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Synthesis and Characterization of the Poly-(2-Methoxycyanurate) of 1,1′-Bis-(4-Hydroxyphenyl)-cyclohexane

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ABSTRACT

The poly-(2-methoxycyanurate) of 1,1′-bis-(4-hydroxyphenyl)-cyclohexane (PMCBC) was synthesized by the interfacial polycondensation technique. The polymer was fractionated by preparative gel permeation chromatography (GPC). The fractions were characterized by viscometry, osmometry, and GPC techniques. The viscosity-molecular weight relationship was established in pure solvent and in different binary solvent mixtures. The unperturbed dimensions, $(\langle R^2 \rangle_0/M)^{1/2}$, and the solvent-polymer interaction parameter, B, were computed by applying the two-parameter theories of the excluded-volume effect.

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INTRODUCTION

Among the heat-resistant polymers, aromatic polyethers are of great interest. They are known for their high resistance to heat and chemical attack, good mechanical and dielectric properties, and ease of processability [1]. Such polymers result when stable ring systems (e.g., borazine, phosphazine, ferrocene, benzene, triazine) are connected with thermally stable linkages.

It has been reported that heat stability is increased considerably when the polymer molecule contains cyclic side groups where one of the atoms also forms part of the main polymer chain [2]. Polymers of this type are known as "cardo" polymers. Corresponding groups include phthalide, phthalimidine, fluorene, anthrone, and cyclohexyl. Most of the properties of polymers are largely dependent on the backbone structure.

The present communication describes the synthesis and solution properties of a cardo polymer. The aromatic polyether of structure I is synthesized from 2-methoxy-4,6-dichloro-S-triazine (MDT) and 1,1'-bis-(4-hydroxyphenyl)cyclohexane (Bisphenol C).

EXPERIMENTAL

Materials

Chemicals used were of laboratory grade and were purified prior to use by methods reported in the literature [3]. 2-Methoxy-4,6-dichloro-S-triazine (MDT) was synthesized according to the method of Dudley [4, 5].

Synthesis of 1,1'-Bis-(4-Hydroxyphenyl)-cyclohexane (Bisphenol C)

Cyclohexanone (49 g, 0.5 mol) and phenol (94 g, 1.0 mol) were reacted in the presence of a mixture of hydrochloric acid and acetic acid (150 mL, 2:1 by volume) at 50-60°C for 3 h. Excess phenol was removed by washing the mixture with boiling water. The solid product was dissolved in 2 M NaOH solution. The suspended impurities were removed by centrifugation at 10 000 rpm for an hour. The clear alkaline solution was neutralized with dilute HCl. The precipitates were filtered, washed with distilled water, and dried at 50°C. It was crystallized from benzene (mp 186°C).

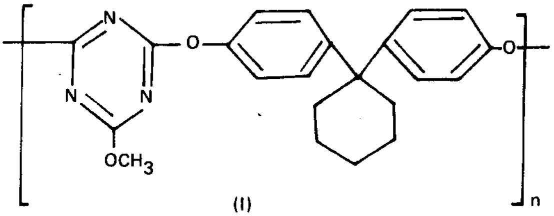
Analysis. Calculated: C, 80.59; H, 7.46%. Found: C, 80.3; H, 6.8%.

Polymer Synthesis

Bisphenol C (2.68 g, 0.01 mol) was dissolved in 0.02 M aqueous NaOH solution (100 mL). The resultant clear solution was cooled to 10°C and cetyldimethylbenzylammonium chloride (0.259) was added. The contents were stirred vigorously. A solution of 2-methoxy-4,6-dichloro-S-triazine (1.8 g, 0.01 mol) in chloroform (25 mL) was added rapidly to the cooled aqueous solution and the emulsion was stirred vigorously at 10°C for 6 h. The organic layer was separated and run into acetone to precipitate the polymeric product. The precipitate was filtered, washed with water and acetone, and dried. It was further purified by dissolving it in chloroform and precipitating with petroleum ether. The yield was 75%.

The polymer, poly-(2-methoxycyanurate) of Bisphenol C (I), hereafter designated as PMCBC, is highly soluble in chloroform. It dissolves only partially or swells in other chlorinated solvents, such as methylene chloride, dichloroethane, trichloroethylene, tetrachloroethane, and chlorobenzene. The polymer forms tough and clear films from chloroform solution.

Analysis. Calculated: C, 70.4; H, 5.6; N, 11.2%. Found: C, 70.21; H, 5.06; N, 10.94%.



(I)

Fractionation

Fractionation of PMCBC was carried out on a Waters Associates Model GPC-200 using chloroform as the solvent at 25°C. A set of two preparative columns (4 ft long) of Styragel having porosities of 10^4 and 10^3 Å and connected in series was used for this purpose. A 2% solution of polymer in chloroform was injected in portions of 10 mL to obtain a sufficient amount of each fraction. In all, 12 fractions were collected. Some of them were refractionated using a set of columns with pore sizes of 10^5 and 10^4 Å.

Measurements

IR. A thin film of PMCBC was prepared by controlled evaporation of solvent from a 1% solution of the polymer in chloroform spread on a glass surface. The IR spectrum of the vacuum-dried thin film was scanned on a UR-10 spectrophotometer.

NMR. The NMR spectrum was taken in $CDCl_3$ solution on a Perkin-Elmer Model-32 ^{1}H-NMR spectrometer (90 MHz) with a sweep time of 10 min at 35°C, with TMS as the internal standard.

Viscometry. Viscosity measurements were carried out with an Ubbelohde suspended-level viscometer. The intrinsic viscosity, $[\eta]$, was evaluated from the reduced viscosities at four different concentrations using the Huggins [6] and Kraemer [7] relationships:

$$\eta_{sp}/c = [\eta] + k[\eta]^2 c \qquad (1)$$

$$(\ln \eta_r)/c = [\eta] - \beta[\eta]^2 c \qquad (2)$$

where k and β are the Huggins and Kraemer constants, respectively.

Osmometry. The osmotic pressure measurements were carried out with a Hewlett-Packard 502 High-Speed Membrane Osmometer at 30°C. Chloroform was used as the solvent. The number-average molecular weight, $\overline{M}_n$, and second-virial coefficient, A_2, were determined by

$$\pi/c = \frac{RT}{\overline{M}_n}(1 + A_2 c) \qquad (3)$$

Gel Permeation Chromatography (GPC). The GPC measurements were carried out on a Waters Associates GPC-200, equipped with a set of four columns containing Styragel (10^6, 10^5, 10^4, and 10^3 Å) at 25°C. Chloroform was used as the solvent. The calibration was carried out by plotting the elution volume (V_R) against log $\overline{M}_w$ for standard polystyrene samples supplied by Waters Associates. The molecular weights used in the following discussion were derived from GPC heterogeneity, corrected for band broadening according to Balke and Hamielec [8], and the value of $\overline{M}_n$ was obtained from osmometry as follows:

$$\overline{M}_w(O) = \frac{\overline{M}_w(h)}{\overline{M}_n(h)}\overline{M}_n(O) \qquad (4)$$

This procedure, proposed by Balke et al. [9], has been employed by others [10-12]. The values of $\overline{M}_w(O)$ are shown in Table 1. For convenience, the symbol "O" with $\overline{M}_w$ is omitted henceforth.

TABLE 1. Corrected Molecular Weights and Polydispersity of PMCBC Fractions from GPC Data in Chloroform at 25°C[a]

No.[b]	$\overline{M}_w(\infty)/\overline{M}_n(\infty)$	h, (count)$^{-2}$	$\overline{M}_w(h)/\overline{M}_n(h)$	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w(O) \times 10^{-4}$
G_1*	3.17	0.58	2.40	28.57	68.54
G_2*	2.16	0.63	1.50	18.04	27.06
G_3*	2.49	0.66	1.95	12.24	23.87
G_4*	1.60	0.70	1.27	13.18	16.74
G_5*	1.76	0.71	1.40	11.43	15.99
G_6	1.78	0.72	1.42	-	-
G_7	1.64	0.76	1.32	8.57	11.31
G_8	1.69	0.78	1.38	6.59	9.09
G_9	1.38	0.81	1.14	5.71	6.51
G_{10}	1.56	0.84	1.29	4.18	5.39
G_{11}	1.36	0.87	1.13	-	-
G_{12}	1.44	0.94	1.22	-	-
UNF	3.54	0.61	2.72	-	-

[a] $V_R = 50.8 - 4.07 \log M$ (counts). $h = 2.02 - 0.26 \log M$ (count)$^{-2}$.

[b] Asterisks indicate refractionated fractions.

RESULTS AND DISCUSSION

The IR spectrum (Fig. 1) shows absorption bands in the 1208-1013 cm^{-1} region, characteristic of the stretching vibrations of the C–O–C linkage of an aryl-ether system [13]. The bands in the 1558-1428 cm^{-1} region are attributed to aromatic double bonds. The band at 815 cm^{-1} is typical of out-of-plane vibrations of the triazine ring [13]. The bands in the 2858-2792 cm^{-1} region are characteristic of C–H stretching vibrations [14]. The 858 and 533 cm^{-1} bands are attributed to out-of-plane ring bending [13, 14].

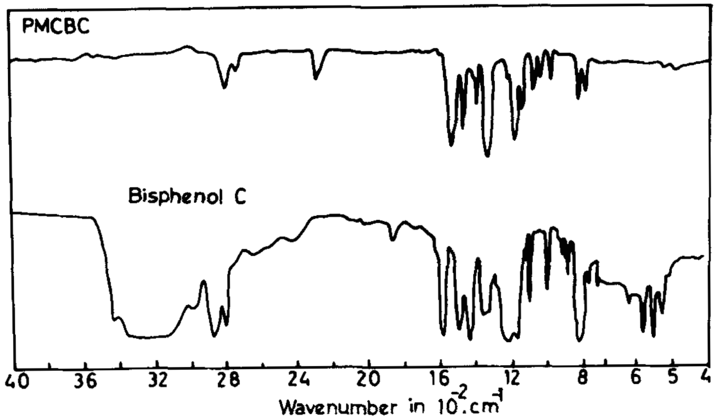


FIG. 1. IR spectrum of PMCBC.

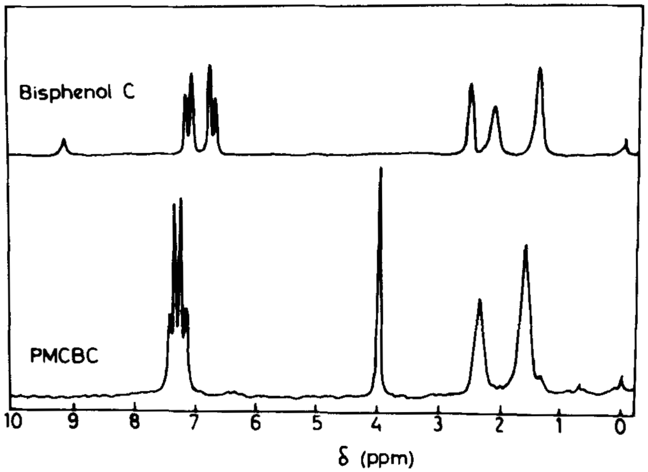


FIG. 2. NMR spectrum of PMCBC.

The NMR spectrum (Fig. 2) shows four distinct signals, viz, a multiplet at δ 7.1-7.38 ppm due to eight aromatic protons, a sharp singlet at δ 3.92 ppm due to three protons of $O–CH_3$, and two singlets at δ 2.28 and 1.56 ppm due to six protons of β, β', γ and four protons of α, α' types of cyclohexylmethylene groups. Thus the spectral characteristics of PMCBC are explicable in terms of the proposed structure (I).

The number-average molecular weights ($\overline{M}_n$) derived from osmotic pressure measurements on PMCBC fractions are shown in Table 1. The molecular weight dependence of the second virial coefficient (A_2) is described by

$$A_2 = 1.04 \times 10^{-2}\ \overline{M}_n^{\,-0.18}$$

The largest possible value of the exponent is about 0.10. This prediction of the theory is in conflict with most of the experimental results. Such a high value of the exponent is also reported in the literature [15, 16].

The intrinsic viscosity $[\eta]$ and the Huggins constant k for PMCBC fractions in chloroform and binary solvent mixtures are listed in Table 2. Both $[\eta]$ and k show no significant variation in magnitude as the polymer experiences the more or less similar chemical environments of chlorinated solvents.

$[\eta]$-M Relationships

The experimental $[\eta]$ is correlated with the molecular weight $\overline{M}_w$ by an empirical relationship of Mark-Houwink-Kuhn-Sakurada (MHKS) [17]. Linear regression analysis of the experimental data (correlation coefficient > 99%) yields the following MHKS relations at 30°C:

$$[\eta],\ \text{dL/g} = 9.90 \times 10^{-4}\ \overline{M}_w^{\,0.57} \quad \text{(chloroform)}$$

$$= 2.10 \times 10^{-3}\ \overline{M}_w^{\,0.50} \quad \text{(chloroform/dichloroethane volume ratio 3:1)}$$

$$= 5.72 \times 10^{-3}\ \overline{M}_w^{\,0.41} \quad \text{(chloroform/tetrachloroethane volume ratio 3:1)}$$

$$= 7.15 \times 10^{-3}\ \overline{M}_w^{\,0.39} \quad \text{(chloroform/chlorobenzene volume ratio 3:1)}$$

The magnitude of the exponent ν, in $[\eta] = KM^{\nu}$, is in the range $0.5 \leq \nu \leq 0.8$ generally observed for polymers which are flexible in solution. Values of $\nu < 0.5$ indicate tightly coiled configurations of macromolecular chains in the solutions.

Unperturbed Dimensions of PMCBC

Several methods [19-25] have been proposed for the estimation of the unperturbed dimensions of polymeric chains from the viscosity

TABLE 2. Intrinsic Viscosity $[\eta]$ and Huggins Constant k for PMCBC Fractions at 30°C[a]

	CF		CF:DCE volume ratio (3:1)		CF:TCE volume ratio (3:1)		CF:CB volume ratio (3:1)	
No.	$[\eta]$, dL/g	k	$[\eta]$, dL/g	k	$[\eta]$, dL/g	k	$[\eta]$, dL/g	k
G_2*	1.16	0.27	1.02	0.34	1.01	0.28	0.98	0.26
G_3*	0.99	0.24	0.91	0.37	0.87	0.21	0.87	0.28
G_5*	0.85	0.29	0.83	0.30	0.83	0.22	0.81	0.23
G_7	0.70	0.33	0.71	0.25	0.67	0.38	0.70	0.34
G_9	0.52	-	0.50	0.40	0.57	0.20	0.56	0.19

[a] CF = chloroform, DCE = dichloroethane, TCE = trichloroethylene, CB = chlorobenzene.

data in nontheta solvents. The methods, based on the current two-parameter theories of excluded volume [19], involve the extrapolation of an appropriate viscosity function to zero molecular weight. Graphical methods based on relations (5) to (8) are employed to estimate the perturbed dimensions in the form of the parameter K_θ. The relation

$$[\eta]/M^{1/2} = 1.05K_\theta + 0.287\Phi_0 BM^{1/2} \tag{5}$$

is the modified Stockmayer-Fixman-Burchard (SFm) equation [19-21] The following equation

$$\frac{[\eta]^{2/3}}{M^{1/3}} = K_\theta^{2/3} + 0.363\Phi_0 B[g(\alpha_\eta)\frac{M^{2/3}}{[\eta]^{1/3}}] \tag{6}$$

where

$$g(\alpha_\eta) = 8\alpha_\eta^{\ 3}/(3\alpha_\eta^{\ 2} + 1) \qquad \text{and} \qquad \alpha_\eta^{\ 3} = [\eta]/[\eta]_\theta$$

was proposed by Kurata, Stockmayer, and Roig (KSR) [22]. Relation (7) is the Flory, Fox, and Schaefgen (FFS) equation [23, 24]

$$\frac{[\eta]^{2/3}}{M^{1/3}} = K_\theta^{2/3} + 0.858K_\theta^{2/3}\Phi_0 B\frac{M}{[\eta]} \tag{7}$$

and relation (8) is based on first-order perturbation (FOP) theory [19, 25].

$$\frac{[\eta]^{2/3}}{M^{1/3}} = K_\theta^{2/3} + \frac{0.44\Phi_0 B}{K_\theta^{1/3}} M^{1/2} \tag{8}$$

The viscosity-molecular weight data were analyzed according to Relations (5) to (8). The values of K_θ and the solvent-polymer interaction parameter (B), evaluated from the above graphical methods, for PMCBC in chloroform and binary solvent mixtures are given in Table 3. Within experimental error, all the above theories lead to more or less similar K_θ values for a given solvent. A given theory, however, does not yield the same K_θ for all the solvents. The value of K_θ is high in binary solvent mixtures. The increase in K_θ, and

TABLE 3. The Unperturbed Dimensions (K_θ) and Solvent-Polymer Interaction Parameter (B) for PMCBC at 30°C

Solvent volume ratio v/vol	$K_\theta \times 10^3$ dL·mol$^{1/2}$·g$^{-3/2}$				$B \times 10^{28}$ cm^3			
	SF	FFS	KSR	FOP	SF	FFS	KSR	FOP
CF	1.81	1.79	1.88	1.89	6.87	2.60	4.65	3.75
CF:DCE (3:1)	2.04	2.12	2.10	2.10	0.97	-0.44	-0.69	-0.54
CF:TCE (3:1)	2.40	2.42	2.46	2.46	-5.07	-2.04	-6.15	-5.18
CF:CB (3:1)	2.50	2.45	2.53	2.54	-7.11	-2.27	-7.74	-6.56

hence in the unperturbed dimensions $(\langle R^2 \rangle_0/M)^{1/2}$, may be due to a specific solvent effect [26-37]. The negative values of B in conjunction with the MHKS exponent $\nu < 0.5$ is indicative of a tightly coiled configurations of PMCBC chains below the theta temperature. The root-mean-square (rms) end-to-end distance, $(\langle R^2 \rangle_{0w}/M)^{1/2}$, at the theta state is obtained by using the heterogeneity correction based on the Schultz-Zimm [38] molecular weight distribution function. The values of $(\langle R^2 \rangle_{0w}/M)^{1/2}$ and the interaction parameter B obtained from the modified SFB plots are given in Table 4.

Free-Rotation Dimensions, $\langle R^2 \rangle_{0f}$ and Chain Stiffness Parameter σ

The stiffness of a polymer chain is generally described in terms of short-range interactions which are characteristic of the backbone. The effect of diminished free rotation about a bond as a result of steric hindrance is defined as

$$\sigma = \frac{(\langle R^2 \rangle_0/M)^{1/2}}{(\langle R^2 \rangle_{0f}/M)^{1/2}}$$

where $\langle R^2 \rangle_{0f}$ is the mean-square end-to-end distance calculated on the assumption of free rotation about bonds where bond angles are restricted. The repeat unit of PMCBC is shown schematically in Fig. 3;

TABLE 4. Unperturbed Dimensions, Solvent-Polymer Interaction Parameter, and Chain Stiffness Parameter Determined from SFm Theory for PMCBC at 30°C

Solvent volume ratio v/v	B × 10^{28} cm^3	$K_\theta \times 10^3$ $dL \cdot mol^{1/2} \cdot g^{-3/2}$	$\left(\frac{\langle R^2 \rangle_{0w}}{\overline{M}_w}\right)^{1/2}$, Å	σ
CF	11.04	1.75	0.85	1.15
CF:DCE (3:1)	0.90	1.96	0.88	1.19
CF:TCE (3:1)	-8.70	2.29	0.93	1.26
CF:CB (3:1)	-11.39	2.35	0.94	1.27

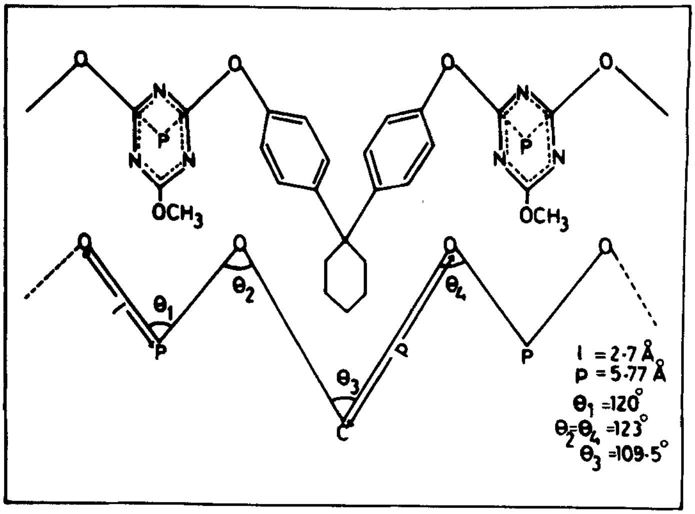


FIG. 3. Schematic representation of the repeat unit of PMCBC: (- -) virtual bond and (—) real bond.

the "rotatable" links in the chain are not all of the same type. The chain consists of three valence angles, denoted by θ_1, θ_2, and θ_3, and two link lengths, denoted by l and p. The link lengths calculated from normal covalent bond lengths are l = 2.8 Å and p = 5.77 Å [12, 33]. These link lengths have been confirmed from the molecular model of the repeat unit. The estimated valence angles are $\theta_1 = 120°$, $\theta_2 = 123°$ [39], and $\theta_3 = 109.5°$. An average end-to-end distance, $(\langle R^2 \rangle_{of}/M)^{1/2}$, is calculated by using

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

where $\alpha = \cos\theta$. The value of $(\langle R^2 \rangle_{of}/M)^{1/2}$ for PMCBC is 0.738 Å. The values of σ for PMCBC in chloroform and binary solvent mixtures are given in Table 4. Although the backbone structure apparently seems to be rigid, the polymers containing X–ϕ–X links show similar low values of σ. A comparison of σ values for polycarbonate ($\sigma = 1.3$) [33], polysulfone ($\sigma = 1.03$ [40], and PMIPT ($\sigma = 1.1$ [12] with that for PMCBC ($\sigma = 1.15$-1.27) indicates that it is the phenylene ring system which causes such low values. The macromolecules containing "long bonds" with chain links which are not simple interatomic bonds but usually aromatic rings have been reported to give unusually small coil dimensions in solution, in that their unperturbed dimensions are only slightly greater than the values theoretically calculated assuming free rotation about chain links. PMCBC also belongs to the class of macromolecules containing "long bonds." This behavior has been attributed to the relatively great average link lengths and the apparently small energy differences between the various rotational isomers since it is noticeable that such polymers not only have $\sigma \approx 1$, but also that the temperature dependence of their dimensions is small.

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