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Tarragona, October 23th 2015

Dear Prof. Advincula:

We send our revised manuscript entitled: *Multifunctional allyl-terminated hyperbranched poly(ethylenimine) as component of new thiol-ene/thiol-epoxy materials*, to be accepted for publication in *Reactive and Functional Polymers*.

We have included practically all the suggestions and corrections made by the reviewers and some answers to their questions have been included in the answer to the reviewer comments file.

Looking forward to hearing from you, I remain.

Yours sincerely,

Prof. Angels Serra

Answers to the reviewer comments

Reviewer #1: This manuscript is polymer preparation of branched structure by changing the monomer proportion and sequence of modifications. The obtained polymer characterization and the predicted polymerization scheme is much understandable. However, some points as follow should be revised,

We thank the reviewer for the favorable comments

- 1) I am not sure in 'big' sample in Abstract. What is the meaning of big? Size, pore, molecular weight, functionalization?

The term big is in our case samples means: rectangular samples (40 mm x 10 mm x 1.5 mm) of size, prepared for thermomechanical tests, we have substituted "big samples" by "samples for thermomechanical tests".

- 2) In introduction, last paragraph is better to move to Para of 'First---' and 'The polymer synthesized---'.

We agree and we have performed changes in the paragraph orders.

- 3) Can you know the reaction rate of each scheme in scheme 3?

It is not possible to measure both reaction rates, but the first is predominant over the second. We have decided to remove the second mechanism of thiol-epoxy condensation in Scheme 3, since the first equation is much more favorable than the second one. This is because the ammonium salt is much more acidic than the thiol, and then the formation of the thioether alcohol should take place only by the first equation.

- 4) Please discuss the basicity of imidazole and so on. This information of base is important in this study.

If we look to the pKa of the ammonium and imidazolium cations we realize that amines are more basic than imidazole (pKa of alkyl ammonium is ~ 10 , whereas pKa of imidazolium is ~ 7). However, the problem arises from the amount of PEIene in the formulation. When the proportion of PEIene is high it catalyzes the second step in which a base is needed and thiol-epoxy reaction takes place overlapped. On the contrary, when the proportion of PEIene is low, then the basicity of the reaction medium is not enough to reach a complete thiol-epoxy conversion and 1-methylimidazole should be added.

- 5) Can you get mobility of electron in photo induced polymerization?

No, there is no electron mobility. As the radical is formed it reacts instantaneously accordingly to a "click" reaction.

- 6) Can you get turn over number in Scheme 2.

The number of cycles is the same than the number of reacting molecules. It is a polycondensation mechanism and not a polyaddition reaction. Thiol-ene is a "click" reaction that occurs in a quantitative way.

- 7) In scheme 3, left side is same. combine it and only right side should be different scheme.

We have suppressed the second mechanism as commented above.

Reviewer #2: Authors synthesized an allyl terminated hyperbranched poly(ethyleneimine). The multifunctional macromonomer has been used as -ene component in thiol-ene/thiol-epoxy curing formulations.

Authors need to address the followings to meet publication requirements:

1. Please add captions for schemes and figures, respectively.

We apologize, but we forgot to add the file with the figure and scheme captions to the manuscript

2. Formats of Table 1, Table 2 and Table 3 are not consistent with each other. Please correct them.

It is true. They have been corrected.

3. There is a lack of discussion on how authors' work in comparison to others. It is important for authors to address this.

In our opinion there are enough references to the previous published work. Up to now, nobody reported a completely dual thiol-ene/thiol-epoxy curing process, but we have cited and explained in the introduction part the related work reported by Carioscia, Saharil and Sangermano groups. The most similar work has been performed by Carioscia et al. and in the results and discussion part (page 11) a comparison of their results with ours has been discussed.

Multifunctional allyl-terminated hyperbranched poly(ethyleneimine) as component of new thiol-ene/thiol-epoxy materials

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ABSTRACT

A new allyl terminated hyperbranched poly(ethyleneimine) was synthesized and characterized and then used in different proportions as multifunctional macromonomer in tetrathiol-diglycidyl ether of bisphenol A formulations. The curing process had a two-stage character and was composed by two click reactions: a first photoinduced thiol-ene addition followed by a thermal thiol-epoxy reaction. The thiol-ene reaction was catalyzed by a radical initiator and the thiol-epoxy curing by tertiary amines. The evolution of the first part of the curing was studied by photo-DSC and FTIR and the results compared with those obtained in a photoirradiation chamber, which was used to prepare samples for thermomechanical tests. These studies showed that the thermal thiol-epoxy process prematurely began during the photoirradiation because the presence of amines in the PEI structure accelerated this process. The thiol-epoxy reaction was more extensively produced when the proportion of the poly(ethyleneimine) increased in the formulation. The overlapping between both processes was greater in the photoirradiation chamber than in the photo-DSC. The intermediate material was completely cured by thermal treatment in an oven. The need of adding 1-methylimidazole as catalyst to complete the thiol-epoxy reaction was derived from the calorimetric studies. The materials

prepared were characterized by thermogravimetry and thermomechanical analysis.

Keywords

Photopolymerization; thiol-epoxy; thiol-ene; dual curing; hyperbranched poly(ethyleneimine).

1. Introduction

In the last years, thiol chemistry has attracted a great deal of attention due to its efficiency and versatility in numerous thiol reactions commonly regarded as *click* reactions [1, 2]. Thiol click chemistry can be divided in two categories which are the base catalyzed nucleophilic reactions: thiol-epoxy [3, 4], thiol-isocyanate [5, 6] and thiol-Michael [7, 8] and radical-mediated reactions: thiol-ene [9, 10] and thiol-yne [11, 12].

Recently, thiol-ene photoinitiated polymerization has attracted a significant interest due to their features. Firstly, a wide range of -ene compounds, including activated and non-activated double bonds as well as multiply-substituted olefins can serve as the substrates and any thiol can be employed, including highly functional compounds. Secondly, such reactions are generally extremely rapid and can be completed in a matter of seconds, are tolerant to the presence of air/oxygen and moisture and proceed with (near) quantitative formation of the corresponding thioether. Finally, the thiol-ene reaction can be employed in combination with living polymerization such as ring opening polymerization (ROP) [13], ring-opening metathesis polymerization (ROMP) [14], cationic polymerization [15] or controlled radical vinyl polymerization [16]. Besides, thiol-ene processes exhibit reduced polymerization shrinkage and stress and show high uniformity in crosslinking density [17].

It has been reported that polysulfides derived from thiol-ene polymerization present some limitations in their physical/mechanical properties, particularly those related to modulus and attainment of high glass transition temperature due to the flexible core of the commercially available thiol monomers [18, 19]. Many different strategies for achieving these improvements have been followed in the literature, as for example the incorporation of significant amounts of

inorganic fillers, particularly nano-sized inorganic structures [20] and the formation of inorganic domains using a sol–gel process [21, 22].

Another approach proposed to enhance these mechanical characteristics is the combination of the photo-curable thiol-ene formulation with an epoxy resin that can be polymerized. This approach was followed by several authors. Carioscia *et al.* [23] combine the properties of polyethers derived from epoxy resins with the polysulfides derived from the thiol-ene polymerization. They developed a thiol-ene/thiol-epoxy system by combining an epoxy resin with a multifunctional thiol and an unsaturated compound in the presence of a tertiary amine as a catalyst. It was found that in addition to thiol-ene photopolymerization, anionic polymerization of the epoxy resin proceeded as a side reaction of the thiol-epoxy process. Saharil *et al.* [24] proposed the use of off-stoichiometric thiol-ene-epoxy mixtures in which a rapid curing of thiol-ene occurs to a simultaneously initiated slow thiol-epoxy reaction. On adding epoxy resins to thiol-ene formulations, the ability to directly react with almost any dry surface is gained, and the two-stage curing facilitates bonding, by providing a compliant bond surface after the first stage of cure that is subsequently hardened fully upon the second cure. This curing system was well suited for self-gluing of micropatterned parts for microfluidics [24] and adhesive wafer bonding [25]. Sangermano *et al.* [26] proposed the use of a pentaallylic triamine curing agent which can react with multifunctional thiols to produce polysulfides *in situ*, and at the same time has the ability to initiate the anionic polymerization of an epoxy resin. Combining the network structure derived from the epoxy curing process with a thiol-ene system an important toughening effect was achieved due to the presence of the flexible polysulfide moieties. In that study, the exothermicity of the thiol-ene UV polymerization activates the amine-epoxy polymerization and during the irradiation time (300 s) the epoxy conversion reached 41%.

In the last years, mechanical and thermomechanical characteristics have also been improved by adding hyperbranched polymers to curing formulations because of their high number of end groups able to participate in the network formation. Moreover, such dendritic structures can be considered as toughness modifiers without drawbacks in the processability, because of the low entanglement that leads to the low viscosity of the reactive mixture [27, 28].

Taking all of this into account, the aim of the present work is the preparation of new materials by the combination of thiol-ene and thiol-epoxy reactions, using an allyl modified hyperbranched poly(ethyleneimine) (PEIene) as a multifunctional comonomer.

In previous studies, we applied the thiol-ene reactions to prepare a hyperbranched polymer with thioether and ester groups in its structure which was used in a photo/thermal epoxy cationic homopolymerization [29]. Moreover, a two-stage thiol-ene/epoxy homopolymerization was employed in another study taking advantage of the multifunctionality of allyl terminated hyperbranched polyesters [30]. In both cases, the high functionality of hyperbranched polymers allowed us to reach a glass transition temperature higher than expected due to the tighter network structure.

In the present paper, we describe the synthesis and characterization of the allyl-terminated hyperbranched poly(ethyleneimine) (PEIene) used as a multifunctional ene-macromonomer in the thiol-ene photoinitiated process. Hyperbranched poly(ethyleneimine) has been extensively used after modification, mainly in encapsulation and molecular transport [31, 32] but also in the improvement of thermosets [33, 34]. The amine groups in its structure allow attaching different moieties [35] or even grow different polymeric branches [34]. The polymer synthesized, PEIene, was mixed in different proportions with diglycidylether of bisphenol A (DGEBA) and the corresponding stoichiometric proportion of pentaerythritol tetrakis (3-mercaptopropionate) (PETMP) and then cured in a photo/thermal two stage consecutive process. On changing the PEIene/DGEBA proportion the contribution of each polymerization mechanism varies and subsequently the properties of the final materials. The presence of tertiary amine in the PEI-ene structure can catalyze the thiol-epoxy reaction which is the second step of the curing. Due to this fact the curing conditions have been deeply studied by FTIR/DSC-UV and in a photoirradiation chamber to know about the separation or overlapping of both processes. The materials obtained were characterized by TGA and DMTA.

2. Experimental Part

2.1 Materials

Poly(ethyleneimine) (PEI) Lupasol[®]FG (800 g/mol) was kindly donated by BASF and used without further purification. From the molecular weight of the polymer and of the repeating unit an average degree of polymerization of 18.6 was calculated. According to the data sheet, the relationship (NH₂/NH/N) was (1/0.82/0.53) and thus by calculations the equivalent number of primary, secondary and tertiary amines resulted to be 0.010, 0.00837, and 0.0053 eq/g. Allyl glycidyl ether, pentaerythritol tetrakis (3-mercaptopropionate) (PETMP), 1-methylimidazole (1-MI) and 2,2-dimethoxy-2-phenylacetophenone (DMPA) were all purchased from Sigma-Aldrich. Isopropanol was purchased from Scharlab. Diglycidylether of bisphenol A (DGEBA) Araldite GY 240 (EEW = 182 g/eq) was provided by Huntsman.

2.2 Synthesis of allyl-terminated hyperbranched poly(ethylenimine) (PElene) (Scheme 1)

In a 50 mL two neck round-bottomed flask provided with magnetic stirrer, addition funnel and Ar inlet, 2 g of PEI (2.5 mmol) were dissolved in 10 mL of i-PrOH. Then, the stoichiometric quantity of allyl glycidyl ether (6.63 g, 58.1 mmol) was added. The reaction mixture was kept at 50°C for a day. The crude product (yellowish oil) was dried at 50°C under vacuum during two days.

¹H-NMR (CDCl₃, δ in ppm) (see **Figure 1**): 5.87 ppm (-CH=CH₂, **5**), 5.2 (-CH=CH₂, **6**), 3.98 ppm (-O-CH₂-CH=, **4**), 3.82 (-CH-OH)-, **2**), 3.38 (-CH-OH-CH₂-O-, **3**) and 2.7-2.4 ppm ((-CH₂-N(CH₂)-, **1** and PEI).

¹³C-NMR (CDCl₃, δ in ppm): 134.7 ppm (-CH=CH₂), 117.9 ppm (-CH=CH₂), 77.5 ppm (-CH(OH)-CH₂-O-), -76.8 ppm (-O-CH₂-CH=), 72.5 ppm (-CH-OH-) and 70-50 ppm (-CH₂-N and PEI nucleus).

T_g, determined by DSC = - 55°C.

Thermal stability, determined by TGA in N₂, *T*_{5%}= 311°C, *T*_{max}= 345°C.

2.3. Preparation of formulations and samples

The formulations were prepared by beating at room temperature different amounts of PETMP-PElene and PETMP-DGEBA stoichiometric mixtures, taking into account that the functionalities of the different reactants are: 4 for PETMP, 2 for DGEBA and 22 for PElene. Compositions of 20, 40, 60 and 80% w/w of PETMP-PElene/PETMP-DGEBA, neat PETMP-PElene and neat

PETMP-DGEBA formulations were tested. The formulations were named as x thiol-ene, being x the proportion of the mixture PETMP-PElene in the formulation. The mixture PETMP-PElene contained 1 phr of DMPA (parts of initiator for 100 parts of mixture). The photoinitiator was dissolved into the formulation by heating at 70°C until the mixture became clear. PETMP-DGEBA formulation contained 2 phr of 1-MI (parts of amine by 100 parts of DGEBA). The composition of the mixtures is detailed in **Table 1**.

Rectangular samples (40 mm x 10 mm x 1.5 mm) were obtained in a Teflon mold covered with a poly(propylene) film by irradiation under light-curing equipment (Dymax ECE 2000 UV light-curing flood lamp system) during 2 min (in intervals of 30 s with 5 min among them, 1 min for each face of the sample) (UV-intensity of 105 mW/cm², 365 nm) and then thermally treated at 100°C for 1 h and 120 °C for 30 min in an oven.

2.4. Characterization techniques

¹H NMR and ¹³C NMR measurements were carried out in a Varian Gemini 400 spectrometer. CDCl₃ was used as the solvent. For internal calibration the solvent signal corresponding to CDCl₃ was used: δ (¹H) = 7.26 ppm, δ (¹³C) = 77.16 ppm.

Photocalorimetric experiments were performed in order to study the thiol-ene stage of the dual curing. The samples were photocured at 30°C using a Mettler DSC-821e calorimeter (Mettler-Toledo, Schwerzenbach, Switzerland) appropriately modified to permit irradiation with a Hamamatsu Lightningcure LC5 (HgeXe lamp) with two beams, one for the sample side and the other for the reference side. Samples weighing ca. 5 mg were cured in open aluminum pans in a nitrogen atmosphere. Two scans were performed on each sample in order to subtract the thermal effect of the UV irradiation from the photocuring experiment, each one consisting of 2 min of temperature conditioning, 6 min of irradiation and finally 2 more minutes without UV light. A light intensity of 30 mW/cm² (calculated by irradiating graphite-filled pans on only the sample side) was employed.

Dynamic postcuring experiments were carried out in a Mettler 822e calorimeter with a TSO801RO robotic arm (Mettler-Toledo, Schwerzenbach, Switzerland), from -100°C to 250°C, under a nitrogen atmosphere at 10°C/min.

The degree of conversion, X_{UV} , during the photocuring stage was calculated in the basis of the heat evolved during the postcuring as follows:

$$X_{UV} = 1 - \frac{\Delta H_{post}}{\Delta H_{tot}} \quad (1)$$

where ΔH_{post} is the heat released during the postcuring process and ΔH_{tot} corresponds to the heat evolved during complete cure of the formulation.

A Bruker Vertex FTIR spectrometer equipment (resolution of 4 cm^{-1}) with an attenuated-total-reflectance accessory with a diamond crystal (Golden Gate heated single-reflection diamond ATR, Specac-Teknokroma) was used to monitor the UV curing. All the measurements were performed at room temperature. An irradiation lamp (Hamamatsu Lightningcure LC5 (HgeXe lamp)) was used to induce the photopolymerization (light intensity of 30 mW/cm^2). The samples were irradiated for 2 min and IR spectra were collected before and after irradiation. The UV process was followed by the thiol band at 2570 cm^{-1} and allyl band at 1643 cm^{-1} .

Thermogravimetric analyses were carried out in a nitrogen atmosphere with a Mettler TGA/SDTA 851e thermobalance. Samples with an approximate mass of 8 mg were degraded between 30 and $800 \text{ }^\circ\text{C}$ at a heating rate of $10 \text{ }^\circ\text{C/min}$ in N_2 ($100 \text{ cm}^3/\text{min}$ measured in normal conditions).

Dynamic mechanical thermal analyses were carried out with a TA Instruments DMA Q800 device. The samples were prepared as described before. Single cantilever bending at 1 Hz and amplitude $10 \text{ }\mu\text{m}$ was performed at $3 \text{ }^\circ\text{C/min}$ from $50 \text{ }^\circ\text{C}$ below T_g to 50°C after T_g for each sample.

3. Results and Discussion

3.1. Synthesis and characterization of the allyl-terminated hyperbranched poly(ethylenimine) (PEIene)

In this work we synthesized an allyl-terminated hyperbranched poly(ethylenimine) (PEIene) by reacting PEI with a molecular weight of 800 g/mol with allyl glycidyl ether at 50°C in isopropanol, taking advantage of the

nucleophilicity of amines of PEI which react with the oxirane ring. The synthetic pathway is depicted in **Scheme 1**.

From the degree of polymerization of PEI and the relationship (NH₂/NH/N) (1/0.82/0.53) published in the data sheet, we calculated the average number of active groups per molecule, NH and NH₂, which resulted to be 6.4 secondary amines and 7.9 primary amines in average per molecule [34]. From this number and taking into account that the secondary amines can react twice in front of the epoxide group the quantity of allyl glycidyl ether was calculated. By ¹H-NMR (**Figure 1**) we confirmed that the practical complete reaction was achieved because of the disappearance of epoxy group signals and the appearance of signal 2, corresponding to the methine group formed by the attack of the amine to the epoxide. Following the procedure previously reported [36] we calculated the degree of modification from the integration of the signals coming from the methine proton (signal 2) and the protons of PEI structure (subtracting the area of signal 3) and applying the following equation:

$$x = \frac{I(2)}{[I(PEI + 1) - I(3)]/4} \quad (2)$$

where, $I(x)$ is the integration of the group of protons assigned in Figure 1. From x and the relationship between primary amine end groups (T), secondary amine linear units (L), and tertiary amine dendrimeric units (D) and taking into account that primary amines can react twice with oxiranes it is possible to calculate the degree of modification (DM) by using the next equation:

$$DM = x(L + 2T + D)x 100/(L + 2T) \quad (3)$$

In this way, a modification degree of 100.2 % was calculated which falls in the range of error for a complete modification complete modification. The knowledge of the degree of modification and the average number of allyl groups in the PEI ene structure is essential to calculate the composition of the curing formulations.

3.2 Study of the photopolymerization and thermal process

Dual curing thermosets are formulations that can be partially cured, with a controlled advancement of the intermediate curing, as an initial stage after being applied onto a substrate and then later completely cured under heat. Usually, they combined two different curing methodologies, photocuring and thermal curing. Dual curing also offers the possibility of tailoring the material properties by changing the monomer and initiator concentrations and curing conditions [23] which can be understood by the mechanism of each reaction. Click reactions are very valuable to be applied for dual curing thermosets because of their orthogonality and selectivity and the high yields without elimination of volatiles.

Thiol-ene polymerization, in which a thiol adds to a carbon-carbon double bond, uses radical species as initiator and is often photochemically induced as represented in **Scheme 2** [37]. DMPA was used as photoinitiator and cleaved by absorbing a photon of light, whereupon it abstracts a hydrogen atom from a thiol monomer, generating a thiyl radical that further reacts.

On the basis of this mechanism, it is generally assumed that, given an initial stoichiometric mixture of thiol and ene functional groups, the thiol and ene components will be consumed at identical rates.

To confirm the completion of thiol-ene reaction between PETMP and PEIene, FTIR spectra of the samples were registered during UV-irradiation. **Figure 2** represents the FTIR of the 100 thiol-ene sample, before and after irradiation. Before irradiation, the spectrum of the liquid film presents the $-SH$ band at 2576 cm^{-1} and $-C=C-$ band at 1643 cm^{-1} , since the reaction mixture consists of stoichiometric amounts of thiol and ene supplemented with a small percentage of photoinitiator. As we can see, after 2 min of irradiation, the absorptions due to the thiol monomer and the double bond have disappeared completely which evidences that the thiol-ene reaction has been completed. It should be commented, that the FTIR spectra during irradiation were taken for all the formulations but the monitoring of the thiol-ene reaction was not always possible, firstly by the presence of the peaks from DGEBA which overlaps the $-C=C-$ band and secondly because unreacted thiol groups are still present in the mixture to react with epoxy monomers.

The second process in the proposed dual curing is the thiol-epoxy reaction, which consists in a simple nucleophilic ring-opening reaction by a thiolate anion, formed by hydrogen abstraction with amine. The alkoxide anion formed is protonated by proton transfer from a quaternary ammonium salt formed in the activation of thiol or by the thiol itself, as depicted in **Scheme 3**. This mechanism puts in evidence the role of tertiary amine as catalyst.

In our case, PElene has several tertiary amines in the structure which can act like a base and promote the thiol-epoxy curing by opening of the oxirane rings. This could be an advantage since no amine should be added but it can be also a drawback because of it can lead to the partial overlapping of thiol-ene and thiol-epoxy reactions, suppressing the dual character of the curing process. Since the concentration of amine (acting as a basic catalyst) is an important issue in the catalysis of the thiol-epoxy process, the composition of the formulation, in which the PElene proportion is varied, is one of the main factors affecting the kinetics of both processes and the characteristics of the materials after the first stage and after complete curing.

First of all, the effect of the basicity of the amines in the PElene structure on the thiol-epoxy reaction was evaluated by DSC experiments. The enthalpy per epoxy equivalent was calculated for each non-irradiated formulation and compared with values reported in the literature [38] to verify that the thiol-epoxy reaction took place completely. Only in formulations containing 60% or 80% of PETMP-PElene the total conversion of epoxy groups was achieved. When the proportion of PETMP-PElene was lower, we realized that the thiol-epoxy reaction was not completed. As an example, in formulation 20 thiol-ene an only 45% of epoxide conversion was evaluated. These results suggest that the basicity of the medium, due to the amines in PElene is not enough to fully catalyze the thiol-epoxy reaction. Taking this into account, 1-methyl imidazole (1-MI) was added to all the formulations and the thiol-epoxy reaction was completed in all of them. Calorimetric curves for the previously irradiated 20 thiol-ene formulation with and without 2 phr of 1-MI are represented in **Figure 3**.

As we can see, on comparing the curves, different shapes can be observed. The addition of 1-MI to the sample produces a faster curing at lower temperatures and in a narrower range. Moreover, whereas the heat evolved in the sample containing 1-MI is 126 kJ/ee, the heat for the non-catalyzed

formulation is only 52 kJ/ee, which indicates that when the proportion of PEIene in the formulation is low the epoxy reaction cannot be completed in the absence of added 1-MI. For this reason, 2 phr of 1-MI (in reference to DGEBA) was added to all formulations.

Carioscia et al. [23] reported that epoxy homopolymerization occurred in thiol-ene/thiol epoxy formulations and this competitive process became more important when the epoxy concentration was decreased. This was attributed to the reduced mobility of the unreacted thiol group in the materials, greater when the vinyl group concentration increased. As a base, the authors selected 2,4,6-tris(dimethylaminomethyl)phenol, which could initiate the homopolymerization process. To investigate if in our system the homopolymerization was a competitive process we could not follow the evolution of both thiol and epoxy bands in the FTIR spectra, but thiol absorptions have disappeared completely in the spectrum of the final material, which indicates that thiol reacts stoichiometrically with the epoxide groups and therefore no appreciable homopolymerization competes.

Once the individual reactions were characterized the combination of a first photochemical reaction followed by the thermal polymerization in the dual curing was studied.

The photoinduced thiol-ene polymerization was investigated by photo-DSC at 30°C. The photocalorimetry experiment was done first of all in an isothermal irradiation curing during 6 min to register the complete exothermal curve. These studies were carried to find out the minimum time necessary to reach the maximum conversion of thiol groups during the irradiation, which was determined to be 2 min. The heat flow per double bond equivalent for all the formulations is reported in **Table 2**. As we can see, the 100 thiol-ene formulation yields an enthalpy per double bond equivalent of 60 kJ. Similar results were obtained for all the formulations, which indicate that in the photocalorimeter the thiol-ene reaction has been completed in all of them. Since 2 min of irradiation were enough to reach the complete thiol-ene reaction, we registered a dynamic scan after 2 min of isothermal photocuring and the T_g s of these materials were determined. As we can see, on increasing the proportion of PEIene in the formulation the T_g also increases, as the result of the

crosslinking by thiol-ene reaction on the hyperbranched structure of the multifunctional PEI.

We also investigated if both processes overlap during photocuring in the DSC. To know about this overlapping, the irradiated samples were subjected to a dynamic scan to determine the heat released by the epoxy-thiol reaction. From this value and the enthalpy per epoxy equivalent in the 0 thiol-ene formulation we can determine by eq. 1, the degree of conversion achieved by thiol-epoxy thermal process. In this way, a partial conversion of epoxides (7 and 14%) could be detected for formulations 60 and 80 thiol-ene, as collected in the table. Thus, by photo-DSC we could determine that the process has a dual character only in formulations 20 and 40 thiol-ene, in which the proportion of amines is low. The explanation to the overlapping between thiol-ene and thiol-epoxy processes can be found in the heat evolved during the thiol-ene process, higher when the extension of this reaction is also higher. It should be taken into account that although the heat evolved by C=C equivalent are quite similar the heat by gram increases on increasing the PEIene content in the formulation. The heat evolved in the thiol-ene photopolymerization was also attributed as the responsible of the overlapping with epoxide homopolymerization in case of using pentallylamine as -ene monomer [18]. However, the extent of epoxide homopolymerization was even larger and could be detected when the proportion of allylic compound was only 10%.

The preparation of films by the present two-stage process requires the use of a UV chamber to perform the first stage of curing. To see if the data and conclusions obtained by photo-DSC were reproducible in a bigger scale, we prepared samples in a mold and they were irradiated for 2 min as described in the experimental part. As we can see in Table 2, the thiol-epoxy reaction overlaps in all the formulations, being this overlapping more evident on increasing the proportion of PEIene in the formulation. The overlapping of the two reactive processes was also confirmed by comparing the T_g values obtained for the irradiated formulations. Only 20 thiol-ene sample has similar T_g values despite the irradiation system applied and the 40 and 60 thiol-ene samples have a higher T_g when the materials were irradiated in the chamber than in the photo-DSC. It was quite surprising that the 80 thiol-ene sample

shows a higher T_g than the 100 thiol-ene, but it can be rationalized by the DGEBA-thiol reaction which cannot occur in 100 thiol-ene formulation. This also confirms that thiol-epoxy reaction is a competitive process occurring during photoirradiation. As we can see, the conversion of thiol-epoxy reaction in this sample was determined to be 54% by measuring enthalpies.

The differences between photo-DSC and chamber can be attributed not only to the different radiation conditions but also to the size of the sample, which diffuse the heat in a different manner. Thus, the presence of amine groups in the formulation which catalyze the thiol-epoxy process, together with the heat evolved in the thiol-ene reaction avoid a pure dual-curing process to occur on preparing samples in the irradiation chamber. Sangermano et al studied by pyrometry the temperature reached during photoirradiation in thiol-ene/epoxy reactions. Although the systems and irradiation conditions were not exactly the same, temperatures of 78°C could be measured, which are enough to start thiol-epoxy reaction.

All the samples prepared were submitted to a post-thermal treatment to complete the epoxy group conversion. The temperature of the cure and post-cure process was chosen taking into account the experiments performed by DSC. The irradiated samples were thermally treated for 1h at 100°C and 30 min at 120°C. Table 2 collects the T_g values determined by DSC of the materials after the thermal stage. On increasing the PEIene content in the formulation the T_g s decreased by the presence of the flexible structure of the polysulfide formed and the lower proportion of aromatic moieties, coming from DGEBA. The aliphatic structure of thiol limits the T_g value up to 55°C for the 0 thiol-ene sample.

3.3 Characterization of the materials

The thermal stability of the complete cured materials was determined by TGA. **Figure 4** shows the thermogravimetric curves and the derivatives of the materials in N₂ atmosphere. As we can see, whereas the neat 0 thiol-ene and 100 thiol-ene present a main degradative process at different temperatures in the derivative curves, the other materials show both processes with contributions depending on the composition of the initial formulation. The main degradative process that appears in the 100 thiol-ene sample occurs at lower

temperature than the process of the 0 thiol-ene sample. Moreover, a shoulder appears in all the samples at temperatures higher than 400°C.

The most typical data extracted from TGA studies are collected in **Table 3**. As we can see, the materials begin to degrade at higher temperature when the proportion of PElene in the formulation is lower, and the highest stability was observed by the thiol-epoxy neat material (0 thiol-ene). $T_{2\%}$ has been taken as the temperature at which the mechanical characteristics of the material usually begin to fail and from the point of view of the behavior of the material at high temperature is more meaningful than T_{max} . $T_{2\%}$ is reduced in 65°C in the neat thiol-ene sample in comparison to the neat thiol-epoxy material. In previous studies we observed the low thermal stability of PEI containing thermosets [33]. The higher the proportion of PEI in the material the more important is the degradation at lower temperature, because of the breakage of the poly(ethyleneimine) structure. The same behavior is observed by looking at the T_{max} and $T_{shoulder}$ in which the degradative processes of the PEI structure leads to a reduction of these temperatures on increasing the proportion of PEI in the material.

Thermomechanical analysis of the materials prepared was performed. **Figure 5** collects the evolution of storage modulus and $\tan\delta$ against temperature. As we can see, the material transforms from the glassy to the rubbery state at lower temperature on increasing the amount of PElene in the formulation, because the higher flexibility of this structure and the lower amount of rigid aromatic structures coming from DGEBA. However, the modulus in the rubbery state tends to increase. The explanation to this fact can be found in the lower molecular weight between crosslinks on increasing the amount of PEI structures, since the structural unit in the HBP is rather short. Thiol-DGEBA polymerization leads to a network structure with a high molecular weight between crosslinking points.

The shape of the $\tan \delta$ curves (Figure 5) is in all cases unimodal indicating a complete homogeneous material. The temperatures of the maximum of $\tan \delta$ decrease on increasing the proportion of PElene in the formulation, similarly as the decrease in T_g observed by DSC.

Figure 6 shows the flexibility and appearance of one of the materials obtained, which are pale yellow and somewhat transparent.

4. Conclusions

A new allyl terminated hyperbranched poly(ethyleneimine) (PElene) was synthesized by reaction of PEI with allyl glycidyl ether. This multifunctional macromonomer has been used as -ene component in thiol-ene/thiol-epoxy curing formulations.

Different formulations of PElene/DGEBA with stoichiometric amounts of pentaerythritol tetrakis (3-mercaptopropionate) were cured by a two-stage process consisting of a first photoirradiation and a second thermal treatment. To catalyze both processes a photoinitiator (DMPA) and a base (1-MI) were necessary.

The presence of amines in the PElene structure together with the heat evolved in the thiol-ene process led to an early initiation of the thiol-epoxy reaction during photocuring. The overlapping of both processes is greater on increasing the amount of PElene in the formulation. This overlapping occurs in different proportions in the photo-DSC and in the photoirradiation chamber, because of the different irradiation conditions and size of the sample.

The materials are thermally more stable by increasing the proportion of DGEBA in the formulation, since the PElene structure begins to degrade at lower temperatures.

The T_g s of the final materials decrease on increasing the proportion of PElene in the formulation, due to the high flexibility of this hyperbranched structure. However, the storage modulus in the rubbery state increases, because of the lower molecular weight between crosslinks in rich PElene materials.

5. Acknowledgements

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Table 1. Composition of the formulations

Sample	PEIene		DGEBA		PETMP	
	(mmol)	(g)	(mmol)	(g)	(mmol)	(g)
0 thiol-ene	-		1.65	0.60	0.82	0.40
20 thiol-ene	0.037	0.12	1.30	0.46	0.86	0.41
40 thiol-ene	0.065	0.22	0.99	0.36	0.86	0.42
60 thiol-ene	0.101	0.33	0.68	0.25	0.88	0.42
80 thiol-ene	0.13	0.44	0.33	0.12	0.90	0.44
100 thiol-ene	0.16	0.55	-	-	0.91	0.45

Table 2. Calorimetric data of the different formulations studied

Sample	DSC data after irradiation in photo-DSC			DSC data after irradiation in the chamber			Final material
	ΔH^a	X^b	T_g^c	ΔH^d	X^e	T_g^f	T_g^g
	(kJ/C=Ceq)	(%)	(°C)	(kJ/ee)	(%)	(°C)	(°C)
0 thiol-ene	-	-		125	-	-	55
20 thiol-ene	60	0	-26	124	2	-26	50
40 thiol-ene	59	0	-18	114	9	-11	42
60 thiol-ene	62	7	-5	70	40	5	30
80 thiol-ene	64	14	0.5	57	54	10	20
100 thiol-ene	60	-	7	-	-	7	7

^a Heat released per ene equivalent during irradiation in the photo-DSC during 6 min at 30 °C.

^b Epoxy group conversion after 2 min of irradiation in the photo-DSC determined by Eq. 1

^c Glass transition of the material after 2 min of irradiation in photo-DSC determined in a second dynamic scan.

^d Heat released by epoxy equivalent after irradiation during 2 min in the irradiation chamber, determined in a dynamic scan at 10°C/min.

^e Epoxy group conversion after irradiation in the chamber determined from DSC data and Eq. 1.

^f Glass transition of the intermediate material after irradiation during 2 min in the chamber determined by DSC

^g Glass transition determined in a second scan in the DSC, of the final material after irradiation and a first dynamic scan at 10°C/min.

Table 3. Thermal stability and thermomechanical data of the cured materials

Sample	TGA			DMTA	
	T _{2%} ^a (°C)	T _{max} ^b (°C)	T _{shoulder} ^c (°C)	E _r ^d (MPa)	T _{tanδ} ^e (°C)
0 thiol-ene	304	360	441	12	58
20 thiol-ene	281	357	436	11	53
40 thiol-ene	270	348	428	19	40
60 thiol-ene	265	334	423	24	30
80 thiol-ene	252	318	422	26	24
100 thiol-ene	239	318	420	28	14

^a Temperature of the 2% of weight loss in N₂ atmosphere.

^b Temperature of the maximum decomposition rate.

^c Temperature of the maximum rate of degradation in the last process.

^d Storage modulus in the rubbery state

^e Temperature of maximum of *tanδ* curve.

FIGURE CAPTIONS

Scheme 1. Synthetic route of allyl-terminated hyperbranched poly(ethyleneimine) (PEIene).

Scheme 2. Mechanism of the radical thiol-ene reaction.

Scheme 3. Mechanism for the thiol-epoxy reaction.

Figure 1. $^1\text{H-NMR}$ spectrum of allyl-terminated hyperbranched poly(ethyleneimine) in CDCl_3 .

Figure 2. FTIR-UV spectra of the 100 thiol-ene formulation before and after UV-irradiation.

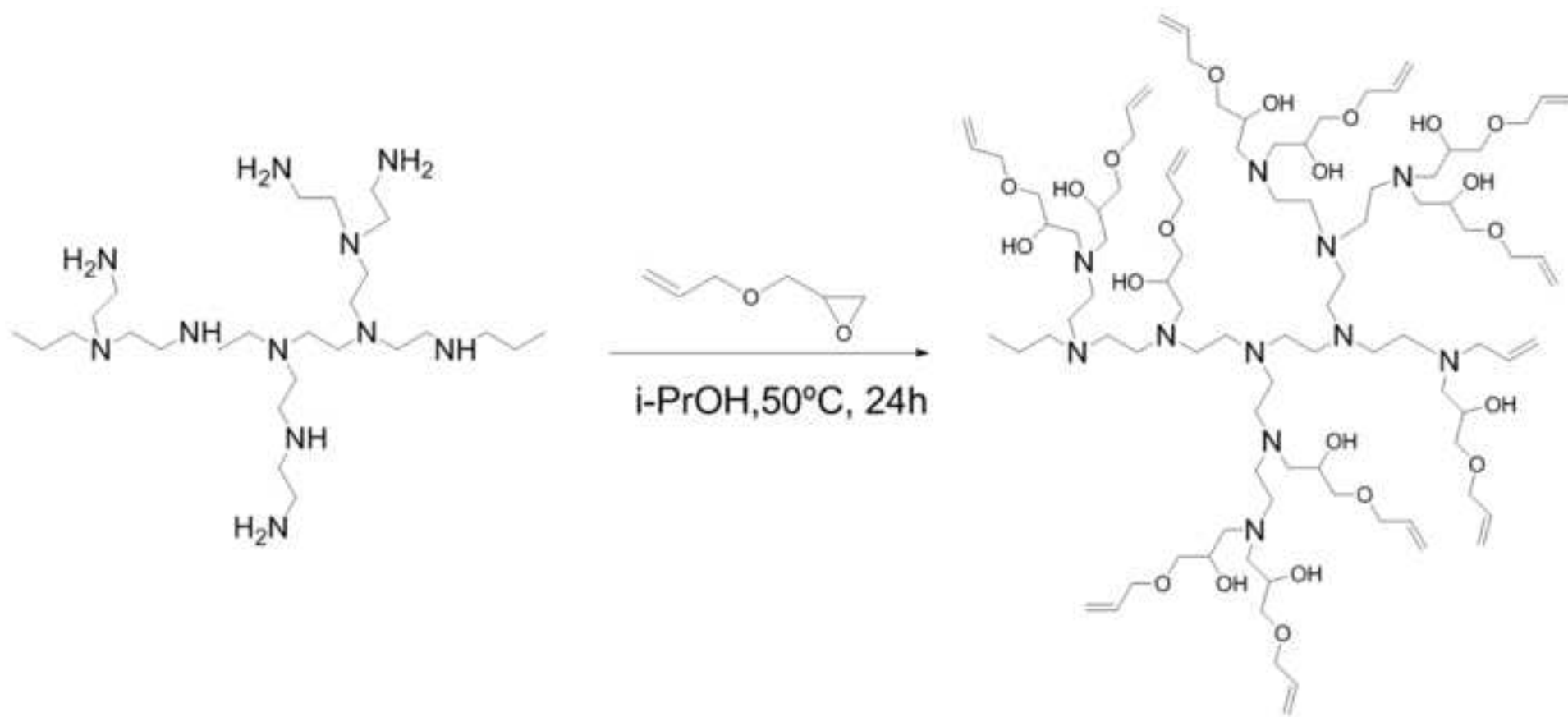
Figure 3. Calorimetric curves of the previously irradiated 20 thiol-ene sample.

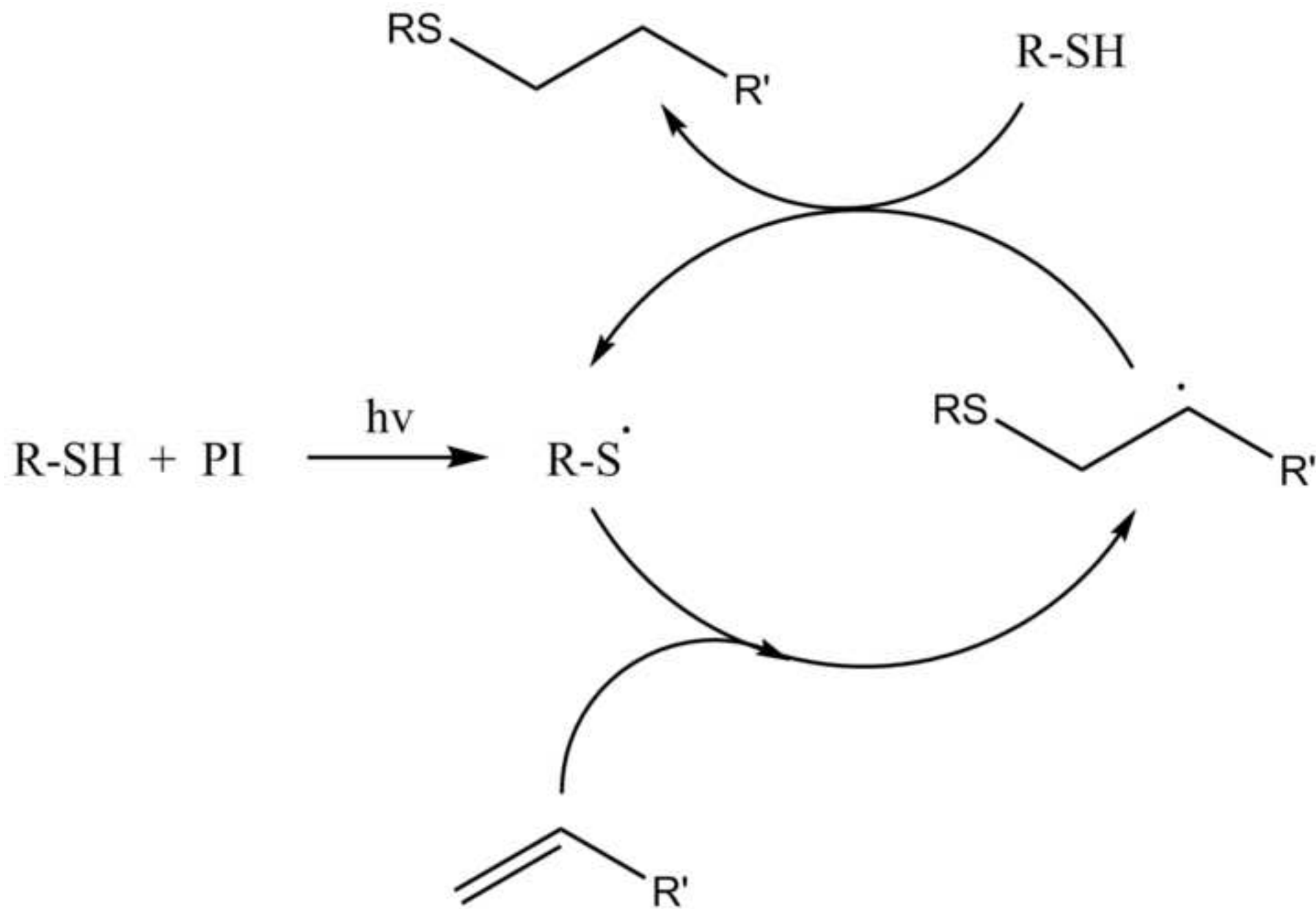
Figure 4. Thermogravimetric curves at $10^\circ\text{C}/\text{min}$ in N_2 atmosphere of cured materials.

Figure 5. Storage modulus and $\tan \delta$ evolution against temperature for the materials obtained.

Figure 6. Photograph of the material prepared from 60 thiol-ene formulation.

Scheme 1
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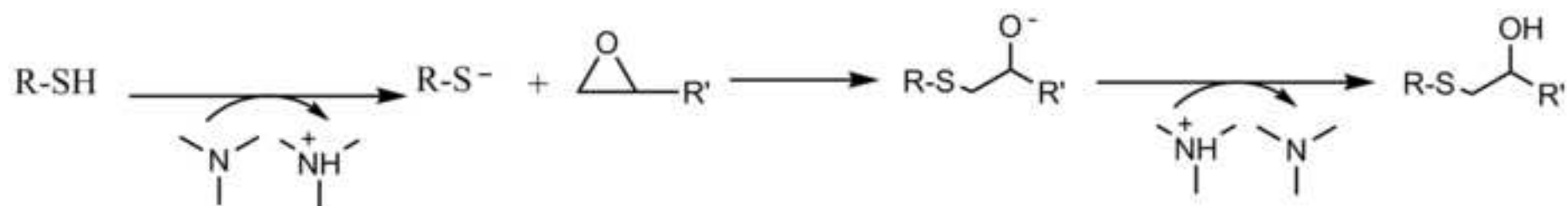


Figure 1
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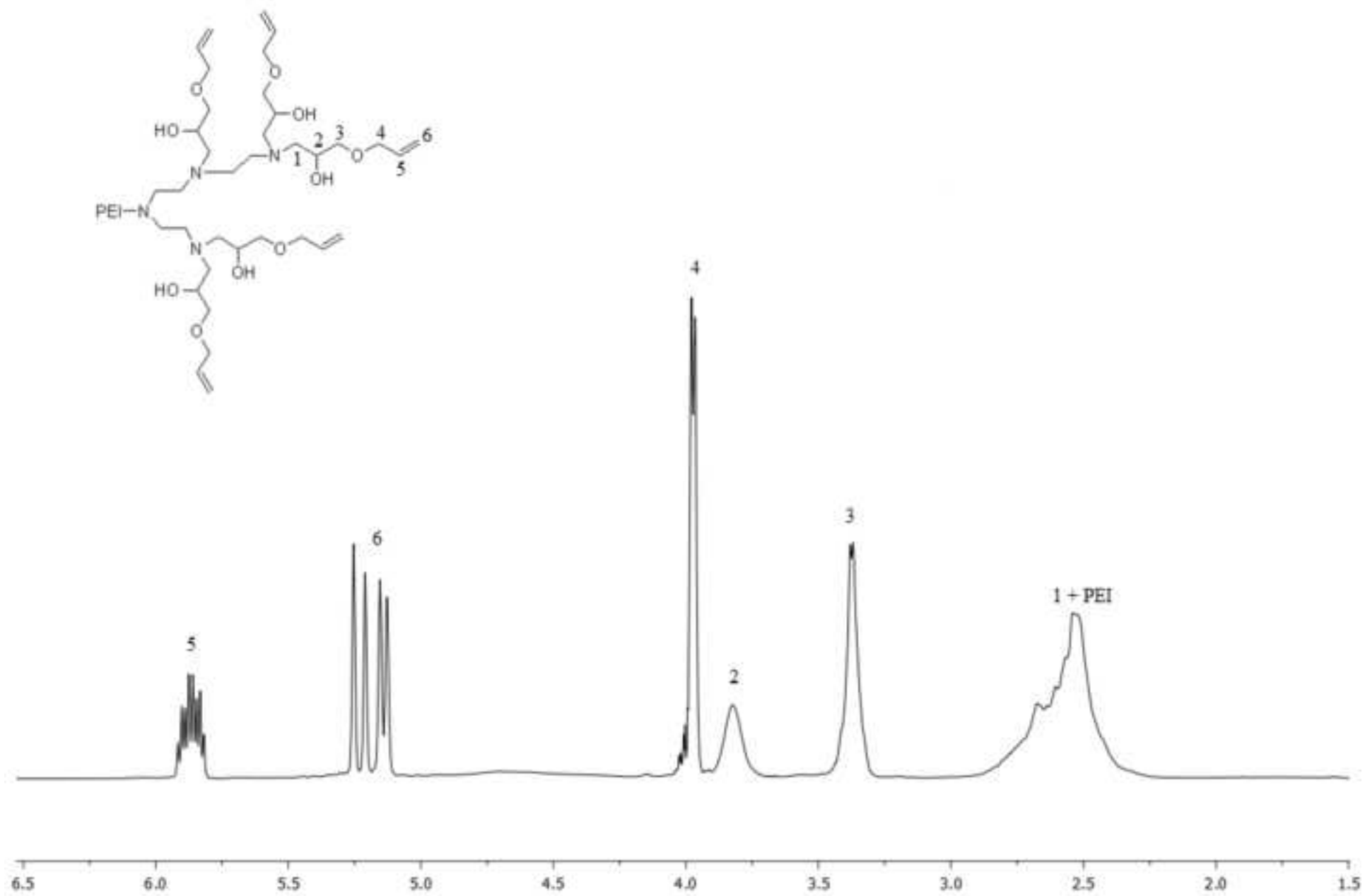


Figure 2
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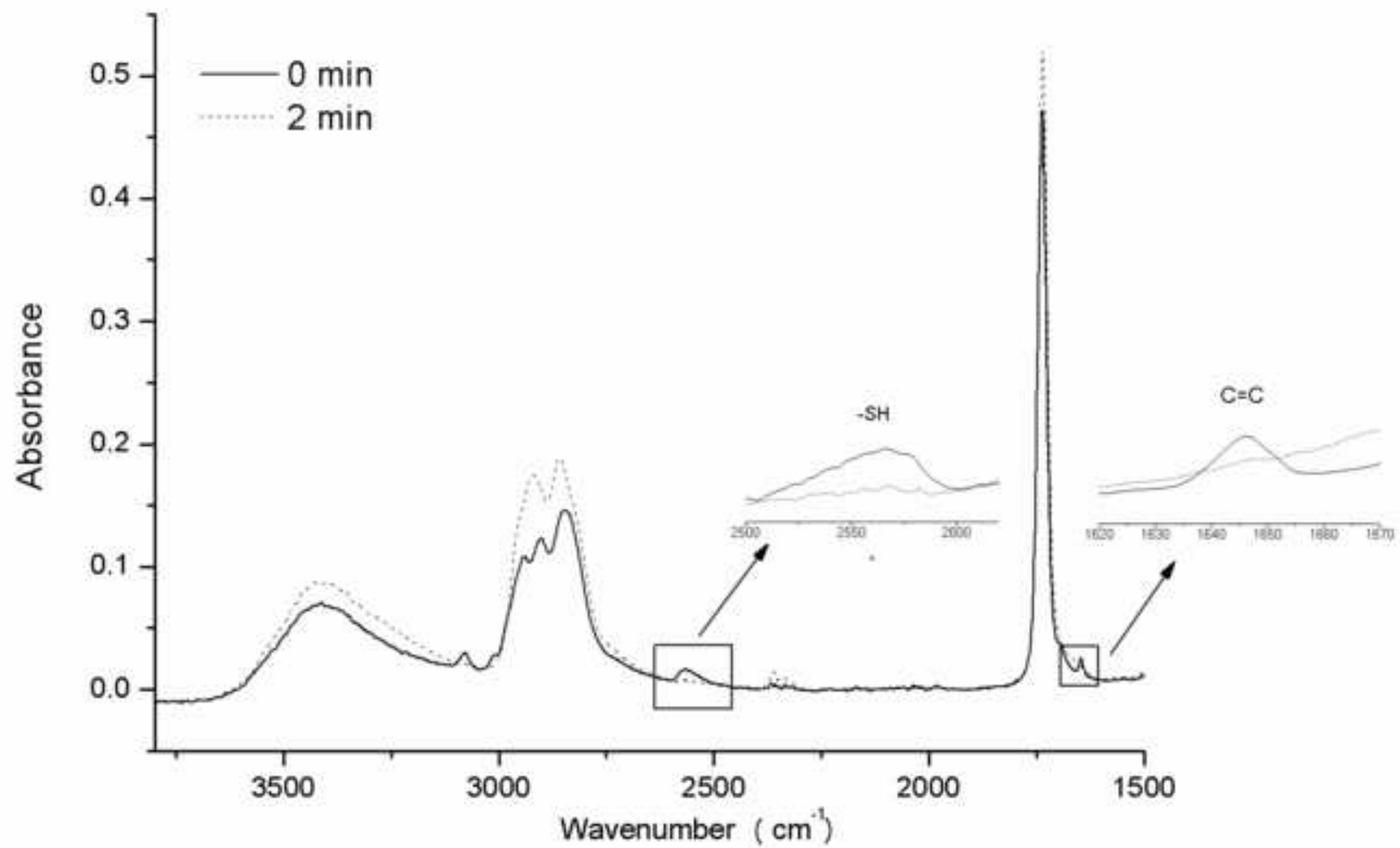


Figure 3
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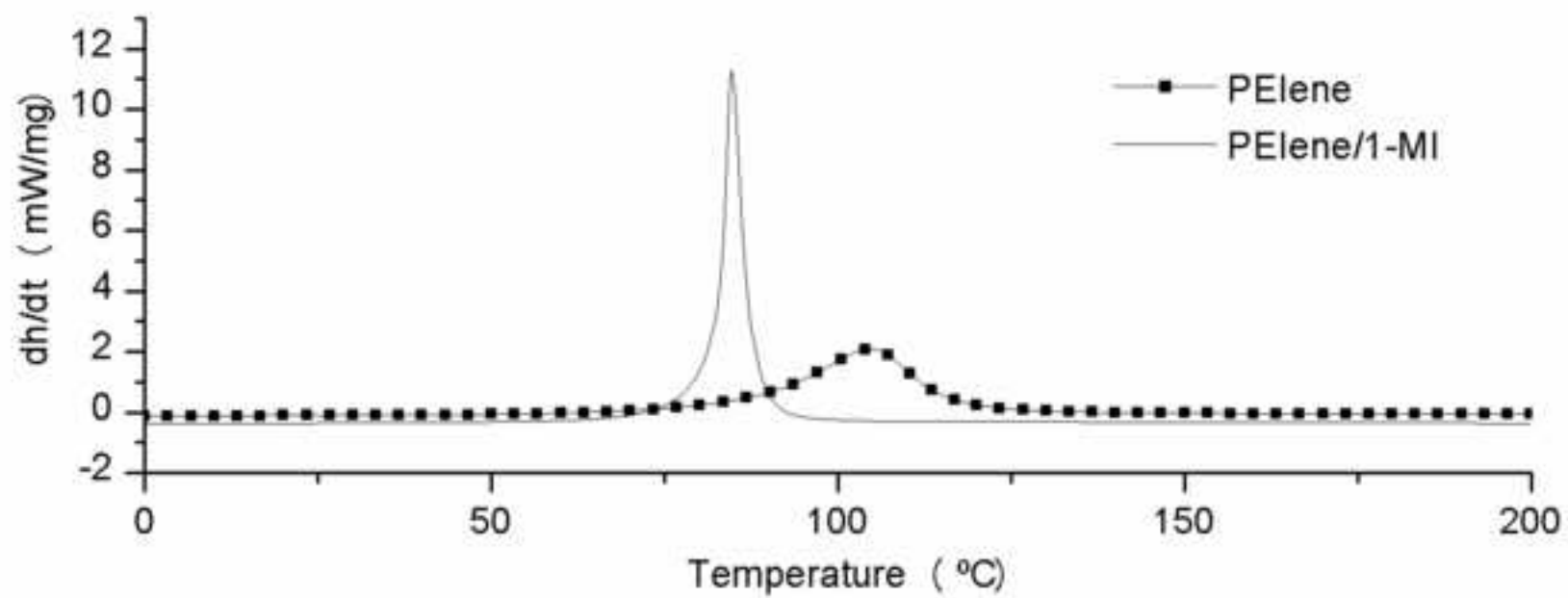


Figure 4
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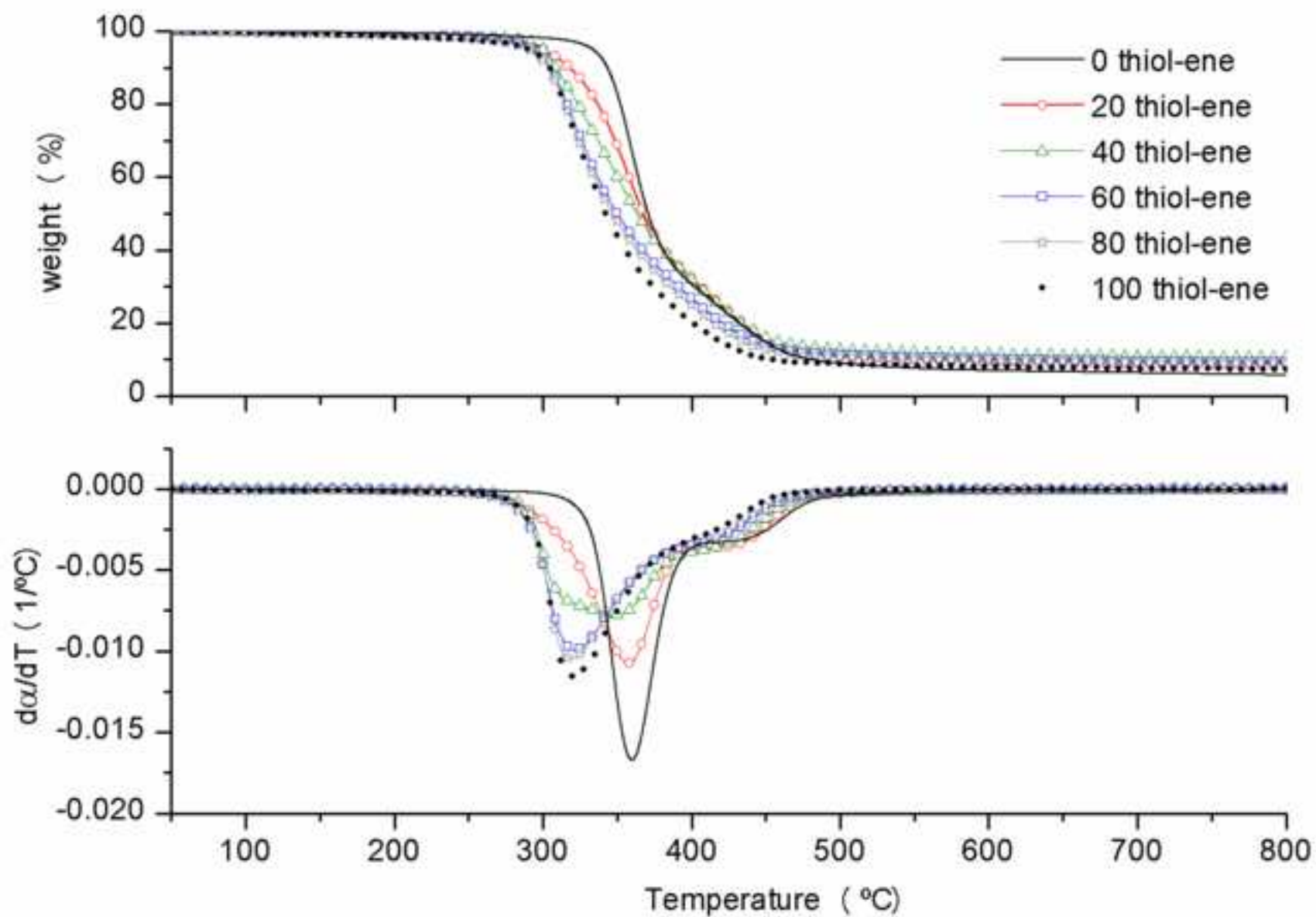


Figure 5
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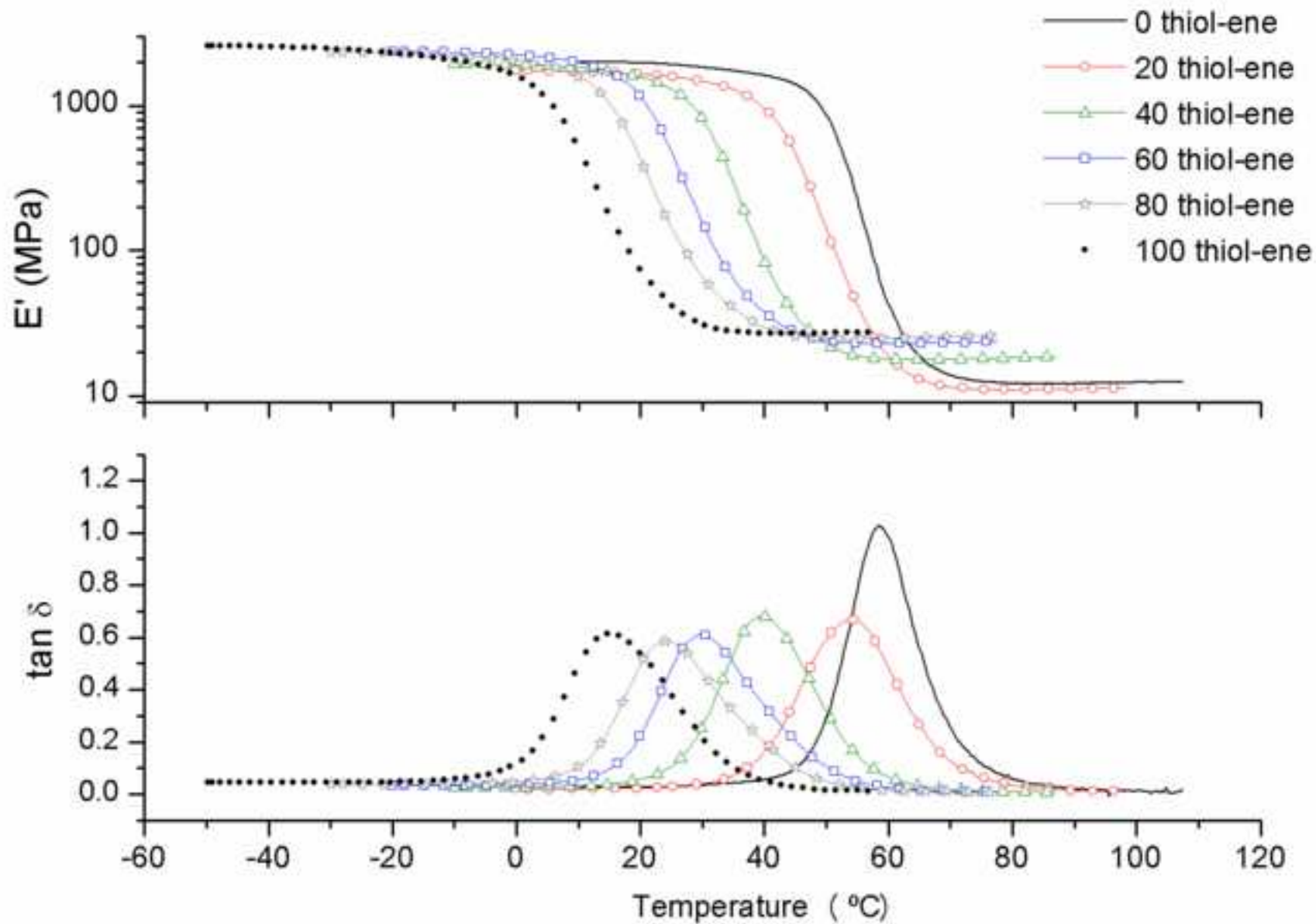


Figure 6
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