This relatively low value may be due to the fact that some of the acetone triplets could be quenched by the alkyl phenyl groups of the polystyrene by a process which does not lead to chain scission. This would be consistent with the observed shorter lifetime of the triplets in toluene.

In conclusion, these experiments show that "photodegradation" processes can be induced in a polymer containing ketone groups by energy exchange from acetone triplets generated by the thermal decomposition of tetramethyl-1,2-dioxetane. The reaction can be completely eliminated by a triplet quencher, COD, and the inhibition seems to follow Stern–Volmer kinetics. The method should be of considerable value for establishing the rate constants for inter- and intramolecular energy exchange in polymer systems.

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Notes

Influence of the Alternate Chair Conformation on the Unperturbed Dimensions of Alginic Acid

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Alginic acid is a 1,4-linked copolymer of β-D-mannuronic acid and α-L-guluronic acid. Haug and coworkers have shown that the molecule contains long homopolymeric blocks of each monomer together with blocks of the alternating sequence;[1] the relative amounts of the two comonomers (and the details of the block structure) depend on the source of the sample.[2] Smidsrϕd and coworkers[3,4] have recently determined the unperturbed dimensions of various alginate samples containing different amounts of the three kinds of structure, and the results are in qualitative agreement with calculations of unperturbed dimensions, provided that the mannuronic acid residues are assumed to adopt the $^4C_1$ conformation and the guluronic acid residues are assumed to adopt the $^1C_4$ conformation.[4,5] Evidence from X-ray crystallography[6,7] and nuclear magnetic resonance[8] strongly favors these as the predominant ring conformations. However, Angyal[9] estimates that the free energy difference between the two chair forms of the guluronic acid monomer is only about 750 cal/mol, so that small, but appreciable, amounts of the guluronic acid units in the polymer will be expected to adopt the energetically unfavorable $^4C_1$ chair form. This is interesting in that, although the calculated and experimental values of the unperturbed dimensions are qualitatively in agreement, the calculated values are higher than the experimental values, especially for samples rich in guluronic acid. In this communication we wish to investigate the effect on the unperturbed dimensions of including small amounts of the alternate chair form of the guluronic acid residues.

The possibility of incorporating some guluronic acid residues in the unfavorable chair conformation raises two interesting questions. The first of these stems from the curious block structure of alginic acid; the effect of such "conformational impurities" might be quite different depending on whether they occur in guluronic acid blocks or in the alternating blocks. The second question concerns the sequence statistics of the conformational impurities themselves. That is, are they likely to occur as isolated impurities along the chain or in blocks of the alternate ring form? Detailed answers to these questions must await estimation of the free energy difference between the $^1C_4$ and $^4C_1$ forms with *different neighbors* in the polymer. In this communication we wish to investigate the first question, with the assumption that the sequence statistics of the conformational impurity are Bernoullian.

We are interested in examining the effect of conformational impurities on the unperturbed dimensions of the polymer, as a function of the block structure with respect to the two chemically distinct comonomers. The averaging process can be thought of in three stages. In the first stage the chemical sequence of the polymer is sampled. That is, a sample of monomer sequences of mannuronic and guluronic acid residues is constructed, consistent with the assumed sequence statistics. In the second stage some of the guluronic acid residues are inverted from the $^1C_4$ to the $^4C_1$ chair form, the residues to be inverted being chosen at random from the guluronic acid residues in the polymer. In the third stage the unperturbed dimensions of this particular sequence of monomers and conformers is calculated. The first two averaging processes are carried out using a Monte Carlo method which has been described elsewhere[10] and the final averaging is effected analytically using the technique described by Flory and Jernigan.[11] The whole process is a straightforward extension of a method which has been described previously.[12] Sample sizes of about 500 chains of 2000 monomers were used, and the error bars shown in the figures correspond to one standard deviation. The monomer coordinates used were obtained by epimerization and inversion of the Arnott and Scott[13] values for β-D-xylose, with a bridge angle of 116°. Other details of the calculations are as described in ref 12.

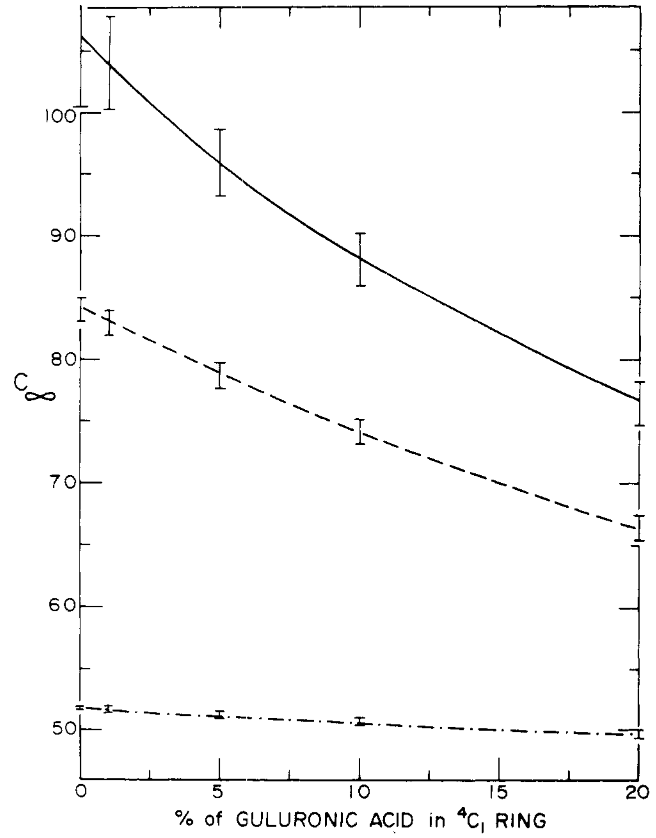

Figure 1. Dependence of characteristic ratio (C_∞) on the percentage of guluronic acid units in the $^4C_1$ ring conformation for a copolymer containing 50% mannuronic acid: (—) no alternating blocks, average guluronic block length = 20; (– – –) Bernoullian; (– • –) strictly alternating.

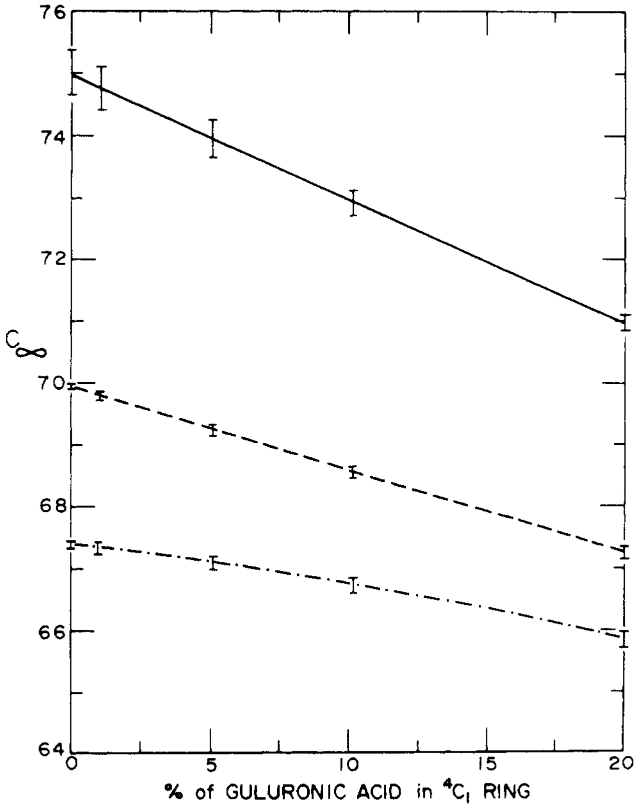

Figure 2. Dependence of characteristic ratio (C_∞) on the percentage of guluronic acid units in the $^4C_1$ ring conformation for a copolymer containing 90% mannuronic acid: (—) no alternating blocks, average guluronic acid block length = 10; (– – –) Bernoullian; (– • –) no homopolymeric blocks of guluronic acid, averaging alternating block length = 8 units.

We first examined the effect of introducing the conformational impurity in poly(guluronic acid). The characteristic ratio decreases dramatically as the percentage of rings in the $^4C_1$ conformation is increased. With 5% of the alternate ring the characteristic ratio has decreased from about 220 (the value for the polymer with all $^1C_4$ rings) to 160, a decrease of about 27%. About 13% of the conformational impurity decreases the characteristic ratio by a factor of 2.

To examine the effect of the conformational impurity on the copolymers of mannuronic and guluronic acids we considered copolymers with 50% and with 10% guluronic acid (the latter has about the overall composition of alginate isolated from *Ascophyllum nodosum*). For the 50% case we examined a Bernoullian copolymer, a strictly alternating copolymer, and a copolymer containing no alternating blocks but with blocks of guluronic acid units of average length 20. The results are shown in Figure 1. The most striking effect is that, for the strictly alternating copolymer, the characteristic ratio scarcely changes as the amount of conformational impurity increases. The characteristic ratio decreases markedly in the other two cases, the fractional decrease being greater for the polymer containing long blocks of guluronic acid.

The results for the 90% mannuronic acid case are shown in Figure 2. The upper curve is for a copolymer with no alternating blocks and with an average guluronic acid block length of ten, the middle curve is for the Bernoullian copolymer and the lower curve is for a copolymer with no guluronic acid blocks and with alternating blocks of average length eight. The effect of the conformational impurity is again less marked in the copolymer containing all the guluronic acid units in alternating blocks.

It appears[14] that for homopolymers variations in the value of the characteristic ratio between different polymers can be qualitatively understood in terms of changes in the bonding geometry and the freedom of rotation about the glycosidic and aglycone bonds, so that it is of interest to examine to what extent the characteristic ratios of copolymers can be understood in the same way. If we consider a block of guluronic acid units in the $^1C_4$ form the bonding geometry is 1a,4a-. Inserting a $^4C_1$ monomer will introduce a 1a,4e- followed by a 1e,4a- linkage, as would introducing a mannuronic acid unit. Since it is known[12] that introducing a small amount of mannuronic acid units into poly(guluronic acid) reduces the characteristic ratio, we would expect the same effect to occur here. However in the $^1C_4$-$^4C_1$ dimer of guluronic acid the carboxyl group is axial in the reducing sugar which will increase the freedom of rotation about the aglycone bond. This will also have the effect of decreasing the characteristic ratio. In the alternating blocks, changing a guluronic acid unit from $^1C_4$ to $^4C_1$ will increase the freedom of rotation but will change the bonding geometry from (1e,4a-,1a,4e-) to (1e,4e-,1e,4e-) which one would expect to lead to an increase in the characteristic ratio. That is, in the alternating blocks, the effects of changing bonding geometry and rotational freedom would be in opposite directions so that the overall effect on the characteristic ratio would be expected to be small.

These results indicate that changing small amounts of the guluronic acid residues from the $^1C_4$ to the $^4C_1$ ring form can considerably decrease the characteristic ratio of the polymer. However, the effect is very much less marked if the insertions are all in the alternating blocks of the copolymer, so that the degree of sensitivity varies with block structure. To understand further the conformational behavior of this type of polymer it will be necessary to know not only the free energy difference between the ring conformations in the monomer but also how this difference is affected by the neighboring units in the polymer.

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Molecular Relaxation of Nearly Monodisperse Polystyrene Melts

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In a recent publication, Forsman and Grand[1] presented a statistical mechanical theory of entanglement for assemblies of monodisperse random-flight chains. They predicted that, because of the symmetry of the chains about their center segments, only the longest *odd-order relaxation* times as defined by Rouse[2] were affected by entanglement. These predictions were shown to be completely consistent with experimental results published by Wolkowicz and Forsman[3] on concentrated solutions of nearly monodisperse polystyrene. In this paper, we analyze dynamic data on polystyrene melts and observe that it is also consistent with the theory.

A number of workers[4-8] have reported dynamic data on polystyrene melts. Of these, only those of den Otter[4] and Onogi, et al.,[5] extend over a sufficiently broad range of frequency to allow interpretation according to molecular theory. We observed, however, that the value of the zero-shear-rate viscosity, η_0, obtained from the terminal zone of the G'' (dynamic loss modulus) data of Onogi, et al.,[5] was inconsistent with the values reported by over 13 groups of investigators[9-11] at corresponding temperatures. We elected, therefore, to study den Otter's[4] data on polystyrene of molecular weight 290,000 at 190°.

Analysis

According to Rouse,[2] the linear viscoelastic behavior of an assembly of monodisperse random-flight chains is described by a multiple Maxwell model in which there is a one-to-one correspondence between each spring and dashpot pair and a normal mode of backbone motion. Each normal mode is designated by an index p and corresponds to movement of the chain backbone in blocks of molecular weight equal to (M/p). In addition, the model predicts relaxation times, τ_{pR}, which can be obtained from the transition region by the relationship[2]

$$\tau_{pR} = \frac{16M^2}{\pi^2 p^2 (\rho RT)^2} \left(\frac{G''^2}{\omega}\right)_{\text{transition}} \tag{1}$$

where M is the molecular weight of the polymer, ρ is its density, RT is the gas constant times absolute temperature, and G'' is the value of the loss modulus at angular frequency ω. The subscript pR is used here to indicate that eq 1 gives the value of each relaxation time of index p as predicted by the Rouse theory for assemblies of unentangled chains. Each normal mode has associated with it a Maxwell-model spring constant, G_R, given by

$$G_R = \rho RT/M \tag{2}$$

According to Forsman and Grand,[1] there is a one-to-one correspondence between the relaxation mechanisms in entangled chains and their unentangled analogs treated by Rouse. The spring constant associated with each normal mode is $(\rho RT/M)$ as in unentangled systems, but some of the first few (longest) relaxation times having odd p are increased. As a measure of the increase in relaxation times, shift factors[3] Q_p were defined by the relationship

$$Q_p = \tau_p/\tau_{pR} \tag{3}$$

where the τ_p are the relaxation times for the entangled system, and τ_{pR} are the corresponding values predicted by the Rouse theory for the unentangled analog. The analysis for entangled systems[1] thus predicted only the first several odd-order Q_p to be greater than unity but did not indicate how Q_p approached unity with increasing p. Because all τ_p approach corresponding values of τ_{pR} with increasing p, the transition zone is predicted to be unaffected by entanglement.

Since the contribution of each normal mode to the dynamic storage and loss moduli G' and G'' are given by the simple expressions

$$G_p' = G_R[\omega^2\tau_p^2/(1 + \omega^2\tau_p^2)] \tag{4a}$$

$$G_p'' = G_R[\omega\tau_p/(1 + \omega^2\tau_p^2)] \tag{4b}$$

testing the predictions of the Forsman–Grand theory is straightforward. Because the transition zone is unaffected by entanglement, eq 1 and 2 are used to predict the G' and G'' for an unentangled analog. One then attempts to match experimental data with a theoretical curve obtained by summing contributions given by eq 4a and 4b but for which the longest several *odd-order* relaxation times have been shifted to longer times. It is important to emphasize that all even-order relaxation times remain fixed at their values predicted by the Rouse theory.

Since theory[1] does not predict the extent to which each relaxation time is affected by entanglement, additional assumptions must be considered in the interpretation of experimental results. The first approach (and that applied previously[3]) is to assume Q_p to be a smooth function of p.

Figure 1 shows a comparison of experiment and theory for such an assumption. We see that by shifting eight relaxation times (p = 1, 3, 5, 7, 9, 11, 13, and 15) experiment and theory are brought into excellent agreement. Figure 2 shows the extent to which entanglement affects these relaxation times as defined by the individual shift factors Q_p.

One might at first dismiss the agreement between the experimental and computed curves as being of little physical significance since there are "8 adjustable parameters." This is, however, an oversimplification. First, it is important to note that the spring constants were assigned their theoreti-