Although rigorously the present spectral evidence can be interpreted along the lines indicated above only for the case of 45° fibril angles, the ordering of the molecules which it suggests is expected to occur more generally. The ordering indicated by the spectra implies that a higher degree of anisotropy prevails in the organization of cellulose in cell walls than had previously been recognized.

Acknowledgment. Support of this work from the Institutional Research Fund of The Institute of Paper Chemistry is gratefully acknowledged.

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Concentration Dependence of Osmotic Pressure in the Semidilute Range

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From scaling laws, it has been predicted[1,2] that the osmotic pressure (π) of a polymer solution in the semidilute range of concentration (c) should in athermal solvents be proportional to $(cRT/M)(c/c^*)^{5/4}$ and hence to $c^{9/4}$. Here M is the molecular weight and c^* is a critical concentration above which the molecular coils overlap each others' domains and may be defined as M/N_0s^3; N_0 is Avogadro's number and s is the radius of gyration. The semidilute concentration range corresponds to $c > c^*$. This relation has been tested by Jannink and co-workers[3] from data of Cotton and co-workers[4] on polystyrene, but the concentration included only a very narrow range in which the $^9/_4$ exponent was valid. Other tests have been deduced indirectly from light scattering measurements.[3,5,6]

Extensive osmotic pressure data obtained by Browning[7] in this laboratory in 1948 can be used to test this prediction. Solutions of a poly(vinyl acetate) fraction with $\bar{M}_n$ = 280 000 in methyl ethyl ketone and 1,2,3-trichloropropane were measured at two temperatures in each solvent over a concentration range up to c = 0.067 g/cm^3. In Figure 1, osmotic pressures reduced to a temperature of 283 K by multiplication by $283/T$ are plotted logarithmically against c in g/cm^3. In each solvent, data at the two temperatures fall together and over a considerable concentration range are described precisely by a line with slope $^9/_4$.

The proportionality constants in the two solvents are clearly different. Although both solvents are "good" (the exponent for intrinsic viscosity in the Mark–Houwink

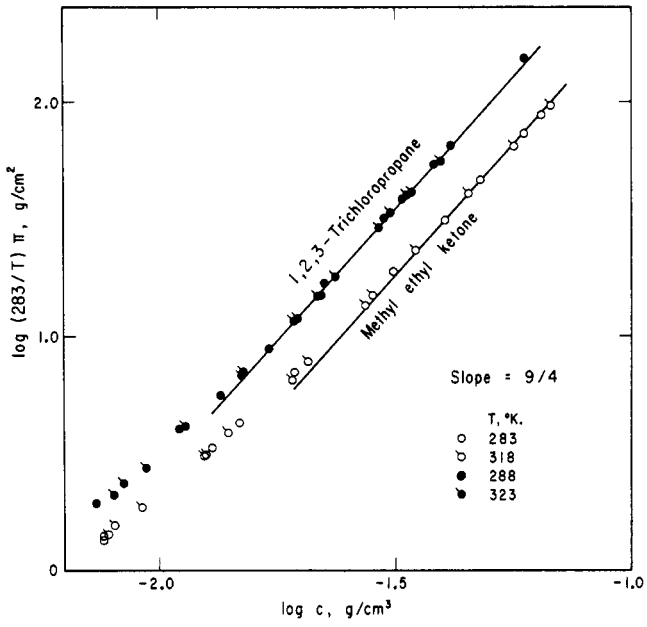

Figure 1. Logarithmic plot of $\pi(283/T)$ in g cm^{-2} against polymer concentration in g cm^{-3} for poly(vinyl acetate) in two solvents at two temperatures each as identified.

equation is 0.71 for methyl ethyl ketone[8]), they are actually "better" than athermal since the partial molal heats of dilution obtained from an earlier analysis[7] are negative, and are more so for the 1,2,3-trichloropropane. The difference in π/T for the two solvents at a given c could be attributed to the $(c^*)^{-5/4}$ factor and would correspond to a c^* ratio of 0.60 for 1,2,3-trichloropropane/methyl ethyl ketone. Another consequence of scaling laws[1] is that the second virial coefficient A_2 should be proportional to s^3 and hence to $(c^*)^{-1}$. These coefficients are[7] 8.0 and 5.0 × 10^{-4} cm^3 g^{-2} for 1,2,3-trichloropropane and methyl ethyl ketone, respectively, corresponding to a c^* ratio of 0.62, in good agreement. A similar ratio would be expected from the inverse ratio of the intrinsic viscosities. The intrinsic viscosity of this sample is available only in methyl ethyl ketone (98 mL/g at 25 °C); however, a qualitative comparison can be made from the specific viscosities of another (unfractionated) sample at a concentration of 0.01 g/cm^3, which are[9] 1.95 and 1.31, respectively; the inverse ratio is 0.67.

The absolute values of c^* are somewhat elusive. They can be estimated from the second virial coefficient by combining the definition $c^* = M/N_0s^3$ with a relation quoted by Fujita[10] for the interpenetration function $\Psi(z)$, which should be approximately 0.25 for this molecular weight; c^* is 0.040 g/cm^3 in methyl ethyl ketone and 0.025 g/cm^3 in 1,2,3-trichloropropane. These correspond to points on the lower portions of the linear regions of the curves in Figure 1. Alternatively, from the empirical approximation[11] that $c^* \cong 3/[\eta]$, in methyl ethyl ketone c^* = 0.031 g/cm^3. On the other hand, the rheological symptoms generally attributed to the onset of entanglement coupling appear at a somewhat higher concentration. The critical molecular weight M_C for the effect of entanglements on viscosity is[12] 22 600 for undiluted poly(vinyl acetate). Dilution increases it[12] by a factor of v_2^{-1} (where v_2, the volume fraction of polymer, is c/ρ and ρ is the polymer density), so the critical entanglement concentration for this molecular weight is 0.10 g/cm^3. The solutions described here may be considered to be semidilute but not entangled.

0024-9297/80/2213-1719$01.00/0

Acknowledgment. This work was supported in part by the National Science Foundation, Grant No. DMR 78-16954, Polymers Program. The author is indebted to Dr. M. Delsanti for helpful discussion.

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Contribution to the Conformational Study of Regularly Alternating Copolymers

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Self-avoiding random walks (SARW) on lattices have long been used as models for flexible macromolecules. These models allow description of the thermodynamic properties of dilute solutions of polymers, taking into account the effect of volume exclusion. A great amount of information about such walks has been gathered by means of Monte-Carlo methods, exact enumeration for short chain lengths, and approximate theories.

In preceding works,[1,2] we established rigorous analytical recurrence formulas for a five-choice SARW on a cubic lattice. Several coefficients characterize such a walk, particularly C_n, the total number of configurations that a chain of n segments can take on the lattice (or the number of self-avoiding walks of $n - 1$ steps) and $\langle r_n^2 \rangle$, the mean-square end-to-end distance of these configurations.

Determination of C_n and $\langle r_n^2 \rangle$

We briefly recall our preceding results. Earlier,[1] we proposed recurrence formulas for the calculation of accurate values of C_n for a three-dimensional cubic lattice. This quantity was obtained as a sum of partial terms. Each of these partial terms corresponds to the population of configurations having a given value of x, the number of primary contacts between nearby segments. A primary contact occurs between segments of the chain if the distance between them is equal to the side of the lattice cell (Figure 1). The value of x can vary between 0 and $(n - 2)/2$ for n even and 0 and $(n - 3)/2$ for n odd. Configurations having a given value of x can present different numbers of primary contacts between segments distant on the chain (segments p and $p + i$, with $i > 3$). Their number, designated by u, can vary between $u = 0$ and $u = u_{max}$, the latter being a function of x that can be calculated.[1] Our independent variable is y, the number of secondary contacts between nearby segments (segments p and $p + 2$). The distance between these segments is equal to the diagonal of the lattice cell (Figure 1), and y varies between 0 and $n - 2$.

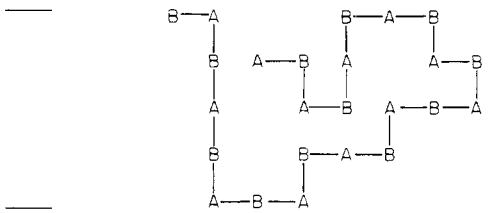

Figure 1. Configuration that can exist when the monomers A and B are compatible with each other in solution and both soluble (identical with a soluble homopolymer configuration). Secondary contacts between nearby segments occur between segments of the same nature and primary contacts between segments of different nature (also true for a cubic lattice).

Let us note that by the manner we have established our recurrence formulas, we can determine separately the number of configurations of a chain n having given values of x and u. Earlier,[2] we have given the following recurrence formula:

$$\langle r_n^2 \rangle = \gamma \langle r_n^2 \rangle_0 + (1 - \gamma) \langle r_{n-2}^2 \rangle \tag{1}$$

where $\langle r_n^2 \rangle_0$ is the mean-square end-to-end distance of the class of configurations of the chain n with $x = 0$ primary contacts, $\langle r_{n-2}^2 \rangle$ is the mean-square end-to-end distance for all the configurations of a chain $n - 2$, and $\gamma = [N]_n^{x=0}/C_n$, where $[N]_n^{x=0}$ is the number of configurations of the chain n having $x = 0$ primary contacts. Also, C_n is the total number of configurations of this chain.

In order to make use of eq 1 we have to establish algebraic relations to determine $\langle r_n^2 \rangle_0$, for each value of n. Letting $\log \langle r_n^2 \rangle_0 = E_n^0 \log n$, the exponent E_n^0 can be calculated with the help of eq 2 and 3 of ref 2.

Regularly Alternating Copolymers

We now apply the preceding results to the study of two types of regularly alternating copolymers. We shall suppose that the constituent monomers A and B are incompatible with each other in solution. We represent this situation by stipulating that two segments A and B cannot be primary neighbors. On a square lattice or on a cubic lattice, primary contacts are of type AB. The configurations with $x \neq 0$ and $u \neq 0$ will then disappear. We now investigate two cases.

(a) A and B are soluble. In this case

$$C_n = \sum_{y=0}^{y=n-2} [N]_n^{x=0,y} \tag{2}$$

and

$$\langle r_n^2 \rangle = \langle r_n^2 \rangle_0 \tag{3}$$

For this type of copolymer and $n = 15$, we find

$$C_{15} = 984\,003\,000$$

$$\langle r_{15}^2 \rangle = 40.37$$

while for a homopolymer we had

$$C_{15} = 4\,468\,955\,764$$

$$\langle r_{15}^2 \rangle = 25.33$$

(b) A and B are poorly soluble. A monomer unit will now have a tendency to draw near a segment of the same nature. The configurations will then reduce to those corresponding to $y = y_{max} = n - 2$, and

$$C_n = [N]_n^{x=0,y=n-2} \tag{4}$$

These configurations obviously have a helicoidal structure. To evaluate their mean-square end-to-end distance,

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