Polymer Bulletin 29, 557–563 (1992)

Polymer Bulletin

Molecular packing at surfaces of oriented polyimide fiber and film observed by atomic force microscopy

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Summary

Molecular morphology of a surfaces of fibers and films from novel segmented polyimides with different rigidity of the backbones was studied by atomic force microscopy. It was observed that surface morphology on a molecular scale is formed by straight segments arranged in a {1-10} plane for polymide fiber and in a {010} plane for polyimide film. Z-shaped backbone segments at the fiber surfaces are arranged at definite angles with respect to the fiber axis. The parameters of unique cells, positional correlations and the arrangement of molecular segments at the interface are discussed.

Introduction

Novel rigid segmented polyimides [1-3] possess excellent physico-mechanical properties and fiber-forming capabilities as compared to classic polyimides [4]. Such polyimides with backbones having different ridigity can be combined to make attractive composite materials [3]. The more rigid polyimides serve as fibers and the softer ones are used as the matrix polymer. For such composite materials the character of interactions between matrix and fibers plays a crucial role in the development of advanced properties. Some preliminary optical microscopy investigations point out the possibility of transcrystallization of matrix polyimide in thin layers on the surface of highly oriented filled fibers [3]. As is known, the mechanical behavior of the matrix polymer in the interface zone strongly depends upon local molecular chain ordering at the surface. Till now only X-ray data are available for characterization of the bulk structure of such novel fibers and matrix polyimides [1-3]. Thus the main goal of this paper is the elucidation of local ordering of the backbone fragments at surfaces of the polyimide BPDA-PFMB fibers and semi-rigid matrix polyimide BTDA films. For chemical structures see Scheme 1. The observation of surface morphology on a molecular scale is possible with atomic force microscopy (AFM) techniques [5-7].

Experimental

Highly oriented fibers of BPDA-PFMB were prepared in the laboratory of Prof. S. Cheng by spinning from an isotropic solution, followed by stretching to a draw ratio of 8. Films of BTDA were prepared by casting the solution on glass substrates. Synthesis, spinning and stretching procedures are described in detail elsewhere [1-3].

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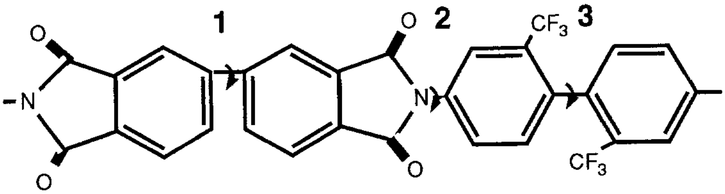
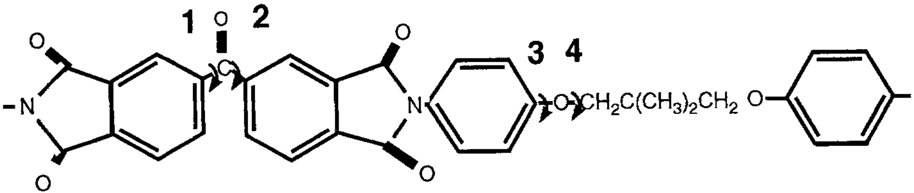
The surfaces of polyimide samples in ambient conditions were observed with an AFM, the Nanoscope II (Digital Instruments, Inc., Santa Barbara) using a pyramidal SiN4 tip. The experimental procedure is well known and described in detail elsewhere [5-7]. Scanning electron micrographs (SEM) of gold coated polyimides were obtained with a JSM-U3 microscope.



BPDA-PFMB (3,3',4,4'-biphenyltetracarboxylic dianhydride + 2,2'-bis(trifluoromethyl) 4,4'-diaminobiphenyl)



BTDA (1,3-bis(4-aminophenoxy)-2,2-dimethylpropane + 3,3',4,4'-benzophenontetracarboxylic dianhydride)

Scheme 1

To analyse the AFM data we processed the raw experimental data and built corresponding computed models of the possible molecular arrangement. The processing of the raw AFM data included the delicate removal of recognizable artifacts on images using one- and two-dimensional Fourier-transforms. Two-dimensional correlation functions G(x,y) and the corresponding geometrical parameters from various one-dimensional sections were calculated also.

The possible molecular arrangements were simulated by building molecular models, minimizing the energy while rotating around various bonds and building sequences of monomers in favourable conformations. All calculations were performed by means of a program called SYBYL (Tripos Associates, Inc., St. Louis) [8] on a Silicone Graphics computer. Having the developed a set of possible molecular models of the backbone fragments we packed them into appropriate crystalline cells using the program CERIUS (Molecular Simulations, Cambridge) [9]. The procedure includes: selection of possible cells (symmetry, parameters, molecular positions, etc.) taking into account all available structural data from [1-3]; searching for dense packing of molecules by minimization of lattice energy; analysis of geometric parameters of models in real and reciprocal spaces in various projections (Miller planes) (for details see [10]).

Results and discussion

The results presented here describe observations of the arrangement of molecular backbones on the molecular scale. The data were obtained repeatedly, at different magnifications, with various experimental conditions at several flat areas of fiber surfaces of PBDA-PFMB and at the free surfaces of cast films of BTDA. As judged from SEM data the fibers of 20-30 μm in diameter have 1-2 μm wide flat areas divided by deep grooves aligned along the fiber axis (Fig. 1a). The surface of the BTDA film had oriented, micronscale features as a result the material was spread to make the film (Fig. 1d).

AFM data. Fig. 1b is a topview of unprocessed image data on scale of 10x10 nm for a fiber of PBDA-PFMB. An unprocessed (8x8 nm) image of a cast BTDA film is presented in Fig. 1e. The axis of the PBDA-PFMB fiber and the preferable orientation in the films are arranged vertically in the images. For the fiber, images show wavy ridges with a wave period of 1.5-2.0 nm in the x- directions. For the BTDA film, a shorter period modulation of heights is detected with a periodicity of 0.5 nm in the x-direction and about 2 nm in the y-one. Image processing was then used to emphasize the important aspects of the observed structures.

Processed images of the polyimides studied were obtained by processing of AFM data and are shown in Fig. 1c, f. As can be seen, all the main features present in the original data are preserved in the processed ones. The main feature of molecular scale morphology of the fiber surface (Fig. 1c) is the presence of thin (0.2-0.4nm) wavy ridges. Each ridge protrudes above the adjacent groove by 0.3 to 0.6 nm. The ridges run at angles of 60-70^o to the direction of the fiber axis. Each wave consists of 4-5 subunits of 0.8-0.9nm length. The ridges run nearly straight for distances of about 3.5-4.5nm, then make a sharp change in direction. Adjacent ridges change direction in the same way so that the wavy ridges fit together. This creates a herringbone-like pattern. At the surface of the BTDA film the wavy ridges form a well defined "layered" array with an periodicity along the y-axis of 2.4 nm and along the x-axis of 0.5 nm (see Fig. 1f).

X-ray diffraction data for BPDA-PFMB fibers and cast BTDA films [1-3] show that the orientation of macromolecular backbones is along the fiber axis of PBDA-PFMB and orientation of the BTDA backbones in the plane of films. This and also our SEM data lead to the conclusion that the observed arrangement of ridges on AFM images can be interpreted as the arrangement of macromolecular chains at the surface examined.

To estimate "average weighted" geometric parameters of molecular ordering (periodicities d_x and d_y along the x and y directions) of observed images in real space, we used two-dimensional correlation functions G(x,y) calculated by self-convolution of the images [8,11] (Fig.2). This function can be considered as self-convolution of repeat units located in separate cells arranged according to the symmetry and periodicity of the lattice. From an analysis of the shape of G(x,y) around the origin, the conclusions about the "average" shape and arrangement of the molecular fragments can be made. The damping of G(x,y) is caused by distortions of positional ordering and can be used to estimate the upper limit of sizes of ordered regions, L_x and L_y. This is analogous to the longitudinal and transverse crystallite sizes calculated from X-ray data [1-3,11]. The same information could be obtained from the analysis of two-dimensional Fourier-images [10,11]. The results of these analyses are presented in Table 1.

Table 1. Molecular parameters of polyimides determined from AFM data.

parameters		**BPDA-PFMB**	**BTDA**
periodicities, nm	d_x	2.0	0.53, 1.05
	d_y	0.7, 1, 1.5	2.4
sizes of ordered regions, nm	L_x	>6	~3-4
	L_y	>4	>4

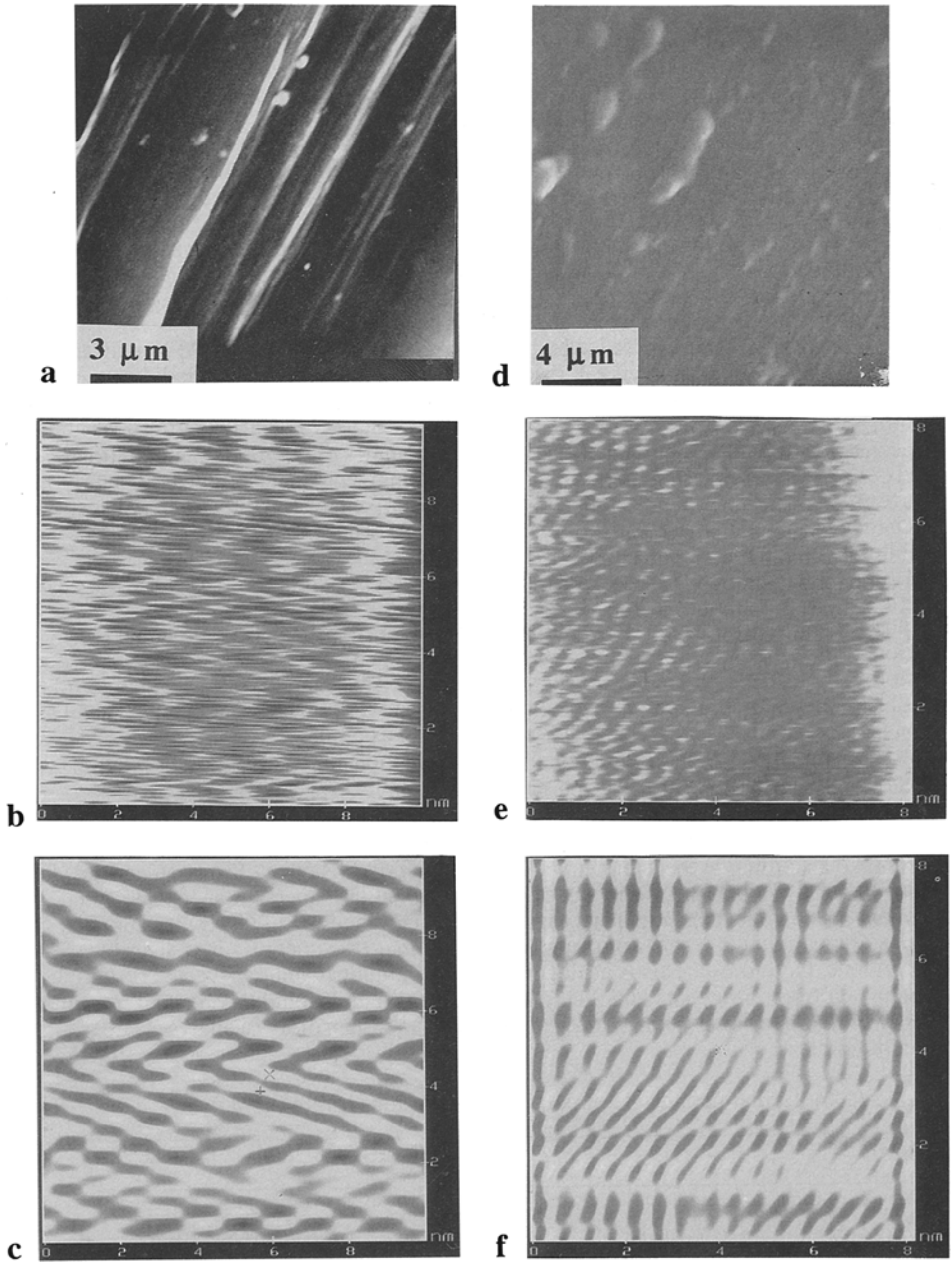


Fig.1 SEM and AFM images of the surfaces of PBDA-PFMB fiber (a, b, c) and BTDA film (d, e, f); a, d - SEM images, b,e - as-obtained AFM images; c,f - AFM images after processing

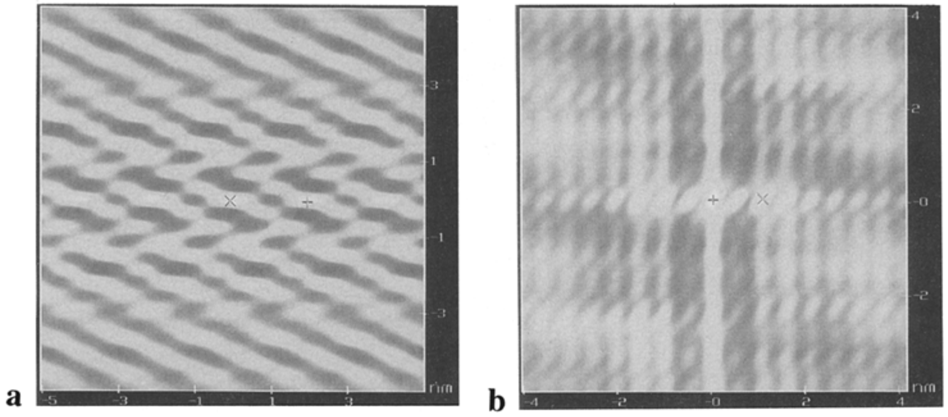


Fig.2 Autocorrelation functions of PBDA-PFMB (a) and BTDA (b).

Molecular modeling. Energy minimization gives a possible minimum potential energy set of torsion angles for bonds (see Scheme 1) **1**, **2**, **3**, **4** in the backbones (Table 2). These angles are close to the ones obtained for similar polyimide fragments [1-3,12]. Based on this data for isolated monomers we built a number of conformers with potential energies which differ by only 1-2 kcal/mol. For further analysis we selected only those which: pack with lowest energy into a cell with parameters fitted to the experimentally obtained; have periodicities along the backbones close to those derived from X-ray data; have the appropriate density of packing and produce Fourier-images and geometrical features that correspond to experimental observations.

Models. The models of proposed molecular packings fitted to the observed data for both polyimides are presented in Fig. 3. The main features of the models are summarized as follows.

PBDA-PFMB fiber. A unique monoclinic cell with a=3.1nm, b=1nm, c=2nm, $\gamma=56^{o}$ and 4 repeat units consists of 2 jointed monomeric fragments. The calculated density of 1.53 g/cm^3 corresponds to the experimental value [1]. The observed image is formed by slightly curved macromolecular segments located in a {1-10} plane and tilted at angle in the range of 60-65^{o} to the c axis. The model presented in Fig.3a shows only double repeat units located in the surface plane. The second layer of the non-primitive three-dimensional unit cell is not shown to avoid confusion from overlapping in the figure. The observed backbone segments are longer, typically 2 to 4 monomeric units. The molecules bend sharply by changing the torsional angles to create the zig-zag shape. The AFM data indicate that positional correlations in the lateral arrangement of macromolecular segments extend over 4-6 nm.

BTDA film. A unique orthorhombic cell with parameters a=2.1nm and c=4.8nm, with 4 repeat units consisting of 2 conjugated monomeric fragments, creating a chain with a large scale zig-zag is shown in Fig.3b. Assuming b=0.58nm (corresponds to X-ray value for the bulk state) the density of packing is 1.32 g/cm^3 which corresponds to the measured value [3]. The image is formed from an {010} plane of the lattice. The main period is 2.4 nm along the c axis. Along the a axis the periods are 0.53 and 1.05nm. Positional correlations extend to 3-4 nm.

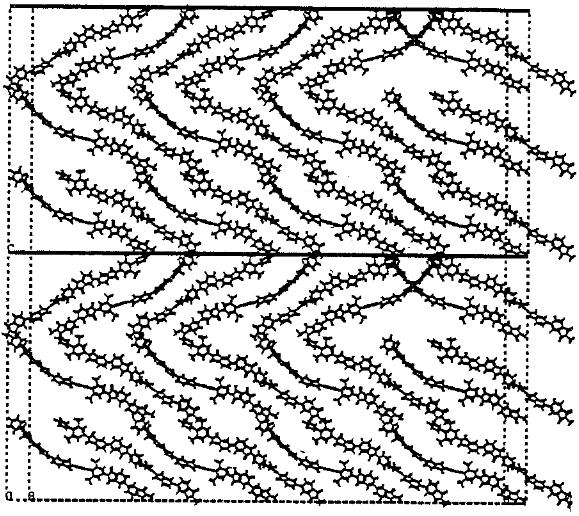
Table 2. Torsion angles in backbones obtained from molecular modeling.

	BPDA-PFMB	BTDA
	torsion angles, ^{o}	
1	60, 124	30, 150
2	39, 141	30, 150
3	90	91
4	-	178

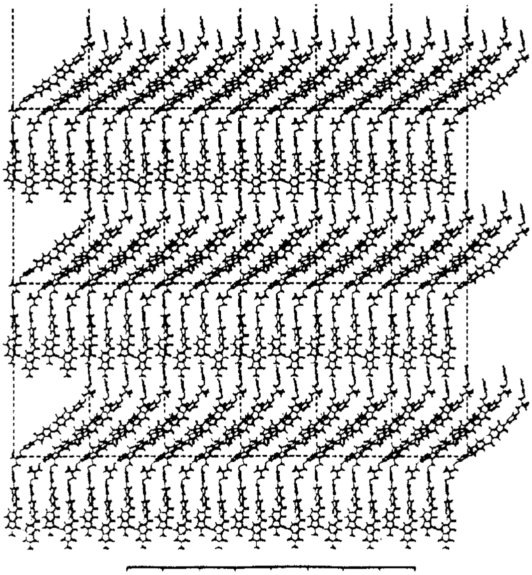
Conclusions

Based on the AFM data obtained from a limited number of observations of flat areas of drawn polyimide fiber and cast film surfaces we can make the following statements about the molecular packing observed at the surface of these polyimide materials.

First, the symmetry of the ordered lattice in the arrangement of macromolecular backbones is the same as has been proposed on the basis of X-ray data for the bulk state of both compounds [1-3]. The unique cell for a two-dimensional array of ordered backbones at the surface of the fibers differs from the X-ray determined unit cell by the presence of 2 conjugated monomeric units which double the length of the *a*-edge. For the film surface, the lengths of *a*- and *c*-edges are similarly doubled. The surface of the BPDA-PFMB fiber is formed by backbone fragments arranged in the {1-10} planes. In the BTDA film the {010} planes are parallel to the free surface.



a



b

Fig.3 Models of molecular ordering at the surfaces of (a) BPDA-PFMB fiber and (b) BTDA film; the bar corresponds to 8 nm

Second, on the surface of BPDA-PFMB fibers, molecular backbones are oriented at a definite angle with respect to the fiber axis while in the core they lie along the *c*-axis, as was concluded from X-ray data in [1].
This effect could be explained by differential shrinkage of the core and the surface during solvent removal and thermal treatment after spinning [1].

Third, from the damping of correlation functions we can conclude that both polyimides are very distorted polymers with positional ordering of the backbones of relatively short-range. Correlations extend over only 3-4 monomer units along and transverse to the backbone directions. This level of positional ordering corresponds to some intermediate, mesomorphic state rather than a crystalline one. Such ordering could be successfully described as biaxial orientational order of stacks of the backbones in the framework of the "sanidic" mesomorphic state classification developed for semi-rigid polyesters and polyimides [13-15].

Acknowledgments

We thank Professor F. Harris and Professor S. Cheng for supplying the samples studied and for helpful discussions. This work was supported by the NSF center for Molecular and Microstructure of Composites and by EPIC, the Edison Polymer Innovation Corporation.

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Accepted August 11, 1992 K