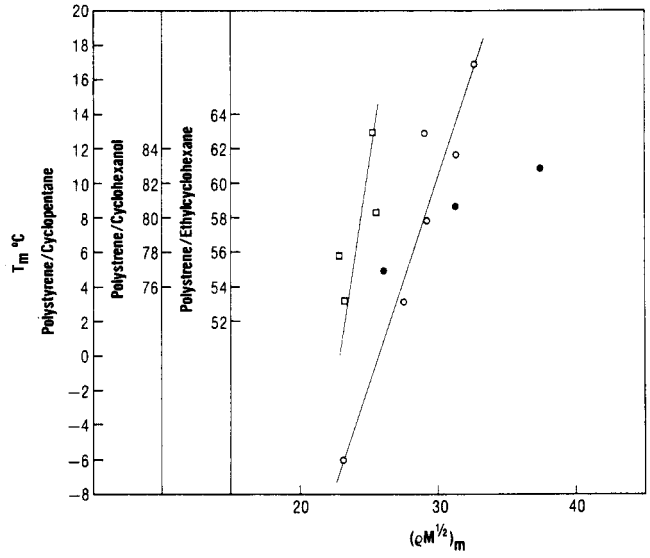

Figure 2. $(\rho M^{1/2})_m$ plotted against the respective T_m for three PS–solvent systems: (●) PS, M_v = 84 000, 236 000 and 881 000 in cyclohexanol, ref 8; (□) PS, M_w = 80 000, 123 900, 152 900, 238 700, and 569 000 in ethylcyclohexane, ref 13; (○) PS, M_w = 37 000, 97 200, 209 000, 400 000, 670 000, and 2 700 000 in cyclopentane, ref 14.

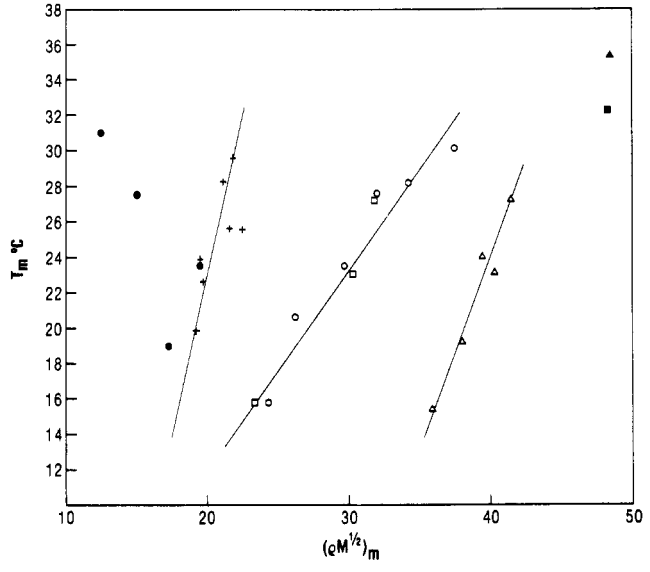

Figure 3. $(\rho M^{1/2})_m$ plotted against the respective T_m for the PS–cyclohexane system: (△) M_w = 51 000, 111 000, 166 000, 200 000, and 527 000, ref 6; (●) M_v = 43 600, 89 000, 250 000, and 1 270 000, ref 15; (○) M_w = 51 000, 93 000, 166 000, 394 000, 527 000, and 1 500 000, ref 16; (+) M_w = 80 000, 123 900, 152 900, 238 700, 253 000, 569 000, and 1 190 000, ref 17; (□) M_w = 51 000, 163 000, and 520 000, ref 18; (■) M_w = 3 200 000, ref 19; (▲) $M_w = 43.5 \times 10^6$, ref 20 and 21.

system Ps–cyclohexane, $(\rho M^{1/2})_m$ increases with M and with the approach to theta temperature, irrespective of the technique employed to obtain T_m, c_m, and the resultant $(\rho M^{1/2})_m$.

A comparison of the three figures reveals that while $(\rho M^{1/2})_m$ for LPE are of the order of 10 or less, the values for PS are 20 and above. Similar differences exist, for example, in the cases of *cis*-polybutadiene[23] whose $(\rho M^{1/2})_m$ are of the order of 10, while those of polyisobutylene in diisobutyl ketone[15] reach a value larger than 35.

From the above it is apparent that: (a) the product $(\rho M^{1/2})_m$ is not a constant for a polymer/solvent system; (b) $(\rho M^{1/2})_m$ is not the same for a given polymer in different solvents; and (c) $(\rho M^{1/2})_m$ is different for different polymers.

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On the Chain Conformation of Poly(tetrafluoroethylene) in the Crystalline Modification above 30 °C

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The possibility that the chain conformation of poly(tetrafluoroethylene) (PTFE), in the crystalline pseudo-hexagonal modification which is stable above 30 °C, may correspond to disordered successions of helical stretches having opposite sense of spiralization has been put forward in the past by De Santis et al.,[1] Brown,[2] Clark,[3] Bates and Stockmayer,[4] and Corradini.[5]

The possibility that neighboring chains may lack a strict periodic correlation in the atomic positions, except that chain axes maintain their parallelism in a pseudo-hexagonal array (with interaxial nearest distances of 5.66 Å instead of 5.59 Å, as in the low-temperature modification), has been discussed and proved feasible by the energetic calculations of Giglio and D'Ilario in a recent paper.[6] In this note, we wish to report a related contribution arising from recent theoretical and experimental work on the subject.

Under atmospheric pressure, poly(tetrafluoroethylene) shows two first-order transitions, at 19 and 30 °C, respectively.[7]

Below 19 °C, the chain conformation may be described as a one-atom helix, characterized by a unit twist $t = 360°$ ($^6/_{13}$) $= 166.15°$ and a unit height $h = 1.292$ Å.[7] Thus, the conformation corresponds locally to a nearly planar zigzag, with internal rotation angles σ all equal to 163.5°[8] or all equal to −163.5°, according to the sense of spiralization (Figure 1a).

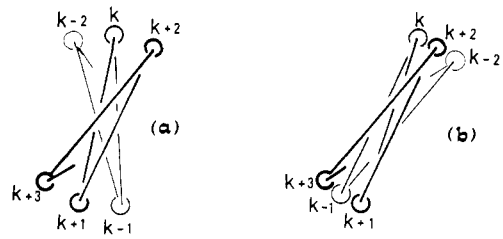

Figure 1. Projection of some carbon atoms of PTFE in a sequence along the chain axis: (a) right-handed helix; (b) junction at the kth bond (between atoms k and $k + 1$) between a section of right-handed and a section of left-handed chain.

(For a strictly planar zigzag, $\sigma = 180°$.) The coordinates of the carbon atoms along the right-handed helix are:

$$\rho = 0.42 \text{ Å}; \quad \varphi_k = kt = k166.15°; \quad z_k - z_{k-1} = 1.292 \text{ Å}$$

Consequently the fiber diagram shows strong diffracted intensities on the equator, the 6th, 7th, and 13th layer lines[9] (with reciprocal lattice corrdinates $\zeta = 0, 0.37, 0.41, 0.77$ Å^{-1}, respectively).

For the purpose of subsequent comparison, Figure 2a reports the square of the average Fourier transform of an isolated helical chain as a function of the reciprocal lattice coordinates ξ and ζ. The average was obtained over a number of different orientations of a chain containing ~200 atoms and having the above described conformation.

In order to perform calculations of the Fourier transforms of chains in which different senses of spiralization succeed each other along the same axis, it is expedient, if possible, to use models in which all the atoms of the chain have the same ρ coordinates as for a perfect helix.

The problem of constructing models of the chain satisfying the above reported conditions has been simplified by us, without loss of significance of the results, in the following manner. Consider an inversion in the sense of spiralization at the kth bond (Figure 1b). Making use of cylindrical coordinates ρ, φ, z, let us put $\rho = 0.42$ Å and $z_k - z_{k-1} = 1.292$ Å for all the carbon atoms of the chain, while

$$t = 166.15° = \varphi_k - \varphi_{k-1} = \varphi_{k-1} - \varphi_{k-2} = \ldots$$

for the atoms below bond k,

$$\varphi_{k+1} - \varphi_k = 180°$$

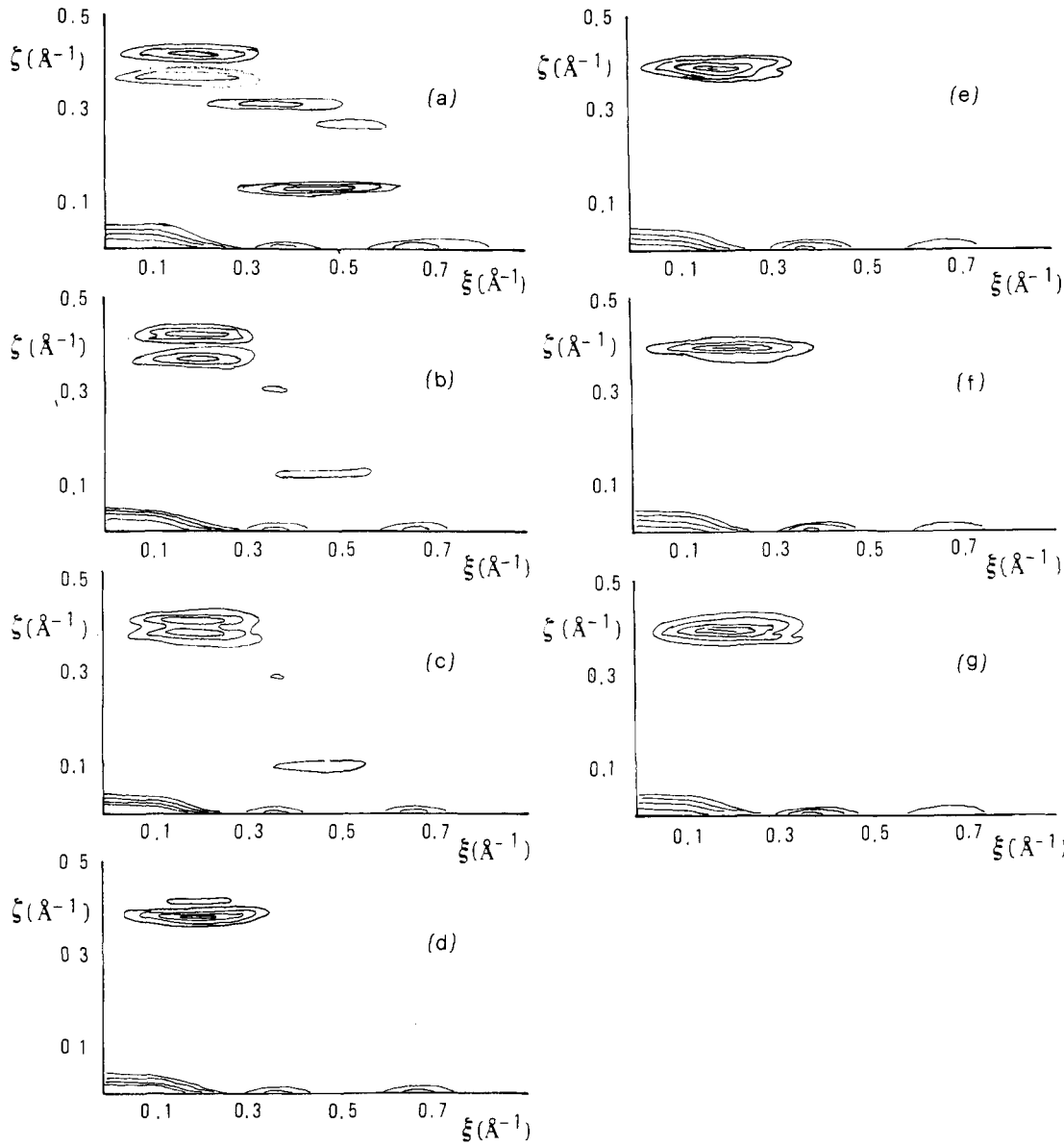

Figure 2. Square of the modulus of the Fourier transform of sections of chain comprising 65 CF_2 groups: (a) one-sense helix; (b–f) straight chains with random inversions in the sense of spiralization; (b) 1 inversion every 15 atoms; (c) 1 inversion every 10 atoms; (d) 1 inversion every 5 atoms; (e) 1 inversion every 3 atoms; (f) 1 inversion every 2 atoms; (g) conformation as arising from energy calculation. For further details see text.

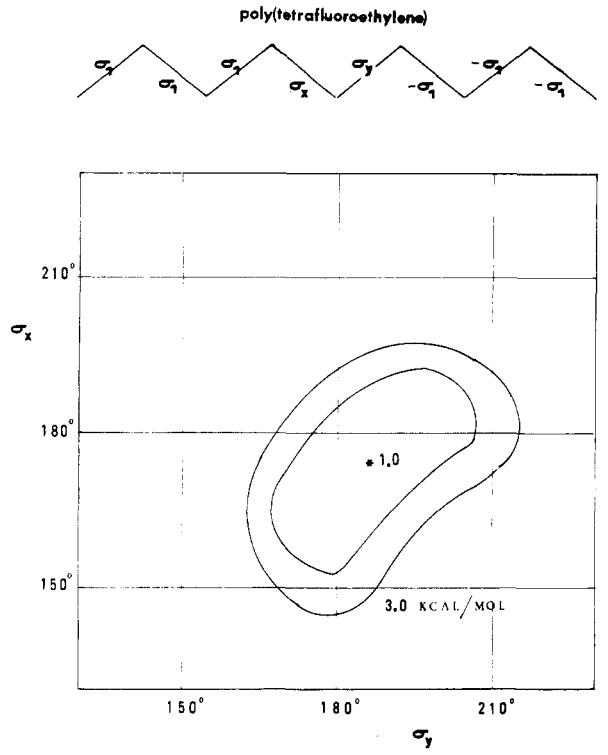

Figure 3. Conformational energy of a section of chain with $\sigma_1 = 165°$ as a function of σ_x and σ_y. The zero of energy is that of the same section of chain with all internal rotation angles $\sigma_1 = 165°$, correspondingly to the minimum of energy with the Bates[10] potential functions.

and

$$-t = -166.15° = \varphi_{k+2} - \varphi_{k+1} = \varphi_{k+3} - \varphi_{k+2} = \dots$$

for all the atoms above bond k.

The constancy of ρ assures us that the chain maintains its axis. The internal coordinates have been thus distorted, in the region of the junction, with respect to those of the single-sense helix; however, it can easily be seen that the distortions of bond lengths and angles are extremely small. In the case described, the succession of relevant internal rotation angles near the junction point is as follows:

σ_{k-2}	= 163.5°	(characteristic of a right-handed helix)
σ_{k-1}	= 167.8°	
σ_k	= 180°	
σ_{k+1}	= −167.8°	
σ_{k+2}	= −163.5°	(characteristic of a left-handed helix)

while the distorsions of the other internal coordinates are minimal as required, and concern only the valence angles $k + 1, k, k - 1; k, k + 1, k + 2$ (0.4°) and the distance $k, k + 1$ (0.003 Å). Though it is not exhaustive, we consider this model as sufficiently representative of possible inversions of the sense of spiralization, and we have calculated a series of Fourier transform maps of an isolated chain, varying the number and positions of the inversions. Figure 2 shows maps of the mean value of the calculated diffracted intensity as a function of the reciprocal-space coordinates ξ and ζ for some representative cases, with inversions distributed randomly every 15(b), 10(c), 5(d), 3(e), 2(f), bonds. For each case, the averaging has been performed on 6 chains of 65 CF_2 groups.

The experimental pattern for the high-temperature modification of PTFE shows only one single diffuse but intense layer line at $\zeta = 0.39$ Å^{-1}, between the equatorial layer and the layer line at $\zeta = 0.77$ Å^{-1}, both of which show sharp diffractions; the experimental pattern is very similar to the calculated pattern of Figure 2e except for the effects of the side-by-side packing of the cylindrically shaped chains, which give rise to the sharp diffractions on the layers with $\zeta = 0$ Å^{-1} and $\zeta = 0.77$ Å^{-1}. The transform of Figure 2b represents well the fiber spectrum between 19 and 30 °C, which is characterized by two distinct, intense but diffuse layer lines at $\zeta = 0.37$ Å^{-1} and $\zeta = 0.41$ Å^{-1}. In fact, the maintenance of distinct layer lines occurs in calculated patterns only when relatively long helicoidal stretches are maintained along the chain.

Table I
Coefficients of the Potentials[a] Used to Describe the van der Waals Interactions in PTFE[10]
$V(r) = a \exp(-br)/r^d - cr^{-6}$

Atom pair	$a \times 10^{-3}$	b	c	d
C–C	301.2	0.000	327.2	12
C–F	188.6	2.304	202.3	6
F–F	105.7	4.608	125.1	0

[a] The energy is in kcal/mol of atom pair if r is in Å.

To investigate the energetic feasibility of such inversions of the helix sense, at least for an isolated chain, we have proceeded as follows. It is necessary to refer to multidimensional conformational maps of a section of chain in which the two extremes are helices of fixed conformation, minimum energy, and opposite sense of spiralization, while the internal coordinates of the atoms at the junction are kept as variables. As an example, in Figure 3 we report the energy map as a function of σ_x and σ_y for a section of chain whose conformation is described by the following set of internal rotation angles (bond lengths and angles being kept fixed):

$$\dots, +163.5°, +163.5°, \sigma_x, \sigma_y, -163.5°, -163.5°, \dots$$

The zero of energy corresponds to the same section of chain in a single-sense minimum-energy spiralization. The calculations have been performed with the potential functions of Bates[10] (Table I); the same calculations were also performed with the slightly different potential functions of Giglio and D'Ilario, with similar results.

In order to evaluate approximately the conformations accessible to the chain we used the rotational isomeric state theory which replaces the configurational integrals by sums over discrete states.[11] The states need not necessarily be identified with energetic minima. Any degree of accuracy may in principle be attained by increasing the number of states, thus diminishing the intervals between torsional angles.

For this reason, we may confine our examination to bond states t_+, t, t_- for which the internal rotation angles are 165°, 180°, −165°; if we allow only passages in which the internal rotation angles vary from a given bond to the successive one in steps of 0° or 15°, the chain axis remains nearly unalterated. We have verified that this restriction does not significantly affect the results obtained.

We indicate as $E_{pack} = RT \ln \alpha$ the difference in packing energy per constitutional unit between the ordered and disordered structure (assuming as a first approximation that it is independent of the number of reversals of the helix sense); β is the statistical weight for a constitutional unit in the single-sense helical conformation, which we do not need to consider explicity here. A reasonable value at room temperature is, for the model chosen, $\beta = 1.3$.[12]

From the calculations with the Bates functions, the energies for different sequences of internal rotation angles and approximately conservative chain axis are:

$$E(\ldots t_+t_+t_+t_+t_+\ldots) = 0 = E(\ldots t_-t_-t_-t_-t_-\ldots)$$

$$E(\ldots t_+t_+tt_+t_+\ldots) = E(\ldots t_+t_+tt_-t_-\ldots) = 0.9 \text{ kcal/mol}$$

$$E(\ldots t_+t_+ttt_+\ldots) = E(\ldots t_+t_+ttt_-\ldots)$$
$$= 1.13 \text{ kcal/mol} = (0.9 + 0.23) \text{ kcal/mol}$$

$$E(\ldots t_+tttt_+\ldots) = E(\ldots t_+tttt_-\ldots)$$
$$= 1.36 \text{ kcal/mol} = (0.9 + 2 \times 0.23) \text{ kcal/mol}$$

The matrix of statistical weights then reads (RT = 600 kcal/mol):

	t_+	t	t_-
t_+	1	0.22	0
t	1	0.68	1
t_-	0	0.22	1

with largest eigenvalue λ. The ratio between the conformational partition functions pertinent to the disordered and ordered states (constant volume assumed) is then

$$Z = (\alpha\lambda/\beta)^N$$

and the free energy difference is

$$G = E_{\text{pack}} + RT \ln \beta - RT \ln \lambda = 0$$

at the transition point.

The frequency of occurrence of bond rotational states is independent of the ratio α/β; hence it is possible, with the methods suggested by Flory, to get the average lengths of the sequences in the three states;[13] $\langle y_t \rangle = \langle y_{t-} \rangle = 2.9$, $\langle y_t \rangle = 1.8$ with the functions of Bates; $\langle y_{t+} \rangle = \langle y_{t-} \rangle = 1.9$, $\langle y_t \rangle = 1.8$ with the functions of Giglio. The Fourier transform calculated according to the model suggested by this energetic calculation is reported in Figure 2g and appears in fairly good accordance with the experimental data.

In summary, it appears to us that a chain conformation of poly(tetrafluoroethylene) in which different senses of spiralization succeed each other frequently while the molecules are confined in a cylindrical envelope is both geometrically and energetically feasible. The x-ray diffraction data are in good agreement with the model proposed.

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The Influence of the Macromolecular Protecting Group in Conformational Studies on Polyoxyethylene-Bound Peptides

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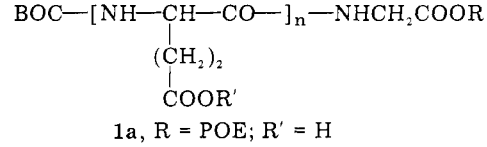
Systematic conformational studies on polypeptides in solution are mainly limited by the time-consuming synthesis and by the insolubility of many peptide sequences. The effective stepwise procedure of synthesizing peptides using solubilizing protecting groups, as realized in the liquid-phase method[1] (LPM), offers a solution to these problems. Here, the C-terminal amino acid of the peptide is attached to a soluble polymer by an ester bond; the macromolecular protecting group solubilizes the growing peptide chain and allows a quick, quantitative separation of all low molecular weight reagents. Owing to the favorable physicochemical properties in respect to the synthesis cycle, polyoxyethylene (POE) has proved to be the most suitable protecting group. The optical properties of this polymer allow investigation of the conformation of the POE-bound peptide without time-consuming deprotection and isolation steps.[2,3] Equally important is the strong solubilizing effect of the protecting group which enables conformational studies of the peptide in a great variety of solvents, including water. For the general reliability of such studies it is important to determine the extent of the influence of the POE chain on the conformational properties of the peptide.

In order to delineate the effect of POE, we synthesized homooligopeptides with a strong tendency to form secondary structures on POE. In each step of the synthesis, the POE



1a, R = POE; R′ = H
b, R = H; R′ = H
2a, R = POE; R′ = benzyl
b, R = H; R′ = benzyl

BOC = *tert*-butoxycarbonyl

group was cleaved from a sample and the conformation of the POE-bound peptide was compared with the free peptide under various conditions. Oligomers of L-Glu (**1**) and L-(γ-Bzl)-Glu (**2**) turned out to be most suitable for this purpose, because they are readily soluble.[4,5]

Oligomers of up to n = 20 were synthesized according to the procedure of the LPM described elsewhere[1] using POE of M_w 2×10^4 esterified by glycine; this residue served as an anchor group between peptide and POE. For the detection of any influence of the POE chain on the conformation of the peptide, the CD was measured after each step under various conditions. The CD spectra of the POE peptides **1a** in H_2O are shown in Figure 1. The formation of a α-helical structure starts at n = 7; at n = 20 the helix content amounts to about 60%.[4] Identical CD spectra were obtained for the free oligomers **1b** for all chain lengths, including the transition region, e.g., for n = 5–7 (Table I); the characteristic CD data of **1b** are in good agreement with (L-Glu) derivatives which have been obtained by polymerization of the corresponding NCA monomers.[4] The addition of POE to **1b** also had no influence upon the CD spectra (Table I). The line shape of the CD spectra was unaffected after adding 10% of POE to the solutions of the free peptides of various chain lengths. The helix–coil transition induced by the continuous neutralization of the COOH side chains did not display any detectable difference