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The Configuration of the Polyoxyethylene Chain

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Stress–temperature coefficients have been determined for networks of polyoxyethylene (*POE*) in the amorphous state. The results yield $d \ln \langle r^2 \rangle_0/dT = 0.23 \pm 0.02 \times 10^{-3}$ deg.$^{-1}$ for the temperature coefficient of the mean-square, unperturbed, end-to-end dimension of the POE chain. According to published intrinsic viscosities in aqueous solvents at the Θ-point, the characteristic ratio $\langle r^2 \rangle_0/nl^2 = 4.1 \pm 0.4$. The ratio and its temperature coefficient are calculated on the basis of structural data using the rotational isomeric state model, a trans and two gauche states being assumed about each bond. Previous theoretical methods are adapted to the treatment of chains having a repeat unit of three bonds. The energy for gauche rotational states about CH_2–O and O–CH_2 bonds appears to exceed that for the trans state owing to interactions, primarily steric, between adjoining methylene groups. The reverse holds for the CH_2–CH_2 bond according to comparison of observed and calculated results. A lower energy for the gauche rotational state compared to the trans for this bond is attributable to a favorable dispersion interaction between the adjoining O atoms. Successive gauche rotations of opposite sign about a CH_2–O–CH_2 pair of bonds are excluded by severe steric repulsions of methylene groups. Analogous rotational states for CH_2–CH_2–O and O–CH_2–CH_2 bond pairs bring about encounters between the adjoining O and CH_2 groups, but, owing to the smaller domain of O and the favorable dipole interaction, these gauche rotations of opposite sign appear not to be greatly suppressed. The dominant effect of increasing temperature is to increase the trans population about CH_2–CH_2 bonds, and this is the main factor causing $d \ln \langle r^2 \rangle_0/dT$ to be positive. The configuration of lowest energy consists of the succession g, t, t for the bond sequence CH_2–CH_2–O–, which duplicates, approximately, the helical conformation occurring in the crystal. An unambiguous assignment of the more important statistical weights for the various rotational states is thus achieved by comparison of calculated and experimental values of both $\langle r^2 \rangle_0/nl^2$ and $d \ln \langle r^2 \rangle_0/dT$.

Introduction

The mean-square, end-to-end length $\langle r^2 \rangle$ of a polymer chain is a convenient index of its configuration and of its domain in space. The value of this quantity which obtains under conditions such that the configuration of the chain is unaffected by interactions between pairs of elements remote in sequence along the chain assumes special importance because it depends on the structure of the chain and very little on its environment. The ratio $\langle r^2 \rangle_0/nl^2$ of this *unperturbed*, mean-square length to the product of the number n of bonds and the square of the bond length l converges to a limit for large n. This dimensionless quantity or *characteristic ratio* for polymer chains of a given chemical and structural type is determined by (i) bond lengths and bond angles, (ii) the nature of the potentials affecting bond rotations, and (iii) steric repulsions tending to suppress rotations of opposite sign about successive bond pairs. Elucidation of the relationship between these structural features and the characteristic ratio is obviously a matter of fundamental importance. With the advent in recent years of adequate theroretical procedures, on the one hand, and of newer experimental approaches, on the other, the characteristic ratio and its temperature coefficient have been successfully interpreted in terms of the chain structure for polyethylene (PE),[2-5] polyisobutylene

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(2) A. Ciferri, C. A. J. Hoeve, and P. J. Flory, *J. Am. Chem. Soc.*, **83**, 1015 (1961).

(3) P. J. Flory, A. Ciferri, and R. Chiang, *ibid.*, **83**, 1023 (1961).

(PIB),[6] poly(dimethylsiloxane) (PDMS),[7-9] and poly-oxymethylene (POM).[10]

The structure of polyoxyethylene, $(CH_2-CH_2-O-)_n$, presents features of special interest to the subject of spatial configurations of long-chain molecules. In the first place, the repeat unit comprises three atoms and, hence, a succession of three bond pairs joined, respectively, at the first CH_2, at the second CH_2, and at the O. Three statistical weight matrices are therefore required to take account of the neighbor dependence of bond rotational potentials in accordance with the rotational isomeric state model.[11] The analysis of the characteristic ratio $\langle r^2 \rangle_0/nl^2$ for POE is consequently more involved than for PE having a one-bond repeat unit and for PIB, PDMS, and POM having repeat units comprising two bonds. On the other hand, the seemingly formidable array of parameters occurring as elements in the three statistical weight matrices for POE may be considerably simplified by symmetry and by other features peculiar to the POE chain.

The two different chain elements CH_2 and O in POE differ markedly in their van der Waals radii. The relevant nonbonded interactions involve $CH_2 \cdots CH_2$ and $O \cdots O$ pairs separated by three bonds, and $CH_2 \cdots CH_2$ and $CH_2 \cdots O$ pairs separated by four bonds. They are uncomplicated by substituents such as occur in vinyl polymers. The fact that the C–O bond is 0.1 Å. shorter than the C–C bond reduces the distances between the interacting groups compared to the distances for corresponding conformations of the PE chain. Where oxygen is a member of the pair, however, its smaller van der Waals radius more than compensates for the effect of this difference in bond distances. The polarity of the C–O bond is also a factor to be considered, but probably a less important one.

As the foregoing remarks suggest, the POE chain can be regarded as an intermediate case manifesting some of the characteristics of both PE and POM. In the former chain the *trans* conformation is of lower energy than the *gauche;* the reverse appears to hold for the latter.[10] Analysis of the chain conformation in POE suggests preference for *trans* rotations about the C–O and O–C bonds and a preference for *gauche* about C–C. As in other examples previously investigated, however, it is essential to take account of the interdependence[12] of neighboring rotations for a proper account of the configuration. Finally, the virtual equality of the bond angles in POE, both being very nearly tetrahedral, is a fact of major significance, for it confers rectilinearity on the planar, all-*trans* conformation. In this respect, POE resembles PE and POM; it differs from PDMS, the unequal bond angles of which render the all-*trans* conformation cyclic. As we have had occasion to point out in comparing these latter three chains,[9,10] the

geometric form of the all-*trans* conformation exerts a pervasive influence on the spatial configuration of the random coil form and on its dependence on temperature.

In this paper we present (i) experimental stress–temperature coefficients for POE networks from which the coefficient d ln $\langle r^2 \rangle_0/dT$ is deduced, (ii) an estimate of the characteristic ratio $\langle r^2 \rangle_0/nl^2$ based on the intrinsic viscosity–molecular weight studies of Bailey and co-workers,[13] and (iii) a theoretical treatment of the POE chain in terms of the rotational isomeric state scheme successfully applied to other polymers.

Experimental

Preparation of Polyoxyethylene Networks. An unfractionated sample[14] of POE bearing hydroxyl end groups was converted to a network suitable for elasticity measurements[15] through reaction with a commercial triisocyanate[16] whose main constituent is reported to be

$$H(-\langle \bigcirc \rangle-CH_2-)_3H$$
$$NCO$$
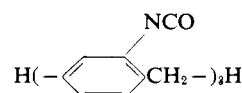
Finely divided POE was intimately mixed with approximately twice its stoichiometric equivalent of the triisocyanate. The mixture was placed in a Teflon mold and heated to 95° under vacuum for approximately 4 hr. The resulting material, which on the basis of the molecular weight of the initial polymer had approximately 90 monomer units between trifunctional network junctions, exhibited high elasticity in the amorphous state. Soluble constituents, removed by extraction with 2-propanol at 75° for approximately 4 hr., amounted to less than 4% by weight. N-Phenyl-β-naphthylamine (PBNA) was incorporated in the network by swelling at 75° in a 5% solution of PBNA in 2-propanol, the solvent being removed subsequently by evaporation. The PBNA thus imparted amounted to 21% of the sample by weight. Besides acting as an antioxidant, it served the further purposes of depressing the melting point so that measurements could be conducted at lower temperatures and of diminishing hysteresis of the network. The composition of the sample remained unchanged during the force–temperature measurements owing to the low volatility of PBNA.

Force – Temperature Measurements. Preliminary studies indicated appreciable network degradation at temperatures in excess of 100° despite presence of the inhibitor. It was necessary, therefore, to conduct the measurements at lower temperatures and, in order to cover an adequate range, to extend them to temperatures below the normal melting point, 66°,[17] of the undiluted, undeformed polymer. Inasmuch as crystallization would have vitiated the stress–temperature results, it was essential to assure that the sample remained completely amorphous. The inhibitor-diluted

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(5) K. Nagai and T. Ishikawa, *ibid.*, 37, 496 (1962).
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(7) J. E. Mark and P. J. Flory, *J. Am. Chem. Soc.*, 86, 138 (1964).
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(9) P. J. Flory, V. Crescenzi, and J. E. Mark, *ibid.*, 86, 146 (1964).
(10) P. J. Flory and J. E. Mark, *Makromol. Chem.*, 75, 11 (1964).
(11) M. V. Volkenstein, "Configurational Statistics of Polymeric Chains," Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 6.
(12) C. Rossi and V. Magnasco, *J. Polymer Sci.*, 58, 977 (1962), have treated the POE chain configuration on the basis of neighbor-*independent* rotational states.

(13) F. E. Bailey, Jr., and R. W. Callard, *J. Appl. Polymer Sci.*, 1, 56 (1959); F. E. Bailey, Jr., J. L. Kucera, and L. G. Inhof, *J. Polymer Sci.*, 32, 517 (1958).
(14) Carbowax 4000, Union Carbide Chemical Co.
(15) Exposure of polyoxethylene to radiation (high energy electrons or γ-rays) gave networks too friable for the force–temperature experiments, probably as a result of excessive chain scission.
(16) Provided by the Carwin Chemical Co., North Haven, Conn., under the trade name PAPI.
(17) L. Mandelkern, *J. Appl. Phys.*, 26, 443 (1955).

networks were observed to retain their elastic properties without evidence of crystallization for several hours after being cooled from 70 to 30°. Moreover, the volume of a sample contained in a dilatometer remained constant for several hours at 30° after having been heated to 70°. These preliminary observations indicated that the required elastic measurements could be conducted in the temperature range 90 to 30° without interference from crystallization, provided that high elongations were avoided.

The dynamometer and associated apparatus have been described in detail.[7] Briefly, the sample is mounted vertically between clamps, the lower one being fixed and the upper one being attached to a strain gauge mounted approximately 25 cm. above the cylindrical cell housing the sample. The cell is immersed in a liquid thermostat. The tension sensed by the strain gauge is delivered to a recorder. The length of the sample can be varied manually by vertical adjustment of the strain gauge assembly and is determined by observing the reference marks with a cathetometer reading to ±0.002 cm. Dimensions of the test sections of the specimens used in this investigation approximated $3.0 \times 0.60 \times 0.10$ cm. The sample was stretched to the desired length and held at the highest temperature of measurement (90°) until the force remained constant for at least 20 min. The temperature was then lowered 15°, the length being fixed, and the force was recorded when it became constant, and so forth. After reaching the lowest temperature (30°) of measurement, the cycle was reversed and the force redetermined at 90°, and sometimes at intermediate temperatures as well. Agreement with forces for the previous temperature descending sequence of determinations was within the limits of accuracy of measurement. Absence of appreciable network degradation in the course of the experiment was thus indicated.

Upon completion of a cycle, the sample was permitted to recover under null force for at least 2 hr. at 90°. The rest length L_i observed thereafter was used to calculate the extension ratio $\alpha = L/L_i$ at this temperature. An exact value of the extension ratio is not explicitly required for analysis of the results; hence, its value for other temperatures was not computed.

The cross-sectional area of the sample, measured by a micrometer at room temperature, was corrected to 90° by application of the thermal expansion coefficient $\beta = \partial \ln V/\partial T = 0.66 \times 10^{-3}$ deg.$^{-1}$ at 60°, determined dilatometrically on a POE sample containing 21% of PBNA.

Results

The Temperature Coefficient of $\langle r^2 \rangle_0$. The forces observed at various fixed lengths are plotted against temperature in Figure 1. Each plot is labeled with the extension ratio $\alpha = L/L_i$ at 90°, where L is the length of the sample at force f and L_i is its undistorted ($f = 0$) length at the same volume and temperature. The ordinate scale represents the observed force divided by the cross-sectional area of the sample at 90°. The method of least squares was used to establish the best straight line through each set of experimental points. The slope $(\partial f/\partial T)_{p,L}$, the force $\bar{f}$ at the mean temperature $\bar{T} = 60°$, and the value of $[\partial \ln (f/T)/\partial T]_{p,L}$, calculated
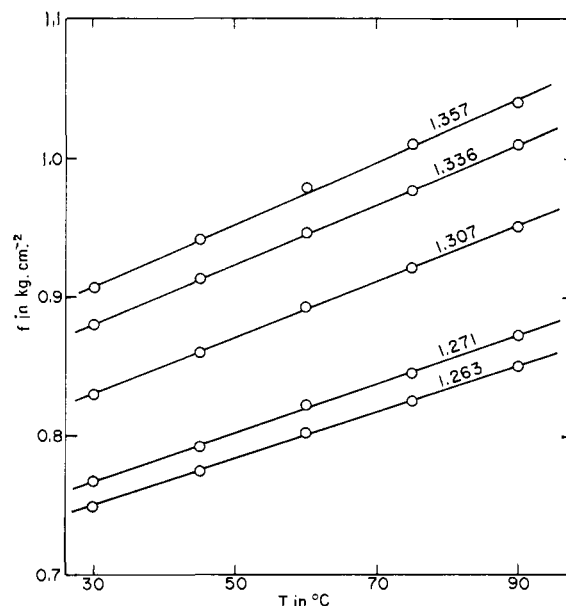

Figure 1. Force *vs.* temperature at constant length. Numerals refer to extension ratios, α, relative to the relaxed length at 90°. Forces are expressed with reference to the undistorted cross-sectional area at 90°.

from these quantities are listed in columns 2, 3, and 4 in Table I.

According to the molecular theory of rubber elasticity[2,18] for gaussian networks

$$d \ln \langle r^2 \rangle_0/dT = -[\partial \ln (f/T)/\partial T]_{p,L} - \beta/(\alpha^3 - 1) = f_e/fT \quad (1)$$

where β is the cubical thermal expansion coefficient, and $f_e = (\partial E/\partial L)_{V,T}$ is the internal energy contribution to the tension f. The ratio f_e/f is a measure of the nonideality of the elastomeric body. Values of f_e/f and of $d \ln \langle r^2 \rangle_0/dT$ given in the sixth and seventh columns of Table I, respectively, were calculated according to eq. 1 from $[\partial \ln (f/T)/\partial T]_{p,L}$ and the correction term $\beta/(\alpha^3 - 1)$. The validity of this term, which corrects measurements at constant pressure to constant volume, has been confirmed by Allen, Bianchi, and Price[19] through direct comparison of force–temperature coefficients for natural rubber determined experimentally at both constant volume and constant pressure.

Crystallization, if it had occurred, would have markedly increased $(\partial f/\partial T)_{p,L}$ and this would have been reflected in large negative values calculated for $d \ln \langle r^2 \rangle_0/dT$. Moreover, the inevitable increase in crystallinity with elongation would have produced a decided decrease in values of this latter quantity with elongation. The constancy of the temperature coefficient of $\langle r^2 \rangle_0$ with elongation (Table I) offers further evidence that the experiments were free of extraneous effects of incipient crystallization.

Although the temperature coefficient of $\langle r^2 \rangle_0$ for POE is small, the experiments show unequivocally that it is positive.

The Characteristic Ratio $\langle r^2 \rangle_0/nl^2$. Bailey and Callard[13] investigated the intrinsic viscosities $[\eta]$ of POE

(18) P. J. Flory, A. Ciferri, and C. A. J. Hoeve, *J. Polymer Sci.*, **45**, 235 (1960); P. J. Flory, *Trans. Faraday Soc.*, **57**, 829 (1961).
(19) G. Allen, U. Bianchi, and C. Price, *ibid.*, **59**, 2493 (1963).

Table I. Force–Temperature Results for Amorphous Polyoxyethylene

α	$\bar{f}$, kg. cm.$^{-2}$	$(\partial f/\partial T)_{p,L} \times 10^3$	$-\left[\dfrac{\partial \ln (f/T)}{\partial T}\right]_{p,L} \times 10^3$, deg.$^{-1}$	$\dfrac{\beta}{\alpha^3 - 1} \times 10^3$, deg.$^{-1}$	f_e/f	$\dfrac{d \ln \langle r^2 \rangle_0}{dT} \times 10^3$, deg.$^{-1}$
1.263	0.800	1.69	0.89	0.65	0.08	0.24
1.271	0.820	1.77	0.84	0.63	0.07	0.21
1.307	0.891	2.02	0.73	0.54	0.06	0.19
1.336	0.946	2.16	0.72	0.48	0.08	0.24
1.357	0.975	2.25	0.69	0.44	0.08	0.25
					Av. 0.07 ± 0.01	Av. 0.23 ± 0.02

samples covering a wide range in molecular weights M using water and various aqueous salt solutions as solvents. They found that both 0.45 M K_2SO_4 at 35° and 0.39 M $MgSO_4$ at 45° gave plots of log $[\eta]$ vs. log M having slopes of 0.5. These solvent media evidently are Θ-solvents for POE at the respective temperatures specified. According to the results of Bailey and Callard, $[\eta]_\Theta/M^{1/2} = 1.15$ (± 0.15) $\times 10^3$ with $[\eta]_\Theta$ in dl. g.$^{-1}$. Inserting this result in the familiar relationship[20]

$$[\eta_\Theta]/M^{1/2} = \Phi[\langle r^2 \rangle_0/M]^{3/2} \qquad (2)$$

with the parameter $\Phi = 2.5 \times 10^{21}$ according to the careful analysis of experimental data in Θ-solvents published by McIntyre, et al.,[21] we find $\langle r^2 \rangle_0/M = 0.60$ (± 0.06) $\times 10^{-16}$ cm.^{2} (mol. wt.)$^{-1}$. Conversion to the characteristic ratio yields

$$\langle r^2 \rangle_0/nl^2 = 4.1 \pm 0.4$$

where n is the number of bonds in the chain backbone and l^2 is the mean of the squares of the lengths of the three bonds comprising the repeat unit (see below).

Theoretical Treatment

The Structure. By inference from structural data[22] for analogous compounds of low molecular weight, the lengths of the bonds comprising the POE chain backbone are $l_{C-C} = 1.53$ Å. and $l_{C-O} = 1.43$ Å. These assignments find partial confirmation in X-ray crystallographic investigations[23] on POE itself. In consideration of the fact that the C–O–C bond angles in ethers and related compounds[22] are approximately tetrahedral, equal values of 70° may legitimately be assigned to each of the three angles θ_1, θ_2, and θ_3 shown in Figures 2–4. The internal rotation angle φ_i about bond i (see Figure 2) is defined as the dihedral angle between the plane determined by bonds $i - 1$ and i and that determined by bonds i and $i + 1$; $\varphi = 0$ is identified with the planar *trans* conformation. The angles of rotation about bonds $i + 1$ and $i + 2$ (see Figures 3 and 4) are defined similarly. Rotation about the C–O bond in dimethyl ether[24] is restricted by a threefold potential barrier of *ca.* 2.7 kcal. mole^{-1};

that for rotation about the C–C bond in ethane[25] is 2.9 kcal. mole^{-1}. With potentials of this magnitude, the validity of the rotational isomeric state model cannot be seriously called into question. Besides the *trans* state at $\varphi = 0°$, we assume the two *gauche* states to occur at $\pm 120°$ in each case. The precise location of the *gauche* minima is invariably uncertain. Minor departures from 120° would not affect the main conclusions.

Formulation of Statistical Weight Matrices for Bond Rotations. The various conformations about the three successive bond pairs of the repeat unit of POE are represented in Figures 2–4. For convenience, the bond pair under consideration in each diagram ($i - 1$ and i in Figure 2, i and $i + 1$ in Figure 3, and $i + 1$ and $i + 2$ in Figure 4) is represented as being retained in the plane of the diagram; rotations are accomplished by turning adjoining bonds out of this plane. Thus, the planar *trans* form is shown by solid lines; atoms and groups turned out of the plane by rotations to *gauche* states are shown by dashed lines.

The steric interactions affecting the statistical weights associated with a given bond conformational state may be gauged by comparing distances between nonbonded atoms and groups with the sums of the appropriate van der Waals radii. Table II lists the distances between nonbonded groups calculated for various rotational states using the structural data given above. Corresponding distances calculated for POM and for PE (with $\theta = 68°$) are included for comparison.

A *gauche* rotation about CH_2–O bond i in Figure 2 decreases the distance between the methylene groups linked by bonds $i - 1$, i, and $i + 1$ from 3.70 to 2.81 Å. At this latter distance, one pair of hydrogen atoms of the opposing CH_2 groups is separated by only about 1.8 Å. (in the staggered conformation), which is substantially less than the sum of their van der Waals radii (*ca.* 1.1 to 1.2 Å.).[26] An appreciable repulsion should therefore be expected. By way of comparison, the *gauche* conformation in an *n*-alkane (or PE) chain places the two analogous methylene groups joined by three intervening bonds at a distance of 3.01 Å., and the pair of nearest H atoms at 2.0 Å. The energy of the *gauche* state for this chain exceeds that of the *trans* by about 500 cal./mole.[27–29] A greater energy difference

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(21) D. McIntyre, A. Wims, L. C. Williams, and L. Mandelkern, *J. Phys. Chem.*, 66, 1932 (1962).
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(24) P. H. Kasai and R. J. Myers, *J. Chem. Phys.*, 30, 1096 (1959).

(25) K. S. Pitzer, *Discussions Faraday Soc.*, 10, 66 (1951).
(26) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960; see also J. B. Hendrickson, *J. Am. Chem. Soc.*, 83, 4537 (1961).
(27) N. J. Sheppard and G. J. Szasz, *J. Chem. Phys.*, 17, 86 (1949).
(28) S. Mizushima and H. Okazaki, *J. Am. Chem. Soc.*, 71, 3411 (1949).
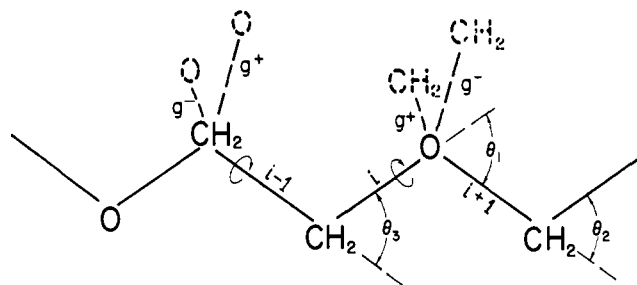(29) W. P. Person and G. C. Pimentel, *ibid.*, 75, 532 (1953).

Figure 2. Rotational conformations about CH_2–CH_2–O bond pairs.

Figure 3. Rotational conformations about CH_2–O–CH_2 bond pairs.

must be expected for the corresponding rotational states for bond i of the POE chain in consideration of the smaller distance (2.81 Å.) separating the pair of

Table II. Distances between Nonbonded Atoms and Groups

Interacting atoms or groups		No. of bonds apart	Con- forma- tion	Dis- tance, Å.	Statistical weight factors
POE	CH_2...CH_2	3	t	3.70	1
		3	$g^{\pm}$	2.81	σ
	O...O	3	t	3.67	1
		3	$g^{\pm}$	2.84	σ'
	CH_2...O	4	$g^{\pm}g^{\pm}$	3.38	α
		4	$g^{\pm}g^{\mp}$	2.46	β
	CH_2...CH_2	4	$g^{\pm}g^{\pm}$	3.34	γ
		4	$g^{\pm}g^{\mp}$	2.37	0
POM	CH_2...O^a	3	t	3.60	1
		3	$g^{\pm}$	2.75	>1
	CH_2...CH_2 or	4	$g^{\pm}g^{\pm}$	3.32	
	O...O	4	$g^{\pm}g^{\mp}$	2.37	
PE	CH_2...CH_2	3	t	3.89	1
		3	$g^{\pm}$	3.01	0.47^b
		4	$g^{\pm}g^{\pm}$	3.65	1
		4	$g^{\pm}g^{\mp}$	2.69	0 to 0.03^b

^{a} See ref. 10. ^{b} In order to achieve correspondence with present results, the statistical weights for PE have been corrected from 160°, the temperature of experimental observation, to 60° assuming each to be represented by a Boltzmann exponential as in eq. 14. See ref. 4 and 5.

CH_2 groups. It may be further increased by dipolar interaction between bonds $i + 1$ with $i - 1$, but, in view of the fairly small dipole moment, 0.86 D.,[30] of the C–O bond, the contribution to the energy of the gauche state from this source should be only of the order of 100 to 200 cal. mole^{-1}. We conclude that the energy of a gauche rotational state about a CH_2–O bond should be at least 1000 cal. mole^{-1} greater than the energy for the trans state. The statistical weight σ of one of the gauche states relative to the trans (see last column of Table II) is thus predicted to be less than the statistical weight associated with the cor- responding conformation in the PE chain. Rotations about an O–CH_2 bond such as bond $i + 1$ in Figure 3 give rise to interactions between methylene groups joined by bonds $i, i + 1$, and $i + 2$, identical with those mentioned above; hence, the same statistical weight σ must apply.

A gauche rotation about the CH_2–CH_2 bond $i + 2$, shown in Figure 4, diminishes the distance between the

(30) C. P. Smyth, J. Am. Chem. Soc., 60, 183 (1930).

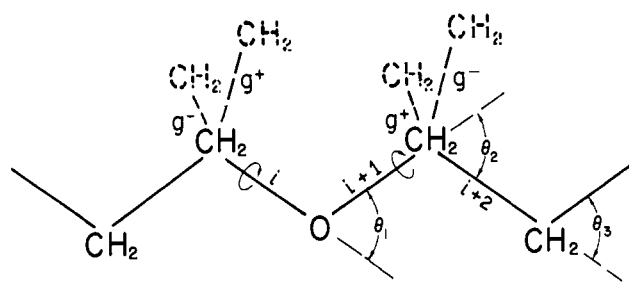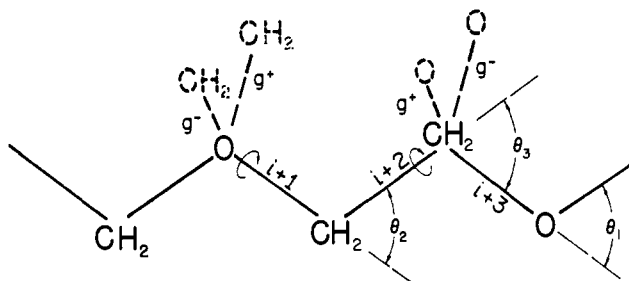Figure 4. Rotational conformations about O–CH_2–CH_2 bond pairs.

attached oxygen atoms from 3.67 to 2.84 Å. (Table II). Since this latter distance is larger than twice the van der Waals radius of the oxygen atom (1.4 Å.), steric effects must be unimportant. As in the previous instance, the repulsive dipolar energy should be fairly small. A significant, favorable London dispersion energy be- tween oxygen atoms at this distance of separation would be expected, however, and this negative contribution to the energy could easily reduce the energy of the gauche states below that of the trans for CH_2–CH_2 bonds. The statistical weight σ' (Table II)[31] associated with this rotation may on this basis be expected to exceed that of the trans, which we arbitrarily equate to unity. In any event σ' must be much greater than σ.

The conformation adopted by a chain molecule in the crystal lattice generally is indicative of the form of minimum intramolecular energy, apart from such minor adjustments of rotation angles as may be required for efficient packing in the lattice. It is instructive, there- fore, to examine the conformation of POE in the crystalline state. The recent X-ray crystallographic investigations of Tadokoro and co-workers,[23] sup- plemented by their analysis of the infrared spectrum, support a helix generated by rotations of $-8°$ 15' about CH_2–O and O–CH_2 bonds, and of 115° about CH_2–CH_2 bonds. The former rotations approximate trans; the latter, gauche. Thus, the form of the helix confirms predictions based on the consideration of interactions between groups separated by three bonds in the chain skeleton.

Adoption of gauche rotational states by each of two successive bonds raises the prospect of interactions between pairs of groups separated by four skeletal bonds. If the gauche rotations are of the same sign, these groups occur on opposite sides of the plane de- fined by the bonds about which rotation occurs (see Figures 2–4). Their distances apart, 3.3 to 3.4 Å.

(31) This parameter is not to be confused with the σ' used in ref. 10 to describe the rotational states of the POM chain.

(Table II), are sufficiently large to suggest absence of strong repulsions. The possibility that their inter- actions may nevertheless be significant has been acknowledged by introducing the statistical weight factors α and γ, given in the last column of Table II, to represent the interactions arising from *gauche* rota- tions of like sign about CH_2–CH_2–O or O–CH_2–CH_2 bond pairs (see Figures 2 and 4) and about CH_2–O–CH_2 pairs (see Figure 3), respectively. In view of the dis- tances involved, these factors may be expected to differ little from unity.

Neighbor *gauche* rotations of opposite sign place the groups on the same side of the plane and at consid- erably smaller distances apart (Table II), where steric repulsions may be severe. A g^+g^- or g^-g^+ conforma- tion about the CH_2–O–CH_2 pair places the adjoining CH_2 groups at the intolerable distance of 2.37 Å. Hence, the statistical weight factor for their conforma- tion may confidently be assigned the value zero, as given in Table II. Rotations of opposite sign about a CH_2–CH_2–O or a O–CH_2–CH_2 pair bring O and CH_2 to a comparable distance, 2.46 Å. The repulsion will be much less severe, however, owing to the smaller van der Waals radius of O. Moreover, the repulsive energy may be partially compensated by the attraction resulting from the dipolar interaction. Hence, the factor β (Table II), through probably less than unity, should not be negligibly small.

Chain conformations which bring groups separated by five or six bonds within range of interaction in- variably involve $g^{\pm}g^{\mp}$ placements of intervening pairs. The infrequency of occurrence of these pairs permits account of higher order interactions to be ignored. This assertion is confirmed by the numerical values deduced for the various statistical weight factors (see below).

Let the statistical weights for "transitions" from states of bond $i - 1$ to those of bond i, as in Figure 2, comprise the elements of a matrix U_1. That is, the element $U_{1;rs}$ of this matrix shall be the appropriate factor for bond i in state s when bond $i - 1$ has been assigned (previously) to state r. The statistical weight for a given conformation of the molecule as a whole will consist of the product of the appropriate set of such factors, one for each chain bond eligible for rotation. The indices r and s will index the rotational states in the order t, g^+, and g^-. It is at once apparent that the rows of U_1 will contain the respective statistical weight factors for the three-bond interactions arising as a result of rotation about bond i. These factors are 1, σ, and σ', respectively (see Figure 2 and Table II). To be combined with them are the factors α and β for the four-bond interactions arising from $g^+{}_{i-1}$ and $g^-{}_{i-1}$ succeeded by $g^+{}_i$ or $g^-{}_i$. It follows at once that

$$U_1 = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \alpha\sigma & \beta\sigma \\ 1 & \beta\sigma & \alpha\sigma \end{bmatrix} \quad (3)$$

Similarly, for bonds $i + 1$ and $i + 2$, respectively

$$U_2 = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \gamma\sigma & 0 \\ 1 & 0 & \gamma\sigma \end{bmatrix} \quad (4)$$

$$U_3 = \begin{bmatrix} 1 & \sigma' & \sigma' \\ 1 & \alpha\sigma' & \beta\sigma' \\ 1 & \beta\sigma' & \alpha\sigma' \end{bmatrix} \quad (5)$$

The matrix U_1 applies to the next bond in the succes- sion, and so forth. Statistical weights for all configura- tions of the chain are generated by multiplication of these matrices in repeating sequence.

Formulation of the Characteristic Ratio for a Chain of Three-Bond Repeat Units. In the limit of large n, the characteristic ratio is given by

$$\langle r^2 \rangle_0 / n l^2 = 1 + (2/3 l^2) \sum_{u,\nu=1}^{3} \sum_{k=0}^{m-1} l_u l_\nu P_k(\mu,\nu) \quad (6)$$

where μ,ν index the three successive bonds of the re- peating triplet, l^2 is the mean of the squares of the bond lengths l_1, l_2, and l_3, $m = n/3$ is the number of repeat units in the chain, and $P_k(\mu,\nu)$ is the statistical mechanical average projection on a bond of type μ of a unit vector along a bond of type ν, the latter being situated in the kth unit succeeding the former bond. Specifically, let bonds like i, $i + 1$, and $i + 2$ in Figures 2–4 be designated as types 1, 2, and 3, respectively. The order (k) is always to be taken in the same direc- tion along the chain—for simplicity from left to right. For $k = 0$, the projections $P_0(\mu,\nu)$ with $\nu \leq \mu$ are to be set equal to zero. In harmony with the assumption of a very long chain, in writing eq. 6 we have taken the various projections to be independent of the location within the chain of the bond pairs separated by k units; *i.e.*, end effects are ignored.

The average projection may be evaluated by the methods[32] previously applied to other chain mole- cules.[9] To this end, matrices $T(\theta_i, \varphi_i)$ for transforma- tion from the coordinate system associated with bond $i + 1$ to that of bond i are introduced. Three such matrices, T_1, T_2, and T_3, are required for the three bonds of the repeat unit. Then, for example

$$P_k(1,3) = [1\ 0\ 0] \langle (T_1 T_2 T_3)^k T_1 T_2 \rangle \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}$$

where angle brackets denote the statistical mechanical average, in keeping with their use above. This average of the matrix product is given by

$$\langle (T_1 T_2 T_3)^k T_1 T_2 \rangle = B(U_1 T_1 U_2 T_2 U_3 T_3)^{k+1} T_3^{-1} A \lambda^{-3(k+1)}$$

where U_μ is the direct product (denoted by $\times$) of the unit matrix E of order three with U_μ, *i.e.*

$$U_\mu = E \times U_\mu = \begin{bmatrix} U_\mu & & \\ & U_\mu & \\ & & U_\mu \end{bmatrix} \quad (7)$$

and T_μ is the $3r \times 3r$ matrix constructed as follows: the v,w (cartesian) element from each of the r matrices $T^{(r)}{}_\mu$, one for each rotational state r, are combined to form a diagonal matrix $T^{(r)}{}_{\mu;vw}$; those for various vw provide the pseudo-elements for T_μ, *i.e.*

$$T_\mu = \|T^{(r)}{}_{\mu;vw}\| \quad (8)$$

Finally, λ^3 is the largest eigenvalue of $U_1 U_2 U_3$, A and B are the corresponding eigencolumn and eigenrow,

(32) T. M. Birshtein and O. B. Ptitsyn, *Zh. Tekhn. Fiz.*, **29**, 1048 (1959); S. Lifson, *J. Chem. Phys.*, **30**, 964 (1959); K. Nagai, *ibid.*, **31** 1169 (1959); C. A. J. Hoeve, *ibid.*, **32**, 888 (1960).

mutually normalized, and

$$A = E \times A$$
$$B = E \times B \tag{9}$$

where $\times$ again denotes the direct product.

The complete set of the required average projections can be written

$$P_k(1,1) = \mathbf{B}^* \mathbf{S}^k \mathbf{A}^*$$

$$P_k(1,2) = \mathbf{B}^* \mathbf{S}^k \mathbf{U}_1 \mathbf{T}_1 \mathbf{U}_1^{-1} \mathbf{A}^*$$

$$P_k(1,3) = \mathbf{B}^* \mathbf{S}^{k+1} \mathbf{T}_3^{-1} \mathbf{A}^*$$

$$P_k(2,1) = \mathbf{B}^* \mathbf{U}_3^{-1} \mathbf{T}_2 \mathbf{U}_3 \mathbf{T}_3 \mathbf{S}^{k-1} \mathbf{A}^*$$

$$P_k(2,2) = \mathbf{B}^* \mathbf{U}_3^{-1} \mathbf{T}_2 \mathbf{U}_3 \mathbf{T}_3 \mathbf{S}^{k-1} \mathbf{U}_1 \mathbf{T}_1 \mathbf{U}_1^{-1} \mathbf{A}^* \tag{10}$$

$$P_k(2,3) = \mathbf{B}^* \mathbf{U}_3^{-1} \mathbf{T}_2 \mathbf{U}_3 \mathbf{T}_3 \mathbf{S}^k \mathbf{T}_3^{-1} \mathbf{A}^*$$

$$P_k(3,1) = \mathbf{B}^* \mathbf{T}_3 \mathbf{S}^k \mathbf{A}^*$$

$$P_k(3,2) = \mathbf{B}^* \mathbf{T}_3 \mathbf{S}^{k-1} \mathbf{U}_1 \mathbf{T}_1 \mathbf{U}_1^{-1} \mathbf{A}^*$$

$$P_k(3,3) = \mathbf{B}^* \mathbf{T}_3 \mathbf{S}^k \mathbf{T}_3^{-1} \mathbf{A}^*$$

where

$$\mathbf{S} = \mathbf{U}_1 \mathbf{T}_1 \mathbf{U}_2 \mathbf{T}_2 \mathbf{U}_3 \mathbf{T}_3 \lambda^{-3} \tag{11}$$

and $\mathbf{A}^*$ and $\mathbf{B}^*$ are the column vector $(3r \times 1)$ and row vector $(1 \times 3r)$ defined by

$$\mathbf{A}^* = \mathbf{A} \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}$$

$$\mathbf{B}^* = \mathbf{B}[1\ 0\ 0] \tag{12}$$

By substitution of these results into eq. 6 and evaluation of the various summations,[33] the final result takes the form

$$\frac{\langle r^2 \rangle_0}{nl^2} = 1 + \frac{2\mathbf{B}^*}{3l^2} \{ l_1^2 \mathbf{S}(\mathbf{E} - \mathbf{S})^{-1} + l_2^2 \mathbf{U}_3^{-1} \mathbf{T}_2 \mathbf{U}_3 \mathbf{T}_3 (\mathbf{E} -$$

$$\mathbf{S})^{-1} \mathbf{U}_1 \mathbf{T}_1 \mathbf{U}_1^{-1} + l_3^2 \mathbf{T}_3 \mathbf{S}(\mathbf{E} - \mathbf{S})^{-1} \mathbf{T}_3^{-1} +$$

$$l_1 l_2 [\mathbf{U}_3^{-1} \mathbf{T}_2 \mathbf{U}_3 \mathbf{T}_3 (\mathbf{E} - \mathbf{S})^{-1} + (\mathbf{E} - \mathbf{S})^{-1} \mathbf{U}_1 \mathbf{T}_1 \mathbf{U}_1^{-1}] +$$

$$l_1 l_3 [\mathbf{T}_3 (\mathbf{E} - \mathbf{S})^{-1} + \mathbf{S}(\mathbf{E} - \mathbf{S})^{-1} \mathbf{T}_3^{-1}] + l_2 l_3 [\mathbf{T}_3 (\mathbf{E} -$$

$$\mathbf{S})^{-1} \mathbf{U}_1 \mathbf{T}_1 \mathbf{U}_1^{-1} + \mathbf{U}_3^{-1} \mathbf{T}_2 \mathbf{U}_3 \mathbf{T}_3 (\mathbf{E} - \mathbf{S})^{-1} \mathbf{T}_3^{-1}] \} \mathbf{A}^* \tag{13}$$

Numerical Results[34] and Discussion

The solid lines in Figure 5 represent the characteristic ratio calculated according to eq. 13 and plotted against $-\ln \sigma$ for the several values of σ' indicated with the curves, other parameters being assigned as follows: $\alpha = \gamma = 1$ and $\beta = 0$. A value of σ' of about 2.0 or greater is indicated to be required by the experimental characteristic ratio, $\langle r^2 \rangle_0/nl^2 = 4.1 \pm 0.4$. A smaller σ' could be reconciled with this result only by allowing σ to exceed unity, a possibility which we reject for the reasons given above.

The tentative inference regarding σ' drawn from the solid curves in Figure 5 is subject, of course, to the arbitrary choice of values for α, β, and γ. The dashed curve in this figure represents the characteristic ratio calculated for $\sigma' = 2.0$ and $\alpha = 1.5$, with $\gamma = 1$

(33) D. A. Brant of these laboratories has independently derived an expression equivalent to eq. 13.

(34) The assistance of Mr. Pietro Balestra in programming the computations carried out at the Stanford Computing Center is gratefully acknowledged.
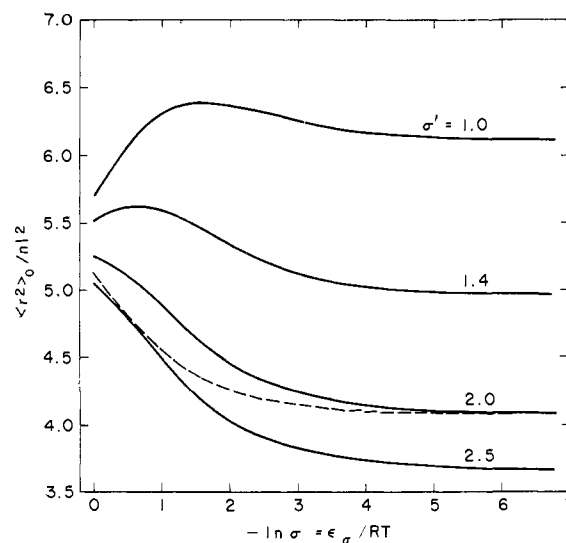
Figure 5. The characteristic ratio vs. $-\ln \sigma$ for $\beta = 0$, $\gamma = 1$, and σ' as indicated. Solid curves for $\alpha = 1.0$; dashed curve for $\alpha = 1.5$ and $\sigma' = 2.0$.

and $\beta = 0$ as for the other curves. This dashed curve and others not reproduced here show the result to be insensitive to α. Other calculations not included demonstrate that the characteristic ratio is insensitive also to the value of γ. We therefore let $\alpha = \gamma = 1$ in all further calculations. The analogous statistical weight factors associated with $g^{\pm}g^{\pm}$ rotational pairs in PDMS[9] were likewise found to be of little importance.

Figure 6 shows the effect of permitting occurrence of gauche states of opposite sign for the bond pair CH_2-CH_2-O, this being accomplished by taking $\beta = 0.4$ (solid curves) and $\beta = 0.9$ (dashed curves). Comparison of the two sets of curves with one another and with those of Figure 5 shows that an increase of β has a marked effect for small values of the abscissa, i.e., for comparatively large σ. The decrease in the characteristic ratio with β is obviously a reflection of the increasing occurrence of compact $g^{\pm}g^{\mp}$ pairs. As σ decreases (i.e., as $-\ln \sigma$ increases), however, the characteristic ratio converges rapidly to the result for $\beta = 0$. This convergence results from the suppression of all gauche pairs as σ decreases, irrespective of the value of β.

The temperature coefficient of $\langle r^2 \rangle_0$ has been computed on the assumption that the statistical weight parameters can be expressed as follows

$$\sigma = \exp(-\epsilon_\sigma/RT)$$

$$\sigma' = \exp(-\epsilon_{\sigma'}/RT) \tag{14}$$

$$\beta = \exp(-\epsilon_\beta/RT)$$

where ϵ_σ, etc., are interaction energies for the relevant conformations. Then

$$d \ln \langle r^2 \rangle_0/dT = -(1/T)[(\ln \sigma) (\partial \ln \langle r^2 \rangle_0/\partial \ln \sigma) +$$

$$(\ln \sigma') (\partial \ln \langle r^2 \rangle_0/\partial \ln \sigma') + (\ln \beta) (\partial \ln \langle r^2 \rangle_0/$$

$$\partial \ln \beta)] \tag{15}$$

As will be apparent from Figures 5 and 6, the first term in brackets is negative for $\beta < 0.5$ and $-\ln \sigma$ in the expected range, i.e., for $-\ln \sigma > 1$; it becomes positive however for larger β. The second term is
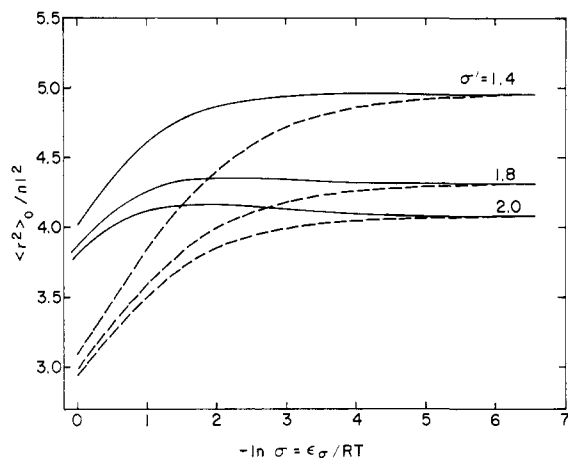
Figure 6. The effect of alleviating the suppression of $g^{\pm}g^{\mp}$ pairs about CH_2–CH_2–O and O–CH_2–CH_2 by taking $\beta > 0$. Solid curves calculated for $\beta = 0.4$; dashed curves, $\beta = 0.9$; $\sigma = \gamma = 1$ throughout.

Figure 7. Characteristic ratio $vs.$ $-\ln \sigma$ for the selected values of β and σ' shown.

negative, and the third is positive. If β is set equal to zero so that the last term in eq. 15 vanishes, and combinations of σ and σ' are chosen which reproduce the experimental value of $\langle r^2 \rangle_0/nl^2$, the calculated temperature coefficient invariably is positive as observed, but at least several-fold too large. Simultaneous agreement with the observed coefficient, $d \ln \langle r^2 \rangle_0/dT = 0.23 \times 10^{-3}$ deg.$^{-1}$, requires $\beta > 0.5$. Figure 7 shows several curves for $\beta = 0.6$ to 0.9 with σ' assigned values of 1.8 or 1.9 as indicated in order to match the experimental data. Values of the parameters β, σ, and σ' affording agreement with the experimental results at a mean temperature of 60° are listed in Table III.[35] Agreement may also be obtained for $\beta > 1$, but values in this range seem implausible in view of the distance between the CH_2 and O groups placed in close proximity by the $g^{\pm}g^{\mp}$ pair.

Table III. Acceptable Parameters and Corresponding Energies for the POE Chain at 60°

β	σ	ϵ_σ, cal. mole^{-1}	σ'	$\epsilon_{\sigma'}$, cal. mole^{-1}	$\sigma\beta\sigma'$
0.60	0.147	1270	1.90	−430	0.167
0.70	0.144	1290	1.80	−390	0.182
0.80	0.109	1470	1.80	−390	0.157
0.90	0.093	1580	1.80	−390	0.151
1.00	0.075	1720	1.80	−390	0.135

The required value of σ' changes little with the choice of β; a value of σ' well in excess of unity obviously is required. The positive temperature coefficient of $\langle r^2 \rangle_0$ for POE (as contrasted to the negative coefficient for PE) arises from the overriding effect of the increase with temperature in the population of $trans$ states about CH_2–CH_2 bonds, and this, of course, reflects the lower energy ($ca.$ −400 cal. mole^{-1}; see Table III) of the $gauche$ state compared to the $trans$ for the bonds considered.

(35) Calculations using eq. 13 could not be carried out for $\beta = 1.0$ by the method set forth above, because U_1 and U_3 are then singular and cannot be inverted. The results given in Table III for $\beta = 1.0$ were obtained by interpolating curves for $\beta = 0.9$ and 1.1.
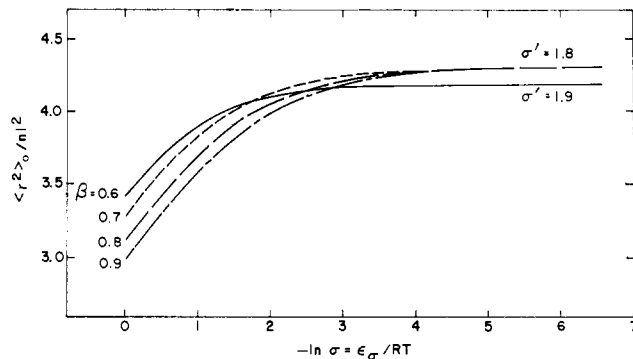
Whereas $\sigma' > 1$, the calculations place $\sigma \cong 0.10$, a value much lower than that for PE. The corresponding energy, $\epsilon_\sigma \cong 1400$ cal. mole^{-1}, accords with expectations based on the comparison of the relevant "three-bond" $CH_2 \cdots CH_2$ distance with that for the $gauche$ conformation in PE chains.

Whereas $gauche$ pairs of opposite sign about CH_2–O–CH_2 have been excluded at the outset on steric grounds, those embracing CH_2–CH_2–O or O–CH_2–CH_2 may be seen to involve the statistical weights $\sigma\beta\sigma'$ given in the last column of Table III. These are small but by no means negligible.

Longer sequences of $gauche$ states of alternating sign generate compact conformations which must be of rare occurrence because of severe steric conflicts between groups separated by more than four bonds. Some of these are included by the present methods, which take account only of interactions between first-neighbor rotations. However, these conformations acquire low statistical weights, even in the present scheme, and, hence, may be presumed to have little effect on the final result. Consider, for example, the only longer conformation sequence of this nature permitted by the present treatment (according to which $g^{\pm}g^{\mp}$ are excluded for CH_2–O–CH_2 pairs), namely, that involving the triad of bonds O–CH_2–CH_2–O which in the $g^+g^-g^+$ conformation would engender a "five-bond" interaction between adjoining CH_2 groups. Even if the first two bonds are g^+g^-, the statistical weight for state g^+ for the third is $\sigma\beta \cong 0.08$ compared with 1.00 for t, and $\sigma \cong 0.10$ for g^-. Hence, the only conformations leading to interactions of this higher order are accorded rare occurrence in the present scheme.

The conspicuous results of the analysis of the random conformation of the POE chain, namely, $\sigma_{POE} < \sigma_{PE}$ and $\sigma'_{POE} > 1$, are gratifyingly confirmatory of predictions based on steric considerations and on comparisons with the other related chains PE and POM. They are also consistent with the conformation adduced by Tadokoro and co-workers[23] for crystalline POE. These successes enlarge the grounds for confidence in the utility of the rotational isomeric model for interpreting the configurations of chain molecules.

The Configuration of Vinyl Polymers.   Experimental Results

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The characteristic ratio $\langle r^2 \rangle_0 / nl^2$ for isotactic poly(n-pentene-1) deduced from intrinsic viscosities of fractions in 2-pentanol at the Θ-point (62.4°) is 9.2 ± 0.5. This result, though larger than the characteristic ratios for polyethylene, polyisobutylene, and poly(dimethylsiloxane), is less than would be expected on the basis of steric interactions within the isotactic chain structure. The temperature coefficients, $d \ln \langle r^2 \rangle_0 / dT$ in 10^{-3} deg.$^{-1}$, determined for several isotactic and atactic vinyl polymers from stress–temperature measurements on crosslinked networks in the amorphous state, are found to be positive but small with values as follows: isotactic poly(butene-1), 0.09; isotactic poly(n-pentene-1), 0.34; atactic poly(butene-1), 0.50; atactic poly(n-pentene-1), 0.53; and atactic poly(isopropyl acrylate), 0.25. The temperature coefficient for isotactic poly(n-pentene-1) deduced from the temperature dependence of its intrinsic viscosity in n-hexadecane is in satisfactory agreement with the stress–temperature value. The significance of these results is discussed in relation to those for other vinyl polymers and also with reference to predictions from analysis of the chain structure and the interactions of its substituents.

Introduction

The studies reported in this paper have been concerned with several vinyl polymer[2] chains ($-CH_2-CHR-)_{n/2}$, namely, poly(butene-1), poly(n-pentene-1), and poly(isopropyl acrylate).   The isotactic and atactic forms of the first two polymers and the atactic form of the third have been investigated.   The occurrence of asymmetric atoms within these chains presents a feature not shared by the examples previously interpreted.[3,4]   Pendant substituents greatly increase the steric interactions as compared with polyethylene or polyoxyethylene.[3]   They are not, however, so great as in the polyisobutylene chain which bears two substituent methyl groups on alternate atoms.   In poly(dimethylsiloxane), which likewise bears two substituents, steric interactions are alleviated by greater bond lengths and bond angles and by the smaller van der Waals radius of the O atom.[5]

Main emphasis has been placed on determination of the temperature coefficient of the unperturbed mean-square, end-to-end length $\langle r^2 \rangle_0$.   The temperature coefficient may be a more significant quantity than the characteristic ratio $\langle r^2 \rangle_0 / nl^2$ from the standpoint of establishing the connection between chain configuration and structure.   The value of the ratio has been determined however for isotactic poly(n-pentene-1).

Experimental

Polymer Samples. Both of the isotactic polymers were recrystallized to obtain material of the highest possible tacticity.   Isotactic poly(butene-1),[6] having a molecular weight of *ca.* 10^6 according to its intrinsic viscosity, was purified by taking advantage of the solubility of atactic poly(butene-1) in both benzene and diethyl ether.   A solution containing approximately 1% of the polymer in benzene was cooled gradually to room temperature; diethyl ether was added to complete the crystallization of the more stereoregular material.   Recovery exceeded 90%, indicating absence of a substantial proportion of atactic constituents in the polymer as received.   The precipitated portion was redissolved in hot benzene, passed through a coarse, fritted-glass filter, and freeze-dried.   The density at 25°, determined by flotation in a liquid of matching density, was 0.93 g. cc.$^{-1}$.   The melting point, determined with a polarizing microscope, was *ca.* 134°.   The size and perfection of the spherulites in the sample indicated a high degree of crystallinity and, hence, of tacticity.

The isotactic poly(n-pentene-1) sample[7] (presumably ether-extracted) was dissolved in toluene, and the resulting solution, *ca.* 1% polymer by weight, was cooled to $-25°$.   It was stirred at this temperature for 30 min.   Precipitated (crystalline) polymer was separated using a cloth filter.   It was redissolved in benzene, passed through a coarse, fritted-glass filter, and freeze-dried.   Approximately 90% of the original material was recovered.   The intrinsic viscosity of the polymer indicated a molecular weight in the range 2 to 3 × 10^6.   The density at 25° of a carefully annealed sample was found to be 0.890 g. cc.$^{-1}$, in good agree-

(1) Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn 1, N. Y.

(2) A preliminary report on a part of this investigation has been published: J. E. Mark and P. J. Flory, *J. Phys. Chem.*, **67**, 1396 (1963).

(3) J. E. Mark and P. J. Flory, *J. Am. Chem. Soc.*, **87**, 1415 (1965).

(4) For a bibliography of previous investigation on this subject, see the footnotes given in ref. 3.

(5) P. J. Flory, V. Crescenzi, and J. E. Mark, *J. Am. Chem. Soc.*, **86**, 146 (1964).

(6) This sample was made available by the Avisun Corp. of Marcus Hook, Pa.

(7) All samples of poly(n-pentene-1) were prepared for this studies by Professor G. Natta and co-workers of the Polytechnic Institute of Milan.   Their cooperation and assistance is gratefully acknowledged.