



Efficient One-Pot Preparation of Thermoresponsive Polyurethanes with Lower Critical Solution Temperatures

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This work reports a simple and scalable strategy to prepare a series of thermoresponsive polyurethanes synthesized via copolymerization of dicyclohexyl diisocyanate with glycerol ethoxylate in a single one-pot system. These polyurethanes exhibit lower critical solution temperatures (LCST) at 57 °C. The LCST of synthesized polyurethane was determined from Dynamic Scanning Calorimetry and UV-vis measurements. Both the LCST and T_g of synthesized polyurethane was tuned by varying the ratio between hard segment (dicyclohexyl diisocyanate) and soft segment (glycerol ethoxylate). Thus, T_g values could be tuned from -54.6 °C to -19.9 °C for samples with different flexibility. The swelling and deswelling studies were

done at room temperature and above the LCST respectively. The results showed that the swelling ratio increases with the increase of soft segment (glycerol ethoxylate) in synthesized polyurethanes. Furthermore, the mechanical properties of the membrane were studied by universal tensile testing measurements. Specifically, stress at break values varied from 0.35 ± 0.07 MPa to 0.91 ± 0.15 MPa for the tested membranes, whereas elongation at break data ranged from $101.9 \pm 20.9\%$ to $192.4 \pm 24.4\%$, and Young's modulus varied from 0.35 ± 0.03 MPa to 1.85 ± 0.19 MPa. Tensile strength of the films increased with the increase of the hard segment and elongation at break decreased.

Introduction

In the last few years there have been large interest to develop smart hydrogels for variety of applications, such as drug

delivery, actuation, tissue engineering and sensing, due to their ability to respond to external stimuli.^[1,2] Additionally, hydrogels have become appealing candidates nowadays because of their high water content inside the three-dimensional (3D) network structure, which closely mimic the natural extracellular matrices of soft tissues.^[3] Compared to other stimuli-responsive hydrogels, thermoresponsive hydrogels are the most common and popular class of materials, which mainly shows temperature dependent deformation of their polymeric 3D network. The most common type of polymers investigated for thermoresponsive behaviour are poly(*N*-isopropylacrylamide) (PNIPAM), polyvinylcaprolactam, poly(ethyleneglycol), and their copolymers.^[4,5]

Recently, thermoresponsive polyurethane (PU) have received increasing attention due to their good mechanical property, biodegradability and biocompatibility.^[6,7,8] Polyurethanes (PUs) are mainly synthesized from various hydroxyl containing components (diols/polyols) and diisocyanates in organic solvents, water^[9] or under solvent-free conditions.^[10] The industrial application of PUs involves its use in the manufacturing of a variety of medical devices including catheters, surgical drains, flexible tubing, vascular grafts,^[11] durable wheels and tyres; high-resilience foam; adhesives; surface coatings and sealant; and so on. PUs with appropriate mechanical properties have long been used in regenerative medicine.^[12,13] Mechanical properties as well as the morphology of the block copolymer can be adjusted by varying the block length, composition, and chemical structure of each domain.^[14,15] In general, the urethane functional group, which connects both the hard segment and soft segments, engage in hydrogen bond interactions and are capable of acting as physical crosslinking points. In presence of water, these urethane groups form hydrogen bond with water molecules.

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The balance between hydrophobic/hydrophilic groups along with the hydrogen bond forming tendency of urethane groups result in the thermoresponsive behaviour of PUs.^[16] Poly (ethylene glycol) (PEG) is one of the widely used polyols for synthesizing PU-based thermoresponsive hydrogels.^[17,18,19] PEG is well studied for biomedical application due to their high solubility in aqueous media, non-toxicity and non-immunogenicity.^[20] By varying the PEG concentration in PU hydrogel it is easy to tune the mechanical property, degradability, and biocompatibility. Recently, Hsu and co-workers designed and synthesized a waterborne PU composed of poly (ϵ -caprolactone) (PCL) diol and an amphiphilic polylactide-poly (ethylene glycol) (PLA-PEG) diblock copolymer which underwent thermoresponsive gelation above 37 °C and able to support proliferation of human mesenchymal stem cells (hMSCs).^[21]

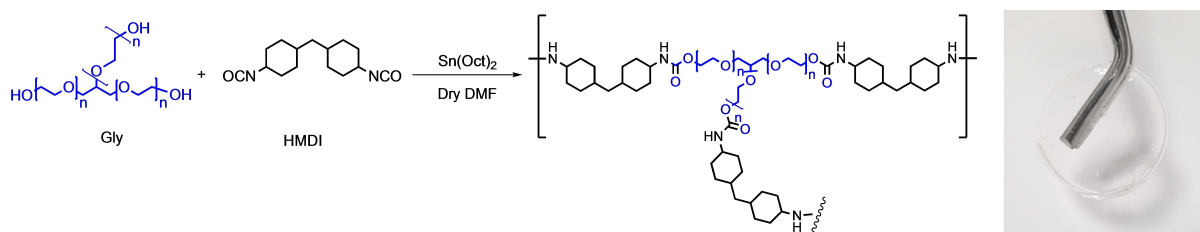
In our previous report we have reported thermoresponsive hydrogel membranes by combining glycerol ethoxylate based trialkyne and different diazide monomers using photo-triggered Cu(I)-catalysed click chemistry.^[22] In this present work we tried to avoid the extra synthetic step which was followed in the previous report (to make different diazide and dialkyne) and showed a very easy and straightforward method to synthesize novel thermoresponsive polyurethane from glycerol ethoxylate,

which is a tri-arm PEG and dicyclohexyl diisocyanate in a one pot system. Herein, glycerol ethoxylate is acting as the soft segment and the hydrophobic dicyclohexyl diisocyanate as the hard segment. By varying the mole ratio between the two monomers we were able to tune the LCST and glass transition temperature of obtained polyurethanes. The swelling and deswelling behavior of the membranes are systematically examined. The mechanical properties of the membranes are studied by universal tensile testing measurements.

Results and Discussion

Synthesis and characterization of crosslinked membranes

Several polyurethanes (PU1-PU5) have been synthesized by copolymerization of diisocyanate with glycerol ethoxylate moiety (Scheme 1). The mole ratio of the two comonomer was varied to prepare different polymers. The FTIR spectra of the pure PU polymers are shown in Figure 1. The FTIR stretching frequency at 3320 cm⁻¹ are attributed to the NH band. The strong isocyanate band 2270 cm⁻¹ are absent in PU1-PU5, indicating complete conversion of the HMDI during synthesis.



Scheme 1. Synthesis of thermo-responsive polyurethane prepared in this work. The picture on the right shows the transparent film obtained after demoulding.

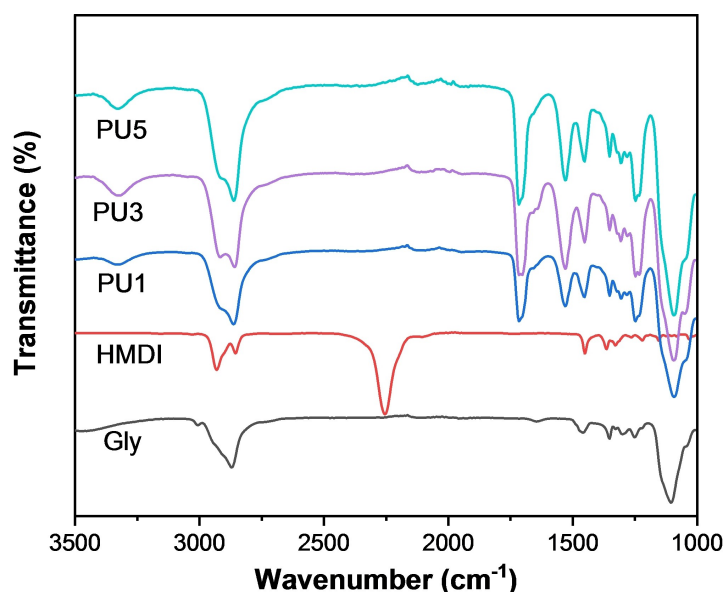


Figure 1. Comparative FTIR spectra of glycerol ethoxylate (Gly), HMDI and different polyurethanes (i.e., PU1, PU3 and PU5).

The signals around 1720 cm^{-1} and at 1550 cm^{-1} confirm successful urethane linkage formation.

It is worth mentioning that we also succeeded to scale up the synthetic process 10 times, leading to the formation of larger membranes (i.e., 10-cm diameter membranes were easily obtained using 10-cm diameter Petri dishes as moulds).

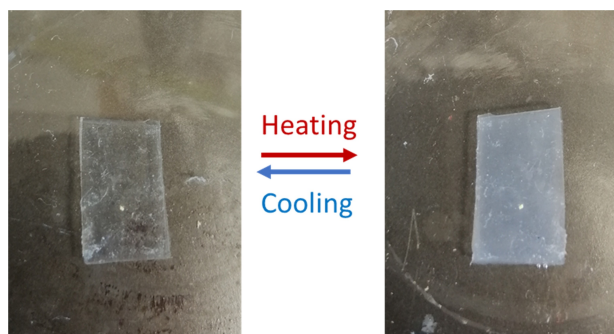


Figure 2. Thermoresponsive behavior of crosslinked gel (PU1).

Table 1. Summary of polyurethane synthesis.					
Polymer	[OH]:[NCO] (ratios in moles)	Topology of the polymer ^[a]	LCST [°C]	T _g [°C]	SR _e [%]
PU1	1:1	Crosslinked membrane	57 ^[b]	-42.8	397
PU2	1:0.5	HB polymer	ND	-54.6	-
PU3	0.5:1	Crosslinked membrane	ND	-19.9	169
PU4	1:0.7	HB polymer	60.3 ^[c]	-50.8	-
PU5	0.7:1	Crosslinked membrane	ND	-32.1	121

[a] Abbreviations: HB = hyperbranched polymer, ND = not determined. [b] LCST determined from DSC. [c] LCST determined from and UV-vis.

Thermoresponsive behavior of membranes

With an increase in temperature, the gel was slowly transformed from transparent to opaque (Figure 2). The LCSTs of the crosslinked PU membranes were determined by differential scanning calorimetry (DSC) and the results are summarized in Table 1. Endothermic peaks in thermograms (Figure 3) represent the LCST of PU membrane where heat is required to break the intermolecular hydrogen bonds existing between water molecules and polymer chains. Figure 3 indicates that the LCST of PU1 is 57°C with an additional signal at $75\text{--}80^\circ\text{C}$. The signals observed at $75\text{--}80^\circ\text{C}$ for PU1-PU3, endothermic in character, are because of the heat change due to the slow evaporation of water. In case of PU2, PU3, we did not observe any phase transition below 75°C .

Furthermore, the polymers such as PU2 and PU4 were soluble in water and LCST was determined by UV-vis spectroscopy (Figure 4). With an increase in temperature, the solution was slowly transformed from transparent to turbid (Figure 4), indicating the thermoresponsive property of polymers due to the presence glycerol ethoxylate moiety. In case of polymer PU2, no LCST have been observed because of the presence of higher amount glycerol ethoxylate or lower amount of hydrophobic monomer (HMDI). Apparently, a higher content of hydrophobic units will decrease the amount of intermolecular polymer-polymer hydrogen bonding and thus less temperature is necessary to break the hydrogen bonds. Moreover, the maintenance of transmittance of pure glycerol ethoxylate within the studied temperature interval (Figure 4) also indicate that the LCST is a consequence of the PU formation.

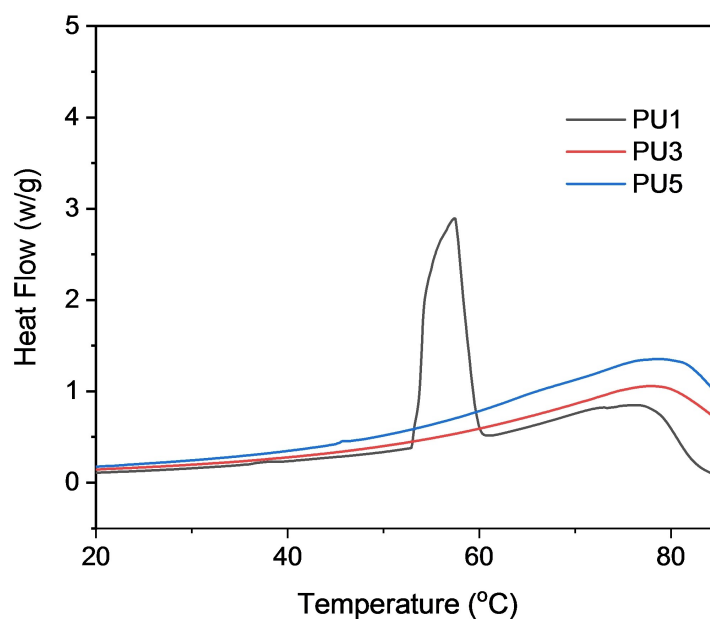


Figure 3. DSC curves of different hydrogel membranes (i.e., PU1, PU3 and PU5).

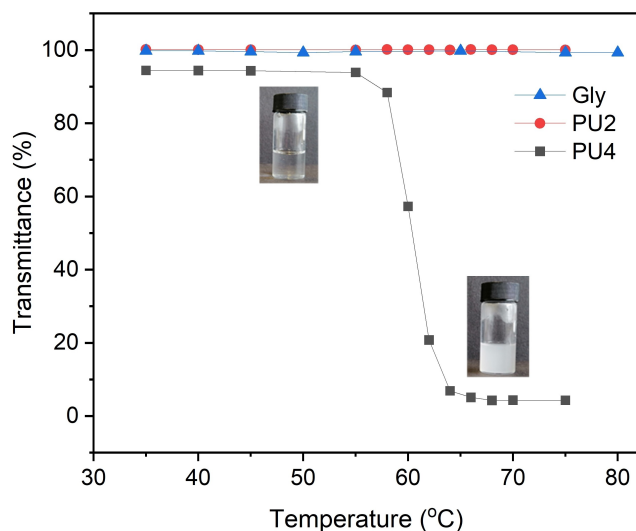


Figure 4. Variation of transmittance with temperature for the aqueous solutions (2.0 mg/mL) of pure Gly (glycerol ethoxylate), PU4 and PU2 polymers.

Swelling and deswelling kinetics

The swelling ratio of different sets of crosslinked membranes was investigated in DI water at 23 °C. Swelling ratios (SR_e) were calculated using equation 1 at room temperature by placing a weighed amount of the hydrogel in water for 24 h to reach the equilibrium swelling. Afterwards, the swollen gel was taken out from the water, wiped with moist tissue paper and weighed. The SR_e values of all the hydrogels are represented in Table 1. As shown in Figure 5A, the PU1 gel showed higher SR_e compared to PU3 and PU5 membrane due to the higher content of hydrophilic glycerol ethoxylate moiety. This result also allows us to understand the lack of endothermic signals attributed to the LCST behavior of PU3 and PU5 in Figure 3, since a lower water content correlates with less water-polymer interactions, reducing the amount of detectable heat.

The deswelling profile of PU hydrogel films are given in Figure 6. The deswelling kinetics of previously swollen hydrogel samples were studied by analyzing the % of water retention as

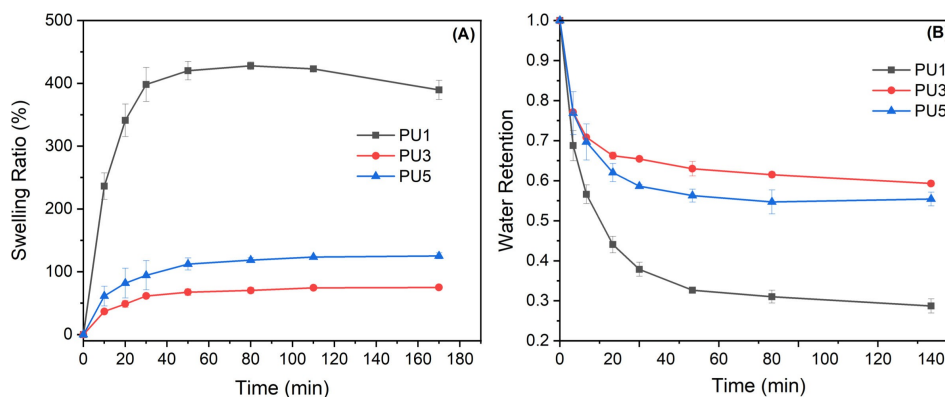


Figure 5. Comparison of (A) equilibrium swelling ratios and (B) water retention upon deswelling of different membranes PU1, PU3 and PU5.

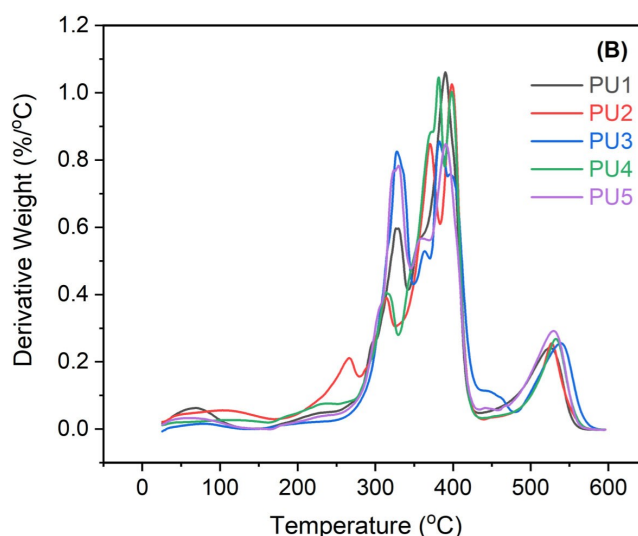
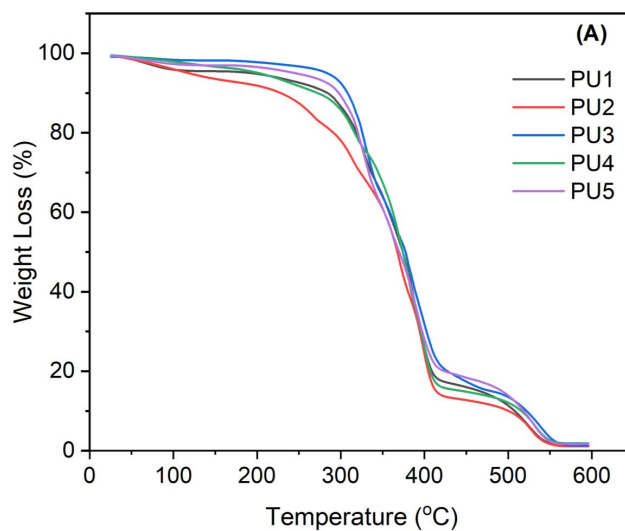


Figure 6. (A) TGA and (B) DTG thermograms of different polyurethanes.

a function of the water absorption time in hot water (50 °C). The deswelling rate of the hydrogel samples varies on the feed ratio of the two different monomers. For all hydrogels, the water

retention dropped quickly in the initial stage of heating and then decreased slowly since the driving force for deswelling was progressively reduced upon the dehydration of the gels and reached its maximum. It is worth to mention that membranes having higher amount of glycerol ethoxylate moiety had more affinity for water molecules, while also acting as a water-releasing channel when dehydration happened, thereby helping the network to shrinkage more sufficiently.^[23] For the water retention of the PU3 hydrogel was reduced to about 65% whereas that of PU1 hydrogel reached a steady-state value of 30% after 60 min (Figure 5B).

Thermal properties

In the next step, TGA and DTG analysis were performed to know the thermal stability of our synthesized polyurethanes in dried state. At first sight, TGA thermograms (Figure 6A) show that all samples exhibit a two-step degradation, being the first step observed at 300–400 °C, while the second one around 400–500 °C. However, when DTG curves (Figure 6B) were analyzed, these materials revealed a more complex degradation profile. In this sense, the mass loss between 300–400 °C can be separated into two main processes. The first one, centered at 330 °C, is characterized by a single peak which intensity can be correlated with the content of dicyclohexyl diisocyanate units present in the material. Thereby, it would seem feasible to relate this degradation with the elimination of fragments containing these entities after the cleavage of urethane bonds, reported to occur below 300 °C.^[24] The second process occurring between 350 °C and 400 °C, can be visualized as a multiple peak signal and could arise from the decomposition of glycerol ethoxylate structures. Indeed, the multiple peaks detected within this region accuse subtle variations of the thermal

resistance for the same type of soft segments inside the sample. The above could be argued in terms of heterogeneity of crosslinking density since the degree of reticulation can modulate the thermal resistance of materials. Additionally, in case of PU2 polymer, we observed a degradation peak at 265 °C is presumably due to the presence of free glycerol ethoxylate. Finally, the mass loss observed in the range 400–550 °C could be attribute to the oxidative degradation suffered by the sample's residues, obtained after the earliest decomposition stages described above.^[25]

The effect of different equivalent glycerol ethoxylate and HMDI during polymerization on the glass transition temperature (T_g) of the synthesized polyurethane was determined by DSC and the results are shown in Figure 7. The T_g of PU1, PU2, PU3, PU4 and PU5 are –42.8, –54.6, –19.9, –50.8 °C and –32.1 °C, respectively. The T_g depends on the mobility/flexibility of the polymer chain, i.e., the higher the flexibility, the lower the T_g is. Herein the mobility or flexibility of the polymer chain depends on the amount of glycerol ethoxylate moiety present in the film. In the case of PU1, PU2 and PU4 the amount of glycerol ethoxylate moiety is higher compared to PU3 and PU5, and the amount of glycerol ethoxylate chain is present in the following order PU2 > PU4 > PU1 > PU5 > PU3 (Table 1) and the T_g is exactly in inverse order PU2 < PU4 < PU1 < PU5 < PU3. Moreover, regarding the crosslinked membranes, it was found that those having a lower [OH]/[NCO] ratio exhibited higher T_g values, which is in total accordance with the well-known relation between crosslinking density and glass transition temperature.^[26]

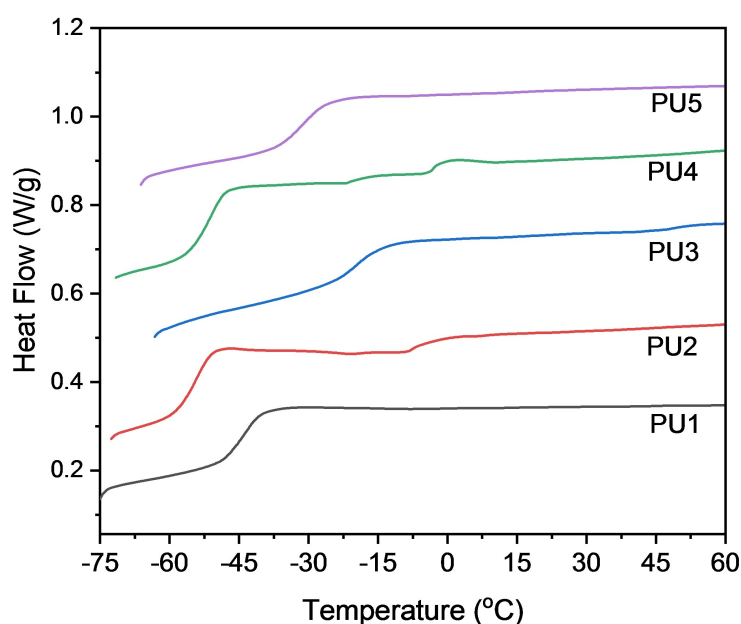


Figure 7. DSC plots corresponding to dry crosslinked membranes and polymers.

Table 2. Comparison of tensile properties of different membranes (i.e., PU1, PU3 and PU5).

Membrane	E [MPa]	[%]	σ [MPa]
PU1	0.35 ± 0.07	192.4 ± 24.4	0.35 ± 0.03
PU3	3.95 ± 0.36	101.9 ± 20.9	1.85 ± 0.19
PU5	0.91 ± 0.15	113.6 ± 36.1	0.56 ± 0.13

Tensile testing of the membranes

The mechanical strength of PU's were investigated by tensile testing. The tensile strength of PU3 was found to be much better than that of PU1 and PU5 (Table 2), showing higher tensile strength and Young's modulus (Figure 8). A correlation of these results with the chemical structures can be explained by considering the percentage of hard segment in each polymer, which was higher for PU3 than for PU5 and PU1. The observed tendency is also in good agreement with the expected crosslinking degree (PU3 > PU5 > PU1) based on the [OH]/[NCO] molar ratio used in each case. Additionally, elongation at break is higher for PU1 due to the presence of higher flexible unit i.e. glycerol ethoxylate moiety.

Conclusion

In conclusion, thermo-responsive polyurethanes can be easily prepared from glycerol ethoxylate and HMDI. Both the LCST and T_g of the polymer can be tuned by varying the monomer ratio. In this work, the crosslinked membrane with highest amount of hydrophilic glycerol ethoxylate showed the highest swelling ratio. The mechanical properties of the membrane were studied by universal tensile testing measurements, showing a Young's modulus, ultimate tensile strength and elongation at break (ϵ) break in the range of 0.35–0.91 MPa, 0.35–1.85 (E) MPa and 101.19–192.4%, respectively. Further efforts are underway in our laboratory to tune the LCST around physiological temperature and explore their potential biomedical application such as tissue engineering, temperature-controlled drug delivery as well as the fabrication of thermoresponsive shape-memory actuators.

Experimental Section

Materials

All reagents and solvents were purchased from commercial suppliers and used as received without further purification: Glycerol ethoxylate (average $M_n = 1000$ g/mol), dicyclohexyl diisocyanate (HMDI) (90 %) tin(II) 2-ethylhexanoate (92.5–100.0%).

Instrumentation

FTIR (Cary 630) spectroscopy was carried out on a spectrometer, equipped with a Diamond Single Reflection ATR-System. Differential scanning calorimetric (DSC) studies were acquired on a TA Instruments Q100 at 10 °C/min from room temperature to 150 °C aiming to test the thermoresponsive behavior of swelled samples and between –75 °C and 60 °C of dried samples to detect glass transition temperatures. The thermogravimetric analysis (TGA) was performed on a TA Instruments Q50 at a heating rate of 10 °C/min in O₂/Air (20:80) atmosphere. The UV-vis spectroscopic measurements were performed using a Perkin-Elmer Lambda 35 UV-vis spectrophotometer.

Synthesis of crosslinked membranes

In a typical example, glycerol ethoxylate (0.7 mmol, 0.7 g), dicyclohexyl diisocyanate (HMDI) (1.05 mmol, 0.305 g) and tin(II) 2-ethylhexanoate (2 mol% of polyol) were dissolved in 1.0 mL of dry DMF and heated at 50 °C for 2 h. Then, the crosslinked membrane was washed by using DI water (i.e., immersion overnight) and dried in a vacuum oven at 35 °C for two days, obtaining a transparent and flexible membrane.

The preparation of 10-cm diameter membrane was achieved following the same procedure using glycerol ethoxylate (7.92 mmol, 7.92 g), dicyclohexyl diisocyanate (11.9 mmol, 3.5 g) and tin(II) 2-ethylhexanoate (2 mol% of polyol) solubilized in 2 mL of dried DMF. A 10-cm glass Petri dish was used as mold. Mass of the dried membrane = 10.768 g; mass of the hydrated membrane = 18.416 g.

Determination of LCST

The LCSTs of the swollen hydrogel films were measured using DSC. Membranes were allowed to swell completely for at least 24 h in deionized water. The extra water on the membrane surface was gently wiped with a wet tissue paper. The sample was sealed in the T-zero pan and the mass was noted and carefully placed along with a reference pan on the heater. Then, samples were heated from 25 °C to 120 °C at a rate of 2 °C/min under a dry nitrogen atmosphere. Nevertheless, for water soluble polymer 2 mg/mL polymer solution was prepared and transferred to a UV cuvette. Then, the turbidity of the solution was measured using a UV-vis

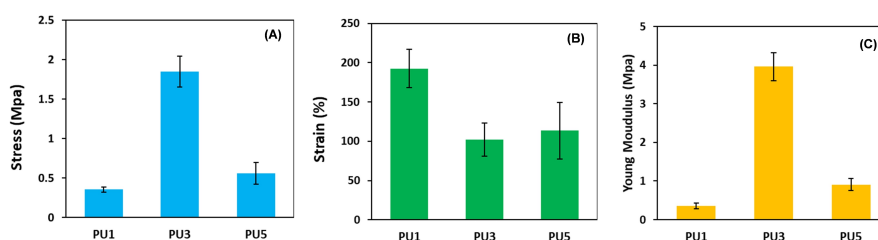


Figure 8. Variation of the (A) stress at break, (B) elongation at break and (C) Young's modulus with different membranes (i.e., PU1, PU3, PU5).

spectrophotometer by monitoring the transmittance (%T) changes at $\lambda = 500$ nm. The temperature was slowly increased from 25 to 70 °C and equilibrated the sample for 5 min at the measurement temperature and the %T value at 500 nm was recorded. The LCST was identified where a reduction of 50%T of the initial polymer solution was recorded.

Measurement of Swelling Kinetics

The equilibrium swelling ratio (SR_e) is defined as the ability to absorb water by the gel matrix with respect to its dry weight until a constant value is reached. The swelling behavior of the hydrogel membranes were carried out by gravimetric analysis at room temperature (23 °C). A small piece of hydrogel membrane was taken in a 20 mL vial and immersed in DI water. Then, the swollen hydrogel membrane was taken out carefully from the vial, wiped with wet tissue paper to remove the excess surface water and weighed on a dry Petri dish in different intervals of time. The SR_e was calculated using [Equation (1)]:

$$\text{Swelling ratio}(SR_e\%) = \frac{W_t - W_d}{W_d} \cdot 100 \quad (1)$$

where W_t is the weight of the swollen hydrogel at time t and W_d is the weight of the dry hydrogel.

Measurement of Deswelling Kinetics

The deswelling study was performed gravimetrically at 50 °C. A small piece of the PU hydrogel was first immersed in water at 22 °C until equilibrium swelling was reached. The equilibrated hydrogels were then immediately transferred into a hot water bath at 50 °C. Then, hydrogels were taken out from the hot water at different time intervals and weighed after wiping off the excess surface water by moist tissue paper. Water retention was calculated by using [Eq. (2)]:

$$\text{Water retention} = \frac{W_t - W_d}{W_o - W_d} \quad (2)$$

where W_t is the weight of the hydrogel at time t and W_o is the weight of the swollen hydrogel below the LCST at equilibrium.

Tensile testing

The mechanical properties were carried out with a Zwick Z2.5/TN1S testing machine in stress-strain experiments, which performed at a deformation rate of 1 mm/min. The mechanical parameters were averaged from a minimum of 5 measurements for each polymer sample. Samples (PU1, PU3 and PU5) with a length of 30 mm, a width of 1 mm, and an average thickness of 500 μm , were cut off from polymer films and used for the evaluation of mechanical properties.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: copolymerization · critical solution temperatures · polyurethanes · tensile strength · thermoresponsive materials

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