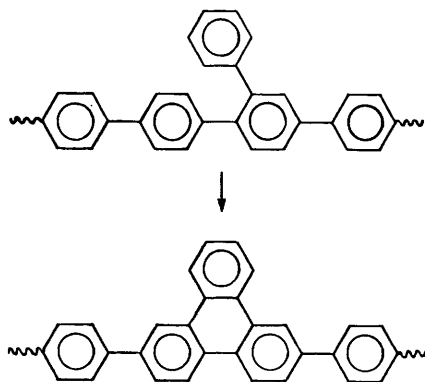


Organic Synthesis using Fused Salt Systems. Preparation of a Polytriphenylene

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THE synthesis of polybenzenes has received considerable attention because of the desirable thermal stability of these polymers. It has been pointed out that chain branching could occur during the polymerization of benzene with Lewis acid catalyst-oxidant,¹ but the presence or absence of such branching has not yet been conclusively shown. If such branching occurs, cyclization to produce a triphenylene nucleus in the polymer chain could occur by the same mechanism proposed for chain growth. Therefore, as part of our study



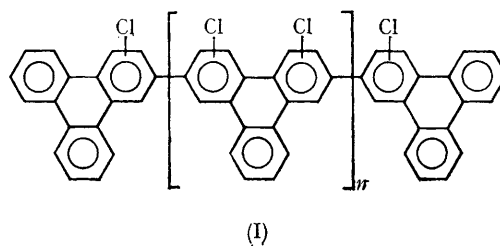
of the preparation and characterization of high-temperature polymers using fused salts as reaction media, we have prepared a polytriphenylene using a eutectic mixture of ferric chloride (60 wt%), sodium chloride (26 wt%), and potassium chloride (14 wt%)² both as "solvent" and source of Lewis acid.

Triphenylene was polymerized at $220 \pm 10^\circ \text{C}$ until hydrogen chloride evolution subsided. The tan polymer was readily formed and isolated in 43% yield; non-polymeric products were not analyzed. On the basis of calculations for possible formulae,³ the elemental composition indicated polymer molecules consisting of sequences of three or more chlorinated triphenylene units. The

C/(H + Cl) ratio (1.805) indicates that the polymer is completely aromatic (theoretical value 1.800). The usually intense absorption peak at 738 cm^{-1} characteristic of triphenylene monomer⁴ was not apparent in the infrared spectrum (KBr disc) of the polymer indicating extensive chlorination and polymerization of the triphenylene nuclei. These observations are consistent with the proposed structure (I), for this polytriphenylene. The polymer is insoluble in the usual organic solvents, but is soluble to the extent of ca. 60% in refluxing phenanthrene.

Differential thermal analysis showed that an exothermic reaction occurred at 457°C when the polytriphenylene was heated under nitrogen at a programmed temperature rate of $10^\circ \text{C}/\text{min}$. A subsequent weight loss corresponding to the weight of the original hydrogen and chlorine in the polymer was indicated by thermogravimetric analysis. The infrared spectrum of the residue compared favourably with the known spectrum for carbon black.⁵ On the basis of these results it is postulated that the exothermic reaction observed is caused by the formation of more highly condensed carbocyclic ring systems.

A copolymer of triphenylene and *p*-terphenyl, a polymer more closely related to that expected for a moderately branched polybenzene, has been prepared by this method and will be reported in the detailed account of this work.



(Received, November 22nd., 1965; Com. 727.)

¹ P. Kovacic and C. Wu, *J. Polymer Sci.*, 1960, **47**, 45.

² D. I. Packham, *Chem. Comm.*, 1965, 207.

³ D. A. Usher, J. Z. Gougoutas, and R. B. Woodward, *Analyt Chem.*, 1965, **37**, 330.

⁴ C. M. Buess and D. D. Lawson, *Chem. Rev.*, 1960, **60**, 313.

⁵ E. K. Plyler and J. J. Ball, *J. Opt. Soc. Amer.*, 1948, **38**, 988.