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Tuning of thermally-induced shape memory properties of low-cost biocompatible linear and
chemically crosslinked isobornyl/isobutylacrylate copolymers

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ABSTRACT

A series of binary low-cost biobased copolymers was elaborated from isobornylacrylate (IBOA) and isobornyl (IsoBA) monomers applying UV-visible induced free radical polymerization, yielding linear and crosslinked architectures. Thermo-mechanical measurements revealed that the elaborated random copolymers exhibit single glass transition temperatures, which can be adjusted on a broad temperature range by varying the amount of IBOA- and HDDA-units. Governed by the glass transition, linear high molecular weight IBOA-isoBA copolymers exhibit good thermally induced shape memory properties related to the occurrence of strong physical entanglements, reinforced by the presence of the voluminous isobornylene groups. Fixity and recovery ratios were found to be in the same order of magnitude when compared to crosslinked thermoplastics and thermosetting polymers. Linear IBOA-isoBA copolymers maintain their form memory properties even after several application cycles, confirming the efficiency of the presence of physical crosslinking. These findings can be explained by the high entanglement molecular weight of 44 kg/mol providing an important elasticity as well as by an elevated glassy/rubbery moduli ratio of around 3000, facilitating deformation and fixing modes.

Keywords: Isobornyl acrylate • isobutyl acrylate • entanglements • shape memory polymers • thermomechanical characterization.

1. Introduction

Shape memory polymers (SMPs) are materials that possess the ability to regain their permanent shapes upon exposure to external stimuli such as temperature [1], electrical field [2], light [3], magnetic field [4], or humidity [5]. Thermoset SMPs deform mechanically at a temperature above a certain transition temperature (T_{trans}), and can be fixed to a temporary shape before being cooled to a temperature below T_{trans} [6]. Heating a SMP above T_{trans} allows to regain its permanent form.

The thermomechanical behavior of SMPs requires generally the existence of two phases which present different thermomechanical properties. The first phase is rigid allowing the fixing of the shape of the polymer at low temperature and the second phase is flexible and represents some mobility, allowing the deformation of the material above a transition temperature, from the first to the second phase. SMPs can be used as an alternative to shape memory alloys (SMAs) in many applications and most importantly, they can be used in applications where SMAs cannot be used. SMPs are less expensive to produce and they can easily be worked into a variety of different shapes and sizes. These performances make it possible to consider industrial applications in several fields such as aerospace [7] namely deformable airplane wings [8], and intelligent textiles [1]. SMPs are classified into two main categories according to the physical and chemical nature of the crosslinking points. For SMPs based on chemical crosslinks, shape memory properties strongly depend on the degree of covalent crosslinking [1-3]. The key aspect of SMPs based on physical crosslinking is crystalline or amorphous rigid segment, and the high molecular weight of their main chains, forming strong entanglements. Among the physically crosslinked SMPs, thermoplastic segmented polyurethanes have been extensively investigated for their shape memory effects [9-12]. Amorphous viscoelastic polymers with high molecular weight ($> 10^6$ g/mol) also show shape memory effects, due to the absence of flow above the glass transition, and their high

elasticity ratio E_g (glassy state modulus)/ E_r (rubbery state modulus). Polynorbornene (Norsorex[®]) [13,14] and poly (methyl methacrylate) (PMMA) with high molecular weight, for example, possess a significant number of molecular entanglements in their chains, serving as (non-covalent) physical crosslinks [15]. These entanglements form a 3D network leading to excellent elasticity in the glassy domain. Polynorbornene and PMMA exhibit efficient shape recovery due to their high entanglement density, highlighted by the lack of flow and large rubbery plateaus [16]. It has already been reported from reptation theory as well as from tube model, that molecular chains tend to form entanglements when the chain length exceeds a critical value M_c [17, 18]. Although the role of hard/soft segments, crystallinity, and molecular entanglements in SMPs has already been discussed in many studies, there is a lack of reports dealing with the influence of entanglement density and elasticity ratio on shape memory performance of amorphous linear acrylate and methacrylate copolymers.

Regardless of the SMP type, the glass transition temperature (T_g) corresponding to T_{trans} represents a crucial parameter for their operation. It can be tailored around body temperature making SMPs attractive for their use in biomedical applications [19] such as catheters [20], stents [21], neural electrodes [22], aneurysms [23], microactuators to remove clots from blood vessels [24], artificial muscles [25], and sutures [26]. SMPs are currently under study for use as fixation of a fractured bone [27]. Each application requires a combination of different properties and functions, therefore, SMPs with well-defined properties are required. However, it is difficult in practice to develop new monomers or crosslinking agents with adjusted properties, for example to obtain appropriate T_g 's. In this context, the use of copolymers allow tuning the thermomechanical properties by playing with their composition and morphology [28]. Acrylate-based copolymers are particularly advantageous because of their ease of use. Their mechanical and rheological properties can be adjusted by varying composition, chemical structure, and molecular weight of the monomers [29]. Many reports in literature

focus on chemically crosslinked polymer networks for synthesizing SMPs [30], which can be triggered near the temperature of the human body. However, there are still several limitations in the synthesis of suitable SMPs, such as the choice of segments and the adjustment of mechanical properties. The most relevant drawbacks of SMPs are high recovery temperatures [31] and long recovery periods [32].

In this work, a simple strategy for modulating T_g of new versatile acrylate-based thermally controlled SMPs functioning near the human body temperature will be proposed, via elaboration of linear and chemically crosslinked random copolymers based on isobornylacrylate (IBOA) and isobutylacrylate (IsoBA) units. Variation of the copolymer composition allows tuning of the glass transition and thus the operational temperature domain of these SMPs. Thermo-mechanical studies by DMA will be carried out to characterize the behavior of the elaborated linear and crosslinked copolymers under the effect of temperature. The effect of shape memory and recovery as well as the efficiency of the SMP performance after several cycles will be investigated.

2. Materials and methods

2.1 Materials

Isobutylacrylate (IsoBA), isobornylacrylate (IBOA) and 1,6 hexanedioldiacrylate (HDDA) were considered as acrylic compounds. 2-hydroxy-2-methyl-1-phenyl-propan-1-one (commercial designation: Darocur 1173) was used as photoinitiator. All these products were purchased from Sigma-Aldrich, France, and used as received.

2.2. Preparation of copolymers

Four IsoBA/IBOA based copolymers were elaborated by varying the weight percentage of IsoBA/IBOA/HDDA as follows: 40/60/0, 50/50/0, 60/40/0, 59.75/39.75/0.5, leading to linear copolymers except for the last composition, which generates a chemically crosslinked network using experimental method described in our previous work [33a, 33b]. Linear acrylic

homopolymers were prepared as well, based on *n*-butylacrylate (*n*BA), 2-ethylhexylacrylate (2-EHA), and tert-butyl acrylate (*t*BA). The amount of photoinitiator was set at 0.5% by weight related to the total weight of monomers. After a stirring time of 3h at room temperature, the monomeric solutions were poured into Teflon molds, and then exposed to UV-visible light at a wavelength of $\lambda=365\text{nm}$ and an intensity of $I_0=1,5\text{mW}/\text{cm}^2$ (Philips black light) (Fig. 1). The monomeric mixtures were exposed to UV-visible light during 40 min under nitrogen atmosphere to ensure maximum conversion of acrylic monomers double bonds.

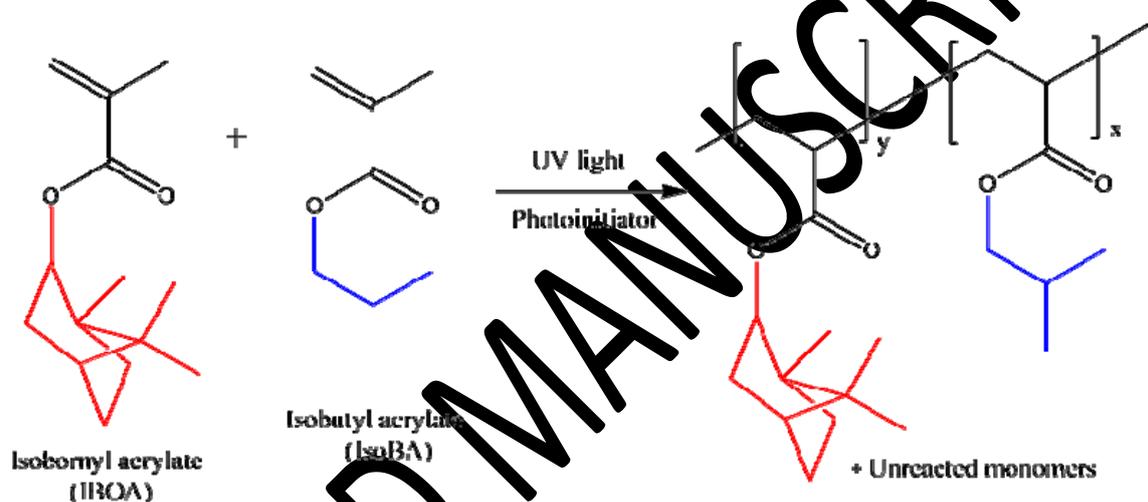


Fig. 1. Schematic representation of the elaboration of linear $[\text{IsoBA}]_x$ - $[\text{IBOA}]_y$ copolymers using UV-visible light induced polymerization of the corresponding monomers in the presence of a photoinitiator. A more detailed presentation of the reaction mechanism is given in Fig. 11.

2.3. Characterization techniques

2.3.1. Molecular weight determination

Gel permeation chromatography (GPC) analysis was carried out at room temperature on a Waters Alliance e2695 system using differential refractive index (Wyatt RI) and Multi Angle Light Scattering (Wyatt MALS, λ (laser) = 670 nm) detectors. Three columns were coupled in

series (Styragel HR1, Styragel HR3, Styragel HR4). THF was used as solvent (flow rate 1mL/min), and calibration was established with polystyrene (PS) standards from Polymer Laboratories.

2.3.2. Differential scanning analysis

Thermal properties of the elaborated copolymers were investigated by means of a DSC (Perkin-Elmer model 8000). The experiments were carried out under nitrogen flow (20 mL/min) applying a heating rate of 10°C/min. Calibration of the instrument was performed with indium and zinc as standards. 8-10 mg of copolymers were introduced from arbitrary positions of the disk-shaped samples into aluminum crucibles.

The program consisted first in cooling the sample, followed by three heating and cooling cycles at a rate of 10°C/min in the temperature range from -72°C to 120°C, separated by one-minute isotherms at maximum/minimum temperatures. Only thermograms from the second heating cycles were considered for the analysis. T_g was determined from the midpoint of the transition range of the thermograms by using a software program from Perkin-Elmer (Pyris).

2.3.3. Thermomechanical studies

Dynamic Mechanical Analysis (DMA) was performed using a Perkin Elmer DMA 8000 device. The thermomechanical studies of the copolymer samples were carried out under nitrogen atmosphere in traction mode at a frequency of 1Hz applying a heating rate of 5°C/min in the temperature range from -60°C to 200°C. Test samples were cutted into rectangular shapes with dimensions of 29 mm x 7mm x 2 mm.

2.3.4. Shape memory polymer evaluation

The dual shape memory experiments were conducted in a controlled force mode measuring strain and stress, using a Perkin Elmer DMA 8000 device. The sample exhibiting identical dimensions as described in section 2.3.3., was heated to a temperature of 80°C (well above

T_{trans} equal to T_g), by application of a constant heating rate of 5°C/min, followed by an isothermal step of 10min, to ensure a good homogeneous temperature distribution throughout the sample. Then, a static force of 0.8N was applied during a period of 10 min to deform the sample uniaxially. The next step consists in cooling down the sample (cooling rate 5°C/min) to 0°C using liquid nitrogen, followed by an isothermal step of 10 min. Then, the applied force was removed and the fixing of the temporary shape was completed. The sample was subsequently heated up again to 80°C, using a constant heating rate of 5°C/min, allowing to recover the initial (permanent) shape. Shape fixity (R_f) and shape recovery (R_r) ratios were calculated using Eqs. (1) and (2):

$$R_f = 100\% \times \frac{\varepsilon}{\varepsilon_{Load}} \quad (1)$$

$$R_r = 100\% \times \frac{(\varepsilon - \varepsilon_{rec})}{\varepsilon} \quad (2)$$

where ε stands for the fixed strain after sample cooling when the external load is removed, ε_{Load} represents the maximum strain under external load, while ε_{rec} corresponds to the strain measured after recovery.

Nota bene : Good fixation of the samples might result in a sudden increase in stress shown in the figures presenting shape memory effects. In fact, polymer chains in this unstable step apply a force in the opposite direction to that applied during fixation, except that this force is not large enough for the chains to relax completely, allowing the sample to return to its stable permanent state. This concurrency between applied force and reverse force causes an increase in the stress of the sample.

2.3.5. Stress-strain behavior of shape memory polymers

Tensile tests to evaluate the yield strain were carried out on a VERSA® machine, equipped with a force transducer of ±100N. The reproducibility of the experiments was evaluated by comparing the response curves of a few specimens analyzed under the same loading

condition. The stretching speed used was 200 mm/s.

2.3.6. Stress-relaxation of shape memory polymers

Stress-relaxation experiments were performed on SMPs using the Perkin Elmer DMA 8000 device. A constant strain was applied on SMPs to induce a fixed deformation (10%) for a defined time, and the change in stress to maintain that strain was measured.

3. Results and discussions

3.1 Molecular weights

Number and weight average molecular weights, M_n and M_w , as well as molecular weight distributions (polydispersities) M_w/M_n of linear [IsoBA]_x-[IBOA]_y copolymers and other linear acrylic homopolymers were gathered in Table 1. M_n of the copolymers varied from

Table 1. Designation, molecular weights and polydispersities of [IsoBA]_x-[IBOA]_y copolymers and *n*BA-, 2-EHA-, and *t*BA homopolymers. ND = Not Determined (crosslinked).

Materials	IsoBA/IBOA/HDEHA ratio (wt%)	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n
[IsoBA] ₆₀ -[IBOA] ₀	60/0/0	322	533	1.65
[IsoBA] ₅₀ -[IBOA] ₁₀	50/50/0	224	528	1.6
[IsoBA] ₅₀ -[IBOA] ₅ (low M_n)	50/50/0	61	122	2
[IsoBA] ₄₀ -[IBOA] ₆₀	40/60/0	374	750	2
[IsoBA] ₄₀ -[IBOA] ₆₀ -R	39.75/59.75/0.5	ND	ND	ND
[IsoBA] ₄₀ -[IBOA] ₆₀ (low M_n)	40/60/0	58	119	2.05
<i>n</i> BA	-	282	402	1.4
2-EHA	-	263	417	1.6
<i>t</i> BA	-	260	423	1.62

224 kg/mol to 374 kg/mol, and their polydispersities from 1.6 to 2. The obtained molecular

weights for all linear copolymers were high enough for physical entanglements to be created [34]. A slight upward trend of the molecular weights was observed when increasing the amount of IBOA in the copolymers.

3.2. Glass transition

The elaborated acrylic copolymers considered here were previously characterized by DSC to investigate their phase behavior and to determine their T_g 's [33b,33c]. In order to compare results from DSC with those obtained from DMA, Fig. 2 reproduces selected thermograms from reference [33b,33c], and the corresponding T_g -data were collected in Table 2. Addition of 0.5wt-% of the bifunctional acrylic HDDA to the monomeric mixture composed of [IsoBA]₄₀ and [IBOA]₆₀ yields a higher T_g of the crosslinked copolymer than that of the linear one. This result was expected, since crosslinking restricts free chain motion, and the polymer requires more energy i.e. higher temperature to transform from glassy to rubbery state.

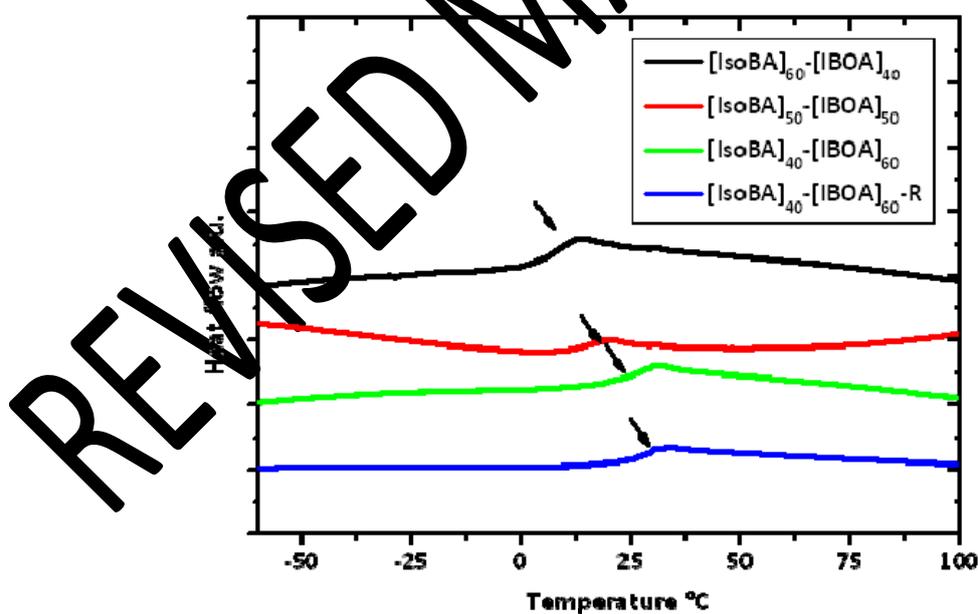


Fig. 2. Thermograms of linear and crosslinked [IsoBA]_x-[IBOA]_y copolymers [33b,33c].

3.3. Dynamic mechanical properties

[IsoBA]_x-[IBOA]_y copolymers were examined by DMA applying a temperature sweep mode

to examine the thermomechanical properties of the samples. At temperatures above T_g , polymer chains follow micro-Brownian motion, leading to rubbery behavior, whereas below T_g , this type of motion is frozen and the copolymers become glassy. The evolution of the storage (E') modulus of $[\text{IsoBA}]_x\text{-}[\text{IBOA}]_y$ copolymers as function of temperature is shown in Fig. 3a. The linear copolymers show apparent rubbery plateaus confirming the formation of physical entanglements of the polymer chains [35]. The storage modulus E' in the glassy state increased by raising the $[\text{IBOA}]/[\text{IsoBA}]$ ratio, which is mainly due to the specific chemical structure of IBOA, containing the voluminous isobornylene group. The latter reduces the free volume of the copolymer and consequently increases the storage modulus.

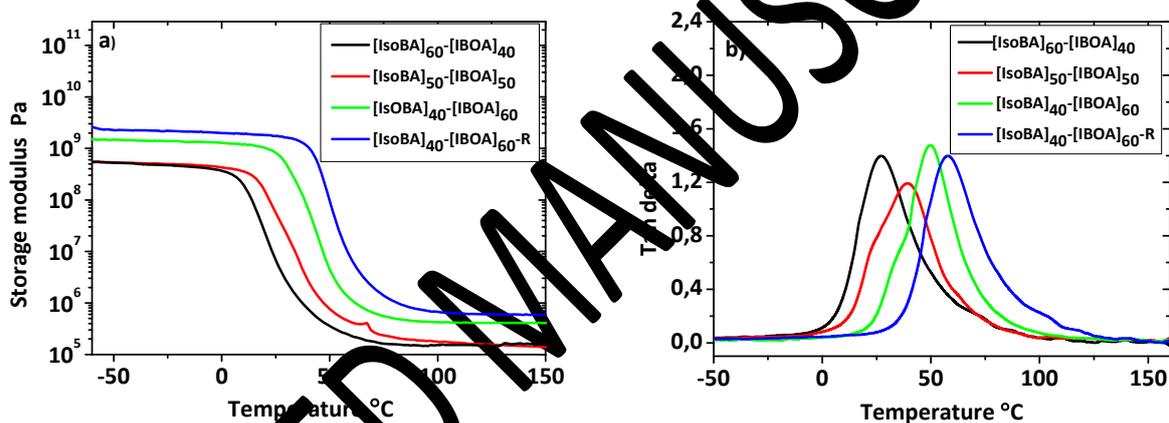


Fig. 3. (a) Storage modulus and (b) $\tan \delta$ as functions of temperature for linear and crosslinked (R) $[\text{IsoBA}]_x\text{-}[\text{IBOA}]_y$ copolymers.

Incorporation of HDDA as crosslinking agent into the copolymer increases the storage modulus compared to the linear copolymer, due to the establishment of covalent permanent crosslinking points (Table 2). Storage moduli values were found to be comparable to those of photochemically synthesized acrylic polymers [36].

Dissipation factors ($\tan \delta$) were obtained by calculating the ratio of loss to storage moduli, and T_g 's were determined from the temperatures corresponding to the peak maxima of the $\tan \delta$ curves. Fig. 3b shows the evolution of $\tan \delta$ as function of temperature, revealing that an

increase of the IBOA concentration in the copolymers shifts the glass transition to higher temperatures, similar to the results obtained by DSC (Fig. 2). The presence of chemical crosslinking points raised T_g to 57°C, 7°C higher than the corresponding value of the linear copolymer.

Table 2. Some thermo-mechanical properties of [IsoBA]_x-[IBOA]_y copolymers.

Materials	E' (Pa) ^a	T_g DSC (°C)	T_g tan delta (°C) ^a	M_e (kg/mol)	ν_e (E/m ³) ^b
[IsoBA] ₆₀ -[IBOA] ₄₀	3.7×10^8	7.7	27.1	4.2	2.57×10^{25}
[IsoBA] ₅₀ -[IBOA] ₅₀	4.2×10^8	15.6	39.1	4.3	2.15×10^{25}
[IsoBA] ₄₀ -[IBOA] ₆₀	1.2×10^9	24.2	50	4.6	2.76×10^{25}
[IsoBA] ₄₀ - [IBOA] ₆₀ -R	2×10^9	29.1	57	6.2	1.18×10^{25c}

^a: storage moduli and tan δ determined at ($T=-25^\circ\text{C}$).

^b: entanglements/m³ calculated using Bersted entanglement model (Eq. 4).

^c: The value of M_n taken to calculate ν_e is that of the linear copolymer.

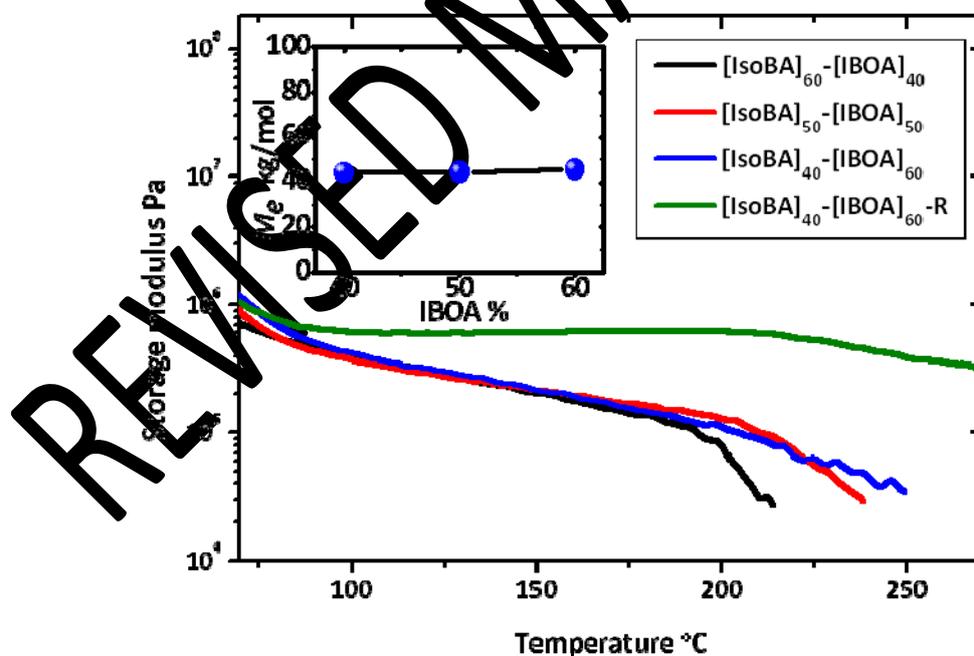


Fig. 4. Storage modulus of [IsoBA]_x-[IBOA]_y copolymers in the rubbery region. The insert shows the dependence of the entanglement molecular weight M_e on the sample composition for linear copolymers.

T_g data obtained by DMA were found to exceed the corresponding values from DSC by several degrees. Indeed, the peak maximum of $\tan \delta$ corresponds roughly to the transition midpoint or inflection point of the decreasing $\log E'$ curve, while T_g values determined by DSC can be related to the initial drop of E' at the transition of glassy to rubbery states.

Fig. 4 illustrates an important difference of the temperature dependant evolution of E' for linear and crosslinked $[\text{IsoBA}]_x\text{-}[\text{IBOA}]_y$ copolymers in the rubbery region. All linear $[\text{IsoBA}]_x\text{-}[\text{IBOA}]_y$ copolymers show overlapping pseudo-plateau rubbery moduli over a broad temperature range (from 90°C to 170°C). Existence of such plateau modulus indicates the presence of molecular entanglements [34]. Indeed, these entanglements play the role of efficient physical crosslinking points, representing one of the salient features leading to desirable shape memory behavior.

Table 3. Some properties of SMPs based on $[\text{IsoBA}]_x\text{-}[\text{IBOA}]_y$ copolymers and *n*BA-, 2-EHA-, and *t*BA-homopolymers.

Materials	E_g/E_r	Shape fixity (%)	Shape recovery (%)
$[\text{IsoBA}]_{60}\text{-}[\text{IBOA}]_{40}$	3131	89	93.7
$[\text{IsoBA}]_{50}\text{-}[\text{IBOA}]_{50}$	2877	88	93
$[\text{IsoBA}]_{50}\text{-}[\text{IBOA}]_{50}\text{-low } M_n$	858	No fixity	No recovery
$[\text{IsoBA}]_{40}\text{-}[\text{IBOA}]_{60}$	3274	97	90.5
$[\text{IsoBA}]_{50}\text{-}[\text{IBOA}]_{50}\text{-R}$	3130	82	88.4
$[\text{IsoBA}]_{40}\text{-}[\text{IBOA}]_{60}\text{-low } M_n$	349	No fixity	No recovery
<i>n</i> BA	3097	91	94
2-EHA	2723	89	91
<i>t</i> BA	2948	91	95

Above 170°C, the storage moduli of the linear copolymers drop significantly, since the increased free volume leads to chain sliding and the material starts to flow. The ability to flow generally depends on the polymer molecular weight, however, no such dependence was observed from Fig. 4, keeping in mind that the molecular weights were roughly situated in the

same range of values (Table 1). On the other hand, the starting flow temperature seems to be composition-dependent: increasing concentration of IBOA units in the copolymers shifts this temperature to higher values, probably related to the increased sterical hindrance effect of the bulky IBOA units, reducing thus chain sliding. In the case of the [IsoBA]₄₀-[IBOA]₆₀-R copolymer, the rubbery modulus remains constant over the entire temperature range from 90°C to 200°C and the material behave like a rubber. This copolymer does not flow under the effect of temperature contrary to the linear copolymers.

Ratios of E_g/E_r of more than 100 facilitate the deformation of the many responsive SMP materials at high temperatures and their fixing at low temperatures [37]. E_g and E_r values were extracted from Fig. 3a at $T=-25^\circ\text{C}$ and $T=100^\circ\text{C}$, respectively, and Table 3 represents the corresponding data showing that all copolymers exhibit ratios around 3000. This means that the elaborated linear as well as the crosslinked [IsoBA]_x-[IBOA]_y copolymers are potentially interesting SMP materials and should present good shape memory properties.

The magnitude of the molecular weight between entanglements (M_e) represents one of the key parameters influencing the mechanical properties of SMP. For linear and chemically crosslinked polymer chains M_e is defined as molecular weight between adjacent temporary and permanent entanglement points, respectively, and is mainly controlled by the molecular architecture. Zosel et al. [23] as well as Jullian et al. [39] demonstrated that high M_e would provide an important elasticity, which is a crucial parameter to obtain optimal SMP properties. Moreover, high M_e values should provide an easy shape recovery. As the physical meaning of rubbery plateau refers to the stress maintain during deformation [30] that would be necessary for an optimal recovery, the lowest shape recovery would be expected for the crosslinked [IsoBA]₄₀-[IBOA]₆₀-R copolymer. M_e can be estimated by writing ([39], and references cited therein) :

$$M_e = \frac{3\rho RT}{E_r} \quad (3)$$

where E_r corresponds to the storage modulus of the rubber plateau taken at $T=T_g + 40^\circ\text{C}$, ρ stands for the polymer density [40], R is the gas constant, and T represents the absolute temperature. Table 2 and the insert of Fig. 4 present the calculated M_e data : The values obtained for the linear copolymers were found to be almost identical; $M_e= 44$ kg/mol for [IsoBA]₆₀-[IBOA]₄₀ and [IsoBA]₅₀-[IBOA]₅₀, and $M_e= 45$ kg/mol for [IsoBA]₄₀-[IBOA]₆₀. However, M_e for [IsoBA]₄₀-[IBOA]₆₀-R was found to be much lower at $M_e= 16$ kg/mol, close to the value of 12.5 kg/mol obtained by Voit et al. [41] from DMA of a low crosslinked methacrylate/IBOA containing copolymer. v_e values (number of entanglements/m³) of SMPs were calculated using Bersted's entanglement model [42]

$$v_e = \left(\frac{2\rho N_A}{3M_c} \left(1 - \frac{M_c}{M_n} \right) \right) \quad (4)$$

where $M_c=2M_e$, and N_A stands for the Avogadro number. The results for v_e are given in Table 2 presenting the same tendency as for M_e , i.e. high values for linear copolymers and a low value for the crosslinked one. It should be pointed out that physical entanglements formed by linear chains are considered efficient only if the polymer molecular weight exceeds at least 8-10 times the value of M_e which is roughly the case here.

3.4. Shape memory behavior

3.4.1. High molecular weight [IsoBA]_x-[IBOA]_y copolymers

Investigation of the shape memory effect of [IsoBA]_x-[IBOA]_y copolymers was carried out as a function of time by performing fixity and recovery tests in pseudo linear deformation regime (see Fig. S2). Fig. 5 shows the result obtained for the [IsoBA]₆₀-[IBOA]₄₀ copolymer, and the graphical presentations belonging to the two other copolymers can be found in the supplementary material (Figs. S3 and S4). These figures show that the three [IsoBA]_x-[IBOA]_y copolymers possess the ability to maintain programmed temporary shapes, due to the presence of a significant number of physical entanglements per chain caused by high

molecular weight ($M_n > 200\text{kg/mol}$). Increasing the amount of IBOA or adding a crosslinking agent (HDDA) show similar effects on shape fixity which was determined as 89%, 88% and 91% for linear $[\text{IsoBA}]_x\text{-}[\text{IBOA}]_y$ copolymers with 40%, 50% and 60% of IBOA, respectively (see Table 3).

Similar data were obtained for SMP materials based on polyurethane, which are known for their high efficiency [43]. In contrast, $[\text{IsoBA}]_{40}\text{-}[\text{IBOA}]_{60}\text{-R}$ presented a lower fixity ratio (81%) compared to linear SMP. This decrease can be attributed to the presence of chemical

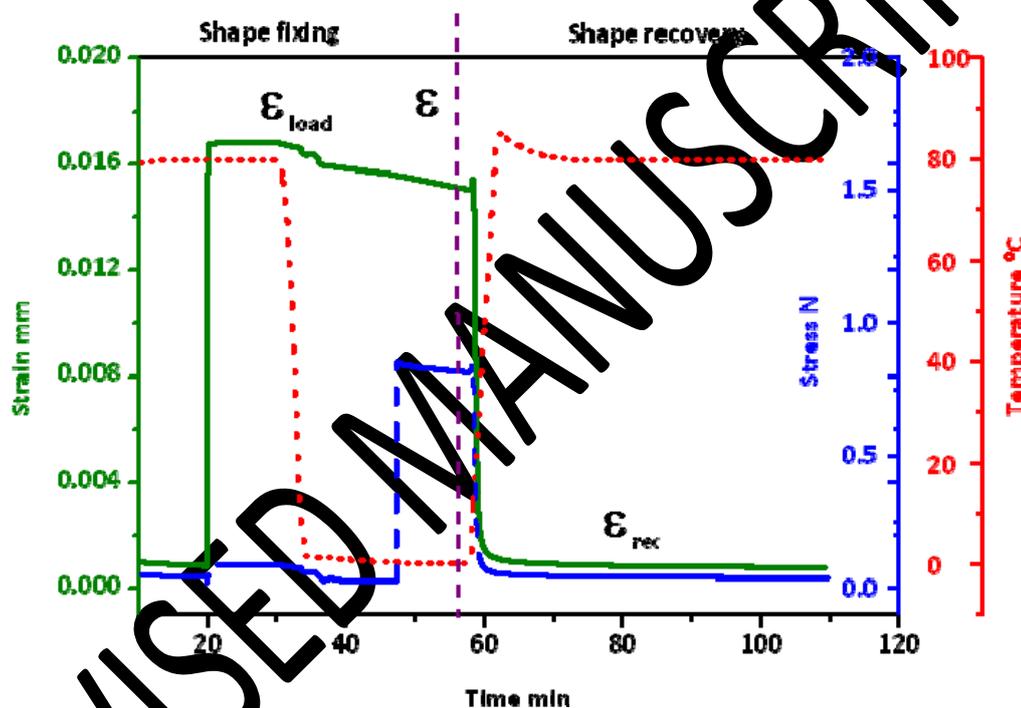


Fig. 5. Shape fixing and recovery for $[\text{IsoBA}]_{60}\text{-}[\text{IBOA}]_{40}$ copolymer. ϵ was determined at the end of the shape fixing period whereas ϵ_{rec} was obtained at $t=80\text{min}$.

crosslinking points which make the fixation of $[\text{IsoBA}]_{40}\text{-}[\text{IBOA}]_{60}\text{-R}$ more complex. Indeed, when polymer chains are stretched between two adjacent chemical crosslinking points, entropy will be largely reduced so that the chains will be forced to return to the energetic favorable equilibrium unstretched state [44].

Fig. 6 and Table 3 show that all ($[\text{IsoBA}]_x\text{-}[\text{IBOA}]_y$ and $[\text{IsoBA}]_{40}\text{-}[\text{IBOA}]_{60}\text{-R}$) samples

recovered nearly their original shape when the applied stress was removed at a temperature above T_{trans} , and the recovery rates were found greater than 88%. Unlike the traditional SMP structure, which requires rigid and flexible segments, the existing entanglements serve as physical crosslinks in the linear copolymers, thus promoting recovery shape while preventing flow at 80°C. Like shape fixity, the shape recovery values of the investigated $[IsoBA]_x$ - $[IBOA]_y$ copolymers were found to be close to those mentioned in literature for thermoplastics [45], thermosets [46], and reinforced composites [47], which means that $[IsoBA]_x$ - $[IBOA]_y$ copolymers can be considered as potential candidates for SMP applications.

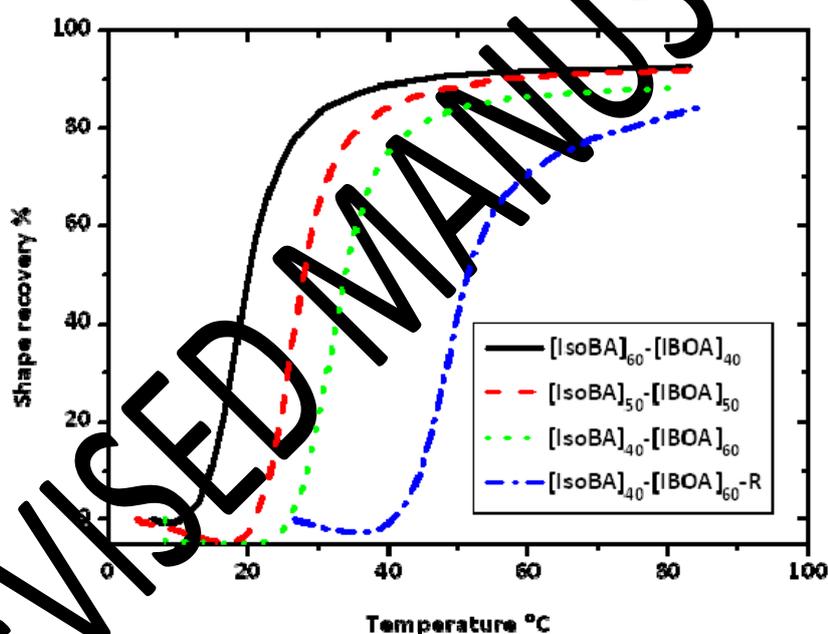


Fig. 6. Tuning of thermally-induced SMPs operating around body temperature: Shape recovery of several linear and crosslinked (R) $[IsoBA]_x$ - $[IBOA]_y$ copolymers.

Fig. 6 represents an extraction of data particularly from Figs. 5, S3 and S4, corresponding to the evolution of ϵ from the end of the shape fixing period at $T=0^\circ\text{C}$ up to the shape recovery cycle at a temperature of 80°C. It can be noticed that shape memory recovery can be tuned as function of temperature, in particular around body temperature, depending on the copolymer

composition. It was found that the shape recovery of a given SMP rises gradually with increasing temperature. A sharp increase of shape recovery was observed when the temperature approaches T_g , until reaching plateau values corresponding to maximum recovery around 80°C. With the increase of IBOA content in the copolymers, the shape recovery curves shift to higher temperatures, in relationship with the corresponding increase of T_g of the examined $[\text{IsoBA}]_x\text{-}[\text{IBOA}]_y$ copolymers, and the storage modulus in the vitreous state (the larger the modulus, the better the recovery) [48]. A difference in the recovery rate is clearly apparent while comparing linear with chemically crosslinked $[\text{IsoBA}]_x\text{-}[\text{IBOA}]_y$ copolymers, indicating that shape recovery was governed by the crosslinking type: physical entanglements in the case of linear SMP and covalent bonds and entanglement for crosslinked SMP. As the temperature increases above 70°C, the shape recovery increases to more than 90% and stabilizes at this percentage for linear $[\text{IsoBA}]_x\text{-}[\text{IBOA}]_y$ copolymers, suggesting that the irreversible deformation of these copolymers presents less than 10%. On the other hand, shape recovery of $[\text{IsoBA}]_{40}\text{-}[\text{IBOA}]_{60}\text{-R}$ was found at a lower value (82%) compared to the linear one. Fig. 6 also shows that the crosslinked SMP tends to exhibit a relatively wide shape recovery temperature range, which may originate from its broader glass transition zone compared to the linear copolymers.

3.4.2. Stress relaxation measurements

The stress relaxation of high molecular weight copolymers was investigated under application of constant strain (10% of strain in flexion configuration). Fig. S5 shows the evolution of stress as function of time for different SMPs at room temperature. The corresponding curves do not present a disentanglement effect, which could be caused by the deformation applied to the films. These findings thus reinforce the results obtained by DMA. The stress-relaxation behavior clearly depends on the amount of IsoBA present in the copolymer. In particular it was found that the copolymer with 60% IsoBA presents the best set properties since it takes

less time than the other copolymers to relax. With the increase of the amount of IBOA in the copolymer, the relaxation becomes more complex and takes longer time compared to the 60% IsoBA film. This is due to the steric hindrance caused by the isobornyl group, which makes it difficult for the chains to rotate by this covalent bond, especially for the crosslinked copolymer.

To describe the relaxation under constant strain, a two-dimensional Maxwell model (Maxwell–Weichert) was applied, which was already employed to study stress-relaxation phenomena [49]. The time-dependent relaxation will thus be described by two characteristic relaxation times instead of one (classical Maxwell model), because of the complexity of the structure, high molar weight and presence of entanglements. The Maxwell–Weichert model can be presented in the following form :

$$\sigma(t) = \sigma_0 + \sigma_1 e^{-t/\tau_1} + \sigma_2 e^{-t/\tau_2} \quad (5)$$

where σ represents the applied stress, and τ_1, τ_2 are the characteristic relaxation times. Fig. S5 shows a good agreement between theory and experimental data, together with high R^2 values around 0.99 for all compositions.

Additional stress recovery experiments were performed on linear and crosslinked [IsoBA]_x-[IBOA]_y copolymers. The corresponding experimental results as well as data fitting by the Maxwell-Weichert model are displayed in Fig. S6 showing the same general tendencies for the relaxation behavior as presented in Fig. S5.

3.4.3. Linear polymers and low molecular weight copolymers

For a better understanding of the effect of molar mass and formulation (using only soft segments) on shape memory effects and elasticity ratios E_g/E_r , an additional series of polyacrylates were synthesized and characterized, including linear homopolymers (poly *n*BA, poly 2-EHA, poly *t*BA), and low molecular weight linear [IsoBA]₅₀-[IBOA]₅₀ and [IsoBA]₄₀-[IBOA]₆₀ copolymers. The results obtained for the E_g/E_r ratios are presented in Table 3. The

two main properties of shape memory (fixity and recovery) have been investigated (Table 3, Figs. S7 and S8a-c). Both low molecular weight copolymers failed to keep their shape in the fixing step, according to the strong decrease of the deformation while decreasing the temperature (Figs. S7 and S8b).

This result was expected, since the low-molecular weight chains cannot form sufficiently strong entanglements to fix the copolymer to a desired deformation in the rubbery state ($T > T_g$). The elasticity E_g/E_r ratios for the low-molecular weight [IsoBA]₄₀[IBOA]₅₀ and [IsoBA]₄₀[IBOA]₆₀ copolymers revealed values of 858 and 349, respectively (Table 3). These two values are higher than 100, but rather low compared to those from copolymers with high molecular weight. The low molar mass of the polymer is responsible for the low values obtained of the elasticity Ratio E_g/E_r (Fig. S9).

Interestingly, linear poly *n*BA (Fig S8b), poly *z*EHAA (Fig S8c) and poly *t*BA, exhibit shape memory effects, with a fixity of (~90%) and recovery of (~94%), despite the absence of rigid segments and chemical crosslinking. These homopolymers are characterized by high molecular weights ($M_n > 260$ kg/mol), presenting thus viscoelastic properties (a large rubbery plateau and a high storage modulus). The elasticity ratios E_g/E_r were calculated as 3097, 2723, 2944, for poly *n*BA, poly *z*EHAA and poly *t*BA, respectively (Table 3), and are in the same order of magnitude as those of the high molecular weight copolymers. The important difference between glassy and rubbery moduli allows an easy shaping (good fixing properties) of the polymer at $T > T_g$ (rubbery state) and great resistance to deformation at $T < T_g$ (glassy state).

An evaluation of cyclic stability is often required to probe the robustness of shape memory performance over several consecutive cycles. This type of experiment is particularly necessary before the SMP could be intended for practical applications. Fig. 7a shows the result for fixity and shape recovery determined by four consecutive thermomechanical cyclic

tests of [IsoBA]₄₀-[IBOA]₆₀ copolymer. It can be concluded from Fig. 7a that the shape memory effect can be repeated several times without risk of any negative effect on thermomechanical properties, indicating that physical crosslinking introduced by strong entanglements maintains its efficiency, in terms of reproducing several times the SMP effect.

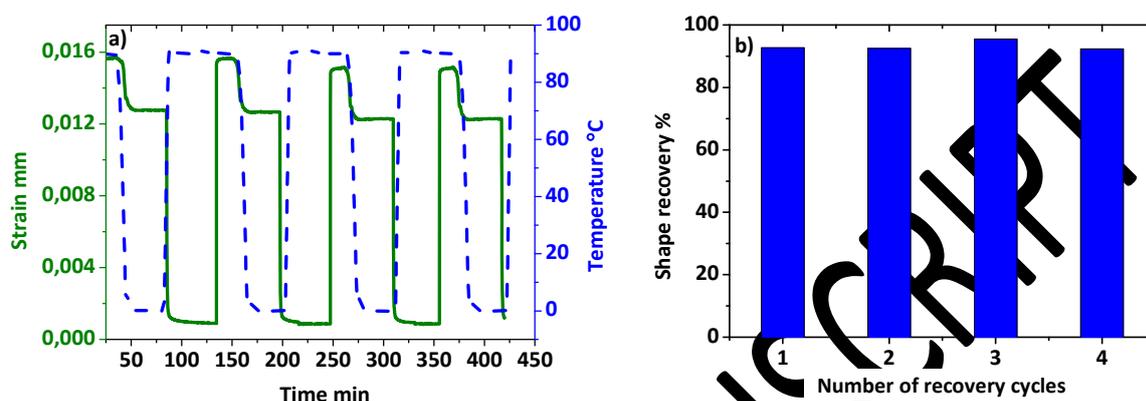


Fig. 7. (a) Deformation-recovery cyclic test and (b) shape recovery of linear [IsoBa]₄₀-[IBOA]₆₀ copolymer as function of the number of recovery cycles.

Fig. 7b presents the shape recovery percentage derived from the thermomechanical cyclic tests (Fig. 7a). As a result, shape recovery remains almost stable during the four cycles and was found equal to more than 90%, demonstrating high stability of cycling performance which is essential for device applications involving multiple cycles.

4. Conclusions

In this work, a simple strategy for modulating the transition temperature of linear and photochemically crosslinked [IsoBA]_x-[IBOA]_y copolymeric SMPs operating near the temperature of human body was proposed. It should be highlighted that no report is known up to now investigating SMPs based on linear poly(acrylate). Characterization of molecular weights by GPC revealed sufficiently high molecular weights of the linear [IsoBA]_x-[IBOA]_y copolymers to form strong physical molecular entanglements. Unlike conventional SMP structures, requiring rigid and flexible segments, these entanglements served as physical

crosslinking points, slowing the flow of the material at high temperature to allow elastic deformation for fixation of the shape. Shape fixity and shape recovery ratios reveal that the SMPs maintain their form memory properties even after four successive recovery cycles, confirming thus the efficiency of the presence of strong physical entanglements in the linear copolymers. The SMP properties of the investigated $[\text{IsoBA}]_x\text{-}[\text{IBOA}]_y$ copolymers were found to be in the same order of magnitude when compared to crosslinked thermoplastics and thermosetting polymers, resulting from high entanglement molecular weight of 44 kg/mol and elevated glassy/rubbery moduli ratio of around 3000.

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c) The thermograms of the linear and crosslinked copolymers poly(BOA-co-IsoBA) shown in Figure 3 were reprinted from reference 20b) with permission from John

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