CHROM. 5136

CAUSES OF SKEWED MOLECULAR WEIGHT DISTRIBUTIONS IN GEL PERMEATION SEPARATION OF NYLON RESINS

E. K. WALSH
Allied Chemical Corporation, P.O. Box 309, Morristown, N.J. 07960 (U.S.A.)

SUMMARY

Gel permeation separations of nylon resins using phenol type solvents are characterized by extended tailing in the low-molecular-weight region. Number average molecular weights ($\bar{M}_n$) calculated from these chromatograms are abnormally low. The resultant molecular weight distributions ($\bar{M}_w/\bar{M}_n$ ratios) are broad.

This report contains investigations of possible causes for tailing of low-molecular-weight nylon species. Studies include thermal and oxidative degradations of resin solutions, flow rate, overloading and elution temperature levels. While none were found to cause tailing, the latter does effect the extent to which the tail is formed. Work with fractions and small molecule homologs of nylon and their comparisons with other resin types in universal calibration plots shows adsorption of low-molecular-weight species on the styrogel separating medium to be the primary cause of tailing. The degree of adsorption is shown to be a function of the ratio of polar ends to polymer chain length.

INTRODUCTION

Gel permeation chromatographic (GPC) separations of nylon 6 resins using phenol solvents in these laboratories have consistently shown tailing of low-molecular-weight species. Similar skewness in the distributions of polyamide resins is evident in the chromatograms shown in published literature[1,2]. Abnormally low number average molecular weights are calculated from these chromatograms. These low values produce broad molecular weight distributions (large weight to number average molecular weight ratios). Molecular parameters measured on nylon resins by classical techniques show nominal values of 2.0 for this ratio. The latter measurements confirm theoretical predictions based on kinetic studies of nylon resin polymerizations.

Broadening in gel permeation defined molecular weight distribution is common to all materials. It is caused by a diffusional process inherent in this type of chromatography. The broadening evident in GPC separations of nylon resin appears substantially different (1) in chromatogram shape from other resin types and (2) in excess of that due to dispersion processes.

Both theoretical and classical definitions of molecular weight distributions in nylon polymerizations have firm foundations. An explanation for molecular weight

distribution broadening, other than that due to a dispersion process, was sought. Verification of an obvious cause, resin adsorption on the styrogel separating medium, was not easily established. To ascertain the cause, all parameters which might conceivably contribute to molecular weight distribution broadening of nylon resins except inherent dispersion, were investigated. This paper relates the results of this investigation.

EXPERIMENTAL

Nylon separations were accomplished with a Waters Associates Inc. Model 200 GPC instrument. Orthochlorophenol was used to prepare and elute solutions of polymers through the instrument. The solvent was distilled under vacuum prior to use. It was continuously purged with purified nitrogen while in the reservoir of the GPC unit. Degassed at 150°, the solvent was metered through the styrogel columns at a 1 cc/min flow rate. Injection port, oven, refractometer and collection areas were maintained at 100°. A Hallikainen temperature controller regulated the temperature of the refractometer heat exchanger.

Two sets of styrogel columns purchased from Waters Associates were used in this work. The majority of separations were accomplished with three columns designated 10^5, 10^4 and 10^3 Å. Comparisons were made with a second set of three columns designated 10^6, 5×10^4 and 5×10^3 Å.

Five tenth percent (0.5 %) concentrations of nylon resin in *o*-chlorophenol, prepared at ambient temperature, were forced through a Waters filter unit maintained at 100°. Prior to injection, the solutions were held for approx. 20 min in an oven maintained at 105°. A 90 sec injection time, 7.5 mg loading, and a 2 × amplification was adopted as standard procedure in this work.

A Brice Phoenix Model 1000 light scattering photometer was used to measure the weight average molecular weights of polymer samples. Nylon whole resins and fractions were dissolved in 90 % formic acid buffered with 0.5 *M* potassium chloride. Measurements were made at ambient temperatures at a wavelength of 546 mμ. The majority of values were calculated from scattered light intensities measured at 90° and 0° angles. Very small corrections for scattering dissymmetry, measured at 45° and 135°, were applied. Multiangle scattered light intensity measurements on three nylon samples gave molecular weights equivalent to those obtained by 90° and 0° angular measurements.

Differential refractive index measurements were obtained with a Brice Phoenix unit. High temperature measurement capability was provided by circulating fluid to the insulated cell area from a bath maintained at the desired level.

Viscosities of polymer solutions were measured in No. 75 Cannon Ubbelohde viscometers at 100°. Flow times of *o*-chlorophenol were 100 sec or greater. No kinetic energy corrections were applied. Initial polymer concentrations of 0.5 g/dl were diluted in three steps to a final concentration of 0.125 g/dl. Intrinsic viscosities were defined by extrapolating four point viscosity-concentration plots to zero concentration.

RESULTS AND DISCUSSIONS

Typical GPC chromatograms of medium- and high-molecular-weight hydrolytically polymerized nylon 6 resins are shown in Figs. 1 and 2. Tailing in the low-

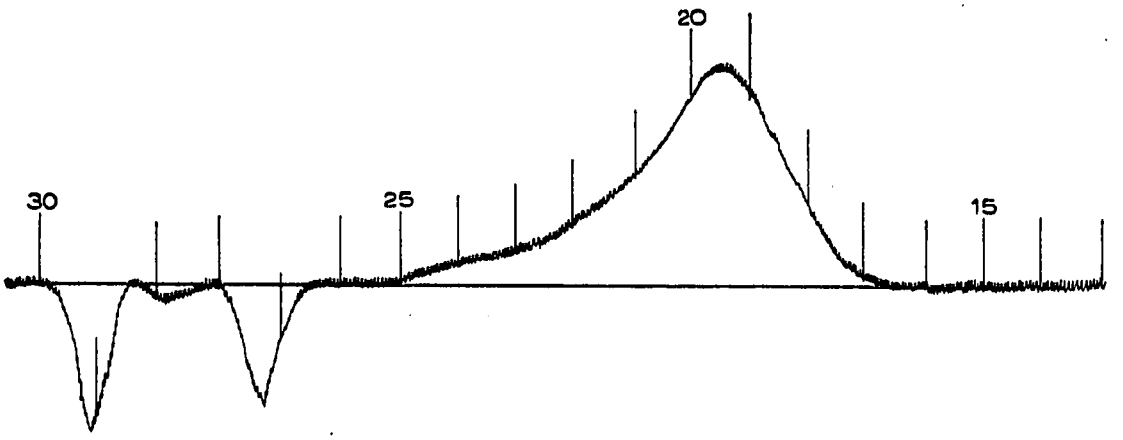

Fig. 1. Nylon 6, 19 500 g/m, water extracted and dried 0.5%, 90 sec, 1 cc/min, 2 ×, *o*-chlorophenol at 100°. Columns: 10^6, 5×10^4, 5×10^3 Å.

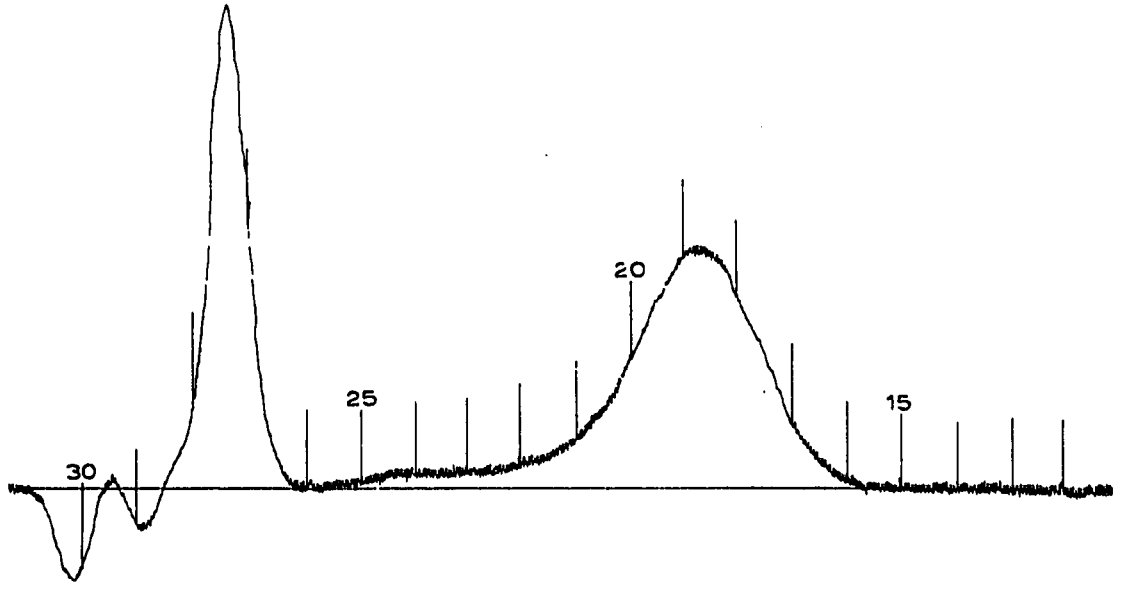

Fig. 2. Nylon 6, 44 000 g/m, water extracted and dried 0.5%, 90 sec, 1 cc/min, 2 ×, *o*-chlorophenol at 100°. Columns: 10^6, 5×10^4, 5×10^3 Å.

TABLE I

NYLON 6 MOLECULAR WEIGHT PARAMETERS DEFINED BY GPC AND CLASSICAL TECHNIQUES

Sample	*GPC*			*Classical*		
	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_w$[a]	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$
Medium $\bar{M}$ nylon 6	44 000	9 300	4.7	38 000	19 500	1.9
High $\bar{M}$ nylon 6	97 700	16 500	5.9	88 700	44 000	2.0

[a] Determined by light scattering techniques.
[b] Determined by end group and osmotic techniques.

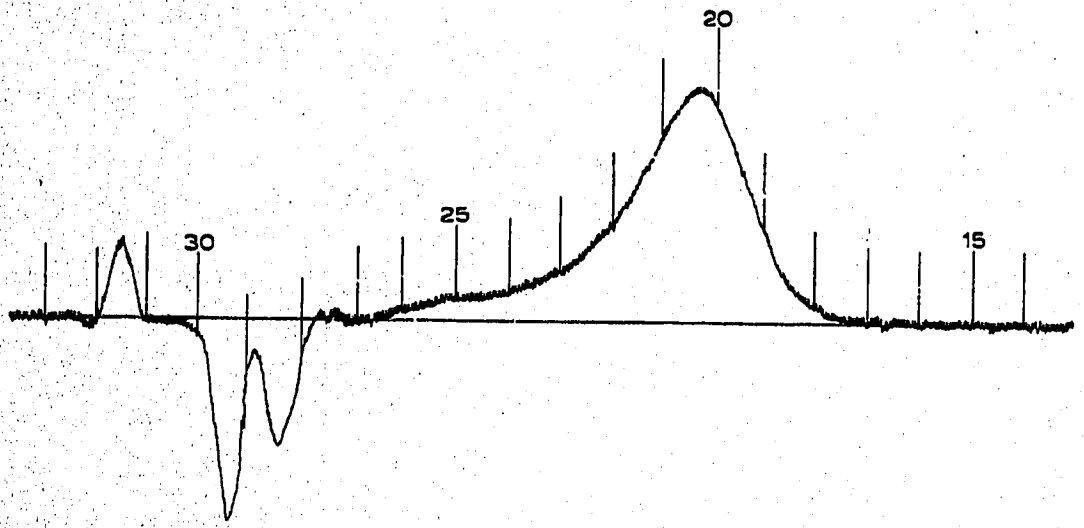

Fig. 3. Nylon 6, 19 500 g/m, water extracted and dried 0.5%, 90 sec, 1 cc/min, 2 ×, *o*-chlorophenol at 100°. Columns: 10^5, 10^4, 10^3 Å.

molecular-weight region appears as the predominant characteristic of these chromatograms. Weight and number average molecular weights calculated from these chromatograms and from classical measurements are shown in Table I. These values illustrate the extent of molecular weight distribution broadening in GPC separations of nylon resins. Since the styrogel columns used in this work were calibrated with nylon fractions, one would expect differences in molecular parameters to be due solely to the inherent diffusional character of the styrogel columns. Yet comparisons with other resins, polystyrene for example, show the nylon resins to be excessively broadened during elution.

In our limited experience, the use of a different column set shown in Fig. 3 did not effect the shape of the low-molecular-weight portion of the chromatogram. Nor could impurities present in the *o*-chlorophenol account for the observed tailing. Such impurities always eluted at retention volumes 5 cc or more (1 or more counts) removed from the area of interest. They have, however, been previously cited as a major contributor to the imperfection of polyamide GPC distributions[1].

One would expect tailing of low-molecular-weight species to be exaggerated in chromatograms of both a low-molecular-weight nylon fraction and the lowest-molec-

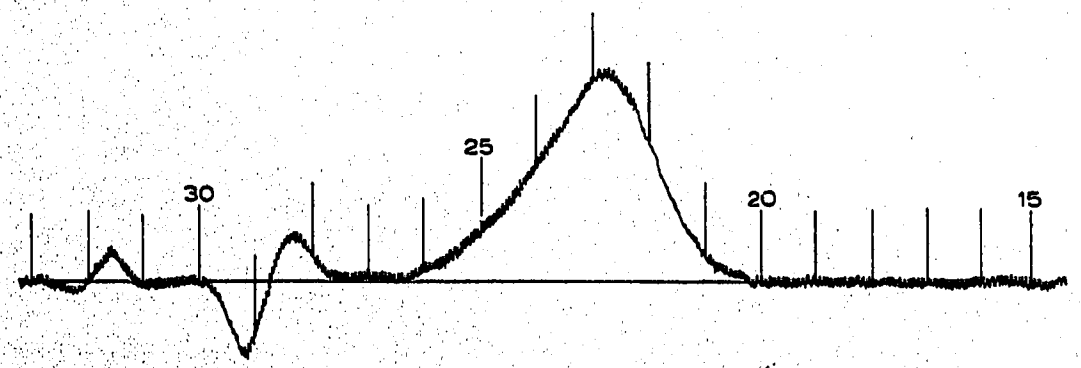

Fig. 4. Nylon 6 fraction, 6900 g/m, 0.5%, 90 sec, 1 cc/min, 2 ×, *o*-chlorophenol at 100°. Columns: 10^5, 10^4, 10^3 Å.

ular-weight nylon homolog, aminocaproic acid. Chromatograms obtained with 5.0 mg loadings of aminocaproic acid are totally obscured by solvent impurities. The results obtained with higher loadings are discussed in a later section of this report. The chromatogram of the lowest-molecular-weight nylon fraction, isolated by preparative scale fractionation techniques, is shown in Fig. 4. Surprisingly little evidence of tailing is observed in this chromatogram. Since no explanation for low-molecular-weight tailing was obtained from this work, it was thought that the problem was caused by some operational variable. An investigation of parameters which could possibly cause molecular weight distribution broadening in nylon resins was initiated. The parameters studied were degradation, overloading, flow rate and temperature. Of these, only the latter gave an indication of causing change in the molecular weight distribution of nylon resins.

Solution degradation of nylon 6 resin in *o*-chlorophenol at 100° was evaluated by viscosity measurements. Three solutions prepared at ambient temperature, each consisting of 0.5 % concentrations of a high-molecular-weight nylon 6 resin, were maintained at 100°–105° for ~ 30 h. Viscosities measured at various time increments over this period decreased at a rate of 0.8 to 1.0 % per h for the first 3 to 4 h and at < 1.0 % per h for the remaining time period. Since the time required to complete elution of nylon species in GPC separations is ~ 3 h, the estimated maximum degradation possible is of the order of 3 %. Degradations of this type are known to be random. Their contribution to extended low-molecular-weight tailing must be minor. In addition, chromatograms of solutions of resins held 4 to 6 h at 100° prior to injection, show no significant difference from chromatograms obtained on samples injected into the system in the normal manner.

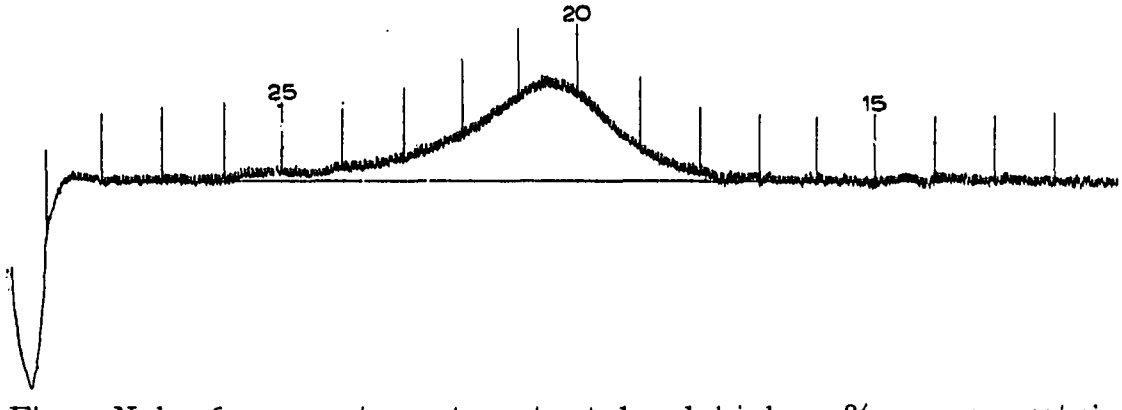

Fig. 5. Nylon 6, 19500 g/m, water extracted and dried 0.25 %, 90 sec, 1 cc/min, (3.75 mg), 2 ×, *o*-chlorophenol at 100°. Columns: 10^5, 10^4, 10^3 Å.

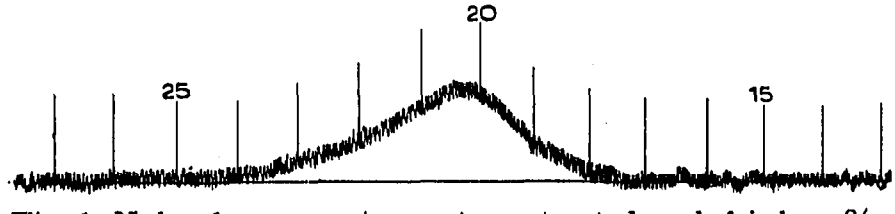

Fig. 6. Nylon 6, 19500 g/m, water extracted and dried 0.1 %, 90 sec, 1 cc/min, (1.5 mg), 4 ×, *o*-chlorophenol at 100°. Columns: 10^5, 10^4, 10^3 Å.

Chromatograms illustrating the effect of various load levels of nylon 6 resins are shown in Figs. 3, 5 and 6. A normal loading of 7.5 mg is shown in Fig. 3. Figs. 5 and 6 show 1/2 (3.75 mg) and 1/5 (1.5 mg) of normal loading level, respectively. Both reduced load levels show definite evidence of low-molecular-weight tails, although close inspection is required to distinguish the tail at the 1.5 mg load level. It is of interest to note that integral plots of data derived from chromatograms obtained using the 7.5 and 3.5 mg loadings are equivalent within experimental error. Overloading effects typified by polystyrene eluted with tetrahydrofuran show a shift in the peak elution volume, but give little or no evidence of tailing.

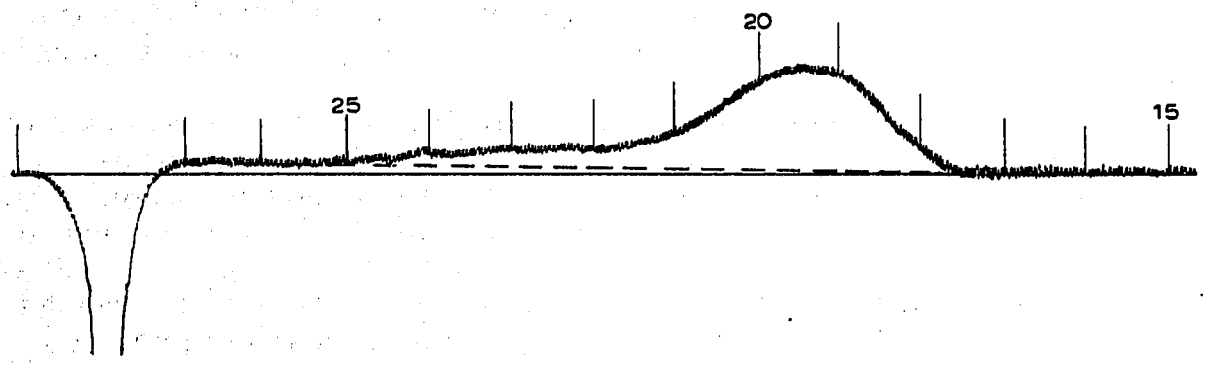

Fig. 7. Nylon 6, 19500 g/m, water extracted and dried 0.5%, 90 sec, 0.27 cc/min, 2×, *o*-chlorophenol at 100°. Columns: 10^5, 10^4, 10^3 Å.

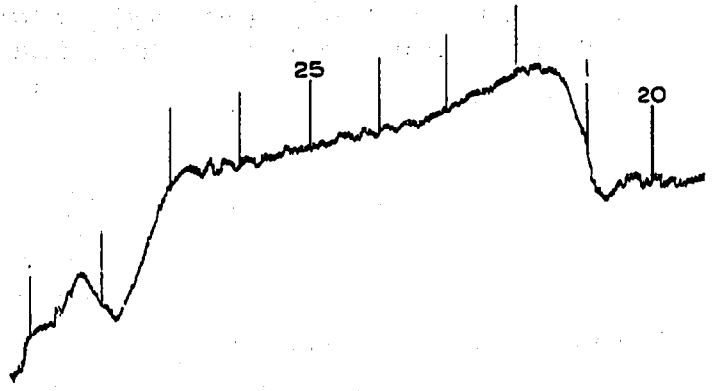

Fig. 8. Nylon 6, 19500 g/m, water extracted and dried 0.5%, 60 sec, 0.85 cc/min, 2×, *o*-chlorophenol at 40°. Columns: 10^5, 10^4, 10^3 Å.

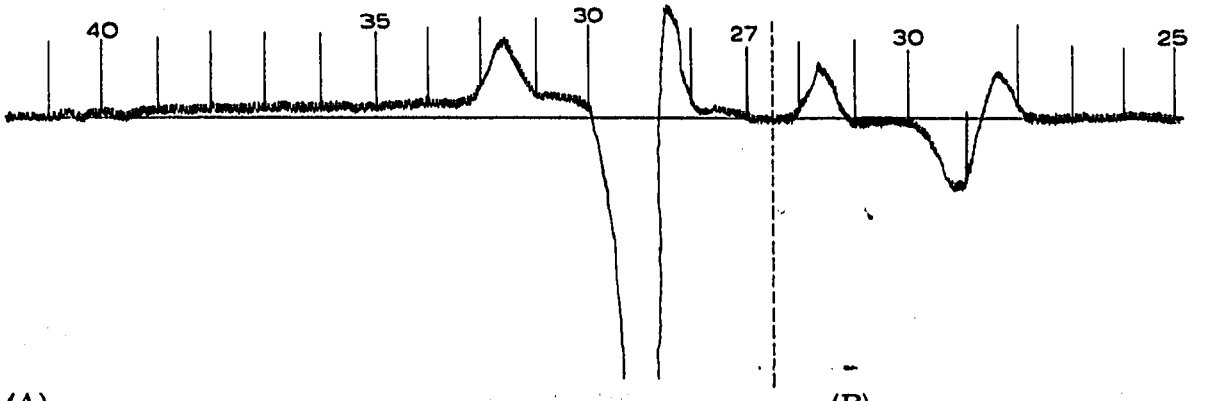

Fig. 9. Aminocaproic acid. (A) 1%, 90 sec, 1 cc/min, 2×, *o*-chlorophenol at 100°. Columns: 10^5, 10^4, 10^3 Å. (B) Solvent; *o*-chlorophenol at 100° C, 90 sec, 1 cc/min, 2×. Columns: 10^5, 10^4, 10^3 Å.

A chromatogram illustrating the effect of change in flow rate is shown in Fig. 7. The flow has been reduced to 0.27 ml/min. It is quite clear from this chromatogram that low-molecular-weight tailing persists at this low flow rate.

The effect of temperature on nylon chromatographic separations is shown in Fig. 8. This reduced temperature level necessitated the use of maximum available pressure to maintain the 1 cc/min flow rate. The high pressure made base line stability untenable. The chromatograph obtained, however, shows evidence of both a delayed response and a drawn out shape. Both are indicative of an absorptive type mechanism.

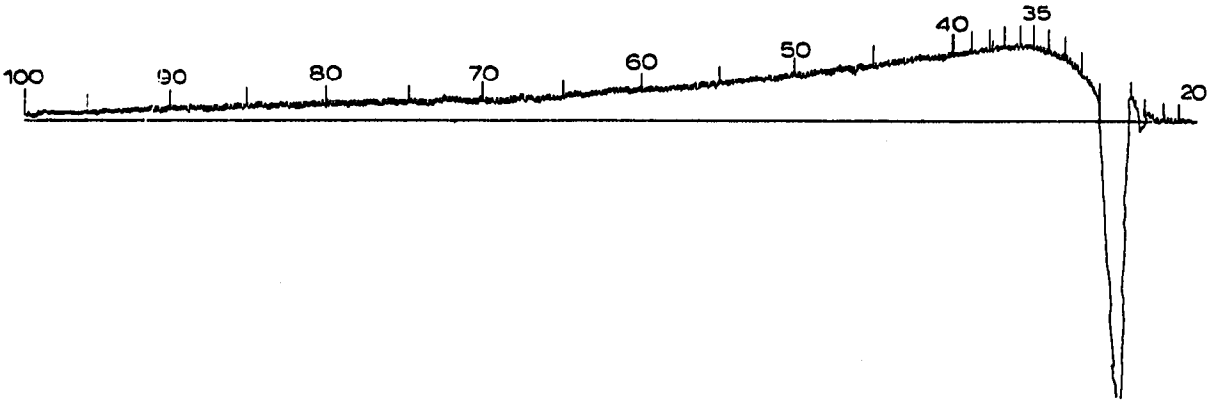

Fig. 10. Aminocaproic acid, 5%, 60 sec, 1 cc/min, 2 ×, *o*-chlorophenol at 100°. Columns: 10^5, 10^4, 10^3 Å.

None of these parameters, either alone or in combination, can explain the cause of tailing in GPC separations of nylon resins. If the cause is due to adsorption, as indicated by chromatogram shifts with temperature change, it must be evident in the chromatograms of the lowest-molecular-weight homolog of nylon 6 resins, aminocaproic acid. As stated previously, a loading of 5.0 mg shows little more than solvent impurity effects. Both, unfortunately, elute at approximately the same retention volume. Chromatograms of higher aminocaproic acid loadings, 15 and 50 mg, are shown in Figs. 9 and 10. Included in Fig. 9 is a chromatogram of the impurities in the *o*-chlorophenol solvent, collected at the same time and treated in the same manner as that used to prepare the aminocaproic acid solution. Both chromatograms of aminocaproic acid are equivalent, the higher loading being an exaggerated copy of the lower loading. Their interpretation is difficult since both down and up scale re-

TABLE II

EFFECT OF POLAR END–DEGREE OF POLYMERIZATION

	Ratio on GPC response			
	A.C.A.	*Nylon 6 fraction*	*Nylon 6 resin*	*Lactam*
$\bar{M}_w$	131	6900	40 000	113
Polar ends/DP	2	0.03	0.005	0
D.R.I.[a]	+0.035–0.040	+0.048	+0.050	+0.040–0.045
GPC response[a]	absorbed on gel	retention volume deviates from U.C.C.	broad distribution	retention volume fits on U.C.C.

[a] *o*-Chlorophenol at 100°.

fractive index changes are clearly evident. Such differences in solute refractive index indicate the presence of two materials having different structures. Their proportion, estimated from Fig. 10, is 15 and 85 %. Yet the use of essentially pure aminocaproic acid was indicated from melt temperature and IR spectral analysis. Also, if the material responsible for the down scale refractive index change is due to aminocaproic acid then its refractive index is appreciably different from the nylon polymer and from caprolactam, both of which show up scale refractive index changes. Such differences or similarities in solute–solvent refractive indexes should be capable of resolution by use of the Brice Phoenix differential refractometer. Table II contains the results of such measurements on aminocaproic acid, a low-molecular-weight fraction of nylon 6, the whole nylon 6 resin and caprolactam. *o*-Chlorophenol was used to prepare all solutions. Measurements were made at 100°. These conditions are equivalent to those used in GPC separations. The positive sign is placed before all the differential refractive index values to indicate that the refractive index of all solutes were observed in these measurements to have values greater than the solvent. The apparent discrepancy between aminocaproic acid values obtained from the two respective measurements, the GPC detector and the Brice Phoenix unit, seems to be a function of the proportions of the two materials present. This ratio is believed affected by the difference in solution residence time at temperature required for each measurement. Solution preparation and measuring time with the Brice Phoenix instrument is approximately one-eighth of that required for GPC measurements. Such time–temperature studies using the Brice Phoenix instrument, however, were inconclusive. Difficulties experienced in accurate measurements of these low values precludes the possibility of establishing a definite conclusion.

The data presented indicates that the material causing the sharp down scale refractive index change in the GPC chromatogram of aminocaproic acid is caused by a reaction product of aminocaproic acid and the solvent. The unreacted aminocaproic acid is responsible for the upscale refractive index change in the chromatogram. It is readily evident from Fig. 10, that this unreacted aminocaproic acid portion is being slowly desorbed from the styrogel separating medium.

It has been shown in Fig. 4, that very little evidence of low-molecular-weight tailing can be observed in a low-molecular-weight fraction of a nylon 6 resin. Tailing, however, is readily evident in the chromatograms of both the whole nylon resin and its lowest-molecular-weight homolog, aminocaproic acid. The GPC response to varying chain length nylon species is shown in Table II on lines 2 and 4. One would normally expect increased adsorption with an increase in functional groups per unit polymer chain length. A convenient means of relating the two parameters, GPC response and functional or polar groups per unit chain length, is provided by the universal calibration concept initially demonstrated by BENOIT *et al.*[3]. Its main tenet implies that if diffusion is the sole mechanism operating in the GPC separation process, then the hydrodynamic volume or size of random coiled polymers is the controlling factor in determining the retention volume at which a given chain length species will elute. A relative measure of the hydrodynamic size is provided by the product of the intrinsic viscosity and molecular weight. Retention volume is the volume measured from sample inject to the peak of the chromatogram. Such measurements are shown in Table III for fractions of polystyrene, polyoxazoline and nylon 6 resins and for caprolactam. Peak retention volumes are given in terms of counts. Molecular weights

TABLE III

RETENTION TIME MOLECULAR WEIGHT DATA

Material	*Count*	$\bar{M}_w$	$[N]^a$	$[N]\bar{M}_w$
PMA[b]	16.55	541 000	1.21	655 000
PMA[b]	17.525	209 000	0.80	167 200
PS[c]	16.16	860 000	1.82	1 565 000
PS[c]	17.11	340 000	0.95	323 000
PS[c]	18.77	89 000	0.39	34 700
PS[c]	21.95	10 300	0.09	1 000
Nylon	18.24	169 000	1.24	210 000
Nylon	18.4	132 000	1.05	138 500
Nylon	18.66	115 000	0.968	115 000
Nylon	19.6	62 000	0.624	38 600
Nylon	21.6	20 600	0.275	5 700
Nylon	23.3	6 900	0.12	827
Caprolactam	26.5	113	0.03	3.39

[a] [N] = intrinsic viscosity.
[b] PMA = polyethyloxazoline.
[c] PS = polystyrene.

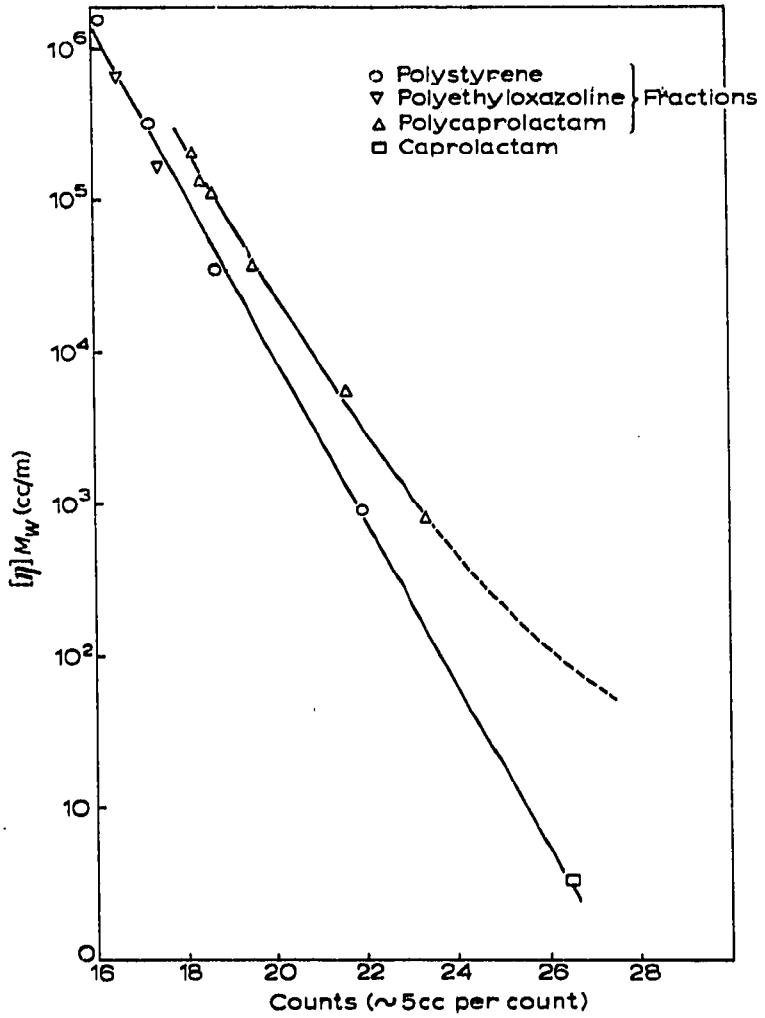

Fig. 11. Universal calibration curve; log $[\eta]M$ *vs.* retention volume.

shown are weight average values. Intrinsic viscosities of polymer fractions were determined in *o*-chlorophenol at 100°, the same conditions used to obtain their GPC chromatograms. A plot of this data is shown in Fig. 11. Readily evident is the conformity of fractions of the non-polar resins, polystyrene, polyoxazoline and of caprolactam, to a common curve in this universal calibration plot. Diffusion is indicated as the sole separation mechanism for these materials. Nylon fractions are displaced from this curve by 0.6 of a count (~ 3.0 cc) at a hydrodynamic volume of 10^5 cc/m. This displacement increases to approximately 2.3 counts (~ 11.5 cc) at a hydrodynamic volume of 10^2 cc/m.

These results show that in addition to dispersion another mechanism is controlling the separation of varying chain length species of nylon resins in styrogel media. The delayed response and extended low molecular weight tailing support an adsorption type mechanism. Both long and short chain length species of nylon resins are adsorbed on styrogel separation media. The strength of the adsorption bond increases as the functional group per unit chain length increases.

Adsorption of a similar type was described in GPC analysis of carboxy terminated polybutadienes[4]. It was reduced by selecting those styrogel columns which by trial and error elution experiments showed little or no adsorption of the resin. It is possible that a similar selection of styrogel columns could affect a reduction, or perhaps elimination, in the adsorption of nylon resins. Our experience with the use of different styrogel columns in this laboratory is very limited.

CONCLUSION

Adsorption accompanied by slow release of molecular weight species in 5000 to 2000 g/m range is primarily responsible for the tailing observed in GPC chromatograms of nylon resins.

ACKNOWLEDGEMENTS

I would like to express my appreciation to A. CLARK and T. CHOU for the GPC and intrinsic viscosity measurements used in this report and to Allied Chemical Corporation for permission to publish this data.

REFERENCES

1 J. D. GOVIER, L. G. PRINCE AND H. E. STAPELFELDT, *6th Intern. Seminar Gel Permeation Chromatog., Miami Beach, 1968.*
2 C. V. GOEBEL, *Proc. 4th Intern. Seminar Gel Permeation Chromatog., Miami Beach, 1967.*
3 Z. GRUBISIC-GALLOT, P. REMPP AND H. BENOIT, *J. Polym. Sci., B*,5 (1967) 753.
4 R. M. SCREATON AND R. W. SIEMANN, *J. Polym. Sci., C*, 21 (1968) 297.