

# Solution Properties and Molecular-Weight Distribution of Nylon 11

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## Synopsis

Molecular, hydrodynamic, and thermodynamic properties of nylon 11 in meta cresol and 1,1,1,2,2,2-hexafluor-2-propanol (HFIP) solutions, as well as its distribution of molecular weights were investigated by means of viscosimetry, conductimetric titration of end groups, light scattering, and fractionation by successive precipitation. The studies were carried out on commercial samples as such ( $\bar{M}_n = 14,900$ ,  $\bar{M}_w = 29,400$ ) and on specimens prepared by solid-state post-polymerization of the former ( $M_n = 35,000$ – $43,000$ ,  $M_w = 91,000$ – $104,000$ ). The results show the expected normal or Flory-Schulz distribution of molecular weights on the commercial sample ( $U = 1.03$ ), and a broadened distribution on the postpolymerized one ( $U = 1.42$ ), in agreement with previous observations on solid-state postpolymerization of other polyamides. The intrinsic viscosity of the individual fractions was determined experimentally and the weight-average molecular weights were calculated from the data of the fractionation (number-average molecular weight and the mass fraction of polymer on each individual fraction) by means of an iterative numerical procedure. The parameters of the Mark-Houwink equation were, then, derived from the data of a large number of samples, including that corresponding to the whole, unfractionated polymers, spanning a range of about 100,000 units of molecular weight. The value of the exponent ( $\alpha = 0.69$ ) for solutions in meta cresol corresponds to the behavior of a linear, flexible macromolecule in a good-solvent medium. The solutions in HFIP employed for the light-scattering studies, on the other hand, display high values of the second virial coefficient ( $A_2 = 7.8 \times 10^{-3}$ – $5.6 \times 10^{-3}$  mol mL/g), suggesting that HFIP is a good solvent for nylon 11.

## INTRODUCTION

Most synthetic polyamides owe their technological importance to the ability of forming fibers with excellent mechanical properties and to their good resistance to a large number of industrial solvents. In addition, nylon 11 is one of the few synthetic polymers of commercial relevance that can be obtained from renewable resources.<sup>1</sup> Furthermore, polyamides derived from higher members of the omega-amino-acids homolog series (high methyl/amino ratios) are particularly interesting inasmuch as they display properties intermediate between those of polyamides and polyolefines. The latter are practically insoluble in all known solvents at room temperature, and the study of their hydro- and thermodynamic properties, as well as the investigation of their molecular weight distributions, must be carried out at elevated temperatures. The methods are thus extremely laborious and require expensive and com-

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plicated instrumentation. The scarce information on properties of these types of polyamides is an incipient manifestation of this characteristic, which turns out more critical as one climbs up along the homolog series.

The situation is even more complicated since it is frequently necessary to study samples with molecular weights below or above the rather narrow range from  $10^4$  to  $5 \times 10^4$  g/mol. The former are too low for absolute methods of measuring weight-average molecular weights, like light scattering, and the latter are without the present limits of resolution of the end-group-titration technique employed to determine number-average molecular weights.

The objective of this project is to investigate the molecular weight distribution of nylon 11 and to study its molecular and hydrodynamic properties in solution. To this end, viscosimetric, end-group-titration, and light-scattering techniques will be adapted and applied to the nylon 11 case. The molecular weight distribution will be studied by means of a fractionation scheme based on the successive precipitation of fractions.

## MATERIALS AND METHODS

The studies were carried out on nylon 11 of commercial origin (Rilsan, Ato Chimie), available as pure monofilament of a rather low molecular weight ( $\bar{M}_n = 14,500$  g/mol). In order to broaden the range of available molecular weights, samples of the commercial polymer were subjected to a solid-state postpolymerization procedure,<sup>2</sup> which more than doubled the original degree of polymerization while slightly broadening the distribution of molecular weights. To conduct the postpolymerization reactions, samples of commercial monofilament were introduced into one of the branches of a U-shaped ampoule while a drying agent ( $P_2O_5$ ) was placed in the other branch. The ampoules were then evacuated to  $10^{-4}$  torr, pumped for a number of hours and flushed with pure  $N_2$ ; the process was repeated several times, and the ampoules were finally sealed under vacuum. The polymer-containing branch was then immersed in a silicon bath at  $172^\circ C$  (mp of nylon 11 =  $183^\circ C$ ) and the  $P_2O_5$  branch was left at room temperature. The reaction times were 168 and 192 h, respectively.

A preliminary investigation on the solubility of nylon 11 pointed to meta cresol, 1,1,1,2,2,2-hexafluor-2-propanol (HFIP) and several mixed systems based on meta cresol, phenol, ethyl alcohol, and water as the most appropriate solvents at room temperature. In order to avoid the complications inherent to mixed solvent systems, the latter were only considered for the end-group analyses. Analytical grade (Fluka) meta cresol, further purified by distillation under reduced pressure, was employed in the viscosimetric measurements, while, in the case of light scattering, HFIP (Merck, pure grade, further purified by distillation) was chosen as the only practical alternative after refractive index and solubility considerations.

### Viscosimetric Measurements

The viscosity studies were carried out in meta cresol solution at  $30^\circ C$  with the help of an Ostwald viscosimeter (capillary diameter = 0.7 mm). Neither velocity gradient nor density effects were taken into account in computing the intrinsic viscosity  $[\eta]$ . The different solutions, to carry out the extrapolations

to zero concentration, were prepared such that the specific viscosities  $\eta_{sp}$  were in the range 0.25–0.75.<sup>3</sup>

### Conductimetric Titration of End Groups

Concerning number-average degree polymerization, the chemical nature of polyamids affords a unique alternative (end-group titration) to the conventional techniques based on measurements of colligative properties.<sup>4</sup>

In order to furnish reliable, number-average molecular weights ( $\bar{M}_n$ ), the end-group-titration technique (EGT) requires that the polymer possesses titratable groups and that the number of such groups per polymer molecule be accurately known. This is the case of nylon 11, originated on a true polycondensation process, whose stoichiometry can be more accurately predicted than that of polyamids prepared by ring-opening-polymerization reactions of lactams.<sup>5</sup> Another usual source of uncertainty, which does not play any role either in the case of nylon 11, is the probability of occurrence of the competing ring-formation reaction. This probability is the lowest, both from the statistical as well as from the energetic point of view, for 11- and 12-member rings.<sup>6</sup> Polyamid 11, therefore, is assumed to possess two titratable ends per molecule, one amine and one carboxylic group, respectively, whereby in the present case the polyamid molecules will be "counted" just by titrating the former.

The solvent system employed in the titrations must fulfill conditions of thermodynamic (solubility of nylon 11) and electrochemical (conductivity) nature. A mixed system, therefore, has to be chosen consisting of meta cresol, ethyl alcohol, and water (10 : 1 : 0.5 in volume). Aqueous 0.1, 0.01, and 0.001*N* HCl was employed as titrating agent, and no phase separation was observed during the titrations, within the whole range of concentrations of nylon 11 and volume of titrant HCl solutions shown in Table II. The equivalence points were established by conductimetric means<sup>7</sup> employing an LKB type 3216B conductivity bridge and a special conductivity cell (const = 0.0207 cm<sup>-1</sup>). The equilibrium position of the bridge was detected with an x-y oscilloscope which allowed to balance not only the conductivity but also the capacity of the cell. This, in turn, made it possible to determine the equivalence point of the titration within very narrow limits of error and to extend the application of the end-group method to samples of polyamid with  $\bar{M}_n$  up to 10<sup>5</sup> g/mol.

### Light Scattering

To carry out absolute measurements of  $\bar{M}_w$  by light scattering, a photogoniometer Sophica Model 42000 was employed. A Philips 500 W, high pressure, water cooled, mercury lamp performed as light source whereby the wavelengths were selected by means of the instruments standard set of filters. Most of the work was carried out with  $\lambda^0 = 546$  nm at 30°C. The cell was immersed in a toluene bath whose temperature was kept constant to  $\pm 0.1^\circ\text{C}$  by means of an external-circulation thermostat.

The solutions of nylon 11 in HFIP were prepared with utmost care, in order to avoid the presence of dust particles, and filtered directly into the cell by means of a syringe fitted with a Sartorius, stainless-steel filter, with two

superimposed membranes featuring pores of 0.45  $\mu\text{m}$ . The glassware was all carefully washed according to the standard procedures.

Four different concentrations of each sample were measured at 19 angular positions between 30 and 150°. Polymer solutions and the corresponding solvent batches were measured alternatively, and, in addition, the primary beam intensity was monitored frequently by means of the scattering of a standard glass slab previously calibrated against pure, dust-free benzene (Rayleigh constant =  $17.2 \times 10^{-6} \text{ cm}^{-1}$  for unpolarized light  $\lambda^0 = 546 \text{ nm}$ ).<sup>8</sup>

The concentration dependence of the differential index of refraction of the system nylon 11/HFIP ( $dn/dC$ ) was considered to be similar to that of nylon 12 (0.25  $\text{cm}^3/\text{g}$ ; Ref. 9) in the same solvent. A good approximation in view of the close chemical similarity between both polymers. The relatively high value of this refractive-index increment constitutes a rather convenient feature of the systems as it enables light scattering studies of low-molecular-weight fractions of nylon 11.

### Fractionation by Precipitation

After a number of practical considerations, the molecular weight distribution of nylon 11 was investigated by a fractionation technique based on successive-precipitation-of-fractions. The method requires a solvent (meta cresol), a nonsolvent (ethyl alcohol or *n*-heptane), and assumes a liquid-liquid equilibrium at each stage of the fractionation. According to thermodynamics, the composition of the pseudoternary system determines the position of the critical points on the phase diagram whereby the distribution of macromolecules in the two liquid phases in equilibrium (gel and sol, respectively) is governed by the chain length of the polymer molecules.<sup>10</sup> This provides the basis for the fractionation procedure.

Temperature is also an important parameter of the equilibrium which, from the experimental point of view, allows one to place each ternary system slightly above or below the corresponding critical point, playing thus the role of a fine-adjustment variable of the fractionation process.

## RESULTS

### Molecular and Hydrodynamic Properties of the Unfractionated Polyamide

To determine the intrinsic viscosities  $[\eta]$ , of nylon 11 in meta cresol solution at 30°C, the system was calibrated in regard to the extrapolation to zero concentration. The studies were carried out on one sample of commercial origin (C-1) and two samples of postpolymerized nylon 11 (PP-1 and PP-2), whereby, a number of solutions of each sample, within the appropriate range of concentrations,<sup>3</sup> were measured. Of all the many available methods of extrapolation,<sup>11-16</sup> that of Schulz and Blaschke<sup>14</sup> [eq. (1)] was applied as it provided the best linear fit of the experimental data. On each individual case, the analysis was carried out by graphical means (Fig. 1) and, alternatively, by a least-squares numerical procedure. The results quoted on Table I show not only the high degree of internal consistency of each set of data but also the

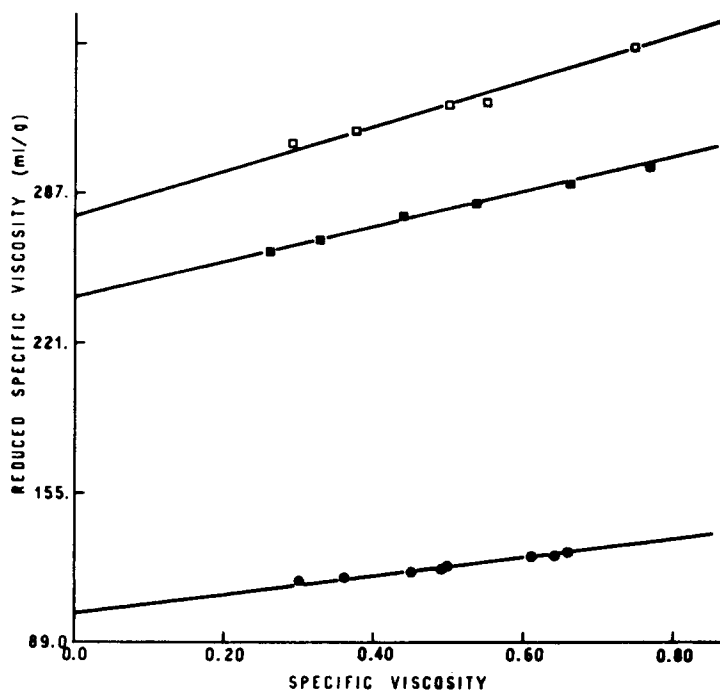


Fig. 1. Graphical extrapolation of the viscosity data for samples C-1 (●), PP-1 (■), and PP-2 (□), of polyamid 11 according to Schulz-Blaschke<sup>14</sup> [eq. (1); See also Table I].

excellent agreement of all three values of  $k_{\eta}$ . In addition, the intrinsic viscosities of the successive samples seem to properly reflect the expected trend of the respective molecular weights:

$$\eta_{sp}/c = [\eta] + k_{\eta}[\eta]\eta_{sp} \quad (1)$$

Regarding end-group titrations, Table II displays a summary of all pertinent data. As mentioned before, the attachment of an oscilloscope to the

TABLE I  
Viscosimetric Data for the Unfractionated Samples C-1, PP-1, and PP-2 of Polyamid 11<sup>a</sup>

	Commercial C-1	Postpolymer PP-1	Postpolymer PP-2
Concentration range (mg/mL)	2.6–5.1	1.0–2.6	0.9–2.1
$\eta_{sp}$ range	0.30–0.66	0.26–0.77	0.29–0.75
Correlation coefficient	0.993	0.989	0.990
$[\eta]$ (mL/g)	105.1	241.0	280.4
$k_{\eta}$	0.33	0.32	0.33

<sup>a</sup>The indicated correlation coefficients correspond to the least squares fit of the individual specific viscosities to eq. (1) carried out over eight, six, and five different concentrations, respectively.

TABLE II  
Number-Average Molecular Weights of Commercial (C-1) and  
Postpolymerized (PP-1 and PP-2) Samples of Polyamid 11<sup>a</sup>

	Commercial		PP-1	PP-2
Sample weight (g)	1.055	0.156	0.178	0.0819
Solvent volume (mL)	50	60	60	60
HCl concn	0.1N	0.01N	0.01N	0.001N
Total HCl volume (mL)	2.0	2.0	1.21	4.0
Conductivity range (mhos $\times 10^5$ )	5-40	1.3-4.9	0.8-3.6	0.6-3.2
Equivalence point (mL)	0.625	1.09	0.5	1.9
$\bar{M}_n$ (g/mol)	14,900	14,100	35,000	43,000

<sup>a</sup>The table also quotes experimental quantities related to typical end-group titration experiments.

conductivity bridge results in a definitive improvement of the method inasmuch as accuracy and the upper limit of the measurable molecular weights are concerned. In a typical experiment, between 25 and 15 pairs of data points (conductivity vs. volume of titrant) were measured. The equivalence points were determined by numerical or graphical means. Figure 2 shows an example of the latter.

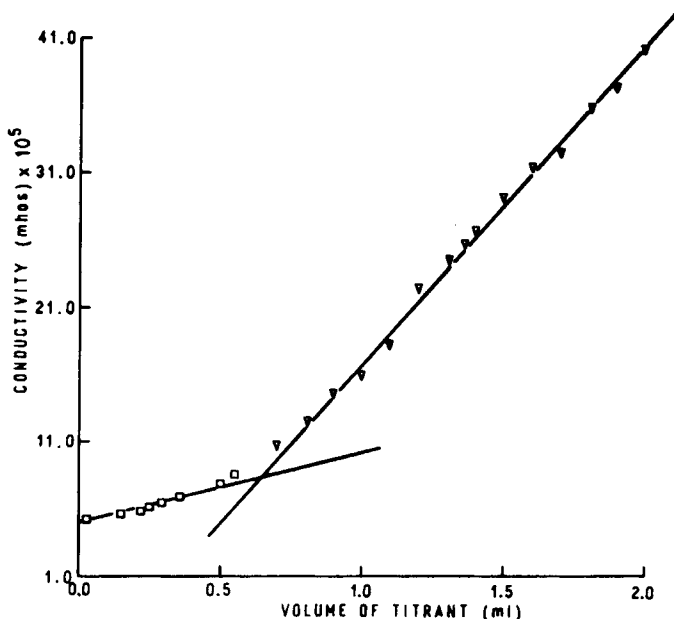


Fig. 2. Conductivity vs. volume plot for a typical run of end-group determination of number-average molecular weight. The data correspond to the first titration of a commercial sample (C-1) shown in Table II, titrated with 0.1N HCl.

TABLE III  
Angular Dependence of the Light Scattered ( $\lambda = 5460 \text{ \AA}$ ) by Pure HFIP and Solutions of Nylon 11 in HFIP at Four Different Concentrations

Concn (mg/mL)	0.00	0.49	0.59	0.974	1.22
Inst <sup>a</sup>	405	405	405	405	404
Angle ( $\theta$ )	Excess Intensities				
30	930	1419	1477	1683	1841
35	690	1094	1139	1312	1435
40	530	876	909	1062	1150
45	420	713	741	876	940
50	370	620	647	761	822
60	290	481	504	590	645
70	250	407	426	498	540
75	240	385	405	477	514
80	225	364	379	448	486
90	230	363	378	448	475
100	240	376	395	466	497
105	247	392	409	478	515
110	257	415	432	510	554
120	290	478	496	593	642
130	360	597	619	741	806
135	398	674	706	839	910
140	450	764	805	961	1043
145	567	945	990	1178	1266
150	700	1159	1208	1433	1555

<sup>a</sup> Intensities dispersed by a glass standard.

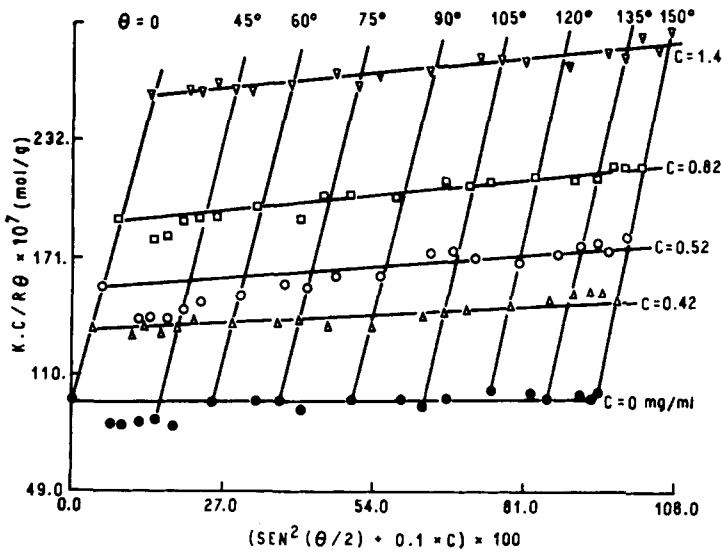


Fig. 3. Zimm plot of the light scattering data corresponding to the postpolymerized sample PP-2. Note the insignificant slope of the line (●) corresponding to  $C = 0$ .

TABLE IV  
Light-Scattering Results Corresponding to Samples C-1 and  
PP-2 Dissolved in HFIP<sup>a</sup>

Sample	Concentration		$A_2 \times 10^5$ (mol mL g <sup>-2</sup> )	$(R_g^2)^{1/2}$ Å
	Range (mg/mL)	$\bar{M}_w$ (g/mol)		
C-1	0.49–1.22	29,400	7.8	< 180
PP-2	0.42–1.40	104,200	5.6	< 180

<sup>a</sup>Radii of gyration are outside the limits of resolution of the wavelength ( $\lambda = 5460 \text{ \AA}$ ) employed, and only an upper limit can be quoted.

Light-scattering experiments were carried out on samples of commercial (C-1) (Table III) and postpolymerized (PP-2) nylon 11 (Fig. 3), respectively. The angular-dependent, excess intensity scattered by four different concentrations of each sample relative to the solvent,  $R(\theta)^{17}$  (Table III), was interpreted according to

$$\frac{K \times C}{R(\theta)} = [\bar{M}_w \times P(\theta)]^{-1} + 2A_2 \times C + \dots \quad (2)$$

where  $K$  is a combination of optical constants,<sup>17</sup> including  $(dn/dc)^2$ ,  $C$  is the concentration in g/cm<sup>3</sup>, and  $A_2$  is the second virial coefficient of the osmotic pressure. The function  $P(\theta)$  describes the angular dependence of the scattered light<sup>18</sup> and, under certain conditions, provides the means to compute the radius of gyration of the dissolved macromolecules. Equation (2) was solved graphically (Fig. 3) for  $\bar{M}_w$  and  $A_2$  after Zimm's extrapolation method.<sup>19</sup> The insignificant slopes of the  $C \rightarrow 0$  extrapolated lines were interpreted as an indication that the radii of gyration are much smaller than  $\lambda/30 \sim 180 \text{ \AA}$ , a rather expected fact in view of the samples' molecular weights. A summary of light-scattering related results is shown in Table IV.

### Fractionation by Successive Precipitations

According to the guide lines sketched in the subsection Fractionation by Precipitation, two different samples of polyamid (C-1 and PP-1) were fractionated. The processes, carried out with ethyl alcohol as nonsolvent, proceeded normally and produced 12 and five fractions, respectively. The amount of polymer, moreover, was sufficient to carry out viscosimetric measurements and end-group titrations on each individual fraction (Table V). The weight losses incurred along the fractionation were attributed to the handling involved in the different steps of the process and were assumed to be proportionally distributed among the fractions. As a further check of the fractionations, the data on Table V provided the means to calculate  $[\eta]$  and  $\bar{M}_n$  of the whole, unfractionated polymers C-1 and PP-1, respectively. The results of the calculation, together with the experimentally measured values, are shown in Table VI. It is immediately apparent that the "calculated" properties are systematically smaller than the experimental ones. This can only be interpreted as the occurrence of molecular degradation during the



TABLE V  
Summary of Results of Two Fractionations Carried Out on Sample C-1 (3.02 g)  
and PP-1 (1.08 g) of the Polyamide 11<sup>a</sup>

Fraction	Mass fraction	Intrinsic Viscosity (mL/g)	$\bar{M}_n$ (g/mol)	$\bar{M}_w^b$ (g/mol)
C1-1	0.020	130	18,500	36,600
C1-2	0.069	129	18,300	35,500
C1-3	0.069	125	16,500	31,800
C1-4	0.064	123	15,400	29,600
C1-5	0.198	113	14,000	27,100
C1-6	0.124	103	12,700	24,300
C1-7	0.149	100	12,200	23,400
C1-8	0.081	94	11,200	21,400
C1-9	0.041	85	10,300	19,800
C1-10	0.084	80	10,000	19,400
C1-11	0.044	76	9100	17,800
C1-12	0.056	72	8400	—
PP1-1	0.255	236	37,600	89,700
PP1-2	0.315	222	33,900	80,154
PP1-3	0.127	217	31,800	75,000
PP1-4	0.233	207	29,700	69,700
PP1-5	0.070	197	22,700	—

<sup>a</sup>The quantitative yield of each procedure was 84 and 86%, respectively, whereby the weight losses were considered to be proportionally distributed among the fractions, and all calculations were carried out accordingly.

<sup>b</sup>Calculated by a numerical procedure<sup>22</sup> based on the data of the fractionation.

<sup>c</sup>In meta cresol at 30°C.

course of the fractionation. In order to verify this interpretation, different samples of polyamid 11 were subjected to conditions similar to those suffered along the fractionation, whereby the intrinsic viscosity was carefully controlled on each initial sample as well as on the polyamids obtained by complete precipitation. Two different solvent/nonsolvent systems were investigated: meta cresol/ethyl alcohol and meta cresol/normal heptane. The results shown in Table VII confirm the hypothesis that the molecules of polyamid undergo degradation during the course of fractionation. In this connection, and regardless of the actual mechanism of the process, the nature

TABLE VI  
Experimental and Calculated Values of  $\bar{M}_n$  and Intrinsic Viscosity for the Whole C-1 and PP-1 Samples<sup>a</sup>

	Fractionation C-1	Fractionation PP-1
$\bar{M}_n$ exptl	14,500	35,000
$\bar{M}_n$ calcd	12,400	32,300
Decrease (%)	14	8
$[\eta]$ exptl (mL/g)	105	241
$[\eta]$ calcd (mL/g)	103	220
Decrease (%)	1.5	9

<sup>a</sup>The experimental values are data quoted in Tables I and II, respectively, and calculated values are calculated from the data in Table V.

TABLE VII  
Intrinsic Viscosity Data for C-1 and PP-2 Samples of the  
Polyamid 11 in Meta Cresol Solution<sup>a</sup>

Sample	Precipitant	$[\eta]$ original (mL/g)	$[\eta]$ pptated. <sup>b</sup> (mL/g)	Decrease (%)
C-1	Ethyl alcohol	105	93 ± 1	12%
C-1	<i>n</i> -Heptane	105	97 ± 1	7%
PP-2	Ethyl alcohol	280	240 ± 5	14%
PP-2	<i>n</i> -Heptane	280	262 ± 9	7%

<sup>a</sup>The measurements were carried out on original samples as well as on samples precipitated by ethyl alcohol or *n*-heptane and redissolved.

<sup>b</sup>Mean values over several experiments.

of the precipitant seems to play an important role in the outcome of the reaction.

## DISCUSSION

The absolute measurements of  $\bar{M}_n$  (Table II) and  $\bar{M}_w$  (Table IV) for both samples of polyamide 11 (conventional C-1 and postpolymerized PP-2) immediately allow the calculation of the polydispersity index  $U = (\bar{M}_w/\bar{M}_n) - 1$ , and provide a preliminary insight into the molecular weight distribution of the specimens. The index corresponding to the commercial sample C-1 ( $U = 1.03$ ) is fully compatible with the Flory-Schulz distribution<sup>20</sup> expected in a polymer prepared by polycondensation. The process of postpolymerization, on the other hand, (sample PP-2) gives rise to a broadening of the distribution ( $U = 1.42$ ) in agreement with a behavior already reported<sup>21</sup> for the solid-state postpolymerization of other polyamides. These observations have been substantiated by the results of the fractionation experiments (Table V). Furthermore, it is possible to correlate the experimental intrinsic viscosity of each fraction with the corresponding value of  $\bar{M}_w$  calculated, by means of a numerical procedure described in the following paper,<sup>22</sup> from the data of the fractionation (mass and  $\bar{M}_n$  of each fraction in Table V). Such correlation [Mark-Houwink, eq. (3)], which is of the utmost importance in the characterization of linear, high polymers in solution, was obtained by means of a least-squares procedure [eq. (3)] (regression coefficient: 0.998) and by graphical means (Fig. 4). In both cases the data points corresponding to the whole unfractionated samples C-1 and PP-2 have been included. The regression, then, is based on an appreciable number of data points and spans a range of 100,000 units of molecular weight (g/mol):

$$[\eta](\text{mL/g}) = K \times \bar{M}_w^a = 9.1 \times 10^{-2} \times \bar{M}_w^{0.69} \quad (3)$$

In conclusion, the exponent  $a = 0.69$  of the Mark-Houwink equation indicates that nylon 11 in meta cresol at 30°C behaves as a linear, flexible macromolecule in a good-solvent medium without reaching, however, the value  $a = 0.80$  for the excluded volume limit.

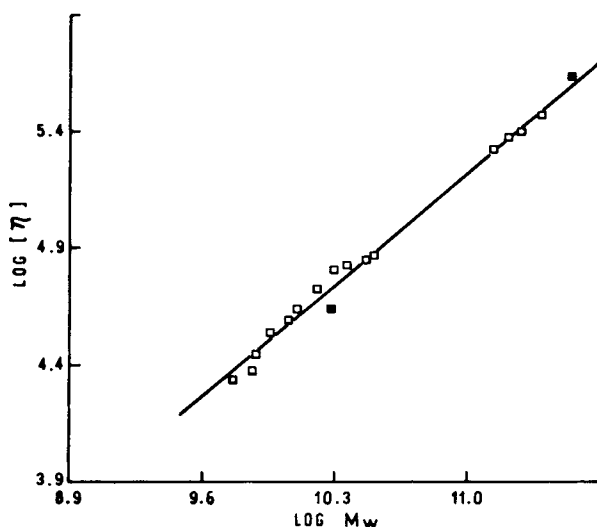


Fig. 4. Intrinsic viscosities and weight-average molecular weights plotted after the logarithmic form of eq. (3) (Mark-Houwink): (□) different fractions of the C-1 and PP-1 samples quoted in Table V; (■) correspond to the whole samples C-1 and PP-2 quoted in Tables I and IV.

HFIP, on the other hand, behaves as a good solvent for nylon 11 as revealed by the light-scattering values (Table IV) of the second virial coefficients ( $7.8\text{--}5.6 \times 10^{-3} \text{ mol mL/g}^2$ ).

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