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Synthesis of Photocrosslinkable Polymers Using Abietic Acid and Their Characterization

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ABSTRACT: Vinylbenzyl abietate (VBA) was synthesized by the reaction of 4-vinylbenzyl chloride with sodium abietate. VBA homopolymer and copolymers of VBA with methyl methacrylate (MMA) were prepared in benzene using azobisisobutyronitrile as an initiator. The compositions of the copolymers were measured with ^{1}H NMR. The monomer reactivity ratios were determined by Kelen–Tüdös plot. The reactivity of VBA for the copolymerization was much larger than that of MMA. The glass transition temperature and the initial decomposition temperature of the homopolymer were higher than those of the copolymers. The polymers with the abietic acid moiety were crosslinked with UV irradiation. This result means that VBA can be a vinyl monomer for the preparation of photocrosslinkable polymers.

KEY WORDS Vinylbenzyl Abietate / Methyl Methacrylate / Monomer Reactivity Ratio / Abietic Acid Moiety / Photocrosslinkable Polymer /

Rosin is a complex mixture of mutually soluble, naturally occurring high molecular weight organic acids and related materials.[1] Abietic acid is the major constituent of rosin. The thermally acid-catalyzed dimerization of abietic acid has been studied by several groups.[2–4] The dimeric product has been in use for about five decades as a source of industrially useful products.[4] In connection with the photodimerization of abietic acid, it was reported that abietic acid was cyclodimerized when irradiated in a molten state for a long time.[5] Owing to the reaction conditions, however, it was ambiguous whether abietic acid was cyclodimerized photochemically or thermally.

Recently, poly(vinylbenzyl abietate) was synthesized by the reaction of poly(vinylbenzyl chloride) with sodium abietate and it was clarified that the abietic acid moiety of the polymer was rapidly photodimerized through the conjugated carbon–carbon double bonds in the moiety by the authors.[6] Accordingly, we expect that abietic acid can be used as a photosensitive group for the preparation of photocrosslinkable polymers.

In this paper, in order to be capable of preparing new various photocrosslinkable polymers through copolymerizations of a vinyl monomer having abietic acid moiety with other vinyl monomers, vinylbenzyl abietate (VBA) was synthesized by the reaction of *p*-vinylbenzyl chloride with sodium abietate and polymerized radically. Its radical copolymerization with methyl methacrylate (MMA) was also investigated. Moreover, the thermal properties and the photocrosslinkings of VBA homopolymer and VBA–MMA copolymers were examined.

EXPERIMENTAL

Materials

Reagents (Aldrich), including 4-vinylbenzyl chloride (VBC), triethylamine (TEA), and chlorobenzene were used as received. Abietic acid was isolated from crude abietic acid (Aldrich, 70%) using dipentylamine.[7] The melting point was 167–169 °C. 2,2′-Azobisisobutyronitrile (AIBN) of reagent grade was recrystallized from methanol. Methyl methacrylate (MMA) of reagent grade was distilled in the presence of hydroquinone under reduced pressure. 1,2-Dichloroethane of reagent grade was distilled in the presence of magnesuim sulfate. Benzene and tetrahydrofuran (THF) as reagent grades were distilled in the presence of sodium, respectively.

Synthesis of Vinylbenzyl Abietate (VBA)

Sodium abietate was prepared as follows.[6] Purified abietic acid (10 g, 33.1 mmol) was added to a 10% aqueous solution (20 mL) of sodium hydroxide and dissolved by stirring at 60 °C for 1 h. The solution was filtered and the filtrate was poured into a large amount of acetone to precipitate sodium abietate. The product was dried at room temperature and the yield was 10.2 g (95.1%).

VBA was synthesized according to Scheme 1 by the esterification of a sodium carboxylate with benzyl chloride.[8] VBC (4.6 mL, 0.031 mol), sodium abietate (11.3 g, 0.035 mol), and triethylamine (4.9 mL, 0.035 mol) were put into chlorobenzene (30 mL) including a trace of *p*-benzoquinone as a polymerization

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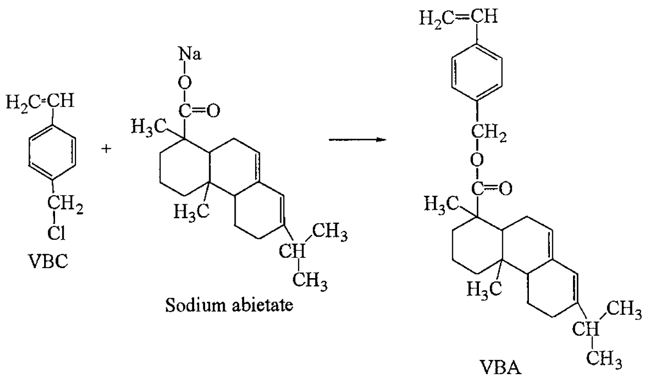

Scheme 1. Synthesis of VBA.

inhibitor. The mixture was stirred at 95 °C for 5 h. Most of the unreacted VBC and chlorobenzene in the mixture were eliminated by vacuum distillation. The viscous mixture was added dropwise to a large amount of distilled water to precipitate the product. The product was dried and recrystallized from acetone-distilled water(v/v : 2/1). The yield of VBA was 10.2 g (78.7%) with the melting point of 70–72 °C.

Polymerization

Homopolymerization of VBA was carried out in benzene at 65 °C for 24 h using AIBN as an initiator in a sealed tube. The concentration of the initiator was 1 mol% with respect to the monomer, and the concentration of the monomer in the solution was 1 mol L^{-1}. The polymerization mixture was gradually added to a large amount of methanol to precipitate poly VBA. Also, the copolymerizations of VBA–MMA for samples of the characterizations were performed under the same conditions as the homopolymerization except for the concentration of the monomer with 2 mol L^{-1}. The copolymerizations of VBA–MMA for samples of the determination of the monomer reactivity ratios were also performed under the same conditions as the homopolymerization except for the polymerization time.

Measurements

IR spectra were recorded on a JASCO-IR 810 spectrometer by KBr method. ^{1}H NMR and mass spectra were measured with a Bruker Advanced Digital 400 FT-NMR spectrometer and with a Hewlet Packard 5985A GC/MSD spectrometer, respectively. UV 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 THF with a Waters Alliance V2000 gel permeation chromatograph (GPC). The intrinsic viscosities of the polymers were measured in chloroform at 25 °C with a Ubbelohde viscometer. Glass transition temperatures of the polymers were obtained 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 were measured in a nitrogen atmosphere at a heating rate of 20 °C min^{-1} with a Dupont 2100 thermal gravimetric analyzer.

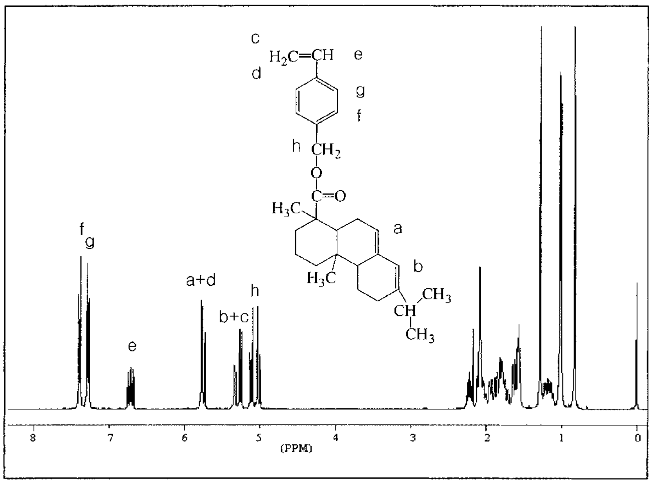

Figure 1. ^{1}H NMR spectrum of VBA in CDCl$_3$.

For the investigation of photochemical reaction of the polymers, 1,2-dichloroethane solutions of the polymers were coated on quartz plates with a spin coater, dried at room temperature, and irradiated with a high pressure mercury lamp for accumulative times. Their UV spectra were then measured with the same UV spectrophotometer described above. Also, for the measurement of insoluble fractions of photocrosslinking for the polymers, 1,2-dichloroethane solutions of the polymers were coated on glass plates with the same spin coater, dried at room temperature, irradiated with the same lamp for different times, and their insoluble fractions were measured by weight after developing the samples in 1,2-dichloroethane for 10 min. The thickness of the samples coated on glass plates was approximately 2.5 μm. The irradiation intensity was 3 m watt cm^{-2}.

RESULTS AND DISCUSSION

Synthesis of VBA

VBA was synthesized by the reaction of VBC with sodium abietate as shown in Scheme 1. To confirm the product of VBA, ^{1}H NMR spectrum of VBA is given in Figure 1. Hydrogens from a to h are assigned in the spectrum by the help of the spectra of VBC and sodium abietate. The peak splitting of hydrogens (h) is interesting. The methylene group is located between two bulky groups, a benzene ring and an abietic acid moiety. Thus, the free rotation of the methylene group is sterically hindered, leading to a splitting for the methylene protons into an AB type quartet. The IR spectrum of VBA evidently showed the peak of carbonyl group of the ester at 1718 cm^{-1}. Also, the weak peak at 1629 cm^{-1} can be attributed to the carbon–carbon double bonds of abietic acid moiety[6] and the weak peak at 1660 cm^{-1} might be due to the vinyl group in VBA. The mass spectrum of VBA showed a peak at the mass number of 418 and the number corresponds to the molecular weight of VBA. The molar absorptivity at 243 nm was determined to be 29900 L mol^{-1} cm^{-1} in 1,2-dichloroethane.

Polymerization

VBA homopolymer (P-1) was prepared by the polymerization of VBA in benzene using AIBN as the initiator. Also, copolymers(P-2 and P-3) were prepared by the polymerizations of VBA–MMA under the same conditions as the preparation of the homopolymer. Among the three polymers, ^{1}H NMR spectrum of P-2 is shown in Figure 2. The hydrogens from a to f are assigned in the spectrum. The peak splitting of hydrogens (f) around 5 ppm can be explained as described above for VBA. A traceable peak on the right side of the peak of hydrogens (c) of the methoxy group around 3.5 ppm appears in the spectrum. For the copolymers used in determining the monomer reactivity ratios of VBA–MMA which will be described later, the two peaks of the copolymers with more VBA content were evidently split. Also, the area of the peak on the right side increased with increasing VBA content in the copolymers. For the discussion of the phenomenon, it can be assumed that two kinds of hydrogens of the methoxy group exist, that is, hydrogens interacted with the pendant group of VBA unit and hydrogens that did not interact with that of VBA unit. Considering this assumption and the variations of the peak along with VBA content in the copolymers, the peak at low chemical shift is due to the former hydrogens and the peak at high chemical shift is attributable to the latter hydrogens.

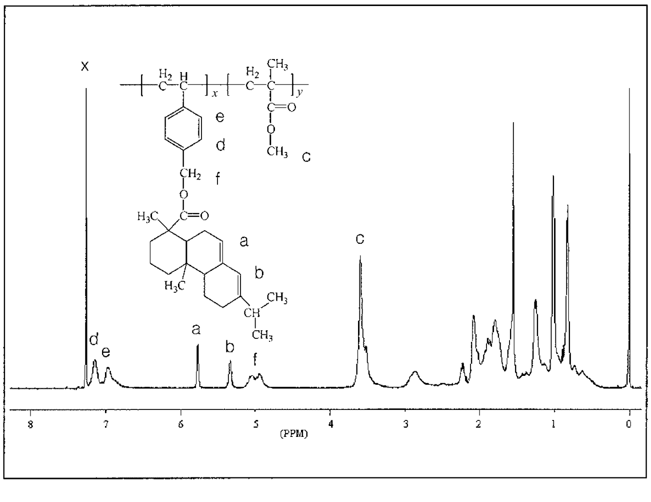

Figure 2. ^{1}H NMR spectrum of poly(VBA-*co*-MMA)(P-2) in $CDCl_3$.

Characterization

The compositions of VBA and MMA in the copolymers P-2 and P-3 were determined from the ratios of the area of the peak (c) to that of the peak (f). The values are shown in Table I together with yields, intrinsic viscosities, M_n, and polydisperties(M_w/M_n).

Also, the data of VBA homopolymer are given in Table I. The contents of VBA in the copolymers P-2 and P-3 were higher than those of VBA in the feeds. This result means that the reactivity of VBA for the copolymerization is larger than that of MMA. The reason will later be described in the section for the monomer reactivity ratios of VBA–MMA.

The polymers were soluble in acetone, THF, chloroform, 1,2-dichloroethane, benzene, etc. The glass transition temperatures of P-1, P-2, and P-3 were around 135 °C, 118 °C, and 120 °C, respectively. Also, the initial decomposition temperatures of P-1, P-2, and P-3 were 422 °C, 386 °C, and 398 °C, respectively. In the polymers, the relation between the temperatures and the contents of VBA was irregular. This might be due to the difference in the molecular weights among these polymers.

Monomer Reactivity Ratios

The VBA–MMA copolymers with low conversions were prepared by the copolymerization of the VBA–MMA system in benzene using AIBN as the initiator for the determination of monomer reactivity ratios. The compositions of VBA and MMA in the copolymers

Table I. Results of polymerization of VBA–MMA[a]

Sample	Feed		Yield	Copolymer[b]		η^{c}	$M_n{}^{d}$	$M_w/M_n{}^{d}$
	[VBA]	[MMA]		[VBA]	[MMA]			
	(mole fraction)		(%)	(mole fraction)				
P–1	1	0	56	1	0	0.22	28100	2.91
P–2	0.186	0.814	83	0.264	0.736	0.28	39100	2.26
P–3	0.093	0.907	80	0.175	0.825	0.32	51500	2.84

[a]Radically polymerized in benzene at 65 °C for 24 h. [b]Measured by ^{1}H NMR analysis. [c]Intrinsic viscosities were measured in chloroform at 25 °C with a Ubbelohde viscometer. [d]Measured in THF with GPC.

Table II. Results of low conversion copolymerizations of VBA and MMA[a]

Run	Feed [VBA] (mole fraction)	Feed [MMA] (mole fraction)	Time (min)	Yield (%)	Copolymer[b] [VBA] (mole fraction)	Copolymer[b] [MMA] (mole fraction)
1	0.186	0.814	30	8	0.388	0.612
2	0.329	0.671	50	7	0.588	0.412
3	0.477	0.523	90	10	0.688	0.312
4	0.628	0.372	110	9	0.774	0.226
5	0.784	0.216	120	11	0.880	0.120

[a]Copolymerized in benzene at 65 °C using AIBN. [b]Measured by ^{1}H NMR.

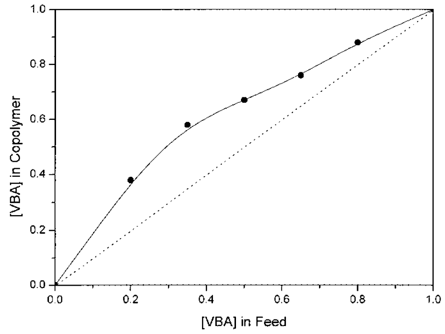

Figure 3. Copolymer composition curve for the copolymerization of VBA–MMA system.

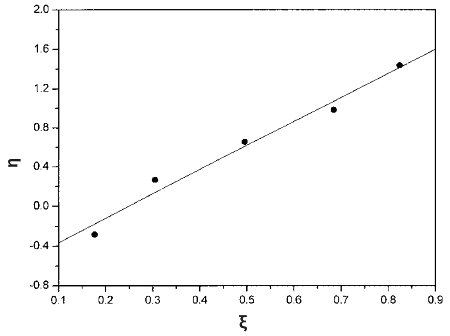

Figure 4. Kelen–Tüdös plot of the VBA–MMA copolymer system.

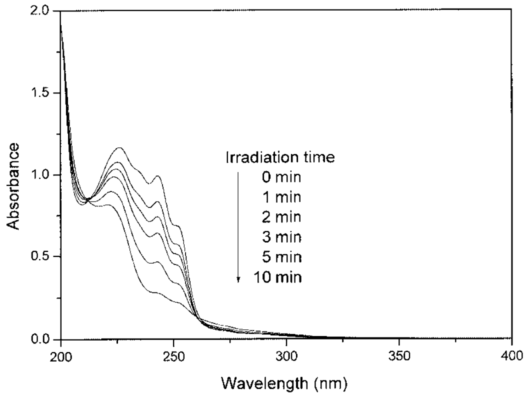

Figure 5. Variation in the UV spectra of the film of P-2 with increasing irradiation time.

were measured by ^{1}H NMR analysis as those in P-2 and P-3. The values are given in Table II together with the polymerization times and the yields.

The copolymerization times were adjusted to obtain low conversions. The contents of VBA in the copolymers were higher than those of VBA in the feeds. In order to visualize the difference between the contents of VBA and MMA, the contents of VBA in the copolymers were plotted against those of VBA in the feeds in Figure 3. As shown in Figure 3, the contents of VBA in the copolymers are located above considerably away from the diagonal line. To know quantitatively the reactivities of VBA and MMA for the copolymerization, two parameters (η and ξ) of Kelen–Tüdös equation[9] were calculated from the compositions of VBA and MMA in the feeds and in the copolymers in Table II, and η were plotted against ξ in Figure 4. The monomer reactivity ratios r_1 and r_2 of VBA(1) and MMA(2) were determined from the Kelen–Tüdös plot as follows : $r_1 = 1.85$ and $r_2 = 0.23$. VBC is the precursor of VBA. The monomer reactivity ratios of VBC–MMA were reported to be 1.02 and 0.46.[10] Qualitatively, the tendency of r_1 against r_2 for our system was in agreement with that of r_1 against r_2 for the reported system. The value of r_1 to r_2 of our system, however, was considerably larger than that of the reported system. Presently, it can not be known what the interaction of the abietic acid moiety of VBA with MMA in the copolymerization is.

Photocrosslinking of the Polymers

In the IR spectrum of P-2, the intensity of the peak of the carbon–carbon double bond in the abietic acid moiety at 1629 cm^{-1} decreased with increasing irradiation time. The changes in the UV spectra of P-2 at the film state with irradiation times are given in Figure 5. The three bands of the polymer in the range of 220 nm to 265 nm can be due to the conjugated carbon–carbon double bonds because the bands disappeared when abietic acid was hydrogenated in the presence of platinum.[6] The intensities of the bands decreased with increasing irradiation time. The results indicate that the conjugated double bonds of the polymer undergo a photodimerization at the film state.[6] The decrease of the

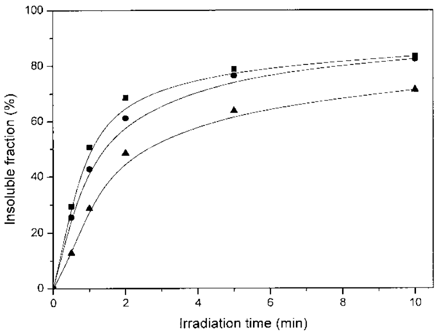

Figure 6. Insoluble fractions of the P-1(■), P-2(●), and P-3(▲) with irradiation times.

intensity of this polymer containing abietic acid moiety with irradiation time was similar to that of the polymer containing styryl-2-pyridine which is known to be photodimerizable group with good photosensitivity.[11]

Since the photochemical reaction of the polymer (P-2) is a photodimerization, the polymer should be crosslinked through the intermolecular photodimerization of the abietic acid moieties. In order to know the relation between the contents of the abietic acid moiety of the three polymers (P-1, P-2, and P-3) and their photocrosslinking amounts, their insoluble fractions with different irradiation times were measured, and the results are displayed in Figure 6. The fractions reached about 68% for P-1, about 61% for P-2, and about 47% for P-3 within 2 min. Considering the contents of abietic acid moiety in the polymers, the fractions of P-2 and P-3 were high in spite of the low contents. P-1 with 100% abietic acid moiety as the pendant group can undergo higher intramolecular reaction than intermolecular reaction owing to neighboring abietic acid moieties in the same molecule. Otherwise, P-2 and P-3 can relatively undergo higher intermolecular photodimerization than intramolecular photodimerization because they contain much less abietic acid moiety than P-1. Accordingly, insoluble factions of the polymers were not proportional to the contents of abietic acid moiety as shown in Figure 6. This suggests that the polymers with abietic acid moiety are photocrosslinkable polymers and VBA can be a new photosensitive vinyl monomer for the preparation of photocrosslinkable polymers.

CONCLUSIONS

VBA was synthesized by the reaction of VBC with sodium abietate in chlorobenzene at 95 °C. Then, VBA homopolymer and copolymers of VBA with MMA were prepared by the radical polymerization. The polymers were soluble in solvents such as acetone, THF, chloroform, 1,2-dichloroethane, benzene, etc. The number-average molecular weights of P-1, P-2, and P-3 were in the range of 28600 to 51800 and their polydispersities were below three. The glass transition temperatures of P-1, P-2, and P-3 were 135 °C, 118 °C, and 120 °C and their initial decomposition temperatures were around 400 °C. The monomer reactivity ratios of VBA(1)–MMA(2) for the copolymerization were determined to be $r_1 = 1.85$ and $r_2 = 0.23$. This result means that the reactivity of VBA is much higher than that of MMA. P-2 or P-3 with much smaller abietic acid moiety than P-1 was crosslinked with UV irradiation. Therefore, VBA with abietic acid moiety can be a new monomer for the preparation of photocrosslinkable polymers.

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