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DILUTE SOLUTION PROPERTIES OF POLYLAUROLACTAM

Z. TUZAR, M. BOHDANECKÝ, R. PUFFR and J. ŠEBENDA

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia

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Abstract—For a number of fractions and unfractionated samples of polylaurolactam, molecular weights ($\bar{M}_w = 1 \times 10^4$–$12{\cdot}5 \times 10^4$) were measured by the light-scattering method in a mixed solvent of *m*-cresol with 60 vol. % 2,2,3,3-tetrafluoropropanol; intrinsic viscosities were determined in *m*-cresol and 96% H_2SO_4, and the constants of the Mark–Houwink equation were calculated. The calculated values of the characteristic ratio of unperturbed dimensions (virtually identical for *m*-cresol and 96% H_2SO_4) were compared with the respective values for polypyrrolidone and polycaprolactam. It was found that the higher frequency of the —CO—NH-groups reduces the rigidity of the polyamide chain.

The literature has very few data on the solution behaviour of polylaurolactam. The main reason is probably the fact that so far polylaurolactam has not been as widely used as, e.g. polycaprolactam. Another reason may be that the study of the solution behaviour is made difficult by phenomena following from the pronounced crystallinity of this polymer (poorer solubility in common solvents of polyamides, aggregation).

Number-average molecular weights ($\bar{M}_n = 5 \times 10^3$–$25 \times 10^3$) have been determined for several unfractionated samples by end-group titration; intrinsic viscosities have been determined for the same samples in *m*-cresol, concentrated sulphuric acid and a mixture phenol–tetrachloroethane, and the constants of the Mark–Houwink equation have been calculated [1]. In another paper [2] unfractionated samples were investigated by osmometry and end-group titration; the resulting values of $\bar{M}_n$ were in good agreement. Another paper [3] gives the constants of the Mark–Houwink equation in *m*-cresol without specifying in detail the samples, range of molecular weights and the method of their determination.

The aim of this work is to measure the intrinsic viscosity of polylaurolactam fractions in several solvents for the broadest possible range of molecular weights, to determine the weight-average molecular weights and the constants of the Mark–Houwink equation by using the light scattering method, to determine the characteristic ratio of the polylaurolactam chain and its dependence on the nature of the solvent and to compare the results with the data for polycaprolactam and polypyrrolidone.

EXPERIMENTAL

Polymers and chemicals

The polymer samples were prepared from laurolactam, purified by threefold crystallization from methanol followed by crystallization from benzene. Two samples were prepared by the polymerization of dry lactam initiated with lauric acid and conducted in sealed glass ampoules in an inert atmosphere; another two samples were obtained by the polymerization of lactam with an excess of water in an autoclave [3] (25 ml. stainless, with a glass lining). The polymerization conditions are given in Table 1.

Table 1. Conditions of preparation of polylaurolactam samples

Sample	Initiator	mol%	T,°C	t,h
A	lauric acid	1.0	260	260
B	lauric acid	1.0	270	97
	water	85		
C	lauric acid	1.0	270	11
	water	85		
D	lauric acid	1.0	270	24

The polylaurolactam samples were reprecipitated from a 1% solution in tricresol into a five-fold excess of diethyl ether. After decanting several times with diethyl ether, the polymer was dried for several days at 25° *in vacuo*. The fractions of the samples B, C, D were obtained by fractional precipitation with decalin from 1% solutions in tricresol. From each sample (starting amount 10 g), at least 10 fractions were obtained, but the marginal ones or those which exhibited weak fluorescence in dilute solutions, due to the effect of residual cresol during the reprecipitation, were not measured. A capital letter denotes the starting polymer; the Arabic numerals denote the fractions according to increasing molecular weights.

2,2,3,3-Tetrafluoropropanol (TFP) (Koch-Light, England) was twice distilled on a laboratory column. Fractions taken at 109° at normal pressure were checked chromatographically (99·8% TFP) and refractometrically ($n_{25}^{D} = 1{\cdot}319$).

m-Cresol (Koch-Light, England), was distilled twice and its purity was checked chromatographically (99·84%) and refractometrically (1·538). Technical *m*-cresol, which after drying and distillation contained 62% of *m*-cresol, was used in the fractionations.

Concentrated sulphuric acid (96%) was checked only for water content. Chloroform and toluene (Lachema, Czechoslovakia) were distilled prior to use and their purities (>99·5%) were again checked chromatographically.

Methods

Light scattering was measured with a Photo-Gonio-Diffusomètre Sofica in a standard angular region. Each mole-

cular weight was determined from measurements at six concentrations. The data obtained were evaluated by the Zimm method using the refractive index increment measured at a dialysis equilibrium between the polymer solution in the mixed solvent and the mixed solvent with a Brice–Phoenix differential refractometer (BP-200V). Experimental details have been described earlier [4].

Intrinsic viscosities were measured with Ubbelohde viscometers by a standard procedure.

The acidic and basic groups in the polylaurolactam samples were determined by conductometric titration [5].

RESULTS AND DISCUSSION

Solvents of polylaurolactam

Owing to very long methylene sequences in the chain, polylaurolactam is soluble in an even more restricted number of solvents than, e.g. polycaprolactam. We have found that, although polylaurolactam dissolves at elevated temperatures in various solvents (such as dimethylformamide, chloroform, TFP, benzyl alcohol, tetrahydrofurfuryl alcohol, cyclohexanol, octyl alcohol and anisole), on cooling to 30–40° it precipitates sooner or later.

Solutions, molecularly disperse at room temperature, can be prepared in cresol, concentrated sulphuric acid, a phenol–50 vol. % tetrachloromethane mixture (cf. [1]) and in an ethanol solution of zinc bromide. We also found several mixed solvents which behave as cosolvent systems, i.e. systems in which neither component dissolves the polymer, but mixtures in a certain composition range are good solvents. These are for instance TFP–30 to 80 vol. % chloroform or TFP–45 to 60 vol. % toluene. While the solutions in the TFP–chloroform mixture are stable for long periods, the polymer in the TFP–toluene mixture (as well as in TFP–benzene, TFP–mesitylene) precipitates spontaneously, sometimes after several days, sometimes after only several hours. However, the turbid solution can be restored to the original state by heating. The intrinsic viscosity values of the sample A in TFP–50 vol. % toluene measured after dissolving the sample several times were well reproducible (1·12 ± 0·03). A comparison with the intrinsic viscosity value in *m*-cresol (1·07) shows that the mixture TFP–50 vol. % toluene cannot be regarded as a thermodynamically poor solvent. The spontaneous aggregation of the polymer from such solutions is therefore explained by a strong tendency toward crystallization (a similar phenomenon is met with polyethylene).

Choice of solvent suitable for light scattering

Cresol, the most frequently used solvent for polyamides, is quite unsuited for light scattering measurements. Its refractive index ($n_D^{25} = 1{\cdot}54$) is close to that of polylaurolactam ($n_D^{25} = 1{\cdot}525$, measured by the Becke line method); polylaurolactam in cresol hardly scatters light due to the very small refractive index increment ($dn/dc = -0{\cdot}03$). Neither can concentrated sulphuric acid or a concentrated solution of zinc bromide in ethanol be regarded as suitable solvents for polylaurolactam as they cannot be optically purified. Moreoever, because of its hygroscopic character, concentrated sulphuric acid can alter its water content during various operations before measurement. The system TFP–chloroform was also ruled out: the strong selective evaporation of chloroform could not be prevented during the optical purification of solutions (i.e. filtration through a bacterial filter), leading to irreproducibility of results. The system TFP–toluene was not considered, as it does not yield stable solutions.

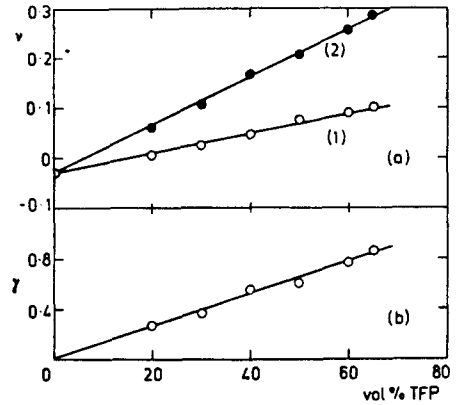

Fig. 1. Dependence (a) of the refractive index increment of polylaurolactam before (1) and after (2) dialysis, (b) of the coefficient of selective sorption of *m*-cresol on polymer on the composition of the mixture *m*-cresol–TFP.

We therefore chose *m*-cresol and sought another component which would help to lower the refractive index of the mixture and to increase the refractive index increment of polylaurolactam. TFP appeared to be such component; owing to its very low refractive index ($n_D^{25} = 1{\cdot}32$), it reduces the refractive index of the mixture very considerably. Polylaurolactam can be dissolved in *m*-cresol containing up to 67 vol. % TFP. A considerable increase in the refractive index increment values after dialysis (mainly in the mixtures with a higher content of TFP) compared to those before dialysis is due to the expected selective sorption on polymer of the better solvent (*m*-cresol) having a high refractive index (Fig. 1). The coefficient of selective sorption was calculated [4] from the equation $\gamma = (\nu_\mu - \nu_c)/\nu_\varphi$, where ν_μ is the refractive index increment measured after dialysis, ν_c is the refractive index increment measured before dialysis, and ν_φ is the refractive index increment of *m*-cresol in the mixture without polymer ($\nu_\varphi = 0{\cdot}217$).

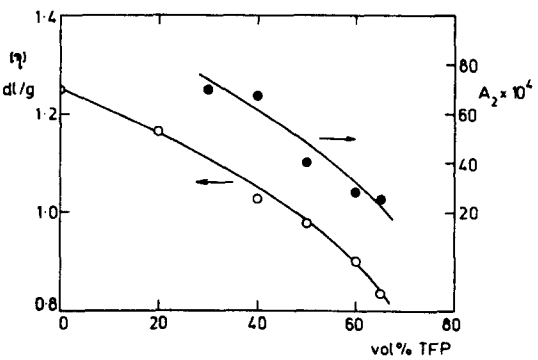

Fig. 2. Dependence of the intrinsic viscosity [η] (○) and of the second virial coefficient A_2 (●) of sample B on the composition of the mixture *m*-cresol–TFP.

Intrinsic viscosity and, in the case of reasonably high refractive index increments, also molecular weights and the second virial coefficient were measured in *m*-cresol–TFP mixtures (Fig. 2). The molecular weight values of sample B were virtually constant in mixtures *m*-cresol–30 to 60 vol. % TFP ($\bar{M}_w = 38 \times 10^3 \pm 5\%$). The decrease in intrinsic viscosity and in the second virial coefficient with increasing coefficient of the selective sorption of *m*-cresol indicates that for polylaurolactam (in contrast with polycaprolactam [6] and polypyrrolidone [7]) TFP is a markedly poorer solvent than *m*-cresol. It is noteworthy that the extremely high value of the second virial coefficient does not drop to zero near the composition at which the polymer precipitates from solution (67 vol. % TFP). A similar phenomenon has been found for polycaprolactam [6] and polypyrrolidone [7]. This probably means that the tendency towards crystallization is so strong that it causes polyamide to aggregate even in some solvents relatively good thermodynamically.

For the determination of the molecular weight of polylaurolactam, the mixture *m*-cresol–60 vol. % TFP was chosen. The reason was the high refractive index increment after dialysis (0·254 ml/g), the partly reduced second virial coefficient and the still sufficient distance from the composition at which the solution becomes unstable. Recently, several papers (cf. [8]) have attempted to prove the more or less considerable dependence of the coefficient of selective sorption in some polymer–solvent precipitating agent systems on molecular weight. As for polycaprolactam [6] and polypyrrolidone [7], we did not observe dependence of the coefficient of selective sorption on molecular weight for polylaurolactam. The refractive index increments before and after the dialysis of five fractions were independent of molecular weight over the range

Table 2. Molecular weights and intrinsic viscosities of polylaurolactam samples

Sample	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	$[\eta]_{m\text{-cresol}}$	$[\eta]_{96\%H_2SO_4}$
A	30	24	1.25	1.07	0.49
B	38			1.25	0.58
B-1	16	15	1.07	0.64	
B-2	40			1.37	0.60
B-3	66			1.85	0.82
C	22	13	1.69	0.86	0.40
C-1	9.5	7	1.35	0.45	0.26
C-2	18	12	1.50	0.75	0.36
C-3	22	13	1.70	0.84	0.42
C-4	24	14.5	1.65	0.94	0.44
C-5	29	21.5	1.35	1.07	0.50
C-6	47	36	1.30	1.53	0.66
C-7	49	37	1.32	1.48	0.69
D	56	38	1.47	1.71	0.77
D-1	18			0.70	0.36
D-2	57			1.79	0.75
D-3	61			1.85	0.80
D-4	80			2.17	0.89
D-5	100			2.62	1.10
D-6	125			3.09	1.29

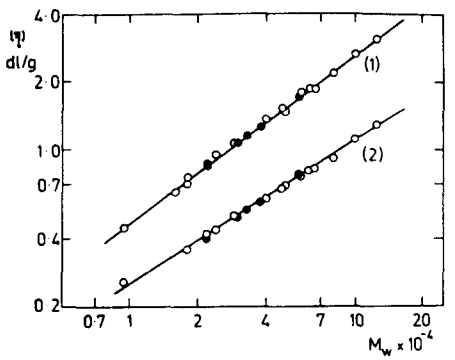

Fig. 3. Dependence of the intrinsic viscosity $[\eta]$ of polylaurolactam on molecular weight $\bar{M}_w$ in *m*-cresol (1) and 96% H_2SO_4 (2); unfractionated samples (●), fraction (○).

$\bar{M}_w = 22 \times 10^3$–$125 \times 10^3$. Neither of the samples exhibited any pronounced dissymmetry of the scattered light; as a result, the dimensions of the polymer coil could not be evaluated even for the highest fractions. On the other hand, the symmetry of the scattered light (even at the limiting angles 30 and 150°) means that the solutions are optically clean, i.e. free of major dust particles. This fact, along with the extremely high refractive index increment value, allows also comparatively low molecular weight samples (say about 10^4) to be measured with good accuracy.

Relationship between intrinsic viscosity and molecular weight

We determined values of $\bar{M}_w$ and $\bar{M}_n$ (by light scattering in the mixture *m*-cresol–60 vol. % TFP or by titration of carboxylic groups) and the intrinsic viscosities in *m*-cresol and concentrated sulphuric acid for a number of unfractionated samples and fractions (Table 2).

Because of the known hydrolytic effect of sulphuric acid on polycaprolactam [9], the stability of polylaurolactam solutions in this solvent had to be ascertained. We found that polylaurolactam (sample B) could be dissolved at 25° in concentrated sulphuric acid. The intrinsic viscosity remained unchanged if the solution was shaken for 2 to 24 hr (0·580 ± 0·005); after another hour of heating, it decreased to 0·558, after 4 hr to 0·421 and after 7 hr to 0·381. We therefore measured the intrinsic viscosities in concentrated sulphuric acid after shaking the samples for 12 hr in sealed ampoules at room temperature.

The constants of the Mark–Houwink equation were determined from logarithmic plots of $[\eta]$ vs $\bar{M}_w$ (Fig. 3) by the least squares method. For *m*-cresol, $[\eta] = 4{\cdot}63 \times 10^{-4}\bar{M}_w^{0{\cdot}75}$ and for 96% sulphuric acid $[\eta] = 6{\cdot}94 \times 10^{-4}\bar{M}_w^{0{\cdot}64}$. The fact that all experimental points satisfy linear dependences can be regarded as proof that the molecules of the samples were linear coils swollen more in *m*-cresol ($a = 0{\cdot}75$) and less in 96% sulphuric acid ($a = 0{\cdot}64$). It seems somewhat surprising (especially in the case of the less good solvent, i.e. concentrated sulphuric acid) that the linear dependences are satisfied both by fractions and by unfractionated samples. This can be explained on the one hand by both solvents being so good that for them

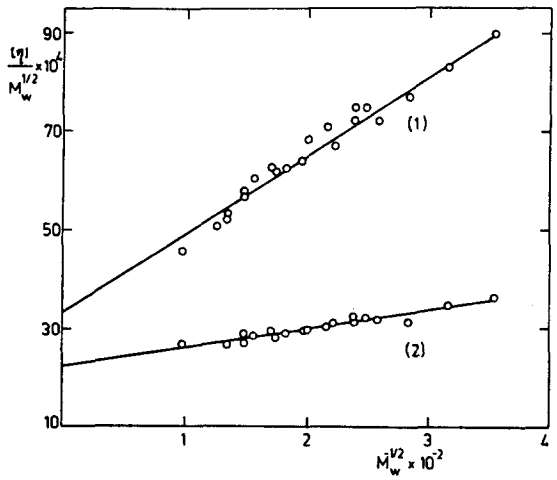

Fig. 4. Determination of the viscometric constant K_0 of polylaurolactam in *m*-cresol (1) and in 96% H_2SO_4 (2).

the difference between the weight and viscometric average molecular weight of polydisperse (unfractionated) samples is not too great, and on the other, that the unfractionated samples are not very polydisperse and the fractions are not very sharp (cf. $\bar{M}_w/\bar{M}_n$ in Table 2).

The number of samples for which $\bar{M}_w$ could be measured, was small. The ratio of $\bar{M}_n$ and $\bar{M}_v$ is more sensitive to polydispersity of samples which may spoil the $[\eta]$–$\bar{M}_n$ correlation. For these reasons we did not evaluate the constants of the Mark–Houwink equation for $\bar{M}_n$. In all the following calculations, the relationship $[\eta]/\bar{M}_w$ was used.

In order to determine the viscometric constant K_0 (used as a basis for the calculation of the characteristics of the conformational rigidity of polymers) use was made of the linear extrapolation of the plots $[\eta]/M^{1/2}$ vs $M^{1/2}$ (Fig. 4). It is known [10, 11] that the intercept of these plots (K'_0) may be identified with K_0 only if the inequality $1 < [\eta]/K'_0M^{1/2} < 1{\cdot}6$ is satisfied. If this condition is not met, empirical corrections are needed. For $1 < [\eta]/M^{1/2}K_0 < 2{\cdot}5$ the ratio K'_0/K_0 equals 1·05 [11] whereas for $1{\cdot}3 < [\eta]/M^{1/2}K'_0 < 2{\cdot}9$ (i.e. $1{\cdot}8 < [\eta]/M^{1/2}K_0 < 4$) the value $K'_0/K_0 = 1{\cdot}40$ has been recommended [10].

The data for polylaurolactam in 96% H_2SO_4 meet the first condition so that $K_0 = K'_0 = 22{\cdot}2 \times 10^{-4}$ (correlation coefficient of linear regression 0·96). For *m*-cresol solutions, the $[\eta]/M^{1/2}$ vs $M^{1/2}$ plot is slightly curved. A linear extrapolation (correlation coefficient 0·98) gives $K'_0 = 33{\cdot}3 \times 10^{-4}$. The values $[\eta]/M^{1/2}K'_0$ (1·4–2·6) are within the limits to be satisfied for the use of $K'_0 = 1{\cdot}40\,K_0$. The value K_0 calculated thus $(23{\cdot}8 \times 10^{-4})$ is very close to that found for solutions in sulphuric acid.

Calculation of the characteristic ratio of polylaurolactam

One of the main characteristics of the polymer is the so-called characteristic ratio of unperturbed dimensions, r_0^2/nl^2, where r_0^2 is the mean square end-to-end distance of a real chain unperturbed by the excluded volume effect and nl^2 is the same quantity for a hypothetical "freely jointed" chain [12a]. The symbol n denotes the number of bonds in the main chain, l stands for the bond length. Since there are several types of bonds having various lengths in the polyamide chain [13] ($l_{CH_2-CH_2} = 1{\cdot}52$ Å, $l_{NH-CH_2} = 1{\cdot}46$ Å, $l_{CO-CH_2} = 1{\cdot}51$ Å, $l_{CO-NH} = 1{\cdot}33$ Å) l^2 must be replaced by the mean square bond length calculated with respect to the number of the individual bonds in the monomer repeating unit [12a, b]. For polylaurolactam, $l^2 = 2{\cdot}28$ Å^2.

The characteristic ratio can be calculated from the viscometric constant K_0 by using the relationships

$$r_0^2/nl^2 = (r_0^2/M)(m/l^2)$$

$$r_0^2/M = (K_0/\Phi_0)^{2/3},$$

where Φ_0 is the Flory universal constant [12a] equal to $2{\cdot}6 \times 10^{21}$, M is molecular weight and m is the mean molecular weight per skeletal bond. m can be calculated from the ratio M_0/n_0 where M_0 is the molecular weight of the monomer unit and n_0 is the number of bonds in the monomer unit.

For polylaurolactam, m = 15·2 and $r_0^2/M = 0{\cdot}94 \times 10^{-16}$ in *m*-cresol and $0{\cdot}90 \times 10^{-16}$ in 96% sulphuric acid. The characteristic ratio in the former case is 6·29 and in the latter 6·01.

In contrast with polypyrrolidone [7] and polycaprolactam [14], where the characteristic ratios are strongly dependent on the dielectric constant of the medium, the values obtained for polylaurolactam in two solvents markedly differing in their dielectric constant are very close to each other. We explain this finding by the fact that the distance between the —CO—NH-groups in the polylaurolactam chain is larger than for the other two polyamides, so that their dipole interaction is weaker, and therefore also the conformational structure is less dependent on the dielectric constant of the medium.

Effect of the frequency of the —CO—NH-groups on the characteristic ratio

By using new and older experimental data, we now attempt to show how the frequency of the —CO—NH-groups influences the characteristic ratio of the polyamide chain. Our calculation of the characteristic ratio of polycaprolactam [14] and polypyrrolidone [7] is based on the data for a solvent having high dielectric constant where the K_0 constant attains limiting values independent of the dielectric constant (Table 3).

Table 3. Comparison of molecular characteristics of various polyamides[a]

Polyamide	q	Solvent	$K_0 \times 10^4$	$\overline{r_0^2/nl^2}$
Polypyrrolidone[b]	0.33	TFP/10 vol.% H_2O	14.3	5.0
Polycaprolactam[c]	0.20	TFP/10 vol.% H_2O/0.1M LiCl	20	6.07[d]
Polylaurolactam	0.09	96% H_2SO_4	22.2	6.01

[a] q is the ratio of the —CO—NH- and —CH_2-groups in a monomer repeating unit of the polymer. K_0 is the viscometric constant. r_0^2/nl^2 is the characteristic ratio.

[b] Cf. ref. [7].

[c] Cf. ref. [14].

[d] The value is lower than in ref. [14] where $\Phi_0 = 2{\cdot}87 \times 10^{21}$ was used.

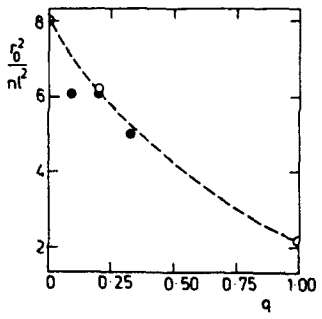

Fig. 5. Dependence of the characteristic ratio on the ratio of the amide and methylene groups in a monomer repeating unit of the polymer q: ○ theoretical values (at 25°) for polyethylene, polycaprolactam and polyglycine (q = 0; 0·2; 1); ● experimental values for polylaurolactam, polycaprolactam, and polypyrrolidone (q = 0·09; 0·2; 0·33).

According to the theoretical considerations concerning the conformational statistics of polyamides [12, 13], the CO—NH bond has the character of a partial double bond with predominant *trans*-conformation. Therefore, the introduction of this group into the polymethylene chain should lead to a higher characteristic ratio. At the same time, however, owing to the presence of the double bond, the interactions associated with rotations of the methylene groups about adjacent bonds are restricted to bonds inside the monomer repeating unit. This effect counteracts the former effect; since it is stronger, the characteristic ratio of poly-ϵ-caprolactam and polyglycine is lower than that for polymethylene, according to theory [12b, c]. The decrease is the more pronounced the higher the ratio of the number of the —CO—NH- and CH_2-groups in the repeating unit (denoted below by q).

In Fig. 5 theoretical values of r_0^2/nl^2 taken from ref. [12b, c] are plotted against q; the values q = 0, 0·2 and 1·0 correspond respectively to polymethylene, poly-ϵ-caprolactam, and polyglycine. (For the latter polymer the characteristic ratio involves also the contribution of the Coulombian dipole interaction of the —CO—NH-groups, amounting to some 15%.)

The experimental value r_0^2/nl^2 for poly-ϵ-caprolactam practically coincides with the theoretical value (probably accidentally, considering the method of determination). No theoretical calculations were carried out for the other two polyamides. An approximate comparison of experimental data with theoretical values could be made if in Fig. 5 a smooth curve is drawn through the theoretical data for polymethylene, poly-ϵ-caprolactam and polyglycine and the graph is then supplemented with experimental data for polypyrrolidone (q = 0·33) and polylaurolactam (q = 0·09). The point corresponding to the former polymer lies in the close vicinity of the curve, that for polylaurolactam is situated about 10% lower. Noting the inaccuracy involved in the determination of the characteristic ratio and the effect of residual polydispersity, the agreement between the experimental and theoretical dependences can be regarded as satisfactory. It suggests that the theoretical model gives an adequate explanation of the observed facts.

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