shape of the correlation function seems to indicate that electrostatic interaction is the main source for the bimodal decay at low ionic strength.

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Angular Scattering Functions for Subchains Defined by a Generator Matrix Treatment of Simple Chains with Excluded Volume

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ABSTRACT: Angular scattering functions, $P(\mu)$, have been computed for subchains located in the middle and at the end of a polymethylene chain. The rotational isomeric state model developed by Flory and co-workers is used for the unperturbed chain. Chain expansion is introduced using a matrix treatment which satisfactorily reproduces several configuration-dependent properties of macromolecules perturbed by long-range interactions. At low angles $P(\mu)$ for subchains in perturbed chains depends on subchain location. This observation simply demonstrates that the mean-square radius of gyration, $\langle s^2 \rangle$, of a perturbed subchain depends on the location of that subchain within the main chain, as expected. Additional effects, arising from further differences in the distribution of chain atoms in perturbed subchains, are apparent at larger angles when $1/P(\mu)$ is examined as a function of $\langle s^2 \rangle \mu^2$. The excluded volume effect produces an increase in $P(\mu)$ for subchains at large $\langle s^2 \rangle \mu^2$. However, subchain location dependence of $P(\mu)$ for perturbed chains occurs only when $\langle s^2 \rangle \mu^2$ is so large that $P(\mu)$ itself is quite small.

Generator matrix methods have been widely used to evaluate the statistical mechanical average of configuration-dependent physical properties of chain molecules unperturbed by long-range intramolecular interactions.[1] These calculations permit a realistic treatment of a chain molecule because they utilize the bond lengths, bond angles, and short-range contributions to torsional potentials appropriate for the polymer in question. Recently generator matrix methods have been devised which permit rapid computation of a reasonable approximation to average configuration-dependent physical properties of chains significantly perturbed by long-range intramolecular interactions.[2-4] Bond lengths, bond angles, and short-range contributions to the torsional potentials are retained at the values appropriate for the unperturbed chain. The first-order a priori probability for occupancy of a particular rotational state by a bond in an infinitely long perturbed chain is identical with that probability in the unperturbed chain. Expansion of the perturbed chain is achieved through alteration in higher order a priori probabilities. This approach, when applied to polymethylene, yields the proper behavior for infinitely long chains because $(\alpha_s^5 - \alpha_s^3)/n^{1/2}$ attains a nonzero asymptotic limit.[2] An adjustable parameter, K, in the generator matrix treatment of perturbed chains can be related to z or $\psi_1(1 - \Theta/T)$ and, hence, is determined by the thermodynamics of polymer–solvent interaction.[2]

The expansion of finite generator matrix chains is asymmetric.[3] It serves to enhance the asymmetry which already exists in the unperturbed chain. Behavior of the asymmetry of infinitely long generator matrix chains depends on the details of the means by which the perturbation alters the properties of the chain. If the generator matrix calculation is performed in a manner which assumes the perturbation is felt uniformly throughout the chain, the expansion of infinite chains is computed to be isotropic.[3] However, if the perturbation is caused to be felt preferentially in the middle of the chain, the expansion of both finite and infinite chains is asymmetric.[3] This latter result is in qualitative agreement with conclusions reached by Monte Carlo studies of lattice chain[5,6] and a smooth-density model.[7] Direct evidence that the perturbation is felt preferentially in the middle of the chain is provided by a Monte Carlo study of finite polymethylene chains in which interacting methylene groups behave as hard spheres. The generator matrix method, when parameterized so that the perturbation is felt preferentially in the middle of the chain, successfully reproduces the position dependence of the expansion of subchains which is observed in the Monte Carlo study.[4]

The foregoing conclusions require that the angular scattering function of an appropriately labeled subchain depend on its location within a perturbed chain. At sufficiently low scattering angle this behavior arises simply because that subchain located in the middle of the chain has the largest mean-square radius of gyration. This conclusion is a direct consequence of the perturbation being felt preferentially in the middle of the main chain. The objective here is to inquire into the possibility that other differences in scattering behavior, observable only at higher scattering angles, might also be present. The rationale for expecting additional effects at higher scattering angles can be presented by considering two subchains. Let the first subchain be located precisely in the middle of the main chain, while the second is located at a chain end. Ends of the former subchain experience an identical expansion, which is smaller than the expansion of the middle portion of this subchain. In contrast, the latter subchain experiences minimal expansion in that portion which lies at the end of the main chain, and this subchain has its maximum expansion at its other end. Thus details of the distribution of chain atoms in the two subchains may differ for reasons in addition to their unequal mean-square radii of gyration. We wish to inquire whether the generator matrix model for perturbed chains predicts that these additional differences in the spatial distribution of chain atoms may give rise to effects potentially observable in the angular scattering function at high angles.

Calculations

The model used for the unperturbed chain is that developed by Flory and co-workers[1,8] for polymethylene. The bond length is 153 pm, the bond angle is 112°, and rotational states available to internal bonds have dihedral angles of 0° and ±120° (t and g$^{\pm}$, respectively). Weighting of unperturbed chains is determined by first- and second-order interactions. The weight of g$^{\pm}$ relative to t is denoted by σ, while $\sigma^2\omega$ denotes the weight of g$^{\pm}$g$^{\mp}$ relative to tt. Energies associated with σ and ω are 500 and 2000 cal mol^{-1}, respectively. The temperature is taken to be 300 K.

The rationale employed in order to introduce excluded volume into the polymethylene chain has been described in detail by Mattice and Santiago.[2] Chain geometry, rotational states, and short-range interactions appropriate for the unperturbed state are retained. Chain expansion is achieved through coordinated manipulation of two additional parameters. This manipulation does not alter the first-order a priori probability for observation of a particular rotational state in a long polymethylene chain. It does, however, alter a priori probabilities of higher order and, hence, the mean dimensions as well. Generator matrix expressions required for computation of α_s^2

$$\alpha_s^2 = \langle s^2 \rangle / \langle s^2 \rangle_0 \tag{1}$$

have been described by Mattice and Santiago.[2] Here $\langle s^2 \rangle$ denotes the mean-square radius of gyration, and zero as a subscript denotes the unperturbed state.

Let $\langle s_{ij}^2 \rangle$ denote the mean-square radius of gyration of a subchain consisting of bonds indexed from $j - (i - 1)/2$ through $j + (i - 1)/2$. Hence there are i bonds in the subchain, and the middle of the subchain is located at bond j. Define a subchain expansion factor as

$$\alpha_{sij}^2 = \langle s_{ij}^2 \rangle / \langle s_{ij}^2 \rangle_0 \tag{2}$$

Generator matrix computations of α_{sij}^2 were performed in the manner described previously.[4] An equivalent generator matrix approach was used in computation of the expansion, α_{rij}^2, of the mean-square end-to-end distance of subchains.

$$\alpha_{rij}^2 = \langle r_{ij}^2 \rangle / \langle r_{ij}^2 \rangle_0 \tag{3}$$

A more compact notation will be employed for expansion factors of those subchains located at the extreme ends and precisely in the middle of the main chain. Thus $\alpha_{s,i,e}^2$ and $\alpha_{s,i,m}^2$ are compact notations for $\alpha_{s,i,(i+1)/2}^2$ and $\alpha_{s,i,(n+1)/2}^2$, respectively.

Angular scattering functions for subchains were computed from a representative sample of chains. Representative samples of perturbed polymethylene chains were generated with a priori and conditional probabilities computed from the configuration partition function.[3] The angular scattering function for a specified subchain of i bonds is[9]

$$P(\mu) = (i + 1)^{-2} \sum_{\beta=k}^{k+i} \sum_{\gamma=k}^{k+i} \left\langle \frac{\sin(\mu r_{\beta\gamma})}{\mu r_{\beta\gamma}} \right\rangle \tag{4}$$

where the subchain includes bonds indexed from k through $k + i$ and $r_{\beta\gamma}$ denotes the distance between atoms β and γ.

Results and Discussion

Two parameters used in the matrix treatment of perturbed polymethylene chains are K and b. The former parameter is a measure of the thermodynamics of polymer–solvent interaction. It can be related to z and $\psi_1(1 - \Theta/T)$.[2] The ratio of b to K reflects the manner in which the perturbation is felt along the chain. If b/K is unity, the perturbation is felt uniformly throughout the chain. This value for b/K can be rejected because it does not

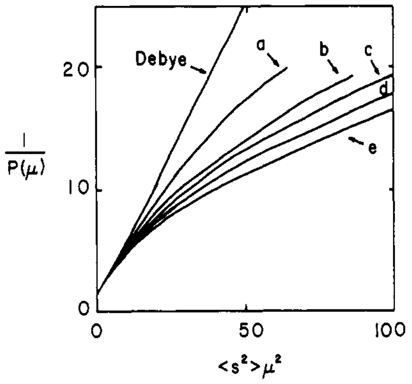

Figure 1. Angular scattering functions for subchains of 100 bonds in a polymethylene chain of 1000 bonds. Curve a depicts results for the unperturbed state. The chain is perturbed in curves b–e, with K being 0.5 for curves b and c, while K is unity for curves d and e. The subchain depicted is that at the middle of the chain for curves c and e and that at the end of the chain for curves b and d. Expansion factors, α_{sij}^2, for subchains whose scattering functions are depicted as curves a–e are 1.00, 1.34, 1.53, 1.73, and 2.00, respectively.

correctly reproduce the effect of excluded volume on the asymmetry of instantaneous configuration of the polymethylene chain[3] or the dependence of α_{sij}^2 on j.[4] These deficiencies are remedied if b/K is less than unity, which signifies that the perturbation is felt preferentially in the middle of the chain.[4] Computations reported here use $b/K = 0.64$, as was the case in earlier studies.[2-4]

Expansion factors were computed for subchains of 100 bonds in a perturbed main chain containing 10^3 bonds. When $K = 0.5$, $\alpha_{s,100,e}^2$ is 1.34, while $\alpha_{s,100,m}^2$ has the larger value of 1.53. If scattering functions computed for these two subchains were to be presented as $1/P(\mu)$ vs. μ, differences would be readily apparent, but these differences would be dominated by contributions due to the unequal $\langle s_{100,j}^2\rangle$. Alternative graphical methods permit examination of additional contributions to the shape of the scattering function. The one adopted here is $1/P(\mu)$ vs. $\langle s_{ij}^2\rangle\mu^2$. Figure 1 presents angular scattering functions computed for subchains of 100 bonds, while Figure 2 presents similar data for subchains comprised of 300 bonds. In both cases the main chain contains 1000 bonds. These figures also include the scattering behavior predicted by the Debye equation.[10]

$$P(\mu) = (2/\langle s_{ij}^2\rangle^2\mu^4)[\exp(-\langle s_{ij}^2\rangle\mu^2) - 1 + \langle s_{ij}^2\rangle\mu^2] \qquad (5)$$

All curves depicted in Figures 1 and 2 are superimposable at sufficiently small $\langle s_{ij}^2\rangle\mu^2$, as expected. As $\langle s_{ij}^2\rangle\mu^2$ increases, scattering curves computed for representative samples of subchains diverge from the Debye curve. Previous calculations of the angular scattering function for rotational isomeric state models of finite unperturbed polymethylene chains also find deviations from eq 5 at high angles.[11,12] These deviations arise because the unperturbed sequences which dominate the scattering in this angular region have neither $\langle r_i^2\rangle$ proportional to i nor a Gaussian distribution of chain atoms.[11] For these reasons $P(\mu)$ for the unperturbed subchain of 300 bonds exhibits less severe deviations from behavior predicted by the Debye equation than does the subchain of 100 bonds.

Perturbation of the chain by the introduction of excluded volume enhances the deviations of $P(\mu)$ for a subchain from the result predicted by eq 5. Expansion of the polymethylene chain is seen to produce an increase in $P(\mu)$ at large angles for all subchains examined. For a given value of the polymer–solvent interaction parameter K, the increase in $P(\mu)$ is most strongly felt by the subchain situated in the middle of the main chain. It is this subchain which experiences the largest expansion.

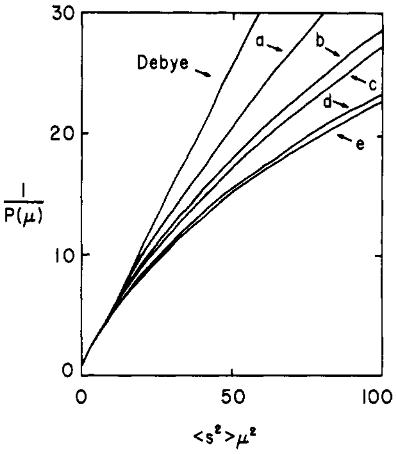

Figure 2. Angular scattering functions for subchains of 300 bonds in a polymethylene chain of 1000 bonds. Curve a depicts results for the unperturbed state. The chain is perturbed in curves b–e, with K being 0.5 for curves b and c, while K is unity for curves d and e. The subchain depicted is that at the middle of the chain for curves c and e and that at the end of the chain for curves b and d. Expansion factors, α_{sij}^2, for subchains whose scattering functions are depicted as curves a–e are 1.00, 1.46, 1.61, 2.13, and 2.37, respectively.

In order to qualitatively describe the manner in which the importance of positioning of a subchain depends on its length and the severity of the excluded volume effect, attention will be directed to that $\langle s_{ij}^2\rangle\mu^2$ at which $P(\mu)$ for subchains in the middle and at the end of the main chain differ by a specified amount. This specified amount will somewhat arbitrarily be selected as 5%. When the subchain contains 100 bonds, the required $\langle s_{ij}^2\rangle\mu^2$ from Figure 1 is about 25 if $K = 0.5$. It falls to near 20 when K is unity. Additional computations (not shown) indicate the pertinent $\langle s_{ij}^2\rangle\mu^2$ falls to 16 when K increases to 1.5. Thus the position of a subchain becomes important at successively lower values of $\langle s_{ij}^2\rangle\mu^2$ as the main chain becomes more strongly perturbed. The longer subchains described in Figure 2 have scattering functions which are less sensitive to positioning of the subchain than were those in Figure 1. When i is 300, $\langle s_{ij}^2\rangle\mu^2$ must be close to 100 if $P(\mu)$ for subchains located in the middle and at the end of the main chain are to differ by as much as 5%.

Values of $P(\mu)$ itself are quite low when the 5% difference in $P(\mu)$ is obtained for subchains located at different positions within the main chain. If the subchain contains 100 bonds, $P(\mu)$ is found to be near 0.1. For the longer subchain of 300 bonds, however, this $P(\mu)$ is only 0.03–0.04. Hence observation of the effect of subchain position upon $P(\mu)$ would require accurate measurements at angles so high that the scattered intensity itself is low. By far the easier demonstration of the dependence of a subchain's expansion upon its position within the main chain would be obtained from the initial dependence of $P(\mu)$ on μ^2, i.e., from the measurement of the j dependence of $\langle s_{ij}^2\rangle$ itself.

While the emphasis here has been on the scattering behavior of perturbed subchains, the results clearly have bearing on the scattering behavior to be expected from the main chain. Consideration of the results depicted in Figures 1 and 2 for subchains of 100 and 300 bonds, respectively, leads to the prediction that $P(\mu)$ at large $\langle s^2\rangle\mu^2$ will increase when the main chain expands. This conclusion is in harmony with earlier theoretical and experimental work[13-15] but is contrary to recent theoretical investigations.[16] The recent study also predicts $P(\mu)$ for perturbed and unperturbed chains should cross when

$\langle s^2\rangle\mu^2$ is near 100. This type of behavior is not evident in either Figure 1 or Figure 2. However, we must point that μ^{-1} must approach the length of a C–C bond if $\langle s_{ij}^2\rangle\mu^2$ is to be near 100 for the subchains considered here. Therefore somewhat different behavior might be observed with much longer subchains.

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Small-Angle Neutron Scattering from Elastomeric Networks. Junction Fluctuations and Network Unfolding

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ABSTRACT: Theoretical calculations of small-angle neutron scattering (SANS) from labeled chains in polymeric networks are presented. These start from the phantom network as a point of departure and include two additional properties of real networks absent in the phantom model. First of all, the reduction of fluctuations of cross-link junctions by network entanglements is introduced according to a model pioneered by Flory. Secondly, a concept of network unfolding without chain deformation is introduced. SANS experiments on deformed networks provide support for the thesis that, in some cases, chain deformation is less than that calculated from the phantom network model. This becomes particularly striking if the model is modified to take into account reduced junction fluctuations.

Introduction

The unique elasticity of rubber polymeric networks arises from the flexibility of the macromolecules of which the network is composed. A statistical thermodynamic theory of these networks, formulated by James[1] and James and Guth[2] and modernized and extended by Graessley,[3,4] Ronca and Allegra,[5] Deam and Edwards,[6] and Flory,[7] is known as the phantom network model. This is an apt name since it emphasizes the hypothetical ability of chains to pass through one another, a property which makes calculations tractable but which is regrettably one of the serious weaknesses of the theory.

There have been a number of indications that the phantom network model is not in accord with experiment. The experiments of Lloyd and Alfrey[8,9] on cross-linked networks prepared under different conditions are not consistent with the phantom model. Pearson and Graessley[10] find that stresses in ethylene–propylene copolymer networks exceed predictions derived for a phantom network. They regard the excess stress as an additional contribution from entanglements. By contrast, Mark and Sullivan[11] find no such discrepancies in their investigation of cross-linked poly(dimethylsiloxane) rubber. Ferry and colloborators[12] conducted a series of studies on polybutadiene networks prepared by cross-linking oriented polymer molecules. The interpretation of these experiments requires the assignment of stress, in large part, to an entanglement network.

Small-angle neutron scattering (SANS) is used to measure the size and shape of deuterium-labeled polymer molecules in an ordinary hydrogenous polymer matrix[13,14] and has been applied to networks[15-17] in a few cases. Benoit et al. have done this with cross-linked polystyrene gels[18] and have found, in some cases, that swelling is less than that given by the phantom network model. An investigation of osmotically deswollen polystyrene networks by Bastide et al.[19] has shown that chain deformation in partially swollen materials changes very little with degree of swelling. Early experiments by Hinkley et al.[20] and Clough et al.[21] show chain deformation consistent with the phantom network, but later experiments by Beltzung et al.[22] on siloxane networks yield results which vary over a range and in which the network with the highest molecular weight between cross-links deforms less than the phantom network. Han, in a SANS investigation of a trifunctional polyisoprene network,[23] has found, depending on the sample, deformation both greater and less than that predicted by the phantom network model.

Flory[24] and Erman and Flory[25] have proposed modifications of the phantom network model in which junction fluctuations are partially suppressed. Flory, referring to previous experiments,[26,27] finds that the suppression of junction fluctuations is considerable.[28] The effect of reducing fluctuations is to predict that chain deformation is greater than that given by the phantom model. This is found in some cases, but the reduction in junction fluctuations cannot account for chain deformations less than that expected from a phantom network.

Network Unfolding without Chain Deformation

Consider the following three explanations for network deformations which are less than would be found in a phantom network.

1. The measurement of dimensions by SANS is inaccurate and unreliable.

2. The preparation of networks is imperfect, dangling chain ends exist, and these lead to lower chain extensions upon deformation than for a perfect network.