

# MOLECULAR MODEL FOR A SOLID SOLUTION OF NYLON6 AND POLY(*p*-PHENYLENE TEREPHTHALAMIDE)

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## ABSTRACT

A molecular model for a substitutional solid solution of nylon6 and poly(*p*-phenylene terephthalamide) has been proposed on the basis of the hydrogen bonding scheme and the unit cell dimensions of the components. The model is compatible with the observed unit cell dimensions of the solid solution. The weight fractions of the components calculated on the basis of the model are in qualitative agreement with those reported earlier.

## INTRODUCTION

THE polymer blend comprising of the wholly aromatic polyamide poly(*p*-phenylene terephthalamide) (PPTA) and the polycaproamide nylon6 has interesting properties<sup>1</sup>. The preparation of polyblends of nylon6 and PPTA has earlier been reported from this laboratory<sup>2</sup>. Kumamaru *et al*<sup>3</sup> have also reported the epitaxial crystallization of nylon6 on PPTA filaments. It is well known that the high strength of rigid rod polymers like PPTA arises from the high degree of molecular order. In composite systems of the type nylon6-PPTA, information on the molecular arrangement is, therefore, essential to understand their properties. From a preliminary x-ray study of polyblends of nylon6 and PPTA, it has been suggested earlier<sup>2</sup> that the polymer blend could be considered as a substitutional solid solution in which some of the chains of nylon6 are replaced by those of PPTA. A model for the molecular arrangement in such a solid solution, based on a comparison of the unit cell dimensions and the pattern of hydrogen bonding in the crystal structures of nylon6 and PPTA is proposed here.

## EXPERIMENTAL

Samples of nylon6<sup>4</sup> were obtained from Garware Nylons Private Limited, India. The observed density<sup>2</sup> of 1.1 g cm<sup>-3</sup> was significantly different from the value of 1.23 g cm<sup>-3</sup> reported earlier for the fully crystalline  $\alpha$ -form<sup>4</sup>. However, it is well known that in polymers, the presence of noncrystalline fractions and imperfections leads to density values different from those for an ideally crystalline sample<sup>5</sup>. Similar low density values for nylon6 have also been reported earlier<sup>4</sup>. X-ray diffraction patterns from the components and the solid

solution have been recorded using CoK $\alpha$  radiation and a Philips powder diffractometer.

## RESULTS AND DISCUSSION

This analysis assumes that the sample under study did not contain segregation of either nylon6 or PPTA. This assumption is supported by the results reported earlier<sup>2</sup> that for the composition 62.7 wt % nylon6—37.3 wt % PPTA analysed by us, the components are completely miscible. Consequently, all the crystallites in the sample are considered to be those of the solid solution. Factors related to the interaction and stability at the interface of the segregated components are, therefore, not considered to be relevant to the proposed model.

### (i) Lattice matching

The unit cell dimensions and some of the other relevant crystal data on nylon6<sup>4</sup> and PPTA<sup>6</sup> are given in table I. A striking equivalence observed in the unit cell dimensions is that

$$^3b_{\text{nylon6}} = ^4b_{\text{PPTA}} = 51.6 \text{ \AA}. \quad (1)$$

The unit cell dimensions of the basal planes are also comparable as follows:

$$^a_{\text{nylon6}} \simeq ^2a_{\text{PPTA}} \text{ and } ^c_{\text{nylon6}} \simeq ^c_{\text{PPTA}}. \quad (2)$$

However, the conspicuous disparity among the monoclinic angles of  $\beta_{\text{nylon6}} = 67.5^\circ$  and  $\beta_{\text{PPTA}} = 90^\circ$ , rules out any matching of the lattices. Perfect lattice matching is, however, necessary only in systems with interfaces. Formation of a stable solid solution, on the other hand, depends on the molecular dimensions of the host

Table 1 Crystal data on nylon6 and PPTA

	Nylon6	PPTA*
<i>a</i>	9.56 Å	5.18 Å
<i>b</i>	17.24	12.90
<i>c</i>	8.01	7.87
	67.5°	90°
<i>V</i>	1219.67 Å <sup>3</sup>	525.89 Å <sup>3</sup>
Space group	<i>P</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>n</i> (or <i>P</i> <sub>n</sub> )
<i>Z</i>	4 units of C <sub>12</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub>	2 units of C <sub>14</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub>
Molecular weight	226.30	238.22

\* The unit cell dimensions of PPTA given by Northolt and Aartsen<sup>6</sup> have been transformed to a conventional monoclinic setting with *b* as the unique axis. The *a* and *c* axes of Northolt have also been interchanged.

and the substituent chains and the ease with which the substituent chains enter the host lattice without disturbing the stability of that structure. Models for the molecular arrangement in the solid solution of nylon6 and PPTA have been analysed here mainly from the criterion of retaining the stability and intermolecular interactions in the host lattice of nylon6.

#### (ii) Random, chain-by-chain substitution model

Schematic representation of the molecular arrangement in the crystal structures of nylon6 and PPTA, viewed along comparable directions perpendicular to the chain axes, is shown in figures 1a and 1b respectively. Crystal structures of nylon6 and PPTA exhibit similarities. Both nylon6 and PPTA form extended chains oriented along the unique axis in their respective unit cells and hydrogen bonds are formed between the CO and NH groups of adjacent chains. Crystal structures of both nylon6 and PPTA consist of layers of extended chains stabilised by interchain hydrogen bonds. Adjacent layers are stabilised by non-bonded van der Waal's interactions.

From these similarities in the crystal structures, it would appear that in a substitutional solid solution of nylon6 and PPTA, with excess of nylon6, the molecular arrangement is likely to be one in which some of the nylon6 chains are randomly replaced by those of PPTA. Such a model conforms to the conventional concept that in a substitutional solid solution, the random substitution corresponds to either atom by atom, or molecule by molecule, or chain by chain replacement. However, such a model is ruled out on account of the following considerations: In the crystal structure of PPTA, the number of hydrogen bonds in a distance of 51.6 Å, along the chain length, is eight, whereas in the

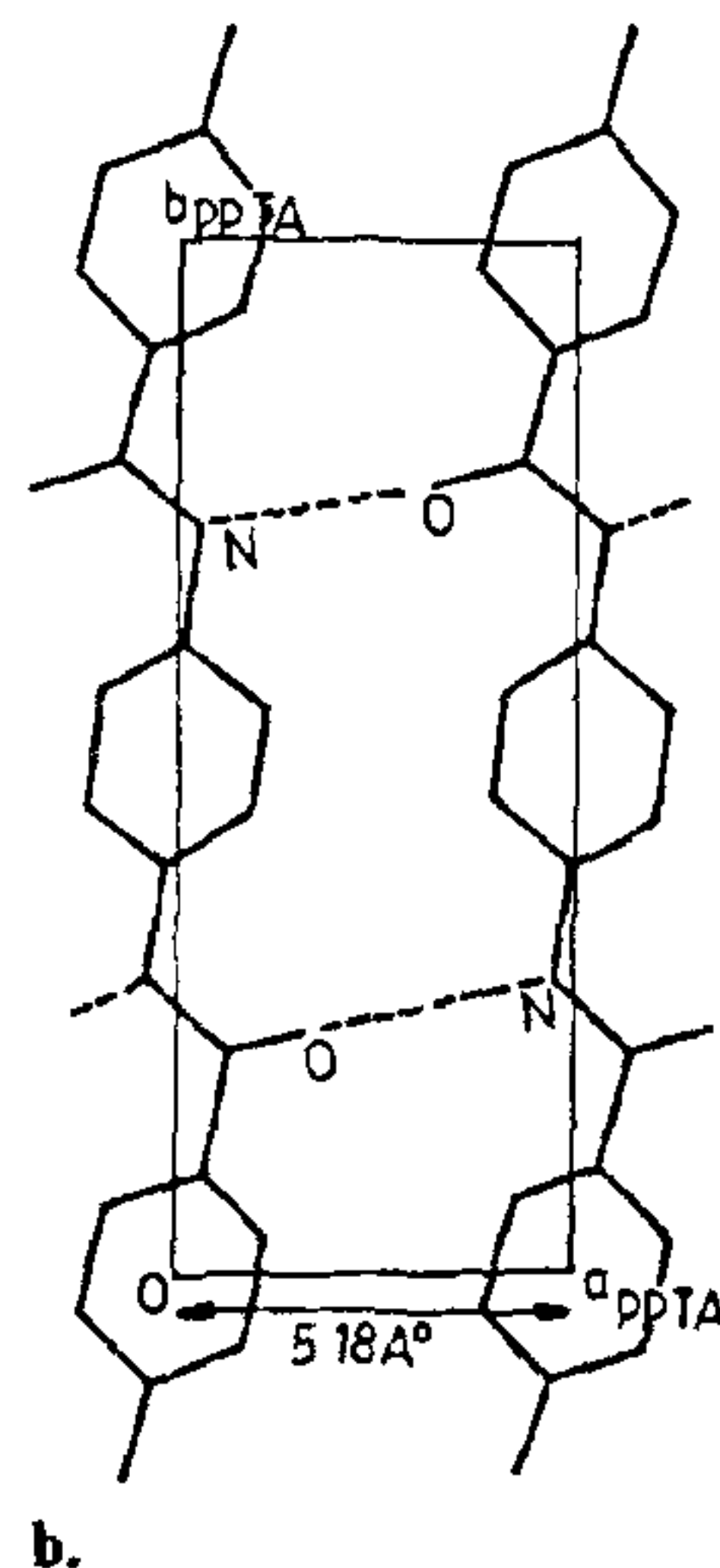
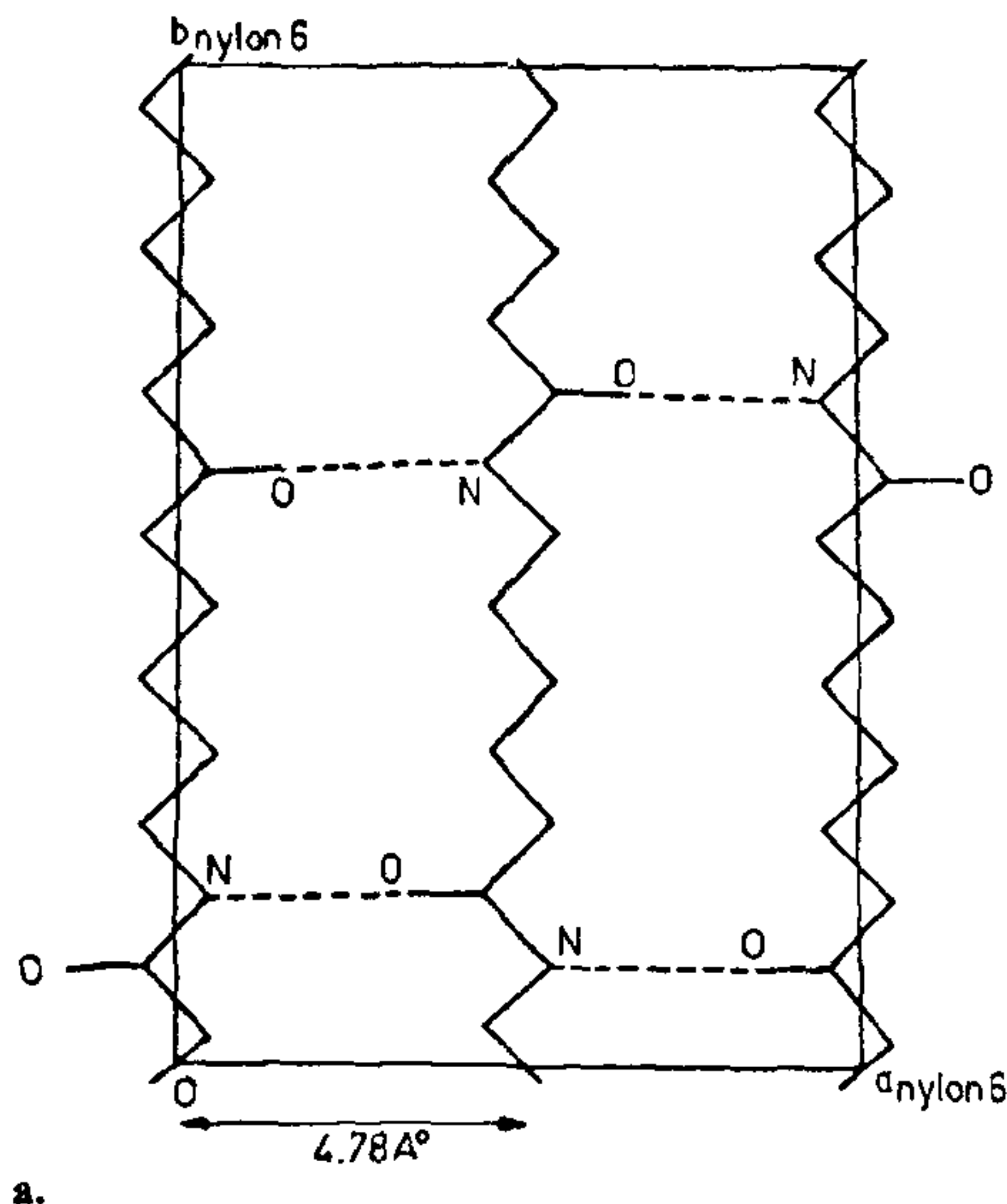


Figure 1. Arrangement of the (a) nylon6 and (b) PPTA chains viewed along the respective *c*-axes. The dashed lines indicate the hydrogen bonds.

crystal structure of nylon6, there are only six hydrogen bonds over the same length. The spacings between adjacent hydrogen bonds along the chains of nylon6 and PPTA are, therefore, significantly different. As a



consequence, the random replacement of a fraction of chains in a layer of nylon6 affects the interchain hydrogen bonding scheme. From trial molecular models, it has been verified that when adjacent chains in a layer are those of nylon6 and PPTA, some of the available CO and NH groups are not juxtaposed to favour the formation of interchain hydrogen bonds. Such a mismatch of the CO and NH groups of adjacent chains in a layer would, therefore, be energetically unfavourable and hence the model with random, chain-by-chain substitution could be ruled out. The only plausible model for a substitutional solid solution appears to be the one in which hydrogen bonded layers of nylon6 are replaced as a whole, by similar layers of PPTA.

### (iii) Random, layer-by-layer substitution model

Comparison of the hydrogen bonded layers of nylon6 and PPTA shows that their dimensions and packing exhibit similarities. The perpendicular distance of 3.70 Å between adjacent layers of nylon6 compares well with the corresponding value of 3.94 Å in PPTA. Also, in each layer, adjacent nylon6 chains are separated by 4.78 Å and those of PPTA are separated by 5.18 Å. These considerations point to the possibility of forming a solid solution by replacing a layer of nylon6 as a whole, by a layer of PPTA. Within each layer, the molecular arrangement is the same as that in the crystal structure of the appropriate component. Hence, unlike in the case of the model with random, chain-by-chain replacement, all the hydrogen bonds formed in the crystal structures of nylon6 and PPTA are fully retained in the model with layer-by-layer substitution. The stability of the solid solution with randomly substituted layers, therefore, is expected to be comparable to those of the components.

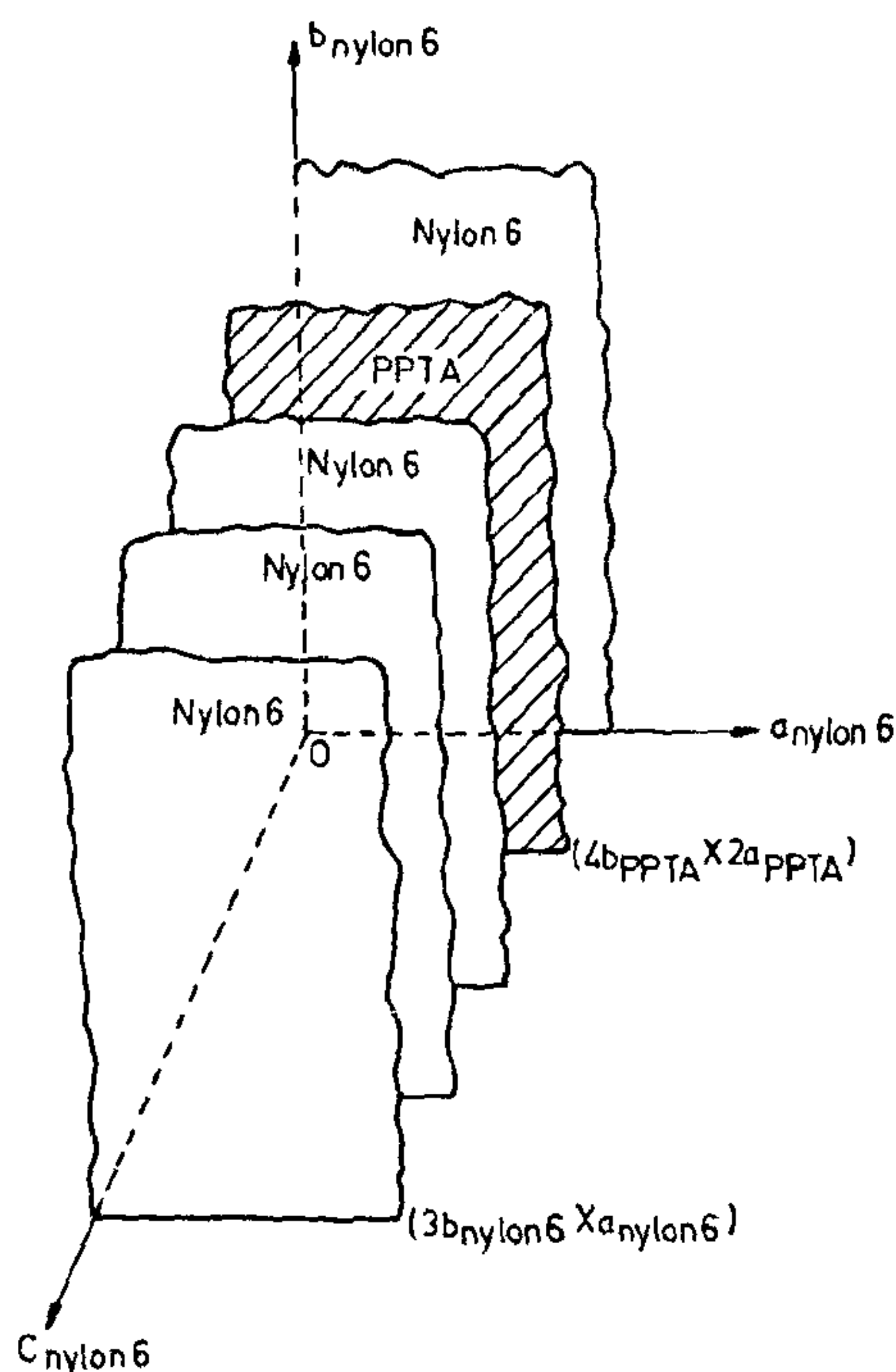
Figure 2 gives a schematic representation of the random, layer-by-layer substitution. Within each crystallite of the solid solution, the arrangement shown in figure 2 extends infinitely along the three crystallographic axes. The unit cell lengths  $b$  and  $a$  of the component crystal structures correspond to the dimensions of the layers along and perpendicular to the chain axes. The equivalences shown in (1) and (2) suggest that when nylon6 layers of dimension

$$(M.3b_{\text{nylon6}} \times N.a_{\text{nylon6}}) \approx (M.51.6 \times N.9.56) \text{Å}^2$$

where  $M$  and  $N$  are non-zero, positive integers, are replaced by PPTA layers of comparable dimension

$$(M.4b_{\text{PPTA}} \times N.2a_{\text{PPTA}}) \approx (M.51.6 \times N.10.36) \text{Å}^2,$$

the strain due to replacement is likely to be very small.



**Figure 2.** Schematic representation of the proposed molecular model with layer-by-layer replacement. The shaded region represents the randomly occurring layer of PPTA chains.

The above mentioned model for the solid solution is found to be compatible with the observed diffraction patterns of nylon6, PPTA and the solid solution, reported earlier from this laboratory<sup>2</sup>. X-ray patterns of nylon6 and PPTA have similar characteristics. Both the patterns consist of two very strong maxima in the  $2\theta$  range of 22 to 28°. These maxima correspond to the reflections (200) and (002) + (202) of nylon6 observed at  $2\theta = 23.4$  and  $27.5$  respectively and the reflections (101) and (002) of PPTA observed at  $2\theta = 24.0$  and  $26.7$  respectively. As could be expected, the diffraction pattern from the solid solution is also characterised by the occurrence of two very strong reflections in the same  $2\theta$  range. However, the observed  $2\theta$  values of 22.95 and 27.3 of the reflections from the solid solution are closer to those of nylon6 than to those of PPTA. This feature is consistent with the composition of the solid solution that has been prepared with excess of

nylon6. The observed  $2\theta$  values of the solid solution indicate that the axial lengths  $a$  and  $c$  of the solid solution are larger than those of nylon6. The observed enhancements are qualitatively consistent with the difference in the cell dimensions of nylon6 and PPTA layers. As noted earlier, the interchain and the inter-layer separations are larger for PPTA than in nylon6. Therefore, when a few layers in nylon6 replaced by PPTA layers, the average effect would obviously be the enhancement of the  $a$  and  $c$  values of the nylon6 unit cell.

Using the experimentally measured values of the unit cell volume and the density of the solid solution, the positional occupancy factors  $P_N$  and  $P_{PPTA}$  of nylon6 and PPTA can be estimated from the relation.

$$M_{SS} = P_N M_N + P_{PPTA} M_{PPTA} \quad (1)$$

Where  $M_{SS}$  = weight in unified mass units of the contents in a volume  $(9.74 \times 51.6 \times 8.2) \sin 67.5^\circ \text{ \AA}^3$  of the solid solution;  $M_N$  = weight unified mass units of the contents in a volume  $(9.56 \times 51.6 \times 8.15) \sin 67.5^\circ \text{ \AA}^3$  of nylon6;  $M_{PPTA}$  = weight in unified mass units of the contents in a volume  $(10.36 \times 51.6 \times 7.75) \sin 90^\circ$  of PPTA and  $P_N = 1 - P_{PPTA}$ . From the above relation,  $P_N$  and  $P_{PPTA}$  have been estimated as 0.90 and 0.10. The corresponding weight fractions of nylon6 and PPTA work out to be 0.84 and 0.16 respectively. These weight fractions are in qualitative agreement with those estimated earlier<sup>2</sup> from the glass transition temperatures ( $T_g$ ), although considerable differences exist in the actual numerical values. These differences are indeed to be expected in view of the probable inaccuracies in the determination of the unit cell parameters,  $T_g$ , etc. It is also possible that the blend

contains substantial non-crystalline regions thus leading to reduced observed density, as appears to be the case with nylon samples<sup>4</sup>. It may be noted that a higher density for the blend would lead to a lower calculated ratio between the weight fractions of nylon6 and PPTA. Considering all these factors, the proposed model appears to explain reasonably satisfactorily the formation and the composition of the blend between nylon6 and PPTA.

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