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# Conformational Properties of Poly(vinyl bromide) and Poly(vinyl fluoride)

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ABSTRACT: The conformational properties of molecules modeling poly(vinyl bromide) (PVB) and poly(vinyl fluoride) (PVF) dimers and trimers have been analyzed using the molecular mechanics method of Boyd et al., which takes into account both steric and electrostatic energies. The geometric and energy results show that the steric effects of changing the halide are greater than the electrostatic effects. Total conformational energies were used to determine a set of intramolecular interaction energies that by means of the rotational isomeric states model allowed estimation of the characteristic ratio, $C_r$, and dipole moment ratio, $C_m$, of PVB and PVF. The results agree satisfactorily with available experimental values.

## Introduction

It is of great interest to find out how the physical properties of polymers are related to their conformational properties.[1] This is especially so in the case of poly(vinyl halides) $(\text{-}CH_2CHX\text{-})_n$, whose important electrical and mechanical properties are to be related to the steric strains and electrostatic interactions of their molecules. This article describes a study of the conformational properties of poly(vinyl bromide) (PVB) and poly(vinyl fluoride) (PVF) by means of a recently published molecular mechanics method including parameters for polar molecules,[2] which has been successfully applied to poly(vinyl chloride)[3a] and poly(vinylidene chloride).[3b] We also calculated characteristic ratios, $C_r = \langle r^2\rangle_0/2xl^2$, and dipole moment ratios, $C_m = \langle \mu^2\rangle_0/xm^2$ (where $x$ is the degree of polymerization, $l$ the length of the C–C bond, and $m$ the dipole moment of the carbon–halogen bond).

The general plan of the calculations performed has been described elsewhere.[3,4] The method used is such that energy minimization (by a modified Newton–Raphson procedure) can involve variation of not only the torsion angles, $\phi_{ijkl}$, but also the bond lengths, $r_{ij}$, and valence angles, $\theta_{ijk}$, of all the atoms of the molecules studied, which in this case were molecules modeling dimers and trimers of PVB and PVF.

The steric energy, DE + NB, is determined by a transferable force field that includes bond stretching terms, $U(r_{ij})$, bending terms, $U(\theta_{ijk})$, twisting terms, $U(\phi_{ijkl})$, and terms for interactions between nonbonded atom pairs (NB). The total conformational energy, ET, is considered to be the sum of the steric contribution, DE + NB, and the electrostatic contribution, EE.

In order not to prolong the calculations, the optimal geometry is taken to be the structure obtained by minimizing the steric energy, DE + NB, while simulating the electrostatic energy, EE, by fixed partial charges; once the sterically optimal geometry has been determined, the total energy is obtained after calculating the electrostatic energy correctly for this structure. For this latter calculation, it is assumed that the carbon–halogen bonds have intrinsic dipole moments, $\mu_0$, that create an electric field, giving rise to induced dipole moments, $\mu$, in each bond, that the induced moments in turn induce further moments in other bonds, and so on. The total moment of each bond is obtained by solving a system of equations,[3a] and the electrostatic energy, EE, is given by the work done on polarization and the energy of interaction between dipoles.

The conformational properties of the most important poly(vinyl halide), poly(vinyl chloride) (PVC), have been studied by Flory and Williams[5] and Mark,[6] who related statistical weight parameters obtained from experimental data to interactions among the bonds of the polymer chain, a procedure that can be generalized to other vinyl polymers. Specifically, they considered three-bond "gauche" and "skew" interactions and the four-bond interactions $w$, $w'$, and $w''$. In his molecular mechanics study of PVC, Boyd and Kesner[3a] subsequently introduced the four-bond interaction, $w_p$, that arises when two adjacent C–X bonds and their corresponding intermediate C–C bonds are all coplanar (Figure 1). Since the statistics used in the present study conform to the rotational isomeric states model,[5,6] which refers to diadic interactions in the polymer, the short-range gauche (g) and skew (sk) interactions are the most important. The energy $E_n = E_{sk} - E_g$ provides the statistical weight parameter, $n$, that Flory and Williams[5] obtained from data for the stereochemical equilib-

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**Table I**
**Calculated Geometries and Total Energies of 2,4-Dibromopentane and 2,4,6-Tribromoheptane**[a,b]

| conformer | $\phi_1$ | $\phi_2$ | $\phi_3$ | $\phi_4$ | $\theta_1$ | $\theta_2$ | $\theta_3$ | $E$, kJ/mol |
|---|---|---|---|---|---|---|---|---|
| | | | 2,4-Dibromopentane[c] | | | | | |
| LDTT | 187.6 | 187.6 | | | 116.0 | 110.8 | | 8.78 |
| LLTG | 183.3 | 58.0 | | | 115.9 | 113.0 | | 9.74 |
| LDG′G′ | −60.9 | −60.9 | | | 114.8 | 112.9 | | 12.21 |
| LLTT | 219.2 | 168.5 | | | 115.2 | 110.9 | | 21.68 |
| LDGG′ | 59.3 | 271.8 | | | 116.7 | 112.7 | | 20.83 |
| LLTG′ | 206.0 | −60.6 | | | 117.1 | 115.0 | | 16.25 |
| LLG′G | 266.3 | 60.2 | | | 114.4 | 114.2 | | 22.05 |
| LDTG | 193.3 | 40.7 | | | 118.0 | 114.0 | | 23.63 |
| LDTG′ | 208.7 | −64.4 | | | 115.3 | 114.6 | | 18.04 |
| | | | 2,4,6-Tribromoheptane | | | | | |
| LDLTTTT | 186.0 | 185.9 | 174.1 | 174.0 | 116.4 | 110.1 | 116.3 | 15.7 |
| LLDG′TTT | −58.0 | 176.4 | 186.2 | 185.4 | 115.8 | 110.4 | 116.3 | 15.9 |
| LLLTGTG | 181.2 | 57.9 | 181.3 | 58.1 | 116.1 | 112.7 | 115.9 | 17.3 |
| LLLG′TTG | −57.7 | 176.2 | 183.8 | 59.2 | 115.8 | 110.7 | 115.8 | 17.5 |
| LLLTTTG | 219.9 | 168.3 | 183.9 | 57.3 | 115.2 | 110.6 | 115.9 | 29.1 |
| LLLGTTG | 60.5 | 152.4 | 183.3 | 57.8 | 117.0 | 110.5 | 115.9 | 23.5 |
| LLLG′GTG | 263.3 | 59.9 | 179.8 | 57.1 | 114.4 | 113.6 | 116.1 | 30.7 |
| LLDTGTT | 181.4 | 58.9 | 182.8 | 184.6 | 116.2 | 112.5 | 116.5 | 17.7 |
| LLDG′TG′G′ | −57.4 | 178.5 | −60.8 | −58.9 | 115.9 | 112.6 | 115.1 | 20.1 |
| LLDTTTT | 221.6 | 170.1 | 187.1 | 185.6 | 115.1 | 110.3 | 116.4 | 27.8 |
| LLDTTG′T | 222.9 | 178.8 | −63.1 | 212.5 | 115.7 | 114.1 | 115.5 | 40.2 |
| LDLTTGG | 185.3 | 184.9 | 62.8 | 59.4 | 116.3 | 112.4 | 115.1 | 18.5 |
| LDLGTTT | 63.3 | 223.4 | 172.7 | 173.6 | 116.2 | 110.6 | 116.3 | 29.4 |
| LDLGG′TT | 85.4 | −58.1 | 181.8 | 178.1 | 119.0 | 113.8 | 117.1 | 28.4 |
| LDLG′GTT | 273.3 | 60.3 | 166.3 | 170.9 | 117.1 | 114.0 | 115.8 | 27.8 |
| LDLG′TTT | −64.0 | 209.4 | 175.1 | 175.6 | 115.3 | 110.5 | 116.5 | 24.7 |

[a] L and D indicate the stereoisomerism of the asymmetric carbon atoms: with the molecule observed end-on from either end, L indicates a halogen on the left and D a halogen on the right. [b] Torsion angles, equivalence between this work (G,G′) and ref 1 ($g^+$,$G^-$): G = $g^-$, G′ = $g^+$. [c] See ref 7.

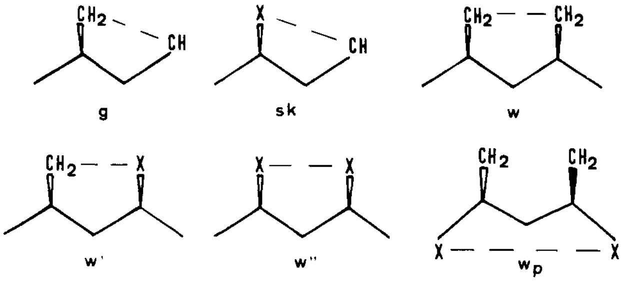

**Figure 1.** Characteristic interactions of poly(vinyl halides).

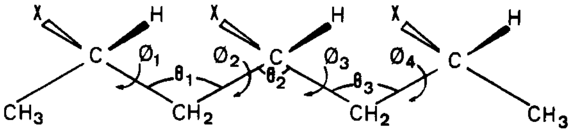

**Figure 2.** Nomenclature and numbering of the PVB and PVF trimer models 2,4,6-tribromoheptane (X = Br) and 2,4,6-trifluoroheptane (X = F).

rium of 2,4-dichloro-*n*-pentane in DMSO at 70 °C in the presence of LiCl.

Instead of using a method similar to the method used by Flory and Williams to obtain the interaction energies that are necessary for estimation of the characteristic ratio, $C_r$, and the dipole moment ratio, $C_m$, the procedure used in this study was first to calculate the geometries and energies of the conformers of the model molecules and then to find the interaction energies (by least squares) after rationalizing the geometric results to take into account the intramolecular interactions in each conformer.

## Results and Discussion

**(A) Conformational Calculations.** The methods indicated above[2-4] were used to calculate the energies and geometries of various conformers of the PVB and PVF dimer models meso and racemic 2,4-dibromopentane and 2,4-difluoropentane and of the trimer models isotactic, syndiotactic, and heterotactic 2,4,6-tribromoheptane and 2,4,6-trifluoroheptane. Figure 2 shows the numbering and nomenclature used for the trimer models; the same left-to-right numbering is used for the valence angles and torsion angles of the corresponding dimer models.

Tables I and III list the geometries and total energies calculated for the most important of the conformers studied. Other conformers located had higher energies; those listed are sufficient for determining the energies of the interactions indicated in Figure 1. The most noteworthy feature of these geometric results is the distortion of the C–C–C skeleton valence angles $\theta_1$, $\theta_2$, and $\theta_3$ from their natural "relaxed" values of 109.5° to mean values of respectively 116°, 113°, and 116° in the bromo molecules and 114°, 113°, and 114° in the fluoro molecules, with an interconformer variation range of about ±2° in each case.

Depending on the conformer, the torsion angles $\phi$ deviate from the standard values 180° (T), 60° (G), and −60° (G′) by 5–15° in either direction in order to alleviate steric and electrostatic repulsions. As in the case of the valence angles, these deviations are more pronounced in the bromo molecules than in the fluoro molecules; this may in part be due to the fact that, of the six basic interactions indicated in Figure 1, only $w''$ and $w_p$ take place between two polar C–X bonds, the other four all being dominated by steric effects, which are more sensitive to the size of the substituent.

In general, the largest contributions to the steric energy of these compounds are made by nonbonding interactions and by the widening of valence angles (Tables II and IV). Twisting energies vary widely from near zero in some conformers to values greater than $U(\theta)$ in others. Stretching energies, which make up about 10% of the total steric energy, generally vary rather little from one conformer to another.

Tables II and IV show that the two most stable conformers of 2,4,6-tribromoheptane have steric energies, DE

**Table II**
**Conformational Energies Calculated for 2,4-Dibromopentane and 2,4,6-Tribromoheptane (kJ/mol)[a]**

| | energies | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| conformer | DE + NB | $U(r)$ | $U(\theta)$ | $U(\phi)$ | NB | EE | ET | parameters |
| 2,4-Dibromopentane | | | | | | | | |
| LDTT | 22.9 | 1.8 | 5.2 | 0.9 | 15.0 | −14.2 | 8.8 | $E_{0d} + 2E_{n} = 8.5$ |
| LLTG | 23.3 | 1.9 | 5.3 | 0.5 | 15.6 | −13.6 | 9.7 | $E_{0d} + E_{n} = 9.7$ |
| LDG′G′ | 23.8 | 2.0 | 4.4 | 0.1 | 17.3 | −11.6 | 12.2 | $E_{0d} + E_{w_p} = 11.8$ |
| LLTT | 31.7 | 1.9 | 6.6 | 7.8 | 15.4 | −10.0 | 21.7 | $E_{0d} + 2E_{n} + E_{w''} = 22.3$ |
| LDGG′ | 33.5 | 2.5 | 8.5 | 4.1 | 18.4 | −12.7 | 20.8 | $E_{0d} + E_{sk} + E_{w} = 20.9$ |
| LLTG′ | 30.7 | 2.1 | 9.3 | 3.3 | 16.0 | −14.5 | 16.2 | $E_{0d} + E_{n} + E_{sk} + E_{w'} = 16.9$ |
| LLG′G | 33.5 | 2.3 | 5.8 | 5.5 | 19.9 | −11.4 | 22.1 | $E_{0d} + E_{w} + E_{w_p} = 22.7$ |
| LDTG | 33.5 | 2.2 | 12.7 | 3.2 | 15.4 | −9.9 | 23.6 | $E_{0d} + E_{sk} + E_{w''} + E_{n} = 22.5$ |
| LDTG′ | 30.7 | 2.1 | 6.4 | 4.8 | 17.4 | −12.6 | 18.1 | $E_{0d} + E_{w'} + E_{n} = 17.9$ |
| 2,4,6-Tribromoheptane | | | | | | | | |
| LDLTTTT | 35.5 | 3.1 | 9.1 | 2.0 | 21.3 | −19.8 | 15.7 | $E_{0t} + 4E_{n} = 15.2$ |
| LLDG′TTT | 36.0 | 3.2 | 9.1 | 1.3 | 22.4 | −20.1 | 15.9 | $E_{0t} + 3E_{n} = 16.5$ |
| LLLTGTG | 37.2 | 3.4 | 9.5 | 1.2 | 23.1 | −19.9 | 17.3 | $E_{0t} + 2E_{n} = 17.7$ |
| LLLG′TTG | 36.5 | 3.4 | 9.1 | 0.8 | 23.2 | −18.9 | 17.6 | $E_{0t} + 2E_{n} = 17.7$ |
| LLLTTTG | 45.2 | 3.4 | 10.3 | 8.0 | 23.5 | −16.1 | 29.1 | $E_{0t} + 3E_{n} + E_{w''} = 30.3$ |
| LLLGTTG | 43.9 | 3.7 | 12.4 | 4.0 | 23.8 | −20.4 | 23.5 | $E_{0t} + 2E_{n} + E_{sk} + E_{w'} = 24.9$ |
| LLLG′GTG | 48.2 | 3.9 | 9.5 | 7.5 | 27.3 | −17.5 | 30.7 | $E_{0t} + E_{n} + E_{w_p} + E_{w} = 30.7$ |
| LLDTGTT | 36.6 | 3.4 | 10.0 | 1.7 | 21.5 | −18.9 | 17.7 | $E_{0t} + 3E_{n} = 16.5$ |
| LLDG′TG′G′ | 37.3 | 3.6 | 8.5 | 0.6 | 24.6 | −17.2 | 20.1 | $E_{0t} + E_{n} + E_{w_p} = 19.8$ |
| LLDTTTT | 44.8 | 3.4 | 10.1 | 9.2 | 22.1 | −17.0 | 27.8 | $E_{0t} + 4E_{n} + E_{w''} = 29.0$ |
| LLDTTG′T | 55.9 | 3.8 | 12.0 | 14.4 | 25.7 | −15.7 | 40.2 | $E_{0t} + 3E_{n} + E_{w''} + E_{w'} = 38.5$ |
| LDLTTGG | 37.0 | 3.5 | 8.5 | 1.3 | 23.7 | −18.5 | 18.5 | $E_{0t} + 2E_{n} + E_{w_p} = 18.5$ |
| LDLGTTT | 46.9 | 3.6 | 11.9 | 9.2 | 22.2 | −17.5 | 29.4 | $E_{0t} + 3E_{n} + E_{w''} + E_{sk} = 29.3$ |
| LDLGG′TT | 48.0 | 4.0 | 18.1 | 2.8 | 23.1 | −19.6 | 28.4 | $E_{0t} + 2E_{n} + E_{sk} + E_{w} = 27.7$ |
| LDLG′GTT | 47.2 | 3.9 | 12.1 | 5.7 | 25.5 | −19.4 | 27.8 | $E_{0t} + 2E_{n} + E_{sk} + E_{w} = 27.7$ |
| LDLG′TTT | 43.9 | 3.6 | 10.4 | 5.4 | 24.5 | −19.2 | 24.7 | $E_{0t} + 3E_{n} + E_{w'} = 24.6$ |

[a] DE + NB is the total steric energy, $U(r)$ the total stretching energy, $U(\theta)$ the total bending energy, $U(\phi)$ the total twisting energy, NB the total energy of interactions between nonbonded atoms, EE the electrostatic energy, and ET = DE + NB + EE the overall total energy.

**Table III**
**Calculated Geometries and Total Energies of 2,4-Difluoropentane and 2,4,6-Trifluoroheptane**

| conformer | $\phi_1$ | $\phi_2$ | $\phi_3$ | $\phi_4$ | $\theta_1$ | $\theta_2$ | $\theta_3$ | $E$, kJ/mol |
|---|---|---|---|---|---|---|---|---|
| 2,4-Difluoropentane | | | | | | | | |
| LDTT | 182.3 | 182.3 | | | 112.7 | 111.7 | | −10.0 |
| LLTG | 174.9 | 63.0 | | | 114.1 | 113.1 | | −7.3 |
| LDG′G′ | −62.4 | −62.4 | | | 114.5 | 113.3 | | −3.8 |
| LLTT | 184.8 | 175.2 | | | 113.4 | 111.6 | | −3.1 |
| LDGG′ | 66.4 | 270.8 | | | 115.8 | 113.2 | | 1.9 |
| LLTG′ | 191.1 | −64.4 | | | 114.7 | 114.1 | | −6.4 |
| LLG′G | 266.1 | 63.8 | | | 115.0 | 114.1 | | 3.0 |
| LDTG | 180.6 | 61.3 | | | 115.0 | 113.4 | | −0.7 |
| LDTG′ | 187.3 | −71.5 | | | 114.5 | 113.9 | | −5.5 |
| 2,4,6-Trifluoroheptane | | | | | | | | |
| LDLTTTT | 182.4 | 181.8 | 178.2 | 177.6 | 112.8 | 111.6 | 112.8 | −14.2 |
| LLDG′TTT | −63.3 | 184.8 | 182.5 | 181.6 | 114.0 | 111.6 | 112.6 | −12.6 |
| LLLTGTG | 174.0 | 62.6 | 174.2 | 63.2 | 114.0 | 113.1 | 114.1 | −10.0 |
| LLLG′TTG | −62.9 | 184.6 | 175.4 | 62.9 | 114.1 | 111.7 | 114.1 | −9.3 |
| LLLTTTG | 183.7 | 174.4 | 174.5 | 62.3 | 113.3 | 111.6 | 114.1 | −5.7 |
| LLLGTTG | 64.8 | 168.7 | 174.7 | 63.1 | 114.7 | 111.4 | 114.1 | −9.1 |
| LLLG′GTG | 266.2 | 64.2 | 169.8 | 61.9 | 115.0 | 114.0 | 114.2 | 0.9 |
| LLDTGTT | 174.7 | 63.9 | 178.1 | 181.8 | 114.3 | 113.1 | 112.8 | −10.8 |
| LLDG′TG′G′ | −62.2 | 178.0 | −61.6 | −61.4 | 114.1 | 113.1 | 115.3 | −6.1 |
| LLDTTTT | 185.5 | 176.5 | 183.0 | 181.3 | 113.3 | 111.5 | 112.7 | −8.5 |
| LLDTTG′T | 186.0 | 180.6 | −77.0 | 185.6 | 113.4 | 113.7 | 114.5 | −3.7 |
| LDLTTGG | 182.0 | 180.1 | 63.9 | 61.7 | 112.6 | 113.2 | 115.4 | −9.1 |
| LDLGTTT | 60.2 | 179.2 | 176.8 | 177.4 | 115.0 | 111.4 | 112.6 | −6.3 |
| LDLGG′TT | 93.1 | −62.4 | 185.0 | 179.2 | 116.2 | 114.1 | 112.9 | −2.3 |
| LDLG′GTT | 270.7 | 65.8 | 169.5 | 176.7 | 115.9 | 114.5 | 112.5 | −3.0 |
| LDLG′TTT | −70.5 | 187.7 | 178.1 | 178.5 | 114.5 | 111.5 | 112.7 | −10.6 |

+ NB, of 35.5 and 36.0 kJ·mol$^{-1}$ and electrostatic energies of respectively −19.8 and −20.1 kJ·mol$^{-1}$, whereas the corresponding figures for the two most stable conformers of 2,4,6-trifluoroheptane are 11.8 and 13.8 kJ·mol$^{-1}$ for DE + NB and −26.0 and −26.4 kJ·mol$^{-1}$ for EE.

Substituting Br for F thus increases the steric energy by about 23 kJ·mol$^{-1}$ but only changes the electrostatic energy by about 6.2 kJ·mol$^{-1}$. Similarly, substituting Br for F in the two most stable conformers of the dimer models increases steric energy by an average of 13.8 kJ·mol$^{-1}$ and changes electrostatic energy by only 4.1 kJ·mol$^{-1}$. The steric effects of changing the size of the halogen thus outweigh the electrostatic effects, which explains why DE + NB is considerably less than the absolute value of EE in the fluoro molecules but is greater in the bromo molecules. In general, it may be noted that in the PVB models the conformers with the smallest steric energies are also those with the smallest total energies, whereas in the PVF

**Table IV**
**Conformational Energies Calculated for 2,4-Difluoropentane and 2,4,6-Trifluoroheptane (kJ/mol)**

| conformer | energies<br>DE + NB | $U(r)$ | $U(\theta)$ | $U(\phi)$ | NB | EE | ET | parameters |
|---|---|---|---|---|---|---|---|---|
| | | | | 2,4-Difluoropentane | | | | |
| LDTT | 8.2 | 0.4 | 1.0 | 0.6 | 6.2 | −18.2 | −10.0 | $E_{0d} + 2E_n = -9.7$ |
| LLTG | 10.4 | 0.6 | 2.5 | 0.3 | 7.0 | −17.7 | −7.3 | $E_{0d} + E_n = -7.1$ |
| LDG′G′ | 11.9 | 0.7 | 4.1 | 0.1 | 7.0 | −15.7 | −3.8 | $E_{0d} + E_{w+} = -4.0$ |
| LLTT | 8.5 | 0.6 | 1.5 | 0.9 | 5.5 | −11.6 | −3.1 | $E_{0d} + 2E_n + E_{w''} = -3.2$ |
| LDGG′ | 18.9 | 0.9 | 5.9 | 3.4 | 8.7 | −17.0 | 1.9 | $E_{0d} + E_{sk} + E_w = 2.0$ |
| LLTG′ | 12.4 | 0.7 | 3.4 | 0.9 | 7.4 | −18.8 | −6.4 | $E_{0d} + E_n + E_{sk} + E_{w'} = -6.3$ |
| LLG′G | 18.7 | 0.9 | 4.6 | 4.9 | 8.3 | −15.7 | 3.0 | $E_{0d} + E_w + E_{w_p} = 3.2$ |
| LDTG | 10.8 | 0.7 | 3.3 | 0.1 | 6.7 | −11.5 | −0.7 | $E_{0d} + E_{sk} + E_{w''} + E_n = -1.2$ |
| LDTG′ | 12.4 | 0.7 | 3.2 | 1.3 | 7.2 | −17.9 | −5.5 | $E_{0d} + E_{w'} + E_n = -5.7$ |
| | | | | 2,4,6-Trifluoroheptane | | | | |
| LDLTTTT | 11.8 | 0.8 | 1.6 | 1.3 | 8.1 | −26.0 | −14.2 | $E_{0t} + 4E_n = -14.6$ |
| LLDG′TTT | 13.8 | 1.0 | 3.0 | 1.7 | 8.1 | −26.4 | −12.6 | $E_{0t} + 3E_n = -12.0$ |
| LLLTGTG | 16.3 | 1.0 | 4.3 | 1.2 | 9.8 | −26.3 | −10.0 | $E_{0t} + 2E_n = -9.5$ |
| LLLG′TTG | 16.0 | 1.0 | 4.2 | 0.8 | 10.0 | −25.3 | −9.3 | $E_{0t} + 2E_n = -9.5$ |
| LLLTTTG | 14.2 | 0.9 | 3.3 | 1.4 | 8.6 | −19.9 | −5.7 | $E_{0t} + 3E_n + E_{w''} = -5.5$ |
| LLLGTTG | 17.9 | 1.1 | 5.1 | 1.3 | 10.4 | −27.0 | −9.1 | $E_{0t} + 2E_n + E_{sk} + E_{w'} = -8.7$ |
| LLLG′GTG | 24.7 | 1.3 | 6.5 | 5.9 | 11.0 | −23.8 | 0.9 | $E_{0t} + E_n + E_{w_p} + E_w = 0.9$ |
| LLDTGTT | 14.3 | 1.0 | 2.9 | 1.2 | 9.2 | −25.1 | −10.8 | $E_{0t} + 3E_n = -12.0$ |
| LLDG′TG′G′ | 17.4 | 1.3 | 5.8 | 0.3 | 10.0 | −23.5 | −6.1 | $E_{0t} + E_n + E_{w_p} = -6.3$ |
| LLDTTTT | 12.0 | 0.9 | 1.9 | 1.6 | 7.6 | −20.5 | −8.5 | $E_{0t} + 4E_n + E_{w''} = -8.1$ |
| LLDTTG′T | 17.6 | 1.2 | 4.1 | 3.1 | 9.2 | −21.3 | −3.7 | $E_{0t} + 3E_n + E_{w''} + E_{w'} = -4.1$ |
| LDLTTGG | 15.5 | 1.1 | 4.6 | 0.3 | 9.5 | −24.6 | −9.1 | $E_{0t} + 2E_n + E_{w_p} = -8.9$ |
| LDLGTTT | 14.2 | 1.0 | 3.6 | 0.8 | 8.8 | −20.5 | −6.3 | $E_{0t} + 3E_n + E_{w''} + E_{sk} = -6.1$ |
| LDLGG′TT | 23.4 | 1.3 | 6.4 | 5.0 | 10.7 | −25.7 | −2.3 | $E_{0t} + 2E_n + E_{sk} + E_w = -2.9$ |
| LDLG′GTT | 22.5 | 1.2 | 6.3 | 4.6 | 10.4 | −25.5 | −3.0 | $E_{0t} + 2E_n + E_{sk} + E_w = -2.9$ |
| LDLG′TTT | 15.9 | 1.0 | 3.8 | 1.8 | 9.3 | −26.5 | −10.6 | $E_{0t} + 3E_n + E_{w'} = -10.6$ |

**Table V**
**Interaction Parameters Deduced from the Conformational Energies (kJ/mol)**[a]

| parameters | PVF | PVB |
|---|---|---|
| $E_{0d}$ | −4.57 | 10.99 |
| $E_{0t}$ | −4.32 | 20.26 |
| $E_{sk}$ | −0.61 | −1.02 |
| $E_n$ | −2.57 | −1.27 |
| $E_{w_p}$ | 0.56 | 0.78 |
| $E_w$ | 7.22 | 10.96 |
| $E_{w'}$ | 1.42 | 8.17 |
| $E_{w''}$ | 6.54 | 13.84 |

[a] $E_{0d}$ and $E_{0t}$ are the base energies calculated for the dimer and trimer models, respectively.

**Table VI**
**Calculated and Experimental Values of Characteristic Ratios, $C_r$, and Moment Dipole Ratios, $C_m$**

| | $C_r = \langle r^2\rangle_0/2xl^2$ calcd | $C_r = \langle r^2\rangle_0/2xl^2$ exptl | $C_m = \langle \mu^2\rangle/xm^2$ calcd | $C_m = \langle \mu^2\rangle/xm^2$ exptl |
|---|---|---|---|---|
| PVB ($t$ = 30 °C) | 6.0[a]–6.9[k] | 6.6[d] | 0.30[a]–0.57[k] | 0.45–0.53[c] |
| PVC ($t$ = 25 °C) | 11.0[e] | 13.0;[f] 8[g] | 0.72[e] | 0.70;[h] 0.59[i] |
| PVF ($t$ = 50 °C) | 5.0;[b] 7–8[j] | | 0.49;[b] 1.2[j] | |

[a,b] Calculated from the set of conformationally deduced parameters of Table V, for a replication probability of 0.46. [c] Reference 9d. [d] Ciferri, A.; Lauretti, M. *Ann. Chim. (Roma)* **1958**, *48*, 198. [e] Reference 3a. [f] Nakajima, A.; Kato, K. *Makromol. Chem.* **1966**, *95*, 52. [g] Reference 6. [h] Imamura, Y. *J. Chem. Soc. Jpn.* **1955**, *76*, 217 [i] Kotera, A.; Shima, M.; Fujisaki, N.; Kobayashi, T. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 1117. [j] Reference 9a. [k] Reference 9b.

models the electrostatic energy is very important, and for this the stability order in the total energy can be different from the stability order in DE + NB.

**(B) Statistical Calculations.** By means of a procedure similar to that employed for polypropylene[3d] and PVC,[3a] the statistical weight matrices used to calculate $C_r$ and $C_m$ were constructed, in accordance with the rotational isomeric states model, from the interaction energies deduced from the total energies of the model molecules (Table V). Comparison of columns 8 and 10 in Tables II and IV shows that the total energies of the conformers are satisfactorily recovered by adding the appropriate calculated interaction energies (Table V and Figure 1). Thus, in spite of their magnitude (especially in the fluoro compounds), the electrostatic interactions appear to be of sufficiently short range as to justify this decomposition. The values of $E_w$, $E_{w'}$, and $E_{w''}$ are in general similar to those reported[3a,5] for PVC, the only striking exception being the low value of $E_{w'}$ for PVF, which in view of the basically steric nature of $w'$ is undoubtedly due to the small size of the fluorine atom. The fact that $E_{w'}$ is in all cases less than $E_{w''}$ may be attributed to $w'$ not involving, as $w''$ does, electrostatic repulsions between almost parallel C–X dipoles. The negative values of $E_n = E_{sk} - E_g$ show that gauche interactions, $E_g$(PVB) = 0.3 kJ·mol$^{-1}$ and $E_g$(PVF) = 2.0 kJ·mol$^{-1}$, are smaller than skew interactions (Figure 1), and it may be noted that $E_g$(PVF) is only slightly greater than the 1.7 kJ·mol$^{-1}$ obtained for PVC.[3a]

In PVB, the sum of the four interactions in which steric effects are expected to predominate (Figure 1) is greater than the sum of the electrostatically dominated interactions $w''$ and $w_p$, 16.8 kJ·mol$^{-1}$ as against 14.6 kJ·mol$^{-1}$. In PVF, the reverse is the case: $E_{sk} + E_n + E_{w'} = 5.5$ kJ·mol$^{-1}$, whereas $E_{w_p} + E_{w''} = 7.1$ kJ·mol$^{-1}$. This is in keeping with the conformational results for valence and torsion angles (see above), indicating that the increase in steric effects on substituting Br for F outweighs the decrease in electrostatic effects.

The statistical weights sk = $\exp(-E_{sk}/RT)$, etc., given by the energies listed in Table V were used to construct statistical weight matrices for the three rotational states T, G, and G′. No solvation energy correction was applied because, possibly due to the lack of coherence with the interactions shown in Figure 1, the practical value of such corrections is doubtful (they sometimes cause standard deviations to almost double).[3a] Since one of the aims of this work was to compare the conformational behavior of PVB, PVC, and PVF, we assumed, like Boyd and Kesner[3a]

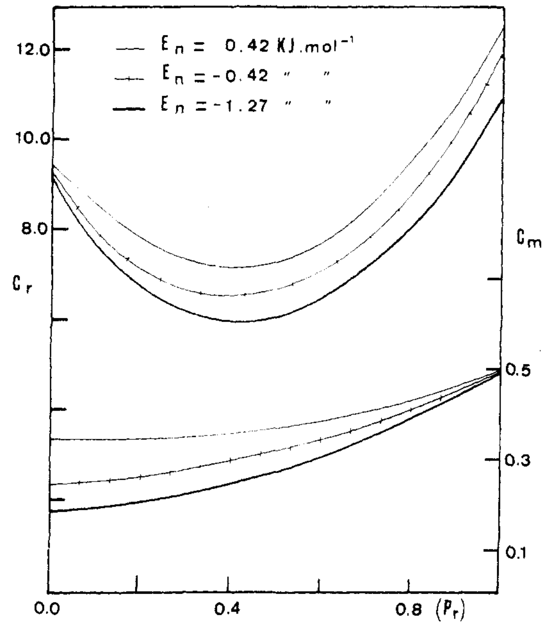

**Figure 3.** Characteristic ratio, $C_r$, and moment dipole ratio, $C_m$, plotted against replication probability, $P_r$, for PVB at 30 °C. Solid curves were calculated directly from the conformationally deduced energies of Table VI ($E_n$ = -1.27 kJ·mol$^{-1}$).

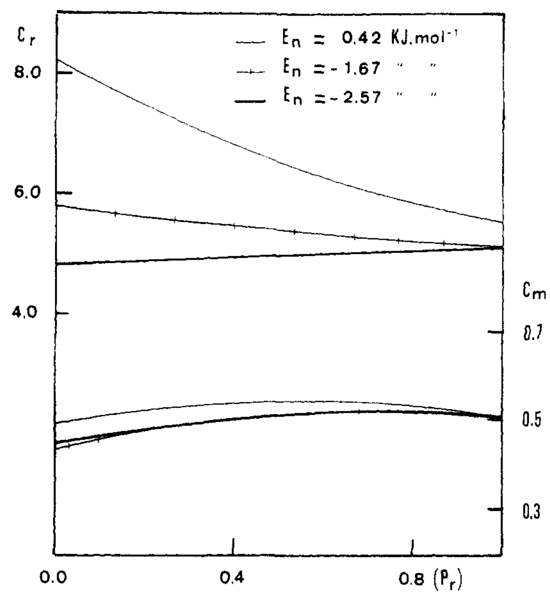

**Figure 4.** Characteristic ratio, $C_r$, and moment dipole ratio, $C_m$, plotted against replication probability, $P_r$, for PVF at 50 °C. Solid curves were calculated directly from the conformationally deduced energies of Table VI ($E_n$ = -2.57 kJ·mol$^{-1}$).

for PVC, that it is sufficient to take $x = 24$ in order for the characteristic and dipole moment ratios to converge. The validity of this assumption was checked for PVB by calculating $C_r$ and $C_m$ using larger values of $x$; the values so obtained did not differ appreciably from those listed in Table VI. Following Flory et al.,[8] stereosequences for stereoirregular polymer chains were generated on the basis of the probability of replicating the steric characteristics of the previous asymmetric carbon atom. The torsion angles employed for T, G, and G′ were the nominal values 180°, 60°, and -60°, and for valence angles the means of the values obtained by the conformational calculations were used.

Table VI lists the calculated values of $C_r$ and $C_m$ for PVB, PVC, and PVF together with the available experimental values; in the absence of experimental data for PVF, the values of $C_r$(PVF) and $C_m$(PVF) calculated by Tonelli[9a] are shown. It can be seen that the agreement between the theoretical and experimental results is good for $C_r$ but less satisfactory for $C_m$. Regardless of whether experimental or theoretical results are considered, $C_r$ is maximum for PVC. The predicted trend in $C_m$ depends on whether Tonelli's results[9a] or ours are accepted for $C_m$; in the latter case, $C_m$ too is maximum for PVC, while in the former $C_m$ increases steadily as the size of the halogen decreases. Tonelli et al.[9c] have recently measured $\langle \mu^2 \rangle$ for the m and r isomers of 2,4-dibromopentane (DBP) in $CCl_4$ at 25 °C, obtaining values of 5.29 and 5.00 D$^2$, respectively. These values are very close to those calculated by Tonelli[9b] (5.46 and 5.64 D$^2$) and by Saiz et al.[9d] (5.27 and 5.52 D$^2$). When converted to $\langle \mu^2 \rangle$ terms, the mean dipole moments implied by the DBP conformations listed in Table I, 2.122 and 2.190 D, exhibit greater discrepancy from the experimental findings,[9c] though they agree with the earlier calculations in that the value for the r isomer is slightly greater than that of the m isomer.

Figures 3 and 4 show $C_r$ and $C_m$ plotted against replication probabilities for PVB and PVF, respectively. In agreement with Tonelli's calculations,[9a] $C_r$(PVF) and $C_m$(PVF) are only slightly affected by the stereosequence of the polymer, whereas the effect on $C_r$(PVB) and $C_m$(PVB) is more pronounced and may be of use for determining stereoregularity. In view of the importance of the interaction *n*, the influence of $E_n$ on $C_r$ and $C_m$ was investigated by carrying out two additional series of calculations for each polymer. Specifically, calculations were performed for $E_n$(PVB) values of ±0.42 kJ·mol$^{-1}$ and the value given by the conformational calculations, -1.27 kJ·mol$^{-1}$, while $C_r$(PVF) and $C_m$(PVF) were calculated for $E_n$(PVF) values of -1.67 and 0.42 kJ·mol$^{-1}$ as well as -2.57 kJ·mol$^{-1}$.

Figure 3 shows that a relatively small correction to $E_n$(PVB) produces a theoretical $C_r$(PVB) practically identical with the experimental value and greatly improves the agreement between theory and experiment for $C_m$(PVB) too. Further refinement would perhaps result from similar corrections to other interaction energies or from their direct calculation (especially with regard to electrostatic contributions). The uncorrected results of Table VI nevertheless support the findings of previous studies of vinyl,[3a] vinylidene,[4c] and oxyalkylene[10] polymers with regard to the utility for polymer research of combining molecular mechanics with the statistical method employed here. Like Miyasaka et al.,[10c] it could be concluded that the use of molecular mechanics for direct calculation of a set of energy parameters for subsequent statistical operations may lead to clearly satisfactory results (as for $C_r$ here) or to less satisfactory results (as for $C_m$). The disparity of $C_m$ could be in part motivated by the limitations in computing the induced dipolar moments, which are more important in PVF. In conclusion, the final results listed in Table VI suggest that the methodology employed in this work does not improve on the results obtained by other rotational isomeric states techniques. In spite of this, we believe that the new approach described here is useful as a first approximation susceptible of correction to improve the modeling of conformational-dependent experimental quantities.

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**Registry No.** PVB, 25951-54-6; PVF, 24981-14-4; *meso*-2,4-dibromopentane, 1825-11-2; *rac*-2,4-dibromopentane, 1625-68-9; *meso*-2,4-difluoropentane, 22464-30-8; *rac*-2,4-difluoropentane, 22464-29-5; isotactic 2,4,6-tribromoheptane, 119242-78-3; syndiotactic 2,4,6-tribromoheptane, 119242-77-2; heterotactic 2,4,6-

tribromoheptane, 119207-04-4; isotactic 2,4,6-trifluoroheptane, 119393-43-0; syndiotactic 2,4,6-trifluoroheptane, 119477-50-8; heterotactic 2,4,6-trifluoroheptane, 119477-51-9.

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# Thermal Degradation of Poly(methyl methacrylate). 2. Vinyl-Terminated Polymer

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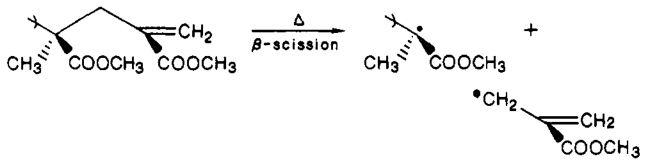
ABSTRACT: It is demonstrated that the thermal degradation kinetics for vinyl-terminated poly(methyl methacrylate) (PMMA-CH=$CH_2$) are dependent on the sample thickness. A systematic study of film thickness on PMMA-CH=$CH_2$ degradation indicates the accepted mechanism of homolytic scission β to the vinyl group is incorrect. A chain-transfer process is proposed that explains the observed results. The source of radicals that initiate degradation is not determined.

## Introduction

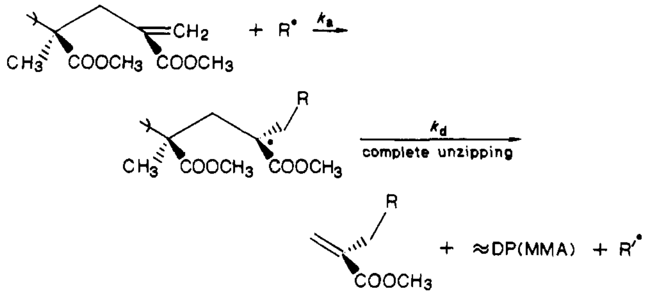
It has been observed that vinyl-terminated poly(methyl methacrylate) thermally degrades at a lower temperature than saturated PMMA (PMMA-H). For example, when free radically polymerized PMMA is heated at 10 °C/min, the unsaturated portion (PMMA-CH=$CH_2$) degrades between 230 and 300 °C, whereas the saturated portion (PMMA-H) degrades between 300 and 400 °C.[1-3] It is generally believed that PMMA-CH=$CH_2$ is less stable due to facile β-scission of the relatively weak C–C bond β to the vinyl group (Scheme I). With short polymer chains the result of Scheme I is end initiation followed by complete unzipping. Accordingly, the rate of degradation will be independent of molecular weight.[4] Studies with model PMMA-CH=$CH_2$ oligomers confirm the low degradation temperature and, in agreement with Scheme I, suggest degradation is independent of molecular weight.[5] The Arrhenius activation energy reported for PMMA-CH=$CH_2$ degradation (~114 kJ/mol) appears low if β-scission is rate limiting.[6]

We are studying the thermal degradation of PMMA-CH=$CH_2$ and report that the major degradation mechanism is not as shown in Scheme I but involves efficient radical transfer to the vinyl chain end (Scheme II). Any reaction that generates a radical R• (including β-scission if it does occur) will degrade a large number of polymer chains by the chain-transfer process. We believe the radical that transfers the active site to the next chain (R′•) will usually be the species present at the initiation end of the PMMA-CH=$CH_2$ chain. With our samples this will be short oligomeric (•C($CH_3$)($COOCH_3$)–R), saturated end group (•C$(CH_3)_2COOCH_3$), or AIBN radicals (•C$(CH_3)_2$CN).

**Scheme I**



**Scheme II**



## Results and Discussion

Samples of vinyl-terminated PMMA were prepared by using a cobalt chain-transfer catalyst[7] (CoCTC) similar to

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† Contribution No. 4860.

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