

***N*-chlorination of aliphatic oligoamides and polyamides by *tert*-butyl hypochlorite in organic medium**

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SUMMARY

Several aliphatic oligoamides and polyamides have been chlorinated by *tert*-butyl hypochlorite in organic medium. Reactions were carried out in mild experimental conditions and no side reactions and degradations were observed. The influence of experimental parameters and of initial polymer structure on the conversion (α) has been examined. The modified polyamides were studied by SEC, chemical titration and ^1H - and ^{13}C -NMR.

INTRODUCTION

The first investigations on the chlorination of polyamides have been carried out by Bamford (1) with gaseous chlorine and Wayman (2) with hypochlorous acid. Schutzenberg and Schulz (3) have perfected the chlorination method of polyamides using various chlorinating reagents : gaseous chlorine, chloromonoxide, *tert*-butylhypochlorite in organic medium and hypochlorous acid in aqueous medium. Polyamide -3 (3,4), polyamide -6 (3-6), polyamide -6,6 (3-9), polyurea (8), optically active polyamides (10, 11) and substituted polyacrylamides (12) have been successfully chlorinated. However the influence of temperature, stoichiometry, solvent and amide concentration is not known.

The present article reports results obtained on the *N*-chlorination of polyamides -11, -12, -6,10, -6 and -6,6 by *tert*-butyl hypochlorite (**tBuOCl**) in organic medium with emphasis on the influence of the various experimental parameters and of the structure of polyamides on conversion.

EXPERIMENTAL PART

Chemicals:

t-butanol (Aldrich, 99%) and trifluoroacetic anhydride **TFA** (Fluka, 99%) were used without further purification. Oligoamides and polyamides were obtained from Elf Atochem and Rhône-Poulenc. The polyamide samples were ground (cryogenic grinder) then fractionated using a series of 100 μm to 1mm sieves.

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Polyamides and oligoamides characteristics are reported in table 1.

Table 1: Oligoamides \overline{M}_n values: (a) chemical titration, (b) SEC and (c) $^1\text{H-NMR}$

sample	Nature	\overline{M}_n^a	\overline{M}_n^b	\overline{M}_n^c	n
1	polyamide -11	-	17700	-	
2	polyamide -12	-	26000	-	
3	polyamide -6,10	-	15000	-	
4	polyamide -6	-	17500	-	
5	polyamide -6,6	-	15200	-	
6	α, ω dicarboxy oligoamide-11	980	950	830	3.6 ^a
7		2000	2070	1600	10.1 ^a
8	α, ω dicarboxy oligoamide-12	1030	1040	1020	4.5 ^a
9		2095	2095	1860	9.9 ^a
10	α, ω dicarboxy oligoamide-6,10	1260	1335	1400	3.74 ^a
11	α, ω dimethyl oligoamide-6,6	-	1040	1180	4.8 ^b
12	α, ω diamino oligoamide-6,6	1430	1500	1625	5.8 ^a
13	α, ω dicarboxy oligoamide-6	1020	-	800	7.73 ^a
14		1430	-	860	11.4 ^a

Synthesis:

1. *t*-butyl hypochlorite (**tBuOCl**) : It was synthesized according to Teeter (13) and was stored in a dark cool place.

2. *N*-Chlorination: Polyamide **2** (0.3954 g, 0.002 mol. of amide group) was placed in a double-walled thermostated reactor protected from light and dispersed in CH_2Cl_2 (20 mL) at 25°C. **tBuOCl** (0.6510 g, 0.006 mol) was added under stirring. After 20 hours the solvent was evaporated off under vacuum at room temperature; the resulting product was dried under reduced pressure for 3 hours and was stored in the dark at 5°C. The same procedure was used for the various samples.

3. *Dechlorination of chlorinated samples* : The procedure of Koutinas (6) was modified as follows. A solution of chlorinated sample **2'** (1 g, 0.0043 mol) in formic acid (50 mL) was placed in an erlenmeyer and maintained at 10°C. Triphenyl phosphite (2.25 mL, 0.0086 mol) was added dropwise and the resulting clear solution was added dropwise into methanol (50 mL) under stirring. Water (50 mL) was added to the white slurry and the mixture was left at room temperature for 24 hours. The polymer was filtered off, washed four times with water (50 mL each time) then with propanone (100 mL) and dried under reduced pressure. The same procedure was used for the various samples.

Analysis:

□ *NMR* : Samples were dissolved in CDCl_3 with an excess of **TFA** (1/3 v/v) and recorded on a Bruker WM 250 spectrometer.

□ *SEC* : - Oligoamide solutions were prepared like those used for NMR; system comprised of a Gilson 302 Pump, a Waters U6K injector, a Gilson 131 refractive index detector and a model 820 Maxima control system; 100Å + 500Å + 1000Å Phenomenex column set was used. The eluting solvent was HPLC grade (stabilized by amylene) CH_2Cl_2 at a flow rate of 1.3 mL/min.

- Polyamides were dissolved in benzyl alcohol at 150°C during 2 hours; Waters system comprised of a 150 Pump, a R410 refractive index detector, and a U6K injector; mixed-bed column was used with 1 mL/min flow rate of benzyl alcohol at 130°C.

□ *Iodometric titration of N-chloroamide groups* : A solution of sample **2'** (0.05 g) in sulfuric acid (10 mL) was dropped in water (50 mL) then was treated with KI (0.17 g, 0.001 mol) in a sodium acetate-acetic acid buffer solution. After 10 min evolved iodine

was titrated with a 0.04 M sodium thiosulfate solution. The precipitate formed during titration did not influence the results.

□ *Titration of carboxy groups* : The oligoamide sample (0.2 g) was dissolved in benzyl alcohol at 110°C; after cooling the solution was titrated with 0.025 M KOH/EtOH. A blank was carried out in the same conditions.

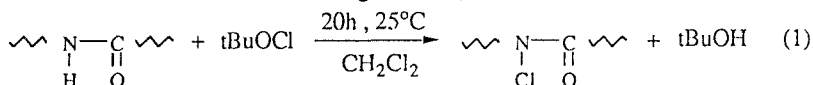
□ *Titration of amino groups* : The sample was prepared as above and titrated with a 0.025 M perchloric acid solution in EtOH.

□ *DSC* : Thermograms were run on a Du Pont 9900 DSC 910 instrument; samples were quenched from melt and heated at 20°C/min under nitrogen atmosphere. Tg was taken at the inflexion point of slope in the DSC curve.

□ *X-Ray diffractometry* : Curves were obtained with a CuK α 1 radiation (40 kV x 30 mA).

RESULTS AND DISCUSSION

Chlorination was carried out according relation (1) :



The initial concentration of amide groups (C_0) was 0.1 M. The molar ratio of tBuOCl to C_0 , $R = [\text{tBuOCl}]/C_0$, was 3 all over the study.

25°C is the upper limit because tBuOCl is unstable above this temperature. The reaction takes place in heterogeneous medium. However when the reaction is carried out in dichloromethane, the medium becomes homogeneous above some conversion.

Conversion α is given by relation 2 :

$$\alpha = \frac{[-\text{NCl-CO-}]}{C_0} \times 100 \quad (\%) \quad (2)$$

where $[-\text{NCl-CO-}]$ is the concentration of chlorinated amide units. α is determined by $^1\text{H-NMR}$ and chemical titration.

Oligoamides and polyamides are labelled **1** to **12** (see table 1). The corresponding chlorinated polymers are labelled **1'** to **12'**.

The $^1\text{H-NMR}$ spectrum of **3'** (granulometry: 100-200 μm , $\alpha=77-79\%$) is shown in figure 1. α was determined from deconvolution of the pattern relative to H_1 and H_1 in spectrum (a) and from the integration of the two H_1' and H_1 triplets in spectrum (b).

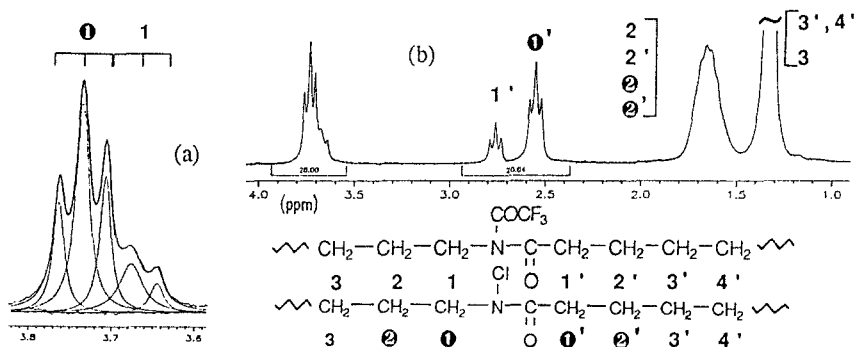


Figure 1 : $^1\text{H-NMR}$ spectrum of **3'** after trifluoroacetylation.

The quadruplet (3.42 ppm) characteristic of N-trifluoro acetylated amino end groups of N-trifluoro acetylated **12** is no longer present in the spectrum of trifluoroacetylated **12'** (fig. 2) ($\alpha=46\%$). On the other hand two triplets at 3.63 and 3.64 ppm are relative to mono (a) and dichlorinated (b) end groups.

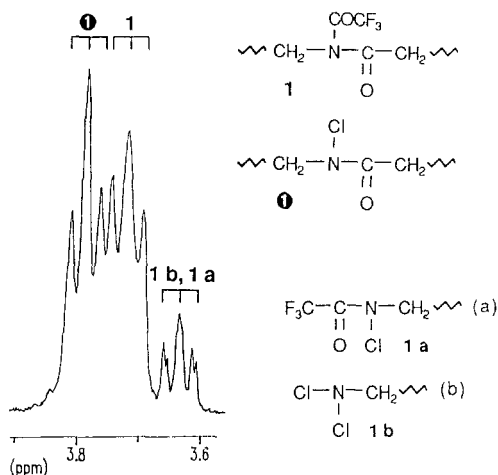


Figure 2 : $^1\text{H-NMR}$ spectrum of **12'** after trifluoroacetylation

The $^{13}\text{C-NMR}$ spectrum of sample **2'** ($\alpha=100\%$, fig.3) shows the absence of any side-compound. No C-chlorination is observed.

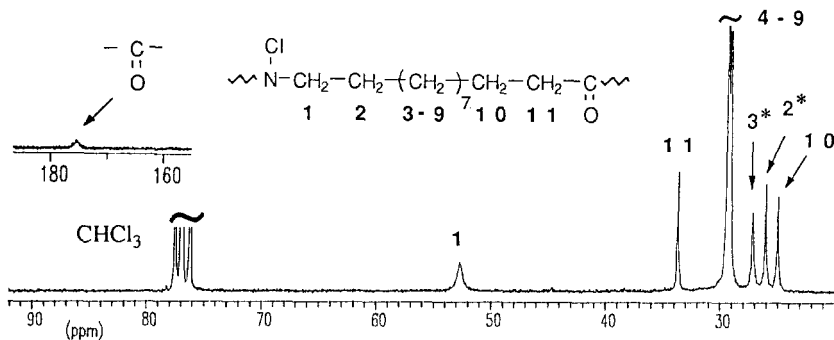


Figure 3 : $^{13}\text{C-NMR}$ spectrum of N-chlorinated sample **2'**

The absence of any degradation product is confirmed by SEC study : the chromatograms of initial polyamides and those of dechlorinated samples are identical (fig. 4).

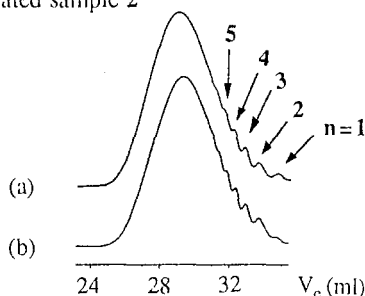


Figure 4 : Chromatograms of trifluoroacetylated **6** (a) and trifluoroacetylated dechlorinated **6'** (b)

Influence of various experimental parameters on α :

The following study is relative to sample 9 which was finely ground (particles size < 100 μm).

■ Solvent nature (table 2)

The best results were obtained in CH_2Cl_2 where the solubility of 9' increases with α . Quantitative conversion was reached. On the other hand 9' is not soluble in the other solvents we studied and the conversion was much lower. A good solubility of chlorinated product is therefore necessary to achieve high conversion.

When the reaction was carried in chloroform or 1,1,2,2- tetrachloroethane, α was very low (10%). The NMR spectra of the resulting product show peaks which are characteristic of C-chlorination and degradation products. It is worth mentioning that the solution developed a yellow color during the reaction and gas evolving is observed. These phenomena originate from tBuOCl degradation which probably induces oligoamide degradation.

■ Stoichiometry (table 3)

α increases with R and reaches 100% for a molar ratio R of 3. The reaction rate depends on the chlorinating reagent.

■ Temperature (table 4)

At 25°C oligoamide 9 remains as a finely dispersed suspension in the solvent. On the contrary, at lower temperatures, agglomerates occur resulting in a lower reactive surface, therefore in a decreasing reactivity.

■ Initial concentration C_0 (table 5)

α reaches 100% when C_0 is greater or equal to 0.1 M and decreases with lower concentrations.

Table 2 : Chlorination of 9
Influence of solvent nature on α

solvent	α (%)	α (%)
	$^1\text{H-NMR}$	titration
CH_2Cl_2	100 ^b	96.0
$\text{CH}_2\text{Cl-CHCl}_2$	44.5 ^a , 48.0 ^b	44.5
CCl_4	45.0 ^a , 41.5 ^b	43.5
$\text{CH}_3\text{-Cl}_3$	40.5 ^a , 40.5 ^b	38.0
$\text{CFCl}_2\text{-CF}_2\text{Cl}$	46.0 ^a , 47.0 ^b	46.0
propanone	59.0 ^a , 58.0 ^b	58.5

α obtained by déconvolution^a and by integration^b

Table 3 : Chlorination of 9
Influence of R on α

R	α (%)	α (%)
	$^1\text{H-NMR}$	titration
1	53.0 ^a	52.0
	52.5 ^b	
2	70.0 ^a	68.0
	72.0 ^b	
3	100 ^b	96.0

a, b see table 2

Table 4 : Chlorination of 9
Influence of temperature T on α

T (°C)	α (%)	α (%)
	$^1\text{H-NMR}$	titration
-20	19.5 ^a	27.0
	27.0 ^b	
5	37.5 ^a	39.0
	39.0 ^b	
25	100 ^b	96.0

a, b see table 2

Table 5 : Chlorination of 9
Influence of C_0 on α

C_0 (M)	α (%)	α (%)
	$^1\text{H-NMR}$	titration
0.01	10 ^b	9.5
0.025	61.5 ^a	59.5
	57.5 ^b	
0.05	73.5 ^a	75.0
	69.0 ^b	
0.1	100 ^b	100
0.2	100 ^b	100

a, b see table 2

Table 6 : Chlorination of oligoamides and polyamides. Influence of granulometry and structure.

sample	T _g (°C)	χ_c^w	G _S ^y	R=3		R=1	
				α (%) 1H-NMR	α (%) titration	α (%) 1H-NMR	α (%) titration
1	36	18.6	1	100	99.0	87.5 ^b	88.0
			3	100	97.0	77.0 ^a , 82.0 ^b	81.0
			5	100	98.0	67.5 ^a , 74.5 ^b	70.5
2	42	34	2	96.0 ^b	99.0	77.5 ^a , 83.0 ^b	82.0
			4	92.5 ^b	98.0	79.5 ^a , 79.0 ^b	79.0
			6	92.0 ^b	86.0	77.5 ^b	76.5
			7	-	-	74.0 ^a , 68.5 ^b	70.0
3	42	<5	1	100	96.0	-	-
			3	75.5 ^a , 78.0 ^b	79.0	-	-
			5	61.0 ^a , 52.5 ^b	50.0	-	-
4	50	16.7	1	59.0 ^a , 60.0 ^b	59.0	-	-
			3	58.0 ^a , 61.0 ^b	57.0	-	-
			5	50.5 ^a , 52.5 ^b	40.0	-	-
			6	30.0 ^a , 32.0 ^b	33.0	-	-
5	53	25.4	1	34.5 ^a , 33.0 ^b	39.0	-	-
			3	39.0 ^a , 41.0 ^b	42.0	-	-
			5	31.5 ^a , 30.0 ^b	31.0	-	-
6	-	-	1	100	95.0	58.5 ^a	56.0
7	-	-	1	100	100	73.0 ^a , 74.5 ^b	75.0
8	-	-	1	78.0 ^b	73.0	67.0 ^b	63.0
9	-	-	1	100	99.5	52.0 ^b	53.0
10	-	-	1	100	98.0	-	-
11	-	-	1	70.0 ^b	68.0	-	-
12	-	-	1	46.0 ^a , 46.5 ^b	-	-	-
13	-	-	1	61.0 ^b	61.0	-	-
14	-	-	1	51.0 ^b	53.0	-	-

(w) χ_c : degree of crystallinity which is the percentage (w/w) of the crystalline phase

(y) G_S : granulometry scale (1 : < 100 μm, 2 : 125-315 μm, 3 : 100-200 μm,

4 : 315-500 μm, 5 : 200-500 μm, 6 : 500-1000 μm et 7 : >1 mm)

a, b see table 2.

Influence of granulometry and structure on α :

For all samples a quantitative conversion was achieved in 3 days or less. Conversions were compared when reaction time was $t = 20$ hours (table 6).

Influence of granulometry

α increases while particles size decreases showing that N-chlorination is favoured by increasing reactive surface.

Influence of structure

The results reported in table 6 indicate that conversion is higher for the samples of type -11, -12 and -6,10 (**1-3** and **6-10**) than for the -6 and -6,6 ones (**4, 5** and **11-14**). The morphological and chemical structures of the compounds must therefore be taken into consideration:

- X-Ray diffractometry shows that the degree of crystallinity of all polyamides is fairly low (< 35%). The contribution of crystalline phase in the N-chlorination reaction should not be the predominant one.

- In addition, the glass transitions of polyamides (36 to 53°C) are above the reaction temperature (25°C). The segmental movements in the amorphous zone are forbidden. Thus all the polyamides should have the same behaviour.

- The chemical structure constitutes therefore the predominant parameter. α increases with the number of methylene segments separating two successive amide groups shows. The conversion of polyamide -6 is 60% and for polyamide -12 100%. The conversion is then higher when the aliphatic chain of polyamide is longer. This can be connected to an easier accessibility of the chlorinating reagent to the amide group in the case of longer chains.

CONCLUSION

The N-chlorination of polyamides in organic medium by tert-butyl hypochlorite is a very clean process. The reaction can be carried out in mild conditions at room temperature, which eliminates side reaction such as degradation and C-chlorination.

Moreover it is possible to obtain samples with different degrees of N-chlorination (from 10 to 100%) by controlling carefully the experimental conditions : nature of solvent, amount of chlorinating reagent, temperature and initial concentration of amide units.

The study of the characteristics of initial polyamides shows that increasing of reactive surface and the number of methylene segments in the chains enhances the conversion.

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