

Multifunctional secondary thiols for UV curing applications

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Abstract

Multifunctional thiols are highly efficient in photoinitiated free radical reactions. Due to the radical chain transfer effect of the mercapto group, they are capable of reducing oxygen inhibition, and can improve the photosensitivity with a small amount of additive. However, the utility of thiol compound is limited by its characteristic odor and a lower pot life in composition with ene compounds. In this paper, we introduce a multifunctional secondary thiol that can address these challenges through presenting reduced odor, and a longer pot life when prepared with the ene compounds. This improved stability is benefited by the steric hindrance of methyl group adjacent to mercapto group.

Introduction

Research of thiol chemistry has been ongoing for a long time. Studies on the free radical reaction of thiols were started in the 1930s^{1,2}, and an excellent review was reported in 1974³. In addition, several reviews addressing photoinitiated free radical reactions using thiol compounds were published since 1993^{4,5}. These reviews highlighted very interesting reports on the kinetics, polymerization processes, storage stability of compositions, odors, applications, etc., regarding the reaction of thiols. In this paper, we report on the characteristics of multifunctional secondary thiol.

Reaction mechanism of thiol compounds

Thiols are known to function as chain transfer agents in free radical reactions⁶. This is due the hydrogen of SH bond, which possess relatively weak bonding energy, can be easily dissociated to form a thiyl radical. The SH group also behaves as a hydrogen donor to the inactive peroxy-radical, thus reducing oxygen inhibition in free radical reactions⁶. In particular, α - and β -mercaptoester types are considered to have a stronger effect as a chain transfer agent because the sulfur-hydrogen bond is weakened by the hydrogen bond between the mercapto and carbonyl group⁷. The thiyl radical plays a critical role in promoting reactions with various unsaturated bonds. For example, compound such as an allyl monomer, which hardly undergoes self-polymerization, proceeds polymerization in a Figure 1 cycle. This is similar to the pathway of Michael addition reaction to enes caused by the thiolate anion⁸. In addition, the polymerization reaction

of a composition containing a compound that undergoes self-polymerization, such as a (meth) acrylic monomer, can proceed via the Figure2 route⁵.

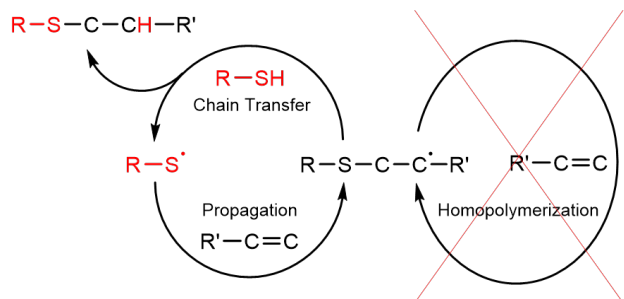


Figure1 The idealized free-radical thiol-ene reaction with alternating chain transfer and propagation.

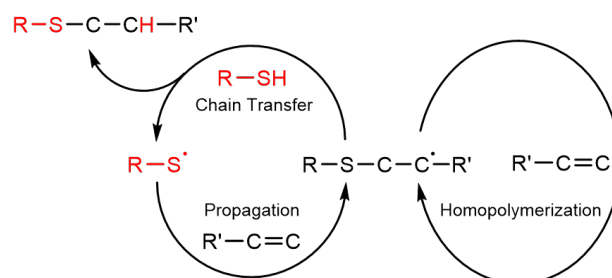


Figure2 Cycles showing reactions of thiol-acrylate and thiol-ene-acrylate polymerization.

History of multifunctional secondary thiols

In the early 2000s, multifunctional secondary thiols were first reported for industrial application⁹. According to this report, secondary multifunctional thiol compounds are synthesized in an esterification reaction between organic acids having a secondary mercapto group and multifunctional alcohol compounds. The multifunctional secondary thiol compounds that are industrially available are shown in Figure3.

In addition, since the inhibition of hydrogen abstraction reaction by the steric hindrance of methyl group adjacent to the mercapto group suppressed the thiol reactivity, multifunctional secondary thiols can generate photo-polymerizable composition with high sensitivity and excellent pot life^{10,11}. Figure4 shows a comparison of the pot life at 60°C of dipentaerythritol hexaacrylate (DPHA) and multifunctional thiol compositions. It can be confirmed that the improved pot life is associated with the application of secondary thiols.

Ene compounds

As aforementioned, various ene compounds can be used for the free radical reaction with thiols. With some exceptions, the reactivity of thiyl radicals for various enes is known to correlate with the electron density of double bonds^{4,7}. In particular, allyl and (meth) acrylic compounds have been applied in electronics application and 3D printing applications because of their moderate stability with multifunctional thiols compounds, and a wide range of available materials¹¹⁻¹⁵.

UV sensitivity of composition

Multifunctional thiols can increase the sensitivity of the composition of UV curable resin through the chain transfer effect. This is highly associated to the fact that the thiyl radical consumes an inactive peroxy radical and polymerization-inhibitor radical existing in the composition and changes it to an active radical. Figure5 shows a comparison of the UV sensitivity when 2 wt% multifunctional thiols are added to acrylic monomer (EO-modified bisphenolA diacrylate) with 2 wt% photoinitiator (2-hydroxycyclohexyl acetophenone). It was evaluated by tracking the viscosity change as a function of time through a photorheometer. It should be stressed that, the sensitivity of the compositions which the thiol compound was incorporated is significantly improved as compared with when thiol was not added. Regarding to the degree of

improvement in the sensitivity, the most responsive primary thiol is followed by PEMB, where a high number of functional groups makes a significant contribution. This observation can be explained by a high number of functional groups contributes a significant gain of crosslinking density during the course of reaction.

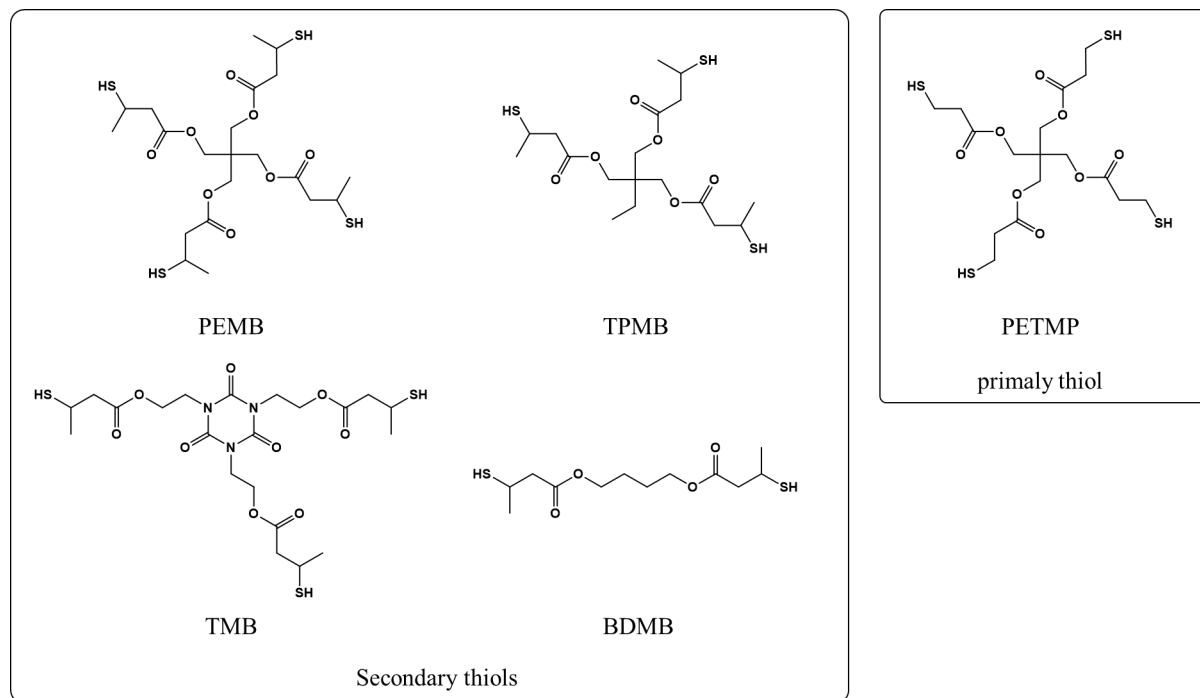


Figure3 Structure of thiols

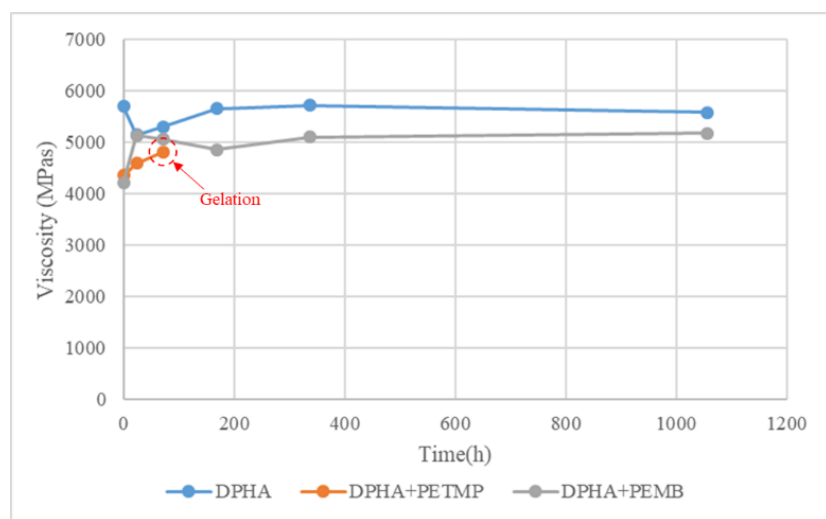


Figure4 Comparison of stabilities between primary and secondary thiols.

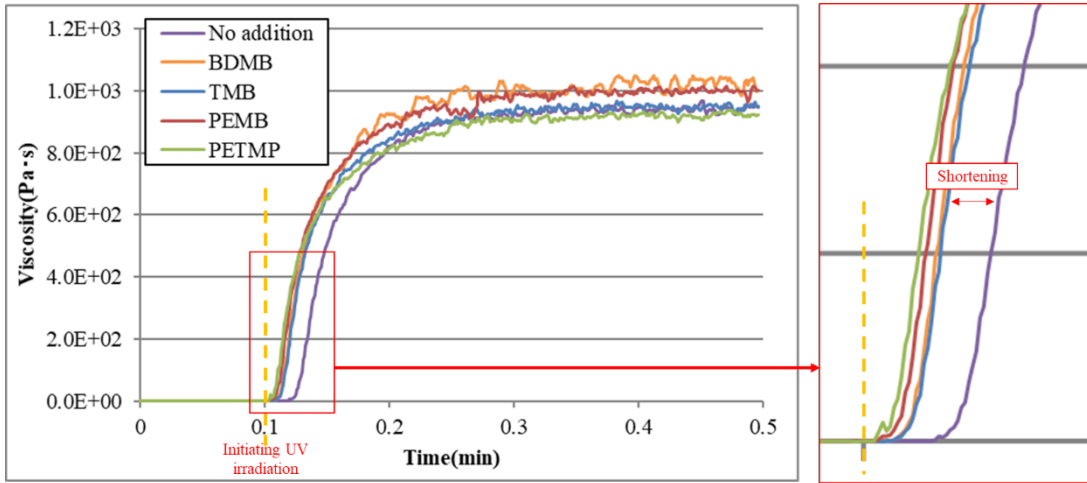


Figure5 Comparison of sensitivities between primary and secondly thiols.

Properties of cured resin by thiol-ene reaction using allyl monomer

The thiol-ene reaction is a class of click reaction⁵ with homogeneous crosslinks compatible, therefore the reaction positively impacts the toughness of the cured product. Figure6 shows a comparison of the breaking strength and the elongation of the cured resin between thiol-ene compositions (TMB and an allyl monomer) and commercially available acrylates. Based on the mechanical characterization, the cured thiol-ene composition achieves both high levels of strength and elongation as compared to the cured acryl resin.

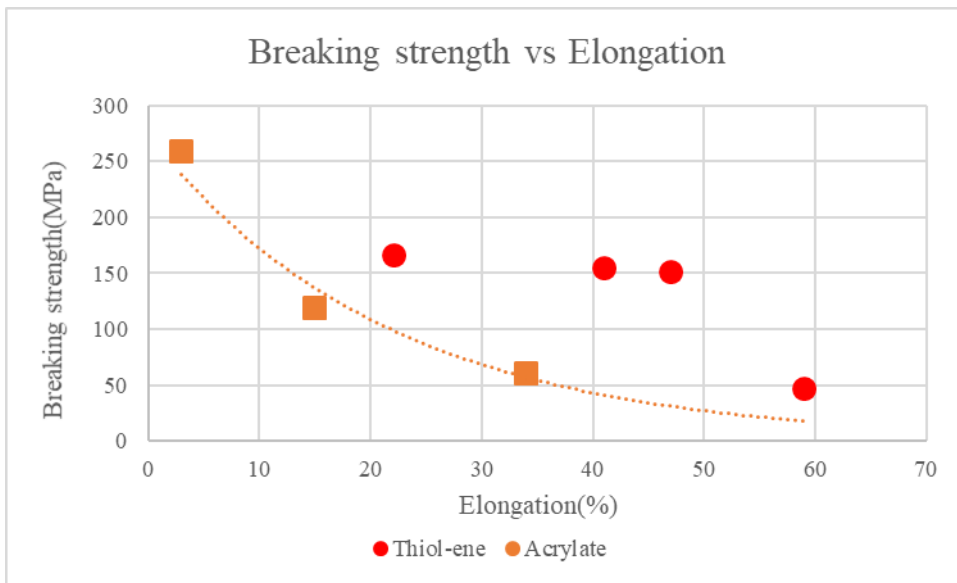


Figure6 Comparison of mechanical properties

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