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Effects of Stereochemical Structure on Distribution Functions for Short Polypropylene and Poly(vinyl chloride) Chains

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The spatial configurations of low molecular weight polymers are of considerable interest, since short-chain molecules occur in a variety of materials, including thermosets,[1,2] bimodal elastomers,[3] adhesives,[1] and thickening agents.[2] Of foremost importance in characterizing chains of this type is the distribution $W(r)$ of their end-to-end separation r.[4-6] Such information would of course not be limited to short chains but would also be relevant to short sequences within long chains[7] and thus to radiation scattering by high molecular weight polymers.

Unlike long flexible chains, short chains do not have distributions that can be approximated by the Gaussian function.[4-9] Fortunately, better approximations[10-14] to $W(r)$ can now be obtained by using Monte Carlo simulations[7-9] based on very realistic rotational isomeric state (RIS) models[5] of the chain molecules of interest. In this way the calculated distributions reflect the geometric characteristics and conformational preferences of the particular chain structure of interest.

The purpose of the present investigation is to use the Monte Carlo–RIS technique[7-14] to obtain distributions for two important vinyl polymers, namely polypropylene (PP) $-[CHCH_3CH_2]-$[5-15] and poly(vinyl chloride) (PVC) $-[CHClCH_2]-$.[5,16-18] Since these two chains contain chiral bonds, the effects of stereochemical structure on $W(r)$ are of considerable interest. Also of interest are comparisons among the distributions of polyethylene (PE) $-[CH_2CH_2]-$,[8-10] PP, and PVC since this will document the effects of replacing one hydrogen atom in the PE repeat unit by the relatively large methyl group or the somewhat smaller chlorine atom. Since one goal of the investigation was to characterize the effect of helicity on vinyl distribution functions, the simplest three-state scheme[5] was employed. In this approximation isotactic PP chains are predicted to have a preference for regular helical conformations. The more realistic five-state scheme[15] does not predict this preference, and in this sense the present calculations should probably be considered more illustrative than quantitative for the PP case.

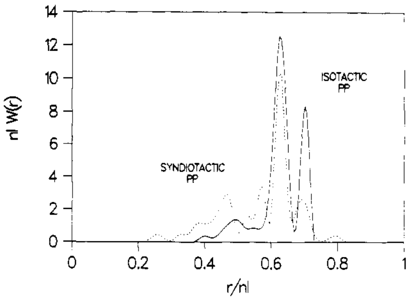

Figure 1. Distributions at 25 °C for the end-to-end separation r of polypropylene chains having $n = 40$ skeletal bonds and of length l. The two limiting stereochemical forms characterized are the syndiotactic (----) and the isotactic (—), with replication probabilities of 0.00 and 1.00, respectively.

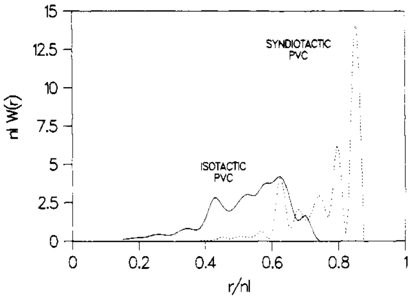

Figure 2. Distributions for poly(vinyl chloride) chains; see legend to preceding figure.

Theory

For all three polymers the bond length l was taken to be 0.153 nm and the bond angle supplement θ to be 68°.[5,15-18] Rotational states were located at values of the dihedral angle ϕ of 0, 120, and −120°, such states being termed trans (t), gauche positive (g^+), and gauche negative (g^-), respectively. Chains having $n = 20$ and 40 skeletal bonds were investigated.

In the case of PP and PVC, the stereochemical modifications studied were the syndiotactic, atactic, and isotactic, corresponding to replication probabilities P_m of 0.00, 0.50, and 1.00, respectively. For the atactic polymers, 80 000 chains having typical stereochemical structures were generated with a Monte Carlo technique,[17] with rejection of any chains having structures differing from that expected for $P_m = 0.50$ by more than ±0.10.

Characterization of conformations in PP and PVC requires three statistical weight factors which are described in detail by Flory.[5] The first, η, accounts for conformations in which the side group is syn (g^+ or g^-) to a CH group separated from it by three bonds, relative to a factor of unity for conformations in which a CH_2 group replaces the side group.[18] The second, τ, is for conformations in which both the side group and a CH_2 group are syn with respect to the CH. Interactions of second order, involving rotations about two consecutive skeletal bonds, were represented by a single average factor ω.

For PE, the factor σ is used for conformations in which a pair of CH_2 groups separated by three bonds are syn to one another and ω for the second-order interactions, as usual.[5,8,10]

Results and Discussion

Calculations were carried out for a temperature of 25 °C, using the following values for the statistical weight factors: For PP, $\eta = 1.0$, $\tau = 0.05$, and $\omega = 0.010$;[5] for PVC, $\eta = 4.5$, $\tau = 0.50$, and $\omega = 0.050$;[5,16-18] for PE, $\sigma = 0.43$, and $\omega = 0.034$.[5,10] Each set of statistical weights were nor-

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Table I
Values of the Most Probable End-to-End Separation and the Characteristic Ratio at 25 °C

		polypropylene[b]			poly(vinyl chloride)[b]			
property[a]	n	syn	atactic	iso	syn	atactic	iso	polyethylene
$(r/nl)_{\mathrm{mp}}$	20	0.62	0.58	0.62	0.85	0.65	0.58	0.60
	40	0.62	0.45	0.62	0.85	0.50	0.63	0.45
$\langle r^2\rangle_0/nl^2$ [c]	20	6.19	5.33	7.43	11.2	7.13	5.57	5.27
	40	7.86	6.45	11.4	19.3	9.83	7.21	6.20

[a] Normalized by using the number n of skeletal bond of length l. [b] Syndiotactic, atactic, and isotactic modifications, with stereochemical replication probabilities of 0.00, 0.50, and 1.00, respectively. [c] The subscript zero acknowledges that excluded-volume interactions are not taken into account in simulations of this type.

malized to probabilities and then used in a Monte Carlo calculation to generate 80 000 typical spatial configurations. They were grouped on the basis of their values of the end-to-end separation normalized by nl, the entire range $r/nl = 0$–1 being divided into 20 intervals. Plots of occupancy numbers against r/nl directly gave the desired distributions.[10–14]

The results obtained for the PP and PVC chains having 40 skeletal bonds are shown in Figures 1 and 2. Most probable values of r/nl (obtained from the locations of the distribution maxima) and values of the second moment (given as the *characteristic ratio* $\langle r^2\rangle_0/nl^2$)[4,5] are presented in Table I. The multimodal nature of some of the distributions could be due to the limited number of states permitted in the RIS approximation[13] applied to the relatively small number of skeletal bonds or to a preference for certain regular conformations[14] (e.g., helices). The latter effect is particularly pronounced in the case of isotactic PP, which forms 3_1 helices[5] ($r/nl = 0.67$), thus decreasing the number of virtual bonds in the chain,[14] and in the case of syndiotactic PVC, which prefers the all-trans planar zigzag conformation[16–18] ($r/nl = 0.83$) that similarly decreases its number of virtual bonds.

As can be seen from Figure 1 and the corresponding information for $n = 20$ and 40 in Table I, substitution of the relatively large CH_3 group into the PP repeat unit in a syndiotactic or atactic manner has relatively little effect on $(r/nl)_{\mathrm{mp}}$ and $\langle r^2\rangle_0/nl^2$. Isotactic substitution, however, could give rise to the helicity already mentioned and thus a rather sharp distribution[14] and increased values of these two parameters. The opposite effect is observed in the case of PVC, where the smaller chlorine substituents have a particularly marked effect on the syndiotactic form. In this case the syndiotactic PVC form has the all-trans conformation as its lowest energy state. The all-trans form leads to the largest possible value of r/nl, as can be seen in Figure 2.

The multimodal distributions could lead to interesting results in calculations of scattering intensities for short PP and PVC chains in solutions or in the undiluted state and of elastomeric properties of such chains in cross-linked networks.[11]

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