

Intrinsic Viscosity–Molecular Weight Relationship for Low Molecular Weight Nylon 6

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Synopsis

Samples of nylon 6 have been prepared by the hexamethylene diamine-initiated polymerization of ϵ -caprolactam at 220°C. Fractionation of these with *m*-cresol-diethyl ether at 26°C yielded 15 amino-terminated fractions of \bar{M}_n of 337–10,940 determined conductometrically. Below $\bar{M}_n = 4,306$ the Mark-Houwink parameters in *m*-cresol at 30°C are $K = 3.0 \times 10^{-3}$ dl/g and $\nu = 0.53 \pm 0.02$. Thereafter ν exhibits a pronounced increase. The value of K is similar to the values of K_Θ derived from Stockmayer-Fixman plots of published data in good solvents. The findings thus corroborate a current hypothesis that fractionated, low molecular weight polymers in good solvents tend to behave viscometrically, as if they were under Θ conditions (i.e., $K = K_\Theta$ and $\nu = 0.50$).

INTRODUCTION

Recent research of Rossi, Bianchi, et al.¹⁻⁷ has indicated that for several fractionated, low molecular weight systems in good solvents the Mark-Houwink viscosity parameters K and ν exhibit values characteristic of Θ conditions, i.e., K_Θ and 0.5. Part of a previous communication⁸ was devoted to our cognate investigations of low molecular weight polytetrahydrofuran and polybutadiene, for which systems the hypothesis was found to be untenable. Current work in this laboratory is concerned with radiation grafting to nylon 6, and solution properties of the parent polymer will need to be established for purposes of overall characterization. A study of the viscometric behavior of nylon 6 has been motivated both by this factor and by (a) the need to elucidate how universally the hypothesis of Rossi et al. may be considered to hold and (b) the discordance among published data on the solution properties of this polymer (see, for example, the review by Korshak and Frunze⁹ and more recent work¹⁰⁻¹⁵).

The polymer has the advantage that molecular weights can be obtained readily by endgroup analysis, and fractionation has also proved feasible by simple conventional techniques. After this program was commenced Rothe and Dunkel¹⁶ reported the synthesis of monodisperse oligomers of ϵ -aminocaproic acid (up to a degree of polymerization of 25) by the Merri-field¹⁷ method. This clearly constitutes an ideal mode of obtaining polymers appropriate to such an investigation. The solution viscosities, however, were not measured.

The following abbreviations are used herein: CL, caprolactam; HMD, hexamethylenediamine; *m*-C, *m*-cresol.

EXPERIMENTAL

Preparation of Polymers

"Nylon grade" CL (B.A.S.F., Ludwigshafen am Rhein, W. Germany), crystallized from petroleum ether (b.p. 60–80°C) and dried over P₂O₅ at 0.5 mm in the dark, yielded white plates of m.p. 68.8–69.6°C. Sublimation of HMD (B.D.H. Ltd., Poole, England) at 0.6 mm yielded white flakes of m.p. 41–42°C, which were stored in the dark. The solvent, *m*-C (B.D.H. Ltd.), was used as supplied, except in viscometry, for which it was purified by distillation (b.p. 69–70°C at 0.5 mm).

Seven polymers of different molecular weights were prepared at 220°C according to the method of Carver and Hollingsworth,¹⁸ with dry HMD as initiator and molecular weight regulator. The molar ratios [CL]/[HMD] ranged from 1:1 to 100:1 for a constant reaction time of 170 hr. Removal of unconsumed reactants by vacuum sublimation proved time consuming. Dissolution of the entire reaction product in 98% formic acid and precipitation in diethyl ether was satisfactory in view of the fact that these two liquids are miscible and that the monomer is soluble in diethyl ether and the initiator fairly soluble. Precipitated samples were washed with diethyl ether and dried *in vacuo* over P₂O₅.

Fractionation

Each of the samples was fractionated at 26°C from *m*-C solution by the addition of diethyl ether. This appears to be a convenient and hitherto unreported system, which has the added attribute of ensuring that any residual reactants remain in solution. Apparent capillary melting points ranged from 64 to 228°C for the lowest molecular weight, sticky solid to the highest molecular weight, white powder. No absolute significance was attached to the values nor were they utilized to estimate the heat of fusion, since traces of residual solvent can drastically influence the melting points of polymers and of oligomers in particular (we are indebted to the referee for emphasizing this point to us).

Molecular Weight Determination

Values of \bar{M}_n for the fifteen fractions were determined in duplicate by conductometric titration against 0.1*N* aq. HCl at 30°C. About 0.03–1.0 g of sample (depending on the molecular weight) was dissolved in 25 ml of *m*-C, and a mixture of 15 ml of methanol and 10 ml of water was added to ensure homogeneity throughout the titration. The precision of duplicate determinations of \bar{M}_n , calculated on the basis of two —NH₂ groups per molecule, was generally better than 1% of the absolute value.

Viscosity Determination

Viscosities were measured at 30°C in an Ubbelohde suspended-level viscometer fitted with a built-in porosity-2 sinter, and values of $[\eta]$ were estimated from the common intercept of plots of η_{sp}/C versus C and $\ln \eta_r/C$ versus C . The latter were of positive slope, indicating the Huggins constants k' to be greater than 0.5. The normal concentration range in m -C (0–1.0 g/dl) was employed for the higher molecular weight samples, whereas to obtain values of η_r significantly greater than 1.1 it was necessary to extend this to 5 g/dl for the lower molecular weights.

RESULTS

Solution Viscosity

In Figure 1, $\log [\eta]$ is plotted against $\log \bar{M}_n$. Despite some experimental scatter it is apparent that a definite increase in slope occurs above $\bar{M}_n \approx 4300$, as emphasized by the dotted extension. Within the interval $4300 > \bar{M}_n > 337$ the Mark-Houwink parameters are $K = 3.04 \times 10^{-3}$ dl/g and $\nu = 0.53$. The points are insufficient to assign legitimately a value to ν applicable within the range $10,940 > \bar{M}_n > 4300$.

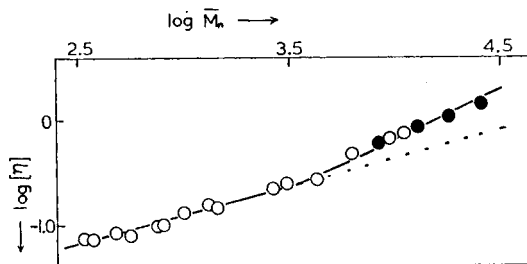


Fig. 1. Intrinsic viscosity versus molecular weight for nylon 6 in m -cresol at 30°C (data of Schaeffgen and Trevissonno²² are indicated by ●).

DISCUSSION

A wide range of ν values has been reported in the literature,⁹ but there is a distinct lack of consistency. Thus, Staudinger and Schnell¹⁹ observed a tendency of ν to increase to 1.0 in m -C at higher molecular weights (20,000), whereas Burnett and MacArthur¹⁰ found this value to hold accurately within the region $4290 > \bar{M}_n > 980$ in another good solvent, trifluoroethanol. Many reported values of ν are, however, considerably lower (e.g., 0.75 in tricresol,¹⁴ 0.70 in 85% formic acid,²⁰ and 0.67 in sulfuric acid²¹). As already stated, it has not been possible to assign values to the Mark-Houwink parameters in this work for fractions of $\bar{M}_n > \text{ca. } 4,000$. In this connection it is illuminating to examine our data in conjunction with those of Schaeffgen and Trevissonno,²² which apply to the same polymer-solvent-temperature system and cover the molecular weight range 4320–26,000.

The three points in Figure 1 above $\bar{M}_n = 4000$ are collinear with a plot of the data of Schaeffgen and Trevisonno (also included in the figure), and the value of ν (0.70) appropriate to the latter may, therefore, be considered to apply to them.

Below $\bar{M}_n \approx 4000$ is found $\nu = 0.53 \pm 0.02$, and there is thus a strong indication that the proposition of Rossi, Bianchi, et al.¹⁻⁷ is valid for this system. Further corroboration would be afforded if the value of K (3.0×10^{-3} dl/g) were the same as that of K_θ . Unfortunately, no value is available for this quantity, although light scattering and viscosity results²³ may well be informative in this respect. We have accordingly been obliged to estimate K_θ (in the relationship $[\eta] = K_\theta M^{0.5} \alpha^{2.43}$) from published data on nylon 6 in good solvents via the Stockmayer-Fixman procedure,²⁴ i.e., from the relationship

$$[\eta]/M^{0.5} = K_\theta + 0.51\Phi BM^{0.5}$$

where Φ is the universal viscosity constant, and B is related to the Flory interaction parameter χ by eq. (1), in which the remaining terms have their customary meanings:

$$B = \bar{v}^2 (1 - 2\chi)/V_1 N_A \quad (1)$$

The intercepts K_θ found from plots of $[\eta]/M^{0.5}$ versus $M^{0.5}$ are listed in Table I and are seen to lie within the same region as K (3.0×10^{-3} dl/g).

TABLE I

Temp., °C	Solvent	$10^3 \times K$, dl/g	Ref. no.
25	<i>m</i> -cresol	1.2	19
25	85% formic acid	1.9	11
25	tricresol	2.4 ^a	14
not quoted	<i>m</i> -cresol	2.6	25
25	concd. sulfuric acid	2.8	26
25	concd. sulfuric acid	3.0	21
30	<i>m</i> -cresol	4.1	22

^a The values of $[\eta]$ and M required for this system were estimated from the published plot of $\log [\eta]$ versus $\log M$, since they were not tabulated separately.

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