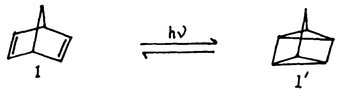
May, 1986] © *1986 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 59, 1501—1504 (1986)*

Synthesis of Photosensitive Poly(2,5-Norbornadien-7-yl Acrylate and Methacrylate)

Hiroyoshi KAMOGAWA* and Makoto YAMADA
Department of Applied Chemistry, Yamanashi University, Takeda 4, Kofu 400
(Received November 25, 1985)

2,5-Norbornadien-7-yl acrylate and methacrylate were synthesized by the esterification of 2,5-norbornadien-7-ol with acryloyl and methacryloyl chlorides, respectively. Polymerization of the monomers with AIBN provided vinyl polymers with pendant norbornadiene units, which could be made to clear films from CH_2Cl_2. UV-irradiations brought about remarkable changes in the 200 nm region of the absorption spectra of the films, indicating the formation of quadricyclane units. These could be partially converted back by immersion in a cobalt(II) 5,10,15,20-tetraphenylporphyrin solution.

It is well-known that norbornadiene (**1**) undergoes a reversible intramolecular [2+2] cycloaddition reaction on irradiation with ultraviolet light to afford the corresponding compound bearing a cyclobutane ring, quadricyclane (**1′**), as indicated in Eq. 1.[1–3]

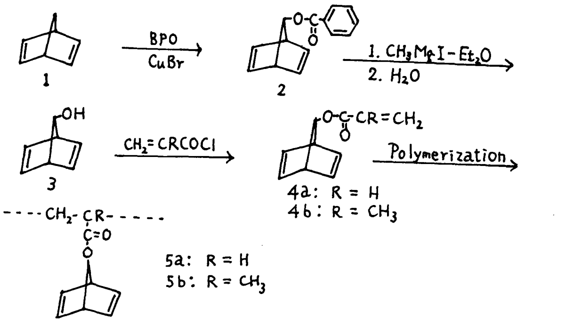


(1)

When the **1** unit is incorporated into the side chain of a vinyl polymer as pendant, a photosensitive polymer is obtained. This exhibits a reversible absorption spectrum change in response to UV irradiation in the solid state such as in a film.

The present study describes the first synthesis and polymerization of vinyl monomers bearing the **1** unit and the investigation of the photosensitivities of the films made of the resulting polymers from the standpoint of photomemory. The polymers made here may also be the first example of photosensitive polymers by the [2+2] cycloaddition mechanism.[4]

The polymers were synthesized via the following route (Eq. 2).



(2)

Absorption spectrum changes of **5a** and **5b** films in response with UV irradiations were also investigated.

Results and Discussion

The 2,5-norbonadien-7-yl group was chosen as the pendant in acrylic and methacrylic ester polymers because this pendant at the 7 position should exert the least steric hindrance to polymerization of the corresponding vinyl monomers as well as the subsequent photoreaction (Eq. 1).

2,5-Norbornadien-7-ol (**3**) was prepared starting with norbornadiene (**1**) via 2,5-norbornadien-7-yl benzoate (**2**).

Table 1. Polymerization Behavior of Norbornadiene Monomers

Monomer	Polymer						
	Conversion %	$[\eta]_{\mathrm{THF}}^{25}$	IR(KBr) cm^{-1}	C[a)] %	H[a)] %	Iodine[a,b)] Value	$\lambda_{\max}^{CH_2Cl_2}$ nm
4a	27	0.45	3070, 2930, 2860, 1720, 1160	73.70 (74.06)	6.60 (6.22)	158 (157)	228 (ε 550)
4b	55	0.49	3070, 2980, 2930, 1720, 1150	74.68 (74.98)	7.07 (6.86)	149 (144)	228 (ε 400)

a) Figures in parentheses indicate calcd values. b) Wjis' method.

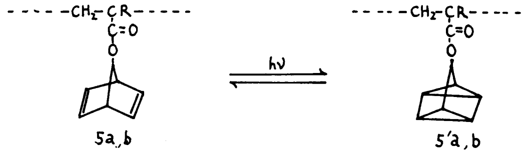
The 7h-reaction of **1** following the method of Tanida and Tsuji[5] provided **2** with satisfactory purity. Attempts to hydrolyze **2** under normal alkaline conditions using potassium hydroxide failed, so that the reaction of a Grignard reagent with the carbonyl group of **2** followed by hydrolysis as in the case of 2,5-norbornadien-7-yl acetate[6] was adopted to afford **3** in 61% yield. The latter was converted to acrylic and methacrylic esters (**4a** and **4b**) by conventional procedures. Thus, the reaction of **3** with acryloyl chloride in the presence of *N*,*N*-dimethylaniline as proton acceptor provided **4a** in 65% yield. With freshly distilled methacryloyl chloride, in the presence of pyridine, a 45% yield of **4b** was obtained. The purity of both products after column chromatography was satisfactory.

Free radical polymerizations of the monomers **4a** and **4b** with α,α'-azobisisobutyronitrile (AIBN) under mild conditions (50 °C, 72 h) provided soluble polymers as indicated in Table 1. Under more severe conditions (e.g., 10 fold monomer concentration) higher conversions were achieved accompanied by lower solubility, presumably due to the participation of the double bonds of the norbonadienyl moiety in polymerization. However, the polymers listed in Table 1 corresponded with **5a** and **5b** structures in all respects. The ultraviolet (UV) absorption spectra of polymer **5a** are indicated in Fig. 1.

The absorption maximum (228 nm) and shape of the curve in CH_2Cl_2 solution are almost identical with those of norbornadiene (**1**) as well as those (229 nm) of the corresponding monomer **4a** in the same solvent. For a film of **5a**, however, no peak is recognized above 200 nm and the absorbance continues to increase down to 189 nm with the decrease of the wavelength. Almost the same results were obtained for polymer **5b**. Both polymers **5a** and **5b** provided clear colorless films from CH_2Cl_2 solutions. This difference of absorption spectra between the film and solution states can be attributed to a solvent effect: Ethanol gives absorption peaks at 209, 212, and 208 nm for **4a**, **4b**, and **1**, respectively.

Films of **5a** and **5b** deposited on the inside walls of quartz cells were irradiated with UV light in a nitrogen atmosphere. Figure 2 and Table 2 indicate the results thus obtained.

The absorbance around 200 nm decreased with irradiation with simultaneous reductions in the iodine value and the 3070 cm^{-1} peak in the IR spectrum, indicating that the reaction given in Eq. 3 occurred.



(3)

This reaction is intramolecular and appears to require little dimensional change, so that a smooth photoconversion of **5a,b** to **5'a,b** may take place even in the solid state. The use of a triplet photosensitizer was avoided to assure [2+2] cycloaddition by the pericyclic mechanism.

It is known that Co(II) porphyrins catalyze the back reaction in Eq. 1.[7] When the films subjected to 48 h irradiation were immersed in a solution of cobalt(II) 5,10,15,20-tetraphenylporphyrin for 24 h, the UV and IR spectra and the iodine values recovered to some extent, indicating that the back

Table 2. Photosensitivities of Norbornadiene Polymer Films

Polymer	Irradiation[a) time h	Absorbance (200 nm)	Iodine Value	IR (3070 cm^{-1})
5a	0	0.540	158(100)[c)	Strong
	24	0.395	—	Weak
	48	0.303	73(46)[c)	Weak
	After immersion[b)	0.345	92(58)[c)	Weak
5b	0	0.510	149(100)[c)	Strong
	24	0.320	—	Weak
	48	0.215	20(13)[c)	Weak
	After immersion[b)	0.382	110(74)[c)	Medium

a) In a nitrogen atmosphere. b) With Cobalt(II) 5,10,15,20-tetraphenylporphyrin. c) Residual **1** unit in %.

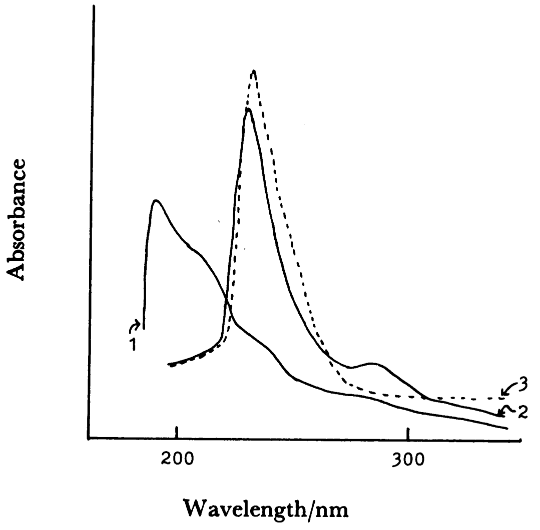


Fig. 1. Ultraviolet absorption spectra of norbornadiene polymer. 1: **5a**-Film; 2: **5a** in CH_2Cl_2; 3: Norbornadiene in CH_2Cl_2. The ordinate has no meaning other than to show the shapes of absorption curves.

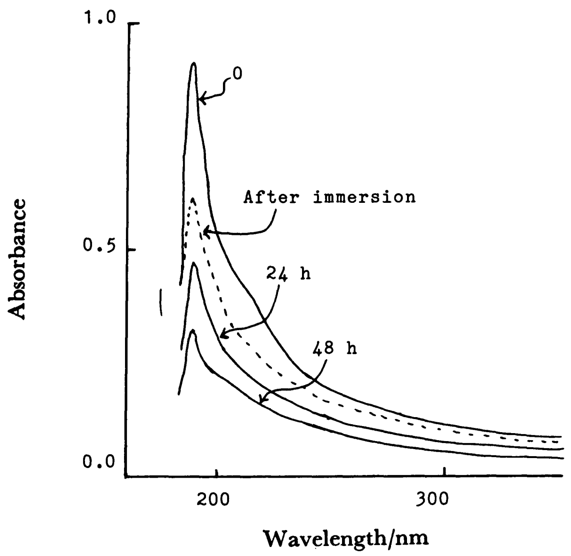


Fig. 2. Change of the absorption spectrum of a norbornadiene polymer (5b) film with UV irradiation. Figures in the diagram indicate the irradiation times in nitrogen atmosphere and the immersion was carried out after 48 h irradiation.

reaction shown in Eq. 3 occurred in the films. The rate and extent of the back reaction depend upon the diffusion of the catalyst into the films, so that a complete reversal would depend on the experimental conditions and the state of the films.

There was no indication of any degradation of the principal polymer chains or decomposition of the carboxyl portion judging from the values of intrinsic viscosity and IR spectra. In fact, the conversion as indicated in Eq. 3 could be repeated.

Experimental

Infrared, ^{1}H NMR, mass, and ultraviolet spectra were recorded on a Hitachi 215 spectrophotometer, a JNM-PMX 60 spectrometer, a Hitachi RMU-6 spectrometer, and a Hitachi 200-10 spectrophotometer, respectively, under standard conditions. Elemental analyses were carried out with a Perkin-Elmer 250 instrument.

2,5-Norbornadien-7-yl Benzoate (2). Refluxing for 7 h of a mixture of norbornadiene (9.2 g, 0.10 mol), copper(I) bromide (50 mg), and benzoyl peroxide (BPO; 6.0 g, 0.025 mol) in benzene (80 ml) and subsequent working up provided colorless needles (mp 54—56 °C, bp 109 °C/0.4 mm; lit,[5] mp 53—54 °C) in 34% yield. Found: C, 79.26; H, 5.66%. Calcd for $C_{14}H_{12}O_2$: C, 79.23; H, 5.70%. IR (KBr) 3070 (CH=CH); 1730, 1280 (ester) cm.$^{-1}$ ^{1}H NMR (CCl_4) δ=3.7 (m, 2H, 2CH), 4.8 (s, 1H, CHO), 6.7 (d, 4H, 2CH=CH), 7.5 (m, 3H, ArH), 8.1 (m, 2H, ArH). Ms (*m*/*z*) 212 (M$^+$).

2,5-Norbornadien-7-ol (3). To a Grignard reagent, prepared from magnesium (2.4 g, 0.10 mol) and methyl iodide (14.2 g, 0.10 mol) in anhydrous ether (100 ml), **2** (4.2 g, 0.020 mol) was added slowly under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 1 h. Saturated aqueous sodium sulfate was added. The ether solution was decanted, washed with water, and dried over anhydrous sodium sulfate. The ether was removed and the product distilled to yield a VPC-pure fluid (bp 81 °C/57 mm; lit,[6] 79 °C/57 mm) in 61% yield. Found: C, 77.75; H, 7.21%. Calcd for C_7H_8O: C, 77.75; H, 7.46%. IR (CCl_4) 3560 (OH), 3070 (CH=CH) cm.$^{-1}$ ^{1}H NMR (CCl_4) δ=2.9 (s, 1H, OH), 3.4 (m, 2H, 2CH), 3.8 (s, 1H, CHO), 6.6 (m, 4H, 2CH=CH). Ms (*m*/*z*) 108 (M$^+$).

2,5-Norbornadien-7-yl Acrylate (4a). To a stirred solution of **3** (2.2 g, 20 mmol), hydroquinone (0.1 g), *N*,*N*-dimethylaniline (4.2 ml, 33 mmol) in anhydrous acetonitrile (50 ml) cooled in an ice bath was added dropwise acryloyl chloride (2.5 ml, 30 mmol) with exclusion of moisture. The reaction mixture was stirred at room temperature for 15 h and poured into ice-water containing conc. hydrochloric acid (20 ml). Ether extraction followed by conventional working up provided a crude product, which was subjected to silica-gel column chromatography (Wakogel C-300) using hexane–benzene (1:1 v/v) as eluting solvent to afford a clear fluid in 65% yield. Found: C, 73.70; H, 6.60%. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.22%. IR (CCl_4) 3070 (CH=CH); 1720 (ester); 980, 900 (vinyl) cm^{-1}. ^{1}H NMR (CCl_4) δ=3.7 (m, 2H, 2CH), 4.6 (s, 1H, CHO), 5.8—6.4 (m, 3H, CH_2=CH), 6.7 (m, 4H, 2CH=CH). λ_{max}^{EtOH} 209 nm (ε 3400), $\lambda_{max}^{CH_2Cl_2}$ 229 nm (ε 440). MS (*m*/*z*) 162 (M$^+$).

2,5-Norbornadien-7-yl Methacrylate (4b). The same procedure as that for **4a** was applied using methacryloyl chloride (3.9 ml, 40 mmol), freshly distilled, and pyridine (3.6 ml, 44 mmol) instead of acryloyl chloride and *N*,*N*-dimethylaniline, respectively. Column chromatographic purification using hexane–benzene (1:1 v/v) as eluting solvent provided a clear fluid in 45% yield. Found: C, 74.63; H, 6.95%. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86%. IR (CCl_4) 3070 (CH=CH), 1720 (ester), 930 (methacryloyl) cm.$^{-1}$ ^{1}H NMR (CCl_4) δ=1.8 (s, 3H, CH_3), 3.6 (m, 2H, 2CH), 4.6 (s, 1H, CHO), 5.5 (s, 1H, CH_2=), 6.0 (s, 1H, CH_2=), 6.7 (m, 4H, 2CH=CH). λ_{max}^{EtOH} 212 nm (ε 8100), $\lambda_{max}^{CH_2Cl_2}$ 229 nm (ε 1100). Ms (*m*/*z*) 176 (M$^+$).

Polymerization of the Monomers. A solution of monomer (0.4 g) and α,α'-azobisisobutyronitrile (AIBN; 0.02 g) in tetrahydrofuran (8 ml) was put into a glass ampule, which was evacuated and sealed in a conventional manner. Polymerization was carried out at 50 °C for 72 h and the resulting polymer was precipitated into hexane–benzene (1:1 v/v) to afford a white powder. The result thus obtained are given in Table 1.

The IR-spectra of the polymers showed absorption in the 2900 cm^{-1} region characteristic of the vinyl polymer backbone with disappearance of the monomeric vinyl absorptions.

Measurements of Ultraviolet (UV) Spectra. Film: A solution of the polymer in dichloromethane was spread over either a quartz plate or an inside wall of a quartz cell, which was air-dried at room temperature overnight and stored for at least a week before measurement. The average thickness of the films thus prepared was 0.01 mm.

Measurement: UV-absorption spectra of films were recorded on a spectrophotometer. The UV irradiation source was a 75W mercury lamp (Toshiba SHL-100UV-2) and irradiation was effected at a distance of 10 cm from the lamp.

Treatment of Irradiated Film for Spectrum Recovery: The films subjected to irradiation were immersed in a 1% solution of cobalt(II) 5,10,15,20-tetraphenylporphyrin in benzene–dichloromethane (4:1 v/v) for 24 h, washed thoroughly with the same solvent mixture, and dried.

References

1) W. G. Dauben and R. L. Cargill. *Tetrahedron,* **15**, 197 (1961).

2) G. S. Hammond, N. J. Turro, and A. Fisher, *J. Am. Chem. Soc.,* **83**, 4674 (1961).

3) N. J. Turro, "Modern Molecular Photochemistry," The Benjamin/Cummings Pub. Co. Inc. (1978), p. 427.

4) H. Kamogawa, *Kōbunshi Kakō,* **33**, 66 (1984).

5) H. Tanida and T. Tsuji, *Chem. Ind. (London),* **1963**, 211.

6) P. R. Story, *J. Org. Chem.,* **26**, 287 (1961).

7) R. R. Hantala, R. B. King, and C. Kutal, "Solar Energy," The Humana Press (1979), p. 333.