Synthesis and characterization of poly(2-methoxycyanurate) of bisphenol-F

Sujata Kansara*

Department of Chemistry, Faculty of Science, Maharaja Sayajirao University of Baroda, Baroda 390 002, India

and N. K. Patel and C. K. Patel

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar 388 120, India

The linear poly(2-methoxycyanurate) of bisphenol-F was synthesized by interfacial polycondensation from bisphenol-F and 2-methoxy-4,6-dichloro-s-triazine. The fractions obtained by fractional precipitation were characterized by light scattering, osmometry and viscosity. The short- and long-range interaction parameters were determined in different solvent systems and at four different temperatures. The results were examined in the light of excluded volume theories to determine the conformation of the polymer.

(Keywords: poly(2-methoxycyanurate) of bisphenol-F; short-range interactions; long-range interactions; excluded volume theories)

INTRODUCTION

The thermal stability of polymeric materials is of particular use in aerospace applications and in instruments where failure of most plastics is observed due to degradation and/or softening. An extensive literature exists on thermally stable polymers in which aromatic and heterocyclic rings are linked together in the main chain[1,2]. A variety of polycyanurates known for their thermal stability because of the s-triazine ring in the main chain have been reported[3-6]. However, systematic studies of solution properties which provide information about the behaviour of macromolecules in solution and may therefore reflect many useful properties are scarce for this class of polymers[7,8].

This paper reports the synthesis of high molecular weight poly(2-methoxycyanurate) of bisphenol-F (PMCBF) and its characterization by using light scattering, osmometry and viscosity. The investigation of the solution behaviour in various solvent systems was carried out to obtain an insight into the conformational behaviour of the polymer.

EXPERIMENTAL

Materials

Monomer 4,4'-dihydroxy diphenylmethane (bisphenol-F) was prepared from phenol and formaldehyde as per reported methods[9]. 2-Methoxy-4,6-dichloro-s-triazine (MDT) was synthesized from cyanuric chloride[10]. Solvents used for dilute solution studies were analytical grade materials.

Polymer preparation

A solution of bisphenol-F (0.25 mol), sodium hydroxide (0.5 mol), cetyl dimethyl benzyl ammonium chloride (0.625 g) in distilled water (250 ml) was stirred vigorously in a 500 ml three-necked flask equipped with a stirrer and thermometer to obtain complete emulsion. To the emulsified mixture a solution of 2-methoxy-4,6-dichloro-s-triazine (0.25 mol) in chloroform (65 ml) was then added and stirring was continued for 5 h at 10°C. The polymer from the organic layer was precipitated out in methanol, and then washed several times with water to remove salt and emulsifier. Finally it was washed with acetone and dried at 60°C. The reaction is shown in *Scheme 1*.

To study the effect of solvent on the behaviour of polymer is solution, the solvents used were chloroform (CF), which was found to be a good solvent, and its
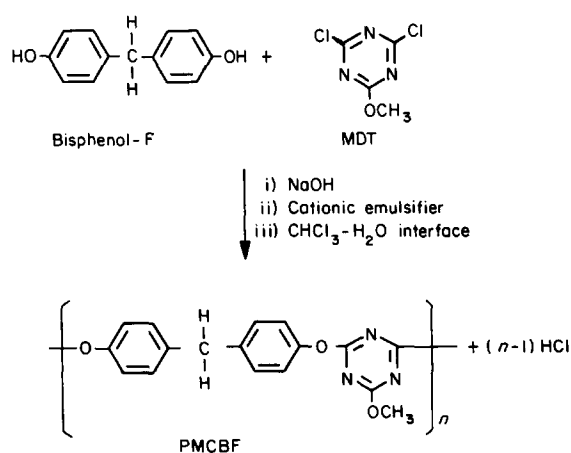
Scheme 1

binary mixtures with dichloroethane, dioxane and n-butanol, which were found to be poor solvents.

The polymer obtained was fractionated by fractional precipitation at 30°C using CF as solvent and n-butanol as precipitant. Intrinsic viscosity measurements of the fractions were carried out using an Ubbelohde suspended level viscometer at four different temperatures (30, 35, 40 and 45°C) and in different solvent systems of CF and its binary mixtures. The binary mixtures employed were CF, CF:dichloroethane (DCE, 70:30 v/v), CF:dioxane (80:20 v/v), CF:dioxane (70:30 v/v) and CF:n-butanol (90:10 v/v).

A Brice–Phoenix light scattering photometer was used to determine the weight-average molecular weight ($\bar{M}_w$) of fractions in CF at 30°C and at a wavelength of 436 nm. Solutions used for the light scattering measurements were centrifuged with an ultracentrifuge machine (Janetzki, VAC 601) at 30 000 rev min^{-1} for ~30 min. The supernatant liquid was transferred into a G5 sintered glass funnel and filtered. The solvent was also filtered through a G5 funnel prior to use. The relative intensity of the incident beam and the response of the photomultiplier tube were standardized by the scattered radiation from a calibrated opal (monitored) reference standard. The instrument was calibrated with a standard polystyrene sample of known molecular weight. The specific refractive index increment was measured on a Brice–Phoenix differential refractometer in CF at 30°C and was found to be 0.173 ml g^{-1}. The determination of the radius of gyration and the solvent–polymer interaction parameter A_2 was carried out by the graphical Zimm method. The number-average molecular weights ($\bar{M}_n$) were determined by osmotic pressure measurements using a Hewlett-Packard 502 high speed membrane osmometer and non-aqueous type O-8 membranes in CF at 30°C.

RESULTS AND DISCUSSION

The intrinsic viscosities ($[\eta]$) of fractions (s-fractions) of PMCBF in different solvents and at different temperatures are shown in *Table 1*. The results indicate that $[\eta]$ and the solvent power for a given fraction at a given temperature are in the following order: CF > CF:DCE (70:30 v/v) > CF:n-butanol (90:10 v/v) > CF:dioxane (80:20 v/v) > CF:dioxane (70:30 v/v). Results reveal that $[\eta]$ decreases with increase in temperature in all solvent systems but the decrease in $[\eta]$ with temperature is more pronounced in binary mixtures than in pure CF.

The $\bar{M}_w$ and $\bar{M}_n$ values, radius of gyration, end-to-end distance and A_2 values (light scattering) of the fractions with the corresponding $[\eta]$ values in CF at 30°C are summarized in *Table 2*.

The viscosity–molecular weight relationships were obtained in different solvents and at different temperatures according to the Mark–Houwink–Kuhn–Sakurada (MHKS) relation. The MHKS constants are shown in

Table 1 Viscosity data (dl g^{-1}) of PMCBF fractions in different solvent systems and at different temperatures

Fraction	$\bar{M}_w$ (× 10^{-5})	Temperature (°C)	CF	CF:DCE (70:30 v/v)	CF:dioxane (80:20 v/v)	CF:dioxane (70:30 v/v)	CF:n-butanol (90:10 v/v)
S$_4$	7.52	30	2.68	–	–	–	2.20
		35	2.54	–	–	–	–
		40	2.44	–	–	–	–
		45	2.38	–	–	–	–
S$_7$	3.19	30	1.56	1.56	1.03	0.77	1.50
		35	1.49	1.49	1.02	0.76	–
		40	1.44	1.43	1.00	0.75	–
		45	1.40	1.39	0.99	0.74	–
S$_8$	2.40	30	1.32	1.24	0.92	0.71	1.05
		35	1.25	1.21	0.90	0.68	–
		40	1.22	1.17	0.89	0.67	–
		45	1.17	1.11	0.87	0.65	–
S$_{10}$	1.25	30	0.94	0.87	0.66	0.55	0.80
		35	0.91	0.85	0.65	0.52	–
		40	0.88	0.81	0.62	0.51	–
		45	0.86	0.77	0.60	0.50	–
S$_{12}$	1.10	30	0.81	0.78	–	0.52	0.73
		35	0.79	0.77	–	0.51	–
		40	0.77	0.75	–	0.50	–
		45	0.75	0.73	–	0.49	–
S$_{13}$	0.86	30	0.70	0.71	0.58	–	0.60
		35	0.68	0.69	0.56	–	–
		40	0.66	0.67	0.54	–	–
		45	0.65	0.65	0.52	–	–
S$_{14}$	0.65	30	0.58	0.56	0.48	0.44	0.55
		35	0.56	0.55	0.47	0.43	–
		40	0.55	0.54	0.46	0.41	–
		45	0.54	0.53	0.44	0.39	–

Table 2 Light scattering and osmometry data of PMCBF fractions in CF at 30°C

Fraction	$[\eta]^{30°C}_{CHCl_3}$	$\bar{M}_w$ ($\times 10^{-5}$)	$\bar{M}_n$ ($\times 10^{-4}$)	$\langle S^2 \rangle^{1/2}_z$ (Å)	$\langle R^2 \rangle^{1/2}_{ow}$ (Å)	A_2 ($\times 10^4$) (cm^3 mol g^{-2})
S_4	2.68	7.52	39.80	498	982	1.40
S_7	1.56	3.19	8.70	310	611	6.60
S_8	1.32	2.40	8.14	251	495	7.09
S_{10}	0.94	1.25	5.50	178	351	7.65
S_{12}	0.81	1.10	5.30	179	353	8.32
S_{13}	0.70	0.86	4.94	145	286	8.41
S_{14}	0.58	0.65	4.40	120	237	8.91

$$\langle R^2 \rangle^{1/2}_{ow} = \left[6\langle S^2 \rangle_z \left(-\frac{h+1}{h+2} \right) \right]^{1/2}$$

where $h = \left(\frac{\bar{M}_w}{\bar{M}_n} - 1 \right)^{-1} = 0.843$

Table 3 Mark–Houwink–Kuhn–Sakurada constants[a] for PMCBF in different solvents at the temperatures indicated

Solvent	Temperature (°C)	a	K' ($\times 10^4$) (dl g^{-1})
CF	30	0.62	6.34
	35	0.60	7.19
	40	0.60	7.40
	45	0.59	7.87
CF:DCE (70:30 v/v)	30	0.61	6.71
	35	0.59	8.17
	40	0.59	8.24
	45	0.58	8.91
CF:dioxane (80:20 v/v)	30	0.46	29.00
	35	0.48	23.20
	40	0.49	20.60
	45	0.50	17.10
CF:dioxane (70:30 v/v)	30	0.37	73.50
	35	0.38	59.70
	40	0.39	55.50
	45	0.40	46.20
CF:n-butanol (90:10 v/v)	30	0.58	8.30

[a] $[\eta] = K'M^a$

Table 3. Results indicate that the MHKS constant K' decreases and the exponent a increases with increasing solvent power as expected. It can be seen from *Table 3* that even though the exponent values in binary mixtures of CF:dioxane (80:20 and 70:30 v/v) are <0.5, the polymer remains in solution. This phenomenon may be attributed to the tightly coiled configuration of the polymer, i.e. the strained compact configuration regarding the bond rotation. Polymer precipitation results as the polymer–polymer interaction increases in the two opposing forces, namely the polymer–polymer interaction and the polymer–solvent interaction, which is normally the case below θ conditions. In the case of PMCBF, the polymer remains in solution even below θ conditions. This is only possible if the polymer configuration is strained and the strain in a polymer molecule minimizes the chance of polymer–polymer interaction as a result of which, even below θ conditions, for the two opposing forces stated above the latter remains predominant. Similar results have been reported[7].

The molecular-weight dependence of the end-to-end distance and solvent–polymer interaction parameter for

PMCBF are given by the following relations:

$$\langle R^2 \rangle^{1/2}_w = 0.464\bar{M}^{0.57}_w \tag{1}$$

$$A_2 = 0.95 \times 10^{-2}\bar{M}^{-0.21}_w \tag{2}$$

Note that $\langle R^2 \rangle^{1/2}_w$ increases and A_2 decreases with increase in molecular weight, which is in accordance with excluded volume theory[11].

In order to obtain short- and long-range interaction parameters and the unperturbed dimensions from the $[\eta]-M$ relation determined under non-θ conditions, various excluded volume theories[12–20] were employed. The values of the short- (K_θ) and long-range interaction parameters (B) thus obtained in different solvents and at different temperatures are presented in *Tables 4* and *5*, respectively. The results indicate that for PMCBF all theories yield linear relations and a common intercept over the entire molecular weight range and in all the solvents studied. However, large variations are observed in B values from theory to theory. The magnitude of B reflects the type of assumptions involved in each of the theories. Qualitatively, all the theories agree very well, stating that B decreases in good solvents and increases in poor solvents with rise in temperature. This suggests that the polymer chain is flexible and the flexibility can be attributed to the ether link in the backbone chain[21]. The K_θ and B values of PMCBF under various experimental conditions and the corresponding molecular weight parameters are shown in *Table 6*. In the unperturbed state the PMCBF chains assume the $(\langle R^2 \rangle_{ow}/\bar{M}_w)^{1/2}$ value to be 0.92 Å at 30°C. This value varied by 2% in different solvents at 30°C which could be explained in terms of minor specific solvent effects. However, the temperature coefficient of unperturbed dimensions changes drastically from a good to a poor solvent. Chlorinated hydrocarbon, when employed as the solvent or in mixed solvents, results in non-ideal polymer solutions with positive non-ideality. On the other hand, CF–dioxane mixtures as solvents result in negative non-ideal behaviour. In the former case, the temperature coefficient of the end-to-end distance remains small whereas it assumes a rather large value in the latter solvent systems. In fact the two opposing phenomena, solubility and rotational potential barrier, are operative in deciding the effect of temperature on polymer configuration. The increase in solubility is greater in a poor solvent than in a good solvent with increase in

Table 4 Estimated values of the short-range interaction parameter K_θ ($\times 10^3$ dl mol$^{1/2}$ g$^{-3/2}$) for PMCBF according to different theories[a]

Solvent	Temperature (°C)	SF	FFS	BJ	FOP	IP	KSR	DB	YT
CF	30	2.06	1.94	2.13	2.09	2.40	2.08	2.03	1.96
	35	2.03	1.93	2.09	2.06	2.40	2.05	2.00	1.94
	40	1.99	1.92	2.04	2.02	2.39	2.00	1.97	1.92
	45	1.97	1.91	2.02	2.00	2.39	1.99	1.94	1.91
CF:DCE	30	2.04	1.92	2.06	2.04	2.13	1.93	1.94	1.94
(70:30 v/v)	35	2.02	1.91	1.96	1.94	2.11	1.93	1.92	1.93
	40	2.02	1.90	1.95	1.93	2.07	1.92	1.92	1.92
	45	2.01	1.88	1.92	1.91	2.06	1.91	1.91	1.91
CF:dioxane	30	1.99	1.99	1.99	1.99	2.10	1.99	1.99	1.99
(80:20 v/v)	35	1.94	1.95	1.95	1.95	2.06	1.95	1.94	1.94
	40	1.84	1.84	1.84	1.84	1.94	1.84	1.84	1.84
	45	1.74	1.74	1.73	1.73	1.82	1.73	1.74	1.74
CF:dioxane	30	1.98	1.91	2.06	2.00	2.40	2.00	1.97	1.92
(70:30*versus*)	35	1.86	1.83	1.95	1.91	2.31	1.90	1.86	1.83
	40	1.82	1.76	1.88	1.84	2.22	1.84	1.82	1.79
	45	1.71	1.69	1.77	1.75	2.14	1.74	1.71	1.69
CF:n-butanol (90:10 v/v)	30	1.93	1.82	1.86	1.84	2.35	1.84	1.88	1.89

[a]SF, Stockmayer–Fixman; FFS, Flory–Fox–Schaefgen; BJ, Bueche–Jame; FOP, first-order perturbation; IP, Inagaki–Ptitsyn; KSR, Kurata–Stockmayer–Roig; DB, Domb–Barrett; YT, Yamakawa–Tanaka

Table 5 Estimated values of the long-range parameter B ($\times 10^{27}$ cm^3) for PMCBF according to different theories

Solvent	Temperature (°C)	SF	FFS	BJ	FOP	IP	KSR	DB	YT
CF	30	0.83	0.55	0.52	0.60	0.94	0.76	0.76	0.96
	35	0.72	0.45	0.46	0.52	0.76	0.67	0.65	0.81
	40	0.68	0.40	0.43	0.49	0.68	0.61	0.59	0.73
	45	0.62	0.36	0.40	0.45	0.60	0.57	0.55	0.66
CF:DCE	30	0.79	0.50	0.49	0.53	0.84	0.67	0.70	0.87
(70:30 v/v)	35	0.68	0.44	0.42	0.48	0.72	0.60	0.63	0.72
	40	0.62	0.36	0.38	0.44	0.65	0.55	0.55	0.68
	45	0.56	0.30	0.31	0.39	0.58	0.49	0.51	0.60
CF:dioxane	30	−0.20	−0.06	−0.15	−0.14	−0.10	−0.17	−0.14	−0.14
(80:20 v/v)	35	−0.16	−0.05	−0.11	−0.12	−0.07	−0.13	−0.12	−0.11
	40	−0.07	−0.03	−0.03	−0.05	−0.02	−0.06	−0.05	−0.05
	45	0.02	0.02	0.03	0.03	0.01	0.04	0.02	0.01
CF:dioxane	30	−0.77	−0.65	−0.81	−0.65	−0.78	−0.75	−0.48	−0.45
(70:30 v/v)	35	−0.65	−0.58	−0.71	−0.58	−0.69	−0.68	−0.48	−0.39
	40	−0.64	−0.52	−0.63	−0.53	−0.61	−0.62	−0.47	−0.38
	45	−0.52	−0.44	−0.52	−0.45	−0.50	−0.53	−0.40	−0.33
CF:n-butanol (90:10 v/v)	30	0.54	0.41	0.42	0.46	0.51	0.58	0.54	0.55

temperature, while the rotational potential barrier is affected equally in both. As a result, in good solvents where appreciable excluded volume effects prevail, either the solubility parameter or the lowering of the potential barrier does not contribute much to the change of configuration. However, the rotational potential barrier takes over the solubility effect to a small extent and the molecular dimensions decrease minutely with rise in temperature. On the other hand, in poor solvents the strained compact configuration attained below θ conditions is made free of strains by raising the temperature through favourable bond rotation. It is justified therefore that the temperature coefficient of the unperturbed end-to-end distance assumes larger values in the 'below θ' state and small values in the 'above θ' state.

To examine the validity of the excluded volume theories for the experimental results, theoretical plots of the excluded volume parameter (z) *versus* the expansion factor (α_s) were constructed according to various theoretical expressions suggested by Cornet[22]. The experimental points of PMCBF in all solvents together

Table 6 The short- (K_θ) and long-range (B) parameters of PMCBF solutions for the given experimental conditions of solvent and temperature

Solvent	Temperature (°C)	K_θ ($\times 10^3$)[a] (dl mol$^{1/2}$ g$^{-3/2}$)	B ($\times 10^{27}$)[b] (cm^3)	$\left(\dfrac{\langle R^2 \rangle_{ow}}{\bar{M}_w}\right)^{1/2}$ (Å)	$\dfrac{-d\ln\langle R^2 \rangle_{ow}}{dT(\times 10^3)}$
CF	30	2.10	0.830	0.92	
	35	2.09	0.720	0.92	1.29
	40	2.06	0.680	0.91	
	45	2.04	0.620	0.91	
CF:DCE	30	2.06	0.790	0.92	
(70:30 v/v)	35	2.03	0.680	0.91	1.63
	40	2.02	0.620	0.91	
	45	2.01	0.560	0.91	
CF:dioxane	30	1.99	−0.196	0.90	
(80:20 v/v)	35	1.94	−0.156	0.89	5.87
	40	1.84	−0.070	0.88	
	45	1.74	+0.020	0.86	
CF:dioxane	30	2.07	−0.770	0.90	
(70:30 v/v)	35	1.97	−0.650	0.88	5.48
	40	1.91	−0.630	0.88	
	45	1.83	−0.520	0.86	
CF:n-butanol (90:10 v/v)	30	1.93	0.540	−	−

[a] Averaged over all theories except IP
[b] According to SF; $q_w = 0.94$ (Schulz–Zimm distribution)

with the theoretical lines are shown in *Figure 1*. In order to avoid clustering of experimental points, the curve is split into separate curves for different theories. All the excluded volume theories give best fit with the experimental data in the vicinity of the θ state and particularly in the range of $0.96 \leqslant \alpha_s \leqslant 1.08$. It is interesting to note that the FOP and BJ theories where inappropriate expansion of polymer chains is considered at higher excluded volume consistently deviate only above $\alpha_s > 1.08$. On the other hand, KSR and F,o deviate only in the below θ state where $\alpha_s < 0.96$, in contradiction to the observations of Orofino[23]. Thus the present analysis not only takes into consideration the adequacy of the theory but also considers its self-consistency. Calculations based on B values derived from various theories and the unique value of K_θ, showed that only the Fixman theory was consistent over the whole range of excluded volume effect covered by the present experiment.

The theoretical plots of ε versus α_η for different theories are shown in *Figure 2*, where ε is the Ptitsyn–Eizner[24] exponent and is related to the MHKS constant a by the relation: $\varepsilon = (2a - 1)/3$. It is also related to α and z by the relation:

$$\varepsilon = \frac{d\ln\alpha}{d\ln z} \qquad (3)$$

This analysis seems to be more sensitive than the previous analysis. The analysis indicates good agreement in the region $0.98 \leqslant \alpha_\eta \leqslant 1.02$, which is a narrow range compared to that of the previous one. The inherent reason for this discrepancy is because in the previous analysis all excluded volume theories have adjusted a constant parameter while in the latter analysis there is no forced constant in the theories. Results indicate that
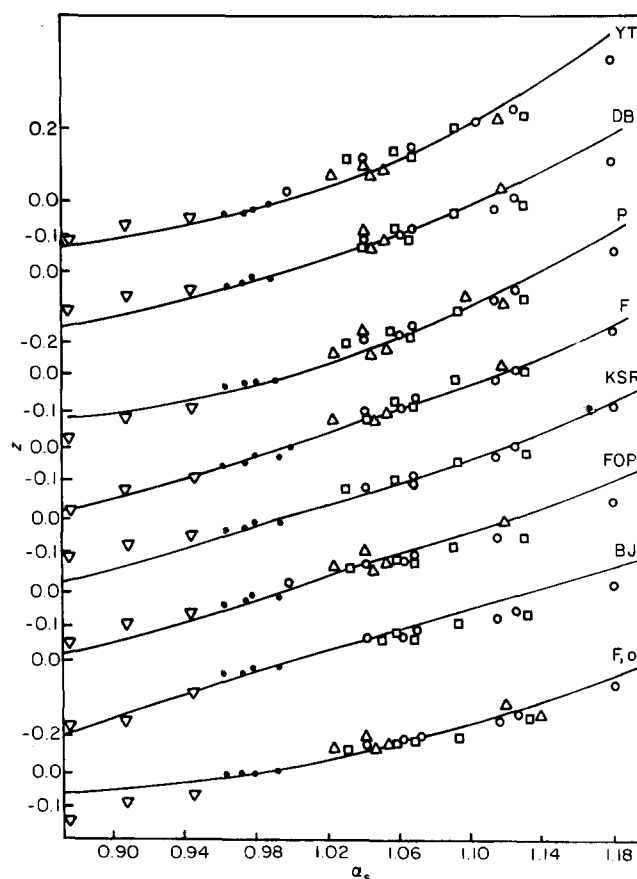

Figure 1 z versus α_s for PMCBF in all solvents with the theoretical curves due to different theories. YT, Yamakawa–Tanaka; DB, Domb–Barrett; P, Ptitsyn; F, Fixman; KSR, Kurata–Stockmayer Roig; FOP, first-order perturbation; BJ, Bueche–Jame; F,o, Flory original
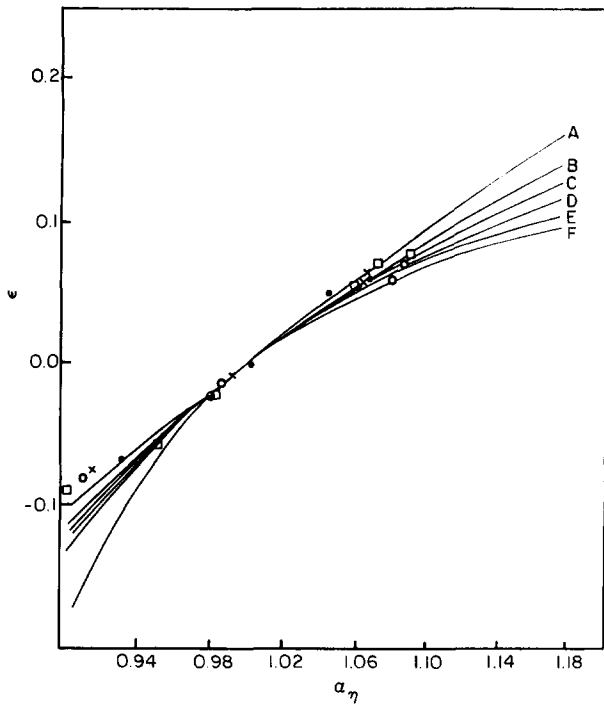
Figure 2 ε *versus* α_η for PMCBF in all solvents with the theoretical curves due to different theories: (A) BJ; (B) FOP; (C) F; (D) KSR; (E) YT; (F) F,o
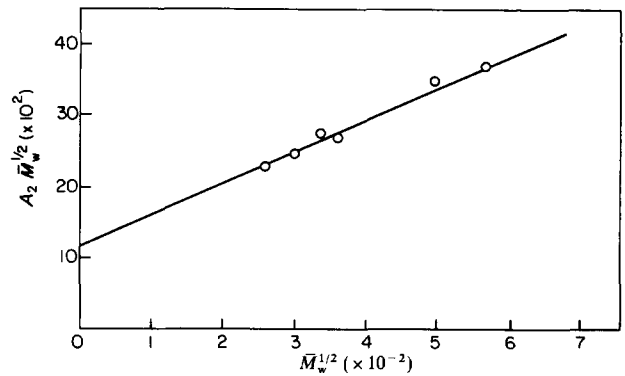

Figure 3 Kurata plot of $A_2 \bar{M}_w^{1/2}$ *versus* $\bar{M}_w^{1/2}$ for PMCBF fractions in CF at 30°C
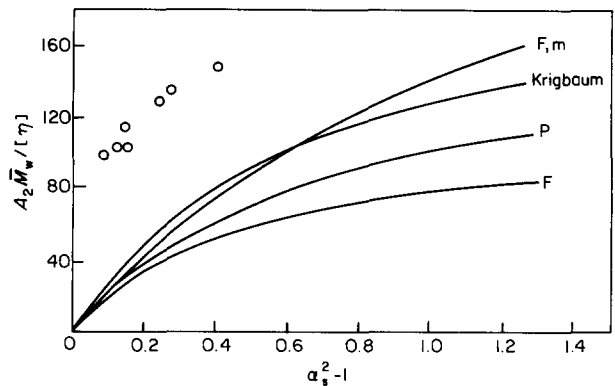

Figure 4 $A_2 \bar{M}_w/[\eta]$ *versus* $\alpha_s^2 - 1$ for PMCBF in all solvents with the theoretical curves for Krigbaum, and for Flory–Krigbaum–Orofino (FKO) theories with the combinations of Flory modified (F,m), Ptitsyn (P) and Fixman (F) theories

except for F,o theory all the theories agree very well with the experimental points at high excluded volume effect which supports the fact that F,o theory overestimates the excluded volume effect. At below θ conditions on the other hand, considering experimental error, all the theories agree well while the F,o theory remains far below the experimental points. This indicates that the F,o theory underestimates the excluded volume effect in the below θ state. It has been reported[23] that the F,o theory is applicable even in θ conditions based on experimental data of polystyrene in cyclohexane below the θ temperature. In the present analysis, the below θ state was achieved by changing the solvent and temperature, and the reliability of our experimental data was verified[25].

The unperturbed dimensions of the chain and the solvent–polymer interaction parameter B were derived for PMCBF using the relation of the two-parameter theory given by Kurata[26]:

$$A_2 M^{1/2} = 1.65 \times 10^{23} \left(\frac{\langle R^2 \rangle_o}{M} \right)^{3/2}$$
$$+ 0.968 \times 10^{23} B M^{1/2} \qquad (4)$$

The linear plot of $A_2 \bar{M}_w^{1/2}$ versus $\bar{M}_w^{1/2}$ shown in *Figure 3* yields an intercept 0.12 and hence end-to-end distance of 0.90 Å. The results show excellent agreement with those derived according to excluded volume theories from $[\eta]$–M data. The theories of A_2 suggest that the ratio $A_2 M/[\eta]$ is a linear function of α alone[27,28].

$$\frac{A_2 M}{[\eta]} = f(\alpha)$$
$$= 200(1 - \alpha^{-3}) \qquad \text{(Ref. 29)}$$
$$= 414 \log[1 + 0.885(\alpha^2 - 1)] \qquad \text{(Ref. 30)(5)}$$

The value of $A_2 M/[\eta]$ for PMCBF in CF is in the range of 99–135.

The A_2 value for real polymer solutions is given by:

$$A_2 = 4\pi^{3/2} N_A \frac{\langle S^2 \rangle^{3/2}}{M^{1/2}} \bar{z} h(\bar{z}) \qquad (6)$$

where N_A is Avogadro's number and $\bar{z} h(\bar{z})$ is a function of intra- and intermolecular interactions. Several theories[11,26,28,31] were used to determine $\bar{z} h(\bar{z})(\Psi)$. The experimental data of $A_2 M/[\eta]$ in the range of 99–135 yield Ψ values of 0.30–0.42. The FKO, o function gives comparatively higher Ψ values, while other theories give very low limiting Ψ values, so the theories were combined with FKO, o to examine the experimental data. *Figure 4* shows theoretical curves of $A_2 \bar{M}_w/[\eta]$ versus $\alpha_s^2 - 1$ for the FKO,o theory combined with the F, m, P and F theories. The semiempirical relation given by Krigbaum is also shown. The points indicate the experimental results from light scattering measurements. It is clear from the figure that all lines are far from the data points, indicating that the behaviour of the parameter cannot be explained by the present theories. The literature[27,32,33] reveals that poly(methyl methacrylate), poly(vinyl acetate), poly(phenylene oxide) and poly(2-methoxy-cyanurate of bisphenol-A) show similar behaviour regarding $A_2 \bar{M}_w/[\eta]$. The discrepancy may be due to an inaccurate determination of A_2 and a contribution from the third virial coefficient. However, the accurate determination of A_2 and reasonably good linearity of the A_2–M relation overruled the above possibilities. Therefore it seems that the deviation shown by several

polymers must have some basis inherent in the basic properties of the polymer chains. To understand this, cellulose nitrate and polystyrene were considered as they show low and intermediate values of $A_2 M / [\eta]$, respectively. The cellulose nitrate is known for its rigidity and assumes an extended chain rod-like configuration while the flexible polystyrene chains assume a loose coil configuration. As rod-like molecules cannot entangle whilst flexible chains can be involved in entanglements between molecules, this implies that $A_2 M / [\eta]$ behaviour is decided by the entanglements. The above examples also indicate that the degree of coiling or the degree of ease of entanglements increases considerably with the flexibility of the chains. It is observed in PMCBF that the chains are highly flexible and possess high temperature coefficients of molecular dimensions. The high flexibility gives rise to excessive entanglements which may be of a tortuous nature. The effects of such entanglements have never been taken into account in the derivation of A_2 theory. Therefore, it is concluded that the present experimental data for highly flexible PMCBF chains may not comply with present A_2 theory.

REFERENCES

1   Critchley, J. P., Knight, G. J. and Wright, W. W. 'Heat Resistant Polymers', Plenum Press, New York, 1983
2   Cassidy, P. E. 'Thermally Stable Polymers', Marcel Dekker, New York, 1982
3   Lin, J. K., Yuki, Y., Kunisada, H. and Kondo, S. *J. Appl. Polym. Sci.* 1990, **40**, 2123
4   Sarwade, B. D., Wadgaonkar, P. P. and Mahajan, S. S. *J. Polym. Sci., Polym. Chem. Edn* 1989, **27**, 3263
5   Melissaris, A. P. and Mikroyannidis, J. A. *Eur. Polym. J.* 1989, **25**, 455
6   Naik, R. B. and Shah, P. P. *Eur. Polym. J.* 1988, **24**, 1057
7   Parsania, P. H. *J. Macromol. Sci. Chem.* 1985, **A22**, 1495
8   Shah, N. A. and Shah, P. P. *J. Macromol. Sci. Phys.* 1985, **B23**, 383
9   Stille, J. K. and Campbell, T. W. 'High Polymers, Vol. 27, Condensation Monomers', Wiley Interscience, New York, 1972, Ch. 8
10   Kaminski, Z. J. *Tetrahedron Lett.* 1985, **26**, 2901
11   Yamakawa, H. 'Modern Theories of Polymer Solution', Harper and Row, New York, 1971
12   Flory, P. J. and Fox, T. G. *J. Am. Chem. Soc.* 1951, **73**, 1904
13   Kurata, M., Stockmayer, W. H. and Roig, A. *J. Chem. Phys.* 1960, **33**, 151
14   Fixman, M. *J. Chem. Phys.* 1962, **36**, 3123
15   Stockmayer, W. H. and Fixman, M. *J. Polym. Sci.* 1963, **C1**, 137
16   Ptitsyn, C. B. *Polym. Sci. USSR* 1962, **3**, 1061
17   Inagaki, H., Suzuki, H. and Kurata, M. *J. Polym. Sci.* 1966, **C15**, 409
18   Patel, K. S., Patel, C. K. and Patel, R. D. *Polymer* 1977, **18**, 275
19   Domb, C. and Barrett, A. J. *Polymer* 1976, **17**, 179
20   Vyas, N. G., Patel, C. K. and Patel, R. D. *J. Polym. Sci., Polym. Phys. Edn* 1979, **17**, 2021
21   Flory, P. J. 'Statistical Mechanics of Chain Molecules', Interscience, New York, 1969
22   Cornet, C. F. *Polymer* 1965, **6**, 361
23   Orofino, T. A. *J. Polym. Sci., Polym. Phys. Edn* 1968, **6**, 575
24   Ptitsyn, C. B. and Eizner, Y. E. *J. Chem. Phys.* 1959, **29**, 1117
25   Prochazka, O. and Kratochvil, P. *Eur. Polym. J.* 1981, **17**, 81
26   Kurata, M. *J. Chem. Phys.* 1964, **41**, 139
27   Kurata, M. and Stockmayer, W. H. *Adv. Polym. Sci.* 1963, **3**, 196
28   Stockmayer, W. H. *Macromol. Chem.* 1960, **35**, 54
29   Krigbaum, W. R. *J. Polym. Sci.* 1955, **18**, 315
30   Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, 1953
31   Orofino, T. A. and Flory, P. J. *J. Chem. Phys.* 1957, **25**, 1067
32   Barrales, J. M. and Pepper, D. C. *Eur. Polym. J.* 1967, **3**, 535
33   Shah, P. P. *PhD Thesis* Sardar Patel University, India, 1983