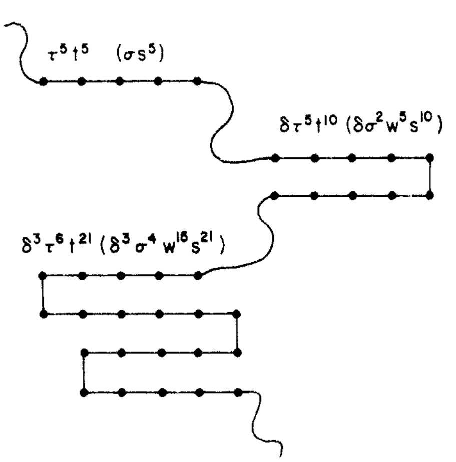

Figure 1. Diagrammatic chain with three ordered regions. Statistical weights outside parentheses are those assigned when the ordered regions are β sheets. Inside parentheses are statistical weights assigned when the ordered regions are comprised of α helices.

bend contributes an addition factor of δ. The weight assigned to the entire chain is the product of the weights for the constituent sheets. One or more additional weighting factors are required when the treatment is generalized so that strands in a particular sheet may be connected by tortuous loops as well as by tight bends.[3]

An alternative set of statistical weights is noted inside the parentheses in Figure 1. The propagation parameter is now symbolized by s. Each tight bend still contributes a factor denoted by β. The factor τ has been replaced by w. The exponent for w is $n_t - n_\tau$, where n_t and n_τ are, respectively, the exponents for t and τ in the weights outside the parentheses. Therefore a factor of w is contributed by every ordered residue that *does* have a partner in a preceding strand. (A factor of τ was contributed by every ordered residue that *did not* have a partner in a preceding strand.) Finally, there is a new statistical weight, denoted by σ. Each strand contributes a factor of σ. The symbolism has been transformed to that used to describe the transition from a statistical coil to a set of interacting helices.[5] The conventional Zimm–Bragg statistical weights are denoted by σ and s, w arises from the helix–helix interaction, and δ arises from the special circumstance where a bend is used to connect two interacting helices. The transformation requires the following four steps: (1) replace each t by ws; (2) replace each τ by $1/w$; (3) replace each δ by $\sigma\delta$; and (4) incorporate one additional σ for each distinct sheet (or set of interacting helices). Steps 1–3 are trivial; they require nothing more than a change in notation. The fourth step is nearly as simple. It merely requires multiplying the second element in the top row of the statistical weight matrix by σ. (It is this element that is used at the beginning of each distinct sheet.) This change is simply implemented, but it may have far-reaching consequences for the manner in which order is developed in a chain. With these changes, the methodology developed for the treatment of intramolecular antiparallel sheets can be directly applied to the study of systems of interacting helices. The number of helices in an interacting cluster is not artificially restricted to two. Its upper limit is instead the largest integer in $n/2$, where n is the number of residues in the chain. The statistical weight matrix can be modified so that contiguous helices in a cluster are connected by loops of arbitrary size.[3]

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Conformational Properties of Poly(1-octadecene/maleic anhydride) in Solution

KEIZO MATSUO† and W. H. STOCKMAYER*

Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755

FELIX BANGERTER

Swiss Federal Institute of Technology,
Technisches-Chemisches Laboratorium, ETH-Zentrum,
CH-8092 Zürich, Switzerland. *Received October 2, 1984*

The regularly alternating copolymer of 1-octadecene and maleic anhydride, hereinafter POMA, has a rather large dipole moment within each repeat unit (over 4 D), and therefore a study of its dielectric behavior in solution has intrinsic interest. This interest is heightened by the fact that alternating copolymers of various 1-olefins with sulfur dioxide show rather unusual dielectric behavior in solution:[1-3] a considerable part of the dipole polarization relaxes slowly, with a peak frequency that varies strongly with molecular weight and has a magnitude corresponding to overall tumbling or to the terminal relaxation time of the Rouse–Zimm model. It is believed[2-4] that the large electric moment and the large steric interactions of the long side chains combine to induce helical structures of moderate stability. We therefore thought it worthwhile to examine the behavior of POMA in solution, and we have found somewhat surprising results which, though fragmentary, are reported at the present time in this note since we have no prospect of being able to extend the work in the near future.

Experimental Part

A commercial sample of POMA was obtained from Gulf Oil Chemical Co., which provides a pamphlet PA-18/78-12-500 describing the general chemical and physical properties of the polymer and its many esoteric[5] uses. Eleven fractions were obtained from ethyl acetate/methanol at 30 °C and dried in vacuo to constant weight. Viscosities in ethyl acetate at 25 °C were measured in Cannon-Ubbelohde viscometers. Weight-average molecular weights were determined from light-scattering measurements in ethyl acetate with a Brice-Phoenix photometer, and the refractive index increment at 546 nm of POMA in ethyl acetate at 25 °C was measured to be $dn/dc = 0.119$ mL/g with a Brice-Phoenix differential refractometer.

Low-frequency dielectric response of POMA solutions in dioxane or benzene (freshly distilled over sodium) was measured with a General Radio 1620-A assembly and a cell described previously.[6] At frequencies above 100 kHz the resonant circuit method[7] was used at the MIT Laboratory for Insulation Research, through the kindness of W. B. Westphal.

For ^{13}C spin-lattice relaxation measurements, a solution of fraction F5 (30% w/w) in toluene-d_8 (Merck Sharp and Dohme Canada Ltd.) was sealed in a 10-mm NMR tube after five cycles of freezing, pumping, and flushing with dry nitrogen to remove

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† Present address: Technisches-Chemisches Laboratorium, ETH-Zentrum, CH-8092 Zürich, Switzerland.

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Table I
Intrinsic Viscosities, Light-Scattering Molecular Weights, and Osmotic Second Virial Coefficients of Poly(1-octadecene/maleic anhydride) in Ethyl Acetate at 25 °C

	$[\eta]/(\mathrm{dL\ g^{-1}})$	$10^{-4}M_w$	$10^4A_2/(\mathrm{cm^3\ mol\ g^{-2}})$
F1	0.138	9.9	2.1
F3	0.113	6.8	2.5
F5	0.099	5.1	2.8
F7	0.092	3.7	2.9
F9	0.075	2.8	3.0
F11	0.073	2.4	

dissolved oxygen. The standard inversion–recovery method with the pulse sequence π–t–$\pi/2$–t_2 ($t_2 \cong 8T_1$), at a frequency of 22.63 MHz and a temperature of 93 °C, was used to determine T_1 of the main-chain carbons in a Bruker WH-90 spectrometer, with complete noise decoupling of the protons. At lower temperatures the spectral peaks were too broad for adequate determination of T_1. Nuclear Overhauser enhancements were evaluated from the ratio of peak areas under complete noise decoupling and under gated decoupling only during data acquisition following each pulse. The magnetic field was locked on the deuterium resonance. The chemical shifts of the methine carbons of the maleic anhydride unit and of the main-chain methylene and methine carbons of the 1-octadecene unit of POMA were found at 35.02, 43.93, and 51.86 ppm, respectively, with respect to $\mathrm{Me_4Si}$.

Results and Discussion

Intrinsic viscosities $[\eta]$, weight-average molecular weights M_w, and osmotic second virial coefficients A_2 for six POMA fractions at 25 °C in ethyl acetate are shown in Table I. The viscosities can be described by the relation

$$[\eta]/(\mathrm{dL\ g^{-1}}) = 5.5 \times 10^{-4}M_w^{0.48} \tag{1}$$

but the molecular weights cover only a fourfold range, so that eq 1 should not be used outside these limits; nor has the exponent 0.48 any great significance. Indeed, the dimensionless ratio $A_2M_w/[\eta]$ falls in the range 1.1–1.5, which is a normal figure for flexible chains in good solvents[8] and close to the value $^8/_5$ characteristic of impenetrable hard spheres. This somewhat unusual behavior is quite similar to that observed for other polymers with large and frequent side groups, including cellulose and amylose tricarbanilates[9] and poly[N-(n-octadecyl)maleimide],[10] as well as of amylose itself,[11] at relatively low molecular weights: the log–log plot of intrinsic viscosity as a function of molecular weight flattens and approaches a constant limit at the low end. The "Einstein density", calculated as $2.5/[\eta]$, is not much below that of bulk polymer; for example, the value for F11 in Table I is 0.34 g/mL. It is thus quite possible that our data fall in the middle of a crossover from random-flight statistics to globular conformations dictated by the space-filling requirements of the side groups.[9-11] If we ignore this possibility and treat the data of Table I as those for unperturbed random-flight chains, we find a characteristic ratio of about 12. The limited range of molecular weights makes both possible interpretations rather speculative. It may be remarked that a characteristic ratio of 18.6 has been reported for poly(1-octadecene) in anisole at 71 °C.

The dipole moment per repeat unit was evaluated from the equation[13]

$$\frac{\langle\mu^2\rangle}{x} = \frac{27k_BTM_1}{4\pi N_Ad_0}\left[\frac{(d\epsilon/dw)}{(\epsilon_0+2)^2} - \frac{2n_0(dn/dw)}{(n_0^2+2)^2}\right] \tag{2}$$

which ignores differences in atomic polarization per unit volume between solute and solvent, and the results are in Table II. In the above equation ϵ_0, n_0, and d_0 are the static dielectric constant, the optical refractive index, and the density, respectively, of the solvent; M_1 is the molecular weight of the polymer repeat unit; k_BT is the thermal energy; N_A is Avogadro's number; and w is the solute weight fraction. Using the dipole moment of succinic anhydride[14] as that of the repeat unit, μ_1 = 4.07 D in benzene and 4.25 D in dioxane, we find a dipole moment ratio, $D = \langle\mu^2\rangle/x\mu_1^2$ = 0.45 in benzene and 0.44 in dioxane. These figures are not unlike those for many other polymers,[15] but elude interpretation in view of the conformational peculiarity mentioned earlier.

Table II
Dipole Moments of POMA F5 at 25 °C

	$d\epsilon/dw$	dn/dw	$(\langle\mu^2\rangle/x)/\mathrm{D}^2$
in benzene	2.25	−0.015	7.40
in dioxane	3.01	+0.066	7.93

Table III
^{13}C Spin-Lattice Relaxation Times (s) of Backbone Carbons, POMA F5 in Toluene-d_8 at 93 °C[a]

methylene carbon	0.067 (2.0 ± 0.3)
methine carbon of octadecene	0.129
methine carbon of maleic anhydride	0.055 (1.9 ± 0.3)

[a] Nuclear Overhauser enhancement factors in parentheses.

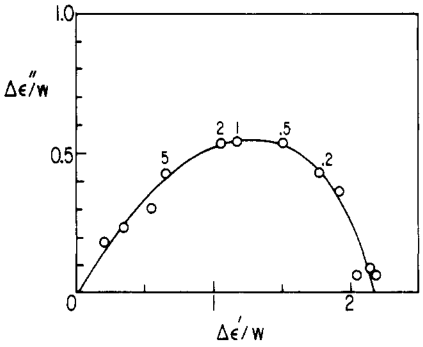

Figure 1. Cole–Cole diagram for fraction F3, 3.88% w/w in benzene at 25 °C. Increments per unit weight fraction of loss factor, $\Delta\epsilon''/w$, are plotted against increments in permittivity, $\Delta\epsilon'/w$. Numerals on the points are frequencies in megahertz.

Dielectric dispersion results for fraction F3 in benzene at 25 °C are displayed as a Cole–Cole plot in Figure 1. It is seen that the entire dispersion falls under a single peak. The maximum loss factor comes at about 0.8 MHz, corresponding to a mean dielectric correlation time of 200 ns. This figure defines a much slower motion than that typical of transverse dipoles even with long side chains, e.g., 4 ns for poly(4-chlorostyrene)[16,17] and 16 ns for poly(1-eicosene/$\mathrm{SO_2}$),[18] both also in benzene at 25 °C. On the other hand, it matches the estimated tumbling or terminal relaxation time, $\tau \cong M[\eta]\eta_0/RT$ = 190 ns for F3. Thus, the true local segmental motion is at least as slow as the observed relaxation rate and may of course be enough slower to be unable to compete[16] with overall tumbling of the globular molecule. A full resolution of this question must await observations of the molecular weight dependence of the relaxation time.

The ^{13}C spin-lattice relaxation time (Tables III) show that the two carbons of the vinyl group move in concert (T_1 for the methylene carbon being half that for the methine carbon) but that the maleic anhydride unit moves somewhat less rapidly. The latter, of course, is more relevant to a comparison with the dielectric data. Analysis with a simple exponential correlation function leads to a correlation time of either 2 or 12 ns for this carbon, but only the former figure is consistent with the observed Overhauser enhancement factor. Roughly similar magnitudes are obtained if more detailed models (e.g., Hall–Helfand[19] or Jones–Stockmayer[20]) are used. There is no quantitative way to extrapolate this result from 93 to 25 °C for comparison with the dielectric result; qualitatively, it looks as though some segmental flexibility is definitely present at the higher temperature. Again, data for a wide range of molecular weights and temperatures are needed.

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Scaling Power Laws for Semidilute Polymer Solutions. A Monte Carlo Simulation in Three Dimensions

HANS CHRISTIAN ÖTTINGER

Fakultät für Physik der Universität Freiburg i.Br.,
D-7800 Freiburg i.Br., West Germany.

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Introduction

In recent years considerable progress has been made in the understanding of semidilute solutions of long, flexible polymers.[1] Much of this progress is based on the discovery of a relation between polymer solutions and magnetic systems by De Gennes[2] and Des Cloizeaux.[3] One of the most important consequences of this relation is Des Cloizeaux's scaling law for the osmotic pressure Π of athermal polymer solutions (these are solutions in good solvents for which only entropy effects are present). If the polymers are represented by self-avoiding walks (SAW model) on a five-choice simple cubic lattice with lattice spacing a, this scaling law reads

$$a^3\Pi/kT = CF(C/C^*) \qquad (1)$$

where the concentration $C = N/Q$ is the number of polymers N divided by the number of lattice sites Q, T is the temperature, k is the Boltzmann constant, and F is a universal function. For monodisperse polymer chains of n monomers (that is, each polymer consists of n sites or $n - 1$ links on the lattice) the critical concentration is defined by

$$C^* = B^{-3}(n-1)^{-3\nu} \qquad (2)$$

where $\nu = 0.588 \pm 0.001$[4] is the exponent for the end-to-end distance R of a single polymer chain ($\langle R^2 \rangle = B^2(n-1)^{2\nu}$, $B \approx 1$). The scaling law (1) is valid for large values of N, Q, and n as long as the monomer concentration is not too high ($nC \ll 1$). In the semidilute region ($C^* \lesssim C \ll 1/n$) the scaling function $F(x)$ is given by a simple power law:[3]

$$F(x) \sim x^{1/(3\nu-1)} \qquad (3)$$

Des Cloizeaux's scaling law for the osmotic pressure can be transcribed into an equivalent scaling law for the partition function $Z(Q,n,N)$:[5]

$$\frac{1}{N}\ln\frac{Z(Q,n,1)^N}{N!\,Z(Q,n,N)} = G\left(\frac{C}{C^*}\right) \qquad (4)$$

where the scaling function G is defined by

$$G(x) = \int_0^x \frac{F(x') - 1}{x'}\,dx' \qquad (5)$$

The quantity $Z(Q,n,1)$ appearing in eq 4 (which is the well-known number of configurations of a single chain on a lattice) is given by

$$Z(Q,n,1) = \frac{Q}{2}A\mu^{n-1}\,(n-1)^{\gamma-1} \qquad (6)$$

with $A = 1.17$, $\mu = 4.6834$, and $\gamma = 1.165$.[6] In the semidilute region one obtains in leading order from eq 3 and 5

$$G(x) \sim x^{1/(3\nu-1)} \qquad (7)$$

By means of the scaling laws (1) and (4) the unknown dependence of the osmotic pressure and of the partition function on three variables (Q, n, N) is reduced to the unknown dependence of the scaling functions on one variable (C/C^*).

Experimental results for the osmotic pressures of polymer solutions seem to be in good agreement with the scaling law (1).[7] However, exact enumeration studies and Monte Carlo simulations in three dimensions disagree slightly but significantly with the scaling law for the osmotic pressure.[8-13]

In the present letter the scaling law (4), (7) will be tested by a direct Monte Carlo estimation of the partition function for chains of length $n = 60$ and $n = 80$ on a simple cubic lattice. In contrast to a previous paper[5] where the properties (virial coefficients) of dilute solutions ($C \ll C^*$) have been estimated, the present letter is concerned with eq 7 for semidilute solutions ($C^* \lesssim C \ll 1/n$). In the next section the Monte Carlo procedure will be described in detail. The results and a discussion will be presented in the third section. A brief summary concludes the paper.

Monte Carlo Procedure

Recently, Meirovitch developed the "scanning method" for the Monte Carlo estimation of the entropy of single polymer chains.[14-17] Using this method which is based on an old paper by Rosenbluth and Rosenbluth[18] one has to scan for allowed continuations in future steps before adding a new monomer. It has been shown in a preceding paper[5] that the scanning method is well suited for the