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New transamidation reaction in molten state: model study

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Abstract

A new transamidation reaction, between an aliphatic secondary amide and an aromatic nitrile, leading to an aromatic amide and an aliphatic nitrile is described in this article. The best conditions have been established: 300°C, no solvent, 2 h, 1 wt.% PPA as catalyst. Yields were found to be independent of the nature of para substituents, but strongly decrease for an ortho substituted compound. NMR studies support the mechanisms such as hydration of the nitrile, amidolysis, dehydration of the aliphatic amide leading to the aromatic amide and the aliphatic nitrile. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Bulk transamidation; Aromatic nitrile + secondary amide; Polyphosphoric acid

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1. Introduction

Transamidation, which is the reaction between a secondary amide and compounds such as an amine (aminolysis), an acid (acidolysis), an ester (esterolysis) or an other amide (amidolysis) is well documented [1–3]. To the best of our knowledge, there is no reference in the literature concerning a one step reaction between a secondary amide and a nitrile. As αω-cyanoaromatic oligomers are easily prepared [4], this reaction would be interesting to prepare block aromatic and aliphatic copolyamides by bulk condensation as a lot of polyamides are commercially available.

To develop this new transamidation reaction in polymer field, it seemed to be interesting to study its scope and limitations using various aromatic nitriles and an aliphatic secondary amide.

$$\mathrm{ArCN} + \mathrm{RCONHR'} \leftrightarrows \mathrm{ArCONHR'} + \mathrm{RCN}$$

The amide used was *N*-hexyl-hexanamide, which can be easily obtained by condensation of hexanoyl chloride and hexylamine [5]. It is an appropriate model for nylon-6,6, which is one of the most commonly used polyamides. Different nitriles with donating or withdrawing groups were also used.

2. Experimental

2.1. General procedure for nitrilolysis

The aromatic nitriles are commercially available, phosphoric acids which were supplied from Aldrich. The experiments were followed by g.l.c. (Hewlett Packard 5890, DB1 capillary column, l: 15 m, ϕ: 0.32 mm, P_{N_2}:70 kPa, t_0: 60°C, 10°C/min, t_f: 300°C). Flash chromatographies were realized with Merck Geduran SI 60 silica gel. NMR spectra (^{1}H and ^{13}C) were recorded in $CDCl_3$ on a BRUKER AC250 apparatus or (^{19}F and ^{31}P) on a BRUKER DRX400. Standards ($\delta = 0.00$ ppm) are TMS, $CFCl_3$, H_3PO_4 and the coupling constants are in Hertz; the following abbreviations are used and correspond to what is observed on the spectrum: s, singlet, bs, broad singlet, d, doublet, t, triplet, q, quadruplet, qu, quintuplet, m, multiplet. Elemental analyses were done by the Service Central d'Analyse du CNRS in Solaize (France).

All reactions were performed in 5 ml stainless steel autoclaves immersed in a thermoregulated sandbath (±3°C). The nitrile (10 mmol) or the dinitrile (2.5 mmol), the *N*-hexylhexanamide (10 mmol) and the PPA (1% weight) were put in the autoclave and heated at 300°C for 2 h. For the monoamides, after cooling, the mixture was dissolved into CH_2Cl_2 and extracted with an aqueous solution of sodium hydrogenocarbonate; the organic layer was then dried, concentrated and the aromatic amide purified by flash chromatography (CH_2Cl_2). For the diamides, after cooling, hot DMF was added and the product crystallized.

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Table 1
Isolated yields of *N*-hexyl-*p*-fluorobenzamide using various catalysts (300°C, 2 h)

Catalysts (5% weight)[a]	Isolated yield of aromatic amide (%)
HPO_3	60
HPO_3 + 1 eq. H_2O	66
H_3PO_4	60
P_2O_5	23
P_2O_5 + 0.5 eq. H_2O	52
P_2O_5 + 1 eq. H_2O	62
P_2O_5 + 2 eq. H_2O	45
PPA	81
PPA + 1 eq. H_2O	65

[a] eq. H_2O refers to the nitrile.

2.2. N-hexylhexanamide

N-hexylhexanamide was synthesized according to Moore [5]. Using Et_3N instead of pyridine, the yield was 93% (B.p. $_{0.07}$ 108°C–111°C [5]). ^1H NMR: $\delta = 6.54$ (s, 1H, NH); 3.21 (t, 2H, NH–C*H₂*); 2.20 (t, 2H, C*H₂*–CO); 1.66–1.32 (m, 14H, CH_2); 0.91 (CH_3). ^{13}C NMR: $\delta = 173.3$ (CO); 39.3, 36.5, 31.3, 31.3, 29.4, 26.5, 25.5, 22.4, 22.3 (CH_2); 13.8, 13.7 (CH_3).

2.3. N-hexyl-p-fluorobenzamide

N-hexyl-*p*-fluorobenzamide is a yellow liquid obtained in 85% yield. ^1H NMR: $\delta = 7.82$ (m, 2H, Ho); 7.27 (bs, 1H, NH); 7.02 (m, 2H, Hm); 3.36 (m, 2H, NH–CH_2); 1.56 (qu, $J = 7$, 2H, NH–CH_2–CH_2); 1.26 (m, 6H, CH_2); 0.84 (t, 3H, $J = 7$, CH_3). ^{13}C NMR: $\delta = 166.9$ (CO); 164.6 (d, $^1J_{C,F} = 251.4$, Cp); 131.0 (d, $^4J_{C,F} = 2.8$, Ci); 129.5 (d, $^3J_{C,F} = 8.7$, Co); 115.2 (d, $^2J_{C,F} = 21.7$, Cm); 40.3 (NH–CH_2); 31.6, 29.7, 26.8, 22.6 (CH_2); 14.0 (CH_3). ^{19}F NMR: $\delta = -109.35$ (dd, $^3J_{HF} = 8.7$, $^4J_{HF} = 5.5$). *Anal.* $C_{13}H_{18}FNO$ calc.: C, 69.95, H, 8.07, N, 6.28, F, 8.52; found: C, 70.09, H, 8.36, N, 6.35, F, 8.15.

2.4. N-hexyl-p-methylbenzamide

N-hexyl-*p*-methylbenzamide is a pale yellow liquid obtained with 75% yield. ^1H NMR: $\delta = 7.66$ (m, 2H, Ho); 7.20 (m, 2H, Hm); 6.25 (bs, 1H, NH); 3.41 (m, 2H, NH–CH_2); 2.37 (s, 3H, ϕ-CH_3); 1.59 (qu, $J = 7$, 2H, NH–CH_2–CH_2); 1.31 (m, 6H, CH_2); 0.88 (t, 3H, $J = 7$, CH_3). ^{13}C NMR: $\delta = 167.4$ (CO); 141.6 (Cp); 132.0 (Ci); 129.1, 126.8 (Co, Cm); 40.0 (NH–CH_2); 31.5, 29.7, 26.7, 22.6 (CH_2); 21.4 (ϕ–CH_3); 14.0 (CH_3). *Anal.* $C_{14}H_{21}NO$ calc.: C, 76.71, H, 9.59, N, 6.39; found: C, 77.08, H, 9.75, N, 6.37.

2.5. N-hexyl-p-cyanobenzamide

N-hexyl-*p*-cyanobenzamide is obtained by mixing equimolar ratio of terephthalonitrile and *N*-hexyl-hexanamide with 68% yield; in these conditions, 10% of diamide was formed. After chromatography and evaporation of CH_2Cl_2, the isolated product spontaneously crystallized (m.p. 77°C). ^1H NMR: $= 7.87$ (m, 2H, Ho); 7.71 (m, 2H, Hm); 6.46 (bs, 1H, NH); 3.44 (m, 2H, NH–CH_2); 1.62 (qu, $J = 7$, 2H, NH–CH_2–CH_2); 1.32 (m, 6H, CH_2); 0.89 (t, 3H, $J = 7$, CH_3). ^{13}C NMR: $\delta = 165.8$ (CO); 138.8 (Ci); 132.4, 127.7 (Co, Cm); 118.1 (CN); 114.8 (Cp); 40.4 (NH–CH_2); 31.5, 29.5, 26.7, 22.6 (CH_2); 14.0 (CH_3). *Anal.* $C_{14}H_{18}N_2O$ calc.: C, 73.04, H, 7.83, N, 12.17; found: C, 73.29, H, 7.77, N, 12.48.

2.6. Bis-N-hexylterephthalamide

Bis-*N*-hexylterephthalamide is obtained by adding 4 eq of amide to terephthalonitrile; the crude product is crystallized in MeOH (m.p. 195°C, yield 70%). ^1H NMR (DMSO d_6): $\delta = 8.11$ (bs, 1H, NH); 7.92 (m, 2H, Ho, Hm); 3.33 (m, 2H, NH–CH_2); 1.57 (qu, $J = 7$, 2H, NH–CH_2–CH_2); 1.33 (m, 6H, CH_2); 0.87 (t, 3H, $J = 7$, CH_3). ^{13}C NMR: $\delta = 166.8$ (CO); 138.3 (Ci); 127.7 (Co); 40.4 (NH–CH_2); 34.9, 30.1, 27.2, 22.9 (CH_2); 14.0 (CH_3). *Anal.* $C_{20}H_{32}N_2O_2$ calc.: C, 72.29, H, 9.64, N, 8.43; found: C, 72.77, H, 9.52, N, 8.10.

2.7. 4,4′-di-N-hexylcarbamoylbiphenyl

The yield for 4,4′-di-*N*-hexylcarbamoylbiphenyl was 68% (m.p. 264°C–266°C, MeOH). ^1H NMR (DMSO d_6): $\delta = 7.93$ (m, 2H, Ho); 7.75 (m, 2H, Hm); 3.33 (m, 2H, NH–CH_2); 2.80 (bs, 1H, NH); 1.60 (qu, $J = 7$, 2H, NH–CH_2–CH_2); 1.39 (m, 6H, CH_2); 0.91 (t, 3H, $J = 7$, CH_3). ^{13}C NMR: $\delta = 165.5$ (CO); 145.8 (Cm); 134.1 (Ci); 127.1 (Co); 125.9 (Cp); 42.1 (NH–CH_2); 34.5, 30.4, 27.1, 22.8 (CH_2); 14.0 (CH_3). *Anal.* $C_{26}H_{36}N_2O_2$ calc.: C, 76.47, H, 8.82, N, 6.86; found: C, 76.56, H, 8.83, N, 6.71.

2.8. 4,4′-dicyano-biphenylether

4,4′-dicyano-biphenylether was synthesized according to Dhanesar and Poole [7] with 77% yield (m.p. 178°C, CH_3CN, lit [7] 176°C–178°C). ^1H NMR: $\delta = 7.71$ (d, H–3, H–3′); 7.10 (d, H-2, H-2′) *Anal.* $C_{14}H_8N_2O$ calc.: C, 76.29, H, 3.63, N, 12.71; found: C, 76.43, H, 3.64, N, 12.71.

2.9. 4,4′-di-N-hexylcarbamoylbiphenylether

The yield for 4,4′-di-*N*-hexylcarbamoylbiphenylether was 72% (m.p.200-202°C, MeOH). ^1H NMR (DMSO d_6): $\delta = 7.87$ (m, 2H, Ho); 7.07 (m, 2H, Hm); 3.30 (m, 2H, NH-CH_2); 2.79 (bs, 1H, NH); 1.57 (qu, $J = 7$, 2H, NH-CH_2-CH_2); 1.38 (m, 6H, CH_2); 0.90 (t, 3H, $J = 7$, CH_3). ^{13}C NMR: $\delta = 167.9$ (CO); 157.8 (Cp); 128.6 (Ci); 127.5 (Co); 117.6 (Cm); 42.1 (NH-CH_2); 34.5, 29.5, 26.5, 22.2 (CH_2); 13.9 (CH_3). *Anal.* $C_{26}H_{36}N_2O_3$ calc.: C, 73.58, H, 8.49, N, 6.60; found: C, 73.43, H, 8.62, N, 6.68.

3. Results and discussion

In order to determine the best bulk reaction conditions,

Table 2
Isolated yields of *N*-hexyl-*p*-fluorobenzamide and *p*-fluorobenzoic acid depending on catalyst amount (300°C, 2 h)

PPA amount (weight ratio %)	Amide (isolated yield %)	Acid (isolated yield %)
20	68	10
10	81	5
5	81	3
2	85	0
1	85	0
0.3	85	0

p-fluorobenzonitrile and *N*-hexylhexanamide were used as models. We first checked whether this reaction occurred without a catalyst; in all runs, less than 2% of aromatic amide was obtained (g.l.c. data). It is well known that transamidation reactions are catalysed by acids [2], hence we tried Lewis acids [$AlCl_3$, $Al(OiPr)_3$, $Ti(OBu)_4$, Sb_2O_3] or sulfonic acids ($MeSO_3H$, CF_3SO_3H), which however gave very low yields (less than 10%) and numerous degradation products. As it is well known that phosphoric acid derivatives are commonly used for polyamides syntheses, various phosphorylated compounds were tested (Table 1); the best one was polyphosphoric acid (PPA). In all cases, *p*-fluorobenzoic acid was obtained as a by-product with a yield increasing up to 25% with the quantity of water. However, only 3% yield was obtained using PPA; another set of experiments using different amounts of PPA shows the catalytic feature of PPA which allows us to obtain a good yield and avoid the formation of *p*-fluorobenzoic acid. Results are summarized in Table 2. Further, the temperature effect was studied to establish the optimal experimental conditions. One per cent PPA was chosen for a more accurate weighing (Table 3). Below 300°C, the reaction was too slow and some degradation products were found to appear after 24 h; above 300°C, the side products were rapidly formed and the yield decreased dramatically. Thus, the best experimental conditions for the nitrilolysis of the *p*-fluorobenzonitrile in a bulk reaction without stirring were: 300°C, 2 h, 1% PPA. By using these conditions, the effect of substituents was studied and the results presented in Table 4. As can be seen, the yields of isolated products are fairly good and we were unable to detect by products coming from nucleophilic attack on the halogen. The low yield observed with *o*-methylbenzonitrile is probably caused by steric hindrance (see ^{31}P NMR), although good yields are obtained with several para substituted nitriles. The poor yield for *p*-cyanoanisole could be explained by the unstability of the ether linkage in the acidic medium [6], leading to the formation of degradation compounds (g.l.c.). The special cases of dinitriles were studied because nitrilolysis could be applied to polyamide syntheses; as expected, the three compounds (Table 5) gave very good yields in diamide using four equivalents of *N*-hexyl-hexanamide during 2 h. A longer time did not affect the yields. It must be mentionned that if only one equivalent of amide was used, it was possible to isolate the nitrilamide with about 70% yield.

Table 3
Best isolated yields of *N*-hexyl-*p*-fluorobenzamide depending on the temperature (1% PPA)

Temperature (°C)	Time (h)	Isolated yield of amide (%)
250	24	71
300	2	85
320	1	57
350	0.5	39

In order to understand the mechanism of this reaction, some additional experiments were carried out. First, we checked the potential reversibility of the reaction by mixing hexanenitrile with *N*-hexyl-*p*-fluorobenzamide. After 2 h at 300°C, fluoroamide and fluoronitrile were obtained in a 94/6 ratio (^{19}F NMR). Thus, although this transamidation is an equilibrium, it is largely shifted to the formation of the aromatic amide with a high yield. Then, two NMR studies (^{31}P and ^{19}F) were performed on the crude mixture in order to detect the transient intermediate taking place along the

Table 4
Influence of the aromatic substituent on nitrilolysis yield (300°C, 2 h, 1% PPA)

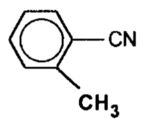
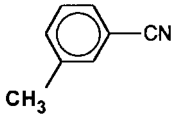
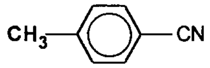
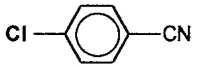
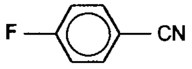
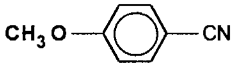
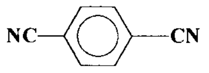
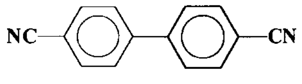
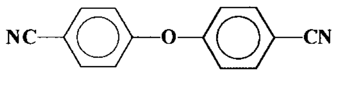
Starting material	% (GLC)
	25%
	72%
	76%
	80%
	87%
	<10%

Table 5
Nitrilolysis of dinitriles with 4 eq. of amide (300°C, 2 h, 1% PPA)

Starting material	Diamide (isolated yield %)
	70
	68
	72

reaction. The ^{31}P NMR spectrum recorded after heating a mixture containing *p*-fluorobenzonitrile, *N*-hexylhexanamide and PPA for 15 or 30 min showed two signals: $\delta = 0$ ppm (PPA) and $\delta = -12$ ppm. In the same conditions, spectra of PPA alone or PPA + *N*-hexylhexanamide show only the PPA signal; thus we can postulate the primary formation of a complex between the aromatic nitrile and the PPA. These observations probably explain the bad results obtained for *o*-methylbenzonitrile: the complex is obtained with great difficulty because of steric hindrance. The ^{19}F NMR spectra showed three signals attributed respectively, by comparison with authentic samples, to *p*-fluorobenzonitrile (−102.71 ppm), *p*-fluorobenzamide (−108.16 ppm) and *N*-hexyl-*p*-fluorobenzamide (−109.35 ppm). Sometimes, there is a fourth signal corresponding to *p*-fluorobenzoic acid (−107.05 ppm), but this by-product can be avoided by using about 1% PPA as catalyst. The ratios of the three compounds which are given in Table 6 shows that *p*-fluorobenzamide is an intermediate of the nitrilolysis as it disappears in the course of time. From the NMR studies, it is possible to propose the following mechanism for the transamidation of an aromatic nitrile:

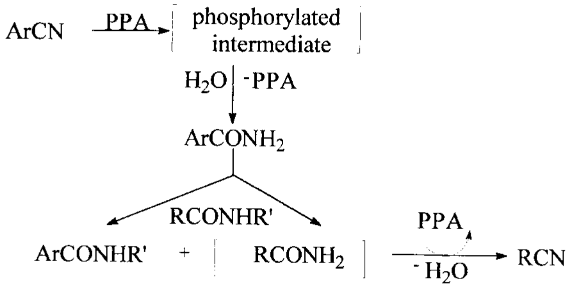


Table 6
Evolution of the mixture during the reaction (300°C, 1% PPA) determined by ^{19}F NMR

Ar compound	0.3 h	0.6 h	1 h	1.5 h	2 h
Nitrile (%)	60	43	34	22	11
Amide I (%)	10	7	4	3	2
Amide II (%)	30	50	62	75	87

It is noteworthy that water concentration is a key point for the reaction: water, like PPA, acts as a catalyst and the quantity needed for the aromatic nitrile hydrolysis is recovered during the aliphatic amide dehydration avoiding the side reaction leading to the acid.

4. Conclusion

This new transamidation reaction can be applied to a large variety of aromatic nitriles. The driving force to displace the equilibrium is the specific reactivity of PPA which is able, in the same conditions, to hydrolyse an aromatic nitrile and to dehydrate an aliphatic amide. These results based on new aromatic nitrilolysis could be applied to obtain block copolyamide by reactive processing; further experiments are in progress in our laboratory.

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