

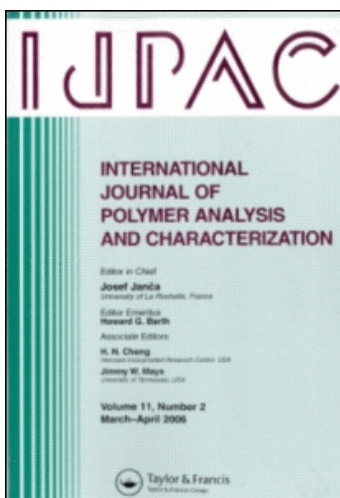
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# Chain Flexibility Characterization of Poly(oxymethylene)

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Flory's characteristic ratio  $C_\infty$  for poly(oxymethylene) (POM) has been measured by Stockmayer from viscosity measurements in hexafluoroacetone sesquihydrate. The value of  $C_\infty$  determined was 10.5, almost the same as that for polystyrene. This  $C_\infty$  value was suspected of being higher than the real  $C_\infty$  value of POM because of the strong solvation power of hexafluoroacetone hydrate and its specific interaction with POM. In this paper, the  $C_\infty$  of POM were determined in *m*-cresol at 100°C and *p*-chlorophenol at 60°C via intrinsic viscosity measurements. Characteristic ratios of 6.72 and 6.97 were found at 60°C and 100°C, respectively. The results show that the POM chain is more flexible than polystyrene and is similar in flexibility to polyethylene chain. The positive temperature coefficient of chain dimensions indicates that more compact chain conformations have lower energies. The Mark–Houwink–Sakurada equations for POM in *m*-cresol (100°C) and *p*-chlorophenol (60°C) have been evaluated simultaneously.

**Keywords:** Poly(oxymethylene); Characteristic ratio  $C_\infty$ ; Chain flexibility; Dilute solution viscosity; MHS equation

## INTRODUCTION

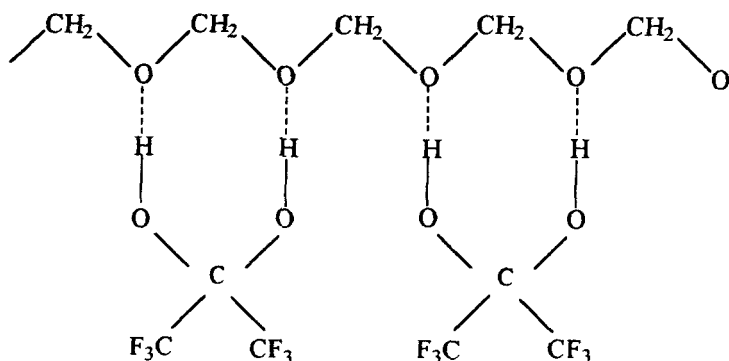
Flory's characteristic ratio,  $C_\infty$ , is the most common parameter for characterization of polymer chain flexibility,<sup>[1]</sup> which is defined as:

$$C_\infty = \lim_{N \rightarrow \infty} \frac{\langle r^2 \rangle_0}{Nl^2}, \quad (1)$$

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where  $\langle r^2 \rangle_0$  is the unperturbed (theta condition) mean-square end-to-end distance, and  $N$  is the number of main chain bonds of length  $l$ . For a freely jointed chain, which has neither rotational hindrances nor bond angle restrictions,  $\langle r^2 \rangle_0$  is equal to  $Nl^2$ . Thus, the value of  $C_\infty$  is equal to 1 for a freely jointed chain, and larger  $C_\infty$  values indicate the departure from freely jointed behavior, that is, diminished flexibility due to fixed bond angles and rotational hindrances. Therefore, the value of  $C_\infty$  is a quantitative measure of polymer chain flexibility.

$C_\infty$  for poly(oxymethylene) (POM) has been estimated by Stockmayer and Chan<sup>[2]</sup> from viscosity measurements in hexafluoroacetone sesquihydrate. The value of  $r_0/M^{1/2}$  was  $1200 \pm 80 \times 10^{-4}$  nm and  $C_\infty$  was 10.5, almost the same as that of polystyrene.<sup>[3]</sup> We suspect that this  $C_\infty$  value of 10.5 is higher than the real  $C_\infty$  value of POM because of the strong solvation power of hydrogen bonds between the hexafluoroacetone hydrate and POM chain. The possible form of solvation was suggested as follows:<sup>[2]</sup>



In this paper we report the  $C_\infty$  values of POM obtained by the combined measurements of weight-average molecular weights and intrinsic viscosities in *m*-cresol (100°C) and in *p*-chlorophenol (60°C). The  $C_\infty$  values of 6.97 in *m*-cresol (100°C) and 6.72 in *p*-chlorophenol (60°C) are quite different from the  $C_\infty$  value of 10.5 and is comparable to the values  $C_\infty = 7.4-8.4$ <sup>[4]</sup> found for other more flexible polymer chains, such as polyethylene. The temperature coefficient of unperturbed chain dimensions for POM and the Mark-Houwink-Sakurada (MHS) equations, both in the POM *m*-cresol system (100°C) and in

the POM *p*-chlorophenol system (60°C) have been evaluated and discussed below.

## EXPERIMENTAL SECTION

The POM samples were POM copolymers (with 5 wt% 1,3-dioxolane) from Shanghai Solvent Company, and thus contain 3% oxyethylene units. This should have a negligible influence on the measurements of  $\langle r^2 \rangle_0$  and  $C_\infty$ , nevertheless, the POM copolymer is more stable than POM homopolymer for solution measurements at higher temperature.

The solvent hexafluoroacetone (Shanghai Institute of Organofluorine Materials) was distilled before use. The solvents *m*-cresol and *p*-chlorophenol were analytical reagent grade and purified by distillation under reduced pressure.

The weight-average molecular weights ( $M_w$ ) of the POM samples were determined with a Brookhaven 200SM laser light scattering photometer. This instrument was equipped with a Spectra-Physics 200 argon laser source and at a wavelength of 514.5 nm. Hexafluoro acetone hydrate was used as the solvent at a temperature of  $25 \pm 0.01^\circ\text{C}$ . The  $dn/dc$  of POM hexafluoroacetone hydrate system ( $25^\circ\text{C}$ ) at 514.5 nm is 0.129 mL/g. The weight-average molecular weights were obtained by Zimm plots.

The polydispersity ( $M_w/M_n$ ) of the POM samples was estimated by Waters 150C size exclusion chromatography with a  $\mu$ -Styragel column set from 500 to  $10^6$  Å. Purified fresh *m*-cresol (with 2%  $\alpha$ -pinene as antioxidant) was the carrier solvent at a flow rate of 1 mL/min. The temperature was  $100^\circ\text{C}$ .

The dilute solution viscosities of POM samples in *m*-cresol at  $100 \pm 0.05^\circ\text{C}$  and *p*-chlorophenol at  $60 \pm 0.05^\circ\text{C}$  were measured in Ubbelohde viscometers having negligible kinetic energy corrections. Two percent  $\alpha$ -pinene was added to the solvents to avoid degradation of POM. The values of intrinsic viscosities were obtained by conventional extrapolation to infinite dilution of the  $\eta_{sp}/c$  and  $\ln \eta_r/c$  vs  $c$  plots.

## RESULTS AND DISCUSSION

The evaluation of  $C_\infty$  is most conveniently accomplished by the combined measurements of weight-average molecular weights and intrinsic

viscosities  $[\eta]$  (assuming Flory's hydrodynamic parameter  $\Phi$  is known).  $[\eta]$  can be measured either in thermodynamically good solvents or in an ideal solvent, that is, under theta conditions. Measurements in good solvents require the application of extrapolation to infinitely low molecular weights as shown by the procedures of Burchard<sup>[5]</sup> and Stockmayer and Fixman.<sup>[6]</sup>

$$[\eta]/M^{1/2} = K_\theta + 0.51\Phi_0 BM^{1/2}, \quad (2)$$

in which a plot of  $[\eta]/M^{1/2}$  vs  $M^{1/2}$ , yields  $K_\theta$  as the intercept. From the value of  $K_\theta$ ,  $\langle r^2 \rangle_0/M$  can be determined from the relationship

$$[\eta]_\theta = \Phi_0(\langle r^2 \rangle_0)^{3/2}/M = K_\theta M^{1/2}, \quad (3)$$

$$K_\theta = \Phi_0(\langle r^2 \rangle_0/M)^{3/2}, \quad (4)$$

where  $\langle r^2 \rangle_0$  represents the mean-square unperturbed end-to-end distance in  $\text{cm}^2$ ,  $[\eta]$  is intrinsic viscosity in  $\text{cm}^3/\text{g}$ , and  $\Phi_0$  is the Flory constant which has been found experimentally to have the value of  $2.5 (\pm 0.1) \times 10^{23} \text{ mol}^{-1}$ .<sup>[7]</sup>

Flory's characteristic ratio,  $C_\infty$ , can then be calculated from the following:

$$C_\infty = \lim_{N \rightarrow \infty} \frac{\langle r^2 \rangle_0/M}{(N'/M_0)l^2}, \quad (5)$$

where  $N$  is the number of bonds in the chain and  $N'$  denotes the number of backbone chain bonds per repeat unit,  $l$  is the mean-square average bond length, and  $M_0$  is the mass per repeat unit. For POM chain,  $N'$  is 2 per repeat unit,  $l$  is taken as 0.143 nm, and  $M_0$  is 30.

The dilute solution characterization results of POM samples, including  $M_w$ ,  $M_w/M_n$ ,  $[\eta]$  and Huggins coefficient  $k'$  are listed in Table I. From the  $[\eta]$  and  $M_w$  data in Table I, a plot of  $\ln[\eta]$  vs  $\ln M_w$ , yields the following relationships for POM:

$$[\eta] = 3.70 \times 10^{-2} M_w^{0.705} \quad (m\text{-cresol}, 100^\circ\text{C}, \text{mL g}^{-1}), \quad (6)$$

$$[\eta] = 1.91 \times 10^{-2} M_w^{0.792} \quad (p\text{-chlorophenol}, 60^\circ\text{C}, \text{mL g}^{-1}). \quad (7)$$

Because polydisperse POM samples ( $M_w/M_n = 1.58\text{--}2.68$ ) were used, the correction for polydispersity effects must be considered.

TABLE I Characteristics of POM samples

Sample	$M_w \times 10^{-4}$	$M_w/M_n$	$[\eta]_1$ (mL g <sup>-1</sup> )	$k'_1$	$[\eta]_2$ (mL g <sup>-1</sup> )	$k'_2$
POM-1	10.8	2.12	130.0	0.39	/	/
POM-2	9.70	1.58	123.9	0.38	169.2	0.35
POM-7	/	2.65	102.2	0.41	136.3	0.33
POM-10	7.50	2.68	99.0	0.36	139.7	0.37
POM-9	7.38	2.00	97.5	0.40	135.5	0.32
POM-3	6.50	1.84	/	/	124.0	0.43
POM-4	5.69	1.73	82.1	0.28	108.0	0.32
POM-8	5.29	/	79.9	0.35	106.7	0.32
POM-6	5.29	1.63	79.7	0.34	105.0	0.41

Subscript 1: *m*-cresol (100°C); 2: *p*-chlorophenol (60°C).

The correction method employed was suggested by Xu *et al.*<sup>[8]</sup> Using Weslau's distribution function to describe the molecular weight distribution of the samples, we get the following equation:

$$K_w = K_m (M_w/M_n)^{\alpha(\alpha-1)/2}, \quad (8)$$

where  $K_w$  is the coefficient of MHS equation from polymer samples with broad distribution,  $K_m$  is the coefficient of the MHS equation from monodisperse polymer samples, and  $\alpha$  is the exponent of the MHS equation.

From Equations (6) and (7) and the  $M_w/M_n$  values for each sample, ( $K_w/K_m$ ) can then be calculated, and the appropriate monodisperse molecular weight  $M_m$  for each polydisperse POM sample can be estimated by the following equation:

$$[\eta] = K_w (K_w/K_m)^{-1} M_m^\alpha. \quad (9)$$

The calculated  $K_w/K_m$  and  $M_m$  results are listed in Table II.

After polydispersity corrections, the more reliable MHS equations for POM in the two systems can be evaluated by  $\ln[\eta]$  vs  $\ln M_w$  plots:

$$[\eta] = 3.76 \times 10^{-2} M_w^{0.710} \quad (m\text{-cresol, } 100^\circ\text{C, mL/g}), \quad (10)$$

$$[\eta] = 1.93 \times 10^{-2} M_w^{0.796} \quad (p\text{-chlorophenol, } 60^\circ\text{C, mL/g}). \quad (11)$$

TABLE II The appropriate monodisperse molecular weights of polydisperse POM samples

Sample	$(K_w/K_m)_1$	$[\eta]_1$	$M_{m1} \times 10^{-4}$	$(K_w/K_m)_2$	$[\eta]_2$	$M_{m2} \times 10^{-4}$
POM-1	0.925	130.0	9.58	0.940	/	/
POM-2	0.954	123.9	9.34	0.963	169.2	9.19
POM-7	0.904	102.2	6.59	0.923	136.3	6.63
POM-10	0.903	99.0	6.29	0.922	139.7	6.83
POM-9	0.930	97.5	6.42	0.945	135.5	6.78
POM-3	0.939	/	/	0.951	124.0	6.11
POM-4	0.940	82.1	5.14	0.956	108.0	5.17
POM-8	/	79.9	/	/	106.7	/
POM-6	0.951	79.7	4.97	0.961	105.0	4.99

Subscript 1: *m*-cresol (100°C); 2: *p*-chlorophenol (60°C).

The appropriate monodisperse molecular weights  $M_w$ , listed in Table II, were used to calculate  $K_\theta$ ,  $\langle r^2 \rangle_0/M$  and  $C_\infty$  by the BSF extrapolation procedure. The results are as follows:

$$\begin{aligned}
 K_\theta &= 0.232, & \langle r_0 \rangle / M^{1/2} &= 975 \times 10^{-4} \text{ nm}, \\
 C_\infty &= 6.97 & & (\textit{m}\text{-cresol}, 100^\circ\text{C}), \\
 K_\theta &= 0.219, & \langle r_0 \rangle / M^{1/2} &= 957 \times 10^{-4} \text{ nm}, \\
 C_\infty &= 6.72 & & (\textit{p}\text{-chlorophenol}, 60^\circ\text{C}).
 \end{aligned}$$

Because of solvent and temperature dependence of unperturbed chain dimension, we obtain two different  $C_\infty$  values for POM in the two systems. If we neglect the solvent influence on unperturbed chain dimensions, the temperature coefficient of unperturbed chain dimensions of POM,  $\kappa = d \ln \langle r^2 \rangle_0 / dT$  (in units of reciprocal absolute temperature), is calculated as  $0.96 \times 10^{-3}$ . This value is similar to the  $\kappa$  value of  $0.78 \times 10^{-3}$  of poly(dimethyl siloxane).<sup>[9]</sup> The positive temperature coefficient indicates that more compact chain postures have lower energies.

From our  $C_\infty$  data, we can conclude that the chain flexibility of POM is greater than that of polystyrene and is comparable to that of polyethylene.<sup>[4]</sup>

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