

# CO<sub>2</sub>-blown Non-isocyanate Polyurethane Foams

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**ABSTRACT:** Polyurethane (PU) foams are produced from toxic, petrochemical- and phosgene-derived isocyanates. Although non-isocyanate polyurethane (NIPU) has shown promise as a replacement for traditional PU, the synthesis of NIPU foams has not been widely studied due to the difficulties in replicating the foaming process of PU – in-situ CO<sub>2</sub> production through the hydrolysis of isocyanates. Hereby, we report the synthesis of amine-CO<sub>2</sub> adducts and their CO<sub>2</sub> adsorption/desorption characteristics under different conditions. The results show that the amine-CO<sub>2</sub> adducts can exhibit up to 87% of CO<sub>2</sub> desorption at 60 °C after aminolysis with cyclic carbonate. The amine-CO<sub>2</sub> adduct is used as both foaming agent and co-monomer to obtain low-density foams (0.203 – 0.239 g.cm<sup>-3</sup>) after heating at 50 – 60 °C for 24 – 48 hrs. This marks the successful synthesis of in-situ CO<sub>2</sub>-blown NIPU foams using amine-CO<sub>2</sub> adduct.

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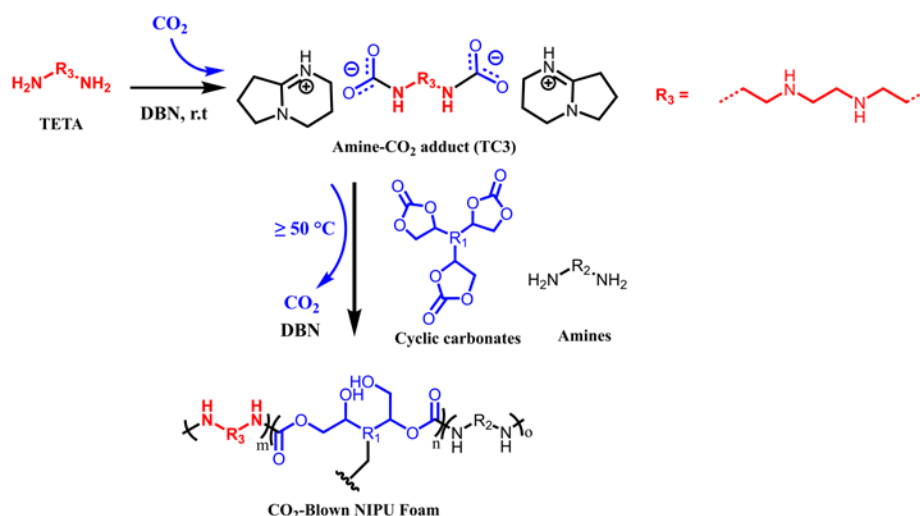
Polyurethane (PU) is widely used in many industries due to its unique mechanical and chemical properties.<sup>1</sup> The largest growth driver in PU market is the molded, rigid, and flexible foams that are used as cushioning and insulation materials.<sup>2</sup> Conventional PU foams are derived from polyols and polyisocyanates, and a simultaneous foaming with in-situ carbon dioxide (CO<sub>2</sub>) generated from hydrolysis of isocyanates.<sup>1</sup> Despite being a versatile foaming method, the use of toxic isocyanate is deemed non-environmentally friendly and not sustainable. In view of this, non-isocyanate polyurethane (NIPU) derived from polyaddition of bis(cyclic carbonate)s and diamines has emerged as safer alternative.<sup>3-6</sup>

The making of NIPU foams is anticipated to differ from that of conventional PU foams owing to the lack of isocyanates in the formulation. Indeed, CO<sub>2</sub> generation from the decarboxylation of stable cyclic carbonate requires high energy.<sup>7</sup> It is therefore imperative to develop other foaming methods under milder conditions. Cornille et al. reported the first NIPU foam by utilizing the hydrogen gas (H<sub>2</sub>) generated from poly(methylhydrogenosiloxane) (Momentive MH 15).<sup>8</sup> This approach was also used to prepare epoxy-based foams<sup>9</sup> and other NIPU foams.<sup>10-13</sup> However, the generation of flammable gas would be a significant concern during production. Physical blowing agents such as Solkane<sup>14-17</sup> (hydrofluorocarbon) and supercritical CO<sub>2</sub><sup>18</sup>, chemical blowing agents such as CO<sub>2</sub> generated from maleic acid/citric acid<sup>19-20</sup> and NaHCO<sub>3</sub><sup>21</sup> were also studied for preparing NIPU foams. Self-blown NIPU foams were reported based on the in-situ carbon dioxide generation from partial decarboxylation of sorbitol-derived bis(cyclic carbonate)s<sup>22</sup> or resorcinol-based bis(cyclic carbonate)s<sup>23</sup> at high temperature (>100 °C). Monie et al. reported a self-blown NIPU foams based on decarboxylation of cyclic carbonates by thiols or latent thiol via S-alkylation at 80 - 100 °C.<sup>24-25</sup> Bourguignon et al. reported self-blown NIPU foams by water-induced decarboxylation of cyclic carbonate at 80 – 100 °C.<sup>26</sup> Recently, Sintas et al. reported a CO<sub>2</sub>-blown NIPU foams through thermal decarboxylation of bis-carbonylimidazolidone monomers at 160 °C.<sup>27</sup> The current foaming processes for NIPU require flammable and

noxious chemicals, non-sustainable blowing agents or high temperatures. Therefore, the development of a sustainable foaming method for NIPU at lower temperature is of great interest.

Amine-CO<sub>2</sub> adducts (e.g carbamates, biscarbonates) have been extensively studied for CO<sub>2</sub> capture and storage,<sup>28-31</sup> and they are known to be formed readily at room temperature. In this work, we synthesized various triethylenetetramine (TETA)-CO<sub>2</sub> adducts by using organic bases such as 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) and 1,5-diazabicyclo(4.3.0)non-5-ene (DBN), and the effects on their CO<sub>2</sub> desorption temperatures were investigated. Finally, we had successfully synthesized the NIPU foam (Figure 1) utilizing amine-CO<sub>2</sub> adducts under mild conditions (50 – 60 °C).

TETA-CO<sub>2</sub> adduct was obtained by introducing purified CO<sub>2</sub> gas (10 mL/min) into the TETA for 15 minutes at room temperature. CO<sub>2</sub> adducts with other polyamines such as pentaethylenhexamine (PEHA), 1,5-diaminopentane (DAP), polyethylenimine (PEI), and Priamine®-1075 had turned into either gel or white solid, which were not suitable for foam formulations. On the other hand, the viscosity (3500 mPa.s<sup>-1</sup>, SI, Fig. S1) of TETA-CO<sub>2</sub> adducts (**TC1**) was suitable for mixing with cyclic carbonates/amines at room temperature.<sup>1</sup> <sup>1</sup>H and <sup>13</sup>C NMR analysis on **TC1** showed the  $\alpha$ -methylene protons (3.30 ppm) of carbamate group (164.5 ppm and smaller peak at 163.9 ppm) (SI, Fig. S7-S8), which accounted for the carbamylations of primary and secondary amines<sup>32</sup> in TETA. The CO<sub>2</sub> adsorption of **TC1** was measured to be 15.8% by <sup>1</sup>H NMR integration of the  $\alpha$ -methylene protons of carbamate (-NHCO<sub>2</sub>) to the sum of  $\alpha$ -methylene protons of carbamate and primary amine. The value is comparable to the CO<sub>2</sub> adsorption (17.9%) calculated based on the mass of adsorbed CO<sub>2</sub> in the **TC1** (SI, Table S1).



**Figure 1. Preparation of CO<sub>2</sub>-blown NIPU foam using amine-CO<sub>2</sub> adduct (TC3).**

The use of organic superbases was found to accelerate the formation of carbamate between amines and CO<sub>2</sub> by increasing the nucleophilicity of the amine and the stabilization of the resulting carbamate, leading to a higher CO<sub>2</sub> adsorption capacity.<sup>33</sup> In this work, TETA-DBU (**TC2**) and TETA-DBN (**TC3**) were obtained as viscous liquids after CO<sub>2</sub> adsorptions. <sup>1</sup>H and <sup>13</sup>C NMR spectra of both **TC2** and **TC3** showed the formation of carbamate groups (3.30 ppm, 163.5 ppm) (SI, Fig. S9-S12). It was found that **TC2** has higher CO<sub>2</sub> adsorption of 27.6% (Table 1). Notably, **TC3** showed highest CO<sub>2</sub> adsorption of 60.4% and highest viscosity (78120 mPa·s<sup>-1</sup>, SI, Figure S1) as compared to **TC1** and **TC2**. The higher CO<sub>2</sub> adsorption found in **TC3** is explained by the higher basicity of DBN,<sup>34-35</sup> which has higher CO<sub>2</sub> adsorption capacity as compared to DBU.<sup>36</sup> In addition, DBN was reported to form carbamate or bicarbonate with CO<sub>2</sub>.<sup>37</sup> A relatively small peak at 162.8 ppm observed in the <sup>13</sup>C NMR of **TC3** was originated from DBN-CO<sub>2</sub> (SI, Fig. S13-14). This suggested that the high CO<sub>2</sub> adsorption found in **TC3** was contributed by formation of both TETA-CO<sub>2</sub>-DBN and DBN-CO<sub>2</sub> adducts.

The use of higher equivalent (3 eq) of DBN had no significant improvement in CO<sub>2</sub> adsorption capacity of adduct (data not shown), probably due to the poor carbamate formation with secondary amines in TETA. Notably, the addition of DBN can be extended to other amine to form adduct with high CO<sub>2</sub> adsorption. In this example, **TC4** with CO<sub>2</sub> adsorption of 54.2% was formed from the DAP-DBN system (SI, Fig. S15-S16). We will only focus on the **TC1-3** in this work.

Next, the CO<sub>2</sub> desorption of **TC** was investigated at lower temperature ranges (60 – 100 °C) since temperatures exceeding 100 °C is not ideal for foam formulation. Generally, CO<sub>2</sub> desorption of amine-CO<sub>2</sub> adduct requires high temperature owing to the thermally stable carbamates. As expected, **TC1** showed low CO<sub>2</sub> desorption (36%, Table 1) even after heating at 100 °C for 24 hr (NMR, SI, Fig. S17-S20). On the other hand, **TC2** exhibited higher CO<sub>2</sub> desorption of 28 % and 70% after heating at 60

°C and 100 °C for 24 hr, respectively (SI, Fig. S21-S26). The initial CO<sub>2</sub> desorption rate of **TC2** was calculated to be 0.023 hr<sup>-1</sup> at 60 °C, which is higher than that of **TC1** (0.009 hr<sup>-1</sup> at 80 °C). The addition of tertiary base (i.e DBU) had catalyzed the formation of TETA-carbamate, as well as reduced the energy needed for CO<sub>2</sub> desorption from the unstable TETA-carbamate.<sup>38</sup> Similarly, **TC3** also showed high initial CO<sub>2</sub> desorption rate (0.021 hr<sup>-1</sup>) at 60 °C (Table 1, SI, Figure S27-S32). The higher desorption kinetic in TETA-DBN system is attributed by its lower enthalpy change of CO<sub>2</sub> desorption and thus a lower energy is required for CO<sub>2</sub> desorption.<sup>39-40</sup> However, the CO<sub>2</sub> desorption of **TC3** remained low (21 %) after 24 hr at 60 °C, which could hinder the NIPU foaming at this temperature.

It was hypothesized that the reaction between cyclic carbonates and free primary amines on **TC** through aminolysis can expedite the CO<sub>2</sub> desorption from carbamate. To test this, the model cyclic carbonates (**M1** and **M2**) were synthesized (SI, Scheme S1 and Figure S5-S6). **M1** with ester linkage should exhibit higher reactivity in aminolysis with **TC3** as compared to **M2**, which has a ether linkage.<sup>41</sup> **M1** or **M2** was mixed with **TC3** at 60 °C and the conversions of cyclic carbonate was analyzed by <sup>1</sup>H NMR (SI, Fig. S33 and S35). A high cyclic carbonate conversion of 94% was found for **TC3:M1** after 2 hr at 60 °C as compared to that of **TC3:M2** (68%). The faster aminolysis in **TC3:M1** had resulted in higher initial CO<sub>2</sub> desorption rate at 0.222 hr<sup>-1</sup> and CO<sub>2</sub> desorption of 87% after 24 hr at 60 °C (Table 1 and SI, Fig. S33-S36). On the other hand, **TC3:M2** showed a slower initial CO<sub>2</sub> desorption (0.132 hr<sup>-1</sup>) and up to CO<sub>2</sub> desorption of 77% after 24 hr at 60 °C. The purified hydroxyurethane products from **TC3:M1** and **TC3:M2** were characterized by NMR (SI, Fig. S37-38). The percentage of amidization as side reaction found on **TC3:M1** was calculated to be 4.5% by NMR analysis.

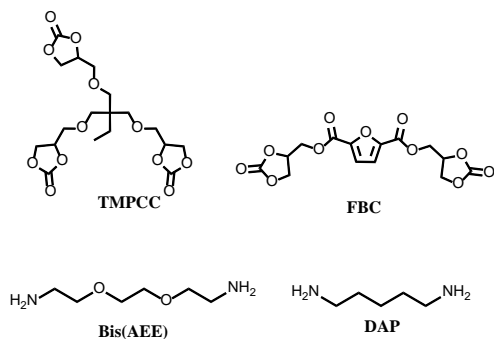
**Table 1. Summary of CO<sub>2</sub> adsorption and desorption of amine-CO<sub>2</sub> adducts at different temperatures.**

	CO <sub>2</sub> adsorption (%)									CO <sub>2</sub> desorption rate (hr <sup>-1</sup> )	CO <sub>2</sub> desorption (%)	
	(Mole of adsorbed CO <sub>2</sub> /mole of primary amines in TETA) <sup>a</sup>											
	Be-fore heating	60 °C			80 °C			100 °C				
	2 hr	4 hr	24 hr	2 hr	4 hr	24 hr	2 hr	4 hr	24 hr			
TC1	15.8	n.d	n.d	n.d	14.0	13.4	11.1	12.9	12.8	10.1	0.009 <sup>b</sup>	36 <sup>d</sup>
TC2	27.6	23.0	21.2	19.8	20.1	18.4	10.2	16.0	10.6	8.2	0.023 <sup>c</sup>	28 <sup>e</sup> ; 70 <sup>d</sup>
TC3	60.4	56.1	52.4	47.7	50.1	48.5	34.1	46.0	39.5	10.7	0.021 <sup>c</sup>	21 <sup>e</sup> ; 82 <sup>d</sup>
TC3:M1	58.4	14.0	9.6	7.5	n.d	n.d	n.d	n.d	n.d	n.d	0.222 <sup>c</sup>	87 <sup>e</sup>
TC3:M2	57.6	31.1	20.5	13.5	n.d	n.d	n.d	n.d	n.d	n.d	0.132 <sup>c</sup>	77 <sup>e</sup>

<sup>a</sup> Determined by the <sup>1</sup>H NMR integration ratio between  $\alpha$ -methylene protons (3.30 ppm) of carbamate group and the sum of  $\alpha$ -methylene protons of both carbamate and free primary amine (2.83 ppm). <sup>b</sup> CO<sub>2</sub> desorption rate at 2 hr at 80 °C. <sup>c</sup> CO<sub>2</sub> desorption rate at 2 hr at 60 °C. <sup>d</sup> CO<sub>2</sub> desorption (%) after heating at 100 °C for 24 hr. <sup>e</sup> Percentage CO<sub>2</sub> desorption (%) after heating at 60 °C for 24 hr. n.d = not done.

Overall, it was shown that the **TC3** has the potential to achieve high CO<sub>2</sub> desorption via aminolysis with cyclic carbonate at 60 °C. This property could be advantageous in its use as both foaming agent and co-monomer for CO<sub>2</sub>-blown NIPU foams. In addition, DBN is preferred in adduct formation owing to the higher CO<sub>2</sub> adsorption and lower toxicity as compared to DBU.

In the following foaming studies, the tris(cyclic carbonate)s, (**TMPCC**) and a bis(cyclic carbonate)s (**FBC**) (Scheme 1) were synthesized and purified based on reported literatures (SI, Scheme S2 and Fig. S2-S3)<sup>42-43</sup>. Subsequently, **F1** and **F2** were prepared by physically mixing **TMPCC** and 1,2-bis(2-aminoethoxy)ethane (BisAEE) or 1,5-diaminopentane (DAP) in the presence of **TC3** (Table 2 and Table S2) at room temperature. The molar ratio between cyclic carbonates and amines used in all foam formulations was approximately 1:1. The viscous liquids were then cured at 60 °C for 24 hr.



Scheme 1. Chemical structures of monomers used in the foam formulation.

No satisfactory foaming was observed for **F1** and **F2** after curing, despite the formation of bubbles in the polymer matrix due to the CO<sub>2</sub> desorption from **TC3**. Both **F1** and **F2** showed high apparent densities ( $p_a$ ) at 1.501 and 1.091 g.cm<sup>-3</sup> (Table 2). This suggested that crosslinking-induced viscosity build-up in the formulation occurred too rapidly, hindering the structural expansion by the blowing reaction. Furthermore, the slower

reaction between **TMPCC** (ether linkage) and **TC3** could explain the insufficient blowing during early stage of foaming. To resolve the rapid viscosity build-up in the formulation, the more reactive **FBC** (ester linkage) was used in the formulation that allowed a slower viscosity build-up and better blowing during foaming. In this context, a reactive groups molar ratio of [TMPCC]/[FBC]/[BisAEE]/[TC3] at 1/0.18/1.05/0.13 was used to prepare **F3**. The gel point of **F3** was determined at 620 minutes (SI, Fig. S39-40), which is significantly longer than those of **F1** and **F2** (190 – 210 minutes). The addition of **FBC** had also reduced the medium viscosity during foaming, resulting in **F3** with low  $p_a$  of 0.203 g.cm<sup>-3</sup> (Table 2). Similarly, **F4** formulated with DAP showed low  $p_a$  of 0.239 g.cm<sup>-3</sup>, indicating a good foam expansion ratio as compared to reported CO<sub>2</sub>-blown foams (0.068 – 0.169 g.cm<sup>-3</sup>).<sup>24-26, 44</sup>

FTIR analysis of **F3** (Figure 2) showed the disappearance of the cyclic carbonate band (C=O stretching) at 1788 cm<sup>-1</sup> and amine band (-NH<sub>2</sub> stretching) at 1605 cm<sup>-1</sup>, and the appearance of characteristic urethane band (C=O stretching) at 1693 cm<sup>-1</sup>. In contrast, **F4** still showed small cyclic carbonates and amines bands, indicating an incomplete polymerization.

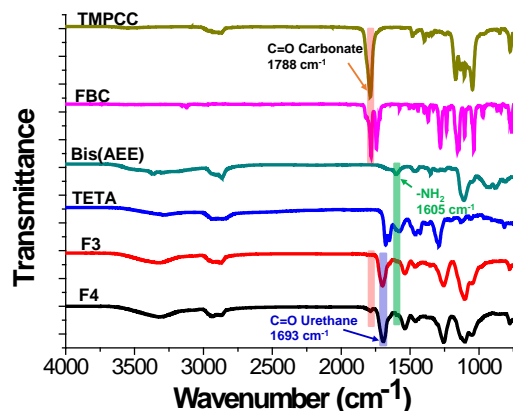


Figure 2. Overlay of FTIR spectra of starting materials and NIPU foams.

**Table 2. Characteristics of NIPU foams.**

NIPU Foam	Diamine	Functional Group Molar Ratio <sup>a</sup> [TMPCC]/[FBC]/[Diamine]/[TC3]	$p_a$ <sup>b</sup> (g.cm <sup>-3</sup> )	SI <sup>c</sup> (%)	GC <sup>d</sup> (%)	Cell Diameter <sup>e</sup> (μm)	Cell Density <sup>f</sup> (10 <sup>7</sup> cells.cm <sup>-3</sup> )	T <sub>d</sub> <sup>g</sup> (°C)	T <sub>g</sub> <sup>h</sup> (°C)	T <sub>α</sub> <sup>i</sup> (°C)	G <sup>j</sup> (MPa)	G <sup>k</sup> (MPa)
F1	Bis(AEE)	1/0/0.88/0.12	1.501	61	95	n.d	n.d	158	12	n.d	n.d	n.d
F2	DAP	1/0/0.88/0.12	1.091	76	96	n.d	n.d	160	27	n.d	n.d	n.d
F3	Bis(AEE)	1/0.18/1.05/0.13	0.203	130	89	232 ± 97	17.4 ± 2.1	200	16	23	88	5.6
F4	DAP	1/0.18/1.05/0.13	0.239	144	93	314 ± 116	8.55 ± 0.63	161	24	35	122	34
F5	Bis(AEE)	1/0.18/1.11/0.07	0.401	160	95	184 ± 79	14.1 ± 0.60	210	15	19	50	2.1
F6	Bis(AEE)	1/0.18/0.93/0.25	0.462	101	91	560 ± 182	1.31 ± 0.19	191	14	23	60	4.0
F7	Bis(AEE)	1/0.18/1.05/0.13	0.289	163	95	590 ± 86	1.25 ± 0.38	195	17	22	48	2.3
F8	Bis(AEE)	1/0.18/1.05/0.13	0.405	121	94	1934 ± 97	0.14 ± 0.03	196	15	21	79	3.2

<sup>a</sup> Molar ratio of reactive functional groups (cyclic carbonates and primary amines) in the respective monomers; thus moles of [cyclic carbonate] = [NH<sub>2</sub>] + [NHCO<sub>2</sub>] in the formulation, see SI for more information on foam preparation. <sup>b</sup> Apparent density was measured by weighting cubic samples (*m*) with dimension (*V*) of 10 x 10 x 10 mm. <sup>c</sup> Swelling index. <sup>d</sup> Gel content. <sup>e</sup> Cell size of each foam was measured by averaging the diameters of foam cells in 3 separate SEM images. <sup>f</sup> Cell density<sup>24</sup> = (*nM/A*)<sup>3/2</sup> *ps/pf*; *n* is the average number of cells in 3 SEM images; *M* is the SEM magnification; *A* is surface area of the image (cm<sup>2</sup>); *ps* is solid sample density and *pf* is foamed sample density; the solid densities (*ps*) were determined to be 1.34 g.cm<sup>-3</sup> for Bis(AEE)-containing polymer and 1.21 g.cm<sup>-3</sup> for DAP-containing polymer. <sup>g</sup> Temperature at 5% weight loss of dry foams. <sup>h</sup> Glass transition temperature of dry foams was measured by DSC (2<sup>nd</sup> heating curve) immediately after drying at 50 °C under vacuum overnight. <sup>i</sup> Maximum of tan δ peak. <sup>j</sup> Storage shear modulus at glassy state at 10 °C. <sup>k</sup> Storage shear modulus at 25 °C. n.d = not done.

It was reported that the 1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea (thiourea) is an efficient catalyst to improve reaction kinetics of cyclic carbonates and amines.<sup>10,45</sup> Thiourea (SI, Figure S4) was synthesized according to the reported literature.<sup>10</sup> In our studies, 0.6 mol% of thiourea with respect to the mole of cyclic carbonate was used to prepare the foam **F3-T** (SI, Table S2). However, there was no significant difference in the conversion kinetics of cyclic carbonates between **F3** and **F3-T** as shown in FTIR analysis (SI, Fig. S42). This could be attributed to the presence of DBN from **TC3** as a catalyst in both formulations.

The effect of different molar ratio of **TC3** on NIPU foams and their corresponding properties were studied. **F5** and **F6** were prepared by using [BisAEE]/[**TC3**] reactive group molar ratios of 1.11/0.07 and 0.93/0.25 in the formulation, respectively, under identical foaming conditions as **F3**. **F5** with higher  $p_a$  (0.401 g.cm<sup>-3</sup>) was obtained owing to the reduced amount of **TC3** in the formulation. In comparison, high amount of **TC3** had resulted in rapid structural expansion of **F6** during foaming process at 60 °C. However, the foam cells collapsed after being removed from the oven, thus resulting in a denser foam ( $p_a$  = 0.462 g.cm<sup>-3</sup>). This was caused by the relatively higher blowing rate in **F6** to the crosslinking rate of polymer.

An investigation was also carried out to understand the effect of foaming temperatures on NIPU foams. The foam formulations were heated at 50 °C and 80 °C to produce **F7** and **F8**,

respectively. FTIR analysis revealed that a lower reaction temperature at 50 °C led to incomplete reaction of cyclic carbonates and amines in **F7** after 24 hrs. Therefore, **F7** was cured at 50 °C for 48 hr to achieve full conversion evidenced by FTIR (SI, Figure S41). **F7** has relatively higher  $p_a$  of 0.289 g.cm<sup>-3</sup> owing to the slow blowing rate at lower temperature. In contrast, a higher foaming temperature at 80 °C resulted in foam cell rupture in **F8**, leading to foam shrinkage and consequently, an increase in  $p_a$  (0.405 g.cm<sup>-3</sup>). It was concluded that a [BisAEE]/[**TC3**] molar ratio of 1.05/0.13 and a foaming temperature of 60 °C are optimal.

The swelling index (SI) and gel content (GC) were measured for all foam samples (Table 2). The lowest SI and highest GC of the sample indicated a higher degree of crosslinking.<sup>10</sup> As expected, both **F1** and **F2** formulated with 100% **TMPCC** showed low SI (61 – 76 %) and high GC (95 – 96 %). The use of **FBC** as extender for **F3 – F8** increased the SI (101 – 163 %) of these foams because of their lower crosslinking densities. All foam samples showed high insoluble contents with high GC (89 – 95 %) owing to the high degree of crosslinking in the polymer.

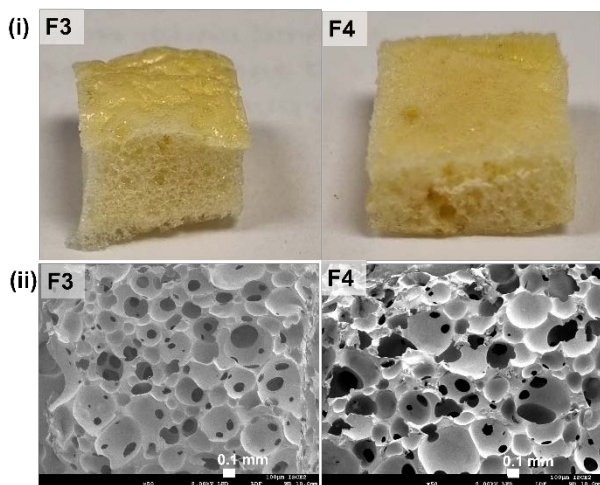


Figure 3. (i) Optical images and (ii) SEM images of NIPU foams.

The cell sizes and cell densities of NIPU foams were analyzed by SEM (Figure 3, SI, Figure S48) following the method reported by Monie et al.<sup>24</sup> **F3** exhibited a homogenous distribution of cell with an average diameter of  $232 \pm 97 \mu\text{m}$  and high cell density of  $17.4 \pm 2.1 \times 10^7 \text{ cells.cm}^{-3}$ . When DAP was used in **F4**, there was an increase in foam cell diameter ( $314 \pm 116 \mu\text{m}$ ) and a decrease in cell density ( $8.55 \pm 0.63 \times 10^7 \text{ cells.cm}^{-3}$ ). Lower molar ratio of **TC3** in formulation had contributed to the smaller foam cell diameter of  $184 \pm 79 \mu\text{m}$  with large distribution found in **F5**. In contrast, a high molar ratio of **TC3** resulted in a significant increase in cell diameter to  $560 \pm 182 \mu\text{m}$  and lower cell density ( $1.31 \pm 0.19 \times 10^7 \text{ cells.cm}^{-3}$ ) found in **F6**. The effects of foaming temperatures on cell diameter and density were also investigated. A slow  $\text{CO}_2$  desorption rate at  $50 \text{ }^\circ\text{C}$  resulted in **F7** with higher cell diameter of  $590 \pm 86 \mu\text{m}$ . A larger cell diameter was also observed for poly(ethylene-co-octene) foams synthesized from a slow  $\text{CO}_2$  desorption rate.<sup>46</sup> A high desorption rate of  $\text{CO}_2$  at  $80 \text{ }^\circ\text{C}$  resulted in a rapid expansion of the foam cell, leading to significant larger cell diameter ( $1934 \pm 97 \mu\text{m}$ ) and smaller cell density ( $0.14 \pm 0.03 \times 10^7 \text{ cells.cm}^{-3}$ ) found in **F8**.

The thermal properties of foams were analyzed by both thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The effect of hydroplasticization on thermal properties of foams was studied. It was found that the moistened **F3** with 5 wt% water (analyzed by TGA) showed decrease in  $T_g$  from  $16 \text{ }^\circ\text{C}$  to  $-6 \text{ }^\circ\text{C}$  (SI, Fig. S43-44). All dry foams showed similar thermal degradation profiles with degradation temperatures ( $T_d$  at 5% weight loss of foam) ranged from  $161 - 210 \text{ }^\circ\text{C}$  (SI, Figure S45 – S46). DSC analysis revealed that the **F4** formulated with DAP showed higher glass transition temperature ( $T_g$ ) of  $24 \text{ }^\circ\text{C}$  (SI, Figure S45) as compared to that of **F3** ( $T_g = 16 \text{ }^\circ\text{C}$ ). Other foams (**F5 – F8**) exhibited rather similar  $T_g$  values of  $14 - 17 \text{ }^\circ\text{C}$ , which is not surprising as the contents of monomers are same in these formulations (SI, Figure S47). The storage shear modulus ( $G'$ ) and loss factor ( $\tan \delta$ ) of foams were analyzed by dynamic mechanical and thermal analysis (DMTA). The  $G'$  of foams was found to decrease when temperature increased; a softer foam like **F3** showed smaller  $G'$  and rapid decrease in  $G'$  as temperature increased (SI, Figure S49). The  $\alpha$  transition temperatures ( $T_\alpha$ ) of foams from glassy state to rubbery state were determined at the maximum of the  $\tan \delta$

curves. It was found that **F4** has higher  $T_\alpha$  ( $35 \text{ }^\circ\text{C}$ ) than that of **F3** ( $23 \text{ }^\circ\text{C}$ ), which was consistent to the  $T_g$  trend analyzed by DSC. Similarly, **F5 – F8** showed  $T_\alpha$  of  $19 - 23 \text{ }^\circ\text{C}$  that followed the same trend as  $T_g$  (SI, Figure S50).

In conclusion, we successfully synthesized the in-situ  $\text{CO}_2$ -blown NIPU foam by utilizing **TC3**, which served a dual purpose as both foaming agent and co-monomer in the preparation of NIPU foams. The high  $\text{CO}_2$  desorption of **TC3** allowed us to prepare NIPU foams at lower temperature ( $50 - 60 \text{ }^\circ\text{C}$ ). Future works will focus on strategies to lower reaction temperature and curing time of NIPU foams.

## ASSOCIATED CONTENT

**Supporting Information.** Experimental details,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of all monomers and **TC1-3**, FTIR spectra, TGA, DSC plots, SEM images, and DMTA plots of NIPU foams. This material is available free of charge via the internet at <http://pubs.acs.org>.

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### Author Contributions

P.S. Choong conceptualized the study, synthesized the foams, performed the characterizations, and drafted the manuscript. Y.L.E. Hui synthesized and purified the monomers and TCs. C.C. Lim performed viscosity, gel points, and DMTA measurements of foams. All authors have given approval to the final version of the manuscript.

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### Notes

The authors declare no competing financial interest.

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