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# Polymer

## Dual reconfigurable network from a semi-crystalline functional polyolefin.

--Manuscript Draft--

<b>Manuscript Number:</b>	POLYMER-23-2989R1
<b>Article Type:</b>	VSI: Dynamic Polymer Networks
<b>Keywords:</b>	semi-crystalline, vitrimers, disulfides exchange, shape-memory
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<b>Abstract:</b>	<p>A statistical copolymer p(E-co-GMA) of ethylene and glycidyle methacrylate (4.5 wt%) is considered as a starting point towards semicrystalline networks with exchangeable links. Application of the binomial law to size exclusion chromatographic data suggests that chains deprived of reactive comonomers would represent less than 6 wt% of the total, allowing to expect the formation of high gel-content networks. Experimentally, up to 98 wt% gel is obtained upon modification with 3,3'-dithiopropionic acid (DTPA). The crosslinking reaction can be performed in the molten state through a 2-steps procedure: 1°) x mol. of a commercial grade p(E-co-GMA), y mol. of DTPA and z mol. of triazabicyclodecene (TBD) are sheared in a twin-screw compounder at 115°C, a temperature right above the melting point of the polymer precursor, without triggering the epoxy-acid addition; 2°) the thermolatent reactive blend thereby obtained is then crosslinked at 170°C. Samples with x = 1, y = 1 to 4 and z = 0 to 0.8 were thus prepared and evaluated. The presence of TBD accelerates disulfide exchange reaction, possibly by involvement of the thiolate anion whereas it decelerates the epoxy-acid addition. The final networks present several characteristic properties of vitrimers such as insolubility in xylene above the melting point, thermo-activated stress relaxation and creep. Particular shape memory regimes, related to the semicrystalline vitrimer character and the high insoluble fraction are demonstrated. Eventually, production scale-up using continuous reactive extrusion is evaluated.</p>

Response to Reviewers' comments and remarks:

First, we thank all Reviewers and Editors for careful examination of our manuscript and interesting comments that helped a lot to improve the quality of the paper.

Below please find the point by point reply to all comments in dialog style. A revised version in the track change mode is attached, where changes are printed in blue.

**Reviewer #1:** *This paper presents a new way of designing semi-crystalline networks with exchangeable bonds and shape memory effect based on a p(E-co-GMA) random copolymer of ethylene and glycidyl methacrylate (4.5 wt.%). The proposed polyolefin-based vitrimers have been thoroughly characterized from the chemical, physical and finally the end-use and application properties points of view. The link between the structure of the network of vitrimers formed and their ability to renew their configuration has been highlighted. The manuscript is well structured and illustrated. The article includes a large number of results from different complementary techniques that argue the subject well. Wherever possible, the results are commented on and discussed in depth to help the reader understand the complex behavior of these systems.*

*My overall opinion is that the paper is convincing in its present form. The article is suitable for Polymer and publication is recommended if the minor revision required takes account of current comments on the form.*

We thank Reviewer 1 for very positive opinion about this work

*Minor Comments :*

**#1 - Page 6, second line after equation (1),** *is it possible to clarify for the reader that E' refers to T=25°C and E'DMA to T=150°C?*

We thank the Reviewer for this remark. When writing this formula, we believed the DMA to take the actual sample length for determination of E'. However, after verification, it turns out that the DMA takes the nominal values of length and section for all determinations, regardless possible variations of the shape during the experiment.

In our case, there is actually change of both length and density during the experiment, the correct formula would write:

$$E_r' = E_n' \frac{\rho_r}{\rho_n} \left( \frac{l_r}{l_n} \right)^2$$

Where subscripts  $r$  and  $n$  stand for "real" and "nominal". As in our case density is decreasing with temperature and length is increasing due to creep and density variation, both factors roughly compensate and in a logarithmic scale, this correction is hardly visible. Thus in the revised version, we have decided to use the DMA value without any correction and clearly indicate the  $E'$  value in equation (1) is the one measured at 150°C. The revised text simply reads:

...The cross-linking density  $\nu_x$  and average molar mass per cross-link  $M_x$  of the polymer networks were then estimated using equation (1):

$$\frac{E'}{3RT} = \nu_x = \frac{\rho}{M_x} \quad (1)$$

where  $\rho$  is the density in the molten state, taken equal to  $\rho_{150} = 0.80 \text{ g/cm}^3$  at 150°C [ref],  $T$  the temperature,  $R$  the perfect gas constant and  $E'$  the value of the dynamic storage modulus at 150°C, as measured by DMA.

Table 2 has been updated with thus calculated  $\nu_x$  and  $M_x$  values. The interpretation remain the same.

**#2 - page 15: eq 5 .** *how can one be sure that the value of residual stress  $G_{inf}$  is not induced by the last point of the  $G(t)$  curve at long times. Similarly, can we consider that this final shoulder may not be of purely elastic origin, but that it is another relaxation mechanism with a higher relaxation time linked to a chemical mechanism with very slow kinetics?*

It should be pointed out that stress-relaxation experiments are carried out on a long-time scale. The end of the experiment can be affected by the evolution of the sample over a long time (especially at high temperature). As mentioned in the main text and revealed in Figure S4.c and d, and Figure S5.c and d, oxidation of disulfide bonds by oxygen affects the stress-relaxation behaviour. Beside disulfide degradation, the appearance of additional permanent cross-links is also observed during network formation.

To highlight this, in the revised version of the article we present the monitoring of gelation of the polymer precursor p(E-co-GMA) blended with different contents of a monocarboxylic

acid and the catalyst TBD (Figure S3). Given the monofunctionality of the carboxylic acid, the epoxy-acid addition with the polymer precursor's pending chains cannot lead to the formation of cross-links. However, a gel point and the formation of a network are observed. The formation of such permanent bonds is attributed to the secondary reactions of the epoxide and their extent depends on the composition of the sample.

In terms of additional relaxation mechanism, transesterification could also participate in network reshuffling and thus affect relaxation curves.

In the revised version of the article, the following text is added:

“A more precise insight into the possible side reactions occurring during gelation was revealed by monitoring the gelation of a blend of the polymer precursor with a monocarboxylic acid (palmitic acid) instead of the dicarboxylic cross-linker (Fig. S3). With palmitic acid, the epoxy-acid addition cannot lead to the formation of interchain links, nevertheless, a gel is formed for all the tested compositions, confirming that the above mentioned secondary reactions take place. Furthermore, when a higher content of TBD is present, the gelation time is shifted to even longer values, thus indicating that TBD preferentially catalyses epoxy-acid addition over the formation of permanent bonds”

Figure S3 is also added to the revised SI.

**#3 - page 6: legend of fig 5:** typos "...normalized relaxation MOULUS...." instead of "...normalized relaxation MODULUS...."; "...to obtain AVARAGE relaxation...." instead of "...to obtain AVERAGE relaxation....".

Corrected in the revised version

**#4 - page 17: Table 3 legend.** Please replace  $Y_0$  by  $G_{inf}$ .

Corrected in the revised version

**#5 - Page 23:** in the sentence "The quantities used are reported in Table 3", table 3 refers to a table that does not exist in this document. Please correct.

Corrected in the revised version

**#6 - Page 24:** in the conclusion, line 6, typo... "Proecess" instead of "processes".

Corrected in the revised version

**#7 - page 24:** in conclusion, line 16, typo... please delete the isolated "o".

Corrected in the revised version

**Reviewer #3:** *This is an attractive work presenting a new(ish) vitrimer system based on polyolefin and disulfide bond exchange. Separately, all these elements forming a vitrimer plastic have been extensively studied before (including by some of the authors), however, there are several nice elements here that, for me, justify publication. The paper is written well, clearly, with adequate references and good discussion of salient points (in a pleasant contrast with the majority of "vitrimer papers" flooding the literature).*

*The authors were clever in identifying a functionalised polyethylene, with 1% of epoxy groups ready for crosslinking (it is lucky this was available, otherwise they would have to go via the 'old' process of functionalisation, e.g. with MA). With such a perfect precursor, and the dicarboxylic acid crosslinker already possessing the disulfide, the epoxy-acid chemistry part of this work is easy and accessible to anyone - I am sure there will be many followers. The 96-98% gel fraction reported is very impressive, because most of the people who tried to swell disulfide-bonded network in hot xylene (as here) have seen a significant network degradation, since at those temperature the stretched chains exert enough force to break the S-S bonds.*

Many thanks for the positive evaluation of our work. The swelling measurements have been repeated 2-3 times for each sample and the measured values were reproducible. Despite the presence of -S-S- bonds that may break during swelling in xylene, the high gel fraction of our samples can be justified by the structure of the network. In contrast to previous works with similar cross-linkers (e.g. in epoxy or polyurethane matrices), the cross-linking density in our case remains very small, with very long PE strands between cross-links. This probably explains why these previous works only reported the soluble fractions whereas in our case the network swelled without breaking and we were able to measure the swelling ratio.

**Comment :** *I don't understand why they needed to use TBD, which is known to make materials black (and not useful) when the S-S exchange is rather fast even in catalyst-free conditions (lots of papers show that): I am sure TBD accelerates the exchange even further, but there are limits for that: a vitrimer with a very fast bond exchange (as in borolates, for instance) is practically indistinguishable from thermoplastic.*

The organic catalyst TBD was not added specifically to accelerate the disulfide exchange, but primarily to control the competition between the epoxy-acid addition (and thus formation of exchangeable bonds) and epoxy homopolymerization (formation of permanent bonds), as shown in Figure S3 in the revised version of the paper. Secondly, it was added to accelerate the transesterification reaction between  $\beta$ -hydroxyester functions.

We have better clarified this point in the reviewed version (see reply to point #3 of reviewer 1). The role of TBD is mentioned in the new text fragment :

“A more precise insight into the possible side reactions occurring during gelation was revealed by monitoring the gelation of a blend of the polymer precursor with a monocarboxylic acid (palmitic acid) instead of the dicarboxylic cross-linker (Fig. S3). With palmitic acid, the epoxy-acid addition cannot lead to the formation of interchain links, nevertheless, a gel is formed for all the tested compositions, confirming that above mentioned secondary reactions take place. Furthermore, when a higher content of TBD is present, the gelation time is shifted to even longer values, thus indicating that TBD preferentially catalyses epoxy-acid addition over the formation of permanent bonds”

Figure S3 is also added to the revised SI.

In the end, we agree that the samples become black with TBD !

**Comment :** *I don't understand (and find it hard to accept) the DMA data in Fig.4. Here a temperature ramp is applied in the constant-frequency low-amplitude shear test (and the frequency not stated) - showing the 'rubber plateau' above the PE melting. Unless it was done at a relatively high frequency (and I am not sure what "high" means in this context), you should not see this plateau because S-S exchange becomes very fast at 150-200C. Why is there no trace of plasticity in this DMA test? This then resonates with the stress-relaxation data in Fig.5 - leaving aside the delicate nature of fitting the curves when the zero-time is hard to set, the apparent relaxation time is very long: 24min at 220C. This (and their activation energy of 120 kJ/mol) is in some contradiction with several studies of disulfide vitrimers, where a lot faster bond exchange was reported with no catalyst at all (and activation energy at least twice this low). The authors should comment on this discrepancy with other studies, as the readers would be confused (like I am) and not develop trust.*

In DMA measurements, frequency was 1 Hz. It was specified in the experimental section. We have added this value to the legend of Figure 4. The drop of  $E'$  at high temperature is not visible in the global DMA trace but it is visible in the insert added to Figure 4. Yet, such a drop is only observable for samples containing enough content of TBD (when the exchange reaction is sufficiently accelerated).

In reference to this point, we also investigated some PE-based vitrimers where the only exchangeable bonds are ester bonds. In that case, the system hardly relaxes stress, and the activation energy is much lower (to be published in a forthcoming paper). However, it is still possible that the influence of a second exchange mechanism affects the stress-relaxation traces at longer time scale. In the revised version of the article, we added the following part (**section 3.6 vitrimer properties**):

“This change in the slope of the stress-relaxation traces may be attributed to various factors, including the presence of a second exchange mechanism between the cross-links. Indeed, in our case, the transesterification reaction can also occur and thus contribute to the overall relaxation of the network. As this exchange reaction is generally slower than the exchange between disulfides, it is likely to become evident over longer periods and only at higher temperatures. In addition, the slower relaxation at longer times can also be related to the...”.

The very low relaxation is not due to the exchange rate of a single disulfide bond but rather to the structure of the network itself, composed of long PE chains and high gel fractions.

We agree that for other disulfide systems, relaxation times are usually shorter.

Comparison with other systems containing similar exchange mechanism is done here.

In the work of *Chen et al. (ACS Macro Lett. 2019, 8, 3, 255–260)*, the authors observed an activation energy of 75 kJ/mol and a relaxation time of 1.5 s at 200°C for a system where both transesterification and disulfide exchange took place (and containing TBD as catalyst).

In the work of *Schenket et al. (ACS Appl. Mater. Interfaces 2023, 15, 39, 46357–46367)*, the authors revealed that stress-relaxation of disulfide-based vitrimers is highly affected by the  $T_g$  of the system, which shows longer relaxation times than similar disulfide-based vitrimers with lower  $T_g$ . As a matter of fact, Ruiz de Luzuriaga et al. observed an activation energy of 55 kJ/mol and a relaxation time of 20 seconds at 200°C. (*Mater. Horiz.*, 2016,3, 241-247).

In these latter systems, the networks are composed of small units (single molecules) linked to each other by exchangeable bonds. In contrast, in our case the network is composed of long unbreakable PE chains. This means that, to obtain a transport of matter within the network, it



is necessary to move the entire chain and reshuffle all the exchangeable bonds attached to it, which considerably delay the relaxation time.

Thus, in the revised version of the article, the following point was added: (**section 3.6 vitrimer properties**),

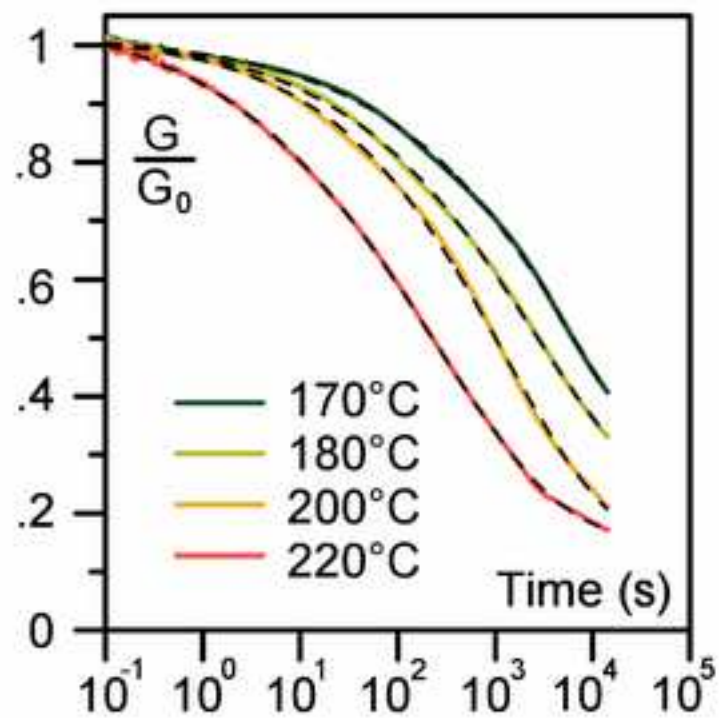
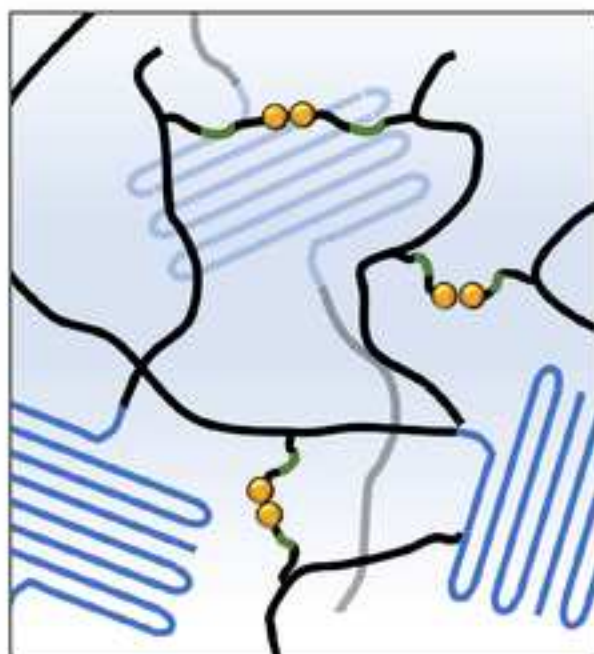
“Interestingly, the obtained relaxation time values differ from those typically observed for disulfide-based vitrimers. While a wide range of activation energy values was extracted from stress-relaxation experiments for disulfide vitrimers (ranging from 55 to over 300 kJ/mol), they have been observed to relax stress within a few seconds at high temperatures, even without the action of an external catalyst. We believe that the slower relaxation times of our system are related to the structure of the network, which is composed of long polyethylene (PE) chains and high gel fractions.

Indeed, disulfide-based vitrimers so far investigated generally consist of networks composed of small units (single molecules) linked to each other by exchangeable bonds. When two bonds exchange, small fragments of the network can interact with a nearby neighbour and locally relax. In contrast, in our case, the network is composed of long unbreakable PE chains. This means that an entire chain must reshuffle all the exchangeable bonds attached to it before moving and achieving a transport of matter within the network, which considerably delays the relaxation time.”

***Editor's comment: (Damien Montarnal)***

*Also, I have an additionnal comment regarding the presence of permanent crosslinks in these materials as determined by fitting the relaxation modulus. Do you have any additionnal experimental evidence of this feature, such as the gel fraction in a solvent containing free disulfide molecules that should cleave the dynamic crosslinks?*

The formation of permanent bonds was highlighted by monitoring the gelation of the polymer precursor p(E-co-GMA) when it is reacted with a monocarboxylic acid. The strategy to reveal the presence of permanent ether bonds is reported in our reply to reviewer 1, point #2 and shown in Figure S3.



Heat



Heat



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## Dual reconfigurable network from a semi-crystalline functional polyolefin

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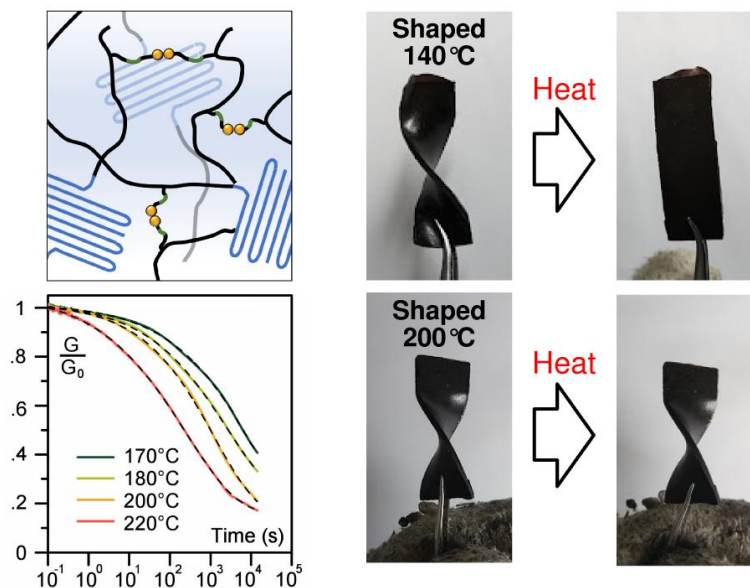
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*Keywords:* semi-crystalline, vitrimers, disulfides exchange, shape-memory

## ABSTRACT :

A statistical copolymer p(E-co-GMA) of ethylene and glycidyle methacrylate (4.5 wt%) is considered as a starting point towards semicrystalline networks with exchangeable links. Application of the binomial law to size exclusion chromatographic data suggests that chains deprived of reactive comonomers would represent less than 6 wt% of the total, allowing to expect the formation of high gel-content networks. Experimentally, up to 98 wt% gel is obtained upon modification with 3,3'-dithiopropionic acid (DTPA). The crosslinking reaction can be performed in the molten state through a 2-steps procedure: 1°) x mol. of a commercial grade p(E-co-GMA), y mol. of DTPA and z mol. of triazabicyclodecene (TBD) are sheared in a twin-screw compounder at 115°C, a temperature right above the melting point of the polymer precursor, without triggering the epoxy-acid addition; 2°) the thermolatent reactive blend thereby obtained is then crosslinked at 170°C. Samples with x = 1, y = 1 to 4 and z = 0 to 0.8 were thus prepared and evaluated. The presence of TBD accelerates disulfide exchange reaction, possibly by involvement of the thiolate anion whereas it decelerates the epoxy-acid addition. The final networks present several characteristic properties of vitrimers such as insolubility in xylene above the melting point, thermo-activated stress relaxation and creep. Particular shape memory regimes, related to the semicrystalline vitrimer character and the high insoluble fraction are demonstrated. Eventually, production scale-up using continuous reactive extrusion is evaluated.



## 1. Introduction

Modifying existing polymers using reactive extrusion provides an attractive approach to synthesize new copolymer materials with tunable additional functionalities and morphologies. [1,2]. The fact that all reactions are performed in the melt, without addition / removal of solvent or by-products makes these processes easily scalable to continuous extrusion techniques. In this context, addition reactions represent a particularly favorable case in that formation of a new bond does not result in release of water or any other molecule [3]. Among possible modifications, transformation of a linear polymer into a branched or cross-linked polymer is an operation which can turn to be interesting insofar as it can improve the usage properties in a temperature range where the pristine thermoplastics tends to flow [4]. It is nevertheless against nature to do it by extrusion since the polymer no longer flows once crosslinked and therefore is no longer extrudable.

A possible exception to this rule is the case of vitrimers. Despite being crosslinked, vitrimers remain flowable due to the involvement of thermoactivated exchange reactions [5]. Production of vitrimers by reactive extrusion has been reported several times [6,7,8,9,10,11]. Nevertheless, the operation remains delicate because the introduction of exchangeable links considerably increases the melt viscosity, typically ranging from  $10^2$ – $10^4$  Pa·s for the molten pristine polymer to  $10^6$ – $10^8$  Pa·s for the vitrimer [6].

In the case of polyolefin vitrimers, it has been observed that the flow behaviour of a cross-linked polyethylene with exchangeable bonds largely depends on the presence of a soluble fraction, which does not participate in the network and imparts a flow behaviour to the vitrimer, which more closely resembles that of a thermoplastic polymer [12]. However, for materials with a higher gel content and greater homogeneity, extrusion can become more challenging, since no soluble fraction can act as a lubricant for the rest of the network.

One way to proceed is to limit the time spent in the extruder to the sole operation of mixing and to carry out the actual crosslinking ex-situ, for example through a curing step after injection. This strategy where the material is extruded in a thermolabile reactive state, called a pre-vitrimer, has been successfully applied to continuous extrusion of a polyester based vitrimer where the branching reactions inside the extruder were limited to below the gel point [13].

In this work, we investigate polyethylene-based vitrimers whose ability to relax stress entirely depends on the rearrangement of the network involving exchangeable disulfide bonds, since almost no soluble fraction is detected in the network. Disulfide functions have already been implemented in different systems, such as polyether elastomers [14,15] poly(urea-urethanes)

[16], epoxy resins [17,18] and proved to be activable by different stimuli including photoirradiation [19], mechanical stress [20], or heat.

The system hereby investigated consists of a statistical copolymer p(E-co-GMA) of ethylene and glycidyl methacrylate, which is transformed into a network using dithiodipropionic acid,  $\text{HOOC}-(\text{CH}_2)_2-\text{S}-\text{S}-(\text{CH}_2)_2-\text{COOH}$  as a crosslinker. The epoxy-acid addition between the polymer epoxide groups and the carboxylic acid functions of the cross-linker molecules leads to the formation of  $\beta$ -hydroxyl links, which are potentially exchangeable by trans-esterification reactions [5]. The disulfide bonds thereby introduced constitute another type of exchangeable bonds [21]. The combination of transesterification and disulfide exchange reactions has previously been explored in other works involving epoxidized natural rubber [21] and epoxy vitrimers [22], which highlighted the potential to enhance the stress-relaxation behaviour of networks compared to using only one type of bond. Here we demonstrate that, by careful design of catalytic and operating conditions, epoxy-acid addition can be accelerated or slowed down and the system can be maintained in a thermolatent reactive state throughout the extrusion process. A catalytic effect is also considered for the exchange reactions, as both transesterification [23] and disulfide exchange [24] are accelerated by basic organocatalysts. Despite being fully crosslinked, the resulting material remains reshapable, as demonstrated by stress-relaxation and erasable shape-memory properties. Furthermore, the effect of topological rearrangement on crystal orientation and its interplay with shape-memory effect will be discussed.

## 2. Experimental

### 2.1 Materials

Polyethylene-co-glycidyl methacrylate, p(E-co-GMA) was obtained from SK functional polymers. The commercial grade used (Lotader® AX8840) has target values of 4.5 wt% glycidyl methacrylate, melt flow index (190°C / 2.16 kg) of 5 g /10 min and density  $\rho = 0.93 \text{ g/cm}^3$ . The cross-linker 3,3'-dithiodipropionic acid (DTPA, 99 %) and catalyst 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, > 98 %) were obtained from TCI; palmitic acid (99%) was obtained from Aldrich. Blending was achieved using a DACA twin-screw mini compounder operating at 300 rpm screw rotation speed. For each sample, 3 g of p(E-co-GMA) was introduced together with the required quantity of DTPA and TBD at 115 °C and mixed for 10 min. Alternatively continuous extrusion was performed using a Rondol "All-in-One" vertical twin screw extruder. In this case, pellets of p(E-co-GMA) were cooled at low temperature with liquid nitrogen and grinded into a powder. DTPA and TBD were mixed in the molten state at

160°C, then cooled down to a solid which was further on pulverized in a mortar. The two powders were finally mixed together and introduced into the extruder through the upper feeding zone of the column.

## 2.2 Gel permeation chromatography (GPC)

GPC analyses were performed using an Agilent HT 220 system equipped with a refractive index (RI) detector in 1,2,4-trichlorobenzene (TCB) stabilized with 0.0125% BHT at 135 °C as mobile phase with two PLgel Olexis columns (Agilent Technology) as stationary phases. P(E-co-GMA) was dissolved in TCB (about 3 g·L<sup>-1</sup>). The elution method consisted in an isocratic step at 1 mL·min<sup>-1</sup> flow of TCB for 30 min at 135°C. The calibration was done with polystyrene (PS) standards. Molar masses of p(E-co-GMA) were then estimated using universal calibration, by considering the Mark-Houwink parameters for PS ( $K_{PS} = 14.1 \times 10^5 \text{ dg}\cdot\text{L}^{-1}$ ;  $\alpha_{PS} = 0.7$ ) and for PE ( $K_{PE} = 95.4 \times 10^5 \text{ dg}\cdot\text{L}^{-1}$ ;  $\alpha_{PE} = 0.640$ ).

## 2.3 Nuclear magnetic resonance (NMR)

The microstructure of the polymer precursor was analysed using <sup>1</sup>H NMR spectra recorded in TCE/C<sub>6</sub>D<sub>6</sub> mixture (volume ratio 2/1) at 363K on Bruker spectrometers working at 400 MHz. The solutions were prepared at 1-2% (w/v) and 1D-<sup>1</sup>H spectra were recorded with a 5 mm BBFO+ probe equipped with a z-gradient coil. Chemical shift  $\delta$  values are given in parts per million (ppm) with the solvent peak as internal standard.

## 2.4 Infrared spectroscopy

The cure monitoring was performed by infrared spectrometry in the 4000 – 600 cm<sup>-1</sup> spectral range. Thin samples (thickness of about 40-60  $\mu\text{m}$ ) were prepared by compressing about 40 mg of extruded material between two silicon paper sheets under a weight of 2 tons (2 minutes at 115°C) Spectra were recorded in transmission using a Bruker Tensor 37 spectrometer equipped with a Specac 5750 heating jacket. The sample was placed between ZnS optically polished windows, previously heated to let the polymer stick on the surface. The cell, isolated by two external ZnS windows was flushed with argon. In-situ monitoring of chemical reactions was carried out at 4 cm<sup>-1</sup> resolution. Before each series of experiments, a background spectrum was taken at the relevant temperature with all windows mounted but no sample present.

## 2.5 Thermal analysis

Thermogravimetric analysis (TGA) is described in the Appendix. Mechanical tests at low strain were performed using a Q800 DMA (TA Instrument, USA) operating in tensile mode on rectangular samples with dimensions of  $35 \times 5 \times 1.5$  mm (nominal length  $\approx 15$  mm), at a frequency of 1 Hz and with a heating regime of  $-115^\circ\text{C}$  to  $180^\circ\text{C}$  at  $3^\circ\text{C}/\text{min}$ . The cross-linking density  $\nu_x$  and average molar mass per cross-link  $M_x$  of the polymer networks were then estimated using equation (1):

$$\frac{E'}{3RT} = \nu_x = \frac{\rho}{M_x} \quad (1)$$

where  $\rho$  is the density in the molten state, taken equal to  $\rho_{150} = 0.80$  g/cm<sup>3</sup> at  $150^\circ\text{C}$  [25],  $T$  the temperature,  $R$  the perfect gas constant and  $E'$  the value of the dynamic storage modulus at  $150^\circ\text{C}$ , as measured by DMA.

## 2.6 Swelling tests

Swelling tests were performed in xylene at  $125^\circ\text{C}$ . About 0.2 g ( $m_i$ ) of sample was placed in a round-bottom flask equipped with a reflux condenser. After 12h, the solid residue was collected and weighed ( $m_s$ ), then dried in a vacuum bell at  $140^\circ\text{C}$  for 12h. The mass of the dried specimen ( $m_d$ ) was finally registered. The swelling ratio ( $Q$ ) and the gel content ( $G$ ) (both expressed in wt%) were evaluated according to equations (2) and (3):

$$Q = 100 \frac{m_s - m_d}{m_s} \quad (2)$$

$$G = 100 \frac{m_d}{m_i} \quad (3)$$

## 2.7 Shape memory and reshaping ability

Q800 DMA was used to quantitatively assess the shape memory behaviour of semi-crystalline networks with exchangeable bonds. A rectangular specimen with dimensions of about  $35$  mm  $\times$   $7.4$  mm  $\times$   $1.5$  mm was placed between DMA clamps in tensile mode. Shape memory behaviour was characterized using the four-step protocol A. Step A1: the sample is annealed during 5 min at  $140^\circ\text{C}$ . Step A2: the rectangular shape is elongated by applying a tensile stress of 100 kPa at  $140^\circ\text{C}$ . Step A3: a cooling ramp of  $-5^\circ\text{C}/\text{min}$  is applied down to  $20^\circ\text{C}$ , while keeping the stress applied. Step A4: external stress is removed and the sample is re-heated to  $140^\circ\text{C}$  at  $10^\circ\text{C}/\text{min}$ . Deformation is measured throughout the different steps to determine shape fixity and shape recovery, as usually defined [26]. Shape memory behaviour was further



characterized on a second sample using the four-step protocol B, featuring different annealing time and temperature: Step B1: the sample is annealed during 35 min at 200°C. Step B2: the rectangular shape is elongated by applying a tensile stress of 100 kPa at 200°C. Step B3: a cooling ramp of 3°C/min is applied down to 20°C, while keeping the stress applied. Step B4: external stress is removed and the sample is re-heated to 200°C at 3°C/min.

### *2.8 Rheological measurements*

The sol-gel transition of the thermolatent blends was monitored by using an Anton Paar MCR501 rotational rheometer equipped with a 25mm parallel plate geometry. The materials here investigated have been first obtained by extrusion and compressed into a cylindrical shape using a stainless-steel mould (radius  $r = 25$  mm, thickness 1.5 mm) at 115°C, applying a pressure of 3 tons on the moulds for 3 min. The upper and lower geometries are a stainless-steel plate and a disposal aluminium plate, respectively. To minimize thermal degradation, the plate geometry was enclosed in a convection oven under a 200L/h nitrogen flow. Before starting every experiment, the oven was preheated at 115°C, above the melting temperature of the pristine polymer, and the sample was placed onto the aluminium plate to ensure good contact. The upper geometry was then gradually lowered onto the sample for proper adhesion. The temperature was then raised to 170°C and kept constant for the rest of the experiment.

Linear viscoelastic properties of the cured samples were evaluated with a strain-controlled Ares-G2 (TA Instrument) rheometer operating in the torsion mode. Rectangular samples were shaped, with a dimension of about  $50 \times 16 \times 5$  mm. During all experiments, a tension force of 100 gram-force ( $\approx 0.98$  N) was applied. Time sweep, amplitude sweep, frequency sweep and stress-relaxation experiments were performed. Time sweep was first carried out at 2% strain to assess the evolution of the storage,  $G'$ , and loss,  $G''$ , moduli over time at 170°C and 1 rad/s (Fig S5a, S6a). Experiments at different strain amplitudes were then performed at the same temperature to determine the linear regime (Fig S5b, S6b). Finally, frequency sweep and stress relaxation experiments were performed on fresh samples for each tested temperature, by applying a constant strain  $\gamma = 2\%$ . Frequency sweeps experiments were performed between 100 rad/s and 0.1 rad/s, while stress relaxation experiments were monitored during up to 4h and then repeated on the same sample.

### 3. Results

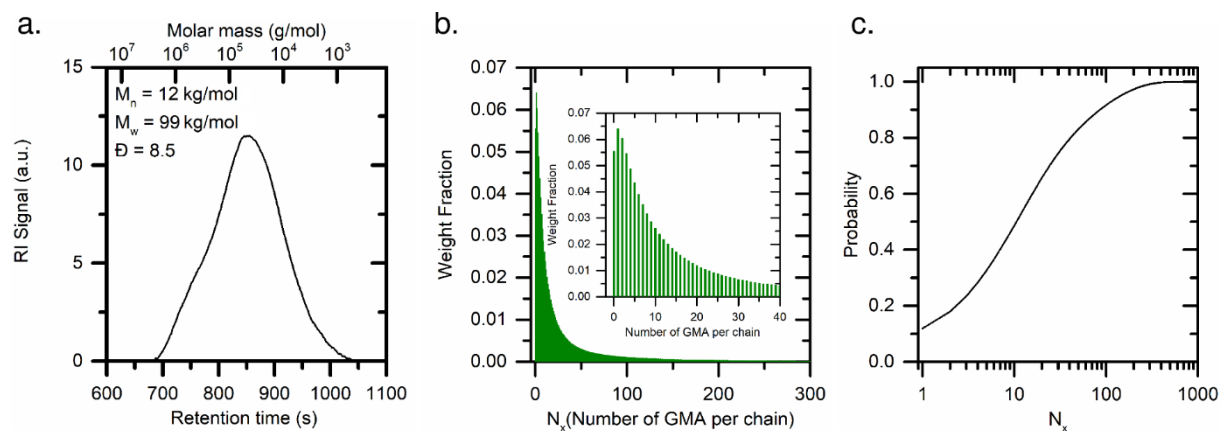
#### 3.1 Precursor copolymer characterization

The semi-crystalline precursor is a commercial statistical ethylene copolymer, p(E-co-GMA), with a nominal fraction of 4.5 wt.% (0.93 mol%) of glycidyl methacrylate (GMA) comonomers. These functional moieties are the reactive sites which will be used as cross-linking points for the formation of dynamic semi-crystalline networks. The effective concentration of the reactive monomer was first assessed by NMR (Fig. S1), which revealed 1.0 mol% of GMA, consistent with the nominal value. The polymer precursor thus presents 1 GMA unit every approximately 110 ethylene units, in average. The p(E-co-GMA) precursor was also analysed by GPC at 135°C in TCB. By applying the so-called universal calibration method based on the Mark-Houwink-Sakurada equation, the initially measured molar masses relative to PS standards have been converted into PE molar masses [27]. The result is reported in Fig. 1a, leading to  $M_n = 12$  kg/mol,  $M_w = 99$  kg/mol and  $\mathcal{D} = 8.5$ . The polydispersity  $\mathcal{D}$  obtained for p(E-co-GMA) indicates a wide distribution of polymer chain lengths. The number of reactive monomer GMA thus increases with the molar mass of the chain. Assuming random copolymerization of ethylene and GMA monomers, further analysis of the GPC signal using the binomial law [28] allowed to determine the respective weight fractions of polymer chains bearing a certain number  $N_x$  of GMA monomers. Such a weight distribution, plotted in Fig. 1b, was obtained by using equation (4):

$$\Phi(N, N_x) = \theta(N) \cdot \Psi(N, N_x) = \theta(N) \cdot \frac{N!}{(N - N_x)! N_x!} p^{N_x} \cdot (1 - p)^{N - N_x} \quad (4)$$

where  $N$  is the degree of polymerization of the chain considered and  $N_x$  the number of GMA comonomers,  $\Phi$  is the number fraction of chains with  $N$  ethylene units and  $N_x$  GMA comonomers,  $\theta$  is the molar mass distribution obtained from the GPC trace of p(E-co-GMA),  $\Psi$  is the binomial distribution and  $p$  the average molar fraction of GMA ( $p = 0.93$  mol%). The product of the two distributions  $\theta$  and  $\Psi$  provides an assessment of the statistical distribution of the reactive groups along the polymer backbone as a function of the chain length. By integrating the resulting distribution  $\Phi$  over  $N$ , it is possible to obtain the weight distribution of chains bearing  $N_x$  GMA, regardless of their length. As it can be observed in Fig. 1b, about 5.5% of polymer chains bear no reactive comonomer and the maximum of the distribution is observed for chains with 1 GMA. Due to the elevated polydispersity of the commercial p(E-co-GMA), it is possible to find polymer chains with up to approximately 300 GMA (Fig. 1c). So, when

forming a gel starting from this polymer precursor, all the chains bearing at least 1 GMA are potentially integrated into the network, contributing to a high gel content value. Here, up to 95% gel content can be expected.



**Fig. 1.** (a) GPC trace of p(E-co-GMA); (b) Calculated weight fraction of chains bearing  $N_x$  reactive units per chain of the p(E-co-GMA) copolymer; (c) cumulative distribution function of the weight fraction distribution

### 3.2 Sample preparation

The compositions of the samples studied in the following are presented in Table 1. The preparation involves two steps as illustrated in Fig. 2. First, the polymer precursor p(E-co-GMA), the cross-linker DTPA and optionally the catalyst TBD are introduced into the twin-screw mini-compounder for 5 min, at 115°C. This preparation strategy allows to mix every component above the melting temperature  $T_m$  of the semi-crystalline polymer without triggering the epoxy-acid addition which would provoke cross-linking inside the machine. We call *pre-vitrimer* the thermolatent mixture thus obtained. In a second step, is the pre-vitrimer is cured for 1 to 7 h at 170°C in a mold of desired shape to obtain the chemically cross-linked network. Whereupon, the obtained compound is cooled down to room temperature causing a partial crystallization of the polyethylene phase, which forms a second, physical, network interpenetrated with the chemical network previously formed. The chemical cross-links formed during the second step contain hydroxy-ester and disulfide bonds which are prone to undergo thermally activated exchange reactions. We anticipate that the chemical network thus obtained is a vitrimer. The whole material therefore combines physically and chemically exchangeable networks; in the following it will be referred to as a *dual reconfigurable network*.

Table 1: Feed ratios and stoichiometry of samples prepared by reactive blending from the polymer precursor (pE-co-GMA), cross-linker (DTPA) and catalyst (TBD).

Compound	p(E-co-GMA) (g)	DTPA (g)	TBD (g)	Epoxy (eq)	COOH (eq)	TBD (eq) <sup>a</sup>
PE-1:1-0	3	0.1	0	1	1	0
PE-1:1-0.2	3	0.1	0.026	1	1	0.2
PE-1:4-0	3	0.4	0	1	4	0
PE-1:4-0.2	3	0.4	0.026	1	4	0.2
PE-1:4-0.8	3	0.4	0.104	1	4	0.8

<sup>a</sup> TBD equivalents are expressed relatively to the number of epoxy functions.

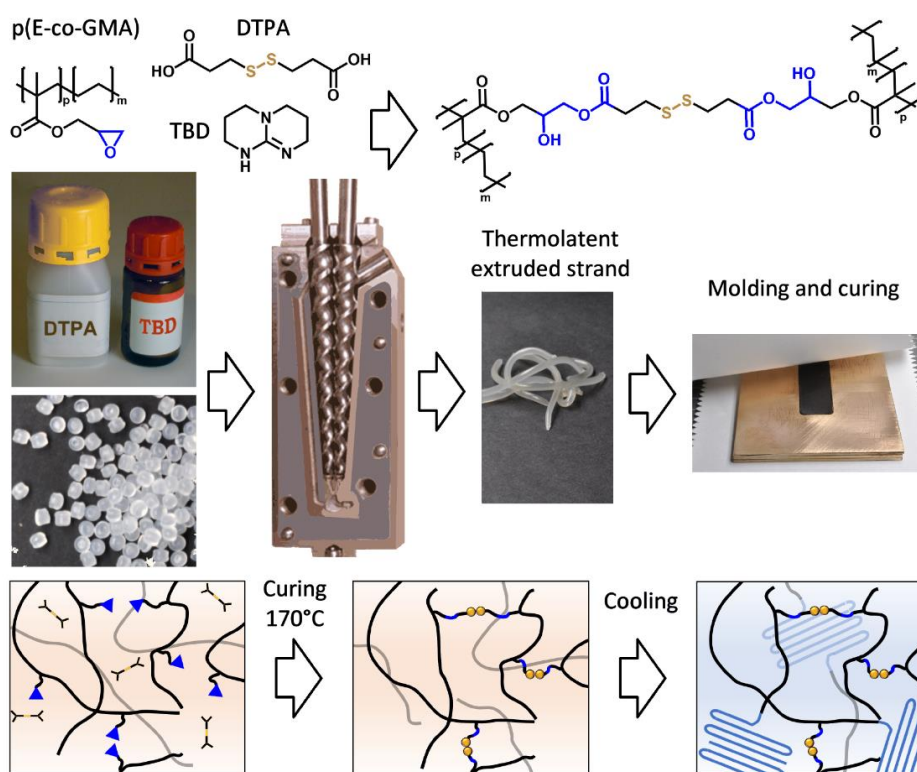


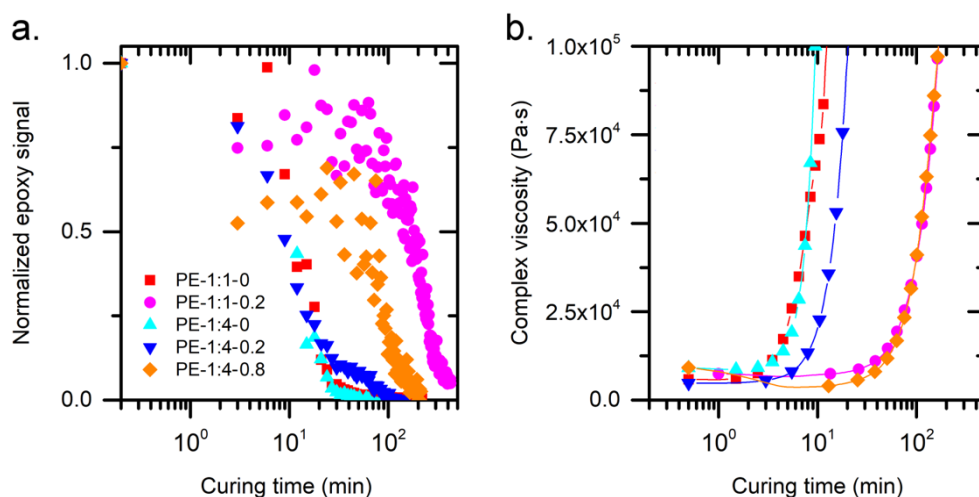
Fig. 2. Top: chemical structure of the p(E-co-GMA) copolymer, DTPA cross-linker, TBD catalyst and the resulting cross-linked polymer chains. Middle: workflow of samples preparation. Bottom: schematic illustration of networks' structure.

### 3.3 Reactive extrusion and curing

Immediately following extrusion, the materials are turbid. Those containing TBD appear brown, whereas those only containing the cross-linker remain colourless. At 170°C, while the precursor copolymer (pE-co-GMA) has a complex shear viscosity of 4000 Pa·s at 1 rad/s, the

extruded compositions listed in Table 1 have viscosities still comprised in a range from  $\eta^* = 5000$  to  $9000$  Pa·s i.e. not much higher. Meanwhile, IR analysis of all samples (Fig. S2) reveal the persistence of the characteristic epoxy band at about  $914\text{ cm}^{-1}$  with almost unchanged intensity. These facts confirm that the compositions at this stage are pre-vitrimerers that are still reactive and not yet cross-linked.

The curing reaction of the pre-vitrimerers was followed by IR spectroscopy and rheology at  $170^\circ\text{C}$  (Fig. 3). The time dependence of the epoxy IR signal (at  $914\text{ cm}^{-1}$ ), normalized by its initial value measured in the pre-vitrimer state (Fig. S2) is plotted in Fig 3a. The decay of this signal demonstrates that full cure is achieved in about 1 to 6 h, depending on the composition. Meanwhile, the effective formation of crosslinks is detected by the sudden rise of viscosity upon approaching the gel point (Fig 3b).



**Fig. 3.** Time dependence of chemical and mechanical signals during curing reaction at  $170^\circ\text{C}$ . a) Decay of the normalized IR epoxy signal ( $914\text{ cm}^{-1}$ ). b) Rise of viscosity showing the onset of the gel point.

From IR kinetics in Fig. 3a, it is observed that the speed of disappearance of the epoxy signal depends on the composition. It is interesting to observe that when TBD is present the drop of the epoxy signal is slowed down. This effect is counter-intuitive since we expect a basic catalyst like TBD to lead to the formation of alkoxide anions, which are more basic than the carboxylate anion, thus favouring transesterification, Fischer esterification and epoxide-hydroxylate reaction [29]. Specifically, TBD is known as a catalyst of ring opening reactions like homopolymerization of lactide [30]. In epoxy-acid systems, TBD was shown to equally catalyse the epoxy-acid addition and the epoxy homopolymerization, whereas a conventional imidazole catalyst clearly favored the former reaction [31]. It remains difficult to accurately follow the kinetics of all the chemical species of interest in our system, due to an overlapping of peaks

related to the carbonyl vibration of the methacrylate moiety ( $1733\text{ cm}^{-1}$ ) and the ester group ( $1725\text{-}1748\text{ cm}^{-1}$ ) that is expected to form. Nevertheless, a global slow-down is observed in the presence of TBD. Alongside reasons attributable to different reactions involved, early works have pointed out how the base-catalysed epoxy-acid addition is hindered in apolar solvents due to the involvement of ammonium/carboxylate ion pairs intermediate, showing poor solubility in low dielectric constant media [32,33], which is also the case here. Another observation in line with such effects is that whenever a higher concentration of acid cross-linker is present for compounds PE-1:4-0.2 and PE-1:4-0.8, the reaction rate further decreases, confirming that the formation of epoxy/carboxylic/TBD complexes influences the reaction kinetics. A more precise insight into the possible side reactions occurring during gelation was revealed by monitoring the gelation of a blend of the polymer precursor with a monocarboxylic acid (palmitic acid) instead of the dicarboxylic cross-linker (Fig. S3). With palmitic acid, the epoxy-acid addition cannot lead to the formation of interchain links, nevertheless, a gel is formed for all the tested compositions, confirming that above mentioned secondary reactions take place. Furthermore, when a higher content of TBD is present, the gelation time is shifted to even longer values, thus indicating that TBD preferentially catalyses epoxy-acid addition over the formation of permanent bonds.

### *3.4 Gel content of cured compositions.*

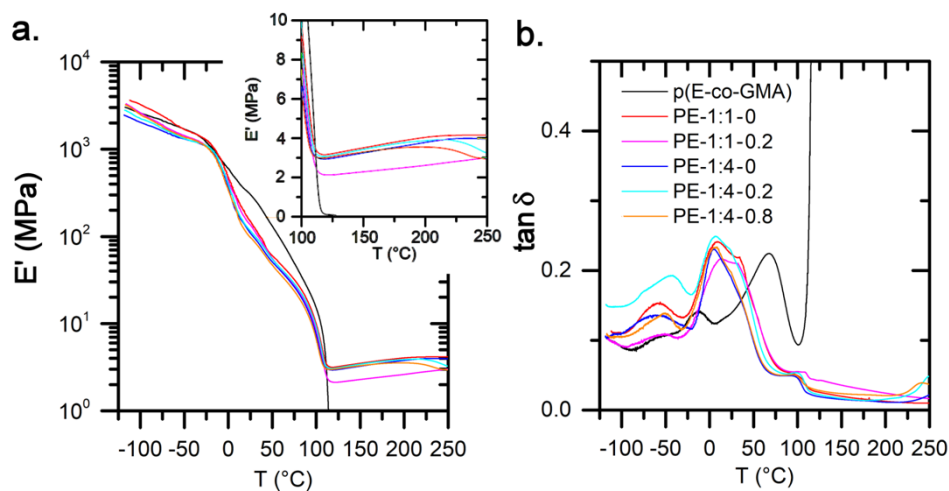
The results of swelling tests are reported in Table 2. Once cured, all samples show gel content values reaching up to  $\sim 98\%$ , in good agreement with the above expected value ( $\sim 95\%$ ) inferred from the GPC analysis. Only the sample PE-1:1-0.2 shows a gel content of  $\sim 64\%$  and a higher swelling ratio, suggesting partial cleavage of the disulfide links in the presence of TBD resulting in a decrease in crosslinking density in this sample where the quantity of crosslinker is not more than stoichiometric. In all other cases, it appears that 4.5 wt% of GMA of the polymer precursor is sufficient to obtain materials that have a negligible amount of soluble fraction, which can potentially lead to macro-phase separation of the non-linked chains in the network [28].

Table 2: elastic modulus  $E'$ , cross-linking density  $\nu_x$ , average molecular weight between cross-links,  $M_x$  as from DMA (see section 2.5) and gel content and swelling ratio from swelling tests (see section 2.6) for the obtained networks.

<b>Compound</b>	$E'$ at 150°C (MPa)	$\nu_x$ (mol/cm <sup>3</sup> )	$M_x$ (g/mol)	Gel content (wt%)	Swelling ratio (wt%)
<b>PE-1:1-0</b>	3.51	$3.3 \cdot 10^{-4}$	2400	97	330
<b>PE-1:1-0.2</b>	2.29	$2.2 \cdot 10^{-4}$	3700	64	1560
<b>PE-1:4-0</b>	3.25	$3.1 \cdot 10^{-4}$	2600	93	370
<b>PE-1:4-0.2</b>	3.41	$3.2 \cdot 10^{-4}$	2500	96	360
<b>PE-1:4-0.8</b>	3.29	$3.1 \cdot 10^{-4}$	2600	98	350

### 3.5 Elasticity of formed networks.

The results of the dynamic mechanical analysis are presented in Fig. 4 and the values of the elastic modulus  $E'$  above the glass transition are reported in Table 2. Different behaviours can be observed depending on the composition. First, in the temperature range between -40°C and 110°C, the elastic modulus  $E'$  for p(E-co-GMA) is larger, due to its greater degree of crystallinity. Moreover,  $E'$  decreases by several orders of magnitude in all the tested samples, and three main transitions can be determined. At ~6°C, a first peak appears in the loss factor measured for the cross-linked networks. At 67°C, the  $\alpha$  transition of polyethylene is only evident for the polymer precursor. This transition depends on the crystallinity of the polymer, which is reduced upon crosslinking (see SI Figure S3, Table S1), and it tends to move towards lower temperatures for lower crystallinity samples [34].  $E'$  keeps decreasing until the melting temperature  $T_m$  of the polymer is reached. At this temperature, the elastic properties of p(E-co-GMA) are no longer measured, whereas the cross-linked samples show a rubbery plateau, whose modulus depends on the composition. The cross-linking density  $\nu_x$  and the average molecular weight between cross-links  $M_x$  are calculated from the rubbery plateau at 150°C, by assuming that the polymer networks is incompressible (Poisson's ratio equal to 0.5).



**Fig. 4** Thermomechanical properties of the obtained networks at 1Hz: a) temperature dependence of the elastic modulus  $E'$ ; b) the loss factor  $\tan \delta$  (right)

Based on the nominal fraction of GMA (0.93 mol%), the expected average mass between crosslinking points is of  $M_x = 3160$  g/mol (weight of 107 ethylene + 1 GMA units). In Table 2, the measured values of  $M_x$  (from DMA), are in good agreement with the calculated one. This may indicate that each epoxy group has reacted with a carboxylic moiety, leading to a cross-linking point. However, when an excess of carboxyl group over epoxies is added, a fraction of crosslinkers should be bound to the polymeric backbone at one end only, thus decreasing the cross-linking density. This scenario would occur in case the epoxy-acid addition is the only reaction contributing to the formation of cross-links. We know instead that other reactions such as Fischer esterification, epoxy homopolymerization and ring opening polymerization can take place [31], making the network denser. Thus, for the majority of samples the rubbery modulus appears to be similar. Only for PE-1:1-0.2 we measured a significantly smaller value, consistent with higher swelling ratio and lower insoluble fraction. The explanation for this result still lies in the multitude of mechanisms involved in network formation. As already discussed above and shown in Fig. S3, the formation of permanent ether bonds is reduced when a higher content of catalyst is present. In addition, the reduction of disulfides to thiols by a basic catalyst, already described in the literature [35], can also lead to the decrease of the cross-linking density and affect the elastic properties of the network. Such a reaction was shown to take place in the presence of amines as reducing agents, which deprotonate thiols to thiolates [36,37,38,39]. In amine-cured epoxy resins containing either aliphatic or aromatic disulfide bridges, a drop in initial shear modulus  $G_0$  was observed at high temperature and attributed in both cases to bond dissociation [18], albeit the effect was more pronounced in the aromatic case. For samples PE-1:4:0.2 and PE-1:4:0.8, a comparable drop is observed above 200°C for the storage modulus  $E'$



(Fig. 4a), showing that bond dissociations have to be taken into accounts in the exchange mechanisms.

### 3.5 Discussion about sulphur exchange mechanisms.

In addition to reducing the network connectivity, the reduction of disulfides to thiols can also influence exchange dynamics through the introduction of a secondary exchange mechanism [40,41,15,24]. When TBD is combined with DTPA, thiol and deprotonated thiolates can exchange with disulfide bonds via a three-step associative mechanism [20,38,42], in parallel with the radical-mediated mechanism generally described for disulfides [38,40,43]. Consequently, the overall network dynamics become faster, causing a drop in the  $E'$  modulus at high temperatures for PE-1:4-0.2 and PE-1:4-0.8 above 200°C in DMA. This observation is generally attributed to a cleavage of the reversible covalent bonds, leading to decrease of the network connectivity with temperature [18]. Therefore, in our systems, both radical and thiol/disulphide exchanges may take place. Since the drop in  $E'$  modulus is evident mainly for compounds PE-1:4:0.2 and PE-1:4:0.8, we believe that the thiolate/disulfide exchange becomes more important in these networks, especially due to the higher TBD content, which can catalyse thiol formation and exchange.

### 3.6 Vitrimer properties.

The rheological analysis of PE-1:4:0.2 is presented in Fig. 5; additional data for PE-1:4:0.2 and PE-1:4:0.8 are reported in Fig. S5 and S6. Frequency sweeps at different temperatures (Fig. 5a) show that PE-1:4:0.2 has a constant shear modulus  $G'$  over all the sampled frequency range, except at 220°C, where a slight drop in  $G'$  is observed at low frequency due to the exchange reaction, as already observed in DMA. More evidently, the loss modulus  $G''$  increases with temperature, indicating that the rearrangement of the network speeds up as the temperature is increased. At a given temperature, the change in slope of  $G''$  occurs at lower frequencies in the case of PE-1:4:0.8 (Fig. S5c), with a higher concentration of TBD, strengthening the hypothesis that the mechanism of the exchange reaction is controlled by the concentration of the catalyst, directly and indirectly through the involvement of thiolates [24]. In Fig. 5a and for all temperatures, the absence of cross-over between  $G'$  and  $G''$  at low frequency indicates the relaxation modes associated with the exchange of dynamic covalent bonds occur at longer times than those accessible using oscillatory measurements.

Stress relaxation experiments under a constant strain of  $\gamma = 2\%$  were performed in order to access long time scales. The time dependant relaxation modulus  $G(t)$  of PE-1:4:0.2 is plotted in Fig. 5b and 5c. The normalized relaxation modulus shown in Fig. 5c is fitted to a stretched exponential function to obtain the average relaxation time  $\langle \tau \rangle$  at each temperature, according to equations (5) and (6).

$$G(t) = G_{\infty} + G_0 e^{-(t/\tau^*)^{\beta}} \quad (5)$$

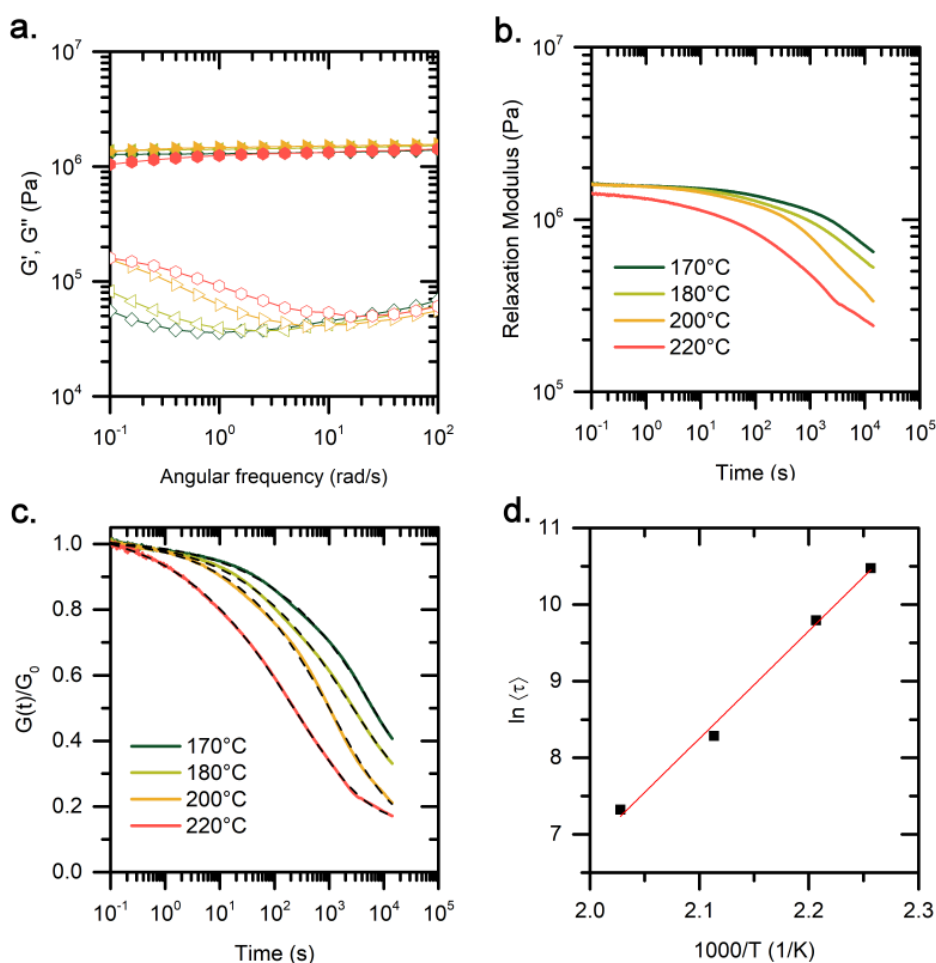
$$\langle \tau \rangle = \frac{\tau^*}{\beta} \Gamma\left(\frac{1}{\beta}\right) \quad (6)$$

where  $G_{\infty}$  is the residual stress obtained from the fitting model,  $G_0$  is the pre-exponential factor,  $\tau^*$  the relaxation time,  $\beta$  the relaxation exponent and  $\Gamma$  the gamma function. The values of  $G_{\infty}$ ,  $\langle \tau \rangle$  and  $\beta$  are reported in Table 3. From the logarithmic plot of  $\langle \tau \rangle$  as a function of  $1/T$ , an activation energy is determined. Such plot for PE-1:4:0.2 is shown in Fig 5d, where the activation energy  $E_a$  is about 120 kJ/mol. The values obtained for  $\beta$  deviate from unity, indicating that the relaxation of the stress involves a distribution of relaxation times possibly reflecting the presence of several mechanisms and the broad size distribution of objects whose relaxation is observed. Indeed, both  $\beta$ -hydroxyl ester and disulfide species can contribute to exchange reactions, whereas permanent crosslinks broaden the size distribution of the polymer precursor. Interestingly, the obtained relaxation time values differ from those typically observed for disulfide-based vitrimers. While a wide range of activation energy values was extracted from stress-relaxation experiments for disulfide vitrimers [17,22,44,45] (ranging from 55 to over 300 kJ/mol), they have been observed to relax stress within a few seconds at high temperatures, even without the action of an external catalyst. We believe that the slower relaxation times of our system are related to the structure of the network, which is composed of long polyethylene (PE) chains and high gel fractions.

Indeed, disulfide-based vitrimers so far investigated generally consist of networks composed of small units (single molecules) linked to each other by exchangeable bonds. When two bonds exchange, small fragments of the network can interact with a nearby neighbour and locally relax. In contrast, in our case, the network is composed of long unbreakable PE chains. This means that an entire chain must reshuffle all the exchangeable bonds attached to it before moving and achieving a transport of matter within the network, which considerably delays the relaxation time.

At 220°C, the relaxation modulus  $G(t)$  of PE-1:4-0.2 reaches a plateau value after 3000 s. This change in the slope of the stress-relaxation traces may be attributed to various factors, including

the presence of a second exchange mechanism between the cross-links. Indeed, in our case, the transesterification reaction can also occur and thus contribute to the overall relaxation of the network. As this exchange reaction is generally slower than the exchange between disulfides, it is likely to become evident over longer periods and only at higher temperatures. In addition, the slower relaxation at longer times can also be related to the presence of permanent bonds originating from secondary reactions such as homopolymerization or ring opening polymerization. Once the network is formed, non-exchangeable bonds limiting the capacity of the thiol/disulfide reaction to relax stress can also form upon the oxidation of thiols, as already observed in disulfide-based systems [46].



**Fig. 5:** linear viscoelastic properties of PE-1:4:0.2 between 170°C and 220°C. For each temperature, a fresh sample undergoes frequency sweep (a), first, and stress-relaxation (b) experiments. (c) Normalized relaxation modulus is fitted (dash line) to obtain the average relaxation time  $\langle \tau \rangle$  and the activation energy  $E_a$  in (d).

This is further observed when a second stress relaxation experiments is performed on the same material: at all temperatures, the stress relaxation in the second experiment is slower than in the first one and the residual stress after 4h,  $\sigma_{r,2}$  is larger than  $\sigma_{r,1}$  (Fig. S5c, d). The difference

between  $\sigma_{r,1}$  and  $\sigma_{r,2}$  increases with the temperature. In addition, after the second stress-relaxation experiment, the relaxation curves cannot be fitted with the same stretched exponential model. In addition to the oxidation of thiols, a degradation of the catalyst can also occur when reaching too high temperatures (Fig. S7). For the sample PE-1:4:0.8, deviation of the stress-relaxation curves from the exponential model is already evident in the first experiment, suggesting that oxidation and/or degradation are more pronounced when a higher catalyst content is present (Fig. S5d).

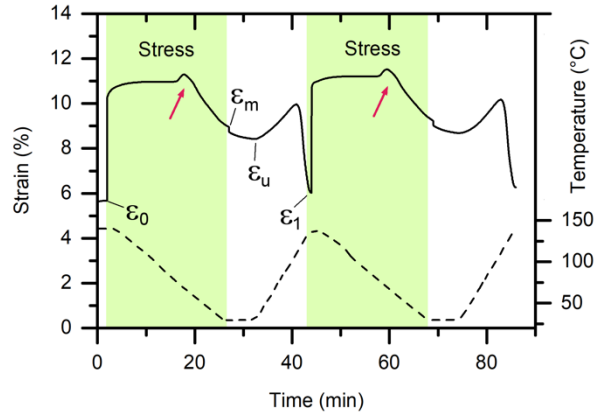
Table 3:  $G_\infty$ ,  $\beta$  and  $\langle\tau\rangle$  of PE-1:4-0.2 after the first stress-relaxation experiment. Relative increment of the residual stress  $\sigma_{r,2}/\sigma_{r,1}$  between the two stress-relaxation.

Temperature (°C)	$G_\infty$	$\beta$	$\langle\tau\rangle$ (min)	$\sigma_{r,2}/\sigma_{r,1}$ (%)
170	0.06	0.35	1090	28
180	0.21	0.37	178	39
200	0.15	0.41	69	50
220	0.15	0.34	24	57

### 3.7 Shape memory properties.

Hartwig and co-workers have investigated the shape memory properties of thermoset/polycaprolactone networks incorporating crystallinity and exchangeable links [47]. The existence of chemical links between the crystallizable part and the network was found to partially decrease crystallinity but on the other hand to improve shape fixity and toughness [48]. The materials hereby investigated are networks wherein the crystallizable sequence is completely bound by chemical links. At room temperature, PE is well above the glass transition ( $T_g \approx -120^\circ\text{C}$ ) and well below the melting point ( $T_m \approx 106^\circ\text{C}$ ). Measurements of crystallinity by DSC are reported in SI (Fig. S4, Table S1). Since the areas of the melting peaks of crosslinked and non-crosslinked samples are of the same order, it is evident that crystallinity is to a large extent preserved after modification. The introduction of covalent bonds along the chains of the semi-crystalline polymer precursor creates a chemically crosslinked network in addition to the crystalline aggregation. Therefore, the synthesized materials gather the structural features of a shape memory polymer being dually crosslinked by chemical links and physical

links. The latter can be easily removed by heating above the melting point. Consequently, the shape memory behaviour of sample PE-1:4:0.2 was assessed in elongation under a cyclic stress of 100 kPa. The result of the shape memory sequence is presented in Fig. 6.



**Fig. 6:** Cyclic shape memory tests of compound PE-1:4:0.2 in tension mode. The green background areas indicate sections of 100 kPa applied stress. The represented variables are used in formulas 7 and 8, their meaning is explained in the text. The overshoots signaled by red arrows are discussed in Section 3.8.

As can be seen from the figure, the initial deformation of the sample is already  $\varepsilon_0 = 5.6\%$  at rest. This deviation from zero might be ascribed to different factors, including the preload force ( $\approx 0.01$  N) applied by the machine to hold the sample in tension. In parallel with this, between clamping at room temperature and equilibration at  $140^\circ\text{C}$ , the sample undergoes regular thermal expansion and volume change upon melting. While in this case the contribution of the preload tension (amounting to about 1 kPa) can be neglected, the other two can be estimated from tabulated volume-temperature diagrams of polyethylenes [49]. For a LDPE grade of similar density (0.92) [25] the linear expansion between these two temperatures is given by formula (7) :

$$\varepsilon_T = \sqrt[3]{\frac{v_{140}}{v_{30}}} - 1 \quad (7)$$

where  $v_{140}$  and  $v_{30}$  are the specific volumes of polyethylene at 140 and  $30^\circ\text{C}$ ; the values retained for calculation are 1.27 and 1.09, respectively. The result  $\varepsilon_T = 5.2\%$  matches the experimental deviation at the beginning of the experiment. Thus the initial strain is attributable to thermal volume changes.

From this initial point, the sample is deformed by applying a constant stress of 100 kPa and then cooled to  $30^\circ\text{C}$  to freeze the deformation. During cooling, the shape of the sample evolves in a non-monotonic way (Fig. 6) this point will be examined below. So far, the final strain, right before removing stress is noted  $\varepsilon_m$ . Then, after removing the stress, the sample is equilibrated

at room temperature and the new strain attained at the end of the equilibration period is noted  $\varepsilon_u$ . During the last segment of the shape memory test, the sample is re-heated without external stress and its shape is recorded. The strain at the end of the first cycle is noted  $\varepsilon_1$  (Fig. 6).

Using above definitions, the shape-fixity  $R_f$  and shape-recovery  $R_r$  performances may be determined in the usual way [26] according to equations (8) and (9):

$$R_f = \frac{\varepsilon_u}{\varepsilon_m} \cdot 100 \quad (8)$$

$$R_r = \frac{\varepsilon_u - \varepsilon_1}{\varepsilon_m - \varepsilon_0} \cdot 100 \quad (9)$$

The results for both cycles are reported in Table 4. From these raw numbers, the material apparently shows good fixity but modest recovery. However, the inconvenience of measuring in tension is that thermal contraction/expansion and the shape memory effects occur along the same axis. To disentangle the effects, one can use another geometry (e.g. flexion, torsion) where thermal expansion is intrinsically compensated. Another approach proposed here is to apply a correction of thermal expansion. In practical terms, this means replacing  $\varepsilon_1$  and  $\varepsilon_0$  (measured at 140°C) in formulas (8) and (9) by their corrected counterparts,  $\varepsilon_1 - \varepsilon_T$  and  $\varepsilon_0 - \varepsilon_T$ . With this correction (Table 4) the performance in shape recovery is close to 90%, while correction has no incidence on the shape fixity value.

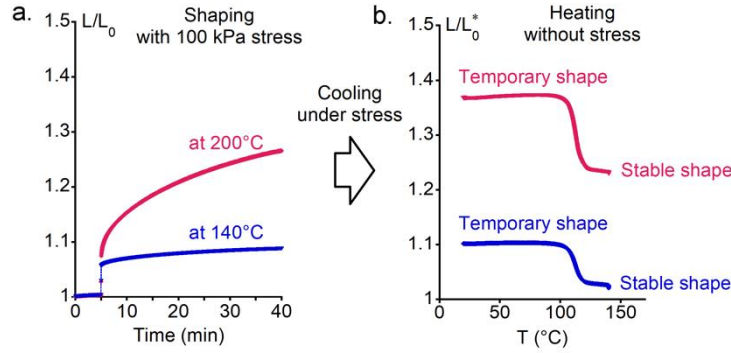
Table 4: shape finixy  $R_f$  and shape recovery  $R_r$  of PE-1:4-0.2 at 140°C and 200°C for 2 different cycles.

Temperature	<i>First cycle (%)</i>		<i>Second cycle (%)</i>		
	$R_f$	$R_r$	$R_f$	$R_r$	
140°C	94	73	95	75	non-corrected
140°C	94	90	95	91	corrected

This demonstrates the efficiency of shape memory properties of these materials as well as the opportunity of applying the thermal expansion correction in this geometry.

In the following of this section, thermal correction will be considered to analyse the interplay between vitrimer properties and shape memory properties which become apparent when the shaping stress is applied at a temperature high enough to activate the bond exchange reactions. Shape memory experiments relevant to such conditions are presented in Fig. 7 where two different experiments at 140°C and 200°C are compared. The first step (Fig. 7a) corresponds to the shaping stage, which is essentially a regular isothermal creep test in response to a constant

100 kPa tensile stress. The stress duration is the same for both temperatures. In these plots, the deformation (draw ratio  $L/L_0$ ) is determined relative to the length of the sample right before application of the stress (normalized to 1). Evidently, the deformation reached after one hour differs depending on whether the 100 kPa stress is applied at 140°C or 200°C. The excess creep observed at 200°C is the result of the plastic deformation of the network permitted by thermally activated bond exchange reactions.



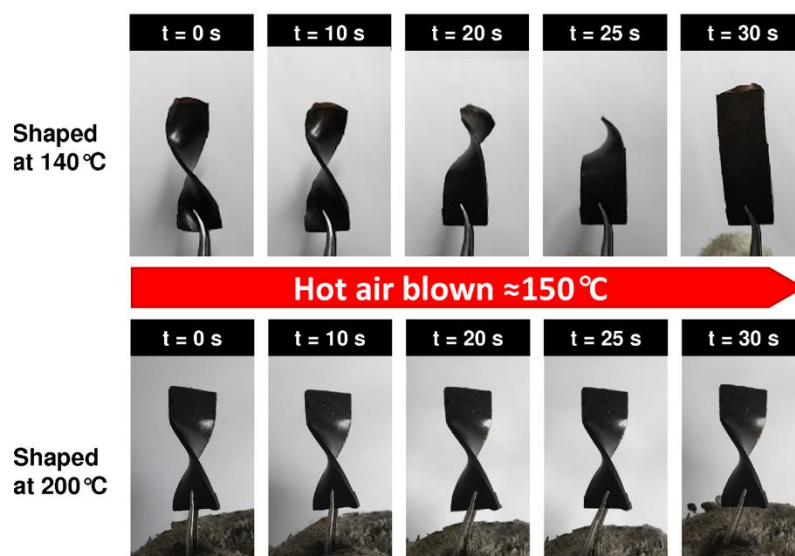
**Fig. 7.** thermomechanical cycles at 140 °C (blue curves) and 200°C (red curves) to assess shape memory behaviour and shape reconfiguration behaviour of PE-1:4:0.2;

The second stage of the experiment is a cooling ramp at  $-10^{\circ}\text{C}/\text{min}$  and the peculiarities of this step will be presented at the end of the section; after cooling, the samples are ready for the strain recovery test. For the recovery stage, which is not isothermal, a real-time thermal correction is achieved the following way: the length of the sample at any time is divided by the length of a reference sample subjected to the same thermal cycle but using a 10 kPa stretching stress, value at which thermal expansion effects are larger than mechanical deformations. The corrected draw ratio ( $L/L_0^*$ ) presented in Fig. 7b is determined through formula (10).

$$\frac{L}{L_0^*} = \frac{L}{L^{\text{Ref}}} \cdot \frac{L_0^{\text{Ref}}}{L_0} \quad (10)$$

Where  $L$  is the length of the sample at any time,  $L^{\text{Ref}}$  the length of the reference specimen at the same instant of the heating/cooling cycle and  $L_0$  and  $L_0^{\text{Ref}}$  their respective initial lengths at 140°C. For the blue curve of Fig 7b (after shaping at 140°C),  $L/L_0^*$  is of about 10% of the starting length. This deformation almost completely vanishes after re-heating. In contrast for the red curve of Fig 7b (after shaping at 200°C under the same stress)  $L/L_0^*$  is more than 35% and part of this deformation remains after reheating, meaning that the permanent (equilibrium) shape of the sample is  $>20\%$  longer than the initial one. Thus after reshaping at 200°C, the sample still shows shape memory properties but the process starts from a new transient shape and ends with a new recovered shape. The sample deformation acquired at the end of this

process is permanent and not recoverable by re-heating. This type of reconfiguration is characteristic of vitrimer materials; it is further illustrated qualitatively in the picture sequence of Fig. 8 where a ribbon shaped at 140° into a helicoïd completely recovers its initial flat shape during next heating whereas another sample twisted and held for enough long time at 200°C (1 hour in an oven) keeps the imprinted shape during further heating.

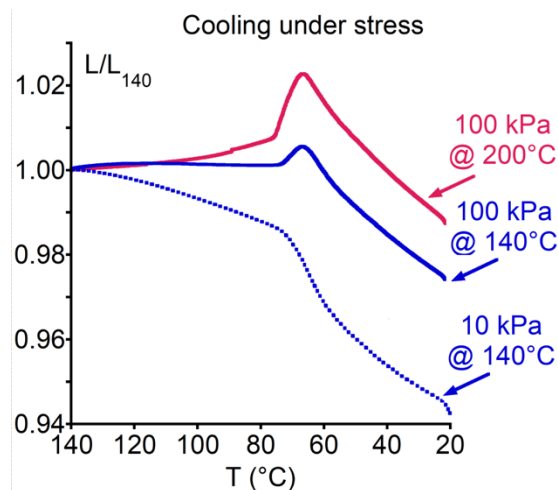


**Fig. 8.** Schematic illustration over 30 s of the double reconfiguration of PE-1:4-0.2 in two distinct conditions.

### 3.8 Strain induced crystallization.

In this section, we focus on another thermomechanical effect, observed with these samples. During a cooling ramp under constant tensile stress and constant cooling rate, the sample first elongates, then shrinks. This peculiarity is already visible and signaled by a red arrow on both cooling cycles shown in Fig. 6. It is further detected on the cooling ramps recorded at the end of the thermal cycles shown in Fig. 7. These cooling ramps are illustrated in Fig. 9, where the draw ratio  $L/L_{140}$ , relative to the initial length at 140°C is plotted together with the cooling ramp of the reference sample (stretched at 10 kPa instead of 100 kPa). The decreasing portions of these plots, present for all samples, is simply attributable to specific volume changes upon cooling and crystallization. For samples stretched at 100 kPa, a distinctive increase of the sample length is also detected in the vicinity of the crystallization temperature.





**Fig. 9.** Temperature variation of the draw ratio  $L/L_{140}$  during cooling under constant tensile stress.

In contrast, there is a continuous decrease of length for the reference sample. The increasing part of the curve therefore correlates with the simultaneous presence of stretching stress and crystallization. Similar effects have been reported in the literature and attributed to the oriented nucleation in stretched crosslinked polymers. This phenomenon sometimes referred to as "crystallization-induced elongation" is a consequence of the orientation of early-formed crystals in the direction of drawing, resulting in further anisotropization of the network [50]. This effect has been observed to be more evident for semi-crystalline networks with high gel content [51]. Interestingly, the phenomenon is amplified in the sample stretched at 200°C suggesting that network nodes in conflict with elongation may rearrange through exchange reactions, resulting in improved anisotropy in the end.

#### 4. Perspective

##### *Production of the pre-vitrimer by continuous extrusion*

The pre-vitrimer mixture of p(E-co-GMA) and dicarboxylate/dicarboxylic acid obtained upon extrusion is a thermolatent mixture that can react and form a network when heated at high enough temperature. Since the gap between the curing temperature and the melting point of the polymer precursor is sufficiently large, the pre-vitrimer can be kept at 115°C (temperature of extrusion and compression molding) without incurring gelation at too short times. This distinctive feature allowed us to convert a thermoplastic polymer into an elastic network in batch extrusion. In the same way, upscaling the production of polyethylene-based vitrimers may be envisioned as the risk of cross-linking inside the extruder is controlled, which is here achieved through proper selection of composition, shear rate and temperature. In this perspective, a powdered mixture according to the PE-1:4:0.2 composition was introduced at the

top feeder entrance of a continuous twin-screw vertical extruder. For this experiment, the temperature was regulated at 115°C all along the different portions of the screws, except for the last zone set at 125°C. The rotational speed of the screws was set on 70 rpm, corresponding to an overall residence time of ~3 min. Right after coming out of the column, the extruded filament slightly expanded and crystallized, resulting to production of a solid wire of about 2.7 mm diameter at a rate of about 15 mm/s eventually pelletized at the end of the extrusion line. We were able to extrude a total of 120 g of the *pre-vitrimer* mixture of PE-1:4:0.2 at an average rate of about 180 g/h. Pictures of extruded strands and pellets are presented in Fig. 10, their regular cylindrical shapes without corrugations strongly suggest that gelation is not attained.



**Fig. 10.** Samples of as-formed (left) and on-line pelletized (right) extruded filament of the PE-1:4:0.2 composition. At this stage, the compound is in its thermolatent pre-vitrimer form.

In the IR analysis (Fig. S8), the characteristic signal of epoxy groups is still present after extrusion. Based on the data presented in Fig. 3b the rise of viscosity takes place after 3 min at 170°C for this composition (dark blue plot). We believe that processing at such moderate extrusion rate is advisable to avoid internal overheating while preserving a large margin of latency for further processing and longer residence time in case of an incidental interruption of the process.

## 5. Conclusions

In this work, we show an example of polyolefin vitrimer where the percentage of chains not linked to the network is close to zero. In contrast to hitherto explored polyolefin vitrimers where

networks featuring a large portion of soluble fraction were obtained by radical grafting of by blending a crosslinkable copolymer with a homopolymer, the current work addresses the use of ethylene copolymers for preparation of homogeneous networks. Considering a random copolymer with an average number of >400 monomers per chain and no more than 1 % of reactive comonomer, the statistical distribution analysis led to the conclusion that chains deprived of any reactive groups represent less than 6 wt% and experimentally a gel content up to 96 wt% was achieved. Nevertheless, such networks have been easily produced by batch and continuous extrusion processes, thanks to the latency of the epoxy-acid addition, which also avoids any release of water, gas or by products. The fully cured networks demonstrated stress relaxation with an activation energy of about 120 kJ/mol. In comparison with epoxidized natural rubber derivatives where the same cross-linking strategy was adopted [21,52] the reaction here did not require the use of one equivalent of amine but only a catalytic quantity. Increase of catalyst content above 20 mol% was found to slow down the addition reaction. The materials of the current work are semi-crystalline and show interesting shape memory properties. In particular, interplay of network's reconfiguration and the crystallization induced orientation under stress that might be exploited to design reversible two-way shape memory polymers especially considering that such properties are critically dependant of high gel content.

## 6. Acknowledgements

Paolo Edera is thanked for his help in torsion rheology. The research leading to these results has received funding from the VITRIMAT program of the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie Grant agreement No 860911, Eric Drockenmuller and Damien Montarnal are thanked for helpful discussions.

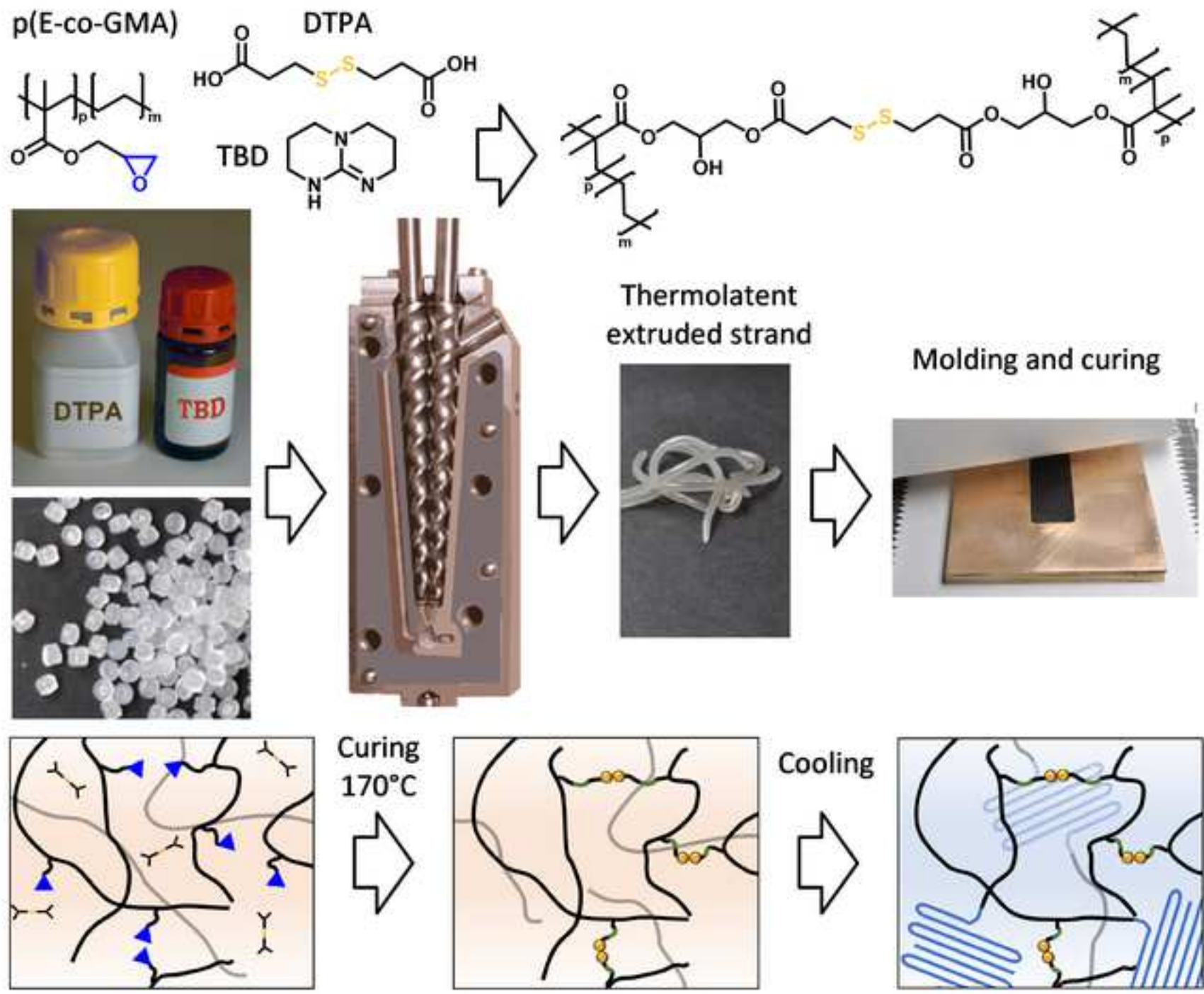
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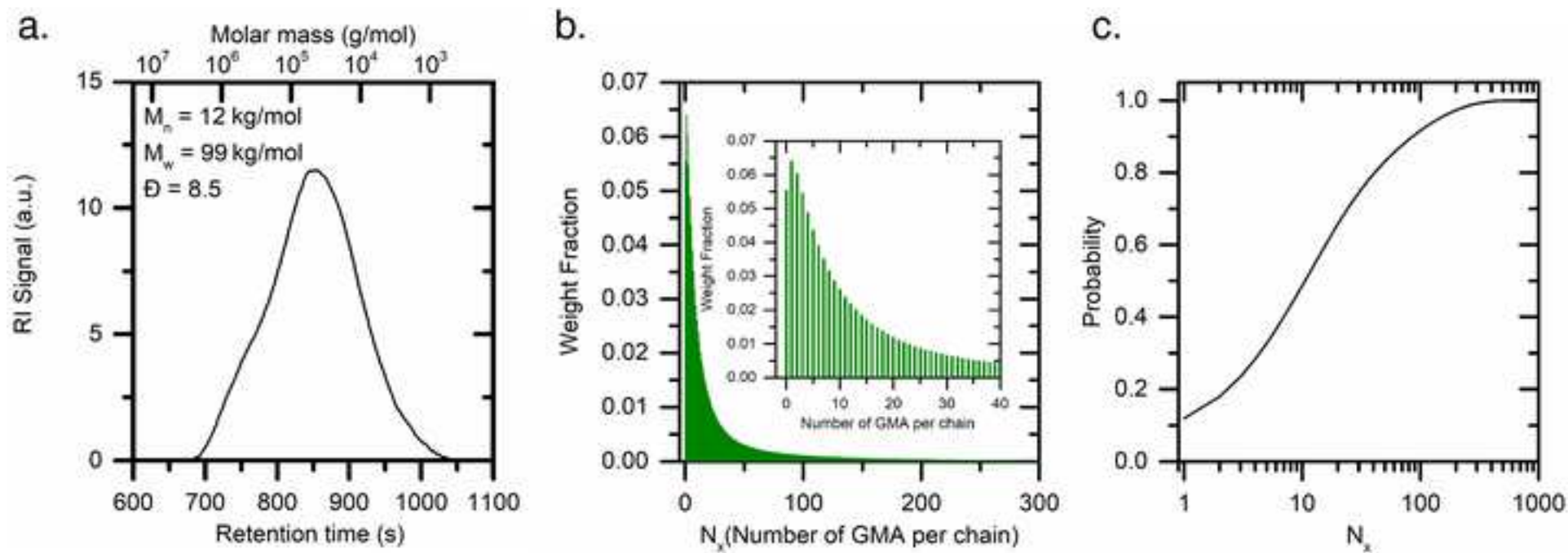
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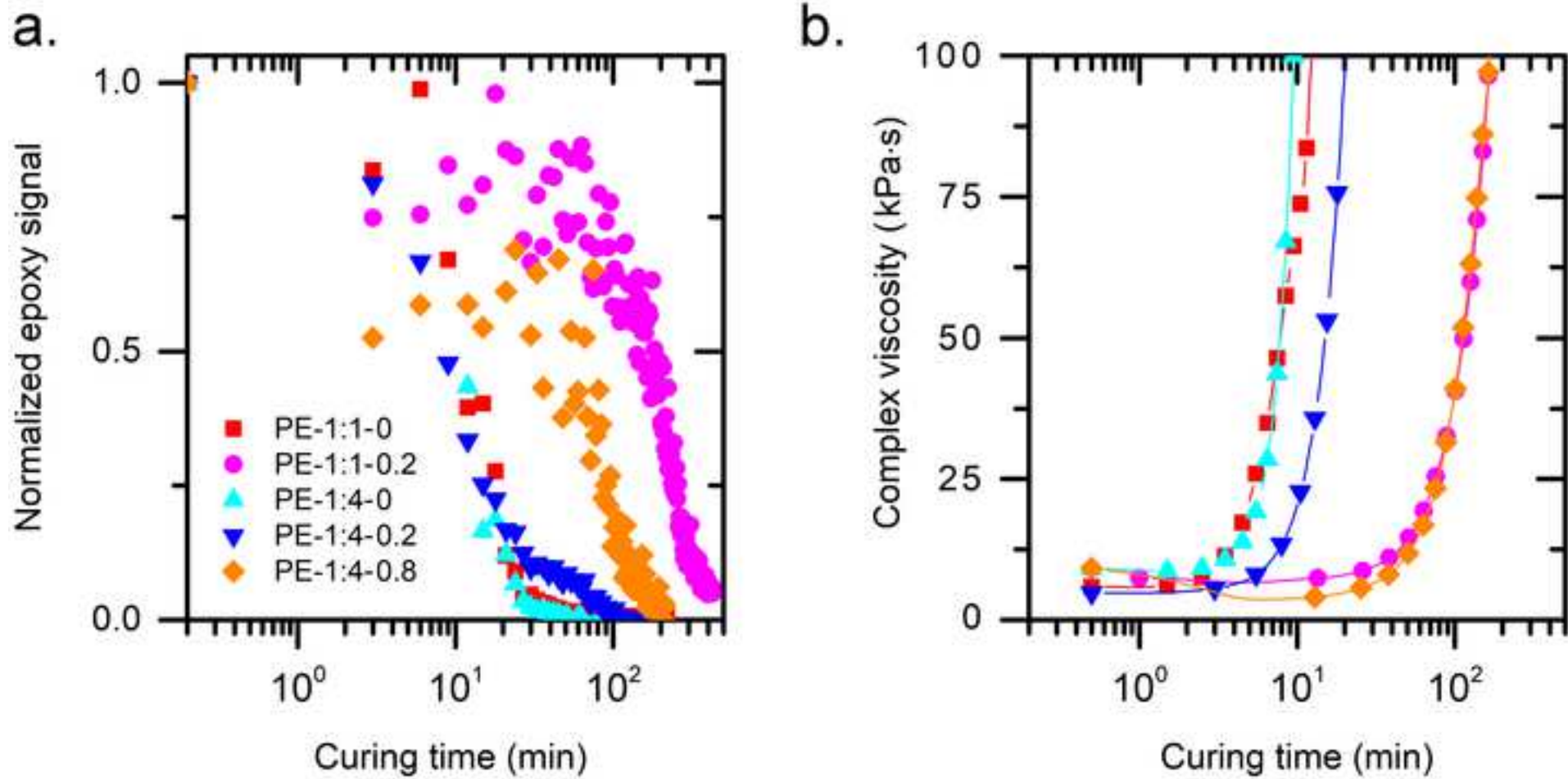
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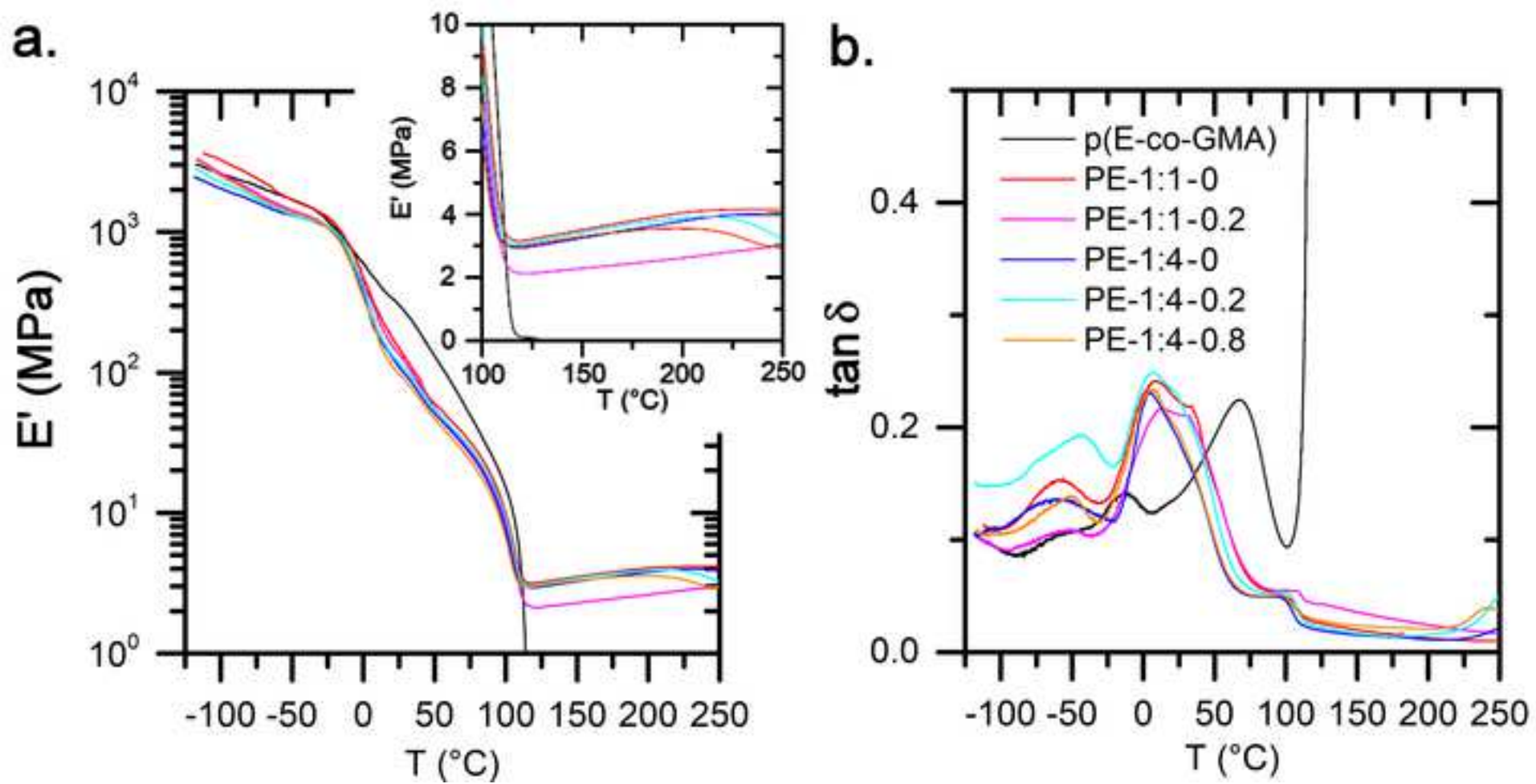


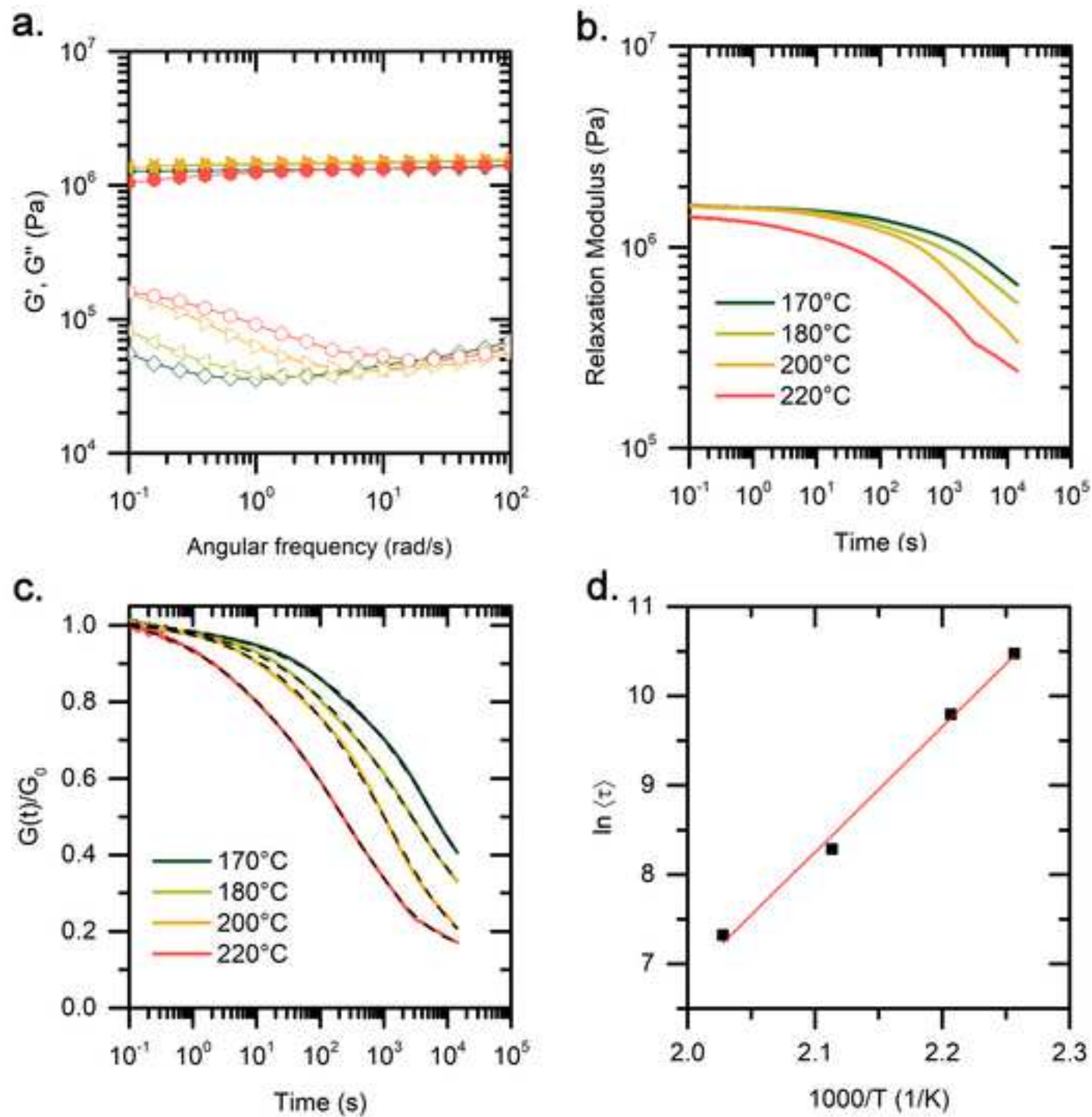


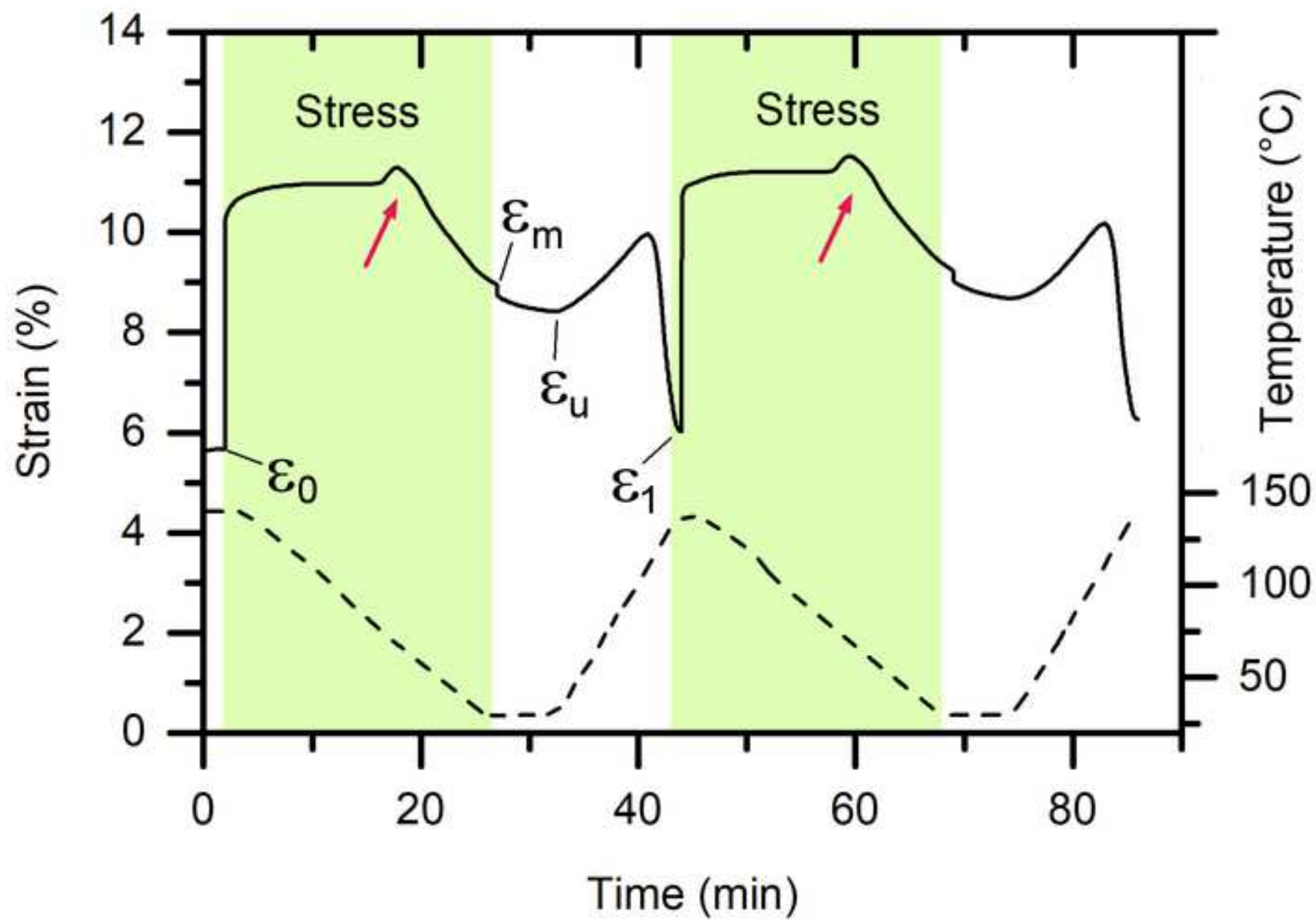


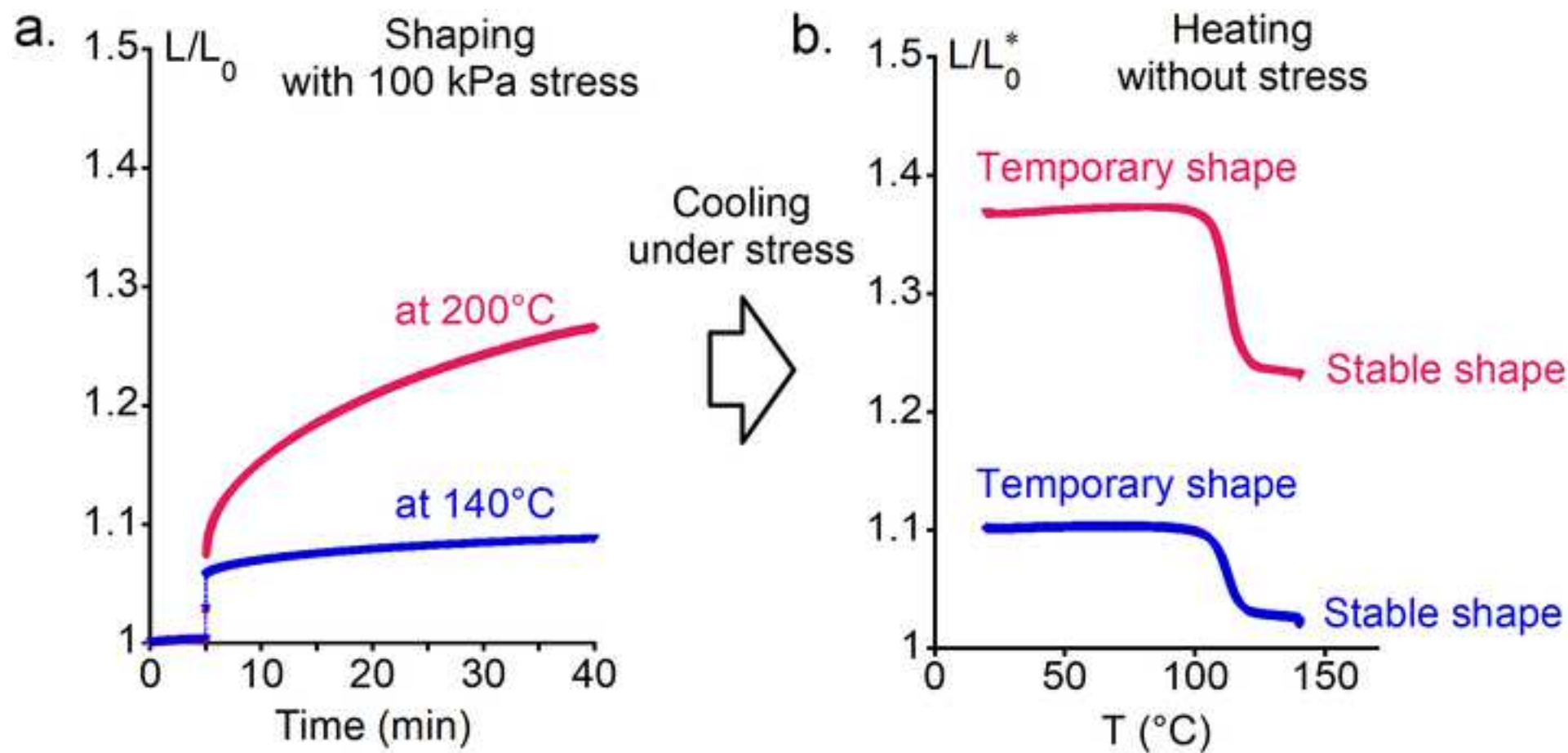






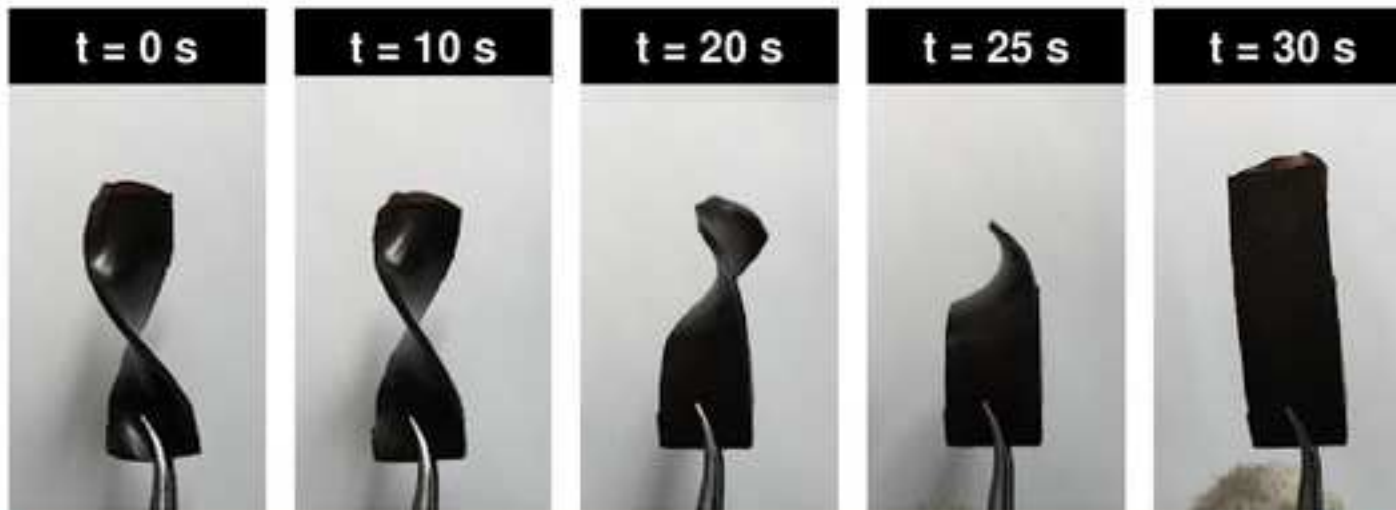






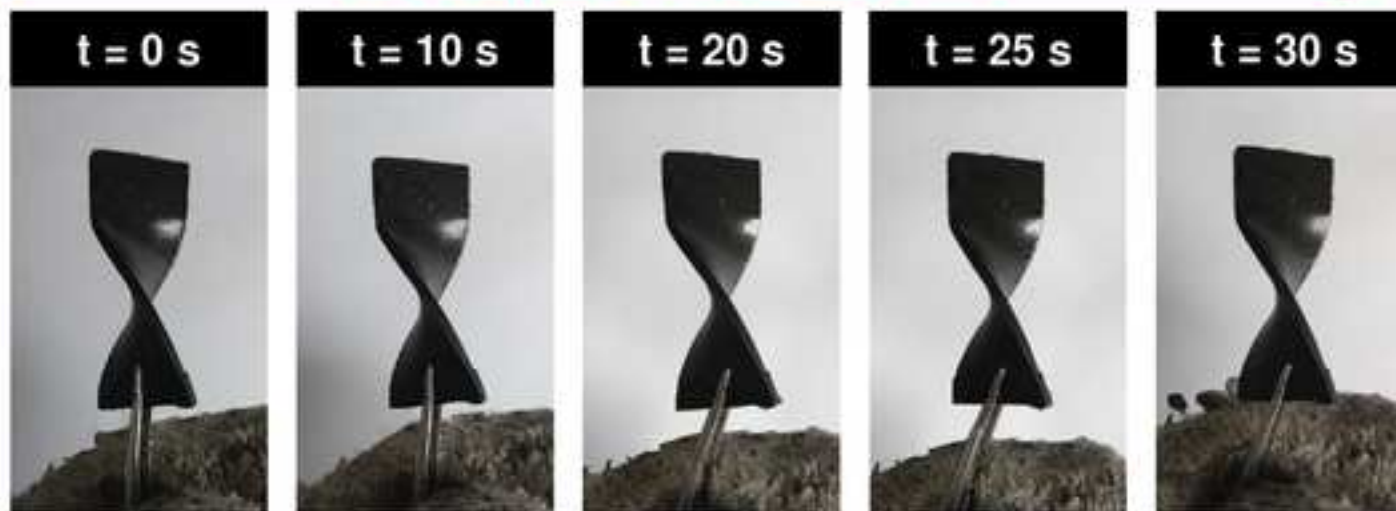


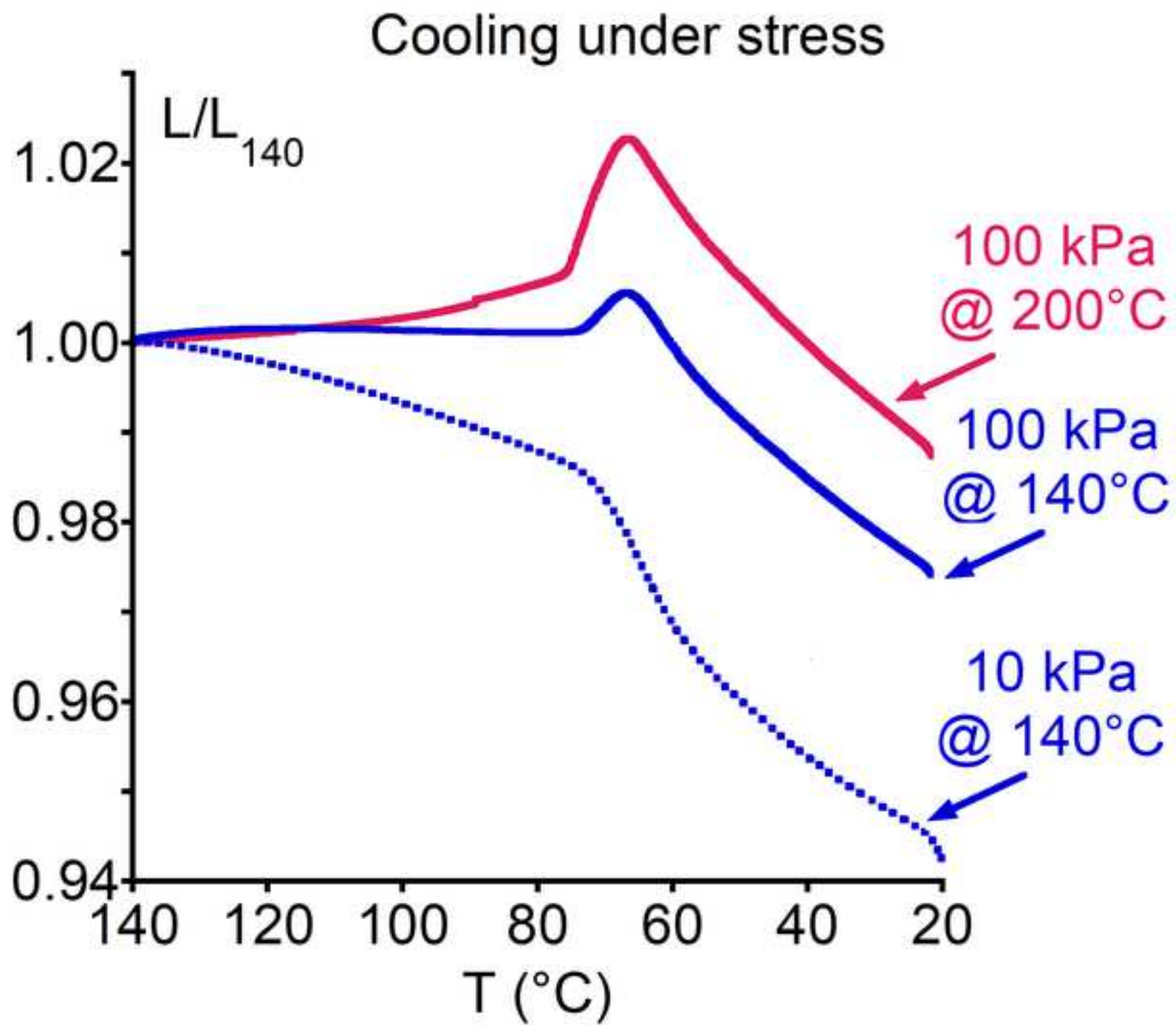
Shaped  
at 140 °C



Hot air blown  $\approx 150^\circ\text{C}$

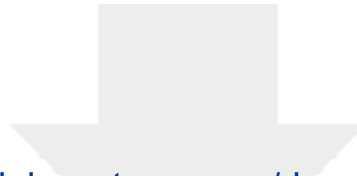
Shaped  
at 200 °C





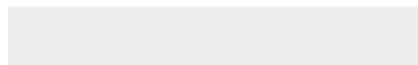


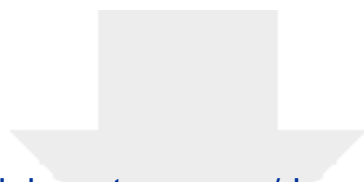




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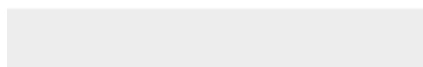
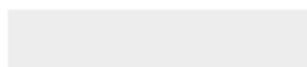
**Supplementary Material (online publication)**  
20240205-SI.docx





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**Supporting Material (not for publication)**  
20240215-Manuscript-track-change.pdf



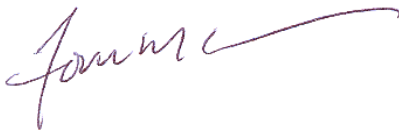
- Semi-crystalline polyethylene-based vitrimers are obtained starting from a commercial thermoplastic ethylene comonomer bearing glycidyl methacrylate function.
- Extrusion design of the polymer precursor with a cross-linker and a catalyst allows to obtain a thermolatent blend, subsequently converted (in a second step) into a network containing  $\beta$ -hydroxyesters and disulfide exchangeable bonds.
- Varying the cross-linker and catalyst content allows to control gelation and networks structural properties, together with stress-relaxation behaviour.
- Investigation of shape-memory properties and reshapeability of cross-linked networks with exchangeable bonds
- Upscaling towards continuous extrusion of a thermolatent blend of polyethylene a

**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

On behalf for all authors

A handwritten signature in dark ink, appearing to read 'François Tournilhac', with a long, sweeping horizontal stroke extending to the right.

François Tournilhac

à Paris, le 30 octobre 2023