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Polymerization of Naphthalene and Reactions of Polynaphthalene

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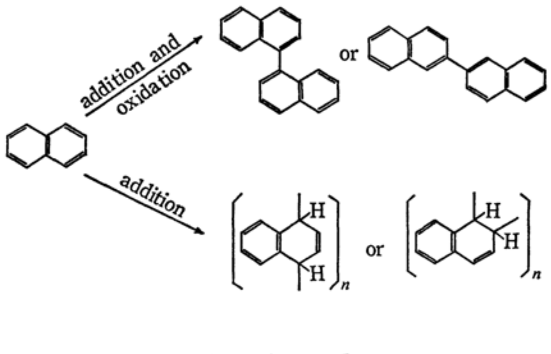
Naphthalene was polymerized by use of anhydrous aluminum chloride. The polynaphthalene formed was soluble in various organic solvents. The molecular weight determination suggested that the average degree of polymerization was six. The NMR spectrum indicated the presence of non-aromatic hydrogens, and the elemental analysis roughly corresponded with $(C_{10}H_8)_n$. The reactions of the polymer was examined such as hydrogenation, bromination, thermal dehydrogenation, chloromethylation and epoxidation.

Kovacic and his coworkers reported on the reactions of various aromatic hydrocarbons such as benzene, toluene, xylene and naphthalene with Lewis acids and oxidizing agents.1) From benzene, polyphenyls were obtained, which were insoluble and infusible. Naphthalene was let to react in *o*-dichlorobenzene with Lewis acids and oxidizing agents, and 1,1′-, 1,2′- and 2,2′-binaphthayls were obtained.

We have been interested in two-step polymerizations of various compounds, and have examined the possibility of performing the addition and the oxidation separately in order to obtain a soluble and fusible polymer.

It was found that benzene, toluene and xylene yields very little polymer when oxidizing agents were not present. However, it was found that naphthalene was converted into polynaphthalene in quite a good yield when it was let to react with anhydrous aluminum chloride without solvent. The results of this polymerization and the reactions of the polymer obtained will be described in this paper.



Experimental

Reagents. Naphthalene used was commercially available extra pure grade naphthalene. Anhydrous aluminum chloride used was commercially available extra pure grade.

Polymerization of Naphthalene. *Procedure A.* Naphthalene, 160 g, was ground in a porcelain mortar and placed in a 500 m*l* three-necked round-bottomed flask. Anhydrous aluminum chloride, 11 g, was also finely powdered and added. They were stirred under a nitrogen atmosphere. When the temperature was raised to 70—72°C, the mixture melted and became homogeneous. The reaction was exothermic at the first stage, and no sooner the reaction started than the color of the mixture started to darken. The reaction mixture was kept at 73—72°C for two hours. The

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1) P. Kovacic and J. Oziomek, *J. Org. Chem.*, **28**, 968 (1963); P. Kovacic and J. Oziomek, *ibid.*, **29**, 101 (1964); P. Kovacic, F. W. Koch and C. E. Stephan, *J. Polymer Sci.*, **2A**, 1193 (1964); P. Kovacic and M. Kyriakis, *J. Am. Chem. Soc.*, **85**, 456 (1963); P. Kovacic and C. Wu, *J. Org. Chem.*, **26**, 767 (1961); P. Kovacic and F. W. Koch, *ibid.*, **30**, 3176 (1965).

TABLE 1. POLYMERIZATION OF NAPHTHALENE

Procedure	Naphthalene g (mol)	Aluminum chloride, anhydrous g (mol)	Mol% $AlCl_3$	Temp. °C	Time hr	Yield g (%)
A	160 (1.25)	11 (0.0825)	6.2	73—75	2	56.0 (35.0)
B	96 (0.748)	25.5 (0.191)	20.3	80—90	2.5	81.0 (84.4)

black product was a viscous liquid at the reaction temperature and solidified at room temperature. The product was all transferred to a 1-*l* round-bottomed flask to which 500 m*l* of water was added. The naphthalene which remained unreacted was steam-distilled out to a receiver through an air condenser. The steam ditillation was continued for 4 hr. The water was discarded, and another 500 m*l* of fresh water was added to run the second distillation for four hours. The same procedure was carried out for the third distillation. After the third distillation, the black product was added in 200 m*l* of warm benzene, and the product completely dissolved. After cooling anhydrous sodium sulfate was added, and the solution was allowed to stand overnight. After the filtration of the sodium sulfate, benzene was evaporated to yield 56 g of a product. The product was a viscous tar-like substance with cohesive properties. The solubility of the product in petroleum ether was 0.154 g/100 m*l* at 27°C.

Procedure B. The procedure was the same as in Procedure A except the quantities of the reagents and the experimental conditions as Table 1 shows. Analyses of the polymers produced by two procedures indicated that the structure and the properties of these polymers were similar. The polymer produced by Procedure A was subjected to various reactions and analyses.

Purification. Naphthalene polymer, 15 g, was dissolved in 10 m*l* of benzene. The solution was added drop by drop into 200 m*l* of petroleum ether with stirring. The naphthalene polymer was dispersed to yield fine, dark brown precipitates which accumulated at the bottom of the beaker. The precipitates were filtered by use of a glass filter, dried and ground in a mortar. Brown powder, 7.0 g was obtained. The weight percent yield was 47%. Again the brown powder was dissolved in 5 m*l* of benzene, and the benzene solution was added dropwise into a 200 m*l* of stirred petroleum ether. Almost all of the substance was recovered in the second precipitation. For the investigation of the structure, further purification was tried. The polymer, 6.5 g, obtained by the above purification, was shaken three times with 100 m*l* of 5% $NaHCO_3$, three times with 100 m*l* of 5% HCl, and three times with 100 m*l* of distilled water. Anhydrous sodium sulfate was added to the benzene solution, and the solution was allowed to stand overnight. The filtered benzene solution was added dropwise to 400 m*l* of stirred petroleum ether. The benzene solution was dispersed to yield brown precipitates. The precipitates were filtered and dried. The final product obtained was 3.5 g and the percentage yield in this prification was 54%.

Results and Discussion

The Analyses of the Polymer. The NMR spectrum of the naphthalene polymer is shown in Fig. 1. The absorptions at 1.9 ppm and 2.9 ppm are due to aliphatic hydrogens. Since there are two peaks instead of one, the 1,2-dihydro-structure seems to predominate in the polymer. The 1,2-dihydro-structure has two kinds of aliphatic hydrogens and the 1,4-dihydro-structure has one kind of aliphatic hydrogen.

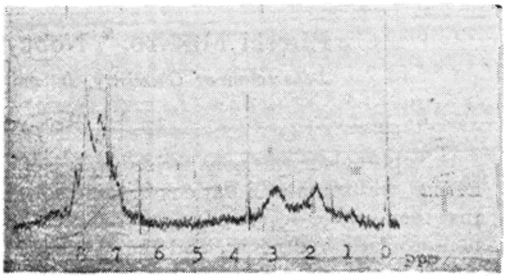

Fig. 1. NMR spectrum of the naphthalene polymer in CCl_4 (reference, tetramethylsilane: 60 Mc).

The results of the elemental analysis of the polymer is summarized in Table 2.
These results indicate the presence of some non-hydrocarbon materials, presumably aluminum chloride. The carbon hydrogen contents correspond with the formula $C_{10}H_{7.37}$. The small difference between this value and theoretical value $C_{10}H_8$ can be ascribed to the dehydrogenation of the polymer, which is likely to take place to some extent even in the absence of any oxidizing agent.

The molecular weight of the polymer was determined by an Osmometer Model 301, Microlab. The determination in chloroform showed that the molecular weight was 761. Since the molecular weight of $(C_{10}H_8)$ is 769, the average degree of polymerization of this napthalene polymer is six.

In order to estimate the number of olefinic double bonds, catalytic hydrogenation of the polymer was carried out by use of platinum oxide. The benzene solution of the polymer was treated with hydrogen for three hours at 28°C/1 atm. Two determinations were carried out independently, and it was found that no hydrogen was absorbed in both cases. The failure of the hydrogenation may be ascribed to the bulkiness of the polymer molecule and the steric hindrance as to the olefinic double bonds.

The polymer was brominated with KBr-$KBrO_3$ in acetic acid according to the method of Johnson and Clark.[2] A $C_{10}H_8$ unit absorbed 0.40 bromine

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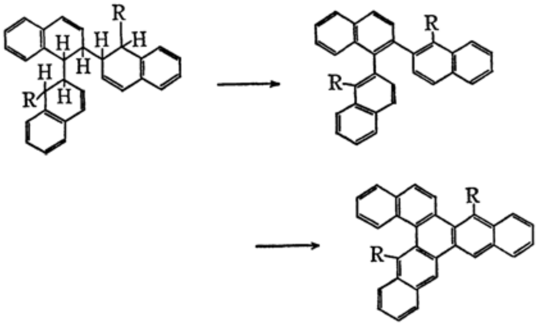
[2] H. L. Johnson and R. A. Clark, *Anal. Chem.*, **19**, 869 (1947).

Table 2. Elemental analysis of naphthalene polymer

	C%	H%	C%+H%	C%/C%+H%	H%/C%+H%
Found	92.30	5.71	98.01	94.18	5.82
Calcd for $C_{10}H_8$	93.71	6.29	100		
Calcd for $C_{10}H_6$	96.00	4.00	100		

molecule in one hour, but after several hours the absorption only increased to 0.43. Theoretically every $C_{10}H_8$ unit of the polymer should absorb 1.0 molecule of bromine.

When the naphthalene polymer was heated in air, it softened near 60°C, and the color darkened at 160—170°C. While being heated, it apparently was aromatized. At 300°C, it was rather hard solid which could be pressed or moved by a spatula. It was thermally very stable and the weight did not decrease at all when heated for 90 min at 220°C and then for 90 min at 290°C. When it was heated for 6 hr at 320°C, some dehydrogenation took place, and the elemental analysis of the polymer indicated that the structure was $(C_{10}H_{5.82})_n$. The analysis shows that some naphthalene units are bound by more than one linkage.

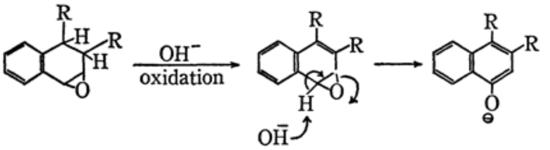


Reactions of the Naphthalene Polymer. *Oxidation with Potassium Permanganate.* The naphthalene polymer was refluxed in an alkaline potassium permanganate solution for 2 hr. The IR spectrum of the product was identical with that of the naphthalene polymer itself. The softening point (about 60°C) of the product was the same as that of the original polymer. It was, therefore, concluded that the naphthalene polymer was not oxidized with the reagent under the conditions mentioned above.

Chloromethylation. The naphthalene polymer was chloromethylated with polyoxymethylene and hydrogen chloride by the usual procedure. The chlorine analysis of the product showed 5.42% chlorine. Since the theoretical value was 20.1%, 27.0% of the initial polymer units was chloromethylated. The IR spectrum showed a new band at 1000 cm^{-1}.

Hydrolysis of the Chloromethylated Polymer. The chloromethylated polymer which was not separated from the unreacted naphthalene polymer was hydrolysed with a potassium carbonate solution. The IR spectrum of the hydrolysis product showed a new band at 1070 cm^{-1} which did not appear in the spectrum of the chloromethylated polymer, while the absorption band at 1000 cm^{-1} in the spectrum of the chloromethylated polymer greatly decreased. The absorption band at 1070 cm^{-1} was assigned to C–O of primary alcohol, and an absorption band due to O–H of primary alcohol appeared at 3400 cm^{-1}.

Epoxidation. The naphthalene polymer was epoxidized according to the method described for the epoxidation of styrene.[3] When the polymer was let to react with perbenzoic acid in benzene at 15°C, the peracid consumed for epoxidation was 71.7% at 113 hr, 78.1% at 165.5 hr and 88.1% at 573.5 hr (after the correction for blanks). In order to remove benzoic acid, the epxoidized polymer solution was treated with 5% sodium bicarbonate solution. Unexpectedly, the epoxidized naphthalene polymer was extracted into the aqueous layer after several extractions. When the alkaline solution was neutralized with hydrochloric acid, brown precipitates were obtained which were benzoic acid and phenolic polymers. Apparently the following reactions took place.



Attempts were made in order to remove benzoic acid without destruction of epoxy group, but in vain. The naphthalene polymer did not form its picrate; the sublimation of benzoic acid resulted in the destruction of the epoxy ring; the column chromatography resulted in the decomposition of the epoxy ring.

In order to have the easier separation of the carboxylic acid after the epoxidation, monoperphthalic acid was used. The rate of epoxidation was a little slower than that with perbenzoic acid, and 39.7% of the peracid was consumed after 44 hr. Phthalic acid precipitated was easily filtered.

The epoxidized naphthalene polymer was mixed with aniline-phenol-formaldehyde resin in the weight ratio of 1 : 0.43, and the mixture was heated at 160°C for 30 min. The mixture solidified completely due to the cross-linking.

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[3] *Organic Reactions,* **1,** 70 (1954).