Monte Carlo Investigation of Chemical Inhomogeneity in Copolymers

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ABSTRACT: Chemical inhomogeneity in copolymers is investigated by a Monte Carlo method. Calculations on the penultimate unit model are compared with results obtained by Painter, *et al.*, using exact enumeration and extrapolation. Although some small differences between the two sets of results are found, these discrepancies are small compared to the inaccuracies in the currently available experimental methods.

A copolymer system is chemically inhomogeneous when the sequence of two or more monomers is not identical in all the chains. When the average length of the homopolymeric blocks is not too small compared to the chain length, the relative amounts of the two monomers in different chains may not be identical,[2] *i.e.*, inhomogeneity with respect to chemical composition may occur. The investigation of such inhomogeneity in synthetic copolymers is still in its preliminary phase.[2f] The problem may, however, be increasingly important in the future when more specific catalytic systems for the polymerization process are developed. Biopolymer samples are very often inhomogeneous with respect to chemical composition, and the evaluation of suitable fractionation techniques is an important aspect of polysaccharide chemistry.[3] The heterogeneity may be so severe compared to the resolution power of the fractionation technique that different fractions may be regarded as different chemical entities.[4,5] When a larger number of fractions is obtained, semantic questions may arise as to the definition of such entities.[6,7]

The first attempt to attack these problems from a theoretical point of view was due to Painter.[8] By applying a statistical modle similar to those used for synthetic addition copolymers,[9,10] Painter, *et al.*, calculated theoretical composition distributions using a digital computer,[11] and applied their results to a study of alginate, a copolymer in which two types of homopolymeric block, composed of residues of mannuronic and guluronic acid, respectively, are linked through long blocks in which these residues are arranged in largely alternating sequences.[12-14] They found that the chemical inhomogeneity, occurring when the alginate is subjected to acid hydrolysis, may be explained qualitatively[15] by applying the penultimate unit theory.[9,10,16,17] The calculation of the composition distribution for chains containing n monomer units was effected by an exact enumeration of all the possible sequences of the chain and by summation of the probability of occurrence of each sequence having identical average composition. Since the computer time increases as the number of possible sequences (2^n) the calculation was limited to $n < 15$. The composition distribution for higher values of n was obtained by an approximate extrapolation method, from the results obtained at low n values.

The object of the present work is to present a Monte Carlo approach to the problem. The essential difference between exact enumeration and the Monte Carlo approach is that in the former all possible sequences are generated, while in the latter only a statistical sample of sequences are generated, and approximate population values are derived from this sample. The method therefore allows longer polymers to be examined (in this work up to $n = 120$) and so provides data with which the approximate extrapolation procedure[15] can be compared.

Simulation of the Polymer. The Monte Carlo approach adopted in this work is essentially a direct simulation of the growth of the polymer molecule. If we represent the two monomer units as A and B, then the parameters needed for the simulation are the

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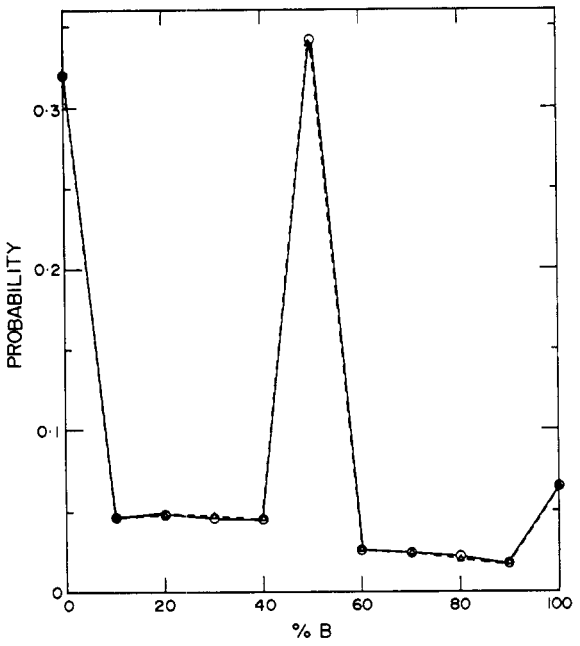

Figure 1. Composition distribution for polymers of length 10: ○, Monte Carlo results; △, results of Painter, *et al.*; $p(BA) = p(AB) = 0.2369$, $p(BB) = 0.1104$, $p(AA) = 0.4157$, $p(A/AA) = 0.9677$, $p(B/BB) = 0.9375$, $p(A/BA) = 0.0566$, $p(B/AB) = 0.0291$.

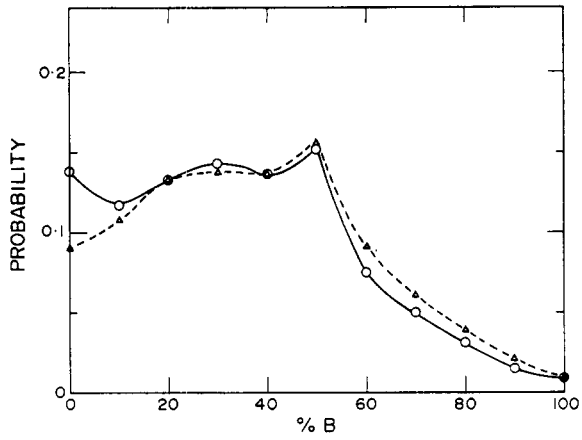

Figure 2. Same as Figure 1, but at length 60.

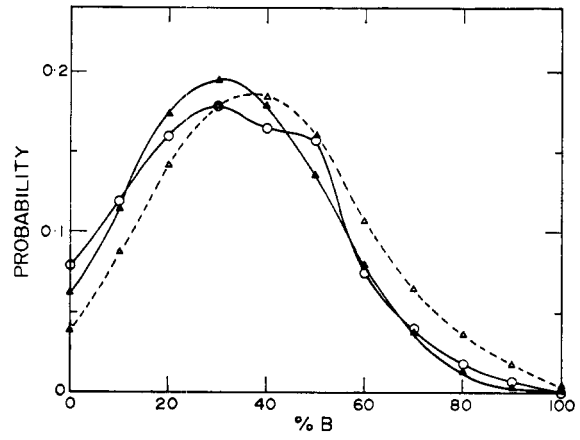

Figure 3. Composition distributions: ○, $n = 100$, Monte Carlo; △, $n = 100$, Painter, *et al.*; ▲, $n = 120$, Monte Carlo. Calculated with the same parameters as in figures 1 and 2.

probabilities that the first two monomer units in the polymer molecule are AA, AB, BA, and BB (which we represent as $p(AA)$ and similar terms) and the conditional probabilities such as $p(A|AB)$ which represent the probability that an A group will be added given that the last monomer is B and the penultimate monomer is A. Clearly, these probabilities must satisfy the relations $p(AA) + p(AB) + p(BA) + p(BB) = 1$ and $p(A|AB) + p(B|AB) = 1$ together with similar relations for the other possible end groups. It is clear that three initial probabilities and four conditional probabilities, together with five equations of the above type, are sufficient to define the stochastic growth of the polymer.

Given the above information, we generate a sample of the possible sequences in the following way. The initial pair of monomers is chosen by generating a uniformly distributed pseudorandom number (u) in the range 0–1. If $u < p(AA)$ then the first pair is AA. If $p(AA) < u < p(AA) + p(AB)$ then the first pair is AB and so on for the other possible initial pairs. That is, the unit interval is divided into four subintervals, each of length equal to the probability of one of the initial pairs. The interval in which u falls determines the initial pair of monomers. The end pair of monomers defines the state of the process and the next monomer to be added is determined by comparing a random number with the appropriate conditional probability; *e.g.*, if the end pair is AA then the next monomer to be added is A if $p(A|AA)$ is greater than the next random number generated, otherwise a B is added. The state of the process is now the new end pair of monomers and the process is continued until a polymer of the required size is generated. During the generation process, the number of A and B units is determined so that the fractional composition can be obtained. The next polymer molecule in the sample is then generated in the same way, and the process is repeated until a sample of the required size is obtained.

Results

The initial and conditional probabilities used were those used by Painter, *et al.*,[15] to allow a direct comparison of the two approaches. Composition distributions were calculated for $n = 10$, 20, 40, 60, 100 and 120 with sample sizes ranging from 10,000 to 100,000. Although results were obtained for all possible compositions the data were grouped in 11 equal intervals to allow direct comparison with the extrapolation data, and some resulting composition distributions are plotted in Figures 1–3. The pseudorandom numbers were generated using a multiplicative congruential generator of the form

$$x_{i+1} \equiv ax_i \pmod{2^b}$$

Discussion

Comparison of the two sets of curves shows that at $n = 10$, the agreement is excellent. For $n = 20$–60 the agreement is good except for the region in which the molecule is predominantly A. The discrepancy in this region is greater than the standard deviation of the Monte Carlo results, and this discrepancy becomes more marked as n increases. At $n = 100$ the difference be-

tween the two sets of results is quite marked, though the uncertainty in the Monte Carlo results is rather large. These results suggest that the extrapolation technique becomes less reliable as the extrapolation range increases. However, the difference between the results obtained by the Monte Carlo and extrapolation techniques is small compared to the inaccuracies in the available experimental methods.

For an infinite polymer, the form of the distribution is a δ function at 34.7%B and both sets of results show signs of the emergence of a peak in this region.

The primary advantage of the Monte Carlo approach over exact enumeration is its ability to provide approximate data on longer polymers. A second advantage is its versatility, in that the method could be applied to nonrandom degradation with little increase in complexity.

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The Viscosity of Liquid Sulfur. A Mechanistic Reinterpretation

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ABSTRACT: The viscosity of liquid sulfur above 160° is calculated assuming that molecular flow is the only flow mechanism. The calculation is based on the values of the degree of polymerization and the monomer concentration as applied to the recent theory of Fox and Allen. It is shown that the calculated viscosity is *ca.* 10^4 times greater than the experimental viscosity. The possibility of bond interchange and of chain-end interchange is introduced, but these mechanisms lead to an underestimated value of the viscosity. In spite of the current inability to calculate the viscosity of sulfur precisely on the basis of chemical reactions, it seems highly probable that the viscosity of liquid sulfur is most probably governed by some type of chemical interchange rather than molecular flow.

The sudden reversible increase in the viscosity of liquid sulfur above 160° has been ascribed to an equibrilium polymerization reaction[1-3] and, by implication, the magnitude of the viscosity was assumed to be in some way proportional to the length of the polymer chains. Two attempts were made to correlate the viscosity with the chain length. In the first of these, Gee[1] was able to compute the molecular weight from the viscosity curve to within a factor of 3 of the currently accepted value by deriving an equation based on the then current theories of polymer viscosity and on the equilibrium theory, and by treating three parameters as adjustable (one of them only within rather narrow limits). Touro and Wiewiorowski,[4] utilizing dilute solution theories with some simplifying assumptions and allowing two parameters to be completely adjustable, correlated the viscosity and molecular weight quite precisely. This work will be discussed more fully below.

In spite of its apparent success, it will be shown here that the assumption that the viscosity of high-polymer sulfur is due to a simple chain slippage (as would be encountered in a polystyrene solution, for example) may be seriously in error. Two lines of evidence will be cited to support this contention, both of them indicating that the viscosity of polymeric sulfur should be very much higher if present estimates of the chain length are to be believed. Furthermore, it will be indicated that two mechanisms other than simple chain slippage may exist, either one of which is more than enough to bring the viscosity way below the value found experimentally. From our present knowledge alone, it is unfortunately impossible to determine whether either or both of these two mechanisms are operative or whether still other possibilities must be considered.

Semlyen[5] has recently shown that there exists a large barrier to internal rotation about the sulfur–sulfur bond. Thus it is not unreasonable that in response to stress a sulfur chain may find it energetically more favorable to relax by some chemical means involving chain scission rather than by a molecular flow mechanism which is based on bond rotation.

The "Theoretical" Viscosity of Sulfur. A. General. Fox and Allen[6] extended the viscosity theory of Bueche[7] to include a wide range of variables, *i.e.*, high molecular

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