(12) Anal. Calcd for $[-NP(CH_3)_{0.34}(OCH_2CF_3)_{1.66}-]_n$: C, 20.42; H, 2.01; N, 6.49; P, 14.36; F, 44.04. Found: C, 20.54; H, 2.16; N, 6.50; P, 14.51; F. 39.51. Calcd for $[-NP(CH_3)_{0.34}(OC_6H_5)_{1.66}-]_n$: C, 60.52; H, 4.55; N, 6.82; P, 15.09. Found: C, 60.32; H, 4.66; N, 6.71; P, 15.12.

(13) ^{31}P NMR peak positions are relative to aqueous 85% H_3PO_4 used as an external reference. Positive chemical shifts are downfield from H_3PO_4.

(14) The $\bar{M}_n$ molecular weights were determined by gel permeation chromatography comparison with polystyrene standards with the use of 10^6, 10^5, 10^4, and 10^3 Styragel columns in series. The solvent was THF.

(15) The glass-transition temperatures (T_g) were measured with the use of a Chemical Instruments Corp. torsional braid analyzer programmed to operate from −120 to +25 °C, with a temperature variation rate of 2.0 °C min^{-1}.

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Chain Conformation of Phase III Poly(vinylidene fluoride)

Recently Weinhold, Litt, and Lando[1] have produced and studied a crystalline form of poly(vinylidene fluoride), PVF_2, having a chain-axis repeat distance of 9.18 Å and identified as phase III. In a previous paper[2] (henceforth called I) we have suggested two possible chain conformations for this form of PVF_2: *tttgtttg′* and *tgtg′tg′tg* (where *t* represents trans, *g* gauche, and *g′* gauche′). This suggestion was based on an intramolecular conformational analysis using molecular mechanics. The interchain energy and the effects of finite temperature were not taken into account. Because of these omissions, we could not unambiguously choose between the two conformations, although *tgtg′tg′tg* was found to be of a higher intrachain energy than *tttgtttg′*.

We present here preliminary results of the calculation of combined intra- and interchain free energy as a function of temperature. Precise *t*, *g*, and *g′* conformations are used, even though such geometries do not exactly allow the observed fiber axis of 9.18 Å to be computed. The interchain energy is modeled by a mean-field approximation. In calculating the partition function, all the bond lengths and included angles are assumed to be hard variables and remain constant. Only the torsional angle θ is allowed to change. Because in both of the known structures (phases I and II) of PVF_2 every second torsional angle is trans, these are fixed. Consequently, only alternate θ are allowed to vary. We write the Hamiltonian of the system as a functional of the distribution of torsional angles. The free energy and the distribution function $n(\theta)$ are calculated self-consistently in a transfer-integral formalism which has been described at length elsewhere.[3]

In order to be able to treat possible phase III PVF_2 structures, we have extended the theory to describe structures in which the repeat distance along the chain contains eight successive torsional angles. Because all the odd-numbered angles have been kept trans, only the angles θ_{2n} are considered. These are divided into four sublattices θ_{8n}, θ_{8n+2}, θ_{8n+4}, and θ_{8n+6}, which we call the *A*, *B*, *C*, and *D* sublattices. (A formalism in which the alternate torsional angles are divided into two sublattices *A* and *B* has been outlined by Boyle.[4]) The intrachain energy is written in the form

$$V_1 = \int \int U(\theta,\theta') \times [n_{AB}(\theta,\theta') + n_{BC}(\theta,\theta') + n_{CD}(\theta,\theta') + n_{DA}(\theta,\theta')] \, d\theta \, d\theta' \quad (1)$$

and the interchain energy

$$V_2 = \tfrac{1}{4} \int \int \int \int W(\theta_1,\theta_1',\theta_2,\theta_2') \times [n_A(\theta_1)n_B(\theta_1')n_A(\theta_2)n_B(\theta_2') + n_B(\theta_1)n_C(\theta_1')n_B(\theta_2)n_C(\theta_2') + n_C(\theta_1)n_D(\theta_1')n_C(\theta_2)n_D(\theta_2') + n_D(\theta_1)n_A(\theta_1')n_D(\theta_2)n_A(\theta_2')] \, d\theta_1 \, d\theta_1' \, d\theta_2 \, d\theta_2' \quad (2)$$

The distribution $n_{AB}(\theta,\theta')$ measures the probability that a pair of torsional angles at adjacent *A* and *B* sites will be found at θ and θ'. The mean-field approximation contains the assumption that V_2 can be written as a function of n_A, n_B, n_C, and n_D alone. The function *U* is the change in potential energy resulting from the addition to a chain whose last torsional angle was θ, an additional unit at angle θ'. The function *W* is the energy of a monomeric unit located between segments in the same chain of torsional angles θ_1, θ_1' in the potential of a neighboring chain with angles θ_2 and θ_2'. The functions *U* and *W* have been computed using molecular mechanics as exists in the molecular structure determination system CAMSEQ II.[5] The requisite atomic charge densities were computed from the semiempirical molecular orbital scheme[6] CNDO/2.

The resulting transfer-integral expression contains four equations of the form

$$\lambda\psi_A(\theta) = \int \psi_A(\theta') \, d\theta' \int \int \int \exp\{-\beta[V_{AB}(\theta,\theta'') + V_{BC}(\theta'',\theta''') + V_{CD}(\theta''',\theta'''') + C_{DA}(\theta'''',\theta')]\} \, d\theta'' \, d\theta''' \, d\theta'''' \quad (3)$$

with

$$V_{AB} = U(\theta,\theta') + \tfrac{1}{2}[h_A(\theta) + h_B(\theta')] \text{ etc.} \quad (4)$$

The function h_i is the mean field at the site *i*. It is related to V_2 through

$$h_i(\theta) = 4 \frac{\partial V_2}{\partial n_i} \qquad (i = A, B, C, D) \quad (5)$$

These equations are solved iteratively from a starting set of trial functions n_A^0, n_B^0, n_C^0, n_D^0, which are first used in eq 5 to give V_{AB}, V_{BC}, etc., in eq 4. Hence a new set of n_A, n_B, n_C, n_D results from eq 3 through relations

$$n_i(\theta) = \psi_i\bar{\psi}_i(\theta) / \int \psi_i(\theta)\bar{\psi}_i(\theta')\theta' \quad (6)$$

with $\bar{\psi}$ the solution of the transposed transfer-integral equation. If more than one such set of solutions is obtained, the one with the lowest free energy is the stable solution. The others are metastable.

In the actual computation, the potentials and distribution functions were found for only six uniformly spaced values of the angle θ (θ = 0° is trans), and the integrations were placed by corresponding uniform summations.

The calculation yields one stable phase and several metastable phases in the low-temperature regime. The chain conformation of the stable low-temperature phase is found to be *tgtg′tgtg′*, the same as the experimental phase II (or α phase). In the high-temperature phase, the gauche and gauche′ states are equally populated, the fractional population increasing with temperature. We identify this as the melt phase. The melting temperature of the α phase is found to be 513 K (Figure 1), which is reasonably close to the experimental value of 460 K. We also find a low-temperature phase with chain conformation *tttttttt*. This is, therefore, identified with the all-trans β phase. It is metastable only with respect to the α phase.

The conformations of the metastable phases that occur with a repeat of eight torsional angles are shown in Table I. The table also contains the free-energy minima of each of these phases and of the α phase and β phase at a

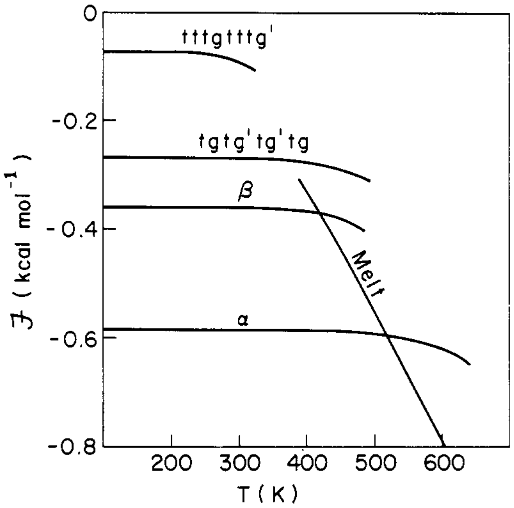

Figure 1. Free-energy minima corresponding to the two suggested chain conformations for a phase III PVF_2 are plotted as a function of temperature. The same quantities for the α, β, and melt phases are also shown for comparison. The termination of each line represents the limit of metastability of that phase.

Table I

chain conformations	repeat distance, Å[a]	free energy (300 K), kcal per monomer unit mol
tttgtttg'	9.11	−0.0954
tgtg'tg'tg	8.78	−0.2752
tttttgtg'	9.43	−0.2710
tgtg'tg'tg'	8.66	−0.2740
tttttttg	8.66	−0.2256
tttttgtg	8.66	−0.1184
tttgtgtg'	8.66	−0.1738
tttgtgtg	8.78	−0.0198
tgtg'tgtg' (α phase)	9.11	−0.5869
tttttttt (β phase)	10.33	−0.3405

[a] 112° bond angle.

temperature of 300 K. The eight conformations shown are the same as those arrived at, in I, from consideration of detailed molecular geometry-dependent intrachain energy. We in I, however, disregarded all but *tgtg'tg'tg* and *tttgtttg'*, because these are the only conformations that pack into a unit cell with an *n*-glide-plane symmetry that has been observed in the X-ray data[1] of the phase III sample. The fiber repeat distances of these two conformations are also close to the experimental value of 9.18 Å.

Figure 1 is a plot of the free-energy minima corresponding to these conformations. We find that *tgtg'tg'tg* is more stable than *tttgtttg'* at all temperatures in which they exist. This supports our suggestion in I that the interchain energy may favor *tgtg'tg'tg* over *tttgtttg'*. We note, however, that the difference in free energy of the two conformations is only 0.18 kcal/mol (per monomer unit) at 300 K. This energy is too small to compensate for the valence bond angle deformation energy needed to stretch the repeat distance of *tgtg'tg'tg* to 9.18 Å. The required deformation energy, as shown in I, is approximately 1 kcal per monomer unit mol, over and above that required for the *tttgtttg'* conformation. It may be mentioned in this connection that the infrared data[7] also favor the *tttgtttg'* conformation.

The present theory also predicts the structural phase transition shown in Figure 2. The transition takes *tgtg'tg'tg* into *tttttgtg'* at about 400 K. This breaks the *n*-glide symmetry of the lattice. Consequently, changes should occur in both the X-ray diffraction pattern and in the infrared spectrum of this structure. The observation of this phenomenon would definitely favor *tgtg'tg'tg* as the conformation of phase III.

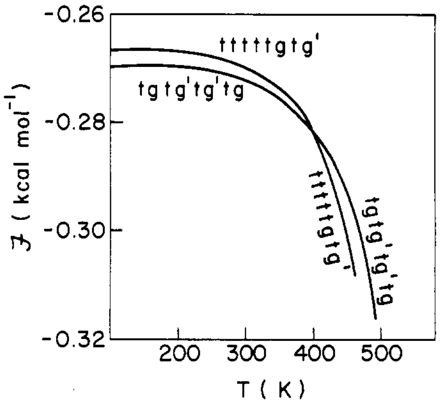

Figure 2. A high-temperature crystal–crystal phase transition, as predicted by the theory, is shown. Two sets of free-energy minima cross at a temperature of about 400 K.

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A New Liquid-Crystalline Material. Transition Metal-Poly(yne) Polymers

In recent years, there has been a growth of interest in extended chain polymers.[1] One of the characteristic features of rigid extended polymers is that their concentrated solutions form lyotropic liquid crystals. An example is poly(γ-benzyl L-glutamate), which exhibits cholesteric liquid crystalline behavior in selected solvents.[2] Some synthetic linear polymers such as polyamides,[1,3] polyesters,[1] and polyisocyanates[4] also form liquid-crystalline solutions. We now wish to report a new class of polymers exhibiting lyotropic liquid-crystalline behavior.

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