

Structure of the hard segments in polyurethane elastomers

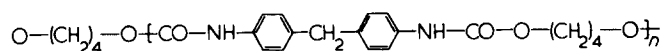
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A new model is proposed for the chain conformation and packing of MDI-butandiol hard segments in polyurethane elastomers. The model is based on the structure of methanol-capped MDI (Me-M-Me), which we have recently determined by single-crystal X-ray methods. Planar zig-zag $-\text{CH}_2-\text{CH}_2-$ sections connect successive Me-M-Me units, which have the same conformation as in the monomer structure. Successive monomer units along the chain are related by a centre of symmetry at the central CH_2-CH_2 bond. The chains are linked together in stacks through $\text{C}=\text{O} \cdots \text{H}-\text{N}$ hydrogen bonds which involve half of the urethane groups. The remaining urethanes are similarly hydrogen-bonded to adjacent stacks, and thus the structure is stabilized by hydrogen-bonding in both directions perpendicular to the chain axis. A triclinic unit cell is proposed for the structure with approximate dimensions $a = 5.2 \text{ \AA}$, $b = 4.8 \text{ \AA}$, $c = 35.0 \text{ \AA}$, $\alpha = 115^\circ$, $\beta = 121^\circ$ and $\gamma = 85^\circ$. The space group is $P\bar{1}$ and the cell contains two repeat units of a single chain.

INTRODUCTION

Polyurethane elastomers are block copolymers consisting of alternating 'soft' and 'hard' segments which are respectively polymer chains above and below their glass-transition temperatures. Phase separation¹ leads to the formation of domains so that the hard segments serve as crosslinks between the amorphous soft segments, which are typically a polyester or polyether. We are interested in the systems in which the hard segments are comprised of diphenylmethane 4,4'-diisocyanate (MDI) with n-butanediol as the chain extender:



The hard segment domains are crystalline and there has been considerable interest in the way that hydrogen-bonding and chain-packing contribute to the structural stability. However, the structures have not been determined by X-ray methods, owing to the low quality of the X-ray diffraction patterns, which typically show only one reflection at $d \approx 7.9 \text{ \AA}$ inclined at $\approx 30^\circ$ to the meridian.^{2,3} This low quality is probably due to the small domain size and the low degree of polymerization, which is generally in the range 1-4.

The most detailed proposals for the structure of the hard segments come from model building studies by Bonart *et al.*³⁻⁶ who considered the possible alignment of chains to form hydrogen-bonded networks. An example of these networks is shown in *Figure 1*. The chains are staggered to allow hydrogen-bonding of half of the urethane groups; the remaining urethanes are hydrogen-bonded to chains in adjacent sheets i.e. in the third dimension. The staggering of the chains results in a tilting of the base plane of the unit cell by $\sim 30^\circ$

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from the perpendicular, (see *Figure 1*) which could account for the off-meridional reflection at $d \approx 7.9 \text{ \AA}$.

The above studies provided considerable insight into the structure of the hard segments, but it was clear that a more detailed picture could not be developed without a knowledge of the stereochemistry of the MDI unit. In particular we need to determine the following: (i) the bond angle at the methylene group; (ii) the orientations of the two phenyl groups with respect to each other and the $\text{C}-\text{CH}_2-\text{C}$ plane; (iii) the degree of planarity of the urethane groups and their orientations with respect to the phenyl groups; (iv) the conformation of the n-butanediol section and its arrangement with respect to the MDI unit.

MODEL URETHANE STRUCTURES

In order to determine the above information and to produce more detailed models, we are investigating the structures of monomers and dimers of the hard segments. We are indebted to Drs C. S. Schollenberger and C. E. Wilkes of B. F. Goodrich Chemical Co. who have provided us with a series of model compounds including Me-M-Me, Et-M-Et, Pr-M-Pr, Bu-M-Bu, and Bu-M-B-M-Bu, where M is the MDI unit which is capped with methanol, ethanol, n-propanol or n-butanol; B corresponds to n-butanediol and serves as the chain extender in the dimer. We have recently determined⁷ the structure of the first of these, Me-M-Me, using single crystal X-ray methods, and studies of three others are in progress, including Bu-M-B-M-Bu. We expect that the general principles for packing of the hard segments will be apparent when we have determined these structures. However, examination of the structure and packing of Me-M-Me reveals many features which can be expected to occur also in the structure of the polymer. The monomer is a long

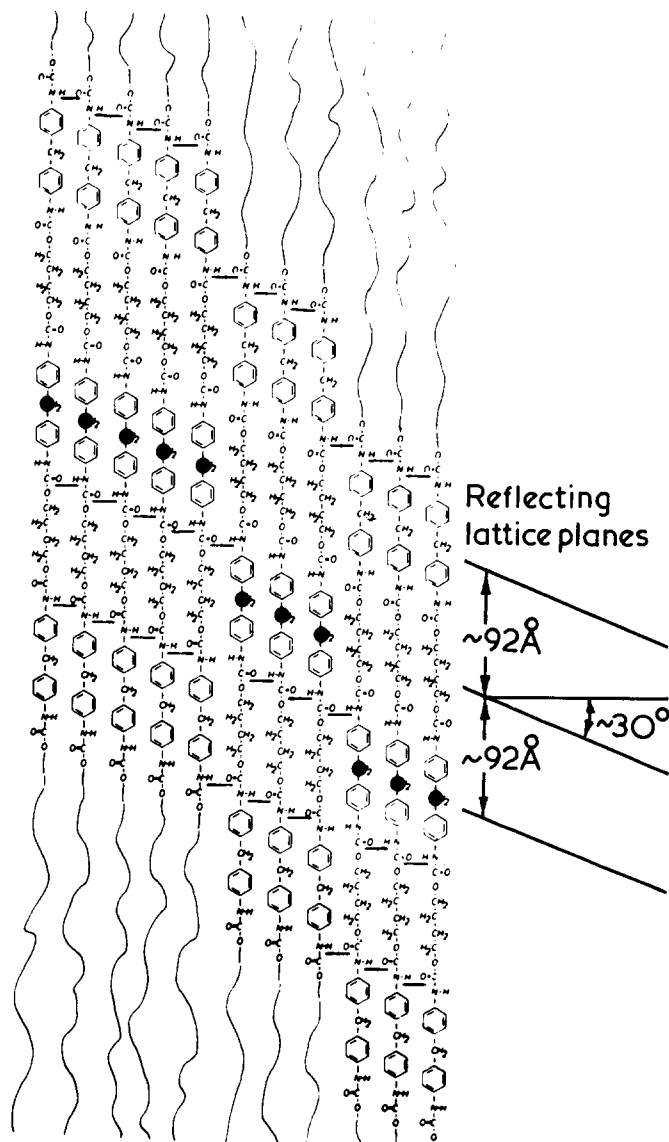


Figure 1 Schematic of the hydrogen-bonding in MDI-butenediol hard segments, as proposed by Bonart *et al.* (Taken from reference 4, with permission). The staggering of the chains leads to planes in this projection at 30° to the perpendicular as indicated

molecule and similarities should exist between the monomer and polymer structures.

Me-M-Me crystallizes with a monoclinic unit cell with dimensions $a = 5.16 \text{ \AA}$, $b = 9.796 \text{ \AA}$, $c = 31.602 \text{ \AA}$, and $\gamma = 93.83^\circ$. The space group is $P2_1/c$ and the unit cell contains four molecules. The bc projection of the structure is shown in Figure 2, and a view of an individual molecule is shown in Figure 3. The following features of the molecule are determined: (i) The bridge C-CH₂-C angle is 115.3° . (ii) The planes of the phenyl groups are mutually inclined at 89.8° , i.e. they are perpendicular to each other. This is to be expected in order to avoid interaction of the π -orbitals, and compares with the 86° reported for this angle in bishydroxydury methane⁸. (iii) The phenyl groups A and B (see Figure 3) are inclined respectively at 75.1° and 34.7° to the C-CH₂-C plane. (iv) Both urethane groups (C-N-C-O) are planar; the terminal carbon atoms of urethanes A and B are, respectively 0.06 \AA and 0.09 \AA out of these planes, i.e.

the entire group C-N-C-O-C is approximately planar. (v) The inclinations of the urethane planes to their respec-

tive phenyl groups are 36.1° (group A) and 10.5° (group B). The mutual orientation of the urethane groups is 51.8° .

As can be seen above, the molecule is not symmetrical, since both the urethane and phenyl groups have different orientations with respect to the central C-CH₂-C plane. This asymmetry probably reflects the necessity to optimize the hydrogen-bonding network. The molecule forms two types of hydrogen bond. The first of these can be seen in Figure 2, where B-urethane groups related by the 2_1 screw-axis are linked by N-H...O=C bonds. The A-urethane groups are approximately perpendicular to the bc plane, and the molecules in adjacent units cells are stacked on top of each other and linked by N-H...O=C bonds along the a axis. The...H-N distances are 2.89 \AA (A-urethanes) and 2.96 \AA (B-urethanes). There is no hydrogen-bonding to the ester oxygens.

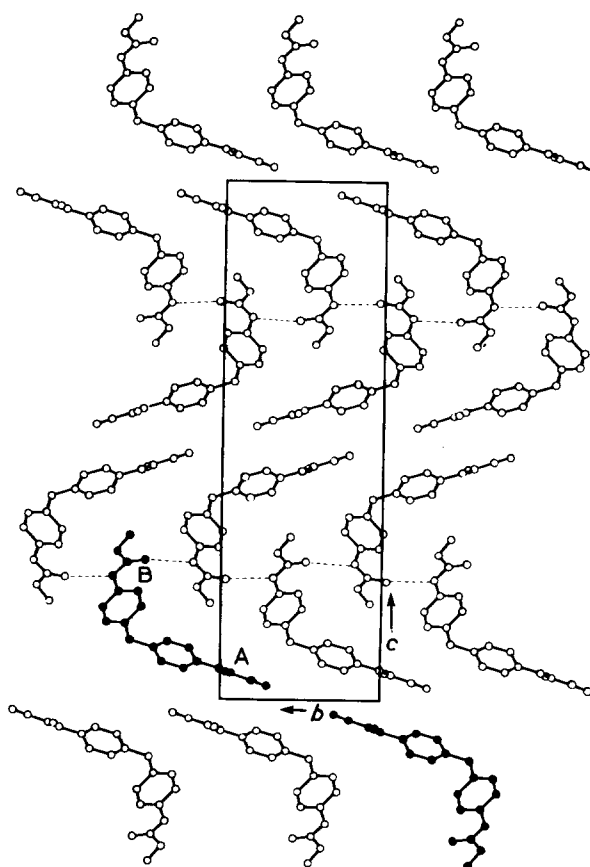


Figure 2 bc projection of the structure of Me-M-Me (4,4'-dimethyloxycarbonyl-4,4'-diamino-diphenylmethane)⁷. The A- and B-urethane groups are indicated, as designated in the text. The shaded molecules are used for construction of the chain

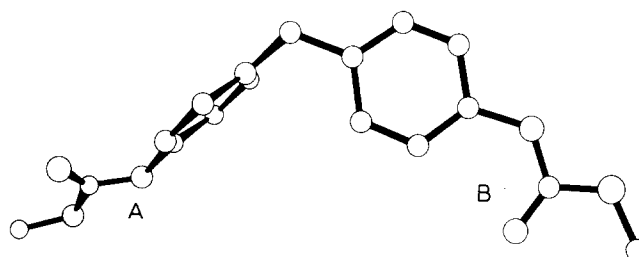


Figure 3 Projection of the Me-M-Me molecule. Note that the phenyl rings are perpendicular to each other

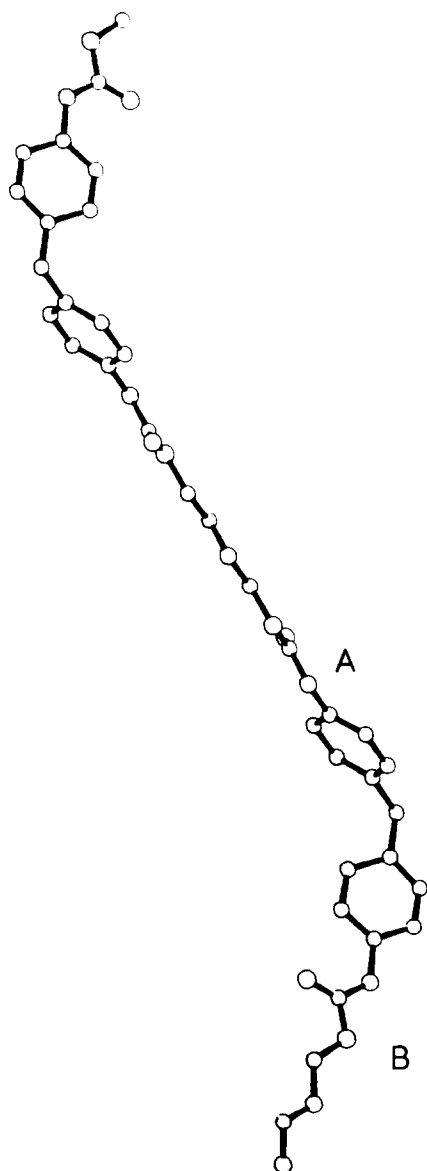


Figure 4 Projection of the polymer chain formed from the pair of molecules shaded in *Figure 2*. A linkage $-\text{CH}_2-\text{CH}_2-$ unit was added after repositioning the two molecules as indicated in the text. The A-urethane groups are hydrogen-bonded to chains stacked above and below the paper. The fibre repeat is $c = 35.0 \text{ \AA}$

HARD SEGMENT POLYMER STRUCTURE

In constructing possible models for the hard segments we have assumed that the MDI conformation of Me-M-Me will be retained, along with some important features of the packing. Specifically, the MDI unit is V-shaped, and can be stacked so that one of the urethanes can be hydrogen-bonded within the stack. The second urethane group cannot be hydrogen-bonded within the stack but will bond across to chains in an adjacent stack, i.e. the structure will be stabilized by hydrogen-bonds in both directions. Therefore, we retained the stacking of the molecules along the a axis of the Me-M-Me and considered how these could be bonded together once they were converted to the polymer by the addition of two CH_2 groups per MDI unit. The butanediol unit was assumed to have a planar zig-zag conformation. This is the most likely conformation although deviations from planarity occur in some analogous linear polyester structures⁹.

The bonds linking the monomer units in this polymer chain cannot be expected to be parallel, and thus successive monomer units are likely to be related by a screw-axis, a glide plane, or a centre of symmetry. The most likely screw axis would be 2_1 but we have found that if we retain the stacking feature of the monomer, then the 2_1 conformation leads to stereochemical overlap of the benzene rings when we attempt to align the chains to form hydrogen-bonds between stacks. A chain generated by a glide-plane can also be eliminated for the same reasons. Higher order screw axes do not appear to be compatible with the stacking requirements, although we have not yet made an exhaustive study of these possibilities.

Examination of the Me-M-Me model, however, reveals that a chain with a centre of symmetry can lead to a very attractive model for the polymer. Two molecules related by a centre of symmetry are shaded black in *Figure 2*. These two molecules were reoriented so that the centres of symmetry between them and at the B ends lay in the plane of the paper. Then after small x , y and z shifts, the polymer chain was produced by linkage of these molecules with a planar zig-zag $-\text{CH}_2-\text{CH}_2-$ chain, as shown in *Figure 4*. The fibre repeat is $c = 35.0 \text{ \AA}$, and contains two MDI-butanediol units. The A-urethane groups are oriented approximately perpendicular to the plane of the paper, and are bonded to chains above and below the plane of the paper. Two such chains are shown in *Figure 5*, where the stack has been rotated by 90° about the chain axis. The A-urethane groups are now in the plane of the paper. The B-urethane groups are inclined at 51.8° and will be bonded to an adjacent stack. The chains are separated by $a = 5.2 \text{ \AA}$, the same dimensions as in Me-M-Me, and a is inclined at ($\beta=$) 121° to c .

The chains have been arranged in the third dimension by working with ORTEP drawings of projections of several chains. We have assumed that the packing will be largely determined by requirement that the B-urethane groups will form hydrogen-bonds between the stacks. Using this requirement, and also the criterion that there should be no bad contacts between the stacks, the proposed packing in the third dimension is as shown in *Figure 6*. The three dimensional structure has a triclinic unit cell with approximate dimensions $a = 5.2 \text{ \AA}$, $b = 4.8 \text{ \AA}$, $c = 35.0 \text{ \AA}$, $\alpha = 115^\circ$, $\beta = 121^\circ$ and $\gamma = 85^\circ$. The space group is $P\bar{1}$ and the unit cell contains two monomers of a single chain. The γ -angle corresponds to the angle between the C=O vectors of the A- and B-urethane groups in the Me-M-Me structure. The values of b and α are then derived from diagrams similar to *Figure 6*.

DISCUSSION

In deriving the above model we have used the same packing for the stack of chains in *Figure 4* as was found in the Me-M-Me structure. It is clear from space filling models that the structure will involve stacking of the phenyl groups, and that the nature of this stacking will depend on the orientation of the phenyls and urethanes. The angle of 90° between the planes of the phenyl groups is thought to be the optimum value, and is likely to be maintained in the oligomers and the polymers. The asymmetry of the rotations of the phenyls about the C- CH_2 -C plane is not likely to affect the packing considerations very much at this relatively unsophisticated level. The orientations of the urethane groups, however, must be determined by the packing requirements,

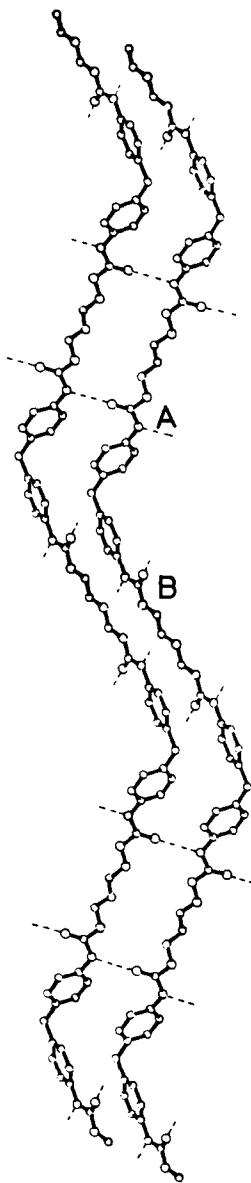


Figure 5 Projection of two chains at 90° to the projection in Figure 4. This is the ac projection of the proposed unit cell, and shows the staggering of chains in this direction. The separation of the chains gives $a = 5.2 \text{ \AA}$ and $\beta = 121^\circ$, based on the packing in the Me-M-Me crystal structure

and are likely to be variable provided hydrogen-bonds can be formed. Exactly how much variation is possible will emerge when we have determined a number of these monomer and dimer structures, but at present we have no alternative but to retain the orientation found for Me-M-Me.

The planar zig-zag conformation for the *n*-butanediol unit is the most likely possibility and it leads to acceptable chain packing. Nevertheless, we need to consider possible distortions from planarity, especially since these could decrease the obvious zig-zag nature of the entire chain and produce a more extended conformation. We now have crystals of the dimer Bu-M-B-M-Bu, and the conformation of the central butanediol unit should throw light on this question for the polymer. The proposed structure could be adopted by hard segments with other diol chain extenders, provided they contain an even number of CH_2 groups. We have yet to consider fully the options with odd numbers of CH_2 groups but it is clear that the stacking of the chains would have to be different.

The off-meridional in the X-ray pattern occurs at $d \approx 7.9 \text{ \AA}$, and is on a layer line spaced at 9.2 \AA (reference 4). Assuming that the chain axes are parallel to the direction of draw, the tilting of the base plane of the unit cell would result in off-meridional $00l$ reflections. In this case the observed reflections could be the 004 , occurring on a layer line which is the fourth order of a chain repeat of 36.8 \AA . This compares with 35.0 \AA for our chain repeat, which could be lengthened, especially if distortions occur in the planar zig-zag assumed for the butanediol section.

As we determine the other monomer and dimer structures, we will gain more insight into the possible variations of the above molecular parameters and their effects on the chain packing. Even for the present chain, the proposed unit cell parameters are necessarily approximate. We need to perform more accurate model building coupled with a packing analysis in order to obtain the best model, and will report on this work in due course. It is clear, that our consideration of the Me-M-Me structure has greatly limited the parameters that need to be analysed.

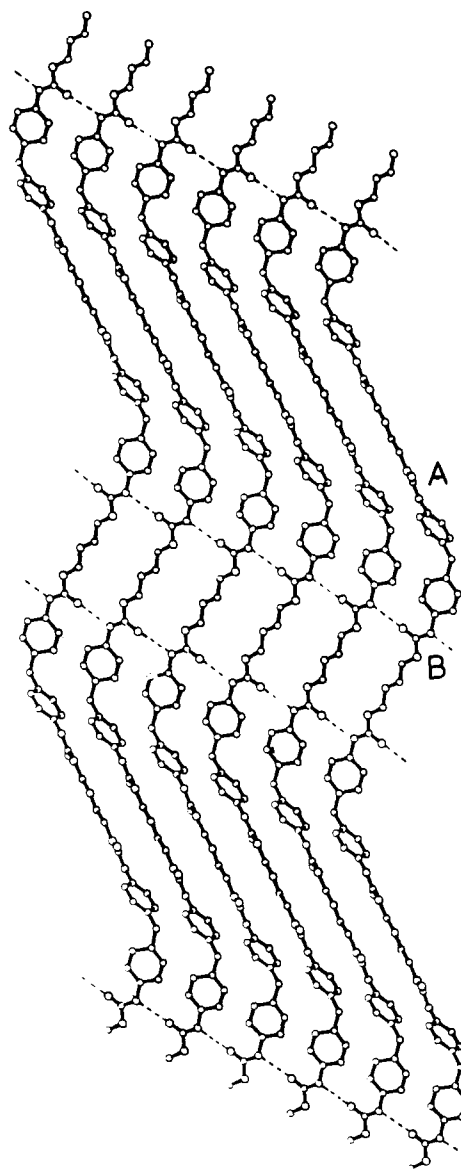


Figure 6 Packing of the chains viewed along the a axis of the unit cell. This is the same projection as in Figure 4. This packing yields the remaining dimensions of the unit cell: $b = 4 \text{ \AA}$ and $\alpha = 115^\circ$

ACKNOWLEDGEMENTS

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