

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ARTICLE

Shape recovery characteristics for shape memory polymers subjected to high intensity focused ultrasound

Guo Li,^{a,b} Guoxia Fei,^a Bo Liu,^a Hesheng Xia^{*a} and Yue Zhao^{*b},

High intensity focused ultrasound (HIFU)-triggered shape memory has distinct features due to the unique heating mechanism based on polymer chain shearing and friction activated by ultrasonic energy. In this study we chose crosslinked poly(methyl methacrylate-co-butyl acrylate) P(MMA-BA) as a model polymer and studied in detail the HIFU induced thermal effect and shape recovery characteristics. It was found that HIFU heating for polymers is quick and spatially localized, and can be controlled by the ultrasound power, which allows for spatiotemporally controllable shape memory process. The effects of various parameters including sample thickness, copolymer composition and crosslinker content on the HIFU-induced thermal effect and shape recovery were investigated. Under HIFU irradiation, there exists an optimum sample thickness for a maximum thermal effect and thus better shape recovery, which is different from conventional heating. Moreover, both the copolymer composition and the crosslinker content have profound effect on the HIFU-induced temperature rise and thus the shape recovery. These effects can be related to changes in the viscoelastic parameter loss tangent ($\tan \delta$) of the copolymer around the glass transition temperature T_g that is the transition temperature for the shape recovery process.

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/MaterialsB

Introduction

Shape memory polymers (SMPs) are a class of stimuli-responsive polymers that are sensitive to environmental condition changes by displaying shape changes. SMPs have potential applications in medical equipment, aerospace, textiles or electronic devices, etc.¹⁻⁴ In most cases, SMPs are crosslinked polymer networks, which have one “permanent” shape and one or several “temporary” shapes. The network can be either physically or chemically crosslinked, enabling the polymer return to its permanent shape after deformation without any damage to its structure, and the network elasticity determines temporary shapes and each temporary shape is fixed by vitrification or crystallization.⁵⁻⁶

Heating is the most conventional stimulus type to trigger the shape recovery of SMPs. Direct heating is not always practical in some special circumstances. Particularly, the desirable spatial and temporal control in activating the shape recovery process requires new and more controllable stimulating means. The external stimuli such as light,⁷⁻⁹ magnetic field,¹⁰⁻¹¹ electrical field¹²⁻¹³ and radiofrequency wave¹⁴ have been investigated as promising triggering mechanisms. However, these stimuli usually need incorporation of responsive moieties or particles in the SMPs, which may raise technical difficulties and restrict their application potential in some fields.¹⁵⁻¹⁷

The use of ultrasound, especially the high intensity focused ultrasound (HIFU), as a remote and controlled stimulus for SMPs has been less explored.¹⁸⁻²¹ In addition to the temporal and spatial control by selecting the HIFU exposure time, intensity and the position of its action, ultrasound wave possesses the ability to penetrate much deeper than light in materials or tissues.²²

In a previous study, we made the first demonstration that HIFU can be used to spatially and temporally control the shape recovery process of SMPs and to obtain multiple intermediate shapes.¹⁹ The HIFU beam can be collimated into a tight focal spot of a small area in the millimetre-scale at a distance from its source. Being focused, HIFU can also have a prominent selective heating effect on SMP materials, since they can absorb the mechanical energy generated by viscous shearing oscillation exerted by focussed ultrasound and subsequently relax, releasing the energy in the form of heat.²³

An important advantage for HIFU stimulus is that there is no need to incorporate responsive particles or functional groups into SMPs, as most polymers can be heated under ultrasound exposure within seconds. However, it was reported that different polymers possess different HIFU-induced thermal effect by our group due to the various inner friction behaviours of macromolecular chains.²⁰ For example, polypropylene has a

much more significant HIFU-induced thermal effect than polyethylene and polystyrene. This endows HIFU triggered shape memory a unique characteristic, different from conventional heating. Under conventional heating, almost all polymers will have a similar temperature rise and be heated to a similar temperature. For HIFU triggered SMPs, in addition to the characteristic T_{trans} of the polymer, the HIFU-induced thermal effect, being related to the inner friction of polymer molecular chains and sound absorption coefficient of the materials, is an important factor for the shape memory behaviour. If a SMP doesn't absorb sound or has a low HIFU induced thermal effect, it will show no or poor HIFU triggered shape memory capability. Moreover, for a same SMP, samples of different dimensions should experience different HIFU-induced thermal effects under the same irradiation conditions, which can also affect the HIFU triggered shape memory behaviour.

In order to obtain an optimal design of HIFU responsive SMP materials for different requirements and a better control capability under the use of HIFU, it is necessary to achieve better understanding of HIFU-induced thermal effect as a function of the polymer viscoelastic properties, and the relationship with the shape memory behaviour.²⁴⁻²⁵ In the present study, we used shape memory P(MMA-BA) as a model copolymer and investigated the effects of sample thickness, copolymer composition and crosslinking density on the HIFU-induced thermal effect and the concomitant shape memory behaviour, as well as the relationship between them. An Infrared Thermal Imager (ITI) was used as an advanced tool to measure the HIFU-induced temperature rise in the SMP.

Experimental

Materials

Methyl methacrylate (MMA), butyl acrylate (BA) and 2,2'-azobis(isobutyronitrile) (AIBN) were purchased from *Chengdu Kelong Chemical Reagent Factory*. MMA and MA were distilled in vacuum, and AIBN was recrystallized prior to use. Ethylene dimethacrylate (EGDMA) was obtained from J&K Technology CO., Ltd. and used as received.

Synthesis of P(MMA-BA) sheet samples

Crosslinked P(MMA-BA) copolymers with different thickness were prepared by *in-situ* free radical polymerization. Typically, monomers at a given MMA/BA molar ratio (2.5:1) were mixed with EGDMA (crosslinker, 1.12 wt% of the reaction mixture) and AIBN (initiator, 0.56 wt% of the reaction mixture). The mixture was then transferred into the glass mold and sealed with silicon rubber of different thickness (0.38 mm, 0.51 mm, 0.78 mm, 1.05 mm, 1.89 mm, 2.91 mm and 3.78 mm) and polymerized at 60 °C for 24 hours. The resulting polymer sheet was then taken out from the glass mold and vacuum dried at 80 °C for 3 h to remove unreacted monomers. Using the same procedure, P(MMA-BA) with different monomer composition were prepared by changing of MMA/BA feed ratio (1.5:1, 2:1, 2.5:1, 3.5:1 and 5:1, mol/mol); P(MMA-BA) with different

crosslinking densities were synthesized by changing EGDMA content (1.12 wt%, 5 wt%, 10 wt% and 15 wt%).

Setup of HIFU and infrared camera imaging system

The setup of HIFU and Infrared camera imaging system are shown in Figure 1. There are three major components: a HIFU generator and transducer module, a sample-holding module and an infrared camera imaging system. The HIFU transducer (H-101, Sonic Concepts, USA) with an active diameter of 64.0 mm and a geometric focal length of 62.6 mm is mounted at the bottom of a tank filled with water and the beams of ultrasound are pointed upwards and focused on a circular spot with a diameter of about 3 mm. The ultrasound power output can be adjusted in the range of 0~200 W and the frequency of ultrasound is 1.1 MHz.

In every run the sample was subjected to HIFU irradiation for 1 min, with the IR camera real-time recording the temperature fluctuation. A Thermovision A20 infrared (IR) camera (FLIR Systems Inc., Wilsonville, OR, USA) equipped with thermal-CAM researcher software (version 2.9) was used in the experiments. The IR camera was positioned directly on the test sample to record the temperature change by thermal imaging. This instrument has a sensitivity of 0.12 °C with an operating temperature range of 0-900 °C. The IR camera recorded the surface temperature of the target by chronophotograph, with a speed of one image per second. After each test, the recorded data could be converted to a series of temperature versus time (T vs. t) curves. This non-invasive temperature recording technique is able to preclude temperature artifacts caused by implanting thermocouple and reduce the temperature errors.

A home-made polystyrene (PS) support was used to fix the sample in position. There was a small hole at the central place of the PS support for ultrasound waves passing through without dissipation. The sample height was fixed to make the downside surface of the sample just in contact with water, as shown in Figure 1. By using this setup, the sample can be horizontally fixed in the same position in each run during the whole experiment. The test should be operated carefully to avoid water sputtering on the top surface of polymer sample during the HIFU treatment. To reduce the scattering of ultrasound waves caused by the gas bubble and cavitation, degassed water was used as HIFU transmission medium. The water temperature was kept constant at 37 °C. By using the sample

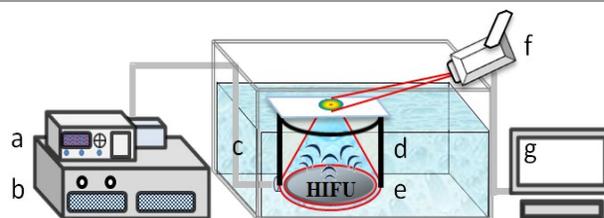


Fig 1. Experimental setup: (a) function generator, (b) power amplifier, (c) tank filled with degassed water, (d) sample holder, (e) ultrasound transducer, (f) Infrared camera and (g) computer used to record data.

holder and the degassed water, the reproducible and reliable temperature data can be obtained (at least three runs were conducted for each sample). The HIFU power should be kept sufficiently low to prevent the occurrence of sample degradation.

Shape memory behaviour of crosslinked P(MMA-BA)

The crosslinked P(MMA-BA) samples were processed into a straight stripe as their original/permanent shape. Then the sample was heated to $T > T_{\text{trans}}$ and deformed to obtain a right-angle bent stripe as the temporary shape, which was fixed by subsequently cooling the sample to room temperature (below T_{trans}). For conventional heating-triggered shape recovery, the deformed sample was placed into an oven at 120 °C to start the shape recovery process, which was monitored by measuring the shape recovery ratio R_r defined as $R_r (\%) = [(\theta_r - 90)/90] \times 100\%$, where θ_t is the deformation angle at the time t .

For HIFU triggered shape recovery of P(MMA-BA), the sample of temporary shape was fixed on the sample holder with the downside surface of the sample in contact with water and the upside surface exposed to air, and the deformed part of the sample (folding area) was placed at the focal spot of HIFU. Once the HIFU with a frequency of 1.1 MHz at a power output of 1–6 W is turned on, the shape recovery starts. The shape recovery, i.e., the unfold process was recorded by a digital camera and the shape recovery ratio was calculated.

Results and discussion

HIFU-induced rapid and localized heating effect

HIFU-induced localized temperature rise was investigated. Unless otherwise stated, in this study P(MMA-BA) copolymer prepared from a MMA/BA monomer ratio of 2.5:1 and with a crosslinker content of 1.12 wt% was used, with a sample having a thickness of 1.89 mm. The recorded infrared thermal images are shown in Fig. 2a. It is seen that at a 2 W power output, the temperature of the polymer at the focal spot increases very fast, while the temperature beyond the focal spot, over about 3 mm, drops quickly, indicating an excellent local heating in the polymer. Nevertheless, it is visible that during HIFU irradiation, the size of heated area expands, and a temperature gradient from the center to the fringe within this area is formed. Fig. 2b shows the temperature distribution in this area upon HIFU irradiation. The temperature in the center of heated area increases from its initial 37 °C to 100 °C within only 9 s at a very low HIFU power of 2 W, and reaches a thermal equilibrium temperature of 120 °C after 15 s. The initial heating rate, defined as the temperature rise of polymer in the first 10 s, is 7.3 °C/s. Bruinewoud et al.²³ reported that the temperature of PMMA disc under conventional ultrasound with 1 MHz frequency and 0.7 W/cm² intensity increased by only ~14 °C, with an initial heating rate of ~0.48 °C/s. This indicates that HIFU heating for polymers is rapid and can be more effective than conventional ultrasound or direct heating. Repeatability is technically important for HIFU induced thermal effect of polymers. Five on-off cycles under different HIFU output

powers were conducted, and the data for the equilibrium temperature in the focused area are plotted in Fig. 2c. In every cycle, the equilibrium temperature changes very little, indicating excellent repeatability. Moreover, as can be expected, the equilibrium temperature increases with increasing the applied ultrasound power, but quite surprisingly, the high rate of temperature rise upon HIFU irradiation appears unaffected by changing the ultrasound power from 1 to 6 W. So is the fast temperature drop after turning off the HIFU beam. All these features point out the excellent controllability of HIFU-induced polymer heating, which provides the basis for SMPs spatiotemporal control by means of HIFU.

Effect of sample thickness on HIFU-induced thermal effect and shape recovery

The ultrasound propagation is highly directional, and ultrasound absorption is related to the sample dimensions. To investigate the effect of the sample thickness on the HIFU-induced thermal effect and shape recovery, a series of P(MMA-BA) sheets of different thicknesses ranging from 0.37 mm to 3.79 mm were prepared, and the HIFU induced temperature rise and shape recovery were measured. The results on temperature rise under 2 W HIFU irradiation are shown in Fig. 3a. The rates of initial temperature rise and the equilibrium temperatures are listed in Table 1. At a thickness of 0.38 mm, the equilibrium temperature can reach just ~48 °C with a rate of initial temperature rise of ~4.7 °C/s, while at a thickness of 1.89 mm, it can reach a much higher temperature of ~136.5 °C with a

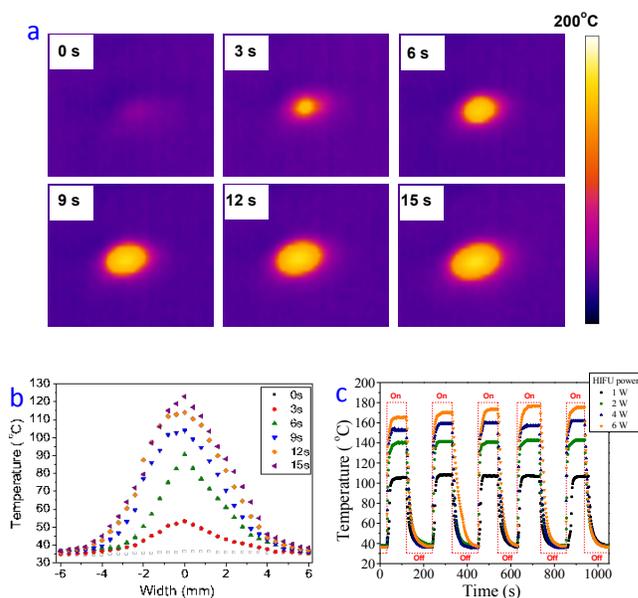


Fig. 2 Localized, fast and repeatable temperature rise in P(MMA-BA) under HIFU irradiation. (a) Infrared Thermal Images recorded within 15 seconds of HIFU irradiation at 2 W. (b) Changes in the temperature distribution in the irradiated area of polymer over time, the curves being obtained from images in (a) and the temperature maxima corresponds to the HIFU focal point. (c) Temperature change profiles upon five consecutive HIFU on-off cycles at different powers output (1, 2, 4 and 6 W). In each on-off cycle, the HIFU beam was turned on for ~90 s and turned off for ~120 s.

rate of initial temperature rise of ~ 5.9 °C/s. The rate of initial temperature rise increases first and then decreases with increasing the thickness, and reaches a maximum value at a thickness of 1.05 mm at a power output of 2 W. The equilibrium temperature shows a similar trend as the rate of initial temperature rise. It reaches a maximum value at a thickness of 1.89 mm at a power output of 2 W. These results clearly show that thickness is an important parameter for HIFU-induced heating. When the polymer sample is thin, like 0.38 mm, the ultrasound waves can easily penetrate through the polymer and only a small portion of sound energy is absorbed and converted into heat, which leads to a slow temperature rise and a low equilibrium temperature. With increasing the thickness, the sample volume interacting with the HIFU beam is enlarged; more sound energy can be absorbed by chain friction to generate heat, which results in increased temperature rise rate and achievable equilibrium temperature. However, after reaching the maximum amount of absorbable sound energy, a further increase in the thickness, meaning increase in the volume and mass of the sample, leads to a decrease in the rate of initial temperature rise and equilibrium temperature. Besides, decreasing the sample thickness means increase in the ratio of surface to bulk, which may result in enhanced heat flux and thus decreased equilibrium temperature.

Shape recovery behaviours of P(MMA-BA) samples of different thicknesses under the same HIFU irradiation conditions were investigated and the results are shown in Fig. 3b. Data of the initial rates of shape recovery and final shape recovery ratios are listed in Table 1. For the sake of comparison, the shape recovery rate obtained by direct heating at 120 °C was also measured for each sample and the results are shown in Fig. 3c. Under 2 W HIFU irradiation, the shape recovery can occur, but the rate and magnitude depends very much on the sample thickness, which is in sharp contrast with the conventional heating that leads to total shape recovery after 20 seconds and for which the thicker sample has a slower shape recovery process. From Table 1, under 2 W HIFU irradiation, the rate of initial shape recovery increases first and then drops with increasing the thickness; it reaches a maximum value at the thickness of ~ 1.05 mm, which is consistent with the change trend in the rate of HIFU-induced temperature rise. The final shape recovery ratio has a similar change trend and reaches a

maximum value at the thickness of ~ 1.89 mm, which also is in agreement with the change trend in the thermal equilibrium temperature.

All P(MMA-BA) samples have the same T_g or T_{trans} regardless of their thickness. From the above results, it is clear that the rate of HIFU-triggered shape recovery depends on the rate of HIFU-induced temperature rise, and the final shape recovery ratio depends on the HIFU-induced thermal equilibrium temperature. Under the used HIFU irradiation condition (2 W) and the setup for exposure of the sample to ultrasound, the shape recovery is slower and less complete than the outcome by direct heating of the whole sample to 120 °C. Nevertheless, the distinct feature of using HIFU to trigger the shape memory effect is the controllability for the shape recovery process, since clearly the ultrasound-induced temperature rise rate and equilibrium temperature can readily be adjusted by HIFU power, sample dimension and the way ultrasound beam is applied to the deformed area of the sample.

Effect of copolymer composition on HIFU-induced thermal effect and shape recovery

For P(MMA-BA) copolymer, the transition temperature T_{trans} for shape recovery (T_g in this case) and mechanical properties can be varied by changing the composition of the two monomer units MMA and BA, i.e., the ratio of hard MMA to soft BA. It is known that with increasing the MMA content, the T_{trans} of P(MMA-BA) copolymer increases. The changing T_{trans} and mechanical properties may affect the HIFU-induced temperature rise and thus the shape memory behaviour. To study the possible effect, several P(MMA-BA) samples of different compositions were synthesized by varying the feed ratio of MMA/BA ranging from 1.5:1 (softest) to 5:1 (hardest). Using the same experimental setup, their HIFU-induced temperature rise and shape recovery were measured by using samples with the same thickness of 1.89 mm and same crosslinker content of 1.12 wt%, with different HIFU powers output (1-4 W). The results are shown in Figs. 4a-4c. In order to understand the relationship between T_{trans} and the ultrasound-induced temperature rise and shape memory, dynamic mechanical analyses (DMA) were also conducted on these copolymers and their measured $\tan \delta$ (ratio of loss modulus to storage modulus) are shown in Fig. 4d.

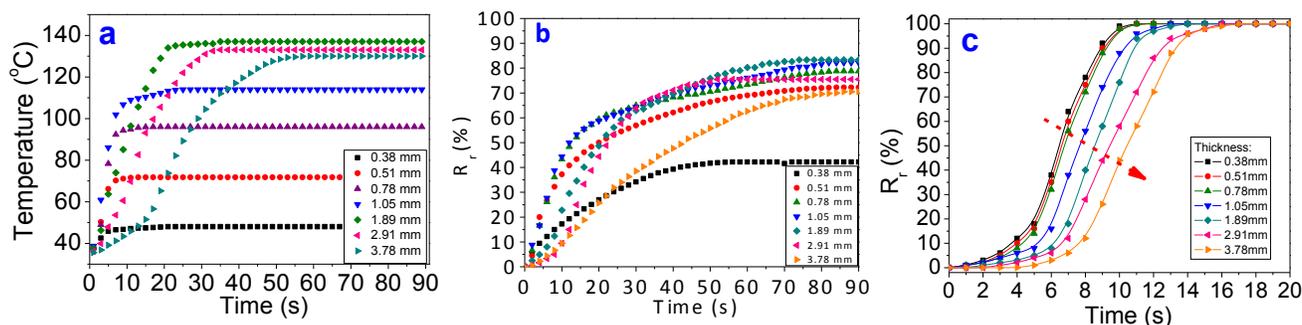


Fig. 3. Results on P(MMA-BA) samples of different thicknesses from 0.38 to 3.78 mm: (a) temperature rise under 2 W HIFU irradiation; (b) shape recovery behaviour under 2 W HIFU irradiation; and (c) shape recovery behaviour under conventional heating at 120 °C.

Table 1. HIFU-induced thermal effect and shape recovery for P(MMA-BA) samples of different thicknesses at a power output of 2 W. Monomer composition and crosslinker content for all the samples were fixed at 2.5:1 (MMA:BA in molar ratio) and 1.12 wt%. The rate of initial temperature rise and the rate of initial shape recovery were determined in the first 10 s of HIFU irradiation.

Thickness (mm)	0.38	0.51	0.78	1.05	1.89	2.91	3.78	3.78
Rate of initial temperature rise (°C/s)	0.8	3.3	5.6	6.9	5.9	2.8	0.9	0.9
Thermal equilibrium temperature (°C)	48.0	71.8	96.0	114.4	136.5	133.6	130.2	130.2
Rate of initial shape recovery (%/s)	1.7	3.7	4.3	4.4	2.2	0.9	0.9	0.9
Final shape recovery ratio (%)	42	72	79	82	83	75	70	70
Shape recovery ratio (%) by conventional heating	99	99	99	99	99	99	99	99

From the temperature rise curves (Figs. 4a-4c), it can be seen that upon HIFU irradiation, the sample temperature first rises relatively slowly and then quickly to reach a final equilibrium temperature. This two-step temperature increase is more prominent under lower HIFU powers (1 and 2 W) and for harder P(MMA-BA) copolymer (MMA/BA ratio 3.5:1 and 5:1). By differentiating the curves, a peak can be obtained which likely is related to the glass transition of the polymer. Knowing that HIFU-induced temperature rise is determined by the amount of heat converted from the ultrasonic energy absorbed by polymer chains undergoing viscous shearing and relaxation motions, the early slow temperature rise implies that the harder copolymers (higher T_g) were in the glassy state at the early stage under HIFU irradiation (lower temperatures). As a matter of fact, when ultrasonic wave passes through the polymer matrix, it forces the polymer chains to vibrate in a confined area, which produces the shear force in the polymer chains and lead to inter- or intra- chain friction and thus result in generation of heat.

On close inspection of Figs. 4a-4c and Table 2 where are summarized the data including the rate of initial temperature rise and the equilibrium temperature calculated from Fig. 4b

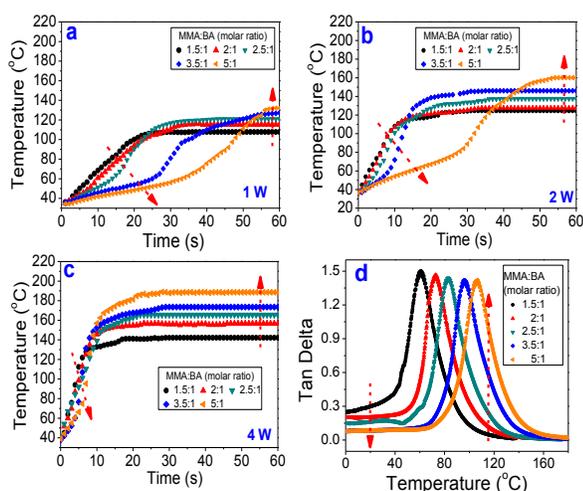


Fig. 4 HIFU-induced temperature rise of P(MMA-BA) copolymer with different MMA/BA ratios and at different ultrasound power outputs: (a) 1 W, (b) 2 W, (c) 4 W; and (d) tan delta of the samples.

(2 W HIFU), and T_{trans} taken as the peak maximum of $\tan \delta$ in Fig. 4d, more insight into the ultrasound-induced local heating can be obtained. It is noticeable that with increasing the MMA/BA ratio the rate of initial temperature rise decreases, while, reversely, the equilibrium temperature increases. This phenomenon is observable for different HIFU powers from 1 W to 4 W. It can be explained by the change trend of the loss factor $\tan \delta$ at different MMA/BA ratios (Fig. 4d). The loss factor $\tan \delta$, being the ratio of loss modulus to storage modulus, is a measure of the lost energy with respect to the recoverable energy, and represents the internal friction or mechanical damping in a viscoelastic system. A high $\tan \delta$ value is indicative of a material that has a high non-elastic strain component, which generates more heat during ultrasonic vibration, and a low $\tan \delta$ value indicates more elastic response, which generates less heat. From Fig. 4d, it can be seen that with increasing the MMA/BA ratio the $\tan \delta$ value decreases at the lower-temperature region (below T_g), but increases at the higher-temperature region (above T_g), as marked by red arrows in the figure. In the beginning stage of HIFU irradiation, the temperature is low (below T_g), P(MMA-BA) copolymer with a higher MMA content has a lower $\tan \delta$ value compared to the one with a lower MMA content. Thus the heat generated by ultrasonic vibration is lower, and the rate of temperature rise is slower. The situation is reversed in the later stage of HIFU irradiation when the reached temperature becomes high (above T_g), P(MMA-BA) copolymer with a higher MMA content has a much higher $\tan \delta$ value, which means that more heat can be generated to lead to a higher equilibrium temperature.

The variations of shape recovery ratio for P(MMA-BA) copolymer of different MMA/BA ratios under HIFU irradiation are shown in Figs. 5a-5c. A couple of observations can be made. First, a higher ultrasound power results in faster shape recovery and a higher shape recovery ratio for all P(MMA-BA) samples due to an increased HIFU-induced thermal effect at higher powers. Second, both the shape recovery rate and the final shape recovery ratio of P(MMA-BA) copolymer decrease with increasing the MMA/BA ratio, which is consistent with the rate of temperature rise and the equilibrium temperature under HIFU irradiation (Fig. 4). Table 2 shows the data for samples at a HIFU power of 2 W. The shape recovery ratio for the sample with the lowest MMA/BA ratio of 1.5:1 can reach ~98% in 30 s. By contrast, for the sample with the higher

MMA/BA ratio of 5:1, even though the equilibrium temperature reaches ~ 160 °C in 60 s at a HIFU power of 2 W, the shape recovery ratio is only about 44%. The main reason for these observations is that the T_g of P(MMA-BA) increases with the MMA/BA ratio. For samples with a higher T_g , it takes a longer heating time to reach that temperature to start the shape recovery process, resulting in a slower rate of shape recovery. To better understand the limited shape recovery ratio for harder P(MMA-BA) samples with a higher T_g , the shape recovery ratio for all samples directly heated to 120 °C was measured. As seen in Fig. 5d, similar behaviours are observable for the samples with various MMA/BA ratios. For these samples, 120 °C (under conventional heating) is in their T_g region and the restricted chain mobility results in restricted chain relaxation and thus limited shape recovery. This result suggests that in the HIFU-induced shape recovery tests, all strained polymer chains in the deformed area may not experience the same temperature above T_g as revealed by the HIFU-induced temperature rise tests (Fig. 2). This issue will be further discussed later.

Fig. 5e shows the photos of shape recovery behaviour of a sample (MMA/BA ratio: 2.5:1, thickness: 1.89 mm, crosslinker content: 1.12 wt%) under gradually increased HIFU power output. The sample was first programmed into a temporary shape "L", then it was fixed on the sample holder and the deformed area was placed at the ultrasound focal spot. At 1 W power output the deformation recovered to a certain extent. Further increasing the power output resulted in an increasingly higher recovery ratio, illustrating that multiple intermediate shapes can easily be obtained by adjusting the HIFU power. The permanent shape was recovered only at a HIFU power of 6 W. The photos in Fig. 5e give a hint on why the shape recovery ratio is still limited at a HIFU power of 4 W (Fig. 5c) for harder P(MMA-BA) samples (MMA/BA ratio: 3.5:1 and 5:1) despite the high ultrasound-induced temperatures above T_g s of these samples (Figs. 4c and 4d). This incomplete shape recovery is likely caused by the experimental setup. With the deformed area of the L-shaped sample exposed to the focal spot of the HIFU beam, it is possible that part of strained polymer chains in the deformed area don't experience a temperature above T_g due to the distribution of ultrasound-induced temperature rise inside the sample, which is dependent on the HIFU power. A power higher than 4 W is necessary to allow all strained polymer chains in this folded area to experience temperatures above T_g , which is required for complete chain relaxation and for complete shape recovery.

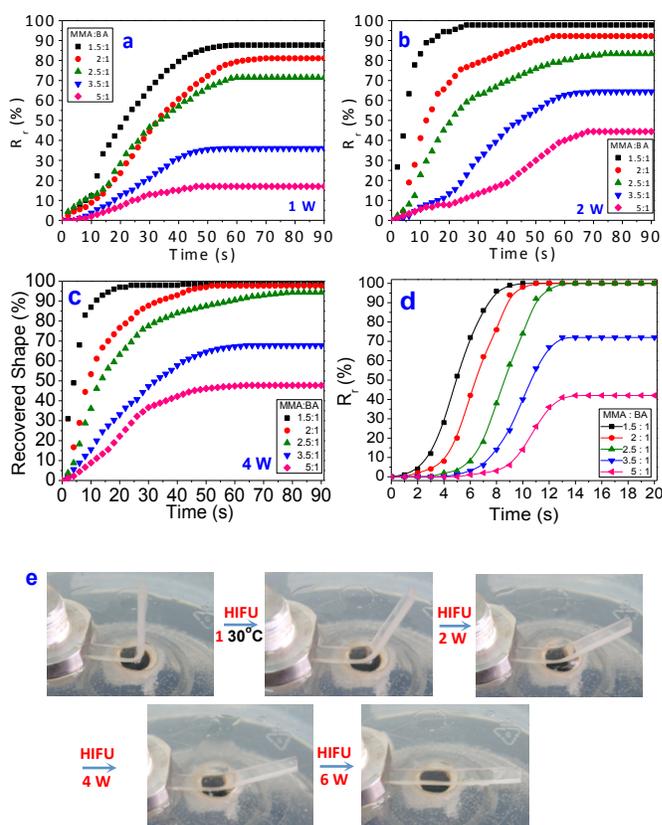


Fig. 5 The shape recovery behaviour of P(MMA-BA) copolymer with different compositions under HIFU irradiation at applied power of (a) 1 W, (b) 2 W and (c) 4 W; and (d) under conventional heating at 120 °C. (e) Photos of shape recovery behaviour of P(MMA-BA) copolymer with different composition under HIFU. The sample with a permanent shape "I" was deformed into a temporary shape "L", and then the deformation area was exposed to HIFU, The power output was changed from 1 W to 6 W gradually.

Effect of Crosslinker Content on HIFU-Induced Thermal Effect and Shape Memory

The crosslinking for P(MMA-BA) copolymer is necessary to assure a good shape memory behaviour as the network enables the polymer to return to its permanent shape under HIFU irradiation. The network crosslinking density, which is determined by the crosslinker content, should be another structural parameter that influences the HIFU-induced temperature rise and the related shape recovery of P(MMA-

Table 2 HIFU-induced thermal effect and shape recovery for crosslinked P(MMA-BA) with different MMA/BA ratio, at 2 W power output. Thickness and crosslinker content of all the samples were fixed at 1.89 mm and 1.12 wt%.

MMA:BA	1.5:1	2:1	2.5:1	3.5:1	5:1
T_{trans}	60.9	72.4	83.4	95.8	106.2
Rate of initial temperature rise (°C/s)	7.1	7.0	5.9	3.5	1.7
Equilibrium temperature (°C)	124.5	127.6	136.5	146.0	160.1
Rate of initial shape recovery (%/s)	8.3	4.1	2.2	0.7	0.5
Shape recovery ratio (%) by HIFU heating	98	92	83	64	44
Shape recovery ratio (%) by conventional heating	99	99	99	75	45

BA). To investigate this, P(MMA-BA) copolymers crosslinked to various extents by using different crosslinker contents while keeping the MMA/BA ratio at 2.5:1 were synthesized. For all the experiments described below, the sample thickness and molar ratio was retained at 1.89 mm and 2.5:1, respectively.

First, the temperature rise for P(MMA-BA) with different crosslinker contents under 2 W HIFU irradiation was measured and the results are shown in Fig. 6a. The rates of initial temperature rise and the equilibrium temperature for all samples are listed in Table 3. With increasing the crosslinker content, the rate of initial temperature rise decreases, while the equilibrium temperature increases. The sample with a crosslinker content of 1.12 wt%, has a rate of initial temperature rise of ~ 5.9 °C/s and a thermal equilibrium temperature of 136.5 °C, while for the sample at a crosslinker content of 15 wt%, these numbers change to ~ 2.3 °C/s and 158.6 °C, respectively. The effect of crosslinker content on the HIFU-induced thermal effect is similar to the effect of the MMA/BA ratio as discussed above, suggesting the same origin of viscoelastic properties. This indeed was confirmed by the measured loss factor crosslinker content, while the opposite is seen at the high-temperature side (indicated by arrows). Consequently, at the beginning of HIFU irradiation, the temperature is low; the heat generated by HIFU is more important for samples at lower $\tan \delta$ as shown in Fig. 6b. It is clear that with increasing the crosslinker content, the T_g of the sample increases. Also, at the low-temperature region, the value of $\tan \delta$ decreases with increasing the crosslinking degrees which are closer to the glass transition and have greater $\tan \delta$. Reversely, in the late stage of HIFU irradiation, the temperature reaches above T_g for all samples and the amount of heat generated by HIFU is greater for samples at higher crosslinking degrees due to higher $\tan \delta$ values. The effect of the crosslinker content on the HIFU-induced thermal effect is similar as the effect of the MMA/BA ratio as stated above. Fig. 6c shows the rate of initial temperature rise for all samples subjected to HIFU irradiation at a power output between 1 W and 6 W. As expected, the rate of temperature rise increases with increasing the ultrasound power. However, at a given HIFU power, the effect of crosslinking density on the temperature rise rate

remains the same, i.e., decreases with increasing the crosslinker content.

The shape recovery behaviour of P(MMA-BA) copolymer with different crosslinker content under 2 W HIFU irradiation is shown in Fig. 7a. Extracted data on the rate of initial and the final shape recovery ratio are also reported in Table 3. It is no surprise to notice that the rate of initial shape recovery decreases with increasing the crosslinker content, since it is dictated by the rate of initial temperature rise. A somewhat surprising finding is shown in Fig. 7b. Although the achievable final shape recovery ratio increases with increasing the HIFU power, it seems little affected by the crosslinker content at a given ultrasound power. Considering the effect of the copolymer composition, the final shape recovery ratio would be expected to become lower for samples with a higher crosslinker content because of the higher T_g . The possible explanation for this observation is that for SMPs with higher crosslinking density, the strain energy stored in the temporary shape usually is greater, which favours the return to the permanent shape. This positive effect for shape recovery may offset the unfavourable effect of increased T_{trans} . To complete the tests, shape recovery behaviour of P(MMA-BA) with different crosslinker contents under conventional heating to 120 °C was also investigated. The results in Fig. 7c show that the shape recovery process is nearly complete regardless of the crosslinker content.

Table 3. HIFU-induced thermal effect and shape recovery for P(MMA-BA) with different crosslinker contents under 2 W HIFU irradiation. Monomer composition and thickness were fixed at 2.5:1 (MMA:BA in molar ratio) and 1.89 mm.

Crosslinker content (wt%)	1.12	5	10	15
T_{trans}	83.4	91.7	98.8	104.8
Rate of initial temperature rise (°C/s)	5.9	3.9	3.2	2.3
Equilibrium temperature (°C)	136.5	142.7	149.1	158.6
Rate of initial shape recovery (%/s)	2.2	1.2	1.0	0.4
Final shape recovery ratio (%)	83	79	82	84
Shape recovery ratio (%) by conventional heating	99	99	99	99

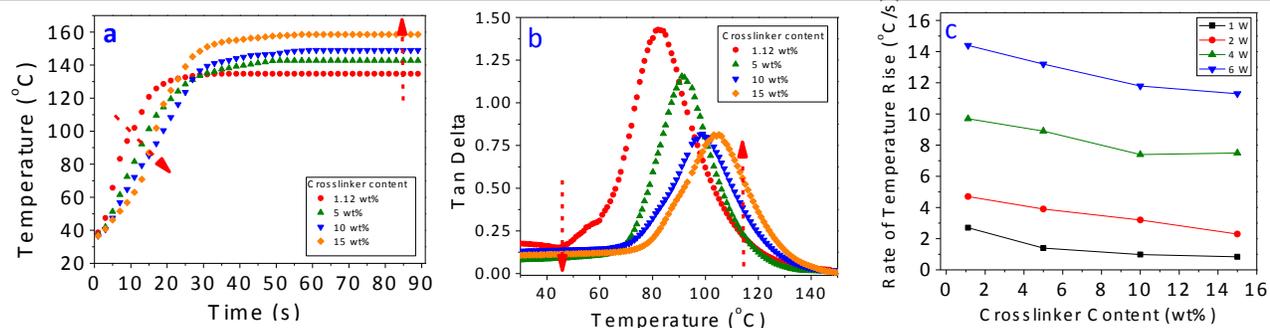


Fig. 6. (a) HIFU-induced temperature rise for P(MMA-BA) copolymer with different crosslinker content under an ultrasound power of 2W. (b) Tan delta of the samples. (c) Rate of initial temperature rise under HIFU irradiation at various powers (1, 2, 4 and 6 W) vs. crosslinker content.

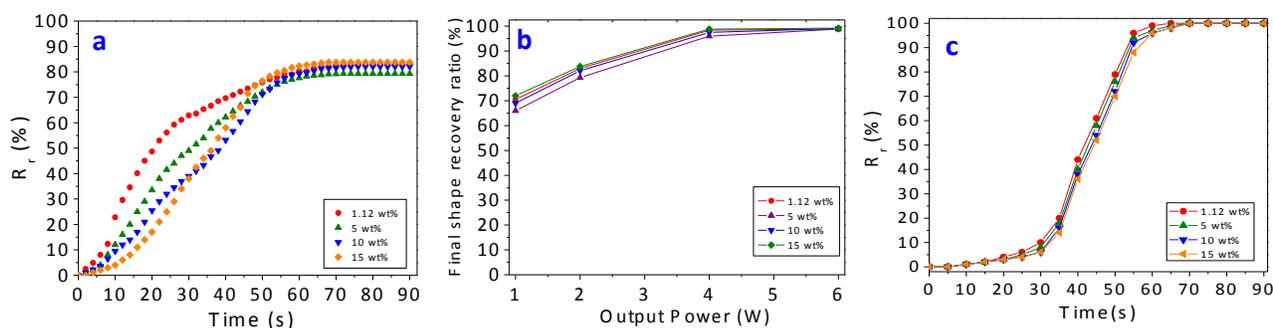


Fig. 7 Results on P(MMA-BA) copolymer with different crosslinker contents: (a) shape recovery ratio vs. HIFU irradiation time at an ultrasound power of 2 W; (b) plots of final shape recovery ratio as a function of HIFU power; and (c) shape recovery under conventional heating at 120 °C.

Conclusions

We have conducted a comprehensive study on HIFU-induced thermal effect and temporary-to-permanent shape transition of crosslinked P(MMA-BA) copolymer chosen as a model shape memory polymer. The results show that HIFU-induced heating is quick and spatially localized, and can be controlled by the ultrasound power, making HIFU an effective remote stimulus to trigger and control the shape recovery process. Under HIFU irradiation, samples of different thickness can experience different HIFU-induced thermal effects and there exists an optimum sample thickness for a maximum thermal effect and thus better shape recovery, which is different from conventional heating stimulus. The shape recovery rate and ratio first increase and then decrease with increasing the sample thickness, which is related to the rate of temperature rise and the equilibrium temperature under HIFU. Moreover, crosslinked P(MMA-BA) at lower MMA/BA ratio displays faster temperature rise and thus quicker shape recovery rate and higher shape recovery ratio. Upon increase of the MMA/BA ratio, while the rate of temperature rise decreases, the equilibrium temperature increases, which can be attributed to smaller loss tangent of the copolymer in the low temperature region (below T_g) and greater loss tangent in the high temperature region (above T_g) with the MMA/BA ratio. Finally, increasing the crosslinking density has the same effect on the HIFU-induced temperature rise and shape recovery as that by increasing the content of hard MMA in the copolymer, which can also be explained by the changing trend in the loss tangent of the sample. This study helps understanding the characteristics of the HIFU trigger for controlling shape memory polymers.

Acknowledgements

H.S. Xia acknowledges financial support from the major project of Chinese Ministry of Education (313036) and National High-Tech Research and Development Program of China (863 Program, 2012AA020504). YZ is grateful to the financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) and le Fonds de recherche du Québec: Nature et technologies (FRQNT). GL thanks China Scholarship Council (CSC) for a scholarship allowing him to study in Canada.

Notes and references

^a State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute, Sichuan University, Chengdu 610065, China.

^b Département de chimie, Université de Sherbrooke, Sherbrooke, Québec, J1K 2R1, Canada.

Corresponding authors: xiahs@scu.edu.cn; yue.zhao@usherbrooke.ca

- M. A. Ward and T. K. Georgiou, *Polymer*, 2011, **3**, 1215-1242.
- I. Tan, F. Roohi and M. M. Titirici, *Analytical Methods*, 2012, **4**, 34-43.
- A. K. Bajpai, S. K. Shukla, S. Bhanu and S. Kankane, *Prog. Polym. Sci.*, 2008, **33**, 1088-1118.
- J. P. Chen and A. S. Hoffman, *Biomaterials*, 1990, **11**, 631-634.
- M. Behl, M. Y. Razzaq and A. Lendlein, *Adv. Mater.*, 2010, **22**, 3388-3410.
- P. T. Mather, X. F. Luo and I. A. Rousseau, *Ann. Rev. Mater. Res.* 2009, **39**, 445-471.
- J. R. Kumpfer and S. J. Rowan, *J. Am. Chem. Soc.*, 2011, **133**, 12866-12874.
- A. Lendlein, H. Y. Jiang, O. Junger and R. Langer, *Nature*, 2005, **434**, 879-882.
- K. C. Hribar, R. B. Metter, J. L. Ifkovits, T. Troxler and J. A. Burdick, *Small*, 2009, **5**, 1830-1834.
- U. N. Kumar, K. Kratz, W. Wagermaier, M. Behl and A. Lendlein, *J. Mater. Chem.*, 2010, **20**, 3404-3415.
- U. N. Kumar, K. Kratz, M. Heuchel, M. Behl and A. Lendlein, *Adv. Mater.*, 2011, **23**, 4157-4162.
- K. Yu, Z. C. Zhang, Y. J. Liu and J. S. Leng, *Appl. Phys. Lett.*, 2011, **98**, 074102-074104.
- Y. J. Liu, H. B. Lv, X. Lan, J. S. Leng and S. Y. Du, *Compos. Sci. Technol.*, 2009, **69**, 2064-2068.
- Z. W. He, N. T. Satarkar, T. Xie, Y. T. Cheng and J. Z. Hilt, *Adv. Mater.*, 2011, **23**, 3192-3196.
- H. Koerner, G. Price, N. A. Pearce, M. Alexander, R. A. Vaia, *Nat Mater*, 2004, **3**, 115-120.
- R. Mohr, K. Kratz, T. Weigel, M. Lucar-Gabor, M. Moneke and A. Lendlein, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 3540-3545.
- A. Lendlein, H. Y. Jiang, O. Junger and R. Langer, *Nature*, 2005, **434**, 879-882.
- M. Bao, Q. H. Zhou, W. Dong, X. X. Lou and Y. Z. Zhang, *Biomacromolecules*, 2013, **14**, 1971-1979.

Journal Name

19. G. Li, G. X. Fei, H. S. Xia, J. J. Han and Y. Zhao, *J. Mater. Chem.* 2012, **22**, 7692-7296.
20. B. Liu, H. S. Xia, G. X. Fei, G. Li and W. R. Fan, *Macromol. Chem. Phys.*, 2013, **214**, 2519-2527.
21. J. J. Han, G. X. Fei, G. Li and H. S. Xia, *Macromol. Chem. Phys.*, 2013, **214**, 1195-1203.
22. J. E. Kennedy, *Nat. Rev. Cancer*, 2005, **5**, 321-327.
23. H. Bruinewoud, PhD thesis, The Eindhoven University of Technology, 2005.
24. R. Xiao, J. W. Choi, N. Lakhera, C. M. Yakacki, C. P. Frick and T. D. Nguyen, *J. Mech. Phys. Solids.*, 2013, **61**, 1612-1635.
25. R. Xiao and T. D. Nguyen, *Soft Matter*, 2013, **9**, 9455-9464.

Table of Contents Entry

A random copolymer shape memory behaviour triggered by high intensity focused ultrasound (HIFU) was studied in detail.

