On the Conformational Isomerism of Poly(vinylidene fluoride)

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Conformationally disordered crystals (condis crystals) were recently found to represent a special class of mesophases of linear, flexible macromolecules.[1] For poly(ethylene) and poly(tetrafluoroethylene) condis crystals are involved, for example, in the extended-chain crystallization. Poly(vinylidene fluoride) can also form extended-chain crystals at elevated pressure, and an involvement of condis crystals was suggested.[1] In addition, poly(vinylidene fluoride) is known to possess pyro- and piezoelectric properties.[2] A change in dipole in a polymer molecule should, however, be connected with a conformational change. Curie temperatures, as recently suggested for copolymers with vinylidene fluoride,[3] could thus be transitions to the condis state. To verify such mobility in poly(vinylidene fluoride) we have started an analysis of motion via heat capacity measurement and interpretation.[4] To expand this study, we undertook a series of conformational energy calculations of the isolated molecule, which we would like to report about in this note. An exceptionally broad potential energy minimum was found that must be considered in discussing the condis state of poly(vinylidene fluoride).

Calculations

Our calculations were done with single-chain molecular mechanics[5] including electrostatic, torsional, and van der Waals interactions. A chain segment of 32 carbon atoms was studied. The charges were taken as follows: $q_C(CH_2) = -0.22$, $q_C(CF_2) = +0.84$, $q_F = -0.35$ and $q_H = +0.04$. These values were transferred to poly(vinylidene fluoride) from small-molecule analogues (less than six-carbon-atom chains). The torsional rotation barrier CH_2–CF_2 was taken to be 12.6 kJ/mol. The nonbonded interactions were calculated from

$$U = \sum_{ij} A_{ij}\rho_{ij}^{-6}[-s_{ij}^{-6} + (6/14)s_{ij}^{-14}] \qquad (1)$$

where $A_{ij} = -(3/2)[(a_i a_j I_i I_j)/(I_i + I_j)]$, where a_i and a_j are the polarizabilities, I_i and I_j are the ionization potentials, ρ_i and ρ_j are the van der Waals radii with $\rho_{ij} = \rho_i + \rho_j$, and the s_{ij} are the reduced distances (s_{ij} = distance/ρ_{ij}) between atoms i and j. Table I lists the parameters for eq 1. The value of U is converted from eV/mol to kJ/mol by the factor 96.485 kJ/eV.

Results

In prior calculations it was assumed that the two gauche conformations were of equal energy at angles $G = -\bar{G}$ and the trans conformation was fixed at $T = 180°$.[6,7] The resulting TGT$\bar{G}$ sequence was then in agreement with the X-ray structure of the α-phase (phase II).[8]

We started our calculations by permitting $G \neq -\bar{G}$ as well as $T \neq 180°$. This resulted surprisingly in not one, but two low-energy conformations for the tetrahedral bond angle of 109.5° for the C bond. The two conformations occurred at $T_1 = 167.5°$, $G_1 = 51°$, $T_1 = 167.5°$, $\bar{G}_1 = -85°$ and at $T_2 = 192.5°$, $G_2 = 85°$, $T_2 = 192.5°$, $\bar{G}_2 = -51°$. These conformations are lower in energy by 20 kJ/mol than those proposed by Farmer et al.[7] ($G = -\bar{G} = 32°$, $T = 180°$) and result in a close to 4*8/1 helix (helix rotation angle 44°, translation 0.4354 nm, helix radius to the C atoms about 0.04 nm). With the conditions $G = -\bar{G}$ and $T = 180°$, our computation program yielded also a minimum at $G = -\bar{G} = 32°$ but, in addition, showed a second, even lower minimum at $G = -\bar{G} = 80°$ not reported by Farmer et al.[7] (lower by 13 kJ/mol).

The helix translation between successive TGT$\bar{G}$ sequences of 0.4354 nm is, however, not in accord with the X-ray repeat distance of 0.462 nm in the α-phase; similarly, a helix does not agree with the close to orthorhombic unit cell in the α-crystal form.[8] To resolve these problems, we attempted to match the torsional angles ϕ and the bond angle β to give a 0.462-nm repeat and to force the helix to a 4*1/1 conformation by requiring $G = -\bar{G}$ and $T = 180°$. Under these conditions the equation

$$(0.462)^2 = \{0.308[\sin(\beta - 90) + 1]\}^2 + \{0.308 \sin(\phi/2) \cos(\beta - 90)\}^2 \qquad (2)$$

gives the repeat distance in terms of torsional angle ϕ and bond angle β, assuming the C–C bond length is 0.154 nm. Table II gives a series of data.

To find now a possible match of the angles of Table II with an energy minimum, new calculations were made for the angles β of Table II ($G = -\bar{G}$ and $T = 180°$). These results are listed in Table III. Also listed in Table III are estimates of the energy of bond angle bending[9]

$$V = 73.2(\beta - 109.5)^2 \quad \text{[in J/mol of bonds]} \qquad (3)$$

The values given by eq 3 agree well with the data of Tripathy et al. based on CNDO/2 calculations.[10]

Two significant observations can be made from the table. First, the double minimum disappears on increasing the

Table I
Parameters Used in Eq 1[a]

atom	ρ, Å	α, Å^3	I, eV
C	1.594	1.116	14.61
H	1.126	0.392	13.60
F	1.30	0.486	18.52

[a] These values were taken from ref 5 and 18; 1 Å = 10^{-10} m, 1 eV = 96.445 kJ.

Table II
Pairs of Bond Angles β (deg) and Torsion Angles ϕ (deg) for Which Eq 2 is Fulfilled

β	ϕ	β	ϕ	β	ϕ
109.5	92.2	113.0	73.9	117.0	47.0
110.0	89.7	114.0	68.1	118.0	37.6
111.0	84.6	115.0	61.8	119.0	24.9
112.0	79.4	116.0	54.8	119.5	15.0

Table III
Minimum Energies[a] of Conformations (kJ/mol of Two-Carbon Repeat) as a Function of Bond Angles β (deg)

β	ϕ	E	V	$E_{tot} = E + V$
109.5	80	162	0	162
	32	175	0	175
110.0	78	149.5	0.04	149.5
	33	158.5	0.04	158.5
111.0	75	145.5	0.08	145.6
	35	151	0.08	151
112.0	71	142	0.92	142.9
	38	145	0.92	145.9
113.0	67	139	1.79	140.8
114.0	61	136	2.96	139.0
115.0	56	133	4.43	137.4
116.0	55	131	6.18	137.2
117.0	54	129	8.24	137.2
118.0	54	127	10.58	137.5
119.0	54	126	13.21	139.2
119.5	54	125	14.64	139.6

[a] The values of the energies E and E_{tot} are only of significance as differences between pairs of data.

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bond angle to 113° or more. Second, the energy needed to distort the bond angle increases rather slowly and reaches values that compete with the steric hindrance only beyond 120°. Checking the energy barrier between the two minima at low bond angle, we found it to decrease from 13 to 7, 2.7 and 0.7 kJ/mol when going from $\beta = 109.5°$ to 110, 111, and 112°, respectively. A further feature of the calculation with different bond angles was to show that relaxing the restraining of $G = -\bar{G}$ and $T = 180°$ does not lead to lower energy conformations at bond angles above 114° ($\beta = 109.5°$, $\Delta E = 7$ kJ/mol; $\beta = 110°$, $\Delta E = 2.5$ kJ/mol; $\beta = 111°$, $\Delta E = 2.0$ kJ/mol; $\beta = 112°$, $\Delta E = 1.8$ kJ/mol; $\beta = 113°$, $\Delta E = 0.8$ kJ/mol; $\beta = 114°$, $\Delta E = 0.3$ kJ/mol). As one would expect from these numbers, the minima above 112° for the bond angle β are rather shallow and rotation from $\phi = 40°$ to 80° shows a potential energy variation of less than 1 kJ/mol. Without intermolecular constraints by the crystal, the chain may thus assume practically any bond angle β between 112 and 118° and any torsional angle ϕ between 40 and 80°. Table II shows that all of these conformations can also satisfy the repeat-length constraint (in any given pairs).

Discussion

These conformation calculations indicate that poly(vinylidene fluoride) should have, at least at high temperatures, increased mobility, i.e., represent perhaps a condis crystal. Indeed, initial heat capacity analyses of crystalline poly(vinylidene fluoride)[11] seem to indicate an elevated heat capacity between the glass transition and the melting temperature when compared to the purely vibrational heat capacity of the solid.[4] There is, however, no indication of a first-order transition, as was observed for the polyethylene and poly(tetrafluoroethylene) crystal to condis crystal change or was reported for a Curie transition.[3]

Other experimental evidence that may be linked to conformational changes are a dielectric relaxation (α_c) above about 325 K, suggested to be due to $TGT\bar{G} \rightarrow G\bar{G}T$ changes.[12] This would give rise to a change in the up and down orientation (inclination) of the –F bonds along the chain, as was observed by X-ray diffraction.[13]

At temperatures above 440 K, changes in the c projection of the chain were attributed to $TGT\bar{G} \rightarrow \bar{G}TGT$ conformational mobility.[13,14] At present, the question of the driving force of these conformational changes is not clear. It seems that intermolecular packing improvement through removal of domain boundaries may prevent reversal of once-induced changes.

At the addition to thermal motion of the electrical field needed for poling, the transformation $TGT\bar{G} \rightarrow T\bar{G}TG$ was proposed[15] as a conformation change, irreversible without the presence of a field. Partial loss of polarity is, however, observed before fusion,[16] so that conformational changes of the earlier described types may also contribute to the poling and reach their Curie temperature range before melting.

Finally, a rather large variability of X-ray structure data with sample[8,17] may point to easy changes in conformation with changes in intermolecular forces, the latter being induced by changes in the concentration of head-to-head sequences.

Summary

Molecular mechanics calculations for isolated poly(vinylidene fluoride) molecules indicate a broad potential energy minimum permitting –C– bond angles between 112 and 118° and rotation angles between 40 and 80°. In the crystal, intermolecular packing considerations must limit the large-scale motion between the given limits. The unfreezing to a conformationally disordered crystal (condis crystal) seems to occur in stages and be driven by intermolecular packing improvements or electric field induced poling strains. Full mobility as needed at the Curie temperature seems to be possible only above the melting temperature.

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Small-Angle X-ray Investigation of Morphological Order in the System Isotactic Polystyrene–Poly(2,6-dimethylphenylene oxide)

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Blends of isotactic polystyrene and poly(2,6-dimethylphenylene oxide) (PPO) can be crystallized by thermal treatment for PPO contents lower than 40%. The samples reveal crystallinities which vary from below 20% to just over 30%.[1,2]

Wide-angle X-ray diffraction results show curves typical for partially crystallized isotactic polystyrene, which suggests that the blends consist of a homogeneous amorphous phase and a discrete crystalline phase. It is concluded from the appearance of a long period in the small-angle X-ray scattering (SAXS) curves of the blends that the crystals are arranged in a partially ordered manner. In an earlier

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