# Short-range interaction parameters of poly(2-methoxycyanurate) of bisphenol-F

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The poly(2-methoxycyanurate) of bisphenol-F (PMCBF), is known for its thermal stability. PMCBF was separated into its various fractions by using a fractional precipitation method, and these fractions were then characterized by viscometry and light scattering methods. The unperturbed dimensions of the polymer chain were computed by using various two-parameter theories and compared with those obtained from calculations based on a freely rotating model. To characterize the flexibility of the polymer, various parameters, such as the stiffness parameter $\sigma$, the effective segment length $B_e$, the characteristic ratio $C_\infty$, and the dihedral angle $\phi$, were determined.

**(Keywords: polycyanurate; short-range interactions; conformation)**

## INTRODUCTION

Polymers containing the s-triazine moiety in the main chain are known as polycyanurates. The polycyanurates which are derived from bisphenols and monosubstituted cyanuric chloride are well known for their thermal stability[1–5]. However, many polycyanurates are infusible and insoluble, and consequently there are only a few reports available on the systematic investigation of the solution properties of such polymers[6–8].

One of the most important characteristics of a polymer chain is its conformation, since this is directly related to both the crystalline and amorphous states, and thus influences the mechanical, optical, and electrical properties of the polymer, and the stiffness of the polymer chains. The single-chain conformation is determined by freedom of rotation which gives the chain its flexibility. This flexibility is characterized by the following parameters:

(i) the conformational parameter, $\sigma$, which is the ratio of the unperturbed coil dimension, $\langle R^2\rangle_o^{1/2}$, to the value with free rotation of the chain unit, $\langle R^2\rangle_{of}^{1/2}$
(ii) the effective segment length, $B_e$;
(iii) Kuhn's equivalent chain segment length, $A_m$;
(iv) the dihedral angle, $\phi$.

We have previously reported[9] the synthesis and dilute solution properties of poly(2-methoxycyanurate) of bisphenol-F. In a continuation of this work, it is interesting to carry out a further study on the conformational behaviour of this polymer. In this present work, only short-range interactions are considered. The polymer is thus treated as a chain which is unperturbed by long-range effects, and the dimensions of the chain therefore depend only on short-range interactions[10].

In this present investigation the above mentioned parameters, based on the freely rotating model, are determined. This model is the basis for a detailed theoretical prediction of the chain dimensions of poly(2-methoxycyanurate) of bisphenol-F.

## EXPERIMENTAL

The poly(2-methoxycyanurate) of bisphenol-F (PMCBF) used in the study was synthesized following a conventional interfacial polycondensation from bisphenol-F and 2-methoxy-4,6-dichloro-s-triazine (MDT), using chloroform/water as the interface system. The detailed procedure is reported elsewhere[9]. The polymer obtained was fractionated by the fractional precipitation method at 30°C using chloroform as the solvent and n-butanol as the precipitant. Intrinsic viscosity measurements of these fractions were made by using an Ubbelohde suspended level viscometer at 30°C in different solvent systems of chloroform (CF) and its binary mixtures. The systems employed were CF, CF:dichloroethane (DCE) (70:30 v/v), CF:dioxane (Di) (80:20 v/v), and CF:Di (70:30 v/v).

A Brice–Phoenix light scattering photometer was used to determine the weight-average molecular weight ($\bar{M}_w$) of the fractions in chloroform at 30°C and at a wavelength of 436 nm. The solutions used for the light scattering measurements were centrifuged with an ultracentrifuge machine (Janetzki, VAC 601) at 30000 rev min$^{-1}$ for ~30 min. The supernatant liquid was transferred into a G5 sintered glass funnel and filtered. The instrument was calibrated with a standard polystyrene sample of known molecular weight. The specific refractive index

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increment was measured on a Brice–Phoenix differential refractometer in CF at 30°C, and a value for d$n$/d$c$ of 0.173 ml g$^{-1}$ was found. The molecular weight determination was carried out by using the graphical Zimm method.

## RESULTS AND DISCUSSION

The unperturbed dimensions $(\langle R^2\rangle_o/\bar{M}_w)^{1/2}$ of PMCBF were determined in different solvent systems by the graphical method using various two-parameter theories of the excluded volume[9]. This method involves the extrapolation of an appropriate viscosity function to zero molecular weight, therefore eliminating the excluded-volume effect.

Values of the viscosities and molecular weights used for the determination of $(\langle R^2\rangle_o/\bar{M}_w)^{1/2}$ of PMCBF are shown in *Table 1*, with the values of $(\langle R^2\rangle_o/\bar{M}_w)^{1/2}$ that were obtained being reported in *Table 4* (see below).

In order to determine the mean square end-to-end distance of PMCBF, the freely rotating chain model is proposed and used. The mean square end-to-end distance for a freely rotating chain can be evaluated from the following general expression:

$$\frac{\langle R^2\rangle_{of}}{(n/p)}=\sum_{i=1}^{p}a_i^2+\frac{2}{\left(1-\prod\limits_{i=1}^{p}\alpha_i\right)}\left[\sum_{i=1}^{p}a_i^2\prod_{i=1}^{p}\alpha_i+a_i\sum_{j=1}^{i-1}a_j\frac{\prod\limits_{j=1}^{p}\alpha_i}{\prod\limits_{k=j}^{i-1}\alpha_k}+a_i\sum_{j=i+1}^{p}a_j\prod_{k=i}^{j-1}\alpha_k\right]\qquad(1)$$

where:

$p$ = number of bonds in a repeat unit;

$i, j$ = sequential number of a bond/angle in the repeat unit $(1, 2, \ldots, p)$;

$a_i$ = bond length of the $i$th bond in a repeat unit;

$\alpha_i$ = cosine of supplement of the bond angle $i$, i.e. $\alpha_i = -\cos\theta_i$.

As can be seen from the repeat-unit model chain of PMCBF (*Figure 1*), not all of the rotatable links in this chain are of the same type. This chain contains three different valence angles, denoted by $\theta_1$, $\theta_2$, and $\theta_3$, and two different bond lengths, denoted by $l$ and $p$. The relevant parameters of the s-triazine ring, taken from the literature, are as follows:

(i) bond lengths C–H = 0.998 Å, C–N = 1.32 Å;
(ii) bond angles C–N–C = 113.2 ± 0.4°,
N–C–N = 126.8 ± 0.4°.

The lengths of the links, applicable to the skeleton, which have been calculated from the normal covalent bond lengths, are 2.7 and 5.77 Å for $l$ and $p$, respectively[11]. These lengths have been confirmed from the molecular model of this chain. The valence angles between the successive bonds, $\theta_1$ (O–P–O), $\theta_2$ (= $\theta_4$) (P–O–C), and $\theta_3$ (O–C–O), have values of 120°, 123° and 109.5° (the tetrahedral angle), respectively. These values are also

**Table 1** Intrinsic viscosity and molecular weight data of PMCBF fractions in various solvent systems at 30°C

| | | $[\eta]$ (dl g$^{-1}$) | | | |
|---|---|---|---|---|---|
| Fraction | $\bar{M}_w$ ($\times 10^{-5}$) | CF | CF:DCE (70:30 v/v) | CF:Di (80:20 v/v) | CF:Di (70:30 v/v) |
| $S_4$[a] | 7.52 | 2.68 | – | – | – |
| $S_7$ | 3.19 | 1.56 | 1.56 | 1.03 | 0.77 |
| $S_8$ | 2.40 | 1.32 | 1.24 | 0.92 | 0.71 |
| $S_{10}$ | 1.25 | 0.94 | 0.87 | 0.66 | 0.55 |
| $S_{12}$ | 1.10 | 0.81 | 0.78 | – | 0.52 |
| $S_{13}$ | 0.86 | 0.70 | 0.70 | 0.58 | – |
| $S_{14}$ | 0.65 | 0.58 | 0.56 | 0.48 | 0.44 |

[a] Viscosity for this fraction could not be measured due to its insolubility in all of the solvent systems studied

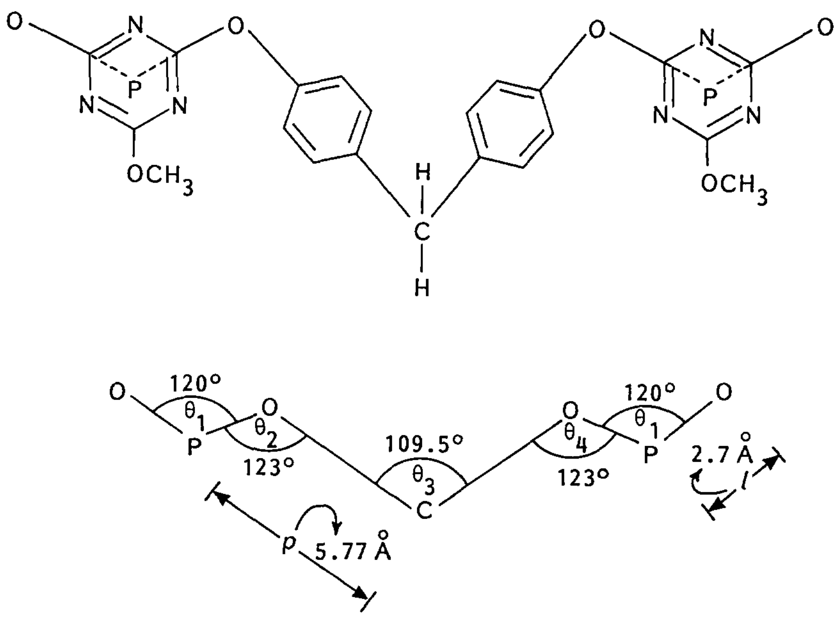

**Figure 1** Repeat-unit model chain of poly(2-methoxycyanurate) of bisphenol-F

**Table 2** Values of $(\langle R^2\rangle_{of}/\bar{M}_w)^{1/2}$ of PMCBF, calculated by using different functions

| Function | Valence angle (deg) | $\langle R^2\rangle_{of}/N$ (Å$^2$) | $(\langle R^2\rangle_{of}/\bar{M}_w)^{1/2}$ | Equation |
|---|---|---|---|---|
| First approximation | $\theta_i = 109.5$ | 37.8 | 0.70 | 2 |
| Exact | $\theta_1 = 120$<br>$\theta_2 = \theta_4 = 123$<br>$\theta_3 = 109.5$ | 50.7 | 0.81 | 3 |
| Equivalent angle | $\theta_i = 117$ | 49.3 | 0.80 | 2 |

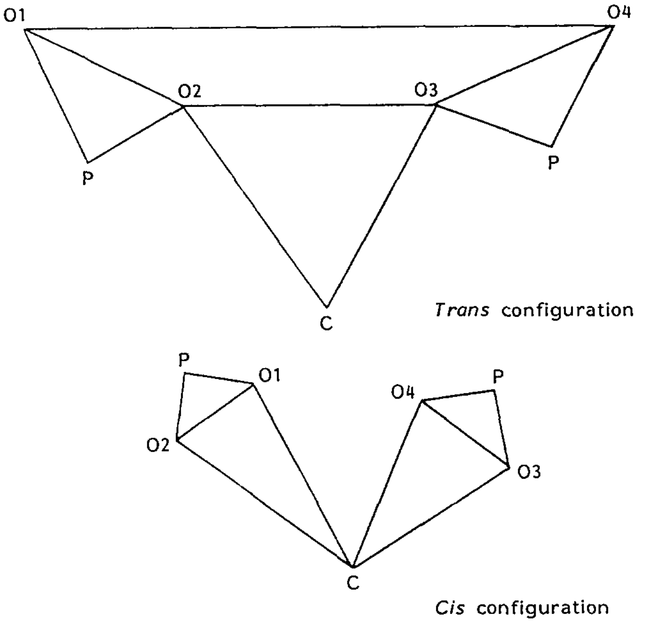

**Figure 2** Geometric representations of the *cis* and *trans* configurations used in calculations of the free-rotation dimensions of poly(2-methoxycyanurate) of bisphenol-F

confirmed from the molecular model[12]. According to a number of authors[13–18], the valence angle at the oxygen atoms in a polyether chain is generally assumed to be approximately equal to the tetrahedral angle, i.e. 109.5°.

We carried out a first approximation in calculating the average end-to-end distance by assuming that the molecule consists of two different bond lengths, with all of the angles equivalent to the tetrahedral angle, i.e. $l$ and $p$ are 2.7 and 5.77 Å, respectively, and $\theta_1$, $\theta_2$ and $\theta_3$ are all equal to 109.5°. The appropriate expression for this case, obtained by solving equation (1) is

$$\frac{\langle R^2\rangle_{of}}{N} = \left[\frac{(l^2+p^2)(1+\alpha^3)}{(1-\alpha)(1+\alpha^2)}\right] + \left[\frac{2lp\alpha(1+\alpha)}{(1-\alpha)(1+\alpha^2)}\right] \tag{2}$$

In fact, the molecule under consideration here consists of three different valence angles and two different bond lengths, as mentioned earlier. The corresponding expression, obtained by solving equation (1), is

$$\frac{\langle R^2\rangle_{of}}{N} = \frac{1}{(1-\alpha_1\alpha_2^2\alpha_3)}[l^2(1+\alpha_1)(1+\alpha_2^2\alpha_3) + p^2(1+\alpha_3)(1+\alpha_1\alpha_2^2) + 2lp\alpha_2(1+\alpha_1)(1+\alpha_3)] \tag{3}$$

The values obtained for $\langle R^2\rangle_{of}/N$, calculated by using equations (2) and (3), are given in *Table 2*.

A concept of an 'equivalent angle' was introduced to simplify calculations of the free-rotation dimensions, $\langle R^2\rangle_{of}$. Two planar configurations, representing two opposite extremes, namely *cis* and *trans*, are introduced in order to check the validity of this equivalent angle approach. With a knowledge of the exact values of the bond angles and bond lengths, we calculated the O1–O4 distances for the *trans* and *cis* configurations, with the help of the simple geometric forms shown in *Figure 2* (see *Table 3*).

With an equivalent angle of 117°, the percentage variation in the value of the O1–O4 distance, obtained by using exact angles in the case of the *trans* configuration, is ~2.0, whereas in the case of the *cis* configuration it is ~0.1. Since this percentage error is less in the case of the *cis* configuration, this latter form was preferred when assessing the equivalent angle. Using this angle the value of $\langle R^2\rangle_{of}/N$ calculated by using equation (1) is 49.32 Å$^2$ (see *Table 2*), differing only by 1.4% from that calculated using exact values of the valence angles. This excellent agreement validates the consideration of the equivalent angle concept.

The conformational parameter, $\sigma$, which characterizes the spatial configuration of the chain molecules and reflects the effect of hindrance to rotation, exclusive of the effect of fixed bond angles, is shown in *Table 4* for different experimental conditions and different values of $(\langle R^2\rangle_{of}/\bar{M}_w)^{1/2}$.

The effective bond length $B_e$ is calculated by using the following equation:

$$B_e = \left(\frac{\langle R^2\rangle_o}{\bar{M}_w}\right)^{1/2} M_o^{1/2} \tag{4}$$

where $M_o$ is the molecular weight of the repeat unit. The Kuhn's equivalent chain segment is defined as follows:

$$A_m = \left[\frac{\langle R^2\rangle_o}{\bar{M}_w}\right] M_o L^{-1} \tag{5}$$

where $L$ is the length of the repeat unit. The dihedral

**Table 3** Values of the O1–O4 distances for *trans* and *cis* configurations of PMCBF

| Angle assumed (deg) | *Trans* configuration (Å) | *Cis* configuration (Å) |
|---|---|---|
| Exact | 18.7 | 4.4 |
| 109.5 | 18.2 | 2.6 |
| 112 | 18.5 | 3.1 |
| 113 | 18.6 | 3.4 |
| 114 | 18.7 | 3.6 |
| 115 | 18.8 | 3.9 |
| 117 | 19.0 | 4.4 |
| 118 | 19.1 | 4.7 |

angle (angle of restricted rotation) $\phi$ is calculated by using the relationship:

$$\sigma^2=\frac{1+\cos\phi}{1-\cos\phi} \tag{6}$$

Values of the unperturbed dimensions and the flexibility parameters of PMCBF, evaluated from the experimental data, are presented in *Table 5*, together with available literature data on other related polymers.

This present value of $\sigma$ of ~1.13 indicates a high flexibility of the PMCBF chains, although the molecular structure apparently seems rigid. Other polymers containing $\Phi$–o–$\Phi$ or $\Phi$–s–$\Phi$ ($\Phi$ = aromatic ring) links show similar low values of $\sigma$. A comparison of the $\sigma$ values of polycarbonate[11] (1.3) and polysulfone[13] (1.03) with PMCBF (1.13) indicates that it is the presence of the oxygen atom in the chain which causes such low values, and not the nature of the links formed by the group of atoms. PMCBF belongs to a class of macromolecules containing skeletal oxygen atoms i.e. those whose chain links are not simple interatomic bonds but groups, which are usually rings of atoms that are connected rigidly together. These types of polymers have been reported to give unusually small coil dimensions in solution, in that their unperturbed dimensions are only slightly greater than the values calculated theoretically when assuming free rotation about the chain links. This behaviour may be attributed to the existence of relatively small energy differences between the various rotational isomers.

The low values of $\sigma$ for PMCBF imply that the polymer chains are tightly coiled in solution. The result also suggests that short-range steric interactions between the nearest neighbour segments are negligibly small. Such short-range steric interactions usually cause a significant increase in $\langle R^2\rangle_o$, relative to $\langle R^2\rangle_{of}$. The values of $\sigma$ for polymers such as poly(dimethylsiloxanes), polyethers and polysulfones are smaller than that of polystyrene[20], except for polyoxymethylene[15], which assumes a helical configuration.

**Table 4** Values of the conformational parameter $\sigma$ of PMCBF in different solvents at 30°C

| | | $\sigma$ | | |
|---|---|---|---|---|
| Solvent system | $\left(\frac{\langle R^2\rangle_o}{\bar{M}_w}\right)^{1/2}=x$ | $\frac{x^a}{0.701}$ | $\frac{x^b}{0.813}$ | $\frac{x^c}{0.801}$ |
| CF | 0.92 | 1.31 | 1.13 | 1.15 |
| CF:DCE (70:30 v/v) | 0.92 | 1.31 | 1.13 | 1.15 |
| CF:Di (80:20 v/v) | 0.90 | 1.28 | 1.11 | 1.12 |
| CF:Di (70:30 v/v) | 0.90 | 1.28 | 1.11 | 1.12 |

[a] First approximation, using equation (2)
[b] Exact angle, using equation (3)
[c] Equivalent angle, using equation (2)

The characteristic ratio, which provides a basis for comparing the average dimensions of unperturbed coils with those of freely jointed chains, is given by the following relationship:

$$C_\infty=\lim_{n\to\infty}\frac{\langle R^2\rangle_o}{nl^2}$$

where $n$ is the number of main chain bonds and $l$ is the average bond length. Values of $C_\infty$ are shown in *Table 5* for various polymers that are known for their flexibility. Although in real chains, certain bond correlations exist, the $C_\infty$ values for the polymers belonging to the class containing skeletal oxygen atoms are all low, thus accounting for their flexibility. PMCBF also belongs to this class, and is highly flexible because of the presence of ether linkage in the backbone, together with aromatic rings. On the other hand, the known data for polystyrene and poly(oxymethylene), where $\sigma$ and $C_\infty$ assume quite large values, indicate the presence of strong steric interactions. In the case of the former polymer, the pendent group is large, while in the latter material, although an oxygen atom is present in the backbone, the pendent hydrogen atoms interact in such a way that the chain assumes a helical, rather than a random, coil structure.

The dihedral angle of PMCBF is ~90°, which indicates that the basic ethane configuration is lost as a result of a cumulative effect of the presence of both oxygen atoms and ring structures in the chain skeleton. The spatial interactions are thus appreciably reduced and the PMCBF chains are found to be quite flexible when compared to other common polymers.

**Table 5** The unperturbed dimensions and flexibility parameters of PMCBF and other related polymers

| Polymer | $\left(\frac{\langle R^2\rangle_o}{\bar{M}_w}\right)^{1/2}$ (Å) | $\left(\frac{\langle R^2\rangle_{of}}{\bar{M}_w}\right)^{1/2}$ (Å) | $\sigma$ | Average link length $l$ (Å) | $B_e$ (Å) | $C_\infty$ | $\phi$ (deg) | Ref. |
|---|---|---|---|---|---|---|---|---|
| Bisphenol-A polycarbonate | 0.880 | 0.680 | 1.30 | 7.00 | 14.0 | 2.8 | 75.0 | 11 |
| Poly(2,6-dimethyl-1,4-phenylene oxide) | 0.830 | 0.690 | 1.20 | 5.34 | 9.1 | 3.0 | 79.6 | 14 |
| Poly(ethylene terephthalate) | 0.985 | 0.687 | 1.45 | 5.00 | 13.6 | 4.2 | 69.2 | 19 |
| Poly(oxymethylene) | 1.200 | 0.520 | 2.30 | 1.43 | 6.6 | 10.5 | 47.0 | 15 |
| Polystyrene | 0.675 | 0.300 | 2.25 | 1.54 | 6.9 | 10.0 | 48.0 | 20 |
| PMCBF[a] | 0.920 | 0.813 | 1.13 | 4.24 | 16.1 | 3.6 | 83.0 | Present data |

[a] $A_m$ for PMCBF = 14.3 Å

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