Molecular weight and temperature dependence of intrinsic viscosity of polymer solutions

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The molecular weight and temperature dependence of the intrinsic viscosity of polymer solutions have been predicted by combining the calculated radius of gyration, R_G, and hydrodynamic radius, R_H, with either the static empirical approach of Mandelkern–Flory or the dynamic argument of Weill–des Cloizeaux. It is found that experimental results can be successfully represented by the dynamic model for a range of five decades of molecular weight and temperature. The discrepancy between the calculated and experimental data at $N \simeq N_\tau$ reveals the crudeness of the discontinuity at the temperature cut-off assumed by current temperature blob theory.

INTRODUCTION

The empirical relation of intrinsic viscosity to molecular weight of polymers in solution given by the Mark–Houwink equation, $[\eta] = KM^a$, is only applicable for a limited molecular weight range at a given temperature and solvent. The exponent a has been shown to change from 0.5 to a value close to 0.8, even in a good solvent, as molecular weight changes[1].

On the other hand, recent advances in experimental and theoretical polymer chain statistics have led to the new working hypothesis of the 'blob theory'[2–4] of a bead-and-spring model. By taking advantage of the simple distribution function provided by the temperature blob model, we were able to calculate the radius of gyration R_G $(\equiv \langle R_G^2\rangle^{1/2})$ and hydrodynamic radius $R_H (\equiv kT/6\pi\eta_0 D_0)$ at any chain length N and reduced temperature τ as a function of a single parameter of N/N_τ. In a previous paper[5] (referred to as I), we compared such calculations with experimental results.

In this paper, we demonstrate the relationship of $[\eta]/[\eta]_\theta$ to N/N_τ by simply combining our previous expressions for R_G and R_H with either the static, empirical model of Mandelkern–Flory[6] or the dynamic argument of Weill–des Cloizeaux[7]. Using the dynamic approach, we can successfully relate $[\eta]/[\eta]_\theta$ to a single reduced parameter of molecular weight and temperature, over both the θ region and the good solvent limit.

THEORETICAL

As in the previous paper (I), the temperature blob theory of the polymer chain is used. In this theory the polymer chain statistics, $\langle |R_n|^2\rangle$ are modelled as:

$$\langle |R_n|^2\rangle = l^2 n \qquad n \leqslant N_\tau$$

and

$$\langle |R_n|^2\rangle = (lN_\tau^{1/2})^2 \left(\frac{n}{N_\tau}\right)^{2\nu}$$

$$= l^2 N_\tau^{1-2\nu} n^{2\nu} \qquad n \geqslant N_\tau \qquad (1)$$

where $\langle |R_n|^2\rangle$ is the mean square distance of two beads n beads apart, l is the statistical length and N_τ is a temperature-dependent cut-off which separates Gaussian and excluded-volume regions. N_τ is approximated by:

$$N_\tau = \frac{\alpha}{\tau^2}$$

and

$$\tau = 1 - \frac{\theta}{T} \qquad (2)$$

where α is an adjustable parameter, and θ is the theta temperature.

Using the above model, the radius of gyration, R_G, or linear expansion factor, $\alpha_s \equiv R_G(x)/R_G(\theta)$ of a polymer chain with a number of statistical segments, N, has been given by Farnoux *et al.*[2] as:

$$\alpha_s^2(x) = x^2(3 - 2x) + 6x^{1-2\nu}\left(\frac{1 - x^{2\nu+1}}{2\nu + 1} - \frac{1 - x^{2(\nu+1)}}{2(\nu + 1)}\right)$$

with

$$R_G(\theta) = l(N/6)^{1/2}$$

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and

$$x = N_\tau / N \tag{3}$$

Also, the hydrodynamic radius, $R_H \equiv kT/6\pi\eta_0 D_0$, where D_0 is the diffusion coefficient at infinite dilution and η_0 is the solvent viscosity, has been calculated in (I) as:

$$\alpha_H \equiv R_H(x)/R_H(0)$$

$$= \frac{4}{(x)^{1/2}} \left[2(3 - x) + 3 \left(\frac{x^{\nu-1} - 1}{1 - \nu} - \frac{x^{\nu-1} - x}{2 - \nu} \right) \right]^{-1}$$

$$\text{with } R_H(\theta) = [(16\pi)^{1/2}/16]\, lN^{1/2} \tag{4}$$

If we use the static empirical approach to intrinsic viscosity by Mandelkern and Flory[6], the relationship between intrinsic viscosity $[\eta]$ and frictional coefficient f_0 is expressed as:

$$f_0/\eta_0 = \beta (M[\eta])^{1/3} \tag{5}$$

with β as a universal constant.

Since

$$D_0 = \frac{kT}{f_0} = \frac{kT}{6\pi\eta_0 R_H} \tag{6}$$

by combining equations (5) and (6), we can obtain the expansion factor for viscosity as:

$$\alpha_\eta^3 = [\eta]/[\eta]_\theta = [R_H(x)/R_H(\theta)]^3$$

$$= \left\{ \frac{3}{4}(x)^{1/2} \left[2\left(1 - \frac{x}{3}\right) + \frac{5}{2}(x^{-2/5} - 1) - \frac{5}{7}(x^{-2/5} - x) \right] \right\}^{-3} \tag{7}$$

assuming the Flory value of $\nu = 3/5$.

Alternatively, if we use the dynamic argument that the intrinsic viscosity is a measure of the weighted-average of relaxation times, Weill and des Cloizeaux[7] have shown that:

$$[\eta] \propto \frac{R_G^2 R_H}{M} \tag{8}$$

Therefore, α_η can be easily expressed as:

$$\alpha_\eta^3 = \alpha_s^2 \alpha_H$$

$$= \left\{ x^2(3 - 2x) + 6x^{-1/5} \left[\frac{5}{11}(1 - x^{11/5}) - \frac{5}{16}(1 - x^{16/5}) \right] \right\}$$

$$\times \left\{ \frac{3}{4}(x)^{1/2} \left[2\left(1 - \frac{x}{3}\right) + \frac{5}{2}(x^{-2/5} - 1) - \frac{5}{7}(x^{-2/5} - x) \right] \right\}^{-1} \tag{9}$$

For the Mandelkern–Flory case, the asymptotic behaviour of α_η at the good solvent limit $(N \gg N_\tau)$ is given by:

$$\alpha_\eta^3 \to \left[\frac{4}{3}(1 - \nu)(2 - \nu) \right]^3 (N/N_\tau)^{3\nu - 1.5}$$

$$= 0.416\, (N/N_\tau)^{0.3} \tag{10}$$

and alternatively for the Weill–des Cloizeaux case is given by:

$$\alpha_\eta^3 \to [4(1 - \nu)(2 - \nu)]/[(2\nu + 1)(\nu + 1)]\, (N/N_\tau)^{3\nu - 1.5}$$

$$= 0.637\, (N/N_\tau)^{0.3} \tag{11}$$

DISCUSSION

In *Table 1*, we have collected some intrinsic viscosity results for polystyrene in cyclohexane and benzene at various temperatures from different laboratories[1,8–10]. We have calculated N/N_τ using:

$$N/N_\tau = \frac{M\tau^2}{M_0(n\alpha)} \tag{12}$$

with the same value of $n\alpha = 4$ obtained from R_G measurements as described in (I) before. There are then no adjustable parameters in this comparison of calculated viscosity with experiment. The experiment results are displayed in *Figure 1*, together with the predictions of our calculations combined either with Weill–des Cloizeaux or Mandelkern–Flory viscosity treatments.

It is clear that the data presented can be successfully represented by the dynamic model for a range of 5 decades of molecular weight and temperature. The exponent changes continuously from 0.5 in the θ region to 0.8 at the good solvent limit. Any attempt to represent $[\eta]$ by a single exponent will clearly result in an a which depends upon the molecular weight range and temperature.

The Mandelkern–Flory model does predict correct limits of $N^{1/2}$ dependence in the θ region and $N^{0.8}$ dependence in the good solvent limit. The lag in actual values as shown in *Figure 1* and as expressed in equations (10) and (11) of 0.416 instead of 0.637 is apparently due to the slower crossover of R_H from the θ region to the good solvent limit compared with R_G as demonstrated in (I).

We did assume that the solvent dependence of the number of monomers per statistical segment, n, and statistical segment length, l, is negligible. Other experiments[11] indicate that this is an acceptable assumption. The crudeness of the discontinuity at the temperature cut-off of the blob theory is clearly revealed as a discrepancy between experimental data and calculations at $N \simeq N_\tau$. The effect is clear in our explicit expression of $[\eta]/[\eta]_\theta$ as a function of N/N_τ, but it could have cancelled out when log $[\eta]/[\eta]_\theta$ was plotted as a function of log $[R_G(x)/R_G(\theta)]^3$ [7]. Nevertheless, the temperature blob theory has provided the opportunity to calculate static and dynamic variables in a unified fashion. In the case presented, viscosity as a function of molecular weight and temperature can be compared with experimental results without any adjustable parameters except the one which has been fixed by R_G measurement.

Equation (9) gives an expression of intrinsic viscosity of polymer solutions as an explicit function of molecular weight for any molecular weight, temperature and solvent. It can be easily transformed for different polymers by obtaining the ratio of the values of n for each polymer, where n is the number of monomers per statistical segment, through characteristic ratios. Also, we suggest that $[\eta]\, MR^2$ with $R = R_H/R_G$ may be a better parameter than $[\eta]\, M$ for the universal calibration of gel permeation chromatography. Intrinsic viscosity from equation (9) can be used, instead of

Table 1 [η] as a function of *M* and *T*

$M \times 10^{-4}$	T(°C)/solvent	[η] (dl/g)	$[\eta]_\theta{}^c$, dl/g	$\ln[\eta]/[\eta]_\theta$	$N/N_T{}^d$	Reference
0.18	25/b[a]	0.041	0.037	0.045	0.27	1, x
0.226		0.045	[0.040][b]	0.047	0.34	
0.60		0.080	[0.067]	0.084	0.91	
0.72		0.085	[0.072]	0.072	1.1	
4.5	30/b	0.276	0.178	0.19	7.5	1, ⊗
5.5		0.305	0.197	0.19	9.2	
7.5		0.387	0.230	0.23	12.6	
8.3		0.42	0.242	0.24	13.9	
15.0		0.67	0.325	0.31	25.2	
21.0		0.85	0.386	0.34	35.2	
23.5		0.90	0.408	0.34	39.4	
34.5		1.25	0.492	0.40	57.8	
50.0		1.60	0.592	0.43	83.8	
82.0		2.21	0.760	0.46	137	
109.0		2.80	0.866	0.51	183	
153.0		3.72	1.04	0.55	256	
41.1	45/c	0.684	0.57	0.079	0.9	8, ○
172		1.57	1.22	0.11	3.8	
1020		4.29	2.35	0.26	22.3	
2780		9.12	4.4	0.32	60.9	
4380		12.7	5.5	0.36	96.0	
41.1	55/c	0.735	0.57	0.11	3.5	8, ●
172		1.75	1.22	0.16	14.8	
1020		5.15	2.35	0.34	87.6	
2780		10.85	4.4	0.39	239	
4380		15.8	5.5	0.46	376	
41.1	40/b	1.34	0.57	0.37	81.7	8, △
172		3.83	1.22	0.50	342	
1020		14.4	2.35	0.79	2027	
2780		36.5	4.4	0.92	5325	
4380		68.0	5.5	1.09	8705	
183	35/b	3.72	1.11	0.53	335	9, □
306		5.40	1.43	0.58	560	
335		6.56	1.50	0.64	613	
350		7.35	1.53	0.68	641	
710		11.4	2.18	0.72	1300	
335	39/c	1.51	1.50	0.003	1.07	9, ▽
350		1.93	1.53	0.10	1.12	
31.0	25/b	1.18	0.487	0.38	47.2	10, ⊠
49.0		1.52	0.603	0.40	74.6	
123		2.93	0.992	0.47	187	
242		5.21	1.33	0.59	369	
363		6.90	1.72	0.60	553	
459		7.98	1.86	0.63	699	

[a] b for benzene and c for cyclohexane

[b] obtained for θ temperature in cyclohexane by $[\eta]_\theta = 8.5 \times 10^{-4}\, M^{0.5}$

[c] intrinsic viscosity of polystyrene in cyclohexane at 35.4°C was used for $[\eta]_\theta$

[d] 35.4°C was used as the θ temperature for polystyrene and −50.0°C was assumed for benzene

the empirical Mark–Houwink equation which requires different coefficients for different molecular weight and temperature ranges.

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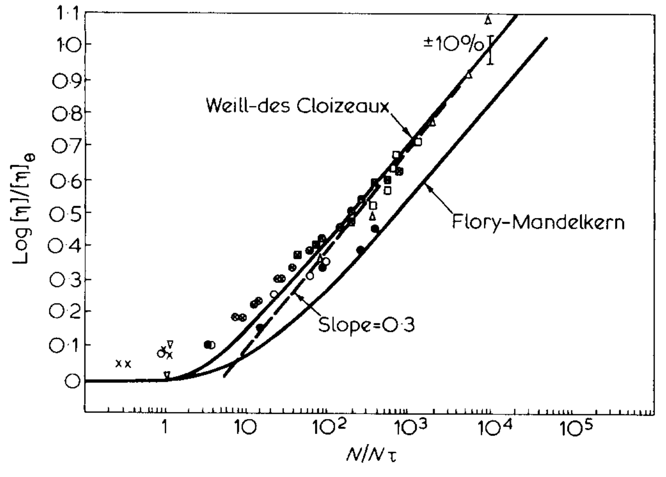

Figure 1 The variation of the expansion factor α_η for intrinsic viscosity with N/N_T. Experimental points are labelled corresponding to *Table 1*. No adjustable parameters are involved in the comparison of theory and experiment

REFERENCES

1 Altares Jr, T., Wyman, D. P. and Allen, V. R. *J. Polym. Sci. (A)* 1964, **2**, 4533

2 Farnoux, B., Boue, F., Cotton, J. P., Daoud, M., Jannink, G., Nierlich, M. and DeGennes, P. G. *J. Physique* 1978, **39**, 77

3 Daoud, M. *Thesis* Université de Paris, VI (1977)

4 Farnoux, B. *Ann. Physique* 1976, **1**, 73

5 Akcasu, A. Z. and Han, C. C. *Macromolecules* 1979, **12**, 276

6 Mandelkern, L. and Flory, P. J. *J. Chem. Phys.* 1952, **20**, 212

7 Weill, G. and des Cloizeaux, J. *J. Physique* 1979, **40**, 99

8 Slagowski, E. L. *Thesis* University of Akron, Department of Chemistry (1972)

9 Yamaguchi, N., Sugiura, Y., Okano, K. and Wada, E. *J. Phys. Chem.* 1971, **75**, 1141

10 Fukuda, M., Fukutomi, M., Kato, Y. and Hashimoto, T. *J. Polym. Sci., (Polym. Phys. Phys. Edn)* 1974, **12**, 871

11 Bazuaye, A. and Huglin, M. B. *Polymer* 1979, **20**, 45