

The use of a coupling agent to obtain copolymers derived from Thiol-Ene/cationic systems

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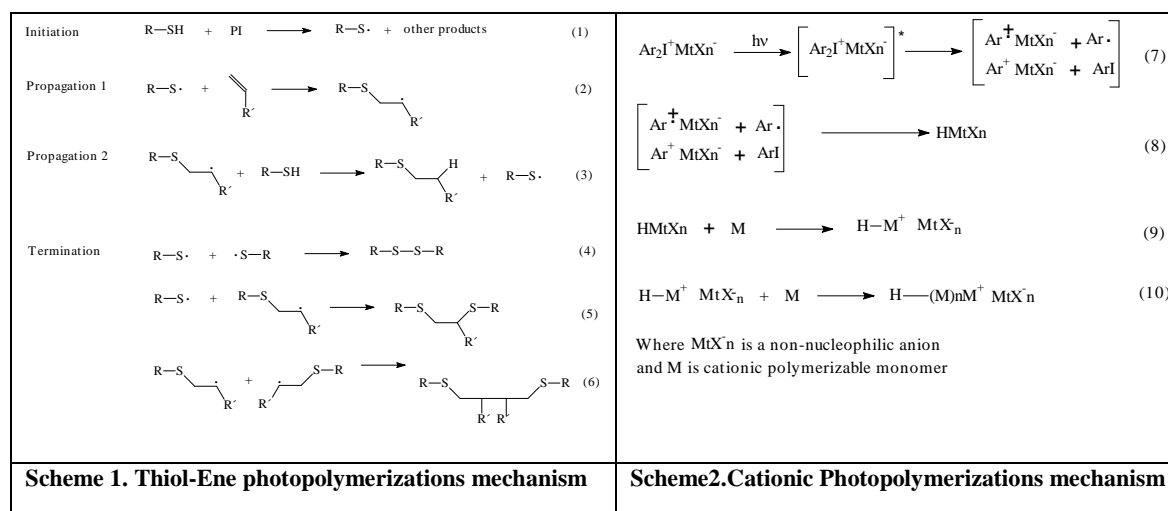
1. Abstract

A bifunctional monomer with methacrylate and epoxycyclohexyl groups linked by a tetramethyldisiloxane moiety was used as a coupling agent for dual photo and thermal polymerizable thiol-ene/cationic systems. The thiol-ene system included a tetrafunctional thiol a trifunctional acrylate and a radical photoinitiator, while the cationic system comprised a difunctional epoxycyclohexyl monomer and a cationic photoinitiator. It was found that in a first stage the methacrylate group of the coupling agent reacted with the components of the thiol-ene system rendering a polysulfide with pendant epoxycyclohexyl groups. In a second stage these pendant groups copolymerized with the epoxy monomer by means of a thermal treatment at 120 °C. When the obtained polymers were analyzed by DMA, an increase in the storage modulus was noticed in comparison with the polymers where no coupling agent was added [1].

2. Introduction

The need for new materials with improved properties has led to the development of novel techniques of polymerization. One of these techniques is the concurrent or sequential polymerizations where two different mechanisms are involved. These hybrids polymerizations generally display advantages over the single components because of the combination of the properties of both systems. In this work was intended to combine two different photopolymerizable systems, namely, the thiol-ene and the cationic. The thiol-ene photopolymerizations proceeds with high regioselectivity under mild conditions, even in the presence of oxygen, reaching high conversions, while cationic systems are not inhibited by oxygen neither and the resultant polymers display excellent mechanical and physical properties. Therefore, it was of interest to combine the properties of both systems to obtain hybrid material with enhanced properties. The mechanisms of both systems are mentioned below for a better understanding of this investigation.

Scheme 1 shows the proposed radical step growth mechanism for the photoinitiated thiol-ene polymerization. The primary radicals produced in the photolysis of the photoinitiator can abstract the hydrogen atom of the thiol group, producing a thiyl radical (eq 1). This thiyl radical would then react with the double bond of the unsaturated monomer to generate a secondary free radical (eq.2), which in turn can abstract the hydrogen atom of a second molecule of the thiol, generating a new thiyl radical to repeat the cycle (eq. 3). Termination occurs by the reaction of two radical species (eq 4,5,6). In Scheme 2 is shown the generally accepted mechanism for the diaryliodonium salt photoinitiated cationic ring opening polymerization of epoxides. When the diaryliodonium salt used as a photoinitiator is activated with UV light, it undergoes photolysis generating cations, radicals and radical-cations (eq. 7). The resulting cationic species interact with the monomer or impurities in the reaction mixture to form a super acid (eq.8). This acid protonates the epoxy monomer generating an activated species. (eq.9). This species reacts further with another molecule of monomer, forming oxonium terminated polyether chains (eq.10).



The aim of this study was to prepare copolymers by photopolymerizing a hybrid thiol-ene /cationic formulation in the presence of a molecule that could serve as a link between the polymers obtained from both thiol-ene and cationic system. The methacrylate group of the compound M1 could react in a first stage with the components of the thiol-ene system. This could give rise to a polymer with pendant epoxycyclohexyl groups. These groups can react further in a second stage with the epoxy monomer of the cationic system, polymerizing by the thermal treatment. By using this methodology a copolymer can be obtained.

3. Experimental Part

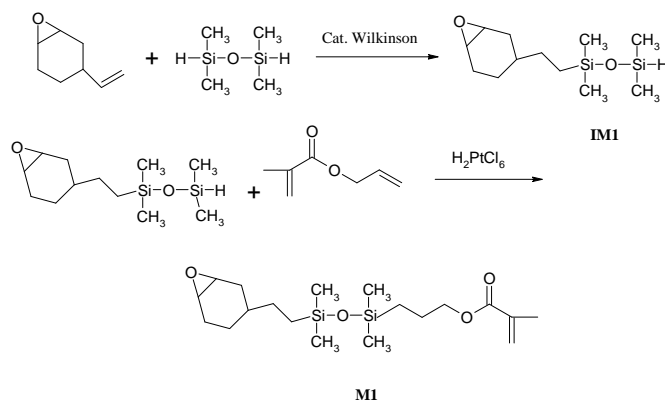
3.1. Synthesis of the Coupling agent M1

The coupling agent was prepared using a method that involves two consecutive hydrosilation reactions onto the tetramethyl disiloxane backbone. In a first stage, it was carried out a regioselective chemical reaction between the 4-vinyl-1-cyclohexene 1,2-epoxide and 1,1,3,3-tetramethyl disiloxane to produce the monofunctional intermediate IM1 (see scheme 3). This reaction took place in the presence of the Wilkinson catalysts at 60 °C. After purification by column chromatography, the compound IM1 underwent a second hydrosylation reaction with allyl methacrylate using chloroplatinic acid as catalyst. The final compound was obtained in 57% yield.

4. Photopolymerization studies

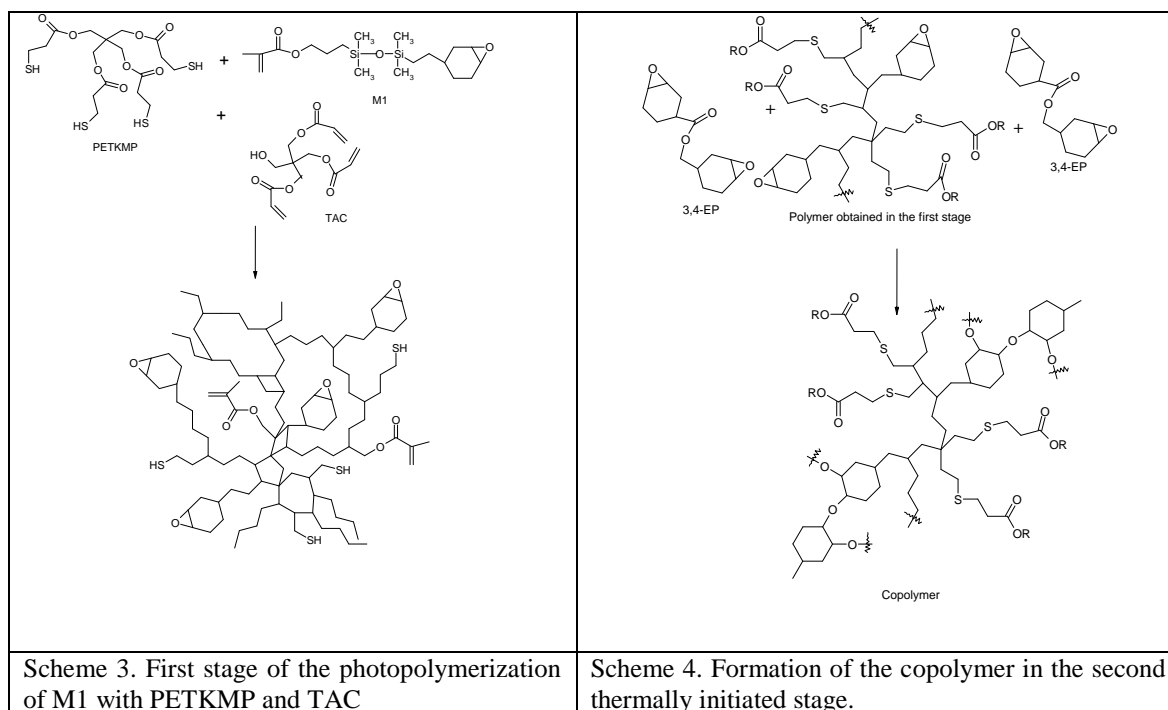
The reactivity of monomer M1 was first evaluated with the thiol pentaerythritol tetrakis mercapto propionate (PETKMP). It was found that M1 can react with PETKMP in a similar fashion that in the thiol-ene mechanism when the system it is irradiated with UV light in the presence of DMPA, undergoing an addition reaction, obtaining in this way a tetrasulfide functionalized with epoxycyclohexyl groups. Although it is also possible that the monomer M1 can homopolymerize, the fact of having an excess of thiol groups (4 to 1) minimize the homopolymerization. Then, once that it was demonstrated that compound M1 could react with the thiol PETKMP, a formulation with 1 equivalent of PETKMP, 1.3 equivalents of pentaerythritol triacrylate (TAC), 1 equivalent of M1, 2 equivalents of the diepoxycyclohexane monomer the 3,4 epoxycyclohexyl 3',4'- epoxy cyclohexancarboxylate (3,4-EP) and

0,01 equivalents of photoinitiators Dimethoxyphenyl acetophenone DMPA and (decyloxyphenyl)phenyl iodonium hexafluoroantimonate (DPPI) was irradiated with UV light.



Scheme 3. Synthetic methodology to prepare M1

It was determined by Real-Time IR spectroscopy that the thiol-ene system (PETKMP, TAC and M1) polymerized rather rapidly in the interval of 10-20 seconds obtaining 85 % conversion. The monomer M1, was incorporated in the obtained polymer, resulting in a polysulfide with pendant epoxycyclohexyl groups (see in scheme 4 the simplified structure). The polymerization of the cationic system was inhibited by the nucleophilic character of the formed polysulfides. As a consequence, the epoxy monomer of the cationic system remained unreacted, acting as a plasticizer in the obtained polysulfide, which has a rubbery nature.



5. DMA Studies.

In the second stage, the epoxy monomer of the cationic system that did not react during the UV irradiation, polymerized thermally at 120 °C for 5 h by the action of the diaryliodonium salt that acted as thermal initiator, copolymerizing at the same time with the polysulfide with epoxycyclohexyl pendant groups (see scheme 4). The obtained solid and rigid polymers were analyzed by DMA to determine the viscoelastic properties. In the following table are shown the components of the formulation that were first irradiated with UV light of 15 mW cm⁻² during 5 minutes and the obtained polymers were subjected to thermal treatment in an oven at 120 °C for 5 hours

Sample	Monomers used in the formulation	Equivalent ratio
F1	PETKMP: HDDA: 3,4-EP : M1 : DPPI: DMPA	1 : 2 : 2 : 1 : 0.01 : 0.01
F2	PETKMP : HDDA : 3,4-EP : DPPI : DMPA	1 : 2 : 2 : 0.01 : 0.01
F3	PETKMP : TAC : 3,4-EP : M1 : DPPI : DMPA	1 : 1.3 : 2 : 1 : 0.01 : 0.01
F4	PETKMP : TAC : 3,4-EP : DPPI : DMPA	1 : 1.3 : 2 : 0.01 : 0.01

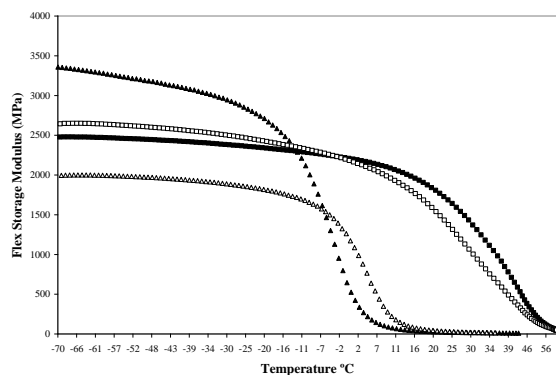


Figure 1. Comparison of the storage modulus of the polymers obtained from the following samples: F1(▲); F2 (△); F3 (□); F4 (■)

It can be seen in figure 1 that the formulations F1 and F3 where the coupling agent M1 was added showed an increment in the storage modulus in comparison with the formulations F2 and F4 that did not include M1. This increase in the storage modulus was due to the incorporation of the epoxy polymer onto the already formed polysulfide. In other words, the coupling agent induced the copolymerization of epoxy monomer with the polysulfide. The differences in the values of storage modulus between F1 and F3 are due to the different level of crosslinking achieved in both cases. In F1 was used a difunctional monomer the hexanediol diacrylate (HDDA) while in formulation F3 it was used a trifunctional acrylate, the pentaerythritol triacrylate (TAC).

6. Conclusions

The use of the coupling agent M1 improved the mechanical properties of the polymers obtained by polymerizing a hybrid formulation that included the components of thiol-ene and cationic systems. This improvement in storage modulus was the result of the copolymerization of the polyether derived from the cationic system with the polysulfide from the thiol-ene photocurable system.

7. References

1. Acosta Ortiz, R.; Garcia, A.E.; Berlanga, M.L.; Ovando, L.R.; Guerrero, R. Soucek, M.D.; Macromol Chem & Phys, 2008, 209, 20, 2157-2168