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Synthesis of Aromatic Polyamides from Isocyanatocarboxylic Acid Chlorides and Dimethylsulfoxide or Water

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SUMMARY:

Aromatic isocyanatocarboxylic acid chlorides (**1a**—**i**) reacted with stoichiometrical quantities of dimethyl sulfoxide in ether to yield poly(*N*-carboxyanhydride)s (**5**) which were converted into polyamides (**6**) by heating them at elevated temperatures. Isocyanatocarboxylic acid chlorides also reacted with water to produce polyamides **6**. The reaction paths were followed by quantitative analysis of carbon dioxide evolved, by measurement of IR spectra, and by thermal analysis of the polymers.

ZUSAMMENFASSUNG:

Aromatische Isocyanatocarbonsäurechloride (**1a**—**i**) reagieren mit stöchiometrischen Mengen von Dimethylsulfoxid in Äther und ergeben Poly(*N*-carboxyanhydride) (**5**), die durch Erhitzen auf höhere Temperaturen in Polyamide (**6**) überführt werden. Isocyanatocarbonsäurechloride reagieren ebenso mit Wasser unter Bildung von Polyamiden **6**. Der Reaktionsweg wurde durch quantitative Analyse des gebildeten Kohlendioxids verfolgt sowie mit Hilfe der IR-Spektren und durch thermische Analyse der Polymeren.

Introduction

Isocyanatocarboxylic acid chlorides (**1a**—**i**) are novel compounds which contain two highly reactive groups, the isocyanate function and the acid chloride function. By reacting them with diamines and diols, "poly(amide-urea)s" and "poly(ester-urethane)s" which contain two different linkages in the main chain of the polymer have been produced directly[1,2]. However, despite of different reactivities of the isocyanate and the acid chloride toward amines or alcohols[3,4], polymers of ordered structures could not be obtained. Recently, we have found that phenol reacts preferentially with the isocyanate group of *p*-isocyanatobenzoyl chloride (**1c**) to yield a new reactive addition product, *p*-phenoxycarbonylaminobenzoyl chloride. By polymer formation reactions using this compound, poly(*p*-benzamide) and ordered "poly(amide-quinazolinedione)s" could be obtained$^{5,6)}$. In the continued investigation of the synthesis of polymers starting from isocyanatocarboxylic acid chlorides, reactions of these compounds with dimethyl sulfoxide (**2**) or with water were undertaken. In this communication, we report the successful synthesis of polyamides from the reactions of aromatic isocyanatocarboxylic acid chlorides with **2** or water.

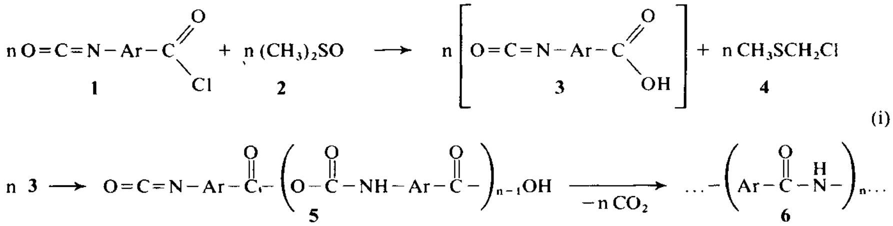
Results and Discussion

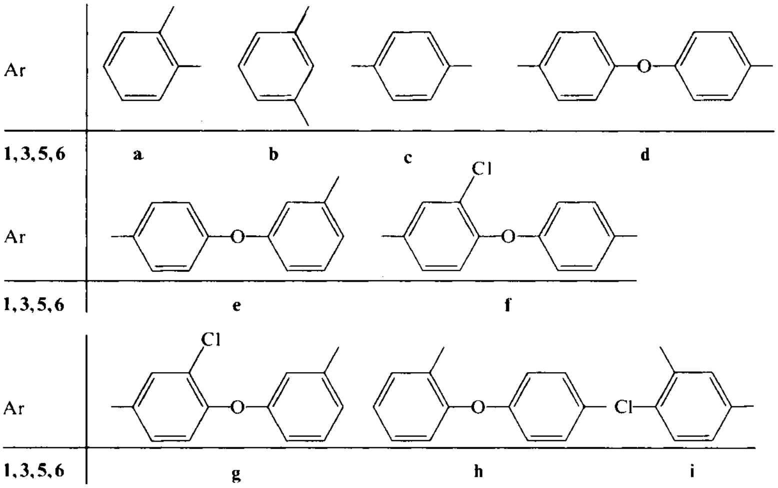
o-, *m*- and *p*-isocyanatobenzoyl chlorides (**1a**—**c**) were prepared in high yields from the corresponding amino acids by the phosgene-phosphorus pentachloride method as previously reported$^{7)}$. In addition, new aromatic isocyanatocarboxylic acid chlorides (**1d**—**i**) containing an ether linkage were also synthesized. The ether linkage introduced into the backbone of the polymer is known to increase the solubility of the polymer formed in organic solvents. The yields and the physical properties of these compounds are presented in Tab. 2 (Exp. Part).

Reaction with dimethyl sulfoxide (DMSO)

It has been reported that carboxylic acid chlorides react with DMSO very rapidly to give the corresponding carboxylic acids$^{8)}$. It was interesting to see if **1a**—**i** will react with DMSO to yield the corresponding isocyanatocarboxylic acids (**3a**—**i**) which contain also two reactive groups. Isocyanatocarboxylic acids have been considered to be produced as intermediates when the urethane derivatives of amino acids are heated at elevated temperatures to form poly(amino acid)s$^{9)}$, but until now they could not be isolated. Recently, Kricheldorf reported that these compounds might be liberated by careful hydrolysis of isocyanatocarboxylic acid trimethylsilyl esters$^{10)}$. In the latter case, however, isocyanatocarboxylic acids could not be obtained; only addition products, cyclic *N*-carboxyanhydrides or poly(*N*-carboxyanhydride)s, were isolated. This meant that a rapid addition reaction did occur between the isocyanate and the carboxylic acid groups.

Here, we also performed a reaction similar to that carried out by Kricheldorf. When a solution of DMSO in ether was slowly added to a chilled solution of **1b**—**g** in ether at 0—5 °C and the reaction mixture was allowed to react at room temperature for ca. 15 h, poly(*N*-carboxyanhydride)s (**5b**—**g**) were obtained.





The reaction was extremely exothermic when the addition of DMSO was carried out without cooling at room temperature or when the DMSO solution in ether was added rapidly. As DMSO is known to react with isocyanates at elevated temperatures, the reaction system had to be cooled and the DMSO solution was added slowly to avoid side reactions. The offensive odor of chloromethyl methyl sulfide (**4**) was detected immediately when the addition of DMSO was started. This indicated that the reaction occurred rapidly.

The reaction product was precipitated by pouring the reaction mixture into hexane. Fig. 1 (a) shows the IR spectrum of the poly(*N*-carboxyanhydride) α-(4-isocyanatobenzoyl)-ω-hydroxypoly(oxycarbonylimino-1,4-phenylenecarbonyl) (**5c**) obtained from the reaction of **1c** with **2**. It shows two characteristic absorption bands of mixed anhydride at 1700 and 1780 cm^{-1}. In addition, two bands at 2275 cm^{-1} and at 2500—3000 cm^{-1} which were assigned to the isocyanate and carboxylic acid groups, respectively, were observed. Because of the relatively weak intensities of these additional bands, the isocyanate and carboxylic acid groups were considered to be two end-groups of the

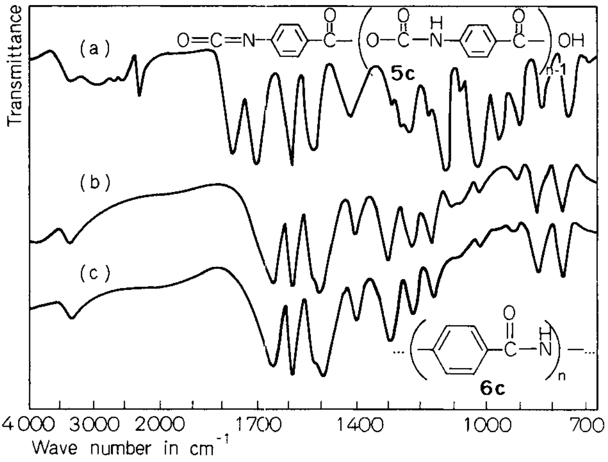


Fig. 1. IR spectra (KBr) of (a): poly(*N*-carboxyanhydride) **5c**, (b): polyamide **6c** from *p*-isocyanatobenzoyl chloride (**1c**) and dimethyl sulfoxide (**2**), (c): polyamide **6c** from **1c** and water after reacting at room temp. for 2h in *N*-methylpyrrolidone

poly(*N*-carboxyanhydride). These results were in agreement with those reported by Kricheldorf.

When the poly(*N*-carboxyanhydride) in solution was stirred at room temperature a slow evolution of carbon dioxide was observed but when poly(*N*-carboxyanhydride) was isolated as a solid it was stable for a long time when protected from moisture. In order to check the above proposed chemical structure of **5c** as described in Eq. (i) as well as to examine its thermal stability, its thermal analysis was carried out. The DTA and TGA curves of **5c** are shown in Fig. 2.

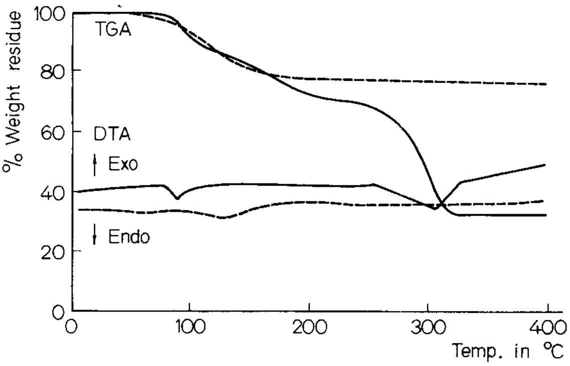


Fig. 2. DTA and TGA curves (heating rate: 10°C/min; in N_2) of (——) poly(*N*-carboxyanhydride) **5c**, and of (– – –) polyamide **6c**, obtained from **1c** and water after reacting at room temp. for 2h in *N*-methylpyrrolidone

Two endothermic peaks at 90 and 305°C appeared in the DTA curve. Corresponding with these two peaks, the abrupt weight decreases at around these temperatures were observed in the TGA curve. Mixed anhydrides obtained by the addition reaction of aromatic isocyanates and carboxylic acids are known to decompose rapidly at 70—100 °C[11]. Therefore, the first endothermic peak was to be due to the rupture of the anhydride linkage in the main chain of **5c**. The second peak was considered to be due to the elimination of carbon dioxide from the anhydride group which is produced by reaction of the isocyanate and carboxylic acid groups at the two ends.

The yields of poly(*N*-carboxyanhydride)s derived from other isocyanatocarboxylic acid chlorides are listed in Tab. 3 (Exp. Part).

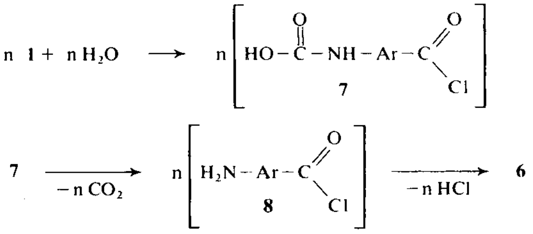
Based on the thermal results described above, we attempted to synthesize polyamides by heating the resulting poly(*N*-carboxyanhydride)s in the solid state. After slowly heating of **5c** up to about 270 °C for 4 h, the polyamide **6c** was obtained as demonstrated in the IR spectrum shown in Fig. 1 (b). All absorption bands characteristic of the poly(*N*-carboxyanhydride) **5c** disappeared completely and a band at 1650 cm^{-1} appeared which was assigned to the amide group. The yields and viscosities of the polyamides obtained by this method are shown in Tab. 3 (Exp. Part).

It has been reported that amide compounds can be obtained easily by heating isocyanates and carboxylic acids in an inert organic solvent[12]. We tried to produce polyamides by mixing isocyanatocarboxylic acid chlorides and **2** at low temperature and then heating the solution at elevated temperatures in an aprotic organic solvent such as *N*-methylpyrrolidone (NMP). Although a violent evolution of carbon dioxide was observed at around 110 °C, there was no polymer precipitated when the reaction mixture was poured into acetone or methanol. In this case, some side reaction accompanied with the evolution of carbon dioxide would have occurred. Furthermore, when poly(*N*-carboxyanhydride) obtained from the reaction in ether was heated in NMP at elevated temperatures there was also no polymer produced.

Reaction with water

It has been reported that water reacts with isocyanates to produce amines and/or ureas depending on the chemical structures of the starting isocyanates and on the substituents in the case of aromatic isocyanates[13]. It is known that in case of electron-withdrawing substituents the amine derivatives are obtained in high yields from aromatic isocyanates and water. Recently, we found that ethanol and phenol reacted preferentially with the isocyanate group of **1c** to yield urethane derivatives[3–6]. Considering the similarity of water with ethanol or phenol as nucleophilic reagents toward the isocyanate group of the isocyanatocarboxylic acid chloride and the electron-negativity of the acid chloride group as substituent, aromatic aminocarboxylic acid chlorides are expected to be produced from the reaction between isocyanatocarboxylic acid chlorides and water. Aromatic aminocarboxylic acid chlorides which are obtained in situ by dissolving aminocarboxylic acid chloride hydrochlorides in basic organic solvents such as pyridine or by reacting sulphinylaminocarboxylic acid chlorides with stoichiometrical quantities of water in polar organic solvents are suitable for the synthesis of aromatic polyamides of high molecular weight[14,15]. From these considerations, an attempt of the synthesis of aromatic polyamides from isocyanatocarboxylic acid chlorides and water was carried out.

In order to obtain polyamides of high molecular weight and definite structure, it is desirable that water reacts preferentially with the isocyanate group and the hydrolysis of the acid chloride group must be kept at the minimum level. On determining the optimum reaction temperature, it was found that the temperature between −15 °C and 0 °C was suitable for the reaction. At this temperature range, no carbon dioxide was observed when a stoichiometrical quantity of water in a pertinent solvent was dropped to a solution of the isocyanatocarboxylic acid chloride in the same solvent. The evolution of carbon dioxide was observed about 1 h after the addition of water. The evolution began violently when the temperature was raised to room temperature. The rapid evolution of carbon dioxide at room temperature was thought to be due to the decomposition of the carbamic acid resulted from the addition of water to the isocyanate group of the isocyanatocarboxylic acid chloride as shown in Eq. (ii).

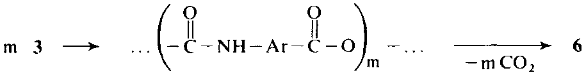


$$n\,\mathbf{1} + n\,H_2O \longrightarrow n\left[HO-\overset{\displaystyle O}{\overset{\|}{C}}-NH-Ar-C\begin{smallmatrix}\diagup\!\!\diagup O\\ \diagdown Cl\end{smallmatrix}\right]_{\mathbf{7}} \qquad \text{(ii)}$$

$$\mathbf{7} \xrightarrow[-n\,CO_2]{} n\left[H_2N-Ar-C\begin{smallmatrix}\diagup\!\!\diagup O\\ \diagdown Cl\end{smallmatrix}\right]_{\mathbf{8}} \xrightarrow[-n\,HCl]{} \mathbf{6}$$

The viscosity of the solution was increased gradually and in case of **1b** and **1c**, the polymers precipitated out within about 10 min after the reaction began. After about 2 h, the evolution of carbon dioxide ceased. Because the hydrolysis of the acid chloride could not be avoided under these reaction conditions, a mixed anhydride similar to that resulted from the reaction between **2** and isocyanatocarboxylic acid chlorides might also be produced in this reaction. Heating, therefore, was applied to achieve the completion of evolution of carbon dioxide.

$$\mathrm{m}\ \mathbf{1} + \mathrm{m}\,H_2O \xrightarrow[-\mathrm{m}\,HCl]{} \mathrm{m}\ \mathbf{3}$$



$$\mathrm{m}\ \mathbf{3} \longrightarrow \underset{\mathbf{9}}{\ldots\left(-\overset{O}{\overset{\|}{C}}-NH-Ar-\overset{O}{\overset{\|}{C}}-O\right)_m-\ldots} \xrightarrow[-\mathrm{m}\,CO_2]{} \mathbf{6} \tag{iii}$$

In order to determine the proportion of the reactions (ii) and (iii), the quantitative analysis of carbon dioxide evolved was carried out in NMP. As indicated in Fig. 3, about 90% of theoretical amount of carbon dioxide was evolved within 1 h after adding water to **1c** or *p*-(4-isocyanatophenyloxy)benzoyl chloride (**1d**) at 25 °C. On the other hand, the evolution of carbon dioxide in the case of the reaction of **1c** and **2** was slow. Considering the similarity of the reactions (i) and (iii), the hydrolysis of the acid chloride in the case of the reaction with water was relatively small. From this result, it may be concluded that water reacts preferentially with the isocyanate group of isocyanatocarboxylic acid chlorides to yield unstable carbamic acid derivatives (**7**) followed by the elimination of carbon dioxide to give aminocarboxylic acid chlorides (**8**). Polyamides **6** are then produced by intermolecular elimination of hydrochloric acid. This reaction path was checked by the IR spectrum and the thermal analysis of the product resulting from **1c** and water. The product was obtained by pouring the reaction mixture into dry ether after stirring at room temperature for 2 h. The IR spectrum shown in Fig. 1 (c)

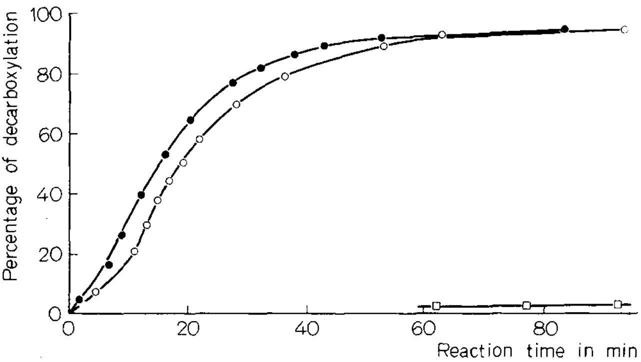


Fig. 3. Decarboxylation reaction of isocyanatocarboxylic acid chlorides with dimethyl sulfoxide and water at 25 °C in *N*-methylpyrrolidone; monomer concentration: 0,25 mol/l. (Before the reaction was started, the reaction mixture was stirred at 0 °C for 1 h). (●): **1d**+H_2O; (○): **1c**+H_2O; (□) **1c**+**2**

was identical with that of **6c**, which resulted from the reaction of **1c** with **2**. No absorption bands of a carboxylic acid group produced by hydrolysis of the acid chloride or the unreacted isocyanate or the mixed anhydride linkage were observed. The TGA curve shown in Fig. 2 exhibited a gradual weight decrease from 50 °C up to 200 °C. From the behaviour of the DTA curve, this weight decrease was considered to be principally due to the evaporation of NMP included in the polymer which could not be removed by drying in vacuo at room temperature. The generation of carbon dioxide from the reaction between the carboxylic acid resulted from the hydrolysis of the acid chloride and the unreacted isocyanate group might also be contained in this weight decrease.

From these results, the reaction between isocyanatocarboxylic acid chlorides and water might proceed via two paths as described in Eq. (ii) and (iii), but reaction (ii) was considered to be the principal one.

The reaction of isocyanatocarboxylic acid chlorides and water to produce polyamides was carried out in various solvents. The results are summarized in Tab. 1.

Tab. 1. Aromatic polyamides from isocyanatocarboxylic acid chlorides and water

Polyamide	Solvent[a]	% Yield	$\frac{10^{-2}\cdot\eta_{\mathrm{inh}}}{\mathrm{cm^3\,g^{-1}}}$[b]
6b	HMPT	99	0,19
	NMP	92	0,15
6c	HMPT	100	0,31
	NMP	95	0,18
	DMAc	91	0,12
6d	HMPT	100	0,34
	NMP	98	0,35
	DMAc	89	0,12
6e	HMPT	77	0,08[c]
6f	HMPT	91	0,19[c]
	NMP	99	0,37[c]
6g	HMPT	94	0,16[c]
6h	HMPT	60	0,06[c]
6i	HMPT	58	0,05[c]

[a] HMPT = Hexamethyl phosphoric acid triamide, NMP = *N*-methylpyrrolidone, DMAc = Dimethylacetamide.

[b] Measured at a concentration of 0,5 g/100 cm³ of concentrated sulfuric acid at 30 °C.

[c] Measured at a concentration of 0,5 g/100 cm³ of NMP at 30 °C.

NMP and hexamethyl phosphoric acid triamide (HMPT) gave the best results. All the polyamides, except the polymers **6b**, **6c**, and **6d** obtained by this method were soluble in dimethylacetamide, NMP and HMPT. Polymers **6b**, **6c** and **6d** were soluble in these solvents containing 5% of lithium chloride and concentrated sulfuric acid. Polymers **6c** and **6d** having inherent viscosities $>30\,cm^3\,g^{-1}$ gave brittle films and **6f** gave a flexible film when a polymer solution in NMP or HMPT was casted.

Experimental Part

All solvents were purified by the usual method. Ether and hexane were refluxed over sodium wire and distilled. Dimethylacetamide, *N*-methylpyrrolidone, hexamethyl phosphoric acid triamide and dimethyl sulfoxide were distilled i. vac. over calcium hydride.

The quantitative analysis of carbon dioxide evolved was performed according to the procedure of Patchornik and Shalitin[16]. The amino acids containing an ether linkage were synthesized according to the method of Lorenz and Nischk[15].

Aromatic isocyanatocarboxylic acid chlorides: They were prepared by treating the corresponding amino acids with phosgene and phosphorus pentachloride as previously described[7]. The preparation of *p*-(4-isocyanatophenyloxy)benzoyl chloride (**1d**) is described as a typical example:

To a mixture of 37 g (0,16 mol) of finely ground *p*-(4-aminophenyloxy)benzoic acid in 400 cm^3 of dioxane, 140 g (1,40 mol) of liquid phosgene was added with stirring at room temp.

After 2 h, the clear solution obtained by adding 33,5 g (0,16 mol) of powdered phosphorus pentachloride was allowed to stand at room temp. for ca. 15 h. Concentration of the solution i. vac. followed by distillation gave 30 g (69%) **1d**; bp_3 181 °C; mp 66—67 °C, with evolution of hydrogen chloride.

The yields, elemental analyses and phys. properties of the prepared isocyanatocarboxylic acid chlorides are summarized in Tab. 2.

Polymerization

Polyamide **6c** *from p-isocyanatobenzoyl chloride* (**1c**) *and dimethyl sulfoxide:* To a solution of 1,815 g (0,01 mol) of *p*-isocyanatobenzoyl chloride (**1c**) in 20 cm^3 of ether, a solution of 0,785 g (0,01 mol) of DMSO in 20 cm^3 of ether was added dropwise over a period of 30 min at 0—5 °C with stirring. After 2 h, the reaction mixture was stirred at room temp. for ca. 15 h. It was poured into hexane and the precipitated solid was filtered, washed with hexane and dried i. vac. over phosphorus pentoxide. 0,978 g (60%) of poly(*N*-carboxyanhydride) (**5c**) was obtained.

This product was then charged into a one-necked flask and heated slowly up to the temp. of 270 °C over a period of 4 h in a thin stream of dry nitrogen. 0,585 g (82%) of a yellow polyamide **6c** was obtained. $\eta_{inh} = 42\,cm^3\,g^{-1}$ (0,5% H_2SO_4, 30 °C).

Tab. 2. Aromatic isocyanatocarboxylic acid chlorides

Isocyanatocarboxylic acid chloride	% Yield	bp in °C (Torr) [mp in °C]	Formula (Mol. Weight)	Elemental analysis Calc. (Found) C	H	N
2-Isocyanatobenzoyl chloride (**1a**)	90	100(4)[a] [32]	$C_8H_4ClNO_2$ (181,5)			
3-Isocyanatobenzoyl chloride (**1b**)	90	100(3)[b]	$C_8H_4ClNO_2$ (181,5)			
4-Isocyanatobenzoyl chloride (**1c**)	92	106(3)[c] [36—37]	$C_8H_4ClNO_2$ (181,5)			
p-(4-Isocyanatophenyloxy)benzoyl chloride (**1d**)	69	181(3) [66—67]	$C_{14}H_8ClNO_3$ (273,5)	61,43 (61,72	2,92 2,90	5,12 5,24)
m-(4-Isocyanatophenyloxy) benzoyl chloride (**1e**)	38	186(4)	$C_{14}H_8ClNO_3$ (273,5)	61,43 (61,24	2,92 2,85	5,12 4,70)
p-(2-Chloro-4-isocyanato-phenyloxy)benzoyl chloride (**1f**)	63	203(3) [71—73]	$C_{14}H_7Cl_2NO_3$ (308,0)	54,55 (53,90	2,27 2,42	4,54 4,40)
m-(2-Chloro-4-isocyanato-phenyloxy)benzoyl chloride (**1g**)	38	193—194(3)	$C_{14}H_7Cl_2NO_3$ (308,0)	54,55 (54,26	2,27 2,41	4,54 4,30)
p-(2-Isocyanatophenyloxy)-benzoyl chloride (**1h**)	62	174—176(3)	$C_{14}H_8ClNO_3$ (273,5)	61,43 (61,11	2,92 2,63	5,12 5,16)
4-Chloro-3-isocyanatobenzoyl chloride (**1i**)	93	110(3)	$C_8H_3Cl_2NO_2$ (216,0)	44,44 (44,38	1,39 1,62	6,48 6,75)

[a] Lit.[7]: bp_6 105°C; mp 32°C.

[b] Lit.[7]: bp_3 100°C.

[c] Lit.[7]: bp_1 95—96°C; mp 36—37°C.

Tab. 3. Aromatic poly(*N*-carboxyanhydride)s and aromatic polyamides from isocyanatocarboxylic acid chlorides (**1b**—**g**) and dimethyl sulfoxide

α-(4-Isocyanatobenzoyl)- -ω-hydroxypoly-[a]	% Yield	Poly[imino-[a] carbonyl-	% Yield[b]	$10^{-2}\cdot\eta_{\text{inh}}/\text{cm}^3\,\text{g}^{-1}$[c]
-(oxycarbonylimino-1,3-phenylenecarbonyl) (**5b**)	65	-1,3-phenylene] (**6b**)	94	0,23
-(oxycarbonylimino-1,4-phenylenecarbonyl) (**5c**)	60	-1,4-phenylene] (**6c**)	82	0,42
-(oxycarbonylimino-1,4-phenyleneoxy-1,4-phenylenecarbonyl) (**5d**)	61	-1,4-phenyleneoxy-1,4-phenylene] (**6d**)	99	0,14
-(oxycarbonylimino-1,4-phenyleneoxy-1,3-phenylenecarbonyl) (**5e**)	20	-1,3-phenyleneoxy--1,4-phenylene] (**6e**)	85	0,11[d]
-(oxycarbonylimino-(3-chloro-1,4-phenyleneoxy)-1,4-phenylenecarbonyl) (**5f**)	57	-1,4-phenyleneoxy-(3-chloro-1,4-phenylene)] (**6f**)	92	0,20[d]
-(oxycarbonylimino-(3-chloro-1,4-phenyleneoxy)-1,3-phenylenecarbonyl) (**5g**)	25	-1,3-phenyleneoxy-(3-chloro-1,4-phenylene)] (**6g**)	—	—

[a] Nomenclature s. IUPAC Inform. Bulletin No. 29 (1972).

[b] Based on poly(*N*-carboxyanhydride)s **5b**—**g**.

[c] Measured at a concentration of 0,5 g/100 cm³ of conc. sulfuric acid at 30 °C.

[d] Measured at a concentration of 0,5 g/100 cm³ of *N*-methylpyrrolidone at 30 °C.

$(C_7H_5NO)_n$ $(119,0)_n$ Calc. C 70,58 H 4,23 N 11,76
Found C 68,93 H 4,17 N 10,70

Yield of other poly(*N*-carboxyanhydride)s and polyamides there of are summarized in Tab. 3.

Polyamide **6d** *from* **1d** *and water:* To a solution of 2,735 g (0,01 mol) of **1d** in 15 cm^3 of hexamethyl phosphoric acid triamide (HMPT), a solution of 0,180 g (0,01 mol) of water in 15 cm^3 of HMPT was added dropwise over a period of 45 min at 0°C with stirring. After 1 h at 0—5°C, the reaction mixture was stirred for 2 h at room temp. The viscous solution was then heated slowly to 150°C for 3 h. The reaction mixture was allowed to cool to room temp. and was then poured into methanol. The solid was filtered, washed thoroughly with methanol and dried i. vac. at 80°C. Yield: 2,10 g (100%). $\eta_{inh} = 34\ cm^3\ g^{-1}$ (0,5% in H_2SO_4, 30°C).

$(C_{13}H_9NO_2)_n$ $(211,0)_n$ Calc. C 73,92 H 4,30 N 6,63
Found C 70,47 H 4,39 N 6,88

Yields and values of η_{inh} of other polyamides are summarized in Tab. 1.

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