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Flame retardant thiol–ene photocured coatings

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ABSTRACT

The low polymerization tendency of allyl compounds can be enhanced by thiol–ene polymerization systems. In this study, allyldiphenyl phosphine oxide (ADPPO) containing thiol–ene based photocured coatings were prepared with the aim to improve their final thermal and flame retardant properties. The photopolymerization kinetics of thiol–ene based formulations were investigated by real-time infrared spectroscopy. The incorporation of ADPPO into the polymer chains was confirmed by monitoring the conversion of acrylate double bonds and measuring the gel content of the crosslinked films. The experiments showed that as the amount of ADPPO was increased, thermal and flame retardant properties of the coatings were also increased.

1. Introduction

Since long it has been shown that allyl compounds polymerize with difficulty and give polymers in low yields and with low molecular weights. It is also accepted that the low molecular weights of homopolymerized allyl compounds are due to the degradative chain transfer to monomer [1].

Thiol–ene polymerization systems in which thiols add to double bonds, e.g. vinyl, allyl, acrylate, methacrylate, have gained a lot of interests from industry and researchers in the last years [2].

Thiol–ene polymerization reactions have superior features such as; photoinitiatorless curing, reduced oxygen inhibition and fast curing, improved adhesion and low shrinkage. In addition, as a result of step-growth mechanism, high viscosities are observed only at high conversions. Moreover, one of the most remarkable features of thiol–ene photopolymerization is that almost any type of ene monomer can be polymerized. Beside these distinct properties; thiol odor, the storage and shelf-life stability of thiol–ene monomer mixtures, the stability of networks formed from thiol–ene polymerizations, low stiffness, low strength and low T_g values can be counted as the disadvantages of the thiol–ene systems. However, low strength and low T_g of the thiol–ene systems can be enhanced by using dendrimers and hyperbranched species and thiol odor can be resolved by using masking agents and low odor thiols [3–9].

Also thiol–ene chemistry allows researchers to synthesize several molecules via click reactions. There are several articles in literature which discuss the mechanism and kinetics [10–12].

Development of flame retardant polymeric materials has become of great importance due to rapid improvement in technology in recent years [13]. Flame retardant polymers can be prepared by the addition of flame retardant additives to the polymer or by attaching flame retardant compounds to the polymer with chemical bonds [14]. The use of flame retardant additives requires high loading to achieve a sufficient level of flame retardation and halogenated flame-retardants generate toxic and corrosive fumes during combustion while chemically bonded compounds can be effective in small amounts [15,16].

When compared with halogen type flame-retardants, phosphorus containing compounds were found to generate less toxic gases and smokes during combustion [17]. Also chemically incorporated phosphorus-containing monomers improve flame retardancy. Thus phosphorus-containing monomers are widely used in flame retardant coatings.

In one of our previous articles we investigated the effect of allyldiphenyl phosphine oxide (ADPPO) on the flame retardancy properties of epoxy acrylate coatings [18]. As a result it was found that ADPPO, instead of undergoing polymerization, undergoes intramolecular dimerization. The tendency of the ADPPO to form dimers, prevented its polymerization within epoxy acrylate resin and caused the gel content to decrease. Thus, its effect on the flame retardancy of the coatings was lower than it was expected.

Therefore in this study we used thiol–ene polymerization system for the preparation of ADPPO containing UV curable coatings and investigated their thermal stability, mechanical and flame

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retardant properties. The main purpose is to increase the low polymerization trend of the monoallyl monomer in coating formulations by using thiol–ene polymerization system.

2. Experimental

2.1. Materials

Triphenyl phosphine and allyl bromide were purchased from Fluka and used as received. 1-Hydroxy cyclohexyl phenyl ketone (Irgacure 184) was obtained from Ciba Specialty Chemicals. Toluene and acetone were received from Merck and they were dried with standard procedures prior to use. Trimethylolpropane tris (3-mercaptopropionate) (TMPMP) was purchased from Aldrich and used as received. CN-922 (a modified aliphatic urethane triacrylate) was purchased from Sartomer.

2.2. Characterization

FT-IR spectrum was recorded on Perkin–Elmer Spectrum100 ATR-FTIR spectrophotometer.

Gel contents of the UV-cured films were determined by Soxhlet extraction for 6 h using acetone. Insoluble gel fraction was dried in vacuum oven at 40 °C to constant weight and the gel content was calculated.

Thermogravimetric analyses (TGA) of the UV-cured free films were performed using a Perkin–Elmer Thermogravimetric analyzer Pyris 1 TGA model. Samples were run from 30 to 700 °C with heating rate of 10 °C/min under air atmosphere.

DSC measurements were performed using Pyris Diamond DSC. Samples were run from −50 to 200 °C with a heating rate of 10 °C/min.

The polymerization conversion was followed by real-time infrared spectroscopy. Experiments were performed using a Perkin–Elmer ATR-FTIR spectrophotometer. Conversion rates were calculated according to the decrease of IR absorption band at 2570 cm^{-1} for thiol and 1630 cm^{-1} for allyl groups. Mixtures were spread on KBr disks and absorption data were collected while UV light was applied on samples. The percentage conversions were calculated by using the following equation:

$$\text{Conversion}\,\% = 100\,[1 - (A_t/A_o)] \tag{1}$$

where A_o is the initial absorbance of allyl or thiol bonds and A_t is the absorbance of the functional groups at time t.

SEM imaging of the films were performed on Philips XL30 ESEM-FEG/EDAX. The specimens were prepared for SEM by freeze-fracturing in liquid nitrogen and applying a gold coating of approximately 300 Å.

The wettability characteristics of free films were performed on a Kruss (Easy Drop DSA-2) tensiometer. The contact angles (θ) were measured by means of sessile drop test method in which drops were created by using a syringe. Measurements were made using 3–5 μl drops of distilled water and diiodomethane.

Mechanical properties of the UV-cured free films were determined by standard tensile stress–strain tests to measure modules, ultimate tensile strength and elongation at break. Standard tensile stress–strain experiments were performed at room temperature on a Materials Testing Machine Z010/TN2S, using a crosshead speed of 5 mm/min.

The LOI values of the coating materials were measured by using a FTT (Fire Testing Technology) type instrument, on the test specimen bar of 120 × 60 × 3 mm^3 according to ASTM D2863-08.

2.3. Synthesis of allyldiphenyl phosphine oxide (ADPPO)

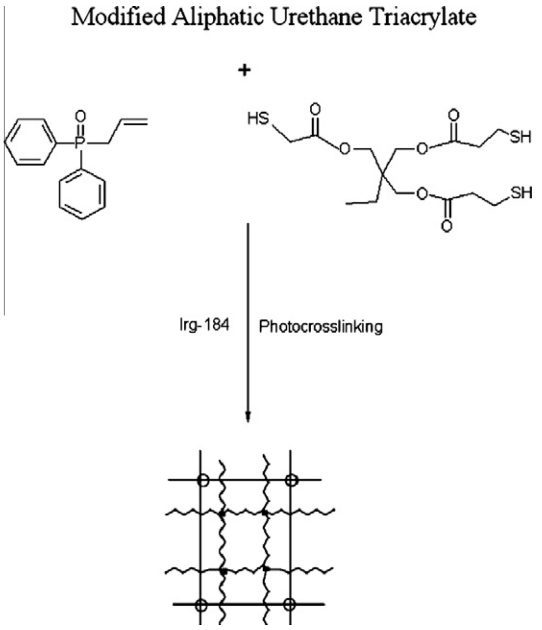
ADPPO was synthesized as described in our previous literature [5]. Briefly, triphenyl phosphine (0.125 mol, 32.79 g) and allyl bromide (0.137 mol, 16.68 g) dissolved in 125 ml of dry toluene, was charged into 1 L round-bottom flask. The reaction mixture was then heated to reflux (at about 110 °C) for 2 h, and then cooled to room temperature. The phosphonium salt as a white powder product was filtered and washed several times with diethyl ether. The product was then refluxed in 225 ml of water for half-an-hour. After this, into the opaque suspension 2.77 M, 225 ml of NaOH aqueous solution was added and gently refluxed for an additional 2 h. After cooling, the mixture was extracted with chloroform and the organic phase was dried with sodium sulphate. The solvent was evaporated off under vacuum. After recrystallization from hexane–diethyl ether, the desired product as a white crystalline solid was obtained.

2.4. Preparation of the polymeric free films

The composition of thiol–ene based photocurable formulations is given in Table 1. Each formulation was prepared in a 10-ml beaker with adequate stirring. Then formulations were kept in an oven at 60 °C until they became clear and homogeneous. Free films were prepared by applying the UV-curable viscous formulations onto a Teflon™ coated mold (10 mm × 50 mm × 1 mm). In order to prevent the inhibiting effect of oxygen, resin in the mold was covered

Table 1
Compositions of the films. Irg-184 was added at 1 wt.% of the total weight for all formulations except for Control 2 in which it was added at 3 wt.% of the total weight.

Samples	CN-922 (g)	TMPMP (g)	ADPPO (g)	Irg-184 (g)	*P* (%)	Gel (%)
Control 1	1	0.5	–	0.015	–	97
F1	1	0.5	0.2	0.017	1.1	98
F2	1	0.5	0.4	0.019	2.2	97
F3	1	0.5	0.6	0.021	3.3	98
F4	1	0.5	0.8	0.023	4.4	96
Control 2	1	–	0.2	0.036	2.1	91



Scheme 1. Formation of photocrosslinked thiol–ene based flame retardant coatings.