

# Synthesis of Polycaprolactone-based Polyurethane Crosslinked by Polyrotaxanes with Exceptional Mechanical and Hydrolytic Properties

Ngoc Mai Chau<sup>1,2,3,\*</sup>, Thuy An Nguyen<sup>3</sup>, Van-Tien Bui<sup>4</sup>, Thi Thai Ha La<sup>3</sup>, Hiroto Murakami<sup>2</sup>



Use your smartphone to scan this QR code and download this article

## ABSTRACT

Polyurethane has been considered as one of the most versatile polymers with a wide range of applications such as elastomers, thermoplastic polymers, foams, and smart coatings by simply combining various polyols and polyisocyanates. In our recent work, polycaprolactone-based polyurethane (PCL-based PU) was, for the first time, crosslinked by half-methylated polyrotaxanes (PRXs) with filling ratios of 37 and 79 %. Besides examining crosslinking extents of PUs through gel fraction and swelling degree, other analyses of PUs were also measured such as differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), dynamic mechanical thermal analysis (DMTA), and hydrolytic tests to evaluate general properties of PUs. The results show that PCL-based PU-PRX acts as an elastic material with low elastic modulus, very high tensile strength, and elongation at break (~ 1200%). The hydrolytic degradation was also achieved when the weight of samples reduced by 21.6 % after 28 days, and the deformation of three-dimensional crosslinking network was shown via the sharp reduction of elongation at break and the stress at break. These results demonstrated that PCL-based PU-PRX is a potential candidate to be used in alkaline and/or acid environment such as human's body, and also used externally to protect our environment and ecological system.

**Key words:** Hydrolytic polymer, polycaprolactone, polyrotaxane, polyurethane

<sup>1</sup>Faculty of Food Science and Technology, Ho Chi Minh City University of Food Industry, Ho Chi Minh City, Viet Nam

<sup>2</sup>Graduate School of Engineering, Nagasaki University, Nagasaki, Japan

## Correspondence

**Ngoc Mai Chau**, Faculty of Food Science and Technology, Ho Chi Minh City University of Food Industry, Ho Chi Minh City, Viet Nam

Graduate School of Engineering, Nagasaki University, Nagasaki, Japan

Department of Polymer Materials, Faculty of Materials Technology, Ho Chi Minh City University of Technology, Ho Chi Minh City, Vietnam; Vietnam National University Ho Chi Minh City, Ho Chi Minh City, Viet Nam

Email: cnmai.sdh21@hcmut.edu.vn

## History

- Received: 28-4-2022
- Accepted: 30-9-2022
- Published: 25-12-2022

DOI : 10.32508/stdjet.v5iS11.992



## Copyright

© VNU-HCM Press. This is an open-access article distributed under the terms of the Creative Commons Attribution 4.0 International license.



VNU-HCM Press

## INTRODUCTION

POLYURETHANE (PU) is prominent as one of the versatile materials formed by combining a variety of polyols and polyisocyanates. Therefore, a wide range of PUs can be produced to satisfy the modern human's goal such as flexible or rigid PU foam, water-borne PU, thermoplastic PU, and elastomers<sup>1,2</sup>. Based on required products, PUs can be tailored by changing soft segment and hard segment to achieve desired properties such as elasticity, resiliency, flexibility, tensile strength, *etc.*, which has been attracting much attention from scientists and researchers all around the world<sup>3,4</sup>. In addition to the original materials, a cross-linking agent also plays a crucial role in determining the ultimate characteristics of PUs and becomes indispensable to produce advanced and smart polymers such as shape-memory PU<sup>5,6</sup>, self-healing PU<sup>7,8</sup>, bio-PU and flame retardant PU<sup>9,10</sup>, *etc.* Among various cross-linking agents, polyrotaxane (PRX) is a potential candidate that can enable PU to be highly strong and stretchable under elongation and compression by its special structure<sup>11,12</sup>. In a PRX molecule, a ring molecule is interlocked by an axle molecule and freely slides along the axle with bulky terminal cap groups as switches that makes PRX

act as shuttles. PRX is usually made of poly(ethylene glycol) (PEG) and cyclodextrin (CD) molecules, enabling PRX to become extraordinarily biocompatible and biodegradable to be applied in biotechnology and medical materials such as drug and gene delivery, scaffold, and tissue engineering<sup>11-14</sup>.

With these aforementioned advantages, several papers were carried out to combine the properties of PUs and PRXs, mainly through crosslinking network<sup>15-17</sup>. Expectedly, based on the uniqueness and specialty of PRX, in this 3D network, PU long chains can be movable alongside PEG axle of PRX molecules as a result of "shuttle property" and therefore enhance tensile strength and elasticity. For instance, Murakami *et al.* proved that PU based on poly(tetramethylene glycol) 2000 (PTMG2000) and PRX4000 could be achieved the highest elongation at break of 1080% compared to PRX1500 and PRX6000<sup>17</sup>. It was also demonstrated that no significant difference in elongation of PTMG-based PU crosslinked by PRX4000 and PRX6000 when using NCO index of 1.0 while NCO index of 2.0 apparently affected elongation at break of PUs<sup>16</sup>. However, to the best of our knowledge, other materials were not used to examine the extraordinary properties of PU-PRX, and the bio-properties of PRX has been wasteful

**Cite this article :** Chau N M, Nguyen T A, Bui V, La T T H, Murakami H. **Synthesis of Polycaprolactone-based Polyurethane Crosslinked by Polyrotaxanes with Exceptional Mechanical and Hydrolytic Properties.** *Sci. Tech. Dev. J. – Engineering and Technology*; 2022, 5(S1):81-90.

<sup>3</sup>Department of Polymer Materials, Faculty of Materials Technology, Ho Chi Minh City University of Technology, Ho Chi Minh City, Vietnam; Vietnam National University Ho Chi Minh City, Ho Chi Minh City, Viet Nam

<sup>4</sup>Department of Polymer Materials, Polymer Research Center, Faculty of Materials Technology, Ho Chi Minh City University of Technology, Ho Chi Minh City, Vietnam; Vietnam National University Ho Chi Minh City, Ho Chi Minh City, Viet Nam

in PU applications because there was no investigation on it. Furthermore, the environmental friendliness is currently attracting great attention to ease the burden on the natural world, leading to an upward trend to use biodegradable and ecologically friendly materials nowadays.

Herein, this study aimed to synthesize a novel biomaterial by introducing polycaprolactone (PCL) into PU as a “soft segment”, which directly determines the degradable property of PU, and then crosslinked by PRXs to generate a 3D network. Its hydrolytic degradability along with the mechanical and thermal properties were thoroughly analyzed to ensure the characteristics of this potential PU-PRX but be easily degraded in the environment.

## EXPERIMENTAL METHODS

### Materials

Polyethylene glycol 4000 (PEG4000,  $M_n = ca. 3,500$ ) and polycaprolactone diol 2000 (PCL,  $M_n = ca. 2,000$ ) were purchased from Nacalai, Japan and carefully dried before use. 4,4-Diphenylmethanediisocyanate (MDI) was supplied by Mitsui Chemical, Japan and directly used. Half-methylated PRXs (PRX-Me) were prepared following previous report<sup>18</sup> using PEG4000 interlocked with 15 and 31  $\alpha$ -CD molecules confirmed by <sup>1</sup>H NMR measurement (corresponding to the filling ratios of 37 and 79%).

### Synthesis of polyurethanes

First, 0.5974 g (0.3 mmol) of PCL was added into a three-necked flask, which was placed in an oil bath at 90 °C for 4 h under N<sub>2</sub> atmosphere. PCL gradually melted, and a viscous and transparent liquid was formed. After 4-hour purging process, 0.2261 g (0.9 mmol) of MDI was put into the flask with the magnetic stirrer for 2 h. Then, 5 mL of dry DMF was introduced into the reaction system, which was continued stirring for 10 minutes to dissolve the formed PU.

The PRX solution was prepared in advance by mixing PRX-Me into 5 mL of dry DMF until PRX-Me was completely dissolved with the NCO index of 1.5. Then, PRX solution was added dropwise into the flask. The viscosity of the mixture was gradually increasing. The reaction was kept in 48 hours (as scheme in Figure 1). The final product was moved to a petri dish and dried in the oven at 60 °C for 24 h to remove the excess solvent. Lately, the created film was post-cured by compression under the pressure of 20 MPa at 95 °C for 24 h to get a perfect crosslinked film for the next analyses.

PU crosslinked by PRXs with filling ratios of 37 and 79% are abbreviated as PU(37) and PU(79), and PU

without crosslinking with  $M_w$  of  $\sim 260,000$  is called PU(0).

### Characterizations

Gel fraction and swelling degree were calculated by the equations as follows:

$$\text{Gel fraction (\%)} = W_g/W_0 \times 100 \quad (1)$$

$$\text{Swelling degree} = W/W_g \quad (2)$$

in which  $W_0$  is the original weight,  $W_g$  is the weight of dried sample after swelling to an equilibrium state in DMSO or toluene at 30 °C,  $W_s$  is the weight of dried sample after swelling to an equilibrium state in toluene at 30 °C<sup>17</sup>. Differential scanning calorimetry (DSC) was measured by DSC-60 (Shimadzu Corporation), TA-60WS (Shimadzu Corporation) from -100 ÷ 150 °C, heating rate of 10 °C min<sup>-1</sup> in aluminum cell under N<sub>2</sub> atmosphere. Dynamic mechanical thermal analysis (DMTA) was performed by DMS6100 - EXSTAR6000 from -100 ÷ 100 °C, heating rate of 2 °C min<sup>-1</sup>, distortion of 0.05%, frequency of 10 Hz, width of sample of 5 mm and initial length of 5 mm. ORIENTEC RTE-1210 was used to test tensile strength. Thermal gravimetric analysis (TGA-50 device) at N<sub>2</sub> atmosphere in aluminum cell, temperature range from 25 ÷ 600 °C and heating rate of 10 °C min<sup>-1</sup>. Hydrolytic property was performed in 1 M NaOH at 30 °C for predetermined times. After hydrolysis, the films were washed with milli-Q water at room temperature 3 times, followed by drying at 60 °C for 24 hours under vacuum. The content of extractable product was determined from the change in the weight of the polymer films before ( $M_0$ ) and after hydrolysis ( $M$ ):

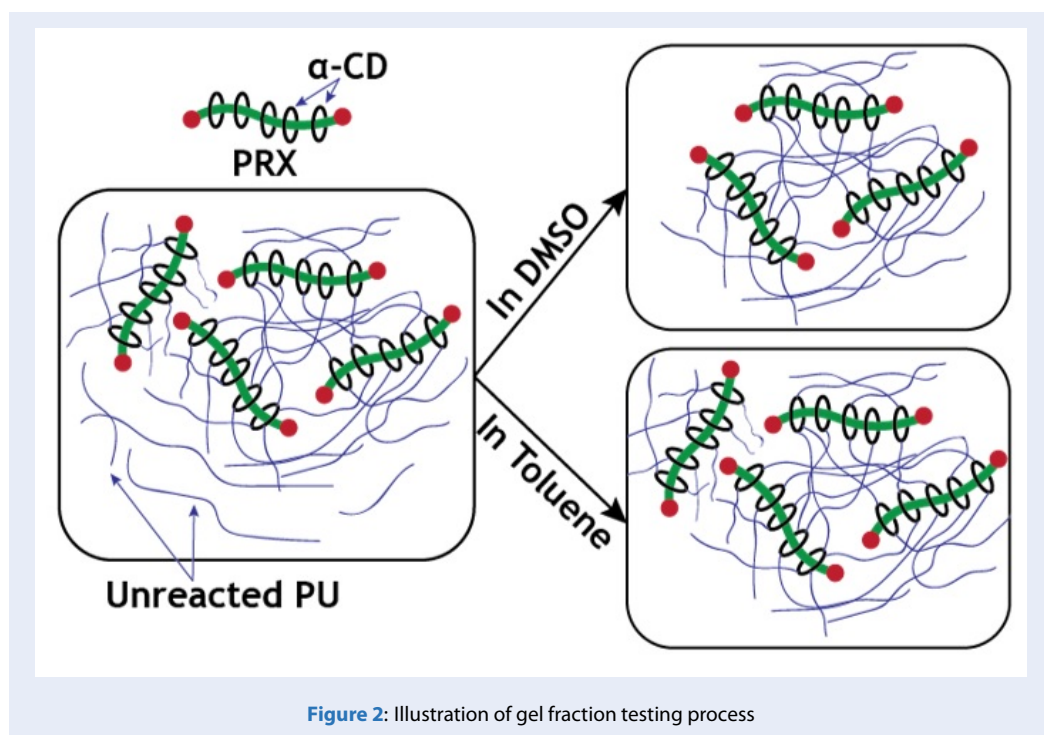
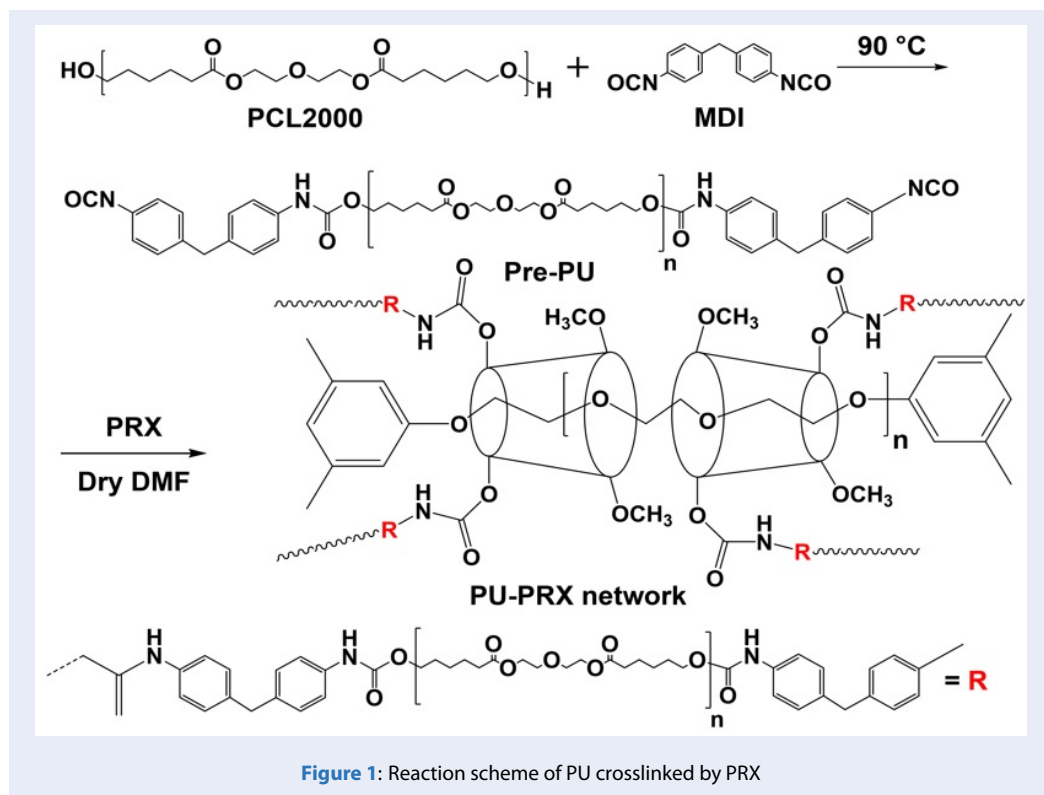
$$\% \text{Extractable products} = 100 \times (M_0 - M)/M_0 \quad (3)$$

After washing out the extractable products, the residual film was used for gel content determination<sup>19</sup>.

## RESULTS AND DISCUSSION

### Gel fraction and swelling test

Gel fractions and degrees of swelling of PUs were summarized in Table 1. Gel fraction is a parameter to confirm the crosslinking network that is calculated by the weight of dry gel component dividing the original weight of the crosslinked sample. When measuring gel fraction in DMSO, the uncross-linked prepolymer chains and imperfectly crosslinked PU will be dissolved and removed from the general network, leaving only the gel components while toluene can just dissolve and remove prepolymer chains (illustrated in Figure 2). Swelling degree is the extent that polymer can absorb solvent calculated by dividing the weight of swollen polymer to the weight of the original crosslinked sample. These two parameters are to

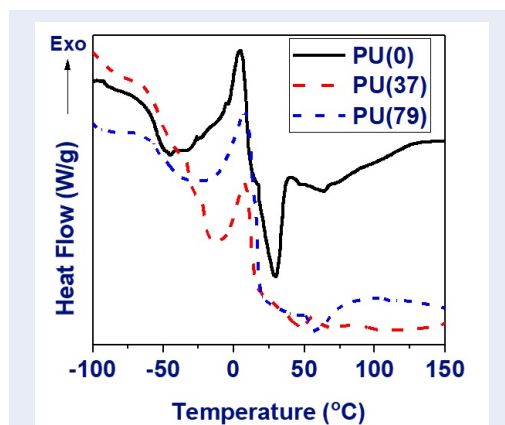


**Table 1: GEL FRACTION AND SWELLING DEGREE RESULTS**

	Gel fraction (%)		Swelling Degree
	DMSO	Toluene	Toluene
PU(37)	62.33 ± 1.01	94.88 ± 1.52	1.61 ± 0.05
PU(79)	69.30 ± 1.84	96.44 ± 1.05	1.21 ± 0.02

compare the crosslinking extent of PUs. As a result, all the PUs left their gel components in DMSO, proving a perfectly crosslinked network of PUs. The gel fraction of PU(37) is lower than that of PU(79) (62.33 and 69.3%, respectively) while the swelling degree of PU(37) is higher than PU(79). This implies that the crosslinking density of PU(79) is higher than PU(37) thereby deterring solvent from penetrating into PU-PRX<sup>20</sup>. Moreover, this high density of crosslinks in PU-PRX may cause insufficient space for the  $\alpha$ -CDs to slide along the axle molecules, thereby leading to the low swelling degree<sup>17</sup>.

**DSC**



**Figure 3: DSC results of PUs**

The thermal properties of PCL-based PUs were determined by DSC results (Figure 3). These results are the second circle of the measurement instead of the first circle to reduce thermal history and obtain the obvious peaks. The first step transition is assigned to the glass temperature of the soft segment. The next exothermal large peak is attributed to the reorganized-crystallization temperature of the soft segment while the endothermal peak is allocated to the melting point of the soft segment. These temperatures of glass transition ( $T_g$ ), reorganized crystallization ( $T_c$ ), and melting ( $T_m$ ) of PUs were summarized in Table 2.

It is well-known that  $T_g$  is basically affected by chain flexibility, intermolecular interaction, and crosslinking of polymer.  $T_g$  of PCL is nearly -60 °C while the melting point is quite low, 60 °C<sup>21</sup>. However, after being polymerized with MDI as a hard segment, the polymer chain was stiffened that made  $T_g$  increase slightly to -55 °C. This value of  $T_g$  is equally similar to PCL-based PU in another research<sup>22</sup>. The reorganized-crystallization process took place at around 5 °C which arranged the amorphous structure to the crystallized structure. Finally, the melting process of these crystals took place at nearly 30 °C, which was also confirmed in another research<sup>23</sup>.

Regarding the crosslinking ones, the values of  $T_g$ ,  $T_c$ , and  $T_m$  are somewhat equal. The  $T_g$  increased moderately to around -50 °C. This is because the polymer chains were crosslinked with one another that limited their chain flexibility, therefore increased the  $T_g$  of both PU(79) and PU(37) as literature. Compared to PTMG-based PU-PRX with similar synthesis conditions,  $T_g$  is much lower (-82 °C)<sup>16</sup> due to the high flexibility of PTMG. The analogous comparison of  $T_g$  between PCL-based and PTMG-based PUs was also verified by Yang et al. (2005)<sup>24</sup>.  $T_c$  of those crosslinked PUs are relatively higher than that of PU(0) mainly because of the limitation of the crosslinking bridges. Finally, the  $T_m$  values are greatly affected after crosslinking, related to crystalline regions. For the PU(79) that was assumed to be the best crosslinking sample with the highest crosslinking density among the three PUs, its  $T_m$  increased to 57.4 °C, which is much higher than that of PU(0). It can be explained that after crosslinking, the polymer chains were connected to one another by the PRX crosslinker, thereby destroying the crystalline regions in polymer matrix and also hindering melting ability of PUs. However, if the temperature was provided high enough, the remaining crystalline regions could be melted, demonstrated through a very small endothermal peak with low enthalpy. Similarly, PU(37) with the lower filling ratio of PRX has a lower  $T_m$  compared to PU(79), achieving at 50 °C.

**Table 2: VALUES OF  $T_g$ ,  $T_c$ , AND  $T_m$  BASED ON DSC RESULTS**

	$T_g$	$T_c$	$T_m$
PU(0)	-55.24	5.32	29.42
PU(37)	-50.03	8.53	49.80
PU(79)	-49.89	8.24	57.40

**DMTA**

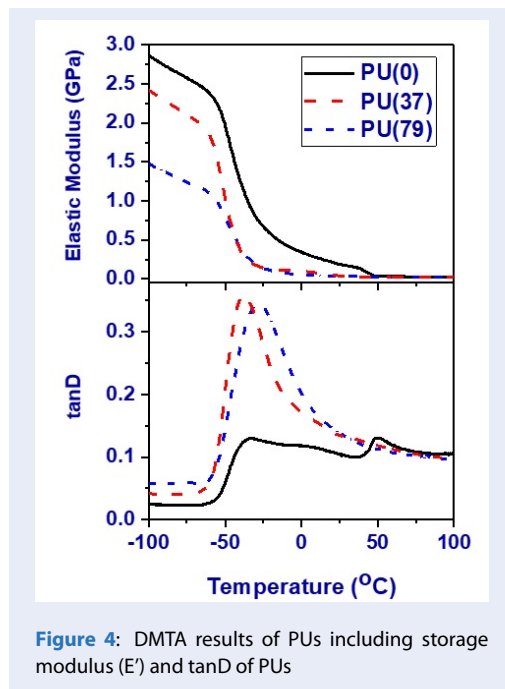
Figure 4 shows the temperature dependence of the elastic modulus ( $E'$ ), and loss tangent ( $\tan\delta$ ) of the PUs.  $E'$  curve represents the elastic modulus or tensile modulus of materials that is used to measure the stiffness of an elastic material and to characterize materials. In Figure 4, PU(0) has the highest modulus, followed by PU(37) and PU(79). Considering these samples at room temperature, PU(0) acts as a plastic material with high stiffness whereas PU(37) and PU(79) are more flexible and act as rubber. Moreover, all of the PCL-based PU gave a peak at around  $-35^\circ\text{C}$  in the  $\tan\delta$  curves, attributable to an  $\alpha$  relaxation corresponding to the glass transition of the soft segment. Among them, PU(79) showed the peak at the highest temperature of  $-26^\circ\text{C}$ , indicating the highest crosslinking density as well as lower flexibility compared to the two others. This result once again confirmed the thermal and elastic properties of PUs.

**TGA**

To evaluate thermal decomposition of the PUs, TGA measurements were carried out. In Figure 5, it can clearly be observed that there is only one decomposition stage in PU(0) sample while there are two stages in the crosslinked ones. This demonstrates the existence of PRX in the crosslinked samples. The onset temperatures of the 3 samples are quite similar at around  $356 - 361^\circ\text{C}$ . This first stage of decomposition process is attributable to the degradation of PCL-PU chains because it appears similarly in the three of them. The next stage is mainly due to the difference in PRX molecules. The onset point of PU(79) is quite earlier than PU(37) but the weight loss of this stage of PU(79) is higher than that of PU(37). This illustrates the higher content of PRX in the PU(79), verifying the higher density of crosslinking bridges in polymer network. Finally, the total weight loss is in an explainable order: PU(0) > PU(37) > PU(79). PU(79) is the most thermally durable samples.

**Tensile strength test**

Figure 6 shows the stress-strain curves of the PUs. Magnitudes of Young's Modulus, tensile strength, and strain at break of the PUs were summarized in Table 3. The Young's moduli are the confirmation of DMTA results when these samples were measured at room temperature (around  $5 \div 10^\circ\text{C}$ ) with the order: PU(0) > PU(37) > PU(79). As mentioned above, PU(0) behaved as a plastic material with high stiffness but was easy to break with the elongation of 375%. After being crosslinked with PRX(37), the Young's modulus was decreasing to 9.88 MPa, which is as low as a third of PU(0) whereas the strain at break increased 2.5 times, reaching at 929.5%. Regarding the best sample in this research, PU(79) possesses the lowest elastic modulus (3.17 MPa) while the strain at break achieved 1166.5% which is a 3-time enhancement compared to that of PU(0), proving the extraordinary mechanical property of PUs with the presence of PRX crosslinkers. The average stress to break the crosslinked samples is around 30 MPa that is nearly 5 times to break the no-crosslinking sample. In comparison with previous research using PTMG2000 under similar conditions to synthesize PU-PRXs, Young's modulus reached 7.5 MPa, tensile



**Figure 4:** DMTA results of PUs including storage modulus ( $E'$ ) and  $\tan\delta$  of PUs

strength was 14.0 MPa, and the elongation at break was 1080 %<sup>17</sup>, which is all lower than the result of our recent work. Furthermore, it is obvious that our new material PCL-PU(79) is not easy to break with low stress, and strain probability is relatively higher than the crosslinked PTMG-PU. Mechanically, the crosslinked PCL-PU is preferably durable than the crosslinked PTMG-PU to be used in reality.

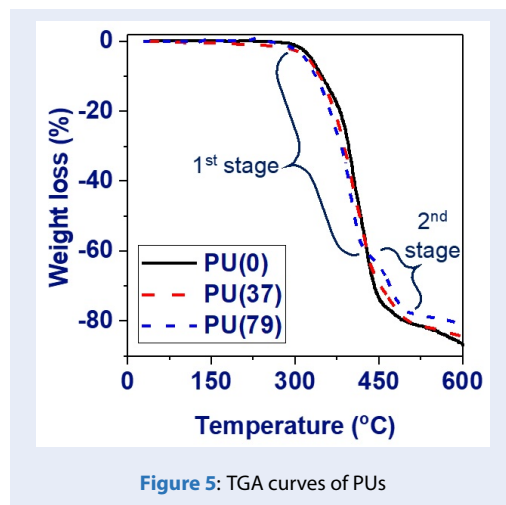


Figure 5: TGA curves of PUs

### Hydrolytic property

#### Weight loss

To easily evaluate the outstanding degradability of PCL, we also tested the hydrolytic property of PTMG-based PU under the completely same synthesis conditions, called PU'(0). The hydrolysis results of PUs can clearly be seen in Figure 7. The weight of PU(0) decreased slightly by 2.08 % after the first 7 days, then stayed unchanged in the next 7 days, decreased by 3.13 % after 21 days, and finally reduced totally by 4.77 % after 28 days. Simultaneously, the change of PU'(0) was insignificant (decreased by 0.22, 0.23, 0.9, and 0.92 % after 7 days, 14 days, 21 days, and 28 days, respectively). As well-known, PCL-PU itself is degradable in water mainly due to the presence of ester groups in the PCL soft segments which is susceptible to hydrolysis, and this degradation reaction is catalyzed by alkaline environment. The fast degradation rate in the first week is attributable to the attack of NaOH to the ester groups in the solution. However, in the second week, it maintained the weight probably because after degradation of ester groups, the carboxylic acid groups would be formed, and then neutralized by NaOH in the solution. Therefore, the concentration of OH<sup>-</sup> was decreased gradually that

slowed down the degradation rate of PCL-PU. This phenomenon did not appear in PTMG-PU sample which was stable during the first two weeks.

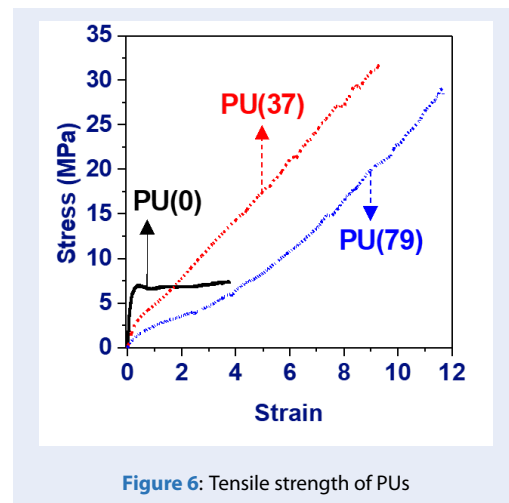


Figure 6: Tensile strength of PUs

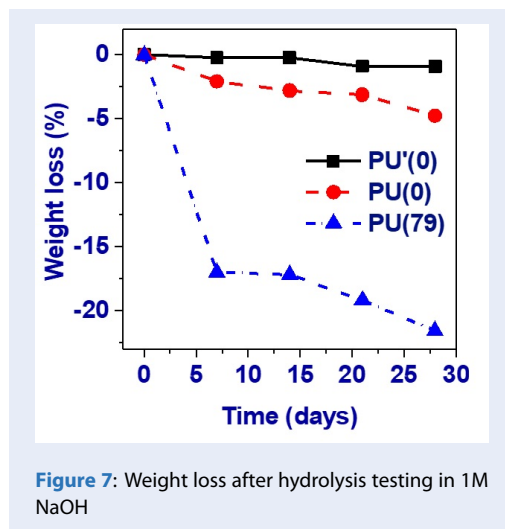
Comparing PU(0) and PU(79), the fast and dramatic loss of weight was observed. It is relatively paradoxical that the crosslinking PU was more degraded than the no-crosslinking one while the thermal and mechanical properties of PCL-PU(79) were outstanding compared to PCL-PU. However, it was also demonstrated in the previous research that PCL-PU after slightly crosslinking is more degradable<sup>25</sup>, and crosslinking is one way to increase the degradation rate<sup>26</sup>. In other words, PCL-PU possesses a high degree of crystallinity that limits hydration through the ordered packing of polymer chains. Therefore, any action reducing crystallinity such as crosslinking will accelerate hydrolytic degradation. As a result, the weight of PU(79) first reduced by 17% in the first 7 days, then almost unchanged in the next 7 days. After 21 days, it fell by 19.2% and finally 21.57% after 28 days. The trend of the weight loss of PU(79) is similar to PU(0) as the reason mentioned above.

#### Tensile strength reduction

As can be seen in the tensile strength results of PUs (Figure 8), the tensile curves changed significantly after degradation. For PU(0), not only did the elastic modulus decrease dramatically, but the values of stress also fell obviously after 14 days and 28 days as the 14-day curve is underlying the 0-day curve but on top of the 28-day curve. Meanwhile, PU'(0) shows a main change in elongation (decreased from 12.3 to 10.2, 9.88, and 9.07 after 7, 14, and 28 days). It is supposed that morphological changes linked with the crystalline and amorphous zones of PCL could be

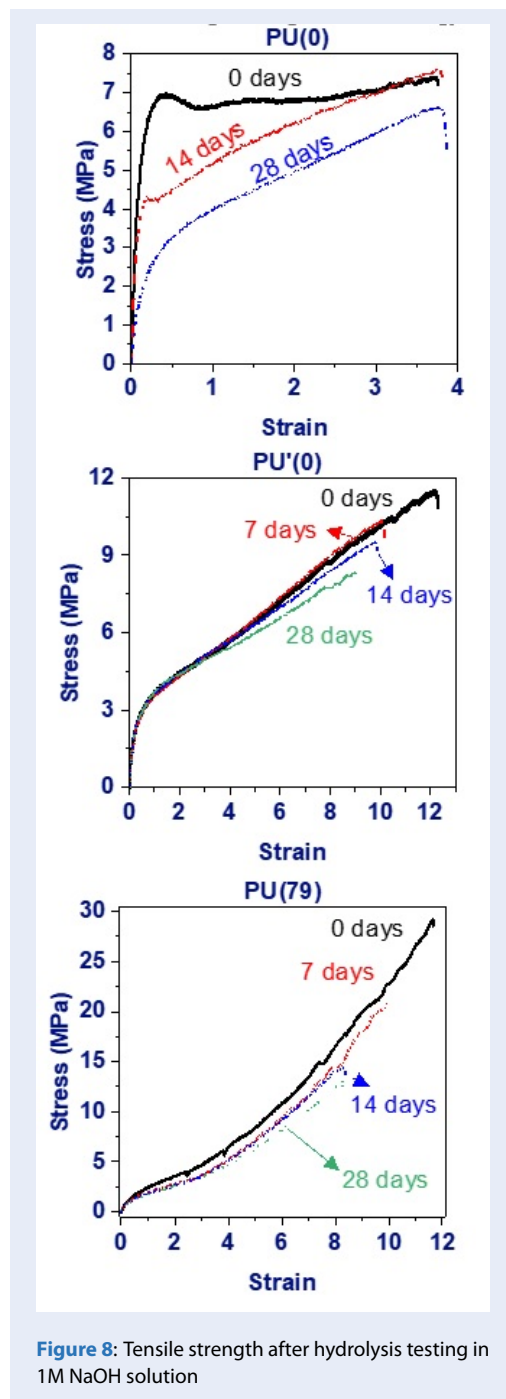
**Table 3: YOUNG’S MODULUS, TENSILE STRENGTH AND STRAIN AT BREAK OF PUs BASED ON THE STRESS-STRAIN CURVES**

Sample name	Young’s Modulus (MPa)	Tensile Strength (Mpa)	Strain at break
PU(0)	82.70	7.29	3.754
PU(37)	9.88	31.7	9.295
PU(79)	3.17	29.18	11.665



**Figure 7:** Weight loss after hydrolysis testing in 1M NaOH

headed onto these results. The first zone to be attacked by the hydrolytic degradation should be the amorphous one since it has lower density and H<sub>2</sub>O molecules could easily penetrate into it. Therefore, this region of PCL was quickly degraded after the first 14 days (weight loss decreased significantly by 2.8%), and mainly the crystalline region was left. That would explain the rapid increase in stress, and the elongation at break presented a bit higher value due to entanglements in the amorphous zones which has higher strain levels than the ordered crystalline chains. After 28-day exposure, hydrolytic degradation would be reaching the crystalline phases, and significantly falling down on mechanical properties is observed as a consequence of hydrolytic degradation progress, possibly leading to a macromolecular breakdown<sup>27</sup>. On the other hand, PU(79) shows no change in curve shape but elongation at break and tensile strength reduced greatly after degradation. After 7 days, elongation at break dramatically dropped from 11.7 to 10.0, and continued to reduce to nearly 8.3 after 14 and 28 days. This proved the potential hydrolytic degradability of PU-PRX crosslinking network in alkaline environment.



**Figure 8:** Tensile strength after hydrolysis testing in 1M NaOH solution

## CONCLUSION

The PCL-PU crosslinked by PRX was successfully synthesized with the analysis of its thermal, mechanical, and hydrolytic properties. PRX crosslinkers enabled PUs to behave as a rubber material at room temperature with low elastic modulus (3.17 MPa) and desirable elongation at break (1167%), corresponding to a 26.6-time decrease in modulus and a 3-time improvement in elongation at break compared to PU without crosslinking. The filling ratios of PRX crosslinkers greatly affect the crosslinking density of PUs and therefore affect the mechanical properties of PUs due to the “shuttle properties” of PRX. The hydrolytic degradability of PU(79) was achieved when after 28 days, the weight decreased 21.6%, and the deformation of 3D crosslinking network was shown via the reduce of 1.5 times elongation at break with the stress as low as 2.5 times of the original one. PCL-based PU-PRX is a potential polymer with the ideal durability and flexibility to be utilized in reality but ecological friendliness due to the possession of hydrolytic degradability.

## ACKNOWLEDGMENT

We acknowledge the support of time and facilities from Nagasaki University and Ho Chi Minh City University of Technology (HCMUT), VNU-HCM for this study.

## LIST OF ABBREVIATIONS

PRX: polyrotaxane  
 PRX-Me: methylated polyrotaxane  
 PCL: polycaprolactone diol 2000  
 PU: polyurethane  
 TGA: thermal gravimetric analysis  
 DMTA: dynamic mechanical thermal analysis  
 DSC: differentiation scanning calorimetry  
 PEG: polyethylene glycol  
 CD: cyclodextrin  
 MDI: 4,4-diphenylmethanediisocyanate

## CONFLICT OF INTEREST

The authors declare no competing financial interest.

## AUTHOR CONTRIBUTIONS

**N.M. Chau:** Conceptualization, Methodology, Formal analysis, Investigation; **T.A. Nguyen:** Investigation, Writing-editing; **V.-T. Bui:** Formal analysis, Investigation, Writing-reviewing and editing; **T.T.H. La:** Supervision, Investigation, Writing-reviewing and editing; **H. Murakami:** Supervision, Funding acquisition, Formal analysis, Investigation, Writing-reviewing and editing.

## REFERENCES

- Akindoyo JO, Beg MDH, Ghazali S, Islam MR, Jeyaratnam N, Yuravaj AR. Polyurethane types, synthesis and applications-a review. *RSC Adv.* 2016;6(115):114453-82; Available from: <https://doi.org/10.1039/C6RA14525F>.
- Das A, Mahanwar P. A brief discussion on advances in polyurethane applications. *Adv Ind Eng Polym Res.* 2020;3(3):93-101; Available from: <https://doi.org/10.1016/j.aiepr.2020.07.002>.
- Jiang L, Ren Z, Zhao W, Liu W, Liu H, Zhu C. Synthesis and structure/properties characterizations of four polyurethane model hard segments. *R Soc Open Sci.* 2018;5(7):180536; PMID: 30109100. Available from: <https://doi.org/10.1098/rsos.180536>.
- Korley LTJ, Pate BD, Thomas EL, Hammond PT. Effect of the degree of soft and hard segment ordering on the morphology and mechanical behavior of semicrystalline segmented polyurethanes. *Polymer (Guildf).* 2006;47(9):3073-82; Available from: <https://doi.org/10.1016/j.polymer.2006.02.093>.
- Kumar B, Noor N, Thakur S, Pan N, Narayana H, Yan SC et al. Shape memory polyurethane-based smart polymer substrates for physiologically responsive, dynamic pressure (Re)distribution. *ACS Omega.* 2019;4(13):15348-58; PMID: 31572833. Available from: <https://doi.org/10.1021/acsomega.9b01167>.
- Ahmed N, Kausar A, Muhammad B. Advances in shape memory polyurethanes and composites: a review. *Polym Plast Technol Eng.* 2015;54(13):1410-23; Available from: <https://doi.org/10.1080/03602559.2015.1021490>.
- Wang H, Xu J, Du X, Du Z, Cheng X, Wang H. A self-healing polyurethane-based composite coating with high strength and anti-corrosion properties for metal protection. *Compos B Eng.* 2021;225(Sep):109273; Available from: <https://doi.org/10.1016/j.compositesb.2021.109273>.
- Jiang C, Zhang L, Yang Q, Huang S, Shi H, Long Q et al. Self-healing polyurethane-elastomer with mechanical tunability for multiple biomedical applications in vivo. *Nat Commun.* 2021;12(1):4395; PMID: 34285224. Available from: <https://doi.org/10.1038/s41467-021-24680-x>.
- Wang X, Cai W, Ye D, Zhu Y, Cui M, Xi J et al. Bio-based polyphenol tannic acid as universal linker between metal oxide nanoparticles and thermoplastic polyurethane to enhance flame retardancy and mechanical properties. *Compos B Eng.* 2021;224(Aug):109206; Available from: <https://doi.org/10.1016/j.compositesb.2021.109206>.
- Acuña P, Zhang J, Yin G, Liu X, Wang D. Bio-based rigid polyurethane foam from castor oil with excellent flame retardancy and high insulation capacity via cooperation with carbon-based materials. *J Mater Sci.* 2021;56(3):2684-701; Available from: <https://doi.org/10.1007/s10853-020-05125-0>.
- Kobayashi Y. Precise synthesis of polyrotaxane and preparation of supramolecular materials based on its mobility. *Polym J.* 2021;53(4):505-13; Available from: <https://doi.org/10.1038/s41428-020-00455-x>.
- Wong SY, Pelet JM, Putnam D. Polymer systems for gene delivery-past, present, and future. *Prog Polym Sci.* Aug 2007;32(8-9):799-837; Available from: <https://doi.org/10.1016/j.progpolymsci.2007.05.007>.
- Rajendan AK, Arisaka Y, Yui N, Iseki S. Polyrotaxanes as emerging biomaterials for tissue engineering applications: a brief review. *Inflam Regen.* 2020;40(1):27; PMID: 33292785. Available from: <https://doi.org/10.1186/s41232-020-00136-5>.
- Li JJ, Zhao F, Li J. Polyrotaxanes for applications in life science and biotechnology. *Appl Microbiol Biotechnol.* 2011;90(2):427-43; PMID: 21360153. Available from: <https://doi.org/10.1007/s00253-010-3037-x>.



15. Takata T et al. Polyrotaxane network as a topologically cross-linked polymer: synthesis and properties. *Supramolecular polymer chemistry*, vol. 1, no. 1. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA, 2012, pp. 331-46; Available from: <https://doi.org/10.1002/9783527639786.ch15>.
16. Murakami H, Kondo T, Baba R, Nonaka N. 'Synthesis and Characterization of Polyurethanes Crosslinked by Polyrotaxanes of Two Filling Ratios of alpha;-Cyclodextrin and with Two Modification Ratios of Polyurethane Chain', *e-journal soft mater. e-J. Soft Mater.* 2014;10(0):9-15; Available from: <https://doi.org/10.2324/ejasm.10.9>.
17. Murakami H, Baba R, Fukushima M, Nonaka N. Synthesis and characterization of polyurethanes crosslinked by polyrotaxanes consisting of half-methylated cyclodextrins and PEGs with different chain lengths. *Polymer (Guildf)*. 2015;56:368-74; Available from: <https://doi.org/10.1016/j.polymer.2014.11.057>.
18. Zhao T, Beckham HW. Direct Synthesis of cyclodextrin-Rotaxanated poly(ethylene glycol)s and Their Self-Diffusion Behavior in Dilute Solution. *Macromolecules*. Dec 2003;36(26):9859-65; Available from: <https://doi.org/10.1021/ma035513f>.
19. Kósa C, Sedláčik M, Fiedlerová A, Chmela Š, Borská K, Mosnáček J. Photochemically cross-linked poly( $\epsilon$ -caprolactone) with accelerated hydrolytic degradation. *Eur Polym J*. 2015;68:601-8; Available from: <https://doi.org/10.1016/j.eurpolymj.2015.03.041>.
20. Yang SL, Wu Z, Yang W, Yang M. Thermal and mechanical properties of chemical crosslinked polylactide (PLA). *Polym Test*. 2008;27(8):957-63; Available from: <https://doi.org/10.1016/j.polymertesting.2008.08.009>.
21. Laurence M W. Permeability properties of plastics and elastomers. 4th ed, Matthew, Deans; 2017;.
22. Haryńska A, Kucinska-Lipka J, Sulowska A, Gubanska I, Kostrzewa M, Janik H. Medical-grade PCL based polyurethane system for FDM 3D printing-characterization and fabrication. *Materials (Basel)*. Mar 2019;12(6):887; PMID: 30884832. Available from: <https://doi.org/10.3390/ma12060887>.
23. Lee SY, Wu SC, Chen H, Tsai LL, Tzeng JJ, Lin CH et al. Synthesis and characterization of polycaprolactone-based polyurethanes for the fabrication of elastic guided bone regeneration membrane. *BioMed Res Int*. 2018;2018:3240571; PMID: 29862262. Available from: <https://doi.org/10.1155/2018/3240571>.
24. Yang YK, Kwak NS, Hwang TS. Effects of physical properties on waterborne polyurethane with poly(tetramethylene glycol) (PTMG) and polycaprolactone (PCL) contents. *Polym (Korea)*. 2005;29(1):81-6;.
25. Chan-Chan LH, Solis-Correa R, Vargas-Coronado RF, Cervantes-Uc JM, Cauich-Rodríguez JV, Quintana P et al. Degradation studies on segmented polyurethanes prepared with HMDI, PCL and different chain extenders. *Acta Biomater*. 2010;6(6):2035-44; PMID: 20004749. Available from: <https://doi.org/10.1016/j.actbio.2009.12.010>.
26. Castilla-Cortázar I, Más-Estellés J, Meseguer-Dueñas JM, Escobar Ivirico JL, Marí B, Vidaurre A. Hydrolytic and enzymatic degradation of a poly( $\epsilon$ -caprolactone) network. *Polym Degrad Stab*. 2012;97(8):1241-8; Available from: <https://doi.org/10.1016/j.polymdegradstab.2012.05.038>.
27. França DC, Bezerra EB, Morais DDS, Araújo EM, Wellen RMR. Effect of hydrolytic degradation on mechanical properties of PCL. *Mater Sci Forum*. 2016;869:342-5; Available from: <https://doi.org/10.4028/www.scientific.net/MSF.869.342>.

# Tổng hợp Polyurethane trên cơ sở Polycaprolactone và Polyrotaxanes với các tính chất cơ học và thủy phân nổi bật

Châu Ngọc Mai<sup>1,2,3,\*</sup>, Nguyễn Thuỳ An<sup>3</sup>, Bùi Văn Tiến<sup>4</sup>, La Thị Thái Hà<sup>3</sup>, Murakami Hiroto<sup>2</sup>



Use your smartphone to scan this QR code and download this article

## TÓM TẮT

Polyurethane (PU) là một loại polyme linh hoạt nhất với phạm vi ứng dụng rất rộng như cao su, polyme nhiệt dẻo, xốp, sơn thông minh bằng cách kết hợp các loại polyol và polyisocyanate khác nhau. Trong nghiên cứu này, PU trên cơ sở polycaprolactone (PCL-PU) lần đầu tiên được nối mạng bằng polyrotaxane đã methylate hoá một nửa nhóm chức -OH với số vòng  $\alpha$ -cyclodextrin là 15 và 31 (tương ứng với chỉ số xoắn vòng 37 và 79%). Bên cạnh việc xác định mức độ nối mạng của PU thông qua chỉ số phần gel và độ trương, những phân tích khác cũng được thực hiện như phân tích nhiệt quét vi sai (DSC), phân tích nhiệt lượng (TGA), phân tích cơ nhiệt động học (DMTA) và thử nghiệm thủy phân để đánh giá tính chất chung của PU. Kết quả cho thấy PCL-PU hoạt động như vật liệu cao su với modul đàn hồi thấp, độ bền kéo và độ giãn dài rất cao (đạt 1200 %). Khả năng thủy phân cũng đạt được trong môi trường kiềm NaOH 1 M khi khối lượng mẫu phân tích giảm 21.6% sau 28 ngày và sự phá hủy của mạng lưới không gian ba chiều được biểu hiện thông qua sự giảm đi đáng kể của độ giãn dài và ứng suất đứt. Do đó, PCL-PU nối mạng bằng PRX là một ứng viên tiềm năng để sử dụng trong môi trường axit hoặc bazơ như cơ thể con người, hoặc sử dụng trong các ứng dụng bên ngoài để góp phần bảo vệ môi trường và hệ sinh thái.

**Từ khoá:** Polyurethane, polycaprolactone, polyrotaxane, polyme thủy phân

<sup>1</sup>Khoa Công nghệ Thực phẩm, Trường Đại học Công nghiệp Thực phẩm TP.HCM

<sup>2</sup>Khoa Kỹ thuật, Đại học Nagasaki, Nhật Bản

<sup>3</sup>Bộ môn Vật liệu Polyme, Khoa Công nghệ Vật liệu, Trường Đại học Bách Khoa – Đại học Quốc gia TP.HCM

<sup>4</sup>Bộ môn Vật liệu Polyme, Trung tâm Nghiên cứu Vật liệu Polyme, Khoa Công nghệ Vật liệu, Trường Đại học Bách Khoa – Đại học Quốc gia TP.HCM

## Liên hệ

**Châu Ngọc Mai**, Khoa Công nghệ Thực phẩm, Trường Đại học Công nghiệp Thực phẩm TP.HCM

Khoa Kỹ thuật, Đại học Nagasaki, Nhật Bản

Bộ môn Vật liệu Polyme, Khoa Công nghệ Vật liệu, Trường Đại học Bách Khoa – Đại học Quốc gia TP.HCM

Email: cnmai.sdh21@hcmut.edu.vn

## Lịch sử

- Ngày nhận: 28-4-2022
- Ngày chấp nhận: 30-9-2022
- Ngày đăng: 25-12-2022

DOI: 10.32508/stdjet.v5iS11.992



**Trích dẫn bài báo này:** Mai C N, An N T, Tiến B V, Hà L T T, Hiroto M. Tổng hợp Polyurethane trên cơ sở Polycaprolactone và Polyrotaxanes với các tính chất cơ học và thủy phân nổi bật. *Sci. Tech. Dev. J. - Eng. Tech.*; 2022, 5(S1):81-90.