Correlations Between Mark-Houwink-Sakurada Parameters for Linear and Star-like Polymers

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SUMMARY: The influence of the excluded volume on the intrinsic viscosity of linear and star-like polymers in dilute solution is reflected on the Mark-Houwink-Sakurada (MHS) parameters k and "a". A correlation between these parameters and the number of arms for star-like polybutadiene in different solvents is proposed. Also, for various linear polymers, a relation describing the decrease of parameter k with increasing "a", the proportionality coefficient being the unperturbed parameter k_θ, is established.

Introduction

The unperturbed parameter, generally designed by k_θ, may be used to assess the unperturbed polymer dimensions as well as chain stiffness of randomly coiled polymers. This important configurational factor is conventionally determined by the viscometric method under theta conditions. In this connection the Mark-Houwink-Sakurada (MHS) relationship is applied to correlate the intrinsic viscosity [η] of a linear polymer in dilute solution with the molecular weight of the polymer M, i.e.

$$[\eta] = k\,M^a \tag{1}$$

where k and "a" are empirical constants. In theta conditions a = 0.5 and $k = k_\theta$ and with the increase of solvent quality "a" increases to 0.8, while k decreases. It is often difficult to determine and keep the theta condition and others techniques, based on experimental

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investigations in thermodynamically good solvents, are used. One of these methods consists on establishing different correlations between "a", k and k_θ parameters[1-7]. Up to now, no investigations of this type on branched polymers have been made.

For the same molecular weight, the density of a branched polymer is higher as compared to that of its linear homologue. Thus, the log-log plot of the intrinsic viscosity vs. the molecular weight for linear and star-like polymers leads to a family of straight lines with the same slope and decreasing intercepts, with respect of the increase of arms number, f [8-14]. This means that the parameter "a" keeps the same value for the linear polymer and the branched homologue, while k decreases with the increase of branching.

The present paper extends previous theoretical investigations on star-like polymers in dilute solution[15,16]. The MHS parameters for linear and star-like polybutadiene (literature data[14]) are evaluated in order to establish an interdependence between k and "a" parameters, taken into account the number of star arms, f. Also, for a number of linear polymers in dilute solution (literature data[17]), a general correlation between k, k_θ and "a" is proposed.

Results and discussion

From the dependences of the intrinsic viscosity on the molecular weight for linear and star-like polybutadienes with f = 18, 32, 64, 128 and 270 in cyclohexane at 25°C, toluene at 35°C and dioxane at 26.5°C (theta condition) (literature data[14]) the MHS parameters were calculated and given in Table 1.

Studying the variations of parameter k with f^{-a}, linear dependences are obtained (Fig. 1), yielding to the following equations:

$$k(f) = 0.298 \cdot f^{-0.500} - 0.012 \qquad \text{for dioxane at 26.5°C} \qquad (2)$$

$$k(f) = 0.058 \cdot f^{-0.697} - 2.877 \cdot 10^{-4} \qquad \text{for cyclohexane at 25°C} \qquad (3)$$

$$k(f) = 0.047 \cdot f^{-0.730} + 2.254 \cdot 10^{-4} \qquad \text{for toluene at 35°C} \qquad (4)$$

The coefficients in these relations depend on the solvent, so that they can be considered as functions of "a" parameter. Thus, for star polybutadiene in dilute solution the variation of parameter k with solvent quality and the number of arms is expressed through equation (5) and plotted in Fig. 2.

$$k(f, a) = 2^{-11.725\,a + 4.109}\,(f^{-a} - 2^{-a}) + 2^{-12.324\,a + 3.823} \qquad (5)$$

The theoretical values of k obtained for a = 0.500, 0.679 and 0.730 and f = 2, 18, 32, 64, 128 and 270 are collected in Table 1. The table also contains the experimental values, which are in good agreement with the calculated ones.

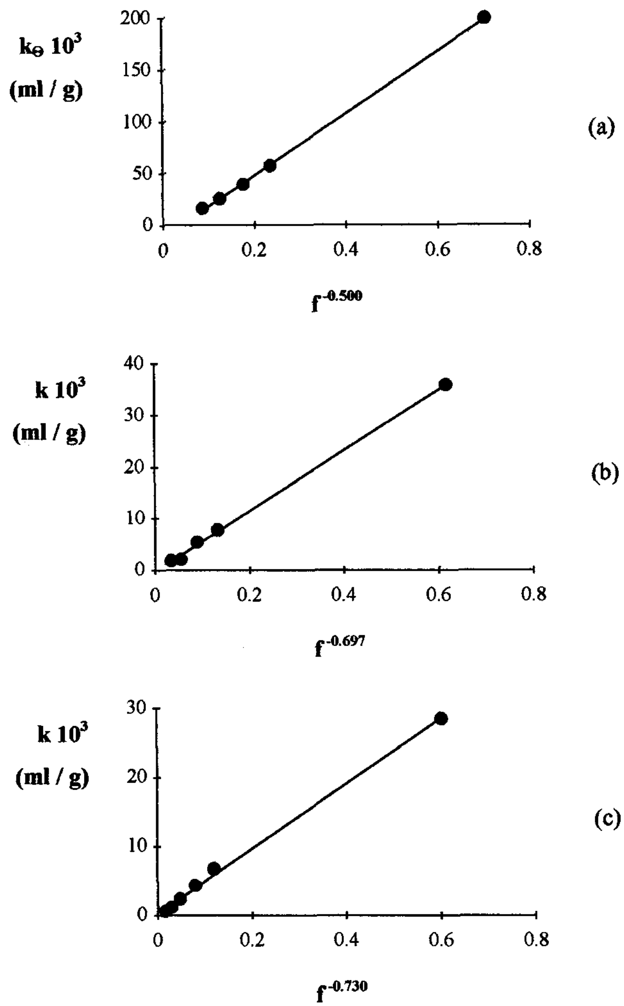

Fig. 1: Variation of MHS parameter k with f^{-a} for star polybutadiene in: (a) dioxane at 26.5°C (a = 0.500); (b) cyclohexane at 25°C (a = 0.697); (c) toluene at 35°C (a = 0.730)

To study the correlation between MHS parameters k and "a" for linear chains, literature data[17)] were evaluated for different polymers with the molecular weight higher than 10^4. For all investigated samples, the obtained dependence is expressed through the relation:

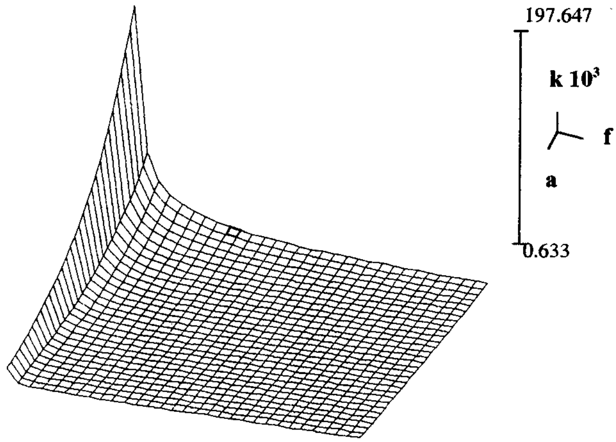

Fig. 2: $k = f(f, a)$ according to equation (5) for star polybutadiene

Tab. 1. Experimental ($k_{\theta,exp}$, k_{exp}, a) and theoretical ($k_{\theta,th}$, k_{th}) MHS parameters (in ml/g) for linear and f-arm star polybutadiene in dioxane at 26.5°C (theta condition), cyclohexane at 25°C and toluene at 35°C

f	Dioxane, 26.5°C a = 0.5		Cyclohexane, 25°C a = 0.697		Toluene, 35°C a = 0.730	
	$k_{\theta,exp}\ 10^3$	$k_{\theta,th}\ 10^3$	$k_{exp}\ 10^3$	$k_{th}\ 10^3$	$k_{exp}\ 10^3$	$k_{th}\ 10^3$
2 (linear)	199.0	197.7	37.5	36.7	28.5	27.7
18	56.9	57.8	7.7	7.8	6.7	5.7
32	39.2	40.4	7.4	5.2	4.3	3.8
64	25.1	25.0	2.1	3.1	2.3	2.3
128	16.1	14.2	1.9	1.9	1.2	1.5
270	-	6.0	-	1.0	0.8	0.9

$$k = s\, 2^{-12.8\, a} \tag{6}$$

where the constant s is given in Table 2. One observes a good agreement between 10 s and the unperturbed parameter k_θ. Fig. 3 presents, as an example, the theoretical curve expressed through the relation (6) as compared to the experimental data[17)] for linear polybutadiene.

Tab. 2. Parameter s from equation (6) and the unperturbed parameter k_θ for the investigated polymers[17]

Polymer	s 10^{-1}	k_θ 10^3 (ml/g)
Polybutadiene	149.9	150.0 – 205.0
Poly(methyl methacrylate)	46.6	39.3 – 78.0
Poly(butyl methacrylate)	28.0	29.5 – 38.0
Poly(methyl acrylate)	50.7	68.0
Polystyrene	65.0	69.9 – 84.6
Poly(vinyl acetate)	86.6	82.0 – 110.0
Poly(vinyl chloride)	187.0	156.0
Polyethylene	257.0	286.0 – 323.0
Polyacrylonitrile	196.5	210.0 – 250.0

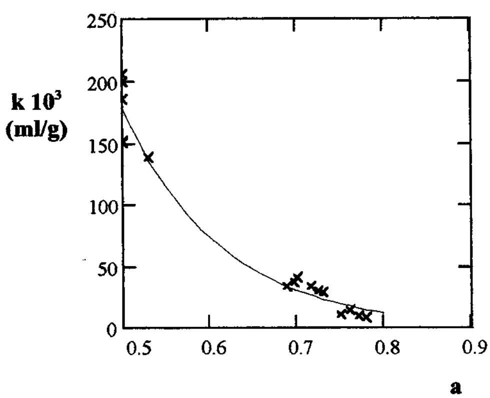

Fig. 3: $k = f(a)$ according to equation (6) for linear polybutadiene

Conclusions

In this study, we have proposed a correlation between MHS parameters k and "a" for f-arm star polybutadiene. This relation allows to evaluate one of the three parameters ("a", k and f) when two of them are known and has proved to yield values consistent with those experimentally determined. The unperturbed parameter k_θ can be evaluated not only for linear but also for star polybutadienes. Also, for a number of linear polymers a relation describing the decrease of the parameter k with incresing “a” was proposed, the proportionality coefficient being related to the unperturbed parameter k_θ.

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