

# Calorimetric study of hydrated poloxamer-based polyurethanes - thermoresponsive transition and peculiar antiplasticization

Izabela Łukaszewska\*, Artur Bukowczan, Edyta Hebda,  
Konstantinos N. Raftopoulos, and Krzysztof Pielichowski

*Department of Chemistry and Technology of Polymers, Cracow University of Technology, Ul. Warszawska 24,  
31-155, Kraków, Poland*

## 1. Introduction

Over years, attentiveness to the field of thermoresponsive polymers has grown, and a significant amount of work has been dedicated to develop temperature sensitive macromolecules that can be crafted into new smart materials.<sup>1</sup> Nevertheless, some issues still need addressing. Predominantly, thermoresponsive polymers have no dimensional stability in the hydrated state, and thus the application range of such materials in topical drug delivery systems is limited. Enhancement of the mechanical properties requires strengthening of the polymer network.<sup>2</sup> Polyurethane block copolymers are the class of materials that is known for good mechanical properties and strong polymer networks.<sup>3</sup> Furthermore, polyurethane systems have been thoroughly studied as the materials for biomedical applications and are widely used in many medical fields, from tissue engineering and scaffolds, through the medical implants and surgical instruments, to ultimately microscale encapsulation devices.<sup>4</sup>

An approach towards the development of dimensionally stable thermoresponsive polymers is to introduce a common thermoresponsive polymer, such as a poloxamer, as a polyol agent in polyurethane block copolymers. Poloxamers are triblock copolymers of poly(propylene oxide) (PPO) and poly(ethylene oxide) (PEO).

This study shows that this approach can be applied to form materials of enhanced mechanical properties in which thermoresponsive transition still persists.

## 2. Experimental

### a. Materials

Polyurethane elastomers were synthesized via the standard two-step prepolymer method. First step of the synthesis consisted of reacting excess amount of Isophorone diisocyanate with the L-64 poloxamer (copolymer PPO-PEO-PPO of average molar mass 2900 g/mol and PEO content 40% wt%). The second step was chain extension by butanediol. The exact synthesis route has been described in our previous work.<sup>5</sup>

Polyurethane elastomers of soft segments content of 40 wt.% (SS-40), 50 wt.% (SS-50), 60 wt.% (SS-60), 65 wt.% (SS-65), 70 wt.% (SS-70) were synthesized.

### b. Equilibrium water sorption isotherms

Samples of approx. 500 mg were conditioned at different relative humidities (RH over saturated solutions of appropriately selected salts [citation to Greenspan]). Upon equilibration the mass was recorded and the water uptake was calculated with respect to the dry sample. Dry mass was determined by equilibration over P<sub>2</sub>O<sub>5</sub>.

### c. Calorimetry

Differential scanning calorimetry (DSC) was used to determine the glass transition temperature of the materials. Experiments were performed with a Mettler Toledo 823e differential scanning calorimeter, purged with argon and calibrated with indium. Samples of 5 to 8 mg were conditioned over saturated solutions of salts were used.

### 3. Results and discussion

Polyurethane elastomers of soft segments content of 40 wt.% (SS-40), 50 wt.% (SS-50), 60 wt.% (SS-60), 65 wt.% (SS-65), 70 wt.% (SS-70) were synthesized.

#### a. Hydration protocol

Figure 1 shows water uptake of conditioned materials as a function of RH (a) and dependence of water uptake on SS content (b). For RH values up to 57% the data exhibit practically linear dependence, whilst at higher RH conditions an upward concaving is observed. A similar behaviour has been reported before by P. Pissis et al.<sup>6</sup> The positive deviations from linear dependence is a result of the formation of water clusters.<sup>6</sup>

Interestingly the water uptake is not monotonic with the poloxamer content with stronger absorption observed at 60 wt% (Figure 1b).

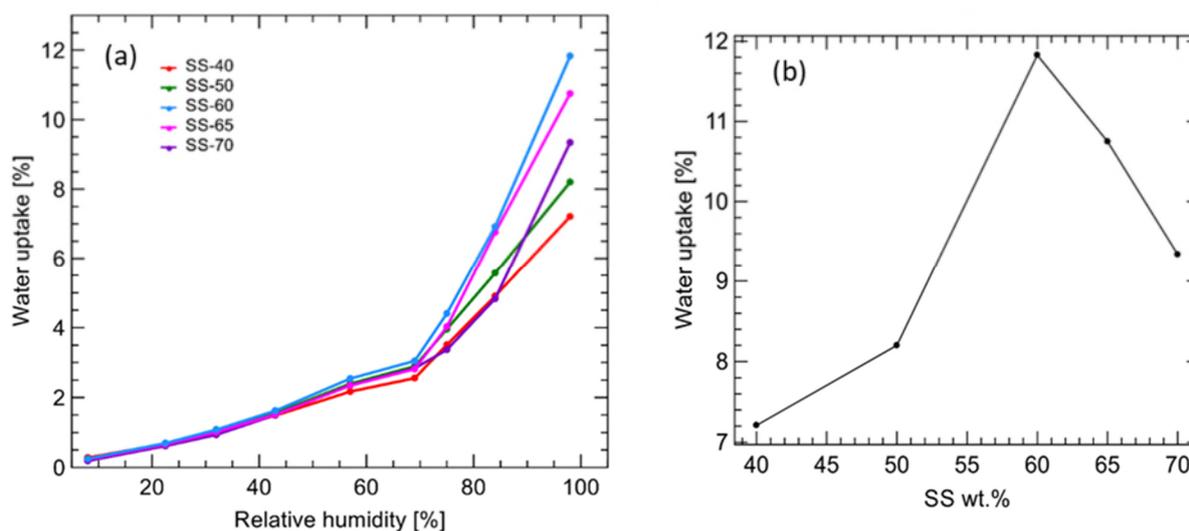


Figure 1: Equilibrium water sorption isotherms at 25°C (a) and water uptake for conditioned materials at RH=98% versus soft segment content (b)

This may be related to a higher degree of phase separation. Water can be absorbed by the poloxamer as well as by the urethane groups along the chain. In better phase separated materials, many urethane groups are h-bonded with each other, not allowing for their hydration.

#### b. Glass transition in the dry materials

Glass transition temperatures ( $T_g$ ) of the dry polyurethanes are higher  $\sim 10$  °C than the glass transition temperature for poloxamer (Figure 2). Higher glass transition temperatures for polyurethane in comparison to the polyol agent is very well known in literature and is associated with incomplete phase separation (mixing of hard and soft segments), which means that hard segments are diluted in the soft phase and slow down its mobility.<sup>7</sup> The glass transition temperatures of obtained elastomers do not differ significantly. The highest value is observed for 60 wt% of soft segments, presumably as a result of the lowest degree of phase separation.

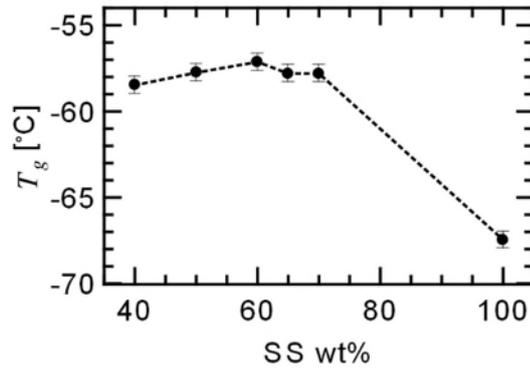


Figure 2:  $T_g$  (a) and  $\Delta c_p$  normalized to soft segment content ratio (b) as a function of soft segment content

**c. Materials equilibrated at 98%. Thermoresponsive transition.**

Figure 3 shows the DSC curves for elastomers conditioned at relative humidity of 98%. In the temperature range 40-70 °C endothermic peaks on cooling curves and exotherm peaks on heating curves are visible for all studied materials. Those peaks correspond to **reversible thermoresponsive transitions**. Indeed, the material at room temperature is transparent, but when mildly heated it becomes milky, and upon cooling down it becomes transparent again (Figure 4). This behaviour should be associated to the thermoresponsive transition of the poloxamer, i.e. its transition from water soluble at low temperatures to insoluble at the so called lower critical solution temperature (LCST) <sup>8</sup>.

The endotherms are broad and asymmetric, and spread over approximately 15-30 °C. Similar behaviour was observed for aqueous solutions of poloxamers and was associated with micellization of poloxamers in solutions as response to temperature change.<sup>9</sup> No significant hysteresis is observed.

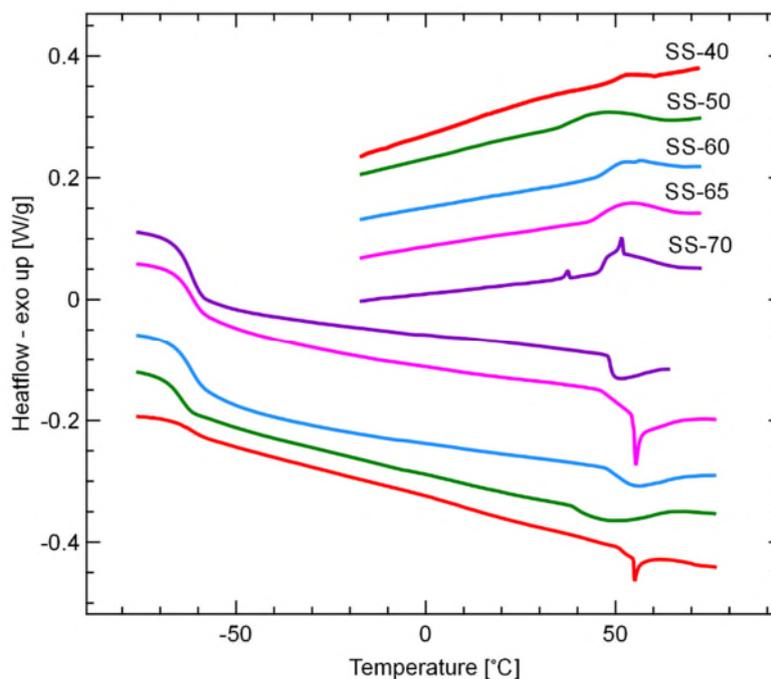


Figure 3: DSC curves for polyurethanes conditioned at relative humidity 98%

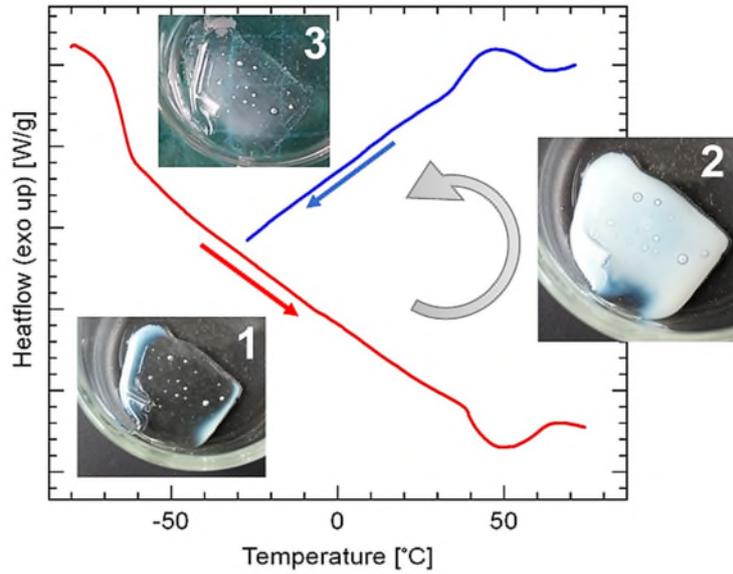


Figure 4: Thermoresponsive behaviour of the synthesized polyurethane SS-50 (DSC spectra and corresponding photographs): 1-before thermoresponsive transition, 2-after thermoresponsive transition, 3-after reverse transition. The curves have been translated for clarity.

#### d. Glass transition and hydration

Figure 5 shows the dependence of  $T_g$  of studied materials on the relative humidity at which the samples were conditioned and the glass transition temperatures of the studied polyurethanes as a function of water uptake. An upward tendency in the values of  $T_g$  is observed in the humidities range up to 75%, which is counterintuitive since due to the plasticization effect the  $T_g$  should be affected contrariwise, as water is expected to accelerate molecular mobility and thus decrease the  $T_g$ .<sup>10,11</sup> Only at higher temperatures the expected plasticization is observed.

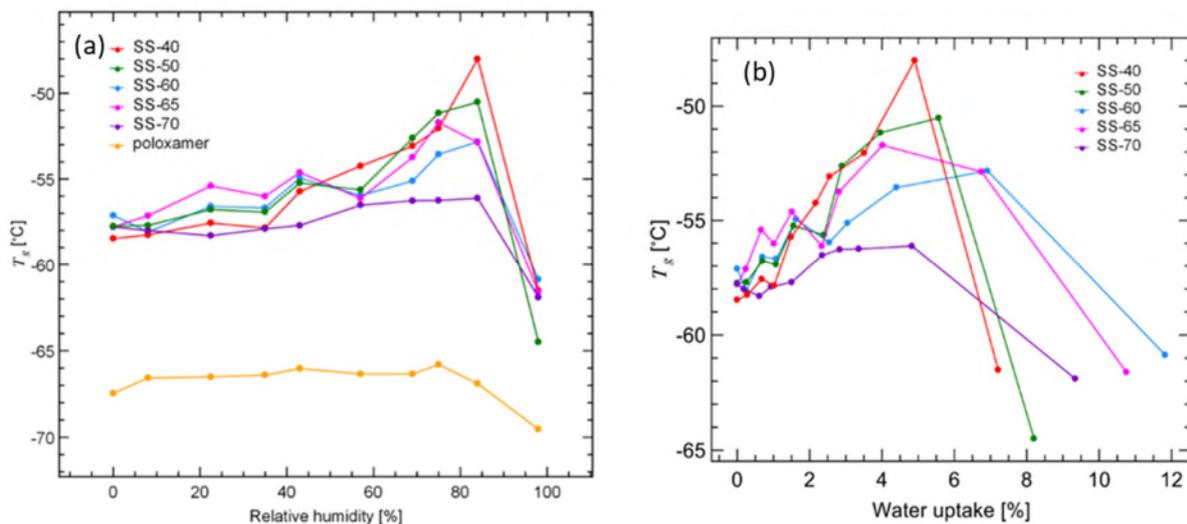


Figure 5: The dependence of  $T_g$  of studied materials on the relative humidity at which the samples were conditioned (a) and the glass transition temperatures of the studied polyurethanes as a function of the water uptake (b)

This counterintuitive behaviour can be a result of two mechanisms. The first is that water molecules may disrupt the hydrogen bonding and thus decrease the degree of phase separation. The second is the often disregarded phenomenon, that when a plasticizer is introduced in a system, the

two components may interact with each other enthalpically, thus causing deviations from Fox or Gordon-Taylor behaviour.<sup>12</sup> In the case at hand, when only few water molecules are in the system, they may be associated with two hydration points and thus act as bridges between adjacent chains or segments, as a result of which the mobility of the polymer is restricted. The effect is counteracted as more water is introduced in the system, and the probability of bridging is reduced.<sup>5</sup>

#### 4. Conclusions

In this work, it is exhibited that poloxamers can retain their thermoresponsive behaviour even when introduced in a dimensionally stable polyurethane elastomer. Immersion in water is not needed, and phenomena associated with the transition are already visible upon exposure at relative humidity of 98%.

The footprint of the thermoresponsive transition in DSC curves is a broad complex endothermic peak during heating. The phenomenon is reversible upon cooling, observed as an equivalent exothermic peak with negligible hysteresis.

As exhibited by an increase of  $T_g$  with water content, small amounts of water cause a counterintuitive antiplasticization, presumably due to disruption of phase separation or bridging of nearby segments by water molecules.

It will be interesting in future works to study the observed phenomena with morphological techniques like small angle scattering.

#### 5. References

1. Roy, D., Brooks, W. L. A. & Sumerlin, B. S. New directions in thermoresponsive polymers. *Chem. Soc. Rev.* **42**, 7214–7243 (2013).
2. Petrini, P., Farè, S., Piva, A. & Tanzi, M. C. Design, synthesis and properties of polyurethane hydrogels for tissue engineering. *J. Mater. Sci. Mater. Med.* **14**, 683–686 (2003).
3. Qiu, Y., Hamilton, S. K. & Temenoff, J. Improving mechanical properties of injectable polymers and composites. *Inject. Biomater.* 61–91 (2011)
4. Davis, F. J. & Mitchell, G. R. Polyurethane based materials with applications in medical devices. in *Bio-Materials and Prototyping Applications in Medicine* (eds. Davis, F. J. & Mitchell, G. R.) 27–48 (Springer, 2008).
5. Raftopoulos, K. N. *et al.* Molecular and charge mobility of a poloxamer in the bulk and as soft component in polyurethanes. *Polymer (Guildf)*. **182**, (2019).
6. Pissis, P., Apekis, L., Christodoulides, C., Niaounakis, M. & Kuritsis, A. Water Effects in Polyurethane Block Copolymers. *J. Polym. Sci. Part B Polym. Phys.* **34**, 1529–1539 (1996).
7. Chen, T. K., Chui, J. Y. & Shieh, T. S. Glass transition behaviors of a polyurethane hard segment based on 4,4'-diisocyanatodiphenylmethane and 1,4-butanediol and the calculation of microdomain composition. *Macromolecules* **30**, 5068–5074 (1997).
8. Ward, M. A. & Georgiou, T. K. Thermoresponsive polymers for biomedical applications. *Polymers (Basel)*. **3**, 1215–1242 (2011).
9. Artzner, F. *et al.* Interactions between poloxamers in aqueous solutions: Micellization and

gelation studied by differential scanning calorimetry, small angle X-ray scattering, and rheology. *Langmuir* **23**, 5085–5092 (2007).

10. Kanapitsas, A. *et al.* Molecular mobility and hydration properties of segmented polyurethanes with varying structure of soft- and hard-chain segments. *J. Appl. Polym. Sci.* **71**, 1209–1221 (1999).
11. Hulleman, S. H. D., Janssen, F. H. P. & Feil, H. The role of water during plasticization of native starches. *Polymer (Guildf)*. **39**, 2043–2048 (1998).
12. Brostow, W., Chiu, R., Kalogeras, I. M. & Vassilikou-Dova, A. Prediction of glass transition temperatures: Binary blends and copolymers. *Mater. Lett.* **62**, 3152–3155 (2008).