have the following simple tenet: the physical properties of the nematic can be described as if every chain consists of L/λ independent rodlike units. Thus, for semiflexible chains eq 2 becomes

$$\alpha \simeq c_\lambda{}^2 \simeq \lambda^4 D^2 \rho_\lambda{}^2 \simeq \alpha^{-2} P^4 D^2 \rho_P{}^2 \tag{9}$$

Here, the number density of deflection segments ρ_λ is α times the number density of persistence segments ρ_P. Equation 9 was previously derived in a different way.[2] Next, the thickness of the depletion layer becomes

$$d_c \simeq \lambda \alpha^{-1/2} \simeq \alpha^{-3/2} P \tag{10}$$

Hence, the increase in surface tension is written as

$$\Delta\tau \simeq k_B T d_c \rho_\lambda \simeq k_B T \left(\frac{\varphi^2}{P D^5} \right)^{1/3} \tag{11}$$

with $\varphi \equiv (\pi/4) D^2 P \rho_P$ the volume fraction. This result can also be obtained by substituting λ for L in eq 7.

These equations show that the interfacial behavior of nematic polymers and rods is markedly disparate. The increment in surface tension increases with concentration for long semiflexible polymers but to leading order it is constant for rods. A similar though reversed disparity occurs for the elastic constants.[4,14] Thus, it seems the influence of semiflexibility in nematic solutions becomes apparent especially in the presence of an external field, whatever its nature.

Equations 10 and 11 yield numerical values amenable to measurement, though it remains to be seen whether experimental conditions can conform to the requirements of the calculation. Intermediately long polymers pose a particular problem because of strong end effects.[3,9] An interesting preliminary analysis of these within a "macroscopic" context has been given by Meyer.[13] A referee has commented on the completely passive role played by the interface: the polymers are hindered by solely steric repulsions. Dispersion forces could well exert a considerable influence on the density profile close to the surface so their effect if any must be assessed when comparing the expressions with experimental results. Little is theoretically understood about the alignment of nematic, anisometric molecules near surfaces,[15] although Meyer has presented convincing arguments why very long semiflexible chains near inert surfaces should align parallel.[13] Anyway, there is some evidence for this in certain cases.[13,16,17]

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(18) Equations 3 and 4 are derived by assuming the rods lose their orientational freedom only in the direction perpendicular to the surface.
(19) When $\alpha = \mathcal{O}(1)$ and $\bar{c}_r(d) \simeq 0$, eq 5 reduces to Auvray's eq 2.[11]

Communications to the Editor

Conformational Characteristics of Polyisobutylene: An Error with Consequences

One of us (L.C.D.) has detected a significant error in a paper by Suter, Saiz, and Flory[1] entitled "Conformational Characteristics of Polyisobutylene", in which a simple and detailed rotational isomeric state (RIS) model had been proposed. The matter requires more than a mere Erratum, since later work[2,3] on the X-ray and neutron scattering of polyisobutylene (PIB) was based on the erroneous RIS model; agreement between prediction and experiment had been unusually good and the questions arise why a "wrong" model is able to so convincingly predict detailed and accurate experimental data[2,3] and if a corrected RIS model would still find such strong experimental support in the same data.

The error consisted of inadvertently switching, in the numerical calculations, the values for the two distinct skeletal bond angles in the PIB chain: actually, $\angle C{-}CH_2{-}C = \pi - \theta'$ lies between 120° and 130°, and $\angle C{-}C(CH_3)_2{-}C = \pi - \theta''$ is approximately equal to the tetrahedral value of ca. 110°, but in the calculations $\pi - \theta'$ was given the smaller numerical value and $\pi - \theta''$ the larger one.

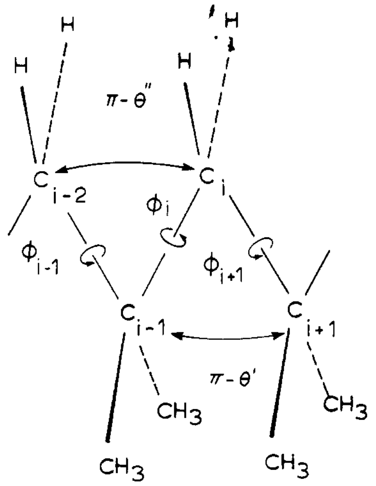

Figure 1. Sequence in a PIB chain.

The limiting value for the characteristic ratio of the end-to-end distance, $C = \langle r^2 \rangle_0 / n l^2$ $(n \rightarrow \infty)$, when calculated[4] from the erroneous RIS model with a predetermined set of statistical weight matrices and a corresponding set of torsion angles, $\{\varphi\} = \{+15°, -15°, +130°, -130°\}$, was 6.7 ($\pm$0.1), in excellent agreement with several sets of experimental data which indicated that $6.6 \leq C \leq 6.9$.[1] If proper bond angles are chosen, however, one obtains, all other

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Table I
Limiting Characteristic Ratio of the End-to-end Distance, $C = \langle r^2 \rangle_0 / nl^2$ ($n \to \infty$), Calculated with the *Erroneous* RIS Model[a]

	$\pi - \theta''$				
$\pi - \theta'$	108°	109°	110°	111°	112°
122°	4.51	4.67	4.83	5.00	5.18
124°	4.58	4.74	4.91	5.08	5.27
126°	4.65	4.81	4.98	5.16	5.35
128°	4.71	4.88	5.06	5.24	5.43
130°	4.78	4.95	5.12	5.31	5.50

[a] $\xi = 0.007$; $\{\varphi\} = \{+15°, -15°, +130°, -130°\}$.

Table II
Limiting Characteristic Ratio of the End-to-end Distance, $C = \langle r^2 \rangle_0 / nl^2$ ($n \to \infty$), Calculated with the *Corrected* RIS Model Proposed Here[a]

	$\pi - \theta''$				
$\pi - \theta'$	108°	109°	110°	111°	112°
122°	6.08	6.29	6.51	6.74	6.98
124°	6.17	6.39	6.61	6.84	7.08
126°	6.25	6.47	6.70	6.94	7.18
128°	6.33	6.55	6.78	7.03	7.28
130°	6.40	6.63	6.87	7.11	7.37

[a] $\xi = 0.007$; $\{\varphi\} = \{+25°, -25°, +120°, -120°\}$.

parameters being kept unchanged, quite unacceptable values for C. Table I shows the results of some such calculations, where the only statistical weight parameter in the model, ξ, was set to 0.007, the value deemed most probable at a temperature of 300 K; other values for ξ in the range $0 < \xi \leq 0.1$ (which spans all possible values[1]) are not significantly different from those given in Table I. If one computes the molecular scattering intensities for X-ray and neutron radiation, with the methods from ref 2, from this erroneous RIS model *without* inadvertently switching the two skeletal bond angles, one obtains scattering patterns significantly different from those observed experimentally.[2,3] Obviously, the RIS model given in ref 1 is in error, and the same mistake has been made, independently, in ref 1 and ref 2 and 3. (The calculations reported in ref 2 and 3 have been repeated by us in order to be certain of this unusual double mistake.)

Closer inspection of all results in ref 1 point, however, to the fact that small changes in the torsional angles associated with the rotational isomeric states, still in accord with the molecular mechanics computations reported in ref 1, are sufficient to bring calculated characteristic ratios to agreement with experiments. Results of computations, identical with those reported in Table I except for the set of torsion angles chosen, are shown in Table II. Hence, we propose here a revision of the four-state RIS model of ref 1:

$$\pi - \theta' = 124°$$

$$\pi - \theta'' = 110°$$

$$\{\varphi\} = \{+25°, -25°, +120°, -120°\}$$

together with the unchanged statistical weight matrices

$$\mathbf{U}' = \begin{bmatrix} 0 & 0 & 1 & \xi \\ 0 & 0 & \xi & 1 \\ 1 & \xi & 0 & 0 \\ \xi & 1 & 0 & 0 \end{bmatrix}$$

$$\mathbf{U}'' = \begin{bmatrix} 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \end{bmatrix}$$

where $\xi = 1.0 \exp(-1500/T)$, with T in units of kelvin. The limiting characteristic ratio at 300 K is then 6.6, in agreement with experiment.

When this new version of the four-state RIS model is used to compute scattering intensities, one obtains curves *indistinguishable* (within the uncertainty inherent to the Monte Carlo simulations) from the ones published by Hayashi, Flory, and Wignall[2,3] and hence in near perfect agreement with experiment.

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Structure and Related Properties of Solution-Cast Perfluorosulfonated Ionomer Films

Methods for obtaining solutions of high equivalent weight Nafion perfluorosulfonated ionomers (PFSI) have been reported during the past few years.[1–3] Dissolution at 250 °C under pressure of the as-received PFSI film in a 50/50 mixture of water and lower aliphatic alcohols such as ethanol is the best procedure for obtaining clear homogeneous colorless solutions.[1,2] It is also of interest to prepare solution-cast films in order to repair pin holes in PFSI chlor-alkali membranes[1,4] or for the coating of modified electrodes.[5] However, the cast film is poor, brittle, and cracked and dissolves readily at room temperature in many polar solvents, especially in water. A first answer to that problem has been given by Grot et al.[1] The procedure consists of adding triethyl phosphate (TEP), dimethyl sulfoxide (Me_2SO), or 2-ethoxyethanol (2EE). The room-temperature evaporation of the mixture then gives rise to a clear uncracked film with good mechanical properties after heating to 120 °C.[1] Quite recently Moore et al.[6] indicated that other polar solvents such as *N*,*N*-dimethylformamide (DMF) and ethylene glycol (EG) can be added to the PFSI solution in order to get good insoluble reconstructed films. Water and alcohol are first removed by evaporation at 80 °C and then the high-boiling solvent is removed by vacuum heating around 20 °C below its boiling point. Grot et al.[1] first suggested that differences observed between reconstructed films, without additive, evaporated at room temperature, and as-received PFSI membranes could arise from the micellar structure of the PFSI solution. In addition Moore et al.[6] assessed morphological differences between films reconstructed at room temperature without additive and as-received membranes as well as films reconstructed at high temperature with additive. In fact, very little is known about reconstructed Nafion membranes and even less about their structure. In this communication, we outline the differences in the properties of membranes reconstructed under various experimental conditions. These differences in

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