

1-Precise Polymer Synthesis and Polymer Modification

The Preparation of Copolymers Derived from Thiol-ene/Cationic Systems by Using a Coupling Agent

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Summary: A bifunctional monomer with methacrylate and epoxycyclohexyl groups linked by a tetramethyldisiloxane moiety was used as a coupling agent for dual photo and thermally 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.

Keywords: cationic; copolymers; coupling agent; Thiol-Ene

Introduction

The need for new materials with improved properties has led to the development of new techniques of polymerization. One of these techniques is the concurrent or sequential polymerizations where two different mechanisms are involved. These hybrid 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 either and the resultant polymers display excellent mechanical and physical properties. Therefore, it was of interest to combine the properties of both systems to obtain a hybrid material with enhanced properties. 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 act as a link between the polymers obtained from both the thiol-ene and the cationic systems.

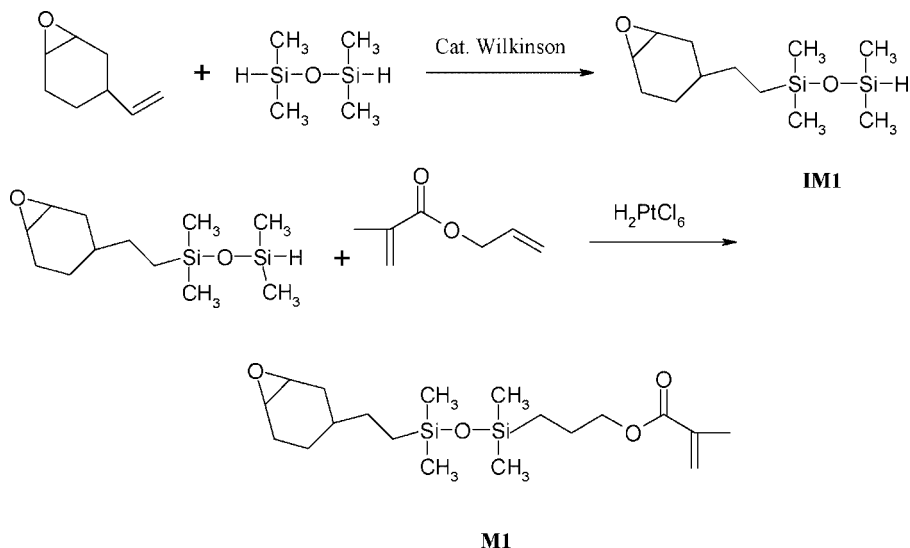
Experimental Part

Materials

To synthesize the coupling agent M1 the following reagents were used:

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Scheme 1.

Synthetic methodology to prepare M1.

1,1,3,3-Tetramethyldisiloxane, 4-Vinyl-1-Cyclohexene-1,2-epoxide, Allyl methacrylate, chloroplatinic acid and Tris(triphenylphosphine) rhodium (I) chloride (Wilkinson catalyst). They were purchased from Aldrich Chemical Co and used as received. The monomer M1 was prepared according to the method reported previously.^[1] In the photopolymerization studies the following monomers and photoinitiators were used: 1,6-hexanedioldiacrylate (HDDA), pentaerythritol triacrylate (TAC), pentaerythritol tetrakis (3-mercaptopropionate) [PETKMP], 3,4-epoxycyclohexyl methyl 3',4'-epoxycyclohexane carboxylate (3,4-EP) were all reagent-quality purchased from Aldrich Chemical Co and used as received. The onium salt cationic photoinitiator, (4-n-decyloxyphenyl) phenyliodonium (DPPI) hexafluoroantimonate, was prepared according to a method reported elsewhere.^[2] The radical photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) was purchased from Aldrich. Routine infrared spectra and photopolymerization kinetics were performed on a Magna Nicolet 550 Infrared spectrometer (Middletown, WI). Viscoelastic properties were determined on a Dynamic Mechanical Analyzer (DMA Rheometrics Scientific)

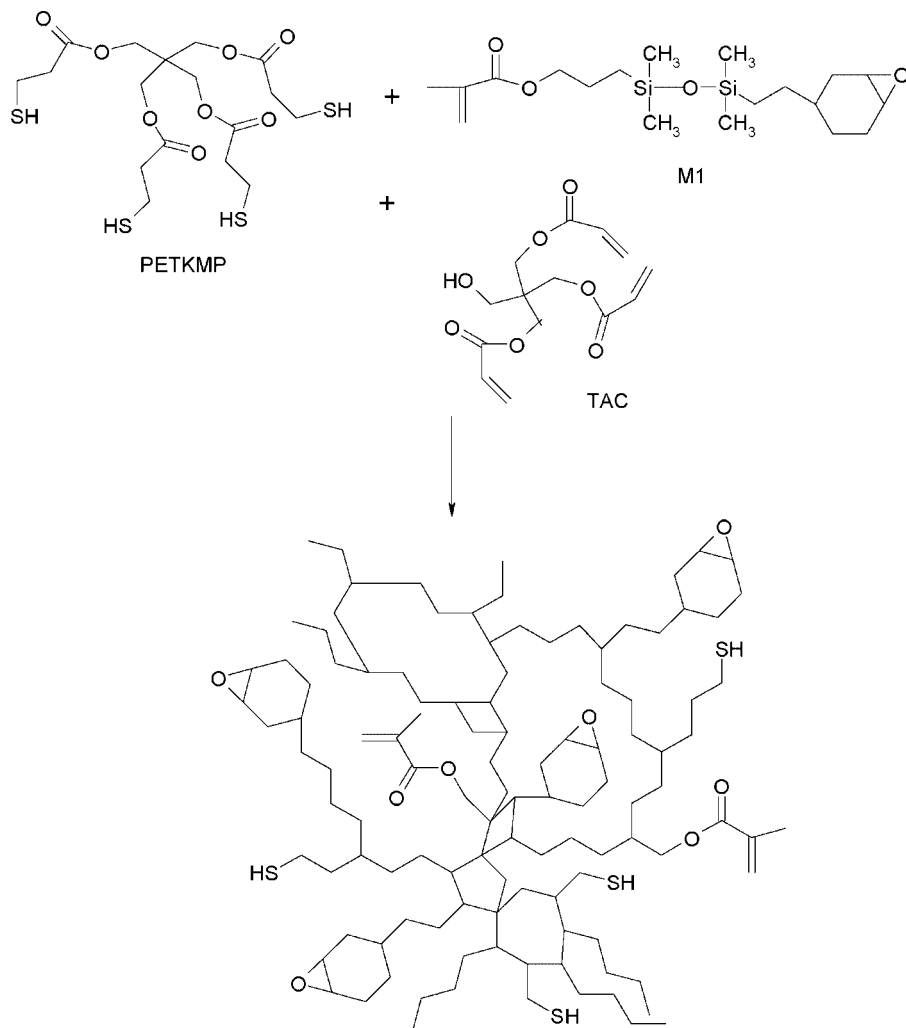
with a frequency of 1 Hz and a heating rate of 5 °C/min over a range of –70 °C to 200 °C in nitrogen. The film geometry was 5 × 25 mm with a thickness of 2 mm.

Synthesis of the Coupling Agent M1

The coupling agent was prepared using a method that involves two consecutive hydrosilylation 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 1). 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 hydrosilylation reaction with allyl methacrylate using chloroplatinic acid as catalyst. The final compound was obtained in 57% yield.

Photopolymerization Study

Previous investigations demonstrated the feasibility to obtain novel hybrid materials by combining the thiol-ene and the cationic systems.^[3,4] It was found that when a formulation containing the components of

**Scheme 2.**

First stage of the photopolymerization of M1 with PETKMP and TAC.

both systems was irradiated with UV light only the thiol-ene system polymerized, letting most of the epoxy monomer without reacting. The nucleophilic character of the generated polysulfides inhibited the cationic polymerization in its early stage. The unreacted epoxy monomer acted as a plasticizer obtaining a rubbery material. After a thermal treatment at 120 °C for 5 hours the epoxy monomer polymerized completely resulting in a rigid material.

Bearing these results in mind, it was anticipated that a bifunctional monomer such as M1 could induce the formation of a

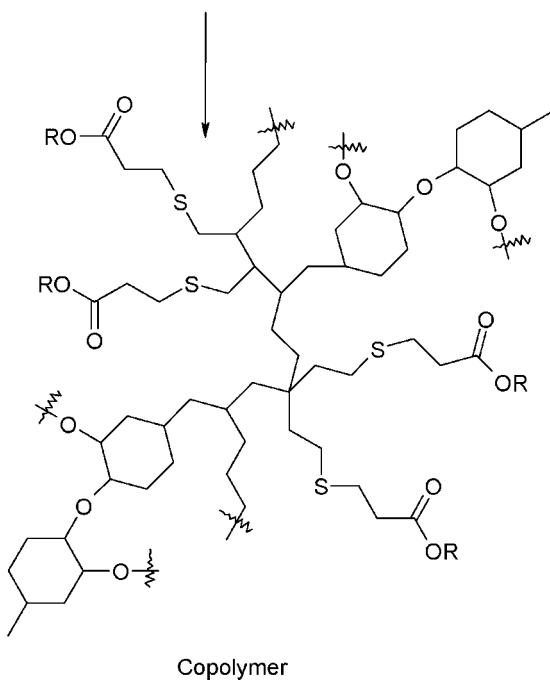
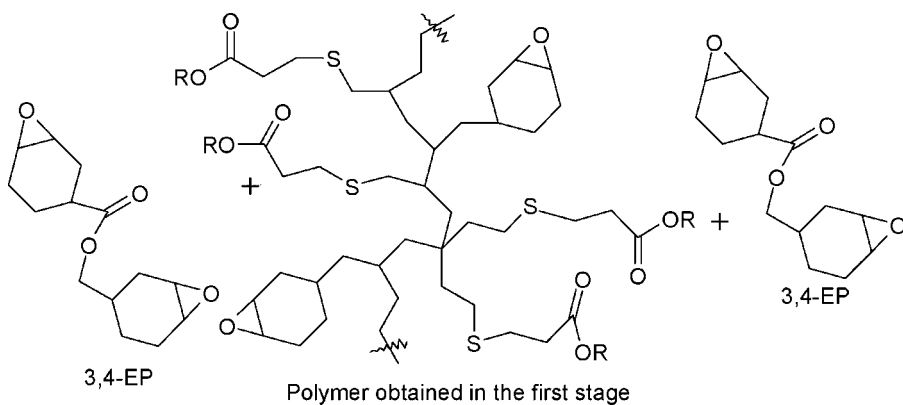
copolymer. The methacrylic group of coupling agent M1 could react in a first stage with the components of the thiol-ene system. This could give rise to a polysulfide with pendant epoxycyclohexyl groups. These groups can react further in a second stage with the epoxy monomer of the cationic system, polymerizing by means of a thermal treatment.

Then, a formulation with 1 equivalent of PETKMP, 1.3 equivalents of TAC, 1 equivalent of M1, 2 equivalents of 3,4-EP and 0,01 equivalents of photoinitiators DMPA and DPPI was irradiated with

UV light. 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 reaching 85% conversion. The monomer M1 was incorporated in the obtained polymer, resulting in a polysulfide with pendant epoxycyclohexyl groups (see in Scheme 2 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.

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



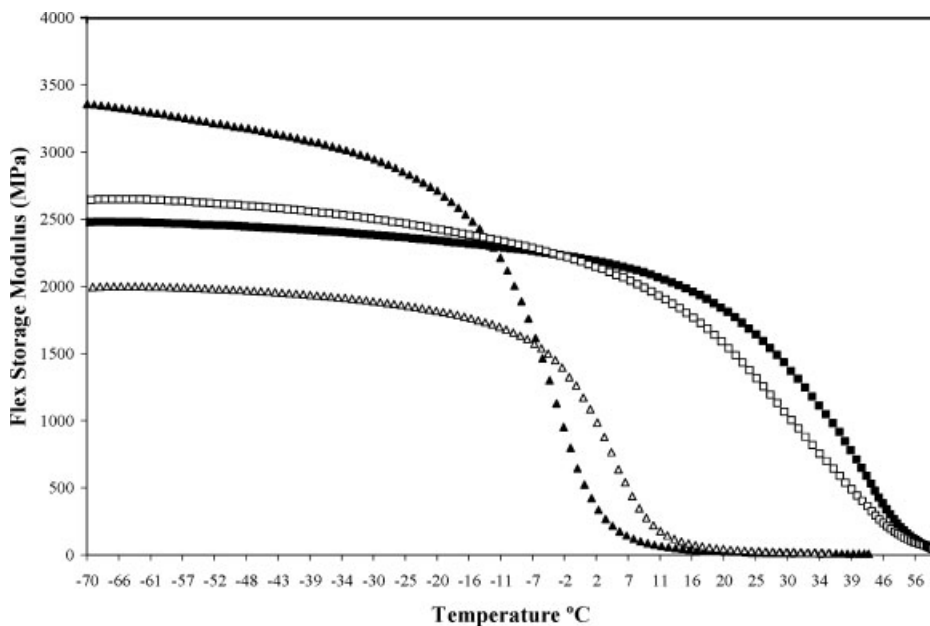
Scheme 3.

Formation of the copolymer in the second thermally initiated stage.

Table 1.

Monomers and photoinitiators used in the studied formulations

Sample	Formulation			Ratio	
	Thiol-Ene	Cationic	Photoinit.	Monomers	Photoinit.
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 (■).

same time with the polysulfide with epoxycyclohexyl pendant groups (Scheme 3).

DMA Study

The copolymers were analyzed by DMA to determine their viscoelastic properties. In Table 1 are shown the components of the formulations 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.

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 included M1. This increase in the storage modulus was due to the reinforcement of the viscoelastic properties as a result of the incorporation of the polyether onto the already formed polysulfide. Here, is noteworthy the effect of the chemical bonding of the polyether to form the copolymer in comparison to the samples where no coupling agent was added. 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

HDDE, that is a difunctional monomer, was used, while in formulation F3 it was used TAC that is a trifunctional one.

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.

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