

Synthesis and Characterization of a Polymethacrylate Containing Photoreactive Abietic Acid Moiety

Tae Hoon Kim and Ji Young Chang

School of Materials Science and Engineering, and Hyper-structured Organic Materials Research Center, College of Engineering, Seoul National University, ENG445, Seoul 151-744, Korea

Jae-Ung Choi and Woo-Sik Kim*

Department of Polymer Science, Kyungpook National University, Daegu 702-701, Korea

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Introduction

Rosin is a complex mixture of mutually soluble, naturally occurring high molecular weight organic acids and related materials.¹ The acidic constituents that make up the major portion of rosin are called resin acids. The major constituent of resin acids is abietic acid. Recently, the acid² has been reported to be cyclodimerized by the irradiation of ultra-violet (UV) light using high pressure mercury lamp in analogy with chalcone derivatives, styrylpyridine derivatives, and cinnamoyl esters which have been widely used as photoreactive groups.³⁻⁷ Thus, we have synthesized polymers bearing vinylbenzyl abietate units, styrene derivative-based polymers, as photoreactive polymers and investigated their photocrosslinking reaction. As the results, the abietic acid moiety was found to show high photosensitivity and thermal stability.^{2,8}

For applications of photosensitive polymers, their properties including transparency are important. Compared to polystyrene, poly(methyl methacrylate) has higher transmittance (lower refractive index), lower thermal expansion, and higher use temperature.⁹ Accordingly, if polymethacrylates with abietic acid moiety were prepared, the polymers can be expected to show high transparency and enhanced thermal stability.

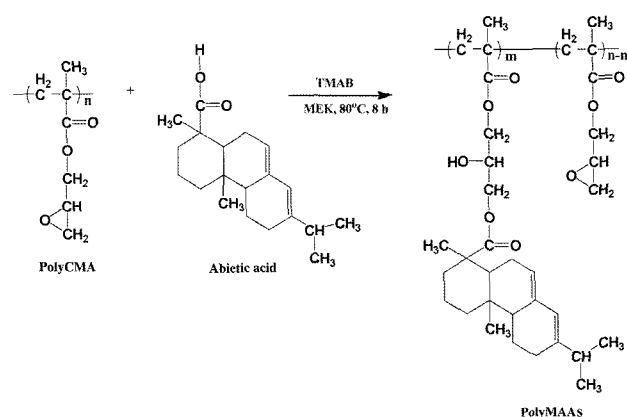
In this paper, we present the synthesis of a polymethacrylate bearing photoreactive abietic acid moiety (polyMAA) by the reaction of poly(glycidyl methacrylate) (polyGMA) with abietic acid, and its photocrosslinking reaction and optical and thermal properties.

Experimental

Materials. Glycidyl methacrylate (GMA) (Aldrich, 97%) was distilled in the presence of hydroquinone under reduced pressure. Abietic acid was isolated from crude abietic acid (Aldrich, 70%) using dipentylamine.¹⁰ Tetramethylammoniumbromide (TMAB) (Aldrich, 98%) was used as received. 2,2'-Azobisisobutyronitrile (AIBN) of reagent grade was recrystallized from methanol. Benzene as reagent grade was distilled in the presence of sodium wire. Methyl ethyl ketone (MEK) (Junsei, 98%) was distilled with calcium sulfate. All other reagents were used as received.

Synthesis of PolyMAAs. The mixture of GMA (10 g, 70 mmol), AIBN (0.5 mol% for GMA), and 15 mL of benzene was put in an ampoule and degassed. The sealed ampoule was heated at 65 °C for 24 h, and the polymerization mixture was gradually added to a large amount of *n*-hexane to precipitate polyGMA. Then, the polymer was dissolved in benzene and the solution was again poured into a large amount of *n*-hexane to purify the polymer. Finally, the polymer was freeze-dried in benzene at room temperature. The yield was 8.98 g (90%).

PolyMAA-1 was synthesized by the reaction of polyGMA with abietic acid as shown in Scheme I.¹¹ PolyGMA (0.43 g, 3 mmol), purified abietic acid (1 g, 3.3 mmol), and TMAB (0.026 g, 0.16 mmol) were put into 6 mL of MEK. The mixture was stirred at 80 °C for 1 h and was poured into 50 mL of methanol to precipitate polyMAA-1. Then, the polymer was dissolved in 10 mL of MEK and the solution was again poured into 100 mL of methanol to purify the polymer. Finally, the polymer was freeze-dried in benzene at room temperature. In order to know the conversions of polyGMA to polyMAA with the different reaction times (2, 4, 6, and 8 h), four different kinds of polyMAA were prepared under the same conditions except for the 1 h reaction time. The



Scheme I. Synthesis of polyMAAs.

*Corresponding Author. E-mail: wskim@knu.ac.kr

Table I. Synthesis of PolyMAAs^a

Sample	Reaction Time (h)	Conversion ^b (mol%)	Yield ^c (%)	M_n^d	M_w/M_n^d
PolyMAA-1	1	19.5	93	42,500	3.1
PolyMAA-2	2	33.3	87	48,900	2.8
PolyMAA-3	4	61.0	82	55,300	2.7
PolyMAA-4	6	76.1	75	62,000	3.2
PolyMAA-5	8	86.7	70	65,700	2.4
PolyGMA ^e	-	-	-	31,600	2.9

^aPrepared by the reaction of polyGMA with abietic acid in MEK at 80 °C. ^bMeasured by H-NMR spectroscopy.

^cPolyMAAs insoluble in benzene were eliminated. ^dMeasured in THF by GPC. ^ePolymerized radically from GMA.

conversions and yields are given in Table I.

Measurements. The IR spectra were recorded on a Jasco-IR 810 spectrometer by the KBr method and the NMR spectra were measured with a Bruker Avance Digital 400 FT-NMR spectrometer. The UV absorbance and transmittance spectra were measured with a Shimadzu Model 2401 spectrophotometer. The number-average molecular weights (M_n) and the weight-average molecular weights (M_w) of the polymers were measured in tetrahydrofuran (THF) with a Waters Alliance V 2000 gel-permeation chromatograph (GPC). In this case, monodisperse polystyrenes were used as standard polymers. The differential scanning calorimetry (DSC) thermograms of the polymers were measured in a nitrogen atmosphere at a heating rate of 10 °C min⁻¹ with a Dupont 2000 differential scanning calorimeter. The initial thermal decomposition temperatures (T_{di}) of the polymers were measured in a nitrogen atmosphere at a heating rate of 20 °C min⁻¹ with a Dupont 2100 thermal gravimetric analyzer (TGA).

For investigating the photochemical reaction of the polyMAA-5, the benzene solution of the polymer was coated on a quartz plate with a spin coater, dried at room temperature, and irradiated with a high pressure mercury lamp for different times. Its UV spectra were then measured with the same UV spectrophotometer described previously. Also, 2% benzene solutions of the polymer were coated on glass plates with the same spin coater, dried at room temperature, and irradiated at different exposure doses with the same lamp. The weights of the insoluble fractions were measured after developing the samples in benzene for 10 min.

Results and Discussion

The synthesis of polyMAAs is outlined in Scheme I. PolyGMA was obtained by radical polymerization of GMA in benzene at 65 °C with AIBN. Abietic acid was reacted with polyGMA in MEK at 80 °C in the presence of TMAB to give polyMAAs. The coupling reaction occurred between the epoxy ring of polyGMA and the carboxyl group of abietic acid.

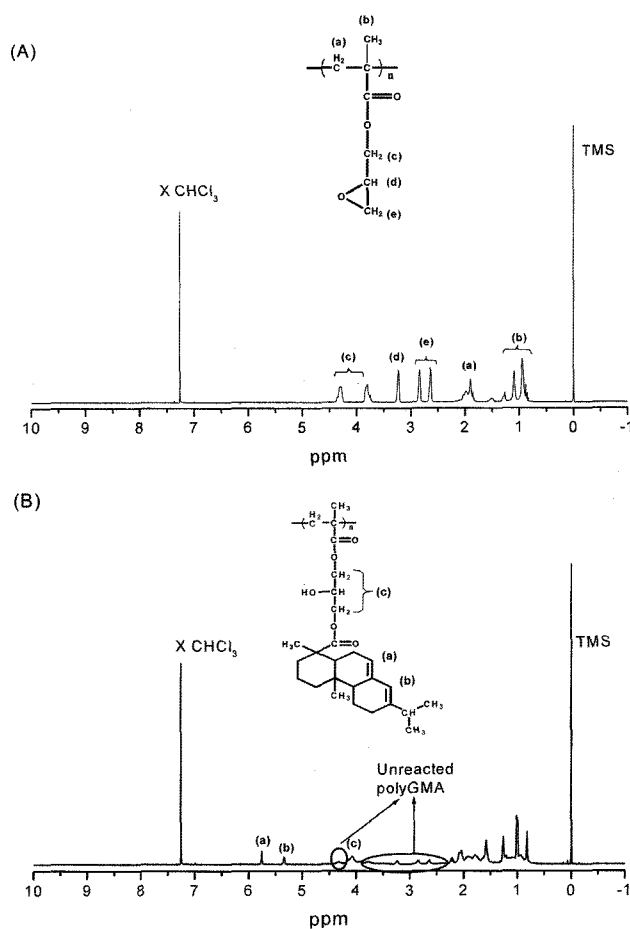


Figure 1. H-NMR spectra of polyGMA (A) and polyMAA-3 (B) in CDCl₃.

Figure 1 shows the ¹H NMR spectra of polyGMA and polyMAA-3 obtained after the reaction for 4 h. The peaks of polyGMA were assigned as given in Figure 1(A). After the reaction of polyGMA with abietic acid, the peaks of two protons (a and b) of vinyl groups of the abietic acid moiety appeared around 5.4 and 5.8 ppm^{2,8} and the peaks of the protons of the unreacted epoxy groups of polyGMA showed up at 2.6, 2.8, 3.2, 3.8, and 4.3 ppm [Figure 1(b)]. The peaks

at 3.9-4.2 ppm were assigned to five protons of the glycerol moieties resulted from the epoxy ring opening.

The conversions of glycidyl groups of polyGMA to abietic acid ester groups with the reaction times were determined from the area ratios of the five peaks in the 2.6-4.3 ppm range to the peaks in the 3.9-4.2 ppm range. They are summarized in Table I and plotted against the reaction time in Figure 2. The conversion increased almost straightly with the reaction times up to 4 h and increased with a lower slope after that. In the case of the reaction for 8 h, the conversion was approximately 87 mol%. The IR spectrum of polyMAA-5 also showed that the intensity of the epoxy group of polyGMA at 848 cm^{-1} decreased as the reaction time increased. The number-average molecular weight of each polyMAA measured by GPC is given together with that of polyGMA in Table I. The number-average molecular weight of polyMAA increased as the reaction time increased. The increase of the molecular weight after the reaction should be due to the coupling of abietic acid on polyGMA. From the conversions and the number-average molecular weight of polyGMA, the number-average molecular weights of polyMAA-1, polyMAA-2, polyMAA-3, polyMAA-4, and polyMAA-5 were calculated to be 44,700, 54,000, 72,600, 82,700, and 90,000. But the measured molecular weights by GPC were smaller than the calculated ones. This deviation was attributed to the formation of the longer side chains (branch structures) after the coupling reaction with abietic acid because it gave rise to the polymer-solvent affinity change, which would have an influence on the GPC results. The yields measured after removing the insoluble part of polyMAAs in benzene decreased with an increase of the reaction time. In other words, the insoluble portion increased with an increase of the abietic acid moiety content in polyMAAs. The insoluble polymers in benzene were not soluble in any solvents including MEK, THF, benzene, and chloroform that dissolved polyMAAs, suggesting that an intermo-

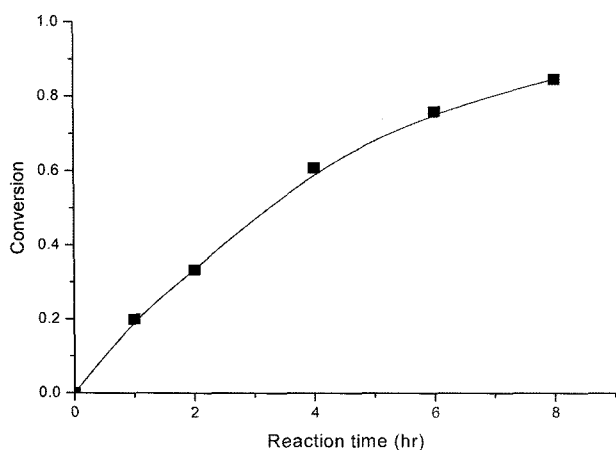


Figure 2. Conversions of polyGMA to polyMAA with reaction times.

lecular reaction of the abietic acid moiety of polyMAAs occurred during the reaction of polyGMA with abietic acid.

DSC thermograms of polyGMA and polyMAAs did not show glass and melt transitions. In the TGA thermograms of polyGMA and polyMAAs, the former polymer exhibited an initial decomposition temperature (T_{di}) around $290\text{ }^{\circ}\text{C}$, and the T_{di} of the latter polymers gradually increased with an increase of the abietic acid moiety content. The polymer containing the abietic acid moiety in 87 mol% of its repeating units (polyMAA-5) showed a T_{di} around $340\text{ }^{\circ}\text{C}$. The rise of the temperature means that the photocrosslinkable abietic acid moieties contribute to the thermal stability of the polymer.

The transmittance spectra of the polyMAA-5 film before and after irradiation of 2 J/cm^2 at several temperatures are given in Figure 3. As shown in this figure, the polymer revealed the transmittance of about 91% at room temperature before irradiation and almost the same as the upper value at $150\text{ }^{\circ}\text{C}$ after irradiation at higher wavelengths than 360 nm . Therefore, this result suggests that the polymer is a photoreactive polymethacrylate with high transparency^{12,13} up to the UV region.

In order to realize the photochemical reaction of polyMAA-5, the UV spectra of the polymer film with exposure doses were measured. The intensities of three bands of the polymer in the range of 230 to 260 nm due to the conjugated carbon-carbon double bonds decreased with increasing the exposure dose. The decreasing tendency of the absorbance of the polyMAA-5 was similar to that of poly(vinylbenzyl abietate).^{2,8} This fact indicates that the polymethacrylate with the photoreactive abietic acid moiety undergoes a photodimerization of the conjugated double bonds in the side chain.²

The intermolecular photodimerization of the abietic acid moieties would result in a crosslinked polymer structure. In

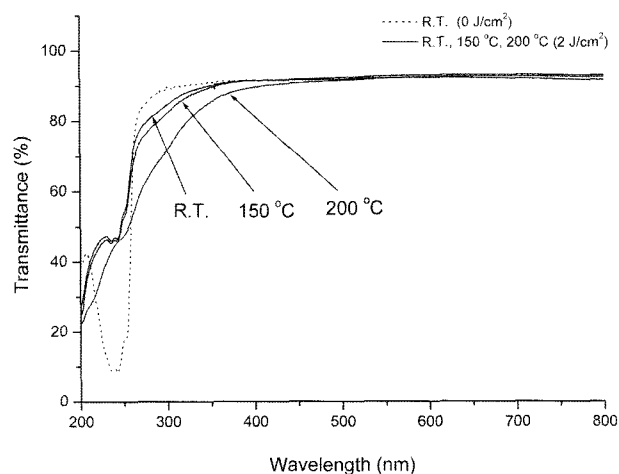


Figure 3. Transmittance spectra of polyMAA-5 film at room temperature and heated at various temperatures after irradiation of 2 J/cm^2 .

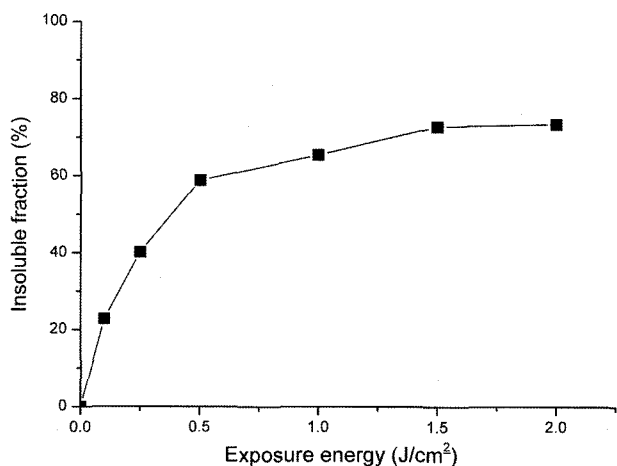


Figure 4. Insoluble fractions of polyMAA-5 films with exposure doses.

order to determine the amounts of the photocrosslinked polymer with various exposure doses, its insoluble fractions were measured and the results are shown in Figure 4. The insoluble fraction increased to about 58% within 0.5 J/cm² and then slowly increased to about 74% after 2 J/cm². The photocrosslinking took place rapidly at the initial stage. The fast initial increase of the crosslinked fraction is characteristic of the photocrosslinking reaction through photodimerization because the concentration of the photoreactive group is initially high, as observed in the photodimerization of polymers with cinnamoyl group.^{14,15}

Conclusions

A polymethacrylate with photoreactive abietic acid moiety (polyMAA) was synthesized by the reaction of poly(glycidyl methacrylate) (polyGMA) with abietic acid in methylethylketone in the presence of tetramethylammonium bromide at 80 °C. The conversion of epoxy groups of polyGMA to abietic acid ester groups increased almost straightly with the reaction times up to 4 h and increased with a lower slope after that. After the reaction for 8 h, the conversion was approximately 87 mol%. The thermal stability of polyMAA-5 was higher than that of polyGMA.

The polymer in the film state showed the transmittance of about 91% in the range of higher wavelengths than 360 nm. Also, the photocrosslinking of the polymer was found to take place rapidly at the initial stage. Therefore, these results indicate that a photocrosslinkable polymethacrylate with high transparency up to the UV region and enhanced thermal stability was prepared.

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