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Internal Rotation and Conformation of Linear High Polymers

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Conformations of various linear high polymers have been collectively discussed on the basis of the result of our study on internal rotation in simple molecules. The basic structures consisting of the *trans* and the *gauche* forms can explain the various conformations of polymers obtained experimentally. The change of a conformation with change of substituent has also been discussed.

Introduction

The structures of a large number of simple molecules have been studied in our laboratory in regard to the internal rotation about single bonds as axes. In the simplest case the *trans* and the *gauche* forms shown in Fig. 1 have been found to be the stable forms.¹

Recently the structures of many linear high polymers have been determined. In this paper the authors wish to report that stable conformations of these polymers can reasonably be explained by the energy relation of the internal rotation obtained from our study on simple molecules. In order to discuss the problem collectively, a part of this paper contains results of our investigations previously reported.

Conformation of Simple Molecules

For all the ethane derivatives so far studied in our laboratory the *trans* and the *gauche* forms are always the stable forms, but the equilibrium ratio between the two forms depends considerably on the state of aggregation (*i.e.*, the gaseous, liquid, and solid states) and also on the nature of the substituent.

In the case of a molecule with a carbonyl group (*e.g.*, Cl-CH₂-CO-CH₃), that with a hydrogen bond (*e.g.*, Cl-CH₂-CH₂-OH), and that forming a coordination bond (*e.g.*, NH₂-CH₂-CH₃-NH₂) the two forms mentioned above have also been found to be stable. However, the stable internal rotation angles of a molecule with a carbonyl group are somewhat different from those of the ideal *trans* and *gauche* forms (*i.e.*, 180 and 60°).

As to the nature of the hindering potential considerable discussion has been made by us as well as by other investigators. The experimental results obtained by us show that the van der Waals repulsive interaction and electrostatic interaction between the movable groups play an important part in hindering force. The change of the energy difference with change of state or with change of substituent can reasonably be explained by taking into account these interactions. However, the fact that in ethane derivatives the staggered forms (*i.e.*, the *trans* and *gauche* forms) are always found to be stable will have something to do with a lack of cylindrical symmetry of the electronic structure of the C-C bond. In this connection the idea proposed by Wilson² is very interesting, because this reasonably explains the stability of the *trans* and *gauche* forms always found for ethane derivatives. In other words, the position of the potential maxima and minima of the internal rotation is mainly determined by this electronic structure although the relative height of the potential minima is affected considerably by the elec-

trostatic and the van der Waals interactions between the movable groups. It may be added that the potential barrier is not so high as that of the double bond; and therefore, there is a rapid transformation from the *trans* form to the *gauche* form or *vice versa*. However, the lifetime is usually longer than the time between collisions so that our treatment as stable separate species is justified.

Basic Structure of Linear High Polymers

It is very probable that even in linear high polymers containing only single bonds the unit structure is either the *trans* form or the *gauche* form. On this basis we can obtain various conformations of linear polymers as shown in Fig. 2. These contain helices and pleated sheets.

It is very interesting to see that conformations of polymers experimentally determined correspond to one of those shown in Fig. 2, although in some cases the internal rotation angles are somewhat different from those of the ideal *trans* and *gauche* forms (see Table I and Fig. 3).

TABLE I
CONFORMATIONS OF LINEAR HIGH POLYMERS^a

TTT	Polyethylene, ^b syndiotactic polyvinyl chloride, ^{c,d} syndiotactic and isotactic polyvinyl alcohol, ^{e,f} syndiotactic polytetrafluoroethylene, ^g etc.
GGG	Polyoxymethylene ^{h,i}
TGTG	Isotactic polypropylene, isotactic polystyrene, and many isotactic polyolefins ^j
TGTG'	Polyvinylidene chloride ^k
TTGTTG	Polyethylene glycol, ^l polyglycine II ^m
TGGTGG	α -Helix of polypeptide ⁿ
TTGG	Syndiotactic polypropylene ^o
TTTGT'TTG'	Rubber hydrochloride ^p

^a T denotes the *trans* form and G the *gauche* form. G and G' are used to discriminate the right-handed and left-handed *gauche* forms, when necessary. ^b C. W. Bunn, *Trans. Faraday Soc.*, **35**, 482 (1939). ^c G. Natta and P. Corradini, *J. Polymer Sci.*, **20**, 251 (1956). ^d T. Shimanouchi, S. Tsuchiya, and S. Mizushima, *Kobunshi Kagaku*, **8**, 202 (1959). S. Krimm, *et al.*, *Chem. Ind. (London)*, 1512 (1958). ^e C. W. Bunn and E. V. Gerner, *Proc. Roy. Soc. (London)*, **A189**, 39 (1947). ^f K. Fujii, *et al.*, *Makromol. Chem.*, **51**, 225 (1962); S. Murahashi, *et al.*, *J. Polymer Sci.*, **62**, 577 (1962). ^g C. W. Bunn and E. R. Howells, *Nature*, **174**, 549 (1954). ^h H. Tadokoro, T. Yasumoto, S. Murahashi, and I. Nitta, *J. Polymer Sci.*, **44**, 266 (1960). ⁱ V. Zamboni, S. Leghissa, and G. Zerbi, Conference on Vibrational Spectra of High Polymers, July 18, 1963, Milan, Italy. ^j G. Natta, *J. Polymer Sci.*, **16**, 143 (1955); *Makromol. Chem.*, **35**, 94 (1960); G. Natta and P. Corradini, *Nuovo Cimento*, [10] **15**, 40 (1960). ^k T. Miyazawa and K. Okuda, private communication. ^l T. Miyazawa, K. Fukushima, and Y. Ideguchi, *J. Chem. Phys.*, **37**, 2764 (1962). ^m F. H. C. Crick and A. Rich, *Nature*, **176**, 780 (1955). ⁿ L. Pauling, R. B. Corey, and H. R. Branson, *Proc. Natl. Acad. Sci. U. S.*, **37**, 205 (1951). ^o G. Natta, *et al.*, *Rend. Accad. Nazl. Lincei*, [8] **28**, 539 (1960). ^p C. W. Bunn and E. V. Garner, *J. Chem. Soc.*, 654 (1942).

(1) S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, New York, N. Y., 1954; S. Mizushima, *Pure Appl. Chem.*, **7**, 1 (1963); see also references cited there.

(2) E. B. Wilson, *Proc. Natl. Acad. Sci. U. S.*, **43**, 816 (1957).

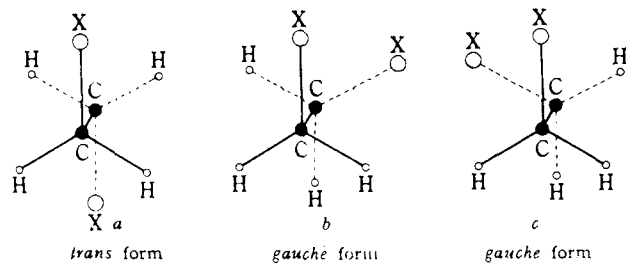


Fig. 1.—Stable conformations of 1,2-dihaloethanes.

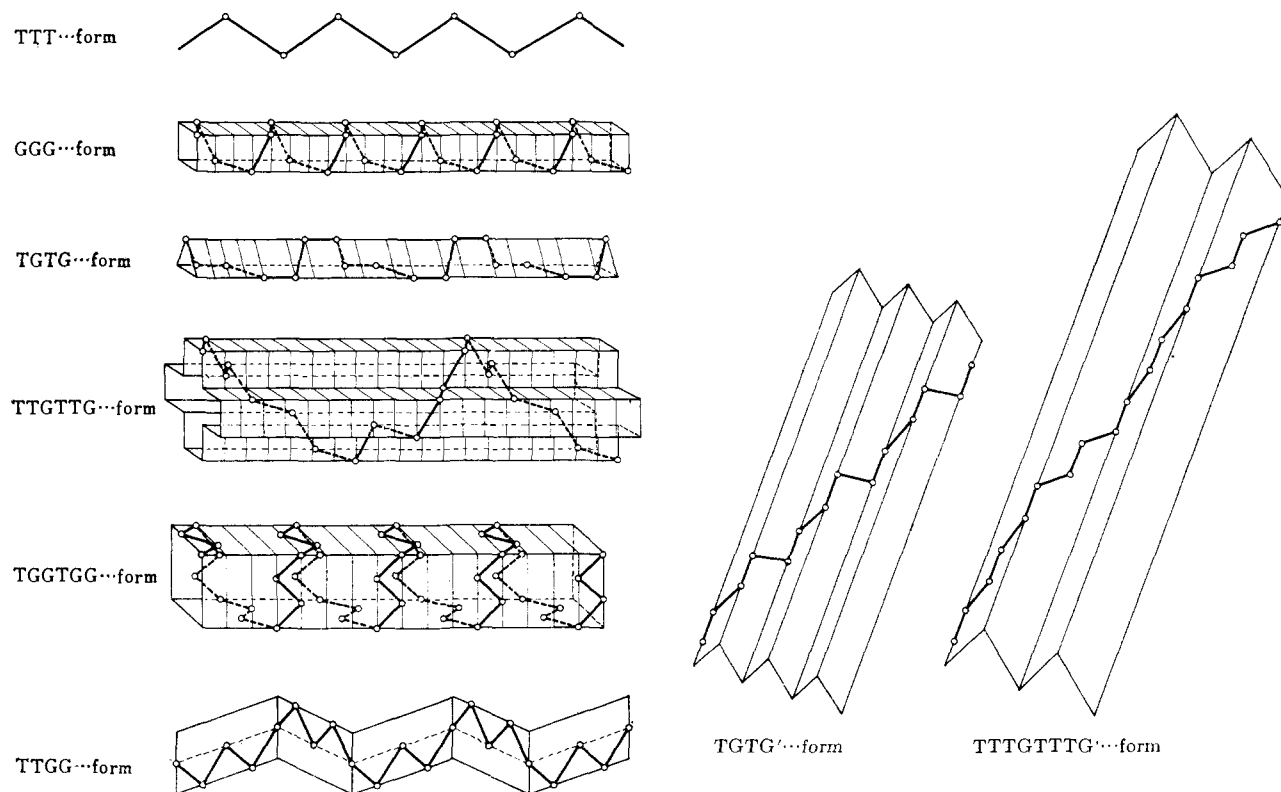


Fig. 2.—Basic structures.

Internal Rotation Angle of Linear High Molecules

The authors derived a mathematical expression for helices of polymer chains as a function of bond lengths, bond angles, and internal rotation angles.³ An extension of this study was made by Miyazawa.⁴ Discussions will be made in the following on the deviations of the bond angles and internal rotation angles from the ideal values.

In the ideal TTT... form (or the extended form) the internal rotation angle is 180°. However, in polytetrafluoroethylene ($-\text{CF}_2-\text{CF}_2-$)_n the angles are changed to 163° because of the steric repulsion between substituents.

In polyoxymethylene ($-\text{CH}_2-\text{O}-$)_n with conformation GGG... the internal rotation angle was found to be 77° instead of 60°. This is due to the replacement of every other CH₂ group of the paraffin chain by an oxygen atom.

A typical chain molecule with TGTG... conformation is that of isotactic polypropylene with internal rotation angles 180 and 60°. Replacement of a CH₃ group by another one results in a change of the angles

(3) T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, **23**, 707 (1955).

(4) T. Miyazawa, *J. Polymer Sci.*, **55**, 215 (1961).

to some extent. For example in poly-*m*-methylstyrene the angles are 164° and 76°, respectively.⁴

The molecular chains of polyethylene glycol ($-\text{CH}_2-\text{CH}_2-\text{O}-$)_n and polyglycine II take the TTGTTG... form (see Table I). In both of them the deviation of the angles from the ideal ones is considerable. The internal rotation angles in the former are 192, 192, and 60° and those in the latter are 216, 180, and 76°. The considerable deviation of the values from ideal

ones in the latter is due to the formation of hydrogen bonding.

This is also the case for polypeptide α -helix which takes the TGGTGG... conformation. The angles are found to be 180, 58, and 47°. (It is to be noted that the peptide bond has partial double bond character and, therefore, stable positions become the *trans* and *cis*, instead of the *trans* and *gauche*.)⁵

The molecular chain of syndiotactic polypropylene takes the TTGG... form. In this case the internal rotation angles are not much different from the ideal values, *i.e.*, 180, 180, 60, and 60°.

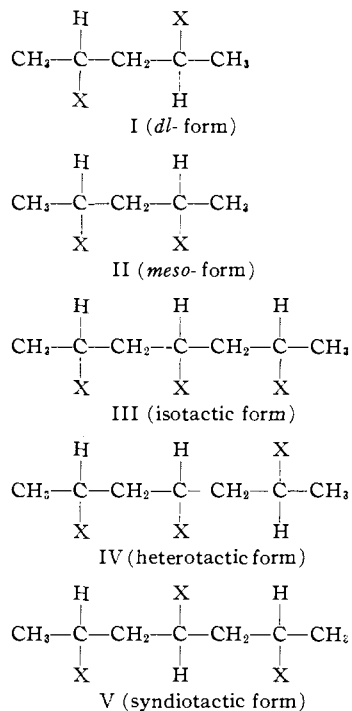
Model Compounds

As shown above, a conformation of a polymer chain is essentially a combination of the T and G units. In this respect there is no problem at all. However, we would like to know how the difference in the sequence of the T and G forms can be explained. For syndiotactic polymers, polyvinyl chloride takes the TTT... form, whereas polypropylene takes the TTGG... form. For isotactic polymers, polypropylene takes the

(5) S. Mizushima, *et al.*, *J. Am. Chem. Soc.*, **72**, 3490 (1950).

TGTG... form, whereas polyvinyl alcohol the TTT... form.

In order to understand this behavior of polymer conformations, a number of model compounds have been studied. They are as follows



Substances with forms I and II were prepared for X = Cl⁶ and X = CN,⁷ and those with forms I, II, III, IV, and V for X = OH.^{8,9} Evidently when X denotes CH₃, I and II become identical with each other (2,4-dimethylpentane).

The existence of many rotational isomers is 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 CH₃ and CH₃, or X and CH₃) 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. 4).

For X = Cl the infrared measurement showed that only one conformation (a, shown in Fig. 4) exists for I. This is in agreement with the fact that syndiotactic polyvinyl chloride takes the TTT... form. In this case II takes only conformation c of Fig. 4, and therefore we expect that the conformation of isotactic polyvinyl chloride will be the trigonal helix TGTG...

If X denotes CH₃, I can take both of the conformations a and b. This is in agreement with the fact that syndiotactic polypropylene takes the TTGG... form. For II only conformation c shown in Fig. 4 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 polyacrylonitrile will take a conformation similar to that of polypropylene. The reason why I takes conformation

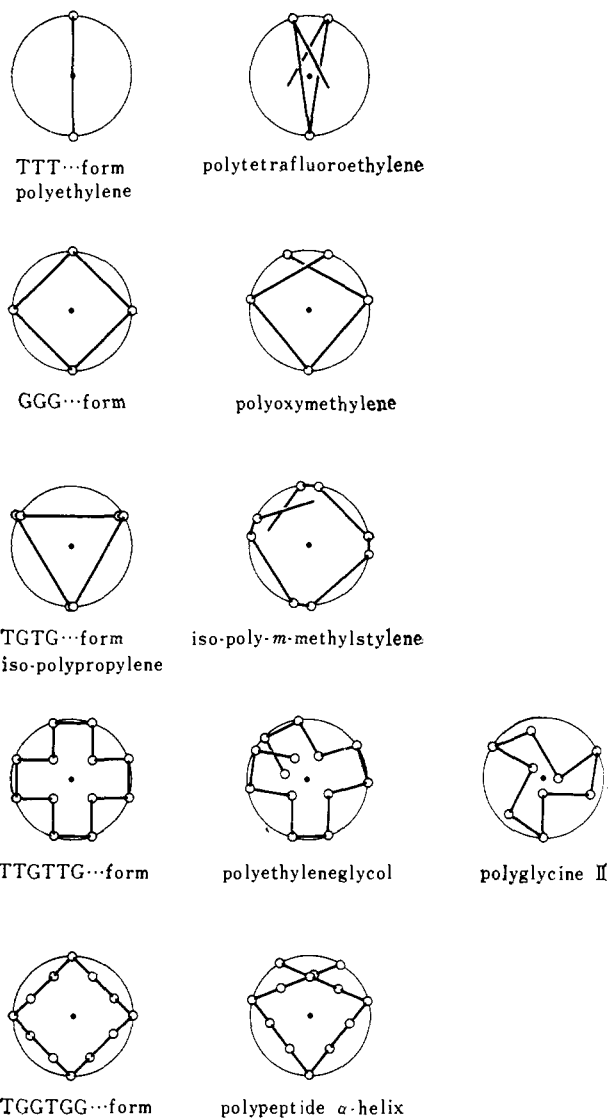


Fig. 3.—Basic structures and helices.

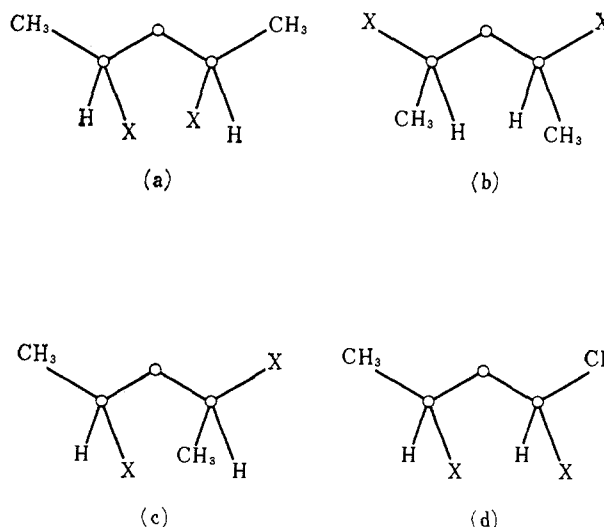


Fig. 4.—Rotational isomers of 2,4-disubstituted pentane.

a for X = Cl and conformations a and b for X = CN is explained by the difference in the relative positions of dipole moments on CCl and CCN groups.¹⁰

(10) T. Fujiyama and T. Shimanouchi, *J. Chem. Phys.*, **39**, 1138 (1963).

(6) T. Shimanouchi and M. Tasumi, *Spectrochim. Acta*, **17**, 755 (1961)

(7) T. Shimanouchi and T. Fujiyama, to be published.

(8) K. Fuji, *et al.*, to be published.

(9) T. Shimanouchi and M. Oka, to be published.

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 of Fig. 4 and, therefore, explains the fact that isotactic polyvinyl alcohol takes the TTT... form. Syndiotactic polyvinyl

alcohol also takes this form because the intermolecular hydrogen bonding is strong enough.

Thus, various conformations of linear high polymers can be explained satisfactorily by taking into account the energy of internal rotation in simple molecules.

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Dimensions of Polymer Molecules in Concentrated Solutions¹

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A concentration-dependent intermolecular potential previously derived from a fluctuation theory of polymer solutions is here used to obtain an analytic expression for the radial distribution function $g(r)$ in concentrated solutions. An approximate equation for $g(r)$ is used, either the Born-Green-Kirkwood or hypernetted chain equation; the two are equivalent under the applicable assumption: $g(r) - 1 \ll 1$. The excluded volume expansion factor α which minimizes the free energy is obtained in terms of $g(r)$ and is shown to decrease toward unity as the concentration is increased. The theory becomes valid in the low concentration region when extensive overlapping of polymer domains occurs and remains valid until the solvent volume fraction drops below *ca.* 10^{-1} – 10^{-2} , depending on the polymer molecular weight. The thermodynamic properties in this concentration range are those of a solution of randomly distributed polymer molecules.

I. Introduction

In earlier work^{2,3} the excluded volume expansion factor α of polymer molecules was calculated for moderately concentrated solutions by minimization of the free energy. The potential energy between polymer molecules was a gaussian function as was used by Flory and Krigbaum⁴ in their theory of the second osmotic virial coefficient. The radial distribution function was obtained by an approximate variational solution of the Born-Green-Kirkwood equation.^{2a} Subsequently, it was noted that the intermolecular potential could not properly be taken independent of polymer concentration, except in the dilute solution range.⁵ A model of polymer solutions was formed on the assumption that the local volume fraction of segments at any point in the system for a given configuration of polymer centers of mass would be close to the bulk volume fraction of segments, and from this assumption a concentration dependent intermolecular potential was derived. The potential was used to calculate the solvent chemical potential in polymer solutions, the same approximate determination of the radial distribution function being made as before. The present work has two purposes. The first is to evaluate the excluded volume expansion factor in concentrated solutions on the basis of the new concentration-dependent intermolecular potential rather than the old concentration-independent potential. The second purpose is to improve the method of calculation of the radial distribution function in concentrated solutions, and therefore also the calculation of the chemical potential and the expansion factor α .

The first stage of the calculation will be an improved version of the free energy minimization which determines α . For reasons not clear in retrospect the earlier calculation^{2b,3} was quite indirect. The osmotic pres-

sure was determined as a function of α and then integrated to obtain the free energy. However, the later work on thermodynamic functions in concentrated solution, using the improved intermolecular potential, gave the free energy as a configurational integral plus a self-energy term, and both of these terms are easy to vary directly with respect to α , to minimize the free energy. This is the procedure followed here. The result is an equation for α whose solution requires knowledge of the radial distribution function at the given concentration and for a given α which occurs implicitly as a scale factor in the segment density function of a single polymer molecule.

The approximate variational solution of the Born-Green-Kirkwood equation used in the earlier work is here replaced by an analytic solution valid when the radial distribution function $g(r)$ is close to unity for all values of the argument r . Our expectation was that this assumption would limit the validity of the analytic solution to very high polymer concentrations. The actual situation is more complicated. As the concentration is raised the approximation becomes valid at concentrations sufficiently high that the polymer domains fill the solution. The approximation then remains valid until some very high concentration is reached, a concentration which is higher the higher the polymer molecular weight. At these very high concentrations an effective repulsion between polymer molecules becomes more effective in causing a nonrandom distribution than is the increased polymer concentration effective in causing a random (or microscopically homogeneous) distribution. A lengthy but inconclusive discussion of this phenomenon is given. For most purposes the breakdown in the linearized theory of $g(r)$ has no importance since it occurs at solvent volume fractions of the order of 0.01 or lower, except for very low polymer molecular weights.

The results may be summed up as follows. The excluded volume factor α , which may be much greater than unity in good solvents, drops rapidly as the polymer concentration is increased in dilute solutions. The rate of decrease moderates during further increases

(1) Supported in part by the National Science Foundation (GP2327), the Division of General Medical Sciences, Public Health Service (GM-0915303), and the Alfred P. Sloan Foundation.

(2) (a) M. Fixman, *J. Chem. Phys.*, **33**, 370 (1960); (b) *J. Polymer Sci.*, **41**, 91 (1960).

(3) M. Fixman, *Ann. N. Y. Acad. Sci.*, **89**, 657 (1961).

(4) P. J. Flory and W. R. Krigbaum, *J. Chem. Phys.*, **18**, 1086 (1950).

(5) M. Fixman, *ibid.*, **35**, 889 (1961).