Soluble and Red-Shifted Sulfonium Salts

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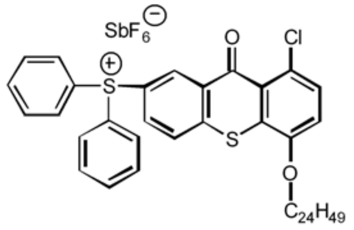
Introduction

One of the primary functions of a UV photoinitiator in Adhesive Industry is to initiate chemical crosslinking reaction or polymerization under UV irradiation. There are two main types of photoinitiators that can be used to initiate UV crosslinking reaction or photopolymerization in adhesive compositions containing UV reactive monomers or prepolymers - radical photoinitiators and cationic photoinitiators. The most frequently used cationic photoinitiators are either organic iodonium or sulfonium salts. Generally speaking, sulfonium salts are more thermally stable than iodonium salts at an elevated temperature and therefore are more often used in adhesive formulations, especially hot melt adhesives. A probable mechanism by which a cationic photoinitiator acts, upon UV irradiation, is that it forms an excited state and then breaks down to a radical cation. This radical cation interacts with a hydrogen donor, such as solvent or other components in the formulation, and eventually forms a protonic acid H^+B^-. The active species that initiates the crosslinking reaction or polymerization is this H^+ ion, and its reactivity towards crosslinking reaction strongly depends on the nucleophilicity of the anion B^-. In this article, we report new types of soluble and red-shifted sulfonium salts. These sulfonium salts can be used not only in adhesives, but also in inks or coatings containing epoxy and vinyl ether functional groups.



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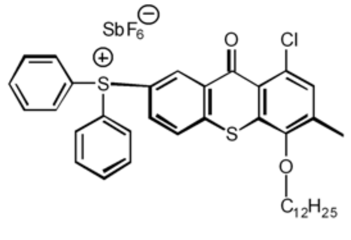

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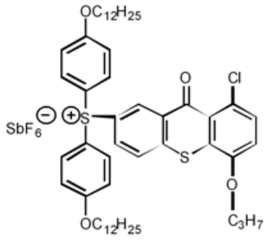

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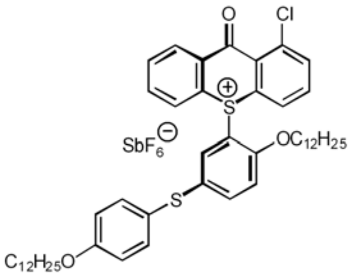

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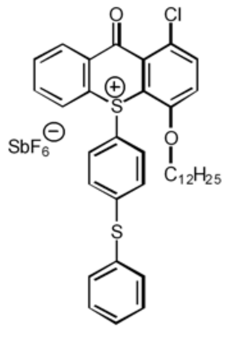

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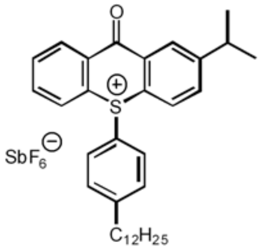

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Figure 1. Soluble and Red-Shifted Sulfonium Salts.

Structure and Synthesis of the Sulfonium Salts

We synthesized a series of sulfonium salts and their chemical structures are shown in Figure 1. They all can be prepared in a similar way. The preparation of sulfonium salt **1** is one step reaction from 1-chloro-4-(2-decyltetradecyl-1-oxy)thioxanthone and diphenylsulfoxide. A solution of the corresponding 1-chloro-4-(2-decyltetradecyl-1-oxy)thioxanthone (1.68 g, 2.8 mmol), diphenylsulfoxide (0.57 g, 2.8 mmol) in dichloromethane (50 mL) was stirred at 10-20º C. Eaton's reagent (P_2O_5/MSA 1:10) (20 mL) was added slowly. The reaction was then warmed to room temperature and stirred for 48 h. Water (30 mL) and $NaSbF_6$ (0.8 g, 2.9 mmol) were then added and the mixture was stirred at room temperature for additional 12 h. The mixture was washed with water and the organic layer was dried with $MgSO_4$. After removal of the solvent, the obtained solid was recrystalized from MeOH to give sulfonium salt **1** as a yellow crystalline solid (1.9 g, 66%). The structure of the product **1** was confirmed ^{1}H, 13C, dept, copy, tocsy and mass spectroscopy.

Sulfonium salt **5** was prepared in a slightly different way. The sulfur at 10-position of 1-chloro-4-dodecyloxy-thioxanthone was firstly oxidized to form sulfoxide. A solution of the obtained 1-chloro-4- dodecyloxy-10-oxythioxanthone (5.0 g, 0.016 mol) in acetonitrile (400 mL) and water (80 mL) was stirred at room temperature. Ammonium cerium (IV) nitrate (44 g, 0.080 mol) was added and the resulting mixture was stirred for 2 h at room temperature. The reaction was followed by LC-MS. The resulted 1-chloro-4- dodecyloxy-10-oxythioxanthone reacted with diphenyl sulfide in a similar way of making **1** to give sulfonium salt **5**. The product was further purified by recrystallization from MeOH at -20º C to give pure **5** in more than 50 % yield. The ^{1}H NMR of **5** was shown below.

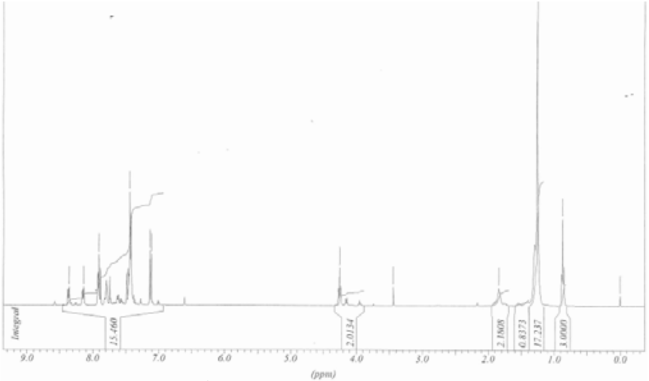

Figure 2. ^{1}H NMR of Sulfonium Salt **5**.

Characterization and Properties

All sulfonium salts in Figure 1 are red-shifted because they contain thioxanthone chromaphor. The UV spectrum of **5** is shown in Figure 3, as an example. Most of these sulfonium salts usually have three distinction UV absorbance peaks λ_{max} = 250-260 nm, ε_{max} = ~50,000; λ_{max} = 300-310 nm, ε_{max} = ~25,000 and λ_{max} = 360-380 nm, ε_{max} = ~10,000. Experiments showed that the sulfonium salts can effectively initiate UV crosslinking reaction of epoxidized acrylic monomers or rubbers in adhesive formulations through glass, PET film, and even in the presence of TiO_2 fillers.

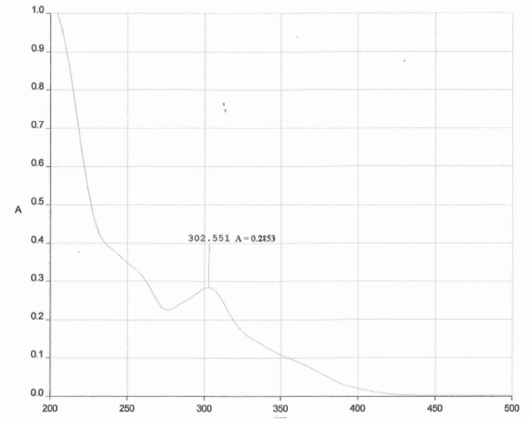

Figure 3. UV Absorbance of Sulfonium Salt **5**.

Another feature of these sulfonium salts is their good solubility in hydrophobic formulations. The length and the numbers of the alkyl or alkoxy groups attached to the aromatic rings of the sulfonium salts can be chemically changed according the solubility requirements of formulations. An example of hydrophobic polymer is Kraton liquid L-207 polymer. L-207 is made of a diblock copolymer of isoprene and butadiene, followed by partially epoxidation and hydrogenation. Commercial sulfonium salt UVI-6974 in 50% propylene carbonate will initially form a fine dispersion in L-207 polymer when mixed together in a fast speed. When a simple formulation of L-207 containing 0.5% wt UVI-6974 was freshly made, a film was coasted with a smooth texture and it cured fast upon UV irradiation, as shown in Figure 4 and 5. However, if the formulation or the film was heated to 110°C for 2 hr, the sulfonium salt was recrystalized and precipitated out from L-207 polymer. Photo DSC showed that the UV cure rate of the formulation was dramatically reduced (Figure 5).

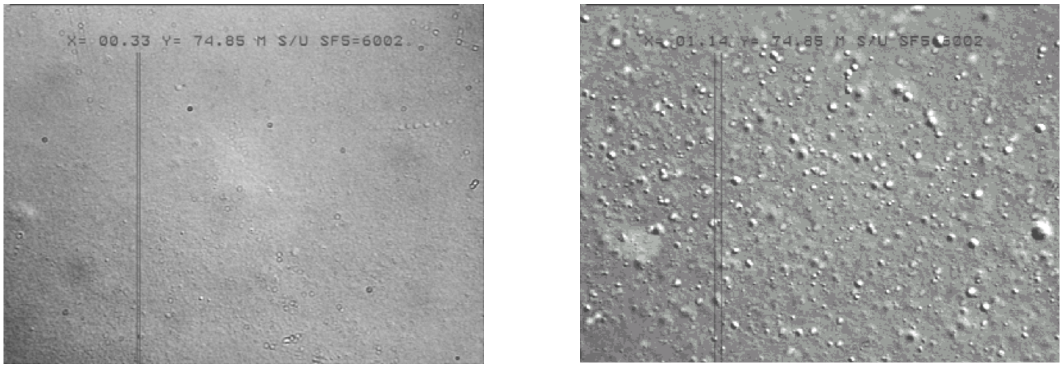

Figure 4. Freshly Prepared Film (Left), Rough film After Heating at 110°C, 2 h (Right)

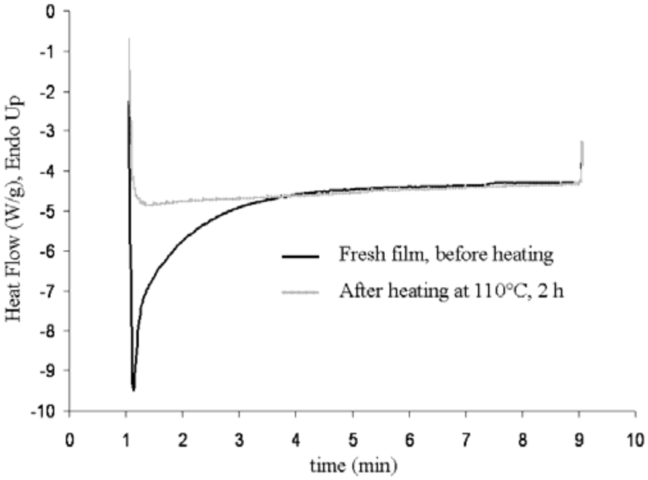

Figure 5. Photo DSC of L-207 in the Presence of 0.5%wt UVI-6974.

All sulfonium salts in Figure 1 have an improved solubility in L-207. When 0.5% wt of any of the sulfonium salts was mixed with L-207, the formulations were usually clear at room temperature. Most of them remained clear even when heating at 110°C for > 2 hr. No crystallization of the sulfonium salts was observed upon heating. Furthermore, these sulfonium salts demonstrated a fast UV cure rate. Figure 6 showed a cure rate comparison of three cationic photoinitiators by photo DSC. All formulations were made of L-207 mixing with 0.5% wt of photoinitiator and they were analyzed by photo DSC under the same UV irradiation condition. UVI-6974 was a commercial sulfonium salt and UV9380C was commercial iodonium salt. As seen in Figure 6, photo DSC showed the UV cure rate of the sample containing sulfonium salt **5** was much faster than samples containing UVI-6974 and UV9380C.

The sulfonium salts in Figure 1 have very low or no smell after UV irradiation. It is obvious from their chemical structures. Most of these sulfonium salts decomposed upon irradiation and generated low vapor pressure photolysis products. The commercially available sulfonium salt UVI-6974 produces sulfide and benzene after photodecomposition. Not surprisingly, none of the sulfonium salts in Figure 1 produces benzene upon UV irradiation.

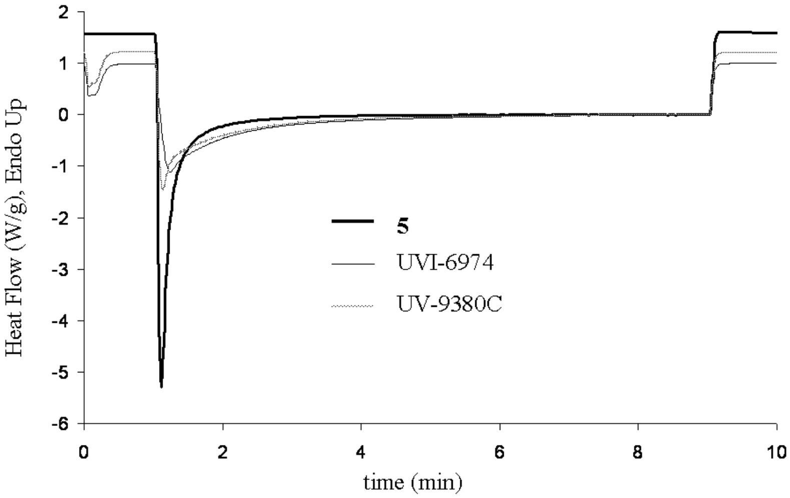

Figure 6. Photo DSC of L-207 in the Presence of 0.5% wt of **5**, UVI-6974, and UV-9380C.