

Practical Evaluation of the $[\eta]$ - M Relationship. III. Estimation of the Exponent a

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Synopsis

A method is proposed for predicting the exponent a of the Mark-Houwink equation, $[\eta] = KM^a$. This method makes use of the solubility parameters of polymer and solvent.

Importance of the Value of a

In Parts I and II of this investigation^{1,2} an attempt was made to correlate the literature data on the Mark-Houwink equation,

$$[\eta] = KM^a \quad (1)$$

Although this equation cannot be derived theoretically, it is of great importance for practical purposes.

It was shown that eq. (1) can be replaced¹ by

$$[\eta] = 32K_{\theta}(M/1000)^a \quad (2)$$

in which K_{θ} is the coefficient of the corresponding equation for θ solutions.

$$[\eta] = K_{\theta}M^{0.5} \quad (3)$$

A method of predicting K_{θ} values, based on polymer structure has been presented.²

Equation (2) can be used for predicting the relationship of $[\eta]$ to M for an arbitrary polymer-solvent combination, if no experimental data are available. The only unknown factor is the exponent a . The exponent has a mean value of 0.7, but proves to be dependent on the nature of both polymer and solvent. A method of predicting the value of a will be given in this article.

Connection with θ Temperatures

As was stated before, eq. (1) may only be considered a practical approximation of the $[\eta]$ - M relationship. Theoretical considerations do not

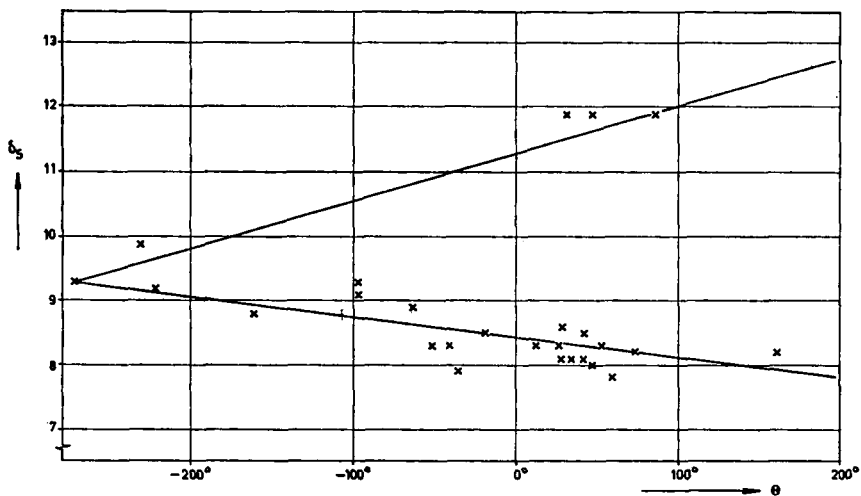


Fig. 1. Solubility parameters and Θ temperatures for poly(methyl methacrylate).

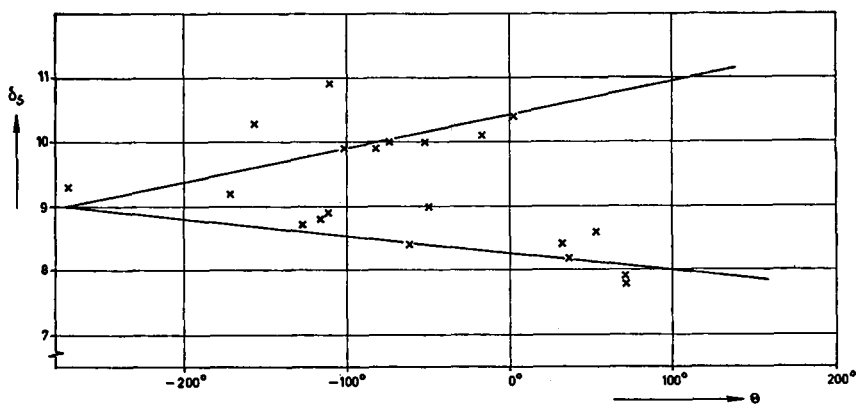


Fig. 2. Solubility parameters and Θ temperatures for polystyrene.

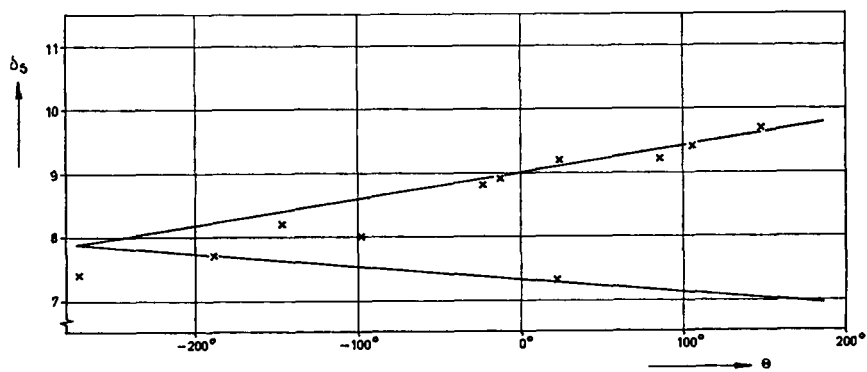


Fig. 3. Solubility parameters and Θ temperatures for polyisobutene.

lead to a simple power function. This appears from eqs. (4) and (5), representing the theoretical relationship given by Flory³

$$[\eta] = K_0 M^{0.5} \alpha^3 \quad (4)$$

$$\alpha^5 - \alpha^3 = c(1 - \Theta/T)M^{0.5} \quad (5)$$

Furthermore, these equations indicate a connection with the temperature Θ , at which for the given polymer-solvent combination there is no net interaction between polymer and solvent molecules.

Fox⁴ used eqs. (4) and (5) for the calculation of Θ temperatures from [η]- M measurements. He succeeded in correlating the Θ values obtained with the solubility parameter δ_s of the solvent. Plots of δ_s as a function of Θ , as given by Fox, are shown in Figures 1, 2, and 3 for the polymers poly(methyl methacrylate), polystyrene, and polyisobutylene. In the figures the points can approximately be connected by two straight lines intersecting at absolute zero at a δ value corresponding to the solubility parameter δ_p of the polymer. As was already stated by Fox, this should be considered a purely empirical, approximate correlation.

At a given temperature the δ values given by the two lines correspond, again very approximately, to the solubility limits of the polymer. If these values are indicated by δ_{\min} and δ_{\max} , the polymer is soluble in solvents for which

$$\delta_{\min} < \delta_s < \delta_{\max}$$

The close connection between Θ temperatures and solubility limits also appears from the method for determining Θ from turbidity measurements.

Estimation of the Exponent α from the Solubility Limits

Equations (4) and (5) and Figures 1-3 suggest that the exponent α should vary between two limits,

$$\alpha_{\min} = 0.5, \quad \text{if } \delta_s = \delta_{\min} \text{ or } \delta_s = \delta_{\max}, \quad \text{i.e., if } T = \Theta$$

$$\alpha_{\max} = 0.8, \quad \text{if } \delta_s = \delta_p, \quad \text{i.e., if } T/\Theta = \infty$$

and for large values of α . Approximate values of δ_{\min} and δ_{\max} , derived from solubility data, are given in Table I for a number of polymers⁵ at a temperature of about 25°C.

In Figure 4 values of α for some polymer-solvent systems⁵ (mentioned in Table II) are plotted against the quotient

$$\Delta = (\delta_s - \delta_{\min})/(\delta_{\max} - \delta_{\min})$$

As was to be expected, the α values show a certain correlation with Δ , although the points spread considerably. For $\Delta = 0$ and $\Delta = 1$ the points tend to the theoretical value of $\alpha = 0.5$. At $\Delta = 0.33$ a maximum value of α of about 0.75 is found.

TABLE I
 Polymer Properties

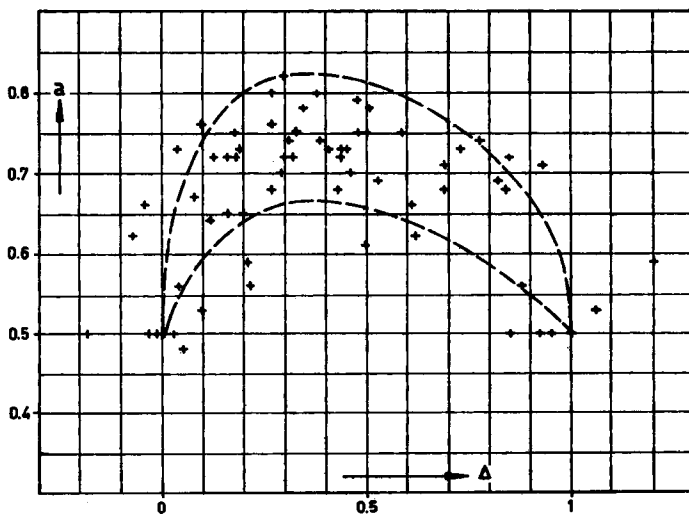
Polymer	δ_{\min}	δ_{\max}	δ_p , calcd.	δ_p , lit.
Polyisobutene	7.5	9.1	8.0	7.1- 8.3
Polypropylene	7.8	9.3	8.3	9.2- 9.4
Poly(octyl methacrylate)	6.9	11.4	8.3	8.4
Poly(hexyl methacrylate)	7.0	11.5	8.4	8.6
Poly(butyl methacrylate)	7.3	11.5	8.6	8.3- 8.8
Poly(ethyl methacrylate)	7.8	11.7	9.1	8.95- 9.1
Poly(methyl methacrylate)	8.2	11.9	9.4	9.1-12.85
Poly(dimethyl siloxane)	8.1	9.4	8.55	7.3- 7.6
Polybutadiene	7.6	10.9	8.7	7.15- 8.6
Polystyrene	8.2	10.4	8.9	8.5-10.3
Polychloroprene	9.0	10.5	9.5	8.1- 9.4
Poly(vinyl chloride)	9.0	11.4	9.8	9.4-10.8
Poly(vinyl acetate)	8.4	13.5	10.1	8.8-11.05
Poly(methacrylonitrile)	9.8	12.5	10.6	10.7
Poly(acrylonitrile)	10.3	15.5	12.0	12.5-15.4

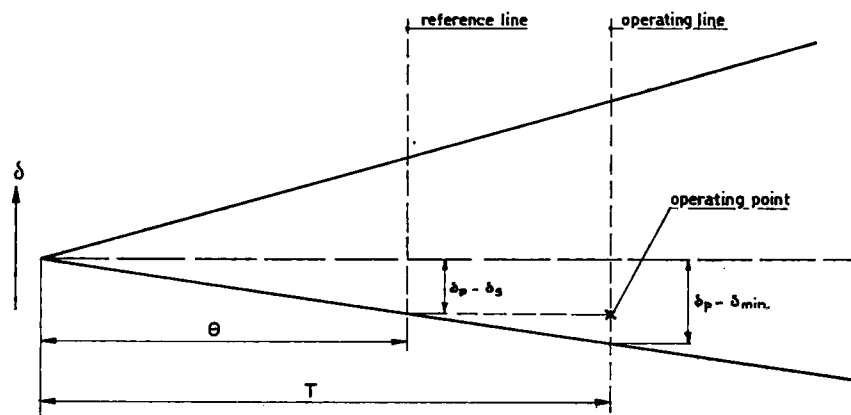
With the aid of the empirical correlations mentioned in Section 2 above the course of a as a function of Δ can be derived by using Flory's theoretical relationship. Equations (2), (4), and (5) permit the calculation of a as a function of Θ/T , the molecular weight M being the only parameter. From Figures 1, 2, and 3 it appears that approximately

$$\delta_p = \delta_{\min} + \frac{1}{3}(\delta_{\max} - \delta_{\min}) \quad (6)$$

From the definition of Δ it follows that

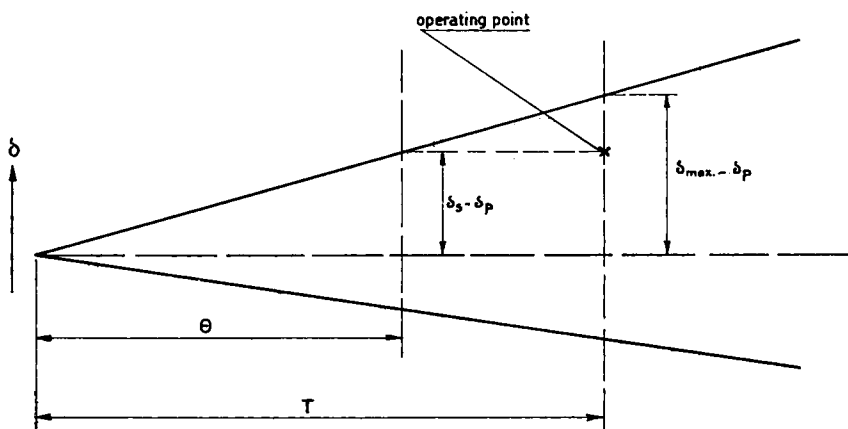
$$\Delta = (\delta_s - \delta_{\min})/3(\delta_p - \delta_{\min})$$


 Fig. 4. Experimental values of a as a function of Δ .



Temperature

(a)



Temperature

(b)

Fig. 5. Derivation of eq. (7).

Now the relationship between Δ and Θ/T can be derived with the aid of Figure 5 as follows.

If $\delta_s < \delta_p$ or $\Delta < 1/3$ (Fig. 5a), then

$$\Theta/T = (\delta_p - \delta_s)/(\delta_p - \delta_{\min}) = 1 - (\delta_s - \delta_{\min})/(\delta_p - \delta_{\min})$$

so that

$$\Delta = 1/3(1 - \Theta/T) \tag{7a}$$

TABLE II
Comparison Between Predicted and Experimental α Values

Polymer	Solvent	δ_s	Δ	α calcd. from Fig. 6	α exptl.	α calcd. from Fig. 7
Polyisobutene	Diisobutylene	7.7	0.12	0.63	0.64	0.70
	Cyclohexane	8.2	0.44	0.71	0.72	0.73
	Carbon tetrachloride	8.6	0.69	0.62	0.68	0.70
Polypropylene	Toluene	8.9	0.88	0.60	0.56	0.65
	Benzene	9.2	1.06	0.50	0.53	0.60
	Cyclohexane	8.2	0.27	0.70	0.80	0.74
	Toluene	8.9	0.73	0.63	0.73	0.70
Poly(octyl methacrylate)	Benzene	9.2	0.93	0.56	0.71	0.66
	Methyl ethyl ketone	9.3	0.53	0.74	0.69	0.65
Poly(hexyl methacrylate)	Methyl ethyl ketone	9.3	0.51	0.69	0.78	0.67
	Isopropanol	11.5	1.00	0.50	0.50	0.50
Poly(butyl methacrylate)	Methyl ethyl ketone	9.3	0.48	0.73	0.75	0.70
	Chloroform	9.3	0.48	0.72	0.79	0.70
	Acetone	9.9	0.62	0.73	0.62	0.61
Poly(ethyl methacrylate)	Isopropanol	11.5	1.00	0.50	0.50	0.50
	Methyl ethyl ketone	9.3	0.38	0.75	0.79	0.74
	Isopropanol	11.5	0.95	0.58	0.50	0.50
Poly(methyl methacrylate)	Butyl chloride	8.1	<0	0.50	0.50	0.50
	3-Heptanone	8.3	0.03	0.57	0.50	0.50
	3-Octanone	8.3	0.03	0.57	0.49	0.50
	4-Heptanone	8.4	0.05	0.58	0.48	0.56
Poly(methyl methacrylate)	Methyl isobutyrate	8.5	0.08	0.64	0.67	0.60
	Methyl methacrylate	8.8	0.16	0.69	0.72	0.67
	Toluene	8.9	0.19	0.72	0.73	0.69
Benzene	9.2	0.27	0.73	0.76	0.73	

Methyl ethyl ketone	9.3	0.30	0.74	0.72	0.74
Chloroform	9.3	0.30	0.74	0.82	0.74
Tetrachloroethane	9.7	0.41	0.70	0.73	0.73
Ethylene dichloride	9.8	0.43	0.70	0.68	0.73
Acetone	9.9	0.46	0.73	0.70	0.72
Nitroethane	11.1	0.78	0.66	0.74	0.60
Acetonitrile	11.9	1.00	0.50	0.50	0.50
Toluene	8.9	0.61	0.67	0.66	0.72
Benzene	9.2	0.84	0.57	0.68	0.70
Methyl ethyl ketone	9.3	0.92	0.58	0.50	0.70
Ethyl iodide	9.4	1.00	0.50	0.50	0.68
Cyclohexane	8.2	0.18	0.68	0.75	0.67
Toluene	8.9	0.39	0.71	0.74	0.74
Benzene	9.2	0.48	0.70	0.75	0.72
Methyl cyclohexane	7.8	<0	0.50	0.50	0.50
Butyl chloride	8.1	<0	0.50	0.66	0.60
Cyclohexane	8.2	0	0.50	0.50	0.62
Ethyl benzene	8.8	0.27	0.71	0.68	0.74
Toluene	8.9	0.32	0.72	0.72	0.75
Benzene	9.2	0.45	0.72	0.73	0.73
Methyl ethyl ketone	9.3	0.50	0.71	0.61	0.72
Chloroform	9.3	0.50	0.73	0.75	0.72
Chlorobenzene	9.5	0.59	0.73	0.75	0.71
Dioxane	10.0	0.82	0.64	0.69	0.66
Toluene	8.9	<0	0.50	0.62	0.67
Benzene	9.2	0.13	0.66	0.72	0.72
Tetrahydrofuran	9.1	0.04	0.56	0.73	0.66
Chlorobenzene	9.5	0.21	0.65	0.59	0.72
Cyclohexanone	9.9	0.38	0.68	0.80	0.75
3-Heptanone	8.3	<0	0.50	0.50	0.50

(continued)

TABLE II (continued)

Polymer	Solvent	δ_s	Δ	α calcd. from Fig. 6	α exptl.	α calcd. from Fig. 7
	Toluene	8.9	0.10	0.60	0.53	0.53
	Benzene	9.2	0.16	0.69	0.65	0.62
	Methyl ethyl ketone	9.3	0.18	0.67	0.72	0.64
	Ethyl formate	9.4	0.20	0.70	0.65	0.67
	Chlorobenzene	9.5	0.22	0.68	0.56	0.68
	Acetone	9.9	0.29	0.72	0.70	0.73
	Dioxane	10.0	0.31	0.71	0.74	0.74
	Acetonitrile	11.9	0.69	0.70	0.71	0.62
	Methanol	14.5	1.20	0.50	0.59	0.50
	Acetone	9.9	0.04	0.60	0.56	0.68
Poly(methacrylonitrile)	Dimethylformamide	12.1	0.85	0.54	0.50	0.67
	Dimethylacetamide	10.8	0.10	0.60	0.76	0.63
Poly(acrylonitrile)	Dimethylsulfoxide	12	0.33	0.72	0.75	0.75
	Dimethylformamide	12.1	0.35	0.71	0.78	0.75
	Butyrolactone	12.6	0.44	0.70	0.73	0.73
	Ethylene carbonate	14.7	0.85	0.61	0.72	0.61

If $\delta_s > \delta_p$ or $\Delta > 1/3$ (Fig. 5B), then

$$\begin{aligned} \Theta/T &= (\delta_s - \delta_p)/(\delta_{\max} - \delta_p) = (\delta_s - \delta_{\min})/(\delta_{\max} - \delta_p) \\ &- (\delta_p - \delta_{\min})/(\delta_{\max} - \delta_p) = (\delta_s - \delta_{\min})/2(\delta_p - \delta_{\min}) - 1/2 \end{aligned}$$

so that

$$\Delta = 1/3(1 + 2\Theta/T) \tag{7b}$$

The course of a as a function of Δ can be calculated from eqs. (2), (4), (5), and (7) for a given value of M at a given temperature. The curves plotted in Figure 6 show this course for a number of values of M . For the majority of the experimental data the M values are between 10^5 and 10^6 .

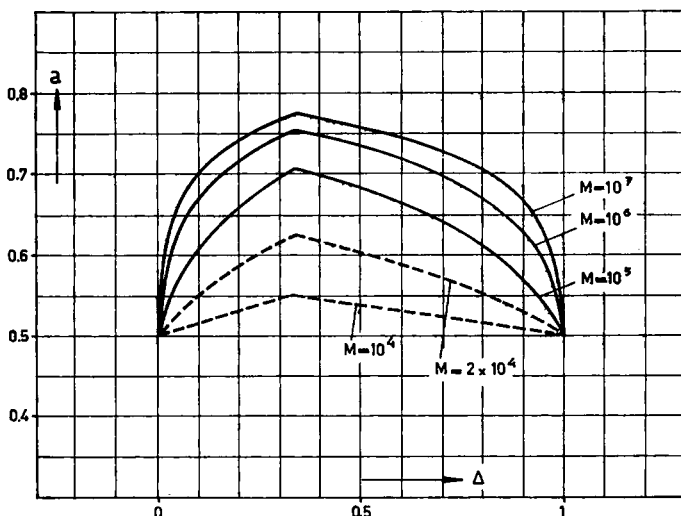


Fig. 6. Theoretical relationship between Δ , M , and a .

There is a reasonable agreement between the experimental points of Figure 4 (temperature, 25°C.) and the calculated curves. So Figure 6 can be used for an estimation of a values when direct experimental data are lacking.

In Table II some a -values calculated according to Figure 6 (fifth column) and experimental values⁴ (sixth column) have been compared. Although for some polymer-solvent systems a good correspondence has been found, rather large deviations occur in some cases. The mean difference between calculated and experimental values amounts to 0.05. Part of these deviations must be due to inaccuracy of the experimental values. For a number of systems the [η]- M relationships have been determined by several different investigators. These data from different sources lead to a mean standard deviation in the a values of 0.035, which is the same order of magnitude as the differences found in Table II.

Prediction of Solubility Parameter of Polymer from Solubility Limits

As was mentioned above, Figures 1, 2, and 3 lead to the conclusion that

$$\delta_p = \delta_{\min} + 1/3(\delta_{\max} - \delta_{\min}) \quad (6)$$

This is also in accordance with the position of the maximum in Figure 4, namely, at $\Delta = 1/3$.

Values for δ_p , calculated with the aid of eq. (6), can be found in Table I. They have been compared with values from the literature,⁵ which spread considerably. In most cases there is a reasonable correspondence between calculated and experimental values. Exceptions are polypropylene and poly(dimethyl siloxane). We expect that in these cases the values obtained from eq. (6) are more reliable.

Prediction of a Values from Solubility Parameters of Polymer and Solvent

According to eq. (6), the solubility limits δ_{\min} and δ_{\max} are closely related to the solubility parameter of the polymer, δ_p . Therefore it might be possible to use only the solubility parameter values δ_p and δ_s for a first estimation of the exponent a .

For this purpose a graph of δ_p versus δ_s was made, the exponent a being a parameter. Experimental a values were plotted on this graph, and equal

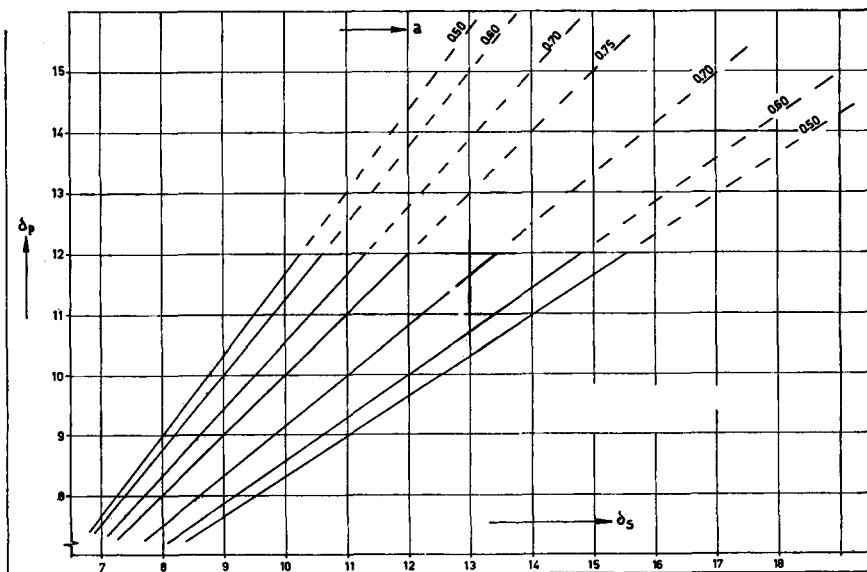


Fig. 7. Relationship between δ_p , δ_s , and a .

parameter values were connected by straight lines. The result, after some smoothing out, is shown in Figure 7.

In Table II the a values predicted with the aid of Figure 7 are listed. Comparison with experimental values show a mean deviation of 0.05 (equal to that of the method described in the Estimation section).

Discussion

In this article methods have been proposed for predicting the exponent a in the Mark-Houwink equation, eq. (1). The application of these methods, however, is liable to a number of restrictions. It is supposed that:

(1) Flory's statistical conformation theory for the coiled polymer molecule does hold. Values for a higher than 0.75 may be expected for very rigid polymer molecules and in the case of special solvent-polymer interactions.

(2) The mean molecular weight should be about 10^5 . Deviations are to be expected for low and very high molecular weights.

(3) The temperature should be about 25°C. Polyethylene was not included in this investigation, because no solvents for this polymer at 25°C. are known.

(4) Our investigation was limited to polymers with solubility parameters not higher than 12. Above this limit no sufficiently reliable experimental data could be found.

Notation

a	exponent in the Mark-Houwink equation
c	constant
K	coefficient in the Mark-Houwink equation
K_{Θ}	coefficient for Θ solutions
M	molecular weight
T	absolute temperature
α	expansion factor
Δ	solubility parameter ratio
δ_{\max}	solubility parameter at maximum solubility limit
δ_{\min}	solubility parameter at minimum solubility limit
δ_p	solubility parameter of polymer
δ_s	solubility parameter of solvent
$[\eta]$	intrinsic viscosity
Θ	temperature at which no net interaction between polymer and solvent results

References

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Résumé

Il est proposé une méthode pour prédire l'exposant a de l'équation Mark-Houwink, $[\eta] = KM^a$. Cette méthode utilise les paramètres de solubilité du polymère et du solvant.

Zusammenfassung

Es wird eine Methode vorgeschlagen, die es ermöglicht, den Exponenten a der Mark-Houwinkschen Gleichung $[\eta] = KM^a$ vorherzusagen. Bei dieser Methode werden die Löslichkeitsparameter von Polymerem und Lösungsmittel angewendet.

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