for 1-2 days and consequently, TMPC-OH was obtained in 56.6 % yield after purification by column chromatography. The ^{1}H and ^{13}C NMR spectra of TMPC-OH are shown in Figure S1 in the appendix section.

The bifunctional TMP-based cyclic carbonate (Ph-TMPC$_2$) was synthesized by the simple reaction of TMPC-OH, terephthaloyl chloride and triethylamine in anhydrous THF. While the reaction proceeded, Ph-TMPC$_2$ and triethylamine hydrochloride precipitated. After washing with distilled water followed by methanol, white solids were isolated in 68.5% yield. The ^{1}H NMR spectrum of the solids is shown in Figure 1. The signal at 3.6 ppm assigned to methylene protons adjacent to a hydroxyl group completely disappears, while the singlet signal ascribed to methylene protons neighboring to an ester bond newly appears at 4.4 ppm. The singlet signal at 8.1 ppm originates from benzene protons, the integral ratio of which is ca. 4.0 and equals to the theoretical value. In addition, the ^{13}C NMR spectrum of the solids gives a signal at 165 ppm originating from ester carbons and signals at 133 and 130 ppm assigned to benzene carbons (Figure S2). FT-IR spectrum of the solids exhibits no absorption at around 3500 cm^{-1} based on hydroxyl groups, while the characteristic absorption of ester bonds appears at 1756 cm^{-1} (Figure S3). These results clearly indicate that Ph-TMPC$_2$ is obtained as white solids. Similarly, Ph-TMPC$_3$ was synthesized from TMPC-OH and trimesoyl chloride and isolated as white solids in 58.6% yield. The ^{1}H NMR

spectrum of Ph-TMPC$_3$ exhibits the signals assigned to the benzene protons at 8.81 ppm and methylene protons adjacent to ester bonds at 4.49 ppm (Figure 2). In FT-IR spectrum of Ph-TMPC$_3$, the streching vibration of hydroxyl groups disappears and ^{13}C NMR spectrum of Ph-TMPC$_3$ shows the signals assigned to carbonyl carbons of ester bonds and benzene carbons (Figure S3 and S4), indicating the formation and purification of Ph-TMPC$_3$.
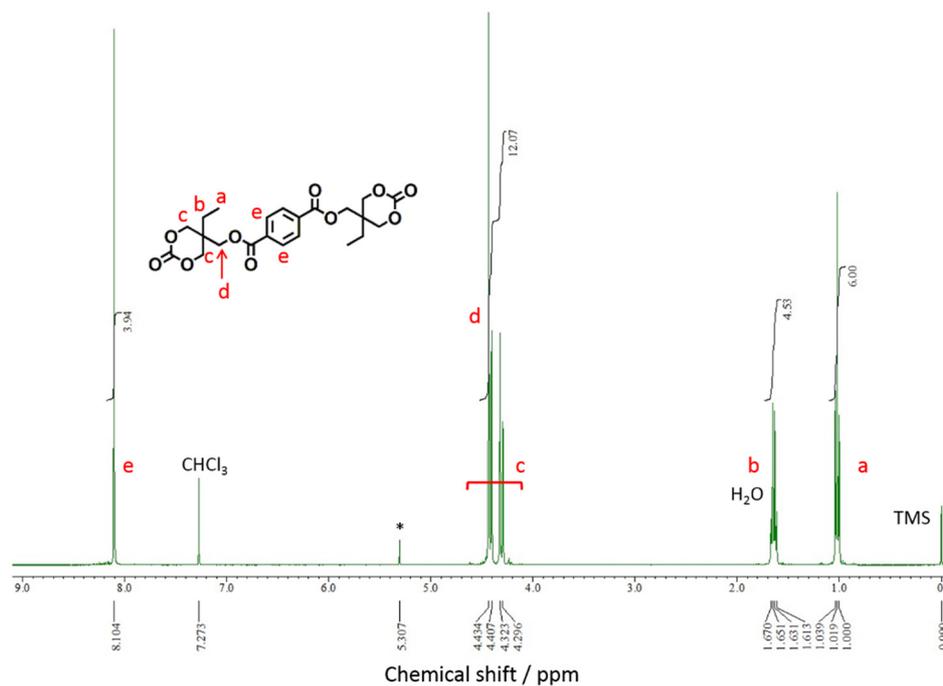

Figure 1. ^{1}H NMR spectrum of Ph-TMPC$_2$ in CDCl$_3$ containing 0.03 v/v% of TMS. An asterisk denotes residual CH$_2$Cl$_2$ used for purification
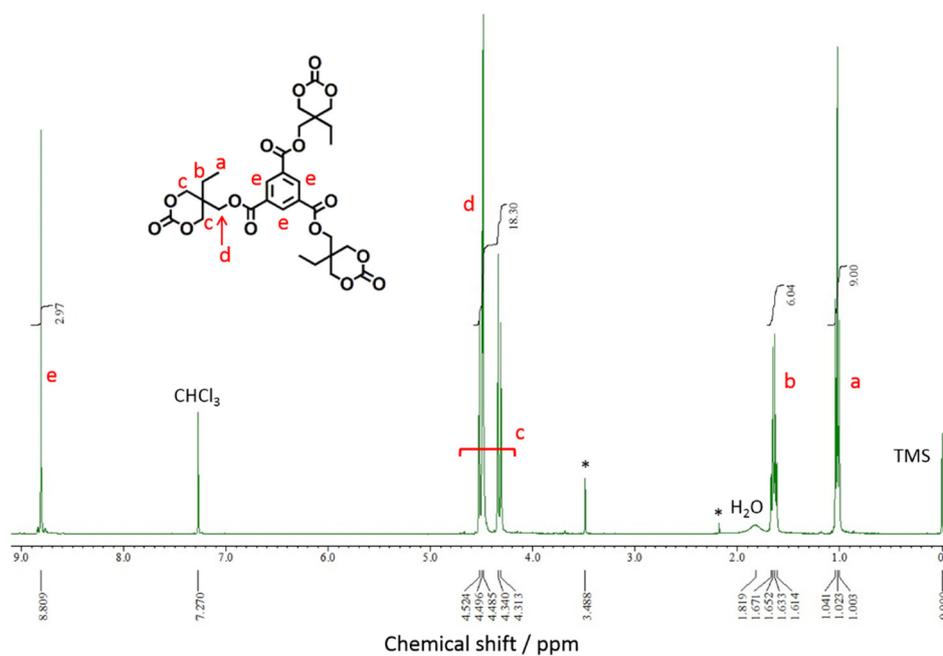
Figure 2. ^{1}H NMR spectrum of Ph-TMPC$_3$ in CDCl$_3$ containing 0.03 v/v% of TMS. Asterisks mean residual MeOH and acetone used for purification
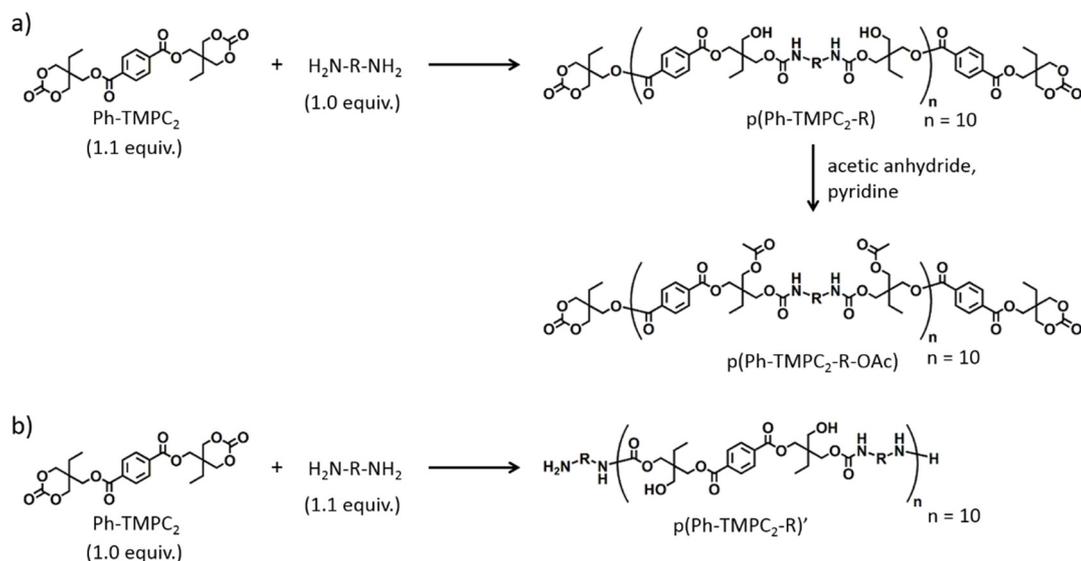
Scheme 4. Synthesis of PHUs with different terminal structures from Ph-TMPC$_2$ and diamine (R = C$_3$H$_6$, C$_6$H$_{12}$ or C$_{12}$H$_{24}$) at different Ph-TMPC$_2$/diamine feed ratios. a) PHUs with cyclic carbonate terminals (p(Ph-TMPC$_2$-R)) by the polyaddition of 1.1 equiv. of Ph-TMPC$_2$ and 1.0 equiv. of diamine and acetylated PHUs with same terminal structures (p(Ph-TMPC$_2$-R-OAc)) after acetylation. b) PHUs with amine terminals (p(Ph-TMPC$_2$-R)') by the polyaddition of 1.0 equiv. of Ph-TMPC$_2$ and 1.1 equiv. of diamine

3.2 Synthesis and Characterization of PHUs Synsized from Ph-TMPC$_2$ and Conventional diamines

Before the fabrication of networked PHUs, we investigated whether the ring-opening polyaddition of Ph-TMPC$_2$ and diamines proceeds to form linear PHUs with well-controlled structures or not. The reaction of Ph-TMPC$_2$ with an equivalent amount of diamine, in which Ph-TMPC$_2$/diamine feed ratio is 1.0, leads to the formation of long-chained PHUs, however, the chain ends of the PHUs are unclear. On the other hand, slight different Ph-TMPC$_2$/diamine feed ratios provide shorter-chained PHUs with cyclic carbonate or amine terminals (Scheme 4). In this paper, we preferred the synthesis of shorter-chained PHUs with well-controlled terminal structures to the formation of longer-chained PHUs.

At first, we carried out the polyaddition of 1.1 equiv. of Ph-TMPC$_2$ with 1.0 equiv. of C$_3$ in DMF at 70 °C for 1 day. The reaction mixture was analyzed by ^{1}H NMR spectroscopy and SEC measurements. The conversion of Ph-TMPC$_2$ was determined by the change in the integral ratio of signals at 4.4-4.3 ppm assigned to methylene protons adjacent to ester and carbonate bonds. In actual, the integral ratio is 1.62, which includes the integral ratio of a slightly excess amount (0.1 equiv.) of Ph-TMPC$_2$ as well as unreacted ones, and then the conversion of Ph-TMPC$_2$ is calculated to be 96.5%. After the reaction mixture was added in distilled water, the resulting precipitate was analyzed by ^{1}H NMR, FT-IR spectroscopy and SEC measurement. Figure 3 exhibits ^{1}H NMR spectrum of the precipitate. The signals at 4.4-4.3 ppm decrease and three signals at 4.1, 3.9 and 3.4 ppm newly appear. These signals are ascribed to methylene protons adjacent to ester, urethane and hydroxyl groups, respectively. In addition, the signals based on NH and OH bonds appear at 7.0-6.7 and 4.7 ppm, respectively. The conversion after purification is calculated to be 98.0%, which is slightly higher than that before purification. This is due to the purification treatment. On the other hand, M_n and M_w/M_n values of the precipitate calculated by its SEC trace are 4,400 g mol^{-1} and 2.11, respectively. These values are close to their theoretical ones (M_n = 4,100 g mol^{-1}, M_w/M_n = 2.00). These results apparently indicate that the reaction of Ph-TMPC$_2$ with C$_3$ proceeds efficiently to form PHUs with cyclic carbonate terminals without the cleavage of ester bonds. When the synthesis of PHUs from Ph-TMPC$_2$ and C$_3$ was performed at lower temperature, the PHUs with similar M_n and M_w/M_n values were obtained (data are not shown).
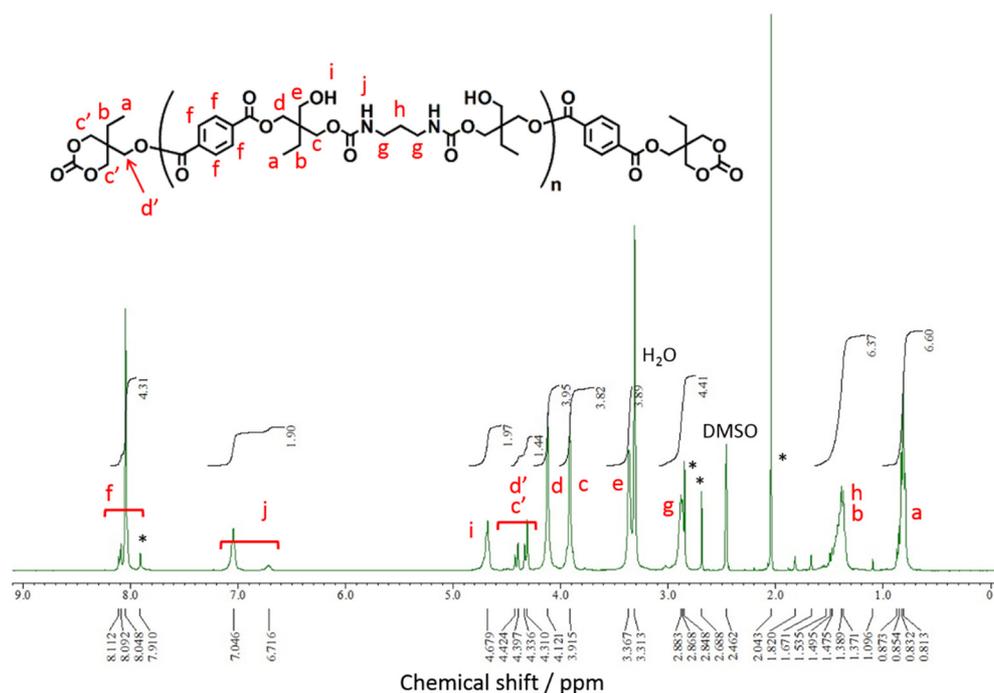
Figure 3. ^{1}H NMR spectrum of p(Ph-TMPC$_2$-C$_3$) in DMSO-d$_6$. Asterisks mean residual DMF and acetone

Table 1. Characterization of PHUs synthesized from Ph-TMPC$_2$ and diamines with different methylene spacers

Entry	PHUs	r [a]	Conv. / % [b]	$M_{n,theor}$ / g mol^{-1} [c]	M_n / g mol^{-1} [d]	M_w/M_n [d]
1	p(pH-TMPC$_2$-C$_3$)	1.1	98.0	4,100	4,400	2.11
2	p(pH-TMPC$_2$-C$_6$)	1.1	99.0	4,300	3,600	2.07
3	p(pH-TMPC$_2$-C$_{12}$)	1.1	97.6	4,700	5,000	2.13
4	p(pH-TMPC$_2$-C$_3$-OAc)	1.1	> 99.9	7,000	3,400	1.92
5	p(pH-TMPC$_2$-C$_3$)'	0.91	> 99.9	5,300	5,300	2.19

[a] Ph-TMPC$_2$/diamine feed ratio. [b] Reactivity of Ph-TMPC$_2$ calculated by ^{1}H NMR spectroscopy. [c] Determined using the conversion values. [d] Determined by SEC traces using polystyrene standards.

Similarly, using C$_6$ or C$_{12}$ instead of C$_3$, the synthesis of PHUs was conducted. The PHUs obtained were characterized by ^{1}H NMR, FT-IR spectroscopy and SEC measurements and the results are summarized in Entry 1-3 in Table 1. The ^{1}H NMR spectrum of these PHUs is similar to that of p(Ph-TMPC$_2$-C$_3$) (Figure S5 and S6). Conversion values are close to 100% and M_n and M_w/M_n values are well corresponded to those of theoretical values.

PHUs can be modified with various functional groups via their hydroxyl side chains. After PHUs are reacted with acetic anhydride, acetylated PHUs can be obtained. Actually, we performed the acetylation of p(Ph-TMPC$_2$-C$_3$) and acetylated PHU (p(Ph-TMPC$_2$-C$_3$-OAc)) was spectroscopically characterized. The ^{1}H NMR spectrum shown in Figure S7 reveals that the acetylation was adequately performed. On the other hand, M_n values determined by its SEC trace is lower than that theoretically calculated by its ^{1}H NMR spectrum (Entry 4 in Table 1), which would be caused by the potential difference of hydrodynamic radius from standard polystyrenes.

As shown in Scheme 4b, it is expected that the polyaddition of Ph-TMPC$_2$ and a slightly excess amount of diamine gives PHUs with amine terminals. We reacted 1.0 equiv. of Ph-TMPC$_2$ with 1.1 equiv. of C$_3$. The ^{1}H NMR spectrum of the resulting PHUs is shown in Figure S8. Differing from the spectrum of p(Ph-TMPC$_2$-C$_3$) (Figure 3), the spectrum exhibits no signals at ca. 4.4 ppm ascribed to cyclic carbonate terminals. The signal at 3.0-2.5 ppm derived from amine terminals is unclear because of the overlapping with other signals, however, its M_n and M_w/M_n

values are close to theoretical values (Entry 5 in Table 1). These results apparently suggest that PHUs with different terminal structures are individually synthesized depending on the changes in Ph-TMPC$_2$/diamine feed ratios.

3.3 Fabrication of Networked PHU Films

To examine the formative ability of networked structures, we at first reacted Ph-TMPC$_3$ with C$_3$ in DMF at 70 °C. The reaction mixture (TMPC/NH$_2$ = 1.0) immediately changed to viscous solution and finally formed gels within 1 h. This behavior apparently indicates the formation of networked structures. Next, the DMF solutions of Ph-TMPC$_2$/Ph-TMPC$_3$/C$_3$, in which mole ratios of Ph-TMPC$_3$ were 5-20 mol% with respect to total carbonate monomer and the TMPC/NH$_2$ ratio was 1.0, were kept in glass petri-dishes at 70 °C overnight. During this treatment, DMF was slowly evaporated and concomitantly the reaction of Ph-TMPC$_2$/Ph-TMPC$_3$ with C$_3$ proceeded to form networked PHU films (Film A) in one-step. These films were quite stable and able to detach from the dishes. These films gave stretching vibrations assigned to carbonyl groups of urethane bonds at ca. 1650 cm^{-1} (data are not shown), indicating the formation of hydroxyurethane linkages. The photographs of these films are shown in Figure 4. All films are well transparent and flexible. Similarly, Film B and Film C, which were prepared using 20 mol% Ph-TMPC$_3$ with C$_6$ or C$_{12}$, respectively, are well transparent and flexible (Figure 5e,f). UV/Vis-NIR absorption spectra of Film A-C are shown in Figure 5. These films show more than 80% transmittance in 440-1600 nm. The Film A prepared at different amounts of Ph-TMPC$_3$ also show same absorption spectra (Figure S9).
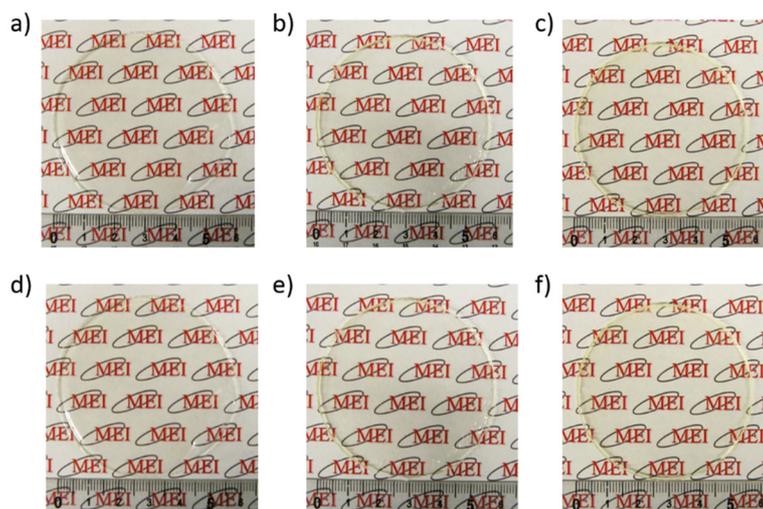

Figure 4. a-d) Photographs of Film A prepared from Ph-TMPC$_2$/Ph-TMPC$_3$/C$_3$. The mole ratios of Ph-TMPC$_3$ are a) 5, b) 10, c) 15 or d) 20 mol% with respect to total carbonate monomers (Ph-TMPC$_2$ + Ph-TMPC$_3$). e) Film B prepared using 20 mol% Ph-TMPC$_3$ and C$_6$. f) Film C prepared using 20 mol% Ph-TMPC$_3$ and C$_{12}$

TGA profiles of these films are shown in Figure 6. For Film A, a slight weight loss occurred at 100-200, which would be caused by the removal of adsorbed water molecules. After that, weights abruptly decreased at 250-300 °C and then the film was completely decomposed at 300-520 °C. Since urethane bonds of polyurethane are decomposed at 300-500 °C (Nayak, 1997), the weight loss at 250-300 °C would be caused by the decomposition of diamine moieties. On the other hand, Film B and Film C gave gradual weight loss at 300-500 °C and showed the slightly higher thermal stability compared to Film A. This could be due to the stronger Van der Waals interactions among longer methylene spacers of diamines. TGA profiles of Film A prepared at different amounts of Ph-TMPC$_3$ are also shown in Figure S10. Without depending on the amounts of Ph-TMPC$_3$, the same thermal decomposition behavior was observed. Since even networked PHUs prepared using 100 mol% Ph-TMPC$_3$ gave the similar TGA profile (data are not shown), the density and amount of cross-linked structures do not seem to affect the thermal properties.
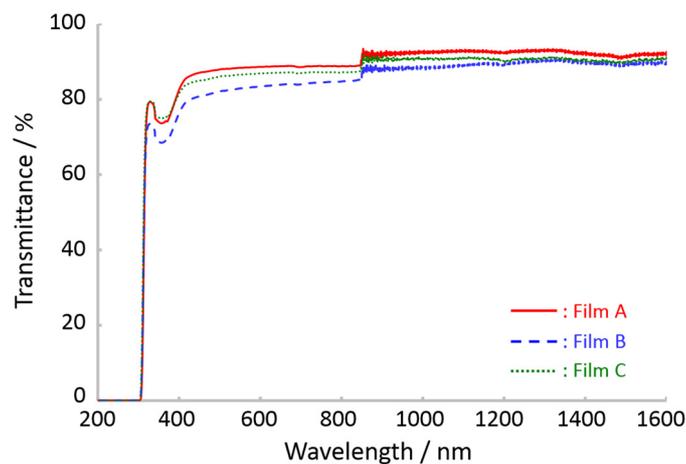
Figure 5 UV/Vis.-NIR absorption spectra of networked PHU films prepared from 20 mol% Ph-TMPC$_3$ and different diamines. Red solid line: Film A. Blue dashed line: Film B. Green dotted line: Film C
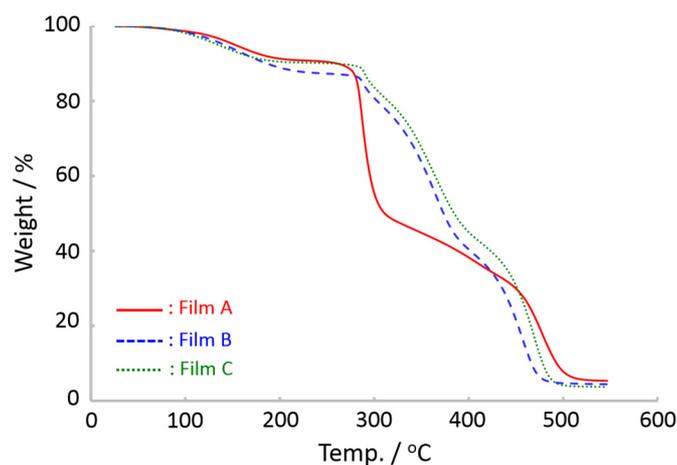

Figure 6 TGA profiles of networked PHU films prepared using 20 mol% Ph-TMPC$_3$ and different diamines. Red solid line: Film A. Blue dashed line: Film B. Green dotted line: Film C

These networked PHU films were investigated for their mechanical properties by tensile test. Representative stress-strain curves of these films are shown in Figure 7 and averaged mechanical parameters obtained from the curves are summarized in Table 2. Although these films showed similar transparency and thermal properties, their mechanical properties were quite different. Film A gave the yield point at 42.4 MPa and then broken at an elongation of 50.1%. Film A prepared using different amounts of Ph-TMPC$_3$ showed similar curves (data are not shown). On the other hands, Film B and Film C elongated gradually without showing yield points and finally broken at longer than ca. 290% elongation points. From these results, it is apparent that mechanical properties of networked PHU films can be regulated by tuning the structures of diamines.

Table 2. Averaged mechanical parameters determined from Stress-strain curves of networked PHU films prepared using 20 mol% Ph-TMPC$_3$ and different diamines.

| Entry	Diamine	E / MPa	σ_{yild} / MPa	σ_{break} / MPa	ε_{break} / %
Film A	C$_3$	7.1	42.4	24.3	50.1
Film B	C$_6$	0.38	-	8.6	296
Film C	C$_{12}$	0.70	-	11.0	402
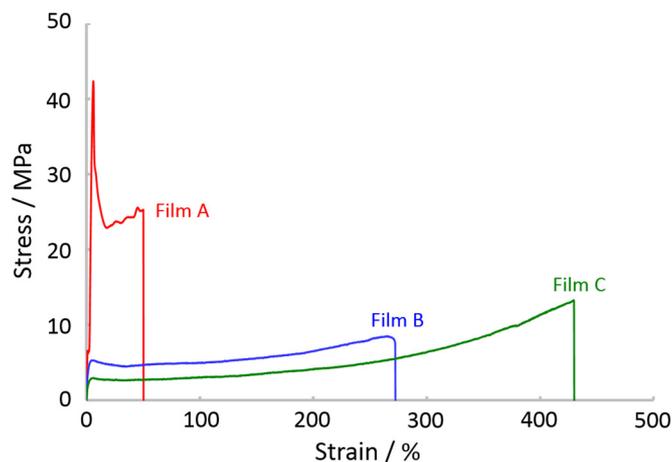
Figure 7 Representative stress-strain curves of networked PHU films prepared using 20 mol% Ph-TMPC$_3$ and different diamines. Red line: Film A. Blue line: Film B. Green line: Film C

4. Conclusions

In this paper, we have described the followings: i) the synthesis of bi- and trifunctional TMP-based cyclic carbonates (Ph-TMPC$_2$ or Ph-TMPC$_3$) from TMPC-OH and the corresponding acyl chlorides, ii) the synthesis of linear PHUs by the ring-opening polyaddition of Ph-TMPC$_2$ and conventional diamines, iii) the fabrication of networked PHU materials by the copolymerization of Ph-TMPC$_2$, Ph-TMPC$_3$ and diamines. The reaction of TMP and 4 equiv. of DPC at 140 °C for 1-2 days gives mainly TMPC-OH and the reaction of TMPC-OH and terephthaloyl chloride or trimesoyl chloride affords Ph-TMPC$_2$ or Ph-TMPC$_3$, respectively. Ring-opening polyaddition of Ph-TMPC$_2$ and conventional diamines effectively proceeded without the cleavage of ester bonds to give PHUs with well-controlled molecular weights and polydispersities. By changing the Ph-TMPC$_2$/diamine feed ratios, we could obtain PHUs with different terminal structures. The copolymerization of Ph-TMPC$_2$, small amounts of Ph-TMPC$_3$ and diamines forms effectively covalently-crosslinked structures and then networked PHU films are readily fabricated. The resulting films showed similar transparency and thermal stability, while the mechanical properties were significantly affected by the methylene spacers of diamines.

In our approach, PHUs are derived from non-expensive reagents via non-phosgene derivatives and non-isocyanate routes in whole processes. Networked PHUs are simply obtainable by copolymerization of bi- and trifunctional cyclic carbonates and diamines in one step without further chemical modification of hydroxyl side chines. Our approach will be one of the fundamental for designing PHU-based networked films.

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Appendix
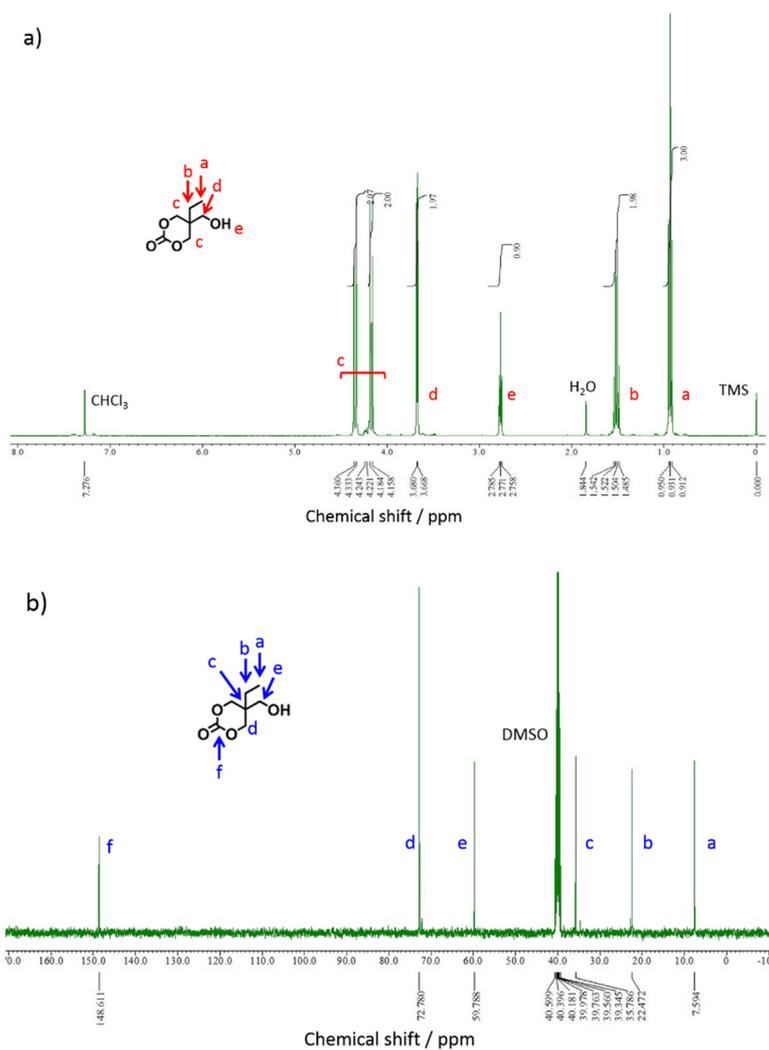
Figure S1. NMR spectra of TMPC-OH after purification by column chromatography. a) ^{1}H NMR spectrum in CDCl$_3$ with 0.03 v/v% of TMS. b) ^{13}C NMR spectrum in DMSO-d$_6$
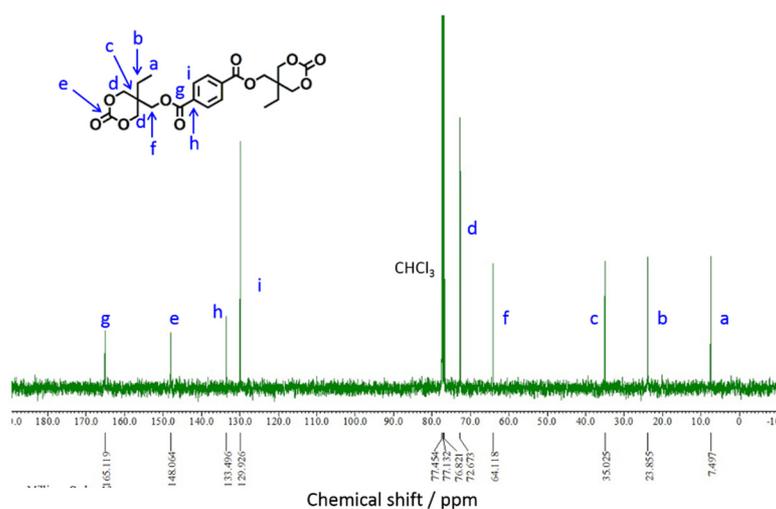

Figure S2. ^{13}C NMR spectrum of Ph-TMPC$_2$ in CDCl$_3$ containing 0.03 v/v% of TMS.
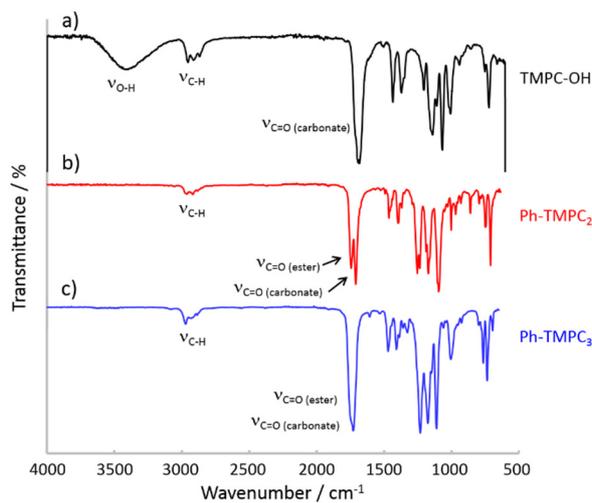
Figure S3. FT-IR spectra of a) TMPC-OH, b) Ph-TMPC$_2$ and c) Ph-TMPC$_3$.
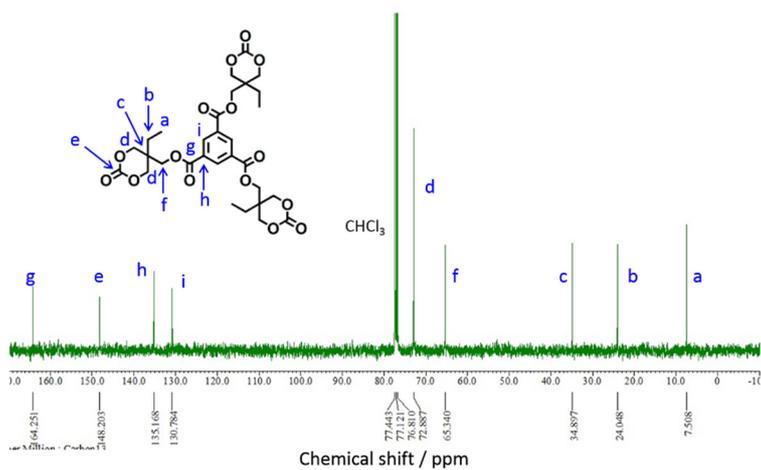
Figure S4. ^{13}C NMR spectrum of Ph-TMPC$_3$ in CDCl$_3$ containing 0.03 v/v% of TMS.
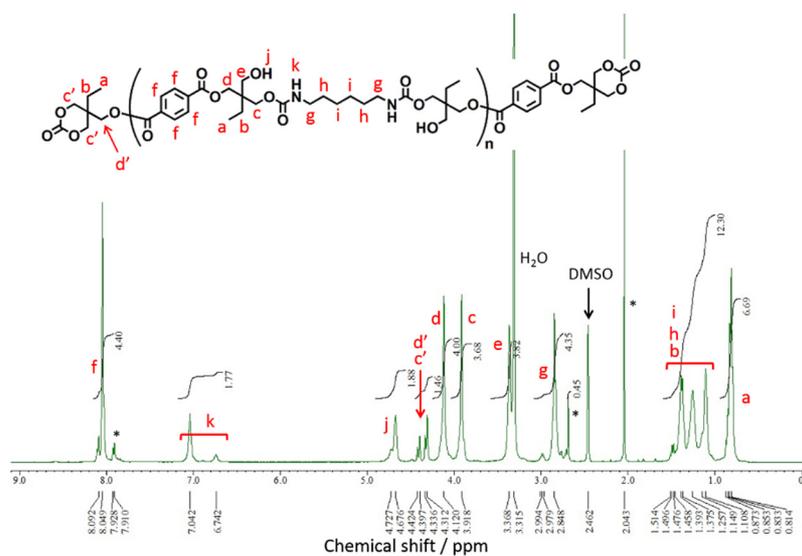
Figure S5. ^{1}H NMR spectrum of p(Ph-TMPC$_2$-C$_6$) in DMSO-d$_6$. Asterisks mean residual solvents (DMF and acetone)
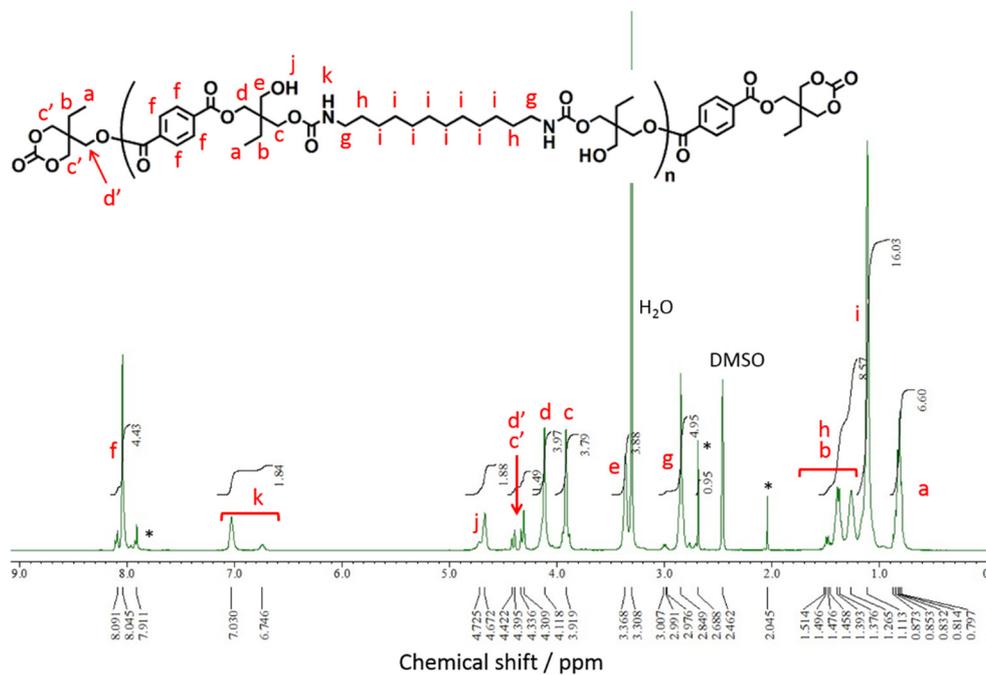
Figure S6. ^{1}H NMR spectrum of p(Ph-TMPC$_2$-C$_{12}$) in DMSO-d$_6$. Asterisks mean residual solvents (DMF and acetone).
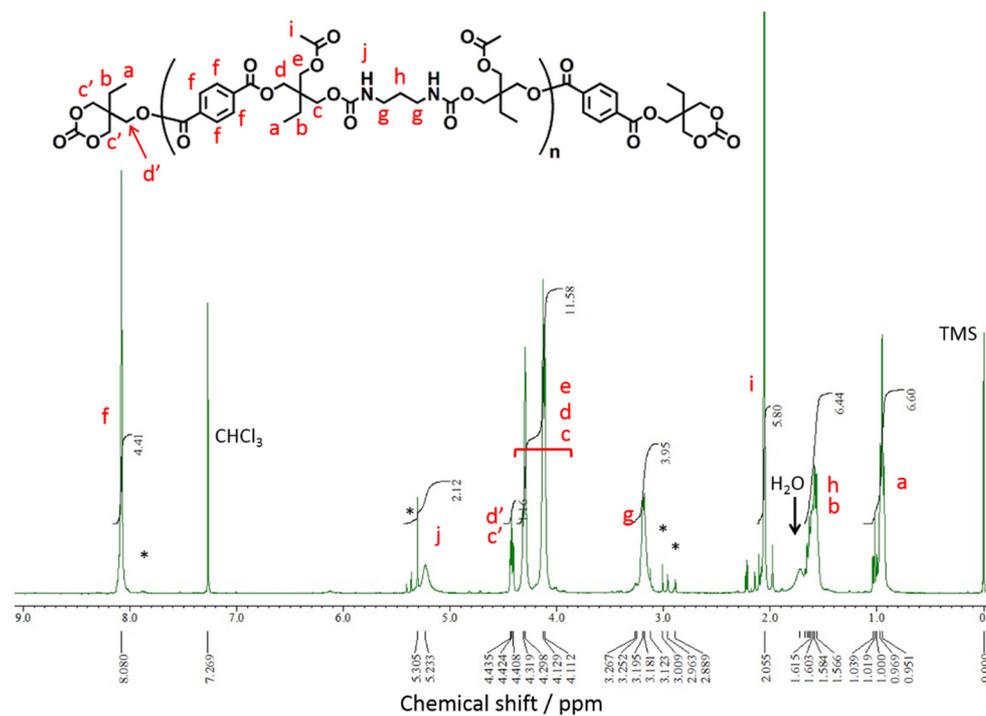
Figure S7. ^{1}H NMR spectrum of p(Ph-TMPC$_2$-C$_3$-OAc) in CDCl$_3$ containing 0.03 v/v% of TMS. Asterisks denote residual solvents (CH$_2$Cl$_2$ and DMF).
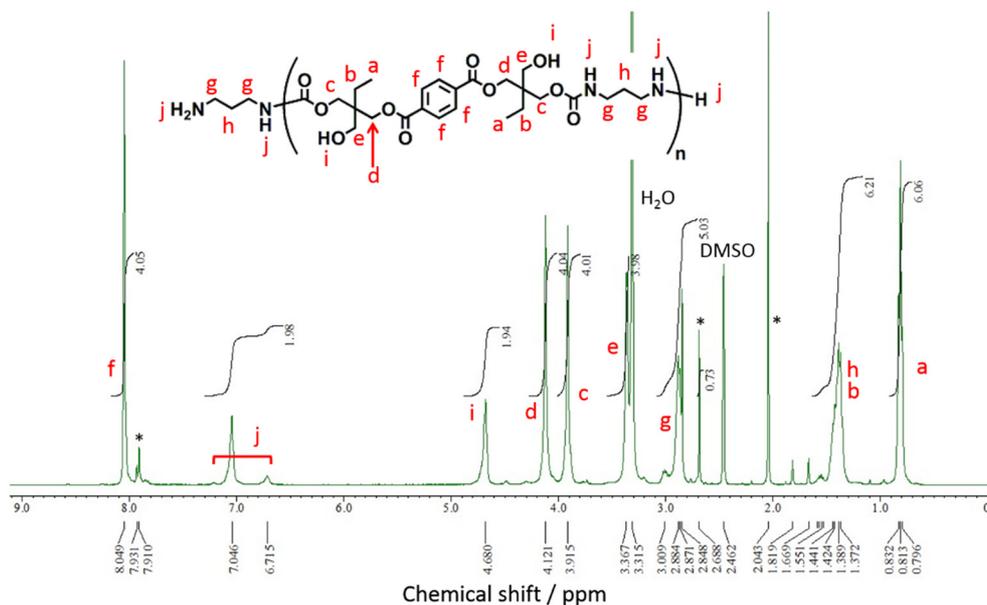
Figure S8. ^{1}H NMR spectrum of p(Ph-TMPC$_2$-C$_3$)' in DMSO-d$_6$. Asterisks denote residual solvents (DMF and acetone)
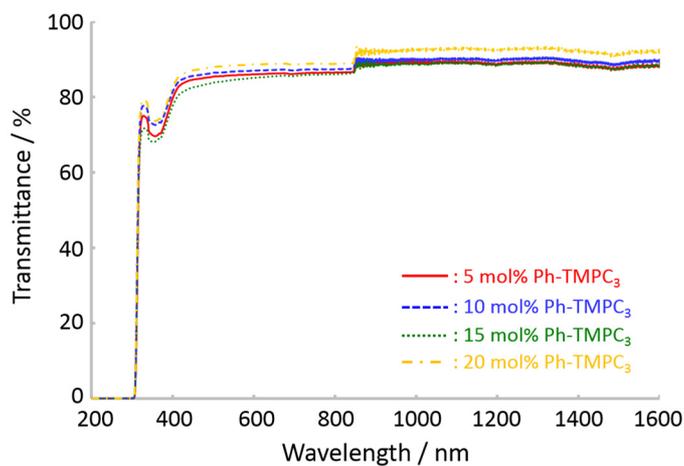

Figure S9. UV/Vis.-NIR absorption spectra of Film A prepared at different Ph-TMPC$_2$/Ph-TMPC$_3$/C$_3$ feed ratios. The mole ratios of Ph-TMPC$_3$ are 5 (red solid line), 10 (blue dashed line), 15 (green dotted line) or 20 mol% (orange dashed and dotted line) with respect to total carbonate monomers (Ph-TMPC$_2$ + Ph-TMPC$_3$)
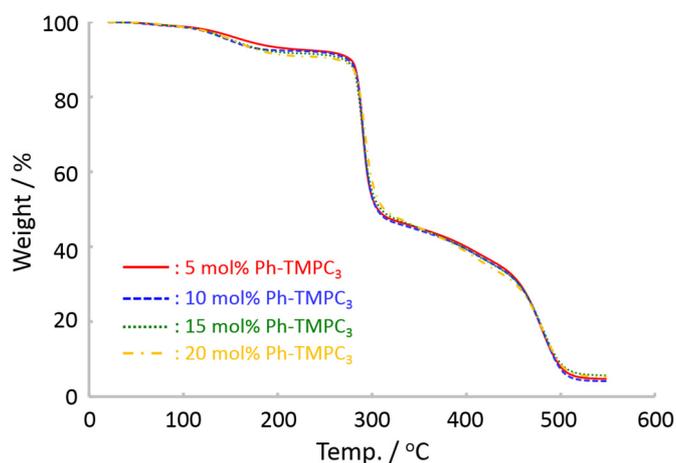
Figure S10. TGA profiles of Film A prepared at different Ph-TMPC$_2$/Ph-TMPC$_3$/C$_3$ feed ratios. The mole ratios of Ph-TMPC$_3$ are 5 (red solid line), 10 (blue dashed line), 15 (green dotted line) or 20 mol% (orange dashed and dotted line) with respect to total carbonate monomers (Ph-TMPC$_2$ + Ph-TMPC$_3$).

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