polymer

Estimation of conformational characteristics of bisphenol-A based poly(hydroxyethers)

A. Kaštánek[a,*], S. Podzimek[a], J. Dostál[b], L. Šimek[b], M. Bohdanecký[c]

[a]*Synpo Ltd, 532 07Pardubice, Czech Republic*
[b]*Faculty of Technology, Technical University, 762 72 Zlin, Czech Republic*
[c]*Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic*

Abstract

Two samples of bisphenol-A based epoxy resins (poly(hydroxy ethers)) were fractionated by precipitation. The fractions were characterized by the weight-average molecular weight ($1.3 < M_w \times 10^{-3} < 40$) and the intrinsic viscosity in tetrahydrofuran and chloroform. Theories based on the worm-like touched-bead model were used to treat the molecular-weight dependence of the intrinsic viscosity and to estimate the conformational characteristics (Kuhn statistical segment length l_K, Flory characteristic ratio C_∞, and steric factor σ). Low values of these characteristics indicating rather high flexibility of the chain are discussed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Bisphenol-A based epoxy resins; Intrinsic viscosity; Worm-like touched-bead chain model

1. Introduction

Reliable values of the parameters characteristic of the conformation and flexibility of polymer chains (e.g. Kuhn statistical segment length l_K, Flory characteristic ratio C_∞, steric factor σ) are needed for the interpretation of various properties, including the rheological behavior of melts [1]. In spite of a high number of papers devoted to the application of epoxy resins based on bisphenol-A and to the mechanism and statistics of curing reaction, no information on the above parameters is available.

Non-linearity of high-molecular-weight fractions ($M_w > 4 \times 10^4$) was probably the most important factor that impeded the estimation of the conformational parameters from the values of the intrinsic viscosity, second virial coefficient and molecular weight [2]. As branching is attributed mainly to the reaction of epichlorohydrin with secondary hydroxyls [3–5], the probability of chain branching is the higher the higher number of CHOH groups, in other words, the longer the chain. We believed that this obstacle becomes negligible when low-molecular-weight fractions are used.

The estimation of conformational parameters of chains of epoxy resins from the intrinsic viscosity data is the object of the present paper. In Appendix A, the calculation of chain dimensions in the free rotation approximation is presented.

2. Experimental

2.1. Polymers

Sample I was prepared by melting bisphenol-A with a low-molecular-weight epoxy resin at 180°C. Sample II was a commercial product Epicote 1009 (Shell International Chemical Co.). They were fractionated by the precipitation method with chloroform as solvent and petroleum ether as precipitant [6]. The initial concentration was 2 g/dl. Both phases, which separated after addition of nonsolvent were liquid.

2.2. Solvents

Chloroform and petroleum ether were products of Lachema (Brno, Czech Republic). Tetrahydrofuran was a product of Aldrich. Before use they were purified by standard methods.

2.3. Molecular weights

The weight-average molecular weights M_w were determined by means of the size exclusion chromatography coupled with a multiangle laser light scattering photometer (SEC–MALLS). The chromatographic system consisted of a 600 pump, a 717 auto-sampler, a 410 differential refractometer (all Waters) and a DAWN-F photometer or a mini DAWN photometer (Wyatt Technology Corporation). The

---

* Corresponding author.

Table 1
Experimental results (THF, tetrahydrofuran (25°C); LS, light-scattering)

$M_w \times 10^{-3}$	$[\eta]/(dl/g)$		$M_w \times 10^{-3}$	$[\eta]/(dl/g)$	
(LS)	THF	CHCl$_3$	(LS)	THF	CHCl$_3$
Fractions of sample I			Fractions of sample II		
9.0	0.165	0.165	40	0.360	0.305
5.6	0.130	–	18.6	0.260	0.225
4.2	0.110	0.105	39	0.330	0.290
3.1	0.090	0.093	22	0.270	0.230
2.2	0.080	0.080	9.0	0.185	0.180
1.6	0.060	0.065	10.6	0.195	0.190
1.32	0.050	0.052	6.8	0.145	0.145
0.34[a]	0.026	–			

[a] Bisphenol-A bisglycidylether (theoretical molecular weight confirmed by vapor pressure osmometry).

data were collected and handled by ASTRA software (Wyatt Technology Corporation) to yield the weight-average molecular weights. Two Styragel HR 5E (Waters) 300 × 7.8 mm columns or two PL gel Mixed-E (Polymer Laboratories) 300 × 7.5 mm columns were used for measurement. Tetrahydrofuran (THF) was used as an eluent at a flow rate of 1 ml/min. The SEC columns were thermostated at 25°C. The samples were injected as solutions in THF in the amount/concentration 100 μl/1.4% (w/v) (Styragel columns) or 100 μl/3% (w/v) (PL gel columns). The molecular weights listed in Table 1 are arithmetic means of two or three analyses.

2.4. Viscometry

Viscosity of solutions in chloroform (at 20°C) and THF (25°C) were measured by viscometers of the Ubbelohde type adapted for subsequent dilution of the stock solution. The temperature of the bath was kept constant within ±0.05°C. The concentrations c of solutions were in the range 0.2–4 g/dl, depending on the molecular weight. Flow times t of four to six solutions were determined with each fraction and the intrinsic viscosities $[\eta]$ were obtained by linear extrapolations to $c = 0$ of the values of $(t/t_0 - 1)/c$ where t_0 is the flow time of solvent.

3. Results and discussion

3.1. Analysis of the intrinsic viscosity data

In view of low molecular weights of PHE fractions used in this study, the chain dimensions could not be determined by light scattering and had to be estimated from the intrinsic viscosity. For the same reason, these data cannot be treated by methods based on the model of non-draining random coil, so more recent theories, which have been developed for the worm-like chain model and take account of the non-Gaussian chain statistics and various strengths of the hydrodynamic interaction, have to be used [7,8]. These theories

do not consider the excluded-volume effect and, therefore, should be applied to solutions at theta condition only where the second virial coefficient is zero. No theta solvent for PHE is known, however. As follows from the ebulliometric measurements [6] of solutions in chloroform, this solvent is a good one. The same holds for THF as evidenced by the intrinsic viscosities being similar to, or even higher than, those in chloroform. Fortunately, as the excluded-volume effect is very weak with short chains, these theories can provide a starting point for the analysis of data.

According to the theory for the worm-like touched-bead model [8], the intrinsic viscosity at theta condition depends not only on the unperturbed mean-square end-to-end distance $\langle R^2 \rangle_0$, but also on the cross-sectional dimensions such as the diameter d_b of the beads forming the model chain. The results of the theory can be expressed in a simple form convenient for use even with very short chains [9]

$$[\eta]_0 = A_\eta + K_0 \cdot M^{1/2} \tag{1}$$

with

$$K_0 = \Phi_{0,\infty} (\langle R^2 \rangle_0 / M)_\infty^{3/2} \tag{2}$$

$$A_\eta = K_0 \cdot A_0(d_{b,r}) \cdot M_K^{1/2} \tag{3}$$

$$d_{b,r} = d_b / l_K \tag{4}$$

$$l_K = (\langle R^2 \rangle_0 / M)_\infty \cdot M_L \tag{5}$$

$$M_K = l_K \cdot M_L \tag{6}$$

where $(\langle R^2 \rangle_0 / M)_\infty$ is the ratio of $\langle R^2 \rangle_0$ and M in the random-coil limit ($M \to \infty$), $\Phi_{0,\infty}$ is the Flory viscosity constant for random coils in the non-draining regime, $A_0(d_{b,r})$ is a function of the reduced bead diameter $d_{b,r}$, d_b is the bead diameter, l_K and M_K are, respectively, the length and molecular weight of the Kuhn statistical segment, and M_L is the shift factor which is usually set equal to the molecular weight per unit contour length of the chain at full extension.

The molecular-weight dependence of the intrinsic viscosity in good solvents has been described by several theoretical and semiempirical equations [8,9]. Though the simplest of them

$$\alpha_\eta^3 = [\eta]/[\eta]_0 = 1 + C_\eta(n_K) \cdot z... \tag{7}$$

is valid for $\alpha_\eta^3 < 1.5$ only [10], it is used here because most of the α_η^3 values are in this range. The symbol α_η stands for the viscosity–radius expansion factor, n_K is the number of Kuhn segments in the chain, and z is the excluded-volume variable

$$z = \left(\frac{3}{2\pi}\right)^{3/2} \cdot \left(\frac{\langle R^2 \rangle_0}{M}\right)_\infty^{-3/2} \cdot B \cdot M^{1/2} \tag{8}$$

and B is a parameter reflecting the polymer–solvent interaction.

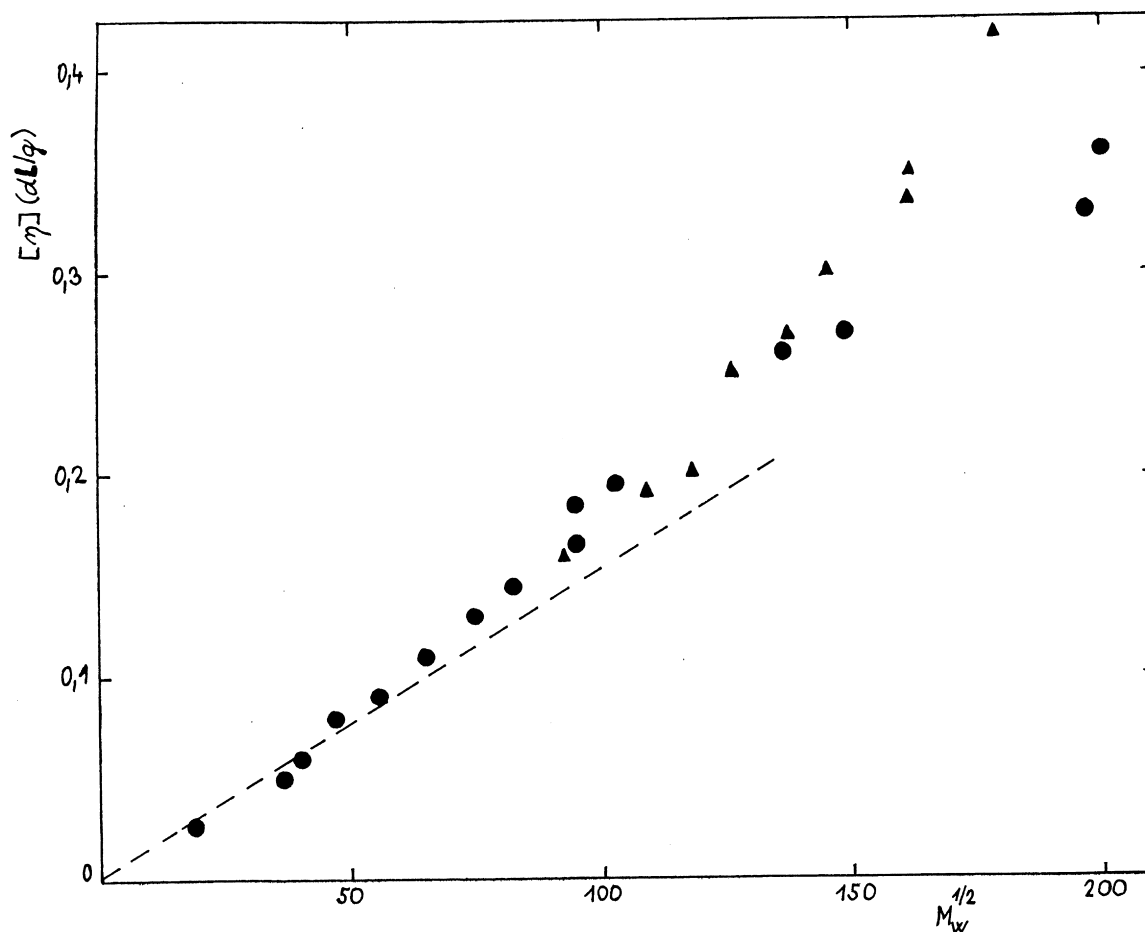When discussing the intrinsic viscosity of short chains,

Fig. 1. Plot of $[\eta]$ vs $M^{1/2}$ according to Eq. (1). Solvent THF (25°C): (●) this paper (Table 1): (□) data from Ref. [2].

attention should be paid to the impact of chain stiffness on the onset of the excluded-volume effect [11–15]. This becomes manifested in the chain-length dependence of the coefficient $C_\eta(n_K)$. This function is not known. In practice, it is usually replaced by the function $(3/4)C_\eta K(n_K)$ where $K(n_K)$ was derived by Yamakawa and Stockmayer [12] for the expansion factor $\alpha_R^2 = \langle R^2 \rangle / \langle R^2 \rangle_0$. This function is approximated by the equations

$$K(n_K) = (4/3)(1 - 2.033 \cdot n_K^{-1/2} + 0.875 \cdot n_K^{-1}) \tag{9a}$$

or

$$K(n_K) = n_K^{-1/2} \exp[-6.611 \cdot n_K^{-1} + 0.9198 + 0.03516 \cdot n_K] \tag{9b}$$

valid for $n_K > 6$ and $n_K < 6$, respectively. Then, Eq. (7) can be modified to

$$\alpha_\eta^3 = 1 + C_\eta(\infty) \cdot \bar{z} + \ldots \tag{10}$$

where $\bar{z}$ is the scaled excluded-volume variable

$$\bar{z} = (3/4) \cdot K(n_K) \cdot z \tag{11}$$

and $C_\eta(\infty) = 1.14$ [10,11].

Combining Eqs. (1), (7), (8), (10) and (11), yields

$$[\eta] = \left(A_\eta + K_0 \cdot M^{1/2} \right) \cdot \left[1 + \frac{3}{4} C_\eta(\infty) \cdot \left(\frac{3}{2\pi} \right)^{3/2} \right. $$
$$\left. \cdot \left(\frac{\langle R^2 \rangle_0}{M} \right)_\infty^{-3/2} \cdot K(n_K) \cdot B \cdot M^{1/2} \right] \tag{12}$$

It can be seen that the interpretation of the intrinsic viscosity of low-molecular-weight polymers such as PHE requires estimation of three characteristic parameters: A (cross-sectional chain diameter), K_0 (flexibility of the chain) and B (polymer–solvent interaction).

Let us briefly examine two plots of the intrinsic viscosity data: (a) $[\eta]$ vs $M^{1/2}$ [9], (b) $[\eta]/M^{1/2}$ vs $M^{1/2}$ (Burchard–Stockmayer–Fixman, BSF plot) [16,17]:

(a) Eq. (12) shows that the plot of $[\eta]$ vs $M^{1/2}$ should be linear over the whole range of molecular weights in theta solvents ($B = 0$) only. In good solvents ($B > 0$), linearity is restricted to a region where the term $B \cdot (\langle R^2 \rangle_0 / M)_\infty^{-3/2} \cdot K(n_K) \cdot M^{1/2}$ is very low, i.e. the ratio $(\langle R^2 \rangle_0 / M)_\infty$ is very high (stiff chains) or $K(n_K) \cong 0$ (short chains, both flexible and stiff). At higher molecular
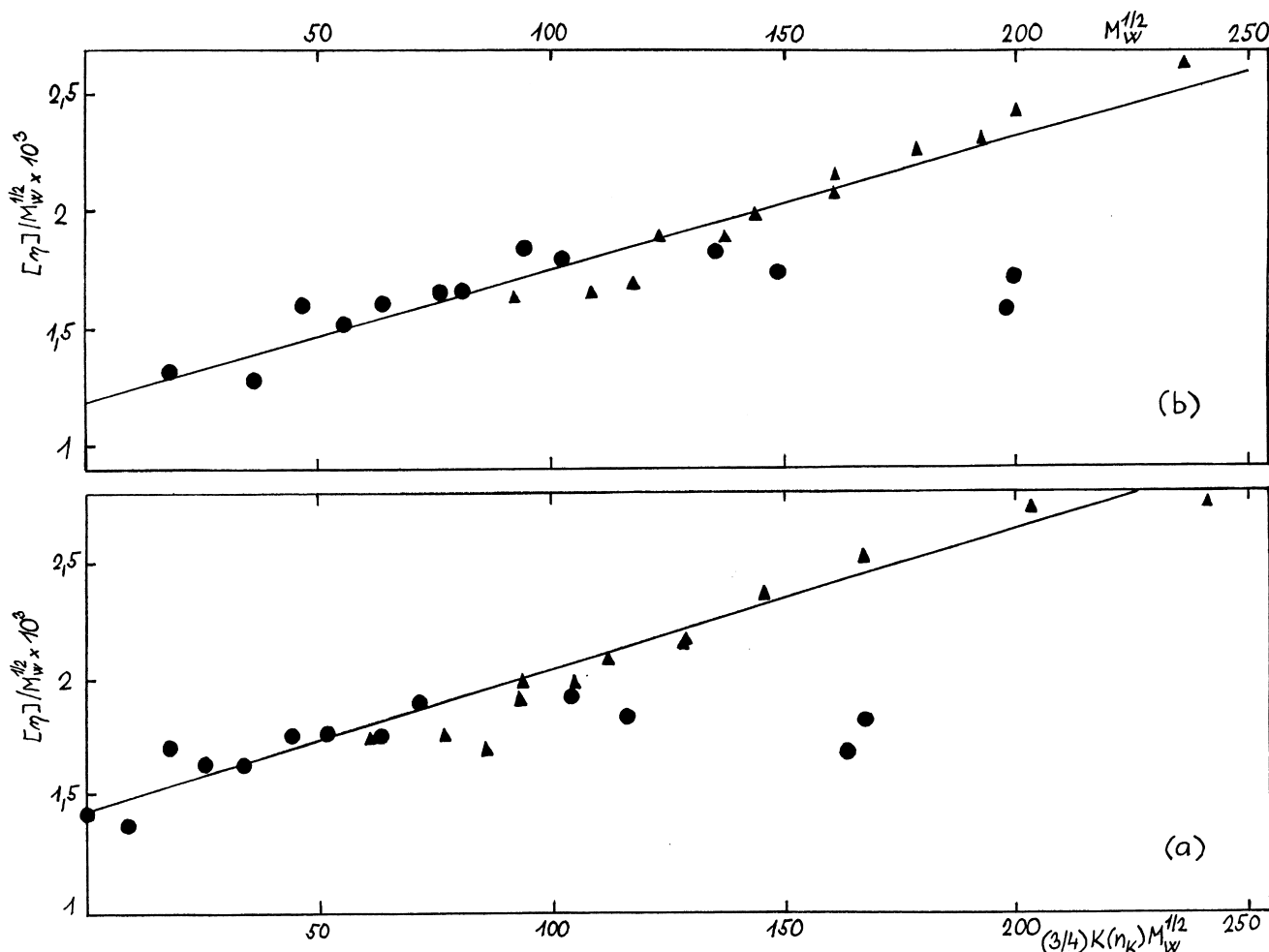
Fig. 2. Burchard–Stockmayer–Fixman plot. Notation of points as in Fig. 1: (a) modified form (for details of calculation see text); (b) standard form.

weights the plot becomes curved upward as the function $K(n_K)$ and the value of z increases with increasing M.

(b) Following Eq. (12), the BSF plot (even for $\alpha_\eta^3 < 1.5$) should be linear only for long enough chains ($n_K > 10^3$) where the absolute value $|A_\eta|$ is much lower than $K_0 \cdot M^{1/2}$ and the function $K(n_K)$ approaches its limit. In the low-molecular-weight region where this condition is not met, precaution is necessary. If $A_\eta = 0$, the BSF plot can be modified to $[\eta]/M^{1/2}$ vs $K(n_K) \cdot M^{1/2}$ which should be linear and can be extrapolated to $M = 0$. This, however, requires an approximate value of the molecular weight of the Kuhn segment to be known. If A_η is not equal to zero, both the original and modified BSF plots are non-linear. They can have a minimum if $A_\eta > 0$ or bend downward with decreasing molecular weight (if $A_\eta < 0$). In either case, the extrapolation to $M = 0$ is not justified [18].

As can be seen in Fig. 1, the plot of $[\eta]$ vs $M_w^{1/2}$ for PHE fractions is curved upward, indicating the excluded-volume to become manifest at rather low molecular weights. However, as the unit –C–Ph–O is rigid the

excluded-volume effect is negligible with the lowest molecular weights. Therefore, the first estimate of the K_0 parameter, $K_0' = 1.5 \times 10^{-3}$ dl/g, can be obtained from the initial slope of the plot in Fig. 1. The estimation of the slope is facilitated by the intercept being very close to zero. By means of Eqs. (2), (5) and (6) with $\Phi_{0,\infty} = 2.5 \times 10^{21}$ [10] and $M_L = 20 \times 10^8$ cm^{-1} (cf. Fig. 3) we obtain $(\langle R^2 \rangle_0/M)'_\infty = 0.71 \times 10^{-16}$ cm^2, $l_K' = 14 \times 10^{-8}$ cm and $M_K' = 284$. In the next step, we calculate $K(n_K)$ by means of Eqs. (9a) and (9b) and construct the "modified" BSF plot (Fig. 2a) assuming $A_\eta = 0$ and including the data also from Ref. [2]. Linear extrapolation yields $K_0 = 1.45 \times 10^{-3}$ dl/g, a value, which differs from the first estimate K_0' by 3% only. Differences in values of the other conformational parameters derived therefrom $((\langle R^2 \rangle_0/M)_\infty = 0.69 \times 10^{-16}$cm^2, $l_K = 13.9 \times 10^{-8}$cm, and $M_K = 278$) are even lower. Therefore, it is not necessary to calculate more accurate values of $K(n_K)$ and repeat the modified form of the BSF plot. The molecular weight M_K of the Kuhn statistical segment is close to that of the chain repeating unit. The PHE chains listed in Table 1 comprise 1–143 Kuhn segments.
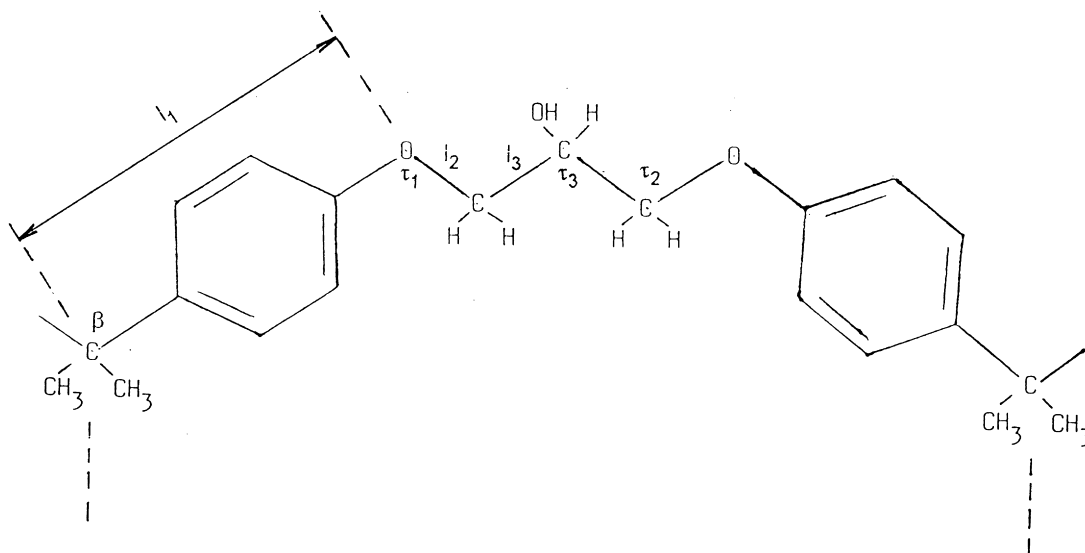
Fig. 3. Chain repeating unit of PHE.

For comparison, the standard BSF plot is presented in Fig. 2b. Linear extrapolation, which would yield $K_0 = 1.3 \times 10^{-3}$ dl/g, would imply an (incorrect) premise that the excluded volume effect is "fully" developed already at the lowest molecular weights so that the coefficient C_η would be equal to the limiting value $C_\eta(\infty)$. In view of the argument presented in the discussion of Fig. 2a, this result may be rejected. Comparison of Fig. 2a and 2b illustrates the limits of the BSF procedure in the low-molecular-weight region. Let us note that lower values of $[\eta]/M^{1/2}$ for some of our fractions of high molecular weight (Fig. 2) are due to chain branching.

According to the Yoshizaki–Nitta–Yamakawa theory [8], the hydrodynamic interaction depends on the reduced bead diameter $d_{b,r}$ which, in the range $0.3 < d_{b,r} < 0.8$, is related to the A_0 parameter by the equation [9]

$$A_0 = -2.9 + 5.36 d_{b,r} \tag{13}$$

As the A_η parameter for PHE chains is close to zero, and so is A_0, the $d_{b,r}$ and d_b values are, respectively, equal to 0.54 and 7.6×10^{-8} cm. They could be somewhat altered if the A_η value could be estimated with better accuracy. Nevertheless, the d_b value seems reasonable.

3.2. Evaluation of conformational characteristics

The conformation of polymer chains is currently characterized by the Kuhn statistical segment length l_K (cf. Eqs. (5) and (6)), the Flory characteristic ratio C_∞ or the steric factor σ. The latter two quantities are defined by the equations [19]

$$C_\infty = (\langle R^2 \rangle_0/M)_\infty \cdot (M_b/\overline{l_b^2}) \tag{14}$$

$$\sigma = \{(\langle R^2 \rangle_0/M)_\infty/(\langle R^2 \rangle_{0,f}/M)_\infty\}^{1/2} \tag{15}$$

The characteristic ratio C_∞ is the random-coil limit of the ratio of the mean-square end-to-end distance of the real

chain and the corresponding quantity $(n_b \cdot \overline{l_b^2})$ for a hypothetical freely jointed chain comprising n_b main chain bonds $(n_b = M/M_b)$ of the mean-square length $\overline{l_b^2}$ and the mean molecular weight M_b each. The symbol $\langle R^2 \rangle_{0,f}$ stands for the mean-square end-to-end distance of the freely rotating model chain. All the chains are assumed to be "unperturbed" by the excluded-volume effect.

In the freely jointed model, only bond lengths are fixed, whereas the mutual orientation of skeletal bonds in random. Thus, the characteristic ratio reflects all directional correlations of skeletal bonds in the real chain. In the freely rotating model, both the bond lengths and bond angles are fixed, but rotation about the main chain bonds is free. Hence, the steric factor reflects only those directional correlations which result from restricted rotations about skeletal bonds.

With polymer chains comprising p-phenylene groups, both C_∞ and σ values may be ambiguous as they depend on the choice of bonds or virtual bonds [19,20] in the model chain. In view of the rigidity of the segment –C–Ph–O–, it is expedient to take it as a virtual bond of length $l_1 = 5.7 \times 10^{-8}$ cm and to compare the results of experiments with the dimensions of the model (freely jointed and freely rotating) chains where the chain repeating unit (Fig. 3) consists of two virtual bonds –C–Ph–O, two real bonds –O–CH$_2$ and CH$_2$–CHOH (each with lengths $l_2 = 1.43 \times 10^{-8}$ cm and $l_3 = 1.54 \times 10^{-8}$ cm [19,20]), the bond angles being equal to $110°$ (τ_1 and τ_2) and $112°$ (τ_3 and β). The values of C_∞ and σ calculated on this assumption are lower than those which would be obtained if the rigidity of the –C–Ph–O unit were not taken into account. It is believed that they give a better account of directional correlations of skeletal bonds in real chains.

Substituting into Eq. (14) the value of $M_b = 47.3$ and $\overline{l_b^2} = 12.3 \times 10^{-16}$ cm, we obtain $C_\infty = 2.65$. The ratio $(\langle R^2 \rangle_{0,f}/M)_\infty$ to be used in Eq. (15) can be computed using

Table 2
Conformational parameters of PHE chains (for details of calculation, see text)

$10^3 \times K_0$ (dl/g)	$10^{16} \times (\langle R^2 \rangle_0 / M)_\infty$ (cm^2)	$10^8 \times l_K$ (cm)	M_K	C_∞	σ
1.5	0.69	13.9	278	2.6	1.3

the equation

$$(\langle R^2 \rangle_{0,f}/M)_\infty = M_0^{-1}(Y + A) \tag{16}$$

where $M_0 = 284$ is the molecular weight of the repeating unit and Y and A are functions of bond angles and bond lengths (cf. Appendix A). By means of Eq. (16) we obtain $(\langle R^2 \rangle_{0,f}/M)_\infty = 0.46 \times 10^{-16}$ cm^2. Substitution into Eq. (15) yields $\sigma = 1.31$.

Low values of C_∞, σ, l_K and M_K (Table 2) suggest rather high flexibility of the PHE chains. This may be surprising in view of the presence of two benzene rings in the repeating unit. The following explanation is acceptable. It has been found that rigid and long units in the main chains such as C–Ph–O in polycarbonates [20] or –C–Ph–NH in polyurethanes [21] can exert two opposing effects on the spatial configuration of the chain. Owing to their length and stiffness, they make the chain more extended. At the same time and for the same reasons, they reduce the spatial interaction between groups separated by three or more skeletal bonds. With PHE chains, this type of interaction is restricted to groups in the segment O–CH$_2$–CH(OH)– CH$_2$–O. If the latter effect predominates, the net result is a low value of the conformational parameters.

Acknowledgements

Appendix A

In a previous paper [22], general equations have been derived for the chain dimensions in the free rotation approximation for the case that the chain repeating unit comprises several types of bonds differing in length and angles but is symmetric around the central group (if the number of skeletal bonds in the repeating unit is even) or around the central bond (for an odd number). As the chain repeating unit of PHE is symmetric around the CHOH group, equation derived for the former case are employed [21]. They can be recast into the following forms:

$$Y = 2l_1^2(1 + \alpha_1 \alpha_2 \alpha_3^{1/2}) + 2l_2^2(1 + \alpha_2 \alpha_3^{1/2}) + 2l_3^2(1 + \alpha_3^{1/2})$$
$$+ 4l_1 l_2 \alpha_1^{1/2}(1 + \alpha_2 \alpha_3^{1/2}) + 4l_1 l_3 \alpha_1^{1/2} \alpha_2^{1/2}(1 + \alpha_3^{1/2})$$
$$+ 4l_2 l_3 \alpha_2^{1/2}(1 + \alpha_3^{1/2}) \tag{A1}$$

$$A/\cos \beta = 2l_1^2(1 + \alpha_1 \alpha_2 \alpha_3^{1/2})^2 + 2l_2^2 \alpha_1(1 + \alpha_2 \alpha_3^{1/2})$$
$$+ 2l_3^2 \alpha_1 \alpha_2(1 + \alpha_3^{1/2}) + 4l_1 l_2 \alpha_1^{1/2}(1 + \alpha_2 \alpha_3^{1/2}$$
$$+ \alpha_1 \alpha_2 \alpha_3^{1/2} + \alpha_1 \alpha_2^{3/2} \alpha_3) + 4l_1 l_3 \alpha_1^{1/2} \alpha_2^{1/2}(1 + \alpha_3^{1/2}$$
$$+ \alpha_1 \alpha_2 \alpha_3^{1/2} + \alpha_1 \alpha_2 \alpha_3) + 4l_2 l_3 \alpha_1 \alpha_2^{1/2}(1 + \alpha_3^{1/2}$$
$$+ \alpha_1 \alpha_3^{1/2} + \alpha_2 \alpha_3) \tag{A2}$$

where

$$\alpha_i = \cos^2 \tau_i \qquad (i = 1, 2, 3). \tag{A3}$$

Notation of bonds and angles (l_i, $\tau_{i,\beta}$) are given in Fig. 3.

References

[1] Kaštánek A, Bohdanecký M. Paper presented at the 14th Annual Meeting of the Polymer Processing Society of Japan, Yokohama, 1998.
[2] Myers GE, Dagon JR. J Polym Sci 1964;A2:2631.
[3] Batzer H, Zahir SA. J Appl Polym Sci 1975;19:601.
[4] Zahir SA, Bantle S. ACS symposium 1983; series 221:245.
[5] Fuchslueger U, Stephan H, Grether HJ, Grasserbauer M. Polymer 1999;40:661.
[6] Kaštánek A. Chem prům 1973;23:143 in Czech.
[7] Yamakawa H, Fujii M. Macromolecules 1974;7:128.
[8] Yoshizaki T, Nitta J, Yamakawa H. Macromolekules 1988;21:165.
[9] Bohdanecký M, Netopilík M. Makromol Chem, Rapid Commun 1993;14:383.
[10] Yamakawa H. Modern theory of polymer solutions, New York: Harper and Row, 1971.
[11] Fujita H. Polymer solutions, Amsterdam: Elsevier, 1990.
[12] Yamakawa H, Stockmayer WH. J Chem Phys 1972;57:2843.
[13] Norisuye T, Fujita H. Polymer J 1982;14:143.
[14] Yamakawa H, Shimada J. J Chem Phys 1985;83:2607.
[15] Shimada J, Yamakawa H. J Chem Phys 1976;85:591.
[16] Burchard W. Makromol Chem 1961;50:210.
[17] Stockmayer WH, Fixman M. J Polym Sci 1963;C1:137.
[18] Bohdanecký M, Kovár J, Fortelný I. Polymer 1979;20:813.
[19] Flory PJ. Statistical mechanics of chain molecules, New York: Interscience, 1969.
[20] Williams AD, Flory PJ. J Polym Sci 1967;5(A2):417.
[21] Kašpárková V, Šimek L, Bohdanecký M. Macromol Chem Phys 1996;197:3757.
[22] Dostál J, Šimek L, Bohdanecký M. Polymer 1999;40:613.