POLYSTYRENE IN *N*-METHYLPYRROLIDONE: INTRINSIC VISCOSITY–MOLAR WEIGHT RELATIONS AND POLYSTYRENE UNPERTURBED DIMENSIONS

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Dedicated to Professor Otto Wichterle on the occasion of his 80th birthday.

Intrinsic viscosity–molar weight relations are reported for polystyrene in *N*-methylpyrrolidone (NMP) and NMP/LiBr solutions at 30, 45, 60, 75, 90 and 105 °C. Also, Mark–Houwink constants K_Θ and the unperturbed dimensions of the polystyrene chains at these temperatures are calculated by applying Stockmayer–Fixman extrapolations of the viscosity/molar weight data. The use of in-line size exclusion chromatography and viscometry is shown to be a facile and accurate method for such studies.

Size exclusion chromatography (gel permeation chromatography), when combined with in-line viscometry, is a rapid and convenient means of measuring the molar weight averages and molar weight distributions of polymers. In our laboratories a large number of new high-performance polymers are being synthesized. *N*-Methylpyrrolidone (NMP) and NMP containing LiBr serve as convenient solvents for many of these polymers. Calibration of the size exclusion chromatographic (SEC) columns and the in-line viscometer with polystyrene standard samples of narrow molar weight distribution permits molar weight characterization of the experimental polymers[1] by means of the universal log ([η] *M*) vs elution volume procedure[2]. The intrinsic viscosity data obtained in such calibration measurements on standard polystyrene samples in NMP and in NMP containing LiBr are reported here. The unperturbed polystyrene chain dimensions were obtained from these data by the Stockmayer–Fixman extrapolation procedure[3] and the theoretical bases of Flory and Fox[4,5].

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EXPERIMENTAL

N-Methylpyrrolidone (Burdick & Jackson, B & J Brand™ GPC grade) and N-methylpyrrolidone solution of lithium bromide (0.5 g LiBr per 100 ml of NMP at 25 °C) were used as solvents. The polystyrene samples were narrow distribution, anionically-polymerized standards obtained from Polysciences, Inc. (Warrington, U.S.A.), except for the 68 000 g/mol sample which was obtained from Polymer Laboratories (Church Stretton, U.K.). These standards were all reported to have M_w/M_n < 1.07. The M_w values specified by the suppliers were accepted as correct. Due to the narrowness of the molar weight distributions we will, for simplicity, refer to the molar weights of these samples as M.

A Waters Model 150-C GPC/ALC chromatograph containing two 300 mm × 7.8 mm columns packed with μStyragel HT (Waters) cross-linked PS beads labelled "10^3 Å and 10^4 Å" (10 μm bead diameter) preceded an in-line Viscotek Model 100 viscometer. Detailed descriptions of the latter have been published[6]. A flow rate of 1 ml/min was chosen for all the measurements except those at 30 °C for which a 0.5 ml/min flow rate was used. Polymer concentrations of 1.0 mg/ml (sample of the highest M) to 2.5 mg/ml (sample of the lowest M) were used. Solution (200 μl) containing a mixture of two or three polymer samples (giving no elution overlap) was injected. The polymer concentrations at the differential refractive index detector of the chromatograph were approximately 1/25 of the injected concentrations due to separation and column dispersion. The chromatograph, connecting line, and viscometer were individually controlled to the same temperature.

RESULTS AND DISCUSSION

The polystyrene molar weights and measured intrinsic viscosities (Table I) are plotted in accordance with the log–log representation of the Mark–Houwink equation

$$\log [\eta] = \log K + a \log M . \qquad (1)$$

The values of K and a obtained from these plots (Figs 1*a* – 1*d*) are presented in Table II. Approximation of the continuously curved $\log [\eta]$ vs $\log M$ by straight lines in the 2 500 to 30 000 g/mol and 30 000 to 400 000 g/mol regions is quite satisfactory for most molar weight determinations from intrinsic viscosity. It is seen from the values of the Mark–Houwink exponent, a = 0.71 – 0.74 in the high molar weight region, that NMP and NMP solution of LiBr (0.5 g per 100 ml) are thermodynamically "good" solvent media for polystyrene.

To obtain information concerning the unperturbed state of the polystyrene chains from viscosity and molar weight data in the present "good" solvents, extrapolations of the data by the Stockmayer–Fixman relation[3]

$$[\eta]/M^{1/2} = K + 0.5 B \Phi_0 M^{1/2} \qquad (2)$$

were performed (Figs 2*a* and 2*b*). The Mark–Houwink constants K_Θ relating $[\eta]$ and M in Θ-solvent (Flory temperature) condition,

$$[\eta] = K_\Theta M^{1/2} \qquad (3)$$

were obtained from the intercepts in these plots and are presented in Table III, where there are also given K_Θ values of Abe and Fujita[7] who used cyclohexane, methylcyclohexane, and their mixtures to obtain Θ-solvent conditions at 34.5, 43, 48, 54 and 70.5 °C; a good correspondence between the findings of Japanese authors and our findings is noted (Fig. 3). Subsequently, the ratios of the unperturbed chain root-mean-square end-to-end distances (r_0) to the square roots of their molar weights were calculated from K_Θ by the relation[5]

$$r_0/M^{1/2} = (K_\Theta/\Phi_0)^{1/3} \qquad (4)$$

TABLE I
Intrinsic viscosities ([η]) of polystyrene samples (molar weights 2 700 – 390 000 g/mol) in *N*-methylpyrrolidone (NMP) solvents

$M \cdot 10^{-3}$ g mol^{-1}	[η], ml g^{-1}					
	30 °C	45 °C	60 °C	75 °	90 °C	105 °C
			NMP			
2.7	4.7	4.5	4.3	4.0	3.8	3.7
4.0	6.0	5.7	5.4	5.3	4.9	4.8
9.2	9.3	8.9	8.4	8.0	7.8	7.5
22.0	15.9	14.9	14.1	13.8	13.5	13.0
30.3	19.1	18.4	17.7	17.1	16.5	16.0
48.9	25.8	24.9	24.0	23.3	22.5	21.7
68.0	34.2	33.0	32.1	31.3	30.7	29.0
90.0	40.1	38.9	37.5	36.4	35.8	34.5
198.4	72.5	70.3	68.7	67.3	65.3	62.3
390.0	118.8	115.9	113.0	109.5	106.7	104.8
			NMP–LiBr (0.5 g per 100 ml)			
2.7	4.5	4.1	4.0	3.9	3.7	3.6
4.0	5.8	5.4	5.1	4.9	4.7	4.5
9.2	8.9	8.5	8.2	7.9	7.5	7.1
22.0	14.9	14.5	13.7	13.3	13.2	12.4
30.3	18.2	17.6	16.9	16.3	16.0	15.4
48.9	25.3	23.9	23.1	22.5	21.9	21.2
68.0	32.5	31.3	30.3	29.0	28.4	27.7
90.0	38.1	37.4	36.2	35.1	34.7	33.4
198.4	67.6	66.5	65.0	62.9	61.2	60.0
390.0	112.4	109.5	106.4	102.9	101.1	97.9

and compared with Abe and Fujita's data in Table III. The value of the universal viscosity constant (Φ_0) used in the calculation was 2.70 . 10^{23} (ref.[8]) which yields r_0 in cm when $[\eta]$ is ml/g and M is g/mol.

Although not pursued here, it is possible to construct the curved log $[\eta]$ vs log M plots for the polystyrene–NMP and polystyrene–NMP/LiBr systems from the relation[5]

$$[\eta] = K_\Theta M^{1/2} \alpha^3 \tag{5}$$

and the approximate proportionality of $\alpha^5 - \alpha^3$ to $M^{1/2}$. Also information concerning the polystyrene–solvent interactions can be extracted in the process.

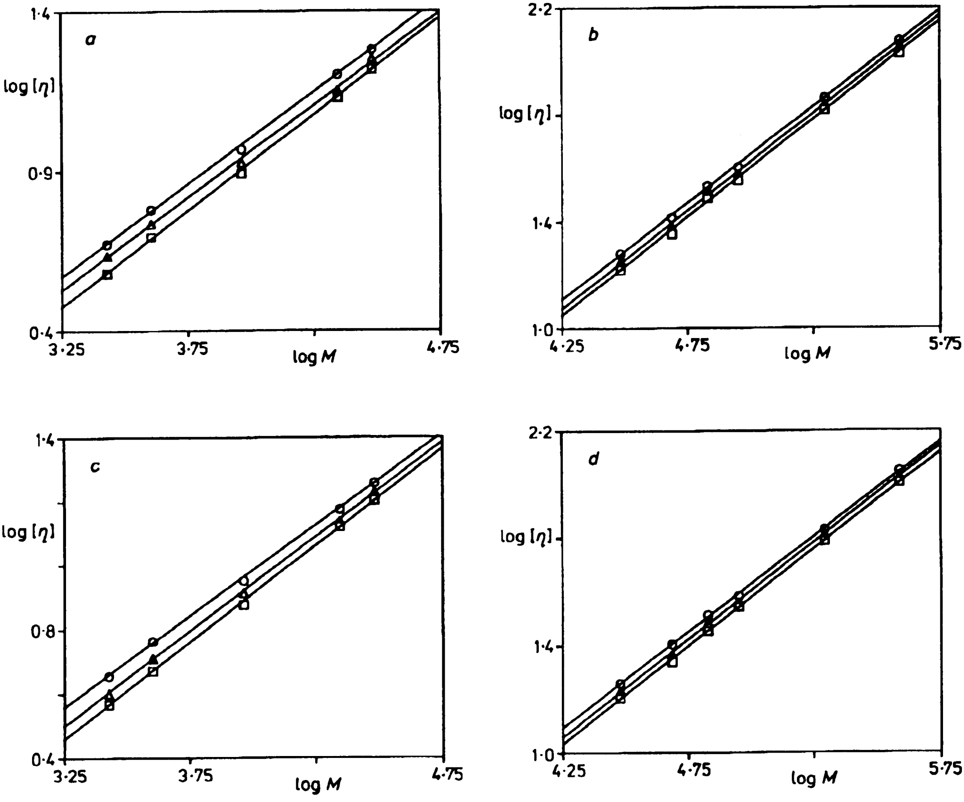

FIG. 1
Mark–Houwink plots for polystyrene at O 30 °C, Δ 60 °C, and □ 90 °C. Molar weight region (M): *a* 2 500 – 30 000 g/mol, *N*-methylpyrrolidone (NMP) as solvent; *b* 30 000 – 400 000 g/mol, NMP; *c* 2 500 – 30 000 g/mol, NMP–LiBr; *d* 30 000 – 400 000 g/mol, NMP–LiBr

TABLE II
Mark–Houwink constants (K, a) in low and high molar weight regions (M in g/mol)

Temperature, °C	M = 2 500 – 30 000		M = 30 000 – 400 000	
	$K \cdot 10^3$, ml g^{-1}	a	$K \cdot 10^3$, ml g^{-1}	a
		NMP		
30	49.2	0.577	11.1	0.720
45	47.4	0.576	10.2	0.725
60	44.4	0.578	9.2	0.730
75	38.9	0.588	8.8	0.732
90	32.4	0.603	8.3	0.735
105	32.8	0.599	7.6	0.739
		NMP–LiBr (0.5 g per 100 ml)		
30	50.2	0.570	11.9	0.710
45	37.8	0.595	10.4	0.719
60	37.7	0.591	9.5	0.724
75	36.8	0.590	9.1	0.724
90	30.7	0.606	8.9	0.725
105	31.2	0.599	8.3	0.728

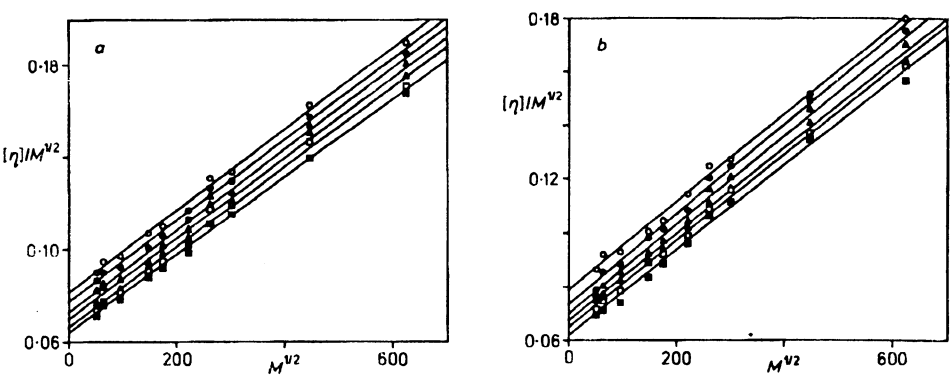

FIG. 2
Stockmayer–Fixman plots for polystyrene at ○ 30 °C, ● 45 °C, Δ 60 °C, ▲ 75 °C, □ 90 °C, and ■ 105 °C. Solvent: *a* *N*-methylpyrrolidone (NMP); *b* NMP–LiBr

TABLE III
Values of K_Θ and $r_0 M^{-1/2}$ for *N*-methylpyrrolidone (NMP), NMP solution of LiBr (0.5 g per 100 ml), and cyclohexane–methylcyclohexane mixtures (S) as solvents

Temperature °C	$K_\Theta \cdot 10^3$, ml mol$^{1/2}$ g$^{-3/2}$			$r_0 M^{-1/2} \cdot 10^2$, nm mol$^{1/2}$ g$^{-1/2}$		
	NMP	NMP/LiBr	S[a]	NMP	NMP/LiBr	S[a]
30	81	78	–	6.69	6.61	–
34.5	–	–	77.9	–	–	6.60
43	–	–	77.6	–	–	6.60
45	77	73	–	6.58	6.47	–
48	–	–	74.8	–	–	6.52
54	–	–	73.0	–	–	6.47
60	72	69	–	6.44	6.35	–
70.5	–	–	69.9	–	–	6.37
75	69	67	–	6.35	6.28	–
90	66	64	–	6.25	6.19	–
105	63	61	–	6.16	6.09	–

[a] Data from ref.[7].

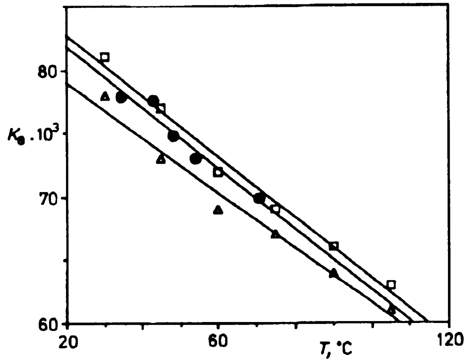

FIG. 3
Correlation K_Θ vs temperature for polystyrene. Solvent: □ *N*-methylpyrrolidone (NMP), Δ NMP–LiBr, ● cyclohexane–methylcyclohexane (data from ref.[7])

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