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DILUTE SOLUTIONS OF NYLON 12—II*

RELATIONSHIP BETWEEN INTRINSIC VISCOSITY AND MOLECULAR WEIGHT

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Abstract—Samples of poly(12-dodecanelactam) (polylaurolactam, nylon 12) with $\bar{M}_n$ 1×10^3–33×10^3 were prepared. Polymerizations initiated with water or with lauric acid proceeded under conditions for minimum changes in end-group concentration. Values of $\bar{M}_n$ were calculated from the end-group content and $\bar{M}_w$ from light scattering in the mixture *m*-cresol/60 vol% of 2,2,3,3-tetrafluoropropanol. From measurements of intrinsic viscosity in *m*-cresol, the relationship $[\eta] - \bar{M}_n$ was established in the given range of $\bar{M}_n$. The relationship $[\eta] - \bar{M}_w$ for $\bar{M}_w$ from 3.3×10^3 to 125×10^3 has been established.

INTRODUCTION

In study of the polymerization of lactams, there is frequently a need to determine the molecular weights of quite low polymers. For low molecular weight samples, the number average molecular weight $\bar{M}_n$ can be found accurately from the content of end-groups, assuming that each molecule is terminated in a specific way with groups which can be determined with sufficient accuracy. However, with polyamides [1–5] this assumption is not always fulfilled. The accuracy of the weight average molecular weight determination, usually by light scattering, is limited by the sensitivity of the method at low molecular weights. Hence, in many cases the only possible way is to characterize the sample by the viscosity average molecular weight, $\bar{M}_v$, calculated from the intrinsic viscosity using the calibrated relationship $[\eta]$ vs M. $\bar{M}_v$ thus determined may be in error due to the choice of an inappropriate relationship and also to experimental inaccuracies. The accuracy of determination of $[\eta]$ of low-molecular weight polyamides may be reduced by an anomalous concentration dependence of reduced experimental values due to the association of amine and carboxylic groups [6].

For nylon 12, methods of determination of both $\bar{M}_n$ and $\bar{M}_w$ have been suggested, allowing in principle measurements of very low molecular weights [7]. In the case of M_w, however, they have not yet been applied for molecular weights below *ca.* 1×10^4. The constants of the Mark–Houwink equation were obtained for *m*-cresol and conc sulphuric acid for $\bar{M}_n$ between 5.3×10^3 and 17.5×10^3, using number average molecular weights [8]. Recently, the $\bar{M}_w$ calibration has been used in the determination of the Mark–Houwink constants in *m*-cresol and 1,1,1,3,3,3-hexafluor-2-propanol [9] for $\bar{M}_w$ between 1.5×10^4 and 1.6×10^5 and in *m*-cresol [7] for $\bar{M}_w$ between 1×10^4 and 1.25×10^5.

The aim of this work is to determine $\bar{M}_n$, $\bar{M}_w$ and the intrinsic viscosity of nylon 12 and to determine the constants of the Mark–Houwink relationship, including molecular weights of about 10^3.

EXPERIMENTAL

Chemicals

12-Dodecanelactam (laurolactam) was crystallized three times under nitrogen from dimethoxyethane purified with calcium hydride. Lauric acid was crystallized four times from 80% aq. ethanol; m.p. 43.4°. 2,2,3,3-Tetrafluoropropanol, TFP (Koch-Light, England), rectified, contained (by gas chromatography) less than 0.3% of impurities. *m*-Cresol, rectified, contained (gas chromatography) 0.5% of *p*-cresol, 0.5% of a mixture of 2,4- and 2,5-xylenol; water content (according to Fischer) was 0.025%. Benzene, analytical purity grade, distilled.

Polymers

The preparation conditions for polymers are summarized in Table 1. Polymerizations initiated with water or with lauric acid proceeded in ampoules sealed under nitrogen. The vapour space occupied roughly 50% of the ampoule volume. Polymerization products were extracted by triple boiling with benzene for one hour. Extracted polymers were dried at 55°/133.3 Pa for 48 hr.

Methods

The end-group content was determined by conductometric titration [10] with an LF 610E, Digi 610, WTW Weilheim conductoscope. The accuracy of the method for basic groups was ±0.5 mmole/kg, and for acid groups ±1.0 mmole/kg. Light scattering was performed with a Photo-Gonio-Diffusomètre Sofica employing a method described earlier [7]. The viscosities were measured with a 5901 B Auto Viscometer Hewlett-Packard apparatus at 25°. The concentration dependences were determined at 5–10 concentrations from various weighed quantities of samples, dissolved with shaking in *m*-cresol at 25° for 18–25 hr, and then at 50° for 0.5 hr.

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* Communication in this series: Z. Tuzar, M. Bohdanecký, R. Puffr and J. Šebenda, this Journal **11**, 851 (1975).

Table 1. Preparation conditions, conversion (p), content of acid (A) and basic (B) groups, number ($\bar{M}_n$) and weight ($\bar{M}_w$) average molecular weights, intrinsic viscosity $[\eta]$ and Huggins coefficients k_M of nylons 12 prepared at 250° in the presence of lauric acid or water as initiators (I)

Polymer	I (mmole kg)	Time (hr)	p (%)	Polym. product A (mmole kg)	Polym. product B (mmole kg)	Polymer A (mmole kg)	Polymer B (mmole kg)	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n	$[\eta]$	k_M
I = lauric acid												
1	24.5	69.0	19.00	24.1	1.15	150.0	2.8	6.7	9.0	1.34	0.530	0.32
2	25.6	145.5	31.16	26.6	1.50	84.7	4.1	11.8	18.0	1.52	0.800	0.27
3	26.0	195.0	37.65	23.2	1.62	58.8	3.8	17.0	24.0	1.41	0.990	0.26
4	25.0	315.0	48.60	22.3	2.20	45.0	2.4	22.2	33.0	1.49	1.280	0.29
5	158.8	16.0	25.95	159.8	0.55	429.4	2.6	2.3	-	—	0.240	0.27
6	155.0	24.0	35.40	155.9	1.10	347.7	3.7	2.9	3.3	1.14	0.290	0.31
7	156.2	45.0	55.80	157.2	1.11	236.3	1.5	4.2	6.0	1.43	0.380	0.35
8	148.2	70.0	70.90	146.0	1.50	176.6	2.0	5.7	9.1	1.60	0.460	0.33
9	151.1	240.0	96.80	139.7	1.58	153.3	1.8	6.5	11.6	1.78	0.590	0.25
10	229.1	74.0	86.24	230.0	1.11	227.3	2.4	4.4	6.6	1.50	0.420	0.22
I = water												
11	205.3	24.0	5.03	25.7	25.4	461.8	430.0	2.2	3.5	1.59	0.215	3.46
12	215.5	48.0	27.13	39.9	37.4	124.1	113.0	8.1	13.0	1.60	0.658	0.74
13	172.2	69.0	38.38	35.9	35.0	76.1	74.5	13.1	20.0	1.53	0.790	0.50
14	211.2	145.5	77.99	37.4	37.3	47.6	47.6	21.0	33.0	1.57	1.300	0.39
15	200.0	195.0	88.14	39.7	41.7	44.3	44.8	22.3	33.0	1.48	1.380	0.30
16	211.0	285.0	95.95	41.6	40.7	42.1	43.4	23.0	39.0	1.69	1.440	0.36
17	502.5	7.5	5.00		—	920.0	797.6	1.1	—	—	0.144	3.50
18	502.5	15.0	25.00			237.0	223.1	4.2	7.7	1.83	0.465	0.73
19	502.5	40.0	74.00		—	95.4	86.9	10.5	19.5	1.86	0.810	0.47
20*	115.6	325.0	98.50		—	30.2	31.3	32.0	—	—	1.760	0.30

* Polymerization temperature 270°

RESULTS AND DISCUSSION

Content of end-groups and weight average molecular weights

The content of end-groups of nylons does not always correspond to values calculated from the consumption of the initiator. The changes in the concentration of acid and basic groups, due to side-reactions, may give rise to branching or even crosslinking. Since this phenomenon has been observed [1–3] also with nylon 12, it has been necessary to prepare samples of nylon 12 under mild conditions.

With acidolytic polymerization products (laurolactam + lauric acid), the content of acid groups corresponded to the starting amount of acid (Table 1, samples 1–10). Only in samples with polymerization times over 200 hr (samples 3, 4, 9) the content of acid groups was lower by approximately 10%, probably because of decarboxylation described earlier [4] for nylon 6. From the beginning of polymerization, all acidolytic polymerization products and extracted polymers contained also basic groups. Their content was low and virtually constant throughout the polymerization. Values of $\bar{M}_n$ for acidolytic polymers were calculated from the content of acid groups. With polymers having long polymerization times (samples 3, 4, 9), this value may be approx 10% in error towards higher molecular weights.

Hydrolytic polymers (Table 1, samples 11–20) contained at the beginning of polymerization up to 10% more acid than basic groups. With increasing polymerization time, the content of acid and basic groups of the polymers became equilibrated. Values of $\bar{M}_n$ for hydrolytic polymers were calculated from those groups which were present in the higher concentration. Here too, however, error is possible because of chains terminated with neutral endgroups.

Treatment of viscometric data

The intrinsic viscosities and Huggins coefficients of *m*-cresol solutions of nylon 12 were determined from specific viscosities by extrapolation to zero concentration. It appeared that the concentration dependence of viscometric data was so much influenced by molecular weight and the type of polymer that the intrinsic viscosity and Huggins coefficient had to be determined with great caution. Methods used in the determination of these quantities have been examined recently e.g. in refs [11–13]. The data were plotted as follows: (1) η_{sp}/c vs c (Huggins [14]), (2) ln η_r/c vs c (Kraemer [15]), (3) $\ln(\eta_{sp}/c)$ vs c (Martin [16], Staudinger and Heuer [17]), (4a) c/η_{sp} vs c, (4b) $c/\ln \eta_r$ vs c, (4c) $\frac{1}{2}(c/\eta_{sp} + c/\ln \eta_r)$ vs c (4a–c Heller [18]), (5) η_{sp}/c vs η_{sp} (Schulz-Blaschke [19]), (6) ln η_r/c vs ln η_r(Arrhenius, Rother, Hoffmann [20]). For methods (1), (2), (3), (5) and (6), the intercept on the y-axis directly gives the intrinsic viscosity (or its logarithm), and the initial slope is (1) k_H^2, (2) $(k_K - \frac{1}{2})^2$, (3) k_M, (5) k_S, (6) $(k_A - \frac{1}{2})$. With method (4), the common part of the three plots on the y-axis gives (intrinsic viscosity)$^{-1}$ and the initial slope of the plot $\frac{1}{2}$ $(c/\eta_{sp} + c/\ln\eta_r)$ vs c is $(\frac{1}{4} - k_{HE})$. In an ideal case, the coefficients k_H, k_K, k_S, k_A, k_M, k_{HE} should all be equal to the real value of the Huggins coefficient k'. All these extrapolation methods are empirical in principle, representing attempts to express the dependence η_{sp} vs c in a linear form suitable for simple treatment of experimental data. Their reliability is limited to the range of relatively low specific viscosities ($\leqslant$ 0.6–0.8); the Heller method is less severely restricted [13]. For method (3), the range of suitability is not delimited with sufficient exactitude [12, 21]. According to a previous analysis [13], the Heller method is the least affected by the contribution of terms of (concentration)^2 and may consequently be regarded as a standard method with respect to the others.

For acidolytic polymers of laurolactam, the plots for all extrapolation methods were linear, and the intrinsic viscosities determined by different methods coincided within the limits of experimental error, if

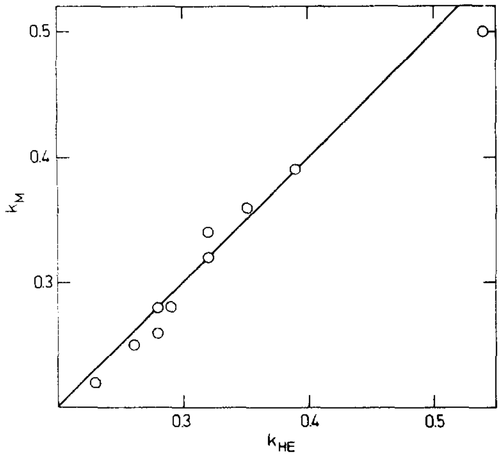

Fig. 1. Comparison of the coefficients k_M and k_{HE}. Acidolytic nylons 12 in *m*-cresol, 25 : ○ experimental points. —— ideal case.

$\eta_{sp} < 0.7$. The coefficients k_M and k_{HE} were virtually identical within the limits of accuracy (Fig. 1), and as usual [12, 13] lower by 10% on the average than k_H, k_K, k_S and k_A. The same was observed with hydrolytic polymers, if the intrinsic viscosity exceeded 0.8 dl/g and $k_{HE} < 0.5$. For low-molecular samples of hydrolytic polymers, the plots using methods (2), (5) and (6) were nonlinear and exhibited maxima, so that these methods could not be employed in the extrapolation. The same effect, though much smaller, was observed if the Heller method (4) was used (Fig. 2). The plots according to the Huggins method (1) were linear in several cases (e.g. Fig. 2) up to rather high specific viscosities (0.9); in other cases, however, there were curvatures even at much lower specific viscosities. All hydrolytic polymers of laurolactam were virtually best satisfied by method (5) i.e. by the dependence ln (η_{sp}/c) vs c. Since also for acidolytic polymers, this method yielded the same intrinsic viscosities and Huggins constants as method (4) regarded as standard, the Martin–Staudinger–Heuer method of extrapolation [method (3)] can be recommended as the most suitable for nylon 12.

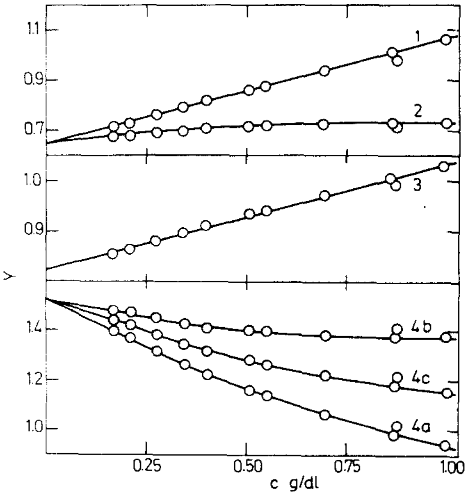

Fig. 2. Concentration dependences of viscometric data. Nylon 12 ($[\eta] = 0.658$) in *m*-cresol, 25 . *Y*: (1) η_{sp}/c; (2) ln η_r/c; (3) 1 + log (η_{sp}/c); (4a) c/η_{sp}; (4b) $c/\ln\eta_r$; (4c) $\frac{1}{2}(c/\eta_{sp} + c/\ln\eta_r)$.

Table 1 shows that the k_M values of hydrolytic polymers are always higher than those of acidolytic ones.

Relationship between intrinsic viscosity and molecular weight

The high refractive index increment of nylon 12 in the mixture *m*-cresol/60 vol % TFP determined under the conditions of the dialysis equilibrium between solution and solvent (0.254 ml/g) [7] permits in principle determination of relatively low molecular weights by the light scattering with sufficient accuracy. Error in $\bar{M}_w$ may be due to a change in the refractive index increment with molecular weight. Such dependence in the range of lower molecular weights has been observed in several polymer/mixed solvent systems as a result of the dependence of the coefficient of selective sorption of one solvent on the polymer [22]. In systems in which the polymer is solvated by a polar mechanism (as in our case, where cresol forms hydrogen bonds with the amide groups), this effect need not be considered [22]. $\bar{M}_w$ values below 1×10^4 were therefore considered to be correct (subjected only to the error of the method, i.e. ±10% at most) and were used to extend and improve the Mark–Houwink relationship determined previously [7]. The dependence involving 38 points in the range of $\bar{M}_w$ from 3.3×10^3 to 125×10^3 is linear (Fig. 3) and has the form $[\eta] = 8.1 \times 10^{-4} \times \bar{M}_w^{0.70}$, coinciding with the previous relationship [7], $[\eta] = 4.6 \times 10^{-4} \times \bar{M}_w^{0.75}$ for higher molecular weights.

Some authors [24] claim a lower slope in log $[\eta]$ vs log M plots for some polymers in good solvents in the M range 10^3–10^4. However, the transition from higher to lower slopes occurs at different molecular weights with different polymers. Our dependence = $11.8 \times 10^{-4} \times \bar{M}_n^{0.73}$ (Fig. 3) demonstrates conclusively the linearity down to $\bar{M}_n = 10^3$ for this particular case. The exponents in the two relationships are similar and the relationships may be regarded as consistent. The $[\eta]$–$\bar{M}_n$ relationship may be employed in the kinetic studies in determinations of $\bar{M}_n$, assuming that the polydispersity of products under investigation corresponds to that of samples used in the

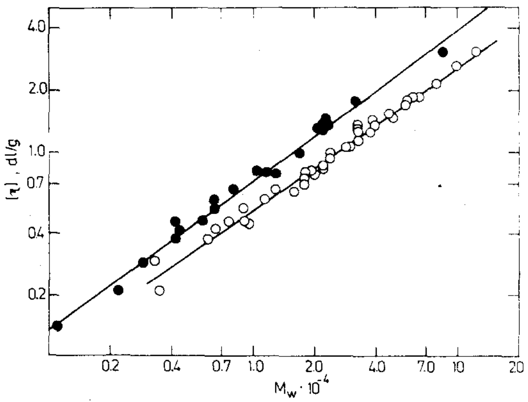

Fig. 3. Dependence of intrinsic viscosity $[\eta]$ of nylons 12 in *m*-cresol at 25° on the number (●) and weight (○) average molecular weights.

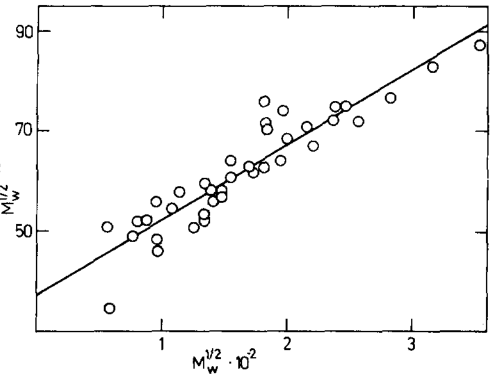

Fig. 4. Determination of the viscometric constant K_0 of nylon 12 in *m*-cresol at 25°.

calibration, i.e. if $1.4 < \overline{M}_w/\overline{M}_n < 1.8$ (Table 1). If the polydispersity were different, the use of $[\eta]$–$\overline{M}_n$ may lead to serious error in $\overline{M}_n$ (e.g. at $\overline{M}_w/\overline{M}_n = 2$, about 20–25%). This point has to be checked very carefully, since recent data indicate [23] that, at very low conversions and under different reaction conditions, the polydispersity may be as high as 6.

The characteristic ratio of unperturbed dimensions, r_0^2/nl^2 (i.e. the ratio of the mean square end-to-end distance of the chain unperturbed with the excluded volume to the same quantity for a freely jointed chain), calculated from the $\overline{M}_w$ data and for all points in Fig. 3 by using the viscometric constant $K_0 = 26.6 \times 10^{-4}$ (Fig. 4) by the same procedure as in ref. [7] is 6.77. This value is higher than in the preceding paper [7] (6.29) and fits better the predicted dependence of the characteristic ratio (which is a measure of the conformational rigidity of the polymer molecule) on the frequency of amide groups in the nylon chain [25]. The characteristic ratio 6.77, which is higher than the value for the more flexible nylon 6 (6.07) and lower than for the more rigid polyethylene [25] (8), may confirm the plausibility of our relationship between intrinsic viscosity and molecular weight.

The Stockmayer–Fixman procedure used in Fig. 4 may not be strictly valid for low polymers because of incipient draining and because the Gaussian statistics are not obeyed. According to theoretical calculations [25], the latter effect will be important at $M < 10^4$. The former effect is difficult to assess but an analysis of data for other low polymers of similar structure (polyethylene, polyethylene oxide) indicates that the draining effect could be important below approximately the same limit. As only a few of data points in Fig. 4 are in this range, we assume that the procedure yields a reasonable estimation of unperturbed dimensions.

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