# Determination of molecular weight averages and molecular weight distribution by g.p.c. of *N*-trifluoroacetylated polyamides

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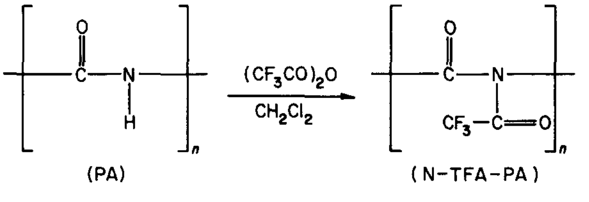
To determine their molecular weight averages and molecular weight distribution, *N*-trifluoroacetylated (TFA) polyamides are studied using gel permeation chromatography in tetrahydrofuran at 25°C. Several calibration methods (calibration with polydisperse standards, universal calibration) are tested; among these, direct calibration of $M_w$ of polydisperse samples vs. peak maximum of the corresponding g.p.c. chromatogram leads to the best results. Calculated molecular weight averages of nylon 6–TFA and Trogamid$^R$–TFA are compared with data from light scattering, viscometry and osmometry.

**(Keywords: polyamides; *N*-trifluoroacetylation; gel permeation chromatography; calibration methods)**

## INTRODUCTION

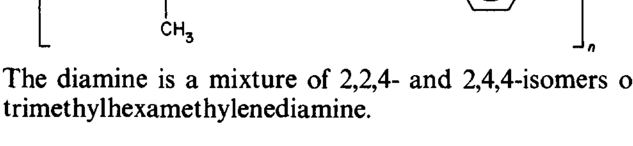
The determination of molecular weight averages and molecular weight distribution of polyamides (PA) is difficult by reason of their insolubility in common solvents. Treating the polyamides with an excess of trifluoroacetic acid anhydride (equation (1)), *N*-trifluoroacetylated derivatives (*N*–TFA–PA) are formed, which are soluble in methylene chloride, chloroform, tetrahydrofuran (THF) and others[1].



(1)

The *N*-trifluoroacetylation leads to nearly quantitative conversion ($\geq 98\%$) without polymer degradation[2].

*N*-TFA-polyamides are already characterized by g.p.c. in methylene chloride qualitatively[3,4]. In this work quantitative analysis of g.p.c.-measurements in THF is described; resulting data are compared with molecular weight determinations by light scattering, viscometry and osmometry. Representative polyamides are nylon 6 (AB-type) and Trogamid$^R$, i.e. nylon 6-3-T (AABB-type). structural unit of Trogamid®



The diamine is a mixture of 2,2,4- and 2,4,4-isomers of trimethylhexamethylenediamine.

## CALIBRATION PROCEDURES

In calibration of a given system 'polymer–column packing–eluent' monodisperse polymer-samples of known molecular weight $M$ are generally used. Ideally, there is a linear relationship of log $M$ and elution volume $V_e$:

$$\log M = A - B\,V_e \qquad (2)$$

If no fractions are available, other methods[5,6] are applicable, i.e. calibration with polydisperse standards or universal calibration.

For calibration with well-characterized polydisperse standards Weiss and Cohn-Ginsberg[7] (WCG) assumed the validity of the generalized Schulz–Zimm distribution:

$$w(M) = (p^{k+1}/\Gamma(k+1))M^k \exp(-pM) \qquad (3)$$

Parameters $k$ and $p$ are determined from $M_w$ and $M_n$. The calibration curve is then calculated by means of g.p.c. chromatogram and equation (3).

If the samples obey the Schulz–Zimm distribution and furthermore the calibration curve is linear (equation (2)), elution volume $V_e$ of the maximum of a given g.p.c. chromatogram ($V_e^{\max}$) corresponds to $M_w$ of the sample[8]. Therefore direct construction of the calibration curve is possible by measuring polydisperse standards of different $M_w$.

The universal calibration most applied is the procedure of Benoit[9]. Knowing the Mark–Houwink parameters of polystyrene (PS) and of the considered polymer ($x$), the calibration curve of PS is converted as follows:

$$\log M_x = \frac{1}{1+a_x}\log\frac{K_{PS}}{K_x} + \frac{1+a_{PS}}{1+a_x}\log M_{PS} \qquad (4)$$

## EXPERIMENTAL

### *Preparation of polymers*

Polymers of nylon 6 were prepared by melt polycondensation of 6-aminohexanoic acid or by hydrolytic polymerization of the corresponding lactam.

Polymers of Trogamid were prepared by solution-polycondensation of terephthalic acid diphenylester and the mixture of 2,2,4- and 2,4,4-isomers of trimethyl-

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**Table 1** Nylon 6–TFA: results of g.p.c. measurements

| | | | Direct calibration | | Universal Calibration | |
|---|---|---|---|---|---|---|
| Sample | $M_w^{TFA}$ (LS) | $M_n^{TFA}$ (Osm.) | $M_w^{TFA}$ | $M_n^{TFA}$ | $M_w^{TFA}$ | $M_n^{TFA}$ |
| R4 | 198000 | 95000 | 191200 | 83100 | 218800 | 102500 |
| B4 | 125000 | 50800 | 120600 | 49700 | 135000 | 56800 |
| B3 | 112200 | 48100 | 112800 | 49300 | 126000 | 55600 |
| R3 | 110400 | 52000 | 103400 | 45700 | 115500 | 51800 |
| R2 | 86000 | 39200 | 84000 | 38300 | 93300 | 43000 |
| B2 | 69900 | 34000 | 71800 | 33600 | 79500 | 37600 |
| B1 | 62700 | 26300 | 62800 | 29000 | 69500 | 32600 |
| N3 | 44500 | — | 40000 | 21600 | 44200 | 24300 |
| N2 | 22500 | — | 24400 | 11500 | 27000 | 12800 |
| N1 | 13800 | 6800* | 13800 | 7900 | 15500 | 9900 |

* Vapour phase osmometry

**Table 2** Trogamid–TFA: results of g.p.c. measurements

| | | | Direct calibration | | Universal calibration | |
|---|---|---|---|---|---|---|
| Sample | $M_w^{TFA}$ (LS) | $M_n^{TFA}$ (Osm.) | $M_w^{TFA}$ | $M_n^{TFA}$ | $M_w^{TFA}$ | $M_n^{TFA}$ |
| L5 | 120000 | 49000 | 108000 | 55900 | 110400 | 58400 |
| L10 | 85000 | 40000 | 88700 | 41900 | 90100 | 42500 |
| L3 | 93500 | 39300 | 88400 | 39600 | 89900 | 40900 |
| L12 | 68500† | 30500 | 67900 | 32200 | 69300 | 33800 |
| L4 | 64800† | 28200 | 62600 | 28700 | 63900 | 29900 |
| L9 | 41800† | 22900 | 41300 | 22600 | 42600 | 23900 |
| L8 | 32000† | — | 32300 | 17400 | 33500 | 18500 |
| L7 | 27400 | — | 29700 | 15100 | 30800 | 16000 |
| L1 | 20100 | 7700* | 21400 | 10100 | 22500 | 11400 |
| L11 | 13200 | 6200* | 14500 | 7200 | 15500 | 8100 |

* Vapour-phase osmometry
† Viscometry (conf. equation (5))

hexamethylenediamine in various aprotic solvents, generally dimethylsulphoxide.

Residual oligomers were eliminated by reprecipitation.

*Preparation of oligomers*

Cyclic oligomers of nylon 6 were extracted from the polymers by hot methanol. Linear oligomers of Trogamid were prepared by a two-fold excess of diester resp. diamine, leading to products with defined endgroups. Equimolar mixtures resulted mainly in a homologous series of oligomers with one amino- and one ester-endgroup (e.g. LO1:0.2 molar in chloroform; 5.5 h, 50°C; conf. *Figure 1*).

Oligomers were separated by g.p.c. and identified by field desorption mass spectrometry[10].

*Gel permeation chromatography (g.p.c.)*

*Column Set 1 (for polymers):*

10$\mu$-styragel columns (Waters): $10^5+10^4+10^3+500$ Å

Detection: $UV_{254nm}$ (Isco UA5)

Solvent: THF, stabilized with 50 ppm 2,6,ditertbutyl-4-methyl-phenol, 25°C, flow = 1 $cm^3$ $min^{-1}$ (1.06 $cm^3$ = 1 count)

Sample concentration: 1 mg $cm^{-3}$ (50 $\mu$l)

After correction for peak spreading applying the method of Balke and Hamielec[11], differences in $M_w$ and $M_n$ did not exceed 3%. This was within reproducability of a single g.p.c.-run; therefore, influence of peak spreading was neglected.

*Column Set 2 (for oligomers):*

5$\mu$-PL gel columns (Polymer Laboratories): 500 + 100 + 100 Å

Detection: $UV_{254nm}$ (Uvidec 100-III)

Solvent: stabilized THF, 25°C, flow = 1 $cm^3$ $min^{-1}$ (1 $cm^3$ = 1 count)

Sample concentration: 1 mg $cm^{-3}$ (100 $\mu$l)

Light scattering, osmometric and viscosimetric measurements of *N*-trifluoroacetylated polyamides were carried out as previously described[2].

## RESULTS AND DISCUSSION

The combination of g.p.c. columns and the experimental conditions were chosen so that a linear calibration curve resulted. Testing the method of Weiss and Cohn-Ginsberg, the calibration curve calculated with two polydisperse PS-standards agreed well with that given by commercially available, nearly monodisperse PS standards.

Assuming the validity of the Schulz–Zimm distribution, direct calibration of log $M_w$ vs. $V_e^{max}$ was used for polyamides. The calibration was completed by the prepared oligomers, which were separated by g.p.c. and identified by field desorption mass spectrometry. *Figure 1* shows the chromatogram of a mixture of oligomers after *N*-trifluoroacetylation; included is the correlation of molecular weights and elution volumes (column set 2).

The resulting calibration curves of nylon 6–TFA and Trogamid–TFA are shown in *Figures 2* and *3* (column set 1). Fractions of Trogamid, prepared by precipitation fractionation[12], support the graph obtained. Direct calibration, as applied here, is simpler than the WCG method and leads to better results. On the other hand, the WCG

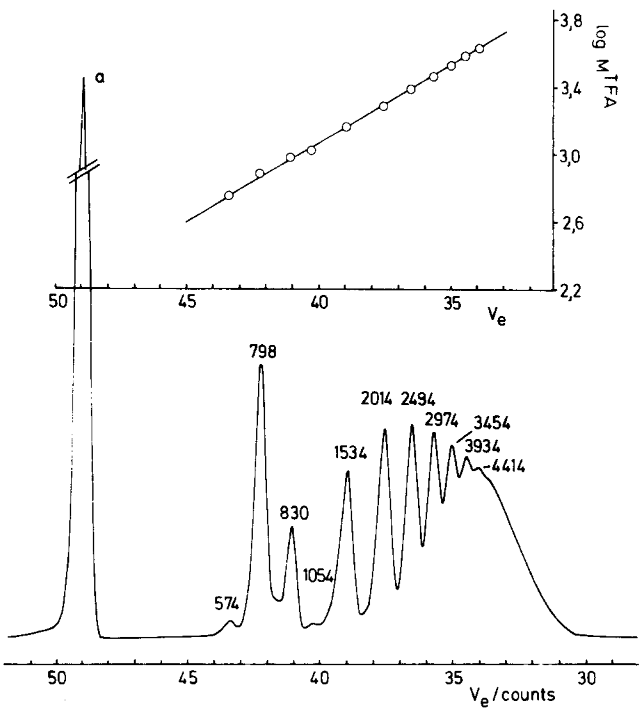

**Figure 1** Chromatogram of a mixture of Trogamid-oligomers after *N*-trifluoroacetylation (LO1–TFA); correlation of molecular weights and elution volumes. (a) Terephthalic acid diphenylester

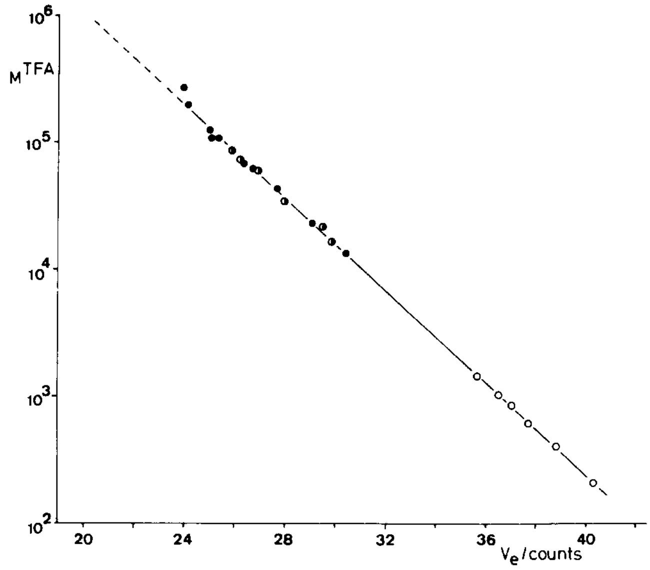

**Figure 2** G.p.c. calibration-curve of nylon 6–TFA. (●) Polydisperse standards ($M_w$ from light scattering); (◑) polydisperse standards ($M_w$ from viscometry); (○) oligomers

method can be utilized to extend the calibration curve to the region of very high molecular weights.

In *Tables 1* and *2* weight and number averages, $M_w^{TFA}$ and $M_n^{TFA}$, of trifluoroacetylated samples are summarized and compared with results of light scattering, osmometric and viscosimetric measurements. The discrepancies in the high molecular weight samples reflect the fact that the calibration curve in this region is not well-defined. However, the overall agreement verified the validity of the assumptions made above.

In addition, *Tables 1* and *2* contain the results of the universal calibration. Equation (4) was calculated using the $[\eta]$-M-relation of polystyrene given by Appelt and

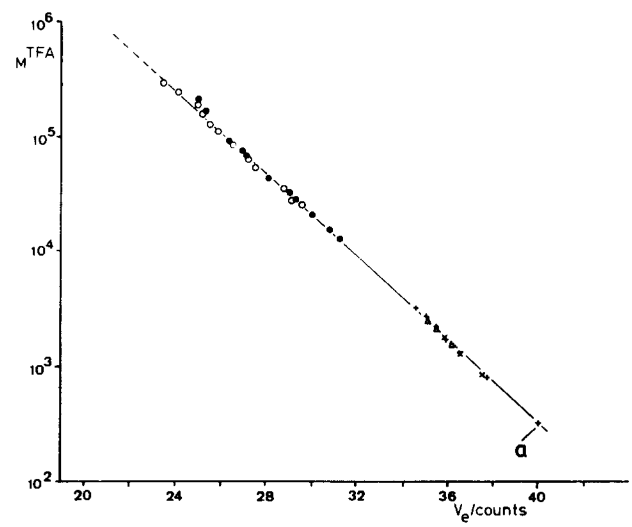

**Figure 3** G.p.c. calibration-curve of Trogamid–TFA. (○) Fractions; (●) polydisperse standards; (+) oligomers with two ester-endgroups; (×) oligomers with two amino-endgroups; (△) oligomers with one ester- and one amino-endgroup; (a) terephthalic acid diphenylester

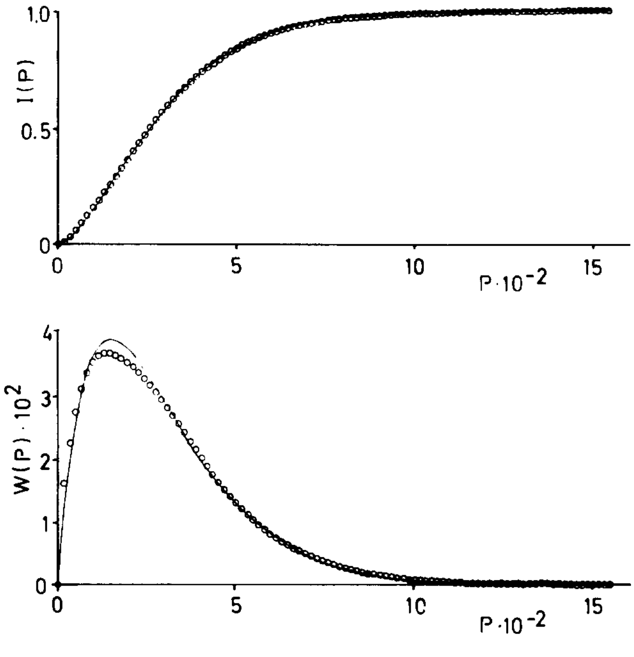

**Figure 4** Integral and differential weight distribution of a nylon 6 sample (B2) (ooooo), compared with the generalized Schulz–Zimm distribution (———)

Meyerhoff[13] and the previously determined relations of nylon 6–TFA and Trogamid–TFA[2]:

$$
\begin{aligned}
&\text{Polystyrene} \quad [\eta]=0.01314\ \mathrm{M}^{0.714} \\
&\text{Nylon 6–TFA:} \quad [\eta]=0.0166\ \mathrm{M}^{0.70} \qquad (5) \\
&\text{Trogamid–TFA:} [\eta]=0.0087\ \mathrm{M}^{0.73}
\end{aligned}
$$

Computed in this manner, molecular weight values of nylon 6–TFA are clearly too high; the same trend is observed with Trogamid, although there is a satisfactory agreement.

Correction of equation (5) according to Coll *et al.*[14] or application of other PS-relations given in the literature[15] do not improve the results significantly.

Cassassa[16] in his theoretical treatment of size exclusion suggested that $[\eta]\cdot M$ is not the truly universal calibration parameter in g.p.c., but remarkable discrepancies are expected only between different types of molecular geometry, e.g. rodlike polymers and polymers with flexible chains. These differences should be indicated by the Mark–Houwink exponent $a$; they are not applied for the $N$-TFA-polyamides and polystyrene because of the similarity of their Mark–Houwink exponents (equation (5)).

However, elution of the polymer is changed by participation of mechanisms other than pure size exclusion, which are discussed for instance by Yau[17]. The specific interactions of polymer and gel matrix, for which the high polarity of the $N$-TFA-group may be responsible, are superimposed on pure size exclusion and may lead to the failure of universal calibration.

Integral and differential weight distributions of the $N$-trifluoroacetylated polyamides were also studied. Choosing the degree of polymerization $P$ as the variable, the distribution of the polyamide-sample under examination may be calculated directly; it is not necessary to consider the change in molecular weight by the TFA-reaction. *Figure 4* shows that the calculated weight distribution closely approximates the generalized Schulz–Zimm distribution as assumed above.

## CONCLUSIONS

For characterizing polyamides with regard to molecular weight averages and molecular weight distribution, $N$-trifluoroacetylated samples were examined using g.p.c. In calibration g.p.c., the direct plotting of log $M_w$ vs. peak-maximum $V_e^{max}$ led to the best results. Only defined oligomers and polydisperse samples of known $M_w$, obeying the generalized Schulz–Zimm distribution, were necessary. A linear calibration-curve was obtained by optimization of experimental conditions. It is possible to extend the calibration method to other polyamides accessible to $N$-trifluoroacetylation.

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