here.

The iPS system with the extended conformation has been visualized in terms of the fringe-micelle model.[6] The present study shows that either extended, threefold, or a mixture of the two conformations can occur in the gel, depending on the solvent. The connectivity between the crystallites containing one conformation is thus provided by the segments of the chain in the other conformations. The tacticity of the chain also seems to have an influence. The differences in the elasticity of the gels provide a good model for correlating the rheological behavior with conformer population and relative crystallinity and crystallite size of the two structures.

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Conformational Characteristics of Poly(vinyl bromide) and Ethylene–Vinyl Bromide Copolymers

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ABSTRACT: Conformational energies are calculated for chain segments in poly(vinyl bromide) (PVB) homopolymer and the copolymers of vinyl bromide (VB) and ethylene (E) (PEVB). Semiempirical potential functions are used to account for the nonbonded van der Waals and electrostatic interactions. Rotational isomeric state (RIS) models are developed for PVB and PEVB from the calculated conformational energies. Dimensions and dipole moments are calculated for PVB and PEVB using their RIS models, where the effects of stereosequence and comonomer sequence are explicitly considered. It is concluded from the calculated dimensions and dipole moments that the dipole moments are most sensitive to the microstructures of PVB homopolymers and PEVB copolymers and may provide an experimental means for their structural characterization.

Introduction

We have recently utilized the chemical shifts observed in the ^{13}C and ^{19}F NMR spectra[1-3] and the molar Kerr constants[4-7] measured in electrical birefringence experiments to characterize the microstructures of vinyl homo- and copolymers. This characterization is achieved by our ability to predict both properties for a given microstructure.

A key ingredient in our recipes for predicting both properties is the conformational characteristics of the polymer chain. We must have knowledge of the allowed conformations and their relative probabilities. The purpose of this investigation is to gather such knowledge for poly(vinyl bromide) (PVB) and the copolymers (PEVB) of ethylene (E) and vinyl bromide (VB).

Recently, ^{13}C NMR studies have been reported[8,9] for PVB and its oligomeric model compounds 2,4-dibromopentane and 2,4,6-tribromoheptane. In addition, PEVB copolymers have been made via the facile reductive debromination of PVB and their ^{13}C NMR specta recorded.[10] We hope to be able to predict the observed ^{13}C NMR chemical shifts of these polymers and oligomers using the conformational characteristics developed here for PVB and PEVB.

Table I
Lennard-Jones 6-12 Parameters for PVB and PEVB

$$E(\text{van der Waals}) = -\frac{C_{ij}}{r_{ij}^{6}} + \frac{A_{ij}}{r_{ij}^{12}}$$

atom pair, ij	$C_{ij}{}^a$	$A_{ij}{}^a$
H,H	46.5	7 180
H,C	126	56 000
C,C	361	393 130
H,Br	420	250 000
C,Br	1200	1 700 000
Br,Br	4000	7 000 000

[a] The values given for C_{ij} and A_{ij} yield E(van der Waals) in kcal/mol when r_{ij} is expressed in Å.

First conformational energy calculations are performed on the various chain fragments occurring in PVB and PEVB. Next a rotational isomeric state (RIS) model[11] is developed for PVB and PEVB from the conformational

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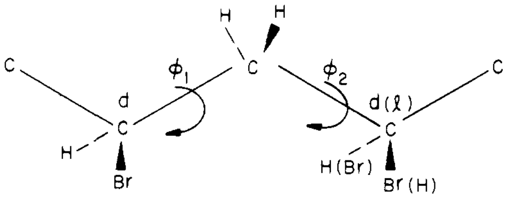

Figure 1. Schematic representation of a meso (dd) and racemic (dl) dyad in PVB in the all-trans conformation $(\phi_1,\phi_2) = 0°, 0°$.

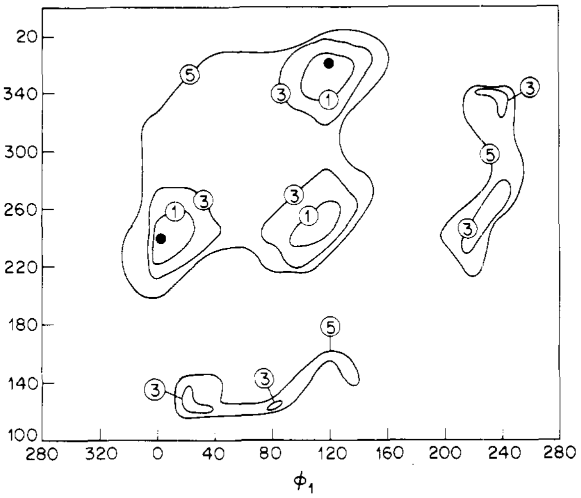

Figure 2. Conformational energy map for a meso (dd) dyad in PVB (see Figure 1). Energy contours are drawn in kcal/mol of dyad fragment relative to the lowest energy conformations indicated by a solid circle at $(\phi_1,\phi_2) = 0°, 240°$ and $120°, 0°$.

energy estimates. Finally the mean-square dipole moments and dimensions are calculated for PVB and PEVB as a function of their microstructures, i.e., stereo- and comonomer sequence.

Conformational Energy Calculations

Each backbone C–C bond was assigned a threefold intrinsic torsional potential with a barrier height of 3.0 kcal/mol.[11] The Lennard-Jones 6–12 potential and a coulombic term were used to evaluate the nonbonded van der Waals and electrostatic interactions.

Lennard-Jones parameters for C and H were taken from Brant, Miller, and Flory[12] and those for Br were evaluated[13] from the Slater–Kirkwood equations using 3.34 Å^3, 16, and 1.85 Å for the atomic polarizability,[14] the effective number of valence electrons,[13] and the van der Waals radius[15] of Br (see Table I). A C–Br bond dipole moment[16] of 1.78 D and a C–Br bond length[15] of 1.91 Å lead to ±0.2 electronic charges for the methine carbon and Br atoms. A dielectric constant of 3.0 was used to mediate the electrostatic interactions.

C–C and C–H bond lengths of 1.53 and 1.10 Å were adopted, and bond angles C–C–C = 112° and H–C–H = H–C–Br = 109° were assumed.[11] Backbone rotation angles were stepped in 20° increments throughout their entire ranges.

In Figure 1 a meso (m or dd) and racemic (r or dl) PVB dyad in the all-trans ($\phi_1 = \phi_2 = 0°$) conformation is illustrated. Conformational energies calculated for the meso and racemic dyads in PVB are presented in Figures 2 and 3. The conformational energies were also calculated for the chain fragments $-C-CH_2-\phi_1\circlearrowright CHBr-\phi_2\circlearrowright CH_2-C-$ and $-C-CHBr-\phi_1\circlearrowright CH_2-\phi_2\circlearrowright CH_2-C-$ found in PVB and PEVB.

RIS Models for PVB and PEVB

It is apparent from Figures 2 and 3 that a 3-state RIS model[11] with allowed rotational states at 0° (t) and ±120° ($g^{\pm}$) is appropriate for PVB. Conformational energies calculated for the chain fragments in PEVB also lead to a 3-state RIS model.

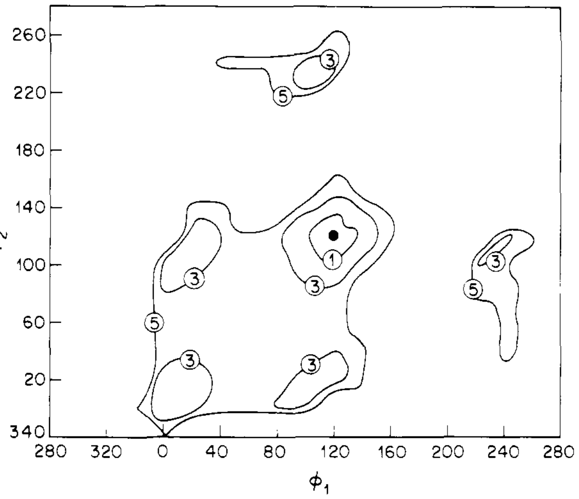

Figure 3. Same as Figure 2 except that meso (dd) is replaced with racemic (dl) and $(\phi_1,\phi_2) = 0°, 240°$ and $120°, 0°$ are replaced with $(\phi_1,\phi_2) = 120°, 120°$.

Statistical weight matrices **U** were calculated at a given

$$\mathbf{U} = \phi_1 \begin{array}{c} \\ \\ t \\ g^+ \\ g^- \end{array} \begin{array}{c} \phi_2 \\ \begin{array}{ccc} t & g^+ & g^- \end{array} \\ \begin{bmatrix} SW_{tt} & SW_{tg^+} & SW_{tg^-} \\ SW_{g^+t} & SW_{g^+g^+} & SW_{g^+g^-} \\ SW_{g^-t} & SW_{g^-g^+} & SW_{g^-g^-} \end{bmatrix} \end{array}$$

temperature from the conformational energies. As an example, SW_{tg^+} is obtained from

$$SW_{tg^+} = \frac{\sum\limits_{\phi_1=-60°}^{60°} \sum\limits_{\phi_2=60°}^{180°} \exp[-E(\phi_1,\phi_2)/RT]}{\sum\limits_{\phi_1=0°}^{360°} \sum\limits_{\phi_2=0°}^{360°} \exp[-E(\phi_1,\phi_2)/RT]}$$

The following statistical weight matrices were derived at 50 °C for the various chain fragments found in PVB and PEVB:

$$U_{dd(CHBr-CH_2-CHBr)} = \begin{bmatrix} 0.005 & 0.006 & 0.370 \\ 0.370 & 0.010 & 0.224 \\ 0.006 & 0 & 0.010 \end{bmatrix}$$

$$U_{dl(CHBr-CH_2-CHBr)} = \begin{bmatrix} 0.184 & 0.061 & 0.001 \\ 0.061 & 0.638 & 0.028 \\ 0.001 & 0.028 & 0 \end{bmatrix}$$

$$U_{d(CH_2-CHBr-CH_2)} = \begin{bmatrix} 0.143 & 0.143 & 0.143 \\ 0.143 & 0.143 & 0 \\ 0.143 & 0 & 0.143 \end{bmatrix}$$

$$U_{de(CHBr-CH_2-CH_2)} = \begin{bmatrix} 0.180 & 0.017 & 0.086 \\ 0.339 & 0.204 & 0.075 \\ 0.086 & 0.009 & 0.004 \end{bmatrix}$$

$$U_{ed(CH_2-CH_2-CHBr)} = \begin{bmatrix} 0.180 & 0.086 & 0.339 \\ 0.086 & 0.004 & 0.075 \\ 0.017 & 0.009 & 0.204 \end{bmatrix}$$

$$U_{e(CH_2-CH_2-CH_2)} = \begin{bmatrix} 0.205 & 0.094 & 0.094 \\ 0.205 & 0.094 & 0.004 \\ 0.205 & 0.004 & 0.094 \end{bmatrix}$$

$\mathbf{U}_{ll}$, $\mathbf{U}_{ld}$, $\mathbf{U}_{l}$, $\mathbf{U}_{le}$, and $\mathbf{U}_{el}$ are obtained by interchanging the second and third columns and rows of $\mathbf{U}_{dd}$, $\mathbf{U}_{dl}$, $\mathbf{U}_{d}$, $\mathbf{U}_{de}$, and $\mathbf{U}_{ed}$, respectively. The columns of **U** correspond to the t, g^+, and g^- states of the second bond in the chain fragment in parentheses and the rows to the t, g^+, and g^- states of the first bond.

Calculated Dipole Moments and Dimensions for PVB and PEVB

Matrix multiplication techniques[11] were utilized to calculate the mean-square dipole moments $\langle\mu^2\rangle_0$ and dimensions $\langle r^2\rangle_0$, where r is the end-to-end distance, of PVB and PEVB chains of 400 bonds. Monte Carlo generation of chains a repeat unit at a time permitted the entire ranges of stereo- and comonomer sequence to be explored.

The trans (t) and gauche ($g^\pm$) states were assigned 0° and ±120° rotations. Dipole moments and dimensions were calculated at 50 and 150 °C.

In Figure 4 the dipole moments calculated for PVB and PEVB at 50 °C are presented as a function of stereosequence and comonomer composition P_{VB}. The results are expressed in two ways as the ratios $C_m = \langle\mu^2\rangle_0/N_{VB}m^2$, where N_{VB} and m^2 are the number of VB units and the square of the C–Br dipole moment[16] (1.780^2), and $C_n = \langle\mu^2\rangle_0/n$, where $n = 400$ bonds.

All PEVB dipole moments were calculated for random distributions of E and VB monomers except for regularly alternating E–VB copolymers, where $P_{VB} = 0.5$. The sizes of the calculated points (filled circles for random and filled triangles for regularly alternating PEVB) indicate the overall dependence of C_m and C_n on stereosequence.

C_n increases and C_m decreases by a factor of 2 over the range of PEVB copolymers corresponding to $P_{VB} = 0.2$–1.0. Clearly, the dipole moments of random PEVB copolymers are sensitive to their VB monomer contents. Also the sequence distribution of E and VB comonomer units in PEVB copolymers significantly affects their calculated dipole moments, as shown by the substantial increases in both C_m and C_n for $P_{VB} = 0.5$ when the E and VB comonomer units are regularly alternating rather than randomly placed.

On the other hand, regardless of comonomer sequence, the calculated dipole moments of PEVB copolymers are virtually independent of the stereosequence of VB monomer units for $P_{VB} < 0.8$, but for $P_{VB} > 0.8$ they depend sensitively upon stereosequence. Clearly, the measurement of PVB ($P_{VB} = 1.0$) dipole moments would aid in the determination of stereosequence.

The dimensions calculated at 50 °C for PVB and PEVB chains are presented in the form of characteristic ratios $C_r = (\langle r^2\rangle_0/nl^2)$ in Figure 5. The addition of VB units decreases the dimensions. A 30% reduction in dimensions occurs for PVB ($P_{VB} = 1.0$) compared to polyethylene ($P_{VB} = 0.0$). Like the calculated dipole moments, the dimensions calculated for PVB do show a sensitivity to stereosequence, with the dimensions of isotactic PVB being 50% and a factor of 2 greater than those calculated for syndiotactic and atactic chains, respectively.

Table II presents the temperature dependence of the calculated dipole moments and dimensions. d ln $\langle\mu^2\rangle_0/\mathrm{d}T$ is small and positive for PEVB copolymers and syndiotactic and atactic PVB, and small and negative for isotactic PVB. The d ln $\langle r^2\rangle_0/\mathrm{d}T$ calculated for PEVB and PVB are negative and similar to that found for polyethylene.[11]

Discussion

We have developed RIS descriptions of the conformational characteristics of PVB and PEVB homo- and copolymers from conformational energy calculations performed on the various chain fragments occurring in these polymers. Dipole moments and dimensions were calculated from these RIS models with full consideration given to comonomer composition and sequence for PEVB chains and to the stereosequence of VB monomers in PVB.

Dipole moments calculated for PEVB are sensitive to comonomer composition and may be used to characterize this aspect of PEVB microstructure. However, the stereosequence of VB units has little effect on the dipole moments calculated for PEVB with $P_{VB} < 0.8$, and information on this facet of their microstructures is not expected to be forthcoming from dipole moment measurements. The dipole moments of PVB are sensitive to stereosequence.

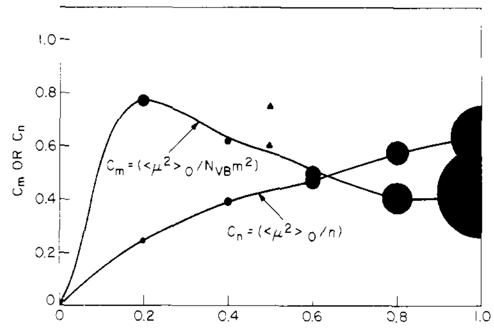

Figure 4. Dipole moments $\langle\mu^2\rangle_0$ calculated at 50 °C for 400-bond PEVB and PVB chains and expressed as the ratios $C_m = \langle\mu^2\rangle_0/N_{VB}m^2$ and $C_n = \langle\mu^2\rangle_0/n$, where N_{VB}, m^2, and n are the number of VB units, the square of the C–Br bond dipole moment, and the number of bonds, respectively. P_{VB} is the fraction of VB monomer units. The filled circles correspond to random copolymers and the filled triangles to regularly alternating copolymers. The sizes of the circles and triangles indicate the calculated dependence on VB monomer stereosequence.

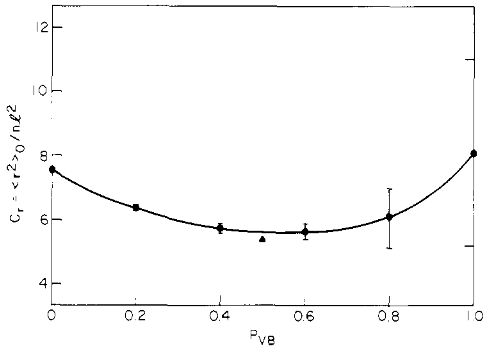

Figure 5. Characteristic ratio of dimensions $C_r = \langle r^2\rangle_0/nl^2$ calculated at 50 °C for 400-bond PEVB and PVB chains and plotted against the fraction of VB monomer units, P_{VB}. Filled circles correspond to random copolymers and the filled triangle corresponds to regularly alternating copolymer. The error bars indicate the calculated sensitivity to VB monomer stereosequence.

Table II
d ln $\langle\mu^2\rangle_0/\mathrm{d}T$ and d ln $\langle r^2\rangle_0/\mathrm{d}T$ Calculated for PVB and PEVB Homo- and Copolymers

P_{VB}	(d ln $\langle\mu^2\rangle_0/\mathrm{d}T$) × 10^4 [a]	(d ln $\langle r^2\rangle_0/\mathrm{d}T$) × 10^3 [a]
0		−1.1
0.2	0.0 to 0.8	−0.8 to −1.1
0.4	0.2 to 1.0	−0.7 to −1.3
0.6	0.2 to 1.3	−0.8 to −1.3
0.8	0.0 to 1.9	−0.6 to −1.9
1.0	−2.3 to 2.6	−0.6 to −3.9

[a] The ranges in d ln $\langle\mu^2\rangle_0/\mathrm{d}T$ and d ln $\langle r^2\rangle_0/\mathrm{d}T$ correspond to the effects of stereosequence.

Table III
Dimensions and Dipole Moments of Poly(vinyl halides) and Their Copolymers with Ethylene at $T = 50$ °C

polymer[a]	C_r exptl	C_r calcd	C_m exptl	C_m calcd
PE[19]	–(6.8)[c]	7.6 (6.7)[c]		
PVF[20]		8.0		1.2
PVC[21,22]	11	12	0.7	0.7-1.2
PVB	6.8	5.4	0.5-0.8	0.4
PEVC[b,19,23]	9	8-10		0.8-1.0
PEVB[b]		5.7		0.6

[a] All polymers containing asymmetric monomers are assumed to have $P_m = 0.5$. [b] 50:50 random copolymer. [c] $T = 140$ °C.

The dimension calculated for PEVB and PVB show only modest dependencies on comonomer composition and VB monomer stereosequence. Consequently, it seems doubtful that the measurement of dilute-solution dimensions can significantly aid in the characterization of PVB or PEVB microstructure, except possibly for isotactic PVB.

Le Fêvre and Sundaran[17] report values of $C_m = 0.49$–0.80 for the dipole moments measured in dioxane on PVB samples with molecular weights ranging from 10 000 to 38 000. According to the ^{13}C NMR studies of Cais and Brown,[8] these PVB samples most probably were atactic with a Bernoullian meso dyad fraction P_m of ca. 0.4. For PVB chains with this stereosequence we calculate $C_m = 0.40$, in good agreement with the results reported by Le Fêvre and Sundaran for the lower molecular weight PVB's but significantly lower than the dipole moments measured for longer PVB chains.

The ratios C_m, C_n, and C_r calculated for 400-bond PVB chains have all reached 99% of their molecular weight independent values. It remains puzzling to us why the dipole moments reported by Le Fêvre and Sundaran[17] do not converge with chain length for molecular weights corresponding to more than 700 bonds per PVB chain.

Ciferri and Lauretti[18] deduce a value of $C_r = 6.6$ from molecular weight–intrinsic viscosity studies at the Θ temperature in THF/methanol solutions. For atactic PVB chains we calculate $C_r = 5.4$, in fairly good agreement with their results.

The RIS model we have developed for PVB is clearly not incompatible with the meager experimental results just quoted from the literature.

Table III summarizes the dimensions C_r and the dipole moments C_m observed and calculated for polyethylene (PE), poly(vinyl fluoride) (PVF), poly(vinyl chloride) (PVC), PVB, and the copolymers of ethylene (E) with either vinyl chloride (VC) (PEVC) or vinyl bromide (VB) (PEVB). PE and PVF have similar dimensions, while PVC and PVB have larger and smaller dimensions, respectively, relative to PE and PVF. The dimensions calculated for PVC are largest for the syndiotactic chain, decrease for the atactic chain, and are smallest for isotactic PVC. Atactic PVF is most extended, while the isotactic and syndiotactic chains have similar dimensions. Atactic PVB is most compact, with the syndiotactic and isotactic chains possessing increasingly larger dimensions. All three poly(vinyl halides) and PE contract with increasing temperature.

The dipole moments of the poly(vinyl halides) increase in the order PVB, PVC, and PVF. Raising the temperature increases C_m for PVB and decreases C_m for PVF and PVC.

Chlorination of PE to form PEVC copolymers leads to an increase in chain dimensions while PEVB copolymers have smaller dimensions than PE. Similarly, the dipole moments of PEVB are smaller than those of PEVC. It would appear that bromine as a substituent in PVB homopolymers and PEVB copolymers results in an increased chain flexibility relative to PE, while the opposite behavior is produced by chlorine substituents, and fluorine substitution has little effect.

In subsequent papers[24,25] we will apply the RIS models derived for PVB and PEVB to calculate the molar Kerr constants expected for these polymers. We are currently studying the electrical birefringence of PVB, its oligomers, and PEVB copolymers in dilute solution. Extraction of molar Kerr constants from these measurements requires[4–7] dipole moment measurements. As a result, we will shortly have experimental data on two microstructurally sensitive properties of PVB and PEVB with which to compare and test their conformational models.

Finally, if we are able to confirm the validity of these conformational descriptions, then they will be utilized in an attempt to calculate the ^{13}C NMR chemical shifts expected for the carbon atoms in the various microstructural environments found in PVB and PEVB. Comparison with the ^{13}C NMR spectra observed for PVB and PEVB should provide another means to characterize their microstructures.

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