viously.[13] A sample of $N_3P_3F_5(C_6H_5)$ (13) (6.0 g, 1.95 mmol) was vacuum-transferred into a small Pyrex tube and the tube was sealed. The tube was then heated in a thermoregulated oven at 290 °C. The contents of the tube gradually polymerized over a 48-h period to give the elastomeric polymer $[N_3P_3F_5(C_6H_5)]_n$ (14) in almost quantitative yield.

Thermal Polymerization of $N_3P_3F_5(C_6H_5)$ (13) with (a) 1% $(NPCl_2)_3$ and (b) 10% $(NPCl_2)_3$ as Initiator. The polymerization reactions with performed as above for $N_3P_3F_5(C_6H_5)$ (13), (13), that $(NPCl_2)_3$ [(a) 1%, 0.06 g, 0.01 mmol; (b) 10%, 0.60 g, 1.0 mmol)] was added as initiator. The tubes were heated to 290 °C in a thermoregulated oven. The contents of the tube a polymerized during a 6-h period, while the contents of tube b polymerized within 20 min to yield $[N_3P_3F_5(C_6H_5)]_{0.99}[N_3P_3Cl_6]_{0.01}$ (16) and $[N_3P_3F_5(C_6H_5)]_{0.9}[N_3P_3Cl_6]_{0.1}$ (17), respectively, in almost quantitative yield.

Attempted Polymerization of $N_3P_3F_5(C_6H_5)$ (13) with 18 mol % of $Fe(\eta\text{-}C_5H_5)_2$. This reaction was carried out as described above for $N_3P_3F_5(C_6H_5)$ (13), except that $Fe(\eta\text{-}C_5H_5)_2$ (0.065 g, 18 mol %) was added. The tube was heated to 290 °C in a thermoregulated oven. An orange, nonviscous, homogeneous solution was obtained. After 30 h, the contents of the tube appeared unchanged. However, after 36 h, the color darkened and after 40 h the contents of the tube became dark brown and immobile. After being cooled, the tube was found to contain an acidic gas. The dark brown, brittle, solid material in the tube was insoluble in all common solvents.

Thermal Polymerization of $N_3P_3F_5(C_6H_5)$ (13) with 18 mol % of $Ru(\eta\text{-}C_5H_5)_2$. The polymerization reaction was performed as above for $N_3P_3F_5(C_6H_5)$ (13) except that $Ru(\eta\text{-}C_5H_5)_2$ (0.82 g, 18 mol %) was added. The tube was heated at 290 °C in a thermoregulated oven. The $N_3P_3F_5(C_6H_5)$ (13) gradually polymerized over a 48-h period to give a mixture of $[N_3P_3F_5(C_6H_5)]_n$ (14) and $Ru(\eta\text{-}C_5H_5)_2$. These were separated by dissolving the mixture in THF (150 mL) and precipitation of the polymer into hexane (2 L). The ruthenocene was recovered quantitatively from the hexane.

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Supplementary Material Available: ^{31}P and ^{19}F NMR spectra of **3a** and ^{31}P NMR spectrum of **7** (1 page). Ordering information is given on any current masthead page.

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Notes

Similar Matrix Expressions Describe Configuration Partition Functions for Intrachain Formation of Antiparallel β Sheets and Interacting α Helices

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Recently we described a tractable matrix formulation for the intramolecular transition from a statistical coil to a β sheet with tight bends (β bends). The formulation can be specialized so that all strands in a particular β sheet have the same number of residues, but in general there is no artificial restraint on the number of residues in a strand. Recently the method has been extended so that contigous strands in a particular β sheet may be connected by loops of arbitrary size.[3] Although statistical weight matrices may become extremely large under some circumstances,[4] computations required for extraction of the statistical mechanical averages of configuration-dependent physical properties require remarkably little memory or execution time. Two features of the matrix formulation are responsible for the ease of implementation: (1) The matrices are sparse, and (2) simple summarizing statements provide the location and identity of all nonzero elements. The computational algorithm is based on the simple summarizing statements. The huge statistical weight matrices need never be formulated and manipulated.

Figure 1 depicts an example of the type of chain that is included in the ensemble that was described in the original formulation.[1] This chain contains three intramolecular β sheets. One "sheet" consists of a single extended strand. Strands in the two multistranded sheets are connected by tight bends. The statistical weights assigned to each of these sheets are noted outside the parentheses in Figure 1. Residues in the disordered regions contribute a factor of 1 to the statistical weight. Each residue in a sheet contributes a β-sheet propagation factor denoted by t. Two additional parameters arise from edge effects. Each sheet residue that does not have a partner in a preceeding strand contributes an additional factor of τ, and each tight

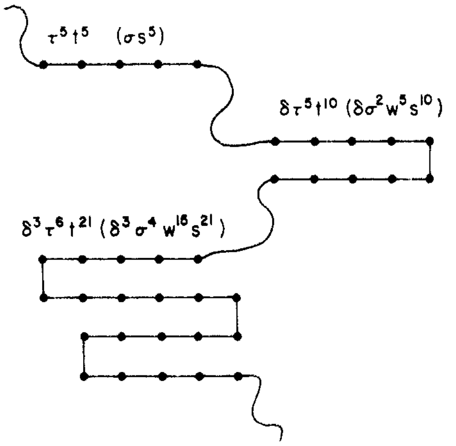

Figure 1. Diagrammatic chain with three ordered regions. Statistical weights outside parentheses are those assigned when the ordered regions are β sheets. Inside parentheses are statistical weights assigned when the ordered regions are comprised of α helices.

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

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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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