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On the Conformations of Poly(*p*-xylylene) and Its Mesophase Transitions

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ABSTRACT: Molecular mechanics calculations for an isolated chain of poly(*p*-xylylene) have been carried out. The results have been used to model the transitions in the polymer that go from the crystal α to condis crystal β_1 at (504 K), to condis crystal β_2 (at 560 K), to the melt (at 700 K). Assuming increasing mobility in the phenylene groups of the trans conformational isomer, the two condis crystal forms could be modeled. It was not necessary to assume the presence of helical chain conformations. For the melt, additional planar chain and helical conformations are likely to account for the observed experimental entropies and enthalpies of transition.

Introduction

Poly(*p*-xylylene) [PPX; structure-based name poly(1,4-phenyleneethylene)] has been of long-standing interest to our laboratory. It is a special, high-temperature polymer,[1] available since 1965 (Union Carbide, trade name Parylene N). Its thermodynamic transition parameters have been determined by extrapolation to equilibrium.[2] They can be summarized as follows:

low-temperature α crystal
504 K ↓ $\Delta H = 5.0$ kJ/mol, $\Delta S = 9.9$ J/(K mol)
high-temperature β_1 condis crystal
560 K ↓ $\Delta H = 1.5$ kJ/mol, $\Delta S = 2.7$ J/(K mol)
high-temperature β_2 condis crystal
700 K ↓ $\Delta H = 10.0$ kJ/mol, $\Delta S = 14.3$ J/(K mol)
melt
followed by decomposition

The glass transition of the amorphous polymer occurs at 286 K with a change in heat capacity, ΔC_p, of 37.6 J/(K mol).[2] The α-to-β-transition was first observed when the polymer was made via Wurtz condensation of *p*-xylylene dichloride,[3] a method now replaced by polymerization of [2.2]-*p*-cyclophane.[1] Niegisch could show later[4] that there is a second high-temperature polymorph β_2 and proposed calling the earlier discovered β-polymorph β_1. A reported γ-polymorph could be shown to be a mixture of α and β_1.[5] Recent suggestions of additional phase structures[6] are most likely incorrect.[7] The observed changes may be due to incomplete conversions of the two condis phases. The often assumed irreversibility of the α to β_1 transition could be shown to be removable by annealing the condis crystal.[7]

The morphology of the PPX crystals grown during polymerization and from solution was studied.[8,9] Orientations, crystal forms, and morphologies change with different conditions of crystallization and polymerization. The crystal structure of the α-polymorph is monoclinic [$C2/m$] with the unit cell dimensions $a = 0.592$ nm, $b = 1.064$ nm, and c(chain axis) = 0.655 nm and $\beta = 134.7°$. Two chains pass through the unit cell with a packing density of 0.705 g/cm^3. One monomer unit makes up the fiber identity period, and the phenylene groups are oriented parallel to each other and are at right angles to the CH_2–CH_2 zigzag (ac)[10] (see Figure 3b, below).

The crystal structure of the β_1 phase is not well established. There is no change in the c axis dimension,[11] and the crystal has already absorbed about $^1/_3$ of the overall entropy of fusion[2] [9.9 J/(K mol)]. Statistical defects in a much enlarged trigonal unit cell [P_3] have been assumed, based on X-ray evidence (see Figure 3a, below).[11] On transition to the β_2-phase, less additional entropy is absorbed[2] [2.7 J/(K mol)], but now the c axis dimension decreases somewhat,[11] indicating the possibility of a kinked or helical chain. The crystal structure changes to hexagonal symmetry. Originally this highly disordered crystal was classified as a "rotor phase".[11] On the basis of this evidence, it was proposed to classify the β-phases of PPX as condis crystals, i.e., crystals with varying conformational disorder and mobility.[12] It was suggested that the β_1-phase has phenylene disorder and mobility and the β_2-phase additional disorder and mobility within its CH_2 conformations. In this paper we present a study of the isolated PPX chain using molecular mechanics and draw conclusions about the detailed nature of the motion in the PPX mesophases.

Computations and Results

A sequence of nine repeating units was selected for study. All thermodynamic changes are reported per single repeating unit. For convenience, the starting conformation is selected as the trans conformation, as found in the

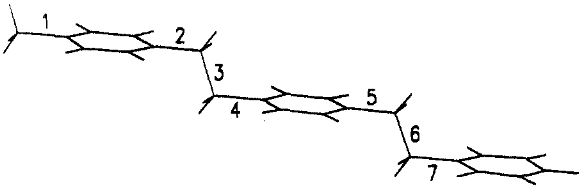

Figure 1. Poly(*p*-xylylene) in the trans conformation. Rotatable bonds are numbered. All conformational angles are adjusted relative to this starting conformation. Three independent bonds, $\phi_b = \phi_{b+3n}$ (n = 1, 2, 3, ..., 7, b = 2–4), $\phi_1 = \phi_4$, and $\phi_{26} = \phi_2$ are rotated cooperatively.

α-crystal form.[9] It has the highest symmetry, and all changes in the torsion angles are measured from this trans conformation, drawn in Figure 1. The calculations were performed by allowing interactions between all atoms not bonded through a common atom but permitting no bond angle and length changes. For rotations about each of the bonds the sum of the steric (U), electrostatic (Q), and torsional (T) energies are adjusted to minimize the total energy, E:

$$E = U + Q + T \tag{1}$$

Relative energies, where $E_{\min}$ is the global minimum, are reported:

$$\delta E = E - E_{\min} \tag{2}$$

The energies of eq 2 are obtained from the sum of two-body interactions between atoms i and j.[13] These energy terms are explained in more detail in a previous publication discussing the mesophase states of poly(diethylsiloxane).[14] Net charges for hydrocarbons are of the order of only 0.01 electron units, so that each pairwise contribution, 138.93 $q_i q_j / r_{ij}$ kJ/mol [q_i and q_j are in electron units and r_{ij} is in nanometers], is small, as is also the total charge. Therefore, in this investigation Q will be neglected. The geometrical parameters used in this computation are r(C–C bond, aromatic) = 0.138 nm, r(C–C, aliphatic) = 0.154 nm, r(C–H) = 0.110 nm, θ(C–C–C) = 108–114°, θ(C–C–H) = 109.5°, and θ(C–C–C, aromatic) = 120°. The torsional energy for each bond (b) is calculated with

$$T_b = (V/2)(1 - \cos \lambda\phi_b) \tag{3}$$

where $\lambda = 3$ and $V = 12.55$ kJ/mol for the rotations about the CH_2–CH_2 bond and $\lambda = 6$ and $V = 5.4$ J/mol for rotations about the CH_2–phenylene bond.

In the starting conformation, illustrated in Figure 1, the torsional energy for orientation of atoms about all bonds is a minimum ($T_b = 0$). The study was conducted by assuming that all equivalent bonds along the polymer rotate in concert. Adjustments to the torsional angles are grouped as follows: ϕ_{b+3n} where n = 0, 1, 2, ..., 7, with the ends of the molecule fixed by $\phi_1 = \phi_4$ and $\phi_{26} = \phi_2$. There are thus only three independent torsional angles with b = 2–4.

In a systematic study, each angle ϕ_b was adjusted to yield the different minimum energy conformations. Table I lists the results. The following minimum energy conformations are found: trans and cis (with parallel phenylene groups[7] that are perpendicular to the ac plane), cis(*) (with parallel CH_2–CH_2 bonds and the phenylene groups perpendicular to the ac plane), and several helical conformations. In the numerous conformations studied an interplay between U and T was found.

The three overall lowest energy conformations are, in order, the two 5/1 helices and the 3/1 helices with relative energies of δE[5/1(LH)] = 0.0, δE[5/1(LH)] = 1.2, and δE[3/1(LH)] = 12.2 kJ/mol. The cis(*), cis, and trans conformations are the only nonhelical conformations and have the considerably higher relative energies of δE = 35.1, 20.6, and 20.6 kJ/mol.

Table I
Minimum Energy Conformations of the Isolated Chain Conformations of PPX[a]

conf	ϕ_2, deg	ϕ_3, deg	ϕ_4, deg	T, kJ/mol	δE, kJ/mol
cis(*)	0	180	180	12.6	35.1
trans	0	0	0	0.0	20.6
cis	0	0	180	0.0	20.6
3/1(LH)	−1	−121	1	0.0	12.2
5/1(LH)	0	121	−180	0.0	1.2
5/1(LH)	−172	129	8	1.4	0.0

[a] 3/1(LH) and 5/1(LH) denote left-handed 3/1 and 5/1 helices. Equivalent conformations are obtained by interchanging ϕ_2 and ϕ_4 or adding 180° to ϕ_2 and ϕ_4. Right-handed helices are obtained by multiplying all angles by −1.

Discussion

Only the higher energy trans conformation of Table I agrees with the X-ray data of poly(*p*-xylylene) in the crystalline and condis crystalline states. The crystal packing energy must thus be of overriding importance for the selection of the conformation. The only other chains of Table I that can be densely packed and oriented in an overall linear fashion are the two cis conformations. Their repeat distances of 0.625 nm for parallel phenylene groups and 0.692 nm for parallel aliphatic CH_2–CH_2 bonds differ, however, sufficiently from the X-ray value of c = 0.655 nm to limit the discussion of the low-temperature crystal and the condis crystal forms to the motion and disorder of the phenylene groups in the trans conformation. In the liquid phase the intermolecular restrictions are removed and one would expect the conformations of Table I to become important in proportion to their single-chain energies.

An effort to simulate structure and motion in poly(*p*-xylylene) by molecular dynamics calculations is in the planning stage. It is most likely that this simulation will take several years for completion because of the large number of atoms involved and the complications caused by inclusion of ring structures with the present code.

In the meantime, to further the understanding of the various phases encountered in going from the rigid, fully ordered crystal to the melt, we are proposing a model fitted to the experimental entropy data. Use is made of the computed trans conformation, the measured transition parameters listed in the introduction, and the changes in crystal symmetry and volume on transition.

Model of the Mesophases

To account for the intermolecular forces, an empirical 6-fold periodic potential

$$W = 5.44(1 - \cos 6\phi) \text{ (in kJ/mol)} \tag{4}$$

is added to the molecular mechanics calculation for the isolated chain. The angle ϕ represents the rotation angle of the phenylene group and is measured from the potential energy minimum of the trans conformation given in Table I and drawn in Figure 1. The potential energy, V_p, becomes

$$V_p = V_{\text{conf}} + W \tag{5}$$

where the intramolecular contribution (δE) measured relative to zero at angle $\phi = 0°$, V_{conf}, is defined for each phase, p, when a cut-off angle, ϕ_{pc}, is introduced for restricted or librational motion. The results of this calculation are presented in Table II in appropriate steps of ϕ and shown schematically in Figure 2. Two equivalent minima occur at ϕ = 0° and 180°. Two equivalent maxima

Table II
Conformational Energies, V_{conf}, of the Trans Conformation PPX for Orientations of the Phenylene Group

ϕ, deg	V_{conf}, kJ/mol	W, kJ/mol	$V_p = V_{conf} + W$, kJ/mol	phases			
0	0.0	0.0	0.0	minimum	α	β_1	β_2
10	−0.1	2.7	2.6		α	β_1	β_2
20	−0.3	8.2	7.9			β_1	β_2
30	−0.4	10.9	10.5	rel max		β_1	β_2
40	0.1	8.2	8.3			β_1	β_2
45	2.4	5.4	7.8			β_1	β_2
50	2.4	2.7	5.1	rel min		β_1	β_2
60	5.9	0.0	5.9			β_1	β_2
70	7.3	2.7	10.0				β_2
80	6.0	8.2	14.2				β_2
90	5.1	10.9	16.0	maximum			β_2

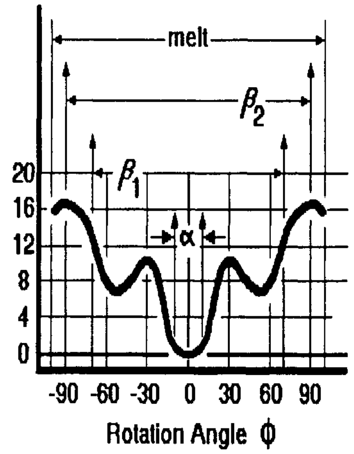

Figure 2. Schematic potential energy curve for rotation of the phenylene groups and of poly(p-xylylene) relative to the trans conformation given in Figure 1.

at 90° and 270° have a potential energy of 16.0 kJ/mol. Of this, 10.9 kJ arise from the empirically chosen intermolecular interaction of eq 4 and 5.1 kJ/mol from the intramolecular interaction of eq 1. Four equivalent relative minima are seen at ±50° and ±130°.

To evaluate the energetics and entropies of the various phases, it is further proposed that the motion in the α- and β_1-phases is limited by a characteristic cut-off potential, V_{pc}. The corresponding rotational angles are $\pm\phi_{pc}$. Up to the cut-off potential the potential is approximated by a harmonic oscillator

$$V_p = K_p \phi^2 \qquad (6)$$

centered at the minimum of the potential given in Figure 2. It is cut off at V_{pc} and continued as a square well with walls at $\pm\phi_{pc}$.

The two best known crystal structures are illustrated in Figure 3. At low temperatures, in the α-crystal phase, the conformations are confined to vibrations about ϕ = 0° and 180°. The cut-off amplitude is chosen as ϕ_{pc} = 10°. The potential is thus nearly a square well with walls at ±10°, as shown in Figure 2. The cut-off potential is V_{pc} = 2.6 kJ/mol. Below T = 504 K two chains per unit cell of the α-form are packed with parallel phenylene groups with restricted motion,[9] as illustrated in Figure 3a and in agreement with this choice of potential. The degeneracy is $g(\alpha) = 2$ because there are two potential wells for the phenyl motion and only one orientation of the entire chain in the crystal. The symmetry factor is also 2 for the phenylene group and the zero-point energy is set at 0 kJ/mol.

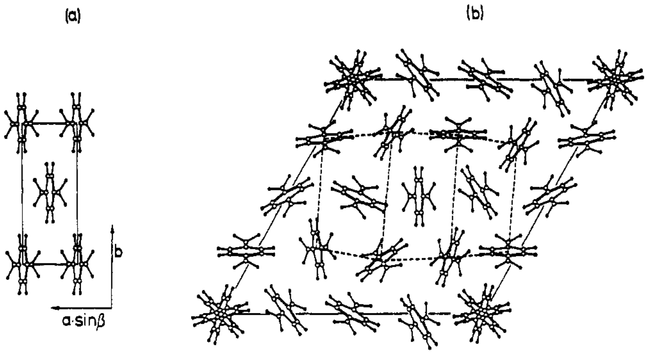

Figure 3. Cross sections of the unit cell structures attributed to the α-crystal structure (a) with parallel phenyl groups and the β_1-mesophase structure (b) with six orientations of the phenyl groups at the unit cell corners.

Between T = 504 and 560 K, the β_1-mesophase is stable. Sixteen chains are observed per unit cell, as illustrated in Figure 3b. The phenylene groups are no longer all parallel; some may reach full hexagonal environment. The two minimum energy conformations at V_p = 0.0 and four at V_p = 5.1 kJ/mol are now assumed to be accessible. These six minima at ϕ = 0°, ±50°, 180°, and ±130° lead to a more isotropic cross section of the chain and to the formation of a more hexagonal cross section of the unit cell. The cut-off potential energy of V_{pc} = 7.0 kJ/mol at cut-off angles of ϕ_{pc} = ±70° models this situation. The zero-point energy is increased to 2.6 kJ/mol to match the experimental energetics. According to the crystal structure of Figure 3b, the phenyl groups are packed such that out of 16, 15 are in well-defined orientations and one has C_3 symmetry relative to its neighbors. The degeneracy is thus calculated by a weighted average of (15 + 3)/16 from these multiple orientations, and 2 for the orientation of each phenylene group, to yield $g(\beta_1) = 2.25$.

Between T = 560 and 700 K, the β_2-mesophase has only one chain per unit cell. We postulate libration of the phenylene group to ϕ_{pc} = ±90° about its axis above the cut-off potential energy, $V_{\beta 2c}$ = 10.0 kJ/mol. This motion distinguishes the β_2-phase from β_1. A zero-point energy of 3.9 kJ/mol is assumed to match the experiment. The detailed crystal structure is not known, but is must be pseudohexagonal. We assign $g_{\beta 2} = 3$ to account for increased mobility of the phenylene groups in this phase.

The observed shortening of the c axis dimension may be caused by the decreased packing density. A normal C(phenylene)–C–C bond angle observed in small-molecule model compounds is about 108°. Due to the crystal packing in the α- and β_1-phases, the poly(p-xylylene) bond angle reaches 114° [$c = 0.644 + 0.0022(\theta - 109.5°)$, in nanometers calculated with our parameters]. We assume thus that the lower density in the β_2-phase alone leads to a smaller θ and a reduced c. Any rotation about the CH_2–CH_2 bonds would also shorten the polymer chain, but this is less likely in the solid phase since it requires considerably more lateral space.

The free rotation of the phenylene groups produces an isotropic cross section of the chain indicated at the corners of Figure 3b. Contour models[15] of three such polymer chain units computed with the present model are shown in Figure 4. Figure 4a shows the all-trans chain with a flat cross section. An average along the chain direction of Figure 4b, in contrast, yields a hexagonal cross section.

Finally, the melt is assumed to contain all possible conformations with unrestricted rotation of the phenyl groups and increased mobility of the chain. This is modeled by assuming that V_{lc} = 14.7 kJ/mol, g_{melt} = 12, and a zero-point energy E_p = 13.3 kJ/mol to reproduce the experimental results. The increased degeneracy

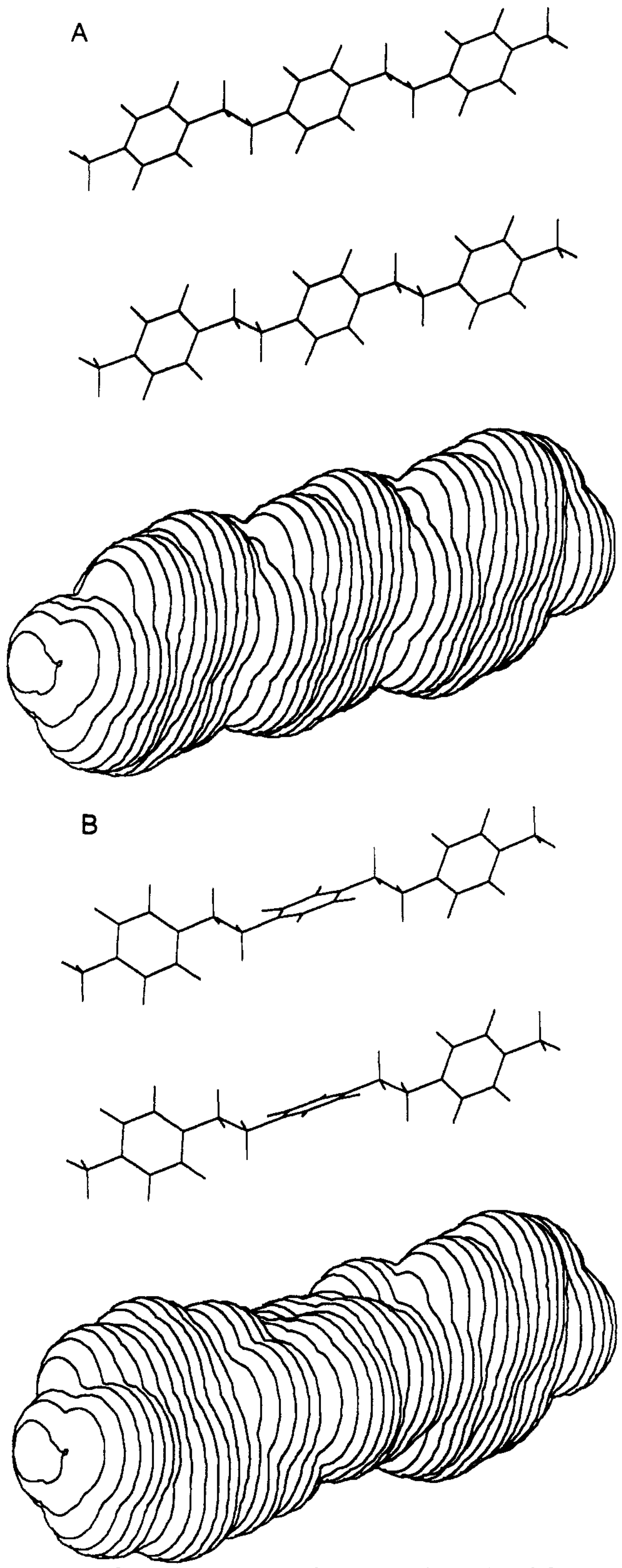

Figure 4. Stereoprojection of three repeating units of the trans chain as found in the α-polymorph (A) and chain illustrating the three rotational isomers for the β_2-polymorph (B).

accounts for the appearance of the helical and kinked conformations listed in Table I.

Table III
Force Constants and K_{eff} for the Harmonic Oscillator and Restricted Rotor at Selected Values in the Cutoff, ϕ_c[a]

K_p	K_{eff}	V_p	amplitude (ϕ_c), deg
195.8	0.9519	0.0	0
170.7	0.8888	2.6	10
76.6	0.5954	10.5	30
restricted rotor	18.7426		10
restricted rotor	3.8250		70
restricted rotor	2.3139		90
free rotor			

[a] $K_{eff} = (h\nu)_{eff} = 0.068027[K_p]^{1/2}$ in kilojoules per mole for the harmonic oscillator, $K_{eff} = 2.3139$ J/mol $(90°/\phi_c)^2$ for the restricted rotor, and $K_p = [d^2V_p/d\phi^2] = 195.8$ at $\phi_c = 0°$ and evaluated numerically at values of ϕ_c with the corresponding V_p in Table II.

Energy Levels, Enthalpies, and Entropies of Transition

The force constants and energies for the harmonic vibrations and restricted and free rotors used in the calculation are listed in Table III. The energies in the harmonic part of the potential are given by

$$E_n^{ho} = (h\nu)_{eff}(n + {}^1/_2) \tag{7}$$

$$E_n^{ho} = K_{eff}(n + {}^1/_2) \tag{8}$$

where the force constants are obtained from the numerical second derivative of V_p

$$K_p = 2V_p/[\Delta\phi]^2 \tag{9}$$

The factor 0.071 92 converts K_p in kilojoules per mole radians squared to $K_{eff} = 0.068027[K_p]^{1/2} = (h\nu)_{eff}$ in kilojoules per mole. Harmonic oscillator energy levels were used up to the cut-off potential, V_{pc}. Then a restricted rotor was implemented with

$$E_m^{rr} = [\hbar^2/(2IL^2)]m^2 \quad m = 1, 2, 3, \ldots \tag{10}$$

and the box defined by $L = \pm(\phi_{pc}/90°)$, where ϕ_{pc} is the cut-off angle. The free rotor levels are given by

$$E_m^{fr} = [\hbar_2/2I]m^2 \quad m = 0, \pm1, \pm2, \ldots \tag{10'}$$

$I = 0.871\ 54$ (amu nm^2) is the moment of inertia of the phenyl group for rotation about the polymer chain, $[\hbar^2/2I] = 2.3139$ J/mol, and $L = \phi_{pc}/90°$ is the fractional dimension of the box relative to the full cycle of ±180°. For the free rotor $L = 2$ in eq 10 yields the same density of energy levels as the free rotor (eq 10′).

The energy levels are calculated with the harmonic oscillator formula when $E_n^{h0} < V_{pc}$ and then with the restricted rotor formula. The cut-off values are indicated in Figure 2 and listed in Table IV. The partition function is written

$$Z_p = \sum_j g_j(p) \exp(-E_{pj}/RT) \tag{11}$$

for each phase $p = \alpha, \beta_1, \beta_2$, and the melt, where

$$E_{pj} = E_p^0 + E_j^{h0}, \quad E_j^{h0} < E_N^{h0} < V_{pc}, \quad j = 0, 1, 2, 3, \ldots, N \tag{12}$$

$$E_{pj} = E_{N+1}^{h0} + E_m^{rr}, \quad j = N + m, \quad m = 1, 2, 3, \ldots \tag{12'}$$

where E_p^0 is the zero-point energy of phase p, also listed in Table IV.

The thermodynamic changes are now calculated for the process

$$\text{crystal } (\alpha) \rightarrow \text{mesophase } (\beta_1) \rightarrow \text{mesophase } (\beta_2) \rightarrow \text{melt (l)} \tag{13}$$

The energy is obtained with

$$E_p = kT^2\, \partial \ln Z_p/\partial T \tag{14}$$

Table IV
Thermodynamic Changes for the Phase Changes Calculated with the Cutoff Harmonic Oscillator Potentials, Restricted Rotor Amplitudes, Zero Point Energies, and Effective Degeneracies in Each Phase

phase	V_{pc}	ϕ_{pc}	$E_p{}^\circ$	g_{pc}	phase change	ΔE(calc), kJ/mol	ΔS(calc), J/mol·K	ΔH(exp), kJ/mol	ΔS(exp), J/mol·K	*T*, K
						$K_{eff} = (h\nu)_{eff} = 0.8888$				
α	2.6	10°	0.0	2	$\alpha \rightarrow \beta_1$	5.0	10.2	5.0	9.9	504
β_1	7.0	70°	2.6	2.25	$\beta_1 \rightarrow \beta_2$	1.5	2.2	1.5	2.7	560
β_2	10.0	90°	3.9	3	$\beta_2 \rightarrow$ melt	9.9	14.1	10.0	14.3	700
melt	14.7	free	13.3	12						
						$K_{eff} = (h\nu)_{eff} = 0.5954$				
α	2.6	10°	0.0	2	$\alpha \rightarrow \beta_1$	4.7	10.1	5.0	9.9	504
β_1	7.0	70°	2.6	2.25	$\beta_1 \rightarrow \beta_2$	1.4	2.5	1.5	2.7	560
β_2	10.0	90°	3.9	3	$\beta_2 \rightarrow$ melt	9.9	14.8	10.0	14.3	700
melt	14.7	free	13.3	12						

and the entropy with

$$S_p = E_p/T + R \ln Z_p/\sigma \tag{15}$$

where the symmetry of the phenyl groups due to interchange of the atoms upon rotation is $\sigma = 2$. The partition function for phase *p* evaluated with the energy levels of eqs 12 and 12′ is Z_p.

The changes in thermodynamic values are largely influenced by the cut-off parameters V_{pc} and ϕ_{pc} and not the harmonic force constant. This is demonstrated by results calculated with $K_{eff} = (h\nu)_{eff}$ at 0.8888 and 0.5954 and reported in Table IV. These two values correspond to fitting a harmonic oscillator through V_p at $\phi = 10°$ and 30° with values reported in Table II. The thermodynamic values change by only 0.7 J mol/K for the range of values of $(h\nu)_{eff}$ used in these calculations. The choice of the zero-point energies, $E_p{}^0$, influence the energy, and the cut-off parameters, ϕ_{pc}, influence both the energy and the entropy. We proceeded by adjusting the parameters in each phase to obtain the thermodynamic changes measured. The equilibrium condition $\Delta G = \Delta H - T\Delta S = 0$ is satisfied for each phase change. The results of these computations are shown in Table IV.

Conclusions

1. The calculated ΔH and ΔS for all changes are not sensitive to the choice of the harmonic force constants at the minima. The zero-point energy, $E_p{}^0$, cut-off potential, V_{pc}, and amplitude, ϕ_{pc}, are important in the calculation of ΔE, ΔH, and ΔS for the $\alpha \rightarrow \beta_1$ transition. These parameters suggest that the phenyl groups become mobile at an amplitude of 70° when the structure changes to the β_1-phase. The amplitude of 70° is sufficient to account for the relatively large change in entropy.

2. Further increases in the amplitude for rotation of the phenyl groups do not add significantly to energy or entropy. Therefore, only a slight increase in the zero-point energy to $E_{\beta_2}{}^0 = 3.9$ kJ/mol and multiple-chain orientation are assumed to occur in the β_1-phase → β_2-phase transition. A degeneracy $g(\beta_2) = 3$ is sufficient to model the results. If the chain is assumed to retain an overall linear shape, then rotation about the CH_2–CH_2 bond is not likely because of limited mobility. Multiple-chain orientations with the associated volume expansion are an alternate explanation of the former interpretation of "mobile" methylene groups.

3. Both ΔH and ΔS are still large for the $\beta_2 \rightarrow$ melt phase change. Further increases in the mobility of the phenyl groups to a free rotation and chain disorder within the trans conformation are not sufficient to be able to account for these changes. However, accessibility to the six helical conformations and the low-energy cis and helical conformations yield sufficient additional states modeled by the postulated zero-point energy of $E_{melt}{}^0 = 13.3$ and degeneracy of 12.

It is thus possible that poly(*p*-xylylene) has only phenylene group disorder and chain mobility in its condis phases. This should be compared to the helical conformation changes in poly(tetrafluoroethylene), the major backbone mobility in polyethylene and *trans*-polybutadiene, and the side-chain disorder in poly(diethyl siloxane). These examples show the large variation in type of disorder and mobility possible in condis crystals and the large difference from liquid crystals with which they are often confused.

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(16) **Note added in proof**: After submission of the paper we completed also a full quantum mechanical approximation, eliminating several of the simplifications and the need to specify the cutoff potentials. The results remained, however, substantially unchanged.