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Free-rotation dimensions of some polyurethane chains

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Abstract

The ratio of the unperturbed mean-square end-to-end distance to the molecular weight in the random-coil limit, $(\langle R^2\rangle_{0,f}/M)_\infty$, in the free-rotation approximation was calculated for chains of linear polyurethanes PUR–D_k prepared from 4,4′-methylenediphenyl diisocyanates and low-molecular-weight diols HO–$(CH_2)_k$–OH (k = 2, 3, 4 and 6). It was found that the experimental values of $(\langle R^2\rangle_0/M)_\infty$ estimated in the previous paper are very close to the values of $(\langle R^2\rangle_{0,f}/M)_\infty$ calculated under the assumption that the groups of bonds CH_2–C_6H_5–NH and NH–CO–O–CH_2 can be replaced by rigid virtual bonds.

Keywords: Polyurethane chains, Free-rotation dimensions, Steric factor σ

1. Introduction

The importance in practice of segmented polyurethanes (PUR) is due to their solid-state properties that result from the combination of 'soft' and 'hard' segments [1]. The former are constituted by oligomeric polyesters or polyethers (mostly aliphatic). The latter comprise urethane units (usually aromatic) and low-molecular-weight diols (as chains extender). By reacting a diisocyanate and a diol, one can obtain polyurethanes which contain no soft component and can therefore serve as a model of the hard segment. In a previous study [2], such polymers (PUR–D_k) (Fig. 1) were prepared from 4,4-methylene diphenyl diisocyanate (MDI) and diols HO–$(CH_2)_k$–OH (with k = 2, 3, 4 and 6). Their dilute solution properties were studied by viscometry and light scattering, and the values of the Kuhn statistical segment l_k were estimated. They are low (~1.3 nm), which is surprising in view of the presence of long and rigid phenylene units in the main chain.

Another characteristic of the flexibility of polymer chains is the steric factor σ, defined [3,4] by

$$\sigma = \left(\langle R^2\rangle_0/M\right)_\infty / \left(\langle R^2\rangle_{0,f}/M\right)_\infty \quad (1)$$

where $\langle R^2\rangle_0$ is the unperturbed mean-square end-to-end distance of the real chain, $\langle R^2\rangle_{0f}$ is the corresponding quantity for a freely rotating model chain, M is the polymer molecular weight, and the subscript ∞ denotes the random-coil limit. In order to estimate σ, one needs the value of $(\langle R^2\rangle_{0,f}/M)_\infty$ for the model chain in which the bond lengths and bond angles are fixed whereas the rotation about the main chain bonds is free. Equations for such a calculation have long been known for relatively simple polymer chains [3–5]. A general equation has been derived for chains containing segments of any number of bonds [6]. It has been applied to several aliphatic and aromatic polyesters and polyamides [7].

The repeating units of polyurethanes comprise, in various proportions, several types of bond differing in lengths and angles. Derivation of general equations for such chains would be tedious. It is easier, and the results are more convenient to handle, if the repeating units are symmetric as is the case for polyurethanes PUR–D_k (Fig. 1). In the present paper, equations for this case are derived and the values of $(\langle R^2\rangle_{0,f}/M)_\infty$ calculated for PUR–D_k chains are compared with the experimental values of $(\langle R^2\rangle_0/M)_\infty$.

2. Theoretical

The end-to-end vector $\bar{r}$ of the chains containing N bonds is calculated as the sum of the individual bond vectors $\bar{r}_i$

$$\bar{r} = \sum_{i=1}^{N} \bar{r}_i \quad (2)$$

and the square end-to-end distance r^2 is obtained as the scalar product

$$r^2 = \bar{r}\cdot\bar{r} = \sum_{i=1}^{N}\sum_{j=1}^{N} \bar{r}_i\cdot\bar{r}_j \quad (3)$$

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-*CH_2-[Ph-NH-CO-O-$(CH_2)_k$-O-CO-NH-Ph-CH_2]-

Fig. 1. Repeating unit of PUR–D_k chains.

If free rotation is assumed, then

$$\bar{r}_i \cdot \bar{r}_j = r_i \cdot r_j \prod_{k=1}^{j-1} \cos \gamma_k \tag{4}$$

(where γ_k is the bond angle between two successive main chain bonds), and the mean-square end-to-end distance $\langle r^2 \rangle_0$ (unperturbed by the excluded-volume effect) is

$$\langle R \rangle_{0,f} = \langle \bar{r}_1 \cdot \bar{r}_1 \rangle + \langle \bar{r}_1 \cdot \bar{r}_2 \rangle + \ldots + \langle \bar{r}_1 \cdot \bar{r}_N \rangle + \langle \bar{r}_2 \cdot \bar{r}_1 \rangle + \langle \bar{r}_2 \cdot \bar{r}_2 \rangle + \ldots + \langle \bar{r}_2 \cdot \bar{r}_N \rangle \ldots + \langle \bar{r}_N \cdot \bar{r}_1 \rangle + \langle \bar{r}_N \cdot \bar{r}_2 \rangle + \ldots + \langle \bar{r}_N \cdot \bar{r}_N \rangle \tag{5}$$

where

$$\langle \bar{r}_i \cdot \bar{r}_j \rangle = \langle \bar{r}_j \cdot \bar{r}_i \rangle \tag{6}$$

Following the method outlined by Evans et al. [5], the calculation is divided into the following steps:

1. The products $\langle \bar{r}_i \cdot \bar{r}_j \rangle$ are evaluated (1.1) for bonds within a repeating unit (term Y), (1.2) for bonds belonging to neighbouring units (term A), (1.3) for bonds belonging to repeating units separated by one repeating unit (term $C \cdot A$), and (1.4) for bonds belonging to repeating units separated by U repeating units.
2. The sum of products sub (1.4) is calculated as [5]

$$\left[(p-1) - U\right] \cdot C^U \cdot A \tag{7}$$

3. The sum of products within the pair of terminal repeating units (1 to p) is computed as

$$C^{p-2} \cdot A \tag{8}$$

where C is the recurrent term

$$C = \sin \beta \cdot \prod_{i=1}^{k} \cos \gamma_i \tag{9}$$

and β is the bond angle between two repeating units. The mean-square end-to-end distance for a freely rotating chain is

$$\langle r^2 \rangle_{0,f} = p \cdot Y + A \cdot B \tag{10}$$

where

$$B = (p-1) + (p-2)C + (p-3)C^2 + \ldots C^{p-2}. \tag{11}$$

Evans et al. [5] have shown that

$$B = \left[p(1-C) + \left(C^p - 1\right)\right] \cdot (1-C)^{-2} \tag{12}$$

From Eqs. (10) and (12) we obtain

$$\langle R^2 \rangle_{0,f}/p = Y + A(1-C)^{-1} + \left(C^p - 1\right)p^{-1} \cdot (1-C)^2 \tag{13}$$

and, for p $\rightarrow \infty$,

$$\left(\langle R^2 \rangle_{0,f}/p\right)_\infty = Y + A(1-C)^{-1} \tag{14}$$

In Section 2.1 and Section 2.2, the terms Y and A are derived for chains where the repeating units are symmetric either around the central group (if the number m of main chain bonds in the repeating unit is even, $m = 2k$) or around the central bond (for odd values $m = 2k - 1$). Calculations are lengthy but straightforward and are simplified by this symmetry.

2.1. *Even number* m *of main chain bonds*

In this case ($m = 2k$) the following relations hold:

$$l_i = l_{2k+1-i} \text{ and } \gamma_i = \gamma_{2k-1} \tag{15}$$

(where $i = 1$ to k). The bond angle at the central group γ_k is unpaired. The general equations (obtained from the results for $k = 2$ to 4) are

$$Y = 2\sum_{i=1}^{k} l_i^2 (1 + C_i) + 4\sum_{j=1}^{k-1} l_j \sum_{i=j+1}^{k} \left(C_j/C_i\right)^{1/2} (C_i + 1) l_i \tag{16}$$

and

$$A/\cos\beta = 2\sum_{i=1}^{k} l_i^2 (1 + C_i)^2 (C_1/C_i) + 4\sum_{j=1}^{k-1} \sum_{i=j+1}^{k} l_j (1 + C_j)\left(C_1/C_j\right)^{1/2} l_i (1 + C_i)(C_1/C_i) \tag{17}$$

where

$$C_1 = \alpha_1 \alpha_2 \ldots \alpha_k^{1/2}, \tag{18}$$

$$C_2 = \alpha_2 \alpha_3 \ldots \alpha_k^{1/2},$$

$$\ldots$$

$$\ldots$$

$$C_k = \alpha_k^{1/2}$$

and

$$\alpha_i = \cos^2 \gamma_i \text{ for } i = 1 \text{ to } k. \tag{19}$$

2.2. *Odd number* m *of main chain bonds*

In the case where $m = 2k - 1$, all bond angles are paired:

$$\gamma_i = \gamma_{2k-1-i} \text{ for } i = 1 \text{ to } (k-1). \tag{20a}$$

The same holds for the bond lengths except for the central bond l_k

$$l_k = l_{2k-1} \tag{20b}$$

Calculations were made for $k = 3$, 5, 7 and 9 and the results

were recast into the forms

$$Y = l_k^2 + 2\sum_{i=1}^{k-1} l_i^2(1+D_i) + 4l_k\sum_{i=1}^{k-1} l_i \cdot D_i^{1/2} + 4\sum_{i=1}^{k-1}\sum_{j=1}^{i-1}(l_i/D_i^{1/2})(1+D_i)l_jD_j^{1/2} \quad (21)$$

and

$$A/\cos\beta = 2D_1\left[l_k^2 + \sum_{i=1}^{k-1}(l_i^2/D_i)\cdot(1+D_i)^2\right] + 4D_1\sum_{i=1}^{k-1}(l_i/D_i^{1/2})\cdot(1+D_i)\cdot\left[l_k + \sum_{j=1+1}^{k-1}(l_j/D_j^{1/2})\cdot(1+D_j)\right] \quad (22)$$

where

$$D_1 = \alpha_1\alpha_2\ldots\alpha_{k-1}, \quad (23)$$

$$D_2 = \alpha_2\ldots\alpha_{k-1},$$

$$\ldots$$

$$D_{k-1} = \alpha_{k-1}$$

and

$$\alpha_i = \cos^2\gamma_i \text{ for } i = 1 \text{ to } (k-1). \quad (24)$$

3. Results and discussion

Eq. (13), together with Eqs. (16) and (17) or with Eqs (21) and (22), is used to calculate the ratio $(\langle R^2\rangle_{0,f}/M)_\infty$ and the σ parameter for PUR–D_k. As follows from the definition, the steric factor reflects the directional correlations of main-chain bonds in the real chain which result from restricted rotations. In the PUR–D_k chains there is a difference in the degree of correlation between the bonds linking the CH_2 and NH groups to benzene rings and other skeletal bonds. The orientation of the bonds CH_2–Ph and Ph–NH with respect to the *p*-phenylene ring is fully fixed by the planarity and rigidity of the latter [8,9]. It is expedient, therefore, to replace the segment CH_2–Ph–NH by one rigid virtual bond (cf. [2]) because such a model chain is closer to the real one so that the σ parameter is more meaningful.

This assumption is used in calculations of the values of $(\langle R^2\rangle_{0,f}/M)_\infty$ for Model **I**. Free rotation is allowed about all main chain bonds except those situated within the segment CH_2–Ph–NH. The repeating unit contains two virtual bonds CH_2–Ph–NH and $(k+5)$ real bonds, i.e. $(k-1)$ CH_2–CH_2 and two NH–CO, CO–O and O–CH_2 bonds each (Fig. 2, **I**).

The CO–NH and CO–O linkages in amides and esters are known to be planar because of their partial double bond character [3,8] (with prevalence of *trans* configuration). Due to this fact, the set of bonds C–CO–O–C in polyesters and C–CO–NH–C in polyamides and polypeptides is usually treated as a hypothetical virtual bond. Therefore, it seems interesting to assess the effect of this factor on the value of $(\langle R^2\rangle_{0,f}/M)_\infty$ for PUR–D_k chains. As, however, the conformation of the urethane group NH–CO–O is not fully known, calculations can be made for two limiting structures, namely NH=C–O and NH–CO=O– (Models **II** and **III**). Details can be seen on Fig. 2.

The following values of bond length (in nm) and bond angles are used in the calculations [3,9]: 0.133 for NH–CO and O–CO, 0.144 for O–C (aliphatic), 0.150 for *C–Ph, 0.153 for C–C (aliphatic), 0.143 for NH–Ph, 125° for < Ph–NH–CO, 119° for < N–CO–O, 117° for < CO–O–CH, 110° for < O–C–C, and 110° for < C–C–C. The lengths of virtual bonds are 0.57 nm for *CH–Ph–NH [9], 0.357 for CO–O–C and 0.776 nm for *CH–Ph–NH–CO. These values, as well as those of angles between the virtual and the real bonds (Fig. 2), have been obtained by simple geometric considerations.

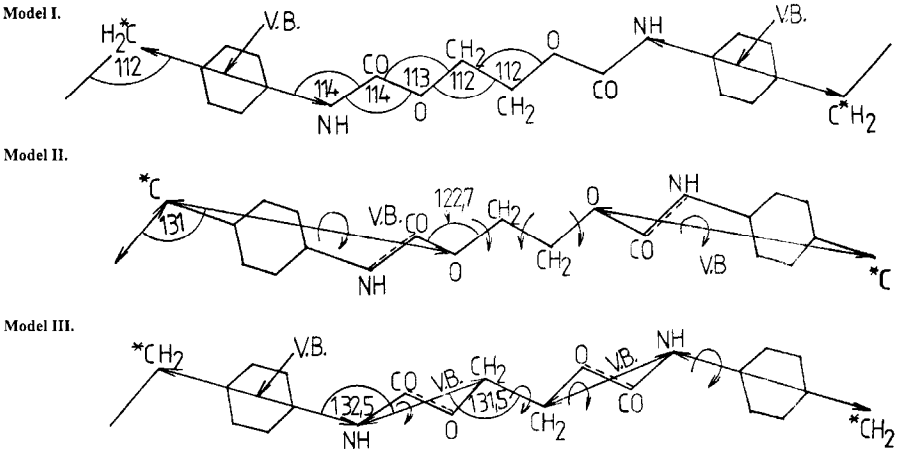

Fig. 2. Models of PUR–D_k chains. Virtual bonds (V.B.) are denoted by arrows ↔ , free rotation by ↻. Bond angles in degrees.

Table 1
Unperturbed dimensions of PUR–D_k chains

k:	2	3	4	6
$(\langle R^2\rangle_0/M)_\infty \times 10^{16}$ (cm^2) (experimental, from [η])	0.8	0.77	0.75	0.78
Model **I**				
$(\langle R^2\rangle_{0,f}/M)_\infty \times 10^{16}$ (cm^2)	0.465	0.44	0.45	0.45
σ	1.31	1.32	1.29	1.32
Model **II**				
$(\langle R^2\rangle_{0,f}/M)_\infty \times 10^{16}$ (cm^2)	0.55	0.54	0.50	0.53
σ	1.21	1.19	1.22	1.21
Model **III**				
$(\langle R^2\rangle_{0,f}/M)_\infty \times 10^{16}$ (cm^2)	0.82	0.67	0.66	0.71
σ	0.99	1.07	1.07	1.05

The values of $\langle R^2\rangle_{0,f}$ and σ depend, to some extent, on the values of bond angles used in calculations. To estimate this effect, calculations have been made with the above basic set of bond angles and with four sets in which all bond angles of the basic set are decreased or increased by 1, 2, 3 and 4°. Variations in this range bring about a variation of $\pm$ 8 in $\langle R^2\rangle_{0,f}$. Though this uncertainty might be serious if dissimilar polymer chains were compared, it is of less importance in the present case where variation in bond angles would probably be the same for all polymers.

The results of calculations for the basic set of bond angles are listed in Table 1. They show that the values of $(\langle R^2\rangle_{0,f}/M)_\infty$ and σ are almost independent of the number k of methylene groups in the diol unit. The result for Model **III** is an exception.

The values of σ for Model **I** (with two rigid virtual bonds per repeating unit) are low and lend support to the conclusion of the previous paper [2] that, in spite of the presence of long and rigid C–Ph–Nh units, the PUR–D_k chains exhibit fairly high flexibility.

Although, because of the character of Models **II** and **III**, the results based on them cannot be taken too literally, an increase in length (Model **II**) or number (Model **III**) of virtual bonds in the repeating unit (with a concomitant decrease in the number of freely rotating bonds) brings about a significant increase in $(\langle R^2\rangle_{0,f}/M)_\infty$. It is remarkable that the values of $(\langle R^2\rangle_{0,f}/M)_\infty$ for Model **III** (with four virtual bonds and unhindered rotation about these bonds as well as about the C–C bonds in diol units, Fig. 2) differ from the experimental values by less than 10% and that the steric factor is close to unity.

4. Concluding remarks

The results of the present and previous papers indicate that 'hard' segments of polyurethanes do not lack freedom in assuming various conformations. Therefore, the 'hardness' does not seem to originate from their stiffness but rather from strong intermolecular interactions. It is felt that this opinion should be checked by adapting to polyurethanes the rotational isomeric state model (RIS) where the restricted rotation about the main-chain bonds as well as the shape and interdependence of rotational potentials are taken into consideration [3,10]. A better knowledge of the conformation of urethane groups is a preriquisite of such work, however.

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