

FRIEDEL-CRAFTS POLYMERISATION

S. L. KAPUR

(Division of High Polymers, National Chemical Laboratory, Poona)

THE use of AlCl_3 and other metallic halides in Friedel-Crafts synthesis of aromatic compounds is well known. When these catalysts are added to such monomers as styrene and its derivatives, or isobutylene, a very rapid polymerization takes place. This polymerization is very sensitive to impurities although the well-known inhibitors like hydroquinone or oxygen have no effect on it. The molecular weight of the resulting polymer is very low and unlike addition polymerization it increases with the rise of temperature. The fact¹ that molecular weight reaches its maximum immediately after start, points it to be a chain reaction rather than a step reaction.

The mechanism of such a polymerization is quite different from that of a free radical polymerization and the nature of the catalyst is indicative of a polar mechanism. The salient features of such type of polymerization are discussed below:

The catalytic activity decreases in the series BF_3 , AlBr_3 , TiCl_4 , TiBr_4 , BCl_3 , BBr_3 , and SnCl_4 . There are certain minimum concentrations of the catalyst and the monomer below which no polymerization takes place. In industry BF_3 is used as the catalyst but in scientific work weak catalysts are used as they are amenable to controlled conditions. No polymerization takes place when thoroughly dried catalysts are used^{2,3}; a third component, usually water or an alcohol is required in small amount.

The monomers in this type of polymerization contain in general an electron rich double bond. Thus substituents in the following typical monomers are of the electron releasing type:— (1) Styrene, (2) α -Methyl Styrene, (3) Isobutylene, (4) Indene, (5) Alkyl Vinyl Ether.

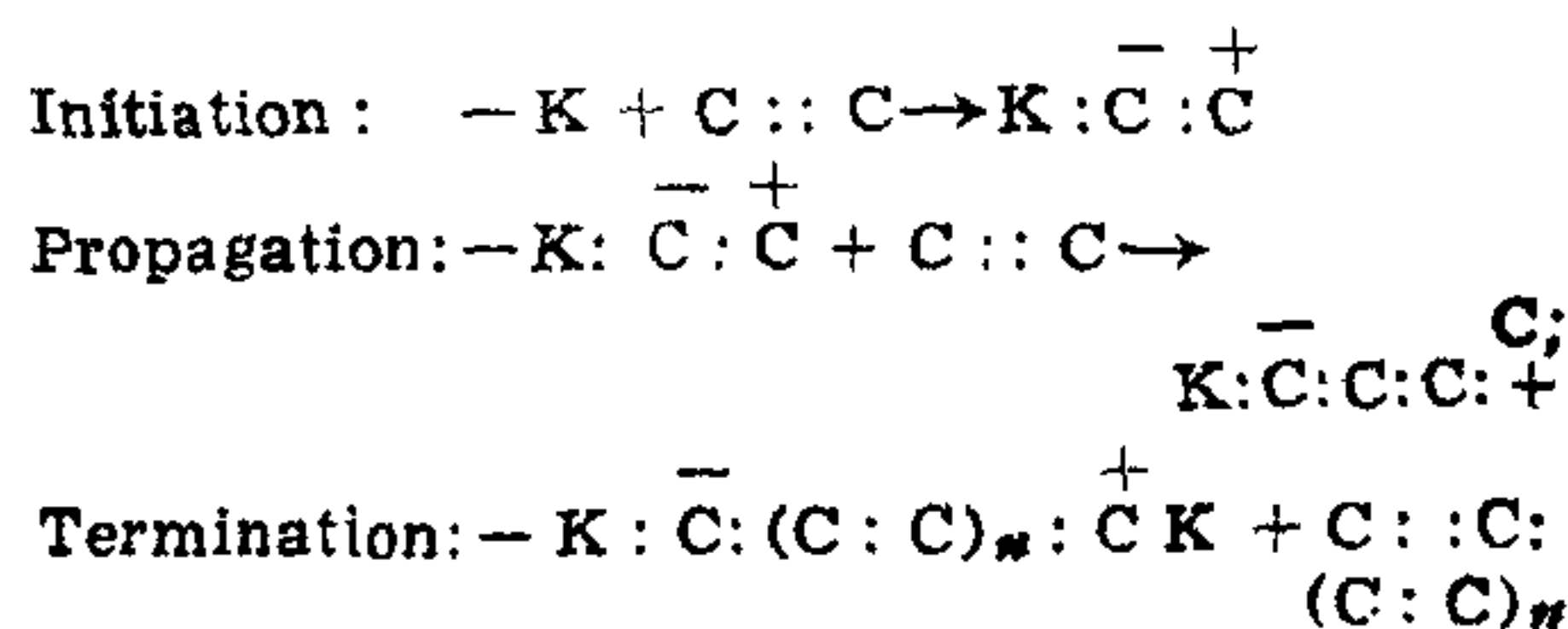
It follows that monomers like vinyl chloride and acrylates which contain electron-attracting substituents cannot be polymerized by such catalysts.

In contrast to inhibition in free radical polymerizations, steric factors play an important role in this type of inhibition. Amines and ethers are some of the typical inhibitors. Amines react with the catalyst to form a complex compound. It has been shown by Brown and Co-workers⁴ that dissociation of the above type of complexes is governed by steric factors. So, it follows that complexes of secondary and tertiary amines with the catalyst will be dissociated to a larger extent than complexes of primary amines. Thus di- and tri-*n*-butyl amines and dimethyl aniline

are about equally effective inhibitors of styrene polymerization while *n*-butylamine is weaker.⁵ This order is however, changed to di-*n*-butylamine, tri-*n*-butylamine, dimethyl aniline and *n*-butyl amine in the polymerization of α -methyl styrene for the likely reason that the reaction between the free amines and chain propagating species (probably a carbonium ion) is also subject to steric hindrance. The α -methyl styrene carbonium ion $\text{R}-\text{C}(\text{CH}_3)\text{C}_6\text{H}_5$ is sterically more hindered than the styrene carbonium ion, which explains the difference in the action of secondary and tertiary amines.

As a consequence of the popular nature of these polymerizations it is to be expected that dielectric constant of the medium strongly influences the reaction, a fact that has been actually observed in the case of α -methyl styrene⁶ and styrene. In the case of styrene, reaction rates show a rapid increase whereas molecular weight is only slightly affected, which indicates that inhibition reaction is strongly favoured while termination is depressed in high dielectric constant media.⁷

Eyring and coworkers⁸ suggested that such a polymerization proceeds through a dipolar intermediate. It is assumed that catalyst merely increases the polarity of the double bond and termination is brought about by the snapping of the catalyst from the chain and they suggested the following mechanism.



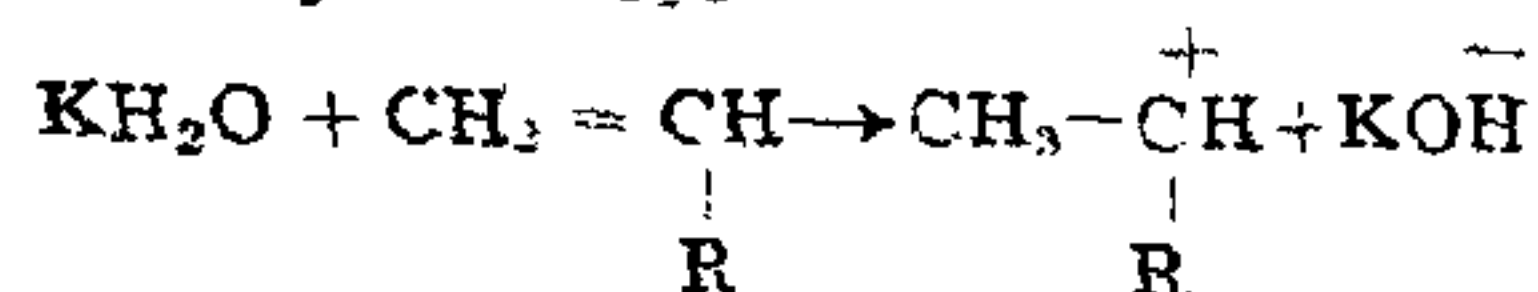
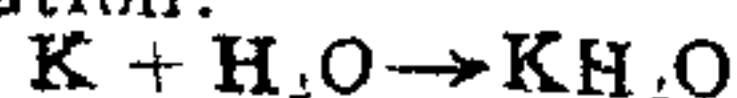
where K denotes the catalyst.

This scheme does not account for the findings of Polanyi and coworkers^{2,3,4} that a co-catalyst is positively required for starting the reaction.

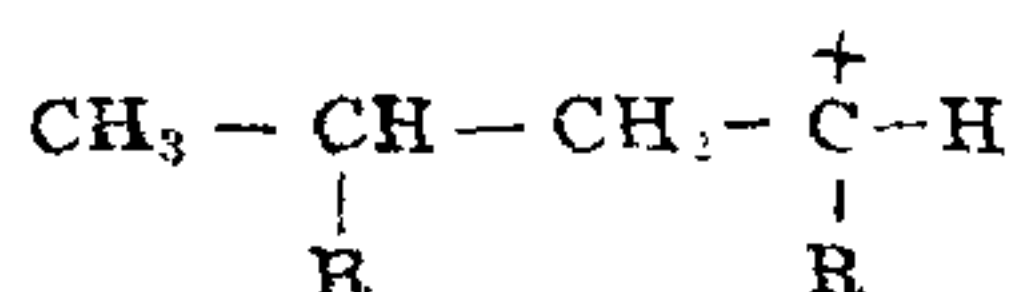
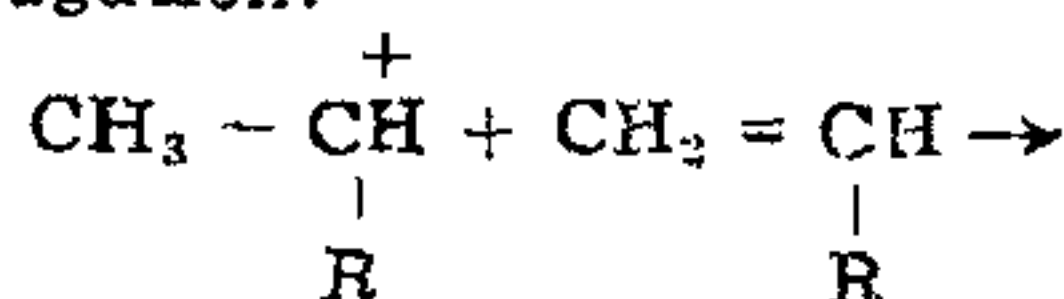
It is clear that if catalyst increases the polarity of the olefinic double bond, BF_3 should be a more effective catalyst than the salt ' $\text{BF}_3 \cdot \text{H}_2\text{O}$ ' in which the electron accepting capacity of BF_3 is satisfied. This is not the case. Moreover the monomolecular termination (also postulated by Price⁹) should be practically unaffected by a change in the dielectric constant of the medium. George and Wechsler⁷ and others⁶ have very recently shown that termina-

tion is depressed by increase of dielectric constant and all these facts support the mechanism approved by Polanyi and coworkers.

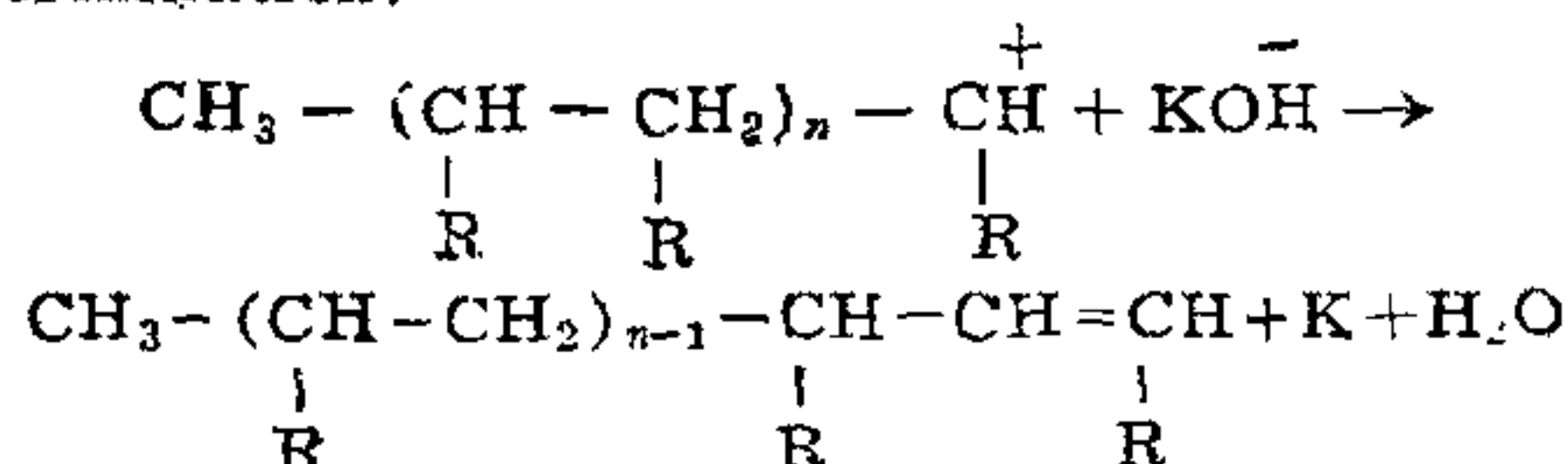
Initiation:—



Propagation:—



Termination:—



The termination being a reaction between oppositely charged ions will be depressed in a medium of high dielectric constant. There is a

note of caution to be observed in accepting this mechanism since we are not dealing with free ions but rather with ion pairs or with potential ions and the proposed mechanism is yet open to criticism.

Progress in this field of polymer chemistry has been slow mainly because of the sensitivity of the reaction to impurities and its high rate in absence of solvents. No reliable kinetic investigations of such polymerizations have been reported as yet.

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ADVANCES IN MICROBIOLOGY*

MICROBIOLOGY has now come of age; separate Research Institutes for the study of microbiology have been founded and the latest in the field is the one organized by Professor Waksman. The rapidly accumulating wealth of fundamental knowledge and the spectacular growth of industries based on the discoveries made in the field of microbiology, have hastened this happy recognition of microbiology as an independent and well-defined branch of science. Microbiology has, in recent years, invaded the fields of genetics, nutrition and intermediary metabolism and micro-organisms have continued to provide for fundamental studies a convenient unicellular unit of life of unexpected flexibility and resourcefulness.

It was inevitable that such a rapidly growing and fruitful branch of science should result in the birth of the *Annual Review of Microbiology*—the third in the lineage of the brilliant family of Annual Reviews.

Seventeen reviews encompassing the morphological, cytological, genetical, immunological, pathological, chemotherapeutical, epidemiological, nutritional, biochemical, medical and industrial facets of microbiology, have been presented

in the first volume by a group of top-ranking and active workers. Of the 17 contributions, thirteen are from the laboratories of the U.S.A., three are from England and one is from France. The total number of references to literature cited in the volume is nearly 2,000.

Protozoa, fungi, bacteria and viruses are all covered. Investigators interested in the various aspects of protozoal diseases including malaria will find the four contributions, morphology and cytology of protozoa by Wenrich, antigenic variation in protozoa by Harrison, life cycle of malarial parasites by Huff, and the problem of growth factors for protozoa by Lwoff, extremely stimulating and suggestive. Those interested in nutrition and intermediary metabolism will welcome the contributions of Woods and Gale on Bacterial Metabolism and Nitrogen Metabolism. Benedict and Langlykke have reviewed the evergrowing field of antibiotics, while the important aspects of Industrial Fermentations are covered by a review by Johnson. The review on chemotherapeutic agents by Lourie constitutes a thought provoking article which will serve to stimulate and rationalise chemotherapeutical research. These reviews have a much wider appeal than what may be apparent from the title. By the publication of the new series of reviews devoted to microbiology, the Annual Reviews Inc. have earned the gratitude of a wide circle of investigators.

* *Annual Review of Microbiology*, Vol. I. Edited by Charles E. Clifton, Sidney Raffel and H. Albert Barker. (Annual Reviews Inc., Stanford, California). 1947. Pp. vii + 104. Price \$ 6.00.