Conformational Energies in Methyl Acrylate and Vinyl Acetate Polymers

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ABSTRACT: The molecular structures and conformational energies of model compounds appropriate to methyl acrylate and vinyl acetate homopolymers and their copolymers with ethylene have been investigated by molecular mechanics techniques. From these calculations a set of geometric and energy parameters to be used in a statistical mechanical rotational isomeric state model was derived.

Introduction

The rationalization of glass–rubber relaxation compared to subglass relaxation in terms of main-chain skeletal bond motion versus flexible side-group motion has been a subject of continuing interest.[1] Pendent ester group polymers appear to be especially appropriate examples. In particular, methyl acrylate (MA) and vinyl acetate (VA) homopolymers and their copolymers with ethylene, Figures 1 and 2, have been selected by us as model systems for both experimental[2,3] and molecular modeling studies.[4] In accomplishing the development of a detailed molecular model for relaxation in such polymers a necessary ingredient is an effective rotational isomeric state (RIS) model for their configurational behavior. The statistical weight matrices employed in RIS models to compute the average configurational properties[5] require a set of interaction energy parameters. Simple examples would be the gauche versus trans energy or the gauche–gauche steric interference energy in polyethylene. The development of such a set of energy parameters can be effected by means of conformational energy or "molecular mechanics" (MM) calculations using a well-calibrated empirical force field. The present paper reports the results of extensive conformational energy calculations on model compounds appropriate to the above polymers and the extraction from them of the necessary interaction energy parameters for RIS statistical weight matrices.

MM calculations on another pendent ester group situation, that in poly(methyl methacrylate), PMMA,[1,6–8] have proven useful in rationalizing relaxation results as have preliminary ones for the polymers considered in the present work.[2,3] However, the intention is somewhat more ambitious here. It is to provide the base for a complete statistical description of the chain to be used in a model for relaxation properties.

Conformational Energy Calculations

The conformational energy model employed considers all internal degrees of freedom. Terms are included for bond stretching, bending, and twisting as well as nonbonded or steric interactions. Polar or electrostatic effects are represented by a mutual induction model where polarizability centers as well as point dipoles are located in the constituent bonds. The appropriate parameters for ester groups have been recently reported[9] as have a summary of parameters for the other types of bonds present.[10]

It was found that a main-chain segment of seven carbon atoms carrying the ester groups was sufficiently long to represent the various steric interactions in the polymer chain and that two adjacent groups sufficed to represent the interactions between pendent esters, higher order interactions being at least approximately additive. Thus calculations of the energies and geometries of a large number of conformers of *n*-heptane substituted at the 4-position with a single MA or VA type ester group and of meso and racemic diads with the substitution of two ester groups at the 3- and 5-positions were made. Specifically, 66 conformations for MA systems and 56 conformations for VA systems were computed to create a data base for statistical weight parameter determination. The structural results were arrived at by complete energy minimization of the conformational energy function with all internal degrees of freedom participating.

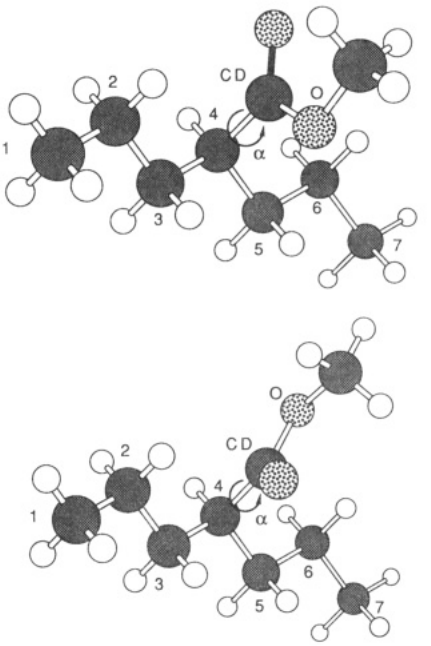

Figure 1. Model for an MA unit in a polyethylene chain. Shown with the main chain all trans. The configuration of the ester side group is *d* according to the convention of the text. Two side-group conformations (rotations about bond labeled α) are shown. The upper one corresponds to $\alpha = 60°$ and a 60° site in Figure 3 and the lower one to $\alpha = -150°$ and a 150° site in Figure 3.

RIS Geometric Parameters. It was found that in general there are three stable positions for the orientation of an ester side group. Some illustrations of these are shown in Figure 3 for a MA-type group and in Figure 4 for a VA-type group. There the energy for the complete rotation of the ester group about the attaching bond, labeled α, determined by complete energy minimization at each step of the constrained bond is plotted. The quoted

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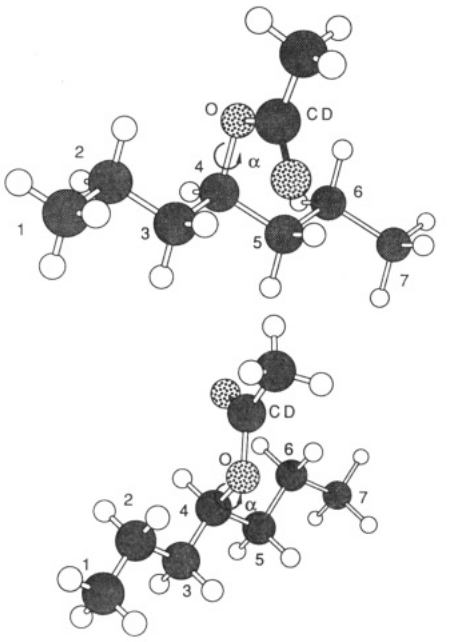

Figure 2. Model for an VA unit in a polyethylene chain. Shown with the main chain all trans. The configuration of the ester side group is *d* according to the convention of the text. Two side-group conformations (rotations about bond labeled α) are shown. The upper one corresponds to $\alpha = 60°$ and a 60° site in Figure 3 and the lower one to $\alpha = -150°$ and a 150° site in Figure 3.

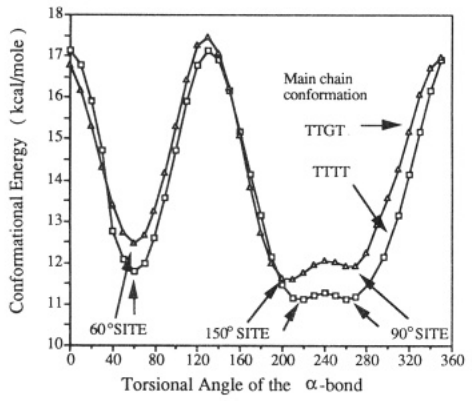

Figure 3. Energy of rotation of the MA ester group about the attaching bond in the model compound of Figure 1. Results for two main-chain conformations, TTTT and TTGT, are shown.

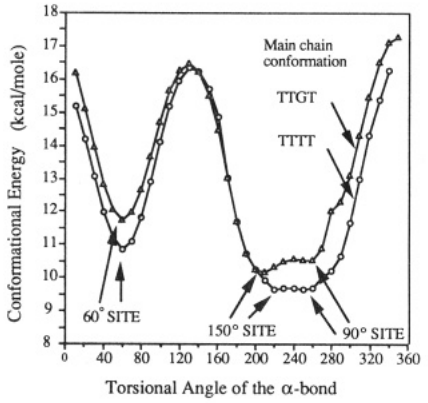

Figure 4. Energy of rotation of the VA ester group about the attaching bond in the model compound of Figure 2. Results for two main-chain conformations, TTTT and TTGT, are shown.

attaching bond torsional angle is based on the four centers, C(3)–C(4)–CD–O, for the MA-type group, Figure 1, and C(3)–C(4)–O–CD for VA, Figure 2, where C(4), is the main-chain carbon at the attachment point, C(3) a main-chain carbon next to it, and CD and O are the ester group doubly bonded sp^2 carbon and divalent oxygen, respectively. If the main-chain torsional angles are written in a sequence, TTGT, for example, or the skeletal atoms numbered as in Figures 1 and 2, the convention is followed of basing tabulated attaching bond torsional angles on the *left-hand* carbon of the two possibilities in the sequence as the C(3) carbon. In addition, another notational convention is required to specify the ester group conformation. Although the main-chain carbon at the attachment point is chiral, the entire monosubstituted heptane molecule possesses a plane of symmetry and is meso. However, it proves convenient if a configurational notation is adopted where the ester group is called "*d*" if the ester group points upward to the right looking down the chain from C(1) near to C(7) far. The configuration *d* corresponds to the torsional angle C(2)–C(3)–C(4)–CD in MA or C(2)–C(3)–C(4)–O in VA being 60° (gauche or G) when the main-chain sequence C(2)–C(3)–C(4)–C(5) is trans (T, 180°). Configuration "*l*" corresponds to upward to the left or the above bonds being −60° (gauche prime or G′) for a trans main chain.

The three side group conformations or states have been designated in general for convenience simply as the "60°, 90°, or 150°" states regardless of the sign or the exact value of the α-bond torsional angle in any given conformer. The notation "MATTGTd150" denotes a singly substituted MA type oligomer as in Figure 1 with main-chain bond C(3)–C(4)–C(5)–C(6) (approximately) G, the other skeletal bonds (approximately) T, the ester group in the *d* configuration above, and the α attaching bond in the indicated one of the two (150° or 90°) sites. No sign + or − on 90° or 150° is implied by the notation. Similarly, MATGTTd601150, describes a C(3), C(5) doubly substituted MA type ester, where the main-chain conformation is TGTT, the side group configurations are *d*,*l* racemic, and the ester orientations are in type 60° and 150° sites, respectively.

In analyzing the results it was further found that, due to four bond "ω" steric interferences,[5] significantly distorted main-chain torsional angles in addition to more or less normal T, G, G′ values occurred. This is similar to the situation in polypropylene.[11] There it is found that T_+, T_-, G_+, G'_- states, where + or − indicates a distortion of ~40° away from the standard value, occur as the result of steric repulsion in four-bond interferences. In the present case, however, it was found that the T_+, T_- distortions were relatively minor and that only G_+, G'_- distorted states need be invoked. The T_- and T_+ states in polypropylene allow relief of the strong steric interactions between substituent methyls in situations such as a TT meso diad. The planar nature of the side groups in MA and VA, the flexibility of rotation about the bond joining the side groups to the main chain, and the much greater distance between the bulky methyl groups and the main chain in these polymers combine to allow relatively small rotations of the main-chain torsions to relieve much of the steric interaction between side groups in this situation.

The conformational energies, torsional (main chain and side group) angles, and dipole moments for the energy minimized set of conformations of the model compounds considered are presented in Tables S-I and S-II of the supplementary material. Values of the torsional angles for the five main-chain states, T, G, G_+, G′, G'_- and the three side group states for both types of polymer are listed in Table I. They were derived from the geometric results in Tables S-I and S-II by Boltzmann energy weighted averaging over the conformers. In addition average bond

Table I
RIS Geometric Parameter and Dipole Moment Values

quantity	average value[a] MA	VA
dipole moment	1.67 D	1.82 D
60° side-group-state torsional angle	62.2° *d*,[b] −62.2° *l*	64.3° *d*, −64.3° *l*
90° side-group-state torsional angle	−97.4° *d*, 97.4° *l*	−107.8° *d*, 107.8° *l*
150° side-group-state torsional angle	−142.8° *d*, 142.8° *l*	−135.9° *d*, 135.9° *l*
T main-chain-state torsional angle	180°	180°
G main-chain-state torsional angle	66°	66°
G_+ main-chain-state torsional angle	96°	96°
G_-' main-chain-state torsional angle	−96°	−96°
G′ main-chain-state torsional angle	−66°	−66°
C–C–C bond angle	112°	112°
bond length	1.54 Å	1.54 Å

[a] Boltzmann energy weighted average over the data base of calculated conformations. [b] *d*,*l* indicates stereochemical configuration of the side group as defined in the text.

lengths and bonds angles were determined and are also given in Table I. These averaged geometrical parameters are to be used in the transformation matrices associated with the statistical weight matrices in the RIS model.

RIS Interaction Energy Parameters. a. Single Side Groups. The RIS model requires that the conformational energy associated with a bond be expressed in terms of a limited set of interaction parameters. The sets of interaction parameters were developed by examining the geometry of the model conformations in order to identify conformationally dependent steric interactions. The energetics of the model conformations were investigated by observation of the geometry using computer graphics to display the energy-minimized conformations and the use of space-filling physical models, along with examination of the values of the energies of the conformational energy functions for the energy-minimized geometries. The conformationally dependent steric interactions that resulted and their corresponding parameter labels are listed and discussed below and illustrated for the MA system in Figure 5 and for VA in Figure 6.

The steric interactions used to model MA systems are as follows:

G. The gauche interaction is first order and is primarily due to steric interactions and intrinsic torsional potentials that occur when main-chain bonds occur in G, G_+, G'_-, or G′ states and is the same interaction as discussed by Boyd and Breitling,[11] Mark,[12] Flory,[5] etc. The energy is assigned to the bond that occurs in one of the states listed above. There is no "skew methyl" like four-center interaction per se analogous to polypropylene[11] invoked for the side groups as the latter are rotatable and side-group-state dependent parameters are included separately.

WMAIN ("ω Main Chain"). The second-order pentane-type interaction that results from the near proximity of the two outer carbons and pendent hydrogens of a five-atom main-chain sequence when the intervening torsions are GG_-', $G_-'G$, G_+G', or $G'G_+$. The pentane interaction is of such high energy that the sequences at the normal undistorted values of GG′ and G′G are precluded. The rotations about the intervening bonds required to relieve the steric interaction are such that the angles are far removed from the G and G′ states (about 30° to 40°), and hence new torsional states, namely, G_+ and G_-', are required to adequately describe the configuration in terms of the RIS model. The energy is assigned to the bond associated with the second of the intervening torsions.

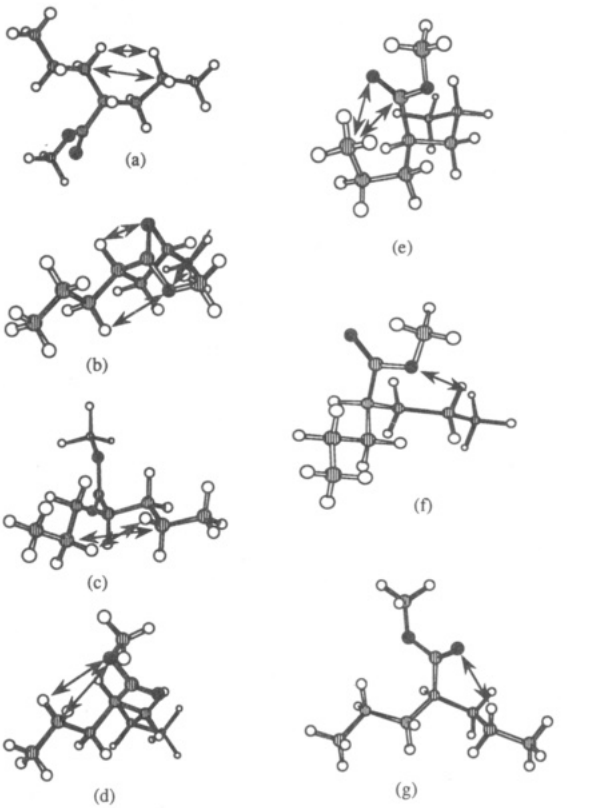

Figure 5. Steric interaction parameters for a single MA group are illustrated. The interaction type label and the conformation label for a circumstance where the interaction occurs are as follows: (a) G interaction (gauche); TTGTd60. (b) S_{60} interaction (side-group-state dependent); TTTTd60. (c) WMAIN interaction (pentane type); TG′GTd60. (d) WCD–O interaction (pentane type); TTGTd90. (e) WC–CD interaction (pentane type); G′TTG′d60. (f) ALPHA interaction (side-group-state dependent); TTG′Td60. (g) BETA interaction (side-group-state dependent); TTG′Td90.

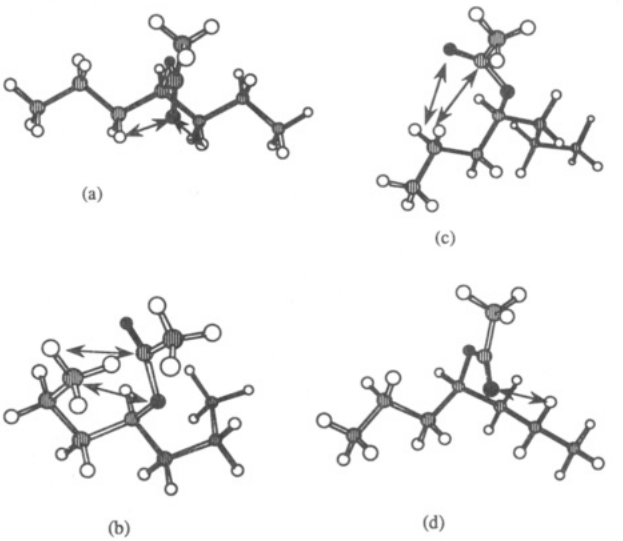

Figure 6. Steric interaction parameters for a single VA group are illustrated. The interaction type label and the conformation label for a circumstance where the interaction occurs are as follows: WMAIN and G types have same definitions as for MA, Figure 5. (a) S_{60} interaction (side-group-state dependent); TTTTd60. (b) WC–O interaction (pentane type); G′TTG′d90. (c) WO–CD interaction (pentane type); TTGTd90. (d) ALPHA interaction (side-group-state dependent); TTG′Td60.

S_{60}. The S_{60} side group interaction is first order and is primarily due to the steric interference between the ether oxygen and nearby main-chain hydrogens when the side group is in the 60° state. The energy is assigned to the bond following the side group.

WCD–O. This interaction is a pentane-type interaction (the intervening torsions being about the α-bond and the main-chain bond adjacent to the α-carbon), considered to be of second order because of the dependence of this interaction on both main-chain bonds adjacent to the α-carbon for the 90° and 150° side-group states, as explained below, and first order for the 60° state. The interaction involves steric effects between the ether oxygen and a main-chain carbon atom and pendent hydrogens two carbons from the α-carbon. In the 90° and 150° side-group states the interaction does not occur when both main-chain bonds adjacent to the α-carbon are in the trans state, due to the ability of the side group to rotate away from the interaction and hence relieve the steric interaction in this conformation. The energy is assigned to the main-chain bond following the α-carbon for the 90° and 150° states. For the 60° state, the interaction is associated with the intervening main-chain bond.

WC–CD. This interaction is a second-order pentane type involving the steric effect between the carbonyl carbon and carbonyl oxygen or ether oxygen and a main-chain carbon atom and pendent hydrogens three carbons from the α-carbon. This interaction can occur for any side-group state. The energy is assigned to the bond associated with the second of the intervening torsions. In addition, the WC–CD interaction is used to model steric interactions between side groups, as discussed below.

ALPHA. This interaction is a second-order interaction that results from the close proximity of the ether oxygen and a hydrogen attached to a main-chain carbon two removed from the α-carbon when the side group is in the 60° state.

BETA. This interaction is a second-order interaction that results from the close proximity of the carbonyl oxygen and a hydrogen attached to a main-chain carbon two removed from the α-carbon when the side group is in the 90° or 150° states.

The steric interactions used to model VA are as follows:

G and WMAIN. These are identical with the analogous interactions in MA and are not shown in Figure 6.

S_{60}. In VA this is analogous to the same interaction in MA. The interaction is first order and is primarily due to the steric interference between the carbonyl carbon and oxygen and nearby main-chain hydrogens when the side group is in the 60° state. The energy is assigned to the bond following the side group.

WO–CD. This interaction is a pentane-type interaction corresponding to the WCD–O interaction in MA. The interaction involves steric effects between the carbonyl carbon and carbonyl oxygen and a main-chain carbon atom and pendent hydrogens two carbons from the α-carbon. The interaction can occur for any side-group state. Because the steric effects involving the carbonyl oxygen cannot be relieved by rotating the side group in the 90° or 150° states away from the interaction, the trans–trans conformation of the two main-chain bonds adjacent to the α-carbon can include a WO–CD for these side-group states, unlike the corresponding situation in MA. Although the interaction is first order, it is assigned in the same manner as the analogous interaction in MA in order to maintain consistent interaction matrices.

WC–O. This interaction is a second-order pentane-type involving steric effects between the carbonyl carbon, carbonyl oxygen, and ether oxygen and a main-chain carbon atom and pendent hydrogens three carbons from the α-carbon. The interaction is similar to the WC–CD interaction in MA, with two major differences, both due to the same effect. In examining the structure of the side group for both methyl acrylate and vinyl acetate, it can be seen that while the volume swept out by rotation of the vinyl acetate group about the α-bond is much greater than that for methyl acrylate, the bulk of the side group is on one side of the rotation axis. In methyl acrylate there is a "backside" steric effect due to the presence of the carbonyl oxygen, which is absent in vinyl acetate. Because of this backside effect, conformations such as MAG′TTG′d150 contain a WC–CD interaction, while the corresponding conformation in VA does not contain a WC–O interaction. The side group must be turned into the interaction, as in VAG′TTG′d90, for the WC–O interaction to occur. This same lack of a backside effect also eliminates the WC–O interaction for conformations were the side group is in the 60° state. The energy for the WC–O interaction is assigned to the bond associated with the second of the intervening torsions.

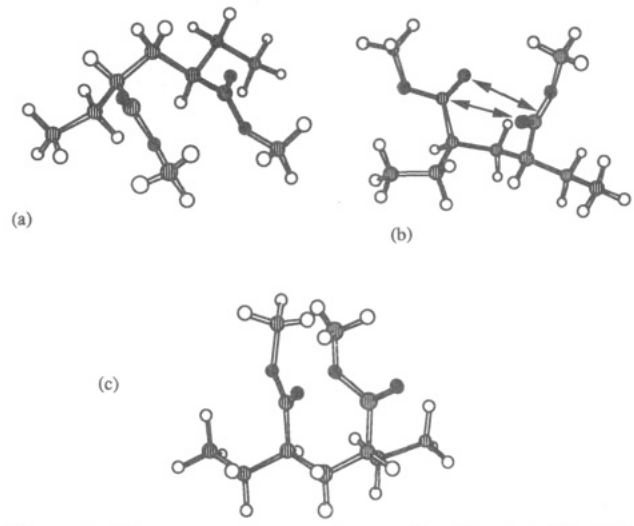

Figure 7. Side-group–side-group interactions illustrated for MA. Where they occur, they could be represented by parameters already invoked for the single-side-group case (a) Conformation TG′TTd601150. Minor skeletal torsional rotations relieve interference, no extra parameter needed. (b) Conformation TG′TTd901160. Interaction resembles and could be handled by interaction type WC–CD. (c) Conformation TTG′Td90160. Not allowed due to steric interference.

ALPHA. This interaction is a second-order interaction analogous to the ALPHA interaction in MA, which results from the close proximity of the carbonyl oxygen and a hydrogen attached to a main-chain carbon two removed from the α-carbon when the side group is in the 60° state.

An interaction corresponding to the MA BETA interaction does not exist in VA because of the lack of the backside steric effects in the latter.

b. Side-Group–Side-Group Interactions. In addition to electrostatic interactions between side groups, which are discussed later, steric interactions can also occur. Examination of the geometries of model conformations indicated whether side group steric interactions were important. When the geometry of the conformations dictated that side group steric interactions must be considered, three situations were found to exist with respect to these interactions for the MA model compounds. The first, in conformations such as MATG′TTd601150, as shown in Figure 7, it was found that small rotations (10–15°) of a main-chain bond would essentially relieve

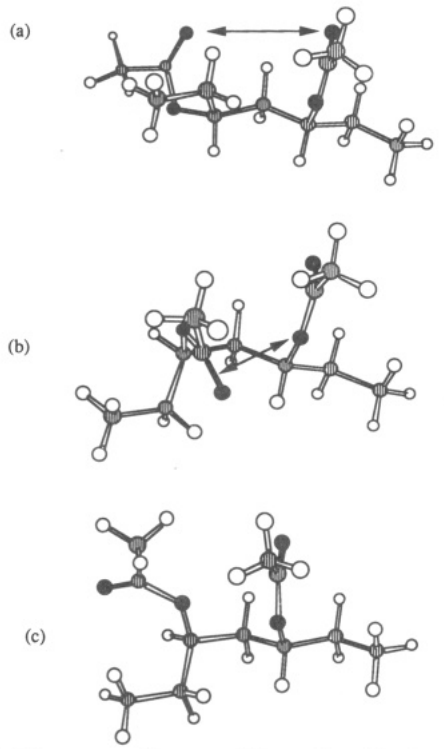

Figure 8. Side-group–side-group interactions illustrated for VA. Where they occur, they could be represented by parameters already invoked for the single-side-group case. (a) Conformation TGTTd601160. Side-group interaction resembles and could be handled by interaction type WC–O. (b) Conformation TG′T-Td601160. Side-group interaction also resembles and could be handled by interaction type WC–O. (c) Conformation TG′T-Td90160. No extra parameter needed.

the steric interaction between side groups and hence no additional energy term was required. In the second situation, such as in MATG′TTd90160, also shown in Figure 7, the geometry was such that a significant steric effect still resulted despite small rotations about the main-chain bond and that greater distortions of the conformational geometry occurred. It was found that the steric interaction, which resembles the WC–CD interaction in geometry, could be well-represented by the WC–CD parameter. In the third case the geometry dictated that the conformation could not exist due to high steric energy, as in MATTG′Td90160, shown in Figure 7.

In VA, any two-side-group conformation that leads to a WC–O geometry or a C–O C–O pentane-type geometry, as shown in Figure 8, results in a side-group interaction steric effect modeled well by the WC–O interaction, unless the side groups are turned away from each other, as in VATG′TTd90160, also shown in Figure 8, in which case no steric effect was noticed in the conformational energy calculations. As in MA the geometries of some conformations resulted in steric energies due to side-group interactions that were so high as to prohibit the occurrence of the conformations.

In both systems the side-group interactions are second order and are therefore assigned to the second of the intervening main-chain torsions.

c. Electrostatic Energy. The electrostatic energy in the disubstituted esters was abstracted for the RIS model in terms of a pair of dipole–dipole interactions. The molecular mechanics results indicate that the dipole moment vector for each side group can be considered approximately as a single vector located along the carbonyl bond. Dipole–dipole electrostatic interaction energy is a function of the relative orientation of the dipoles and the distance between them. Relative energies of a few coplanar orientations are shown in Figure 9. By examination of the geometry of the dipole configurations on this basis and from the consideration that the distances are fairly uniform, it proved possible to estimate the relative electrostatic energy by classifying a configuration as one of those in Figure 9. More formally and generally, especially for nonplanar configurations, however, the following scheme was used. The dipole–dipole electrostatic energy is

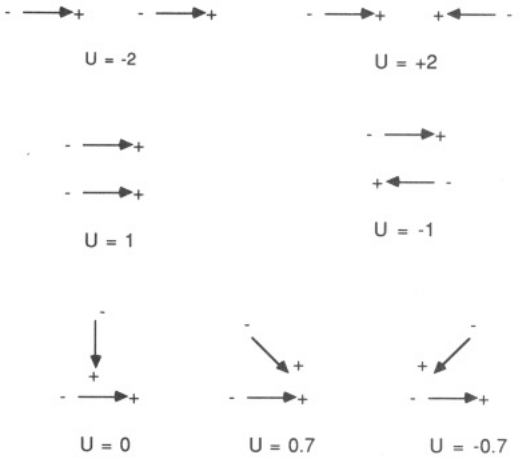

Figure 9. Orientational dependence of electrostatic dipole–dipole energy.

$$U = {}^1/_2\mu^2(\cos\theta - 3\cos\gamma_1\cos\gamma_2)/R^3 \qquad (1)$$

where θ is the angle formed by the dipole vectors and γ_1, γ_2 are the angles they form with the distance vector. The geometric factor, $(\cos\theta - 3\cos\gamma_1\cos\gamma_2)/R^3$, for a configuration was calculated and assigned as one of nine integer values spanning the range −4 to +4. This latter integer was used as the multiplier of the electrostatic energy parameter, EELECTRO, in computing the RIS electrostatic energy. The electrostatic energy is second order and is assigned to the second of the interacting side groups.

A complete enumeration of the numbers of each type of the above interactions, both steric and electrostatic, occurring in all of the MA system conformers considered is given in Table S-III and for the VA system in Table S-IV of the supplementary material.

Results and Discussion

The Energy Parameters. Once the numbers of each type of the above steric and electrostatic interactions have been established for a given conformer, its energy can be expressed as a linear combination of the interaction energy parameters. Thus the energy, $E(i)$, of conformer i is

$$E(i) = \sum_{\{\text{set of interactions } j\}} \nu_{ij}E_j + E_{\text{base}} \qquad (2)$$

where the ν_{ij} are the number of interactions of type j with energy parameter E_j in the conformer. Resulting for each polymer system, MA or VA, is an overdetermined system of linear equations in the unknowns, E_j and E_{base}, where the latter is a base energy. The relative energies of the conformations of a molecule of fixed chemical composition are independent of the base energies. The $E(i)$ set is also available as "data" from the molecular mechanics energy minimization for each conformer in the computed data base. Thus eq 2 constitutes an overdetermined system from which the parameters E_j can be determined by standard least-squares techniques. The resulting values are listed in Table II. The difference between the energy computed via eq 1, using the parameters of Table II, and

Table II
RIS Energy Parameters

polymer type	label	value, kcal/mol	no. of conformers fit	RMS, kcal/mol
MA	G	0.52	66	0.22
	WMAIN	1.57		
	WC–CD	0.70		
	WCD–O	0.63		
	ALPHA	0.33		
	BETA	0.73		
	S60	0.97		
	EELECTRO	0.38		
	EB1[a]	11.19		
	EB2[b]	20.00		
VA	G	0.89	56	0.25
	WMAIN	1.62		
	WO–CD	0.83		
	WC–O	0.68		
	ALPHA	0.83		
	S60	1.96		
	EELECTRO	0.26		
	EB1[a]	8.76		
	EB2[b]	14.87		

[a] To be used with monosubstituted heptanes. [b] To be used with disubstituted heptanes.

that computed from molecular mechanics energy minimization is listed for each conformer in Tables S-III and S-IV. The RMS difference for each system was approximately 0.2 kcal/mol.

Direction of the Dipole Moment Vector. The direction of the dipole moment for each side-group conformational state is critical in determining the mean-square dipole moments of the polymer chains studied by using the parameters of this work. Previous work[13] has indicated that the dipole in simple esters points to within a few degrees of the carbonyl bond from the oxygen to the carbon atom, the angle being 4 ± 3° toward the ether oxygen. Simple ester analogues of the side groups, ethyl acetate and methyl propionate, were examined here by molecular mechanics employing the mutual induction model. The angles were determined to be 1° for ethyl acetate and 3° for methyl propionate. The angle of the dipole moment with respect to the carbonyl bond was determined for each compound, averaging the angles over the ester conformations. The angle was set at 2° for both VA and MA and used in all further calculations.

It was also necessary to express the dipole moment vector for each side-group state in terms of the coordinate system attached to the main-chain bond following the side group. The angles of the dipole moment with respect to the carbonyl bond, the geometry of the side group, and the geometry of the main chain in the vicinity of the side group all affect the direction of the dipole moment. Table III gives the dipole moment vectors in terms of local bond coordinates. All values were determined by examination of the geometry of the model compounds discussed above using average values as given in Table I.

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Table III
Dipole Moment Vectors

state	dipole components[a]					
	x	*y*	*z*	*x*	*y*	*z*
d 60°	0.9201	1.3627	−0.2860	−0.9914	−1.4684	0.4118
d 90°	−0.6549	−0.0101	1.5359	0.6309	0.2462	−1.6894
d 150°	0.2369	−0.6125	1.5359	−0.0092	0.6785	−1.6894
l 60°	0.9201	1.3627	0.2860	−0.9914	−1.4684	−0.4118
l 90°	−0.6549	−0.0101	−1.5359	0.6309	0.2462	1.6894
l 150°	0.2369	−0.6125	−1.5359	−0.0092	0.6785	1.6894

[a] The coordinate system is centered on the main-chain atom to which the polar group is attached, the *x* axis points down the bond to the next main-chain atom, the *y* axis is in the plane of this bond and the previous main-chain one and points interior to these two bonds, and *z* is normal to *x*,*y* in a right-handed sense. The components are based on the dipole vector pointing 2° off the carbonyl bond toward the ether oxygen with magnitude 1.67 d for MA and 1.82 d for VA.

Supplementary Material Available: Tables S-I and S-II containing conformational energies, torsional angles, and dipole moments for MA and VA conformations, respectively, and Tables S-III and S-IV containing a complete enumeration of steric and electrostatic interactions computed from molecular mechanics energy minimization for MA and VA conformations, respectively (7 pages). Ordering information is given on any current masthead page.

References and Notes

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Registry No. MA (homopolymer), 9003-21-8; VA (homopolymer), 9003-20-7; (MA)(H_2C=CH_2) (copolymer), 25103-74-6; (VA)(H_2C=CH_2) (copolymer), 24937-78-8.