

# Communication

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# Re-workable Polyhydroxyurethane Films with Reversible Acetal Networks Obtained from Multi-functional Six-membered Cyclic Carbonates

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Supporting Information Placeholder

**ABSTRACT:** Multi-functional 6-membered cyclic carbonates (6-CCs) comprising acetal structures have been synthesized via phosgene-free routes and utilized for the fabrication of reworkable networked poly(acetal-hydroxyurethane) (PAHU) films. Dibenzoyl-protected di(trimethylolpropane) (DTMP) reacts with multi-functional aldehydes derived from non-expensive alcohols to afford protected multi-functional DTMPs. After deprotection, the multi-functional DTMPs can react with diphenyl carbonate to efficiently form multi-functional 6-CCs. The polyaddition of the 6-CCs and diamines effectively proceeds in DMF to give networked PAHU films with good transparency and flexibility. These films possess the re-workability based on acid-catalyzed reversibility of acetal linkages. In particular, the film fabricated using large amounts of hexa-functional 6-CCs can re-form reproducibly with maintaining to some degree its mechanical properties.

Poly(hydroxyurethane)s (PHUs) have been attracting huge attentions as the promising alternatives of widely-used polyurethanes because PHUs can be synthesized by the ring-opening polyaddition of di-functional cyclic carbonates and diamines without using toxic isocyanates.<sup>1-5</sup> PHUs reported are basically synthesized from 5-membered cyclic carbonates (5-CCs) because 5-CCs can be derived from epoxides and CO<sub>2</sub> under environmentally benign conditions.<sup>1-4</sup> Furthermore, various epoxides including multi-functional structures are commercially available.<sup>1-4</sup> Using these epoxides, multi-functional 5-CCs have been designed and used to build networked PHU materials.<sup>1a,4</sup> On the other hand, PHUs from 6-membered cyclic carbonates (6-CCs) are not reported much.<sup>1a,6</sup> Although 6-CCs are highly reactive,<sup>5,8</sup> they are basically synthesized from the corresponding 1,3-diols using toxic phosgene or its derivatives except a few cases.<sup>1a,5</sup> Moreover, commercially-obtainable 1,3-diols are structurally limited. In particular, multi-functional 6-CCs requires special designs and multi-step synthetic procedures.<sup>7</sup> These problems hinder the practical usage of 6-CCs and their application to PHU-based materials

We have previously reported that trimethylolpropane (TMP) and di(trimethylolpropane) (DTMP) efficiently react with diphenyl carbonate (DPC) to afford the corresponding 6-CCs in good yields.<sup>8</sup> DPC can be synthesized without phosgene and its derivatives<sup>9</sup> and thus, the synthesis of 6-CCs using DPC is one of phosgene-free routes. The excellent formative ability of these alcohols to 6-CCs helps us to design the unique strategy in synthesizing Scheme 1. a) Synthesis of Tri-functional 6-CC (Tri-DTMPC) via phosgene-free routes. b) Chemical structures of tetra- and hexa-functional 6-CCs (Tetra-DTMPC and Hexa-DTMPC).



i) DPC, 140°C, 2 d. ii) Benzaldehyde/TsOH/MeOH, 50°C, overnight. iii) DPC/MgCl<sub>2</sub>/DMF, 100°C, overnight. iv) BzCl/pyridine/CH<sub>2</sub>Cl<sub>2</sub>, 0°C to r.t., overnight. v) Neopentylgly-col/TsOH/MeOH, 50°C, overnight. vi) TsCl/pyridine, 0°C to r.t., 2 d. vii) Vanillin/K<sub>2</sub>CO<sub>3</sub>/DMF, 100°C, 3 d. viii) TsOH/CH<sub>2</sub>Cl<sub>2</sub>, 40 °C, 2 d. ix) NaOH/THF/MeOH. r.t., overnight.

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## Scheme 2. Synthesis of networked PAHUs by the ringopening polyaddition of multi-functional 6-CCs and DAP.



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multi-functional 6-CCs. Based on this concept, we designed the synthetic route to multi-functional DTMP-based 6-CCs via the acetal linkages (Scheme 1). Using these 6-CCs bearing acetal structures and diamines. networked poly(acetalhydroxyurethane)s (PAHUs) comprising acetal and hydroxyurethane structures are obtainable (Scheme 2). Generally, acetal bonds are reversible under acidic conditions with H<sub>2</sub>O and/or alcohols<sup>10</sup> and, therefore, there are many efforts to develop acetalbased functional polymers such as chemical recyclable materials<sup>11</sup> and pH-responsive drug/gene-delivery carriers<sup>10,12</sup>. In our system, the acetal-incorporated networks potentially show reversible crosslinking/de-crosslinking functions based on acetal linkages, i.e., PAHU materials expect to show re-workable properties. Here we report the phosgene-free synthesis of multi-functional DTMPbased 6-CCs from commercially-available polyols and the fabrication of re-workable networked PAHU films.

Multi-functional 6-CCs were synthesized according to the route shown in Scheme 1a. Details are summarized in Figure S1-25 and Table S1. Our strategy utilizes the acetal formations between 1,3diols of DTMP and multi-functional aldehvdes to build multifunctional polyols. During this reaction, to avoid the generation of undesired polyacetals, the protection of one 1,3-diol of DTMP is required. Besides, relatively-stable 6-membered cyclic acetals formed from 1,3-diols and aromatic aldehydes are favorable to construct re-workable PAHU networks. From these needs, we synthesized benzoyl (Bz) protected-DTMP (DTMP-Bz<sub>2</sub>) and multi-functional aldehydes (Tri-Van) derived from vanillin and  $TMP^{13}$ . After that, three **DTMP-Bz**<sub>2</sub> arms were introduced into **Tri-Van** core<sup>14</sup> and then a tri-functional polyol (**Tri-DTMP**) was obtained by de-protection. The model reaction of mono-functional **Ph-DTMP** and DPC with MgCl<sub>2</sub> proceeded without the cleavage of acetal structures and consequently, Ph-DTMPC was obtained in high yields (Figures S3 and S4), which suggests that multifunctional 6-CCs are also obtainable by the same procedure. Actually, the MALDI-TOF-mass spectrum of the product from the reaction of Tri-DTMP shows one major peak at m/z of 1,334 (Figure 1a). This value equals to  $M_w$  of **Tri-DTMPC** with Na<sup>+</sup> (1,312+23), indicating that **Tri-DTMPC** is successfully synthesized. Similarly, Tetra-DTMP and Hexa-DTMP were synthesized from DTMP and dipentaerythritol (DPE), respectively and then reacted with DPC. These products also show the peaks which equals to M<sub>w</sub> of the corresponding target structures (Figure 1b, c). Apart from these major peaks, minor peaks are confirmed, which are mainly assigned to multi-functional 6-CCs having less number of DTMPC arms and those bearing acvelic carbonate structures (Figure S22). Although these products contain the by-products, the amounts of acetal structures and bis(phenoxycarbonyl) groups originating from these impurities are extremely lower than those of target structures (Table S1). Hence, we can conclude that the multi-functional 6-CCs can be efficiently synthesized by our approach.

Next, we reacted these 6-CCs with 1,3-diaminopropane (DAP) to fabricate networked PAHU films. As shown in Figure 2a, DMF solutions of **Hexa-DTMPC** and **DTMPC** were mixed with the DMF solution of DAP and then the mixtures (5-20 mol%)



**Figure 1**. MALDI-TOF-mass spectra of multi-functional 6-CCs. a) **Tri-DTMPC**. b) **Tetra-DTMPC**. c) **Hexa-DTMPC**.



Figure 2. a) Fabrication of networked PAHU films (PAHU-Hexa-n) from Hexa-DTMPC, DTMPC and DAP. Mole fractions of Hexa-DTMPC per total carbonate monomer (Hexa-DTMPC + DTMPC) were 5 (n = 5), 10 (n = 10), 15 (n = 15), or 20 mol% (n = 20). b) Representative S-S curves of PAHU-Hexa-15, PAHU-Tetra-15 and PAHU-Tri-15. c) Effect of monomer feed ratios on averaged tensile strength (bars, left axis) or averaged elongation (plots, right axis) at fracture points of networked PAHU films. Top: PAHU-Hexa-n. Middle: PAHU-Tetra-n. Bottom: PAHU-Tri-n. Error bars denote standard deviations.

**Hexa-DTMPC**,  $[6-CC]_0/[NH_2]_0 = 1/1$ ) were heated at 60°C overnight. During this treatment, the polyaddition effectively proceeded to form networked PAHU films (**PAHU-Hexa-n**, n denotes the feed ratio of multi-functional 6-CCs used). Hydroxyurethane structures in these films are confirmed by the appearance of stretching vibrations ascribed to OH groups and by the slight shift of stretching vibrations originating from carbonyl groups (Figure S26).<sup>4</sup> Similarly, **PAHU-Tetra-n** and **PAHU-Tri-n** were successfully obtained from **Tetra-DTMPC** and **Tri-DTMPC**, respectively. All the resulting films are transparent and flexible (Figure S27) at 0.084-0.168 mm thickness and exhibit the similar FT-IR spectra 1

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(Figure S28). Although the remaining monomer terminals cannot be detected in their FT-IR spectra, unreacted 6-CC structures and amino groups in **PAHU-Hexa-20** are calculated to be ca. 22 mol%, which are described later. Furthermore, these films swelled well in MeOH and DMF. In particular, **PAHU-Tri-5** showed higher swelling properties (Figure S29). The weight of these films decreased by ca. 15% after the immersion in these solvents and oligomeric PHUs mainly composed of **DTMP** and DAP were collected from the supernatant.

Representative stress-strain (S-S) curves of these PAHU films are shown in Figure 2b. The tensile strength of PAHU-Hexa-15 linearly increased at < ca. 1.5% elongation and then nonlinearly increased and the film was finally broken at ca. 140% elongation. Its averaged tensile strength at the fracture point ( $\sigma_f$ ) was 26.4 MPa and higher than that of other two films. On the other hand, an averaged tensile strength at the fracture point ( $\varepsilon_{\rm f}$ ) of **PAHU**-Hexa-15 was the lowest and PAHU-Tri-15 showed the highest  $\varepsilon_{f}$ . These results suggest that more rigid but fragile films tend to form with increasing the number of DTMPC arms of multi-functional 6-CCs. This tendency is adequately rational because multifunctional 6-CCs bearing greater numbers of monomer units tend to afford polymer networks at higher densities. S-S curves of the other films were measured (Figure S30-32) and their  $\sigma_f$  and  $\varepsilon_f$  are summarized in Figure 2c. For all films,  $\sigma_f$  increased when the molar fraction of multi-functional 6-CCs increased from 5 to 15 mol%. On the other hand,  $\varepsilon_f$  tended to decrease in this range. However,  $\sigma_f$  decreased or remained unchanged with an increase in the molar fraction of multi-functional 6-CCs to 20 mol%. This would be due to that excessive amounts of multi-functional 6-CCs sterically hinder the proceeding of the polyaddition and the formation of polymer networks.

Finally, we describe the re-workable properties of these films. As these films involve reversible acetal bonds, it is expected that these films can be dissolved in solvents containing acids and H<sub>2</sub>O and then can be re-formed by the elimination of H<sub>2</sub>O (Figure 3a). As a preliminary study, we synthesized a linear PAHU (LPAHU) and investigated its reversible fragmentation/extension behavior (Scheme S1 and Figure S33-39). After LPAHU was heated in DMF containing TsOH monohydrate at 60°C, its  $M_n$  decreased dramatically from 9,300 to 1,600 g mol<sup>-1</sup> (Figure S38). In its <sup>1</sup>H NMR spectrum, the signal of acetal proton at 5.3 ppm apparently decreased to ca. 60%, while the signal of aldehyde proton newly appeared at 9.8 ppm (Figure S39). These result obviously indicate the fragmentation of LPAHU chains via the formation of aldehydes. After all solvents (H<sub>2</sub>O and DMF) were removed at 60 °C under reduced pressure, the signal of acetal proton adequately recovered and its SEC trace gave a peak based on higher molecular mass structures with a relatively-narrow polydispersity ( $M_{\rm n}$  = 4,600 g mol<sup>-1</sup>,  $M_w/M_n = 2.86$ ). These results indicate that the fragmented LPAHU chains are partially extended by acetal formations between their aldehyde and 1,3-diol chain ends.

Similar to LPAHU, networked PAHU films were examined for their crosslinking/de-crosslinking properties. These films were dissolved to afford pale yellow solutions (Figure 3b) by heating in DMF containing TsOH monohydrate (0.2-0.4 equiv. per acetal structure). Because these films were insoluble in DMF without acids, this solubilization clearly indicates the partial cleavage of PAHU networks. The <sup>1</sup>H NMR spectrum of dissolved PAHU-Hexa-20 reveals that ca. 60% acetal bonds converted to aldehydes (Figure S40). After the elimination of the solvents, PAHU-Hexa-20 was again obtained as a transparent and flexible film (Figure 3b). This result suggests the crosslinking of partially-cleaved networks caused by the elimination of H<sub>2</sub>O. Unfortunately, selfstanding films were not reproducibly obtained for other films, which implies that larger amounts of acetal linkages would need



**Figure 3**. a) Schematic illustration of crosslinking/de-crosslinking functions of **PAHU-Hexa-n** under acidic conditions. b) Photographs of **PAHU-Hexa-20**. The film was dissolved in DMF containing TsOH monohydrate by heating to afford a pale yellow solution. After solvents were removed, a transparent and flexible film formed again. c) Changes in  $\sigma_f$  and  $\epsilon_f$  obtained from S-S curves of re-formed **PAHU-Hexa-20**. Cycle represents the repetition number of re-formation processes.

to form re-workable films. By the solubilization of these films, we can obtain detailed information about their networked structures. As mentioned above, the remaining amino groups in PAHU-Hexa-20 are determined to be approximate 20% (Table S2). Since these amino groups trap acids, the cleavage of networked structures needed slightly larger amounts of TsOH at the following decrosslinking treatment (0.4 equiv. per acetal structure). The reworkable treatment was carried out 10 times and each re-formed film was analyzed for its mechanical properties by tensile tests (Figure S41). The  $\sigma_f$  and  $\varepsilon_f$  of each re-formed film are plotted in Figure 3c. After the 1st re-formation process, its  $\sigma_f$  decreased, while its  $\varepsilon_f$  marginally decreased. This change suggests that the film became more flexible by the decrease in the amount of crosslinking points. After that, its  $\sigma_f$  and  $\varepsilon_f$  varied at the range at 6.0-21.5 MPa and 74-143%, respectively. There are no relationship and tendency between its mechanical properties and the repetition number of the re-formation process. Because acetal-based networks are strongly affected by coexisting H<sub>2</sub>O, we consider that the changes in its mechanical properties would be caused by the humidity. The averaged  $\sigma_f$  and  $\varepsilon_f$  of the film during 1st-10th reformation processes are 13.0 MPa and 112%, respectively. Compared to the non-re-formed film, the decreases in its  $\sigma_f$  and  $\varepsilon_f$  are only 3 and 33%, respectively. Therefore, we conclude that the film maintains to some extent mechanical properties after the repetitive re-formation process and has a potential to be applied to a re-workable film.

In this paper, we designed multi-functional DTMP-based 6-CCs bearing acetal structures from non-expensive materials and used them for the fabrication of re-workable networked PAHU films. Our strategy utilizing acetal linkages makes it possible to extend the variation of the design of 6-CCs via phosgene-free conditions. In addition, the resulting acetal linkages are stable in basic condition and therefore, PHUs can be obtained without the cleavage of acetal bonds. Furthermore, these acetal linkages can serve as reversible crosslinking points under acidic conditions, which affords re-workable properties. Although remendable PHU materials utilizing Diels-Alder reactions have been reported<sup>4d</sup>, our films need catalytic amounts of acids, water and thermal energy, i.e., our system does not work by a simple addition of thermal energy and is applicable under higher temperature conditions. To our best knowledge, our study is the first report discussing networked PHU materials comprising acetal linkages and their reworkable feature based on their acetal linkages. Our approach will be one of the fundamental for designing multi-functional 6-CCs under phosgene-free conditions and for fabricating re-workable networked PHU materials.

## ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website:. Experimental details including spectroscopic data, characterization of polymers and networked films: photographs, spectroscopic measurements, swelling properties and tensile tests (PDF)

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#### Notes

The authors declare no competing financial interests.

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| Polyaddtion<br>Polyaddtion<br>Polyaddtion<br>Polyaddtion<br>Polyaddtion<br>Polyaddtion<br>Crosslinking<br>Crosslinking<br>Re-workable Networked poly(acetal-hydroxyurethane) film |
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