Vinyl Polymerization. LXX*. Preparation of 3-(4′-Pentenyl)cyclopentene-1 and its Alternative Copolymerization with Maleic Anhydride

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3-(4′-Pentenyl)cyclopentene-1 (PCP) was prepared from tetrahydrofurfuryl alcohol and cyclopentadiene, by the scheme as shown in Fig. 1.

Tetrahydrofurfuryl alcohol was chlorinated by thionyl chloride into tetrahydrofurfuryl chloride, and the ring cleavage of the chloride formed by metallic sodium led to the formation of 4-penten-1-ol. By the bromination of 4-penten-1-ol with phosphorous tribromide, the unsaturated alcohol was transformed into 5-bromo-1-pentene, which was then converted into its Grignard compound.

3-Chlorocyclopentene-1 was prepared by

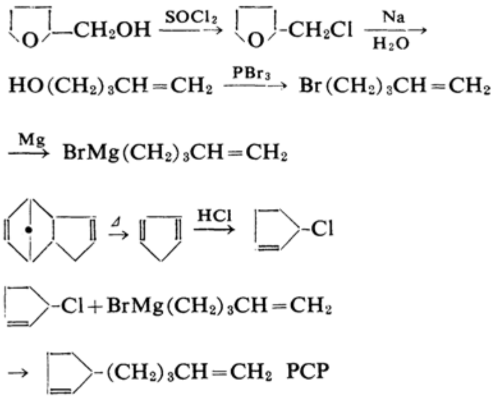

Fig. 1. The process of PCP synthesis.

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* Part LXIX of this series: M. Imoto, T. Otsu and M. Nakabayashi, *Makromol. Chem.*, in press.

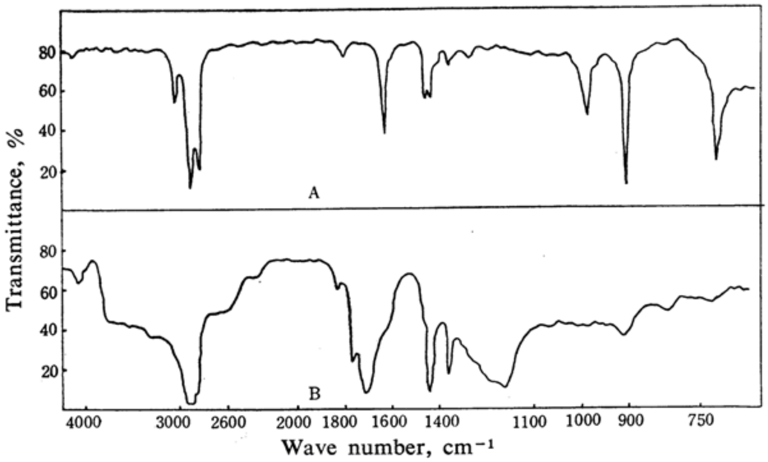

Fig. 2. Infrared absorption spectra.
A PCP (liquid)
B Copolymer (in Nujol)

TABLE I. COPOLYMERIZATION OF PCP WITH MALEIC ANHYDRIDE AT 60°C FOR 3 hr.

Exp. No.	Monomer composition			Copolymer composition*		
	[PCP]	[MA]	[PCP]/[MA]	[PCP]	[MAd]**	[PCP]/[MAd]
	mol. %		mol. ratio	mol. %		mol. ratio
1	50.78	49.22	1.032	35.03	64.97	1/2.004
2	69.07	30.93	2.234	—	—	—
3	33.09	66.91	0.4948	36.07	63.93	1/2.024
4	74.26	25.74	2.7911	34.21	65.79	1/2.011
5	63.91	36.09	1.2912	35.06	64.95	1/2.016

* After hydrolyzed ** [MAd] : Maleic acid

hydrochlorination of cyclopentadiene, which was the pyrolysis product of dicyclopentadiene. A coupling reaction was carried out between the 1-pentenylmagnesium bromide and the 3-chlorocyclopentene-1 at $-30\sim-35$°C. By this reaction, PCP was yielded. The infrared spectrum of PCP is shown in Fig. 2A.

In order to synthesize polyperhydroazulene or poly(methyleneperhydroindene) by intra- and inter-molecular polymerization, radical polymerization was attempted by azobisisobutyronitrile (AIBN) at 60°C for 30 hr. Polymerization by Ziegler catalyst was also tried at 30, 5 and −70°C for 72 and 120 hr., respectively. In the case of using Ziegler catalyst, the Al/Ti molar ratio was changed from 0.93 to 3.39. A little brown methanol-soluble oil was obtained and most of the monomer PCP was recovered in both cases. Cationic polymerization was performed by titanium tetrachloride or boron trifluoride etherate at 30, 5 and −70°C for 72 and 120 hr., respectively, under nitrogen atomosphere. When titanium tetrachloride was employed, the results were the same as in radical and Ziegler polymerization, but by boron trifluoride etherate initiator, a trace of reddish brown gel polymer was obtained. This polymer did not dissolve in common organic solvents, and most of the monomer PCP was recovered. From the above results, it may safely be said that PCP does not homopolymerize under these conditions.

PCP was copolymerized with maleic anhydride (MA) by the use of a radical initiator at 60°C for 3 hr. Under these conditions, neither maleic anhydride nor PCP homopolymerized and the copolymers of PCP with MA were obtained in a good yield.

When the molar ratio in the monomer mixture of PCP to maleic anhydride was varied from 1 : 1 to 1 : 2, 2 : 1 and 2.8 : 1, no change was observed in the copolymer composition (the proportion of PCP to maleic anhydride being 1 to 2), as shown in Table I. The infrared absorptions of vinyl type double bond and unsaturated cyclopentene ring of PCP in copolymer disappeared in the infrared absorption spectrum as shown in Fig. 2B, so it is assumed that both the double bonds participated in the copolymerization and formed glassy gelled pale-yellow copolymer. These results indicated an alternative copolymerization.

Experimental

Preparation of 4-Penten-1-ol.—Tetrahydrofurfuryl chloride was obtained by Brooks and Snyder's method[1]. Tetrahydrofurfuryl alcohol was chlorinated by thionyl chloride; yield 68～72% (lit. 73～75%); b. p. 40～42°C/11mmHg (lit. 41～42°C/11mmHg).

4-Penten-1-ol was prepared with ring cleavage of tetrahydrofurfuryl chloride by metallic sodium. The yield of b. p. 136～137°C was 71～74% (lit. 76～83%); n_D^{20} 1.4300 (lit. 1.4299). (Found: C, 69.75; H, 12.31. Calcd. for $C_5H_{10}O$: C, 69.77; H, 11.63%.)

Preparation of 5-Bromo-1-pentene.—5-Bromo-1-pentene was prepared by a modification of La Forge's method[2]. 1.6 mol. of 4-penten-1-ol and 0.5 mol. of pyridine were placed in a four-necked flask. The contents of the flask was held, being stirred, at about −30 to −35°C and 0.6 mol. of phosphorus tribromide was added into the flask over a period of about 5 hr. dropwise to prevent vigorous exothermic reaction; stirring was continued one hour more. The reflux condenser was then replaced by a Vigreux column and the product of the reaction was distilled on an oil bath until the temperature in the flask rose to 160～170°C. The distillate was washed with water, dilute sodium hydroxide, and lastly with water. After being dried on calcium chloride, the product was distilled several times. The yield of pure 5-bromo-1-pentene, boiling between 125.5 and 126.0°C at atmospheric pressure, was 55～57%: d_{25}^{25} 1.2595; n_D^{25} 1.4645.

Found: C, 40.55; H, 6.30; Br, 53.60*. Calcd. for C_5H_9Br: C, 40.31; H, 6.08; Br, 53.65%.

3-Chlorocyclopentene-1. — The chlorohydrogenation of cyclopentadiene, which was obtained by the pyrolysis of dicyclopentadiene, yielded 3-chlorocyclopentadiene[3].

Synthesis of PCP.—3.3 g. of magnesium was placed in a four-necked flask, and the mixture of 5-bromo-1-pentene and ether contained in a funnel was added dropwise into the flask which was cooled in a water bath. Stirring was continued two more hours even after the addition was made to complete the reaction. To this 1-pentenylmagnesium bromide, a mixture of 3-chlorocyclopentene-1 (15 g.) and ether (25 g.) was added dropwise, during which time the flask was cooled between −30 to −35°C under nitrogen atmosphere. A vigorous reaction followed immediately and white magnesium halide was precipitated. The addition was made for about 1 hr. and stirring was continued for an additional 2 hr., and then the temperature of the reaction mixture was risen gradually to 25°C. Stirring was carried on for another 2 hr. The reaction product was then poured into a large amount of water and the unreacted compound was decomposed. The ether layer was separated and dried over magnesium sulfate. After the removal of the ether by distillation, the residue was distilled through a Vigreux column. The yield of PCP was 88～91%; b. p. 46.0～47.0°C/7 mmHg. n_D^{25} 1.4582: d_{25}^{25} 0.8267.

Found: C, 88.05; H, 11.91. Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84%.

Polymerization of PCP.—*Radical Polymerization.*—AIBN, m. p. 102.0～102.5°C, recrystallized twice from methanol, was used for radical polymerization. The polymerization was carried out in benzene. The benzene solution of PCP (3 ml. of PCP mixed with 7 ml. of benzene or 3 ml. with 3 ml.) and AIBN ($2.303～6.911 \times 10^{-2}$ mol./l. and $1.352～3.577 \times 10^{-1}$ mol./l.) as initiator, were charged into a tube, and sealed in vacuo under cooling in a dry ice-methanol bath. The polymerization was carried out in a thermostat at 60°C under shaking for 30 hr. After polymerization, the content of the tube was poured into methanol.

Anionic Polymerization.—Anionic Polymerization was carried out in *n*-hexane, which was distilled twice over sodium wire. Commercial *n*-butyl lithium was used as initiator which was diluted with *n*-hexane to 0.193～0.385 mol./l. The hexane solution of PCP (2 ml. of PCP in 1 ml. of *n*-hexane) and of *n*-butyl lithium were fed into a tube, and sealed under nitrogen atmosphere. The polymerization was carried out at 30, 5 and −70°C from 72 to 120 hr.

Polymerization by Ziegler Catalyst.—The triisobutylaluminum ($Al(i\text{-}Bu)_3$), supplied by Ethyl Corporation, was diluted with *n*-hexane and titanium tetrachloride was distilled three times and used as *n*-hexane solution. The hexane solution of triisobutylaluminum was charged into a tube and then titanium tetrachloride solution was added under nitrogen atomosphere, and a reddish brown precipitate appeared immediately. An addition of titanium tetrachloride was made and then the tube was stood for 15 min., the monomer, PCP, was added and the tube was sealed under nitrogen atomosphere. The polymerization was carried out at 25, 5 and −70°C for 120 hr. and the tube was shaken at times during the process. In these polymerizations, Al/Ti molar ratio was changed from 0.93 to 1.23, 2.16, 2.47 and 3.39, and the total catalyst concentration to the monomer was varied between 2.04～4.18 wt.%.

After polymerization, the content of the tube was poured into a large amount of methanol, but no polymer was precipitated. In the polymerizations by radical and Ziegler type initiators, a small quantity of brown methanol-soluble oil was obtained, when monomer PCP was recovering.

Cationic Polymerization.—Cationic polymerization was carried out by titanium tetrachloride or boron trifluoride etherate catalysts.

A mixture of 2 ml. of PCP, 2 ml. of *n*-hexane and $6.593～13.19 \times 10^{-2}$ mol./l. of titanium tetrachloride were fed into a tube and sealed under nitrogen atomosphere. The polymerization was carried out at 30 and 50°C for 120 hr. Then the content of the tube was poured into excess methanol. The same results were obtained as both in radical and

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[1] L. A. Brooks and H. R. Snyder, "Organic Syntheses", Coll. Vol. 3 (1955) p. 698.

[2] F. B. La Forge and N. Green et al., *J. Am. Chem. Soc.*, 70, 3703 (1948).

* By micro Carius method.

[3] R. B. Moffett, "Organic Syntheses", Vol. 32 (1952), p. 41.

TABLE II. COPOLYMERIZATION OF PCP WITH MALEIC ANHYDRIDE AT 60°C FOR 3 hr.

Exp. No.	[PCP]	[MA]	Total monomer	AIBN	Polymer Yield	Elementary* analysis		
	g.	g.	g.	g.	g.	C, %	H, %	O, %
1	1.6534	1.1535	2.8069	0.0065	0.6340	58.80	7.43	33.77
2	4.9602	1.5986	6.5588	0.0085	0.6774	—	—	—
3	1.6534	2.4059	4.0593	0.0069	0.6099	59.38	7.44	33.17
4	5.7042	1.4233	7.1275	0.0077	1.2291	59.01	6.76	34.24
5	3.3068	1.3438	4.6506	0.0076	0.8055	59.15	7.10	33.75

* After hydrolyzed by 10% KOH for 50 hr. Theoretical value for 1 : 2 copolymer : C, 58.69% ; H, 6.57% ; O, 34.75%.

Ziegler catalyst polymerizations and no polymer was formed.

Freshly distilled boron trifluoride etherate was added to a tube containing 2 ml. of PCP and 2 ml. of benzene. The concentration of boron trifluoride etherate was changed between $3.910\sim7.820\times10^{-2}$ mol./l. When the initiator was added to the benzene solution of PCP, the solution immediately turned pale brown. Polymerization was performed at 30, 5°C and room temperature for 72 hr.

After polymerization, when the mixture in the tube was poured into a large excess of methanol, a trace of brown polymer precipitated.

In view of the above results, another polymerization, in which the concentration of boron trifluoride etherate was increased to 1.56×10^{-1} and 7.95×10^{-2} mol./l. was performed at 50°C and room temperature. The results obtained in the secnd series of these polymerizations were the same as those in the first series of the same polymerization of boron trifluoride etherate initiated polymerization. This polymer was swelled a little in tetrahydrofuran only. No double bond being found in infrared absorption spectrum, we assume that PCP is polymerized by boron trifluoride etherate to form a cross-linked polymer. The polymer obtained was a very small quantity.

Copolymerization of PCP with MA.—MA, m. p. 53∼54°C, was recrystallized three times from chloroform. AIBN was used as polymerization initiator. Polymerization was carried out as usual, monomers and initiator being charged into a tube and sealed in vacuo, in a thermostat at 60°C under shaking. During the polymerization, a pale yellow waxy polymer precipitated from polymerization system. After 3 hr., the content of the tube was poured into a large amount of methanol. The precipitated polymers were filtered and dried under 40°C in a desiccator. The polymers appeared like a pale yellow glassy substance and swelled a little in tetrahydrofuran, dioxane and dimethylformamide.

The polymers were refluxed in tetrahydrofuran and methanol for 3 hr. to remove as much initiator as possible. Then the polymers were hydrolyzed by 10% potassium hydroxide or hydrochloric acid as catalyst in water for 50 hr. Hydrolyzed polymers by potassium hydroxide catalyst is shown in Table II. The values of carbon % in Table II are somewhat larger than the theoretical value and the values of oxygen % are rather small due to the difficulty in complete hydrolysis : these polymers were gelled and did not dissolve in the solvent.

As Table II shows, PCP and maleic anhydride were copolymerized and when the monomer mixture ratio was changed, the polymer composition was not changed but always kept the constant ratio of 1 to 2. After hydrolysis, the absorption band of carboxyl group appeared in the infrared absorption spectrum.

These results indicate that two unsaturated double bonds of PCP participate in the copolymerization with maleic anhydride to form a glassy gelled alternative copolymer, the ratio of PCP to maleic anhydride being 1 to 2.

Summary

3-(4'-Pentenyl)cyclopentene-1 (PCP) was prepared through the reaction of 1-pentenyl magnesium bromide and 3-chlorocyclopentene-1. An attempt was made for the polymerization and copolymerization of PCP. In the polymerizations by radical (azobisisobutyronitrile) and Ziegler $[Al(i\text{-}Bu)_3\text{-}TiCl_4]$ initiators, a little brown methanol-soluble oil was obtained. By cationic initiator ($BF_3\cdot OEt_2$), however, a trace of reddish brown polymer which did not dissolve in common organic solvents was formed.

PCP was copolymerized with maleic anhydride by the use of a radical initiator. When the monomer mixture ratio of PCP to maleic anhydride was varied, no change was observed in the copolymer composition (the proportion of PCP to maleic anhydride being 1 to 2). In the infrared spectrum of the copolymer, the absorption bands of the vinyl type double bond and the unsaturated cyclopentene ring of PCP disappeared in the copolymer, so it was to be assumed that both double bonds participated in the copolymerization to form glassy gelled pale-yellow copolymer. These results indicate that an alternative copolymerization took place.

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