of the orientation parameter determined by the hypersonic velocity obtained from the Brillouin scattering with that obtained from Raman scattering and birefringence indicates the inadequacy of Moseley's model, which relates the sonic velocity with the orientation parameter. We have discussed the effect of crystallinity and chain segment orientation as well as the effect of pair orientation correlation on the elastic constants. The pair correlation effect is left out in Moseley's model. Further experimental work together with theory is needed to develop a reliable microscopic model for the determination of the orientation parameter from Brillouin scattering for the deformed semicrystalline polymer.

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End Effects and Asymmetries of the Distribution of Chain Atoms in Polymethylene Chains Perturbed by Attachment to an Impenetrable Interface

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ABSTRACT: Polymethylene chains in which the chain atom at one end is attached to an impenetrable interface have been studied by using a rotational isomeric state model which accurately reproduces configuration-dependent physical properties of the unperturbed chain in free solution. Properties investigated are the mean-square radius of gyration, asymmetry of the distribution of chain atoms, and the probability of observing a particular rotational state at bonds near the site of attachment to the impenetrable interface. Limiting behavior of infinitely long chains was characterized by studying finite chains with up to 1000 bonds. Attachment of the chain to an impenetrable interface produces only a small expansion in the mean-square radius of gyration. The mean-square end-to-end distance, in contrast, increases significantly due to the perturbation produced by the impenetrable interface. Nonidentity of the effect of the interface on the mean-square end-to-end distance and radius of gyration should be kept in mind in any experimental characterization of the thickness of an attached polymer layer. The increase in the mean-square radius of gyration is not isotropic. It serves to change the symmetry of the average distribution of chain atoms about the first two bonds in the chain from spherical to that of a prolate ellipsoid. Individual configurations become, on the average, more asymmetric. The probability for observation of a trans placement is not changed when a long polymethylene chain is attached to an impenetrable interface. End effects on the probability for a particular placement extend only about 20 bonds into the chain. The maximum disturbance of this probability is only slightly greater than that seen with an unperturbed chain in free solution.

If bond lengths and bond angles in the chain molecule are considered to be constant, its configuration becomes a function solely of the rotational state occupied by internal bonds in the chain. One means of characterizing the rotational state occupancy is through p_η, the first-order a priori probability that an internal bond will occupy rotational state η.[1] For an unperturbed simple linear chain (e.g., polymethylene) containing a large number of bonds, p_η should be identical with the a priori probability for occupancy of rotational state η by bond i (denoted $p_{\eta;i}$) for most i. Exceptions are provided only by bonds sufficiently close to either end of the chain so that they are influenced by end effects. A measure of the importance of end effects is therefore given by the dependence of $p_{\eta;i}$ on i. End effects are found to be small in the case of unperturbed polymethylene.[1] If the number of bonds, n, is large, p_η differs significantly from $p_{\eta;i}$ only for i less than five and i greater than $n - 4$. Similar behavior is exhibited by the second-order a priori probabilities, $p_{\xi\eta}$ and $p_{\xi\eta;i}$. Here $p_{\xi\eta;i}$ denotes the a priori probability that bond i is in rotational state η, with bond $i - 1$ simultaneously in rotational state ξ.

In the spirit of first- and second-order a priori probabilities, p_η and $p_{\xi\eta}$, we can also define $(n - 2)$-order a priori probabilities, which equate to the probability for observation of a specified chain configuration. Perturbation of the chain will reduce certain of the $(n - 2)$-order a priori

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probabilities while increasing other of these probabilities. The modification produced in the $(n - 2)$-order a priori probabilities need not, however, require alteration in a priori probabilities of low order. For example, the perturbation produced by the intramolecular excluded-volume effect for a chain molecule in solution certainly demands a change in the $(n - 2)$-order a priori probabilities. Self-avoiding-walk studies, however, show that the perturbation need not modify the probability for a trans placement.[2] Consequently the well-known chain length dependence of the expansion factor[3] can be reproduced by using matrix calculations in which p_η is unaffected by the perturbation.[4]

A different type of perturbation is produced when the excluded volume is not of intramolecular origin but arises instead through attachment of one end of the chain to an impenetrable interface.[5] This type of pertubration should be expected to modify $p_{\eta;i}$ and $p_{\xi\eta;i}$ for bonds near the end at which the chain is attached. If this end effect were to propagate a substantial distance into the chain, changes would also be seen in p_η and $p_{\xi\eta}$. One objective of the present study is to examine the behavior of these a priori probabilities when a polymethylene chain is perturbed by attachment of one end to an impenetrable interface.

Perturbation of the chain by the impenetrable interface is known to produce an increase in the mean-square end-to-end distance.[5,6] The increase in dimensions arises from extension of the end-to-end distance in the direction normal to the interface.[5,6] This behavior suggests an alteration in the asymmetry of the chain, as assessed by ratios of the principal moments of the averaged inertia tensor. If components of this tensor are averaged in a coordinate system defined by the first two bonds in the chain, long flexible free chains are found to have spherical symmetry.[7] The symmetry might be expected to change to that of a prolate ellipsoid if the first atom in the chain is attached to an impenetrable interface. If an alternative measurement of asymmetry, based on averages of the corresponding principal moments of the inertia tensors for individual chain configurations, is employed, it is not immediately obvious that asymmetries of free and attached chains will differ. A second objective is to evaluate the asymmetry of attached chains from both points of view.

Calculations

Representative Samples of Chains. A rotational isomeric state model was used for the polymethylene chain.[8,9] The bond length, l, is 153 pm, and trans placements have a dihedral angle, φ, of 0°. Most calculations were performed by using $\theta = 68°$ for the supplement of the bond angle and $\varphi = \pm 120°$ for gauche states. In a few selected cases, θ was 70.5° or $\varphi_{g\pm}$ was $\pm 112.5°$. These latter cases are specifically noted in the text.

Representative chains were grown by Monte Carlo methods, using a random number generator and the conditional probabilities, $q_{\xi\eta}$ shown in matrix for below.

$$\mathbf{Q}_{\xi\eta} = \begin{bmatrix} 0.5396 & 0.2302 & 0.2302 \\ 0.6830 & 0.2914 & 0.0256 \\ 0.6830 & 0.0256 & 0.2914 \end{bmatrix}$$

Here $q_{\xi\eta}$ denotes the probability a given bond will occupy rotational state η, given that its predecessor is in rotational state ξ. Rows index the state of the preceding bond, columns index the state of the bond in question, and the order of indexing is trans (t), gauche$^+$ (g$^+$), gauche$^-$ (g$^-$). The same expression for $\mathbf{Q}_{\xi\eta}$ was used for bonds 3 to $n - 1$. Only the top row was used for bond 2. This set of conditional probabilities will not properly reflect the small end effects in unperturbed polymethylene. It will, however, permit an accurate reproduction of the unperturbed dimensions of long polymethylene chains.

Certain of the chains grown by the above procedure must be eliminated if one chain atom is attached to an empenetrable interface. This objective was achieved by establishing a Cartesian coordinate system centered on the atom at one end of the chain. The X axis is considered to run from this atom to the second chain atom, and the Y axis is in the plane of the first three chain atoms and oriented so that the y coordinate of the third chain atom is positive. Growing chains were discarded if any atom had a negative x coordinate. The surface is therefore considered to be an impenetrable plane. The first chain atom is located on the surface, and the first bond is normal to the surface. A more detailed description of this method has been given in an earlier study of polymers attached to an inert surface.[5]

Chains with n ranging up to 1000 were studied. The number of chains started at each n ranged from 5000 to 65000. Survivors were divided into five (occassionally four) groups. Configuration-dependent properties were averaged for chains in each group. Reported averages are those for the five (or four) groups, and standard deviations are those arising from differences in averages for the groups. Error bars in figures denote ±1 standard deviation, and the standard deviation for values cited in the text is presented in parentheses.

Configuration-Dependent Properties. A priori probabilities, p_η, $p_{\eta;i}$, $p_{\xi\eta}$, and $p_{\xi\eta;i}$, were obtained by simply noting placements for the bonds in the surviving chains. The persistence vector, $\mathbf{a}$, is the average of the vector from the zeroth to the nth chain atom. The mean-square distance between these atoms is denoted by $\langle r^2 \rangle$. The center-of-mass vector, $\mathbf{g}$, for a specified configuration is

$$\mathbf{g} = (n + 1)^{-1} \sum_{i=0}^{n} \mathbf{r}_{0i} \tag{1}$$

where $\mathbf{r}_{0i}$ denotes the vector from the zeroth to the ith chain atom. Its average is denoted by $\langle \mathbf{g} \rangle$. Both $\mathbf{a}$ and $\langle \mathbf{g} \rangle$ are expressed in the coordinate system defined by the first two bonds in the chain.

The inertia tensor for each configuration was calculated as

$$\mathbf{S}_{x2} = (n + 1)^{-1} \sum_{i=0}^{n} \mathbf{r}_{0i}^{x2} - \mathbf{g}^{x2} \tag{2}$$

where x2 as a superscript denotes the self-direct product, and $\mathbf{S}_{x2}$ is generated as a column with the nine elements in reading order. The squared radius of gyration, s^2, is the trace of the 3 × 3 representation of $\mathbf{S}_{x2}$, and $\langle s^2 \rangle$ denotes its average over all surviving chains. Diagonalization of $\mathbf{S}_{x2}$ via an appropriate similarity transform yields the principal moments, $L_1^2 \geq L_2^2 \geq L_3^2$, their sum being

$$s^2 = L_1^2 + L_2^2 + L_3^2 \tag{3}$$

Asymmetry of a particular chain configuration can be assessed by examination of the departures from unity of L_2^2/L_1^2 and L_3^2/L_1^2.

The significance to be attributed to an average asymmetry of all surviving chains depends on whether averaging is achieved before or after the similarity transformation. The average tensor obtained by averaging corresponding elements of $\mathbf{S}_{x2}$ for all surviving configurations is denoted by $\langle \mathbf{S}_{x2} \rangle$. Averaging is achieved in the coordinate system established by the first two bonds in the chain. In this coordinate system the surface to which the chain is attached lies in the YZ plane. Diagonalization of $\langle \mathbf{S}_{x2} \rangle$ yields

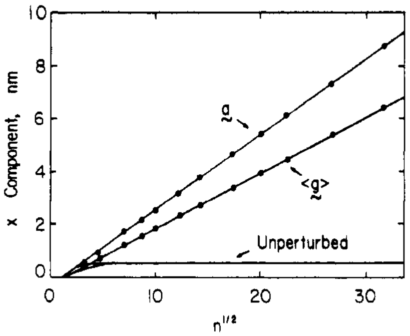

Figure 1. x component of **a** and $\langle \mathbf{g} \rangle$ for polymethylene chains perturbed by attachment to an impenetrable interface. Also depicted are the x components of **a** and $\langle \mathbf{g} \rangle$ for unperturbed polymethylene chains, as reported by Yoon and Flory.[7]

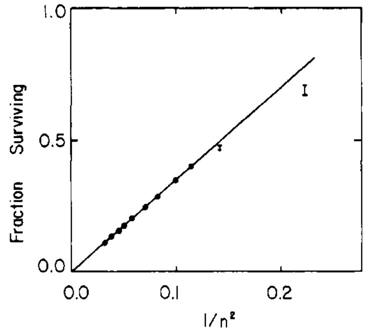

Figure 2. Fraction of the chains surviving as a function of n^{-2}. Filled circles have radius equal to or greater than one standard deviation.

principal moments denoted by $\langle S_{2;i} \rangle$. Ratios of these principal moments reflect the asymmetry of the average distribution of chain atoms in the coordinate system rigidly attached to the first two bonds in the chain. Hence the $\langle S_{2;i} \rangle$ measure the asymmetry of the average distribution from the site at which the chain is attached to the impenetrable interface.

An alternative assessment of asymmetry is provided by averages, $\langle L_i^2 \rangle$, of corresponding principal moments of the individual inertia tensors. Thus $\langle L_1^2 \rangle$ denotes the average value of the largest principal moment for each configuration. This method retains the asymmetry of individual configurations. Ratios formed from the $\langle L_i^2 \rangle$ reflect the average instantaneous asymmetry of surviving chains.

Results and Discussion

Validity of the Representative Samples of Chains. Two of the configuration-dependent physical properties evaluated (**a** and $\langle r^2 \rangle$) have been independently calculated by Feigin and Napper.[5] Behavior of these properties for the samples described here is identical with that reported in their earlier study. Thus $\langle r_2 \rangle / nl^2$ is convergent, but the length of the persistence vector is divergent. At $n = 1000$, $\langle r^2 \rangle / nl^2$ is 8.9 (0.2), which is nearly $^4/_3$ the value obtained for unperturbed chains in free solution. In all cases the z component of **a** differs from zero by less than one standard deviation. As n increases, the y component approaches 0.4 nm, but the x component grows without limit. Behavior of the x component of **a** is depicted in Figure 1.

Chain Attrition. Figure 2 depicts the fraction of the chains started which successfully avoid contact with the impenetrable interface. Attrition becomes more severe as n increases. The fraction surviving becomes inversely proportional to n^2 when n is greater than about 75. As n approaches infinity, the fraction of the chains surviving approaches zero.

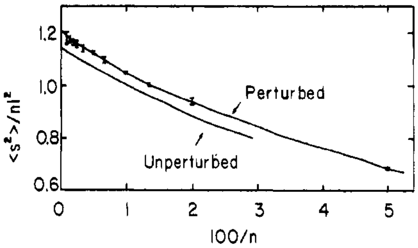

Figure 3. Mean-square radii of gyration for polymethylene chains attached to an impenetrable interface. Also depicted is the behavior of an unperturbed chain, as reported by Jernigan and Flory.[11]

Average Center-of-Mass Vector. The persistence vector and average center-of-mass vector for unperturbed chains converge to the same limit at large n.[7] This limit is attained more rapidly by **a** than by $\langle \mathbf{g} \rangle$.[7] When one end of the chain is attached to an impenetrable interface, $\langle \mathbf{g} \rangle$ remains smaller than **a** even as n becomes large. Nonidentity of $\langle \mathbf{g} \rangle$ and **a** at large n arises solely from the behavior of their x components. In each case this component becomes proportional to $n^{1/2}$ at large n, as is shown in Figure 1. However, the x component for $\langle \mathbf{g} \rangle$ is only about $^3/_4$ as large as the x component of **a**.

In a large unperturbed chain, the nth chain atom occurs with equal probability in any direction from the center of mass. Hence **a** and $\langle \mathbf{g} \rangle$ become identical at large n. The presence of the impenetrable interface preferentially eliminates configurations whose nth chain atom has an x component smaller than the x component of $\langle \mathbf{g} \rangle$. Surviving chains therefore have larger **a** and $\langle \mathbf{g} \rangle$ than unperturbed chains, with the increase in **a** being larger than that in $\langle \mathbf{g} \rangle$. Inequality of **a** and $\langle \mathbf{g} \rangle$ at large n suggests $\langle r^2 \rangle$ and $\langle s^2 \rangle$ are affected differently by the perturbation produced by the impenetrable interface.

Mean-Square Radius of Gyration. Figure 3 depicts behavior of $\langle s^2 \rangle / nl^2$ for polymethylene chains perturbed through attachment of one end to an impenetrable interface. Also shown are values for unperturbed chains, as computed by Jernigan and Flory.[11] The impenetrable interface produces only a small expansion of the radius of gyration. If α_s is defined as

$$\alpha_s^2 = \langle s^2 \rangle / \langle s^2 \rangle_0 \qquad (4)$$

then α_s approaches a value of about 1.028 as n goes to infinity. In contrast, α_r, defined as

$$\alpha_r^2 = \langle r^2 \rangle / \langle r^2 \rangle_0 \qquad (5)$$

approaches the much larger value of 1.15.[5] The small value of α_s reflects the small perturbation of the segments about the center of mass, which itself moves somewhat away from the interface.

An equivalent means of contrasting the effect of the impenetrable interface on the end-to-end distance and radius of gyration is through examination of $\langle r^2 \rangle / \langle s^2 \rangle$. This ratio approaches 6 for unperturbed polymethylene as n goes to infinity,[11] as would be the case for any flexible chain. Behavior of $\langle r^2 \rangle / \langle s^2 \rangle$ is depicted in Figure 4. In both cases, $\langle r^2 \rangle / \langle s^2 \rangle$ decreases as n increases. However, the limiting value is about 7.5 when chains are perturbed through attachment on one end to an impenetrable interface.

Note that any experimental measurements that use $\langle r^2 \rangle^{1/2}$ as an indicator of the thickness of the attached polymer layer would display a significant increase in the dimensions of the polymer resulting from terminal attachment. In contrast, the change produced by the interface would be so small that it might well escape de-

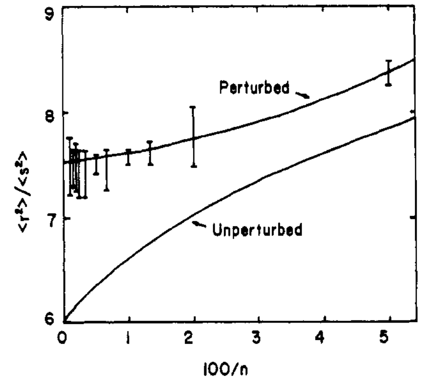

Figure 4. $\langle r^2\rangle/\langle s^2\rangle$ for polymethylene chains attached to an impenetrable interface.

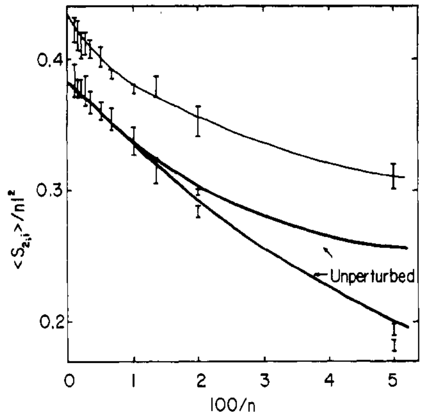

Figure 5. Principal moments of the averaged inertia tensor, $\langle \mathbf{S}_{x2}\rangle$. Averaging takes place in the coordinate system established by the first two bonds in the chain. Heavy solid lines denote behavior reported by Yoon and Flory[7] for unperturbed polymethylene chains. Bars denote the behavior for chains attached to an impenetrable interface. In the former case $\langle S_{2;b}\rangle$ and $\langle S_{2;c}\rangle$ are essentially identical for all n shown. They are therefore represented by the same heavy line. When attached to an impenetrable interface, $\langle S_{2;b}\rangle$ and $\langle S_{2;c}\rangle$ become so similar when n exceeds 100 that they are then represented by a common error bar.

tection if $\langle s^2\rangle^{1/2}$ were the parameter used to characterize the polymer dimensions.

Asymmetry of the Averaged Inertia Tensor. Figure 3 demonstrates that the surface produces a small increase in the trace of the averaged inertia tensor. How is this increase reflected in the principal moments of $\langle \mathbf{S}_{x2}\rangle$? Behavior of the reduced principal moments, $\langle S_{2;i}\rangle/nl^2$, is depicted in Figure 5. The smaller two principal moments are so nearly identical that they are represented by a common error bar at sufficiently large n. The remaining principal moment is larger than the other two at all n. Hence the time-averaged distribution of chain atoms in the internal coordinate system established by the first two bonds in the attached chain has the asymmetry of a prolate ellipsoid. The axial ratio for the prolate ellipsoid differs from unity by only a few percent. The major principal axis for $\langle \mathbf{S}_{x2}\rangle$ is nearly normal to the surface; i.e., it is nearly collinear with the first bond in the chain.

Heavy solid lines in Figure 5 denote the behavior of the reduced principal moments for $\langle \mathbf{S}_{x2}\rangle$ when the polymethylene chain is unperturbed.[7] Unperturbed chains have the asymmetry of a prolate ellipsoid at small n, but the distribution becomes spherically symmetric at large n. At sufficiently large n the common behavior of the three principal moments of $\langle \mathbf{S}_{x2}\rangle$ for unperturbed chain provides a good description of the smaller two principal moments for perturbed chains.

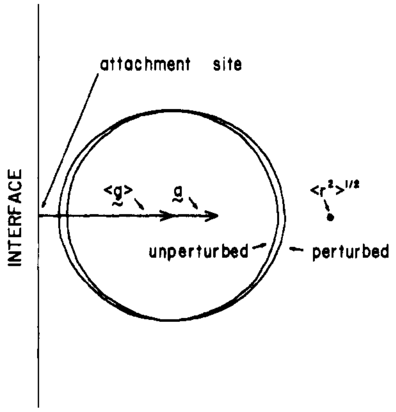

Figure 6. Schematic representation of a linear polymethylene chain with one end attached to an impenetrable interface.

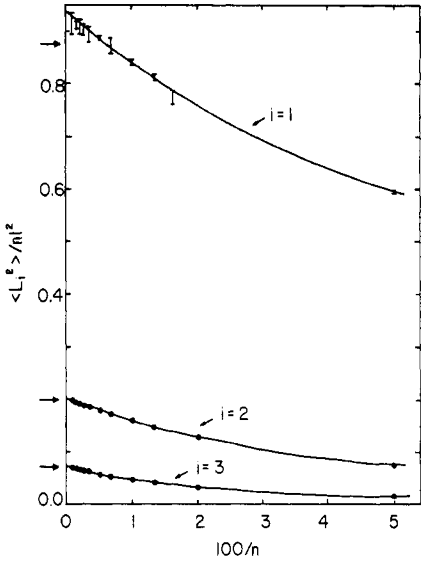

Figure 7. Averaged values of corresponding principal moments of the inertia tensors for individual configurations. The radius of plotted points is larger than one standard deviation.

Figures 1, 3, and 4 demonstrate that $\mathbf{a}$, $\langle \mathbf{g}\rangle$, $\langle r^2\rangle^{1/2}$, and $\langle s^2\rangle^{1/2}$ become proportional to $n^{1/2}$ at sufficiently large n. This limiting behavior yields

$$(\langle r^2\rangle/\mathbf{a}^{\mathrm{T}}\mathbf{a})_\infty^{1/2} = 1.6 \qquad (6)$$

$$(\langle s^2\rangle/\langle \mathbf{g}\rangle^{\mathrm{T}}\langle \mathbf{g}\rangle)_\infty^{1/2} = 0.8 \qquad (7)$$

where $\mathbf{a}^{\mathrm{T}}$ denotes the transpose of $\mathbf{a}$. These two equations, as well as the limiting behavior depicted in Figures 4 and 5, are summarized in a highly schematic fashion in Figure 6. The circle in Figure 6 has a radius given by the root-mean-square radius of gyration of the *unperturbed* chain. An equivalent representation of the *perturbed* chain is provided by the ellipse. The area enclosed in the ellipse is larger by a factor of α_s^2 than that in the circle, and the axial ratio of the ellipse if given by the limiting $((\langle S_{2;a}\rangle/\langle S_{2;b}\rangle)^{1/2}$ from Figure 5. The center of the ellipse is located at the tip of the average center-of-mass vector. The origin of $\langle \mathbf{g}\rangle$ is at the site where the chain is attached to the impenetrable interface. Equation 7 provides the ratio of $\langle s^2\rangle^{1/2}$ to the length of $\langle \mathbf{g}\rangle$ for the perturbed chain. Figure 6 also depicts $\mathbf{a}$ (scaled relative to $\langle \mathbf{g}\rangle$ via Figure 1) and a point (scaled via eq 6) a distance $\langle r^2\rangle^{1/2}$ from the site at which the chain is attached to the interface. The schematic picture in Figure 6 bears little resemblance to a half-sphere with a radius comparable to $\langle s^2\rangle^{1/2}$, which has been suggested as a model for an attached chain.[12]

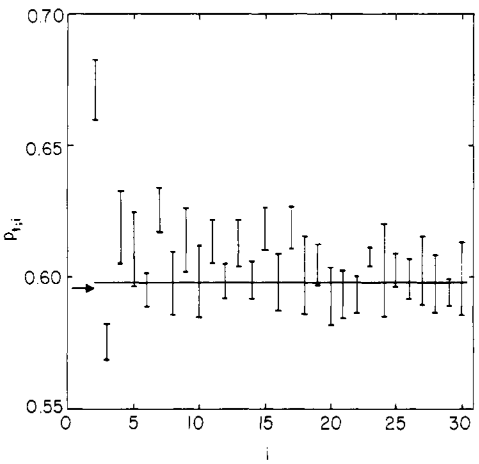

Figure 8. A priori probability for a trans placement at bonds 2–30 in an attached polymethylene chain of 300 bonds. The horizontal line denotes the average $p_{t;i}$ for all internal bonds in the attached chain. The arrow denotes p_t for a long unperturbed chain in free solution.

Average Asymmetry of Individual Configurations. Figure 7 depicts behavior of averages of corresponding moments of the inertia tensors for individual configurations. Arrows to the left of the ordinate axis denote asymptotic limits for unperturbed polymethylene chains. These limits are obtained from the limiting $\langle s^2\rangle/nl^2$ for unperturbed polymethylene[11] and the relationship $\langle L_1{}^2\rangle:\langle L_2{}^2\rangle:\langle L_3{}^2\rangle = 0.765:0.172:0.0627$, which is valid for any unperturbed flexible linear chain containing a sufficiently large number of bonds.[7,13-19] The smaller two averaged principal moments for the perturbed chains approach these limits as n increases. In contrast, $\langle L_1{}^2\rangle/nl^2$ has a slightly higher asymptotic limit when the chains are perturbed through attachment to an impenetrable interface. Surviving configurations tend to be somewhat more asymmetric than those found in the absence of the perturbation. The intramolecular excluded-volume effect for chain molecules in free solution also causes $\langle L_1{}^2\rangle$ to increase relative to $\langle L_2{}^2\rangle$ and $\langle L_3{}^2\rangle$.[20]

In summary, attachment of one end of a long polymethylene chain to an impenetrable interface produces an increase in both $\langle r^2\rangle$ and $\langle s^2\rangle$, with the much larger change being seen with $\langle r^2\rangle$. The increase in $\langle s^2\rangle$ occurs primarily in $\langle S_{2;a}\rangle$ and $\langle L_1{}^2\rangle$. Thus individual configurations are slightly more asymmetric, and the time-averaged distribution of chain atoms in the internal coordinate system established by the first two bonds is no longer spherically symmetric but instead has the asymmetry of a prolate ellipsoid.

End Effects in Attached Chains. Perturbation in the probability for occupancy of a rotational state is conveniently described by examination of the first 30 bonds in a polymethylene chain containing 300 bonds. First-order probabilities for occupation of a trans state at bonds 2–30 are depicted in Figure 8. Of course, $p_{g^+;i} = p_{g^-;i} = (1 - p_{t;i})/2$. The horizontal line in Figure 8 denotes the average of $p_{t;i}$ for all internal bonds in the attached chain. The arrow at the left of this figure denotes the value of p_t obtained by Jernigan and Flory[1] for a long unperturbed polymethylene chain. Essentially identical p_t are obtained for the unperturbed chain and the chain perturbed through attachment of one end to an impenetrable interface.

In a long unperturbed chain, the end effect is apparent in $p_{t;i}$, $i = 2$–4, but is no longer detectable at $p_{t;5}$.[1] The $p_{t;i}$ for $i = 2$–4 are 0.537, 0.606, and 0.594, which can be compared with 0.596 for p_t. Data reported in Figure 8 demonstrate that the end of the attached chain, as well as the unperturbed chain, exerts its largest effect on $p_{t;2}$. However, the end effects are in opposite directions, serving to depress $p_{t;2}$ by 0.06 in the unperturbed chain and to enhance $p_{t;2}$ by about 0.07 when the chain is attached to an impenetrable interface. The direction of the perturbation produced by the chain end oscillates and becomes smaller as one proceeds from bond 2 to bond 4 in both the attached chain and the chain in free solution, as is shown in Table I.

Table I

Comparison of End Effect on $p_{\eta;i}$ and $p_{\xi\eta;i}$ in Free and Attached Long Polymethylene Chains[a]

		$p_{\eta;i} - p_\eta$ or $p_{\xi\eta;i} - p_{\xi\eta}$	
i	η or $\xi\eta$	free[b]	attached
2	t	−0.059	0.074 (0.012)
3		0.010	−0.023 (0.007)
4		−0.002	0.021 (0.014)
3	tt	−0.033	0.025 (0.014)
4		0.004	−0.007 (0.013)
5		−0.001	0.023 (0.014)
3	$tg^\pm$	−0.013	0.024 (0.007)
4		0.002	−0.008 (0.010)
5		−0.001	−0.001 (0.009)
3	$g^\pm g^\pm$	0.009	−0.008 (0.005)
4		−0.001	−0.002 (0.006)
5		0.000	−0.004 (0.005)
3	$g^\pm g^\mp$	0.0007	−0.0051 (0)
4		−0.0001	−0.0006 (0.0016)
5		0.0000	−0.0015 (0.0013)

[a] Listed only for those bonds where an appreciable end effect is seen in the free unperturbed chain. [b] Reported by Jernigan and Flory.[1]

While end effects on $p_{t;i}$ disappear at bond 5 for the unperturbed chain in free solution, they extend considerably further into the chain when the chain is perturbed through attachment to an impenetrable interface. Figure 8 demonstrates that the $p_{t;i}$ show a definite pattern for i in the range 5–20. The $p_{t;i}$ with even i are indistinguishable from p_t for the entire chain. In contrast, those $p_{t;i}$ with odd i are somewhat larger than p_t. Not until i exceeds 20 do the $p_{t;i}$ generally agree with p_t. Therefore the presence of the impenetrable interface causes recognizable end effects out to bond 20 in a chain of 300 bonds. The magnitude of the end effects, however, is not sufficient to cause p_t to be significantly different for the attached and free chains.

If $\varphi_{g\pm}$ is placed at ±112.5°, rather than ±120°, the effect of the impenetrable interface on $p_{t;i}$ dies out when i is about 15. On the other hand, if $\varphi_{g\pm}$ is retained at ±120°, but θ is increased to 70.5°, end effects on $p_{t;i}$ are recognizable until about $i = 20$. In neither of these two cases is the alternating pattern at $i = 5$–20 as dramatic as that depicted in Figure 8.

Comparison of end effects on $p_{\xi\eta;i}$, $i = 3$–5, for free and attached chains is presented in Table I. As was the case with $p_{\eta;i}$, end effects on $p_{tt;i}$ and $p_{tg\pm;i}$ tend to be in opposite directions. On the other hand, $p_{g\pm g\pm;i}$ and $p_{g\pm g\mp;i}$ in this range are all diminished by the end effects arising from a surface, while changes in either direction are noticed for the chain in free solution.

Detailed behavior of $p_{\xi;i}$ for bonds 3–30 in the attached chains is depicted in Figure 9. With the exception of $p_{tt;4}$, all $p_{tt;i}$ for $i = 3$–20 are slightly higher than p_{tt} for the entire chain. On the other hand, $p_{g\pm g\pm;i}$ and $p_{g\pm g\mp;i}$ for $i = 3$–20 tend to be smaller than $p_{g\pm g\pm}$ and $p_{g\pm g\mp}$ for the entire attached chain. The effect of the surface on $p_{tg\pm;i}$ and $p_{g\pm t;i}$ manifests itself primarily by causing $p_{tg\pm;i} \neq p_{g\pm t;i}$ for $i < 21$. Effects of the impenetrable interface on the various $p_{\xi\eta;i}$ extend into the chain to about $i = 20$. The $p_{\xi\eta}$ for

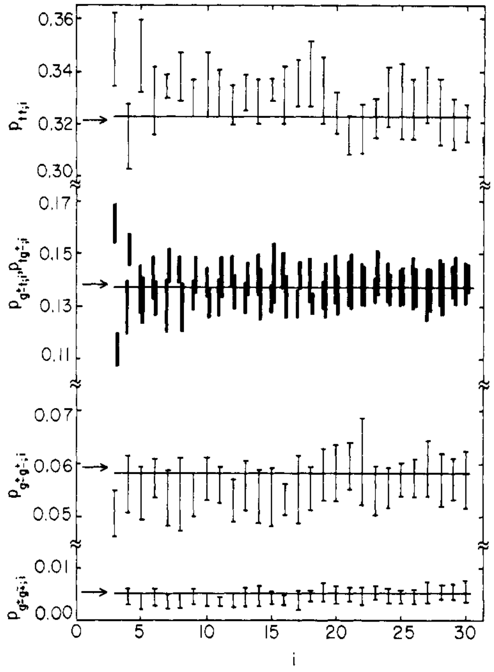

Figure 9. Second-order a priori probabilities for bonds 3-30 in an attached polymethylene chain of 300 bonds. Horizontal lines denote averages of $p_{\xi\eta;i}$ for bonds 3-299. Arrows denote $p_{\xi\eta}$ for a long unperturbed chain in free solution.

bonds 3-299 in the attached chains are essentially identical with the $p_{\xi\eta}$ reported by Jernigan and Flory[1] for long unperturbed polymethylene chains.

The general conclusion from Figures 8 and 9 and Table I is that end effects extend somewhat further into the chain when one end is attached to an impenetrable interface. However, the largest displacement of $p_{\eta;i}$ from p_η, or $p_{\xi;i}$ from $p_{\xi\eta}$, is of comparable size for free and attached chains. Furthermore, the end effects produced in a chain of 300 bonds by the impenetrable interface do not cause either p_η or $p_{\xi\eta}$ to differ from values obtained with the free unperturbed chain. It would seem appropriate, therefore, to categorize the end effects produced by the impenetrable interface as being "small".

One means of placing the size of the end effects discussed here in their proper perspective is to compare the largest $p_{\eta;i} - p_\eta$ and $p_{\xi\eta;i} - p_{\xi\eta}$ (Table I) with the largest perturbations produced in the main chain when a butyl group is attached to an atom in the interior of a long polymethylene chain. When a butyl group is present, $p_{t;i} - p_t$ and $p_{tt;i} - p_{tt}$ can be as negative as -0.20 and -0.22, respectively.[21] Perturbations produced by the butyl group are much larger than those arising from the end effects produced by the impenetrable interface.

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Elasticity Theory. 5. Mean Field Solution of the Network Collapse Problem

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ABSTRACT: The problem of network collapse is solved by combining the asymptotic form of the unperturbed distribution function of the radius of gyration with a mean field representation of the repulsive forces of volume exclusion. The theory gives well-behaved thermodynamic densities for elastomers.

Introduction

Networks formed by cross-linking linear polymer chains have properties unlike those of the parent molecules. Linear chains in the bulk (or in certain dilute solutions) can be brought to a state where their configurations are unperturbed by the influence of neighboring molecules. In this state molecular dimensions are determined solely by the short-ranged intramolecular potential, the intermolecular influences having been nullified by fundamental cancellation with the nonbonded part of the intramolecular potential.[1] This ideal or Flory Θ state is firmly established; it is realized in practice[2] and it serves as the reference state for rigorous perturbation theory of the influence of nonbonded interactions upon molecular dimensions.[3] The decomposition of potentials into inter- and intramolecular components is not possible for networks, however. Upon cross-linking the collection of molecules into a single reticulated molecule, the forces that had been intermolecular

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