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Synthesis and Polymerization of 2-(β -Substituted Acryloyl)- 1-Methacryloyloxynaphthalenes

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ABSTRACT

Some 2-(β -substituted acryloyl)-1-methacryloyloxy-naphthalenes (II) were synthesized by the reaction of the corresponding 2-(β -substituted acryloyl)-1-naphthols with methacryloyl chloride. These monomers were polymerized with 2,2'-azoisobutyronitrile. The properties of the resulting oligomers as photosensitive resins are described.

INTRODUCTION

In the past almost 20 years, there have been numerous reports of the syntheses and properties of photosensitive resins [1-5]. These studies have received renewed interest in recent years [6-8]. In connection with these studies, we have recently reported the preparation and polymerization of 2-methacryloyloxyethyl 4-chalcone-

carboxylate and 2-methacryloyloxyethyl 4'-chalconecarboxylate [9]. Additionally, we have demonstrated that the resultant polymers are excellent as photosensitive polymers.

In the course of our investigation of photosensitive polymers, we have now found that the oligomers produced by the radical polymerization of some 2-(β -substituted acryloyl)-1-methacryloyloxynaphthalenes (II) act as efficient photocrosslinkable resins.

The present paper is concerned with the synthesis and polymerization of some 2-(β -substituted acryloyl)-1-methacryloyloxynaphthalenes. The properties of the resultant oligomers as photocrosslinkable resins have also been examined.

EXPERIMENTAL

Reagents

1-Naphthol, furfural, 2-thiophenaldehyde, benzaldehyde, 3-nitrobenzaldehyde, acetic acid, and triethylamine were obtained commercially and purified by distillation and recrystallization, respectively. Zinc chloride was reagent grade and used without further purification. Methacryloyl chloride was prepared by the reaction of methacrylic acid with benzoyl chloride [10]. All other reagents were commercially supplied and purified by the usual methods.

2-Acetyl-1-naphthol, mp 102°C (lit. [11] mp 102°C), was prepared by the reaction of 1-naphthol with acetic acid in the presence of zinc chloride, according to the procedure described by Torrey and Brewster [12].

2-(2'- β -Furanacryloyl)-1-naphthol (Ia) was prepared by the reaction of 2-acetyl-1-naphthol with furfural in ethanol in the presence of 10% sodium hydroxide, following the method of Torrey and Brewster [12]. The product was recrystallized from methanol to give a 25% yield of orange needles; mp 121°C (lit. [13] mp 121-122°C).

2-(2'- β -Thiophenacryloyl)-1-naphthol (Ib) was prepared from 2-acetyl-1-naphthol and 2-thiophenaldehyde by the procedure described above for Ia. The product was recrystallized from methanol to give a 50% yield of dark red needles; mp 152-154°C.

2-Cinnamoyl-1-naphthol (Ic) was prepared from 2-acetyl-1-naphthol and benzaldehyde in the above manner. The product was recrystallized from acetone to give a 40% yield of an orange-colored solid; mp 124°C (lit. [14] mp 125-126°C).

2-(3'-Nitrocinnamoyl)-1-naphthol (Id) was prepared from 2-acetyl-1-naphthol and 3-nitrobenzaldehyde in the above manner. The product was recrystallized from acetone to give a 35% yield of a brown colored solid; mp 198-204°C.

2-(2'- β -Furanacryloyl)-1-methacryloyloxynaphthalene (IIa)

In a 300-ml three-necked round-bottomed flask equipped with a mechanical stirrer, a dropping funnel, an efficient refluxed condenser, and a calcium chloride tube were placed 3.4 g of Ia, 2.7 g of triethylamine, and 100-ml of benzene. The solution was heated at 50°C and 2.8 g of methacryloyl chloride was added dropwise to the solution over a period of 0.5 hr with stirring. The reaction was allowed to continue for an additional 3 hr and then allowed to cool to room temperature. Then 60 ml of water were added to the reaction mixture. The organic layer was washed with dilute hydrochloric acid, water, and then dried over anhydrous sodium sulfate. The dried organic layer was evaporated in vacuo with a stream of nitrogen for 3 hr to give 3.6 g (80%) of a brown viscous liquid.

Analysis. Calcd for $C_{21}H_{16}O_4$: C, 75.89%; H, 4.85%. Found: C, 75.74%; H, 4.94%.

IR (KBr): 3180 (furyl), 2860 (CH_3), 1730 (C=O), 1650, 1010 ($CH=CH$), 1620, 970, 925 ($H_2C=C$), 1590, and 1495 cm^{-1} (naphthyl); NMR ($CDCl_3$): δ 2.10 (s; CH_3 , 3H), 5.78 (m; $-CH=$, 1H), 6.46 (s; $-CH=$, 1H), and 6.47-7.98 ppm (m; aromatic protons and $-CH=CH-$, 11H).

2-(2'- β -Thiophenacryloyl)-1-methacryloyloxynaphthalene (IIb)

The same procedure as described for the preparation of IIa was used to prepare IIb from 7.1 g of Ib and 5.3 g of methacryloyl chloride in 100 ml of benzene in the presence of 5.1 g of triethylamine. The product was recrystallized from methanol to yield 5.2 g (60%) of IIb as yellow crystals; mp 95°C.

Analysis. Calcd for $C_{21}H_{16}O_3S$: C, 72.39%; H, 4.63%. Found: C, 72.13%; H, 4.63%.

IR (KBr): 3100 (thienyl), 2890 (CH_3), 1730 (C=O), 1650, 945 ($H_2C=C$), 1626 ($CH=CH$), and 1580 cm^{-1} (naphthyl); NMR ($CDCl_3$): δ = 2.09 (s; CH_3 , 3H), 5.84 (m; $-CH=$, 1H), 6.53 (s; $-CH=$, 1H), and 6.97-8.08 ppm (m; aromatic protons and $-CH=CH-$, 11H).

2-Cinnamoyl-1-methacryloyloxynaphthalene (IIc)

The same procedure as described for the preparation of IIa was used to prepare IIc from 5.9 g of Ic and 4.6 g of methacryloyl chloride in 100 ml of benzene in the presence of 5.1 g of triethylamine. The product was recrystallized from methanol to afford 4.4 g (60%) of IIc as yellow crystals; mp 90°C.

Analysis. Calcd for $C_{23}H_{18}O_3$: C, 80.68%; H, 5.30%. Found: C, 80.58%; H, 5.15%.

IR (KBr): 300 (CH_3), 1730 (C=O), 1660, 980 ($CH=CH$), 1620, 940 ($H_2C=C$), 1600, 1580, and 1500 cm^{-1} (naphthyl); NMR ($CDCl_3$): δ 2.05 (s; CH_3 , 3H), 5.75 (m; $-CH=$, 1H), 6.45 (s; $-CH=$, 1H), and 7.00-8.03 ppm (m; aromatic protons and $-CH=CH-$, 13H).

2-(3'-Nitrocinnamoyl)-1-methacryloyloxynaphthalene (IId)

The same procedure described for the preparation of IIA was used to prepare IId from 6.0 g of Id and 4.0 g of methacryloyl chloride in 100 ml in the presence of 3.8 g of triethylamine. The product was recrystallized from methanol to give 4.6 g (60%) of IId as yellow crystals; mp 132°C.

Analysis. Calcd for $C_{23}H_{17}O_2N$: C, 71.31%; H, 3.38%; N, 3.62%. Found: C, 71.35%; H, 4.43%; N, 3.56%.

IR (KBr): 1730 (C=O), 1660, 980 (CH=CH), 1625, 940 ($H_2C=C$), 1350 (NO_2), 1605, 1560, and 1525 cm^{-1} (naphthyl); NMR ($CDCl_3$); δ 2.10 (s; CH_3 , 3H), 5.95 (m; =CH=, 1H), 6.67 (s; -CH=, 1H), and 7.35-8.67 ppm (m; aromatic protons and -CH=CH-, 12H).

Polymerization

The monomers IIA-IId were polymerized in benzene by 2,2'-azobutyronitrile (AIBN) in degassed sealed tubes with shaking in a thermostat maintained at given temperature. The products were isolated by pouring the reaction mixture into an excess of methanol and purified by reprecipitation from benzene solution with methanol.

The IR spectra of the resulting oligomers showed no peak due to vinyl group.

The molecular weights of the oligomers were determined by vapor pressure osmometry with a Knauer vapor pressure osmometer. Chloroform was used as solvent for oligo(IIa), while benzene was used for oligo(IIb).

Ultraviolet Irradiation

A 300-ml Eiko high-pressure mercury lamp (PIH-300) was used as the source of UV light.

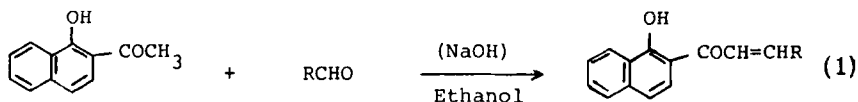
Thin polymer films were prepared as follows. The THF solution of the polymers was cast on a quartz plate (or KBr plate), followed by drying slowly. The distance between the film and the lamp was 15 cm. The film was irradiated with the lamp at $30 \pm 1^\circ C$.

Spectroscopic Measurements

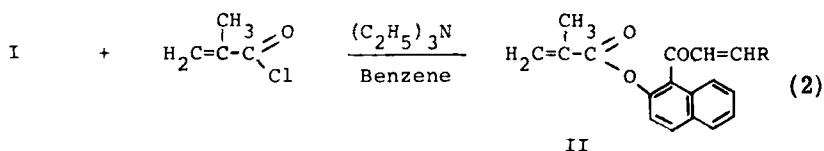
UV spectra were recorded on a Hitachi-EP5-3T spectrophotometer; IR spectra were recorded on a Jasco Model IR-G spectrophotometer. A 60 MHz Hitachi-Perkin Elmer Model R-20 spectrometer was used to obtain 1H -NMR spectra.

RESULTS AND DISCUSSION

2-(β -Substituted acryloyl)-1-methacryloyloxynaphthalenes (IIa-IId) were synthesized as shown in eqs. (1) and (2),



I



II

where

IIa: R = 2-Furyl

IIb: R = 2-Thienyl

IIc: R = Phenyl

IId: R = 3-Nitrophenyl

The synthesis of 2-(β -substituted acryloyl)-1-naphthols (Ia)-(Id) was achieved by the reaction of the corresponding aldehydes with 2-acetyl-1-naphthol in ethanol in the presence of 10% sodium hydroxide. 2-(β -Substituted acryloyl)-1-methacryloyloxynaphthalenes (IIa)-(IId) were prepared by reacting the naphthols with methacryloyl chloride in benzene in the presence of triethylamine. These monomers were characterized by IR, NMR, and elemental analysis, as described in the Experimental Section. For example, the IR and $^1\text{H-NMR}$ spectra of IIb are shown in Figs. 1 and 2, respectively.

The polymerization of 2-(β -substituted acryloyl)-1-methacryloyl-naphthalenes was carried out in benzene with AIBN as initiator. The results are summarized in Table 1.

The molecular weights of the resulting polymeric materials derived from polymerization of IIa and IIb were determined by vapor pressure osmometry. As can be seen from Table 1, these molecular weights are low. This finding is attributable to the bulky pendant group of these monomers. The solid oligomers thus obtained are generally soluble in common organic solvents such as chloroform, benzene, and THF. In the IR spectrum of oligo(IIb), the 950 and 995 cm^{-1} bands characteristic of the methacrylic double bond are absent, although the 970, 1580, and 1645 cm^{-1} bands characteristic of the photoreactive

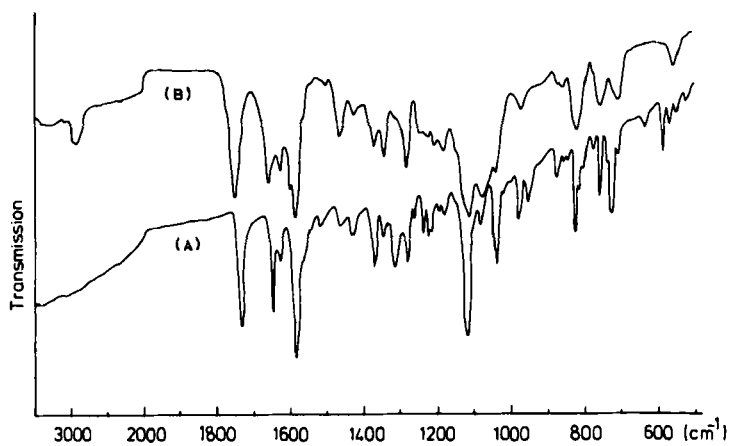


FIG. 1. IR spectra of: (A) IIb in KBr and (B) oligo(IIb) film.

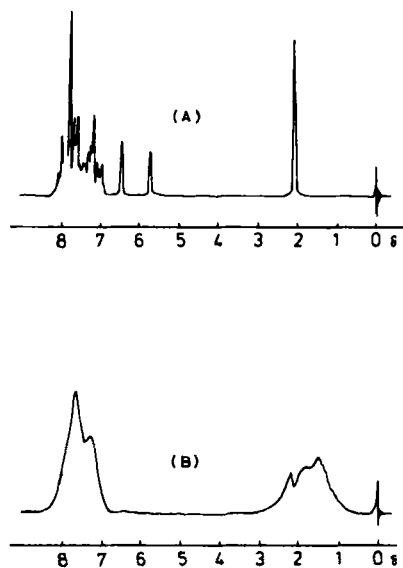


FIG. 2. ¹H-NMR spectra: (A) IIb and (B) oligo(IIb). In CDCl₃; TMS as internal standard.

TABLE 1. Data for Polymerization of 2-(β -Substituted Acryloyl)-1-Methacryloyloxy-naphthalenes in Benzene at 70°C

Monomer	[Monomer] (mole/liter)	[AIBN] (mole/liter)	Time (hr)	Conversion (%)	Molecular weight	Melting point (°C)
IIa	0.42	2.1×10^{-2}	22	17.5	2000	163-184
IIb	0.44	2.0×10^{-2}	20	7.8	1400	173-185
IIc	0.27	2.0×10^{-2}	20	2.1	-	145-165
IId	0.23	2.0×10^{-2}	20	13.9	-	140-165

unsaturated double bond are still present, as shown in Fig. 1. If the radical polymerization of these monomers follows a cyclization reaction to lead to the formation of lactone, a band should appear around 1750 cm^{-1} [7]. However, there was no absorption band in this region. In the $^1\text{H-NMR}$ spectrum of oligo(IIb), the absorption peaks at 5.84 and 6.53 ppm due to the terminal vinyl protons disappeared, whereas a broad absorption peak at 1.1-2.0 ppm due to the methylene protons of oligo(IIb) appeared, as shown in Fig. 2. The other oligomeric materials showed similar IR and $^1\text{H-NMR}$ spectroscopic behavior. From these results, it may be said that the resultant oligomers are linear and the pendent photoreactive groups are quantitatively preserved.

Films of these oligomers, which had relatively good film-forming properties, were subjected to photocrosslinking under an Eiko 300-W high-pressure mercury lamp. After exposure of the films to the lamp at 15 cm distance for a given time, the films became insoluble in organic solvents such as chloroform, benzene, and THF; the photoreactive unsaturated double bonds of the oligomers undergo intermolecular dimerization by UV rays.

Figures 3 and 4 show successive changes in the IR and UV absorption spectra of oligo(IIb) on UV irradiation.

The IR absorption peaks at 970, 1580, and 1645 cm^{-1} due to the photoreactive double bond decreased markedly with UV irradiation time, as shown in Fig. 2 whose IR spectrum recorded at several irradiation times.

As can be seen from Fig. 3, the UV absorption diminished in intensity with irradiation time. In the above manner, similar IR and UV spectral changes were observed for the other oligomeric materials. On monitoring at a fixed wavelength (275 nm) of the oligomeric materials, the changes in absorbances were measured after a constant period (1 min) of UV irradiation. The photosensitivity of these oligomeric materials was defined as the decreasing percentage of the absorbance of the oligomeric materials, which was evaluated as $100(A_b - A_a)/A_b$, where A_a is the absorbance for the oligomer after 1 min UV irradiation and A_b is that before UV irradiation. The results are listed in Table 2.

We examined the effect of addition of some sensitizers to the oligomers on the photosensitivities. Oligomeric product containing 10 wt-% sensitizer was dissolved in THF. The THF solution was cast on a quartz plate, followed by drying slowly. Using an analogous procedure to that described above, the photosensitivity of these oligomeric materials containing sensitizers was evaluated, as shown in Table 1. As shown in Table 2, the photosensitivity of the oligomers was scarcely affected by the addition of sensitizers, though the reason is still not known.

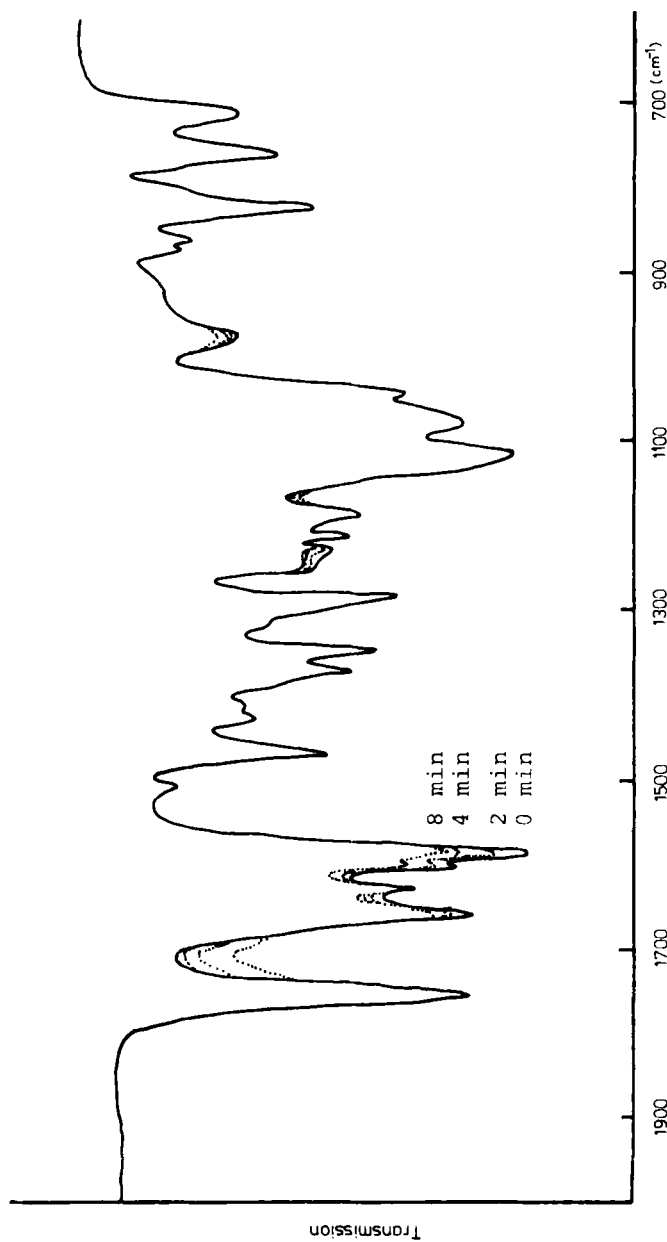


FIG. 3. IR changes in of oligo(IIb) film with irradiation time.

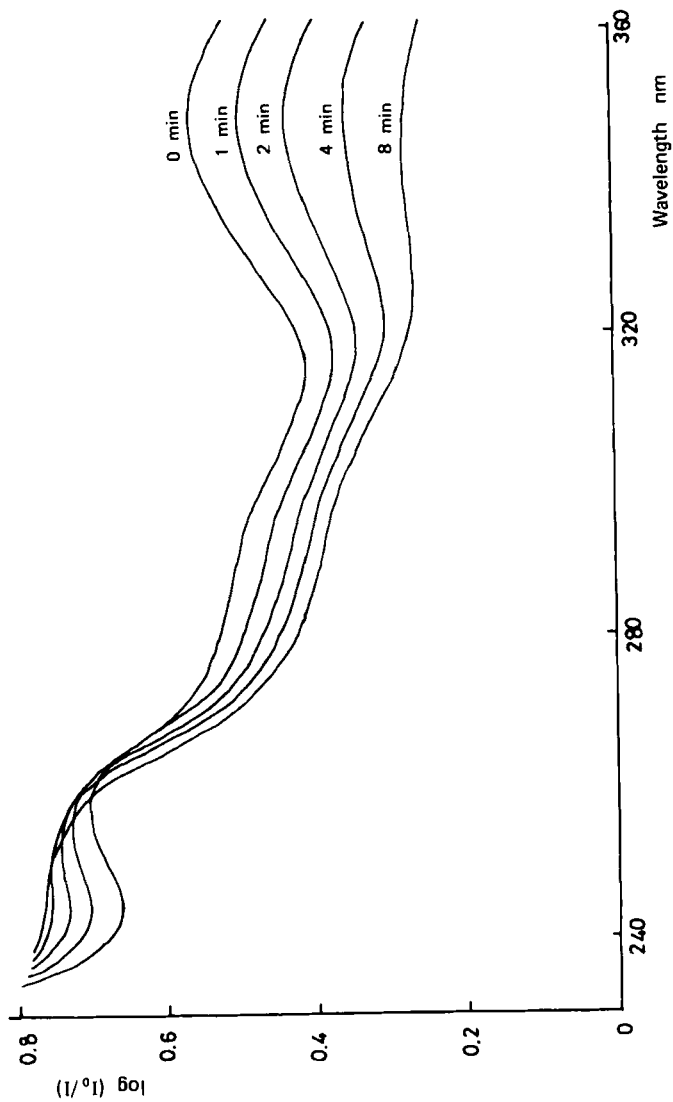


FIG. 4. UV changes in of oligo (IIb) film with irradiation time.

TABLE 2. Photosensitivity of Oligomers Resulting from 2-(β -Substituted Acryloyl)-1-methacryloylnaphthalenes with or without Sensitizers (UV Irradiation Time = 1 min)

Oligomer	Photosensitivity with or without sensitizers (%)				
	None	Benzophenone	Michler's ketone	5-Nitroacenaphthene	2,4,5,7-Tetra-nitro-9-fluorenone
Oligo(IIa)	30.8	31.4	23.2	21.4	18.1
Oligo(IIb)	14.8	15.0	16.2	13.5	11.1
Oligo(IIc)	13.8	11.9	18.1	13.0	11.0
Oligo(IIId)	3.5	7.8	4.8	8.5	5.5

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