

Molecular weight determinations of polyamides by N-trifluoroacetylation

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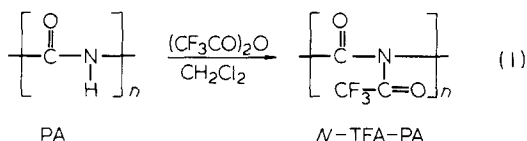
By *N*-trifluoroacetylation (TFA) polyamides become soluble in ordinary organic solvents such as acetone, butanone, methylene chloride, chloroform and tetrahydrofuran. In these solvents light scattering and osmotic measurements (membrane and vapour-phase osmometry) were carried out to determine the weight and number average degrees of polymerization. Comparison with the results on non-TFA-polyamides in various solvents clearly shows that no polymer degradation takes place. The $[\eta]$ - P relationships of Trogamid[®]-TFA and nylon-6-TFA in tetrahydrofuran at 25°C were determined and corrected for polydispersity.

Keywords Polyamides; *N*-trifluoroacetylation; light scattering; osmometry; viscometry; gel permeation chromatography

INTRODUCTION

The characterization of polyamides (PA) in solution is complicated by their restricted solubility: common solvents of PA are concentrated acids, phenols, aliphatic fluorinated alcohols and concentrated solutions of salts in alcohols¹. Owing to the possibility of hydrolytic degradation, polyelectrolyte effects, the presence of aggregates and apparatus problems like corrosion or decomposition of membranes, molecular weight determinations may be difficult or even impossible.

To avoid these problems, one can use the *N*-trifluoroacetylation reaction (equation (1)) developed by Schutzenberg and Schulz²; in this way polyamides become soluble in ordinary organic solvents such as acetone, butanone, methylene chloride, chloroform and tetrahydrofuran (THF):



This reaction can be applied to many PA and leads to nearly quantitative conversion ($\geq 98\%$) without polymer degradation³. Thus the number and weight average degrees of polymerization P_n and P_w can be determined in *N*-TFA-PA by osmotic and light scattering measurements, respectively. Furthermore, viscosity measurements and quantitative evaluation of g.p.c. measurements on *N*-TFA-PA are possible⁴.

EXPERIMENTAL

The polyamides investigated and their structural formulae are shown in Table 1. The samples are industrial and laboratory products; by previous g.p.c. measurements³ residual monomer and oligomers were

detected and removed by reprecipitation and extraction, if necessary.

The *N*-trifluoroacetylation was carried out as described in ref. 3. The *N*-TFA-PA are completely soluble in the solvents used within 15–30 min at room temperature; however, in acetonitrile only Trogamid-TFA is soluble. The solvents (Merck, Darmstadt) are methanol and butanone (p.a.), acetone and acetonitrile (Uvasol), chloroform (LiChrosolv), methylene chloride (dried with Al_2O_3 , distilled over CaH_2), DMF (LAB, distilled over bis-(4-isocyanatophenyl)methane) and THF (distilled over K).

Light scattering measurements were carried out at 25°C with vertically polarized light of $\lambda = 4.36 \times 10^{-5}$ cm (FICA 50) using benzene as the standard. The refractive index increments were determined at the referred wavelength and temperature using a high-precision differential refractometer according to Bodmann⁵. The results are: for nylon-6-TFA, $0.0748 \text{ cm}^3 \text{ g}^{-1}$ (acetone); for nylon-6,6-TFA, $0.0756 \text{ cm}^3 \text{ g}^{-1}$ (acetone); for nylon-12-TFA, $0.0883 \text{ cm}^3 \text{ g}^{-1}$ (acetone); for Trogamid-TFA, $0.117 \text{ cm}^3 \text{ g}^{-1}$ (acetone) and $0.105 \text{ cm}^3 \text{ g}^{-1}$ (acetonitrile); for non-TFA Trogamid, $0.144 \text{ cm}^3 \text{ g}^{-1}$ (DMF) and $0.191 \text{ cm}^3 \text{ g}^{-1}$ (chloroform:methanol 53:47 vol.%).

The osmotic measurements were performed in an automatic 'High-speed membrane osmometer' (Hewlett-Packard) with pre-tested 'Ultracellallerfeinst' membranes (Sartorius GmbH, Göttingen) at 25°C, in DMF at 40°C. For vapour-phase osmometry a Knauer instrument (Knauer KG, Berlin) thermostatted to 37°C was employed using chloroform as the solvent. For the calibration in the corresponding molecular weight range, polystyrene standards of defined P_n were used (PCC 4000, PCC 10000, PCC 17500; Pressure Chemical Company).

Viscosity measurements were performed at 25°C in an automatic viscometer of the Ubbelohde type. The dimension of the viscometer was chosen in such a way that the Hagenbach-Couette correction can be neglected. The

Table 1 Investigated polyamides; molecular weight of the structural unit M_0 for PA, M_0^{TFA} for *N*-TFA-PA

Name/abbreviation	M_0	M_0^{TFA}	Structural formula
Nylon-6 $x = 5$ Nylon-12 $x = 11$	113 197	209 293	$\left[(\text{CH}_2)_x - \text{C}(=\text{O}) - \text{NH} \right]_n$
Nylon-6,6 ($y = 6; z = 4$) Nylon-6,10 ($y = 6; z = 8$)	226 282	418 474	$\left[\text{N}(\text{H}) - (\text{CH}_2)_y - \text{N}(\text{H}) - \text{C}(=\text{O}) - (\text{CH}_2)_z - \text{C}(=\text{O}) \right]_n$
Trogamid T ^{®a}	288	480	$\left[\text{N}(\text{H}) - \text{CH}_2 - \text{C}(\text{CH}_3)_2 - \text{CH}_2 - \text{CH}(\text{CH}_3) - (\text{CH}_2)_2 - \text{N}(\text{H}) - \text{C}(=\text{O}) - \text{C}_6\text{H}_4 - \text{C}(=\text{O}) \right]_n$
Polyesteramide 6NT6	494	686	$\left[\text{C}(=\text{O}) - \text{C}_6\text{H}_4 - \text{C}(=\text{O}) - \text{N}(\text{H}) - (\text{CH}_2)_6 - \text{N}(\text{H}) - \text{C}(=\text{O}) - \text{C}_6\text{H}_4 - \text{C}(=\text{O}) - \text{O} - (\text{CH}_2)_6 - \text{O} \right]_n$
Copolyamide 6/6.6			$\left[\text{N}(\text{H}) - (\text{CH}_2)_6 - \text{N}(\text{H}) - \text{C}(=\text{O}) - (\text{CH}_2)_4 - \text{C}(=\text{O}) \right]_m \left[\text{N}(\text{H}) - (\text{CH}_2)_5 - \text{C}(=\text{O}) \right]_n$

^a Trogamid T[®] is a trade name of Dynamit Nobel AG. The diamine is a mixture of 2,2,4- and 2,4,4- isomers of trimethylhexamethylenediamine

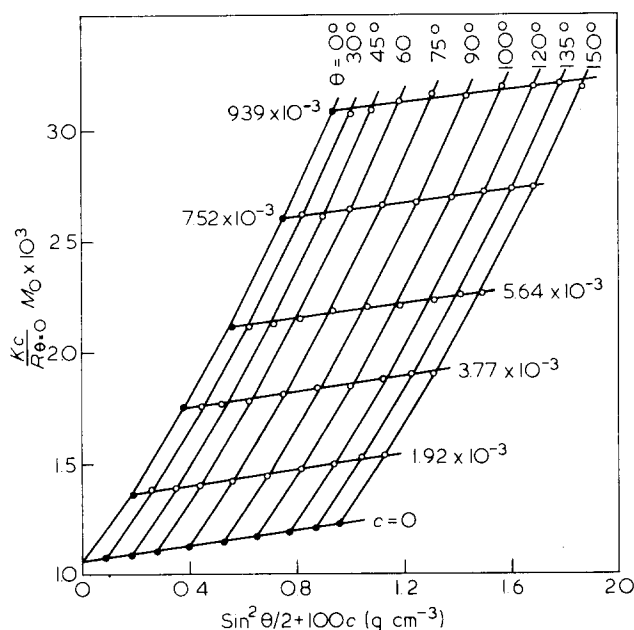


Figure 1 Zimm plot of a nylon-6-TFA sample in acetone, at 25°C. $R_4; P_w = 947, M_w = 107\,000 \text{ g mol}^{-1}$

intrinsic viscosity $[\eta]$ was calculated from the extrapolation of η_{sp}/c for $c \rightarrow 0$. The *N*-TFA-polyamides were measured in THF, freshly distilled over K and stabilized with 50 ppm 2,6-di-tertbutyl-4-methylphenol.

RESULTS AND DISCUSSION

Light scattering

In treatment of data the reciprocal reduced intensities of scattered light were extrapolated to zero concentration and, if necessary, to zero angle. Figure 1 shows a typical Zimm plot of a nylon-6-TFA sample ($R_4; P_w = 947$,

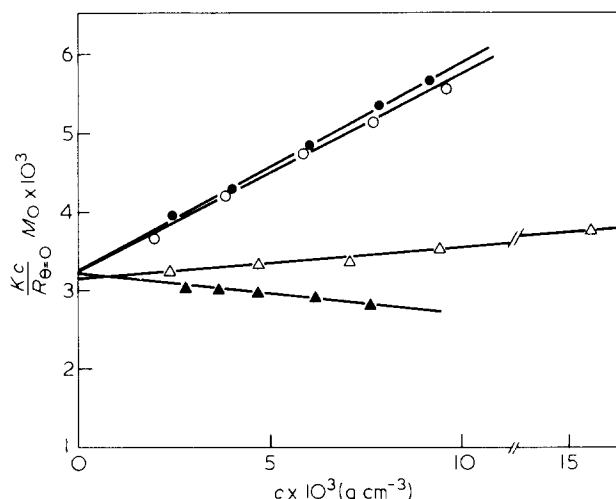


Figure 2 Light scattering measurements on Trogamid, at 25°C. TAGR-TFA: \circ , acetone, $P_w = 154$; \triangle , acetonitrile, $P_w = 159$. TAGR: \bullet , DMF, $P_w = 152$; \blacktriangle , chloroform:methanol (53:47 vol.%), $P_w = 158$

$M_w = 107\,000 \text{ g mol}^{-1}$). For Trogamid, which is already soluble in DMF and mixtures of methanol and chloroform without *N*-trifluoroacetylation, the method employed can be examined directly. Using equation (2)

$$\frac{Kc}{R_0} M_0 = \frac{1}{P_w} + 2A_2 M_0 c \quad (2)$$

where R_0 is the Raleigh ratio at zero angle, K the optical constant and M_0 the molecular weight of the structural unit, the correspondence between measurements on non-TFA (TAGR) and TFA-Trogamid (TAGR-TFA) is clearly shown in Figure 2. In this way it is confirmed that there is no polymer degradation in *N*-trifluoroacetylation as already shown by g.p.c. and viscosity measurements³.

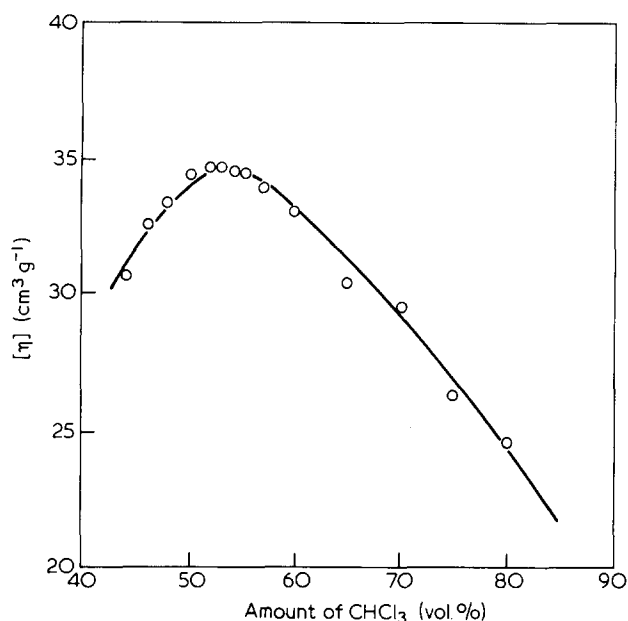


Figure 3 Intrinsic viscosity $[\eta]$ of Trogamid (TAGR) in the co-solvent mixture chloroform : methanol

To minimize possible complications by selective sorption¹ in the mixed solvent, the measurements were carried out at the composition 53:47 vol.% chloroform:methanol where the intrinsic viscosity $[\eta]$ shows a maximum (Figure 3). The negative second virial coefficient A_2 in Figures 2 and 4 is explained by the fact that chloroform and methanol, respectively, alone are non-solvents and the mixture only solves samples of molecular weight $< 10^5$.

In Table 2 the results of the molecular weight determinations are summarized.

Membrans osmometry/vapour-phase osmometry (VPO)

Determinations of the number average P_n (equation (3)) also leads to corresponding results between TFA- and non-TFA-Trogamid within experimental error:

$$\Pi M_0 c F T = \frac{1}{P_n} + A_2 M_0 c \quad (3)$$

where R is the universal gas constant and T the temperature in Kelvin.

In Figure 4 the measurements of the osmotic pressure Π in four solvents are included.

Table 2 Molecular weight averages M_w and M_n (solvent)

Polyamide	Sample	Light scattering, M_w (g mol ⁻¹)	Membrane osmometry, M_n (g mol ⁻¹)	v.p.o., M_n (g mol ⁻¹)
Nylon-6	N1	7500 (ac)	—	3700 (CHCl ₃)
	B1	33900 (ac)	14200 (CHCl ₃)	13700 (CHCl ₃)
	B2	37800 (ac)	18500 (CHCl ₃) 18300 (THF)	17300 (CHCl ₃)
	B3	60700 (ac)	26000 (CHCl ₃) 26100 (bu) 25300 (THF)	—
Trogamid	TAGR	44400 (ac)	26100 (CHCl ₃) 24700 (bu) 25500 (THF)	
		45800 (CH ₃ CN)	25300 (DMF) ^a 25000 (CC) ^a	
		43900 (DMF) ^a		
		45400 (CC) ^a		
	L3	56100 (ac)	23900 (CHCl ₃) 24000 (bu) 23600 (DMF) ^a 24000 (CC) ^a	
		56700 (CC) ^a		
L4	—	18000 (CHCl ₃) 18600 (bu) 17400 (DMF) ^a 17800 (CC) ^a		
L5	71900 (ac)	29400 (CHCl ₃) 29100 (bu) 29700 (THF)		
Nylon-12		33300 (ac)	13900 (CHCl ₃)	14400 (CHCl ₃)
Nylon-6,6	N6	44400 (ac)	—	
	N7	59800 (ac)	27800 (CHCl ₃)	
Nylon-6,10		—	13800 (CHCl ₃)	
Copolyamide 6/6.6		—	16300 (CHCl ₃)	
Polyesteramide 6NT6		—	19000 (CHCl ₃) 18000 (<i>m</i> -Cresol) ^{a,b}	

CC = CHCl₃/CH₃OH 53 : 47 vol.%; ac = acetone; bu = butanone
^a Non-TFA-polyamides

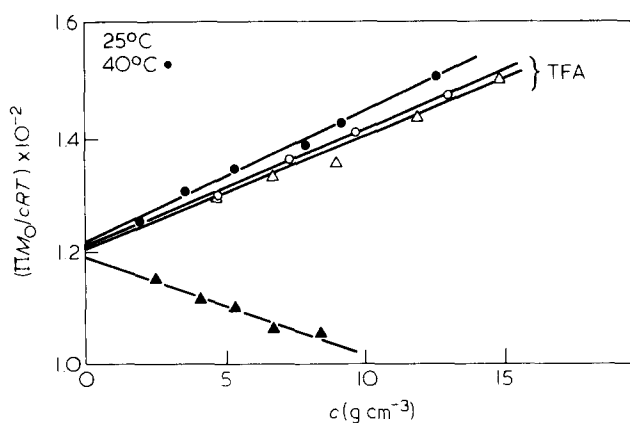


Figure 4 Osmotic measurements on Trogamid. L3-TFA: ○, chloroform, P_n = 83; △, butanone, P_n = 83. L3: ●, DMF, P_n = 82; ▲, chloroform:methanol (53:47 vol.%), P_n = 84

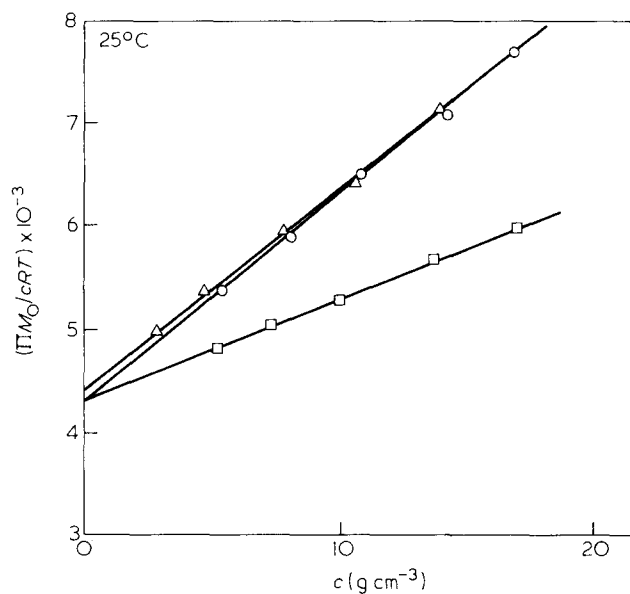


Figure 5 Osmotic measurements on nylon-6-TFA. B3-TFA: ○, chloroform, P_n = 230; △, THF, P_n = 224; □, butanone, P_n = 231

In a similar way nylon-6-TFA was analysed in several solvents (Figure 5), and the results are given in Table 2.

By means of v.p.o. the determination of P_n is completed for lower molecular weight samples.

Viscometry

The [η]-P relationship of Trogamid-TFA and nylon-6-TFA in THF at 25°C was determined. The data of Table 3 are plotted in Figure 6. Fractions of Trogamid were at our disposal, and they had been characterized in DMF by ultracentrifugation, viscosity and g.p.c. measurements^{7,8} and by light scattering. P_w of broad Trogamid-TFA samples derived from light scattering in acetone are also included in Figure 6 and they show the same dependence. P_w values of nylon-6 were obtained by light scattering on broad TFA samples exclusively as described above.

Least-squares treatment of data in Table 3 resulted in the following [η]-P relationships.

For Trogamid-TFA in THF (only fractions were used):

$$[\eta] = 0.79P_w^{0.73} \quad (4)$$

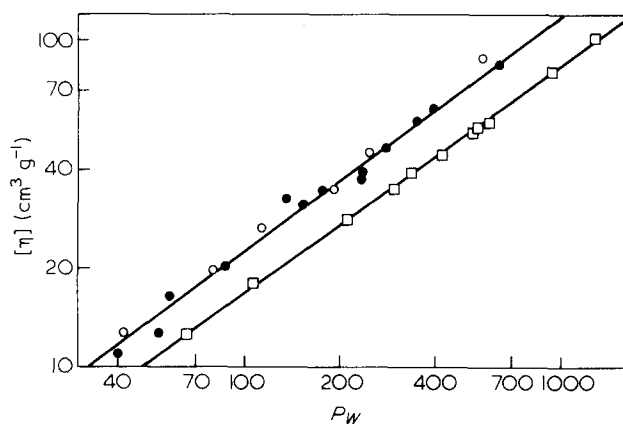


Figure 6 [η]-P_w plot of Trogamid-TFA (●, fractions; ○, broad samples) and nylon-6-TFA (□) in THF at 25°C

Table 3 Intrinsic viscosity [η] in THF at 25°C, degrees of polymerization P_w and non-uniformities (U = P_w/P_n-1)

Trogamid-TFA				Nylon 6-TFA			
Sample	[η] (cm ³ g ⁻¹)	P _w	U	Sample	[η] (cm ³ g ⁻¹)	P _w ^b	U
6L1 ^a	10.9	40	0.32	N1	12.9	66	1.03 ^d
7D7,7 ^a	12.8	54	0.41	N2	17.8	108	1.30 ^c
6D7,7 ^a	16.3	58	0.43	N3	28.3	213	1.05 ^c
7D7,6 ^a	20.4	88	0.32	B1	35.0	300	1.39 ^d
7D7,5 ^a	26.4	115	0.28	B2	39.4	334	1.05 ^d
7D7,4 ^a	32.8	137	0.15	R2	44.5	412	1.22 ^c
TAGR ^a	30.8	154 ^b	0.70	R3	52.7	528	1.40 ^c
7D7,3 ^a	34.4	180	0.18	B3	54.0	537	1.29 ^d
TGA7 ^a	37.5	236	0.41	B4	56.5	598	1.43 ^d
7D7,2 ^a	40.0	237	0.14	R4	80.3	947	1.41 ^c
TGA3 ^a	47.1	272	0.42	N5	103.3	1292	1.30 ^d
7D7,1 ^a	56.9	354	0.14				
6D7,2 ^a	62.0	401	0.34				
6D7,1 ^a	85.1	651 ^b	0.74				
L1	12.7	42 ^b	1.12 ^c				
L2	19.9	79 ^b	1.07 ^c				
L3	34.5	195 ^b	1.35 ^d				
L5	45.8	250 ^b	1.45 ^d				
L6	90.4	595 ^b	-				

^a Sample codes, P_w and U from Herold and Meyerhoff^{7,8}

^b From light scattering on TFA samples

^c U from g.p.c. measurements on TFA samples

^d P_n from osmotic measurements on TFA samples

For nylon-6-TFA in THF:

$$[\eta] = 0.67P_w^{0.70} \quad (5)$$

Assuming a generalized Schulz-Flory distribution of the nylon-6 samples, the data of Table 3 were corrected⁹ in order to eliminate the influence of polydispersity; using the given non-uniformities this leads to

$$[\eta] = 0.70P_w^{0.70} \quad (6)$$

CONCLUSIONS

By using the *N*-trifluoroacetylation reaction (equation (1)), the determination of molecular weight averages of polyamides in many dipolar aprotic solvents is possible. Comparative light scattering and osmotic measurements on non-TFA- and TFA-polyamides verified that no polymer degradation takes place.

By *N*-trifluoroacetylation the molecular weight is enlarged thus compensating for the rather small refractive index increments and reduces experimental errors due to the remaining permeability of osmotic membranes. Because of the nearly quantitative conversion it is not necessary to determine the exact degree of substitution with regard to the experimental accuracy (5–10%) of methods used in the determination of the degree of polymerization.

It seems to be possible to extend the molecular weight characterization to other polymers accessible to *N*-trifluoroacetylation, e.g. polyurethanes and polyureas.

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