

Possible conformational change in compressed poly(*p*-phenylene terephthalamide)

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Under compression poly(*p*-phenylene terephthalamide) (PPTA) fibres fail in a ductile mode without apparent bond cleavage and fracture. However, the molecular origins of this are not well understood. We propose a possible molecular mechanism dominated by change in the amide-carbon-phenyl bond, as opposed to the amide bond.

(Keywords: conformation; compression; poly(*p*-phenylene terephthalamide); modelling)

Introduction

An interesting property of poly(*p*-phenylene terephthalamide) (PPTA) is its resistance to compressive breakage due to a ductile compressive failure mode¹. This occurs without apparent bond cleavage. It has been proposed previously² that the molecular source of this ductility might be a molecular rotation of the amide bond from a *trans* conformation to a *cis* conformation. In this note, we present another possible molecular mechanism which does not require a conformational change in the more rigid amide bond but instead relies on the torsional rotation of the less rigid phenyl-nitrogen bond, causing a rotation of the molecular axis.

Modelling

Using the Tripos force field³, a chain segment of PPTA was built in the conformation found in the crystal⁴. (We chose the Northolt structure as most representative of fibres spun from solution concentrations exceeding 15%^{1,5}.) By analysing the minimum energies of successively stretched and compressed conformations of this model, the stress needed to compress the molecule could be computed.

Results and discussion

As shown in Figure 1, at approximately 1.5% compressive strain, a yielding occurs in which very little further compressive stress is needed to drastically change the length of the molecule. This unstable state is due to excessive torsional rotations of bonds in the free molecule as opposed to the initially dominant mechanism of bond angle and bond length compression.

At moderate strains the above effect is reversible; however, at larger compressive strains the amide group 'flips' (a discontinuity in torsion angle and energy) into a lower energy state (the torsion angle enters a new potential minimum) adding a kink to the molecule. A comparison of this state with that of the known crystal form is shown in Figure 2. If this flipped state is stretched it is found to be stable and further stretching will not cause the molecule to revert to the crystal form. While the computational path for arriving at this state (extreme

compression) may be aphysical, it does indicate that there are possible pathways from the crystal conformation to this new locally stable flipped conformation. Notice that the rigid amide bond remains unchanged in the *trans* conformation.

Figure 3 illustrates the energy of the molecule as it is successively stretched and compressed. The large discontinuity in energy represents the flip to the new state. Figure 3 also shows that the flipped state has a

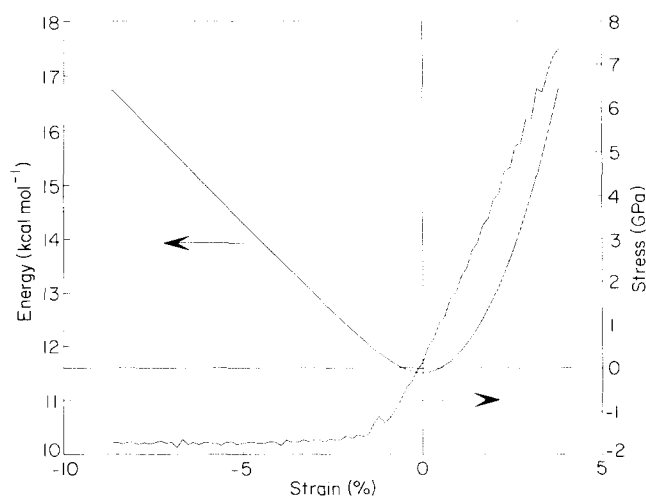


Figure 1 Stress and energy of a PPTA molecule as a function of strain

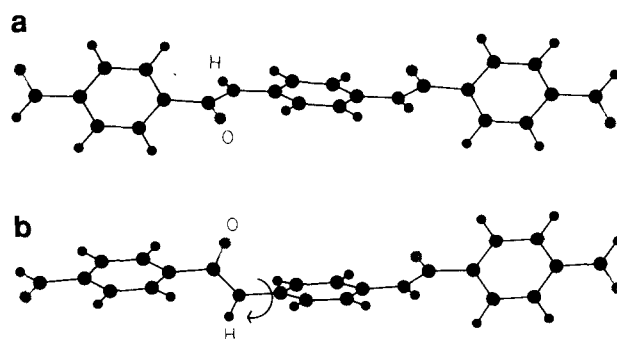


Figure 2 Illustration of the conformational differences in (a) the crystal conformation and (b) the compressed ('flipped') conformation

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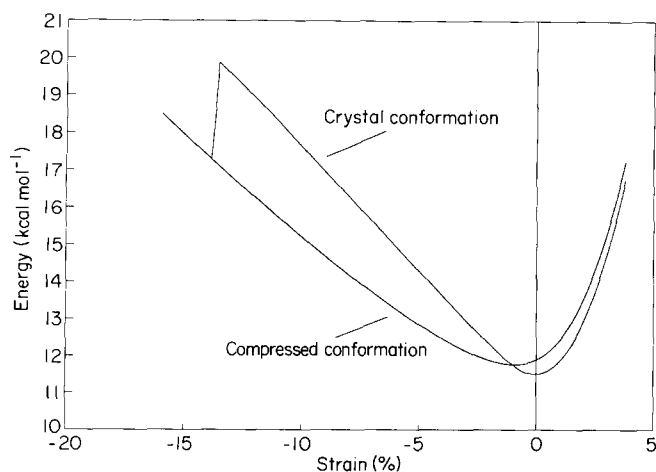


Figure 3 Energy as a function of strain for both the crystal conformation and the 'flipped' conformation. The large discontinuity in the curve indicates the actual 'flip' to the new conformation

shorter minimum-energy end-to-end distance (due to the kink) as well as a higher minimum energy than the corresponding quantities for the crystal conformation, and thus is metastable. However, upon compression, the energy of the flipped state becomes equal to that of the compressed crystal form at about -1% strain, and at greater compression the flipped state becomes energetically favourable. Thus, at least for an isolated molecule, this new conformation becomes the preferred state. If the barrier to this transition at -1% strain is too high, the transition may occur at a greater compressive strain. One possibility is when the crystal form begins to yield at a strain of -1.5% (see *Figure 1*).

In PPTA there are three rotatable bonds (shown in *Figure 2*); the amide-carbon-phenyl bond, the nitrogen-phenyl bond and the amide (amide-carbon-nitrogen) bond. The occurrence of the flip (more precisely defined as the torsion angle entering the domain of a non-equilibrium potential minimum) in the amide-carbon-phenyl bond as opposed to the others can be inferred qualitatively from a compressive buckling model⁶. The smaller torsional stiffness for this bond implies that buckling will occur at this 'weakest link'.

Note that the above statement is not the same as saying that the bond of interest has a lower rotation barrier. In fact electrostatic and van der Waals' interactions impart significant barriers of rotation to all the rotatable bonds, with the nitrogen-phenyl bond possessing the lowest. However, the calculated torsional stiffness of this well is greater than that for the amide-carbon-phenyl bond. The amide bond has steeper 'walls', a higher barrier to rotation and a greater torsional stiffness. It is this emphasis on the 'torsional spring constant' over the ultimate barrier to rotation that is consistent with the link-hinge chain model⁶. Of course, the presence of neighbouring molecules in a crystal would affect the effective torsional stiffness and, indeed, the nature of the failure mode.

Similar computational experiments have also been carried out on hydrogen-bonded sheets of three chains, each three repeat units long, as well as small three-dimensional structures of crystals (seven chains, three repeat units long). The hydrogen bonding was modelled using a 6-12 non-bonded term⁷ standard in the Tripos force field. In all cases, a similar flipped conformation was observed. In one compress-stretch cycle one chain was observed to flip. On subsequent cycles this chain

remained in its conformation and neighbouring chains were observed to flip in the same manner. Once created, the flip remains and, with our protocols of cycling strain using minimum energy, cannot be undone.

How this defect might fit into the crystal is of importance and may be relevant in the formation of the experimentally observed pleats⁸ and shear bands⁹. The amide group is flipped by approximately 75° , breaking the hydrogen bond. However, if a similar flip in a chain above or below the original hydrogen-bonded sheet flips, these two amide groups can reform the hydrogen bond. One can envisage a plane of these flips perpendicular to the chain axis, forming a twin in the crystal with the flipped chain departing at an angle of about 12° to the original chain. However, there would have to be some further smaller distortions of the bonds and angles in the twin boundary in order to assure crystallographic packing in the new crystal.

Another mechanism for localizing the effects of the rotation and tilt of the chain could be crankshaft-type rotation or correlated flips on the same chain. The defect would be a flip of 75° of the nitrogen-phenyl bond and a counter-rotation of approximately -75° of the amide-carbon-phenyl adjacent to the amide group. This amounts to a rigid rotation of the amide group. The combination of rotations results in the tilt of the phenyls being in register with the nearby chains and a much smaller departing angle from the original chain. The net cost in energy of these correlated flips (or the rotation of the amide group) for an isolated chain is about 1 kcal mol^{-1} (4.19 kJ mol^{-1}).

Examination of the model in *Figure 2b* indicates that the energy to 'bend' the chain back into its original course is about 4 kcal mol^{-1} ($16.75 \text{ kJ mol}^{-1}$), where the 'bend' extends over two monomer units. This value is surprisingly low because most of the geometric rearrangement of the molecule is done by using the relatively flexible bond-torsion degrees of freedom. This simple bending has not been studied in detail but it suggests that not only can the chain regain its original direction after a flip, but the pitch (torsional angle) of the phenyl groups can also regain registry with the neighbouring chains using the same mechanism.

Conclusion

The compressive buckling of PPTA chains may occur using a flipped state requiring a change of a single amide-carbon-phenyl torsion angle. This might play a mechanistic role in the shear bands observed under compressive failure of fibre⁹ and in the formation of the pleated structure⁸ of PPTA. It is a different mechanism to that previously discussed^{2,10}, in which rotation of the amide bond undergoes a *trans* to *cis* conformational change.

Acknowledgement

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