A Suggested Unit Cell for it-Poly(methyl methacrylate)

Introduction. A new proposal for the crystal structure of it-PMMA is presented in which the unit cell consists of five straight-chain molecules, each with four polymer units in two combinations of cis–trans methacrylate groups, ctct... and cttt... sequences, in an end-centered monoclinic or an orthorhombic unit cell. These conformations are more stable than, and appear to fit within, the geometric constraints of the experimentally determined unit cell better than the previously proposed two double helices each with five polymer units.

A recent conformational study of poly(methyl methacrylate) (PMMA) reports a global minimum with the C=O of the ester and the α-CH_3 groups alternating in a cis and trans conformation, ctctctctc, and a less stable all-trans, ttttttttt sequence.[1] These are more stable than any of the single helices, the 9/1 helix being the most stable. The results of this study suggest that the X-ray structure of it-PMMA, in which various kinds of helices were proposed, might be revised to be more consistent with the space available in the experimentally determined unit cell with the more stable straight-chain conformations. In this paper, the conformations of relative minima are reported, the unit cell and the packing of helices are analyzed, and a new chain conformation is proposed for packing in a unit cell.

Stroupe and Hughes[2] suggested a 5/2 helix to explain the first X-ray diffraction pattern. Subsequent X-ray, infrared, and normal-mode studies[3,4] suggested a 5/1 helix, then a 12/1 helix was found to be more stable,[5] and finally a double helix of 10/1 chains was proposed[6] and shown to be more consistent with the X-ray pattern[7] and then disputed.[8,9] A normal-mode analysis of IR and Raman spectra of crystalline it-PMMA supports a 10/1 single helix[10] best of all the conformations proposed prior to this paper. This 10/1 helix[10] and the 9/1 helix with the ttttttttt sequence[1] are essentially the same. As more elaborate conformational studies were undertaken to consider more carefully the intramolecular effects of the nonbonded contacts, less wound helices were proposed to describe the conformation of the PMMA for use in the unit cell.

Conformational studies of straight-chain and helical PMMA[1] showed that an overall linear chain with alternating cis–trans C=O and α-CH_3 groups in a ctctctctc sequence and the all-trans, ttttttttt, sequence are more stable than any helix. In our calculations[1] the backbone conformation was minimized in the all-trans conformation to retain the overall linear shape. Vacatello and Flory[11] have shown that there are g^+ and g^- combinations in the backbone which yield conformations within a few kilocalories per mole of the global minimum, but the backbones are not overall linear. The global minimum they reported with four polymer units is the same sequence as the one we report,[1] ctctctctc, and our all-trans one, ttttttttt, is 0.23 kcal/mol higher in their paper. We did not pursue the gauche variants or helices because the overall linear conformations fit best into the unit cell.

The X-ray patterns reported[5,7] do not clearly exhibit closing-of-the-cross characteristic of a helix, and conformational studies reveal some alternation and randomness in the chain.[1,11] This also suggests that the structure may not consist of helices. In addition, an analysis of the stereographic projections of the proposed two double helices in a unit cell in Figure 6 of ref 7 permits the following direct measurements. If the vertical axis with c = 10.56 Å is used to obtain the scale, then the distance between carbonyl oxygen atoms across the helix is determined to be 9.08 Å. Adding two van der Waals radii for a carbonyl oxygen of 1.5 Å yields b = 12.08 Å and, because each helix is nearly cylindrical, $a = 2b$ = 24.16 Å. The reported experimentally determined cell parameters[3,5,7] average to a = 20.9 ± 0.4 Å, b = 12.3 ± 0.2 Å, and c = 10.53 ± 0.03 Å and the cell angles are within ±2° of 90°. The discrepancy of 4 Å between the experimental and theoretical (two double helices) a axis suggests that crystalline it-PMMA may not be composed of helical or double-helical forms but rather some combination of straight-chain units.

A conformational analysis on the polymer containing nine repeat units was undertaken to eliminate end effects. Standard bond lengths[12] (C–H, 1.08 Å; C–C, 1.54 Å; C–O, 1.36 Å; C=O, 1.23 Å; C=C, 1.40 Å) and bond angles (C–C–C, 112.0°; C–C–H, 109.5°; C–C–O, 109.5°; C—C=O, 120.0°; C–O–C, 109.5°) were used in methyl methacrylate repeat units (Figure 1 of ref 1). The sum of the steric (U), Coulombic (Q), and torsional (T) energies was minimized[1] by rotating about equivalent bonds along the chain. The steric energy if $U_{ij}(s_{ij}) = [A_{ij}/\rho_{ij}^6][1/s_{ij}^6 - 6/(ns_{ij}^n)]$, where $s_{ij} = r_{ij}/\rho_{ij}$ is the reduced distance, r_{ij} is the distance between the two atoms, and $\rho_{ij} = \rho_i + \rho_j$ is the sum of the van der Waals radii. $A_{ij} = -1.5\alpha_i\alpha_j I_i I_j/(I_i + I_j)$ is the London dispersion coefficient with atomic polarizabilities (α_i and α_j) and ionization potentials (I_i and I_j). These parameters are presented elsewhere.[13,14] The Coulombic energies were calculated with $Q_{ij}(r_{ij}) = q_i q_j/(\epsilon r_{ij})$, where the net charges were obtained from the MINDO/2[15] procedure and listed in Figure 1 of ref 1. The sum is over all atoms i and j not bonded directly or through a common atom. A macroscopic dielectric constant, ϵ = 4 was used.[1] The parameters for the bonds are (bond, V_b, λ_b) = (CTE–CTE, 3.0, +3), (CTE–CTR, 0.001, +6), (CTR–OTE, 2.0, +2), (OTE–CTE, 3.0, +3), and (CTR–CTR, 50.0, −2) where CTE and CTR are tetrahedral and trigonal carbon atoms and OTE is a tetrahedral oxygen atom.

Discussion and Models. Various conformations were studied. The C=O was oriented either cis (c) or trans (t) to the α-CH_3 in a regular pattern. The conformations [ttttttttt], [ccccccccc], and [ctctctctc] provide a starting point from which the trends due to increasing numbers of cis and trans conformations can be studied. Minimum-energy conformations are reported in Table I. Stereographic projections of the best conformation, ctctctctc, are shown in Figure 3b of ref 1. Several trends are apparent. The it-PMMA with the alternating ctctctctc sequence is the most stable, and the ctctctctc and ttttttttt sequences are more stable than the helices. The energy change for reorientation of the C=O from the alternating cis–trans to the all-trans for the it-isomer increases monotonically in energy when there are odd numbers of trans conformations between each cis conformation, i.e., c[(2n + 1)t]c. Even numbers of trans conformations, as well as any number of cis conformations between each trans conformation, rise more rapidly in energy and are larger than the all-trans energy of 1.49 kcal/mol.

Based on a distribution of each of the conformations given in Table I, the ctct... and cttt... alternating sequences with translational repeats of two and four are selected as the combination of conformations to fit into the unit cell with an overall net repeat of four to reproduce the c axis. In Figure 1, a stereographic projection of one possible unit cell with these polymer units is presented. An alternate presentation in which four cttt conformations share the four corners but contribute one strand to the unit cell and four ctct conformations occupy the interior in a monoclinic or an orthorhombic cell is presented in Figure 2.

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Table I
Energy of it-PMMA with Regular Sequential Methyl Ester Group Orientations of the C=O Relative to the α-CH_3[a]

conformn	ΔE	exp($-\Delta E/RT$)	repeat[b]
tttttttt	1.49	0.081	2
c[(2*n*)t]c...	h		2*n* + 2
c[(2*n* + 1)t]c...	0.71–1.49		*n* + 1
cttttctttt...	2.50	0.015	10
ctttctttc	0.71	0.300	4
cttcttctt	1.67	0.059	6
ctctctctc	0.0	1.000	2
tctctctct	0.0	1.000	2
tcctcctcc	3.50	0.003	6
tcctcctct	2.78	0.009	4
t[(2*n*)c]t...	h		2*n* + 2
t[(2*n* + 1)c]t...	2.78–4.32		*n* + 1
ccccccccc	4.32	0.001	2
ttttttttt (9/1 L)	3.7	0.002	9
ccccccccc (9/1 L)	5.1	0.000_2	9
ctctctctc (9/1 L)	5.3	0.000_1	9

[a] ΔE (in kcal/mol) is calculated relative to the minimum ctctctctc conformation. High (h) refers to a large ΔE. [b] The repeat along the chain for translation with the chain.

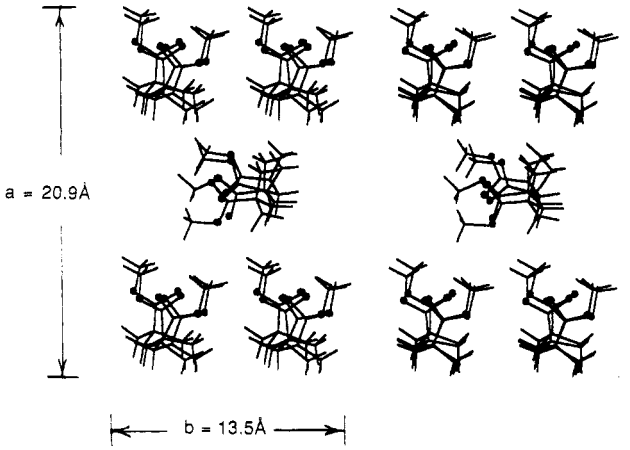

Figure 1. Stereographic projection of one possible unit cell of it-PMMA with four ctct conformations at the corners and one centered cttt conformtion in an end-centered monoclinic or orthorhombic unit cell. Cells with more than one cttt are possible.

Alternatively, four ctct conformations can share the four corners but contribute one strand to the unit cell with four cttt conformations occupying the interior in a monoclinic or an orthorhombic cell. The intermolecular energy was not minimized, but rather the strands were adjusted until the nonbonded distances between the atoms were at least equal to the sum of the appropriate van der Waals radii. The structure fits well into the experimentally determined cell dimensions. For backbone angles of 109.47°, 112°, and 114°, the *c* axis is 9.84, 10.03, and 10.18 Å, respectively, and reasonable agreement with the experimental value of 10.5 Å is achieved. Further relaxation of the conformations packed into this cell should result in an elongation and slight compression of the proposed structure and yield a structure which describes the unit cell only better. Other possible unit cells include any combination of the ctct and cttt sequences for any of the five chains, but at least one cttt sequence is needed to yield the appropriate value for the *c* axis.

There is no homologue polymer to it-PMMA which can be used to compare the proposed unit cell. The orthorhombic *β-trans*-1,4-poly(2-methylbutadiene) and *β-cis*-1,4-poly(2-methylbutadiene), each with four molecules per unit cell, provide some hints for use in the present analysis.[16] The conformation of the trans isomer derives from substitution of a methyl group in the 2 or 3 positions to yield right and left local regions in the chain. The crystal structure consists of a random mixture of these right and left chains. Similarly, the conformation of the cis isomer derives from substitution of a methyl group in the 1 and 5 or 2 and 6 positions, and reversal of the chain axes yields two more for a total of four different possible chains for insertion into the unit cell. The present proposal requires five chains in some statistical distribution of the two chains, tctc and cttt, to yield the required cell dimensions, and especially the *c* direction of 10.5 Å. The intent of this study is to show that there may be conformations other than helices which describe the unit cell of it-PMMA.

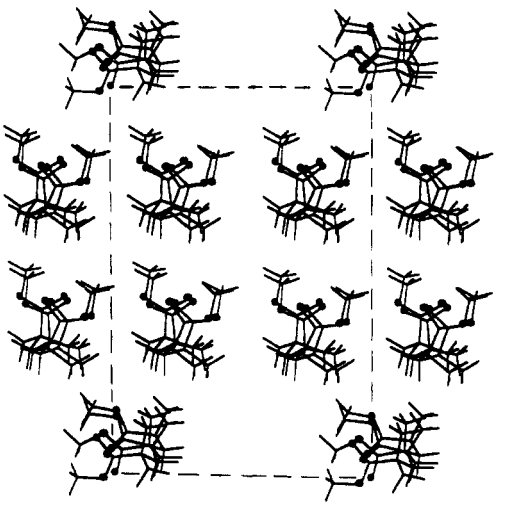

Figure 2. Unit cell of it-PMMA with four cttt conformations at the corners contribuging one strand to the unit cell and four ctct conformations in the interior of a monoclinic or an orthorhombic unit cell. Other cells with various combinations of cttt and ctct conformations are possible.

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