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Configurational Statistics of Methyl Vinyl Ether–Maleic Anhydride Copolymer: Selection of Important Atomic Interactions and Conformations

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ABSTRACT: The conformations of methyl vinyl ether–maleic anhydride copolymer (MVEMA) are investigated by determining and analyzing the most important conformers of an appropriate subunit of the copolymer. Average dimensions of the unperturbed MVEMA copolymer chain are calculated by using the rotational isomeric state model. The relative energy of each rotational isomer has been approximated three ways: (1) by analogy to known atomic interactions as reported for small molecules and derived from polymer properties, (2) by computation of atomic interaction energies with the MM2 molecular mechanics program, and (3) by calculation of the relative energy of each conformation of the entire subunit using MM2. Each of these three methods leads to statistical weights for the individual conformers. When these weights are used, the characteristic ratio, $\langle r^2\rangle_0/nl^2$, at the limit of large n, is calculated separately for each of the four most important stereoisomers and compared to the experimental characteristic ratio. The characteristic ratios computed by using the three different sets of weighting factors for the first isomer were 9.0, 9.2, and 8.9. These values are in virtual agreement with the experimental characteristic ratio of 9.01 ± 0.90. The characteristic ratios of the other three stereoisomers are significantly larger with average values of 25.0, 18.6, and 20.9. The large differences in the characteristic ratio between the first stereoisomer and the other three directly imply that the polymer consists principally of the first stereoisomer, with any of the other stereoisomers present only in insignificant amounts.

Introduction

The exact atomic positions of a flexible macromolecular chain in dilute solution cannot usually be determined. However, the dimensions of the chain can be measured and also evaluated statistically.

Many factors govern the spatial arrangements that the atoms of a polymer in dilute solution may assume. Structural features such as the stiffness of the chemical bonds and the relative rigidity of the valence bond angles constrain the chain. Rotations about the bonds, on the other hand, are relatively freer and usually impart the chain its flexibility. The many combinations of rotational states for these bonds permit the polymer to adopt a large number of possible conformations. Other factors that strongly influence the conformation of a polymer are the attractions or repulsions between the various atoms.

In this work only short-range interactions will be considered. The polymer will be treated as a chain unperturbed by long-range effects. Experimental Θ conditions can be chosen by changing solvent and temperature, under which the effects of long-range interactions are compensated and under which the dimensions of the chain depend only on short-range interactions.[1]

In the following analysis, attention will be focused on a single subunit of the polymer. The structural parameters, the rotational conformations, and the short-range interactions of the subunit will be investigated. The important conformations of the polymer chain can then be represented as a statistical combination of contributions from these individual repeating units. The relative energy of the most important conformations of the polymer will then be approximated in three ways: (1) by analogy to known atomic interactions reported for small molecules and derived from polymer properties, (2) by computation of atomic interactions with the MM2 molecular mechanics program (MM2 80, QCPE, Indiana University, Bloomington, IN), and (3) by calculation of the relative energy of each conformation of the entire subunit with MM2. Finally, the mean dimensions of the chain will be computed by weighting each polymer conformation and averaging over all conformations.

The experimental molecular dimensions of this polymer were determined by Yang and Strauss.[2] The polymer was obtained from the GAF Corp. It was fractionated by phase separation into five samples with different ranges of molecular weights. The molecular weight of each fraction was determined by light scattering. The molecular weights ranged from 53.30×10^5 to 7.45×10^5. The Θ solvent for the polymer, 10% hexane and 90% THF, was also determined by phase separation. Yang and Strauss found the characteristic ratio of this sample of MVEMA to be 9.06 ± 0.90.

The characteristic ratio determined under Θ conditions is defined as

$$C_n = \langle r^2\rangle_0/nl^2$$

where n is the number of backbone bonds of the polymer and l the length of the backbone bonds. Usually the characteristic ratio increases with n, but as n becomes large the characteristic ratio converges to become independent of n. C_∞ is the characteristic ratio at this asymptotic limit where the ratio is independent of n.

This experimentally determined characteristic ratio of $C_\infty = 9.06$ will be used as a principal test of the molecular calculations to be described in this work. The polymer MVEMA is shown in the extended trans conformation:

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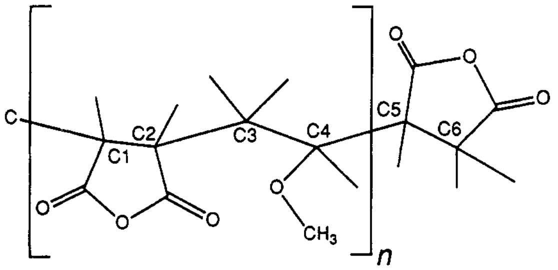
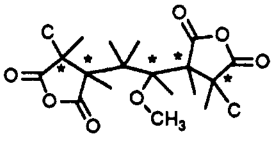


The backbone of the repeat unit consists of a sequence of four bonds, one of which is fixed in the succinic anhydride ring. The bonds are indexed as follows: Bond 1 is between atoms C1 and C2, bond 2 between C2 and C3, bond 3 between C3 and C4, and bond 4 between C4 and C5. All but bond 1 can undergo restricted rotation. The corresponding dihedral angles will be designated ϕ_1, ϕ_2, and ϕ_3.

In the statistical analysis of MVEMA, the conformational energy will be computed as a function of the torsional rotation of each bond of the repeat unit. Because the succinic anhydride rings are bulky and are a fixed part of the backbone, the conformational energy of the repeat unit depends on both the preceding and the following ring. Consequently for these energy calculations, a unit larger than the repeat unit must be used and is taken to be the repeat unit together with the next succinic anhydride ring. The stiffness of the rings also makes interactions between the atoms of adjacent units unlikely. Thus, as with polyamides[3] and polypeptides,[4] to a good approximation, the interactions between the neighboring rings can be treated independently of other units. This independent subunit will be used in all energy calculations to follow.

The MVEMA copolymer has a relatively complex stereochemistry. When the subunit is part of the polymer, it has five chiral carbons: each ring has two chiral carbons and the carbon with the ether side group is also a chiral carbon. Therefore, 2^5 or 32 isomers are possible. The five chiral carbons of the subunit are depicted.



In the evaluation of the stereoisomers of this unit, the asymmetric carbons of the succinic anhydride ring will be considered first. The substitution on the ring can be either meso (cis) or racemic (trans). There is a substantial amount of experimental data to indicate that most of the MVEMA copolymer exists in the *racemic* configuration;[5-8] it will be assumed in this study that the MVEMA copolymer occurs only in the racemic form. This reduces the number of stereoisomers. Assuming only the racemic form, each ring can have only two stereoisomers. Thus 2^3 or 8 stereoisomers are possible instead of 32. Since four isomers are mirror images of the other four and since the energy of a pair of enantiomers is identical, the number of stereoisomers that must be considered is further reduced to four.

Figure 1 depicts these four stereoisomers.

Geometric Parameters

In order to compute the average chain dimensions, it is necessary to specify the lengths of the backbone bonds and the bond angles between consecutive backbone bonds.

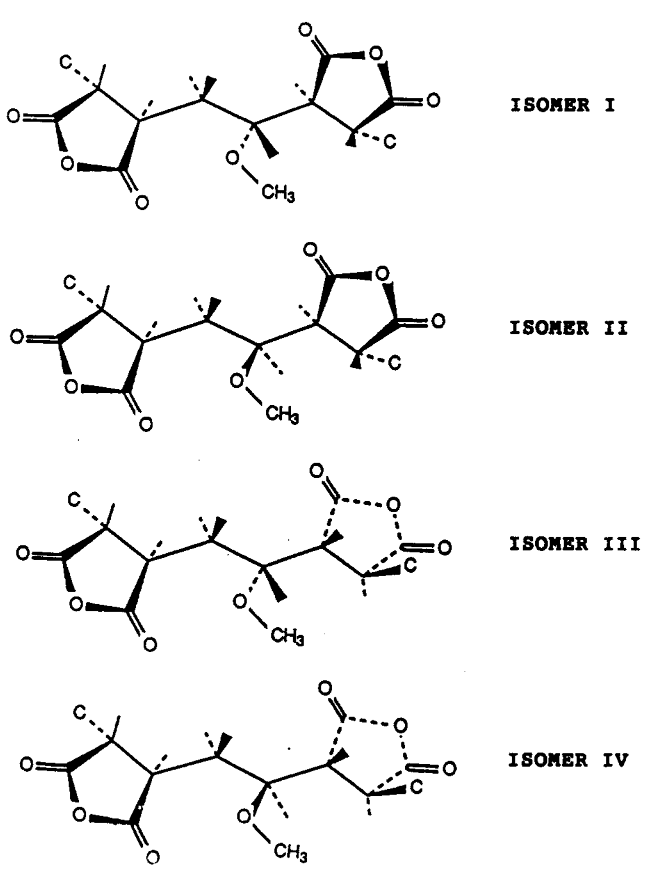


Figure 1. Stereoisomers of the MVEMA subunit.

Structural parameters for the MVEMA repeat unit were chosen from the crystal structure of succinic anhydride[9] and polypropylene.[10] The bond lengths used were 1.51 Å for bond C_1–C_2 and 1.53 Å for bonds C_2–C_3, C_3–C_4, and C_4–C_1. The bond angles used were as follows: ∠C1C2C3, 113.6°; ∠C2C3C4, 114.0°; ∠C3C4C1, 110.0°; and ∠C4C1C2, 113.8°.

Conformational Energies Based on Model Compounds

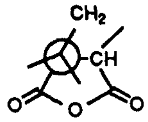
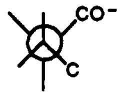
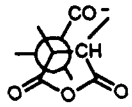
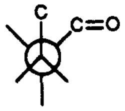
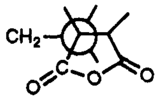
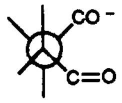
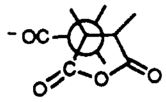
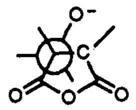
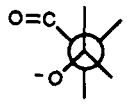
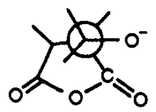
For simple hydrocarbons such as ethane and butane the torsional potential energies have three minima for the dihedral angle near trans (0°), gauche$^+$ (120°), and gauche$^-$ (-120°). These minima are separated by well-defined energy barriers and are usually called rotational isomers. Some positions of the torsion angles are more probable than others. The preferences for these states are determined by the specific atomic interactions.

To analyze the contributions of each of these individual atomic interactions to the total conformational energy, CPK models and computer modeling have been used to generate structures of all the allowed conformations of the subunit. From these, all the possible *first-order* interactions (involving one bond rotation) and *second-order* interactions (involving two bond rotations) have been categorized. Six different types of close interacting atom pairs have been found. Four of these are between pairs of carbon atoms with different substituents. The other two interactions are betwen oxygen and carbon atoms.

There are basically three types of *second-order* interactions: those between two carbon atoms, those between a carbon atom and the ether oxygen, and those between two oxygen atoms. The interactions are further classified as to the type of substitution on the interacting atom, resulting in six different *second-order* interactions.

In this approximation the energy contribution of each pair of interacting nonbonded atoms in MVEMA is

Table I
Summary of First-Order Interactions

	model compd	energy, cal/mol	MVEMA	energy, cal/mol	statistical wt
σ -CH2-, -CH2-		500		500[a]	0.43
σ′ -CH2-, -CO-				500[b]	0.43
σ″ -CH2-, -C=O		0		500[c]	0.43
σ‴ -CO-, -C=O				500[d]	0.43
δ -CH2-, -O-		-200		0[e]	1.00
δ′ -C=O, -O-				-400[f]	1.96

[a] Based on polymethylene.[11] [b] Based on poly(tetramethylene oxide).[13] [c] Based on polyamide[3] and polymethylene.[11] Because the carbonyl is fixed in the succinic anhydride ring and directed toward the hydrogens of the interacting group, there is greater steric interference in MVEMA than in polyamide. The steric arrangment of the closest atoms is similar to polymethylene. [d] No analogous atomic arrangement was found in the previous theoretical treatments of other polymers. In the absence of further information, the same initial energy assigned to σ″ will be used. [e] Based on poly(oxymethylene).[15] [f] No model for this interaction could be found in the previously analyzed polymers. However, the interaction between the ether oxygen and the carbonyl carbon is judged to be electrostatically somewhat more favorable than that between an ether oxygen and methylene, δ.

assumed to be the same as that found for analogous atom pairs in other polymers. Thus the increase in energy resulting from a gauche$^+$ rotation about a carbon–carbon bond that brings two -CH2- groups into contact is assumed to be the same in MVEMA as it is in polymethylene.[11] In other words, it is assumed that the statistical weight for an interaction involving a given atom type is independent of the polymer, as long as Θ conditions are maintained. This assumption has been successfully used in applying statistical weights found in polymethylene to analogous interactions in poly(oxyethylene)[12] and higher poly(oxyalkanes),[13] to polyamides,[3] and to poly(ethylene terephthalate).[14]

Clearly, there may be differences between the interacting groups in this polymer and those found in the simpler polymers used here as models. However, it is of interest to learn whether weights determined for simpler polymers can be applied to MVEMA.

Table I gives the approximate energy of the first-order interactions. The energies from simpler polymers that serve as models are given in the third column, and the analogous interactions found in MVEMA are given in the fifth column. The Greek symbols represent the statistical weights to be estimated for each type of interaction. Table II summarizes the approximate energies for the second-order interactions.

As shown in Tables I and II, there are basically two types of first-order interactions: between carbon atoms and between carbon and oxygen atoms. The carbon–carbon interactions are taken to have interaction energies of 500 cal/mol. The carbon–oxygen interactions are taken to be attractive and by analogy to the poly(oxyalkanes) have negative energies. Second-order interaction energies are larger. Between carbon atoms they are estimated at 2000 cal/mol, based on polymethylene. Second-order interaction energies between carbon and oxygen or between two oxygens are much smaller but not negative, between 800 and 250 cal/mol, respectively.

Calculation of Characteristic Ratios

To compute the average end-to-end distance, the mathematical representation developed by Flory and Abe[16] will be used. However, an additional major simplification can be made for MVEMA, if it is assumed that the conformation of each subunit is independent and depends only on the rotation of the bonds between the fixed succinic anhydride rings. In other words, it is assumed that interactions do not occur that depend upon rotational positions of bonds outside this unit. This simplicication was made in treating polyamides, with the bonds between amide bonds constituting the independent unit.[3] This method will now be applied to MVEMA.

In this approximation the end-to-end distance for a chain of x repeat units, each comprised of y bonds, is

$$\langle r^2 \rangle = \mathbf{J}^*[\mathbf{H}]^{x-1}\mathbf{H}'\mathbf{J}$$

where

$$\mathbf{H} = (\mathbf{G}_1\mathbf{G}_2\mathbf{G}_3...\mathbf{G}_y)/z$$

is the average of the serial product of the G matrices of each bond of the repeat unit divided by the partition function of the repeat unit. The terminal unit of the chain is represented by

$$\mathbf{H}' = (\mathbf{G}_1\mathbf{G}_2\mathbf{G}_3...\mathbf{G}_t)/z'$$

The form of the **G** matrix can be found in ref 16.

The partition function used in the averaging for the repeat unit can be written as

$$z = \mathbf{J}^*(\mathbf{U}_1\mathbf{U}_2\mathbf{U}_3...\mathbf{U}_y)\mathbf{J}$$

and for the terminal unit as

$$z' = \mathbf{J}^*(\mathbf{U}_1\mathbf{U}_2\mathbf{U}_3...\mathbf{U}_t)\mathbf{J}$$

where $\mathbf{G}_t$ and $\mathbf{U}_t$ are the matrices for the terminal bond.

The **U** matrices for isomer I are

$$\mathbf{U}_1 = \begin{bmatrix} 1 & 0 & 0 \\ 1 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix}$$

$$\mathbf{U}_2 = \begin{bmatrix} \sigma'''\rho' & \sigma' & \sigma'\sigma''' \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$\mathbf{U}_3 = \begin{bmatrix} \delta & \sigma\omega' & \sigma\delta\omega'' \\ \delta & \sigma & \sigma\delta\omega \\ \delta\omega'' & \sigma\omega & \sigma\delta\omega'\rho \end{bmatrix}$$

$$\mathbf{U}_4 = \begin{bmatrix} \sigma''\delta\rho' & \sigma\delta'\delta & \sigma'\sigma''\delta'\rho \\ 0 & \sigma\delta'\delta & 0 \\ \sigma''\delta\rho' & \sigma\delta'\delta\omega & \sigma\sigma''\delta'\rho\omega'' \end{bmatrix}$$

The final assembly of matrices for MVEMA gives

$$\langle r^2\rangle_0 = \left(\frac{\mathbf{J}^*(\mathbf{G}_1\mathbf{G}_2\mathbf{G}_3\mathbf{G}_4)\mathbf{J}}{z}\right)^{x-1} \frac{\mathbf{J}^*(\mathbf{G}_1\mathbf{G}_2\mathbf{G}_3\mathbf{G}_4\mathbf{G}_t)\mathbf{J}}{z'} \qquad (1)$$

with

$$\mathbf{J}^* = [1 \;\; 0 \;\; 0 \;\; 0 \;\; 0]$$

and

$$\mathbf{J} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}$$

Characteristic Ratios Using Statistical Weights from Model Compounds

With this formulation to compute $\langle r^2\rangle_0$, the asymptotic characteristic ratios, C_∞, are calculated by using the geometric parameters given above and the statistical weights given in Tables I and II. The results are as follows: isomer I, 9.01; isomer II, 23.15; isomer III, 14.49; isomer IV, 24.61. The result for isomer I is in excellent agreement with the experiments of Yang and Strauss,[2] who reported a value of 9.06. The values for the other isomers are much larger than the experimental values. This suggests that the MVEMA samples consist primarily of isomer I.

Characteristic Ratios Using Statistical Weights Calculated with the Molecular Mechanics Program MM2

In the previous section the characteristic ratio has been calculated with statistical weights estimated from empirical values determined for analogous atomic arrangements in model compounds. The characteristic ratio thus calculated was in excellent agreement with the experimentally derived characteristic ratio. However, it is of interest to compare the above results with values obtained from more detailed energy calculations. In the following section the statistical weights will be determined by using molecular mechanics.

Using the MM2 molecular mechanics program is in principal very similar to the method described above. In both cases all the important nonbonded atom pair interactions are enumerated. In the first method only atom pairs separated by three and four bonds are considered. Here we use MM2 to treat all nonbonded atom pairs; thus, this method will provide a test of the assumptions made in the previous method. In both methods, each type of nonbonded atomic pair interaction has a corresponding energy. The energy values determined by Flory et al. originate in small-molecule data as well as from fitting calculated mean chain dimensions to experimental chain dimensions of long-chain polymers. MM2 is parametrized mainly to reproduce experimentally derived geometries of hydrocarbons and small organic molecules with simple functional groups such as alcohols, ethers, esters, etc. One reason that the MM2 results are of particular interest in this analysis is the need to treat more accurately the possible effects of crowding due to the branching of the ether side chain. This was considered only in an approximate manner in the above analysis. If a particular interaction was judged from CPK models to be more hindered on average, it was given a higher energy than that found in the model compounds. However, the degree of crowding depends on the rotational state of all three of the rotatable bonds of the subunit and, therefore, cannot be represented only by *second-order* interactions. The energies calculated by MM2 should reflect more completely all steric interactions as well as permit deformations of bond angles and dihedral angles.

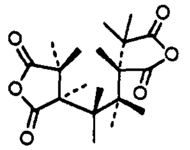
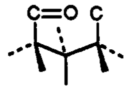
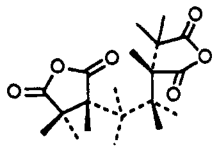
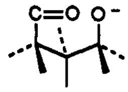
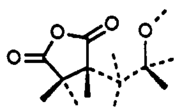
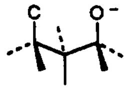
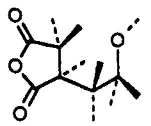
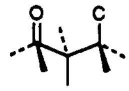
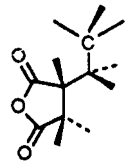
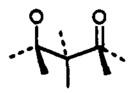
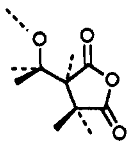
The resulting energy of each conformation of the subunit can be fit with the expression

$$E = c_1E^{\sigma} + c_2E^{\delta} + c_3E^{\delta'} + c_4E^{\omega} + c_5E^{\omega'} + c_6E^{\omega''} + c_7E^{\rho} + c_8E^{\rho'} + c_9E^{\tau}$$

where E is the energy calculated by MM2 for the given conformational isomer relative to the energy calculated for the reference state. The E subscripted with a Greek letter is the pairwise interaction energy for each type of first- and second-order atomic interaction. The coefficients c_1, c_2, etc., are constants and represent the number of times that interaction occurs in each conformation. Because only a few interactions occur in a given conformation, many of the coefficients are zeros.

The energies of 108 conformations, 27 for each of the four stereoisomers, have been calculated. The initial conformations with the dihedral angles fixed at 0° and ±120° are used as starting conformations. During the minimization all the structural parameters including the dihedral angles are allowed to vary until the minimum energy is obtained. Energy minimization in MM2 is by

Table II
Summary of Second-Order Interactions

	model compd	energy, cal/mol	MVEMA	energy, cal/mol	statistical wt
ω $-CH_2-$, $-CH_2-$		1700–2000		2000[a]	0.034
ω' $-CH_2-$, $-C{=}O$		1400		2000[b]	0.034
ω'' $-C{=}O$, $-O-$				2000[c]	0.034
ρ CH_2-, $-O-$		350, 340		800[d]	0.26
ρ' $=O$, $-CH_2-$				400[e]	0.51
τ $=O$, $-O-$		250		250[f]	0.65

[a] Based on polymethylene.[11] [b] The steric clash is greater than that in polyamide, and this interaction is judged to be at least as unfavorable as ω. [c] No analogous situation could be found among the published conformational analyses of polymers. Inspection of the CPK models indicates severe steric interference. Therefore, in the absence of further knowledge, ω'' is assumed to be as unfavorable as ω'. [d] There is considerably more steric interference in this case than in the analogous case in poly(oxyethylene).[12] However, the steric interference is not as large as that found in the previous three interactions involving two carbon groups. Therefore, as an initial estimate a value between these cases will be used. [e] Based on poly(oxyethylene)[12] and poly(tetramethylene oxide).[13] [f] Based on poly(trimethylene oxide).[13]

the block-diagram Newton–Raphson method. It is assumed that the geometries of the structures, although altered by minimization, are still sufficiently close to the conformations modeled with CPK models in the first method to have the same first- and second-order nonbonded atomic pair interactions. There are 69 conformations with an energy less than 4.5 kcal/mol. The conformations with energies above 4.5 kcal/mol contribute insignificantly and are ignored. From these, a set of conformations in the lower energy range is selected that gives the most unambiguous representation of the different types of nonbonded interactions. The higher energy conformations have so many atom pairs in contact (hence their high energies) that it is difficult to assess clearly which interactions are the most important. The set selected for this analysis is comprised of 47 different conformations.

Table III gives the 47 conformations, their relative energies, and the statistical weights for the *first-* and *second-order* interactions found in each conformation normalized relative to the reference conformation.

To determine the values of each type of atomic interaction energy, E^{σ}, E^{δ}, ..., etc., a set of 47 equations with nine unknown energies must be solved. No algebraic solution can be found to this set of overdetermined equations. Therefore, the problem reduces to finding the most consistent set of values to fit the total energies.

The SAS[17] nonlinear regression procedure is used to determine the best values of the interaction energies with fitting. Starting values for each variable are chosen. For this analysis the values approximated from analogous polymers are used as the starting values. An iterative process is used in which these starting values are improved until the error sum of squares, SSE, is minimized. SSE here is the difference between the total energy calculated by MM2 and that predicted by the addition of all the interactions for a given conformation.

Table IV gives the results of the various estimates of the nonbonded interaction energies and the corresponding statistical weights. For most cases the values found in this analysis agree well with those given in Tables I and II. An exception is the value for τ, which is much larger

Table III
MM2 Energies and Atomic Interactions of Each Conformation

	energy, kcal/mol	atom pair interacts[a]
	Isomer I	
ttt	0	1
ttg^{+}	−0.82	$\sigma, -\delta, \delta', -\sigma\omega$
ttg^{-}	1.25	$\sigma, \sigma'', -\delta, -\sigma\omega, \tau$
tg^{+}g^{+}	1.68	$2\sigma, -2\delta, \delta', -\sigma\omega, \omega'$
tg^{-}t	1.62	s, s$''$, ω''
g^{+}tt	1.48	$\sigma', -\delta, -\sigma\omega, \rho$
g^{+}tg^{+}	−0.65	$\sigma, \sigma', \delta', -2\sigma\omega, \rho$
g^{+}tg^{-}	1.21	$\sigma, \sigma', \sigma'', \delta, -2\sigma\omega, \tau, \rho$
g^{+}g^{+}g^{+}	−0.63	$2\sigma, \sigma', -\delta, \delta', -2\sigma\omega$
g^{+}g^{-}t	0.69	$\sigma, \sigma', -\sigma\omega, \omega$
g^{-}tt	2.35	$\sigma', \sigma''', -\sigma\omega, \omega''$
g^{-}tg^{+}	0.38	$\sigma, \sigma', \sigma''', -\delta, \delta', -2\sigma\omega, \rho$
g^{-}tg^{-}	3.11	$\sigma, \sigma', \sigma'', \sigma''', -\delta, -2\sigma\omega, \tau, \omega''$
g^{-}g^{-}t	3.76	$\sigma, \sigma', \sigma''', -\sigma\omega, \rho, \omega'$
	Isomer II	
ttg^{-}	1.29	$\sigma, \sigma'', -\sigma\omega, \omega', \omega$
tg^{-}t	−0.82	$\sigma, -2\delta, \delta'$
g^{+}tt	1.18	$\sigma', -\delta, \delta', -\sigma\omega$
g^{+}tg^{+}	1.08	$\sigma, \sigma', -2\sigma\omega, \tau$
g^{+}tg^{-}	−0.73	$\sigma, \sigma', \sigma'', -2\sigma\omega$
g^{+}g^{+}t	1.03	$\sigma, \sigma', \sigma'', -\delta, -2\sigma\omega, \rho, \omega'$
g^{+}g^{+}g^{+}	0.67	$2\sigma, \sigma', -2\sigma\omega, \tau, \rho$
g^{+}g^{+}g^{-}	2.50	$2\sigma, \sigma', \sigma'', -2\sigma\omega, \rho, \omega'$
g^{-}tg^{+}	2.14	$\sigma, \sigma', \sigma'', -2\sigma\omega, \tau, \omega'$
g^{-}tg^{-}	0.24	$\sigma, \sigma', 2\sigma'', -2\sigma\omega, \omega'$
g^{-}g^{-}g^{-}	2.03	$2\sigma, \sigma', 2\sigma'', -\delta, -2\sigma\omega, \omega', \omega$
	Isomer III	
ttt	−0.28	$-\delta, \delta'$
ttg^{+}	−0.08	$\sigma, \sigma'', -\sigma\omega$
ttg^{-}	0.49	$\sigma, -\sigma\omega, \tau$
g^{+}tt	0.75	$\sigma', -\delta, \delta', -\sigma\omega, \rho$
g^{+}tg^{+}	−0.18	$\sigma, \sigma', \sigma'', -2\sigma\omega, \rho$
g^{+}tg^{-}	1.17	$\sigma, \sigma', -2\sigma\omega, \tau, \rho$
g^{+}g^{+}t	0.32	$\sigma, \sigma', -2\delta, \delta', -\sigma\omega$
g^{+}g^{+}g^{+}	2.00	$2\sigma, \sigma', \sigma'', -\delta, -2\sigma\omega, \omega$
g^{+}g^{+}g^{-}	3.00	$3\sigma, -\delta, -2\sigma\omega, \tau, \omega$
g^{-}tt	3.10	$\sigma', \sigma''', -\delta, -\delta', -\sigma\omega, \omega''$
g^{-}tg^{+}	0.48	$\sigma, \sigma', \sigma'', \sigma''', -2\sigma\omega, \omega''$
g^{-}tg^{-}	3.08	$\sigma, \sigma', \sigma''', -2\sigma\omega, \tau, \omega''$
	Isomer IV	
tg^{-}g^{-}	−0.19	$2\sigma, -2\delta, \delta', -\sigma\omega$
g^{+}tt	0.43	$\sigma', -\sigma\omega$
g^{+}tg^{+}	1.75	$\sigma, \sigma', \sigma'', -2\sigma\omega, \tau$
g^{+}tg^{-}	−0.86	$\sigma, \sigma', -\delta, \delta', -2\sigma\omega$
g^{+}g^{+}t	0.49	$\sigma, \sigma', -\sigma\omega, \rho$
g^{+}g^{+}g^{+}	2.71	$2\sigma, \sigma', \sigma'', -2\sigma\omega, \rho, \omega$
g^{+}g^{+}g^{-}	0.30	$2\sigma, \sigma', -\delta, \delta', -2\sigma\omega, \rho, \omega$
g^{-}tg^{+}	1.60	$\sigma, \sigma', \sigma'', \sigma''', -2\sigma\omega, \rho, \tau$
g^{-}tg^{-}	0.07	$\sigma, \sigma', \sigma''', -\delta, \delta', -2\sigma\omega, \rho$
g^{-}g^{+}t	2.71	$\sigma, \sigma', \sigma'', -\sigma\omega, \rho, \omega$
g^{-}g^{-}g^{-}	1.47	$2\sigma, \sigma', \sigma'', -2\delta, \delta', -2\sigma\omega, \omega$

[a] Normalized relative to a value of 0 for the ttt of isomer I.

Table IV
Interaction Energies and Statistical Weights

	approxd by analogy to model compds		computed with MM2	
	energy, cal/mol	stat wt	energy, cal/mol	stat wt
σ	500	0.43	356.4	0.55
δ	0	1.00	−98.0	1.18
δ'	−400	1.96	−70.0	1.12
ω	2000	0.034	1461.0	0.086
ω'	2000	0.034	1744.6	0.054
ω''	2000	0.034	1121.1	0.15
ρ	800	0.26	576.5	0.38
ρ'	400	0.51	409.2	0.50
τ	250	0.65	1430.0	0.09

than that approximated by using polyamide as a model compound. Examination of a CPK model of the subunit reveals that, for some conformations where τ occurs, there is considerable crowding by the ether side chain. This increase in steric interference due to side-chain crowding did not occur in the model compounds used in the previous analysis.

The characteristic ratios calculated by using the energy values given in Table IV and the structural parameters given above are as follows: isomer I, 9.16; isomer II, 26.11; isomer III, 15.87; isomer IV, 28.26. The characteristic ratio for isomer I, 9.16, is extremely close to the experimental value of 9.06.

It can be concluded that, the statistical weights determined by MM2 using the minimized structures that had the three rotational isomeric state conformations as starting conformations give a characteristic ratio in virtual agreement with that derived from viscosity. The values of the statistical weights from the MM2 calculations are not identical with the values approximated earlier. However, with the exception of τ, the overall trend of low energies for the favorable interactions, somewhat higher energies for the σ-type interactions, and very high energies for the sterically hindered conformations is the same.

Computation of the Characteristic Ratios with Subunit Conformational Energies Computed with MM2

In the previous part of this work, the relative energy of the subunit is determined by first enumerating all the important nonbonded atomic pairs found in each conformation. This was done by inspecting CPK models. Next, a relative energy was assigned to each interaction. These energies were obtained first by analogy to model compounds from the work of Flory et al. and, subsequently, by computation with the MM2 molecular mechanics program. To obtain the relative energy of a given conformation of the subunit, the energies of all the interactions that occur in the conformation are summed. Knowing the relative energy of each of the important conformations of the subunit permits the determination of the mean dimensions of the polymer.

This method was previously used successfully by Flory and his co-workers to calculate conformation-dependent properties of a series of different, usually relatively simple, polymers. This method is also successful for the present, more complicated MVEMA copolymer. However, properly identifying all the significant atomic interactions is a complicated procedure. It is also difficult to arrive at a unique set of statistical weights that will reproduce the experimental conformation-dependent properties. In Flory's method the statistical weights are first approximated and then adjusted so that they will reproduce parameters derived from experimental measurements such as the characteristic ratio, the dipole moment, and their temperature dependences. This procedure should lead to a complete set of statistical weights that will successfully characterize the polymer. However, in a complex polymer often the experimental values are difficult to obtain and there are too many parameters.

In this section a third different method will be used to determine the relative energy of the conformations. The statistical weights of each entire subunit conformation will be obtained directly from energies computed with MM2. Instead of enumerating all important nonbonded atomic interactions, approximating their energy, constructing statistical weight matrices for each bond, and then representing the subunit by the product of the matrices of the component bonds, the statistical weight of individual conformations of the entire subunit is calculated directly with MM2.

In the previous analyses, the MVEMA subunit was treated as though the energy were a function of two consecutive bonds. Actually the subunit energy can be a function of three bonds: the three rotatable bonds between the succinic anhydride rings. The presence of the succinic anhydride rings and the ether side chain makes this a crowded structure. Therefore, the assumption of interdependence beyond neighboring bonds is somewhat overly simplified for some cases. It can be demonstrated that the energy is a function of the conformation of all three bonds by comparing the differences in energy between ttt and ttg^+ and between g^+tt and g^+tg^+. In this example, the conformation of bond 2 is constant and that of bond 3 is changed. If the energy depends on the conformation of bonds 2 and 3 and is independent of bond 1, then the differences in energy for each pair should be the same. The difference between the energy of ttt and of ttg^+ for isomer 1 is −0.82 kcal/mol and the difference between g^+tt and g^+tg^+ is −2.13 kcal/mol (Table III). Clearly, according to these energies computed by MM2, the conformation of bond 1 greatly influences the energy of the other two bonds. The magnitude of these differences suggests that the MM2 calculation is a somewhat better method in this case for obtaining statistical weights.

In the following analysis, the interdependence of all three bonds will be treated by expanding the statistical weight matrices. If each bond is allowed three rotational states, than a 9 × 9 matrix will represent the statistical weights of a pair of bonds and the dependence of this pair on the preceding bond.

For the MVEMA subunit the first matrix $\mathbf{U}_1$ is

$$\begin{array}{ccc} t_0|t_1 & t_0|g^+_1 & t_0|g^-_1 \\ \hline u_{11}\ (t_0t_1) & u_{12}\ (t_0g^+_1) & u_{13}\ (t_0g^-_1) \\ u_{21}\ (t_0t_1) & u_{22}\ (t_0g^+_1) & u_{23}\ (t_0g^-_1) \\ u_{31}\ (t_0t_1) & u_{32}\ (t_0g^+_1) & u_{33}\ (t_0g^-_1) \end{array}$$

The matrix $\mathbf{U}_1$ consists of only three rows instead of nine since it is assumed that the energy of the subunit consisting of two succinic anhydride rings and the intervening three rotatable bonds is independent of the adjacent subunits. Therefore, the bond pair, bond 1 and bond 2, is not dependent on any previous bond. Furthermore, the $\mathbf{U}_1$ matrix consists only of three columns because bond 1 is fixed in the succinic anhydride ring and can only adopt the trans conformation.

The $\mathbf{U}_2$ matrix is a 3 × 9 matrix in the case of MVEMA instead of a 9 × 9 matrix, again because bond 0 can only have one conformation instead of three. The $\mathbf{U}_2$ matrix has the form of the first three rows of the matrix. The matrices $\mathbf{U}_3$ and $\mathbf{U}_4$ have the form below.

$$\begin{array}{c|ccccccccc} & t_2|t_3 & t_2|g^+_3 & t_2|g^-_3 & g^+_2|t_3 & g^+_2|g^+_3 & g^+_2|g^-_3 & g^-_2t_3 & g^-_2|g^+_3 & g^-_2|g^-_3 \\ \hline t_1|t_2 & u_{111} & u_{112} & u_{113} & 0 & 0 & 0 & 0 & 0 & 0 \\ t_1|g^+_2 & 0 & 0 & 0 & u_{121} & u_{122} & u_{123} & 0 & 0 & 0 \\ t_1|g^-_2 & 0 & 0 & 0 & 0 & 0 & 0 & u_{131} & u_{132} & u_{133} \\ g^+_1|t_2 & u_{211} & u_{212} & u_{213} & 0 & 0 & 0 & 0 & 0 & 0 \\ g^+_1|g^+_2 & 0 & 0 & 0 & u_{221} & u_{222} & u_{223} & 0 & 0 & 0 \\ g^+_1|g^-_2 & 0 & 0 & 0 & 0 & 0 & 0 & u_{231} & u_{232} & u_{233} \\ g^-_1|t_2 & u_{311} & u_{312} & u_{313} & 0 & 0 & 0 & 0 & 0 & 0 \\ g^-_1|g^+_2 & 0 & 0 & 0 & u_{321} & u_{322} & u_{323} & 0 & 0 & 0 \\ g^-_1|g^-_2 & 0 & 0 & 0 & 0 & 0 & 0 & u_{331} & u_{332} & u_{333} \end{array}$$

The G matrices, as given by Flory and Abe,[13] are derived from the U matrices to enable the computation of the required averages.

The average end-to-end distance is calculated by using the same method as presented in eq 1 but with the expanded matrices based on the larger U matrices described just above instead of the previous matrices.

Table V
Conformational Statistical Weights

	isomer I	isomer II	isomer III	isomer IV
ttt	1.00	0.0057	1.6	0.0047
ttg^+	3.9	0.0008	1.2	0.0052
ttg^-	0.12	0.11	0.43	0.12
tg^+t	0.024	0.084	0.0067	0.025
tg^+g^+	0.059	0.0040	0.064	0.013
tg^+g^-	0	0.0018	0	0.080
tg^-t	0.065	3.9	0	0.036
tg^-g^+	0.0060	0.0099	0.0015	0
tg^-g^-	0	0.0092	0.0068	1.4
g^+tt	0.083	0.13	0.28	0.49
g^+tg^+	3.0	0.16	1.4	0.053
g^+tg^-	0.13	3.4	0.14	4.2
g^+g^+t	0.068	0.17	0.58	0.44
$g^+g^+g^+$	2.9	0.32	0.034	0.011
$g^+g^+g^-$	0	0.015	0.0065	0.60
g^+g^-t	0.31	0.069	0.016	0.0063
$g^+g^+g^+$	0.015	0	0.0008	0
$g^+g^-g^-$	0	0.010	0.053	0.24
g^-tt	0.019	0.066	0.0054	0.066
g^-tg^+	0.53	0.027	0.44	0.068
g^-tg^-	0.0054	0.066	0.0056	0.89
g^-g^+t	0.0026	0	0.018	0.013
$g^-g^+g^+$	0.010	0.0021	0	0
$g^-g^+g^-$	0	0	0	0
g^-g^-t	0.0018	0.0009	0.0049	0.023
$g^-g^-g^+$	0.0035	0	0	0
$g^-g^-g^+$	0.0045	0.033	0.018	0.085

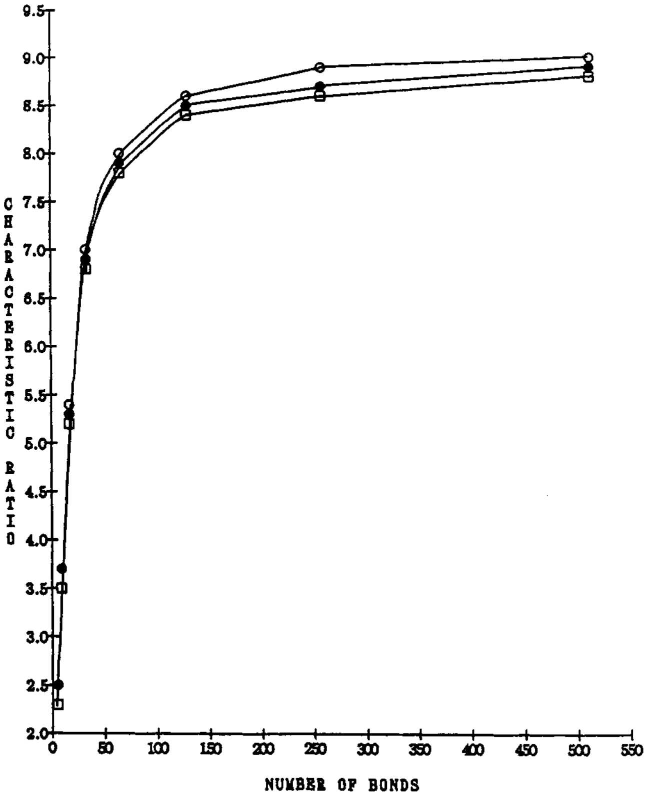


Figure 2. Characteristic ratio versus number of bonds for (●) method 1, (○) method 2, and (□) method 3.

To calculate the average end-to-end distance and the characteristic ratio, the statistical weights and the structural parameters for all the important conformations of the subunit must be determined.

Table V gives the statistical weights for each conformation of the stereoisomers. These are the Boltzmann factors of the energies calculated for each entire subunit conformer with MM2. The characteristic ratio using these

Table VI
Characteristic Ratios

	method 1: atom pair stat wts by analogy	method 2: atom pair stat wts from MM2	method 3: subunit energy from MM2
isomer I	9.01	9.16	8.88
isomer II	23.15	26.11	26.96
isomer III	14.49	15.87	25.69
isomer IV	24.61	20.81	17.33
exptl		9.06 ± 0.91	

Table VII
Statistical Weights of the Conformations of Isomer I

	method 1: stat wts by analogy to model compds	method 2: stat wts from MM2	method 3: min energy subunit conformn from MM2
ttt	1.00	1.00	1.00
ttg^+	3.8	1.9	3.9
ttg^-	1.1	0.094	0.12
tg^+t	0	0	0.024
tg^+g^+	0.058	0.047	0.059
tg^+g^-	0	0	0
tg^-t	0.015	0.084	0.065
tg^-g^+	0.002	0.014	0.006
tg^-g^-	0	0.0004	0
g^+tt	0.51	0.76	0.083
g^+tg^+	2.0	1.4	3.0
g^+tg^-	0.056	0.071	0.13
g^+g^+t	0	0	0.068
$g^+g^+g^+$	3.2	1.8	2.9
$g^+g^+g^-$	0	0	0.0004
g^+g^-t	0.030	0.094	0.31
$g^+g^+g^+$	0.004	0.015	0.015
$g^+g^-g^+$	0.001	0.0005	0.0005
g^-tt	0.030	0.167	0.019
g^-tg^+	0.113	0.316	0.53
g^-tg^-	0.032	0.016	0.0054
g^-g^+t	0	0	0.0026
$g^-g^+g^+$	0.049	0.083	0.010
$g^-g^+g^-$	0	0	0
g^-g^-t	0.003	0.0123	0.0018
$g^-g^-g^+$	0.0004	0.002	0.0035
$g^-g^-g^-$	0.0001	0.0001	0.0045

statistical weights and the structural parameters of these minimum energy conformations are as follows: isomer I, 8.8842; isomer II, 26.9572; isomer III, 25.685; isomer IV, 17.333. The correlation of isomer I with the experimental characteristic ratio of 9.06 is good. The inconsistency with the other three isomers' values is again a clear indication that the polymer consists principally of isomer I. The good agreement between the characteristic ratio calculated by this method and the experimental value supports the use of such methods to distinguish among stereoisomers.

Figure 2 gives the characteristic ratios computed by all three methods as a function of the number of bonds. The curve resulting from the present method is almost identical with that from the earlier procedures.

Although $\langle r^2 \rangle_0$ was computed with the above equation and matrices, the method being considered here reduces the computation of $\langle r^2 \rangle_0$ for a polymer with independent repeat units to a simpler procedure. The partition function is computed by summing the Boltzmann factors of the energies of all the conformations of the subunit. These energies can be determined by molecular mechanics. The weighted dot products of all the bond vectors are represented by a sum of terms, one term for each conformation of the subunit. These terms have the form

$$u\mathbf{g}_1\mathbf{g}_2 \cdots \mathbf{g}_y$$

where u is the Boltzmann factor of the given conformation and $\mathbf{g}$ is the matrix for calculating the geometry transformations; these are summed to obtain r^2 for one conformation. The geometrical parameters are those of the minimum energy structure of the conformation.

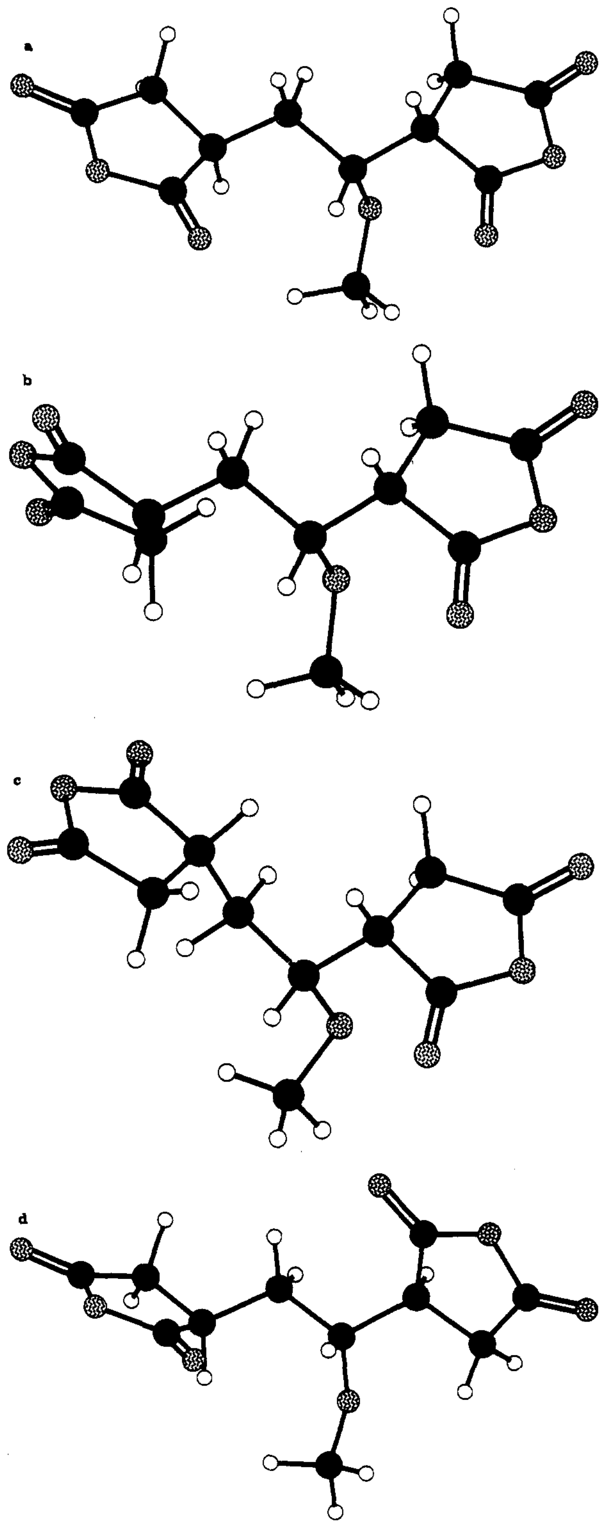


Figure 3. Lowest energy conformations of the MVEMA subunit: (a) ttg^+, (b) g^+tg^+, (c) $g^+g^+g^+$, (d) ttt.

This procedure simplifies the calculation. Any number of conformations and any number of bonds of a subunit can easily be treated. Additional conformations do not require reconstruction of matrices but are simply more terms in a sum.

The use of the minimum energy to represent a conformation in the computation of mean dimensions is an approximation that ignores the *shape* of the potential well of that minimum. Flory has pointed out that the entire potential surface should be considered.[1] However, in the present study very good agreement with experimental data was obtained with the approximate treatment.

Comparison of the Three Methods

The three different methods that have been used to approximate the relative energies of each rotational isomer give similar characteristic ratios. In the first method, CPK models have been inspected to determine the most important atom–atom interactions. Analogous interactions found in polymers previously treated by Flory et al. served as a starting point in approximating the statistical weights of each of these interactions. In the second method, the atom–atom interaction energies have been computed by using the MM2 molecular mechanics program, and, finally, the relative energy of each conformer, as a whole, has been calculated by using MM2. All three methods yield a similar characteristic ratio. The characteristic ratios for the four isomers calculated by the three different methods are given in Table VI.

In a comparison of the methods used, the statistical weights of the 27 conformations of isomer I are given in Table VII. In the first two methods, the relative energy of a single conformation of the subunit is the sum of the nonbonded atom pairs that occur in that conformation. In the third method, the minimum energy of a conformation is calculated directly with MM2.

As shown in Table VII, each of the methods gives similar statistical weights for each of the conformations. The only important discrepancies are the values computed for ttg$^-$ and g$^+$tt. In both cases the statistical weights for the conformers computed by summing the atom pair interactions are larger than that determined from energy minimization of the whole subunit. The reason is that the relative crowding of the side chain, which increases the energy, is not included in the determination of the energies in the first two methods but is included directly in the energy minimization of the subunit. In all other cases, the three methods give similar weights for each of the conformations. Therefore, it can be concluded not only that all three methods give similar characteristic ratios but that there is also agreement in the relative energies of the individual conformers. This agreement between statistical weights obtained with two different force fields, Flory's and MM2, is noteworthy.

Conclusions

The close agreement between the computed and the experimental characteristic ratios verifies the three approaches. Rotational states provide a complete representation of this complex molecule's conformations. The intuitive approach of selecting the important atomic interactions and weighting them with appropriate statistical weights is also shown to be successfully verified even for this very complex polymer.

All three methods used give similar energies for the subunit conformations and similar characteristic ratios. As shown in Table VI, only the characteristic ratio of isomer I is similar to the experimental value. Thus we conclude that isomer I must be the dominant species, with only trace amounts of the other isomers possibly present.

Examination of Table VII shows clearly that the conformational space is dominated by very few conformations. Methods II and III give only four conformations with statistical weights greater than one: ttg$^+$, g$^+$tg$^+$, g$^+$g$^+$g$^+$, and ttt. Because all other conformations have significantly smaller statistical weights, these four conformations dominate and the other conformations occur infrequently. In conclusion, methyl vinyl ether–maleic anhydride copolymer occurs principally as stereoisomer I and consists mostly of a mixture of four conformations: ttg$^+$, g$^+$tg$^+$, g$^+$g$^+$g$^+$, and ttt. These four lowest energy conformations are shown in Figure 3.

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Registry No. MVEMA (alternating copolymer), 124660-07-7.