

## Manuscript Details

<b>Manuscript number</b>	EUROPOL_2019_1055_R1
<b>Title</b>	A NEW CLASS OF VITRIMERS BASED ON ALIPHATIC POLY(THIOURETHANE) NETWORKS WITH SHAPE MEMORY AND PERMANENT SHAPE RECONFIGURATION
<b>Article type</b>	Research paper

### Abstract

Vitrimeres are a new promising class of polymeric materials which are attracting increasing attention thanks to their thermosetting characteristics with their capability of being reprocessed and recyclable, which make them more environmentally friendly in reference to the conventional thermosets. In the present study, we report a new class of vitrimeric materials consisting in poly(thiourethane) networks. These materials can be easily prepared from readily available isocyanate and thiol monomers in the presence of dibutyltin dilaurate (DBTDL) as the catalyst. The reaction has a click nature and therefore leads to highly homogeneous networks. The materials studied behave as conventional thermosets until topological rearrangement started. Freezing topological temperatures ( $T_v$ ) between 132 and 95 °C were determined depending on the amount of catalyst in the material. The vitrimers prepared showed good shape memory and welding abilities and a high optical transparency and therefore they have a great potentiality in advanced engineering applications. The occurrence of the trans-thiocarbamoylation reaction, responsible of the rearrangement, has been confirmed by using model compounds. The materials remained unaltered after reprocessing, which was proved by means of FTIR and thermomechanical studies.

<b>Keywords</b>	vitrimers; poly(thiourethane); thermosets; shape-memory; click reaction.
<b>Manuscript category</b>	Regular Paper
<b>Corresponding Author</b>	Angels Serra
<b>Corresponding Author's Institution</b>	Universitat Rovira i Virgili
<b>Order of Authors</b>	Francesco Gamardella, Federico Guerrero, Silvia De la Flor, Xavier Ramis, Angels Serra
<b>Suggested reviewers</b>	zhou changlin, Guy Van Assche, Roberto Williams, Francois Tournilhac, Damien Montarnal

## Submission Files Included in this PDF

### File Name [File Type]

Letter editor.docx [Cover Letter]

Answers to Reviewers.docx [Response to Reviewers]

Highlights.docx [Highlights]

graphical abstracts.pptx [Graphical Abstract]

revised text.docx [Manuscript File]

To view all the submission files, including those not included in the PDF, click on the manuscript title on your EVISE Homepage, then click 'Download zip file'.

## Research Data Related to this Submission

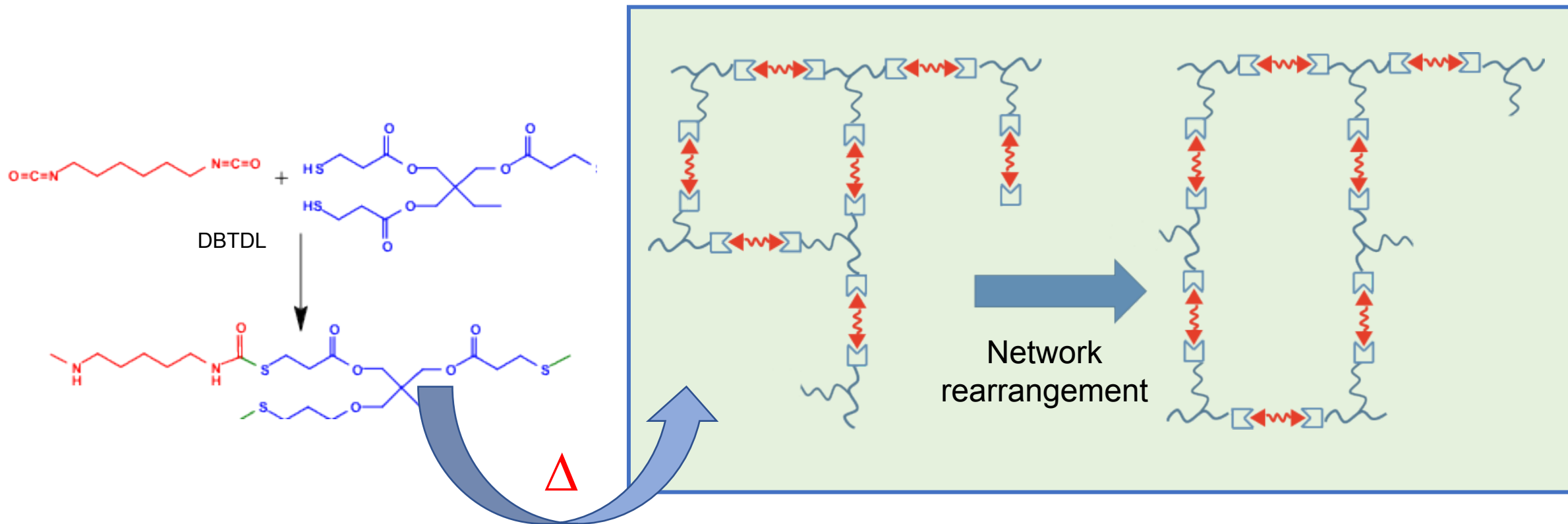
There are no linked research data sets for this submission. The following reason is given:  
Data will be made available on request

## **Highlights**

Novel poly(thiourethane) vitrimeric materials have been developed

Trans-thiocarbamoylation reaction has been proved using model compounds

Self-welding and shape memory abilities have been demonstrated



# A NEW CLASS OF VITRIMERS BASED ON ALIPHATIC POLY(THIOURETHANE) NETWORKS WITH SHAPE MEMORY AND PERMANENT SHAPE RECONFIGURATION

Francesco Gamardella,<sup>1</sup> Federico Guerrero,<sup>1</sup> Silvia De la Flor,<sup>2</sup> Xavier Ramis<sup>3</sup> and Angels Serra<sup>1\*</sup>

<sup>1</sup> Dept. of Analytical and Organic Chemistry, Universitat Rovira i Virgili, C/ Marcel·lí Domingo, Edif. N4. 43007, Tarragona, Spain.

<sup>2</sup> Dept. of Mechanical Engineering, Universitat Rovira i Virgili, Av. Països Catalans, 26, 43007 Tarragona, Spain.

<sup>3</sup> Thermodynamics Laboratory, ETSEIB Universitat Politècnica de Catalunya, Av. Diagonal, 08028, Barcelona, Spain.

Corresponding author: A. Serra. E-mail: [angels.serra@urv.cat](mailto:angels.serra@urv.cat) +34 977559558

## Abstracts

Vitrimeres are a new promising class of polymeric materials which are attracting increasing attention thanks to their thermosetting characteristics with their capability of being reprocessed and recyclable, which make them more environmentally friendly in reference to the conventional thermosets. In the present study, we report a new class of vitrimeric materials consisting in poly(thiourethane) networks. These materials can be easily prepared from readily available isocyanate and thiol monomers in the presence of dibutyltin dilaurate (DBTDL) as the catalyst. The reaction has a *click* nature and therefore leads to highly homogeneous networks. The materials studied behave as conventional thermosets until topological rearrangement started. Freezing topological temperatures ( $T_v$ ) between 132 and 95 °C were determined depending on the amount of catalyst in the material. The vitrimers prepared showed good shape memory and welding abilities and a high optical transparency and therefore they have a great potentiality in advanced engineering applications. The occurrence of the trans-thiocarbamoylation reaction, responsible of the rearrangement, has been confirmed by using model compounds. The materials remained unaltered after reprocessing, which was proved by means of FTIR and thermomechanical studies.

**Keywords:** vitrimers; poly(thiourethane); thermosets; shape-memory; click reaction.

## 1. Introduction

Thermosetting polymers are very useful in a broad range of industrial applications, due to their chemical, thermal and environmental resistance and because of their excellent mechanical performance. However, the existence of covalent bonding in the three dimensions of the network prevents reshaping, reprocessing, or recycling and makes difficult their reparation. To avoid these drawbacks a new family of materials, called vitrimers, has been developed. These new materials combine the excellent performance of thermosets with some of the processability advantages of thermoplastics [1, 2, 3].

Vitrimers consist in three-dimensional polymeric structures with dynamic covalent bonds within an organic network, which can lead to topological changes without affecting the average crosslinking degree. This fact allows reshaping, self-welding, reprocessing and not less important, the elimination of internal stresses, which appear during their curing or service-life [4].

This type of materials shows a characteristic transition temperature,  $T_v$ , also called topology freezing transition temperature, that corresponds to a reversible transition from viscoelastic solid to a viscoelastic liquid. This temperature depends on the kinetics of the reversible reaction, responsible of the topological changes in the network structure [5].

In advanced technologies, there is a great demand for smart materials, especially shape memory thermosets. They are quite advantageous in comparison to thermoplastics, since they have higher thermal stability, fixation ability and shape-recovery rate and can perform higher levels of mechanical work [6, 7].

Bearing this idea in mind, the introduction of a new class of vitrimers with good shape memory behaviour can overcome the limitations of the traditional thermosets, in the formation of sophisticated and geometrically complex forms, thanks to the combination of elasticity (shape memory) and plasticity (vitrimers). In addition, these materials, after recycling, can also exhibit comparable mechanical performance [8, 9, 10].

In recent years, different reversible exchange reactions have been explored for the preparation of vitrimers [4]. Among them, transesterification [1, 5] transamination [11]

disulfide exchange [12, 13] transalkylation [14] siloxane equilibrium [15] dioxaborolane metathesis [16] amine-urea exchange [17] and transcarbamoylation [18, 19] can be mentioned. These exchange reactions are the responsible of the reformation of the network structure. **These chemical processes are triggered by external stimuli, usually by heating, and occurs to reach the most thermodynamically stable state of the materials after deformation.** The exchange rate can be enhanced by the addition of catalysts [4].

Polyurethanes have a broad application because of their versatility. They are durable and tough, and they have been applied in the field of elastomers, coatings, rigid foams and adhesives [20]. The vitrimeric characteristics of polyurethane thermosets has been already reported [21, 22]. Dynamic exchange reactions have already been demonstrated in a variety of poly(hydroxyurethane) materials [23]. In addition, their shape memory behaviour has also been reported.

Poly(thiourethane)s, also called poly(thiocarbamate)s, are related to the above-mentioned materials, but they present several advantages. Since they are obtained by *click-type* reactions from isocyanates and thiols, **the network structure is highly homogeneous and consequently relaxation processes occur in a narrow temperature range [24].** Thiol-isocyanate reaction does not present by-reactions such as occurs in the polyurethane synthesis, which leads to the formation of allophanate units in the network structure. In addition to that, poly(thiourethane) thermosets have quite valuable properties such as biocompatibility, flexibility and excellent optical transparence [25].

Herein, we report a new type of vitrimers with shape memory performance based on poly(thiourethane) networks. Because the vitrimeric behaviour in poly(urethanes) was attributed to a transcarbamoylation reaction, it was hypothesized that trans-thiocarbamoylation could also lead to a rapid exchange allowing reshaping, self-welding and stress dissipation, even in a more efficient way, due to the presence of sulphur, which has an enhanced reactivity in front of its oxygen analogues.

The materials prepared can be easily obtained from commercially available precursors. In the present case, hexamethylene diisocyanate (HDI) and trimethylolpropane tris(3-mercaptopropionate) (S3) in stoichiometric proportions have been selected as starting monomers. A Lewis acid (dibutyltin dilaurate, DBTDL) has been

used as a catalyst, but it is also possible to use a Lewis base, such as 1-methylimidazole, 1MI, as demonstrated in a previous article [24]. Although this type of materials can be obtained from different monomers, the study was carried out with only one type of material as a proof of concept.

It should be noticed that in the literature, there are no references to the trans-thiocarbamylation process in absence of thiol in excess, nor in the field of materials science, nor in the field of pure organic chemistry. Moreover, the trans-carbamylation previously proposed by Yan et al., as the responsible of the reversible structural change in those vitrimers, was not structurally demonstrated by these authors [21].

## **2. Experimental part**

### *2.1. Materials*

Trimethylolpropane tris(3-mercaptopropionate) (S3), hexamethylene diisocyanate (HDI), n-butanethiol, 2-methyl-1-propanethiol, n-butyl isocyanate, tert-butyl isocyanate and dibutyltin dilaurate (DBTDL) from Sigma-Aldrich were used as received.

### *2.2. Preparation of the formulations*

HDI and S3 were mixed in stoichiometric proportions, 2 mol of S3 per 3 mol of HDI. The selected amount of DBTDL was first dissolved in the isocyanate and the corresponding amount of thiol was then added. Different formulations were prepared with 1, 2 and 4 phr of DBTDL (parts of catalysts per hundred parts of thiol). The mixtures were manually stirred until homogeneity at room temperature and freshly used.

### *2.3. Synthesis of the model compounds*

S-Butyl butylcarbamothioate (L-L) was prepared by reacting stoichiometric proportions of n-butanethiol and n-butyl isocyanate with a 5 wt% of DBTDL at 90 °C in a 10 mL flask under argon atmosphere for 96 h. The final product was purified by eliminating unreacted volatile products at vacuum in the rotary evaporator. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ in ppm) (see Figure S1): 5.25 (1H), 3.28 (2H), 2.90 (2H), 1.59 (2H), 1.50 (2H), 1.39 (2H), 1.35 (2H), 0.93 (3H) and 0.90 (3H).

S-isobutyl tert-butylcarbamothioate (I-T) was prepared as described before for L-L, starting from stoichiometric proportions of 2-methyl-1-propanethiol and tert-butyl

isocyanate.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  in ppm) (see Figure S2): 5.15 (1H), 2.75 (2H), 1.80 (1H), 1.33 (9H) and 0.95 (6H).

#### 2.4. *Trans-thiocarbamoylation assessment*

An equimolar mixture of S-butyl butylcarbamothioate (L-L) and S-isobutyl tert-butylcarbamothioate (I-T) with 5 wt.% of DBTDL was heated under argon atmosphere at 120 °C for 24 h. The mixtures before and after heating were analyzed by gas chromatography equipped with a mass detector (see Figure 1). The mass spectra registered for each compound can be visualized in Figures S3, S4, S5 and S5 in SI.

#### 2.5. *Sample preparation*

For DMTA analysis, films were prepared by pouring the formulations on pre-silanized glasses and using Teflon spacers to ensure a homogeneous thickness of 0.5 mm. The formulations were cured at 60°C, 80°C, 100°C and 150°C for two hours at each temperature. The films were die-cut to obtain a rectangular specimen of 20 x 5 x 0.5 mm<sup>3</sup> dimensions.

#### 2.6. *Characterization techniques*

$^1\text{H}$  NMR spectra were registered in a Varian Gemini 400 spectrometer.  $\text{CDCl}_3$  was used as the solvent. For internal calibration the solvent signal corresponding to  $\text{CDCl}_3$  at 7.26 ppm.

Separation and detection of the mixture components were performed in a HP6890 gas chromatograph and 5973 Mass selective detector (Agilent Technologies, Waldbronn, Germany), using a HP-5MS capillary column (30 m × 0.25 mm × 0.25 m) provided by Agilent.

FTIR spectra were registered with a Bruker Vertex 70 equipped with a Golden Gate heated single reflection diamond ATR in the absorbance mode at a resolution of 4 cm<sup>-1</sup> in the wavelength range of 400 to 4000 cm<sup>-1</sup>. The typical absorption bands of the poly(thiourethane) vitrimer obtained with a 4% of DBTDL were followed during heating in the ATR in the temperature range from 155 to 200 °C keeping the temperature of the ATR for 10 min at each temperature tested. The material before and after being reprocessed at 180 °C for 40 min was analyzed at room temperature.



The viscoelastic and thermo-mechanical properties were evaluated by using a DMA Q800 analyzer from TA Instruments (New Castle, DE, USA).

## 2.7. Stress relaxation tests

Tensile stress relaxation tests were conducted using a film tension clamp on samples with the same dimensions as previously defined. The sample was firstly equilibrated at 160 °C and left isothermally at this temperature for 3 min, then a constant strain of 1.5 % (to ensure the material is within the linear range) was applied on the sample and the consequent stress level was measured as function of time. Then the strain was removed, and the process was repeated every 5 °C until the final test temperature, 190 °C, is reached.

The relaxation stress  $\sigma(t)$  was normalized by the initial stress  $\sigma_0$  and the relaxation times ( $\tau$ ) were determined as the time necessary to relax  $0.37 \cdot \sigma_0$ . With the relaxation times obtained at each temperature, the activation energy values  $E_a$  were calculated for each vitrimer, using an Arrhenius-type equation:

$$\ln(\tau) = \frac{E_a}{RT} - \ln A$$

where,  $\tau$  is the time needed to attain a given stress relaxation value (37 %),  $A$  is a pre-exponential factor and  $R$  is the gas constant. From the Arrhenius relation, the temperature of topology freezing ( $T_v$ ) was obtained as the temperature at which the material reaches a viscosity of  $10^{12}$  Pa·s. For our system the value of  $T_v$  could also be extrapolated from the Arrhenius fitting to a relaxation time of around  $10^5$  s. This time is deduced from the Maxwell's relation ( $\eta = E' \cdot \tau^*$ ) and assuming  $E'$  (obtained from the DMTA experiments) being relatively invariant in the rubbery state.

To compare the time to reach the complete relaxation of the stress (i.e. a normalized stress less than  $10^{-2}$ ) of poly(thiourethane)s vitrimers obtained with different contents of DBTDL, a single stress relaxation test was performed at the temperature of 180°C with the same constant strain of 1.5%.

## 2.8. Creep experiments

Creep and recovery properties were studied by the same DMA Q800 apparatus equipped with a film tension clamp.

All the samples were stretched under a stress of 0.1 MPa at 180 °C for 30 min, then the stress was immediately released, and the sample was left to recover for 30 min. For comparative purposes between the rubbery and the vitrimeric state, a sample with a 4% of DBTDL content was also tested, under the same creep conditions, at 70°C (slightly above  $T_g$ ).

For the determination of the viscosity at each temperature needed for the representation of the Fragility Angell Plot, a series of creep experiments were carried out on films at temperatures between 70 and 180 °C, increasing 10 °C in each scan. To perform the tests, the selected temperature was equilibrated for 3 min and then a stress level of 0.1 MPa was applied for 30 min. The viscosity  $\eta$  (Pa·s) was then obtained from the slope of the graph strain-temperature and represented in front of  $T_v/T$  thus obtaining the Angell Fragility Plot.

### 2.9. *Tan $\delta$ determination*

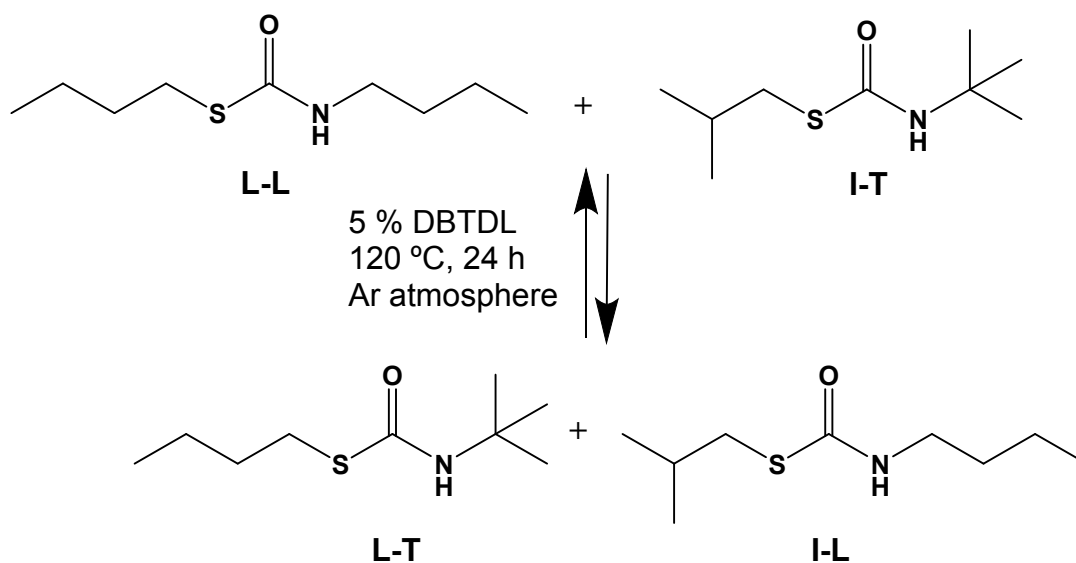
To study the influence of the trans-thiocarbamoylation process on the thermo-mechanical properties, the evolution of **tan  $\delta$  and storage modulus with temperature** was investigated after performing several stress relaxation experiments. A sample was tested in tension in the DMA Q800 analyzer, at a heating rate of 3°C/min from 30 to 125°C with a frequency of 1 Hz and 0.1 % of strain. Then the sample was left to completely relax at 180 °C with a strain level of 1.5 % for 25 minutes. After the sample was relaxed, another thermomechanical tests, with the same conditions as the initials, was performed. This process was repeated 2 times.

### 2.10. *Dilatometry tests*

Dilatometry was performed with the tension film geometry in the DMA Q800 analyzer on the samples with the same dimensions as described before. The length of the sample was continuously measured while increasing the temperature at a heating rate of 1 °C/min from 25 to 250 °C. A slight stress of 0.01 MPa was applied during the experiment to avoid buckling.

### 3. Results and discussion

To prove that trans-thiocarbamylation can occur on heating thiocarbamates in the presence of a Lewis acid such as DBTDL, we synthesized and characterized two different model compounds (L-L and I-T) and then, they were heated for 24 h at 120 °C under inert atmosphere. Scheme 1 depicts the structure of the model compounds and the structure of the rearranged compounds expected.

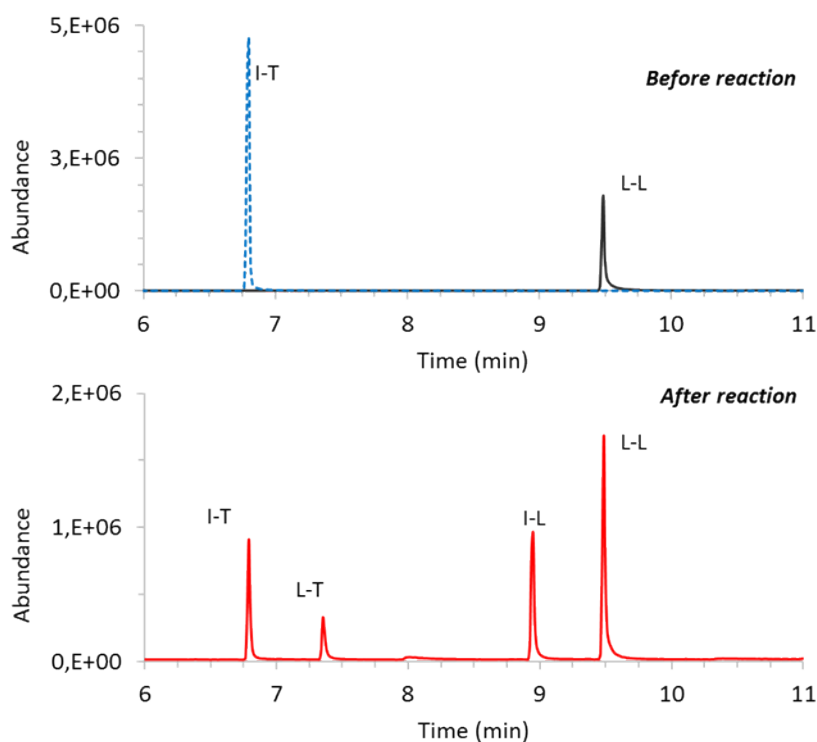


**Scheme 1.** Model compounds synthesized and structure of the compounds formed by trans-thiocarbamylation rearrangement.

The mixture before and after heating was investigated by gas chromatography coupled to a mass spectrometer detector and the chromatograms are represented in Figure 1. As we can see in the figure, the two peaks of the mixture before reaction were transformed into four peaks after reaction. By mass spectrometry the structure of the two new compounds appearing as two new peaks was characterized and corresponds to the products designed as L-T and I-L in Figure 1. The characterization of the model compounds and the mass spectra obtained of these eluted products are given in the supporting information (Figures S1- S6).

As we can see in the chromatogram, after reaction no traces of initial thiol or isocyanate were observed, which indicates that the trans-thiocarbamylation reaction

occurs through a concerted mechanism and not by dissociation of thiourethanes to form thiol and isocyanate and further coupling.



**Figure 1.** Trans-thiocarbamoylation reaction scheme and gas-chromatograms of the mixture before and after reaction.

Once confirmed the viability of the interchange process the characterization of the crosslinked materials was performed. The preparation of the material from HDI and S3 with different proportions of DBTDL (1, 2 and 4 phr) is described in the experimental part. Three different proportions of catalyst were used in the formulation to investigate if in these materials, the increase in the amount of catalyst also increases the rate of interchange reaction, enhancing the reshaping velocity as it was reported for other vitrimeric materials [4].

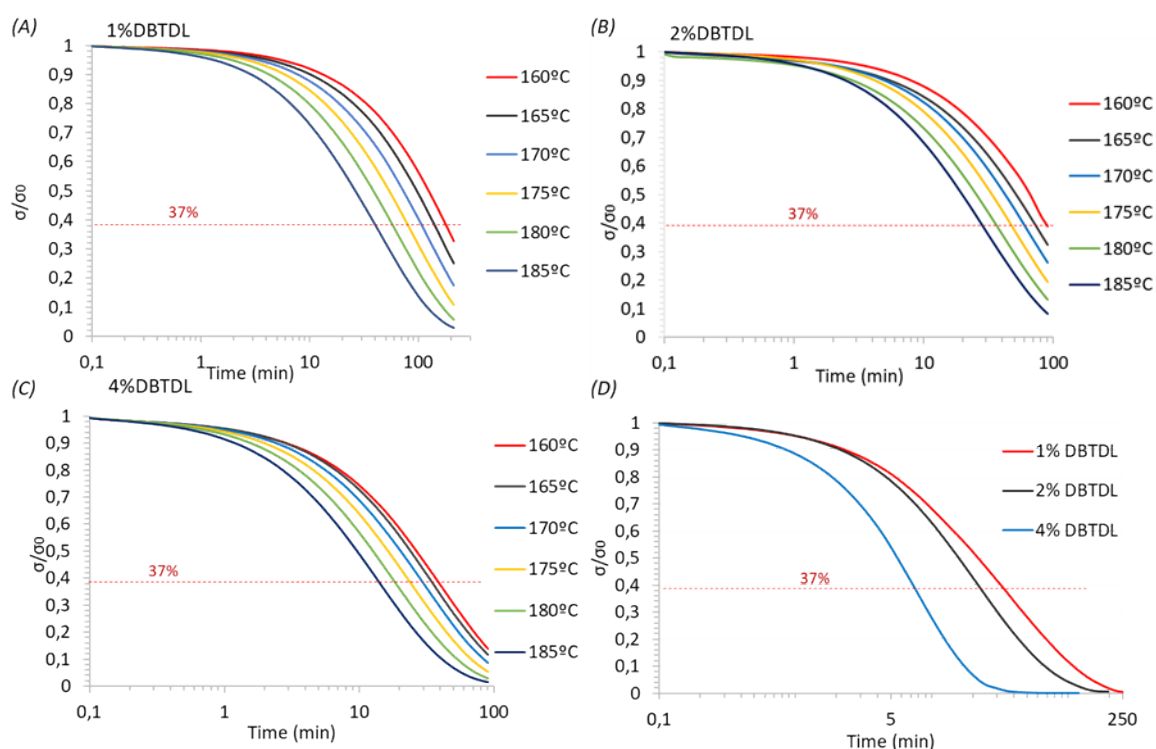
From the DMTA analysis the values of the temperature at peak of  $\tan \delta$  for the materials prepared with different proportions of DBTDL were determined and they are collected in Table 1. As we can see, both the  $\tan \delta$  evolution (and the corresponding peak of  $\tan \delta$ ) and the storage modulus are not influenced by the amount of catalyst (see Figure S7 and S8 in SI) which indicates that the materials have similar thermomechanical

behavior, i.e. the evolution of the  $\tan\delta$  and the storage modulus present the same shape and almost the same values throughout all the temperature range.

**Table 1.** Temperature at peak of  $\tan\delta$  and topology freezing temperature, activation energy and time for complete stress relaxation at 180 °C. Adjusting parameters for the Arrhenius eq. have also been included.

Sample	$T_{\tan\delta}$ (°C)	$T_v$ (°C)	$\tau_{180^\circ\text{C}}$ (min)	$E_a$ (kJ/mol)	$\ln A$ (s)	$r^2$
1% DBTDL	57	132	126	102	18.9	0.99
2% DBTDL	57	109	79	73	11.6	0.99
4% DBTDL	57	96	20	72	12.0	0.98

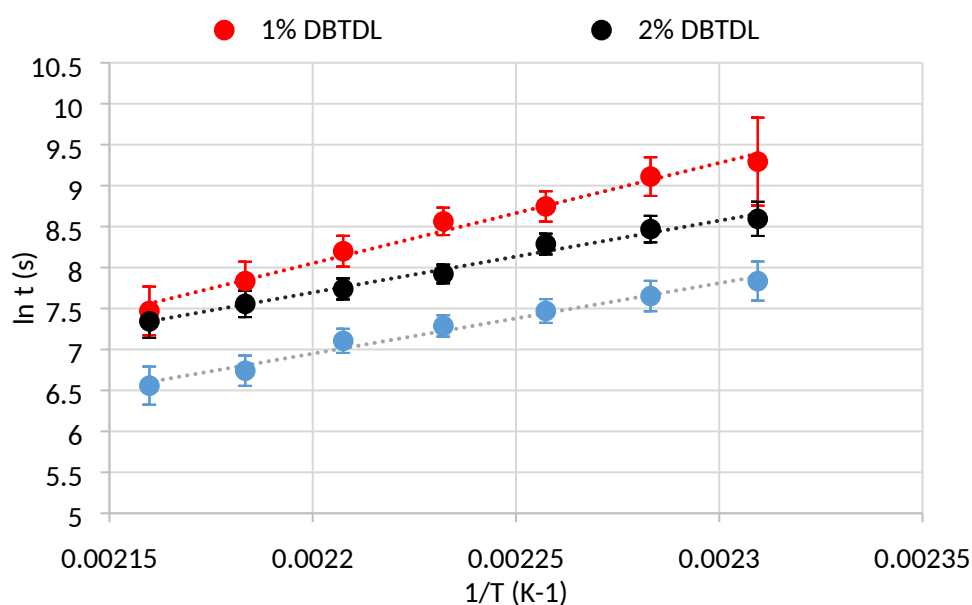
The time and temperature dependent relaxation modulus of the dynamic network was investigated in order to determine the vitrimeric nature of the materials. With this purpose, the stress relaxation behaviour of the samples prepared containing different proportions of DBTDL was studied by DMTA to evaluate the trans-thiocarbamoylation reaction rate and the results are shown in Figure 2.



**Figure 2.** Normalized stress relaxation plot as a function of time at various temperatures from (160 to 185 °C) during 90 min for the samples with 1 % (A), 2% (B) and 4 % of catalyst (C). Normalized stress relaxation behaviour at 180 °C, for the samples with different DBTDL amounts (D). The reference  $\sigma/\sigma_0=0.37$  is highlighted.

As observed in the figure, the amount of catalyst in the sample has a big influence in the stress-relaxation behavior. This fact agrees with the results obtained by Zheng et al. [18] in poly(urethane) vitrimers and confirms that DBTDL acts as catalyst in both the formation of poly(thiourethane)s and in the trans-thiocarbamoylation process. The greater the catalyst amount the faster is the relaxation process. The times needed to achieve the complete stress relaxation at 180 °C ( $\tau_{180^\circ\text{C}}$ ) are collected in Table 1. As we can see, the time needed to reach a complete relaxation state (zero stress) that enables the permanent reshaping of the material is drastically reduced by more than 80% (from 126 to 20 min) on increasing the amount of DBTDL from 1 to 4 phr.

A property that distinguishes vitrimers from dissociative CANs is that, at higher temperatures, the viscosity of the vitrimers is controlled by chemical exchange reactions leading to a temperature-viscosity relation that follows the Arrhenius' law like in inorganic silica materials. **In contrast, in dissociative covalent adaptable networks, the drop-in viscosity usually is more abrupt with temperature if compared to the associative CANs [2].** According to that, to further characterize the vitrimeric behaviour of poly(thiourethane)s, the stress relaxation time at different temperatures for a relaxation value of 63% ( $\sigma/\sigma_0=0.37$ ) was obtained from Figure 2. Using an Arrhenius-type equation the activation energy ( $E_a$ ) of the rearrangement process can be determined (see Figure 3 and Table 1).



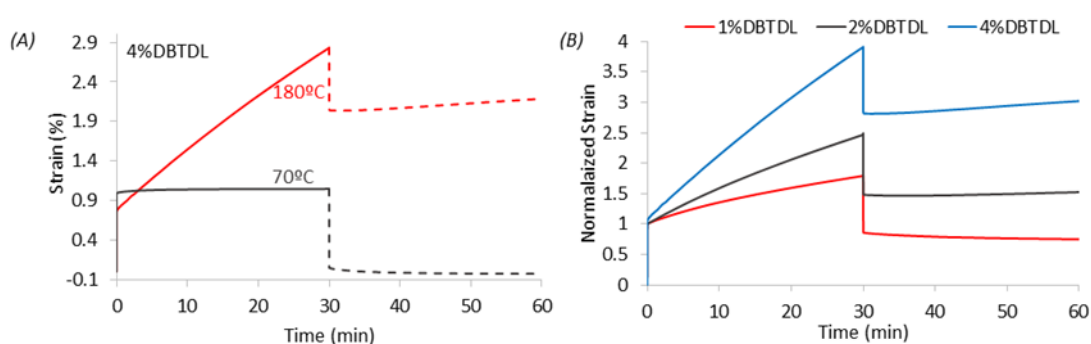
**Figure 3.** Arrhenius plot of relaxation times against temperature for the materials with different proportions of catalyst, measured from stress relaxation experiments.

As we can see in Figure 3, because of the associative character of the bond exchange, the rate of the relaxation process increases with the temperature and fits perfectly with an Arrhenius-like relaxation time dependence.

From the Arrhenius plot, we can also determine the topology freezing transition temperature,  $T_v$ , that is defined, as explained before, as the temperature at which the material reaches a viscosity of  $10^{12}$  Pa·s [1]. Table 1 collects the values calculated that are reduced from 132 to 96 °C on increasing the catalyst content. It is noteworthy that, although the correlations are very strong and the models are significant in all cases for a 95% confident level, limited errors in activation energy give great errors in the relaxation time and, consequently, in the  $T_v$ .

It is important to highlight that the values reported in Table 1 for  $E_a$  are significantly lower than those reported for poly(urethane) transcarbamoylation processes, which are 130.5 and 183.7 kJ/mol [21]. Besides, whereas Leibler et al. [5] described that the  $E_a$  in polyester vitrimers was about 90 kJ/mol and did not vary with the amount of catalyst, in our case  $E_a$  is higher with 1 phr of DBTDL but similar when the amount of catalyst was 2 or 4 phr (72-73 kJ/mol). As the activation energy allows us to predict the relaxation stress rate within a temperature range [26,27], these values indicate that the sensitivity of the trans-thiocarbamoylation reaction rate to a change in the temperature would be similar with proportions of catalyst of 4 and 2 phr (similar  $E_a$ ) but the relaxation time would be lower for a given temperature with 4 phr for values predicted inside the limits of the experimental data (higher pre-exponential factor).

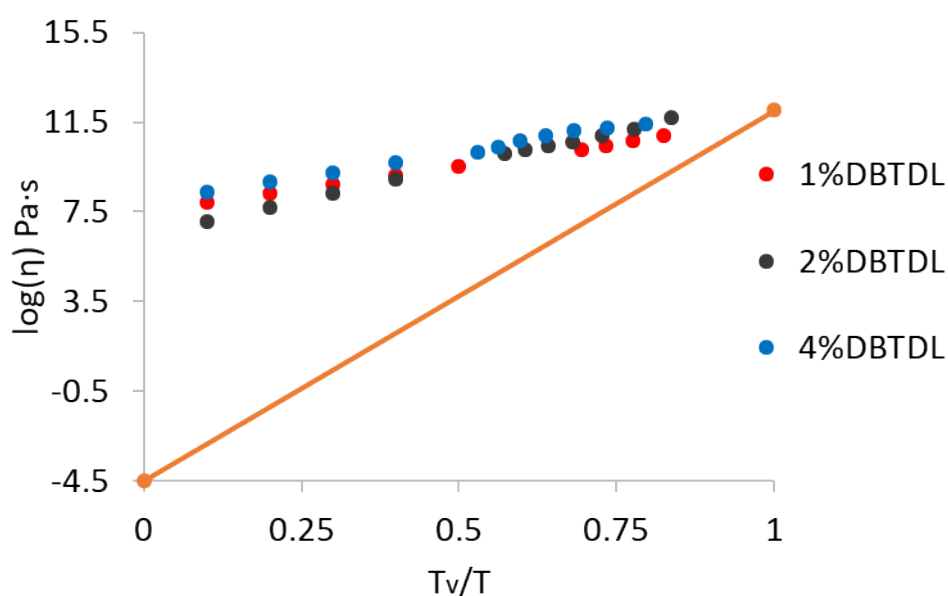
The effect of the temperature on the creep behavior was studied in order to confirm that the materials flow at temperatures higher than  $T_v$ . Figure 4A shows the creep plot at 70 and 180 °C for the material containing 4 phr of DBTDL.



**Figure 4.** Creep and recovery curves at 70 and 180 °C for the sample with 4 % of DBTDL (A) and with different proportions of DBTDL at 180 °C (B).

As we can see, at the lowest temperature (70°C) the material does not present plastic deformation when the stress is released, behaving like a thermoset above its  $T_g$  (rubber-like behavior) whereas at a temperature higher than  $T_v$  the material elongates as a viscoelastic liquid and in the recovery process a permanent deformation remains, due to the topology rearrangement produced by the trans-thiocarbamoylation process. In Figure 4B the effect of the amount of catalyst in the creep behavior is shown up. On increasing the DBTDL proportion both the elongation and the plastic deformation increase, but in all materials, after the instantaneous stress release, the strain cannot be recovered which confirms the vitrimeric characteristics of these materials. From these tests we can state that poly(thiourethane) networks can be deformed, reshaped and reprocessed at temperatures higher than their  $T_v$ .

The Angell fragility plot is represented in Figure 5, where it is shown how the materials prepared behave like thermosetting vitrimers.

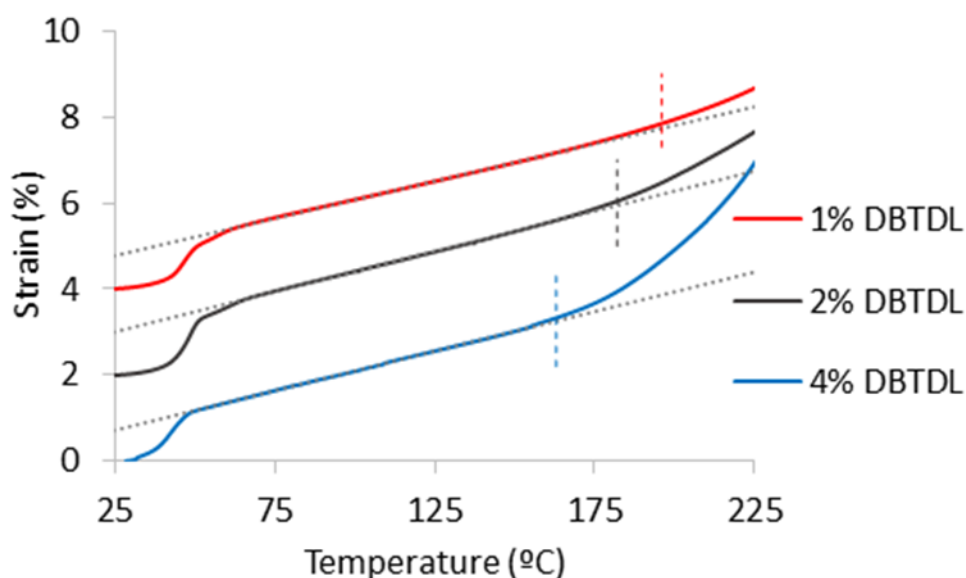


**Figure 5.** Angell fragility plot of the logarithm of the viscosity as a function of the inverse temperature, scaled to  $T_v$ , for the different materials. For comparative purposes, the relation for silica is included as a reference of an ideal strong liquid [28, 29].



At temperature above  $T_v$ , the exchange reactions are active, and the relaxation time and the viscosity follow the Arrhenius law, as occurs in “strong glass formers” like inorganic silica materials (taken as ideal strong liquids) [28, 29]. This is in contrast with the behaviour of thermoplastic materials and dissociative covalent adaptable networks, which are “fragile liquids”. At higher temperature, as stated before, the viscosity of such materials suffer a very sharp decrease [2].

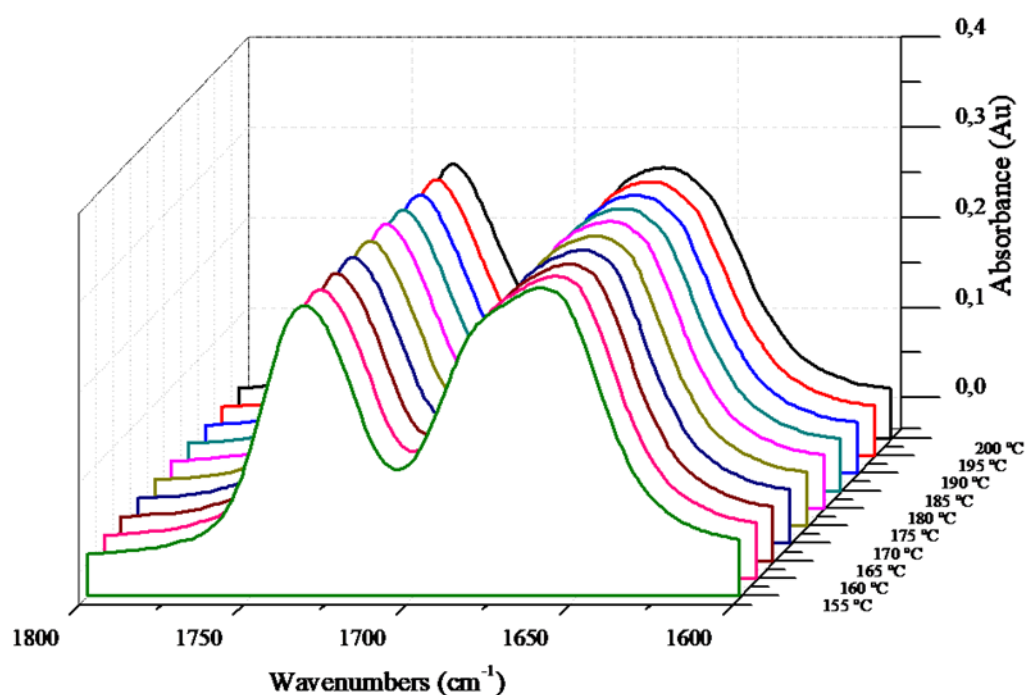
The vitrimeric behaviour of these materials was studied by tensile dilatometry experiments (Figure 6) where a slight stress of 0.01MPa was applied to prevent buckling. At low temperatures, the glass transition,  $T_g$ , is evidenced by a first change in the slope of the strain, produced by the change of thermal expansion coefficient, CTE. After that, CTE remains constant, such as in a typical thermosetting polymer, until at a certain point where the exchange reactions are so evident that they lead to a significant increase in CTE, more evident with a higher proportion of catalyst.



**Figure 6.** Dilatometry experiments with heating rate of 1 °C/min for the materials with 1, 2 and 4% of DBTDL (the curves are shifted only for a better understanding).

The non-dissociative character of the trans-thiocarbamoylation interchange in poly(thiourethane) vitrimers, was structurally studied by FTIR spectroscopy in an ATR at different temperatures to see if there was any change in the carbonyl region, in which the absorptions of the ester group in the thiol structure at  $1730\text{ cm}^{-1}$  and thiourethane group at  $1670\text{ cm}^{-1}$  appear. In Figure 7, we can see how these bands remain practically unaltered

during the heating process, considering the thermosensitivity of the bands. Moreover, any typical absorption of isocyanate groups at  $2270\text{ cm}^{-1}$  appeared during the heating process. It should be noted that in case of thiourethane dissociation, isocyanate band would appear and thiourethane band would be decreased. In this way, FTIR-ATR studies structurally confirm that thiourethane groups are not broken in the  $155\text{--}200^\circ\text{C}$  temperature range and that the rearrangement of this group is purely associative with a concerted mechanism.

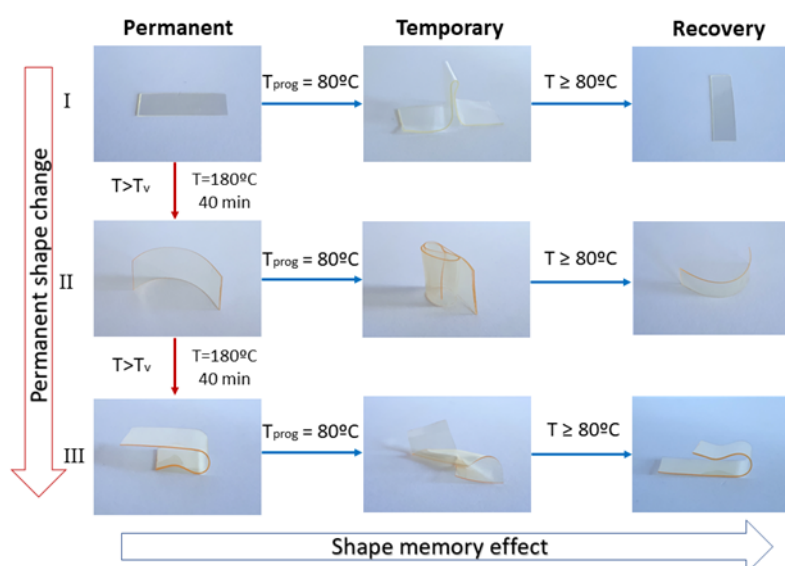


**Figure 7.** FTIR carbonylic absorptions of the ester ( $1730\text{ cm}^{-1}$ ) and thiourethane groups ( $1670\text{ cm}^{-1}$ ) of a cured sample with 4% of DBTDL registered after heating for 10 min at each temperature from 155 to  $200^\circ\text{C}$ .

The thermal stability of these materials in the reprocessing range was studied by thermogravimetry. The TGA curves are shown in SI Figure S9. By this study we could see that **the materials with different proportions of DBTDL** began to lose weight (1% and 2%) at temperatures **around 260** and  $270^\circ\text{C}$ , respectively, much higher than the interchange temperature.

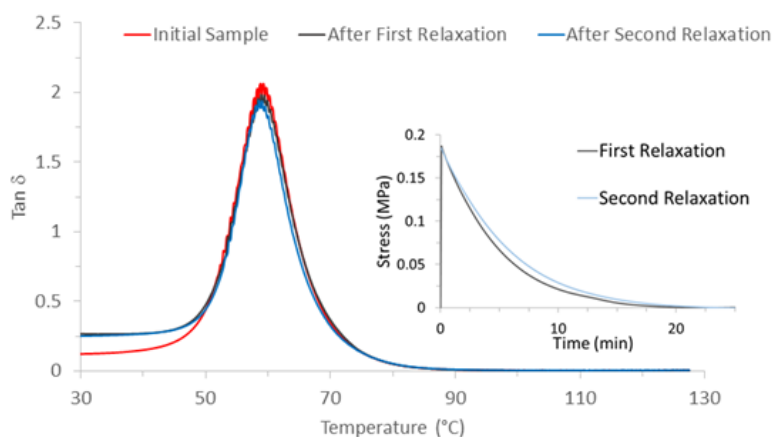
Besides the vitrimeric behaviour, the materials prepared also possess shape memory effect (SME). Figure 8 shows a visual qualitative assessment of the shape memory and vitrimeric behaviour. The rectangular initial sample (I) was programmed at  $80^\circ\text{C}$  to a

folded temporary shape, followed by a rapid cooling to room temperature. When heating at  $T > 80^{\circ}\text{C}$ , the initial shape was recovered as a consequence of its elasticity-based shape memory effect. By annealing for 40 min at  $180^{\circ}\text{C}$  ( $T > T_v$ ), the initial sample can be permanently bended to a new shape (II) as a result of the plasticity of the vitrimer. This new permanent shape can be programmed into another temporary shape that can be recovered on heating at  $T > 80^{\circ}\text{C}$ . The figure shows a third plastic reshape (III) with the same annealing treatment, which further shows a third temporary shape after the corresponding programming cycle. These cycles can be repeated many times, according to the good thermal stability of these materials at this range of temperature and their elastic/plastic characteristics. It should be noted the high transparency of the samples prepared that is not lost after reshaping.



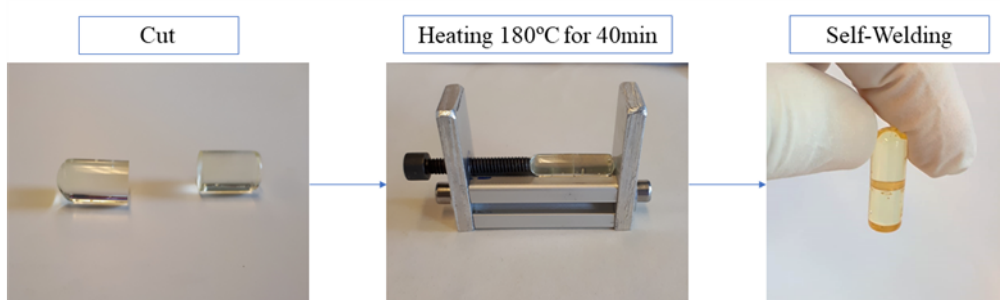
**Figure 8.** Qualitative demonstration of shape memory behaviour and permanent/plastic shape change for the poly(thiourethane) vitrimer with a 4% of DBTDL.

Once reprocessed, the sample was investigated by FTIR (Figure S10), confirming that no variation in the structure of the network had occurred. The material was also subjected to two thermal reprocessing cycles (relaxation process at  $180^{\circ}\text{C}$ , 25 min), verifying that the **peak of  $\tan \delta$**  remained stable without any variation, as can be seen in Figure 9.



**Figure 9.** Tan  $\delta$  against temperature of the poly(thiourethane) with a 4% of DBTDL sample before and after two relaxation processes. Inset: stress relaxation process in front of time.

From these experiments we can state that the materials can be reprocessed at high temperatures under a mechanical action. In addition to their vitrimeric characteristics and the shape memory capabilities, they also possess a high welding ability, as it is visually shown in Figure 10.



**Figure 10.** Visual demonstration of the self-welding ability of the poly(thiourethane) vitrimer heating under pressure for 40 min.

Quantitative studies on shape memory behaviour and welding will be reported in a further paper with different poly(thiourethane) structures.

#### 4. Conclusions

In the present study, we have demonstrated that aliphatic poly(thiourethane)s networks are a new class of vitrimers with shape memory and self-welding characteristics. These materials can be prepared from commercially available monomers, by an easy procedure, using DBTDL as the catalyst. The synthetic reaction has *click* characteristics, which assures a great homogeneity of the network structure.

The trans-thiocarbamylation reaction, which has a non-dissociative mechanism, responsible of the reshaping ability of these vitrimers has been chemically assessed by the use of model compounds and gas chromatography coupled to mass spectrometry. The non-dissociative character of the trans-thiocarbamylation process has been confirmed in the materials by FTIR spectroscopy.

The materials prepared with different amounts of DBTDL present lower freezing topological temperature on increasing the amount of catalyst. The activation energy is different for 1 phr of DBTDL but similar with 2 or 4 phr indicating that the dependence of the trans-thiocarbamylation reaction rate on the temperature change is similar with these proportions of catalyst but with different relaxation times for a given temperature. As emphasized by the Angell fragility plot the materials prepared resulted strong glass formers.

By performing thermomechanical analyses before and after several reprocessing test, it has been proved that the materials kept their thermomechanical characteristics. Also the FTIR spectra remained unaltered after heating and reprocessing.

Finally, it has been qualitatively demonstrated that the vitrimers developed show good shape memory characteristics, self-welding ability and high transparency, which

combined with the possibility of topological rearrangements, confer these materials promising possibilities for smart technological applications.

### Acknowledgements

The authors would like to thank MCIU (Ministerio de Ciencia, Innovación y Universidades) and FEDER (Fondo Europeo de Desarrollo Regional) (MAT2017-82849-C2-1-R and MAT2017-82849-C2-2-R) and Generalitat de Catalunya (2017-SGR-77) for the financial support.

### References

1. Montarnal, D.; Capelot, M.; Tournilhac, F.; Leibler, L. Silica-Like Malleable Materials from Permanent Organic Networks. *Science* **2011**, 334, 965-968.
2. Denissen, W.; Winne, J.M.; Du Prez, F.E. Vitrimers: permanent organic networks with glass-like fluidity. *Chem. Sci.* **2016**, 7, 30-38.
3. Kloxin, J.C.; Bowman, C.N. Covalent adaptable networks: smart, reconfigurable and responsive network systems. *Chem. Soc. Rev.* **2013**, 42, 7161-7173.
4. Zhang, Z.P.; Rong, M.Z.; Zhang, M.Q. Polymer Engineering based on reversible covalent chemistry: A promising innovative pathway towards new materials and new functionalities. *Prog. Polym. Sci.* **2018**, 80, 39-93.
5. Capelot, M.; Unterlass, M.M.; Tournilhac, F.; Leibler, L. Catalytic control of the vitrimer glass transition. *ACS Macro Lett.* **2012**, 1, 789-792.
6. Zhao, Q.; Qi, J.; Xie, T. Recent progress in shape memory polymer: New behavior, enabling materials, and mechanistic understanding. *Prog. Polym. Sci.* **2015**, 79, 49-50.
7. Santiago, D.; Fabregat-Sanjuan, A.; Ferrando, F.; De la Flor, S. Recovery stress and work output in hyperbranched poly(ethyleneimine)-modified shape-memory epoxy polymers. *J. Polym. Sci. B.* **2016**, 54, 1002.
8. Zhao, Q.; Zou, W.; Luo, Y.; Xie, T. Shape memory polymer network with thermally distinct elasticity and plasticity. *Sci Adv.* **2016**, 2, e1501297.
9. Zou, W.; Dong, J.; Luo, Y.; Zhao, Q.; Xie, T. Dynamic Covalent Polymer Networks: from Old Chemistry to Modern Day Innovations. *Adv. Mater.* **2017**, 29, 160610.
10. Wang, Y.; Pan, Y.; Zheng, Z.; Ding, X. Reprocessable and Multiple Shape Memory Thermosets with Reconfigurability. *Macromol. Rapid Commun.* **2019**, 1900001 DOI: 10.1002/marc.201900001

11. Denissen, W.; Rivero, G.; Nicolaÿ, R.; Leibler, L.; Winne, J.M.; Du Prez, F.E. Vinylogous Urethane Vitrimers. *Adv. Funct. Mater.* **2015**, *25*, 2451-2457.
12. Canadell, J.; Goosens, H.; Klumperman, B. Self-Healing Materials Based on Disulfide Links. *Macromolecules* **2011**, *44*, 2536-2541.
13. Azcune, I.; Odriozola, I. Aromatic disulfide crosslinks in polymer systems: Self-healing, reprocessability, recyclability and more. *Eur. Polym. J.* **2016**, *84*, 147-160.
14. Hendriks, B.; Waelkens, J.; Winne, J.M.; Du Prez, F.E. Poly(thioether) Vitrimers via Transalkylation of Trialkylsulfonium Salts. *ACS Macro Lett.* **2017**, *6*, 930-934.
15. Wu, X.; Yang, X.; Yu, R.; Zhao X-J.; Zhang, Y.; Huang, W. A facile access to stiff epoxy vitrimers with excellent mechanical properties via siloxane equilibration. *J. Mater. Chem. A*, **2018**, *6*, 10184-10188.
16. Röttger, M.; Domenech, T.; van der Weegen, R.; Breuillac, A.; Nicolaÿ, R.; Leibler, L. High-performance vitrimers from commodity thermoplastics through dioxaborolane metathesis. *Science* **2017**, *356*, 62-65.
17. Erice, A.; Ruiz de Luzuiraga, A.; Matxain, J.M.; Ruipérez, F.; Asua, J.M.; Grande, H.J.; Rekondo, A. Reprocessable and recyclable crosslinked poly(urea-urethane)s based on dynamic amine/urea exchange. *Polymer* **2018**, *145*, 127-136.
18. Zheng, N.; Fang, Z.; Zou, W.; Zhao, Q.; Xie, T. Thermoset Shape-Memory Polyurethane with Intrinsic Plasticity Enabled by Transcarbamoylation. *Angew. Chem. Int. Ed.* **2016**, *55*, 11421-11425.
19. Fortman, D. J.; Brutman, J. P.; Cramer, C. J.; Hillmyer, M. A.; Dichtel, W. R. Mechanically Activated, Catalyst-Free Polyhydroxyurethane Vitrimers. *J. Am. Chem. Soc.* **2015**, *137*, 14019-14022.
20. Akindoyo, J. O.; Beg, M. D. H.; Ghazali, S.; Islam, M. R.; Jeyaratnama, N.; Yuvaraj, A. R. Polyurethane types, synthesis and applications—a review. *RSC Adv.* **2016**, *6*, 114453-114482.
21. Yan, P.; Zhao, W.; Fu, X.; Kong, W.; Zhou, C.; Lei, J. Multifunctional polyurethane-vitrimers completely based on transcarbamoylation of carbamates: thermally-induced dual-shape memory effect and self-welding. *RSC Adv.* **2017**, *7*, 26858-26866.
22. Zheng, N.; Hou, J.; Xu, Y.; Fang, Z.; Zou, W.; Zhao, Q.; Xie, T. Catalyst-Free Thermoset Polyurethane with Permanent Shape Reconfigurability and Highly Tunable Triple-Shape Memory Performance. *ACS Macro Lett.* **2017**, *6*, 326-330.

23. Delebecq, E.; Pascault, J.P.; Boutevin, B.; Ganachaud F. On the Versatility of Urethane/Urea Bonds: Reversibility, Blocked Isocyanate, and Non-isocyanate Polyurethane. *Chem. Rev.* **2012**, *113*, 80-118.
24. Gamardella, F.; Ramis, X.; De la Flor, S.; Serra, A. Preparation of poly(thiourethane) thermosets by controlled thiol-isocyanate click reaction using a latent organocatalyst. *React. Funct. Polym.* **2019**, *134*, 174-182.
25. Jaffrennou, B.; Droger, N.; Mechin, F.; Halary, J. L.; Pascault, J.P. Characterization, structural transitions and properties of a tightly crosslinked polythiourethane network for optical applications. *e-Polym.* **2005**, *82*, 1618-7229.
26. Altuna, F.I.; Hoppe, C.E.; Williams, R.J.J. Shape memory epoxy vitrimers based on DGEBA crosslinked with dicarboxylic acids and their blends with citric acid. *RSC Adv.* **2016**, *6*, 88647-88655.
27. Altuna, F.I.; Hoppe, C.E.; Williams, R.J.J. Epoxy vitrimers with a covalently bonded tertiary amine as catalyst of the transesterification reactions. *Eur. Polym. J.* **2019**, *113*, 297-304.
28. Kelton; K.F. Kinetic and structural fragility-a correlation between structures and dynamics in metallic liquids and glasses. *J. Phys.: Condens. Matter* **2017**, *29*, 023002.
29. Angell, C.A. Formation of Glasses from Liquids and Biopolymers. *Science* **1995**, *267*, 1924-1935.



## SUPPORTING INFORMATION

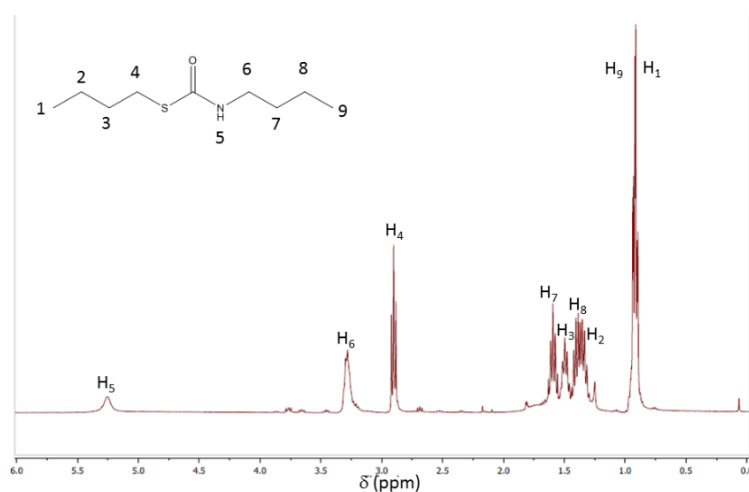
### A new class of vitrimers based on aliphatic poly(thiourethane) networks with shape memory and permanent shape reconfiguration

Francesco Gamardella,<sup>1</sup> Federico Guerrero,<sup>1</sup> Silvia De la Flor,<sup>2</sup> Xavier Ramis<sup>3</sup> and Angels Serra<sup>1\*</sup>

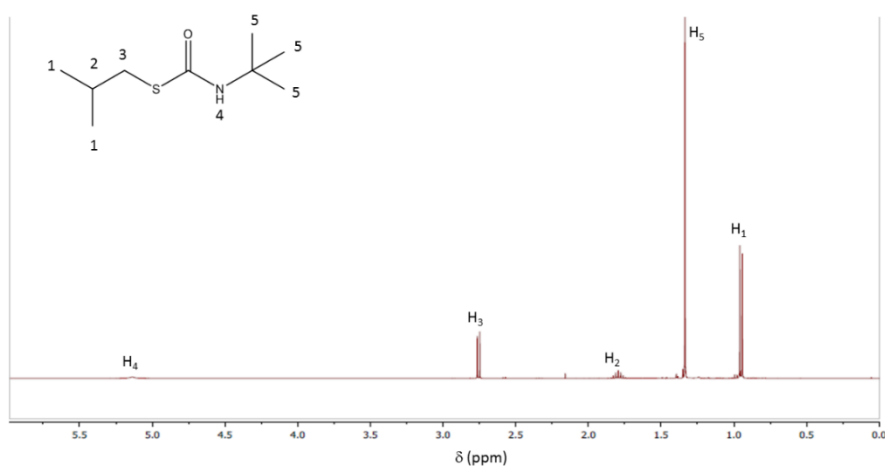
<sup>1</sup> Dept. of Analytical and Organic Chemistry, Universitat Rovira i Virgili, C/ Marcel·lí Domingo, Edif. N4. 43007, Tarragona, Spain

<sup>2</sup> Dept. of Mechanical Engineering, Universitat Rovira i Virgili, Av. Països Catalans, 26, 43007 Tarragona, Spain

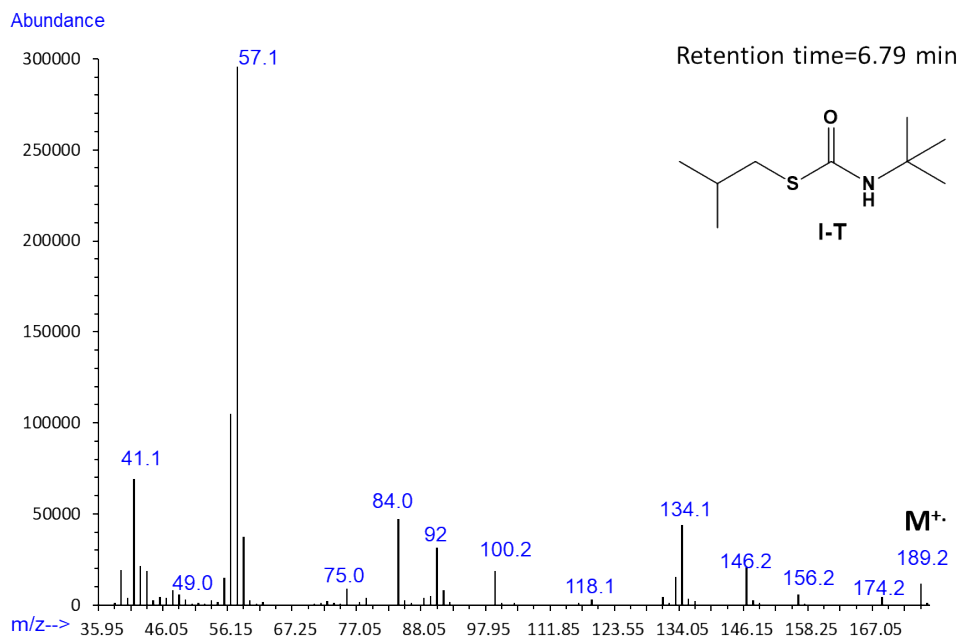
<sup>3</sup> Thermodynamics Laboratory, ETSEIB Universitat Politècnica de Catalunya, Av. Diagonal, 08028, Barcelona, Spain



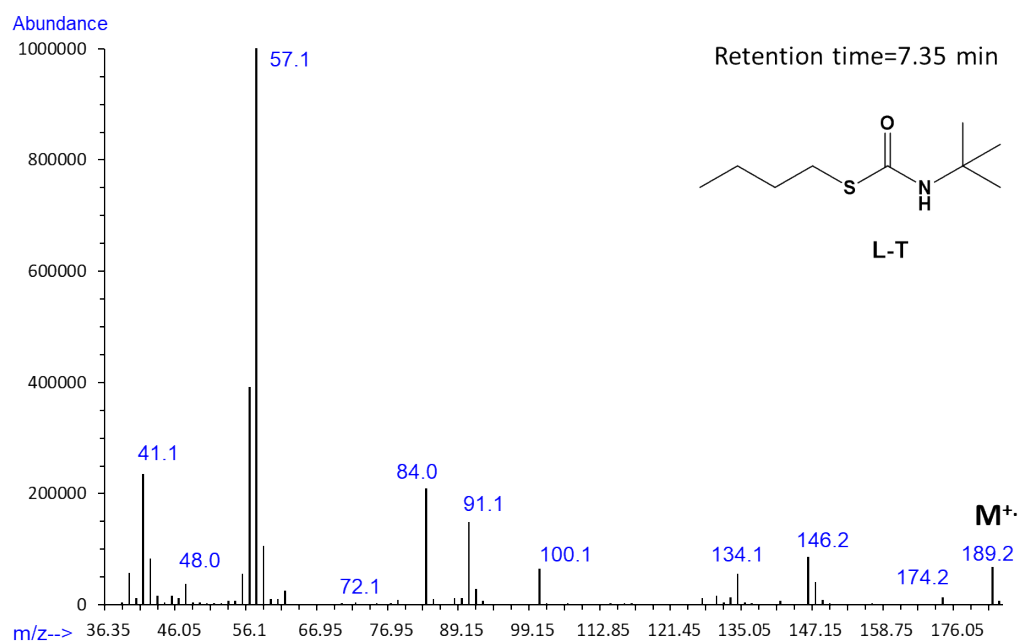
**Figure S1.** <sup>1</sup>H NMR spectra of S-butyl butylcarbamothioate (L-L) in CDCl<sub>3</sub>.



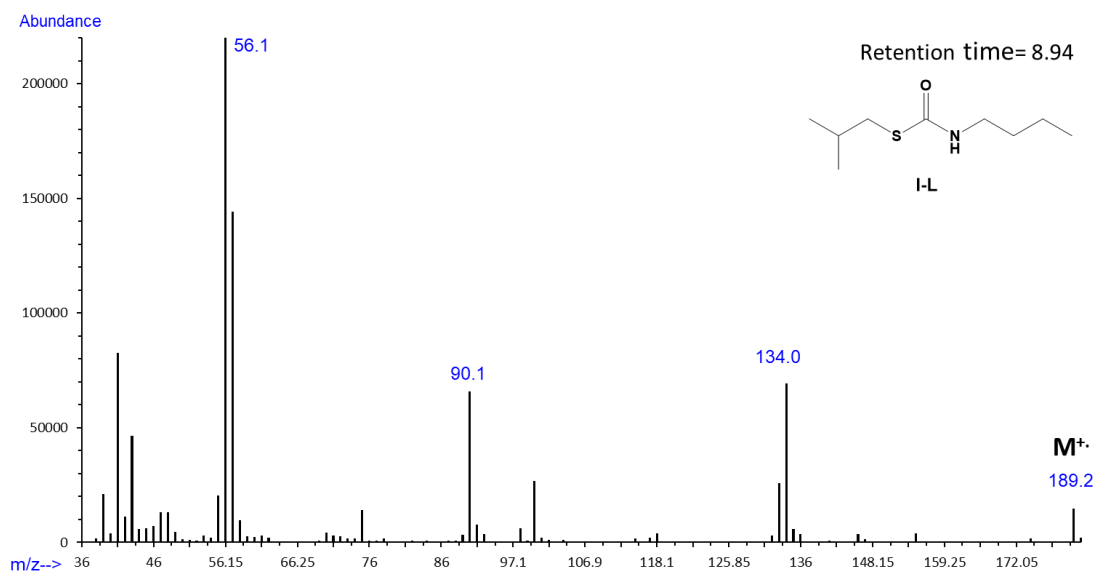
**Figure S2.** <sup>1</sup>H NMR spectra of S-isobutyl tert-butylcarbamothioate (I-T) in CDCl<sub>3</sub>.



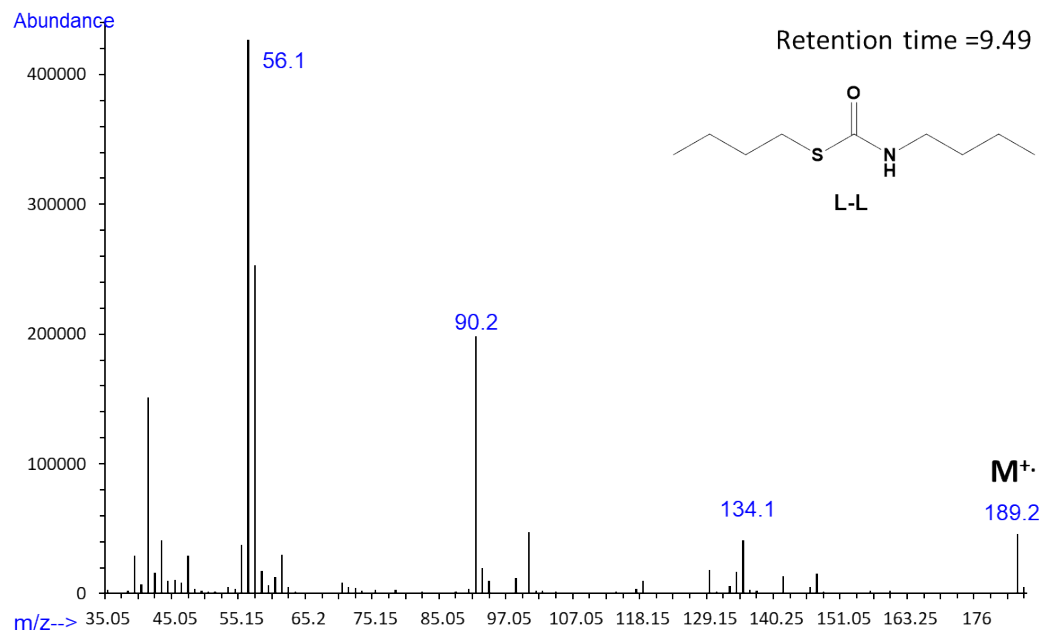
**Figure S3.** Mass spectra of the eluted product that corresponds to the S-isobutyl tert-butylcarbamothioate.



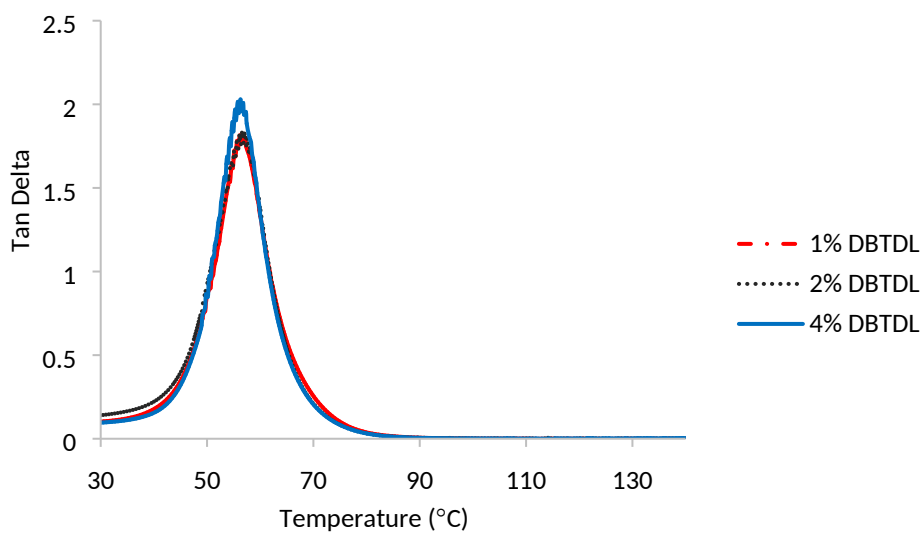
**Figure S4.** Mass spectra of the eluted product that corresponds to the S-butyl tert-butylcarbamothioate.



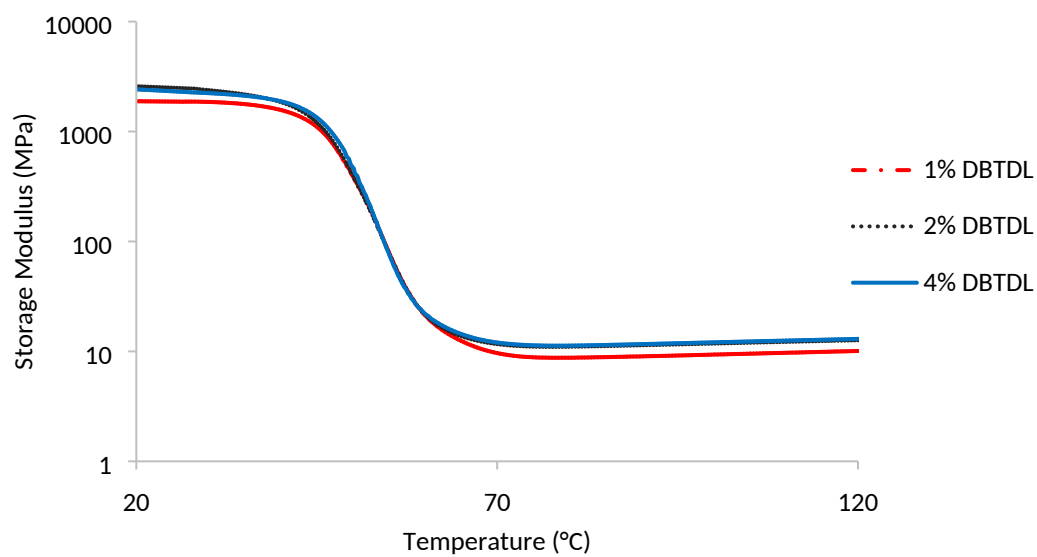
**Figure S5.** Mass spectra of the eluted product that corresponds to the S-isobutyl butylcarbamothioate.



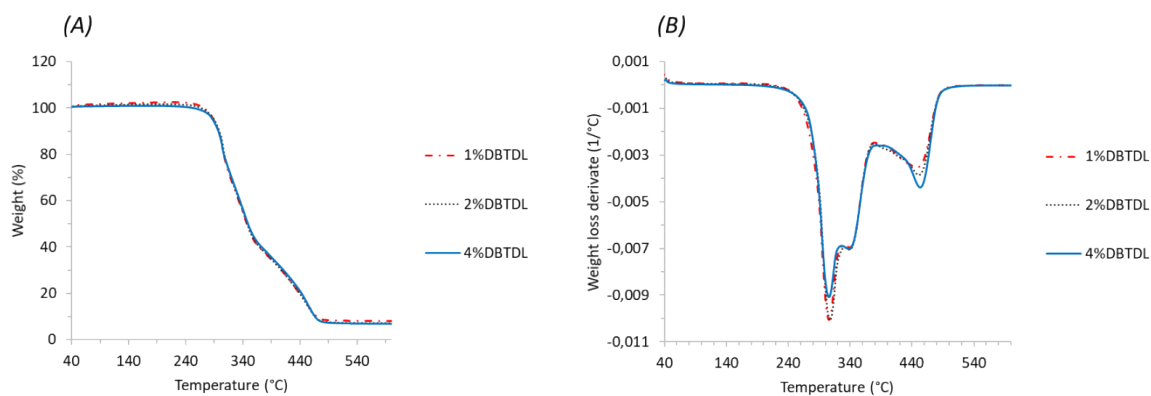
**Figure S6.** Mass spectra of the eluted product that corresponds to the S-butyl butylcarbamothioate.



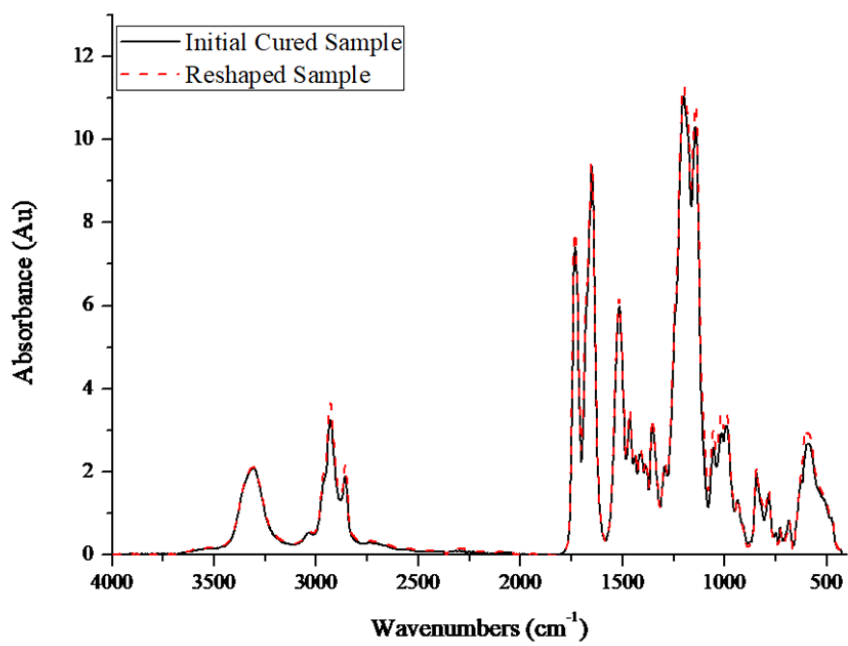
**Figure S7.** Tan  $\delta$  against temperature of the materials prepared with different proportions of DBTDL.



**Figure S8.** Storage Modulus against temperature of the materials prepared with different proportions of DBTDL.



**Figure S9.** TGA curves of the samples prepared with different proportions of DBTDL (A). The rate of weight loss against temperature, DTGA (B).



**Figure S10.** FTIR of poly(thiourethane) with a 4% of DBTDL before and after reshaping at 180 °C for 40 min registered at room temperature.