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Structure of the hard segments in trans,trans-diisocyanato dicyclohexylmethane based PU elastomers

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Abstract: A model for the structure of the hard segments and the hydrogen bonded network in the hard domains of segmented polyurethane elastomers with trans,trans-diisocyanato dicyclohexylmethane (*tt*-HMDI)/1,4-butanediol (BDO) based hard segments is proposed. The structure of the bis(methylurethane) of *tt*-HMDI (Me-*tt*HMDI-Me) has been determined by single crystal x-ray diffraction analysis and the conformation and packing of the polyurethane hard segments are constructed by connecting the successive Me-*tt*HMDI-Me units via $-CH_2-CH_2-$ groups using the principle of isomorphic substitution. The conformation and hydrogen bonds of the monomer units are retained. The resulting polyurethane structure is highly crosslinked by a three-dimensional hydrogen bond network. The special packing principle may explain the high melting point as compared to the well-known structure of 4,4′-diisocyanato diphenylmethane (MDI)-BDO hard segments and the differences in the material properties.

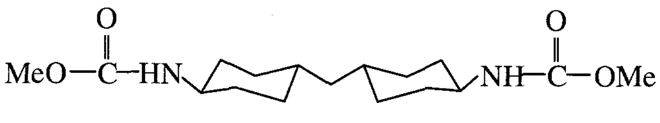
Key words: Structure determination – polymer hard segments – polyurethane elastomers

Introduction

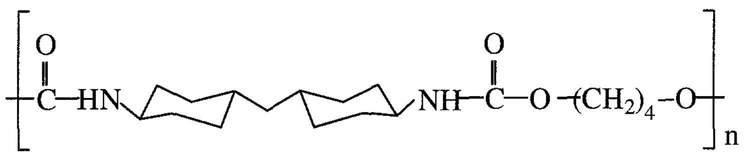
Segmented polyurethane (PU) elastomers are multiblock copolymers $(A - B)_n$ with an alternating sequence of so-called soft and hard segments. Such materials show distinct elastic properties due to microphase separation [1–3]. At working temperature the urethane segments form crystalline domains, which act as multifunctional, thermoreversible crosslinks and as fillers in a more or less liquid soft segment phase, usually with a polyether or polyester forming the elastic matrix. The material properties of thermoplastic PU elastomers are directly related to the morphology and especially to the hard domain structure. The hydrogen bonding between the urethane groups in the hard domains is an important factor of the non-covalent crosslinking of segmented PU elastomers [4, 5].

PU elastomers with hard segments based on commercial 4,4′-diisocyanato dicyclohexylmethane (HMDI) and 1,4-butanediol (BDO) as chain extender are materials with excellent optical clarity, light stability and hydrolysis resistancy. Because HMDI is prepared by nonstereospecific hydrogenation of 4,4′-diamino diphenylmethane (MDA), followed by phosgenation of the 4,4′-diamino dicyclohexylmethane (HMDA), the hydrogenated compounds consist of a mixture of three geometrical isomers (trans,trans, cis,trans and cis,cis isomer) [6, 7]. It has been shown that the physical and mechanical properties of the elastomers increase with increasing trans,trans-HMDI content, and this was discussed in connection with a crystal structure of the bisurethane of trans-4-isocyanato dicyclohexylmethane (*t*-HMMI) and BDO [8].

It has been successfully demonstrated that the structural analysis of model compounds of polyurethanes allows the construction of the packing and conformation of the corresponding polyurethane chains [9–18]. This has led to a better understanding of the structure-property relationships for both hydrogen bond forming and hydrogen bond free systems. In this study we report on the single crystal and x-ray analysis of the dimethylurethane of the isomeric pure trans,trans-diisocyanato dicyclohexylmethane (*tt*-HMDI), and a structure and packing model for the *tt*-HMDI-BDO based polyurethane are deduced from the Me-*tt*HMDI-Me model compound structure.



Me-tt-HMDI-Me



tt-HMDI-BDO Polyurethane

The advantage of this model compound as compared to the previously investigated bisurethane of *t*-HMMI with BDO is first that it contains part of the repeat unit of the *tt*-HMDI-BDO polyurethane; secondly, because of the methyl end groups, the principle of isomorphic substitution of 2 opposing methyl groups by a tetramethylene chain, which has been successfully demonstrated for deriving the structure of 4,4′-diisocyanato diphenylmethane (MDI)/BDO based polyurethanes [9, 10] as well as piperazine (PIP)/BDO-bischloroformate based *N*-alkylpolyurethanes [19] can be explained.

The structure of the bisurethane model compound

The Me-*tt*HMDI-Me model compound has been synthesized by addition of excess methanol to *t,t*-HMDI in chloroform solution and purified by recrystallization from methanol; melting point: 215 °C. The *tt*-HMDI was provided by Bayer AG and has been purified by recrystallizing twice from *n*-hexane. An alternative route is to react the isomeric pure trans,trans-diaminodicyclohexylmethane with methanol chloroformate; this will be described elsewhere [20]. Clear and colourless crystals were grown by slow evaporation from dilute chloroform solution at a constant temperature (20 °C) over a period of 14 days.

The model compound crystallizes with a monoclinic unit cell with the dimensions a = 17.963 Å, b = 6.290 Å, c = 18.214 Å and $\beta = 116.59°$. The space group is $P2_1/n$ and the unit cell contains four molecules. Details of the x-ray diffraction data will be given elsewhere [21]. The projection of the crystal structure of Me-*tt*HMDI-Me is shown in Fig. 1. The molecules are aligned perpendicular to the bc-plane.

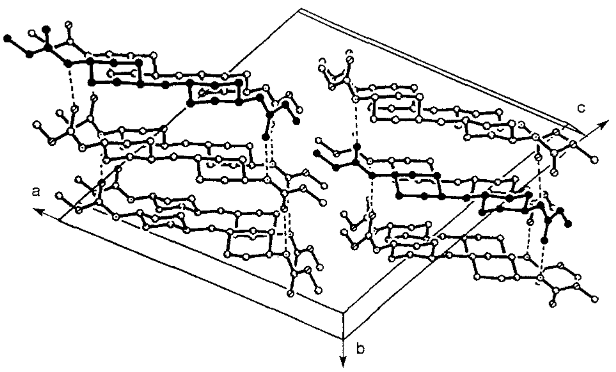


Fig. 1. Centrosymmetrical projection of the crystal structure of the Me-*tt*HMDI-Me model compound in the b direction; hydrogen bonds between neighboring molecules are indicated by dotted lines. The shaded molecules have a short intermolecular distance of terminal methyl groups and are used for construction of the polymer chain (see Fig. 9)

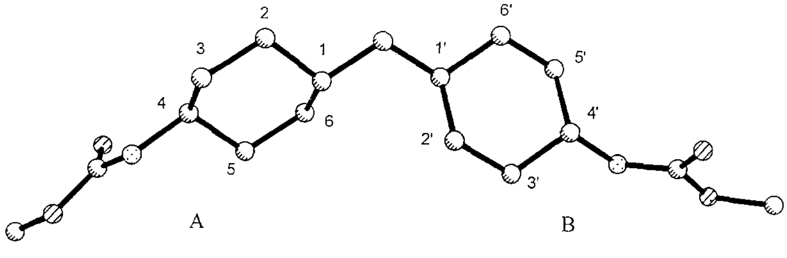


Fig. 2. Projection of the trans,trans-4-4'-di(methoxycarbonylimino) dicyclohexylmethane (Me-*tt*HMDI-Me) molecules

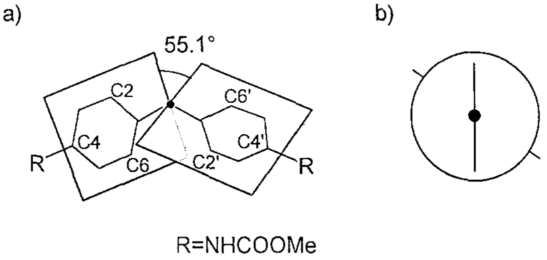


Fig. 3. Schematic representation of the angle between the cyclohexyl planes of the dicyclohexylmethane constitutive unit (a) and simplified Newman projection along the C4-C4' axis (b). The plane of the ring A is defined by the carbon atoms C2, C4 and C6, and of ring B by C2', C4' and C6'

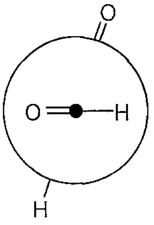
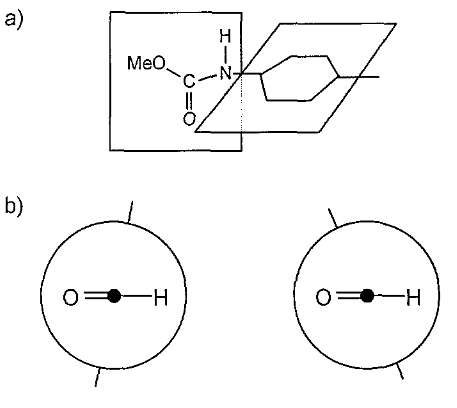


Fig. 5. Scheme of the mutual orientation of the two urethane bond planes of the 4,4'-bis(oxycarbonylimino)dicyclohexane constitutive unit in simplified Newman projection, view in A → B direction (● = C–N axis of the urethane A)



urethane A (101.5°) urethane B (66.2°)

Fig. 4. Scheme of the twist of the urethane bond planes to their respective cyclohexyl planes in the oxycarbonyliminocyclohexyl constitutive units; the planes of the cyclohexyl A and B rings are again defined by the carbon atoms C2/C4/C6 and C2'/C4'/C6' respectively. Perspective view of the A group (a) and the simplified Newman projections (b, ● = C–N axis of the urethanes A and B)

A projection of the crystal structure of Me-*tt*HMDI-Me (individual molecule) is shown in Fig. 2. Both cyclohexyl rings crystallize in the chair conformation, and both urethane groups and the central methylene group occupy equatorial ring positions. The bridge C1–CH_2–C1' angle is 116.1°. The planes of the cyclohexyl rings are mutually inclined at 55.1°, as shown schematically in Fig. 3. The angle between the A and B cyclohexyl rings and the central Cl-CH_2-Cl' plane is 29.2° and 25.9°, respectively. The urethane groups -O–C(=O)–NH– are both planar and the carbon atom of the respective methoxy group also lies in this plane. The urethanes are inclined at 101.5° (urethane A) and 66.2° (urethane B) to the respective cyclohexyl ring as shown schematically in Fig. 4. The urethane carbonyl groups are mutually inclined at 109.1° (Fig. 5).

The conformational asymmetry of the molecule seems to be necessary to optimize the hydrogen bonding network. Each molecule forms four hydrogen bonds, but with only three of the four next neighbouring molecules; this is illustrated in Fig. 6 for the centre molecule of an array of 5 molecules in a section of the crystal structure. Similar to a dimerization, two hydrogen bonds are formed with one neighbour; the two residual H-bonds are formed to different molecules. The distance of the $\underline{N}H \cdots \underline{O}=C$ hydrogen bonds nos. 1 and 2 of the "twin" is 2.95 Å, and the distance of the two hydrogen bonds nos. 3 and 4 both are 2.88 Å. No

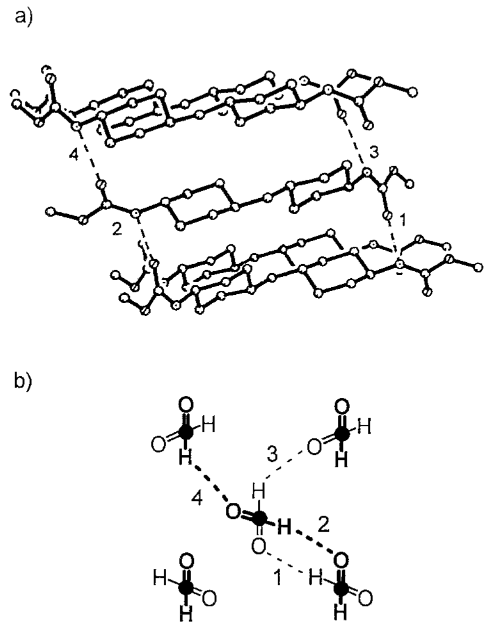


Fig. 6. Section of the crystal structure (projection of the ac plane as in Fig. 1) and the scheme of the hydrogen bonding of an individual Me-*tt*HMDI-Me with its four next neighbouring molecules (a), and simplified Newman projection (see Fig. 5) of this array of five molecules (projection of the bc plane, see Fig. 1). The numbering of the four hydrogen bonds in the crystal structure projection and the simplified Newman projection (view from the left, parallel to the molecular chain axis; ● = C–N axis of the urethane) is the same. Note that hydrogen bonds are only formed with three neighbouring molecules

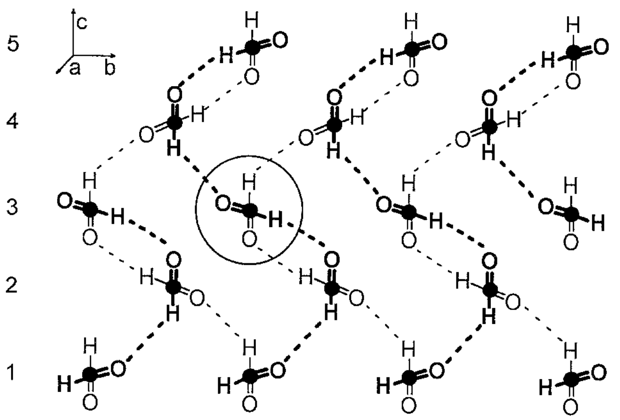


Fig. 7. Scheme of the hydrogen bonding network and molecular packing of Me-*tt*HMDI-Me in simplified Newman projection (cf. Fig. 5; view on a staggered layer of molecules along the molecular axis (a-axis). The central molecule of Fig. 6 is marked by a circle

hydrogen bonding to the oxygen of the methoxy group is found. It is evident from both Figs. 6a and 6b that the two molecules involved in the twin formation are anti-parallel to each other, i.e., there is a point symmetry.

The schematic bc-projection of a larger section of the structure (Fig. 7) illustrates the two types of hydrogen bonds between the molecules which are aligned side by side with their long axis parallel to the a axis. The molecules are staggered in a layer-like close pack. There are no hydrogen bonds within a stack, but the urethanes are hydrogen bonded to the adjacent stack below and above, e.g., stack no. 3 to stacks no. 2 and no. 4. Along the b axis, every 3rd layer is crystallographically identical, whereas along the c axis only every 5th layer shows identical motives.

Hard segment polymer structure model

In the crystal structure of the Me-*tt*HMDI-Me, the shortest intermolecular distance between two carbon atoms of methyl end groups of successive molecules along the a axis is 3.51 Å. In Fig. 1 two such molecules in the ac-plane with this short distance are shaded black. A similar distance of the terminal methyl groups has been obtained from the single crystal x-ray structure analysis of the bis(methyl urethane) model compound of PIP/BDO-bischloroformate based hard segments [19]; there the terminal methyl groups of two neighbouring molecules are separated by 3.63 Å. For comparison, the intramolecular distance between C1- and C4-atoms of a $-(CH_2)_4-$ sequence in all-trans conformation is 3.81 Å.

The principle of isomorphic substitution of the methyl end groups of the Me-*tt*HMDI-Me by a $-(CH_2)_4-$ chain extender is applicable without further influence on the crystal structure. The polymer chain can be constructed by placing the two missing CH_2 groups between the methyl end groups and assuming a gauche-trans-gauche (gtg) conformation of the resulting oxytetramethyleneoxy chain extender unit (cf. [19]). The conformation of the model compound Me-*tt*HMDI-Me is retained. The urethane planes of the bridged monomers are mutually twisted by 109.1° (Fig. 8). The bridging of the molecules with the shortest methyl group distances by replacing these two

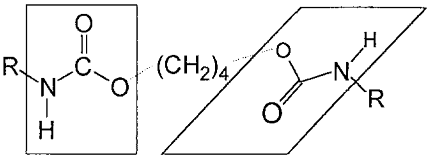


Fig. 8. Scheme of the mutual inclination of the urethane planes, linked by a tetramethylene unit; the angle is 109.1 °

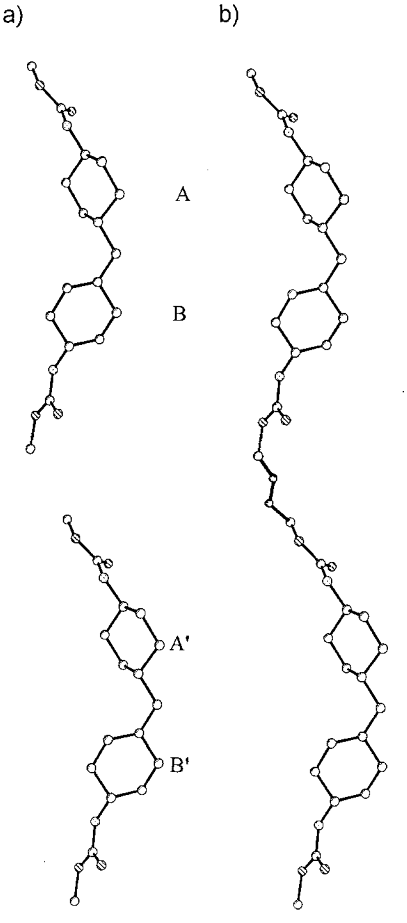


Fig. 9. Projection of the structure of two consecutive Me-*tt*HMDI-Me molecules (a) and structural model for the polyurethane hard segment chain (b); construction by connection of the methyl end groups of the shaded molecules in Fig. 1 by a CH_2CH_2-unit

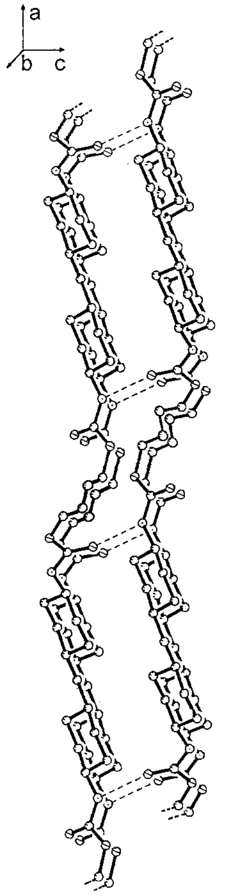


Fig. 10. Projection (ac plane, as in Fig. 1) of parts of four chains consisting of *tt*-HMDI building units connected by BDO chain extender; the packing is based on the Me-*tt*HMDI-Me structure (see Fig. 1)

methyl groups by a tetramethylene bridge (see Fig. 8) leads to a structure of the polymer hard segments as shown in Fig. 9; the two methyl substituents of the two opposing urethane end groups have been replaced by a tetramethylene unit connecting the two molecules and form the *tt*-HMDI/BDO polyurethane. In analogy to the crystal structure of the bisurethane model compound (see Fig. 1), a packing model of parts of 4 next neighbour chains which form two hydrogen bonded twins, each consisting of two HMDI building units connected by a BDO chain extender is depicted in Fig. 10. The conformation of a single chain in the crystal as depicted in Fig. 9 when starting with the urethane A bond plane and going in B direction is given by the following sequence of mutual inclinations of bond plane; 101.5° g + rotation of cyclohexane A ring plane respective to urethane A bond plane; 55.1° g − rotation of the B cyclohexane ring respective to cyclohexane A ring plane; 66.2° g + rotation of B urethane bond plane respective to cyclohexane B ring plane; 109.1° g + rotation of urethane A′ bond plane respective to B urethane bond plane. The urethane A′ bond plane is crystallographically identical with the urethane A bond plane and conformation continues as described for the A – B sequence.

The structural model is in agreement with the crystal structure of BDO-bis(*t*-HMMI), the bisurethane of BDO with trans-4-isocyanato dicyclohexylmethane (*t*-HMMI) [8, 22], which is a model compound for the BDO-based structural unit in the *tt*-HMDI/BDO polyurethane; BDO-bis(*t*-HMMI) has a kink in the tetramethylene unit leading to a shortening of the intramolecular distances of the urethane groups as compared to the zigzag conformation. The assumed conformation of the polymer chain in the crystalline state (Fig. 9) infers a fiber repeat of about 18 Å as given by 1 carbonyliminocyclohexylmethylene cyclohexyliminocarbonyloxy tetramethyleneoxy repeat unit; this figure is in good agreement with the hk3 and hk4 spacings observed in the fiber diffraction pattern of a *tt*-HMDI-BDO spaced polyurethane fiber.

When constructing a model for the hard segment packing, the optimization of the intermolecular hydrogen bond formation with regard to an efficient 3-dimensional hydrogen bond network perpendicular to the fibre axis has to be considered. Figure 11 shows the top view (bc-plane) of an array of single chains; for the sake of better illustration of the intermolecular hydrogen bond network, the projection of the individual chain is restricted to the simplified Newman projection of the urethane bond planes of the 4,4′-bis(oxycarbonylimino) dicyclohexylmethane constitutive units, $-OOCNHC_6H_{10}CH_2C_6H_{10}NHCOO-$. The scheme represents a slice cut perpendicularly through a stack of chains with the packing as found for the Me-*tt*HMDI-Me model compound (cf. Fig. 7); thus, the slice represents a bundle of constitutive units with urethane ends.

The twins formed between two neighboring 4,4′-bis(carbonylimino) dicyclohexylmethane constitutive units through hydrogen bonds between their urethane end groups are illustrated by the rectangulars; these dimers ("twin") for a regular pattern in the bc-plane, and the two chains are anti-parallel as far as the sense of the mutual orientation of the two urethane bond planes is concerned, and as indicated by the abbreviations r (right) and s (sinister). The volume filling stacks of layers in the b direction are identical for every third layer; in the c direction, only every fifth layer is crystallographically identical. This periodicity is indicated by the numbering of the stacks put in brackets. The hydrogen bond pattern reiterates in the very same manner for each repeat unit along the chain; this is further illustrated by the projection of an array of 4,4′-bis(oxycarbonylimino) dicyclohexylmethane constitutive units normal to the ac-plane (Fig. 12); the numbering of the stacks in the c- and b- direction is the same as in Fig. 11. Both projections (Figs. 11 and 12) show the meander type hydrogen bond pattern of the double hydrogen bonded "twins" perpendicular the fiber axis.

This well ordered and very dense network of hydrogen bonds tightly connects the chains with

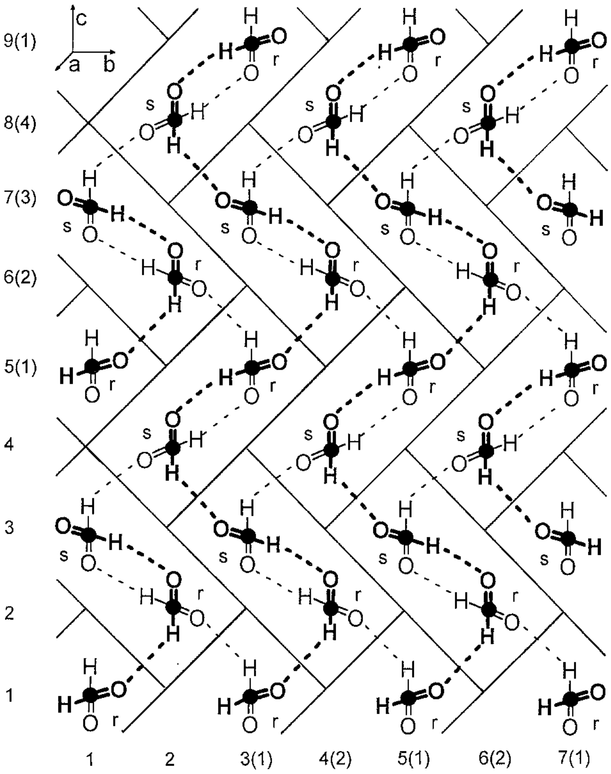


Fig. 11. Scheme of the hydrogen bonding network and packing of the chains viewed along the chain (a-axis): simplified Newman projection of an array of stacks of 4,4′-bis(oxycarbonylimino)dicyclohexylmethane constitutive units ($-OOCNH-(C_6H_{10})CH_2(C_6H_{10})NHCOO-$). The numbers indicate the stacks in b and c direction (numbers put in brackets illustrate periodicity); r and s symbolize the sense of inclination of the urethane bond planes and the dicyclohexylmethane unit

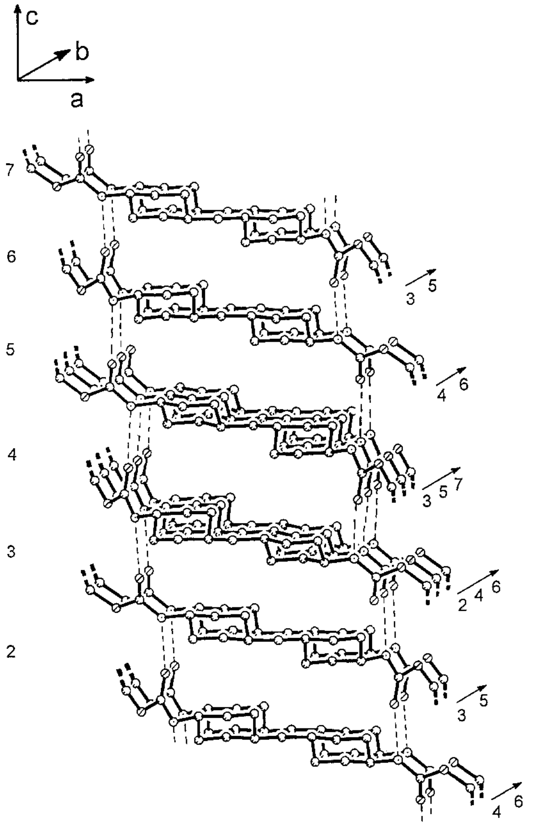


Fig. 12. Packing of part (4,4′-bis(oxycarbonylimino) dicyclohexylmethane constitutive unit) of an array of polyurethane chains (ac plane); the numbering is the same as for the stacks in Fig. 11

each other. As it is evident from the view on the bc plane (Fig. 11), irrespective of the direction, stacks of chains cannot be shifted against each other without the breaking of at least two different kinds of hydrogen bonds pointing in different directions.

Conclusion

A possible model for the hard segments of the polyurethane of trans,trans-HMDI (*tt*-HMDI) and 1,4-butanediol (BDO) has been constructed on the basis of the crystalline structure of the dimethylurethane of *tt*-HMDI; the conformation of the single units, the chain packing and the hydrogen bond network of the model compound structure is retained and the bridging $-(CH_2)_4-$ groups connect the *tt*-HMDI dimethylurethane (Me-*tt*HMDI-Me) stacks shown in Fig. 7. The resulting polymer chain (Fig. 9 and 10) forms hydrogen bonds within the stacks in a very specific manner, in that all chains are repeatedly hydrogen bonded in three directions, i.e., through the formation of double hydrogen bonded twins of next neighbouring urethane-dicyclohexylmethane-urethane units and the two remaining hydrogen bonds with two other next neighbouring urethanedicyclohexylmethane-urethane units pointing in different directions (Figs. 11 and 12). There is no possibility to shift stacks of polymer chains by dissolving only one type of hydrogen bond.

The meander-like hydrogen bond network is very different to the two by two and perpendicular hydrogen bonds of the 4,4′-bis(oxycarbonylimino) diphenylmethane constitutive unit with its four next neighbouring constitutive units of polyurethanes of 4,4′-diisocyanato diphenylmethane (MDI) and BDO [9, 18]. This distinct difference of the structure of MDI-BDO polyurethanes, where one stack is linked to the adjacent stack with one hydrogen bond per monomer unit [9, 18], certainly effects the hard domain stability: if these bonds at one side along the chain are dissolved, the stacks can slide off on this gliding-plane, a “creep”, which is not possible in the *tt*-HMDI-BDO polyurethane.

The more effective hydrogen bond network of the *tt*-HMDI-BDO polyurethane and also the generally observed increase in the melting temperatures of low molecular weight molecules and polymers when replacing a phenyl by a cyclohexyl unit can explain the higher thermal and mechanical stability of HMDI-based polyurethanes as compared to the MDI analogues [23, 24]. E.g., the calculation of the differences in the melting temperature of the dimethylurethane of MDI and *tt*-HMDI by using the group contribution method and incrementals given in the literature [25] leads to $\Delta T = 22\,°C$, which is in excellent agreement with the experimentally determined melting temperature of 191° and 215° respectively. In this context the good packing of stereoregular cyclohexane chairs could also be considered, since there are structural analogies between the *tt*-HMDI-based polyurethanes and cellulose fibers with the 1,4-linked β-D-glucose residues, which are also in the chair conformation (cf. [26]).

Further insights into the superior stability of the presented polyurethane structure will be obtained by investigations of longer bis(methylurethanes) based on *tt*-HMDI and BDO, which in the meantime have been synthesized. The structure of the bis(methylurethane) of trans,trans-HMDI as the simplest model compound alone shows a lot of interesting features and already allows a feasible explanation for the macroscopic properties of the polymer hard segments. The implications of the structural differences of the *tt*-HMDI and MDI polyurethanes on their properties will be discussed in detail in a subsequent publication.

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References

1. Noshay A, McGrath JE (1977) Block Copolymers, Academic Press New York, p 365
2. Meckel W, Goyert W, Wieder W (1987) In: Legge, NR, Holden G, Schroeder HE (eds) Thermoplastic Elastomers, Carl Hanser Verlag München Wien, p 13
3. Eisenbach CD, Baumgartner M, Günter C (1986) In: Lal J, Mark JE (eds) Advances in Elastomers and Rubber Elasticity, Plenum Publ Corp New York, p 51
4. Bonart R, Morbitzer L, Müller EH (1974) J Macromol Sci Phys 9:447
5. Bonart R (1977) Angew Makromol Chem 58/59:259
6. Barkdoll AE, Gray HW, and Kirk W Jr (1951) J Am Chem Soc 73:741
7. Prince FR, and Pearce EM (1971) Macromolecules 4:347
8. Seneker SD, Born L, Schmelzer HG, Eisenbach CD, Fischer K (1992) Colloid Polym Sci 270:543
9. Blackwell J, Gardner KH (1979) Polymer 20:13
10. Gardner KH, Blackwell J (1980) Acta Cryst B36:1972
11. Blackwell J, Nagarajan MR, Hoitink TB (1981) Polymer 22:202
12. Blackwell J, Nagarajan MR, Hoitink TB (1981) Polymer 22:1534
13. Blackwell J, Nagarajan MR, Hoitink TB (1982) Polymer 23:950
14. Born L, Hespe H, Crone J, Wolf KH (1982) Colloid Polym Sci 260:819
15. Born L, Hespe H (1985) Colloid Polym Sci 263:335
16. Born L, Crone J, Hespe H, Müller EH, Wolf KH (1984) J Polym Sci, Polym Phys Ed 22:163
17. Blackwell J, Quay JR, Nagarajan MR, Born L, Hespe H (1984) J Polym Sci, Polym Phys. Ed 22:1247
18. Quay JR, Blackwell J, Lee CD, Hespe H, Born L (1985-1986) J Macromol Sci Phys. B24:61
19. Eisenbach CD, Nefzger H, Enkelmann V, Makromol Chem, submitted
20. Steinlein C, Fischer K, Eisenbach CD, to be published
21. Milius W, Steinlein C, Eisenbach CD, Acta Cryst B, in press
22. Born L, Fischer K, Eisenbach CD, to be published
23. Martin EV, Busch H (1962) Angew Chem 74:624
24. Kibler CJ, Bell A, Smith JG (1964) J Polym Sci A2:2115
25. Van Krevelen DW (1990) Properties of Polymers, Elsevier, Amsterdam
26. Kolpek TJ, Blackwell J (1976) Macromolecules 9:273

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