Macromolecules **1986**, *19*, 2707–2712

Conformational Rigidity of Polychloral: Effect of Bulky Substituents on the Polymerization Mechanism

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Received April 29, 1986

ABSTRACT: Conformational energy calculations have been carried out for polychloral and its oligomeric model compounds, $(CH_3)_3CO[CH(CCl_3)O]_xC(O)CH_3$, by using the MM2 program. Among the dimer models ($x = 2$), (*S*,*R*)-g$^-$g$^+$, (*S*,*S*)-tg$^-$, and (*S*,*S*)-g$^-$g$^-$ were found to be low-energy conformations. The meso (*m*) and racemic (*r*) fractions in an equilibrium mixture were estimated to be nearly equivalent. These results are compatible with gas chromatographic data, which clearly indicate that both *m* and *r* isomers are produced during the early part of the polymerization process. Calculations further suggest that the *mm* isomer may be the only growing species at the trimer level ($x = 3$). For the polymer, the isotactic sequence leads to the most preferred conformation. Experimental values of the dihedral angles for the acetal linkage obtained from the X-ray fiber diagram can be reasonably reproduced by the calculation. The geometries and conformational energies deduced for polychloral and related compounds by the MM2 program were thus found to be consistent with various experimental observations.

Introduction

Polymerization of chloral has been extensively studied by Vogl and co-workers[1] since 1963. The high polymers prepared by anionic initiators are infusible at ordinary temperatures and start depolymerizing around 220 °C. Polychloral is insoluble in conventional organic solvents. Due to its high chlorine content, the polymer is nonflammable. Crystallographic studies reported by Furukawa and collaborators[2] indicate that the polymer has an isotactic structure and that it forms a 4/1 helix in the crystalline state. Vogl et al.[3] investigated the mechanism of chain growth by terminating the polymerization reaction at an embryonic stage:

$$t\text{-BuO}^- + \text{O}{=}\text{CH(CCl}_3) \rightarrow t\text{-Bu(OCH(CCl}_3))_x\text{O}^- \xrightarrow{\text{Ac}_2\text{O}} t\text{-Bu(OCH(CCl}_3))_x\text{OC(O)CH}_3$$

Gas chromatographic studies on a mixture of end-capped oligomeric species revealed that (1) the dimer ($x = 2$) exists in the two stereochemical forms (i.e., the meso (*m*) and racemic (*r*) isomers) and (2) as the degree of polymerization increases (i.e., $x = 3$ and 4), the individual oligomeric fraction tends to exhibit one main peak, accompanied by some small satellite peaks. These results may suggest that during the course of polymerization, the propagation reaction proceeds only via the meso addition. Occasional reversal of the isotactic arrangement from ···*SS*··· to ···*RR*··· or vice versa by incorporation of a racemic unit seems to be suppressed.

In this work, we have performed conformational analyses for the dimer and trimer as well as for a tetramer sequence buried in a long polymeric chain. These molecular systems are sterically hindered by the presence of bulky side groups. Full optimization of the molecular geometry is required to elucidate the energy minima. The molecular mechanical force field (MM2) scheme developed by Allinger and co-workers[4] serves for this purpose. Since the molecules comprise many rotatable bonds, difficulties were encountered, as usual, in determining the global energy minimum. Careful examination of a proper molecular model was found to be very helpful. The results of our calculations seem to be consistent with the experimental observations cited above.

Conformational Energy Calculation

Molecular mechanics calculations were carried out by employing the MM2 force field program.[5] Conventional values of the bond lengths and bond angles were assembled in the structural parameter set for the initiation of the iterative geometry optimization.[6-8] Bond angles associated with the *tert*-butoxyl group were taken from the crystallographic data reported on a cage dimer of 7-*tert*-butoxynorbornadiene.[9] Structural parameters for the acetyl group are well established.[10] Parameters required for the description of the torsional potentials for the internal bond rotation are mostly provided in the MM2 program and used without modification. Various force constants defined in the valence force field scheme were also adopted as specified in the program. Unless otherwise indicated, the effective dielectric constant was set equal to 1.5, the value provided in the program as the standard for the gas phase.

Results and Discussion

Dimer Model Compounds. Molecular mechanics calculations were first performed on the dimer model compounds (Figure 1), both for the meso (*S*,*S*) and racemic (*S*,*R*) configuration. Here, *R* and *S* denote the stereochemical character of the asymmetric carbon, reading from the terminal carrying the *tert*-butoxyl group. The skeletal atoms are numbered from left to right. Primes are used to distinguish the pendant atoms from the acetal carbon to which they are bonded. In conformity with the rotational isomeric state approximation, optimizations were performed by starting from the regularly staggered conformation. Those arrangements that involve exceedingly high steric conflicts were omitted from the treatment. Each conformer may be characterized by bond rotations from ϕ_2 to ϕ_5 defined for the skeletal sequence O_1–C_2–O_3–C_4–O_5 (cf. Figure 1). The g$^-$g$^-$g$^+$t form of the racemic isomer was calculated to be the lowest energy arrangement. Six conformers were found to fall within the range of 4 kcal mol^{-1} above the minimum value. They can be distinguished by specifying the rotational states around the central bond pair, C_2–O_3 (ϕ_3) and O_3–C_4 (ϕ_4), in addition to their stereochemical character. The rotational angles for the neighboring bonds, ϕ_2 and ϕ_5, may be so specified as to minimize the total molecular energy. Accordingly, the lowest energy conformation mentioned above may be expressed as (*S*,*R*)-g$^-$g$^+$, and hereafter, the same rule applies to the other conformers. The results of the preliminary screening are summarized as follows: *m* isomer, (*S*,*S*)-g$^-$g$^-$ (1.07), (*S*,*S*)-tg$^-$ (2.14), (*S*,*S*)-g$^+$t (2.87), (*S*,*S*)-g$^-$t (3.04); *r* isomer, (*S*,*R*)-g$^-$g$^+$ (0.0), (*S*,*R*)-tg$^+$ (3.27), (*S*,*R*)-tt

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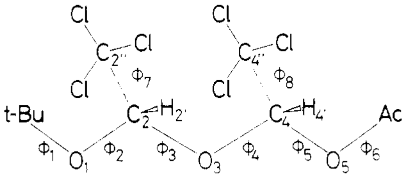


Figure 1. Schematic representation of a dimer model compound: t-Bu = $C(CH_3)_3$ and Ac = $C(O)CH_3$. The skeletal carbons are expressed in the meso (S,S) configuration. (In this instance, the (S,S) arrangement is identified as the meso configuration. Note that this is true only when the acetyl group is of higher priority than the t-butoxyl group.) The location of atoms and rotation angles may be identified by the numerical suffixes: for the planar backbone conformation, $\phi_1 = \phi_2 = \phi_3 = \phi_4 = \phi_5 = \phi_6 = 0°$. The rotational states t, g$^+$, and g$^-$ around each bond may be defined in the conventional manner.[6]

Table I
Dihedral Angles for the Skeletal (Acetal) Sequence Calculated for the Dimer, (S,R)-g$^-$g$^+$, (S,S)-tg$^-$, and (S,S)-g$^-$g$^-$

	m		*r*
dihedral angle/deg	(S,S)-tg$^-$	(S,S)-g$^-$g$^-$	(S,R)-g$^-$g$^+$
ϕ_2	-88.9	-87.5	-96.8
ϕ_3	29.5	-131.6	-111.6
ϕ_4	-119.2	-103.5	118.2
ϕ_5	45.3	37.6	-30.5

(3.61). The values in parentheses indicate the relative energy expressed in kcal mol^{-1}. From these results and supplemental use of a molecular model, we concluded that (S,S)-g$^-$g$^-$, (S,S)-tg$^-$, and (S,R)-g$^-$g$^+$ are the three most important conformers.

In the next step, the energy contour map (ϕ_3, ϕ_4) was prepared in the vicinity of the minimum for each of these conformers. In these calculations, geometrical parameters other than ϕ_3 and ϕ_4 were set equal to the values deduced by the optimization treatment. For the (S,S)-g$^-$g$^-$ and (S,R)-g$^-$g$^+$ forms, the energy minima were well-defined, and no extra minimum appeared in the map (see Figure 2b,c). In the case of (S,S)-tg$^-$, however, an additional minimum with greater depth was found on the potential energy surface, suggesting that the one obtained previously was a local minimum. The energy minimization was again conducted from this newly detected geometry. The conformational energy of the (S,S)-tg$^-$ form turned out to be nearly equivalent to that of (S,R)-g$^-$g$^+$. Illustrated in Figure 2a is the energy map for the minimum thus derived. The energies indicated in the diagrams shown in Figure 2 are expressed relative to the minimum of the *r* isomer, (S,R)-g$^-$g$^+$. Dihedral angles around the bonds associated with the skeletal conformation are summarized in Table I. The rotational angles for the C_2–O_3–C_4 portion, i.e., ϕ_3 and ϕ_4, correspond to the minimum of the energy contour map shown in Figure 2. Large deviations from the regular staggering are due to severe steric conflicts among the bulky pendant groups. The planar trans configuration of the ester group is practically unaffected by the geometry optimization (i.e., $\phi_6 < 5°$). Displacements of the rotational state for the articulated side chains, i.e., ϕ_7 and ϕ_8, were found to vary over a range from 2° to 20°.

In Table II, contributions from various components involved in the conformational energy expression are listed for the three most stable conformers. As implied by the magnitude of the stretching and bending term, bond angles are least constrained in the (S,S)-tg$^-$ conformer. The van der Waals interaction and torsional potential terms are smaller in the *r* isomer, (S,R)-g$^-$g$^+$, than those for either of the two meso forms. The dipole–dipole interaction is less conspicuous in the (S,S)-g$^-$g$^-$ conformer. The total energies, given as the sum of these contributions, and the relative energies, expressed with respect to the (S,R)-g$^-$g$^+$ conformer, are indicated in the last two rows. The energy difference between the (S,R)-g$^-$g$^+$ and (S,S)-tg$^-$ forms was thus estimated to be 0.33 kcal mol^{-1}. At this stage, we need to comment on the contribution from the long-range (van der Waals) interaction taking place between the *tert*-butyl (t-Bu) and acetyl (Ac) groups situated at the terminals (cf.

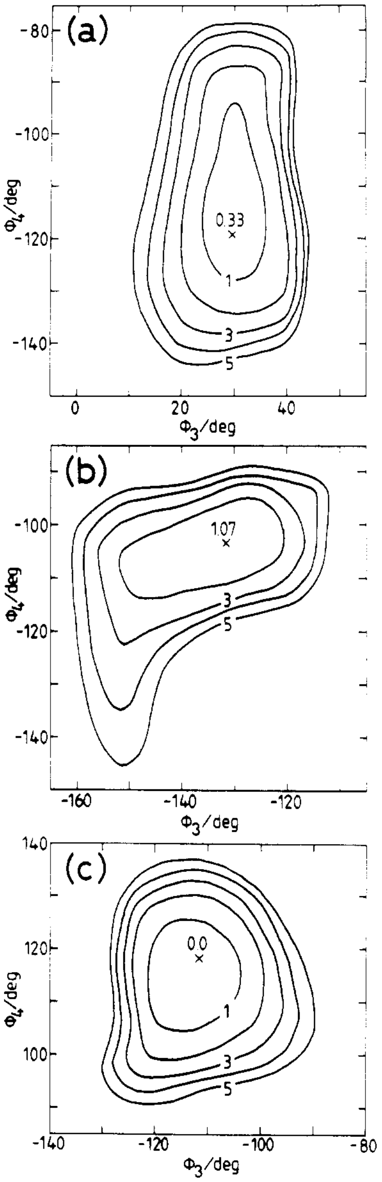


Figure 2. Energy contour diagrams (ϕ_3, ϕ_4) calculated for the dimer model compounds: (a) (S,S)-tg$^-$; (b) (S,S)-g$^-$g$^-$; (c) (S,R)-g$^-$g$^+$. The energies are expressed in kcal mol^{-1} relative to the minimum of the (S,R)-g$^-$g$^+$ form.

Table II
Contribution from the Individual Components Comprising the Conformational Energies for the Dimer Model Compounds[a]

	m		*r*
	(S,S)-tg$^-$	(S,S)-g$^-$g$^-$	(S,R)-g$^-$g$^+$
stretching and bending	15.52	17.54	17.54
van der Waals	7.10	7.47	6.07
dipole–dipole	19.54	17.69	19.26
torsional	6.32	6.51	5.27
total energy	48.47	49.21	48.14
relative energy	0.33	1.07	0.00

[a] Energies are given in kcal mol^{-1}.

Table III
Bond Lengths Deduced by the Geometry Optimization for the Dimer and Trimer Model Compounds

bond	bond length/Å	
	dimer	trimer
C-H (acetal)	1.115 ± 0.001	1.114 ± 0.004
C-O (acetal)	1.432 ± 0.005	1.433 ± 0.007
C-C (Cl_3)	1.577 ± 0.005	1.577 ± 0.005
C-Cl	1.794 ± 0.004	1.794 ± 0.005

Table IV
Bond Angles Deduced for the Skeletal Portion of the Dimer and Trimer Model Compounds

bond angle	angle/deg	
	dimer	trimer
$\angle C_{t\text{-Bu}}O_1C_2$	118.2 ± 0.7	118.2 ± 1.0
$\angle O_1C_2H_{2'}$	109.1 ± 1.0	108.9 ± 0.9
$\angle O_1C_2C_{2''}$	108.8 ± 2.6	108.5 ± 2.5
$\angle O_1C_2O_3$	112.0 ± 4.4	111.7 ± 2.5
$\angle C_2O_3C_4$	119.3 ± 1.0	119.6 ± 1.4
$\angle O_3C_4H_{4'}$	108.5 ± 0.4	108.3 ± 0.7
$\angle O_3C_4C_{4''}$	107.0 ± 0.9	106.4 ± 0.6
$\angle O_3C_4O_5$	111.8 ± 0.8	110.4 ± 2.0
$\angle C_4O_5C_6$		118.0 ± 2.0
$\angle O_5C_6H_{6'}$		108.9 ± 0.9
$\angle O_5C_6C_{6''}$		108.3 ± 0.6
$\angle O_5C_6O_7$		110.2 ± 1.5

Figure 1). As inspection of a molecular model reveals, these groups are located in a close proximity in the (*S*,*R*)-g^-g^+ conformer: the van der Waals interactions were calculated to be negative and large (−0.7 kcal mol^{-1}). A similar value (−0.63 kcal mol^{-1}) was obtained for (*S*,*S*)-tg^-. The (*S*,*S*)-g^-g^- conformer takes the most extended form, and therefore, the van der Waals interaction between the aforementioned groups is less negative (−0.19 kcal mol^{-1}). One can make an argument that the energy difference arising from this source is unrealistic in the liquid or in solution, in which a molecule is entirely surrounded by the other molecular species.[4] Then, for example, the calculated (relative) energy of (*S*,*S*)-g^-g^- should be lowered by ca. 0.5 kcal mol^{-1}. On the other hand, the dipole–dipole interaction energy critically depends on the magnitude of ϵ_{eff} used in the calculation. An increase in ϵ_{eff} from 1.5 to 3.0 should reduce the dipole–dipole interaction term to half of those given in Table II. As shown in the table, the (*S*,*S*)-g^-g^- form may be destabilized by ca. 0.7 kcal mol^{-1}: the effect is opposite to the correction in the van der Waals interaction mentioned above. The relative energy of (*S*,*S*)-tg^- is practically unaffected by such modification.

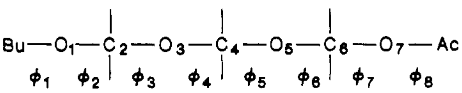
Table V
Dihedral Angles for the Skeletal (Acetal) Sequence Calculated for the Trimer, (*S*,*S*,*S*)-tg^-tg^-, (*S*,*S*,*R*)-tg^-tg^+, (*S*,*R*,*R*)-$g^-g^+tg^+$, and (*S*,*R*,*S*)-$g^-g^+tg^-$, Forms

dihedral angle/deg	*mm* (*S*,*S*,*S*)	*mr* (*S*,*S*,*R*)	*rm* (*S*,*R*,*R*)	*rr* (*S*,*R*,*S*)
ϕ_2	−91.6	−89.4	−94.3	−93.0
ϕ_3	35.0	33.6	−111.0	−110.6
ϕ_4	−117.4	−119.2	119.4	107.2
ϕ_5	49.5	27.3	−17.0	−25.2
ϕ_6	−106.2	71.9	125.2	−85.4
ϕ_7	49.2	−35.9	−44.6	36.5

Variation of the bond length caused by the energy minimization is generally small. The averaged values and the range of deviations are given in Table III. The largest deviation from the initial value was observed for the articulated CH–CCl_3 bond, elongated from the starting value (1.54 Å) by ca. 2%. The bond lengths associated with the terminal groups, i.e., the *tert*-butyl and acetyl groups, are nearly unaffected by the geometry optimization and are omitted from the table. Shown in Table IV are the averaged values of the bond angles for the skeletal portion resulting from the optimization. Location of bond angles may be identified by the suffixes appended to the individual atoms (cf. Figure 1). Bond angles associated with the terminal groups of the molecule are not much perturbed by the steric interactions: values of ∠CCH = 111.5 ± 1.5° and ∠CCCl = 110.0 ± 1.6° were obtained for the methyl and trichloromethyl groups, respectively. The bond angle deformation is most pronounced at the acetal oxygen; i.e., $\angle C_{t\text{-Bu}}O_1C_2$ = 118.2 ± 0.7° ($C_{t\text{-Bu}}$ = tertiary carbon in the *tert*-butyl group) and $\angle C_2O_3C_4$ = 119.3 ± 1.0°. A similar value is reported for compounds carrying bulky substituents on both sides of the ether linkage.[11] The acetal carbon, C_2, is somewhat unique. The bond angle $\angle O_1C_2O_3$ is sizably widened in the (*S*,*R*)-g^-g^+ (113.8°) and (*S*,*S*)-g^-g^- (114.7°) forms, while that of (*S*,*S*)-tg^- (107.6°) is slightly smaller than the standard value (108.5°) provided in the MM2 program. In the former conformers, bond C_2–O_3 is placed in the g^- state, which brings the terminal *tert*-butyl group into severe steric repulsion with one of the trichloromethyl groups in the molecule. The latter conformer ((*S*,*S*)-tg^-) is free from such interactions.

The stabilities of the conformers under examination may be given as Boltzmann factors for the relative energies listed in Table II. The meso and racemic fractions in an equilibrium mixture are estimated to be $f_m = 1 - f_r = 0.5$ for the temperature 190 °C. Gas chromatographic data[3] on the dimer mixture derived from the polymerizate gave an estimate of $f_m = 0.23$ at about 190 °C. Since this does not necessarily represent an equilibrium value, a quantitative comparison may be unrealistic. Nevertheless, the results of the present analysis are consistent with the experimental observations, which clearly indicate coexistence of the *m* and *r* isomers in the steady state.

Trimer Model Compounds. Similar studies were extended to the trimer model compounds ($x = 3$) with stereochemical arrangements such as *mm* (*S*,*S*,*S*), *mr* (*S*,*S*,*R*), *rm* (*S*,*R*,*R*), and *rr* (*S*,*R*,*S*). For each isomer, the most stable conformer can be easily elucidated by utilizing the information acquired through the analysis of the dimer model as well as by examination of a proper molecular model. For these conformations, a preliminary assessment of the energy minimum was performed by adjusting the rotation angles for the skeletal bonds, i.e., ϕ_3, ϕ_4, ϕ_5, and ϕ_6, the other parameters being kept invariant:



$$t\text{-Bu}-O_1-C_2-O_3-C_4-O_5-C_6-O_7-Ac$$

The full optimization of geometry was then conducted by starting from the spatial arrangement derived above. Adjustments of the rotation angle required in this process were found to be generally small (within a few degrees). Values of the internal rotation for the skeletal portion thus deduced are listed in Table V. The bond lengths and bond angles obtained concomitantly are compared with those for the dimer model compounds in Tables III and IV, respectively. Since variation of the bond length caused by the geometry optimization is small, averages were taken for all of the chemically equivalent bonds of the trimer model compounds. Following the previous treatment, locations of the bond angle along the skeletal chain are distinguished by numerical suffixes. The numbers are appended according to the rule applied for the dimer model (cf. Figure 1). Variations among the conformers are indicated by the deviation. Bond lengths and bond angles critically depend on the short-range steric interactions. As can be shown by inspection of a molecular model, similar

Table VI
Contribution from the Individual Components Comprising the Conformational Energies for the Trimer Model Compounds[a]

	mm (*S*,*S*,*S*)	*mr* (*S*,*S*,*R*)	*rm* (*S*,*R*,*R*)	*rr* (*S*,*R*,*S*)
stretching and bending	19.64	21.84	23.97	24.75
van der Waals	5.77	7.36	6.00	7.33
dipole–dipole	27.46	27.11	27.83	27.20
torsional	9.46	11.00	9.68	9.61
total energy	62.32	67.30	67.48	68.88
relative energy	0.0	4.98	5.16	6.56

[a] Energies are given in kcal mol^{-1}.

interactions take place in the dimer and trimer model compounds. Comparison shown in Tables III and IV confirms such expectation. Structural parameters established for these oligomers will be used in the analysis of the polymer chain in the following section.

The conformational energies and their components estimated for the aforementioned conformers are summarized in Table VI. The conformational energies of the optical antipodes, i.e., (*R*,*R*,*R*), (*R*,*R*,*S*), (*R*,*S*,*S*), and (*R*,*S*,*R*), can be obtained by symmetry from those listed in the table and are therefore omitted. Among the models investigated, the *mm* isomer, (*S*,*S*,*S*)-tg$^-$tg$^-$, was found to be the most stable: the difference amounts to more than 5 kcal mol^{-1} (see the last row of the table). In this conformation, the stretching and bending, van der Waals, and torsional potential terms are low. The dipole–dipole interactions are nearly equivalent in all the conformers. In contrast to the situation discussed above for the dimer model compounds (Table II), the *mm* isomer may be the only growing species at the trimer level. It should be noted here that the tg$^-$tg$^-$ conformation of the meso (*S*,*S*,*S*) isomer corresponds to one of the most preferred helical arrangements of the isotactic polymer.

Gas chromatographic studies on the oligomeric mixture gave a diagram comprising a main peak immediately followed by two small bumps in the trimer region. The major peak should correspond to the *mm* isomer. The present calculation does not provide any explanation for the nature of the two minor peaks. The analysis on the trimer model compounds is moderately in agreement with observations.

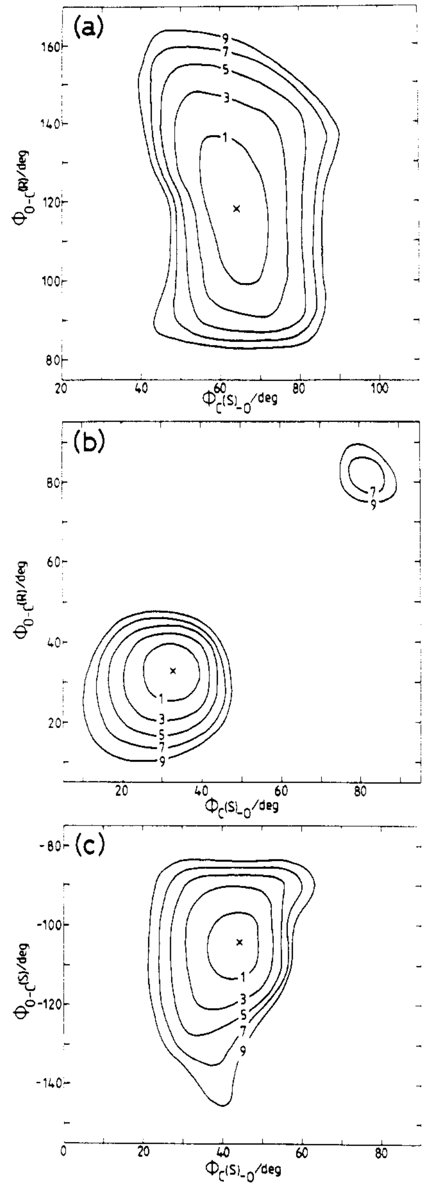
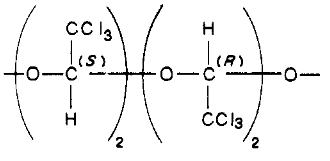


Figure 3. Potential energy contours calculated for a pair of consecutive bonds in polychloral: (a) the (*S*,*R*)-tg$^+$ form burried in an ···*SSRR*··· sequence; (b) the tt conformation of the same diad; (c) the most preferred conformation, (*S*,*S*)-tg$^-$, of the isotactic ···*SSSS*··· sequence. The energy contours are given in kcal mol^{-1} relative to the minimum (×) of each diagram. The altitudes of these minima are estimated to be (a) 5.6, (b) 8.7, and (c) 0 kcal mol^{-1}.

Polymeric Chains. In general, polyaldehydes are known to have a highly isotactic sequence.[12] Indeed, crystallographic examinations of polychloral revealed that the polymer chain is isotactic and crystallizes with a 4/1-helical conformation.[2] The results of the analysis on the trimer model compounds suggest that the stability of the isotactic helical conformation is enhanced by the bulky side groups (CCl_3) peculiar to the polychloral system. However, some stereoirregular placements may take place occasionally in an otherwise perfect isotactic chain:[13] in a conventional isotactic polymer system, either polyaldehydes or vinyl polymers, inversion of the isotactic arrangement occurs easily via placements such as ···*SSRR*··· or vice versa.[14] Conformational energy calculations are, therefore, carried out for a moiety such as



$$\left(-O-\overset{CCl_3}{\underset{H}{C^{(S)}}}-\right)_2\left(-O-\overset{H}{\underset{CCl_3}{C^{(R)}}}-\right)_2 O-$$

where superscripts (*S*) and (*R*) appended to the skeletal carbon indicate the stereochemical character of the site. Calculations were also performed for a quartet (*SSSS*) in the all-*S* configuration. Geometrical parameters were taken from the optimized conformation of the trimer model having a closely related arrangement. For the isotactic portion, dihedral angles were set equal to the lowest energy conformation: tg$^-$ and tg$^+$ for the *SS* and *RR* diad, respectively. The transition from one helix (tg$^-$) to the other (tg$^+$) takes place most probably through the tg$^+$ conformation at the SR diad.[15] Shown in Figure 3 are the energy contour diagrams derived for the central C–O–C bond pair, geometrical parameters other than rotations for these bonds being kept invariant. In each diagram, energies are expressed relative to the minimum shown by ×. Because of the limitation in computing capacity, optimization of the geometry was not attempted for the polymer. In Figure 3a, the tg$^+$ minimum for the *SR* diad can be located at (64.2°, 118.1°). The minimum found in this figure is higher by 5.6 kcal mol^{-1} than the corresponding value of the preferred isotactic conformation of the *R* and

S sequences (cf. Figure 3c) joining on both sides of this diad.

Conformational energy calculations were also carried out for other possible pathways from the ···*SS*··· to ···*RR*··· sequence. In an isotactic polymer carrying less bulky substituents, a transition such as ···tg$^-$ttg$^-$t··· is readily permitted at the *SR* junction.[15] The transition takes place with retention of the sense of helix. Figure 3b indicates the result of computation for such tt conformation of the *SR* diad. As dictated by the molecular structure, the energy diagram is symmetric with respect to the $\phi_{O-C^{(R)}} = \phi_{C^{(S)}-O}$ axis. The minimum located at (33.0°, 33.0°) is estimated to be higher by 8.7 kcal mol^{-1} as compared to that of Figure 3c. By one-by-one sequential inspection, we further found that the transformation from the stable conformation of ···*SS*··· to that of ···*RR*··· may occur via ···tg$^+$tg$^+$g$^+$tg$^+$t··· with an extra energy of 5.9 kcal mol^{-1}. Conformations other than those described above require much higher energy. It follows from these considerations that a configurational transition such as ···*SSRR*··· may be highly restricted from the conformational point of view.

As shown in Figure 3c, the energy minimum for the all-*S* polymer was calculated to occur at $\phi_{C^{(S)}-O} = 44.2°$ and $\phi_{O-C^{(S)}} = -104.5°$. The potential well is fairly broad and shallow in the vicinity of the minimum. The energy is less than 1 kcal mol^{-1} in the range $\phi_{C^{(S)}-O} = 35°$ to 48° and $\phi_{O-C^{(S)}} = -95°$ to $-115°$. Furukawa and collaborators[2] reported values of $\phi_{C^{(S)}-O} = 22°$ and $\phi_{O-C^{(S)}} = -96°$ from the analysis of the X-ray fiber diagram. In their calculation, bond angles are all assumed to be tetrahedral. If we substitute our values in their expression, a set of dihedral angles such as $\phi_{C^{(S)}-O} = 32.4°$ and $\phi_{O-C^{(S)}} = -100.1°$ can be deduced. The agreement with experimental observations is considerably improved.

Concluding Remarks

For the dimer and trimer model compounds, fractions estimated under the equilibrium condition were found to be consistent with gas chromatographic data on the oligomers derived at an embryonic stage of the polymerization reaction. Calculations were extended to the estimation of the helical conformation of the isotactic polymer chain. The geometrical parameters established in the analysis of the oligomers were adopted in this treatment. The dihedral angles estimated in this manner were found to be in reasonable agreement with those elucidated from the X-ray fiber diagram. In general, a conventional isotactic polymer can form either a left- or right-handed helix. Reversal of the screw sense from left to right, or vice versa, may be permitted occasionally along the chain. As the side chain becomes larger, conformational rigidity of the chain increases, and transition from one screw sense to the other tends to be suppressed. These characteristic features of an isotactic chain have been extensively studied for the vinyl polymer system.[13] The same argument should hold for polyaldehydes.[16]

Vogl et al.[3] prepared polychloral samples with some optically active initiators. The polymer exhibited high optical activities: a specific rotation of 5000° was measured in films. The observed optical rotatory power is believed to be due to the asymmetric (helical) nature of the polymer backbone. Severe steric conflicts arising from bulky side groups may be responsible for the persistence of one helical screw along the chain. Vogl et al.[17] have also shown that the trihalomethyl group in perhaloacetaldehydes has to have at least the size of two chlorine atoms to provide the bulkiness to have only insoluble, presumably isotactic, polymers formed. Other examples have been reported by Okamoto et al.,[18] who polymerized triphenylmethyl methacrylate with several optically active anionic initiators. The polymer was found to be highly optically active in solution. They claimed that no fragment of the initiator should remain attached to the polymer. As the temperature is raised, the optical activity decreases drastically and the change is irreversible. When the bulky side groups were removed by hydrolysis, the optical rotatory power was entirely lost.[18]

Allinger et al.[4] have introduced some low-periodicity torsional potential terms in their MM2 program to account for the anomeric effect, a well-known characteristic of the acetal linkage. The torsional potential function is in general given by

$$E_{\mathrm{tor}} = (E_1/2)(1 + \cos\phi) + (E_2/2)(1 - \cos 2\phi) + (E_3/2)(1 + \cos 3\phi) \quad (1)$$

For the moiety OC–OC, $E_1 = 0.50$, $E_2 = -0.42$, and $E_3 = 0.0$, and for OC–OLp (Lp = a lone pair of electrons), $E_1 = E_3 = 0.0$ and $E_2 = 1.00$, units being in kcal mol^{-1}. The E_2 terms render the twofold character to the potential. In a recent paper, Norskov-Lauritsen and Allinger[19] proposed a revised set of parameters (MM2(82)) for the acetal linkage. For the torsional part, the aforementioned parameters are replaced by $E_1 = -0.17$, $E_2 = -1.20$ (OC–OC), and $E_2 = 0.50$ (OC–OLp). With these revisions, the gauche form around the OC–OC bond tends to be more stabilized by ca. 0.8 kcal mol^{-1}. Alterations are also required in the stretching and bending terms. The conformational energy of dimethoxymethane was calculated by using these newly defined parameters and compared with the previous estimation. The energy difference between the tg and gg forms is slightly raised (0.36 kcal mol^{-1}) by adoption of these revisions.[19] Judging from these results, we do not expect the conclusion reached for polychloral in this work to be affected by the use of the new version of the MM2 program.

In our recent paper,[20] we have examined the applicability of the MM2 program to the gauche oxygen effect associated with the moiety O–C–C–O in glycol ethers such as 1,2-dimethoxyethane, 1,2-dimethoxypropane, and 1,2-dimethoxy-2-methylpropane. In brief, the energy calculation failed to reproduce the observed trend for such a homologous series of compounds. In these molecules, steric interactions are moderate, and the chains are flexible. It was concluded that the torsional potential energy functions should vary more sensitively with the degree of methyl substitution. In polychloral, very severe steric interactions take place among the bulky side groups. Only a few stable conformers survive, and, in general, locations of the energy minima are largely displaced from those for the regular staggering. An accurate estimation of the substituent effect on the torsional potential energy expression is difficult. The correspondence between the calculated and observed results for the polychloral system should be subject to the ambiguity arising from this source.

Acknowledgment. We thank J. Zhang for his work on the preparation and gas chromatographic analysis of the oligomers of polychloral, work that was supported by the National Science Foundation. This paper is part 31 of the O. Vogl perhaloaldehyde polymer series.

Registry No. Chloral, 75-87-6; chloral dimer, 104156-78-7; chloral trimer, 104241-94-3; polychloral (homopolymer), 25154-92-1.

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Assignment of Monomer Sequences in the ^{13}C and ^{1}H NMR Spectra of Several Ethylene-Containing Co- and Terpolymers by Two-Dimensional Nuclear Magnetic Resonance Spectroscopy

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ABSTRACT: Two-dimensional nuclear magnetic resonance spectroscopy has been applied to the sequence assignments of the proton and carbon-13 spectra of the ethylene-containing polymers ethylene/methyl acrylate/carbon monoxide, ethylene/carbon monoxide, and ethylene/methyl acrylate. The proton NMR spectra of these polymers are extremely complex due to the occurrence of resonance lines corresponding to many different monomer sequences in a small chemical shift range of the spectra. Despite this complexity, the proton monomer sequence assignments can be made unambiguously at the triad level through application of homonuclear two-dimensional correlated spectroscopy (COSY). Furthermore, several different types of end groups are observed in the proton spectra of these polymers, and these end-group resonances were assigned from the coupling patterns seen in the COSY spectra. Once the proton assignments were known, the carbon-13 assignments were made from two-dimensional ^{13}C–^{1}H heteronuclear shift-correlated spectroscopy. These assignments were confirmed by performing distortionless enhancement by polarization transfer (DEPT) spectroscopy.

Introduction

Nuclear magnetic resonance (NMR) spectroscopy is a powerful tool for determination of the chemical microstructure of synthetic copolymers since the chemical shift is sensitive to differences in comonomer and stereochemical sequences. However, analysis by NMR requires that the lines in the spectrum be assigned to specific sequences in the polymer. Traditional line assignment techniques, such as theoretical chemical shift calculations, comparison of relative intensities of resonances to those predicted from reaction probabilities, and various synthetic techniques, are often tedious and/or subject to some ambiguity in complex copolymers. Two-dimensional (2D) correlated spectroscopy (COSY) provides an experimental basis for making unambiguous line assignments in the straightforward manner.

Two-dimensional correlated spectroscopy has been applied extensively to line assignment in the NMR spectra of biopolymers,[1–11] but application of these techniques to synthetic polymers has been less widespread. One of the first applications to polymers was by Gerig, who applied ^{19}F–^{1}H correlation NMR to poly(*p*-fluorostyrene).[12] Proton COSY has been applied to stereosequence assignments in poly(vinyl alcohol)[13] and poly(methyl methacrylate).[14] Bruch et al. have applied ^{19}F homonuclear 2D correlated spectroscopy to stereosequence assignments in the ^{19}F spectrum of poly(vinyl fluoride),[15] and Ferguson et al. have applied ^{19}F COSY to poly(vinylidene fluoride).[16] More recently, Cheng and Lee have applied 2D ^{13}C–^{1}H correlated spectroscopy to comonomer sequence assignments in ethylene/propylene copolymers[17] and stereosequence assignments in polypropylene,[18] and Mirau and Bovey have used a variety of 2D correlated techniques to make stereosequence assignments in poly(vinyl chloride).[19]

We report the application of 2D COSY, 2D ^{13}C–^{1}H correlated, and ^{13}C distortionless enhancement by polarization transfer (DEPT) spectroscopy to line assignment in the ^{1}H and ^{13}C spectra of a terpolymer containing ethylene, methyl acrylate, and carbon monoxide (E/MA/CO). This terpolymer is more complex than the homopolymers and copolymers studied previously due to the large number of possible comonomer sequences. Sequences containing methyl acrylate are further complicated by stereochemistry since methyl acrylate has a pseudoasymmetric center. Furthermore, the ^{13}C NMR spectrum of E/MA/CO was previously unassigned. Despite this complexity, ^{1}H and ^{13}C assignments can be made unambiguously at the triad level by a combination of 2D correlated and DEPT experiments on a single sample of E/MA/CO. In addition, several different types of end groups are observed and assigned in the ^{1}H spectrum of E/MA/CO. All of the line assignments are confirmed by COSY spectra and ^{13}C spectra of the two copolymers E/MA and E/CO.

Experimental Section

All spectra were recorded on a Bruker AM-300 spectrometer equipped with an Aspect 3000 computer. Chemical shifts were

0024-9297/86/2219-2712$01.50/0