A THEORY FOR THE STEREOSPECIFIC POLYMERIZATION OF PROPYLENE OXIDE BY FERRIC CHLORIDE

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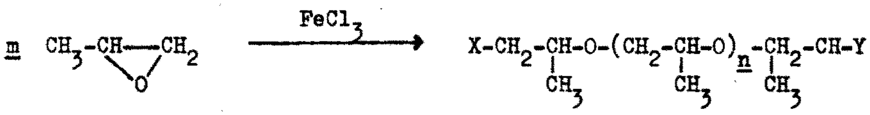
THE polymerization of d,l-propylene oxide under the catalytic influence of ferric chloride may be described grossly by equation (1) in which X and Y represent terminal units, possibly Cl, OH or an unsaturated group.



$$\underline{m}\ CH_3\text{-}\underset{\diagdown\ O\ \diagup}{CH\text{—}CH_2} \xrightarrow{FeCl_3} X\text{-}CH_2\text{-}\underset{CH_3}{CH}\text{-}O\text{-}(CH_2\text{-}\underset{CH_3}{CH}\text{-}O)_{\underline{n}}\text{-}\underset{CH_3}{CH_2}\text{-}CH\text{-}Y \qquad (1)$$

Although the catalyst for the reaction and the gross structure of the polymer are unexceptional, the stereochemistry of the polymerization is extraordinary. Under the conditions which have been utilized for the polymerization, about 30-40 per cent of the polymeric product from d,l-propylene oxide is the isotactic [1] variety in which essentially all of the asymmetric carbons of a given polymer molecule possess the same configuration.[2] Thus, the optically inactive crystalline polymer consists of a mixture of all d- and all l-polymer molecules.

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[1] G. Natta, J. Polymer Sci. **16**, 143 (1955); G. Natta and P. Corradini, Makr. Chem. **16**, 77 (1955); C. W. Bunn and E. R. Howells, J. Polymer Sci. **18**, 307 (1955).

[2a] H. Staudinger, Hochmolekulare Organische Verbindungen p. 295. Springer, Berlin (1932); [b] U.S. Pat. 2,706,181 (April 12, 1955), M. E. Pruitt and J. M. Baggett (to the Dow Chemical Co.); U.S. Pat. 2,706,182 (April 12, 1955), M. E. Pruitt, J. M. Baggett, R. J. Bloomfield and J. H. Templeton (to the Dow Chemical Co.), cf. Chem. Abstr. **49**, 2395 (1955).

Price and coworkers [3,4] have shown that the polymer formed from l-propylene oxide with ferric chloride catalyst possesses the same specific rotation as that which results from l-propylene oxide using potassium hydroxide as catalyst, a clear indication that the ferric chloride-catalyzed polymerization proceeds with retention of configuration at the asymmetric center. Thus, it becomes necessary to assume that in the polymerization of d,l-epoxide the growing chain reacts selectively with that enantiomer which becomes involved in the initial stages and also that epoxide opening occurs by front-side displacement at the asymmetric carbon of the epoxide.

Based on the observations that solid gradually separates from the polymerization mixture and that the crystalline polymer possesses a higher average molecular weight than the amorphous product, it has been proposed [4] that stereospecificity is consequential to heterogeneity and is dependent on the generation of an asymmetric surface. The purpose of this note is to indicate an alternative and simpler explanation which derives from the availability of a reasonable, stereoselective mechanism for reaction in solution and which is not dependent on complex surface effects (although these might pertain). The essential features of the process are formalized in Fig. 1. In this scheme the activity of the catalyst is associated with the well-known tendency of iron to form octahedral complexes and the initial step is the reaction of ferric chloride with a molecule of propylene oxide, the d-form, for example, and some terminating

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[3] C. C. Price, M. Osgan, R. E. Hughes and C. Shambelan, J. Amer. Chem. Soc. 78, 690 (1956).

[4] C. C. Price and M. Osgan, J. Amer. Chem. Soc. 78, 4787 (1956).

group X to give the unstable complex I.[5] This is converted reversibly by co-ordination with a second propylene oxide molecule to the octahedral complex II. Complex II may react internally by attack of the nucleophilic alkoxide donor group on the nearby epoxide ring, specifically by displacement at the asymmetric carbon atom with retention of configuration,

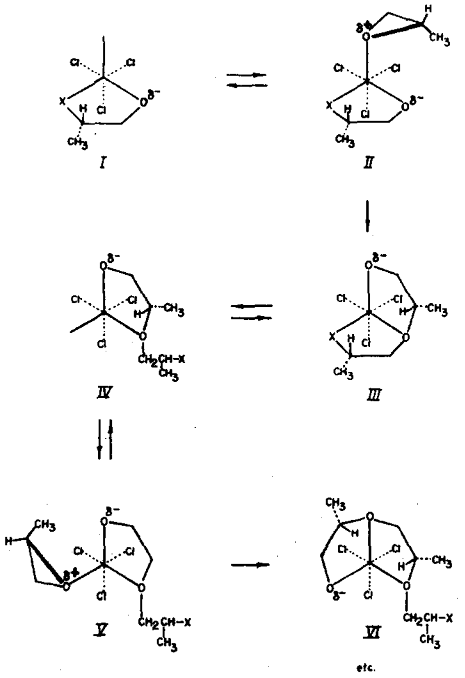

FIG. 1.

to form complex III in which the first and second units have been joined.

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[5] The five-co-ordinated intermediates in Fig. 1 are represented as possessing the tetragonal pyramid arrangement. This type of structure seems to be favored generally over the trigonal bipyramid form in S$_N$1 reactions of octahedral complex ions; see F. Basolo and R. G. Pearson, Mechanisms of Inorganic Reactions, Chap. 5. John Wiley, New York (1958).

To the extent that the transition state for this reaction resembles the product in structure, the conversion of II to III will be more facile when the second unit is derived from the same enantiomer of propylene oxide as was the first, i.e. _d_ as specified above, since this leads to a folded system of two _cis_-fused five-membered rings in which both methyl substituents are situated external to the fold, free of serious steric repulsions and both equatorial*.[6] If the second unit is derived from the other enantiomer, _l_-propylene oxide, a much less stable structure would result and it is suggested that instead of forming a new chelate ring the _l_-propylene oxide dissociates making room for the more reactive _d_-enantiomer. Complex III rearranges to IV which co-ordinates reversibly with another monomer unit to give V. If the third monomer unit is the _d_-isomer, V is converted rapidly to VI, otherwise dissociation to IV takes place. Additional monomer units unite with the growing chain by the process represented by III → VI. According to this interpretation formation of the polymer involves three orthogonal valences of the octahedral metal ion which co-ordinate singly and in turn with monomer units as the polymer is removed from the catalyst by dissociation of one donor group at a time. Construction of the polymer takes place cyclically about these three catalytic valences with constant control over the asymmetry of each unit being appended, a unique feature of this mechanism.

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[6] The five-membered chelate rings derived from 1,2-disubstituted ethanes are puckered to the extent that the substituents on carbon possess about 80 per cent axial or equatorial character (designated as axial* or equatorial*, respectively). For a detailed discussion of the geometry of such chelates and of stereospecific effects therein, see E. J. Corey and J. C. Bailar, Jr., _J. Amer. Chem. Soc._ In press.

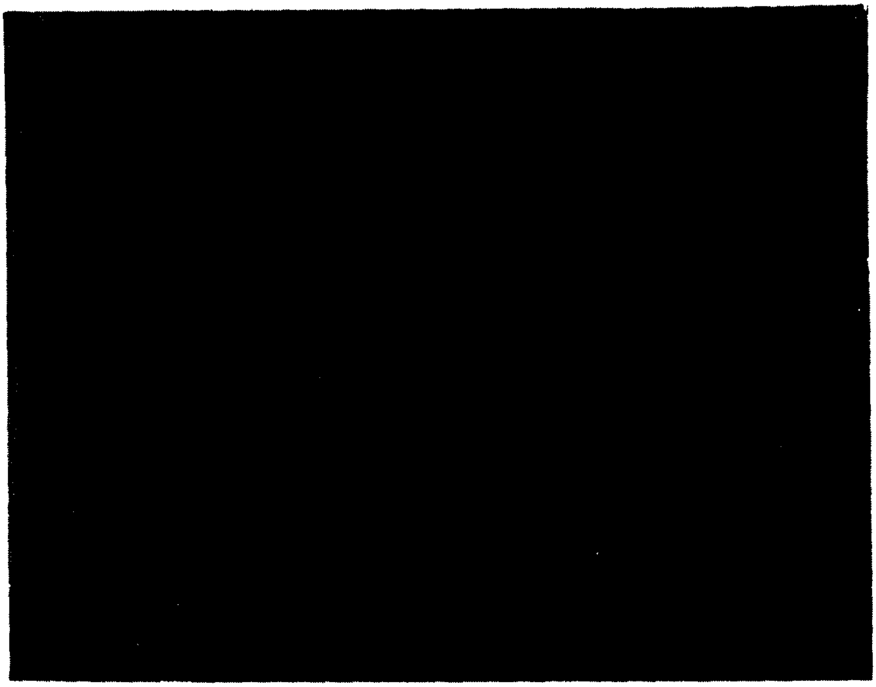

FIG. 2.

A model of complex VI is shown in Fig. 2 to illustrate the geometry of this type of intermediate and the preference for incorporation of units having the same configuration.

It is also conceivable that the polymerization might take place by a process similar to that above, but involving four of the iron valences which lie in the same plane. Here again, a cyclic addition-unwinding process in which new monomer units are added one at a time as the formed polymer units unwind is possible. Consideration of the structures involved in this process, however, makes it seem doubtful that such a polymerization would be very specific and hence this mechanism may be discounted. Other possibilities involving five or six of the iron valences can be discarded with confidence both because they do not account at all for the observed stereospecificity and because they do not present a sterically favorable reaction path.

Formation of isotactic polymer from propylene oxide has also been observed with other catalysts, e.g., aluminum isopropoxide-zinc chloride and titanium alkoxide-zinc chloride. Although these reactions are considerably less stereospecific than in the case of ferric chloride, it is possible that three of the metal valences (probably tetrahedral) are involved in co-ordination with the reactants, in a fashion analogous to the process in Fig. 1.