Tetrahedron Letters No. 11, pp. 467-469, 1962. Pergamon Press Ltd. Printed in Great Britain.

# POLYMERIZATION OF BENZENE TO p-POLYPHENYL

Peter Kovacic and Alexander Kyriakis

Department of Chemistry, Case Institute of Technology, Cleveland 6, Ohio

(Received 22 March 1962; in revised form 11 April 1962)

ALTHOUGH benzene is known to give tars and other uncharacterized higher molecular weight products under certain conditions,[1] there appear to be no reports on the use of benzene as a monomer in well-defined polymerizations leading to homopolymers. This communication concerns an apparently novel method for this type of transformation involving aromatic nuclei, which is designated oxidative cationic polymerization.

We have found that benzene can be polymerized smoothly in the system, catalyst-cocatalyst-oxidizing agent, to a solid product possessing the properties of p-polyphenyl. For example, in the presence of aluminum chloride (0.5 mole), water (1 ml), and cupric chloride (0.5 mole), benzene (1 mole) was converted under remarkably mild conditions (36-37° for 1/2 hr to a brown solid (12 g).

Evidence for the p-polyphenyl structure is based upon the C/H atomic ratio (1.47) obtained from elemental analyses (Found: C, 92.87; H, 5.25; Cl, 0.73; O, 0.89. Calc. for $C_6H_4$: C, 94.70; H, 5.30), infrared spectrum, X-ray diffraction pattern, thermal stability, pyrolysis products, and insolubility. The polymer is very similar (color, insolubility, thermal stability, infrared and X-ray data) to the p-polyphenyl prepared[2] by Marvel

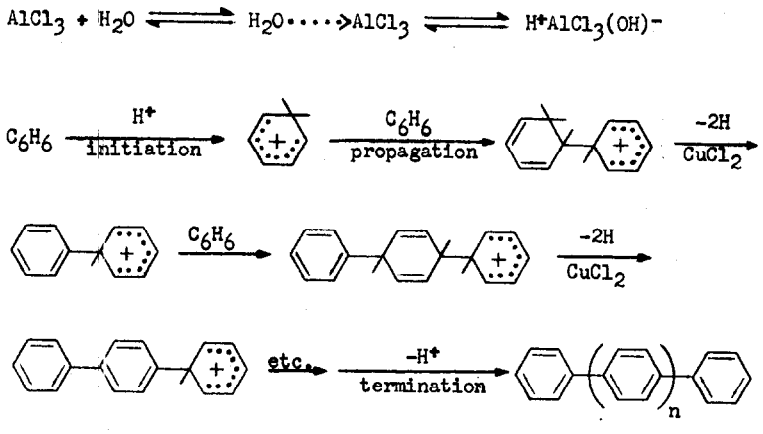
---

[1] For pertinent references see C.A. Thomas, Anhydrous Aluminum Chloride in Organic Chemistry p. 713. Reinhold, New York (1941).

[2] C.S. Marvel and G.E. Hartzell, J. Amer. Chem. Soc. 81, 448 (1959).

and Hartzell by another method. In addition to residual material, pyrolysis in vacuo yielded volatile lower p-polyphenyls including biphenyl, terphenyl, quaterphenyl, and quinquephenyl. There were no more than trace amounts of isomeric lower polyphenyls in the pyrolysis product.

The following reaction sequence is suggested for oxidative cationic polymerization of aromatic nuclei.




Less than 0.2 per cent of soluble material was obtained from the polymer by successive extractions with boiling ether, chloroform, and p-xylene.

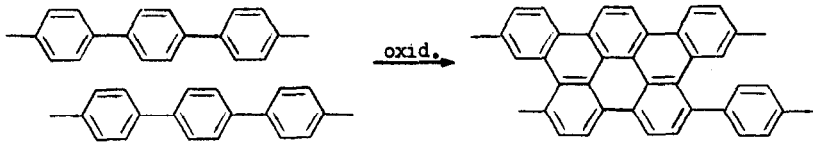
In control experiments, no solid product resulted when either aluminum chloride or cupric chloride was omitted from the reaction mixture. The effect of variation in water content is currently being studied.

The roles of catalyst and oxidizing agent can be assumed by a single reagent, such as ferric chloride.[3] In this case, it is possible to obtain polymers possessing higher C/H atomic ratios (1.8-2.5) and darker colors. This suggests that the p-polyphenyl is converted to some extent subsequently to polynuclear structures.[4] A minor number of cross-links may be present

[3] P. Kovacic and C. Wu, J. Polymer Sci. 47, 45 (1960).

[4] P. Kovacic, C.E. Stephan and F.W. Koch, unpublished work.

in the polymer prepared by means of aluminum chloride-cupric chloride.




Our investigations of the reaction scope and polymer properties are continuing.

Acknowledgements - We wish to thank the Petroleum Research Fund of the American Chemical Society, and the National Science Foundation for their support of this work.