

# Renewable Monomer Based on Rosin in Photoinitiated Radical Polymerization

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**Abstract** : Rosin moiety-containing monomer was prepared by the reaction of abietic acid with 2-hydroxyethyl methacrylate in tetrahydrofuran(THF) using diethyl azodicarboxylate as a catalyst. This new monomer was photo-polymerized to give thin films in the presence of a radical type initiator. The rate of photo-polymerization and amount of cured polymer were determined using the residual yield method. A thermogravimetric analysis of the cured polymer showed that the film was stable up to 170 °C, at which point the polymer film has lost 10 wt % of its weight.

## 1. INTRODUCTION

In recent years, a growing interest on chemical research is to develop polymeric materials, which were environmentally compatible. Many synthetic and natural polymers have been tested for environmental compatibility.<sup>1-3)</sup> One interesting discovery is that synthetic polymers that biodegrade tend to have structure similar to those found in naturally occurring polymers, suggesting that the enzymatic activities produced by microorganisms may not differentiate between polymers of similar structure.<sup>4, 5)</sup> Accordingly, structure-modified monomers that come from renewable resources instead of petrochemical sources are particularly attractive. At the same time, there is also a demand that curing processes employ energy efficient, nonpolluting methods. UV curing is based on the photoinitiated polymerization of functional monomers into a crosslinked polymer network.<sup>6, 7)</sup> This process is controlled by a photoinitiator system, which absorbs and converts UV light into reactive intermediates such as free radicals, radical ions, acids, and bases, initiate the

crosslinking process. Generally, an UV cure is comprised of 100% reactive monomers, which provide environmentally acceptable coatings. The utilization of UV curable monomers eliminates or reduces the need for solvent to achieve appropriate viscosity. In addition, UV cure can provide long term storage stability together with a lower curing temperature than corresponding thermo-curing.<sup>8-10)</sup>

On the other hand, rosin has been developed as intermediate of functional polymers and extensively used as a raw material, such as adhesive, print-ink, paint and then coating material for surface protection. Abietic acid is a major ingredient of rosin, which is obtained from pine trees. However, rosin by itself can not be used as a coating material due to its poor impact resistance.<sup>11, 12)</sup> Thus, it is used with an impact absorber to overcome this impact weakness, and needs a solvent to make liquid paste for easy use. In this study, we modified the molecular structure of abietic acid by the reaction of 2-hydroxyethyl methacrylate and examined it as a potential photo-crosslinkable monomer.

## 2. EXPERIMENTAL

### Materials and Measurements

Abietic acid (AA, Aldrich) was purified by recrystallization from ethanol/water mixture. 2-Hydroxyethyl methacrylate (HEMA, Aldrich) was purified by distillation under reduced pressure. Diethyl azodicarboxylate (DEAD, Aldrich) and 2,2-dimethoxy-1,2-diphenylethan-1-one (IRGACURE 651, Ciba-Geigy) was used without further purification. The <sup>1</sup>H-NMR data were recorded with a Jeol Lamda 300 spectrometer using CDCl<sub>3</sub> as a solvent. FT-infrared studies were performed on a Perkin-Elmer Model BX Infrared Spectrometer. A thermogravimetric analysis was obtained with the aid of a Cahn TG-131 Thermal System. The measurement was made at a heating rate of 20°C min<sup>-1</sup> in air.

### Preparation of Model Compound

**Ethyl Abietate:** A mixture of 3.00g (10mmol) of abietic acid and 1.14mL (20mmol) of ethyl alcohol in 70mL of THF under an atmosphere of nitrogen was treated dropwise with stirring 5.20g (20mmol) of triphenylphosphine in 20mL of THF. The diethyl azodicarboxylate (3.15mL, 20mmol) was added slowly, keeping at the temperature in the range of 0~25°C, and then the reaction mixture was stirred for an additional 1h. After removing THF using rotary evaporator, the resulting residue was dissolved in 50mL of methylene chloride and washed with 30ml of 5wt% aqueous sodium bicarbonate. The organic layer was dried over anhydrous magnesium sulfate and evaporated under reduced pressure to give a crude oil. This oil was purified using column chromatography (1:1 v/v hexane/ethyl acetate) to obtain 2.15g (yield: 65 %) of pure product. <sup>1</sup>H-NMR (300MHz, CDCl<sub>3</sub>): 6.0-5.0 (d, 2H, 2=CH), 4.5-0.8ppm (m, 32H, saturated CH). IR (NaCl): 3200 (vinyl C-H stretching), 2980 (saturated C-H stretching), 1720 (C=O stretching), 1591 (vinyl C=C stretching), 998 cm<sup>-1</sup> (vinyl C-H bending)

### Preparation of Rosin Modified Monomer (RMM)

To a stirred solution of 5.00g (16.5mmol) of abietic acid and 4.01mL (33mmol) of 2-hydroxyethyl methacrylate in 150mL of THF under N<sub>2</sub> at 25°C was added 8.66g (33mmol) of triphenylphosphine in 40mL of tetrahydrofuran. The diethyl azodicarboxylate (5.2mL, 33mmol) was slowly added dropwise at room temperature. After stirring for 1hr, the solution was evaporated to remove THF. The resulting residue was dissolved in 100mL of methylene chloride and washed with 50ml of 5% aqueous sodium bicarbonate. The organic layer was dried over anhydrous magnesium sulfate and evaporated under reduced pressure to give a crude oil. This oil was purified using column chromatography (1:1 v/v hexane/ethyl acetate) to obtain 4.11g (yield: 60%) of pure product. <sup>1</sup>H-NMR (300MHz, CDCl<sub>3</sub>): 6.2-5.0 (q, 4H, 4=CH), 4.5-0.8 ppm (m, 34H, saturated CH). IR (NaCl): 3100 (vinyl C-H stretching), 1720 (C=O stretching), 1640 (vinyl C=C stretching), 940 cm<sup>-1</sup> (vinyl C-H bending)

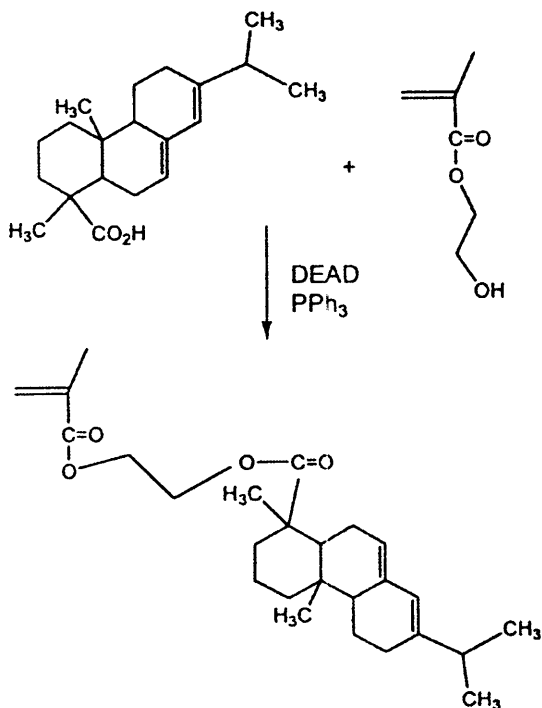
### Photo-Crosslinking Reactions

The following general procedure was performed for the photo-crosslinking studies. 1g of the monomer and 0.15mol % of the photoinitiator were placed in a 2mL vial. The photoinitiator was dissolved in the monomer by shaking and the mixture was placed onto glass plates. The photocrosslinking studies were carried out by drawing 5m films of the monomer containing the radical-type photoinitiator and then irradiating them at room temperature for 110 minutes using Spectra Energy, 200W mercury-xenon lamp mounted approximately at a distance 5cm from the samples. To isolate the crosslinked moieties, the irradiated samples were dipped into acetone for 1 minute and then dried in vacuum.

## 3. RESULTS AND DISCUSSION

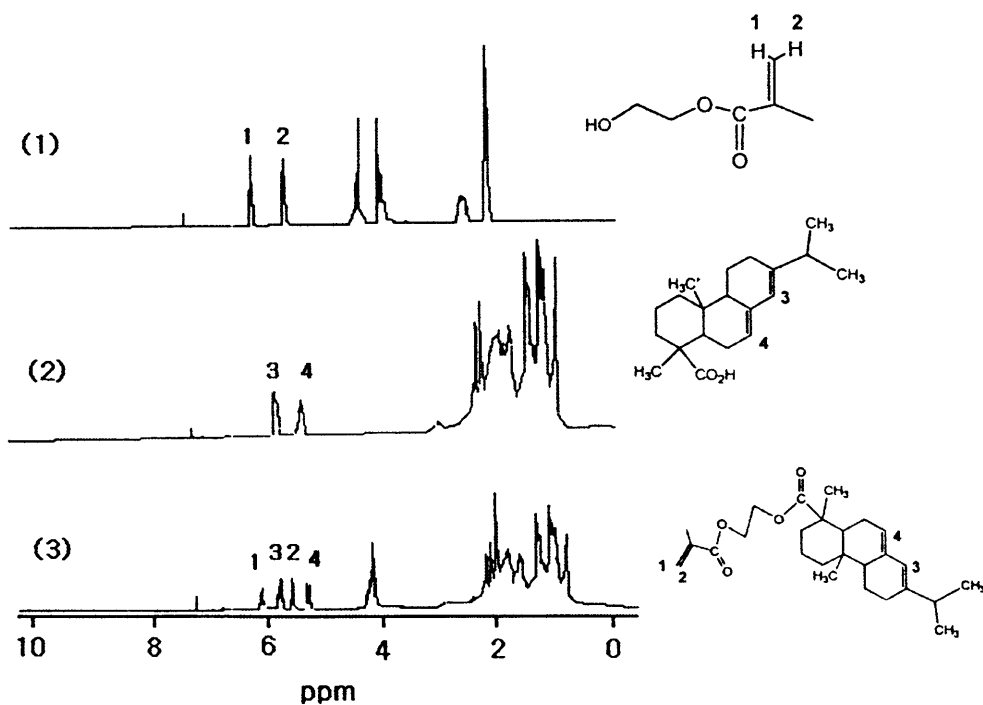
### Synthesis of Photo-reactive Monomer

Rosin modified monomer (RMM) was



Scheme 1. Synthetic route to monomer.

synthesized by the reaction of abietic acid with HEMA in the presence of diethyl azodicarboxylate as a catalyst (Scheme 1). The prepared monomer was characterized by comparing with  $^1\text{H-NMR}$  of AA, HEMA, and RMM in  $\text{CDCl}_3$  (Figure 1). The vinyl proton of HEMA showed peaks at 6.1 and 5.6 ppm (1) and doublets at 5.8, 5.3 ppm corresponding to the vinyl proton of AA (2). The spectra for RMM (3) revealed quartet in the range of 6.2-5.0 ppm with each of the same integration and IR spectra of RMM showed strong  $\text{C}=\text{O}$  stretching band at  $1720\text{ cm}^{-1}$  and disappearance of broad  $\text{O-H}$  stretching band assigned to abietic acid. From the above results, it was confirmed that RMM was successfully prepared. This monomer is attractive because it can be prepared using abietic acid, which is obtained from a renewable source. However, abietic acid by itself has a physical weakness in coating applications, such as poor impact strength and solvent requirement due to its high melting temperature. The modified structure by the reaction with HEMA exhibited

Figure 1.  $^1\text{H-NMR}$  spectra of HEMA(1), AA(2), and RMM(3).

a liquid phase at normal temperature, which would make it easy to use without a solvent and contains highly photo-reactive methacryl and vinyl structure, which means it can be used as a photo-crosslinkable monomer.

### Model Curing Studies

To investigate the curing chemistry that occurs in the thin film, a model experiment was carried out. The radical-catalyzed polymerization of acrylic group was fairly well understood. However, it was not clear the vinyl bond of abietic acid was participated in the crosslinking-reaction. For that reason, it was decided to investigate the effect of vinyl bond of abietic acid in curing chemistry. For this study, ethyl abietate was chosen and synthesized because it structurally resembles with RMM. The examination of ethyl abietate/IRGACURE 651 (100/5mol ratio) as a model compound by UV absorption spectra, showed that the absorbance at 270 - 290nm derived from the vinyl group of ethyl abietate decreased upon irradiation, indicating that the vinyl bond of ethyl abietate was participated in photo-crosslinking reaction (Figure 2).

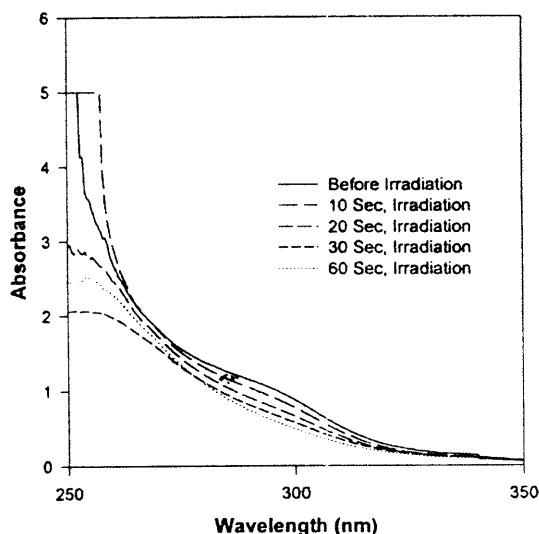
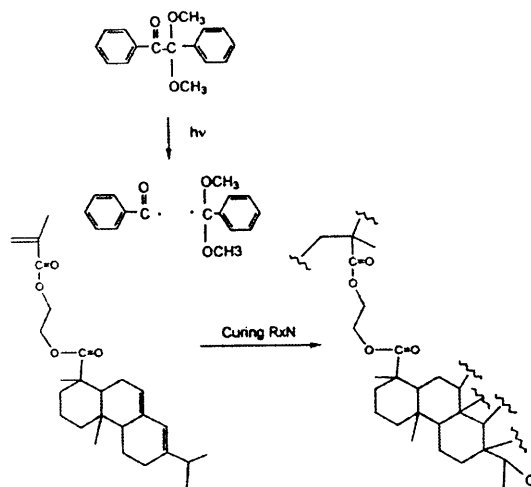


Figure 2. UV absorption spectra of ethyl abietate / IRGACURE 651(100/5mol ratio) with irradiation times.

### Photolysis Studies

The photo-polymerization of a renewable monomer was carried out using a radical-type photoinitiator. The photo-crosslinking reaction of the monomer was attempted by spreading thin films (approx. 5m) of the monomer containing 0.5 ~ 2mol % of the photoinitiator (IRGACURE 651) onto a glass plate using a bar-coater and then irradiating the films with a 200W Hg-Xe lamp. The infrared spectra of a film of RMM/IRGACURE 651 (100/1) before and after UV irradiation, confirmed the crosslinking reaction of the vinyl group by the disappearance of the sharp vinyl C-H stretching band at  $3100\text{ cm}^{-1}$ , C=C stretching band at  $1640\text{ cm}^{-1}$  and vinyl C-H bending band at  $940\text{ cm}^{-1}$  corresponding to the saturated C-H band (Figure 3). The cured film was not soluble in any solvents, such as acetone, dichloromethane, ethyl acetate etc. due to the photocrosslinking reaction of the acrylic double bond and the vinyl bond of the abietic acid by the radical-type photoinitiator (Scheme 2). Figure 4 shows a direct comparison of the conversion versus the time curves as determined by the solubility of the cured film. As shown in Figure 4, as the contents of photoinitiator increased, the UV cure rate of RMM also increased. Increasing the photoinitiator concentration up to 2mol % had a beneficial effect on the UV cure rate such that even with less than 1 min irradiation, the



Scheme 2. The photocrosslinking reaction.

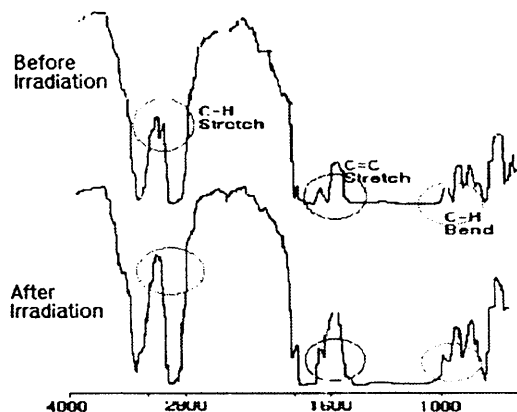


Figure 3. IR spectra of the RMM/IRGACURE 651 (100/1 mol ratio); Before and after UV irradiation (irradiation time : 5 min).

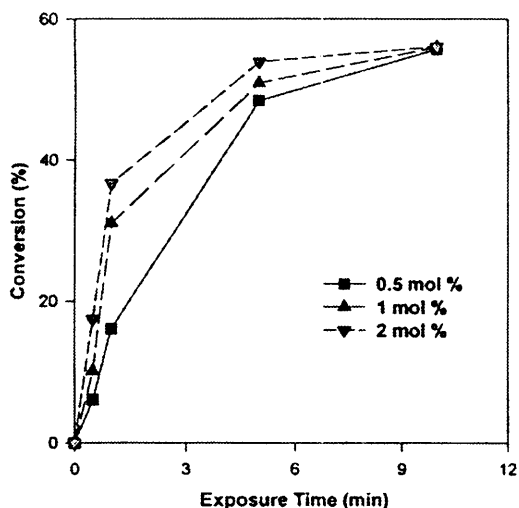


Figure 4. Conversion measured by insoluble.

conversion was almost completed. The cured film had quite a good thermal stability as can be seen in Figure 5. A thermogravimetric analysis of the cured polymer showed that the film was thermally stable up to 170°C, at which point the polymer film has lost 10% of its weight.

#### 4. CONCLUSIONS

A rosin modified photo-curable monomer was

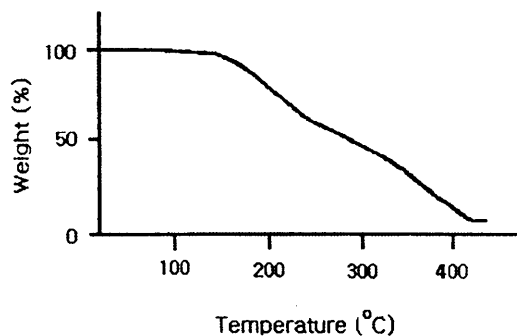


Figure 5. Thermogravimetric analysis fractions of the RMM/IRGACURE 651 curve for RMM/IRGACURE 651 as a function of irradiation time. (100/2 mol ratio : irradiation time = 4 min) at a heating rate 20°C/min under air.

designed and synthesized. This modified structure lowered the melting point of abietic acid due to a flexible ethylene linkage. The synthesized RMM became an oily product at room temperature, which is advantageous, as this reactive monomer will not require any organic solvents to control its viscosity. The photopolymerization of the RMM was performed with a radical-type photoinitiator. A crosslinked structure was formed by the photopolymerization reaction between the photo-reactive methacryl and vinyl groups in the monomer. The resulting product was insoluble in organic solvents such as acetone, chloroform, THF, hexane and exhibited high thermal stability.

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