Conformational analysis of poly(MDI-butandiol) hard segment in polyurethane elastomers

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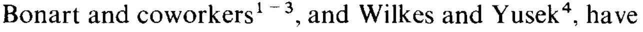
As part of our study of the structure of the hard segments of polyurethane elastomers, we have used conformational analysis to predict the conformation of the polyurethane chain formed from diphenylmethane 4,4'-diisocyanate (MDI), with butandiol as the chain extender. X-ray diffraction indicates the chain conformation is highly extended in the solid state, with a monomer repeat of 18.95 Å. The chain conformation can be predicted from the interaction between the large contiguous groups. Semi-empirical and CNDO/2 molecular orbital calculations have been used to investigate the phenyl–phenyl, phenyl–urethane, and urethane–butandiol interactions. Minimum energy for the diphenyl-methane section occurs for a C–CH_2–C bridge angle of $\theta = 110°$. However, the more likely conformation in the polymer is probably that at the subsidiary minimum at $\theta = 118°$, in which the phenyl rings are mutually perpendicular, which is comparable to the conformation seen for model compounds. For the phenyl–urethane interactions the energy minimum is at $\chi = \pm 90°$, with the combination $(\chi_1, \chi_2) = (-90°, +90°)$ leading to the necessary extended conformation. Calculations for the butandiol segment favour an all-*trans* conformation which is coplanar with the urethane groups. The predicted conformation of the polymer chain has a fibre repeat which matches the observed value, and this cannot be attained if the butandiol unit contains any *gauche* bonds. Model compounds show large variations for the phenyl–urethane conformation from the predicted minimum at $\chi = \pm 90°$, indicating the importance of intermolecular stacking forces in determining the polymer conformation. However, provided the adjacent butandiol and urethane groups are coplanar, the fibre repeat is relatively insensitive to variations of χ.

INTRODUCTION

In previous papers we have described work on the structure of poly(MDI–butanediol), which forms the hard segments in an important group of polyurethane elastomers. These copolymer systems derive their useful properties from the phase separation into hard and soft domains: the soft segments are polyesters or polyethers and are amorphous, whereas the hard segments are crystalline. There has been interest in the three dimensional structure of these hard domains e.g. in the chain conformation, packing, and intermolecular hydrogen bonding, since the development of crystallinity leads to enhanced phase separation.

The MDI (diphenylmethane 4,4'-diisocyanate)-butanediol hard segments have the following chemical structure:



where *n* is variable and is frequently in the range 1–4. Bonart and coworkers[1–3], and Wilkes and Yusek[4], have shown that X-ray fibre diagrams of the hard segments can be obtained in the following manner. When the copolymer is stretched the resulting fibre diagram is due to oriented crystalline domains of both the hard and soft segments [the soft segment polymer was poly(tetramethylene adipate)]. However, annealing at a temperature above the melting temperature for the soft segment (but below that for the hard segments) destroys the crystallinity of the soft segments and the remaining X-ray pattern is attributable to the hard segment domains. The X-ray patterns obtained by both groups showed a single Bragg reflection at $d \approx 7.9$ Å, inclined at ~30° to the meridian, and an intense amorphous halo. Bonart *et al.*[2] suggested that this arises due to staggering of the chains to form a hydrogen bonded array, as shown in *Figure 1*.

However, the structure in *Figure 1* does not take account of present knowledge of stereochemistry, and we have attempted to produce more detailed models by the following approaches. Using single crystal X-ray methods we determined the structure of a model compound methanol-capped MDI (MeMMeI)[5]. Assuming that the MeMMe conformation is retained in the polymer, and that the butanediol section is a planar zigzag, we were able to predict the structure of the hard segments[6], as shown in *Figure 2*; the predicted unit cell is triclinic with dimensions $a = 5.2$ Å, $b = 4.8$ Å, $c = 35.0$ Å, $\alpha = 115°$, $\beta = 121°$, and $\gamma = 85°$, and space group $P\bar{1}$. The packing in the *bc* projection was derived from ORTEP projections and the unit cell dimensions are necessarily only approximate. Nevertheless the tilted base plane was in keeping with the earlier ideas of Bonart *et al.*[2].

Recently we have obtained improved X-ray patterns of the hard segments[7]. Twelve reflections are observed from which the unit cell is determined to be triclinic, with dimensions $a = 5.05$ Å, $b = 4.67$ Å, $c = 37.9$ Å, $\alpha = 116°$, β

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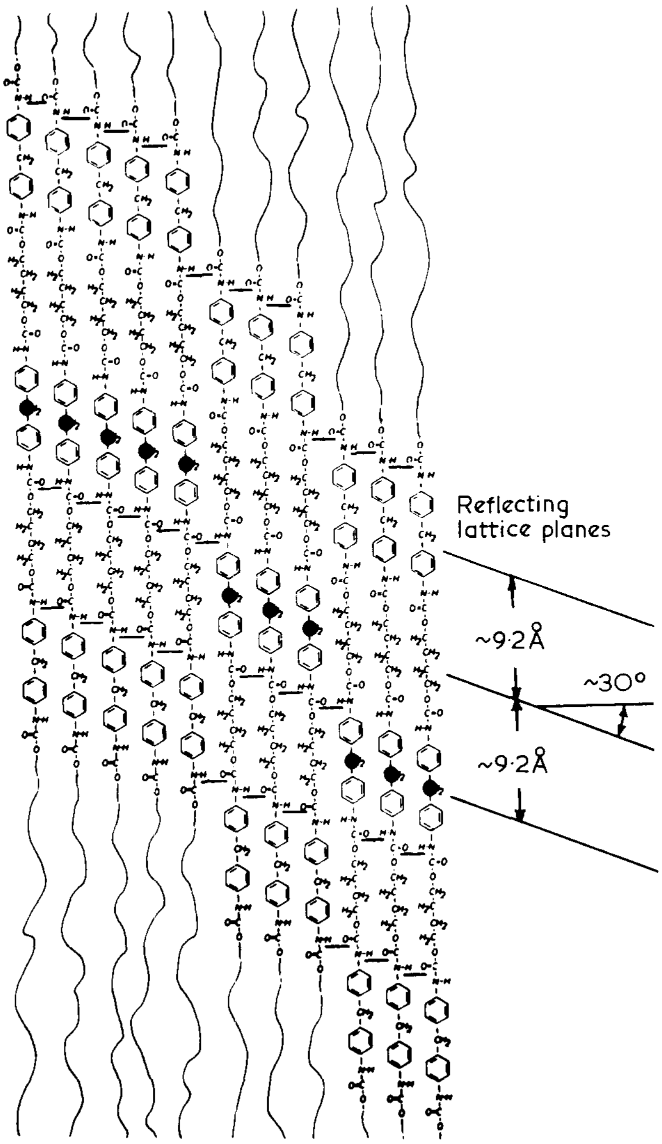


Figure 1 Scheme of the hydrogen bonding in MDI-butandiol hard segments, as proposed by Bonart *et al.*[2] The staggering of the chains leads to planes in this projection at 30° to the perpendicular as indicated

=116°, and $\gamma = 83.5°$. The agreement obtained is good considering experimental errors in the X-ray measurements and the approximations in the model building. The most significant difference is probably the longer fibre repeat, which may indicate a less linked conformation than that shown in *Figure 2*.

The techniques of conformational analysis have been used to determine the most likely chain conformation. In addition to the crystal structure of methanol-capped MDI determined in this laboratory (MeMMeI), a second polymorphic structure of this compound, MeMMeII, has been determined by Hocker and Born[8]; we have also recently determined the structure of butanediol-capped MDI (HO–BMB–OH)[9] and thus three model structures are available for comparison with our predictions.

EXPERIMENTAL

Model building

The numbering of the atoms in the MDI–butanediol repeat unit and the labelling of the torsion angles are shown in *Figure 3*. The initial conformation is defined as follows:

$\omega_1 = 0$ when O(22)—C(20) is *cis* to C(23)—C(24);

$\chi_1 = 0$ when C(16)—C(17) is *cis* to N(19)—C(20);

$\varphi_1 = 0$ when C(12)—C(1) is *cis* to C(13)—C(18);

$\varphi_2 = 0$ when C(1)—C(2) is *cis* to C(12)—C(13);

$\chi_2 = 0$ when N(7)—C(8) is *cis* to C(4)—C(3),

and

$\omega_2 = 0$ when C(11)—C(26) is *cis* to O(10)—C(8).

Clockwise rotation is considered positive.

The bond lengths and bond angles used for the aromatic rings and $-(CH_2)_4$ chain were standard values taken from the literature:

$$\text{aromatic C–C} = 1.39\ \text{Å},\ \text{C–H} = 1.00\ \text{Å},\ \text{C–}\hat{\text{C}}\text{–C} = 120°,$$
$$\text{C–}\hat{\text{C}}\text{–H} = 120°$$

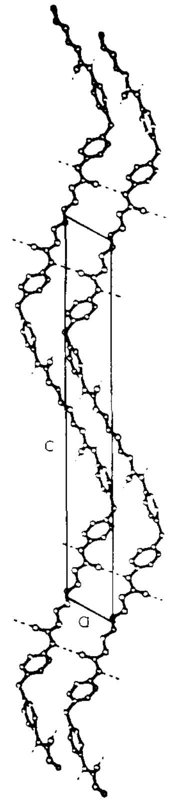


Figure 2 ac Projection of the structure of poly(MDI-butandiol) hard segments proposed by Blackwell and Gardner[6]

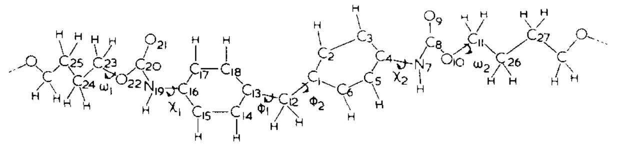


Figure 3 Poly(MDI-butandiol) chain showing the torsion angles that define the conformation

Table 1 Crystal structure data for urethane fragment

Bond length (Å)			
N–C	C–O	C–O	Reference
1.348	1.206	1.364	5
1.350	1.231	1.326	9
1.339	1.223	1.333	10
1.373	1.192	1.335	11
1.336	1.211	1.326	12
1.330	1.201	1.330	13
1.356	1.210	1.301	14
1.360	1.180	1.360	15
1.340	1.190	1.340	16
1.349	1.223	1.333	17
1.324	1.231	1.324	18
1.347	1.195	1.349	19
1.325	1.223	1.345	20
1.344	1.225	1.319	21
1.334	1.209	1.320	22
1.368	1.211	1.328	23
1.347	1.219	1.332	24
1.357	1.210	1.334	25
1.330	1.221	1.363	26

$$\text{aliphatic C–C} = 1.52\ \text{Å},\ \text{C–H} = 1.00\ \text{Å},\ \text{C–}\hat{\text{C}}\text{–C} = 110°,$$

$$\text{C–}\hat{\text{C}}\text{–H} = 110°$$

To establish the stereochemistry of the urethane group we surveyed crystallographic studies of nineteen urethane containing compounds[5,9–26]. The reported bond lengths and angles are given in *Table 1*, and yield the following averages:

$$N_7\text{–}C_8 = 1.35\ \text{Å},\ C_8{=}O_9 = 1.20\ \text{Å},\ C_8\text{–}O_{10} = 1.35\ \text{Å}$$

$$C_4\text{–}N_7 = 1.44\ \text{Å},\ N_7\text{–H} = 1.00\ \text{Å},\ O_{10}\text{–}C_{11} = 1.42\ \text{Å}$$

The urethane group C–NH–CO–O–C was assumed to be planar and all the bond angles were set at 120°. For the central C–CH$_2$–C bridge, the C–C bond length was taken as 1.56 Å, as in the MeMMel structure[5]; the C–Ĉ–C bridge angle (τ) was varied over the range 105°–120°, as detailed below.

CONFORMATIONAL ANALYSIS

Semi-empirical calculations

The total potential energy (V_{tot}) for the polymer chain was calculated by summing the contributions of the non-bonded (V_{nb}), electrostatic (V_{es}), and torsional (V_{tor}) interactions, and the bond-angle (V_τ) deformations:

$$V_{tot} = V_{nb} + V_{es} + V_{tor} + V_\tau$$

The above terms are calculated using the equation given by Scheraga and coworkers[27,28]:

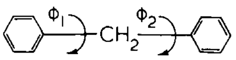
$$V_{nb}(i,j) = \varepsilon_{ij}\left(F\left(\frac{\langle r_g\rangle_{ij}}{r_{ij}}\right)^{12} - 2.0\left(\langle r_g\rangle_{ij}/r_{ij}\right)^{6}\right) \quad (1)$$

where r_{ij} is the distance between the ith and jth atoms, and ε_{ij} and $\langle r_g\rangle_{ij}$ are constants depending on the types of atoms.

$$V_{es}(i,j) = 332\frac{q_i q_j}{\varepsilon' r_{ij}} \quad (2)$$

where q_i and q_j are the partial charges on the ith and jth atoms, calculated using the CNDO/2 method[29]. These partial charges were calculated for the minimum energy conformation derived using partial charges obtained by classical Del Re[30] and Hückel methods[31] and the actual values obtained by CNDO/2 method are shown in *Figure 4*.

The torsional potential function associated with the rotation about



used by Scheraga and coworkers[32] can be expressed as

$$V_{tor}(\varphi_1, \varphi_2) = V_{tor}(\varphi_1) + V_{tor}(\varphi_2) \quad (3)$$

where $V(\varphi_1)$ and $V(\varphi_2)$ are the inherent potentials arising from the bond torsion of C–CH$_2$–C bonds are of the form:

$$V_{tor}(\varphi_1) = \frac{V_{rot}}{2}(1 + \cos 6\varphi_1) \quad (4)$$

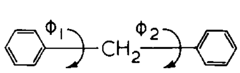
$$V_{tor}(\varphi_2) = \frac{V_{rot}}{2}(1 + \cos 6\varphi_2) \quad (5)$$

where V_{rot} is the barrier height; a value of 0.58 kcal mol^{-1} has been assigned for V_{rot} by Scheraga *et al.*[32]. The torsional potential about the C–N (phenyl–urethane) bond has been assumed to be zero[33]. The energy associated with deformation of the bridge C–CH$_2$–C angle, τ, was calculated using the expression given by Hendrickson[34]

$$V_\tau = K_{CCC}\alpha^2 + 2K_{HCC}(\nu_1^2 + \nu_2^2) + K_{HCH}\beta^2 \quad (6)$$

The angles α, ν_1, ν_2, and β are related to the distortions from the assigned normal values, and the constants K_{CCC}, K_{HCC}, and K_{HCH} are given in ref 34.

The potential energy in the central



unit was minimized using the Fletcher–Powell–Davidson method[35,36]. In this procedure, a number of possible conformations were chosen with different (φ_1, φ_2) conformation angles, and these variables were allowed to reach a local minimum on a two dimensional surface. The lowest minimum obtained was taken as the global minimum.

Molecular orbital calculations

In addition to using the CNDO/2 method[29] for calculation of the partial charges for use with the electrostatic potential functions in the semiempirical energy calculations above, it was also used to calculate the energy

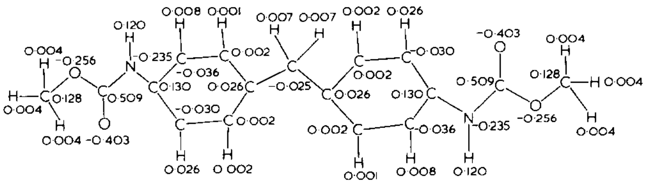


Figure 4 Charge distribution in MDI

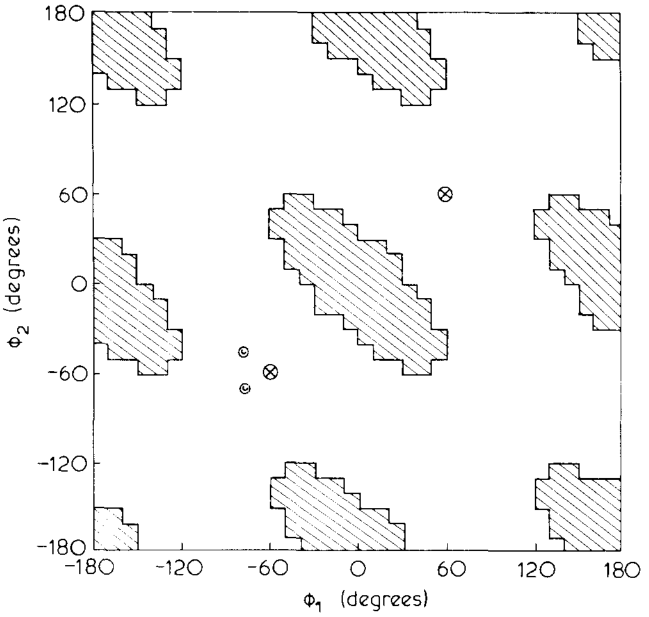
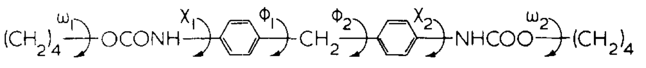


Figure 5 Extreme-limit contour for phenyl$\xrightarrow{\phi_1}$CH$_2$$\xrightarrow{\phi_2}$phenyl fragment (for $\tau = 118.3°$). The shaded regions represent disallowed conformations. x Position of minimum energy; © ϕ_1, ϕ_2 conformations observed in the crystal structures of model compounds (see text)

of sections of the molecule. This approach was used to investigate the possible effects of interaction between the π orbitals on the phenyl and urethane groups, which is not included in the treatment of the atoms as points in the semi-empirical calculations.

RESULTS AND DISCUSSION

The phenyl and urethane groups are planar and will be assumed to be rigid. Hence the conformation of the chain can be described in terms of the following torsion angles:



This is a long repeat, but as a result of the chemistry, the conformation of the chain will be determined largely by the interactions between contiguous groups. Thus we need to examine the phenyl–phenyl and phenyl–urethane interactions, the possible conformations of the $(CH_2)_4$ chain, and finally the $(CH_2)_4$–urethane interactions.

Phenyl–phenyl interactions

Conformational calculations for the diphenyl methane unit were initiated by calculating the extreme limit contour[37], based on contact criteria applied to the conformations obtained when φ_1 and φ_2 were varied in 10° increments. The results obtained are presented in *Figure 5*, which shows the allowed and disallowed regions for (φ_1, φ_2). For this map the bridge C–CH$_2$–C angle was set at 118° (see below). Only minor changes occur in the allowed region of the contact map when the bridge angle is varied between 110° and 120°.

In the second step the minimum energy conformation was found using the Fletcher–Powell–Davidson minimization method. The energy was minimized for 180 different starting conformations taken from throughout the allowed region in *Figure 5*. Two symmetry related global minima were obtained, at $(\varphi_1, \varphi_2) = (-60°, -60°)$, and $(+60°, +60°)$. In these conformations the planes of the benzene rings are perpendicular to each other, and this inclination is observed (approximately) in all diphenyl methane structures studied so far. In addition to the global minima, five other subsidiary minima exist, as shown in *Table 2*. These have energies 0.91–1.86 kcal mol^{-1} higher than the global minimum. The coordinates of these minima are fully refined, and they correspond to other staggered conformations of the CH$_2$–phenyl grouping: the phenyl–CH$_2$ interactions are acceptable but there are unsatisfactory phenyl–phenyl interactions. In these conformations the phenyl groups are not mutually perpendicular, and this appears to be an important feature in stacking the molecules as discussed below. For this reason, the subsidiary minima were rejected in favour of the $(-60°, -60°)$ and $(+60°, +60°)$ conformation. In MeMMeI, the molecule is not symmetrical with $(\varphi_1, \varphi_2) = (-74°, -36°)$ and has an energy 1.12 kcal mol^{-1} above the minimum; in HO–BMB–OH, the molecule is symmetrical and the values of $(\varphi_1, \varphi_2) = (-74°, -74°)$ set the energy 0.53 kcal mol^{-1} above the minimum.

Finally we investigated the dependence of the minimum energy conformation on the C–CH$_2$–C bridge angle (τ). With (φ_1, φ_2) at the $(-60°, -60°)$ starting position, the value of τ was varied in 1° increments from 105° to 120°, and held constant so that the conformational energy could be minimized at each position, using the semi-empirical method. The (φ_1, φ_2) angles changed by less than 0.1° from the $(-60°, -60°)$ starting position. The energy due to distortion of the bridge angle V_τ was computed separately and added to the conformational energy at the minimum, and the total conformational energy is plotted as a function of τ in *Figure 6*. The minimum is at 110°, the tetrahedral angle, and increases smoothly on either side, except that there is a small inflection at 118.3°, 1.9 kcal mol^{-1} higher than the minimum. The angle between planes of the phenyl groups, θ, was calculated for each minimum energy conformation and is also shown in *Figure 6*, where it can be seen that $\theta = 90°$ at the energy inflection point, $\tau = 118.3°$.

In order to check for possible effects due to interactions of the π orbitals of the phenyl groups, the CNDO/2 method was used to calculate the energy for the $(\varphi_1, \varphi_2) = (-60°, -60°)$ conformations having different values of τ. The plot of energy against τ is shown in *Figure 6*, and is not significantly different in shape from that obtained by the semi-empirical method.

The predicted values of τ and θ are in good agreement with those seen for model compounds. The observed values of $\tau = 115.3°$ and 114.5° and $\theta = 89.6°$ and 89.2° for the two forms of MeMMe[5,8] are in very good agreement

Table 2 Minimum energy conformations of the phenyl$\xrightarrow{\phi_1}$CH$_2$$\xrightarrow{\phi_2}$phenyl fragment

	Initial conformation (degrees)		Minimized conformation (degrees)		Relative energy
No	ϕ	ϕ	ϕ_1	ϕ_2	(kcal mol^{-1})
1	− 60	− 60	− 60	− 60	0.00
2	+ 60	+ 60	+ 60	+ 60	0.00
3	− 60	+ 60	− 60	+ 60	0.91
4	+ 60	− 60	+ 60	− 60	0.91
5	− 70	+170	− 60	+180	1.03
6	+ 80	+160	+ 60	−180	1.03
7	−140	+110	−125	+125	1.86

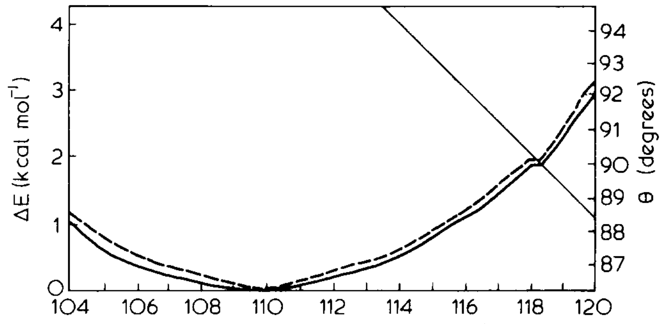


Figure 6 Plot of the relative energy of the minimum energy conformation of the phenyl–CH_2–phenyl unit as a function of τ, the bridge C–CH_2–C angle: ——— CNDO/2 method; — — — — semi-empirical method. The straight line curve (top right) is a plot of θ, the inclination of the phenyl rings at the energy minimum, as a function of τ

with the predictions for the point of inflection. Early work on non-urethane diphenyl methanes gave $\tau = 119.2°$ and $\theta = 104°$ in 3,3'-dichloro-4,4'-dihydroxy diphenylmethane[38], and $\tau = 116.7°$ and $\theta = 95.0°$ in 4,4'diamino–diphenylmethane[39]. Recently we have determined the structure of HO–BMB–OH[9] for which $\tau = 105°$ and $\theta = 98°$. Of these structures the MeMMe compounds are most analgous to the polymer: the structure of HO–BMB–OH appears to be complicated by hydrogen bonding of the terminal hydroxyls, leading to a hydrogen bonding network completely different from any possible in the polymer, and the other diphenylmethanes do not have urethane groups. We have selected $\tau = 118.3°$ for the bridge angle in the model described below, since this leads to perpendicular phenyl rings. This choice is not critical to the rest of the discussion, except to the extent that a lower value of τ would lead to a small contraction of the fibre repeat.

Urethane–phenyl interactions

Using the semi-empirical energy calculations, the potential energy of the phenyl–urethane unit was calculated, varying χ in 10° intervals. A plot of relative energy against χ is shown in *Figure 7* (curve A). It can be seen that two minima are predicted at $\chi = \pm 90°$, corresponding to the symmetry related orientations of the urethane groups exactly perpendicular to the benzene rings. The values for χ in the structure of MeMMeI are $\chi_1 = -143.2°$ and $\chi_2 = 16.2°$; for HO–BMB–OH, $\chi_1 = \chi_2 = -156.3°$. All these values are away from the predicted minima and the differences are too large to be accounted for solely by hydrogen bonding. It seemed possible that favourable interaction between π orbitals of the urethane and phenyl groups may occur in the region of $\chi = 0°$ and $\chi = 180°$, when these groups are coplanar. For this reason the calculation was repeated using the CNDO/2 method and the resultant energy curve is plotted in *Figure 7* (curve B). The curve has the same form as that obtained using the semi-empirical functions, but the difference between maxima and minima has declined. Nevertheless the observed values for χ above are respectively 2.5, 4.0, and 4.0 kcal mol^{-1} higher than at the minimum. It is likely that the need to form hydrogen bonds will account for some of these differences. In addition, the energy of interaction due to stacking of the diphenylmethanes may be responsible for stabilizing the molecular conformation. Similar problems have been reported in the conformational and packing analyses of nucleic acid constituents where the experimentally observed conformation frequently has a relative energy of 2–5 kcal mol^{-1} higher than that of the predicted minimum. This has been discussed in detail[40–42] and is thought to be due to the effect of hydrogen bonding and stacking of the bases.

Conformation of the $(CH_2)_4$ group

The conformation of $(CH_2)_4$ chains has been studied considerably, and it is known that the all *trans* planar zigzag conformation corresponds to the energy minimum. It is significant that the planar zigzag conformation for $(CH_2)_4$ is found in HO–BMB–OH. However, the energy differences due to inclusion of some *gauche* conformations in the $(CH_2)_4$ chain are small compared to the increases resulting from changes in the urethane–phenyl conformation, and alternatives to the planar zigzag need to be considered for the polymer.

Indications of the conformation of the $(CH_2)_4$ unit come from the observed fibre repeat, $c = 37.9$ Å, which corresponds to 18.95 Å per $c/2$ repeat. Considerations of the phenyl and urethane interactions above, lead to the following conformational combinations for the diphenylmethane diurethane unit:

$$\chi_1 = \pm 90°,\ \varphi_1 = -60°,\ \varphi_2 = -60°,\ \chi_2 = \pm 90°$$

plus the symmetry related set for $(\varphi_1, \varphi_2) = (+60°, +60°)$. Taking $\tau = 118°$, which is close to the upper limit for this angle, then the lengths of this unit are: 12.3 Å for $(\chi_1, \chi_2) = (+90°, +90°)$; 13.0 Å for $(\chi_1, \chi_2) = (-90°, +90°)$ and $(+90°, -90°)$ and 14.0 Å for $(\chi_1, \chi_2) = (-90°, -90°)$, as measured between the terminal oxygens. Only small variations in (φ_1, φ_2) are seen in model compounds ($\pm 15°$) and these have little effect on the overall length. Large variations occur in χ_1 and χ_2 in the model compounds, but since the terminal oxygen is almost colinear with N–C(phenyl), the length of the diphenylmethane diurethane unit is relatively insensitive to χ_1 and

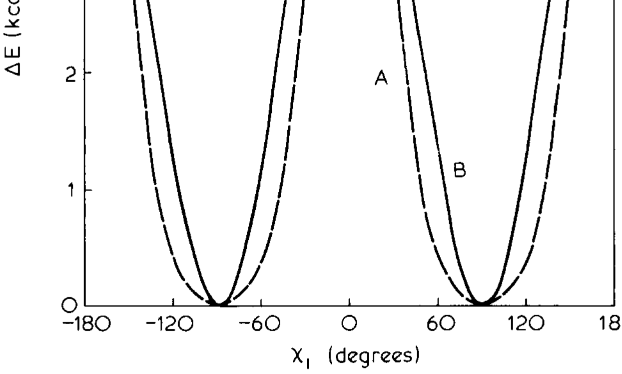


Figure 7 Plot of the relative energy of the phenyl-urethane fragment as a function of χ_1. A, — — — semiempirical method; B, ——— CNDO/2 method

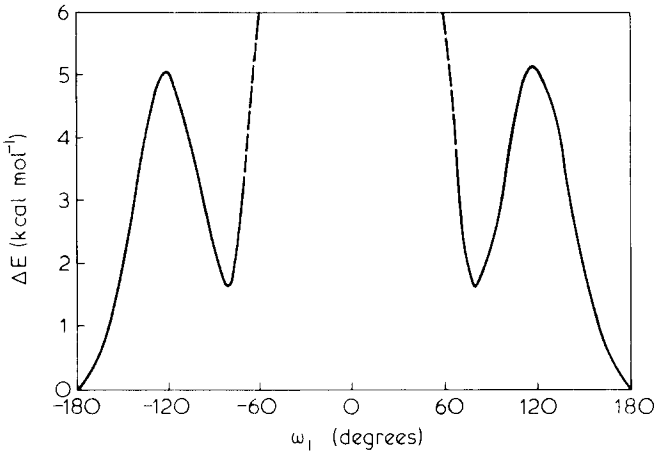


Figure 8 Plot of the relative energy of the urethane–$(CH_2)_4$ unit as a function of ω_1. A planar zigzag conformation was assumed for the butandiol (see text)

χ_2 (this is illustrated by the small effect of 180° changes in χ). Thus the remaining length of the repeat must be made up by the O $(CH_2)_4$ O chain. In the most extended planar zigzag conformation, the O···O length for the O–$(CH_2)_4$–O unit is 6.25 Å. With only a single *gauche* bond, the length is reduced to 5.34 Å. From this it is clear that the observed repeat of 18.95 Å cannot be achieved unless the O–$(CH_2)_4$–O unit is a planar zigzag. In addition, as a result of the extended fibre repeat, the χ_1, χ_2 conformation will be closer to (−90°, +90°) than to the other ±90° combinations.

Urethane $(CH_2)_4$ *interaction*

The results of a semi-empirical calculation to determine the most likely urethane–$(CH_2)_4$ conformation are shown in *Figure 8*, where the conformational energy is plotted as a function of ω_1. Not surprisingly the plot shows a minimum at $\omega_1 = 180°$, corresponding to the all *trans* conformation, in which the urethane–$(CH_2)_4$–urethane unit would be completely planar. Subsidiary maxima of 1.5 kcal mol^{-1} higher than that at 180° are predicted at $\omega_1 = \pm 80°$, which are close to the *gauche*$^+$ and *gauche*$^-$ conformations. These are 20° from the ±60° position to avoid interaction between the terminal (CH_2) and the carbonyl oxygen. A torsion angle of $\omega_1 = -69.5°$ is seen for HO–BMB–OH, where the planar $(CH_2)_4$ OH group is not coplanar with the urethane.

Conformation of the polymer chain

Consideration of contiguous group interactions have predicted the following conformational angles as the most likely for the isolated chain:

phenyl–phenyl:

$$\tau = 118.3°, \ \theta = 90°, \ \varphi_1 = -60° \text{ and } \varphi_2 = -60°$$

phenyl urethane:

$$\chi_1 = -90 \text{ and } \chi_2 = 90$$

urethane butanediol:

$$\omega_1 = \omega_2 = 180$$

Fletcher–Powell–Davidson minimization for a variety of starting conformations, taking χ_1 and χ_2 as variables always resulted in final conformations close to the above values. A projection of the polymer chain in this conformation is shown in *Figure 9*.

We can be reasonably confident that these angles are close to those in the solid state structure, except for χ_1 and χ_2. The values seen for the χ angles in the model compounds suggest that large deviations in χ_1 and χ_2 may be acceptable in order to optimize the intermolecular interactions. It is probable that the stacking interactions for the diphenylmethanes are the major contribution to this effect for the model compounds. As indicated above, the fibre repeat is relatively insensitive to χ_1 and χ_2. *Table 3* shows fibre repeats for centrosymmetric chains with different values of χ_1 and χ_2, and it can be seen that deviations from $(\chi_1, \chi_2) = (-90°, +90°)$ in the range seen in model compounds do not change the residue repeat by more than 0.2 Å. The values of (χ_1, χ_2) used in *Table 3* all lead to chains which are not only centrosymmetric but have a perpendicular two-fold axis through the CH_2 of the diphenylmethane. This is a consequence of the chemical symmetry. Such two-fold symmetry is seen for MeMMeII[8] and HO–BMB–OH[9], but not for MeMMeI[5], which is thought to be the best model for the likely hydrogen bonding in the polymer. A non-two-fold chain results for non-symmetrical deviations of (χ_1, χ_2) from the (−90°, +90°) position; the centre of symmetry is retained provided $\chi_2 = \chi_1' + 180°$, where χ_1' is the value of χ_1 for the next monomer unit along the chain. The effect on the fibre repeat of this type of deviation from two-fold symmetry can be estimated by interpolation of the data in *Table 3*, and will be relatively minor within the possible range of variation for χ_1 and χ_2. The structure proposed by Blackwell and Gardner[6] has a non-two-fold conformation for the chain, as a consequence of the asymmetry of the MeMMeI structure.

We are now proceeding on a packing analysis of this polymer, starting with the $(\chi_1, \chi_2) = (-90°, +90°)$ chain and then considering many possible variations of χ_1 and χ_2. This work will be published in due course. Our research is supported by ARO Grant No. DAAG29-79G-0070.

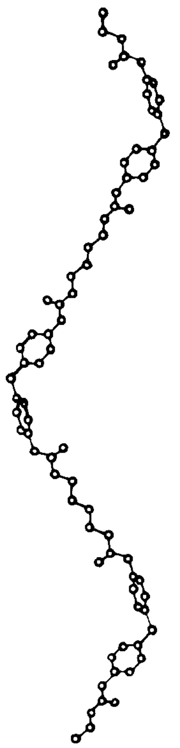


Figure 9 Projection of the conformation of the poly(MDI-butandiol) chain as defined in *Table 3*. The repeat is 37.9 Å and contains two monomers (i.e. the rise per monomer along the chain axis is 18.95 Å)

Table 3 Minimum energy conformations of the MDI-butanediol fragment

No	Initial conformation (degrees) ω_1	χ_1	ϕ_1	ϕ_2	χ_2	ω_2	Relative energy (Kcal mol^{-1})	Length of the MDI-butanediol fragment c/2 (Å)
1	−180	− 90	−60	−60	90	180	0.00	18.95
2	−180	−100	−60	−60	80	180	0.32	19.02
3	−180	−110	−60	−60	70	180	0.88	19.06
4	−180	−120	−60	−60	60	180	1.62	19.09
5	−180	−130	−60	−60	50	180	2.58	19.06
6	−180	−140	−60	−60	40	180	3.92	19.02
7	−180	−150	−60	−60	30	180	5.35	18.95
8	−180	−160	−60	−60	20	180	7.03	18.86
9	−180	−170	−60	−60	10	180	9.12	18.77

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NOTE ADDED IN PROOF

In a recent paper by Hummel and Flory (*Macromolecules* 1980, **13**, 479), these authors have considered the conformations of *p*-phenylene polyamides and polyesters, and their conclusions with respect to the phenyl–amide and phenyl–carboxyl orientations are relevant to our discussion of the phenyl–urethane conformation. Specifically in the case of the phenyl–amide orientation, semi-empirical calculation of non-bonded, strain, and coulombic energies led to a minimum at $\chi = \pm 90°$, i.e. perpendicular phenyl and amide groups, whereas model compounds generally crystallize with χ close to $\pm 30°$ (or $\pm 150°$). With regard to this the results are very similar to ours for the phenyl–urethane conformation. Hummel and Flory therefore apply a torsional potential function to model the effect of electron delocalization, which would tend to produce a planar phenyl–amide conformation: the potential function has the form $E_{\text{delocalization}} = -B \cos^2 \chi$, and leads to a total energy minimum at $\chi = \pm 30°$ when $B = 7$ kcals mol^{-1}. Such an approach has been used previously for the same structure by Tadokoro and coworkers, (*Macromolecules* 1977, **10**, 413), who proposed $B = 16$ kcals mol^{-1}. Application of a similar torsional potential function to our phenyl–urethane system would lead to values of χ_1 and χ_2 that match the model compound data, and would produce only small changes in the fibre repeat of the polymer (see *Table 3*).

The magnitude of B for the phenyl–amide system was selected simply to achieve the best fit between the observed and calculated values of χ. This assumes that the polymer conformation is determined exclusively by intramolecular effects, although packing forces such as ring stacking and hydrogen bonding should also play a role. When chains poly(MDI-BDO) in the χ_1, $\chi_2 = -90°$, $+90°$ conformation are hydrogen bonded together, large holes occur between the chains; these holes are eliminated and the phenyl rings stack on top of each other when the conformation is changed e.g. to χ_1, $\chi_2 = +150°$, $-30°$. At this point it is not clear what is the extent of the role of electron delocalization, in addition to packing forces, in determining the chain conformation in the crystalline hard segments.