UNDERSTANDING CRYSTALLINITY IN AROMATIC POLYIMIDES

by

Professor Edward A. Colarier
Department of Chemistry
Hampton University
Hampton, VA 23668

Aromatic polyimides are a class of polymers that show remarkable thermal stability, strength, and toughness. These properties make them attractive candidates for use in high-performance carbon fiber composites for airborne and spaceborne structural components.

The range of possible polymers one could produce in the laboratory is vast. Consequently, there is a need to develop an understanding of the relationship between some of the thermochemical or thermomechanical properties of polyimides and their chemical structures and processing histories, in order to guide the selection of candidate polymers for synthesis.

The physical properties of a polymer are determined not only by the chemical identities of the monomeric units, but also by the microscopic morphology (amorphous, polycrystalline, distribution of voids) of the material, and by the presence of foreign material. Change in morphological properties with time accounts for the physical process of polymer aging; foreign material (fillers) are widely employed (for example in the rubber tire industry) to tailor physical properties.

Polymer microcrystallites are, in a way, like foreign particles embedded in the amorphous polymer, but since they are also intimately involved in the amorphous phase, they are less prone to exclusion as the material ages than particles of an inhomogeneous filler. The profound effects the presence of microcrystallites can have on the physical properties of polymers make it desireable to be able to control their formation during synthesis and processing. Our research centered on the development of an understanding of the underlying process of crystallite formation in a particular class of aryl polyimides for which there are some x-ray crystallographic data available. The ultimate aim of the project is to be able to develop a model sufficiently flexible to be able, on the basis of the chemical structure of a polymer in this class, to predict: (1) whether it will be prone to form crystallites; (2) crystallographic features of the crystallites; and (3) synthesis and/or processing conditions that will be favorable or unfavorable to crystallite formation. This will provide guidance to the laboratory chemists in their choice of candidate polymers and processing methods.

The process of crystal formation in high polymers is dominated by kinetic factors; the true state of thermodynamic equilibrium is virtually unattainable. The kinetic factors are dependent upon bond rotations within the molecule, as well as the interactions between adjacent lengths of polymer. Characteristically, aromatic polyimides have monomeric units that are relatively long (on the order of 15-30 Å), but have relatively few (2-5) articulations, and thus have few rotatable bonds per monomeric unit. The imide functionality endows the monomers with localized dipole moments, more or less in the chain direction, and other pendant or in-chain groups, such as trifluoromethyl or carbonyl groups, may also contribute to local dipole moments. Both the interaction between these local dipoles along the chain, and ordinary dispersion (van der Waals) interactions are thought to dominate inter-chain cohesion which may be inter- or intra-molecular.

The model compounds studied were (see Figure 1) poly(N-*para*phenylenebisphthalimide) (I), poly(N-*para,para*biphenylenebisphthalimide) (II), and poly(N-*meta*phenylenebisphthalimide) (III). Of these, (II) and a number of its functionalized analogs are known to crystalize, and x-ray crystallographic data have been published for drawn fibers. It is strongly suspected that (I) does and (III) does not crystallize.

C-2

Cheng *et al.*[1] have studied analogs of (II), and the data indicate that the crystallites that form, both in spun and in drawn fibers, have thicknesses of only about 18-22Å, *i.e.* the length of a single monomeric unit in the polymer chain direction. They also found that, with increasing draw ratio, the crystals tend to get larger in the directions transverse to the chain, but do not grow in the chain direction. These conclusions rest on a number of assumptions about the origin of the x-ray reflections, starting with the assumption that the ordering is really crystalline, as opposed to smectic or nematic; for such small crystllite sizes, the data are difficult to interpret rigorously.

Semiempirical quantum chemical calculations (*MOPAC/AM1*) were carried out to investigate the potential energy versus bond rotation about all of the rotatable bonds in the monomeric units. In each of these bonds (the bisphthalimide bond, the phenylene-phthalimide bond, and the biphenylene bond), the energy minima correspond to dihedral angles of 25 - 35 degrees between the aromatic ring systems, the potential energy barrier to rotation through the coplanar conformation is at most on the order of kT at 300K above the minima, the minima are relatively flat (small second derivative of potential energy with respect to dihedral angle), and there is a very large barrier to rotation through the conformation with the rings perpendicular to each other, of around 10 kT. In practical terms, these results mean that, once the conformation around a bond has been established in synthesis, it is essentially frozen in excursions of up to 90 degrees are thermally accessible, but not excursions through larger angles. This point is illustrated in Figure 2: Both sets of conformations indicated can result from the synthesis of the polyimide by the usual synthetic techniques, but a single such bond, once formed, may not cross the barrier around $\varphi = 90°$.

As the polymer is formed, the conformations at the bisphthalimide bonds are random. Since to form a crystallite that is extended for two or more monomer units along the chain direction, all the involved monomers must have the same conformation type, the fact that the conformations are random along the chain means that that condition generally won't be met. Furthermore, besides a correlation of conformations along the chain, there must be a correlation of monomeric conformations on adjacent chains. Again, the randomness of the conformations frustrates this crystallinity. See Figure 3.

These observations lead us to the suggestion that the crystallites are of the fringed micelle type. This is also consistent with the observation that the crystallites seem to grow as the fiber is drawn, but transverse to the chain direction. It is proposed that, as the fiber is drawn, the polymer chains undergo reptation, which would lead both to extension of the crystallites at their edges (Figure 4a), and perfection of the crystallites (Figure 4b). The latter occurs as conformational impurities, whose interactions with the rest of the crystal are weaker, are drawn out of the crystallite, and replaced by monomers with the correct conformation, located further down the polymer chain, which would "click" into place, owing to their stronger interactions with the rest of the crystal. The removal of conformational impurities could also enhance coöprative effects contributing to extension.

This understanding of the nature of crystallinity in this family of aromatic polyimides suggests a number of approaches to increasing the degree of crystallinity: The correlation of conformations along the polymer chains must be brought under control. One possible approach to that might be to synthesize the amic acid polymer precursor to the polyimide, and draw it into sheets or fibers to effect conformational alignment, and then dehydrate it to form the polyimide. Another approach might be to employ bulky functional groups attached to the phthalic 6-rings at the position *ortho* to the bisphthalic bond to enhance conformational purity in the polymer. Finally, surface "template", or enzyme-mediated syntheses might be developed to produce polymers in a conformationally specific way.

[1] S.Z.D. Cheng, Z-Q Wu, M. Eashoo, L.C. Hsu, and F.W. Harris: "A high-performance aromatic polyimide fibre: 1.," *Polymer*, **32**, 1803 (1991).
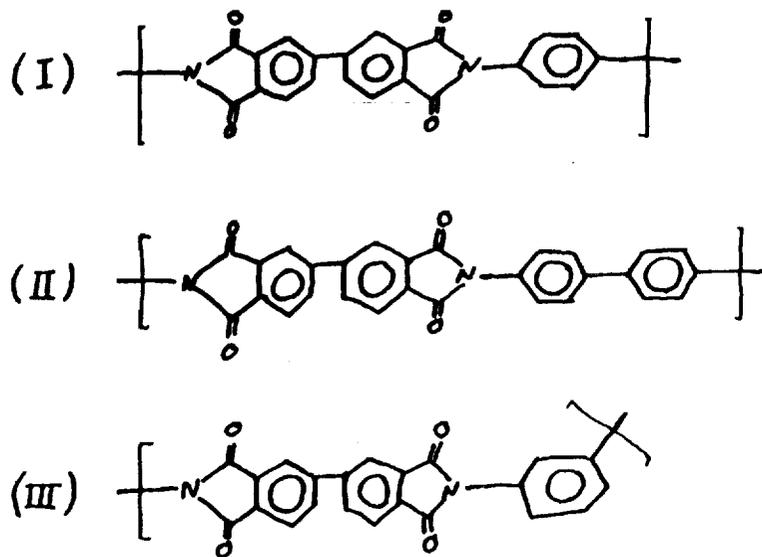
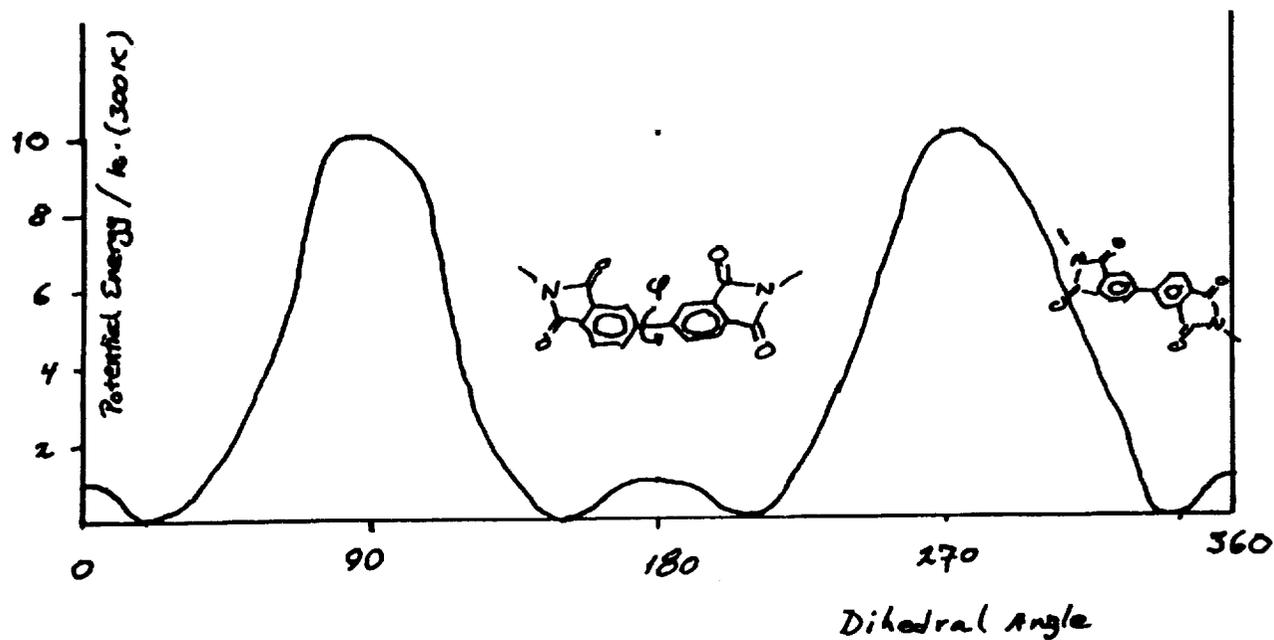**Figure 1.** Three model polymers used in the study.

Figure 2. Schematic representation of the potential energy curve corresponding to rotation about the bisphthalimide bond. The lower barriers are on the order of kT at $T = 300K$, while the higher barriers are on the order of $10 \times kT$ so, once formed in a particular conformation, excursions of dihedral angle may range over only about 90°, and may not pass over the barrier. Hence, there will be very few transitions between the conformers shown.
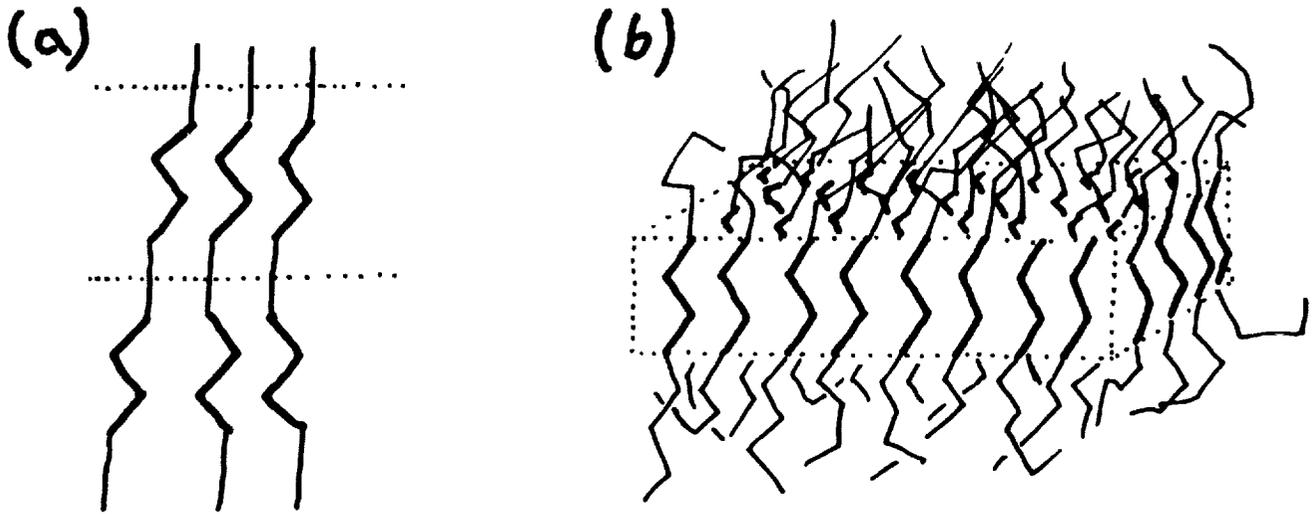
89

Figure 3. Schematic representation of monomer conformations in polymer chains involved in crystallite formation. (a) The conformationally significant region is shown as the bold zig-zag, and the two conformers are represented by the two possible orientations of the zig-zag. Because there is no correlation in conformations of adjacent monomer units along the chains, even though within the crystallite (between the dotted lines) the monomers establish conformational order, that order cannot be retained above or below. This leads to crystallites whose thickness is the length of a monomer unit. (b) Schematic representation of a crystallite, showing conformational order within the crystallite, and the remainder of the polymer chains involved in the amorphous regions above and below the crystallite. A single polymer chain could be involved in a number of such crystallites. These crystallites are a special instance of the "fringed micelle" type.
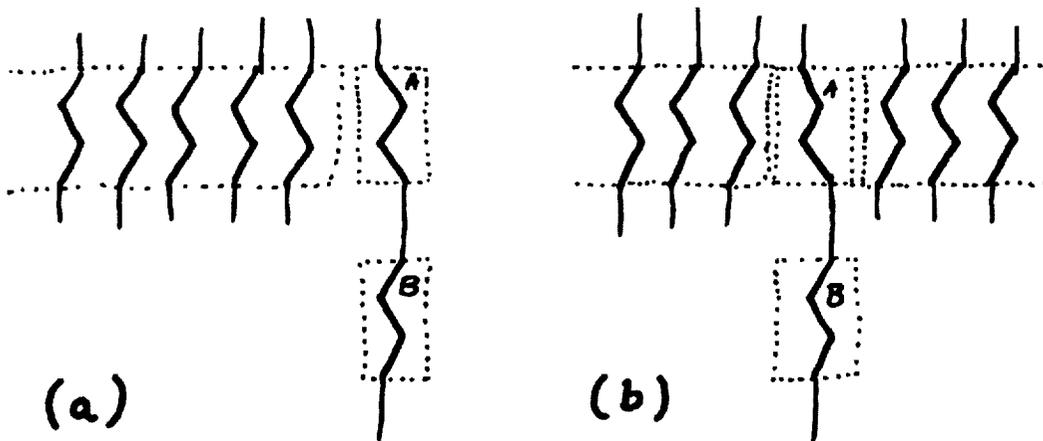

Figure 4. The process of reptation (vertical motion of the chains in the figures) can result in: (a) lateral extension (growth) of the crystallite as monomers with the appropriate conformation are drawn alongside an existing crystallite; and (b) perfection of a crystallite which contained a conformational impurity. In both cases, reptation leads to the removal of monomer unit 'A', and its replacement by the monomer unit 'B', which fits into the existing crystallite structure. Reptation is a typical mode of motion in polymers, and would probably be a prevalent mode when the material is being stretched or drawn.