Predicted Chain Conformation for a Possible Phase III Form of Poly(vinylidene fluoride)

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ABSTRACT: Intramolecular conformational analysis of PVF_2 suggests two possible chain conformations for a form of this material identified as phase III by Lando and co-workers. The two chain conformations are perturbations of *TTTGTTTG'* and *TGTG'TG'TG*. Both are consistent with X-ray data. Although *TTTGTTTG'* is preferred on the basis of intrachain molecular energetics and FTIR data, it is not possible to select between these two conformations.

Extensive work has been carried out to elucidate the polymorphic forms of poly(vinylidene fluoride), PVF_2. Originally, two principal phases, termed phase I and phase II, were found. Crystal structures of these phases have been determined by both Lando and co-workers[1-3] and Tadokoro et al.[4-6] There are differences in the structural details of the crystals reported by these two groups. However, both groups agree that the phase I chain conformation is, essentially, an all-trans (*T*) structure, while the phase II chain conformation consists of a trans-gauche-trans-gauche', *TGTG'*, repeating structure. Interconversion between the two phases depends upon physicochemical conditions as well as inherent structural defects.[7]

A third phase of PVF_2 has also been identified and characterized by various workers. However, oriented samples for this polymorphic form have been difficult to obtain since attempts to orient phase III (or γ form) have led to a transformation to phase I similar to the stress-induced II–I phase transition.[8] Prest and Luca[9] identified weak infrared bands at 430, 776, and 810 cm^{-1} as characteristic phase III bands. However, a strong band at 1230 cm^{-1} has been prescribed as a distinctive phase III band by Kobayashi et al.[10] Hasegawa et al.[5] have suggested that phase III consists of all-trans chains, as in phase I, which are presumed to be packed in a lattice intermediate between phases I and II with respect to pressure treatment. The characterization of these and other polymorphic forms of PVF_2 continues to be pursued by various workers.[11,12]

Recently Lando and co-workers have further studied a PVF_2 structure they believe to be phase III.[13] They have produced very high molecular weight samples of PVF_2 films approximately 20–25-μm thick by casting them from *N,N*-dimethylacetamide solution. The samples were found to have the characteristic IR bands observed by Kobayashi et al.[10] and Prest and Luca.[9] Oriented samples were produced by drawing a thin film of the material at 178 °C. The samples were then cooled under tension. The drawn sample retained a predominant phase III IR spectrum. X-ray analysis of this sample indicated a "*c*" axis repeat of 9.18 Å, and "*a*" and "*b*" repeats of 4.97 and 9.66 Å, respectively. Fourier transform infrared studies (FTIR) of this material revealed, in addition to the characteristic phase III bands,[9,10] many other bands analogous to those of phases I and II.[14]

The purpose of this paper is to report the results of performing single chain conformational analyses on segments of PVF_2 in order to identify which intramolecular low-energy states possess conformational features consistent with the X-ray and FTIR data. The goal of this work is twofold. First, the structures found in these analyses are to be used as trial X-ray structures. Second, we wish to make *actual predictions* of the chain conformation of phase III prior to the experimental structure determination.

Table I[a]

structure	helicity	θ, deg	*D*, Å	*E*, kcal/mol
(a) The Unique Intrachain Energy Minima which Can be Modified to Possess a $D = 9.18$ Å				
TTTTTTTT	2_1 (RH)	180	10.33	−52.87
TTTGTTTG'	25_{12} (LH)	−172.65	9.11	−53.90
TTTTTGTG'	9_4 (RH)	159.56	9.43	−52.89
TTTTTG'TG	9_4 (LH)	−159.56	9.43	−53.28
TTTGTGTG	49_3 (RH)	21.94	8.78	−53.27
TTTG'TG'TG'	31_2 (RH)	17.56	8.78	−53.27
TGTGTG'TG'	13_6 (RH)	165.31	8.78	−53.02
TGTG'TGTG'	11_5 (RH)	163.10	9.11	−52.80
(b) Some Intramolecular Energy Minima which Cannot be Stretched to a Conformation Having $D = 9.18$; These Structures Have LH Analogues				
TTTGTTTT	3_1 (RH)	120	8.66	−53.32
TTTTTG'TG'	3_1 (RH)	120	8.66	−52.91
TTTG'TTTG'	3_1 (RH)	120	8.66	−53.04
TTTGTTTG	3_1 (RH)	120	8.66	−53.17
TTTGTGTG'	3_1 (RH)	120	8.66	−52.89
TGTGTGTG	3_1 (RH)	120	8.66	−53.59
TGTG'TG'TG'	3_1 (RH)	120	8.66	−53.01

[a] θ, angular turn per monomer unit. *D*, projection length of the tetramer on the helical axis. *E*, intrachain energy. LH and RH, left- and right-handed helix.

Method: Conformational Analysis

The valence geometry reported in ref 5 was used to construct $X(-CH_2-CF_2-)_4CH_2-X$ where X has the energy features of a backbone carbon. This segment was chosen because it is the shortest unit which can incorporate, equally, phase I and II chain conformations. The fixed valence geometry molecular mechanics segment of the CAMSEQ-II[15] was used in the conformational analysis. The atomic charge distribution was determined using CNDO/2.[16] The conformational analysis scheme considered all possible backbone torsional rotations at 60° (starting with the $T = 0°$ state) increments, with alternate torsional rotations held in the *T* states. Figure 1 defines the valence geometry, atomic charges, and torsional bond rotations. In all, $6^4 = 1296$ conformations were considered.

Results and Discussion

Table I gives a list of possible energy minima for a tetramer repeat unit and the corresponding intramolecular energies and helical properties.

In the next series of calculations, only the intramolecular conformer energy minima were considered. In these

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Table II
PVF_2 Chain Structures which Possess the Observed Fiber Axis Repeat, D

structure	backbone ∠CCC, deg	torsional angles[a]	fiber axis repeat, D, Å	energy above[b] min, kcal/mol
TTTTTGTG′ (*a*)	112	*TTTTT129T231*	9.18	0.64
TTTTTGTG′ (*b*)	111	*TTTTT121T239*	9.18	0.16
TGTG′TG′TG	116	*T100T260T260T100*	9.18	9.6
TTTGTTTG′	114	*TTT115TTT245*	9.18	2.2
TTTGTGTG	118	*T370T110T120T110*	9.18	extremely high stretching energy needed
TGTG′TG′TG′	118	*T120T100T260T220*	9.18	
TG′TG′TG′TT	118	*T260T220T260T330*	9.18	
TTTGTTTT	119.4	*TTT120TTTT*	9.18	

Table III
Suggested Phase III Structures of PVF_2 and Corresponding Intrachain Properties of Phase I and Phase II Chains

structure	phase	backbone ∠CCC, deg	E, kcal/mol	helix	θ, deg
TGTG′TG′TG	IIIa	116	−43.42	11_3 (RH)	97.98
TTTGTTTG′	IIIb	114	−51.70	17_6 (RH)	127.05
TTTTTTTT	I	114	−52.87	2_1 (RH)	180
TGTG′TGTG′	II	114	−52.80	11_5 (RH)	163.10

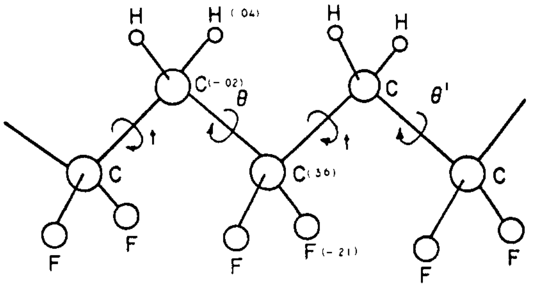

Figure 1. The valence geometry and partial atomic charges used in the intrachain conformational analysis of PVF_2. The charges are in electronic units and are given in parentheses. T refers to a trans conformer state and θ and θ' to allowed bond rotations. The bond lengths are C–C = 1.54 Å and C–F = 1.39 Å. The bond angles are ∠CCC = 112°, ∠HCH = 109.5°, and ∠FCH = 110.5°.

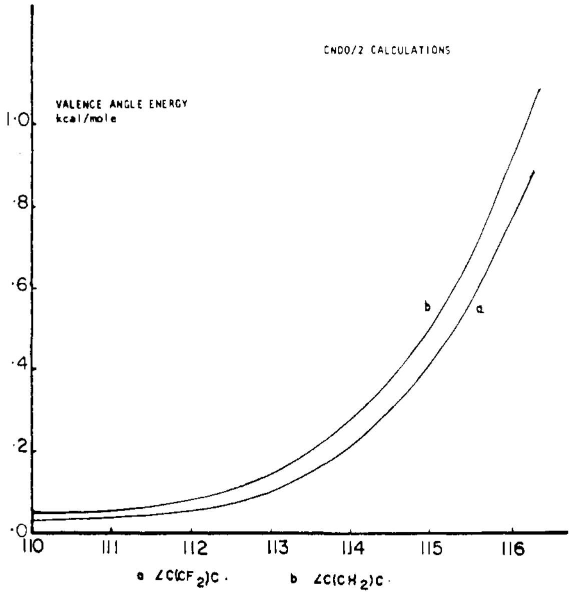

Figure 2. Valence bond angle deformation energy as a function of backbone valence bond angle: (a) $\angle C(CF_2)C$; (b) $\angle C(CH_2)C$.

structures, the backbone valence bond angles were varied, and the torsional bond rotations were allowed to deviate about their minimum energy conformations in order to arrive at the experimental "c" axis repeat obtained by X-ray analysis. Of course, these structural excursions yield a deviation from the intramolecular energy minima. Presumably, intramolecular stabilization energy lost may be gained as the chains pack into the crystalline structure, although one would tend to favor those structures that go over to the observed dimensions by expending little intramolecular energy. The results of these analyses are listed in Table II. The energy needed to convert from the isolated energy minimum to a structure consistent with X-ray studies was computed using the following approach. A single bond torsional potential, $E(\theta) = E^*(1 - \cos 3\theta)$, for $\theta = 0°$ being T, was used to calculate the excursion energy about the torsional angles corresponding to energy minima. The half barrier height, E^*, is 1.45 kcal/mol. The energy expended in stretching the valence bond angle was evaluated through CNDO/2[16] calculations. The valence angle deformation energy is plotted against the backbone C–C–C valence bond angle in Figure 2. Of the structures listed in Table II, *TTTGTTTG′* and *TGTG′TG′TG* seem to be the most appropriate structures to fit the X-ray data. The *TTTTTGTG′* structure does not satisfy the glide plane symmetry as inferred from systematic absences in the X-ray pattern[13] and, as such, is excluded in spite of its very low intrachain energy. Ball-stick models of the *TTTGTTTG′* and the *TGTG′TG′TG* structures, both on the same dimensional scale, are shown in Figure 3. It appears that both conformations can pack to have approximately the same basal plane as phase II. However, a detailed interchain energy calculation is needed to confirm these inferences.

The FTIR findings suggest equal numbers of phase I and II diads are present in the phase III structure. The conformation *TTTGTTTG′* satisfies this criterion while *TGTG′TG′TG* does not. However, we do not feel sufficiently confident to completely rule out the *TGTG′TG′TG* structure on the basis of the available information. This structure might pack into a lattice with a high efficiency because of a uniform distribution of G and G' induced kinks in the chain.

There is a series of structures (see Table I) having D = 8.67 Å. These structures can only be "stretched" to the required chain axis of 9.18 Å for C–C–C angles of 119.4°. It was also necessary to stretch the C–C–C angle to about 118° for *TTTGTGTG* and *TGTGTGTG′* structures in order to obtain the experimental chain axis for small excursion of the torsional angle. Although large backbone angles of this order have been observed in other materials, such deformations for PVF_2 chains require a large amount of compensating interchain energy to facilitate crystalline packing. We do not believe this is reasonable, since alternate, lower energy conformations have been identified.

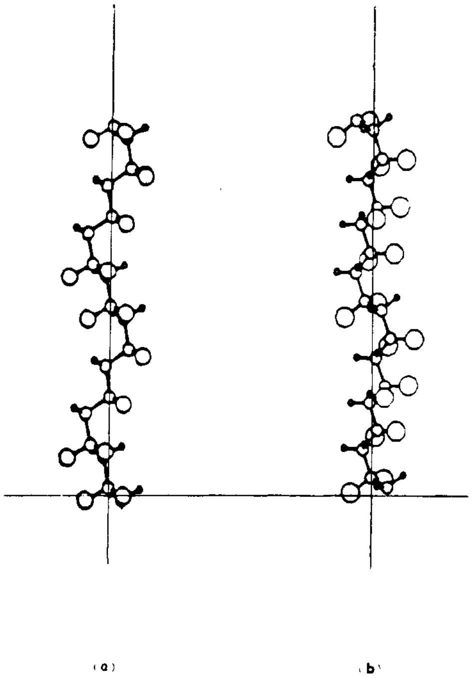

Figure 3. Ball-stick models of possible phase III PVF$_2$ chain conformations: (a) *TTTGTTTG′*; (b) *TGTG′TG′TG*.

Table III contains a description of the final two conformations we believe are most appropriate for phase III PVF$_2$. The phase I and II structures are also listed for comparison. Of the two possible phase III structures, *TTTGTTTG′* is preferred on the basis of FTIR data and also intrachain molecular energetics.

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References and Notes

(1) J. B. Lando, H. G. Olf, and A. Peterlin, *J. Polym. Sci., Part A-1*, 4, 941 (1966).
(2) W. Doll and J. B. Lando, *J. Macromol. Sci., Phys.*, 4 (2), 309 (1970).
(3) J. B. Lando and W. Doll, *J. Macromol. Sci., Phys.*, **2**, 205 (1968).
(4) H. Tadokoro, R. Hasegawa, M. Kobayashi, Y. Takahashi, and Y. Chantani, IUPAC preprints, Boston, 1971 unpublished.
(5) R. Hasegawa, Y. Takahashi, Y. Chatani, and H. Tadokoro, *Polym. J.*, **3**, 600 (1972).
(6) R. Hasegawa, M. Kobayashi, and H. Tadokoro, *Polym. J.*, **3**, 591 (1972).
(7) B. L. Farmer, A. J. Hopfinger, and J. B. Lando, *J. Appl. Phys.*, **43**, 4293 (1972).
(8) Ye, L. Gal'perin, B. P. Kosmynin, and R. A. Bychkov, *Vysokomol. Soedin., Ser. B*, **12**, 555 (1970).
(9) W. M. Prest, Jr., and D. J. Luca, *J. Appl. Phys.*, **46**, (10), 4136 (1975).
(10) M. Kobayashi, K. Tashiro, and H. Tadokoro, *Macromolecules*, **8**, 158 (1975).
(11) P. Naegale, D. Y. Yoon, and M. G. Broadhurst, *Macromolecules*, **11**, 1297 (1978).
(12) A. J. Lovinger and H. D. Keith, *Bull. Am. Phys. Soc.*, **24** (3), 414 (1979).
(13) S. Weinhold, M. H. Litt, and J. B. Lando, *J. Polym. Sci., Polym. Lett. Ed.*, to be published.
(14) M. A. Bachman, J. L. Koenig, W. L. Gordon, and J. B. Lando, *Bull. Am. Phys. Soc.*, **24** (3), 414 (1979).
(15) R. Potenzone, Jr., E. Cavicchi, H. J. R. Weintraub, and A. J. Hopfinger, *Comput. Chem.*, **1**, 187 (1977).
(16) J. A. Pople and D. C. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, 1970.

A Study of Concentration Fluctuations during the Thermal Polymerization of Styrene Using Photon Correlation Spectroscopy

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ABSTRACT: The cooperative diffusion coefficient D_c for concentration fluctuations is studied as a function of polymer concentration during the thermal polymerization of styrene using photon correlation spectroscopy. Measurements were carried out from the semidilute region to approximately 90% polymer. From 2–10%, polymer D_c rose linearly with concentration. The value of D_c eventually reached a plateau with a value of 4.5×10^{-6} cm^2/s which corresponds to a minimum dynamic screening length between 10 and 15 Å. At higher polymer concentrations, the local viscosity increases sharply, and the value of D_c falls accordingly.

Introduction and Theory

The Rayleigh spectroscopy of dilute polymer solutions is now well understood.[1] The spectrum due to concentration fluctuations can be explained in terms of the dynamics of isolated polymer molecules. There has been considerable recent interest in the Rayleigh spectroscopy of semidilute and concentrated polymer solutions.[2–7] Experimentally, it has proven difficult to clarify such solutions sufficiently to study the intrinsic homodyne correlation function. However, a convenient technique exists to prepare optically clear polymer solutions. Stevens and co-workers[8,9] have studied the thermal polymerization of styrene using Rayleigh–Brillouin spectroscopy and have shown that the spectrum obtained can be accounted for by intrinsic thermal fluctuations. In the present paper, we report a study of the concentration fluctuations in semidilute and concentrated polymer solutions obtained

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