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Molecular modelling of poly(aryl ether ketones): 2. Chain packing in crystalline PEK and PEEK

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A molecular mechanics study of the crystal structures of aryl ether ketone materials has been undertaken using a model based on *ab initio* calculations and crystal data of small, aromatic molecules. The model can reproduce the global minima of the poly(phenylene oxide), PE, and PEK crystals and also correctly estimate the ring conformation in these materials. The calculations show the different unit cell dimensions in PEK, relative to PE (suggested to be due to the additional bulk of the carbonyl group) to favour a lower ring twist angle and therefore complement the respective single chain conformations which, due to the increased torsional barrier around the ketone bridge, also predict a lower twist angle for PEK. To reproduce the PEEK ring conformation satisfactorily it is necessary to considerably reduce the torsional terms employed. This change can be rationalized by n.m.r. evidence which suggests the conjugation of the PEEK chain to be somewhat reduced relative to PEK. The nature of the chain packing in PEK and PEEK has also been examined with respect to the alignment of the ether and ketone bridges and, for both materials, it is suggested that increased packing order involves horizontal (*bc* plane) E..K alignment and vertical E..E (and K..K) alignment. The relative energy difference between ordered and disordered packing is much greater for PEK and it is suggested that this provides an explanation for the differing behaviour of the two unit cells with increased crystallization temperature.

(Keywords: molecular mechanics; poly(aryl ether ketone); crystal; conformation; chain packing)

INTRODUCTION

The preceding paper of this series[1] described the parameterization of a molecular mechanics model of the aryl ether ketone polymeric materials, using data from relevant small molecule crystal structures. Emphasis was placed upon obtaining a good description of the aryl..aryl interaction and, with the inclusion of parameters for the oxygen atoms, the applicability of the model was demonstrated. Hence good agreement was obtained between calculated and experimental crystal structures of poly(phenylene oxide), PE and poly(aryl ether ketone), PEK. We now describe two applications of the model to the PE, PEK and poly(aryl ether ether ketone), PEEK crystals, considering first the intra- and intermolecular forces which influence the unit cell dimensions and ring conformations in the three materials. The second study is concerned with the packing of the ether and ketone functionalities and the differing behaviour of the PEK and PEEK cells with crystallization temperatures. Prior to this the question of chain geometry, with particular reference to the bridge bond angles, will be discussed at some length.

RESULTS AND DISCUSSION

Chain geometry

Semi-empirical (MNDO)[2,3] and *ab initio*[4,5] optimizations of various molecular conformations of diphenyl ether and benzophenone have indicated that, other than for near planar conformers, the molecular geometry does not distort to any great extent, allowing a rigid rotor approach to calculation of the polymer conformation to be used. In the constrained environment of the polymer crystal there is even less likelihood of geometrical change. The rigid rotor model does, however, make the selection of the chain geometry, particularly that of the ether and carbonyl bridges, of some importance. This has already been a matter of some debate in the literature[2] since the COC and CCC bridge angles in the crystals have been reported to be several degrees larger than those measured and calculated for the corresponding small molecules. This has been interpreted[2] in PE in terms of the decreased ring twist angle (about 40°)[6] in the polymer crystal relative to that in diphenyl ether (about 45°)[4,5]. This, in turn, causes additional repulsion of the *ortho* hydrogen atoms and a consequent opening of the COC angle. This is an entirely reasonable argument and is supported by MNDO calculations[2,13] which predict similar behaviour in diphenyl ether conformers with decreased ring twist angles. Extension of this idea to the COC angles in PEEK and PEK is also justifiable, but a problem arises with the CCC (carbonyl) bridges. It has been stated that the two bridge types in PEEK and PEK are crystallographically equivalent[7]. However the ring twist angles in PEK (34°)[8] and PEEK (37–40°)[7,9] are larger than those in the low energy benzophenone conformer, which has a CCC angle of about 121° (ref. 3). The increased CCC angle in the polymers cannot, therefore, occur because of ring

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Table 1 Unit cell parameters of PE, PEEK and PEK

Reference	Polymer	*a* axis	*b* axis	*c* axis
6	PE	8.07	5.54	9.72
10	PEEK	7.75	5.86	10.00
11	PEEK	7.78	5.92	10.06
7	PEEK	7.83	5.94	9.86
9	PEEK	7.75	5.89	9.88
12	PEK	7.65	5.97	10.09
10	PEK	7.63	5.96	10.00

flattening around the carbonyl bridge although it could perhaps be argued that, in order to improve the chain packing, the CCC angle opens to maintain equivalence with the ether bridge. This is not an energetically expensive process[3] and any increase in intramolecular energy could be offset by favourable intermolecular interactions. The approximate geometrical equivalence of the two bridge types is clearly shown by the similarity in the *c* axes' lengths of PEK and PEEK (see *Table 1*).

Because the validity of the above arguments is unclear it is perhaps useful to examine the derivation of the experimental bond angles more closely. Usually these values are not directly observed but rather calculated from the measured *c* axis length using 'standard' C–O and C–C bond lengths (1.36 Å and 1.47–1.50 Å respectively)[6–12]. MNDO and STO-3G optimizations referred to earlier suggest a lengthening of these bonds in benzophenone and diphenyl ether, which, if extended to the polymers, clearly demands a smaller bond angle to reproduce the experimental *c* axes. We have calculated energy curves based on STO-3G energies of MNDO optimized benzophenone[3] and diphenyl ether[13] helical conformers and the geometries of the low energy conformers are used in the following calculations with, for PEK and PEEK, averaging giving equivalent carbonyl and ether bridges (a reasonable approximation because experimentally only a small increase in the length of the *c* axis is observed for PEK relative to PEEK; see *Table 1*). The values employed (1.376 Å and 121.79° for the ether bridge and 1.515 Å and 121.28° for the carbonyl) give (using 1.395 Å ring C–C bond lengths and 120° ring bond angles) *c* axes of 9.68 Å for PE (experimentally 9.72 Å) and 9.91 Å for (since the bridges are taken as equivalent) both PEK and PEEK (experimentally 9.9–10.0 Å). Thus whilst the reduction in the dihedral angles around the COC plane may well produce some opening of the bridge angle it is possible that this effect has, in the past, been somewhat exaggerated because of the smaller bond lengths employed in calculating the bond angle. Only a small increase in the bridge bond angles (about 0.5°) is required to reproduce the experimental *c* axes' lengths.

Ring conformation in the PE, PEEK and PEK crystals

Because there clearly are conformational differences in the PEK, PEEK and PE crystals it is of some interest to assess the intra- and intermolecular interactions that influence this behaviour. To this end six-ring units (to accommodate a crystallographically and chemically symmetric PEEK unit) were used with the interacting unit positioned centrally in chain 1 and within a matrix of chains as shown in *Figure 1*. Intra and intermolecular interaction energies were evaluated between the central unit and the remainder of the matrix with each of the chains of sufficient length to encompass all significant interactions. Van der Waals, electrostatic and torsional components of the total energy were calculated using previously described equations and parameters[1]. The conjugative barriers to rotation about the ring to carbonyl and ring to ether bonds were calculated to be 4.8 and 2.6 kcal mol^{-1} respectively (from *ab initio* calculations[3,13]) and these values were employed in evaluation of the torsional energy component. Charges were calculated using the CHARGE2 program (with a minor modification[1]) and these are given for PE, PEK and PEEK in *Figure 2*. Chain conformations were generated such that all bridges were maintained in the *bc* plane (*Figure 1*) and averaged experimental unit cell dimensions were employed for all three materials. It has been stated[7] that one twist angle (from the *bc* plane) is sufficient to describe the conformations of the two distinct ring types, diether flanked and ether-ketone flanked, in PEEK and this approach is used here.

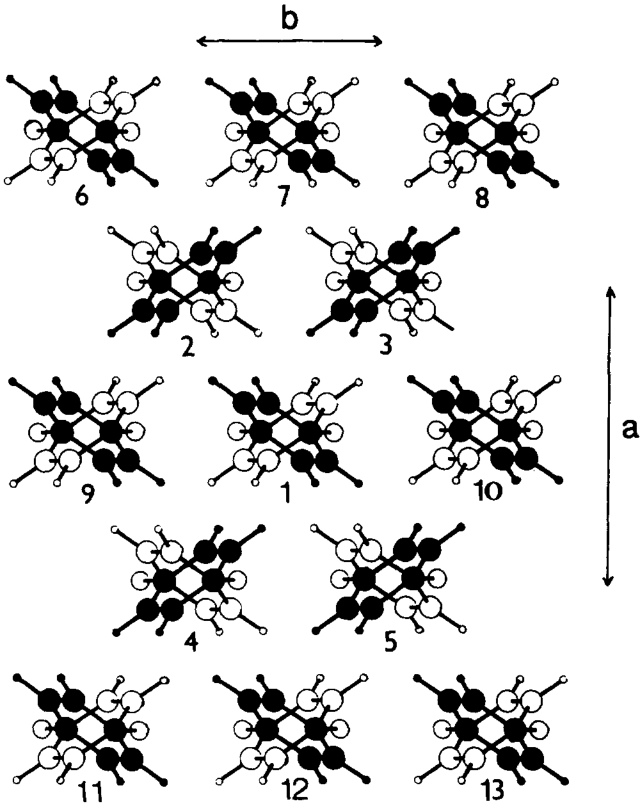
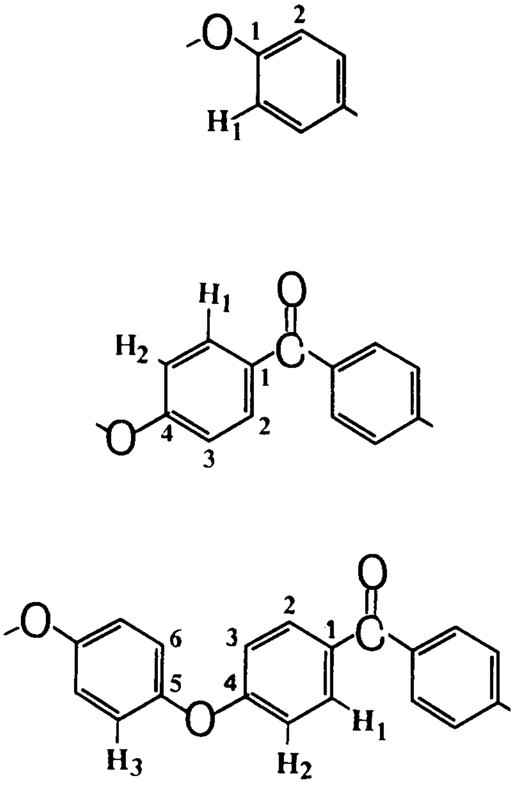


Figure 1 Schematic representation of the PE crystal (viewed along the *c* axis) showing the positioning of chains in the matrix

The conformational energy curves for PE ($a = 8.07$ Å, $b = 5.54$ Å) and PEK ($a = 7.64$ Å, $b = 5.96$ Å) crystals are shown in *Figure 3c* with the contributing intramolecular (i.e. chain 1 energy) and intermolecular component curves shown in *Figures 3a* and *3b*, respectively. The intramolecular minima are essentially dependent upon the torsional energy contributions and it is, therefore, not surprising to find the energy minimum in the PE chain occurs at a slightly higher twist angle to that in the PEK chain. The intermolecular energy is greatly dependent on the aryl..aryl interaction, making the intermolecular curves much less predictable. The calculations indicate a relatively lower twist angle to be favourable in a cell in which the *a* axis is relatively shorter and the *b* axis length is increased, i.e. in the PEK crystal



	Cca	C1	C2	C3	C4	C5	C6	H1	H2	H3	Oca	Oct
PE		60	-114					133				-195
PEK	248	-22	-98	-117	79			130	133		-363	-191
PEEK	248	-22	-98	-117	79	60	-114	130	132	133	-363	-193

Figure 2 Charges (me) calculated for PE, PEK and PEEK

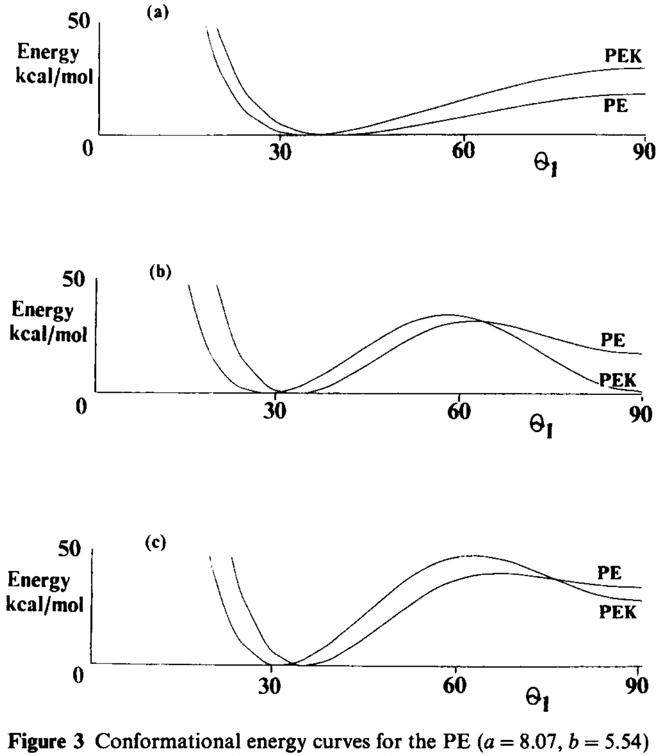


Figure 3 Conformational energy curves for the PE ($a = 8.07$, $b = 5.54$) and PEK ($a = 7.64$, $b = 5.96$) crystals; (a) intramolecular, (b) intermolecular and (c) total energy as a function of ring twist angle

relative to the PE unit cell, and clearly in PE and PEK there is no conflict between intra and intermolecular energy requirements. Thus the increased twist angle observed in PE is consistent with relative internal torsional energies and relative unit cell dimensions of PE and PEK. The increased *b* axis length in PEK can be attributed to the additional bulk of the carbonyl function in the *bc* plane, this in turn allowing a decreased *a* axis because the horizontal spacing is increased. This in turn favours (intermolecularly) a decreased twist angle which is compatible with the conformation of an isolated PEK chain.

Because PEEK is intermediate between PE and PEK in terms of relative ether to ketone ratios it is not unreasonable to assume that structural features such as unit cell dimensions and ring twist angles might also be intermediate between the two extremes. This is the observed behaviour, but the lengths of the *a* and *b* axes are much closer to those observed in PEK. In contrast the experimental ring twist angle is much closer to that observed for PE. The explanation of the increased *b* axis length in PEK is also applicable to the PEEK crystal and helps to explain the greater similarity between the PEEK and PEK unit cell dimensions, in contrast to those of PE (the slightly reduced *b* axis in PEEK relative to PEK presumably reflects the lower ketone to ether ratio). Intermolecular aryl..aryl interactions will, therefore, favour a twist angle close to 30°, somewhat lower than that found experimentally. Furthermore, the internal torsional energy of a six-ring PEEK unit, based on the derived V_2 values, does not differ greatly from a six-ring PEK unit and it is, therefore, not possible to balance the low twist angle favoured intermolecularly with a high intramolecular value and thus obtain an overall angle which matches experimental determinations (37–40°). This can be achieved by excluding the torsional energy term (see *Figures 4a* and *4c*), giving an overall conformation having a slightly lower twist angle than that observed experimentally (the final calculated values for PE and PEK were also 1–2° too low). Whilst at first sight this might appear a somewhat arbitrary modification there is some justification in reducing, if not entirely removing, the torsional energy contribution in PEEK relative to PEK. Solution state ^{13}C n.m.r. spectra of related materials[14] clearly indicate different behaviour for EK-alternating (i.e. PEK-like chains) which has been interpreted in terms of enhanced conjugation (i.e. a greater torsional barrier to the rotation of the rings from the *bc* plane) in such chains. Introduction of EE units appears to break this conjugative interaction, behaviour which can be understood in terms of simple resonance structures (i.e. the opposing effect of neighbouring, electron donating ether functions *versus* the complementary effect of the ether group neighbouring an electron withdrawing ketone function). Thus whilst the intermolecular constraints in the PEK and PEEK crystals favour almost identical twist angles it is the overall conjugative interactions in the chain, rather than the small, isolated effect of replacing 33% of the carbonyl bridges with ether functionality, that causes the increased twist angle in PEEK.

Chain packing in the PEK and PEEK crystals

The calculations in the previous sections were carried out under the assumption that, in PEK and PEEK, all chains are perfectly aligned, i.e. all ether bridges in chain

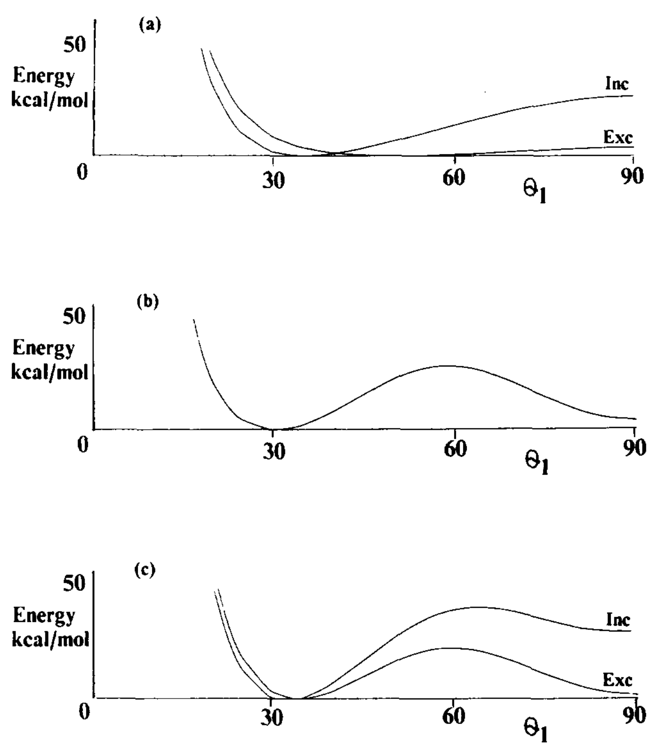


Figure 4 Conformational energy curves for the PEEK crystal ($a = 7.80$, $b = 5.90$) including and excluding torsional energy; (a) intramolecular, (b) intermolecular and (c) total energy as a function of ring twist angle

1 are aligned with ether bridges in the remaining chains, etc. The conformation of the rings is not, it would seem, greatly dependent on this aspect of the packing because the major determining factors are the aryl..aryl interactions and torsional energies. However, the manner in which the bridging groups pack together is a matter of some interest in itself and may also provide an explanation for the different behaviour of PEK and PEEK at different crystallization temperatures. This has already been the subject of a number of experimental studies[15–17] which have suggested the general trend of decreased *a* and *b* axes lengths in PEEK as the crystallization temperature is increased. Within this there have been some contradictions, hence Wakelyn[17] observed a constant *a* axis for crystallization temperatures of 189–241° followed by a regular decrease to 323°, a general decrease in the *b* axis over the entire range and variation but no general trend in the *c* axis length (attributed to experimental error). Hay *et al.*[15] reproduced the general decrease of *a* and *b* axis lengths (but over the entire temperature range) and also suggested the same behaviour characterized the *c* axis. Similar trends do not occur for PEK, discounting crystal surface effects as a possible explanation because these should be similar in both materials[15].

In the following calculations the interaction energies of the various possible combinations of chains will be evaluated in an attempt to gain an insight into the nature of crystalline PEK and PEEK and, furthermore, to provide a rationale for the differing behaviour of the two polymers with respect to crystallization temperature. The interchain energy between a six-ring unit of chain 1 and all surrounding chains (with the latter extended such as to include all significant interactions) has been evaluated using the fixed geometries described above, the unit cell dimensions previously employed and the experimentally determined ring twist angles (i.e. 34° in PEK and an average of 38° for PEEK). The nomenclature used refers to eclipsed (ecl) and staggered (stg) PEK chains as illustrated in *Figure 5* (it should be noted that the chain 1–chain *x* stg interaction differs from the 1–*y* stg interaction, particularly when *x* and *y* are 9 and 10

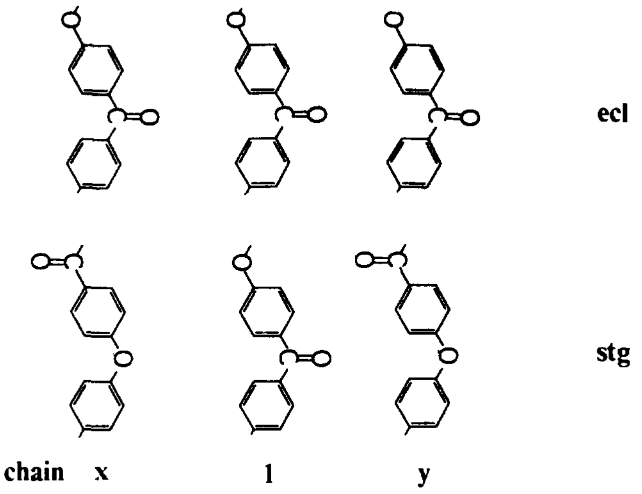


Figure 5 Modes of chain packing in the PEK crystal, chain $x = 2$, 4 or 9, chain $y = 3$, 5 or 10 (see *Figure 1*)

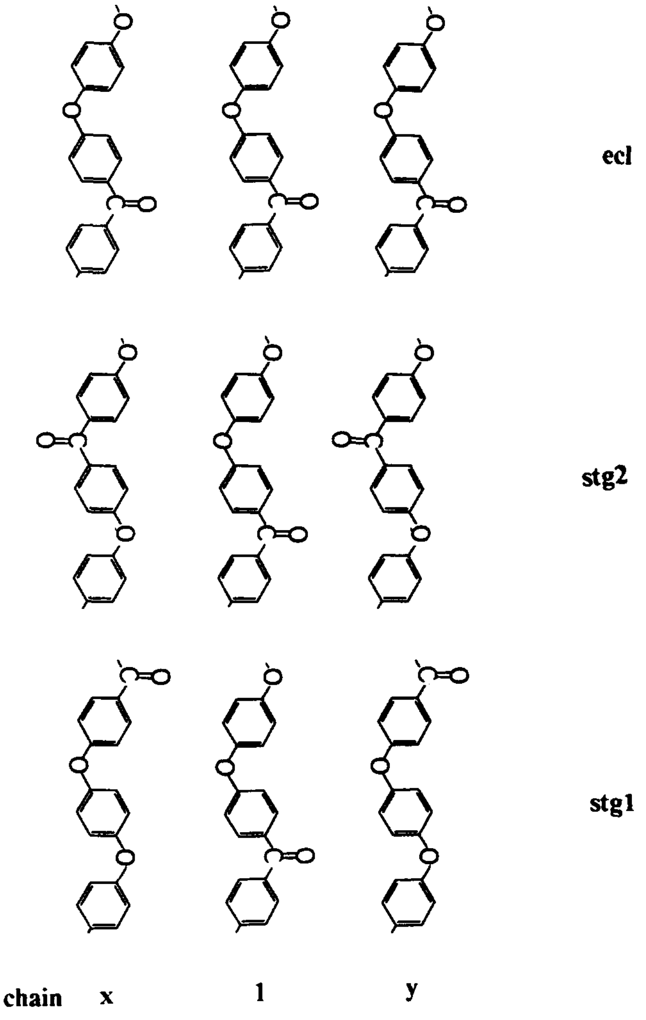


Figure 6 Modes of chain packing in the PEEK crystal, chain $x = 2$, 4 or 9, chain $y = 3$, 5 or 10 (see *Figure 1*)

Table 2 Interaction energies for chain packing in the PEK and PEEK crystals

Interaction	PEK[a] stg[c]	PEEK[b] stg1[c]	 stg2[c]
chain 2	−0.83	−0.17	−0.08
chain 3	−1.08	−0.20	−0.08
chain 4	−0.69	−0.17	−0.04
chain 5	−1.20	−0.19	−0.09
chain 9	−3.91	+0.77	+0.90
chain 10	+5.72	+0.76	+0.86
vertical[d]	−3.80	−0.73	−0.29
horizontal[e]	+1.81	+1.53	+1.76

[a] $a = 7.64$ Å, $b = 5.96$ Å, $\theta = 34°$
[b] $a = 7.80$ Å, $b = 5.90$ Å, $\theta = 38°$
[c] Energies relative to eclipsed interaction of 0.0 kcal mol^{-1}
[d] Total for chains 2, 3, 4 and 5
[e] Total for chains 9 and 10

respectively) whilst for PEEK the two staggered interactions are denoted by stg1 and stg2 (see *Figure 6*). The partial interaction energies of chain 1 with each of the other chains in the staggered orientation are given in *Table 2*, in each case the eclipsed interaction is taken as 0.0 kcal mol^{-1}.

The vertical packing (i.e. that in the *ac* plane) in both PEK and PEEK is energetically favourable when neighbouring chains are staggered. However, because for PEK the 'perfect' staggered arrangement is possible (i.e. all E aligned with all K whilst for PEEK there must be one E to E alignment for each three-ring unit) there is a much greater stg–ecl energy difference. This may provide an explanation for the differing crystallization behaviour with temperature. If it is accepted that for crystallization at higher temperatures the chains will possess more energy and hence more mobility this provides for a greater possibility of crystallization into the more preferential arrangement. The energetic driving force for staggered vertical packing in PEK is such that even at low temperatures it seems quite likely that this orientation will occur because for a six-ring unit the stabilization energy is 3.8 kcal mol^{-1}. Conversely for PEEK there is a much lower stabilization gained from chains 2 to 5 being staggered with respect to chain 1 (for the best possible situation only about 0.7 kcal mol^{-1}) which suggests a much more disordered packing at low crystallization temperatures (low chain mobility). With increasing temperature a more staggered vertically packed structure may be produced with a consequent decrease in the *a* axis length (the additional stabilization could presumably manifest itself in a slightly closer packing of the chains).

The arguments for the horizontal packing and (for PEEK) the decrease in the *b* axis length with temperature have some similarities to those given for the *a* axis but also have some essential differences. In PEK there is a considerable driving force for unit *q* (*Figure 7*) to adopt a staggered orientation to unit *p* (−3.9 kcal mol^{-1}). However following this occurrence units *p*1 and *q*1 can only adopt eclipsed orientations with respect to units *p* and *q* respectively because the carbonyl..carbonyl interaction produced by the alternative staggered relationship is highly destabilizing (+5.7 kcal mol^{-1}). Thus the horizontal packing is essentially eclipsed with one possible staggered orientation (although even this is doubtful, see below) with a large energy loss if the packing is disordered, i.e. once again the PEK crystal structure should be highly ordered, even at low crystallization temperatures. The situation for PEEK is quite different, first there is no energy saving for even one staggered orientation. Secondly, and much more significantly, the worst possible staggered orientation is only disfavoured by 0.9 kcal mol^{-1} relative to an eclipsed horizontal packing, suggesting a disordered structure which will approach a more horizontally eclipsed arrangement as chain mobility (i.e. temperature) increases.

The overall picture the above calculations give is, for 'perfect' crystals of both polymers, very similar, i.e. horizontal packing with alignment of like bridges and vertical packing with non-alignment of similar bridges (in PEEK there must be vertical alignment of half the ether bridges). The energy difference between these 'perfect' crystals and the more disordered arrangements is much larger for PEK than for PEEK, this being reflected in the differing behaviour at different crystallization temperatures and the higher degree of crystallinity attainable for PEK[10]. Energetically there is a suggestion that one staggered horizontal orientation may occur in PEK. However the stabilization provided in the *bc* plane is offset by the disorder introduced into the vertical packing and it is impossible to construct an extended structure which includes an ecl–stg horizontal interaction that is lower in energy than the ordered 'perfect' crystal described above.

Hay *et al.*[15] argue that, if the improvement in the packing order (in terms of the ether and ketone bridges) is the explanation for the increased *a* and decreased *b* axis in PEK relative to PEEK, then this cannot be the explanation for the contraction in both axes (for PEEK) with crystallization temperature (because for the *b* axis the trend is opposite). The latter part of this statement is only correct, however, if the former is true and the above results suggest this is not the case. The increased *b* axis from PE to PEEK to PEK is simply caused by the additional bulk of the carbonyl function in the *bc* plane and the increasing ketone to ether ratio, with the additional space created allowing closer vertical packing. Additionally, for the PE *versus* PEK comparison, there is an intramolecular driving force because the PEK single chain conformation is energetically more suited to a cell with an expanded *b* axis and a contracted *a* axis. These arguments do not depend on the relative alignment of the ether and ketone bridges and improvement in the order of the chain packing does, therefore, account for the decreased PEEK *a* and *b* axes with increased crystallization temperature.

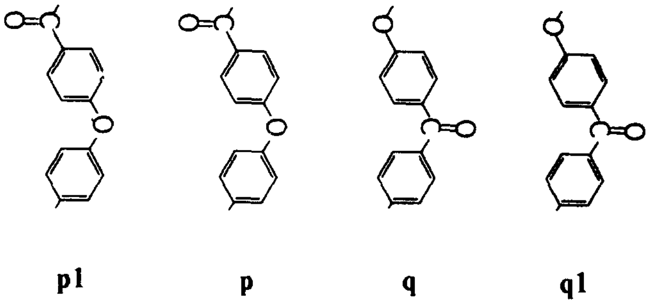


Figure 7 Possible horizontal packing in the PEK crystal

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