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The crystal structure of a rigid-rod aromatic polyimide: application of a molecular simulation technique to calculate the structure

Yukishige Kitano*
Toray Research Center Inc., Sonoyama, Otsu, Shiga 520, Japan

and Itaru Usami†
Rikei Corporation, Nishi-sinjyuku, Sinjyuku-ku, Tokyo 163, Japan

and Yutaka Obata and Kenji Okuyama
Tokyo University of Agriculture and Technology, Nakamachi, Koganei, Tokyo 184, Japan

and Takuma Jinda
Kyusyu Women's Junior College, Yahatanishi-ku, Kitakyusyu, Fukuoka 807, Japan
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A molecular simulation technique, combined with X-ray diffraction measurements, was applied to the determination of the crystal structure of poly(4,4'-diphenylene pyromellitimide), a high-modulus aromatic polyimide. Simulation of the crystal structure was carried out with the programs POLYGRAPH and CERIUS (Molecular Simulations Inc.) using the Dreiding force field approach. Initial models optimized by molecular mechanics were set up in order to minimize the energy of an isolated chain and then located in the crystalline lattice by using the unit cell parameters obtained from the X-ray diffraction measurements. These structures were then optimized by the anneal-dynamics method by fixing the unit cell. The computed diffraction patterns calculated for the simulated structure agree well with the X-ray diffraction patterns obtained experimentally. The two benzene rings of the biphenyl group are coplanar and rotated by 65° from the pyromellitimide group. The extended polymer chains run along the direction of the c-axis, with the pyromellitimide plane being inclined at 58° to the (010) plane. The structure has the space group Pbam, with unit cell parameters of $a=8.45$, $b=5.71$ and c (fibre axis)$=16.78$ Å. Two adjacent pyromellitimide groups are aligned side-by-side at the same height along the c-axis and form a zigzag plane along the a- and b-axes.

(Keywords: molecular simulation; X-ray diffraction; polyimide)

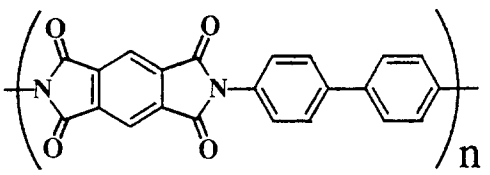
INTRODUCTION

Due to their excellent thermal stability, high glass transition and high melting temperatures, low thermal expansion, good mechanical properties, and low dielectric constants, polyimides have found significant applications in the microelectronics and aerospace industries[1–4]. Easy processability in their precursor states to form smooth thin films has made them attractive dielectric materials for multilayer chip packing modules and for high-quality insulating films in microelectronics and potential matrix materials for high-performance composites in the aerospace industry. To achieve the optimum properties for such applications, it is important to establish the chemical and molecular structure–property relationships in these polymers.

For investigation of molecular and crystal structures, X-ray diffraction analysis is perhaps the most definitive technique for assigning atomic placements within the individual unit cells. In general, however, aromatic heterocyclic polyimides, which have received much attention recently, show very poor X-ray fibre patterns with quite a small number of broad reflections, making it practically impossible to carry out any detailed structural analysis[5–7].

In such a situation, the utilization of model compounds may provide much useful information which can lead to a better understanding of the conformation and the relationships between the structure and the mechanical properties of various related polymers[6,8]. Moreover, with recent advances in simulation software, molecular simulation techniques, which involve molecular mechanics and molecular dynamics, have been shown to be powerful methods when used to complement the X-ray diffraction technique[9–11].

* To whom correspondence should be addressed
† Present address: Teijin Systems Technology Ltd, 4-1-11 Yushima, Bunkyo-ku, Tokyo 113, Japan



Scheme 1

In this study, poly(4,4′-diphenylene pyromellitimide) (DPI, see *Scheme 1*), a member of the class of high-modulus aromatic polyimides, was selected for determination of its molecular and crystal structure by applying such molecular simulation techniques.

DPI has the ability to form well-oriented fibre samples whose diffraction pattern may provide comparatively more crystallographic information than many other polyimides. Therefore, the crystal structure of DPI was also analysed independently by a linked-atom least-squares method, using the X-ray diffraction data that had been collected on an imaging plate[12].

EXPERIMENTAL

Materials

Polyimide fibres were prepared from pyromellitic dianhydride and an aromatic diamine, namely benzidine, by wet-spinning *N*-methylpyrrolidone solutions of their precursor poly(amic acid)s and then imidizing the fibres thermally and chemically. Poly(amic acid)s were partially imidized by adding the appropriate amount of acetic anhydride to their solutions, which were then wet-spun. The fibres that were produced were then chemically converted to polyimides by immersing them in an acetic anhydride–pyridine mixture, followed by heat-drawing treatment[13].

X-ray diffraction

X-ray diffraction patterns were recorded with a cylindrical camera using CuKα radiation. The fibre sample was also examined on a diffractometer in order to obtain meridional and equatorial X-ray scans.

Simulation techniques

Simulation of the crystal structure was carried out with the programs POLYGRAPH and CERIUS (Molecular Simulations Inc.) on an IRIS Indigo computer using the Dreiding force field approach[14] for molecular mechanics and molecular dynamics calculations. The diffraction pattern for the polymer was obtained using the CERIUS program. Diffraction patterns for both powders and oriented fibres can be generated and compared to the experimental data.

Energy minimization (molecular mechanics) and molecular dynamics were used alternatively for each initial structure determination, with only the structure obtained with the lowest energy over several runs being further analysed. Simulation of the polymer using a single-chain approximation was first carried out. Initial models, which were optimized by molecular mechanics, were used to minimize the energy of an isolated chain, and then located in the crystalline lattice containing two chains, using the space group and unit cell parameters obtained from X-ray diffraction. These structures were then optimized by the anneal-dynamics method by fixing the unit cell.

RESULTS AND DISCUSSION

An X-ray fibre photograph of DPI is shown in *Figure 1*; all of the reflections can be indexed in terms of an orthorhombic unit cell. The equatorial diffractometer scan of the reflections on the zero-layer line gives more accurate values of the spacings and indicates lateral cell parameters of $a=8.57$ and $b=5.51$ Å. The meridional diffractometer scan revealed twelve clear 001 diffraction peaks up to $2\theta=70°$, which correspond to twelve layers. These spacings give a chain repeat length c of 16.78 Å, and it would require two chains per unit cell to achieve a realistic density for the cell. The calculated density of 1.50 g cm^{-3} agrees well with the observed one (1.45 g cm^{-3}).

From the extinction rule, possible space groups for this crystal structure are Pbam or $P2_12_12$. The simulation was first attempted by assuming $P2_12_12$ as the space group, in which the polymer chain has twofold symmetry and the two chains must be arranged in an antiparallel fashion, due to the fact that the chains are related by 2_1 symmetry perpendicular to the c-axis. In the course of optimization, the rotational angle of the pyrommelitimide group from the (010) plane is nearly constant ($\sim 58°$), but the dihedral angle between the two phenyl rings became narrower, finally reaching a value below 1°. As the molecular dynamics simulation was performed for P1 symmetry, this fact meant that the diphenyl group was substantially coplanar and therefore the structure had a pseudo-mirror symmetry perpendicular to the c-axis and an inversion symmetry, which suggested the space group Pbam, as a special case of $P2_12_12$.

The molecular arrangements of the simulated crystalline structure are shown in *Figure 2*. X-ray diffraction patterns calculated using CERIUS satisfactorily reproduced those that were obtained experimentally. The simulated pattern of the highly oriented DPI fibre shown in *Figure 3* clearly

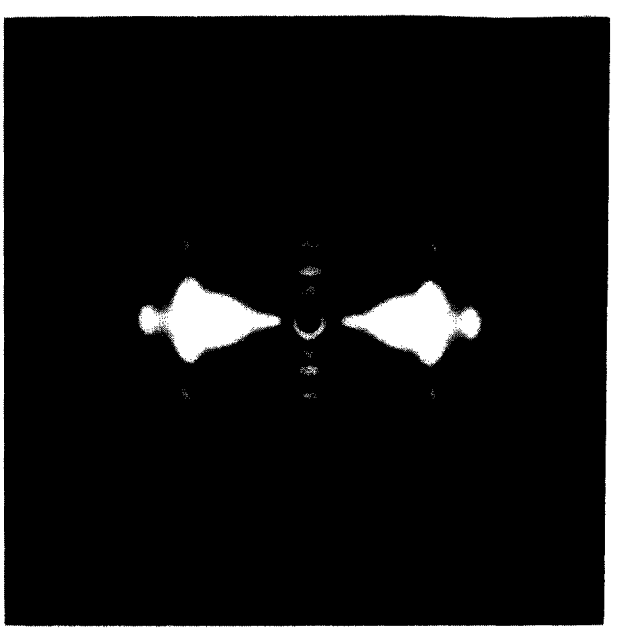


Figure 1 X-ray fibre photograph of DPI

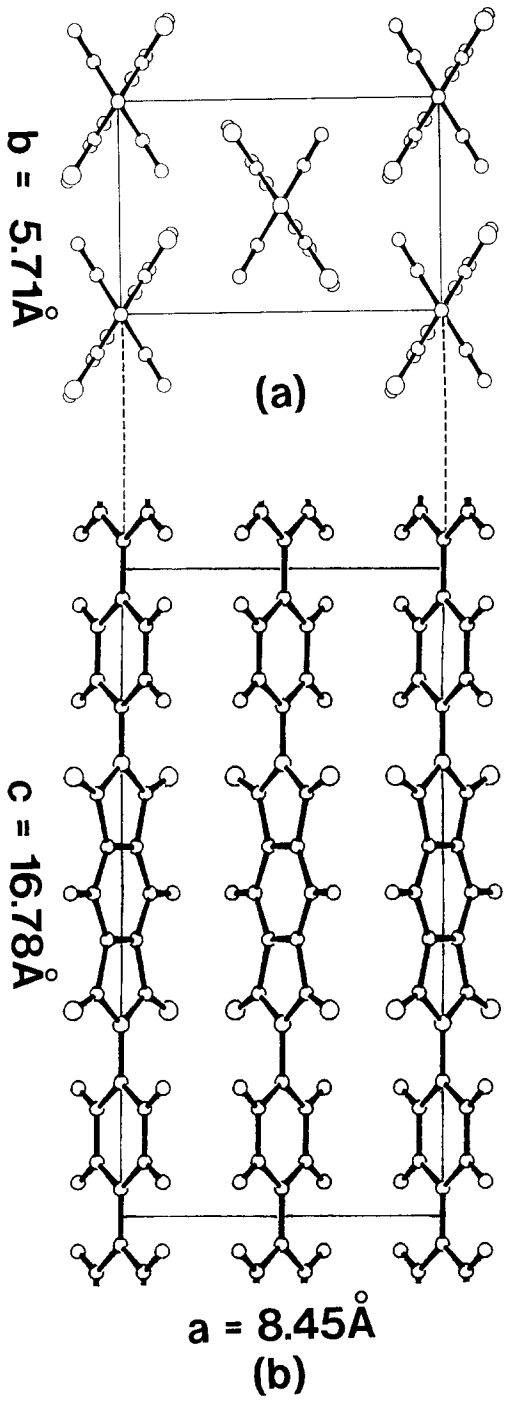


Figure 2 Molecular arrangements of the simulated crystalline structure of DPI, projected along (a) the *c*-axis and (b) the *b*-axis

indicates that coincidence was attained between the photograph obtained experimentally and the simulated one.

As a check of the preciseness of the simulated structure the dihedral angle between the two phenyl rings was opened. As a result of this, not only does the packing energy become higher than the lowest energy state, but in addition the simulated X-ray fibre photograph and powder diffraction patterns were different from those obtained experimentally.

The two benzene rings of the biphenyl group are coplanar and rotated by 65° from the pyromellitimide group. Regarding the torsional angle between the two benzene rings of the biphenyl group, two types

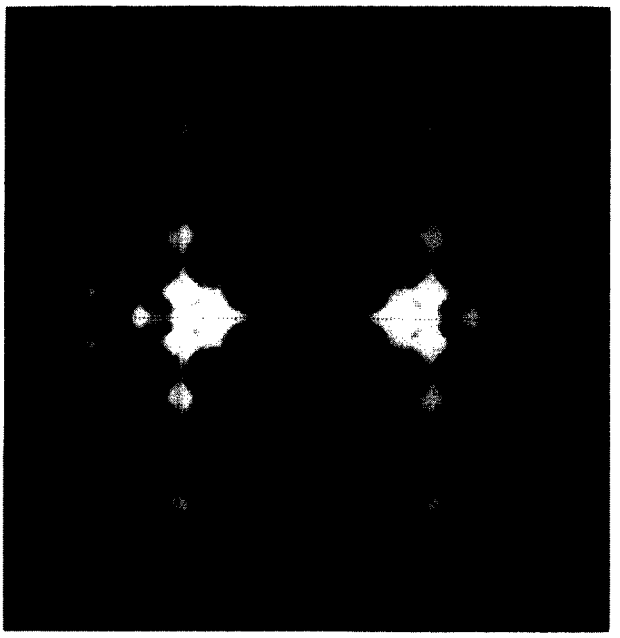


Figure 3 Simulated fibre pattern of highly oriented DPI based on the molecular arrangements shown in *Figure 2*. The half-width at the half-height of the crystalline orientation distribution is 5°, which is equivalent to an orientation function of 0.995

of conformation have been reported in the solid state. The dihedral angles of 4-hydroxybiphenyl[15], 4,4′-bis(4-fluorobenzoyl)biphenyl[8], 4,4′-difluoro-*p*-terphenyl[16], 4,4‴-difluoro-*p*-quaterphenyl[16], and biphenyl itself[17], were almost 0° in every case. In contrast, the angles were 31.0° in 3-chlorobiphenyl-4-carbonitrile[18], 46° in 4-biphenyl thioketone[19], and 36° and 40° in *p,p′*-bitolyl[20]. These results indicate that the biphenyl ring has a comparatively low energy barrier in the ring–ring internal rotation potential[21].

The extended polymer chains run along the direction of the *c*-axis, with the pyromellitimide plane being inclined at an angle of 58° to the (010) plane. The structure has the space group Pbam, with unit cell parameters of $a=8.45$, $b=5.71$ and $c=16.78$ Å. Two adjacent pyromellitimide groups are aligned side by side at the same height along the *c*-axis and form a zigzag plane along the *a*- and *b*-axes. These results are consistent with those obtained by the X-ray diffraction method, which were refined, with 32 observed reflections, to give a final *R*-value of 0.202. Details of the X-ray structure analysis will be presented elsewhere[12]. Consequently, we are fully convinced from this investigation that molecular simulation methods have advantages of being powerful and time-saving procedures in the conformational analysis of polymer chains when compared with the conventional X-ray structural analysis approach.

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