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## VISCOSITY BEHAVIOR OF POLY(2-METHOXYCYANURATE) OF BISPHENOL F AND BISPHENOL A

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### ABSTRACT

Activation parameters of viscous flow of poly(2-methoxycyanurate) of bisphenol F and bisphenol A of different molecular weight fractions in chloroform and dioxane were calculated using the Frenkel-Eyring equation. Voluminosity of the polymer was also computed. From voluminosity data 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 their solution properties which would provide information about the behavior of these macromolecules in solution and might therefore reflect on their useful properties are scarce for this class of

polymers [7–9]. In previous publications [10, 11] we reported the synthesis and solution behavior of poly(2-methoxycyanurate) of bisphenol A and bisphenol F (PMCBFA).

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

## EXPERIMENTAL

Poly(2-methoxycyanurate) of bisphenol A and bisphenol F (PMCBFA) was synthesized by interfacial polycondensation of bisphenol A (1 mol), bisphenol F (1 mol), and 2-methoxy-4,6-dichloro-*s*-triazine (MDT) (2 mol). The procedure for the synthesis is reported elsewhere [10].

PMCBFA was fractionated by the fractional precipitation method using chloroform as the solvent and *n*-butanol as the precipitant at  $30 \pm 2^\circ\text{C}$ . Dilute solution viscosities of some of the fractions of PMCBFA were measured with the help of an Ubbelohde-type suspended level dilution viscometer in chloroform (CF) and dioxane (Di) at four different temperatures.

The efflux flow times for all solutions were more than 100 seconds, and hence kinetic corrections were not made. As the concentrations of polymer solutions used were very low, the densities of the solutions at different temperatures were assumed to be those of the solvents at those temperatures [12].

The number-average molecular weights of some of the fractions were measured on a Hewlett-Packard 502 high speed membrane osmometer using nonaqueous-type 0-8 membranes in chloroform at  $25^\circ\text{C}$ .

The GPC experiments were carried out on a Waters Associates 200 gel permeation chromatograph equipped with a set of four columns ( $10^6$ ,  $10^5$ ,  $10^4$ ,  $10^3$  Å) at  $30^\circ\text{C}$ . Chloroform was used as the solvent. The sample solution (0.2–0.4%) was injected for 1 minute. The flow rate was 1.25 mL/min. Calibration was carried out using standard polystyrene samples supplied by Waters Associates.

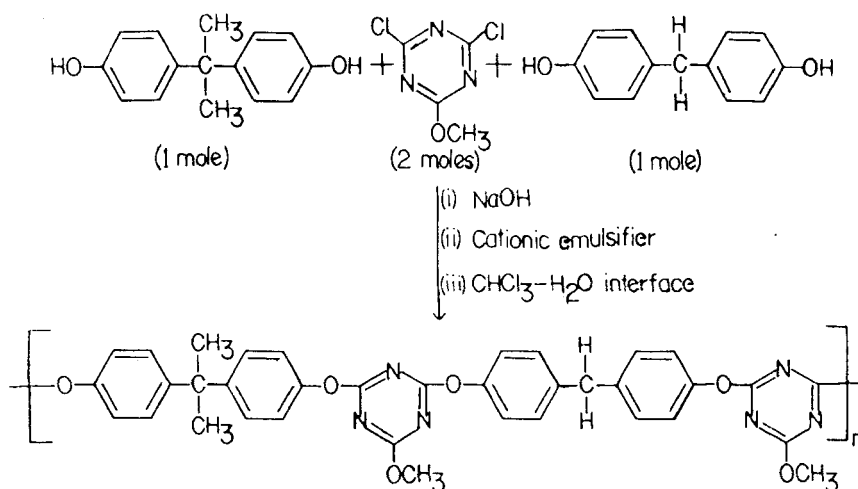
## RESULTS AND DISCUSSION

The structure of PMCBFA is outlined in Scheme 1. The weight-average molecular weight  $\bar{M}_w(o)$  was determined by combining the number-average molecular weight  $\bar{M}_n(o)$  obtained from osmometry and the GPC polydispersity with the following relation [13, 14]:

$$\bar{M}_w(o) = \frac{\bar{M}_w}{\bar{M}_n} \bar{M}_n(o)$$

For convenience, the symbol “o” of  $\bar{M}_w$  is omitted.

Intrinsic viscosity data of PMCBFA fractions in CF and Di obtained [11] at four different temperatures were used to establish the viscosity–molecular weight relationship according to Mark–Houwink–Kuhn–Sakurada (MHKS) relation. The



SCHEME 1.

MHKS constants are shown in Table 1. It can be seen from the results that CF shows higher  $\alpha$  and lower  $K$  values than Di. Hence, CF has better solvent power than Di.

Activation parameters of viscous flow were evaluated using the well-known Frenkel-Eyring equation [15]:

$$\eta = \frac{Nh}{V} \exp(\Delta G_{\text{vis}}^{\ddagger}/RT) \quad (1)$$

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

TABLE 1. Mark-Houwink-Kuhn-Sakurada Constants for PMCBFA in Chloroform and Dioxane at Various Temperatures

Solvent	Temperature, $^{\circ}\text{C}$	$\alpha$	$K \times 10^4$ , $\text{dL} \cdot \text{g}^{-1}$
Chloroform	30	0.77	1.41
	35	0.76	1.46
	40	0.76	1.45
	45	0.75	1.57
Dioxane	30	0.63	4.57
	40	0.63	4.40
	50	0.63	4.18
	60	0.62	3.18

$$\ln \frac{\eta V}{Nh} = \frac{\Delta G_{\text{vis}}^{\ddagger}}{RT} = \frac{\Delta H_{\text{vis}}^{\ddagger}}{RT} - \frac{\Delta S_{\text{vis}}^{\ddagger}}{R} \quad (2)$$

where  $\Delta H_{\text{vis}}^{\ddagger}$  and  $\Delta S_{\text{vis}}^{\ddagger}$  are the activation enthalpy and entropy change for the viscous flow, respectively. The molar volume  $V$  of the solution was taken to be that of the solvent. The linearity was observed by plotting  $\ln(\eta V/Nh)$  against  $T^{-1}$  with correlation coefficient 0.99 or better for all systems. The slope and intercept give  $\Delta H_{\text{vis}}^{\ddagger}$  and  $\Delta S_{\text{vis}}^{\ddagger}$ , respectively. The values of  $\Delta H_{\text{vis}}^{\ddagger}$  and  $\Delta S_{\text{vis}}^{\ddagger}$  for PMCBFA of various molecular weight fractions in CF and Di at several concentrations are presented in Table 2. Some representative plots are shown in Fig. 1.

It is observed from the results that heats of activation of viscous flow,  $\Delta H_{\text{vis}}^{\ddagger}$ , are low and positive, and decrease as the concentration of polymer in solution decreases. The decrease in  $\Delta H_{\text{vis}}^{\ddagger}$  is significant in CF;  $\Delta H_{\text{vis}}^{\ddagger}$  remains almost constant for Di. It is also observed from Table 2 that the CF variation in  $\Delta H_{\text{vis}}^{\ddagger}$  with concentration is relatively more in high molecular weight fractions. It is also interesting to note from Table 2 that for solutions in CF,  $\Delta H_{\text{vis}}^{\ddagger}$  decreases in all concentrations as the molecular weight of the polymer decreases. This seems to be logical. But when the relatively poor solvent dioxane was used, such regularity 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 poorer, such regularity disappears.

The entropies of activation of the viscous flow  $\Delta S_{\text{vis}}^{\ddagger}$  are also low and negative, indicating that the polymer structures are poorly ordered. Moreover, the variations of  $\Delta S_{\text{vis}}^{\ddagger}$  with concentration in both solvents indicate that the change in  $\Delta S_{\text{vis}}^{\ddagger}$  is significant in CF while in the poorer solvent Di it is practically independent of the concentration of the polymer solution. The values of  $\Delta G_{\text{vis}}^{\ddagger}$  at various concentrations also show a behavior similar to that observed for  $\Delta H_{\text{vis}}^{\ddagger}$ .

TABLE 2. Enthalpy  $\Delta H_{\text{vis}}^{\ddagger}$  and  $\Delta S_{\text{vis}}^{\ddagger}$  of Activation of Viscous Flow of PMCBFA Fractions in Chloroform (CF) and Dioxane at Various Concentrations

Sample	$\bar{M}_w \times 10^{-5}$	Solvent	$\Delta H^{\ddagger}$ , kJ·mol <sup>-1</sup>				$\Delta S^{\ddagger}$ , J·mol <sup>-1</sup> ·°K <sup>-1</sup>			
			Concentration, g/dL				Concentration, g/dL			
			0.25	0.20	0.15	0.10	0.25	0.20	0.15	0.10
1	2.24	CF	8.50	8.20	7.89	7.50	14.6	14.7	15.1	15.7
2	1.55		8.50	8.20	7.89	7.50	13.6	14.1	14.6	15.4
3	0.99		8.27	7.98	7.67	7.33	13.6	14.2	14.8	15.5
4	0.73		7.46	7.32	7.16	7.06	15.7	15.9	16.2	16.3
5	0.46		7.24	7.12	6.99	6.85	16.2	16.4	16.5	16.8
6	0.38		7.24	7.11	6.96	6.85	16.2	16.4	16.5	16.7
1	2.24	Dioxane	11.28	11.21	11.13	11.07	10.5	10.1	10.0	9.7
2	1.55		11.25	11.19	11.13	11.07	9.9	9.7	9.6	9.5
2a	1.23		11.49	11.38	11.29	11.18	9.0	9.0	9.0	9.1
4a	0.66		11.32	11.26	11.19	11.12	9.0	9.0	9.0	9.1
6	0.38		11.30	11.25	11.19	11.12	8.8	8.8	8.9	9.0

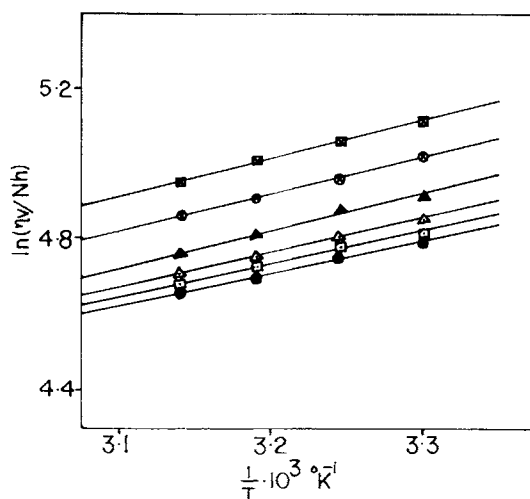


FIG. 1. Plot of  $\ln(\eta V/Nh)$  versus  $T^{-1}$  for various molecular weights of PMCBFA in CF at a concentration of 0.25 g/dL: ( $\boxtimes$ ) 1, ( $\otimes$ ) 2, ( $\blacktriangle$ ) 3, ( $\triangle$ ) 4, ( $\square$ ) 5, ( $\bullet$ ) 6.

The values of  $\Delta H_{\text{vis}}^{\ddagger}$  and  $\Delta S_{\text{vis}}^{\ddagger}$  are tabulated in Table 2. It is possible to plot one parameter against the other to see whether a linear compensation effect exists. In Fig. 2 the  $\Delta H_{\text{vis}}^{\ddagger}$  and  $\Delta S_{\text{vis}}^{\ddagger}$  values taken from Table 2 are plotted for the CF system, and indeed the plot is linear. It follows the relationship

$$\Delta H_{\text{vis}}^{\ddagger} = k_1 + k_2 \Delta S_{\text{vis}}^{\ddagger} \quad (3)$$

where  $k_1 = 14.5$  and  $k_2 = 450$  with the best data points. In dioxane the two parameters were found to be relatively random, which may be due to dioxane's poor solvent power. Equation (3) can be combined with the thermodynamic equation

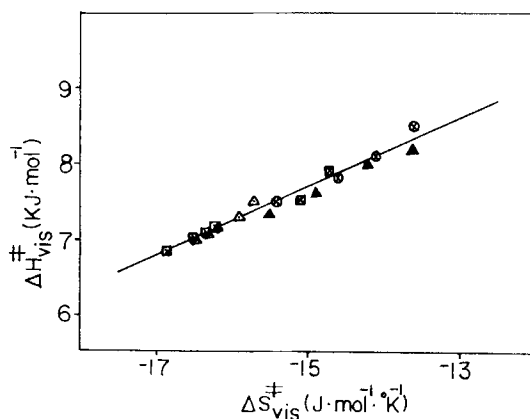


FIG. 2. Plot of  $\Delta H_{\text{vis}}^{\ddagger}$  against  $\Delta S_{\text{vis}}^{\ddagger}$  of PMCBFA of various molecular weights in CF. Notations as in Fig. 1.

$$\Delta G_{\text{vis}}^{\ddagger} = \Delta H_{\text{vis}}^{\ddagger} - T\Delta S_{\text{vis}}^{\ddagger}$$

to give

$$\Delta G_{\text{vis}}^{\ddagger} = k_1 + (k_2 - T)\Delta S_{\text{vis}}^{\ddagger} \quad (4)$$

Such linear free energy relationships have been reported previously for many systems [16]. The constant  $k_2$ , called the structural temperature, is found to be 450°K where  $\Delta G_{\text{vis}}^{\ddagger} = k_1 = 14.5 \text{ kJ}\cdot\text{mol}^{-1}$  in CF. This indicates that at 450°K,  $\Delta G_{\text{vis}}^{\ddagger}$  becomes totally independent of the structural changes in the system.

The activation parameter  $\Delta H_{\text{vis}}^{\ddagger}$  at infinite dilution for PMCBFA fractions in both solvents was obtained by plotting  $\Delta H_{\text{vis}}^{\ddagger}$  against concentration and extrapolating to  $C = 0$ .  $\Delta S_{\text{vis}}^{\ddagger}$  values were similarly obtained. All these activation parameters are compiled in Table 3. The results summarized in Table 3 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 viscosity is determined by the dimensions of the small parts/segments but not of macromolecules as a whole, which were kinetically independent structural elements of a polymer [17].

Intrinsic viscosity data  $[\eta]$  were also used to calculate the voluminosity  $V_E$  of the polymer solutions at different temperatures in both solvent systems. It was recently used to determine the shape of protein molecules [18], some acrylic polymers [19, 20], and poly(2-methoxycyanurate) of bisphenol F [21] in solution, i.e., the so-called "shape factor"  $\nu$ .

$V_E$  was calculated by plotting  $Y$  against concentration  $C$  in g/mL where

$$Y = (\eta_{\gamma}^{0.5} - 1) / [C(1.35^{0.5} - 0.1)] \quad (5)$$

The plot was linear and extrapolated to  $C = 0$  (Fig. 3), from which  $V_E$  was obtained as an intercept as  $\lim_{C \rightarrow 0} Y = V_E$ . The shape factor [22] was obtained from the equation

$$\eta = \nu V_E \quad (6)$$

The shape factor gives an idea about the shape of the polymer molecules in solution. It is 2.5 for spherical particles but has a different value if the particles in solution are not spherical [23, 24]. Table 3 shows that  $\nu$  is 2.5 for all the PMCBFA fractions studied at all four temperatures in both solvent systems, indicating that the polymer coils are spherical. The shape factor was not affected by molecular weight, solvent, and temperature of the study.

The voluminosity (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 4 presents the variation of  $V_E$  with molecular weight of PMCBFA in CF and Di 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 Di because the former is a good solvent for the polymer. It is also to be noted that as the molecular weight decreases the solvated volume ( $V_E$ ) also becomes smaller. Moreover, the poor solvent certainly is not expected to solvate the polymer molecules, and hence the system in Di will have lower  $V_E$  values. This fact can also be clearly seen from Table 3. But in both cases the shape factor is 2.5, indicating that the polymer conformation in solution was

TABLE 3. Viscosity Activation Parameters at Infinite Dilution, Voluminosity  $V_E$ , and Shape Factor  $\nu$  of PMCBFA Fractions in Chloroform (CF) and Dioxane

Fraction	CF				Dioxane				Dioxane			
	$\bar{M}_w \times 10^{-5}$	$\Delta H^\ddagger$ , $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta S^\ddagger$ , $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	Temperature, $^\circ\text{C}$	$\Delta H^\ddagger$ , $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta S^\ddagger$ , $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	Temperature, $^\circ\text{C}$	$V_E$ , $\text{mL/g}$	$\nu$	$V_E$ , $\text{mL/g}$	Temperature, $^\circ\text{C}$	$V_E$ , $\text{mL/g}$
1	2.24	6.79	16.58	10.92	9.31	30	74.2	2.52	40.1	30	40.1	2.49
						35	69.5	2.50	39.9	40	39.9	2.48
						40	67.9	2.50	39.4	50	39.4	2.49
						45	64.7	2.52	38.9	60	38.9	2.49
2	1.55	6.74	16.72	10.96	9.2	30	57.4	2.51	30.8	30	30.8	2.50
						35	54.7	2.50	30.4	40	30.4	2.50
						40	52.0	2.50	30.0	50	30.0	2.50
						45	50.0	2.50	29.5	60	29.5	2.51
2a	1.23	—	—	10.98	9.14	30	—	—	27.6	30	27.6	2.50
						40	—	—	26.4	40	26.4	2.50
3	0.99	6.67	16.83	—	—	30	39.4	2.51	24.8	30	24.8	2.50
						35	39.1	2.51	24.8	35	24.8	2.50
						40	34.8	2.50	24.8	40	24.8	2.50
						45	34.0	2.50	24.8	45	24.8	2.50

(continued)



TABLE 3. Continued

Fraction $\bar{M}_w \times 10^{-5}$	CF		Dioxane		CF		Dioxane			
	$\Delta H^{+}$ , $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta S^{+}$ , $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\Delta H^{+}$ , $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta S^{+}$ , $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	Temperature, $^{\circ}\text{C}$	$V_E$ , $\text{mL/g}$	$\nu$	Temperature, $^{\circ}\text{C}$	$V_E$ , $\text{mL/g}$	$\nu$
4	0.73	6.68	16.91	—	30	28.4	2.50	30	18.4	2.50
					35	27.6	2.50	40	18.4	2.50
					40	26.8	2.49	50	17.6	2.50
					45	25.2	2.50	60	16.4	2.50
4a	0.66	—	—	11.00	9.10	—	—	30	18.4	2.50
								40	18.4	2.50
								50	17.6	2.50
								60	16.4	2.50
5	0.46	6.60	17.16	—	—	22.8	2.50	30	18.8	2.50
						22.0	2.50	35	18.0	2.50
						21.6	2.50	40	17.2	2.50
						20.4	2.50	45	16.6	2.51
6	0.38	6.60	17.17	11.00	9.08	—	—	30	14.4	2.49
								35	13.2	2.50
								40	12.8	2.50
								45	12.4	2.49

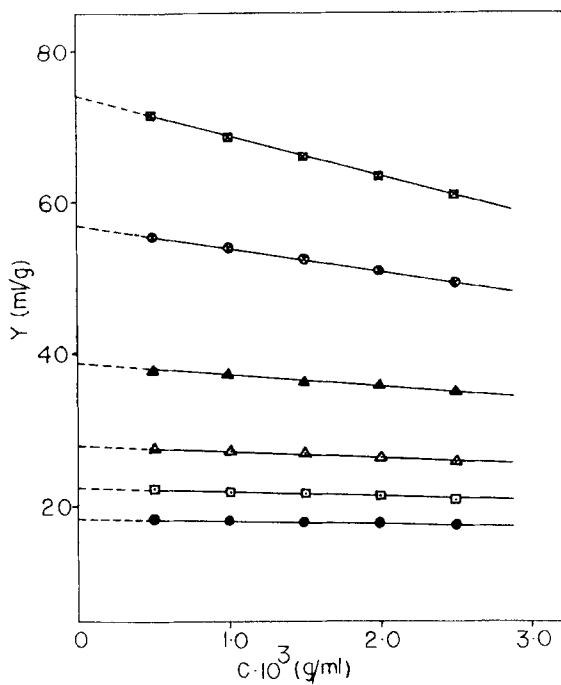


FIG. 3. Plot of  $Y$  versus concentration (g/mL) where  $Y = (\eta_r^{0.5} - 1)/[c(1.35^{0.5} - 0.1)]$ . Notations as in Fig. 1.

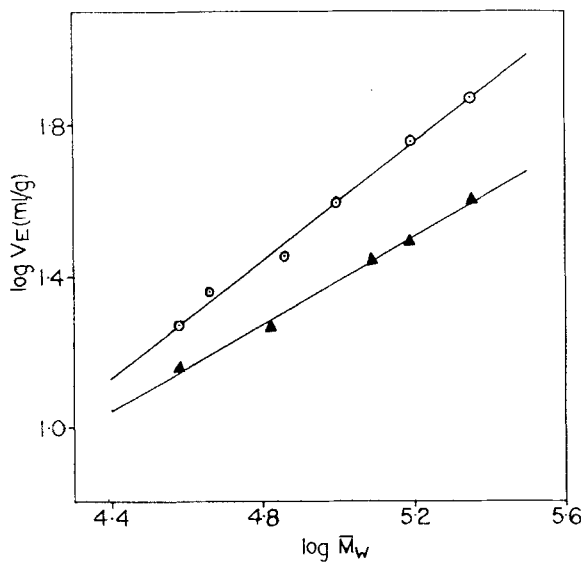


FIG. 4. Log-log plot of  $V_E$  against  $\bar{M}_w$  of PMCBFA fractions in CF ( $\odot$ ) and Di ( $\blacktriangle$ ) at 30°C.

spherical and independent of temperature, molecular weight, and the nature of the solvent.

### CONCLUSION

The activation parameters of viscous flow at infinite dilution for PMCBFA depend only on the nature of the solvent and are independent of the molecular weight of the polymer. The polymer molecules are rigid spheres in the solvent systems studied, and the conformation does not depend on temperature, nature of solvent, and molecular weight.

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### REFERENCES

- [1] J. P. Critchley, G. J. Knight, and W. W. Wright *Heat Resistant Polymers*, Plenum Press, New York, 1983.
- [2] P. E. Cassidy, *Thermally Stable Polymers*, Dekker, New York, 1982.
- [3] J. K. Lin, Y. Yuki, H. Kunisada, and S. Kondo, *J. Appl. Polym. Sci.*, **40**, 2123 (1990).
- [4] B. D. Sarwade, P. P. Wadgaonker, and S. S. Mahajan, *J. Polym. Sci., Polym. Chem. Ed.*, **27**, 3263 (1989).
- [5] A. P. Melissaris and J. A. Mikroyannidis, *Eur. Polym. J.*, **25**, 455 (1989).
- [6] R. B. Naik and P. P. Shah, *Eur. Polym. J.*, **24**, 1057 (1988).
- [7] P. H. Parasania, *J. Macromol. Sci. - Chem.*, **A22**, 1945 (1985).
- [8] N. A. Shah and P. P. Shah, *J. Macromol. Sci. - Phys.*, **B23**, 383 (1985).
- [9] S. Kansara, N. K. Patel, and C. K. Patel, *Polymer*, **34**, 1309 (1993).
- [10] V. Vangani, S. S. Kansara, and N. K. Patel, *Macromol. Rep.*, **A28**, 193 (1991).
- [11] G. M. Patel, N. K. Patel, and S. S. Kansara, *Polym. Int.*, In Press.
- [12] H. Tompa, *Polymer Solutions*, Butterworth, London, 1956, p. 287.
- [13] S. T. Balke, A. E. Hemielec, B. P. Leclair, and S. L. Pearce, *Ind. Eng. Chem., Prod. Res. Dev.*, **8**, 54 (1969).
- [14] P. P. Shah, *Eur. Polym. J.*, **20**, 519 (1984).
- [15] G. V. Vinogradov and A. Ya. Malkin, *Rheology of Polymers*, Mir, Moscow, 1980, p. 106.
- [16] B. G. Sharma and A. K. Rakshit, *J. Colloid Interface Sci.*, **29**, 139 (1989).
- [17] A. Tager, *Physical Chemistry of Polymers*, Mir, Moscow, 1978, p. 283.
- [18] A. S. Narang and V. L. Garg, *J. Indian Chem. Soc.*, **66**, 214 (1989).
- [19] R. Joseph, S. Devi, and A. K. Rakshit, *Polym. Int.* **26**, 89 (1991).
- [20] A. K. M. Asaduzzaman, A. K. Rakshit, and S. Devi, *J. Appl. Polym. Sci.*, **47**, 1813 (1993).

- [21] S. Ajitkumar, D. Prasadkumar, S. Kansara, and N. K. Patel, *Eur. Polym. J.*, In Press.
- [22] R. Simha, *J. Phys. Chem.*, *44*, 25 (1940).
- [23] J. W. McBain, *Colloid Science*, Heath, Boston, 1950.
- [24] A. B. Mandal, S. Ray, A. M. Biswas, and S. P. Moulik, *J. Phys. Chem.*, *84*, 856 (1980).

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