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Solvent stimulated actuation of polyurethane-based shape memory polymer foams using dimethyl sulfoxide and ethanol

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Abstract

Solvent exposure has been investigated to trigger actuation of shape memory polymers (SMPs) as an alternative to direct heating. This study aimed to investigate the feasibility of using dimethyl sulfoxide (DMSO) and ethanol (EtOH) to stimulate polyurethane-based SMP foam actuation and the required solvent concentrations in water for rapid actuation of hydrophobic SMP foams. SMP foams exhibited decreased T_g when submerged in DMSO and EtOH when compared to water submersion. Kinetic DMA experiments showed minimal or no relaxation for all SMP foams in water within 30 min, while SMP foams submerged in EtOH exhibited rapid relaxation within 1 min of submersion. SMP foams expanded rapidly in high concentrations of DMSO and EtOH solutions, where complete recovery over 30 min was observed in DMSO concentrations greater than 90% and in EtOH concentrations greater than 20%. This study demonstrates that both DMSO and EtOH are effective at triggering volume recovery of polyurethane-based SMP foams, including in aqueous environments, and provides promise for use of this actuation technique in various applications.

Keywords

shape memory polymer; SMP foam; solvent; actuation

1. Introduction

Shape memory polymers (SMPs) are promising materials due to their ability to maintain a temporary shape and subsequently recover their original shape in response to a thermal, chemical, or optical stimulus [1–3]. Thermoresponsive SMPs act about a transition temperature (T_{trans}), where below T_{trans} , low polymer chain mobility holds the SMP in its temporary shape and above T_{trans} , high polymer chain mobility allows entropic forces in the polymer chains to recover the original shape of the SMP. Porous SMPs exhibit volume expansion, high surface area-to-volume ratios, permeability, and thermomechanical properties that are advantageous for several applications including biomedical, aerospace, self-healing materials, and textiles [1, 4, 5].

Conflict of Interest

Shape Memory Therapeutics, Inc. holds the license for medical application of the technology discussed in this work. The authors disclose that DJ Maitland is a founder, board member, shareholder, and employee of SMT. Furthermore, A J Boyle, L D Nash, and S M Hasan are employed by SMT and, in addition to A C Weems, hold stock options with SMT.

Solvent exposure has been investigated to trigger SMP actuation as an alternative to direct heating or stimulation by electricity, light, or magnetic fields [6–8]. Solvent exposure promotes SMP actuation by plasticizing the polymer chains, thereby increasing chain mobility and lowering T_{trans} below the environment temperature. Previous studies have focused on water as the actuating solvent, which is not ideal for several applications where water exposure is common to the environment [6, 7, 9]. With water-responsive SMPs, water exposure can result in decreased stiffness and stimulate actuation prior to successful placement of the material, reducing the effectiveness of porous SMPs for applications such as water filtration, textiles, and clinical embolic vascular devices. Porous polyurethane SMP foams have been reported as water-responsive materials [10, 11]. Singhal *et al* reported that increasing SMP foam hydrophobicity resulted in delayed actuation in aqueous environments, but the actuated volume was severely reduced [10]. Actuation of non-water-responsive SMPs with an alternative solvent can provide controlled SMP expansion without direct heating and minimize the negative effects of water plasticization on material performance and mechanical properties.

This study aims to investigate the feasibility and sensitivity of solvent-stimulated SMP foam actuation with an initial focus of aqueous environments of biomedical applications. Two organic solvents were chosen due to an expectation of effective polyurethane plasticization and their previous use in biomedical applications: dimethyl sulfoxide (DMSO) and ethanol (EtOH). DMSO has been used as a solvent in trans-dermal drug delivery and liquid embolic materials [12, 13]. EtOH has also been studied for liquid embolic applications and for use as a parenteral solvent [14–16]. However, both DMSO and EtOH have been shown to have concentration dependent toxicological effects, indicating a need for using diluted solvent solutions for biomedical applications [14, 15]. SMP foam compositions with varying hydrophobicity were investigated for changes in thermo-mechanical properties and shape recovery when exposed to water and varying concentrations of organic solvents.

2. Methods

2.1. SMP foam fabrication

Polyurethane-based SMP foams were synthesized using a two-step method with aliphatic isocyanate and hydroxyl monomers as previously reported [10, 17]. Trimethyl-1,6-hexamethylene diisocyanate, 2,2,4- and 2,4,4- mixture (TMHDI, TCI America Inc.), isophorone diisocyanate (IPDI, 98%; Sigma-Aldrich Inc.), N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine (HPED, 99%; Sigma-Aldrich Inc.), triethanolamine (TEA, 98%; Sigma-Aldrich Inc.), DC 198 (Air Products and Chemicals, Inc.), DC 5943 (Air Products and Chemicals, Inc.), T-131 (Air Products and Chemicals, Inc.), BL-22 (Air Products and Chemicals, Inc.), Enovate 245fa Blowing Agent (Honeywell International, Inc.) and deionized (DI) water (>17 M Ω cm purity; Millipore water purifier system; Millipore Inc.) were used as received. SMP foam compositions were synthesized with 0, 10, and 20 mol% of IPDI, with the remaining isocyanate mol% comprised of TMHDI, as previously reported by Hasan *et al* [17]. The SMP foam compositions are denoted by the respective mol% of IPDI as 0IPDI, 10IPDI, and 20IPDI.

After the synthesis, SMP foams were processed before being cut into blocks for reticulation. As reported by Rodriguez *et al* a mechanical wire punch apparatus was used for reticulation [18]. 8 mm diameter, 2 to 3 cm long cylindrical samples were cut from the foam blocks using a biopsy punch. The foam samples were radially compressed to 1 mm diameter using a SC250 stent crimper (Machine Solutions, Inc., Flagstaff, AZ), heated to 100 °C, and subsequently heated to expand to their original shape. SMP foam cylinders were then acid etched, cleaned under sonication, and dried under vacuum, as previously reported [17]. Foam samples were stored in a sealed container with desiccant.

2.2. SMP foam density and pore diameter

SMP foam density was measured for each composition. Bulk foams were cut into cubes using a resistive wire cutter from three sections along the foaming axis in accordance with ASTM standard D-3574. The length of each cube edge was measured using calipers to calculate volume, mass was measured for each foam cube, and density was calculated.

Pore diameter was measured for each SMP foam composition. Each pore is approximately uniform in diameter in the transverse direction and elongated in the axial foaming direction. Cleaned SMP foam cylinders were cut into 2 to 3 mm thick slices along the axial and transverse directions. The samples were mounted on a stage and sputter coated with gold for 60 s at 20 mA using a Cressington Sputter Coater (Ted Pella, Inc., Redding, CA). Images were taken using a Joel NeoScope JCM-5000 scanning electron microscope (Nikon Instruments, Inc., Melville, NY) at 10 kV and 24× magnification under high vacuum. ImageJ software (National Institutes of Health, Bethesda, MD) was used to measure the maximum diameter of seven pores per sample in the axial and transverse directions for two samples of each foam composition.

2.3. Differential scanning calorimetry (DSC)

DSC using a Q-200 DSC (TA Instruments, Inc., New Castle, DE) was used to measure the glass transition temperature (T_g) for approximately 9 ± 3.0 mg of dry and solvent-swelled samples. The dry sample heating profile was ambient to -40.0 °C, isothermal for 2 min, ramp to 120 °C, isothermal for 2 min and repeat. The second heating cycle was used to find the half height transition (T_g) using TA instrument analysis software.

Solvent-swelled samples were first submerged in the selected solvent at 37 °C for 10 min before being mechanically compressed for 2 min to remove residual solvent. The samples were then sealed in TZero pans and placed in the DSC. Samples were cooled to -40 °C from ambient temp, followed by heating to 80 °C (DMSO and Water) or 60 °C (EtOH), isothermal for 2 min, cooled back to -40 °C, and then reheated to the same peak temperature. For all testing, the heating rate was 10 °C min^{-1} . A sample size of 3 was used for analysis.

2.4. Dynamic mechanical analysis (DMA)

DMA was performed to determine the mechano-thermal transitions in various solvents. A TT-DMA (Mettler-Toledo AG, Schwerzenbach, Switzerland) was used to perform kinetic and temperature sweeps, applying a static force of 0.04 N at a rate of 1 Hz, with a static to

dynamic force ratio of 1.5. Foam cylinders (6 mm diameter and 5 mm length) were heated to 100 °C and axially compressed to 0.8 mm before cooling to room temperature under compression.

Temperature sweeps were used to find the storage modulus (E') and loss modulus (E'') with the T_g measured as the temperature of the peak ratio of E'/E'' ($\tan \delta$). Solvent was cooled to 5 °C or the freezing point of the solvents before being ramped to approximately 70 °C at a rate of 1 °C min⁻¹. E' was normalized for each sample to the first measurement and plotted versus time. T_g values for each composition were compared to dry T_g values at $\tan \delta$ reported by Hasan *et al* [17]. Four samples were examined for each composition for each solvent.

Kinetic experiments were used to analyze the actuation of SMP foams submerged in solvent over time. Solvent was isothermal at 37 °C for 20 min before the sample was submerged, and measurements were recorded for 30 min. E' was normalized for each sample to the first measurement and plotted versus time. The n -values for each foam composition in water, DMSO, and EtOH were three, seven, and four, respectively, to account for variability in kinetic behavior. Kinetic experiments were correlated with temperature sweeps to ensure measurement accuracy.

2.5. Swelling ratio in solvent solutions

Swelling volume ratio was measured over time for each SMP foam composition in solvents. SMP foam discs (6 mm diameter and 4 to 5 mm length) were cut from cleaned and dried samples. A 0.09 mm diameter nickel–titanium (nitinol) wire (Nitinol Devices & Components, Inc., Fremont, CA) was placed through the disc axis. Sample were then imaged, and the sample diameter and length were measured using ImageJ software.

SMP foam samples were submerged in solvent solutions held at 37 °C ± 1 °C and imaged at fixed time intervals. An aluminum fixture was used to suspend the foam samples in the solution and act as a reference scale. Samples were submerged in solution and were imaged at 1 min intervals for 5 min of submersion and then at 5 min intervals to 15 min total submersion time. ImageJ software was used to measure the diameter and length of samples at each time point. Volume was calculated for the samples at each time point. Volume ratio % at each time point was calculated using (1). Volume ratio of 100% represents the initial volume, while 150% and 200% volume ratio indicate radial swelling of 1.14x and 1.26x, respectively. Swelling volume ratio was measured for 3 samples of each SMP foam composition in water, DMSO, and EtOH.

$$\text{Volume ratio \%} = \left(\frac{\text{Volume}_{\text{Submersion time point}}}{\text{Volume}_{\text{Initial}}} \right) \times 100. \quad (1)$$

2.6. Shape recovery in solvent solutions

Shape recovery was measured over time for each SMP foam composition in solvent solutions with varied concentrations. SMP foam cylinders (2.5 mm diameter and 1 cm

length) were cut from cleaned and dried samples using a biopsy punch. A 0.09 mm diameter nitinol wire was placed through the cylinder axis. The sample diameter and length were measured for each SMP foam sample using calipers to calculate pre-compressed volume. The SMP foam cylinders were radially compressed to 0.30–0.34 mm diameter using a SC250 stent crimper heated to 100 °C. Compressed samples were stored in a sealed container with desiccant for minimum of 24 h before testing.

SMP foam samples were submerged in solvent solutions held at $37\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$ and imaged at fixed time intervals. An aluminum fixture was used to suspend the foam samples in the solution and act as a reference scale. Samples were submerged in solution and were imaged at 1 min intervals for 10 min of submersion and then at 5 min intervals to 30 min total submersion time. ImageJ software was used to measure the diameter and length of actuated sections at each time point. Actuated volume was calculated for the cylindrical samples at each time point. Volume recovery at each time point was calculated using (1) where volume ratio of 100% represents the initial volume. Volume recovery was measured for three samples of each SMP foam composition in water, DMSO, and EtOH solutions. SMP foam samples were tested in DMSO concentrations of 100, 90, 80, 40, and 0 vol% in water and in EtOH concentrations of 100, 80, 50, 20, and 0 vol% in reverse osmosis (RO) water, where 0 vol% is the control in 100% RO water.

3. Results and discussion

3.1. SMP foam morphology

SMP foams were fabricated with similar stable morphology, as shown in figure 1. Cell membranes are still present with small pinholes created during the reticulation process, resulting in a high total surface area with interconnected pores that allow fluid flow through the foam volume [18]. SMP foams were fabricated with varying isocyanate ratios and similar average densities and average pore sizes, as shown in table 1. All SMP foam compositions exhibited transverse anisotropy, where pore diameter is greater in the axial direction than in the transverse direction.

3.2. Glass transition temperature shift

SMP foam glass transition temperatures varied in response to exposure to different solvents with greatest decreases in T_g after exposure to EtOH. Average T_g values for each SMP foam composition measured using DSC and DMA in the dry condition and after submersion in water, DMSO, and EtOH are shown in table 2. 20IPDI was the only composition to exhibit a water-submerged T_g above body temperature ($37\text{ }^{\circ}\text{C}$), indicating minimal actuation at body temperature. Increasing IPDI content resulted in an increase in T_g in all cases when measured by DMA, due to decreased bond rotation. However, 10IPDI foams demonstrated lower T_g than both 0IPDI and 20IPDI foams with solvent exposure when measured by DSC. This suggests increased plasticization of 10IPDI foams, particularly in DMSO, though there is insufficient data to conclude any statistical significance. From these results, it is suggested that increasing IPDI content is effective at muting or preventing SMP actuation in water while allowing for actuation in DMSO and EtOH.

3.3. Actuation kinetics and profiles

Kinetic experiments exhibited distinct actuation transitions in the relaxation behavior of the SMP foams submerged in DMSO and EtOH at 37 °C. Relaxation times were longest in water and shortest in EtOH as shown in figure 2, where the normalized storage modulus is shown for 20IPDI in each solvent. For water and DMSO, no relaxation behavior was seen within 30 min, as demonstrated by the lack of a decreasing inflection in the normalized modulus. However, DMSO does begin to show reduction in modulus within the examined time, contrasted to the modulus increase exhibited in water. In contrast, SMP foams in EtOH demonstrated rapid relaxation within 1 min. The increased rate of actuation for all foams in EtOH compared to in DMSO is supported by table 1, where average T_g values are 8 °C–19 °C less in EtOH compared to DMSO values. Figure 3 illustrates the actuation behavior of all foam compositions submerged in EtOH. 0IPDI and 10IPDI foams actuated at a slightly increased rate in EtOH compared to 20IPDI, though high variance was observed and relaxation time differed by less than 1 min.

Swelling tests showed significant increase in SMP foam volume after submersion in DMSO and EtOH and minimal to no volume increase in water. All SMP foam compositions exhibited noticeable swelling within 5 min of exposure to DMSO and within 2 min of exposure to EtOH as shown in figure 4. Volume ratio of 100% represents the initial volume, while greater than 100% volume recovery represents solvent swelling into the polymer, where 150% and 200% volume recovery indicate radial swelling of 1.14x and 1.26x, respectively. 10IPDI foam experienced swelling to greater than 175% volume in both solvents. However, decreased IPDI resulted in greater swelling in DMSO while increased IPDI resulted in greater swelling in EtOH. SMP foams experienced less swelling in water, exhibiting volume ratio % values of $104\% \pm 1.7\%$ for 0IPDI, $109\% \pm 8.3\%$ for 10IPDI, and $108\% \pm 1.4\%$ for 20IPDI after 15 min exposed to water.

Volume recovery testing demonstrated that submersion in water resulted in minimal foam actuation for all compositions while DMSO and EtOH both stimulated actuation with a solvent concentration dependence, as shown in figures 5 and 6. Figure 7 shows selected images of the foam actuation in 100% and 20% EtOH solutions. All SMP foam compositions actuated to less than 15% volume recovery in water after 30 min, with 20IPDI actuating the least amongst compositions to less than 3% volume recovery. All SMP foam compositions exhibited greater than 100% volume recovery in 100% and 90% DMSO solutions after 20 min submersion. However, minimal actuation was observed in DMSO concentrations less than 90%, with only 10IPDI in 80% DMSO actuating greater than 30% volume recovery. All SMP foam compositions exhibited greater than 100% volume recovery in 100% and 80% EtOH solutions after 3 min submersion. 0IPDI and 20IPDI actuated to greater than 100% volume recovery in 50% EtOH within 3 min, and 0IPDI and 10IPDI actuated to greater than 100% volume recovery in 20% EtOH within 25 min. Volume recovery testing demonstrates a plasticization sensitivity to EtOH that is not shown with DMSO, where the EtOH is sufficiently more effective as a plasticizer over water, even in dilute concentrations.

Both swelling and shape memory effects are critical factors in the SMP foam volume recovery shown in this study. Previous studies on solvent stimulated actuation have reported

that swelling of solvent into the polymer matrix changes the internal energy and decreases the relaxation time [19, 20]. As shown in figures 4–6, all foam compositions exhibited swelling to greater than their original volumes during submersion in 100% solutions of both DMSO and EtOH. The rates of volume ratio increase during the swelling experiment and the volume recovery experiments are very similar for all foam compositions. However, while EtOH exposure resulted in an expected decrease in relaxation time and T_g ($\tan \delta_{\max}$) values below 37 °C for all foam compositions, DMSO exposure did not cause the same result. Rather, as shown for 20IPDI in figures 2, 4, and 5, DMSO exposure resulted in polymer swelling but minimal to no relaxation in DMA kinetic experiments. This suggests differing mechanisms through which DMSO and EtOH influence volume recovery. During swelling, solvent penetrates into the polymer matrix and separates the polymer chains, increasing overall volume and enabling viscous migration between polymer network and solvent [19]. During shape recovery, heating the polymer above T_{trans} increases chain mobility, allowing entropic forces to orient polymer chains from the organized state of the temporary shape to the disorganized state of the original shape [2]. This study suggests that DMSO exposure primarily causes volume change due to solvent swelling separating polymer chains, increasing volume, but stimulation the conformational change during polymer chain orientation expected during shape recovery is less of a factor. Thus, both swelling and shape recovery influence volume recovery, but swelling may dominate the volume change that occurs without chain relaxation expected. However, EtOH exposure was observed to cause both volume change from swelling as well as relaxation during shape recovery. Thus, rapid volume recovery occurs as a result of both swelling and shape recovery as indicated by the expected chain relaxation.

We hypothesize that the mechanism and effectiveness of solvent stimulated actuation is heavily dependent on the relative molecular interactions of the solvent and polymer backbone. In these studies, EtOH proved to be a much more effective plasticizer of the polyurethane-based SMP foams than DMSO and water. This is likely caused by two primary factors: (1) the solvent's ability to penetrate the SMP and plasticize the polymer backbone and (2) the availability of isocyanate species to plasticization and mobility. Lu *et al* demonstrated that submersion in EtOH decreased the T_g of polyurethanes as a function of time due to hydrogen bonding interactions between the solvent and the urethane linkages [9]. However, previous studies of solvent-stimulated actuation of polyurethanes reported opposite results to this study; namely, decreased shape recovery was observed with EtOH compared to water, which was attributed to stronger hydrogen bonding interactions between urethane linkages and water relative to those with EtOH [6, 9]. These differing results reinforce that interactions between the chosen solvent and specific polymer chemistry are critical to the shape recovery effect. The SMP foam chemical compositions used in these studies were designed for increased hydrophobicity and decreased water plasticization, as reported by Hasan *et al* [17]. Methyl groups in the isocyanate monomers in combination with the ring structure of IPDI hinder water penetration into the polymer backbone, reducing available isocyanate linkages for water plasticization [17]. We hypothesize that the presence of both polar and non-polar regions in the EtOH molecule allow for drastically increased interactions with this polymer backbone compared to water and DMSO. Specifically, the OH functionality in the EtOH molecule will readily interact with urethane linkages while the C–

C tail will interact with the non-polar regions of the isocyanates. Further investigation is required to fully characterize and understand the mechanisms underlying the solvent stimulated SMP foam actuation observed in this study.

4. Conclusion

Solvent-stimulated volume recovery of hydrophobic polyurethane-based SMP foams using DMSO and EtOH was shown. Dramatic decreases in T_g were observed with exposure to water, DMSO, and EtOH. EtOH was shown to decrease SMP foam relaxation times to less than 1 min in DMA kinetic experiments. Furthermore, rapid shape recovery and volume swelling was observed for SMP foams in high concentrations of both DMSO and EtOH, as well as in decreased concentrations of EtOH. This study demonstrates effective control of SMP foam volume recovery using both DMSO and EtOH, including in aqueous environments, and that pairing of polymer composition and solvent selection is critical to the effectiveness of this actuation technique. Future work should investigate other solvents, as use of EtOH and DMSO are not ideal solvents in many applications, including biomedical applications due to moderate to severe toxicological effects [14, 15]. However, this work serves as a proof of concept of SMP foam actuation control using non-water solvents and provides insight into mechanisms that can be investigated for future material and device design work. Overall, this work demonstrates great potential for use of solvents as an alternative actuation stimulant for polyurethane-based SMP foams and may improve feasibility of using SMP materials in a variety of applications.

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Figure 1. SEM images of SMP foams. Foam pores in the transverse direction are shown on the top row for (a) 0IPDI, (b) 10IPDI, and (c) 20IPDI compositions. Foam pores in the axial direction are shown on the bottom row for (d) 0IPDI, (e) 10IPDI, and (f) 20IPDI compositions.

Figure 2. Actuation of 20IPDI foam immersed in varying solvents at 37 °C, demonstrated with measurements of storage modulus over time normalized to the initial modulus value.

Figure 3. Actuation of varying SMP foam compositions immersed in 37 °C EtOH, demonstrated with measurements of storage modulus over time normalized to the initial modulus value.

Figure 4. Swelling volume ratio in 37 °C solvent solutions. Volume ratio is shown over time of submersion in (a) DMSO and (b) EtOH.

Figure 5.

Volume recovery in 37 °C DMSO solutions. Volume recovery is shown over time of submersion in DMSO solutions of varying concentrations for SMP foam compositions of (a) 0IPDI, (b) 10IPDI, and (c) 20IPDI, where 0% DMSO is 100% RO water. Note the break in the time axis between 5 and 10 min.

Figure 6.

Volume recovery in 37 °C EtOH solutions. Volume recovery is shown over time of submersion in EtOH solutions of varying concentrations for SMP foam compositions of (a) 0IPDI, (b) 10IPDI, and (c) 20IPDI, where 0% EtOH is 100% RO water. Note the break in the time axis between 5 and 10 min.

Figure 7.

Images of 20IPDI actuation in 37 °C EtOH solutions. (a), (b), (c) and (d) Show 20IPDI actuation in 100% EtOH at 0, 1, 2, and 5 min, respectively. (e), (f), (g) and (h) Show 20IPDI actuation in 20% EtOH at 0, 5, 10, and 20 min, respectively.

Table 1SMP foam density and pore diameter (mean $\pm$ standard deviation).

	Density	Transverse pore diameter	Axial pore diameter
Foam ID	(g cm ⁻³) (<i>n</i> = 2)	(μ m) (<i>n</i> = 14)	(μ m) (<i>n</i> = 14)
0IPDI	0.0138 $\pm$ 0.0009	680 $\pm$ 130	1070 $\pm$ 300
10IPDI	0.0111 $\pm$ 0.0003	600 $\pm$ 150	1070 $\pm$ 220
20IPDI	0.0121 $\pm$ 0.0002	660 $\pm$ 130	1090 $\pm$ 210

Table 2

Summary of actuation transitions of SMP foams in solvent (mean $\pm$ standard deviation).

Foam ID	Dry			Water			DMSO			EtOH		
	T_g (DSC) ($^{\circ}\text{C}$) ($n = 3$)	T_g ($\tan \delta_{\max}$) ($^{\circ}\text{C}$) [17]	T_g ($\tan \delta_{\max}$) ($^{\circ}\text{C}$) ($n = 3$)	T_g (DSC) ($^{\circ}\text{C}$) ($n = 3$)	T_g ($\tan \delta_{\max}$) ($^{\circ}\text{C}$) ($n = 3$)	T_g ($\tan \delta_{\max}$) ($^{\circ}\text{C}$) ($n = 7$)	T_g (DSC) ($^{\circ}\text{C}$) ($n = 3$)	T_g ($\tan \delta_{\max}$) ($^{\circ}\text{C}$) ($n = 3$)	T_g (DSC) ($^{\circ}\text{C}$) ($n = 3$)	T_g ($\tan \delta_{\max}$) ($^{\circ}\text{C}$) ($n = 4$)		
0IPDI	66 $\pm$ 1	105 $\pm$ 2	46 $\pm$ 1	35 $\pm$ 2	46 $\pm$ 1	28 $\pm$ 6	8 $\pm$ 3	-6 $\pm$ 4	-6 $\pm$ 4	18 $\pm$ 1		
10IPDI	74 $\pm$ 1	118 $\pm$ 2	51 $\pm$ 1	33 $\pm$ 1	51 $\pm$ 1	33 $\pm$ 1	-1 $\pm$ 3	-9 $\pm$ 5	-9 $\pm$ 5	18 $\pm$ 3		
20IPDI	79 $\pm$ 2	131 $\pm$ 1	61 $\pm$ 1	44 $\pm$ 4	61 $\pm$ 1	41 $\pm$ 3	12 $\pm$ 3	2 $\pm$ 4	2 $\pm$ 4	22 $\pm$ 8		