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INTERNAL ROTATION AND CONFORMATION OF LINEAR HIGH POLYMERS

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SVMMARIVM — Quorumdam linearium altorum polymerorum conformationes ita determinantur, ut constent ex formarum T et formarum G sequentia.

As reported in previous sessions (in 1961 and 1962), the unit structure of a linear high polymer is either the trans form (T) or the gauche form (G), and in each polymer there is a specific sequence of the T and G forms. The research has been continued with Prof. SHIMANOUCHI et al.

In Table 1 conformations of linear polymers determined by many investigators are shown in terms of a sequence of the T and G forms.

TABLE 1 — *Conformations of linear high polymers*

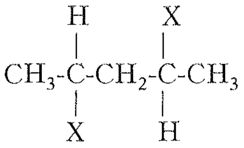
TTT...	polyethylene, syndiotactic polyvinyl chloride, syndiotactic and isotactic polyvinyl alcohol, syndioctactic polytetrafluoroethylene etc.
GGG...	polyoxymethylene

Paper presented on October 2, 1964, during the Plenary Session of the Pontifical Academy of Sciences.

TGTG...	isotactic polypropylene, isotactic polystyrene, and many isotactic polyolefins
TGTG′...	polyvinylidene chloride
TTGTTG...	polyethylene glycol, polyglycine II
TGGTGG...	α-helix of polypeptide
TTGG...	syndiotactic polypropylene
TTTGTTTG′...	rubber hydrochloride

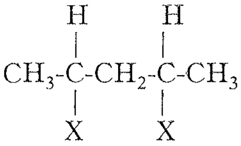
In order to understand the specific sequence of the two unit forms in these polymers, the following model compounds have been prepared in addition to those reported previously.

I. dl-form:



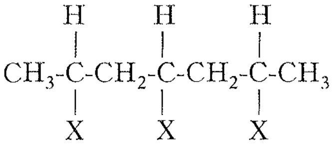
$$CH_3\text{-}\underset{X}{\overset{H}{C}}\text{-}CH_2\text{-}\underset{H}{\overset{X}{C}}\text{-}CH_3$$

II. meso-form:



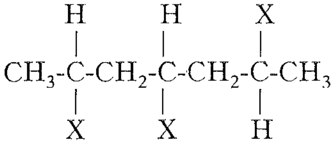
$$CH_3\text{-}\underset{X}{\overset{H}{C}}\text{-}CH_2\text{-}\underset{X}{\overset{H}{C}}\text{-}CH_3$$

III. isotactic form:



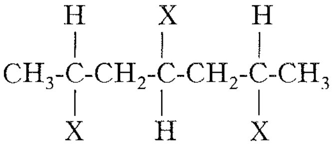
$$CH_3\text{-}\underset{X}{\overset{H}{C}}\text{-}CH_2\text{-}\underset{X}{\overset{H}{C}}\text{-}CH_2\text{-}\underset{X}{\overset{H}{C}}\text{-}CH_3$$

IV. heterotactic form:



$$CH_3\text{-}\underset{X}{\overset{H}{C}}\text{-}CH_2\text{-}\underset{X}{\overset{H}{C}}\text{-}CH_2\text{-}\underset{H}{\overset{X}{C}}\text{-}CH_3$$

V. syndiotactic form:



$$CH_3\text{-}\underset{X}{\overset{H}{C}}\text{-}CH_2\text{-}\underset{H}{\overset{X}{C}}\text{-}CH_2\text{-}\underset{X}{\overset{H}{C}}\text{-}CH_3$$

Substances with forms I and II were prepared for X=Cl and X=CN, and those with forms I, II, III, IV and V for X=OH. Evidently when X denotes CH_3, I and II become identical with each other (2,4-dimethylpentane).

The existence of many rotational isomers are expected for the substances mentioned above. Forms I and II contain two axes of internal rotation and, therefore, nine rotational isomers are conceivable. However, those in which two larger atoms or groups (i.e. X and X, or CH_3 and CH_3, or X and CH_3) are very close to each other will be unstable, and we consider two conformations *a* and *b* for I and only one conformation *c* for II. (See Fig. 1).

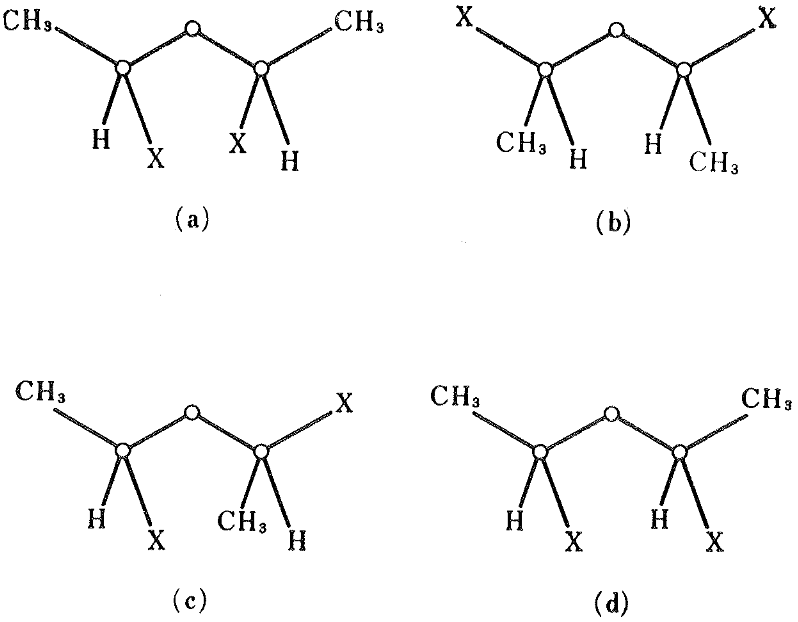


FIG. 1

For X = Cl the infrared measurement showed that only one conformation *a* exists for I. This is in agreement with the fact that syndiotactic polyvinylchloride takes TTT... form. In this case II takes only conformation *c* and, therefore, we except that the conformation of isotactic polyvinylchloride will be the trigonal helix TGTG...

If X denotes CH_3, I can take both of the conformations *a* and *b*. This is in agreement with the fact that syndiotactic polypropylene takes TTGG... form. For II only conformation *c* is conceivable. This is consistent with the observed conformation TGTG... of isotactic polypropylene.

If X denotes CN, I takes both of the conformations *a* and *b* and II only *c*. This suggests that polyacrylonitile will take a conformation similar to that of polypropylene. The reason why I takes conformation *a* for X = Cl and conformations *a* and *b* for X = CN is explained by the difference in the relative position of dipole moment on CCl and CCN groups.

For X = OH strong internal hydrogen bonding has been found to exist for both II and III. This results in the stability of conformation *d* and, therefore, explains the fact that isotactic polyvinylalcohol takes TTT... form. Syndiotactic polyvinylalcohol also takes this form, because the intermolecular hydrogen bonding is strong enough.

Details of this research will be published shortly in Prof. DEBYE's Anniversary Issue of the Journal of the American Chemical Society.