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VISCOSITY BEHAVIOUR OF POLY(2-METHOXYCYANURATE) OF BISPHENOL F

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Abstract—Activation parameters of viscous flow of poly(2-methoxycyanurate) of bisphenol F having different molecular weight fractions and in different solvent systems were calculated using the Frenkel–Eyring equation. The volume-related parameter V_E of the polymer in solution was also computed. From data of V_E it is concluded that the polymer molecules are rigid spheres in the solvent systems studied.

INTRODUCTION

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 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 on many useful properties are scarce for this class of polymers [7, 8]. In our previous publication [9] we reported the synthesis and solution behaviour of poly(2-methoxycyanurate) of bisphenol F (PMCBF).

In continuation of our studies on solution behaviour, the present investigation reports determination of activation entropy and enthalpy of viscous flow for PMCBF of various molecular weight fractions in different solvent systems. This gives an insight into the conformational properties of the polymer molecules as a function of molecular weight in these solvents.

EXPERIMENTAL

Poly(2-methoxycyanurate) of bisphenol F (PMCBF) was synthesized by interfacial polycondensation of bisphenol-F and 2-methoxy-4,6-dichloro-s-triazine. The polymer was divided into several molecular weight parts by a fractional precipitation method using chloroform as solvent and *n*-butanol as precipitant. Intrinsic viscosity measurements of the solutions of these fractions were carried out using an Ubbelohde suspended level viscometer at four different temperatures (30, 35, 40 and 45°C) and in three solvents, viz; chloroform (CF) and two chloroform (CF):dioxane (Di) mixtures. The mixtures were 80:20 and 70:30 (%v/v) of CF and Di respectively. The efflux flow times for all solutions were more than 100 sec and hence kinetic corrections were not performed. The density of the polymer solutions was taken to be that of the solvent.

The weight average molecular weight of each fraction was determined by light scattering method. The experimental details of synthesis and characterization of polymers were reported elsewhere [9].

RESULTS AND DISCUSSION

The structure of PMCBF is outlined in Scheme 1.

Intrinsic viscosity data of PMCBF fractions in various solvent systems obtained [9] at four different temperatures are used to evaluate various activation parameters of viscous flow using the well-known Frenkel–Eyring equation [10]:

$$\eta = \frac{\mathrm{N}h}{V}\exp(\Delta G^{\ddagger}_{\mathrm{vis}}/RT) \tag{1}$$

where V is the molar volume of the solution, N is Avogadro's number, h is Planck's constant, R is the gas constant, T is temperature in K and $\Delta G^{\ddagger}_{\mathrm{vis}}$ is the activation free energy for the viscous flow. Equation (1) can be rewritten as:

$$\ln\left(\frac{\eta V}{\mathrm{N}h}\right) = \frac{\Delta G^{\ddagger}_{\mathrm{vis}}}{RT} = \left(\frac{\Delta H^{\ddagger}_{\mathrm{vis}}}{RT}\right) - \frac{\Delta S^{\ddagger}_{\mathrm{vis}}}{R} \tag{2}$$

where $\Delta H^{\ddagger}_{\mathrm{vis}}$ and $\Delta S^{\ddagger}_{\mathrm{vis}}$ are the activation enthalpy and entropy changes for the viscous flow. The molar volume V of the solution was taken to be that of the solvent. The linearity was observed by plotting $\ln(\eta V/\mathrm{N}h)$ against T^{-1} with correlation coefficient 0.99 or better for all systems. The slope and intercept gave $\Delta H^{\ddagger}_{\mathrm{vis}}$ and $\Delta S^{\ddagger}_{\mathrm{vis}}$ respectively. Some representative plots are shown in Fig. 1. The values of $\Delta H^{\ddagger}_{\mathrm{vis}}$ and $\Delta S^{\ddagger}_{\mathrm{vis}}$ for PMCBF of various molecular weight fractions in different solvent systems and at several concentrations are presented in Table 1.

It is observed from the results that the heat of activation of viscous flow, $\Delta H^{\ddagger}_{\mathrm{vis}}$ is low and positive, and decreases as the concentration of polymer in solution decreases. The decrease in $\Delta H^{\ddagger}_{\mathrm{vis}}$ is significant in CF while $\Delta H^{\ddagger}_{\mathrm{vis}}$ values remain practically constant for mixed systems. It is also observed from Table 1 that in CF variation in $\Delta H^{\ddagger}_{\mathrm{vis}}$ with concentration is relatively more for high molecular weight fractions. From Table 1, it is also interesting to note

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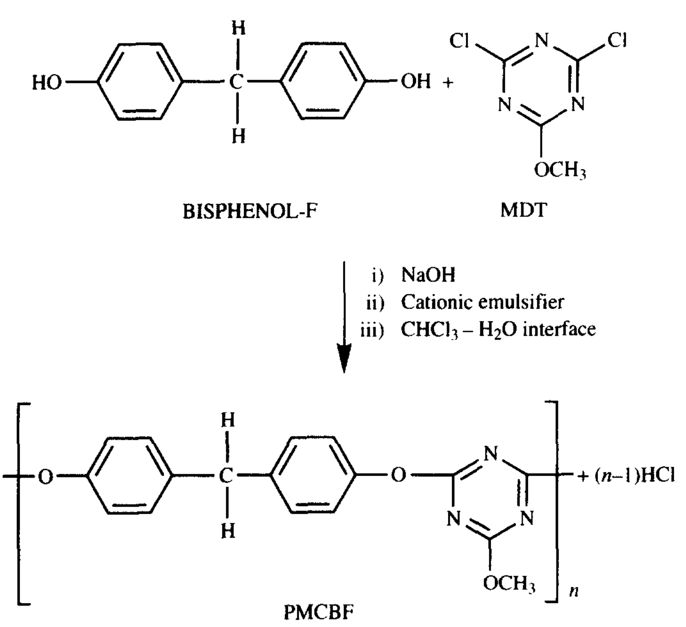

Scheme 1

that for solutions in CF the $\Delta H^{\ddagger}_{\text{vis}}$ decreases for all concentrations as the molecular weight of the polymer decreases. This seems to be logical. But when the non-solvent dioxane was added, such a trend was not observed. It seems that for a good solvent the activation enthalpy of viscous flow is a function of molecular weight but as the solvent becomes gradually poor such an observation disappears.

The entropies of activation of the viscous flow $\Delta S^{\ddagger}_{\text{vis}}$ are also low and negative indicating that the polymer structures are poorly ordered. Moreover, the variation of $\Delta S^{\ddagger}_{\text{vis}}$ with concentration in different solvents indicates that a change in $\Delta S^{\ddagger}_{\text{vis}}$ is significant in CF while in mixed solvent systems it is practically independent of the concentration of polymer solution. The values of $\Delta G^{\ddagger}_{\text{vis}}$ at various concentrations also show the similar behaviour as observed for $\Delta H^{\ddagger}_{\text{vis}}$.

Using the values of $\Delta H^{\ddagger}_{\text{vis}}$ and $\Delta S^{\ddagger}_{\text{vis}}$ tabulated in Table 1, it is possible to plot one parameter against the other to see if a linear compensation effect exists. In Fig. 2 the $\Delta H^{\ddagger}_{\text{vis}}$ and $\Delta S^{\ddagger}_{\text{vis}}$ values taken from Table 1 are plotted for the CF system and indeed the plot is linear following the relationship:

$$\Delta H^{\ddagger}_{\text{vis}} = k_1 + k_2 \Delta S^{\ddagger}_{\text{vis}} \tag{3}$$

where $k_1 = 17.5$ and $k_2 = 628$ with a correlation coefficient 0.99. In the other two solvent systems, correlation in two parameters was found to be in a relatively random manner which may be due to the poor solvent power. With the best data points k_1 and k_2 in the mixed solvent systems also were determined. Equation 3 can be combined with the thermodynamic equation, $\Delta G^{\ddagger}_{\text{vis}} = \Delta H^{\ddagger}_{\text{vis}} - T\Delta S^{\ddagger}_{\text{vis}}$, to give:

$$\Delta G^{\ddagger}_{\text{vis}} = k_1 + (k_2 - T)\Delta S^{\ddagger}_{\text{vis}}. \tag{4}$$

Table 1. Enthalpy $\Delta H^{\ddagger}_{\text{vis}}$ and $\Delta S^{\ddagger}_{\text{vis}}$ of activation of viscous flow of PMCBF fractions in different solvents and at various concentrations

			$\Delta H^{\ddagger}_{\text{vis}}$ kJ/mol				$-\Delta S^{\ddagger}_{\text{vis}}$ J/mol K			
			conc. (g/dl)				conc. (g/dl)			
Sample No.	$\bar{M}_w$ 10^{-5}	Solvent	0.25	0.15	0.10	0.05	0.25	0.15	0.10	0.05
S_7	3.19	CF	8.18	7.58	7.24	6.86	14.9	15.7	16.2	16.8
S_8	2.40		7.98	7.45	7.14	6.81	15.1	15.9	16.3	16.9
S_{10}	1.25		7.43	7.07	6.87	6.66	16.2	16.7	16.9	17.2
S_{12}	1.10		7.31	6.98	6.81	6.64	16.3	16.8	17.0	17.3
S_{13}	0.86		7.04	6.83	6.71	6.60	17.0	17.2	17.2	17.4
S_7	3.19	CF:Di (80:20% v/v)	8.63	8.43	8.31	8.20	14.6	14.6	14.5	14.5
S_8	2.40		8.67	8.43	8.31	8.20	14.3	14.4	14.4	14.4
S_{10}	1.25		8.85	8.56	8.40	8.24	13.2	13.7	13.9	14.2
S_{13}	0.86		8.73	8.48	8.35	8.22	13.5	13.8	14.0	14.2
S_{14}	0.65		8.60	8.39	8.29	8.19	13.7	14.0	14.1	14.3
S_7	3.19	CF:Di (70:30% v/v)	9.34	9.21	9.14	9.07	12.8	12.6	12.5	12.4
S_8	2.40		9.64	9.41	9.27	9.14	11.7	11.8	12.0	12.1
S_{10}	1.25		9.51	9.32	9.21	9.11	11.8	12.0	12.1	12.2
S_{12}	1.10		9.29	9.18	9.13	9.07	12.4	12.4	12.3	12.3
S_{14}	0.65		9.59	9.39	9.27	9.14	11.3	11.6	11.8	12.0

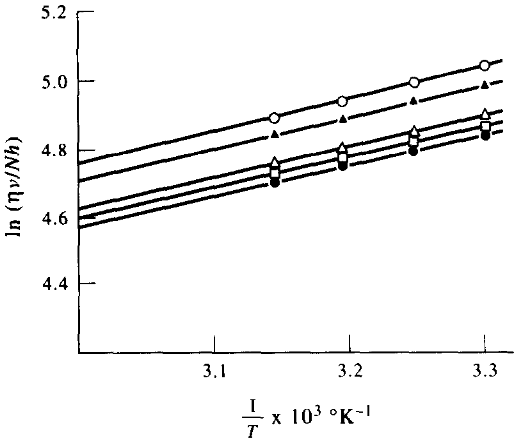

Fig. 1. Plot of $\ln(\eta V/Nh)$ vs T^{-1} for various molecular weights of PMCBF in $CHCl_3$ at concentration 0.25 g/dl. (○) S_7; (▲) S_8; (△) S_{10}; (□) S_{12}; (●) S_{13}.

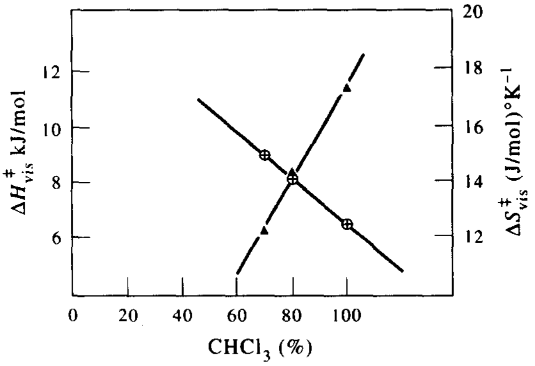

Fig. 3. Plot of $\Delta H^{\ddagger\circ}_{\mathrm{vis}}$ (⊗) and $\Delta S^{\ddagger\circ}_{\mathrm{vis}}$ (▲) with % composition of $CHCl_3$.

Such linear free energy relationships have been reported previously for many systems [11]. The constant k_2 called the structural temperature is found to be 628 K where $\Delta G^{\ddagger}_{\mathrm{vis}} = k_1 = 17.5$ kJ mol^{-1} in CF. This indicates that at 628 K, $\Delta G^{\ddagger}_{\mathrm{vis}}$ becomes totally independent of the structural changes in the system. The structural temperatures found for CF:Di (80:20%v/v) and CF:Di (70:30%v/v) are 655 and 894 K. The corresponding $\Delta G^{\ddagger}_{\mathrm{vis}}$ values are 17.6 and 20 kJ mol^{-1}. The values of structural temperature are in increasing order with decreasing solvent power which is in agreement with our expectation.

The activation parameter $\Delta H^{\ddagger\circ}_{\mathrm{vis}}$ at infinite dilution for PMCBF fractions in different solvent systems was obtained by plotting $\Delta H^{\ddagger}_{\mathrm{vis}}$ against concentration and extrapolating to $c = $ o. $\Delta S^{\ddagger\circ}_{\mathrm{vis}}$ values were also similarly obtained. All these activation parameters are compiled in Table 2. Results in Table 2 clearly indicate that for a given solvent system, all the activation parameters of viscous flow are independent of molecular weight. It follows that the temperature dependence of η was determined by the dimensions of the small part-segments, but not of macromolecules as a whole which were kinetically independent structural elements of a polymer [12]. Figure 3 shows the linear relationship of $\Delta H^{\ddagger\circ}_{\mathrm{vis}}$ and $\Delta S^{\ddagger\circ}_{\mathrm{vis}}$ with the % composition of CF. Both the parameters decrease with increasing the % of CF, indicating that with increasing solvent power, a higher degree of order is observed. However, the variation of $\Delta H^{\ddagger\circ}_{\mathrm{vis}}$ and $\Delta S^{\ddagger\circ}_{\mathrm{vis}}$ with % composition of CF is not very high as slope values in both curves are small in magnitude. The $\Delta G^{\ddagger\circ}_{\mathrm{vis}}$ values also show the same behaviour with % of CF.

Intrinsic viscosity data, $[\eta]$, were also used to calculate the volume-related parameter V_E of the polymer solutions at different temperatures and in different solvent systems. Recently it was used to determine the shape of the protein molecules [13] and some acrylate copolymers [14, 15] in solution, i.e. by the so called "shape factor" ν. V_E was calculated by plotting Y against concentration c in g/ml where

$$Y = (\eta_r^{0.5} - 1)/[c(1.35^{0.5} - 0.1)]. \tag{5}$$

The plot was linear and extrapolated to $c = 0$ (Fig. 4) from which V_E was obtained as an intercept as

$$\lim_{c \to 0} Y = V_E.$$

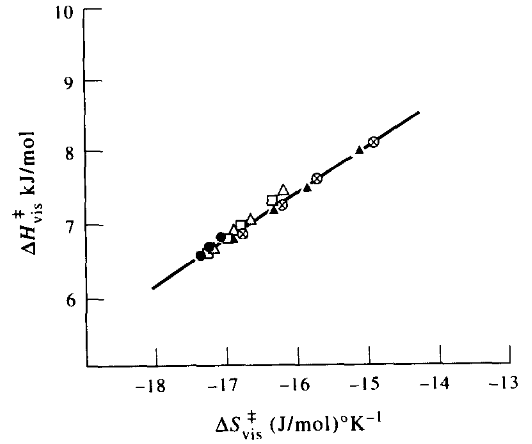

Fig. 2. Plot of $\Delta H^{\ddagger}_{\mathrm{vis}}$ against $\Delta S^{\ddagger}_{\mathrm{vis}}$ of PMCBF of various molecular weights in $CHCl_3$. Notations as in Fig. 1.

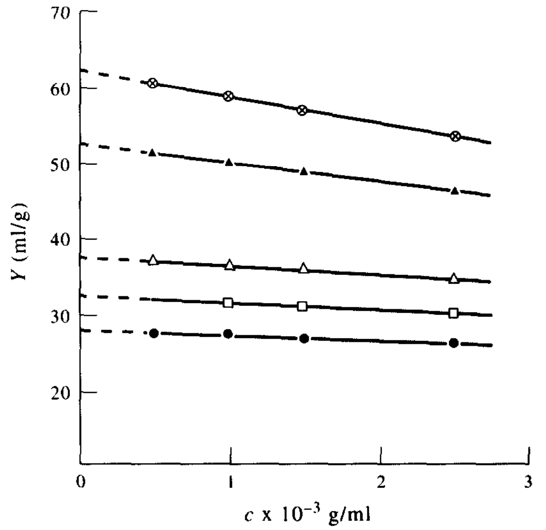

Fig. 4. Plot of Y vs concentration (g/ml) where $Y = (\eta_r^{0.5} - 1)/[c(1.35^{0.5} - 0.1)]$. Notations as in Fig. 1.

Table 2. Viscosity activation parameters at infinite dilution, voluminosity V_E and shape factor ν of PMCBF fractions in various solvent systems

		CF		CF:Di(80:20% v/v)		CF:Di(70:30% v/v)			CF		CF:Di(80:20%v/v)		CF:Di(70:30%v/v)	
Fraction	M_w 10^{-5}	$\Delta H^{\ddagger\circ}$ (kJ/mol)	$-\Delta S^{\ddagger\circ}$ (J/mol K)	$\Delta H^{\ddagger\circ}$ (kJ/mol)	$-\Delta S^{\ddagger\circ}$ (J/mol K)	$\Delta H^{\ddagger\circ}$ kJ/mol K)	$-\Delta S^{\ddagger\circ}$ (J/mol K)	Temp (°C)	V_E(mg/g)	ν	V_E(ml/g)	ν	V_E(ml/g)	ν
S_7	3.19	6.56	17.2	8.10	14.4	9.00	12.3	30	62.1	2.51	41.1	2.51	30.5	2.49
								35	59.7	2.50	40.6	2.51	30.5	2.49
								40	57.6	2.50	39.7	2.52	29.9	2.49
								45	55.9	2.50	39.2	2.52	29.5	2.49
S_8	2.40	6.55	17.2	8.03	14.5	9.02	12.2	30	52.6	2.51	36.5	2.51	28.3	2.49
								35	49.9	2.51	35.9	2.51	27.2	2.50
								40	48.7	2.51	35.5	2.51	26.6	2.50
								45	46.9	2.51	34.7	2.51	26.1	2.50
S_{10}	1.25	6.48	17.4	8.09	14.4	9.01	12.3	30	37.6	2.50	26.3	2.49	21.9	2.49
								35	36.2	2.50	25.9	2.51	20.9	2.49
								40	35.2	2.50	24.8	2.50	20.6	2.49
								45	34.5	2.50	23.8	2.50	20.1	2.49
S_{12}	1.10	6.47	17.5	—	—	9.01	12.3	30	32.4	2.50	—	—	20.8	2.50
								35	31.6	2.50	—		20.3	2.49
								40	30.4	2.50	—	—	20.0	2.49
								45	29.7	2.51	—	—	19.7	2.49
S_{13}	0.86	6.49	17.4	8.10	14.4	—	—	30	28.0	2.50	23.0	2.51	—	—
								35	27.2	2.50	22.3	2.49	—	—
								40	26.7	2.50	21.6	2.50	—	—
								45	26.1	2.51	20.8	2.50	—	—
S_{14}	0.65	—	—	8.03	14.4	9.04	12.2	30	—	—	19.1	2.51	17.8	2.50
								35	—	—	19.0	2.50	17.0	2.49
								40	—	—	18.4	2.51	16.4	2.50
								45	—	—	17.5	2.51	15.5	2.50

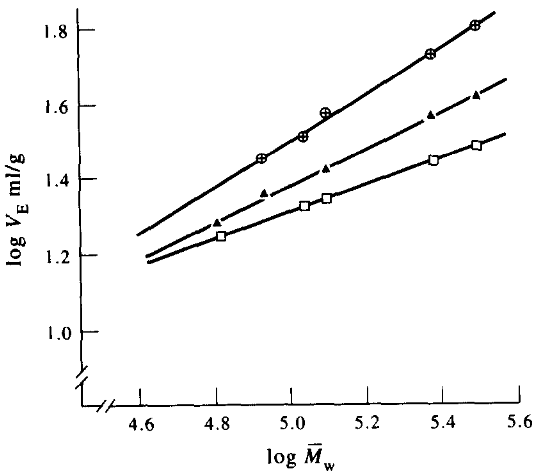

Fig. 5. Log–log plot of V_E against $\bar{M}_w$ of PMCBF fractions in different solvent systems at 30°C. (⊗) CF; (▲) CF:Di (80:20%v/v); (□) CF:Di (70:30%v/v).

The shape factor v [16] was obtained from the equation,

$$[\eta] = vV_E. \tag{6}$$

The shape factor gives an idea about the shape of the polymer molecules in solution. It is 2.5 for spherical particles but is different if the particles in solution are not spherical [17, 18]. Table 2 shows that v was 2.5 for all PMCBF fractions studied at all four temperatures and in all solvent systems indicating polymer coils were spherical in nature. These were not affected by molecular weight, solvent and temperature of the study.

The volume-related parameter V_E (ml/g) is a function of temperature and is a measure of the volume of solvated polymer molecules. As the temperature increases the solvation decreases and hence V_E decreases. Figure 5 represents the variation of V_E with molecular weight of PMCBF in different solvents at 30°C. It is observed from the slope of the curves that variation of V_E with molecular weight is higher in CF than in mixed solvents as the former is a good solvent for the polymer. It is to be noted also that as the molecular weight decreases the solvated volume (V_E) also becomes smaller. Moreover the poorer solvent certainly was not expected to solvate the polymer molecules and hence the systems with higher dioxane content will have lower V_E values. This fact can also be clearly seen from Table 2. But in all cases the shape factor is 2.5 indicating that the polymer conformation in solution was spherical and independent of temperature, molecular weight and nature of the solvent.

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