

# Synthesis and characterization of two-stage curing reactive bio-based polymers

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## Abstract

Two-stage curing reactive bio-based polymers network namely, poly(octanediol-co-dodecanedioate-co-citrate-co-itaconate) (PODCI) were successfully synthesized using 1,8-octanediol, citric acid, itaconic acid and 1,12-dodecanedioic acid. In the first curing stage, a prepolymer of PODCI was thermally crosslinked. At a later time, a second curing was completed thru photo-initiated free-radical polymerization. Here, we discovered that permanent shape of the thermally crosslinked PODCI was successfully reconfigured by application of second stage curing. The molar ratio of itaconic acid (IA) to citric acid (CA) and time of photo-curing was varied. Based on XRD analysis, the polymer crystallinity of the bio-based polymer decreased with time of photo-curing. The swelling ratio of bio-based polymer decreased from 2750 % to 250 % as soon as completion of second stage curing. PODCI existed as a semi-crystalline polymer with a melting transition temperature of 40.2 °C. Also, PODCI exhibited excellent shape memory properties with shape recovery by nearly 100%.

**Keywords:** Bio-based polymer, shape memory property, photo-induced free radical polymerization

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## INTRODUCTION

Petroleum-based polymers are widely used in packaging and plastics manufacturing industry. Due to the environmentally unfriendly and waste disposal landfill problem, the petroleum-based polymers raised the warning sign to worldwide. Replacing the petroleum-based polymers with those derived from bio-masses may seem to be a cost-effective and sustainable approach. Bio-based precursors can be derived from bio-masses, which may include but not limited to crops, aquatic plants, wood and animal waste. Consequently, bio-based polymers sound sustainable, eco-efficient, and environment-friendly whereas petroleum-based polymers are the major components of landfill due to non-biodegradable (Miao *et al.*, 2013).

The thermally crosslinked bio-based polymer possessed irreversible crosslink within the polymer network. Due to major bio-based polymer undergone thermally crosslink process, in this way they cannot be remolded or reshape (Yang *et al.*, 2004, & Serrano *et al.*, 2011). However, by incorporating a second crosslink curable monomer, new crosslinks will be formed within the polymer network. Some of the polymers that use to create a new shape configuration by undergoing two different curing stages, which are thermal curing first then followed by the photoinitiated curing process. A UV curable monomer was incorporated into the polymer network, which is assisting for new shape configuration. (Meng *et al.*, 2014, & Yakacki *et al.*, 2015).

Interestingly, shape-memory properties of these bio-based polymers also have been revealed. The first US patent related to shape memory polymer was registered in the year 1941, it is about synthesis and testing on a dental material that made use of methacrylic acid ester resin. This material was found able to recovers its original shape when triggered by heat (Liu *et al.*, 2007). Shape-memory polymers (SMP) are a class of smart materials that can be fixed in a temporary shape and regain its permanent shape upon triggered by an external stimulus, typical heat (Xie, 2011). SMP was can be found in a number of applications ranged from aerospace, automotive, and most promisingly, in the medical field.

In this project, a series of two stages curing reactive polymer networks were successfully synthesized using 1,8-octanediol, citric acid, itaconic acid, and 1,12-dodecanedioic acid. Here, it was expected that the two-stage curing method can be utilized to the re-configure permanent shape of a thermally crosslinked polymer. We studied the change in structural, thermal, and shape-memory properties of the bio-based polymers upon two-stage curing.

## EXPERIMENTAL

### Materials

1,8-octanediol (98 %), citric acid, itaconic acid ( $\geq 99$  %), 1,12-dodecanedioic acid (99 %), and 2,2-dimethoxy-2-phenylacetophenone (99 %) were purchased from Sigma-Aldrich. Tetrahydrofuran (THF) was purchased from EMSURE. All of the chemicals were directly used as received.

### Synthesis of bio-based pre-polymer

The bio-based pre-polymer was synthesized by catalyst-free polyesterification. First, 1,8-octanediol, citric acid, itaconic acid and dodecanedioic acid in certain molar ratio was melted in an oil bath at 160 °C. As soon as all monomers melted, the temperature of the oil bath was lowered to 150 °C. The photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (DMPA) was added in 20 wt% into reactant mixtures. After vigorously stirred for 6 hours, pre-polymer was obtained.

### Two-stage curing reactive method of bio-based polymer

In first stage curing, the prepolymer was cured thermally at 100 °C for 24 hours. It was followed by second stage curing thru photo-induced free radical polymerization. The samples were exposed under ultraviolet irradiation (365nm, 6-10 W). Time of exposure under UV irradiation was varied from 0 to 60 min. Here, the obtained bio-based polymer was named as  $PODC_xI_yT_z$ , where x is the molar ratio of citric

acid,  $y$  is the molar ratio of itaconic acid, and  $z$  is the time of UV irradiation. Fig. 1 presents the schematic diagram for the synthesis of two-stage curing reactive bio-based polymer.

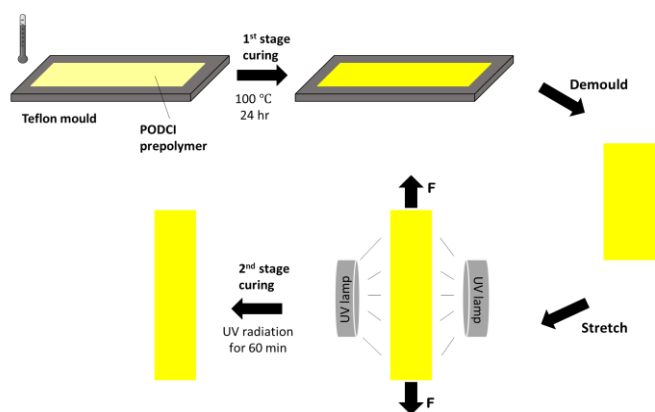


Fig. 1 Schematic diagram for the synthesis of a two-stage curing reactive process.

### Characterizations and testing

The light transmission of PODCI was evaluated via ultraviolet-visible light spectrometer (Shimadzu UV-3101PC, Japan). Fourier transform infrared spectra of PODCI was obtained from ATR-FTIR (NICOLET IS10-IR Spectrometer). Sol and gel content of PODCI was quantified by immersion in THF solvent via sol-gel analysis. The gel fraction ( $G$ ) and swelling ratio ( $Q$ ) were calculated according to Cardoso et al. (2011). The X-ray diffraction testing was conducted at ambient temperature on a Rigaku Dmax/III diffractometer using  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) with accelerating voltage of 40 kV and current of 30 mA respectively. The heating and cooling curve of PODCI was recorded under a nitrogen atmosphere by using a Differential scanning calorimetry (DSC) 820 (Mettler Toledo) within the temperature range of  $-50$  to  $100 \text{ }^\circ\text{C}$ . In the first heating, the sample was heated from room temperature to  $100 \text{ }^\circ\text{C}$  with a rate of  $10 \text{ }^\circ\text{C min}^{-1}$  and hold for 10 min. It was followed by cooling to  $-50 \text{ }^\circ\text{C}$  with a rate of  $10 \text{ }^\circ\text{C min}^{-1}$  and then hold for another 10 min. In second heating, the sample was reheated to  $100 \text{ }^\circ\text{C}$  with the same heating rate as used in first heating. The shape memory property of PCI was quantified by determining the shape recovery from bending angle to original angle upon heating.

## RESULTS AND DISCUSSION

### Light transmission study of PODCI

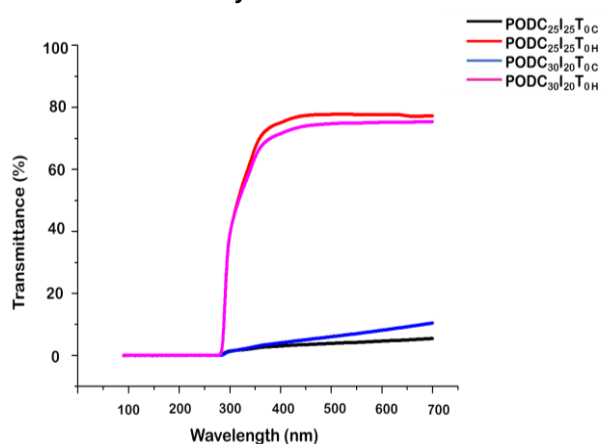


Fig. 2 UV light transmittance of PODCI.

Fig. 2 reveals the light transmittance of UV and visible spectral within 200-800 nm wavelength. At room condition, the light transmittance of all of the synthesized PODCI only achieved a maximum of 10 %. When it was heated above  $50 \text{ }^\circ\text{C}$ , the light

transmittance increased to 77 %. At room temperature, the PODCI existed at semi-crystalline state, and it possessed opaque appearance. As soon as heated above the melting-transition temperature ( $T_m$ ), all of the crystalline structures were melted and it became transparent. Herein, second stage curing was conducted at a temperature higher than  $T_m$ . We found that the PODCI cannot undergo UV-initiated free radical crosslink at a lower temperature.

### Chemical and structural properties of PODCI

The gel fraction of one stage cured and two stages cured PODCI polymers were evaluated by quantifying the mass loss of sample after immersing into THF solvent. Fig. 3 shows the sol-gel analysis results of PODCI. Gel content refers to the crosslinked polymer network which is not soluble in THF. Due to network structure integrity, a prepolymer of PODCI able to undergo stage-wise curing. A prepolymer which soluble in THF was firstly thermally crosslinked and then followed by UV-initiated photocuring. From the result, the gel fraction of PODCI increased with increasing photocuring duration. It is well-known that crosslinked polymer cannot be remolded (reshaped). In this work, we presented that thermally crosslinked PODCI can be remolded easily upon completion of second stage curing. Photographs in Fig. 4 presents that a PODCI slab sample was successfully reshaped into helix dimension.

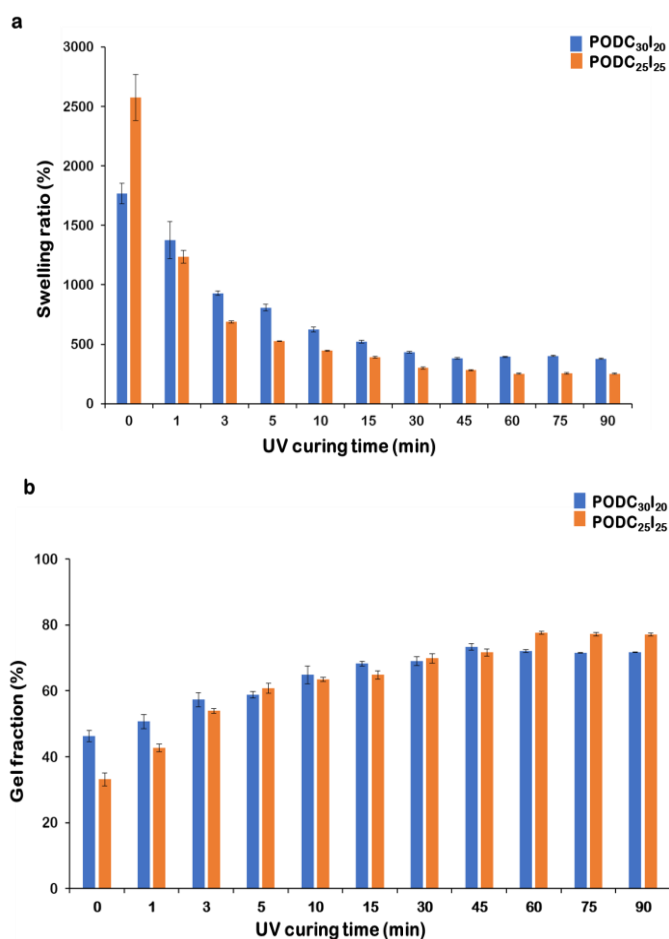


Fig. 3 (a) Swelling ratio and (b) Gel fraction with different photo-curing duration.

Fig. 4 presents a schematic diagram of crosslink formation during the stepwise-curing of PODCI. By introducing a UV light curable monomer, the IA, PODCI network can be further crosslinked upon application of UV irradiation. Swelling degree of PODCI was found decreased from 2570 % to 250 % after exposed under UV light for 60 min. PODCI with a greater content of IA was also found swelled lesser. As an alternative, the swelling degree is also an indication for crosslinking density which higher swelling degree indicates lower crosslinking density.

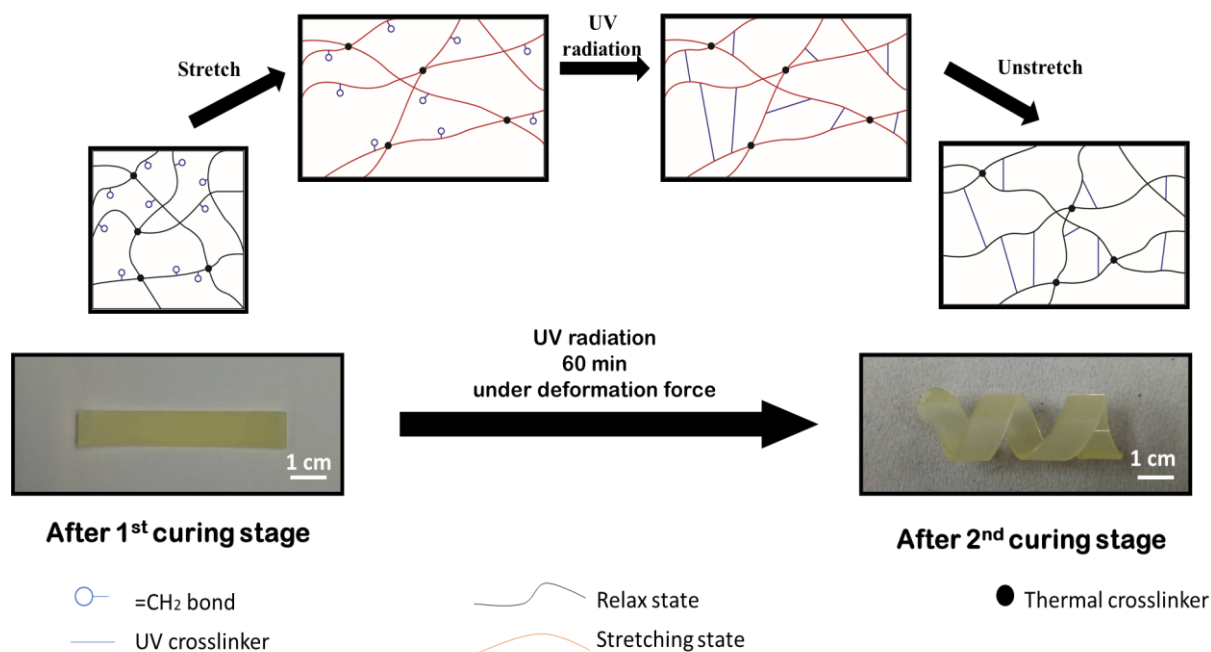


Fig. 4 Schematic diagram of crosslinks formation and photo for reshaping of PODCI upon second curing process.

Fig. 5 shows FTIR spectra of PODCI. The transmission peak at 1370-1470  $\text{cm}^{-1}$  is corresponding to =C-H stretching from branches due to the presence of IA. The transmission peaks at 1735-1750  $\text{cm}^{-1}$  attributed to the stretching of C=O (ester bond) within the polymer network. Upon UV irradiation exposure, the carbon-carbon double bond (=C-H) of IA was transformed into alkyl group (-CH<sub>3</sub>). It was clearly shown that peak intensity due to =C-H double bond (absorption band at 1375  $\text{cm}^{-1}$ ) was decreased while the band at 2930  $\text{cm}^{-1}$  corresponding to the vibration of the alkyl group (-CH<sub>3</sub>) was increased. While the transmission peak at 1370-1470  $\text{cm}^{-1}$  still showed at FTIR spectra because the uncrosslinked =C-H still remains at the branches of PODCI networks.

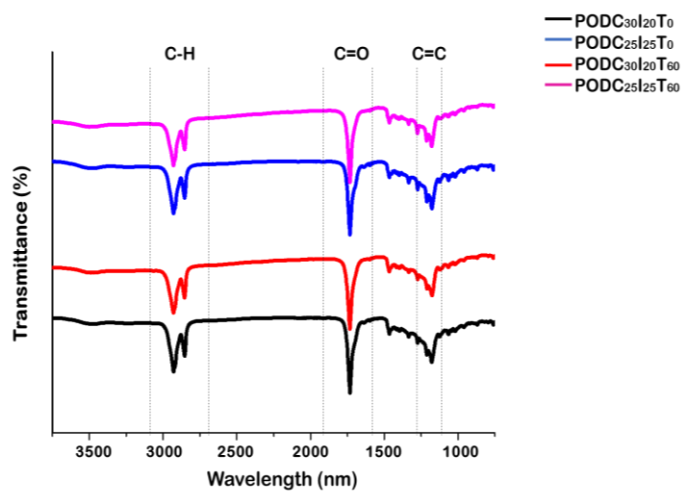


Fig. 5 FTIR spectra of PODCI.

Fig. 6 presents X-ray diffraction (XRD) pattern of the PODCI with a different stoichiometric ratio of CA to IA and different photocuring time. From the diffraction pattern of PODC30I20T0, the diffraction peaks around 21.3 and 23.9 are significantly high. After second stage curing, the intensity of these diffraction peaks remarkably decreased. The degree of polymer crystallinity ( $X_c$ ) was calculated using Eq. (1).

$$X_c = \frac{\sum_{i=1}^n A_{ci}}{A_t} \quad (1)$$

where  $A_{ci}$  is the under each crystalline peak with index  $i$  and  $A_t$  is the total area under the diffractogram (Lopez-Rubio *et al.*, 2008). The  $X_c$

of PODCI were recorded in Table 1. The  $X_c$  of PODCI was found decreased after further curing under UV light. The increment in polymer crosslinking inhibits polymer crystallization.

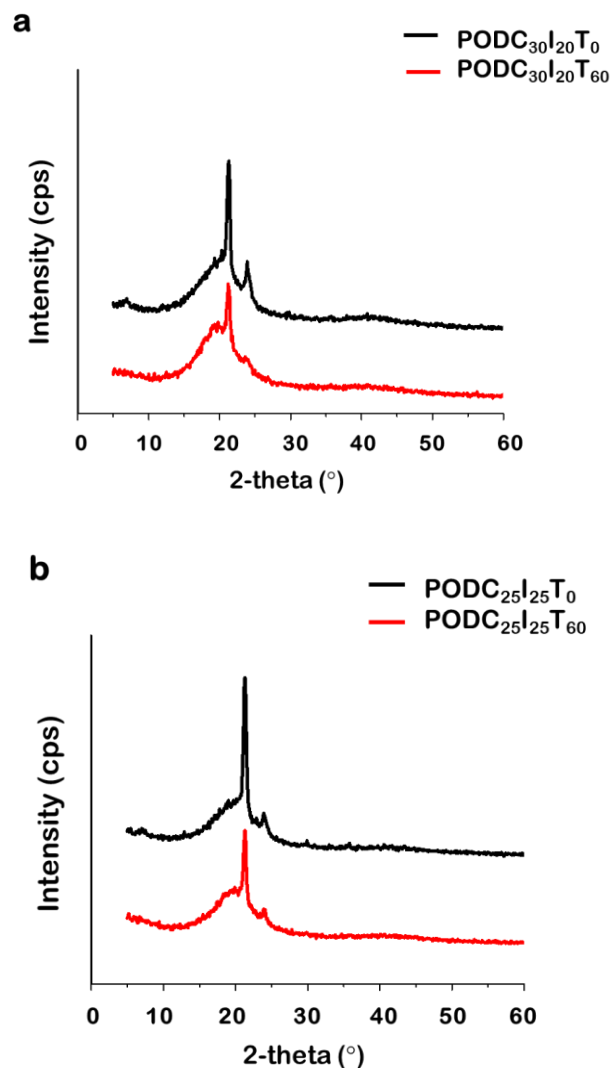


Fig. 6 XRD spectra for (a) PODC30I20 and (b) PODC25I25 with two different photo-curing time.

**Table 1** Thermal data and degree of polymer crystallinity of PODCI.

Formulation	T <sub>c</sub> <sup>a</sup> (°C)	T <sub>m</sub> <sup>b</sup> (°C)	X <sub>c</sub> <sup>c</sup> (%)
PODC <sub>30I20T0</sub>	1.5	40.4	17.7
PODC <sub>30I20T60</sub>	-17.8	28.9	9.6
PODC <sub>25I25T0</sub>	9.2	44.2	20.5
PODC <sub>25I25T60</sub>	9.1	40.2	10.4

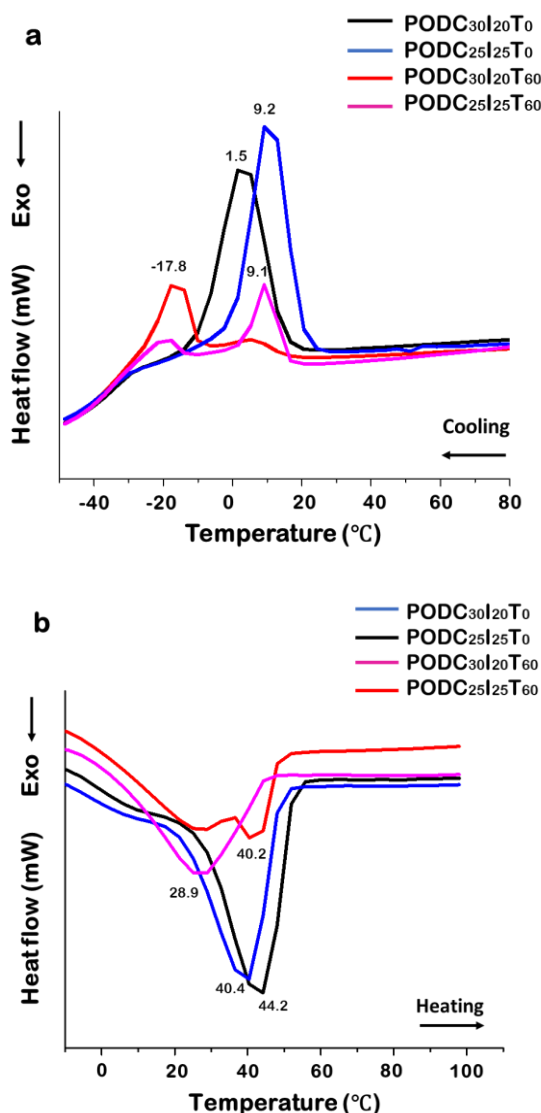
a Crystallization transition temperature determined by a first cooling curve of DSC.

b Melting transition temperature determined by a second heating curve of DSC.

c Polymer crystallinity of PODCI calculated by Eq. (1).

**Thermal properties of PODCI**

Fig. 8 depicts the DSC thermograms curve of PODCI during cooling and second heating process. The thermal properties of PODCI were displayed in Table 1. From thermograms, it was found that the crystallization transition temperature (T<sub>c</sub>) of PODCI is below 9.2 °C. When IA content is increased, leading to the decreased possibility of branch forming by CA after first stage curing. Therefore, the melting transition temperature of PODC<sub>30I20</sub> is lower than it's of PODC<sub>25I25</sub>. Melting transition temperature of PCI decreased after second stage curing, as the crystalline of PCI decreased with increasing crosslinking formed. The DSC results indicate that PCI exhibits semi-crystalline state at room condition.



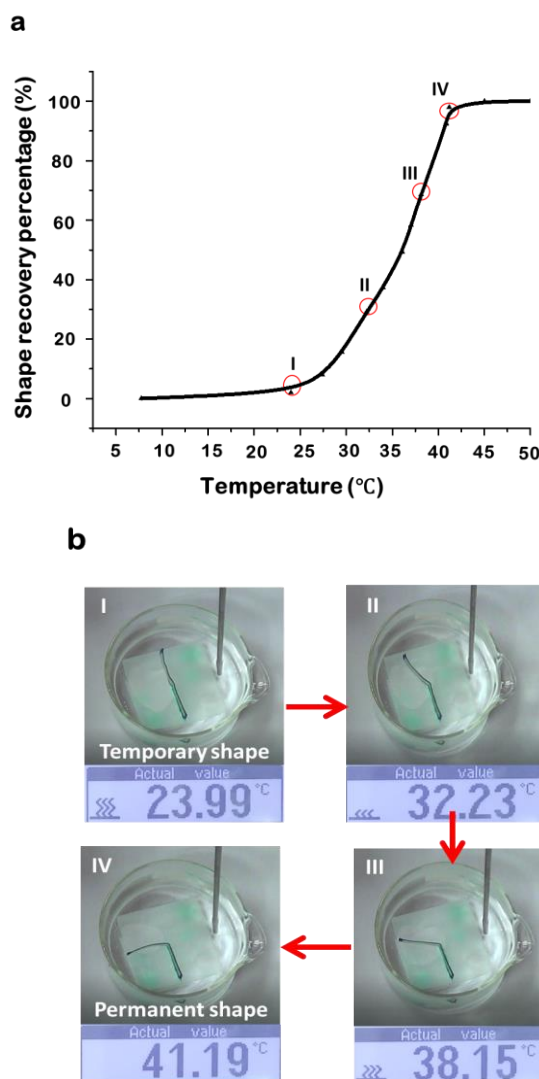
**Fig. 8** DSC curve for (a) cooling curve and (b) second heating curve of PODCI.

**Shape memory effect of PODCI**

PODCI is a shape memory polymer as it can be fixed in a temporary shape and only regain its permanent shape upon heating. Fig. 9a presents the relationship between shape recovery percentage and change in temperature upon heating and Fig. 9b displays the images of PODCI in water bath upon heating. The shape recovery percentage (R<sub>r</sub>) was calculated using Eq. (2).

$$R_r = (180^\circ - A_d) / A_o \times 100\% \quad (2)$$

where A<sub>d</sub> is deformed angle and A<sub>o</sub> is original angle. With the increasing temperature of the water bath, the temporary shape of PODCI started to recover at 23 °C, and it fully recovered to its permanent shape at a temperature of 42 °C. As well as the higher deformation recovery temperature of PODCI is 36 °C. PODCI possessed an excellent shape memory behavior with shape recovery temperature of 36 °C. Therefore, PODCI can act as an actuator or drug capsules within the human body.



**Fig. 9** (a) Relationship between shape recovery percentage of PODCI and temperature (b) Image of angle deformation change of PODCI with temperature.

**CONCLUSION**

A two-stage cured bio-based polymer was successfully synthesized. The shape of the polymer can be tailored after the second stage by free-radical photopolymerization. PODCI possessed different chemical, structural, and thermal properties between one stage and two stages curing reactive process. Two-stage cured PODCI possessed an excellent shape memory property.

## ACKNOWLEDGEMENT

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