Structure of polyurethane elastomers. X-ray diffraction and conformational analysis of MDI–propandiol and MDI–ethylene glycol hard segments

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X-ray diffraction and conformational analysis have been used to investigate the structure of polyurethane hard segments prepared from diphenylmethane 4,4'-diisocyanate (MDI) with propandiol (PDO) and ethylene glycol (EDO) as chain extenders. The results are compared with those obtained previously for MDI-butandiol (BDO) hard segments. In the latter system, the poly(MDI–BDO) chains are fully extended with an all-*trans* conformation for the $O-(CH_2)_4-O$ unit, and a monomer repeat of 18.95 Å. The unit cell is triclinic with a tilted base plane such that adjacent chains are staggered along the fibre axis. In contrast both poly(MDI–PDO) and poly(MDI–EDO) adopt unstaggered structures, i.e. the chains are in register and the unit cell base planes are perpendicular to the chain axis. The monomer repeats of 16.2 Å for poly(MDI–PDO) and 15.0 Å for poly(MDI–EDO) are shorter than the predicted repeats for fully-extended chains, indicating that these polymers have contracted conformations containing some *gauche* CH_2 groups. Conformational analysis shows that the 16.2 Å repeat for poly(MDI–PDO) can be achieved with the $O-(CH_2)_3-O$ unit in the *trans–gauche*$^+$*–gauche*$^+$*–trans* or *gauche*$^+$*–trans–trans–gauche*$^+$ conformations. Similarly the 15.0 Å repeat for poly(MDI–EDO) is predicted for the *gauche*$^+$*–trans–gauche*$^-$ conformation for the $O-(CH_2)_2-O$ unit. These conformations are of higher energy than the all-*trans* fully-extended chains. This may explain the higher crystalline perfection of the poly(MDI–BDO) hard segments, for which crystallization in the all-*trans* form will probably provide a greater driving force for phase separation.

INTRODUCTION

Previous papers from this laboratory[1-3] have described our X-ray diffraction and model building work in determining the structures of the hard segments in polyurethane elastomers. These papers concentrated on hard segments formed from diphenylmethane 4,4'-diisocyanate (MDI) with butandiol (BDO) as the chain extender. The bulk properties of polyurethane elastomers vary significantly depending on the choice of chain extender, and we are investigating whether or not this can be correlated with differences in the solid state structures of their hard segments.

Polyurethane elastomers are block copolymers which derive their useful properties from phase separation into hard and soft domains. The hard domains contain the polyurethane segments: these are below their T_g and form domains which serve as crosslinks between the flexible soft segment chains, which are usually polyethers or polyesters above their T_g. In preparations containing poly(MDI–diol) hard segments, crystallization of the hard segments is an important determinant of the extent of phase separation, and the development of crystallinity is likely to be dependent on the hydrogen bonding and other interactions between the chains in the hard domains.

The structures of poly(MDI–diol) hard segments have been considered previously by Bonart and coworkers[4-6] and by Wilkes and Yusek[7]. The X-ray patterns obtained by these workers showed a single Bragg reflection in the diffraction pattern of the poly(MDI–BDO) hard segments at $d \simeq 7.9$ Å, azimuthally inclined at $\sim 30°$ to the meridian. In addition, an intense amorphous halo at $d \simeq 4$ Å was observed. Bonart *et al.*[5] assigned the Bragg reflection to planes inclined at $\sim 60°$ to the fibre axis, and proposed that these planes arise from a staggering of adjacent chains so that intermolecular C=O···H–N hydrogen bonds are formed between the urethane groups. This staggered chain structure is analogous to that for the α-form of nylon-6,6[8].

Figure 1 shows the X-ray diffraction pattern obtained in this laboratory[2] for poly(MDI–BDO) hard segments. This pattern is much more detailed than those obtained previously: twelve reflections are resolved and can be indexed by a triclinic unit cell with dimensions $a = 5.05$ Å, $b = 4.67$ Å, $c = 37.9$ Å (fibre axis), $\alpha = 116°$, $\beta = 116°$ and $\gamma = 83.5°$. The base plane of the unit cell is tilted, i.e. it is not perpendicular to the fibre axis, and the off-meridional reflection at $d = 7.65$ Å is indexed as 004. We have also predicted the conformation and packing of the poly(MDI–BDO) chains[1], based on the structure of the model compound, methanol-capped MDI (MeMMe*), determined by single crystal methods[9]. The predicted polymer structure has a triclinic unit cell with dimensions $a = 5.2$ Å, $b = 4.8$ Å, $c = 35.0$ Å, $\alpha = 121°$, $\beta = 116°$ and γ

* Two polymorphic structures of MeMMe are known, designated MeMMe I and II, and have been determined respectively by Gardner and Blackwell[9] and Born *et al.*[10].

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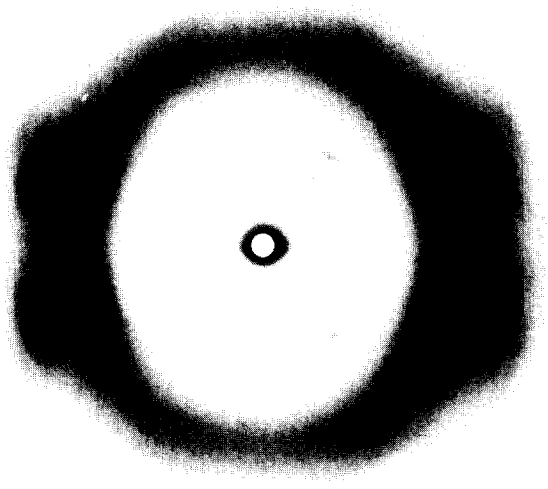


Figure 1 X-ray diffraction pattern of an oriented MDI/BDO/PTMA film[2] prepared by stretching 700% at 130°C. The reflections are due to the crystalline poly(MDI–BDO) hard segments

$=85°$; the space group is $P\bar{1}$ and the unit cell contains two repeat units of a single chain related by a centre of symmetry. The *ac* projection of this structure is shown in *Figure 2*. Adjacent chains are staggered along the *c*-axis, and are linked by hydrogen bonds which are directed along the *a* and *b* axes, i.e. there is hydrogen bonding in both dimensions perpendicular to the chain axis.

Given the assumptions in the model building and the experimental uncertainties in the X-ray work, the two unit cells are in good agreement. The most obvious difference is in the fibre repeat, indicating that the actual chain is more extended than that predicted from the structure of MeMMeI. We have reported conformational analysis for the poly(MDI-BDO) chains[3], for which the minimum energy conformation has a fibre repeat of 37.9 Å and a planar zigzag butandiol coplanar with the adjacent urethane groups.

In examining the PDO and EDO preparations we have used similar procedures: X-ray fibre diagrams have been obtained for the hard segments from which the fibre repeats have been determined. Conformational analysis has then been used to determine the likely conformation of the chains.

X-RAY DIFFRACTION

Experimental

Specimens of the polyurethanes were generously provided by Dr C. S. Schollenberger of B. F. Goodrich Co., Brecksville, Ohio, in the form of films ~0.5 mm thick prepared by hot rolling. The molar ratio of reactants was 6:5:1 for MDI:diol:PTMA [poly(tetramethylene adipate)] ($M_n=2089$), corresponding to approximately 50% hard segment content. Oriented films for the PDO preparation were produced by stretching to ~700% elongation at 130° and annealing at 70°C (above T_m for PTMA) for 24 h, followed by cooling to room temperature. As will be seen, these specimens gave the crystalline diffraction pattern for the hard segments only, i.e. the soft domains were amorphous. This procedure was unsuccessful for the EDO polymer in that all the films broke during preparation at high temperature. For this polymer, oriented specimens were prepared by stretching to 300% elongation at room temperature and annealing at 55°C for 24 h. The resultant pattern contained crystalline reflections for both the hard and soft domains. X-ray fibre diagrams were recorded using a Searle toroidal focussing camera and CuKα radiation from a Rigaku-Denki rotating anode source. The *d*-spacings were calibrated using CaF_2 powder.

Results

X-ray diffraction patterns of the PDO and EDO preparations are shown in *Figures 3* and *4*. The poly(MDI–PDO) pattern has meridional reflections at $d=16.2$ and 8.1 Å: these are the first and second orders, respectively, and there is a weak fourth order meridional at $d\simeq4.0$ Å that is difficult to resolve due to the amorphous halo. One row line is visible with reflections at $d=4.7$, 4.05, and 3.5 Å on the zeroth, second, and third layer lines, respectively. These reflections are not seen for either α- or β-PTMA, and can confidently be assigned to the crystalline hard segments. These results indicate that the base plane of the unit cell is perpendicular to the fibre axis, such that the 00*l* reflections occur on the meridian. There is insufficient data to define the unit cell, but it is either monoclinic or orthorhombic, with an interchain separation of ~4.7 Å.

The X-ray pattern of the oriented EDO preparation shows meridional reflections at 15.0 and 7.5 Å which can

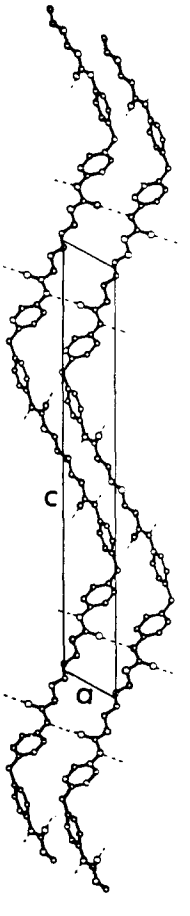


Figure 2 *ac* Projection of the model of the structure of poly(MDI–BDO) proposed by Blackwell and Gardner[1]

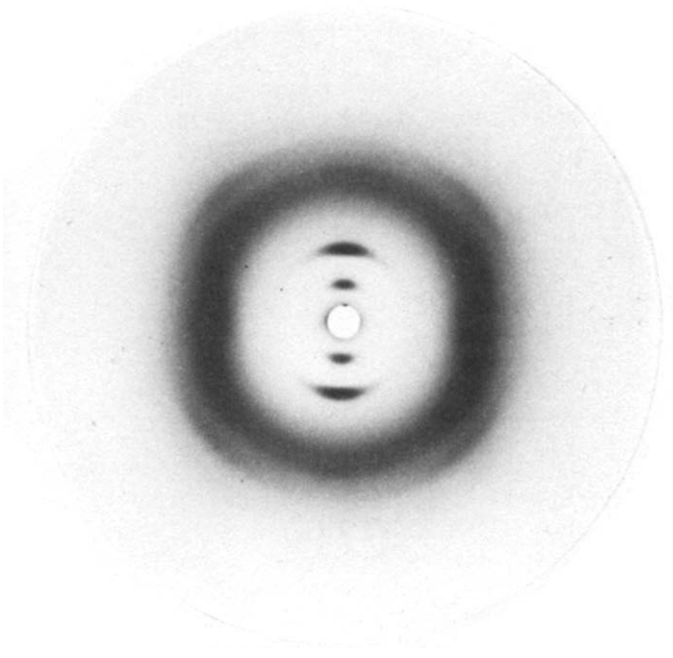


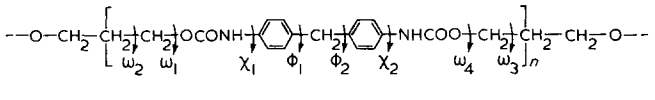
Figure 3 X-ray diffraction pattern of an oriented MDI/PDO/PTMA film prepared by stretching 700% at 130°C. The reflections are due to the crystalline poly(MDI–PDO) hard segments

be assigned to the hard segments. (These meridional *d*-spacings were first reported by Wilkes and Yusek[7].) The strong equatorial at $d=4.05$ Å corresponds to the observed 110,020 reflection of α-PTMA. (The soft segments are crystalline due to low annealing temperature.) Analogy with the data for the PDO polymer suggests that poly(MDI–EDO) has a similar conformation and non-staggered chain packing.

Thus although these X-ray patterns are not as detailed as that of poly(MDI–BDO) it can be seen that poly(MDI–PDO) and poly(MDI–EDO) have significantly different structures. For poly(MDI–BDO) the monomer repeat is 18.95 Å, and conformational analysis indicates that the butandiol unit is fully extended, i.e. all-*trans*. Deletion of a *trans* CH_2 group from such a chain would reduce the monomer repeat by approximately 1.2 Å. This is the difference between the fibre repeats of the PDO- and EDO-containing hard segments, and it is reasonable to conclude that these two polymers have the same type of conformation with the addition or deletion of a *trans* CH_2 group. However, the difference between the monomer repeats for the PDO and BDO polymers is 2.75 Å. Since the poly(MDI–BDO) chain is known to be fully extended, it is clear that the poly(MDI–PDO) and poly(MDI–EDO) chains must be contracted conformations, i.e. there must be some *gauche* bonds in the diol section of the chains.

Conformational analysis

The labels for the torsion angles are shown below: the origins for these angles are defined in Ref. 3.



The chemical repeat is relatively long, but the predictions are simplified by the fact that the urethane and phenyl groups are planar. We have already considered the phenyl–phenyl and phenyl–urethane interactions in our analysis of the poly(MDI–BDO) chain[3]. The conclusions from the latter work were as follows:

(a) The energy of the phenyl–CH_2–phenyl section was determined as a function of φ_1, φ_2, and the C–CH_2–C bond angle (τ). The global minimum occurred at $\tau=110°$, but there was a subsidiary minimum at $\tau=118.3°$, for which $\varphi_1,\varphi_2=(60°,60°)$, and the phenyl planes are mutually perpendicular as in the structure of MeMMeI[9]. The latter conformation is more extended and was selected for the polymer chain, although this selection is not critical to other conclusions below.

(b) In the case of the phenyl–urethane conformation, semi-empirical calculations predict minimum energy when the planes of the phenyl and urethane groups are mutually perpendicular, i.e. χ_1 or $\chi_2=\pm90°$. However the observed conformations of diphenyl methane diurethane model compounds[9–11] have χ angles in the range 10–36°. These large variations from the perpendicular conformation are probably due to either or both intermolecular packing forces and the effect of urethane–phenyl electron delocalization. The latter effect has been considered for aromatic polyamides and polyesters[12,13], for which the electron delocalization has been modelled by a torsional potential function of the form $E=-B\cos^2\chi$, where B is an empirical constant. In the case of poly(MDI–BDO), the fibre repeat is relatively insensitive to the value of χ: the planar –NHCO.O–$(CH_2)_4$–O.CONH– chain can be rotated about the linkage N–C (phenyl) bonds like a crankshaft, with only small changes in the separation of successive diphenyl methane units.

Thus our procedure, in predicting the conformations of poly(MDI–PDO) and poly(MDI–EDO), has been to take the extended minimum energy conformation for the diphenyl methane diurethane ($\chi_1,\chi_2=-90°,+90°$) and to add the diol section in different possible conformations. The resultant chains have then been compared in terms of their relative energies and fibre repeats. Thereafter the effects of changes in χ_1 and χ_2 due to possible packing forces and electron delocalization have been considered.

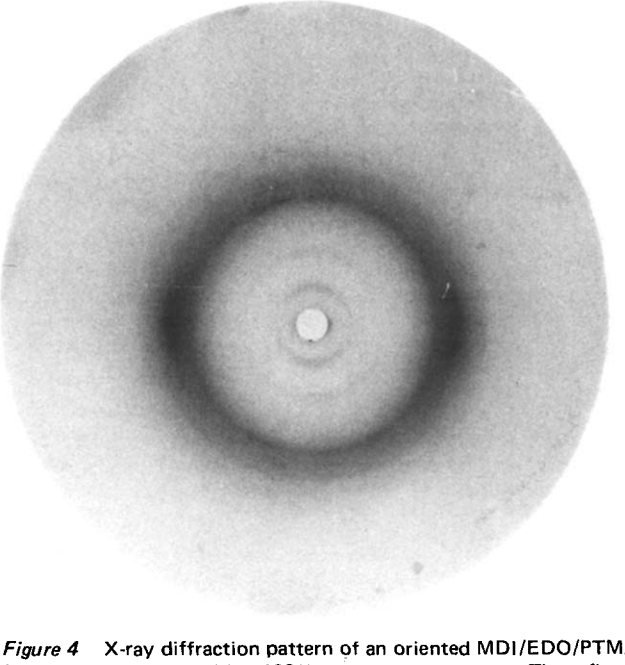


Figure 4 X-ray diffraction pattern of an oriented MDI/EDO/PTMA film prepared by stretching 400% at room temperature. The reflections are due to both the hard and soft segments

The conformations of the diol segments are defined by ω_1, ω_2, ω_3 and [for poly(MDI–PDO)] ω_4. The chemical repeat is symmetrical and it is likely that this will lead to symmetry in the conformations on either side of the centre of the diol unit, i.e. $\omega_1 = \omega_4$ and $\omega_2 = \omega_3$ for poly(MDI–PDO) and $\omega_1 = -\omega_3$ for poly(MDI–EDO).

The energy map for the (ω_1,ω_2) conformations for poly(MDI–PDO) is shown in *Figure 5*. A similar map is obtained for poly(MDI–EDO). The energies for the predicted minima in *Figure 5* are listed in *Table 1*. Not surprisingly, the lowest energy is for $\omega_1,\omega_2 = 180°,180°$, corresponding to the all-*trans* conformation, for which the entire urethane–$(CH_2)_3$–urethane is coplanar. This chain has a fibre repeat of 17.6 Å, which is significantly longer than the observed value of 16.20 Å. In addition, it can be seen that this all-*trans* chain cannot form straight intermolecular hydrogen bonds, since the N–H groups of urethanes adjacent to the central $(CH_2)_3$ point in the same direction.

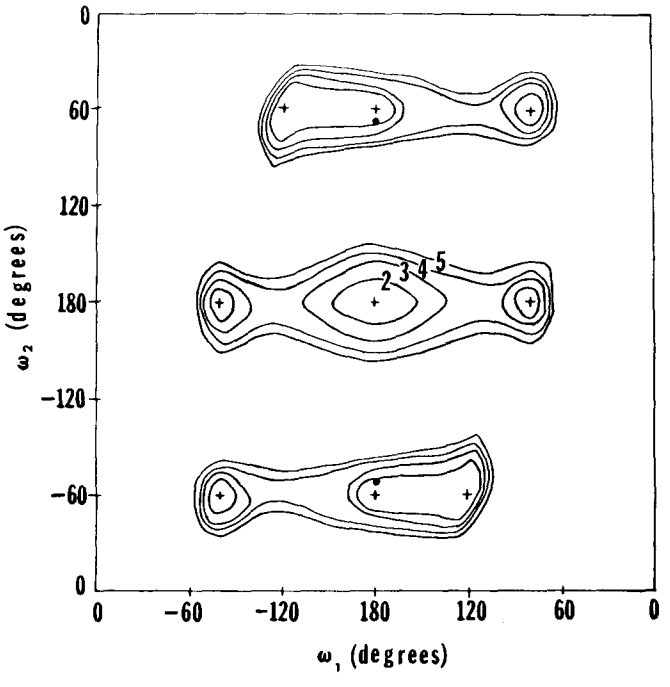


Figure 5 ω_1, ω_2 energy map for poly(MDI–PDO). The energy contours are in kcal mol^{-1}. +, Energy minima; ●, observed conformations for model compounds

The next lowest minimum, 0.9 kcal mol^{-1} above the all-*trans* conformation, is for $\omega_1,\omega_2 = 180°, \pm 60°$; $+60°$ and $-60°$ corresponding to the *gauche*$^+$ and *gauche*$^-$ conformations respectively for the CH_2 groups. This *trans–gauche*$^+$ *gauche*$^+$*–trans* (and *trans–gauche*$^-$ *gauche*$^-$*–trans*) option has a fibre repeat of 16.2 Å. The third lowest minimum has a calculated energy 1.4 kcal mol^{-1} higher than all-*trans*. This has $\omega_1,\omega_2 = \pm 80°, 180°$ and corresponds approximately to the *gauche*$^+$*–trans trans–gauche*$^+$ (and *gauche*$^-$*–trans–trans–gauche*$^-$) option: $\omega_1 = \pm 80°$ rather than $\pm 60°$ in order to avoid an unfavourable methylene–carbonyl interaction. The fibre repeat for this conformation is 16.24 Å. The remaining minima are for the all-*gauche* options; the most extended of these conformations has a fibre repeat of 15.31 Å.

The above conformations all have $\chi_1,\chi_2 = -90°, +90°$, i.e. the phenyl and urethane groups are mutually perpendicular. *Table 2* shows the effect on the fibre repeat and relative potential energy for the polymer with the *trans–gauche*$^+$*–gauche*$^+$*–trans* conformation for the diol of symmetrical variations of χ_1 and χ_2. It is seen that the fibre repeats are in the range of 16.36 to 16.10 Å, and are all compatible with the observed value. This occurs because the ether oxygen is almost colinear with the N–C (phenyl) bond, and hence the length of the diphenyl-methane–diurethane is relatively insensitive to χ. Furthermore, symmetrical changes of χ_1 and χ_2 simply move the $(CH_2)_3$ chain like a crankshaft, and have only small effects on the separation of adjacent diphenyl methanes. Similar behaviour is seen for the *gauche*$^+$ *trans–trans–gauche*$^+$ option. The values of χ in *Table 2* are in the range observed in model compounds and thus energy differences of the magnitude shown can clearly be overcome by packing and/or electron delocalization effects.

Table 1 Minimum energy conformations of MDI–PDO fragment

Conformational angles (degrees)								Relative energy (kcal mol^{-1})	Length of MDI–PDO fragment c (Å)
ω_1	ω_2	χ_1	ϕ_1	ϕ_2	χ_2	ω_3	ω_4		
180	180	−90	−60	−60	90	180	180	0.00	17.60
180	±60	−90	−60	−60	90	±60	180	0.90	16.20
±80	180	−90	−60	−60	90	180	±80	1.39	16.24
±60	±80	−90	−60	−60	90	±80	±60	1.64	15.31

Table 2 Effect of changes in phenyl–urethane orientation (χ) on the fibre repeat and relative energy for poly(MDI–PDO) for the *trans–gauche*$^+$*–gauche*$^+$*–trans* diol unit

Conformational angles (in degrees)								Relative energy (kcal mol^{-1})	Length of the MDI–PDO fragment c (Å)
ω_1	ω_2	χ_1	ϕ_1	ϕ_2	χ_2	ω_3	ω_4		
180	±60	− 90	−60	−60	90	±60	180	0.00	16.20
180	±60	−100	−60	−60	80	±60	180	0.21	16.26
180	±60	−110	−60	−60	70	±60	180	0.78	16.31
180	±60	−120	−60	−60	60	±60	180	1.44	16.36
180	±60	−130	−60	−60	50	±60	180	2.05	16.31
180	±60	−140	−60	−60	40	±60	180	3.24	16.26
180	±60	−150	−60	−60	30	±60	180	4.35	16.21
180	±60	−160	−60	−60	20	±60	180	5.16	16.16
180	±60	−170	−60	−60	10	±60	180	6.98	16.10

Thus two groups of symmetrical conformations are compatible with the observed fibre repeat. The two $\chi_1,\chi_2 = -150°,+30°$ conformations for poly(MDI–PDO) are shown in *Figure 6*. Evidence in favour of the lower energy form (*trans–gauche*$^+$*–gauche*$^+$*–trans*) comes from the crystal structure of butandiol-capped MDI $[CH_2\{C_6H_4NHCOO(CH_2)_4OH\}_2$; HO–BMB–OH$]$[11]. This molecule is shown in projection in *Figure 7*. The terminal $-C_4-O$ chains are approximately planar but are *gauche*$^+$ to the adjacent urethanes, i.e. $\omega_1,\omega_2 = 170.7°,69.5°$. The $CH_2\cdots CH_2$ distance that corresponds to the poly(MDI–PDO) repeat is 16.3 Å, calculated from the refined atomic coordinates of HO–BMB–OH[11]. We are currently studying packing models for both poly(MDI–PDO) conformations, allowing for the possible variations in χ_1 and χ_2.

The equivalent energy data for the possible poly(MDI–EDO) conformations is shown in *Table 3*. The symmetrical possibilities for the diol section are: all-*trans*; *trans–gauche*$^+$*–trans*; *gauche*$^+$*–trans–gauche*$^-$; and combinations of all-*gauche*. The minimum energy form is all-*trans* and this leads to a centrosymmetric dimer repeating in 32.90 Å, i.e. 16.45 Å for the monomer repeat, which must be rejected in view of the 15.0 Å repeat determined from the X-ray pattern. The next minimum, *trans–gauche*$^+$*–trans*, has a repeat of 15.8 Å and is also rejected in favour of the third minimum, *gauche*$^+$*–trans–gauche*$^-$, for which the repeat of 15.0 Å matches the observed value. The all-*gauche* combinations all have repeats which are too short. As was the case for poly(MDI–PDO), the fibre repeat is relatively insensitive to the χ_1 and χ_2 values. Thus the analysis suggests a single option for the poly(MDI–EDO) conformation, *gauche*$^+$*–trans–gauche*$^-$, and this is shown in *Figure 8*.

The conformations in *Figures 6* and *8*, and most of the others considered above have monomer repeats. Multimonomer repeats, in which successive monomer units are related, e.g. by a 2_1 screw axis, may be compatible with the limited X-ray data, and can be obtained by conversion of certain *gauche*$^+$ conformations to *gauche*$^-$. These conformations also need to be considered, although at present there is no definite evidence for anything other than monomer repeats for both poly(MDI–PDO) and poly(MDI–EDO). We are now looking at possible models of packing of the proposed conformations, and will report on this work in due course.

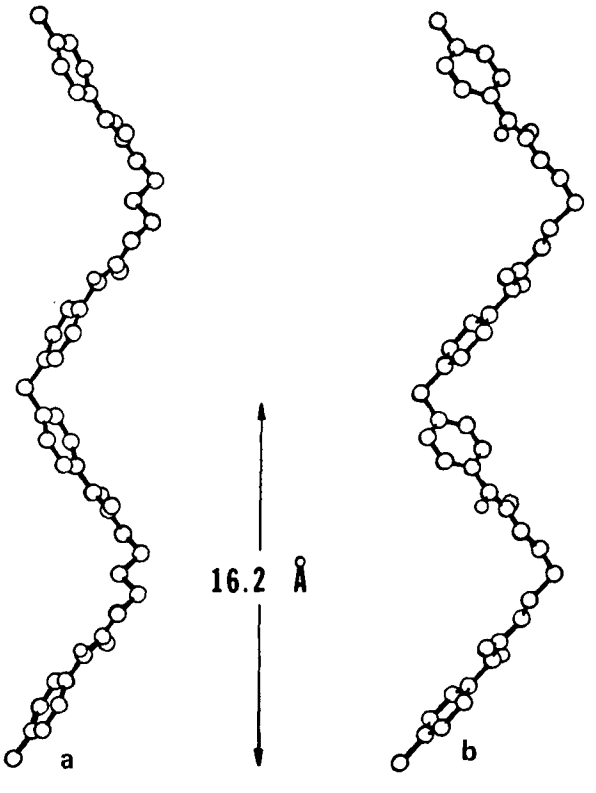


Figure 6 Conformations of poly(MDI–PDO) compatible with the observed fibre repeat of 16.2 Å. (a) *gauche*$^+$*–trans–trans–gauche*$^+$; (b) *trans–gauche*$^+$*–gauche*$^+$*–trans*

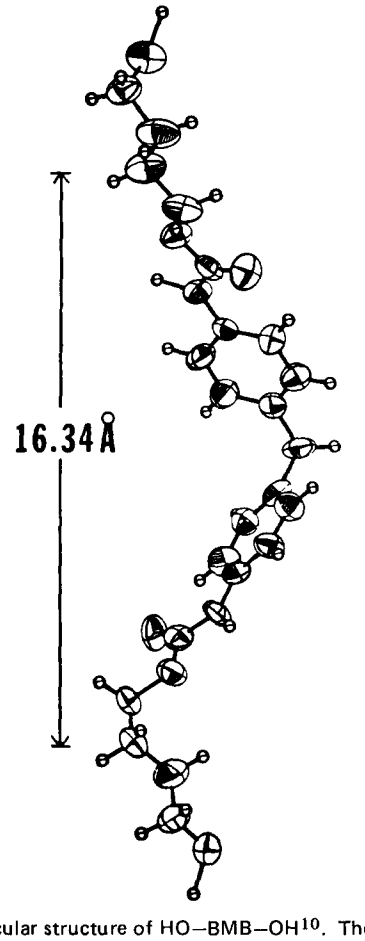


Figure 7 Molecular structure of HO–BMB–OH[10]. The C ··· C distance corresponding to the poly(MDI–PDO) repeat is 16.34 Å

Table 3 Minimum energy conformations of MDI–EDO fragment

Conformational angles (degrees)							Relative energy (kcal mol^{-1})	Fibre repeat c (Å)
χ_1	ϕ_1	ϕ_2	χ_2	ω_1	ω_2	ω_3		
−90	−60	−60	90	180	180	180	0.00	16.45
−90	−60	−60	90	180	60	180	0.94	15.80
−90	−60	−60	90	60	180	−60	1.28	15.00
−90	−60	−60	90	±60	±60	±60	1.98	14.16

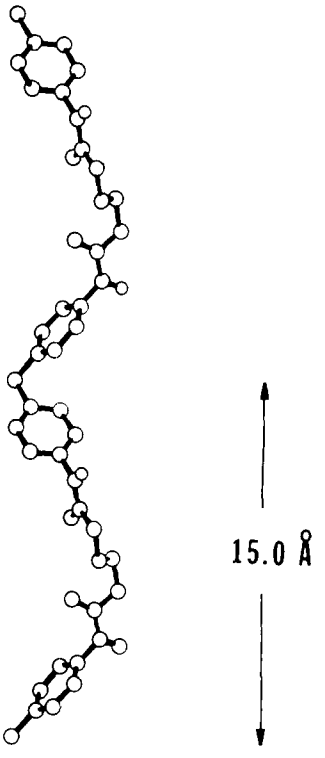


Figure 8 *Gauche*$^+$*–trans–gauche*$^-$ conformation for poly(MDI–EDO). Fibre repeat of 15.0 Å matches the observed value

At this point it can be seen that the BDO hard segments have better crystalline order than the PDO hard segments, suggesting more effective phase separation in the BDO preparation. This may have the simple explanation that the poly(MDI–BDO) chains can crystallize more easily, because they adopt the lowest energy fully extended conformation, which allows the formation of straight intermolecular hydrogen bonds. However, the all-*trans* conformation of poly(MDI–PDO) cannot form the same type of hydrogen bonding network because the odd number of CH_2 groups results in the N–H groups being on the same rather than the opposite side of the planar zigzag. Therefore this polymer needs to adopt a higher energy contracted conformation in order to crystallize. The resulting structure will probably be of a higher energy than that for poly(MDI–BDO) and hence there will be less of a driving force for phase separation due to crystallization of the hard segments. The results for poly(MDI–EDO) are more surprising since one might have expected the even diol to result in a similar structure to poly(MDI–BDO) with fully extended chains. It may be, however, that the ethylene glycol chain is too short to allow for satisfactory packing of the diphenyl methane diurethanes in the staggered array of extended chains, resulting in adoption of a contracted conformation more analogous to poly(MDI–PDO).

ACKNOWLEDGEMENT

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