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2 **Fully Bio-based Polymers Derived from Acrylated** 3 **Epoxidized Soybean Oil by Thiol-ene Reaction**

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12 **Abstract:** It has been estimated that more than 8.3 billion tonnes of plastics have been produced
13 over the past decades and about 60 % of plastics have ended up either in landfills or in the natural
14 environment. With the rapid growth of consumerism, research on innovative starting materials for
15 preparation of polymers may help to reduce the negative impact of petroleum-based plastic
16 materials on the global ecosystem and on animal and human health. Therefore, photochemical
17 thiol-ene coupling reaction of squalene was performed to obtain thiol functional groups. Then,
18 hexathiolated squalene was used as a cross-linker in UV curing reactions with acrylated epoxidized
19 soybean oil. Two photoinitiators, 2-hydroxy-2-methylpropiophenone and ethylphenyl
20 (2,4,6-trimethylbenzoyl) phosphinate, were tested in different quantities. Rheological properties of
21 compositions were monitored by real time photorheometry. The obtained polymers were
22 characterized by differential scanning calorimetry and thermogravimetry. Polymers possessed
23 higher storage modulus and thermal characteristics due to the higher yield of insoluble fraction
24 when ethylphenyl (2,4,6-trimethylbenzoyl) phosphinate was used as photoinitiator.

25 **Keywords:** thiol-ene; soybean oil; hexathiolated squalene; UV curing; biobased polymer
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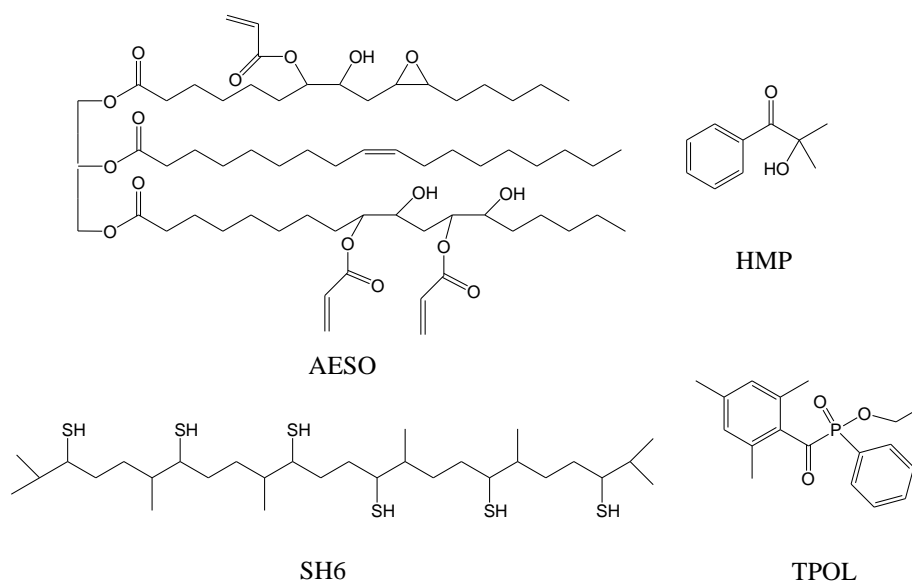
27 **1. Introduction**

28 The availability of petroleum-based resources has decreased significantly with the increase of
29 worldwide demand for energy. Indeed, the depletion of fossil reserves associated with serious
30 ecological problems related to greenhouse gas emissions forced researchers to develop new
31 polymeric materials based on renewable and sustainable sources.

32 Acrylated epoxidized soybean oil (AESO) is already used in industry due to the various
33 functional groups such as acrylic, epoxy, and hydroxy groups, and has Ebecryl 860 trademark [1].
34 AESO was already polymerized with various petroleum-derived compounds, such as styrene,
35 divinylbenzene [2,3], as well as plant-derived compounds such as vanillin acrylates [4].

36 Biobased thiols synthesized from squalene and eugenol have been reported as suitable for
37 thiol-ene reaction with the occurrence of side reactions that led to incomplete thiol-ene reaction [5].
38 Incomplete curing in case of using hexathiolated squalene (SH6) as thiol has been reported
39 previously [6]. SH6 has a compact structure with a short distance among thiol groups and a quite
40 hindered position of these groups in the whole molecular structure. These characteristics can lead to
41 serious topological restrictions leading to an incomplete reaction and therefore to an undesired
42 imbalance between thiol and acryloyl groups.

43 Commercially available petroleum-derived thiols have been already tested in photochemical
44 thiol-ene reaction with AESO [7,8]. Bio-based SH6 has been tested in thermal polymerization of AESO
45 using 1-methylimidazole as a catalyst previously [9]. Photopolymerization is quite advantageous in
46 front of thermal polymerization due to high reaction rates and performance at ambient conditions.
47 Therefore, hexathiol synthesized from squalene (SH6) was selected for stoichiometric UV curing
48 thiol-ene reaction with AESO (Scheme 1). Two photoinitiators, 2-hydroxy-2-methylpropiophenone
49 (HMP) and ethylphenyl (2,4,6-trimethylbenzoyl) phosphinite (TPOL), were examined in thiol-ene
50 reaction in different quantities to find out the highest yield of insoluble fraction (Scheme 1).
51



52 **Scheme 1.** Chemical structures of acrylated epoxidized soybean oil (AESO), hexathiolated squalene
53 (SH6), 2-hydroxy-2-methylpropiophenone (HMP), and ethylphenyl (2,4,6-trimethylbenzoyl)
54 phosphinite (TPOL).
55

56 2. Experiments

57 2.1. Materials

58 Acrylated epoxidized soybean oil (AESO, having an average number of acryloyl groups per
59 molecule calculated from ^1H NMR spectrum as 2.7 and 0.3 of epoxide groups), squalene, thioacetic
60 acid, 2,2-dimethoxy-2-phenylacetophenone, 2-hydroxy-2-methylpropiophenone (HMP), and
61 ethylphenyl (2,4,6-trimethylbenzoyl) phosphinite (TPOL) were purchased from Sigma-Aldrich
62 (Darmstadt, Germany). Inorganic salts were received from Scharlab (Barcelona, Spain). Methanol
63 and chloroform were purchased from Carlo Erba (Barcelona, Spain). All materials were used
64 without further purification.

65 2.2. Synthesis of Hexathiolated Squalene (SH6)

66 The product was obtained following a two-step procedure as previously reported [10], which
67 includes photochemical thiol-ene coupling reaction of squalene with thioacetic acid and
68 saponification of the resulting thioacetates. The purification of SH6 was carried out by silica gel
69 column chromatography using hexane/ethyl acetate 8/2 mixture as eluent. The yield of the pale
70 yellow viscous liquid was 70%.

71 ^1H NMR (CDCl_3 , δ in ppm), 2.60 broad ($-\text{CH}-\text{S}-$, 6H), 1.10–1.95 unresolved broad signals ($-\text{CH}_2-$,
72 $-\text{CH}-$ and $-\text{SH}$, 32H), and 0.8–1.05 broad (CH_3- , 24H).

73 IR (KBr): 2955 (ν CH_2 aliph.), 2923, (ν $\text{C}-\text{H}$ aliph.) 2570 (ν $\text{S}-\text{H}$) cm^{-1} .

74 2.3. *Chemical Structure Analysis*

75 A Varian Gemini 400 spectrometer (Palo Alto, CA, USA) was used to register the ^1H NMR
 76 spectra. CDCl_3 was used as a solvent. For internal calibration the solvent signal corresponding to
 77 CDCl_3 was used: $\delta(^1\text{H}) = 7.26$ ppm.

78 A Perkin-Elmer (Llantrisant, UK) Spectrum BX II FT-IR spectrometer was used to record IR
 79 spectra of cross-linked polymers. The spectra were performed in KBr pellets and acquired from 10
 80 scans. The range of wavenumber was $(400\text{--}4000)$ cm^{-1} .

81 2.4. *Real-Time Photorheometry*

82 UV/Vis curing tests were performed with stoichiometric AESO and SH6 compositions (ratio of
 83 acrylate/S_H groups 1:1) using 1-5 mol.% of photoinitiator (HMP or TPOL) (Table 1) on a MCR302
 84 rheometer (Anton Paar, Graz, Austria) equipped with the plate/plate measuring system. The
 85 Peltier-controlled temperature chamber with the glass plate (diameter 38 mm) and the top plate
 86 PP15 (diameter 15 mm) was used. The measuring gap was set to 0.1 mm. The samples were
 87 irradiated by UV/Vis light in a wavelength range of 250-450 nm through the glass plate of the
 88 temperature chamber using UV/Vis spot curing system OmniCure S2000 (Lumen Dynamics Group
 89 Inc., Mississauga, Ontario, Canada). Shear mode with the frequency of 1 Hz and shear strain of 1 %
 90 were used in all cases. Storage modulus G' was recorded as a function of irradiation time.

91 **Table 1.** Compositions of photopolymerization

Composition	Photoinitiator (mol.%)
1HMP	1
2HMP	2
3HMP	3
4HMP	4
5HMP	5
1TPOL	1
2TPOL	2
3TPOL	3
4TPOL	4
5TPOL	5

92

93 2.5. *Soxhlet Extraction*

94 A Soxhlet extractor was used to determine the amount of insoluble polymer fraction. The
 95 samples of the cross-linked polymers (0.2 g) were put into a filter package and placed in a Soxhlet
 96 apparatus. Extraction was performed with chloroform for 24 h. Insoluble fractions were dried under
 97 vacuum to a constant weight. The amount of insoluble fraction was calculated as the difference of
 98 the sample weight before and after extraction.

99 2.6. *Differential Scanning Calorimetry*

100 The glass transition temperature (T_g) of the photocross-linked polymers were estimated by
 101 differential scanning calorimetry (DSC). The measurements were performed on a DSC 8500
 102 apparatus (Perkin Elmer, Llantrisant, UK) with a heating-cooling-heating rate of 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$ under a
 103 nitrogen atmosphere (nitrogen flow rate 50 $\text{mL}\cdot\text{min}^{-1}$). The T_g value was taken as the middle point in
 104 the heat capacity step of the glass transition.

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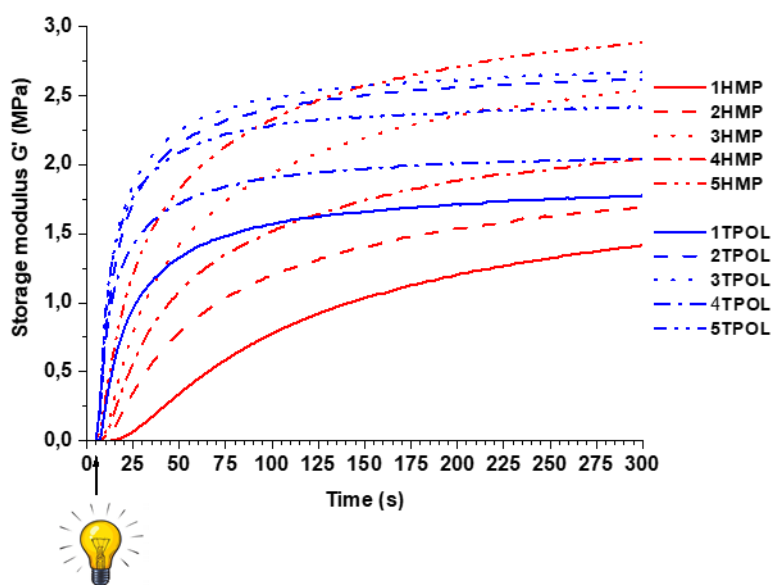
106 2.7. *Thermogravimetric Analysis*

107 Thermal stability of polymers prepared was determined by thermogravimetric analysis (TGA).
 108 The measurements were performed on a Perkin-Elmer TGA 4000 apparatus in the temperature
 109 range from room temperature to 800 °C at a heating rate of 20 °C·min⁻¹ under nitrogen atmosphere
 110 (nitrogen flow rate 100 mL·min⁻¹).

111 3. Results

112 3.1. Kinetics of Photocross-linking

113 The kinetics of photocross-linking was monitored by real-time photorheometry. As an example,
 114 the typical curves of storage modulus G' are presented in Figure 1. G' increased very fast when
 115 irradiation of the reaction mixture started. This shows the quick chain size growth and the network
 116 formation in the initial part of photocross-linking. With the increase of concentration of
 117 photoinitiator, storage modulus changed unevenly. The highest storage modulus was obtained
 118 when 5 mol.% of HMP and 3 mol.% of TPOL were used (2.89 MPa and 2.67 MPa, respectively). These
 119 values were similar to those of AESO polymers with aromatic dithiols tested with the same real-time
 120 photorheometry method (2-9 MPa) [8]. G' of compositions with TPOL increased very fast during the
 121 first 10 s and continued to increase slowly with time due to the gel aging and settled down into a
 122 steady-state (plateau) indicating the end of the gelation process. While G' of compositions with HMP
 123 increased evenly until plateau was reached. Thus, the rate of photopolymerization and the value of
 124 G' of the composition was the highest when 3 mol.% of TPOL was used.



125

126 **Figure 1.** Curves of storage modulus G' versus irradiation time of the compositions with different
 127 photoinitiators.

128 3.2. Thermal Properties

129 Thermal characteristics of polymers investigated by DSC and TGA are summarized in Table 2.
 130 Glass transition temperatures (T_g) of polymers prepared using TPOL as photoinitiator (from -2 °C to
 131 0 °C) were higher than those of polymers prepared with photoinitiator HMP (from -20 °C to -6 °C).
 132 The same behavior was noticed with the temperature at the weight loss of 10 % ($T_{dec-10\%}$). This could
 133 be explained by the higher yield of insoluble fraction of the crosslinked polymers (Table 2). Polymer
 134 **3TPOL** with the highest yield of insoluble fraction (98 %) exhibited the highest T_g and $T_{dec-10\%}$ values

135 (0 °C and 344 °C, respectively). These values were similar to those of AESO polymer with aromatic
 136 dithiol (1 °C and 342 °C respectively) [8].

137 **Table 2.** Yield of the insoluble fraction and thermal characteristics of the cross-linked polymers.

Polymer	Yield of Insoluble Fraction ¹ (%)	T _g ² (°C)	T _{dec.-10%} ³ (°C)
1HMP	68	-20	333
2HMP	85	-6	333
3HMP	90	-7	330
4HMP	88	-9	331
5HMP	88	-11	331
1TPOL	96	-1	340
2TPOL	97	-1	342
3TPOL	98	0	344
4TPOL	97	-2	340
5TPOL	96	-2	334

138 ¹ After Soxhlet extraction with chloroform for 24 h; ² Glass transition temperature estimated by DSC; ³
 139 Temperature at the weight loss of 10 % obtained from TGA curves.

140 4. Conclusions

141 Hexathiol was prepared from squalene as a starting biobased material. Hexathiolated squalene
 142 was used as monomer in the thiol-ene reaction with acrylated epoxidized soybean oil using two
 143 different photoinitiators, 2-hydroxy-2-methylpropiophenone and ethylphenyl
 144 (2,4,6-trimethylbenzoyl) phosphinate, in different quantities. Polymers had the higher storage
 145 modulus and thermal characteristics due to the higher yield of insoluble fraction when ethylphenyl
 146 (2,4,6-trimethylbenzoyl) phosphinate was used in the compositions. The obtained polymers of the
 147 present study can be considered as fully bio-based.

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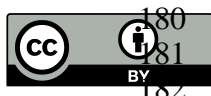
149 **Author Contributions:** S.K., J.O. and A.S. conceived and designed the experiments; S.K. and D.V. performed
 150 the experiments; S.K., J.O. and A.S. analyzed the data; S.K., J.O. and A.S. wrote the paper.

151 **Conflicts of Interest:** The authors declare no conflict of interest.

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