Structure of polyurethane elastomers: effect of chain extender length on the structure of MDI/diol hard segments

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X-ray diffraction and conformational analyses have been used to study the structure of the hard segments in MDI/diol/PTMA polyurethanes, and to investigate the differences in structure that result from the use of different chain lengths for the aliphatic diol component. It is found that for butandiol and longer diol chain extenders (up to octandiol) the structure depends on whether the diol has an even or odd number of CH_2 groups. The even diol polymers adopt the lowest energy fully extended conformations that allow for hydrogen bonding in both directions perpendicular to the chain axis. Such a hydrogen bonding network would not be possible for the odd diol polymers in the extended conformation, and these adopt contracted, higher energy conformations. Both the odd and even diol polymers adopt staggered chain structures with triclinic unit cells, but the even diol polymers have higher crystalline order. The first two members of the homologous series, prepared using ethylene glycol and propandiol, are exceptions to the above behaviour and adopt contracted unstaggered structures. It is possible that these two diols are too short to permit packing of the MDI units in the same way as for the longer chain extenders. The results suggest the simple explanation for the better overall properties of the elastomers prepared using butandiol and the higher even diols. The hard segments of these polymers can crystallize more easily in the lowest energy extended conformation, and hence there is more of a driving force for phase separation.

Keywords X-ray diffraction; conformational analysis; polyurethanes; MDI/diol/PTMA; hard segments

INTRODUCTION

We are using X-ray diffraction and conformational analyses to investigate the structure of the hard segments in polyurethane elastomers, concentrating on the polymers prepared from diphenylmethane diisocyanate (MDI), with a linear diol as the chain extender, and poly(tetramethylene adipate) (PTMA) as the soft segment. Polyurethane block copolymers derive their elastomeric properties from phase separation into hard (polyurethane) and soft (polyester or polyether) domains[1,2], such that the hard domains serve as physical cross-links and also as a reinforcing filler[3]. In MDI/diol/polyurethanes, the bulk properties are very sensitive to the length of the diol chain extender[4,5]. The hard domains are crystalline, and we have investigated the structure of these domains for polymers prepared using different chain extenders. Crystallinity is an important determinant of the extent of phase separation in block copolymers[6], and the features of the structure developed, i.e. the chain conformation, hydrogen bonding and packing, can be expected to be factors in this process. In previous papers[7-11] we have looked at the structures of hard segments prepared using ethylene glycol (EDO), propandiol (PDO), and butandiol (BDO) (i.e. C_2–C_4) as the chain extenders. We have now extended this work to the C_5–C_8 linear aliphatic diols, which has allowed us to draw some general conclusions on the effect of diol length on the structure of the hard segments.

Figure 1 shows the X-ray diffraction patterns of oriented films of elastomers prepared using EDO, PDO, and BDO[8,10]. The PDO and BDO polymers were stretched 700% and annealed at 130°C, resulting in relaxed specimens containing amorphous soft segments. All the observed reflections are due to the crystalline hard segments. The EDO specimen could not be prepared in this manner, but was stretched 400% at room temperature, and the resultant X-ray pattern shows identifiable soft segment reflections as well as those due to the hard segments.

The MDI/BDO pattern (*Figure 1c*) was indexed[8] by a triclinic unit cell with dimensions $a = 5.05$ Å, $b = 4.67$ Å, $c = 37.9$ Å (chain axis), $\alpha = 116°$, $\beta = 116°$, and $\gamma = 83.5°$. The triclinic structure is apparent from the absence of meridional reflections and the lack of obvious row lines. The reflection at $d = 7.65$ Å inclined at 36° to the meridian is indexed 004, and arises from the tilted base plane of the unit cell. As was first suggested by Bonart and coworkers[12,13], this reflection arises from a staggering of neighbouring chains along the fibre axis so that C–O···H–N hydrogen bonds can be formed between adjacent urethane groups. Based on our structure determination of the model compound methanol-capped MDI[14], we proposed a staggered chain model for poly(MDI/BDO)[7], as shown in *Figure 2*. This triclinic structure has unit cell dimensions comparable to those proposed from the X-ray data. The butandiol unit has the fully extended planar zigzag conformation, and the adjacent chains are linked by hydrogen bonds in both directions perpendicular to the chain axis. Minimum

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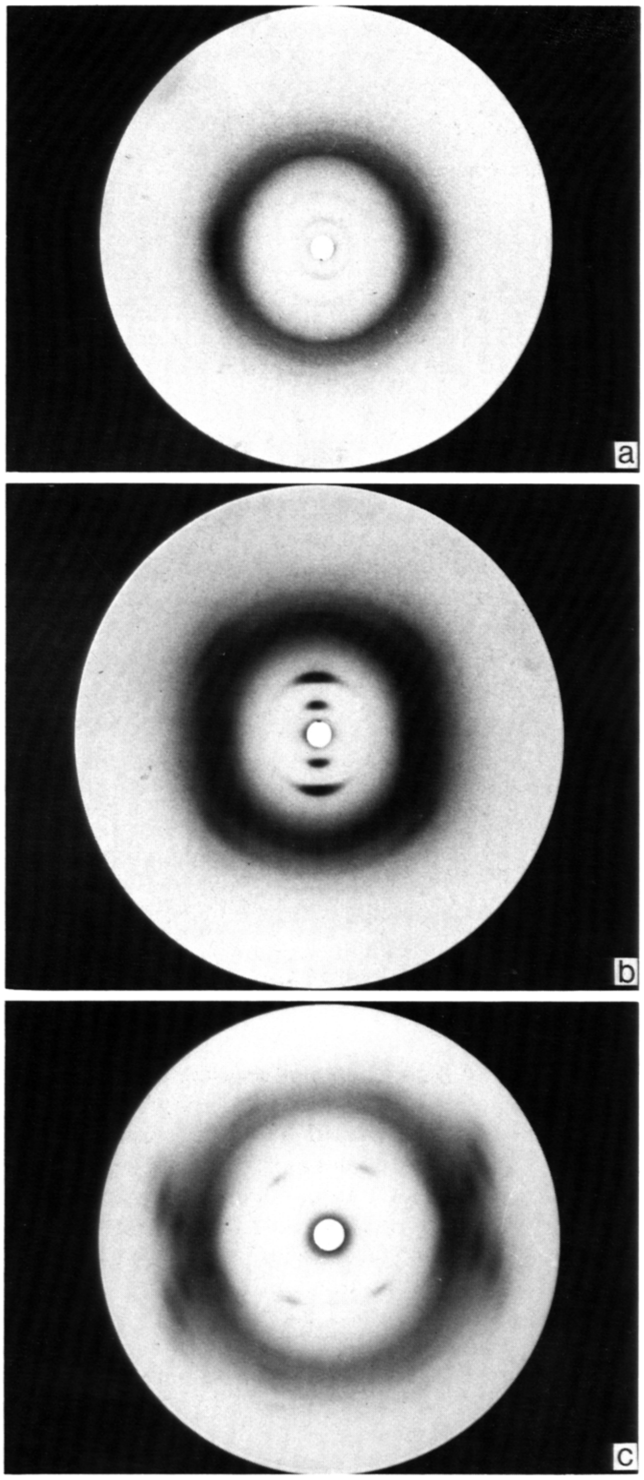


Figure 1 X-ray diffraction patterns of drawn films of C_2—C_4 diol polyurethanes[8,10]. (a) MDI/EDO/PTMA (Hard and soft segment reflections); (b) MDI/PDO/PTMA (Hard segment reflections only); (c) MDI/BDO/PTMA (Hard segment reflections only)

energy conformational analysis[9] predicts a fully extended chain, similar to that in *Figure 2*, with a fibre repeat of 37.9 Å. The proposed lateral aggregation of the chains probably accounts for the lamellar and spherulitic morphology seen in the electron microscope for MDI/BDO/polyester preparations[15,16]. A lamellar structure is also indicated by small angle X-ray studies[17,18]. The proposed structure is compatible with the observed infra-red dichroisms for the urethane groups[19,20]. It should be noted, however, that the proposed unit cell leads to a calculated density of 1.57 g cm^{-3}. We have recently obtained specimens of the MDI/BDO homopolymer, for which the measured density is 1.30 g cm^{-3}, and this difference is too large to be explained by the crystalline–amorphous ratio. The fibre repeat (*c*) can be determined fairly accurately, and thus it is possible that larger values of *a* and *b* are necessary in order to explain this discrepancy. We have therefore reexamined this unit cell, as is discussed below.

The X-ray pattern for poly(MDI/PDO)[10] (*Figure 1b*) is very different from that for poly(MDI/BDO) just discussed. The PDO polymer gives fewer reflections, and there are also broader, indicating a lower degree of order in the hard segments than for the BDO polymer. The X-ray pattern shows meridional spacings that are orders of 16.2 Å, probably corresponding to the monomer repeat. Also there are reflections on a row line at $d = 4.7$ Å. These data point to a unit cell with a base plane perpendicular to the *c* axis, i.e. monoclinic or orthorhombic, and thus the adjacent chains must be in register rather than staggered as in poly(MDI/BDO). The reduction in the monomer axial repeat from 18.95 Å for poly(MDI/BDO) to 16.2 Å for poly(MDI/PDO) suggests that the latter has a contracted conformation. Our analysis shows that a fully extended poly(MDI/PDO) chain would have a monomer length of 17.6 Å when the propandiol unit is all-*trans*, and thus there must be some *gauche* conformations in the propandiol, since the length of the diphenylmethane diurethane section is not sufficiently variable. Poly(MDI/PDO) chains with *trans*–*gauche*$^+$–*gauche*$^+$–*trans* and *gauche*$^+$–*trans*–*trans*–*gauche*$^+$ conformations

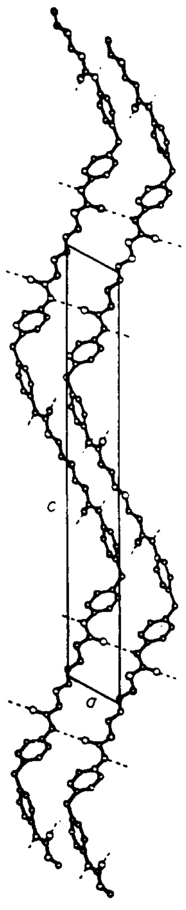


Figure 2 Proposed structure for poly(MDI/BDO)[7]

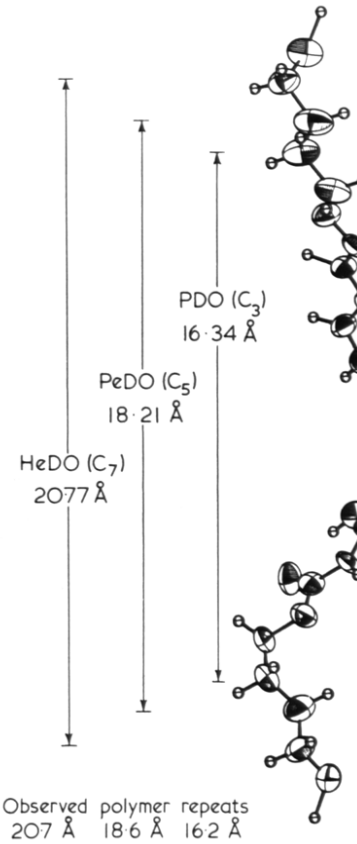


Figure 3 **Conformation of butandiol-capped MDI in the crystal structure[21]. The monomer repeats for poly(MDI/PDO), poly(MDI/PeDO) and poly(MDI/HeDO) are shown, corresponding conformations with planar zigzag C_x chains oriented *gauche*$^+$ to the urethane groups**

for the $-O\text{-}(CH_2)_3\text{-}O$ section have fibre repeats of 16.20 Å and 16.24 Å respectively, comparable with the observed repeat. Of these two conformations, the former has the lower potential energy, and is also suggested by the conformation of the model compound, butandiol-capped MDI[21]. This model compound crystallizes with a planar zigzag $-C_4\text{-}O(H)$ chain that is *gauche* to the urethane group. As shown in *Figure 3*, the repeat for the MDI/PDO unit derived from this model is 16.34 Å, and has approximately *trans–gauche*$^+$*–gauche*$^+$*–trans* conformation.

The MDI/EDO polymer[10] also gives hard segment meridional reflections (*Figure 1a*) in this case at $d = 15.0$ and 7.5 Å, as was first observed by Wilkes and Yusek[22]. The monomer repeat of 15.0 Å is 1.2 Å less than the poly(MDI/PDO) repeat and suggests that poly(MDI/EDO) has a conformation similar to the PDO polymer, except for the deletion of a *trans* CH_2 group. Conformational analysis yields a single symmetrical conformation with a *gauche*$^+$*–trans–gauche*$^-$ conformation for the $O\text{-}(CH_2)_2\text{-}O$ section, and a fibre repeat of 15.0 Å. This conformation for poly(MDI/EDO), and the two possible conformations for poly(MDI/PDO) are shown in *Figure 4*.

Thus both the EDO and the PDO hard segments have contracted conformations, which have higher potential energy than the all-*trans* chain of poly(MDI/BDO). This may account for the lower crystallinity of poly(MDI/PDO) for which there will be a lower potential energy as the driving force for phase separation. (A different preparation method was used for the EDO polymer, and the crystallinity cannot be compared with the PDO and BDO polymers.) These considerations have now been extended to preparations using C_5–C_8 linear aliphatic diols as the chain extender, and we can now draw general conclusions for a longer homologous series.

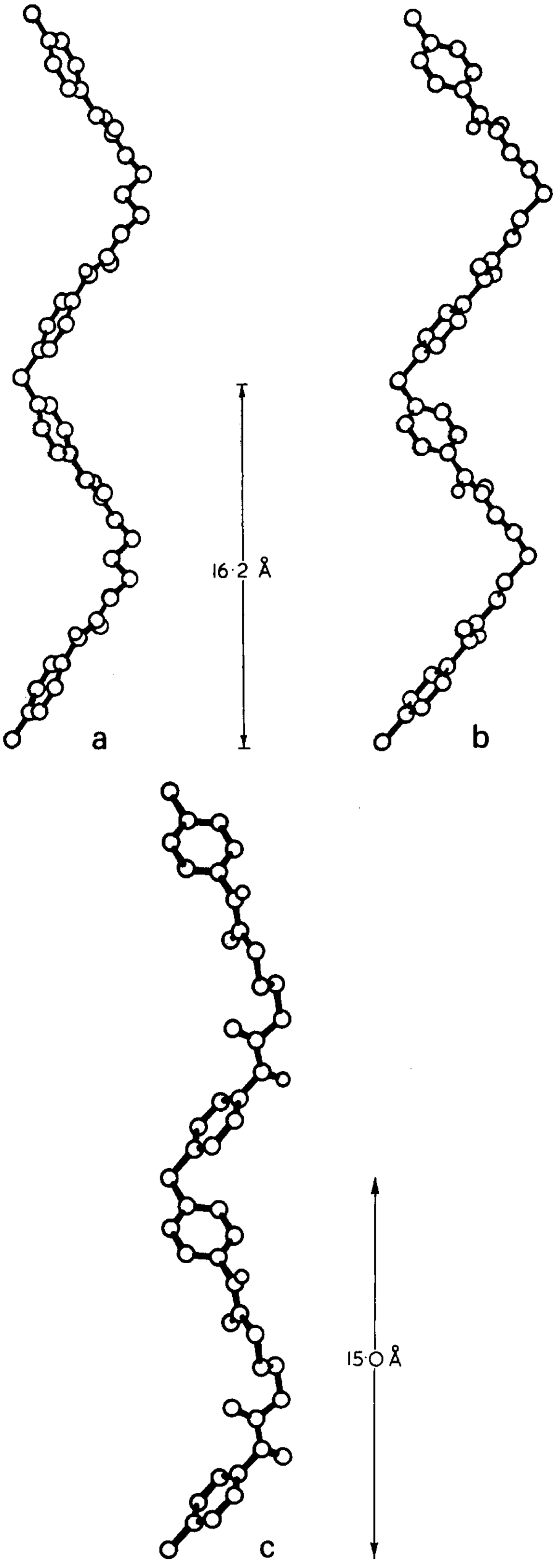


Figure 4 Conformations of poly(MDI/PDO) and poly(MDI/EDO) that are compatible with the observed fibre repeats. (a) Poly(MDI/PDO) with a *gauche*$^+$*–trans–trans–gauche*$^+$ diol; (b) Poly(MDI/PDO) with a *trans–gauche*$^+$*–gauche*$^+$*–trans* diol; (c) Poly(MDI/EDO) with a *gauche*$^+$*–trans–gauche*$^-$ diol

EXPERIMENTAL

Specimens of the polyurethane were generously synthesized by Dr C. S. Schollenberger of B. F. Goodrich, Brecksville, Ohio, and were supplied in the form of films, 0.5 mm thick, prepared by hot rolling. The molar ratio of reactants for the pentadiol (PeDO) and hexandiol (HDO) extended polymers were 7:6:1 for MDI:diol:PTMA, where $\bar{M}_n = 2089$ for the soft segments. 6:5:1 molar ratios were used for the heptandiol (HeDO) and octandiol (ODO) extended polymers.

Strips of the PeDO and HDO polymer films were stretched $\sim 700\%$ at 130°C and annealed at the same temperature for 24 h. Samples of the HeDO and ODO polymers were prepared in a similar manner except at ~ 80°C. (The films broke if prepared at 130°C.) Some evidence of soft segment crystallinity is seen for the latter specimens.

X-ray diffraction patterns were recorded on Kodak no-screen film using a Searle toroidal focusing camera, with nickel-filtered CuKα radiation from a Rigaku–Denki rotating anode generator.

CONFORMATIONAL ANALYSIS

The potential energies for the C_5–C_8 diol-extended polymers were computed by summing the contributions from non-bonded, electrostatic and torsional energies, and bond angle distortions. The models were constructed using standard bond lengths and angles. These data and the potential functions and coefficients are given in Ref. 9, and the analyses have followed exactly the same procedures as used in our previous work[9,11]. The polymers have long, complex repeating units, but the X-ray data indicate highly extended chains, and consequently the conformations will be determined largely as the interaction between contiguous sections of the chain, i.e. phenyl–phenyl, phenyl–urethane, and urethane–diol interactions. In our calculations for poly(MDI/BDO) we predicted the preferred conformation for the diphenylmethane diurethane unit, which proves to be similar to that adopted by model compounds[14,23,24], except that the adjacent phenyl and urethane groups were predicted to be perpendicular, i.e. $\chi = \pm 90°$, whereas $\chi = 10° - 40°$ in the model compounds. It is likely that χ is determined by hydrogen bonding, packing and effects such as orbital delocalization that were not included in the calculations. However, variation of χ has little effect on the overall length of the diphenylmethane diurethane section of the chain, with a result that the fibre repeat is largely dependent on the diol conformation. We have set the phenyl–urethane inclination at 30° ($\chi_1 = -150°$, $\chi_2 = 30°$) and have proceeded to calculate the potential energies and fibre repeats of the polymer chains with the chain extenders in different conformations that are all possible combinations of *trans* and *gauche*. Only centrosymmetric conformations have been considered, in view of the symmetry of the chemical structures.

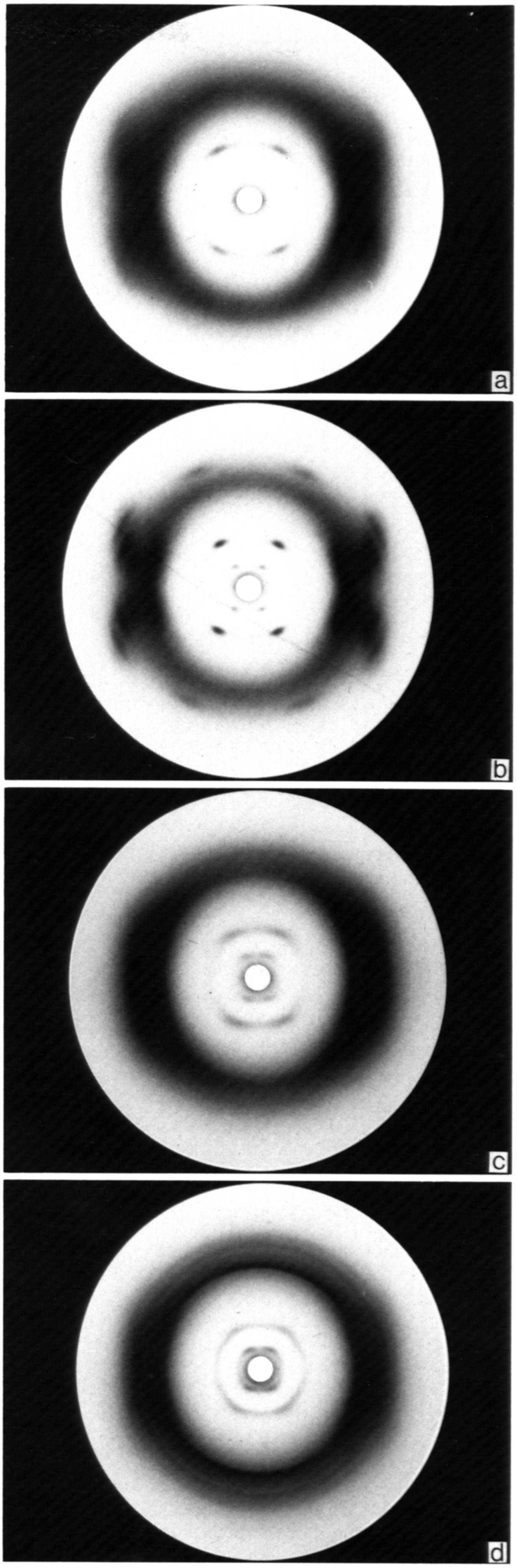
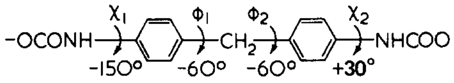


Figure 5 X-ray diffraction patterns of drawn films of C_5–C_8 diol. (a) MDI/PeDO/PTMA (Hard segment reflections only); (b) MDI/HDO/PTMA (Hard segment reflections only); (c) MDI/HeDO/PTMA (Hard and soft segment reflections); (d) MDI/ODO/PTMA (Hard and soft segment reflections)

Table 1 Minimum energy conformations for poly(MDI/PeDO)

Diol section $O–CH_2–CH_2–CH_2–CH_2–CH_2–O$						Relative energy (kcal mol^{-1})	Monomer repeat (Å)
t	t	t	t	t	t	0.00	19.69
g^+	t	t	t	t	g^+	0.54	18.65
t	t	g^+	g^+	t	t	0.72	18.38
t	g^+	t	t	g^+	t	0.98	18.15
g^+	g^+	t	t	g^+	g^+	1.52	18.03
g^+	t	g^+	g^+	t	g^+	1.84	17.86
t	g^+	g^+	g^+	g^+	t	2.09	17.52
g^+	g^+	g^+	g^+	g^+	g^+	2.53	17.16

t = *trans* (ω = 180°) g^+ = *gauche*$^+$ (ω = 60°)



held constant (see Ref. 9).

N.B. The conformations listed above are those that have the longest repeats. Conversion of all the *gauche*$^+$ to *gauche*$^-$ (ω = –60°) does not affect the repeat, e.g., g^+ttttg^+ and g^-ttttg^- have the same repeat. Conformations containing combinations of *gauche*$^+$ and *gauche*$^-$ e.g. $g^+g^-ttg^-g^+$ all have repeats shorter than 17.16 Å

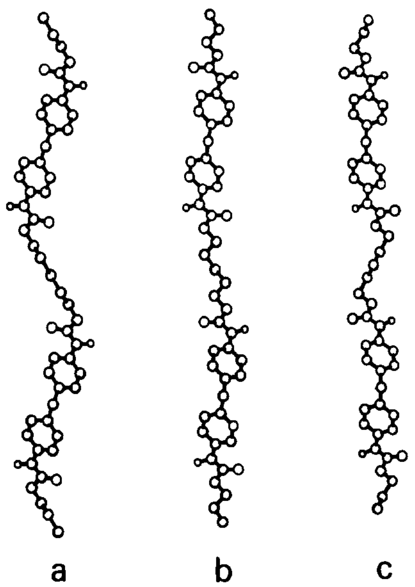


Figure 6 Conformation of poly(MDI/PeDO) that are compatible with the observed monomer repeat (18.6 Å). (a) *gauche*$^+$–*trans*–*trans*–*trans*–*trans*–*gauche*$^+$; monomer repeat 18.65 Å; (b) *trans*–*trans*–*gauche*$^+$–*gauche*$^+$–*trans*–*trans*; monomer repeat 18.38 Å; (c) *trans*–*gauche*$^+$–*trans*–*trans*–*gauche*$^+$–*trans*; monomer repeat 18.15 Å

RESULTS AND DISCUSSION

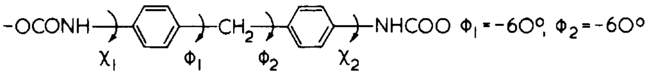
The X-ray diffraction patterns of the four polymers are shown in *Figure 5*, and the important features of these patterns are summarized below.

The poly(MDI/PeDO) pattern is similar in appearance to that for poly(MDI/BDO), and is characteristic of a triclinic structure with staggered chains. A strong off-meridional reflection is seen at $d = 7.8$ Å, which is an order of the very weak reflection at $d \simeq 15$ Å. The fibre repeat measured from the former reflection is 18.6 ± 0.4 Å, which is shorter than the monomer repeat for poly(MDI/BDO) and indicates a contracted chain conformation. *Table 1* shows the fibre repeats predicted for chains with different (symmetrical) $–O–(CH_2)_5–O$ units, and it can be seen that all three conformations possessing two *gauche* and four *trans* bonds are within experimental error of the observed fibre repeat. These three conformations are shown in *Figure 6*. There is insufficient data to obtain unit cell dimensions and the crystalline order is clearly lower than for poly(MDI/BDO). The relative insensitivity of the monomer repeat to the phenyl–urethane orientation is demonstrated in *Table 2*. This Table shows the monomer repeat for a poly(MDI/PeDO) chain with the *gauche*$^+$–*trans*–*trans*–*trans*–*trans*–*gauche*$^+$ diol conformation varies by 0.35 Å as the urethane groups are rotated symmetrically from perpendicular to coplanar with the phenyl groups.

The X-ray pattern of poly(MDI/HDO) contains ten reflections which are sharper than those on all the other patterns, although poly(MDI/BDO) is a close second in this regard. The d-spacings of the reflections are listed in *Table 3*, and are indexed by a triclinic unit cell with dimensions $a = 4.99$ Å, $c = 41.5$ Å, $\alpha = 114.5°$, $\beta = 113.8°$, $\gamma = 84.3°$; all the reflections are indexed by $h0l$ planes and thus b is not defined, unless $a = b$, in which case the

Table 2 Effect of changes in the phenyl-urethane orientation on the monomer repeat and relative potential energy for a poly(MDI/PeDO)

$O–(CH_2)_5–O$ Conformation: *gauche*$^+$–*trans*–*trans*–*trans*–*trans*–*gauche*$^+$



χ_1 (degrees)	χ_2 (degrees)	Relative energy (kcal mol^{-1})	Monomer repeat (Å)
–90	90	0.00	18.15
–100	80	0.32	18.23
–110	70	0.89	18.27
–120	60	1.65	18.29
–130	50	2.24	18.27
–140	40	3.41	18.23
–150	30	4.64	18.15
–160	20	5.97	18.08
–170	10	7.28	18.00
–180	0	9.23	17.94
–190	–10	7.28	18.00
–200	–20	5.97	18.08
–210	–30	4.64	18.15

Table 3 Observed and calculated *d*-spacings for poly(MDI/HDO)

hkl	*d* (obs) Å	*d* (calc) Å
002	17.45	17.32
004	8.71	8.66
$\bar{1}01$	4.79	4.76
101	4.33	4.30
$\bar{1}02$	4.90	4.91
102	4.04	4.02
103	3.72	3.75
104	3.46	3.49
105	3.28	3.25
$\bar{1}09$	3.78	3.78

Unit cell dimensions:
a = 4.99 Å　c = 41.5 Å
α = 114.5°　β = 113.8°　γ = 84.3°

N.B. b is not defined. If $b = a$ then calculated density = 1.423 g cm^{-3}
b not defined
if $b = a$ = 5.0 Å calculated density 1.423 g cm^{-3}

Table 4 Observed and calculated *d*-spacings for poly(MDI/BDO)[a]

hkl	*d* (obs) Å	*d* (calc) Å
$\bar{1}01$	4.75	4.77
101	4.25	4.21
$\bar{1}02$	4.91	4.96
102	3.89	3.90
103	3.56	3.59
004	7.65	7.66
$0\bar{1}4$*	4.60	4.61
104	3.30	3.31
$\bar{1}06$*	4.53	4.49
$\bar{1}07$	4.15	4.18
018	3.75	3.75
$\bar{1}\bar{1}9$*	3.42	3.43

Unit cell dimensions:
a = 5.05 Å b = 4.67 Å c = 37.9 Å
α = 116° β = 116° γ = 83.5°
calculated density = 1.571 g cm^{-3}
observed density = 1.30 g cm^{-3}
* Reflections due to second phase?
if $b = a$ = 5.05 Å calculated density = 1.453 g cm^{-3}

reflections are multiply indexed as *h*0*l* and 0*kl*. In this case the calculated density is 1.423 g cm^{-3}. If $b \neq a$ then the absence of the 0*kl* reflections would need to be explained by much poorer lateral order in the *b* direction. Nevertheless, the *c* dimension indicates that the chain is fully extended. We have predicted the poly(MDI/HDO) repeats for different O–(CH$_2$)$_6$–O conformations, and obtain a monomer repeat of 20.8 Å, i.e. 41.6 Å for the dimer, when the hexandiol section is all-*trans*; all the other options containing *gauche* CH$_2$ conformations are significantly shorter than the observed repeat. The fully extended all-*trans* conformation is similar in appearance to that in *Figure 2* for poly(MDI/BDO) with the addition of an extra –(CH$_2$)$_2$– zigzag. This addition would be 2.53 Å long in polyethylene, but the diol section is tilted with respect to the chain axis, which accounts for the 1.9 Å increase in the monomer repeat over poly(MDI/BDO).

The poly(MDI/HeDO) pattern shows recognizable reflections for oriented PTMA, notably the strong equatorial reflection at $d = 4.05$ Å, which is characteristic of the α-form. The hard segment reflections have a similar disposition to those for poly(MDI/PeDO), and the fibre repeat of ~20.7 Å identifies the structure as a staggered array of contracted chains. The pattern is more diffuse than that of poly(MDI/PeDO) indicating relatively poor lateral order.

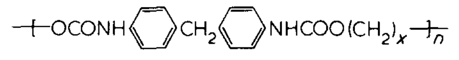
Finally poly(MDI/ODO) has a pattern similar to that of poly(MDI/HDO), with off-meridional reflections giving a layer line repeat of ~22.8 Å. The increase in fibre repeat over that for poly(MDI/HDO) is approximately the same as the increment for the latter polymer over poly(MDI/BDO). Conformational analysis predicts a monomer repeat of 22.8 Å for a fully extended chain, and thus the data show that poly(MDI/ODO) fits into the even series from poly(MDI/BDO) onwards. Polymers prepared using BDO, HDO, and ODO as the chain extender have similar properties[3,4] such as tensile strength, elongation at break, 300% modulus, permanent set, and melt flow temperature, and these data suggest that the polymers have similar physical structures. For poly(MDI/ODO), however, there is a weak meridional at $d = 20.2$ Å that cannot be explained by the ordered PTMA: fibre repeats of 14.2 and 14.7 Å are reported for α- and β-PTMA[25]. It is possible that this reflection, which is outside the layer line of the neighbouring off-meridionals, could be due to the presence of a second contracted polymorphic form of poly(MDI/ODO), but it will be necessary to obtain better patterns to investigate this further.

The above results led us to reexamine the unit cell for poly(MDI/BDO), in view of the discrepancy between the observed and calculated density. *Table 4* lists the observed *d*-spacings and compares them with the calculated *d*-spacings as indexed by Blackwell and Ross[8]. All of the reflections are indexed *h*0*l* except three, and the latter define the *b* axis. It is interesting that the equivalent three reflections are not seen for poly(MDI/HDO). Two of the three reflections are the outermost of the twelve observed and are too diffuse to be used to define a dimension of the unit cell, and hence the value of *b* depends largely on the reflection at $d = 4.60$ Å, indexed as $0\bar{1}4$. This reflection has a different appearance from the *h*0*l* reflections, in that it is sharper but much more arced. It is possible that this reflection is due to the presence of some other structure, perhaps a less well oriented second phase. Assignment of these three reflections to a second structure would leave a set of indexed *h*0*l* reflections with *b* undefined, unless $a = b = 5.05$ Å. In the latter case the calculated density is 1.453 g cm^{-3}, which is in better agreement with the observed value. Evidence in favour of polymorphism for the MDI/BDO hard domains also comes from the multiple d.s.c. peaks seen in the 200°–240°C range and assigned to melting of the hard segments[26,27].

CONCLUSIONS

The fibre repeats for the poly(MDI/diol) homologous series are shown in *Table 5*. It can be seen that for diols above and including butandiol the even and odd extended polymers form two systems: the even polymers have fully extended conformations in which the diol is all-*trans*, as shown for poly(MDI/BDO) in *Figure 2*. In contrast, the odd polymers adopt contracted conformations, in which the O–(CH$_2$)$_x$–O chain has some *gauche* bonds. Both the odd and even series of polymers adopt triclinic unit cells with tilted base planes. For the even series this is seen to arise from a staggering of the fully extended chains to form straight C=O···H–N hydrogen bonds, as can be seen in *Figure 2*. The urethane–(CH$_2$)$_x$–urethane sections of the chain are oriented to allow for hydrogen bonding in both directions perpendicular to the fibre axis, which should serve to stabilize the structure of the hard domains. It is easy to see that this type of structure could not occur for

Table 5 Observed fibre repeats for poly(MDI/diol) hard segments



O–(CH$_2$)$_x$–O x	Monomer repeat (Å)	Conformation
2	15.0 ± 0.2	Contracted
3	16.2 ± 0.2	Contracted
4	18.9$_5$ ± 0.2	Extended
5	18.6 ± 0.4	Contracted
6	20.8$_5$ ± 0.2	Extended
7	20.7 ± 0.4	Contracted
8	22.8 ± 0.4	Extended

the odd polymers if they had extended conformations, because the C=O bonds adjacent to the diol section would point in the same rather than the opposite direction, resulting in highly non-linear hydrogen bonds when the chains are packed. Thus the contracted conformations probably arise in order to form a more favourable hydrogen bonding network, which is sufficient incentive to overcome the approximately 1 kcal monomer increase in potential energy on contraction from the extended conformation. It appears that once in their contracted conformations, the odd polymer chains are able to adopt staggered (triclinic) hydrogen bonded structures analogous to those for the even series. Thus the major difference between the odd and even series of polymers is that the former must adopt higher energy conformations.

The first two members of the series, poly(MDI/EDO) and poly(MDI/PDO) do not fit the pattern described above, as frequently happens for the early members of a homologous series. Both of these polymers adopt contracted conformations, which is surprising for poly(MDI/EDO), if not for poly(MDI/PDO). In addition they pack with the chains in register rather than in the triclinic staggered arrays formed by the higher diol containing polymers. We can only speculate that EDO and PDO are both too short to allow for adequate packing of the MDI units in arrangements analogous to those for the higher members of the series, and thus another alternative must be found, which in the case of poly(MDI/EDO) results in a contracted conformation similar to those of the odd series.

As mentioned previously the model compound butandiol-capped MDI[21] crystallizes with a planar zigzag butandiol unit oriented *gauche* to the adjacent urethane group. As shown in *Figure 3*, the $CH_2 \cdots CH_2$ distances corresponding to the fibre repeats of the PDO, PeDO, and HeDO polymers are 16.34 Å, 18.21 Å, and 20.77 Å respectively, which are close to the observed and predicted monomer repeats of the polymers.

It is clear that the highest crystallinity is obtained for the extended even series of polymers, which in general have the better properties. We are presented with the simple explanation that this arises due to the fact that these polymers can crystallize more easily in the lower energy conformation. Development of crystallinity is an important component of the driving force for phase separation: there will be a greater decrease in potential energy when the even diol polymers crystallize in the extended conformations, leading to better phase separation and hence to better properties for the elastomers.

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