Table IV
Monomer Composition, *n*-ad Sequence Distribution, and r_1 and r_2 Values for Samples C–H

	ethylene feed, mol %					
	5.0 C	8.5 D	10.1 E	21.2 F	38.6 G	50.4 H
P	0.85	0.78	0.75	0.51	0.28	0.25
E	0.15	0.22	0.25	0.49	0.72	0.75
PP	0.76	0.66	0.61	0.33	0.13	0.10
EP	0.19	0.25	0.27	0.37	0.31	0.29
EE	0.05	0.09	0.11	0.31	0.57	0.61
PPP	0.67	0.57	0.50	0.22	0.07	0.04
PPE	0.17	0.18	0.21	0.21	0.13	0.10
EPE	0.02	0.03	0.04	0.08	0.09	0.11
PEP	0.07	0.10	0.10	0.11	0.07	0.05
EEP	0.03	0.06	0.07	0.15	0.16	0.17
EEE	0.04	0.06	0.08	0.23	0.49	0.52
r_1	9.3	7.5	7.0	6.3	6.0	4.2
r_2	0.4	0.5	0.5	0.5	0.5	0.7
r_1r_2	4.2	3.8	3.7	3.0	3.1	2.9

Table V
Observed vs. Calculated Triad Distributions

sample		PPP	PPE	EPE	PEP	EEP	EEE
C	obsd	0.67	0.17	0.02	0.07	0.03	0.04
	calcd	0.68	0.17	0.01	0.06	0.06	0.02
D	obsd	0.57	0.18	0.03	0.10	0.06	0.06
	calcd	0.58	0.20	0.02	0.07	0.10	0.03
E	obsd	0.50	0.21	0.04	0.10	0.07	0.08
	calcd	0.49	0.23	0.03	0.08	0.12	0.05
F	obsd	0.22	0.21	0.08	0.11	0.15	0.23
	calcd	0.22	0.23	0.06	0.07	0.23	0.19
G	obsd	0.07	0.13	0.09	0.07	0.16	0.49
	calcd	0.06	0.14	0.08	0.03	0.24	0.45
H	obsd	0.04	0.10	0.11	0.05	0.17	0.52
	calcd	0.04	0.12	0.09	0.03	0.23	0.50

predicted by a first-order Markovian scheme and the EEP triad is obviously less. In other words, ethylene (strangely) tends to copolymerize either in alternation or in runs. As speculated by several investigators,[17–22] this result may suggest that multiple active sites are present: on one active site ethylene preferentially polymerizes and on another site less ethylene polymerizes.

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Random-Coil Configurations of Poly(vinyl bromide) Chains

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ABSTRACT: Two samples of poly(vinyl bromide) were prepared and purified. Sample A was synthesized by radical polymerization of vinyl bromide at 35 °C, and sample B was obtained by extraction of sample A with dioxane at room temperature. Both samples had an isotactic content (determined by ^{13}C NMR) of 46%. Molecular weight averages were calculated from viscometric measurements in THF solutions and were found to be 52 100 and 27 400 for samples A and B, respectively. Dielectric measurements were performed in solutions of both samples in dioxane and 1-methylnaphthalene at several temperatures, and dipole ratios $D_x = \langle \mu^2 \rangle / xm^2$ were found to be 0.53 and 0.45 in dioxane and 1-methylnaphthalene, respectively. No noticeable dependence of D_x with molecular weight was found; the variation of D_x with temperature was too small to allow an accurate determination of its temperature coefficient. A rotational isomeric state model was derived and used to calculate dipole and characteristic ($C_n = \langle r^2 \rangle_0 / nl^2$) ratios. Theoretical values of both D_∞ and C_∞ are in good agreement with experimental results.

Introduction

The available information on the physical and physicochemical properties of poly(vinyl bromide) (PVB) is meager in comparison with that existing for most vinyl polymers. The reason is that instability of the polymer decreases the precision of the measurements, so that most of the results are considered to be qualitative in nature. In view of recent work aimed at understanding the stereoconfigurational dependence of the dipole moment ratio of poly(vinyl chloride) (PVC),[1] it seemed of interest to analyze the next higher homologue of the poly(vinyl halides).

A characteristic common to all of the vinyl chains is the extreme sensitivity of the configuration-dependent properties to the stereochemical composition.[2-4] Early dipole moment studies of PVC[2] and poly(*p*-chlorostyrene) (PCS)[3,5] have shown that the dipole moment ratio increases significantly with syndiotactic content. In both cases theoretical calculations for extreme tacticities reveal an almost sixfold increase, although it has not yet been confirmed by experimental measurements due to difficulties in preparing samples with these tacticities. The effect of stereochemical structure on statistical properties is much less pronounced in the case of a chain like poly(oxypropylene),[6-8] poly(thiopropylene),[9,11] or poly(4-methyl-1,3-dioxolane),[12] where the substituted carbons are separated by more than two bonds.

One reason for our interest in the properties of PVB lies in the similarity of PVB and PVC. For instance, the C–Br bond length is ca. 5% longer than the C–Cl bond length;[13] furthermore, the value of the dipole moment associated with the C–Br bond should be similar to that of the C–Cl bond, because the dipole moments of ethyl chloride and ethyl bromide are similar.[14] It is of interest to investigate whether these similarities manifest themselves in the conformational characteristics of the PVB chains, mainly in their dipole moments and molecular dimensions. The study of the dependence of the configurational properties of PVB on the polymer stereoconfiguration would therefore highlight the difference in steric influence of bromine and chlorine backbone substituents.

Studies on the solution properties of PVB by Ciferri et al.[15,16] led to the conclusion that the polymer does not present the aggregation effects observed in PVC solutions. As a consequence, the study of the dielectric properties of the former polymer should also help to elucidate a dilemma that appears in the analysis of the dipole moments of the PVC chains. We are referring to the discrepancy between the theoretical and experimental dipole moments of PVC.[1] Actually, assuming that the vector dipole moment corresponding to the repeating unit coincides with that of the C–Cl bond, the theoretical values of $\langle \mu^2 \rangle$ are significantly higher than the experimental results. This may be attributed either to the presence of molecular aggregates in the solutions or to the fact that the angle between the vector dipole moment of the repeat unit $\mathbf{m}$ and the C–Cl bond is not zero. In a recent work[1] it was shown that agreement between theory and experiment is achieved if the contribution to $\mathbf{m}$ from the C–H bond of the HCCl group, $\mathbf{m}_{\mathrm{CH}}$, is considered.

This work, therefore, focuses on the determination of the unperturbed dipole moments of PVB chains, using both methylnaphthalene and dioxane as solvents. The approach taken is probably the best method available for this purpose, because those solvents are the only nonpolar media in which slightly syndiotactic PVB chains are sufficiently soluble at room temperature. The results will be interpreted in terms of the rotational isomeric state model, emphasizing the effects of the contribution of $\mathbf{m}_{\mathrm{CH}}$ of the HCBr group on the dipole moment ratio of the chains.

Experimental Part

Preparation of Poly(vinyl bromide). The monomer, vinyl bromide, was obtained by reaction of 1,2-dibromoethane with sodium ethylate according to the method described by Regnault.[17]

Table I
Summary of Dielectric Results

sample	T, °C	ϵ_1	ρ_1	$\mathrm{d}(\epsilon - \epsilon_1)/\mathrm{d}w$	$\mathrm{d}(n^2 - n_1^2)/\mathrm{d}w$	$\langle \mu^2 \rangle / xm^2$
			Dioxane Solvent			
B	30	2.2010	1.023	2.86	0.26	0.531
A	60	2.1507	0.9955	2.58	0.26	0.548
			1-Methylnaphthalene Solvent			
B	30	2.6829	1.0101	2.68	0.00	0.447
	40	2.6696	1.0027	2.56	0.00	0.448
	50	2.6499	0.9953	2.46	0.00	0.450
	60	2.6308	0.9880	2.39	0.00	0.457

All operations needed for the polymerization of vinyl bromide were carried out under high-vacuum conditions (10^{-5} mmHg) using conventional techniques. Thus the monomer was distilled under reduced pressure into a Pyrex glass tube containing 2,2′-azobis(isobutyronitrile). The sealed tube was introduced into a water bath at 35 °C for 24 h and was kept in darkness. The solid material was dissolved in purified THF, precipitated with methanol, filtered, and washed several times with lukewarm methanol to remove the last traces of initiator. Finally, the polymer was dried in a vacuum oven at 40 °C for 25 h to constant weight.

Characterization of the Polymer. The characterization of the polymer was carried out by ^{13}C NMR, using the method developed by Cais and Brown.[18] Its isomeric composition was 46% meso and 54% racemic. The bromine content of the polymer was 74.02%. The viscosity-average molecular weight was estimated by viscometry in THF at 20 °C by means of the Mark–Houwink equation reported by Ciferri et al.[15] for fractionated PVB

$$[\eta] = 1.59 \times 10^{-2} M_{\mathrm{v}}^{0.64}$$

and a value of 52 100 was obtained for M_{v}.

Dielectric Measurements. Dielectric measurements were carried out on solutions of the polymer in dioxane and in 1-methylnaphthalene. The purification and physical constants of dioxane have been reported elsewhere.[19] The purification of 1-methylnaphthalene was accomplished by shaking commercial grade product (Ferosa SA) with several portions of 10% sulfuric acid until no appreciable dark reddish color was observed. Then it was successively treated with dilute sodium hydroxide and distilled water. Finally, it was allowed to stand over finely ground sodium sulfate for 24 h, with occasional shaking. The product was separated from the drying agent by filtration and then distilled from fresh calcium hydride under reduced pressure (10 mmHg), using a 70-cm thermostated column packed with glass helices. The first and the tail fractions were rejected, and the fraction having refractive index $n^{20}{}_{\mathrm{D}} = 1.6143$ with $\mathrm{d}n/\mathrm{d}T = -4.67 \times 10^{-4}$ K^{-1} was collected and used in further dielectric measurements. The density of the solvent, measured by dilatometry, obeys the equation $\rho(t) = 1.0321 - 7.35 \times 10^{-4} t$ (°C). The values of both ρ and n are in good agreement with those reeported in the literature.[20-22] The dielectric constants of the solutions and of the solvents were determined with a capacitance bridge (General Radio Type 1620 A) operating at a frequency of 10 kHz. The three-terminal cell (Foxboro Model 2HV35) was calibrated at several temperatures of interest by using the procedure described elsewhere.[23] Values of the dielectric constant ϵ_1 of 1-methylnaphthalene at several temperatures are given in the third column of Table I. These values are in disagreement with those reported by Rampolla and Smith,[24] who found values of 2.853 and 2.797 at 40 and 60 °C, respectively, much higher than the corresponding values shown in Table I (2.670 and 2.631). This may be the cause of the anomalously high dipole moment found by these authors for this solvent. Values of the index of refraction of the solutions in dioxane were measured at 546 nm using a Brice-Phoenix differential refractometer. For the solutions in 1-methylnaphthalene, these indices were measured with a Carl Zeiss interferometer.

Results

Two samples were used for the dielectric measurements: the polymer obtained at 35 °C from the radical polymer-

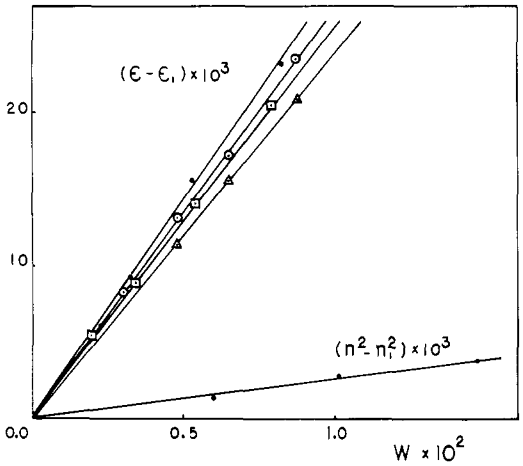

Figure 1. Typical data showing the concentration dependence of the increments in dielectric constant and squared index of refraction. Data of dielectric constant were obtained as follows: (●) sample B in dioxane at 30 °C; (○) sample A in 1-methylnaphthalene at 30 °C; (□) sample A in dioxane at 60 °C; (△) sample A in 1-methylnaphthalene at 60 °C. Data of refractive index were obtained with sample A in dioxane and do not change with temperature.

ization of vinyl bromide (sample A), which is totally soluble in dioxane at temperatures above 50 °C, and the polymer chains obtained from the extraction of sample A with dioxane at room temperature (sample B). The viscosity-average molecular weight of sample B was found to be M_v = 27400, and its NMR spectra were indistinguishable from those of sample A; therefore the tacticity of both samples should be the same. Dielectric measurements were carried out on solutions of sample A in dioxane at 60 °C. Similar measurements were made on solutions of sample B in dioxane at 30 °C. In another series of experiments at 30, 40, 50, and 60 °C dielectric measurements were made on solutions of sample A in 1-methylnaphthalene. Since some dielectric results were obtained above room temperature, at which severe degradative effects may occur, the influence of these effects on the dielectric results was examined. Thus, experimental measurements were made over several minutes on a solution of sample A in dioxane at 70 °C. It was found that $d\epsilon/dw$ increases about 5.6% over an interval of 30 min. This increase is 5.2% if the solution is kept at 60 °C for 85 min. Therefore, dielectric results obtained at moderately high temperatures should be considered with caution.

The dielectric constant and indices of refraction for each PVB solution were expressed relative to the corresponding values for the pure solvent in the incremental quantities $\epsilon - \epsilon_1$ and $n^2 - n_1^2$. These quantities were then plotted against the weight fraction w of the polymer in solution. Typical curves are shown in Figure 1; the slope of the curves obtained in the limit $w \to 0$ gave values of the derivatives of eq 1. Since the values of $n^2 - n_1^2$ in 1-methylnaphthalene were practically 0.00 in all the intervals of temperatures, $d(n^2 - n_1^2)/dw$ was taken to be null for all the temperatures. On the other hand, the slope $d(n^2 - n_1^2)/dw$ in dioxane did not show a noticeable dependence on temperature.

The dipole moment ratio $\langle\mu^2\rangle/xm^2$ was calculated from the dielectric results by using the equation of Guggenheim and Smith[25,26]

$$\langle\mu^2\rangle/xm^2 = \frac{27kTM}{(xm^2)4\pi\rho_1 N_A(2+\epsilon_1)^2}\left[\frac{d(\epsilon-\epsilon_1)}{dw} - \frac{d(n^2-n_1^2)}{dw}\right] \quad (1)$$

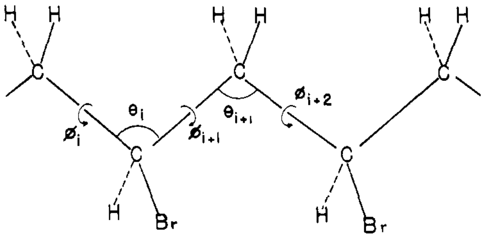

Figure 2. Segment of meso PVB chain shown in its planar all-trans conformation.

where k is the Boltzmann constant, T is the absolute temperature, $M = xM_0$ (where M_0 = 106.92 is the molecular weight of the repeating unit), N_A is Avogadro's number, and ρ_1 is the density of the solvent. The magnitude of the dipole moment corresponding to the repeat unit was taken to be 2.08 D, the observed value of the dipole moment of ethyl bromide in the gas phase.[14]

All of the values obtained are given in the last column of Table I. It can be observed that the value of the dipole moment ratio at 50 °C for sample A in dioxane is similar to that obtained at 30 °C for sample B. Both values are significantly higher than the value of the dipole moment ratio of sample A measured in 1-methylnaphthalene. This difference should not be attributed to long-range perturbations whose effects should be null in PVB because, for these chains, the resulting dipole moment of each repeat unit lies in a plane bisecting one of the skeletal bond angles.[27-30] It is more reasonable to expect that such a difference is due to specific solvent effects possibly arising from the dependence of the coulombic part of the conformational energy on the dielectric constant of the medium as well as from the changes in conformational distribution due to a weak complex ion of the solvent molecules with the segments of the polymer chains. These solvent interactions also have a marked effect on the dimensions and dipole moments of other polar chains such as poly(dimethylsiloxane)[30-33] and poly(propylene sulfide).[9,10] Finally, it should be stressed that the present experimental results in dioxane are quite in line with those obtained by Le Fèvre and Sundaran[34] in the same solvent for PVB fractions of high solubility.

It is not possible to give a value for the temperature coefficient of the dipole moments due to the increasing instability of the polymer with increasing temperature. Actually, this coefficient is generally a small quantity, corresponding to changes of only a few tenths of a percent per degree. Therefore, even for stable polymers the temperature coefficient is difficult to determine with accuracy.

Theoretical Calculations

A segment of an isotactic PVB chain in the all-trans conformation is shown in Figure 2. The conformational energies were calculated with the use of Lennard-Jones potential functions for estimating nonbonded interactions, with the same parameters used for other vinyl chains. Thus values of 1.53, 1.10, and 1.95 Å were taken for C–C, C–H, and C–Br bond lengths, respectively.[13,35] The skeletal CH_2–C–CH_2 and C–CH_2–C bond angles were taken to be 112 and 114°, respectively;[35] all remaining bond angles were considered to be tetrahedral. The attractive term c_{ij} of the potential function was calculated according to the Slater–Kirkwood formula.[35,37] The a_{ij} values of the repulsive term were assigned so as to minimize the pair potential V_{ij} for a given pair of atoms when their distance r_{ij} is set equal to the sum of the corresponding adjusted van der Waals radii. The parameters used to compute a_{ij} and c_{ij} are given in Table II. A threefold intrinsic torsional potential, with a barrier of 2.8 kcal mol^{-1},[38] was assigned

Table II
Parameters Used for Nonbonded Interactions

atom	van der Waals radius, Å	effective no. of electrons	polarizability, Å^3
C	1.8	5	0.93
H	1.3	0.9	0.42
Br	2.05	23	3.34

to the rotations ϕ_i and ϕ_{i+1}. Electrostatic contributions were calculated by assigning partial charges ($q_C = -q_{Br} = 0.223$) to atoms joined by the C–Br bond;[39,40] as usual, a value of 3 was given to the effective dielectric constant.[41] In some calculations a truncation procedure, similar to that used in PVC, was followed to allow for the conformational dependence of solvent interaction.[35] That is, the potential V_{ij} was truncated when the distance r_{ij} reached a given value σ. It was found, however, that, as in the case of PVC,[1] the statistical factors are scarcely affected by the value of σ chosen; therefore, no truncation procedure was used in the present study.

The molecule 2,4-dibromopentane was used as a model compound for a dyad of PVB. Calculations were performed for meso and racemic configurations, allowing for rotation over two consecutive skeletal bonds (ϕ_i, ϕ_{i+1} in Figure 2). A preliminary calculation was conducted by using increments of 20° in both rotational angles in order to locate the approximate position of the minima; a second calculation was then carried out for regions of ±40° over each minimum at intervals of 5°, and the partition functions, averages of energies, and rotational angles were computed at 300 K.

Comparison of the partition functions Z with the statistical weight matrices for vinyl polymers[42] allows the calculation of all statistical weights (e.g., $\eta = Z_{tg}{}^{m}/Z_{gg}{}^{r}$), which are then written as Boltzmann exponentials of the corresponding energies (e.g., $\eta = \exp(-E_\eta/RT)$); the results of these calculations were $E_\eta = -0.15$, $E_\tau = 0.5$, $E_\omega = 2.5$, $E_{\omega'} = 2.0$, and $E_{\omega''} = 3.6$ kcal mol^{-1}. The conformational averages of ϕ_i and ϕ_{i+1} differed from the perfectly staggered values (i.e., 0, +120, and −120°) by less than 5° in all instances; these staggered values were thus used in all calculations.

The resulting statistical weights are similar to those of PVC,[1] the major difference being in the value of η (4.2 for PVC and 1.3 for PVB). Standard methods of matrix multiplication[31,33] were used to compute $\langle \mu^2 \rangle$ and $\langle r^2 \rangle_0$ of chains consisting of up to $x = 200$ repeat units, with Bernoullian placement of meso and racemic dyads at different tacticities (i.e., at different values of the total fraction of isotactic dyads, p_i). Dipole ratios $D_x = \langle \mu^2 \rangle / xm^2$ and characteristic ratios $C_x = \langle r^2 \rangle_0 / nl$ (with $n = 2x$) were computed and extrapolated to $x \rightarrow \infty$ by plotting D_x and C_x vs. $1/x$; the increase of both ratios from $x = 200$ to ∞ was of the order of 1%. Twenty chains were generated for intermediate tacticities, and the averages of their results are represented in Figures 3 and 4, where vertical bars represent standard deviations in the averages. Figure 3 also shows the dipole moment ratios obtained for different orientations, indicated by β, of the dipole moment m of the repeat unit. Earlier studies carried out on PVC[1] show that a reasonable value for the angle β should lie in the interval 10–20°.

Discussion

The major difference between the conformational characteristics of PVC and PVB lies in the high value of η for the former polymer[1] (4.2) in comparison with the value of this parameter for the latter (1.3). This difference is due to the difference in size between Cl and Br atoms; in a racemic dyad in its tt conformation, there is still a significant interaction between the Br and the H atom attached to the next tertiary C, and even between this tertiary C and Br, these interactions are relieved in the gg conformation. Despite these interactions, tt is the preferred conformation, but the difference with gg is much smaller than in the case of PVC, where such interactions are negligible. For a meso dyad, the value of η is not so important, since it is still much higher than the value of ω, and therefore, the conformations tg and gt are by far the preferred ones.

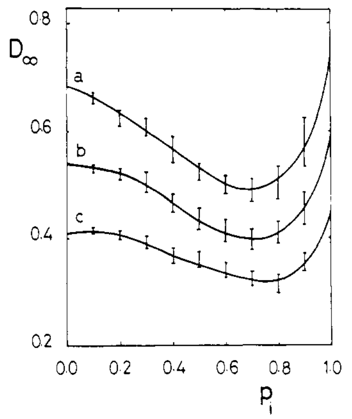

Figure 3. Theoretical values of D_∞ as a function of the isotactic fraction p_i at $T = 30$ °C obtained with (a) $\beta = 0$, (b) $\beta = 5°$, and (c) $\beta = 10°$. Results shown for $0 < p_i < 1$ are averages over 20 Monte Carlo chains; values of standard deviations of these averages are denoted by vertical bars.

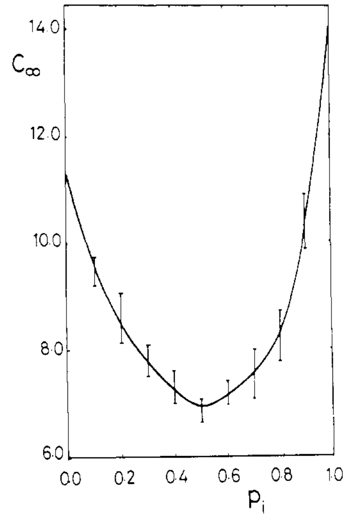

Figure 4. Dependence of the theoretical values of C_∞ on the isotactic fraction p_i at $T = 30$ °C. See legend for Figure 3.

Let us examine now how the value of η affects the results of the dipole moment ratio for syndiotactic PVC and PVB. A high value of η means that the probability of tt conformations is much higher than that of gg, and as a consequence, the polymer will have longer ttt... sequences along the chain. These sequences are mainly responsible for the increase in $\langle \mu^2 \rangle$ and the strong dependence of D_∞ on β, since the projections of m on the backbone plane are additive for these sequences. However, for values of η close to unity, the tt and gg conformations have almost the same probability, and the fraction of long ttt... sequences is very small, the addition of projections of m takes place practically on isolated dyads, and hence the value of $\langle \mu^2 \rangle$ is low.

For the reasons outlined above, the comparison between theoretical and experimental results requires a close ex-

Table III
Sensitivity of the Theoretical Value of the Dipole Ratio to the Parameters Used in Calculations Written As $10^3[\delta \ln D_\infty/\delta(\text{parameter})]$

	tacticity (p_i)					
parameter	0.0	0.2	0.4	0.6	0.8	1.0
E_η	−2488.4	−1577.5	−1118.5	−842.3	−167.0	−27.7
E_τ	−4.7	−4.8	−48.2	−71.2	18.3	268.9
E_ω	−9.5	12.4	−16.8	29.3	79.4	279.9
$E_{\omega'}$	−156.3	−130.5	−152.4	−99.5	−39.8	268.7
$E_{\omega''}$	2.3	−33.1	−34.0	20.2	11.9	17.6
θ	9.0	1.1	−4.5	−19.4	−14.4	−31.9
$\Delta\phi$	32.9	27.9	20.6	22.8	30.2	30.4
T	−0.2	−0.1	0.6	1.2	3.4	−4.8
			$\beta = 10°$			
E_η	−2313.7	−1368.1	−691.2	−421.9	−29.5	−18.2
E_τ	−15.2	−24.3	−53.4	−133.4	−91.6	152.9
E_ω	−18.1	4.0	−4.3	−25.9	83.0	270.3
$E_{\omega'}$	−244.1	−182.8	−164.1	−225.5	−145.7	152.4
$E_{\omega''}$	1.0	3.9	−1.1	−41.1	−51.3	5.7
θ	18.6	10.5	−6.4	−5.7	−12.8	−30.4
$\Delta\phi$	45.1	33.4	28.8	18.3	37.4	41.8
T	0.5	0.2	1.4	−0.8	2.6	−3.7

Table IV
Sensitivity of the Theoretical Value of the Characteristic Ratio to the Parameters Used in Calculations Written As $10^3[\delta \ln C_\infty/\delta(\text{parameter})]$

	tacticity (p_i)					
parameter	0.0	0.2	0.4	0.6	0.8	1.0
E_η	−1077.7	−1000.8	−879.7	−704.9	−178.1	−156.7
E_τ	77.5	80.8	92.9	182.7	220.9	626.3
E_ω	80.8	39.7	17.7	52.5	72.0	259.4
$E_{\omega'}$	0.9	2.6	32.7	81.1	190.1	548.4
$E_{\omega''}$	5.3	36.1	34.9	1.3	0.8	30.7
θ	8.7	13.3	19.0	27.4	26.0	32.7
$\Delta\phi$	−27.5	−23.9	−24.4	−21.8	−1.2	−3.7
T	−1.2	−0.1	−0.4	−4.4	−1.7	−7.1

amination of the stereochemical composition of PVB chains. In a recent work, Cais and Brown[18] examined the stereoconfiguration of PVB by NMR and found that racemic placement becomes more likely with decreasing polymerization temperature, just as in PVC. For samples obtained at 30 °C, the probability of meso dyads is 46%, which is in very good agreement with our results. The value of 0.53 found for the dipole moment ratio of PVB chains in dioxane is in good agreement with the value 0.57–0.52 obtained by the RIS model assuming that $\beta = 0$ and $p_i = 0.4$–0.5. The experimental result $D_\infty = 0.45$ obtained in 1-methylnaphthalene requires a value of $\beta \simeq 5°$. As was indicated above, much of the discrepancy between the results for both solvents might be due to specific solvent effects, which are probably greater in 1-methylnaphthalene. Le Fèvre and Sundaran[34] measured the dipole moment for six PVB fractions that, on the basis of their solubility characteristics, would be expected to have increasing syndiotacticity. The samples showed an increase of dipole moment ratio from 0.49 for fraction 1 to 0.80 for fraction 6. The high value of D_∞ obtained for the last fractions should be considered, however, with caution. Actually, obtaining these fractions by extraction probably involved considerable handling of the polymer (at least in the fractions of higher molecular weight), so that possible oxidative effects that enhance the polarity of the chains should not be disregarded.

Comparison between theoretical and experimental results of D_∞ indicates that a value of $\beta = 0$–$5°$ is required for PVB chains. This value is significantly lower than the $\beta = 10$–$20°$ needed for PVC chains.[1] Actually, a lower value of β for PVB than for PVC was expected because of the smaller partial charge located over the tertiary carbon of the former polymer due to the longer C–Br bond length compared with that of C-Cl. However, the range $\beta = 0$–$5°$ obtained here is probably a lower bound because of difficulties in the experimental measurements that might increase the polarity of the samples.

Values of the characteristic ratio $C_n = \langle r^2\rangle/nl^2$ were calculated for PVB chains as a function of isotactic content. The results, plotted in Figure 4, show that perfectly isotactic chains have the largest value of C_∞. The reason is that for isotactic chains the preferred conformation is a helix tgtg, which gives a highly expanded molecule. Syndiotactic placements in the chain, even in a small proportion, cause disruptions of the helix, giving rise to small fragments with different orientations that reduce the dimensions of the chains. There are few experimental data with which to compare the theoretical results. The most reliable determination of C_n for this polymer is based on a study of a number of fractions in 83:17 THF/methanol.[15,16] Molecular weights and intrinsic viscosities determined for these fractions at the Θ point gave a value of $\langle r^2\rangle/nl^2$ of 6.6. As can be observed in Figure 3 this experimental value of C_n is in good agreement with the calculated value 7.3–6.9 for chains with $p_i = 0.4$–0.5. The value of 13.1 reported by Kratky and Porod[44] for the characteristic ratio of the polymer is in disagreement with our calculations unless the determination of this parameter was carried out on polymeric chains with an isotactic content of 0.9–1.0. This case, however, is very improbable because it was shown elsewhere[18] that the isotactic content of PVB chains obtained by radical polymerization lies in the range 0.386 (at −78 °C) to 0.477 at +100 °C.

The sensitivity of both D_∞ and C_∞ to the different conformational energies is shown in Tables III and IV. The

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data concerning the dipole moments were obtained by assuming that $\beta = 0$ and 10°. The absolute values of the temperature coefficient of D_∞ and C_∞ obtained from Tables III and IV are smaller than those corresponding to PVC due to, among other reasons, the small contribution of E_η in the case of PVB chains. The value of $10^3(\mathrm{d}\ln\langle\mu^2\rangle/\mathrm{d}T)$ for PVB chains with $p_i = 0$ is -0.2 and for those with $p_i = 1$ the value is -4.8. For chains with a tacticity similar to that of the chains used in the present study the value of $\mathrm{d}\ln\langle\mu^2\rangle/\mathrm{d}T$ is 0.6×10^{-3} K^{-1}. The temperature coefficient of the molecular dimensions of PVB chains is negative for all stereochemical compositions and has an unusually high value of -7.1×10^{-3} K^{-1} for isotactic chains. This is due to the fact that an increase in temperature also increases the disruptions of tgtg... conformations and, for the reasons explained above, drastically decreases the value of the molecular dimensions.

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Phenomenology of Self-Diffusion in Star-Branched Polyisoprenes in Solution

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ABSTRACT: We have measured polymer and solvent self-diffusion at 50 °C in equiarmed star-branched polyisoprenes of low molecular weights in solution with C_6F_5Cl and CCl_4, using pulsed-gradient spin-echo methods supplemented by NMR T_2 relaxation. In solutions and melts of stars with M(arm) $\simeq 10^4$ and $f \leq 18$, entanglements are less pronounced than in linear polymers of equal molecular weight. Polymer diffusion depends differently on M(arm) and f, the f dependence becoming weak at high f at all solvent concentrations. In dilute solution, diffusion behavior shows that these stars are relatively highly expanded; at high polymer concentrations, segmental diffusion mechanisms begin to contribute. Free volume theories explain solvent but not polymer diffusion.

Introduction

Star-branched polymers with arms of equal length are the simplest model systems that allow the effect of branching to be studied in the absence of the usual architectural randomness. This permits the most convenient testing of theories describing branched polymer behavior. Thus, star-branched polymers have attracted considerable experimental[2-4] and theoretical[5-12] attention, much of which has been directed toward their hydrodynamic and rheological properties. Of particular interest are their

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