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Synthesis of Aromatic Polyamides from Reactive *N,N'*-Isophthaloyldi(thiolactam)s and Aromatic Diamines under Mild Conditions

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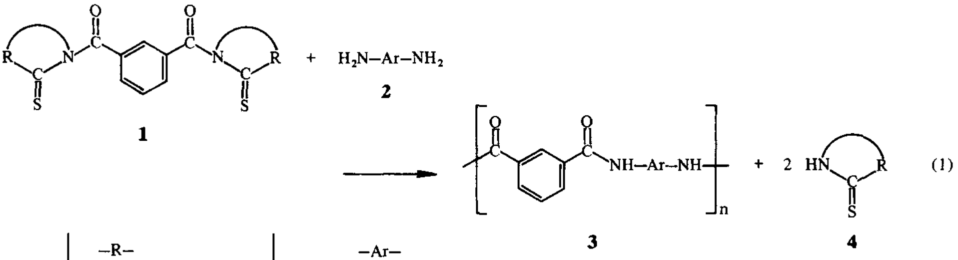
SUMMARY:

Solution condensation polymerization of new reactive diamides, *N,N'-isophthaloyldipyrrolidine-2-thione* (**1a**) and *N,N'*-isophthaloyldiperhydroazepine-2-thione (**1b**), with aromatic diamines **2** in 1-methyl-2-pyrrolidone at room temperature or above leads to polyamides **3** with moderate molecular weights. The ease of aminolysis of these diamides is discussed in relation to the good leaving nature of the thiolactam moieties and an intramolecular general base catalysis. The condensation polymerization is strongly catalyzed by 1-hydroxybenzotriazole giving aromatic polyamides with higher inherent viscosities up to 0,9 $dl \cdot g^{-1}$.

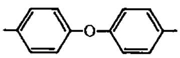
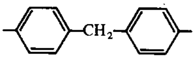
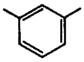
Introduction

In recent years our interest has been directed particularly to polyamide syntheses from reactive dicarboxylic acid derivatives and diamines under mild conditions[1-7]. On a similar standpoint, Ogata et al.[8] reported the use of *N,N'*-diacyldilactams as one of the polyamide-forming monomers. It is expected that *N,N'*-diacyldi(thiolactam)s are more reactive toward amines than *N,N'*-diacyldilactams, because of the higher acidic nature of the leaving groups of thiolactams in comparison with those of the corresponding lactams. This article reports on the syntheses of aromatic polyamides from reactive *N,N'*-isophthaloyldi(thiolactam)s (**1**) and aromatic diamines (**2**) under mild conditions.



1 **2** **3** **4** (1)

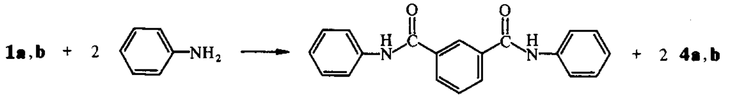
	–R–
1a,4a	$-(CH_2)_3-$
1b,4b	$-(CH_2)_5-$

	–Ar–
2a,3a	
2b,3b	
2c,3c	

Results and Discussion

Two new reactive diamides, *N,N'*-isophthaloyldipyrrolidine-2-thione (**1a**) and *N,N'*-isophthaloyldiperhydroazepine-2-thione (**1b**), were synthesized by condensation of isophthaloyl dichloride with the corresponding thiolactams, 2-pyrrolidinethione (**4a**) and perhydroazepine-2-thione (**4b**), in THF in the presence of triethylamine as an acid acceptor.

A study of the model compounds was performed before the polymer syntheses, to obtain information regarding the reactivity of these diamides toward amines. The reactions of **1a** and **1b** with aniline (Eq. (2)) proceeded readily in 1-methyl-2-pyrrolidone (NMP) even at room temperature giving isophthalanilide (**5**) in excellent yields (Tab. 1).



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(2)

Tab. 1. Model reaction of diamides **1a** and **1b** with aniline leading to isophthalanilide (**5**)

Diamide	Reaction conditions[a]		Product yield in %
	temp. in °C	time in h	
1a	20	48	88
1a	70	24	92
1b	20	48	90
1b	70	7	88

[a] Reaction was carried out with 2,5 mmol of diamide and 5,0 mmol of aniline in 5 ml of 1-methyl-2-pyrrolidone.

However, the diamides reacted with benzylamine with evolution of hydrogen sulfide, producing only low yields of *N,N'*-dibenzylisophthalamide.

In accordance with the model reaction, the condensation polymerization of the reactive diamides **1** with aromatic diamines **2** (Eq. (1)) was carried out in a polar aprotic solvent like NMP or *N,N*-dimethylacetamide (DMA). The results of the polymerization are summarized in Tab. 2. Aromatic polyamides of moderate molecular weights were readily obtained from diamide **1b** and aromatic diamines **2** in NMP at 70 °C or above. When **1a** was used as diamide component, the color of the polymerization mixture changed from pale yellow to deep purple, which resulted in the formation of a polyamide with lower inherent viscosity, probably due to some side reactions.

It has been reported that the condensation polymerization of *N,N'*-adipoyldilactams with aromatic diamines in DMSO at 60 °C did not afford any polyamides[8]. The higher reactivity of *N,N'*-diacyldi(thiolactam)s like **1** than that of *N,N'*-diacyldilactams can be explained by the fact that thiolactams are good leaving groups, being more acidic than the corresponding lactams, and with an intramolecular general base catalysis as shown in Eq. (3).

It has previously been shown from our laboratory[9] that the condensation polymerization of some reactive diesters with aromatic diamines was effectively catalyzed by 1-hydroxybenzo-

Tab. 2. Conditions and results of the condensation polymerizations of diamides **1** with aromatic diamines **2** leading to polyamides **3**

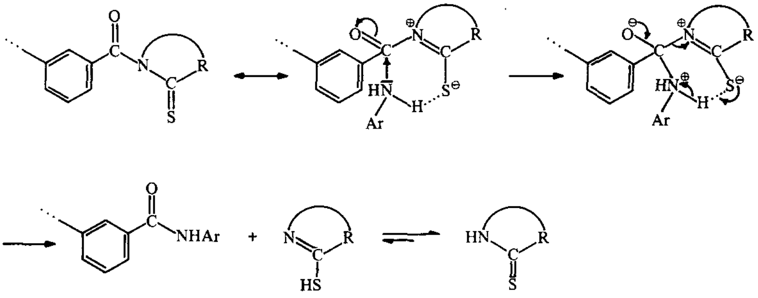
Diamide	Diamine	Reaction conditions[a]			Polymer	
		solvent	temp. in °C	time in day	yield in %	$\frac{\eta_{inh}{}^{b)}}{dl\cdot g^{-1}}$
1a	**2a**	NMP	20	1	99	0,28
1a	**2a**	NMP	40	1	99	0,27
1a	**2a**	NMP	70	1	99	0,23
1a	**2a**	DMA	70	1	99	0,24
1b	**2a**	NMP	20	3	96	0,21
1b	**2a**	NMP	70	1	99	0,41
1b	**2a**	NMP	100	1	99	0,44
1b	**2a**	NMP[c]	70	1	99	0,82
1b	**2a**	DMA[c]	70	1	99	0,56
1b	**2b**	NMP[d]	70	1	99	0,41
1b	**2c**	NMP	70	1	98	0,29
1b	**2c**	NMP[c]	70	1	99	0,48

[a] Polymerization was carried out with 2,5 mmol of the diamide and 2,5 mmol of the diamine in 5 ml of the solvent. NMP: 1-methyl-2-pyrrolidone; DMA: *N,N*-dimethylacetamide.

[b] Measured at a concentration of 0,5 g·dl⁻¹ in conc. sulfuric acid at 30 °C.

[c] 1-Hydroxybenzotriazole (HOBt, 0,37 mmol) was added as catalyst.

[d] Lithium chloride (5 mmol) was added.



(3)

triazole (HOBt) yielding high molecular weight polyamides. In the present study, it was also found that the condensation polymerization of **1** with **2** is strongly accelerated by using HOBt as catalyst. Fig. 1 shows the course of the condensation polymerization in NMP at 70 °C in terms of the inherent viscosity of the resulting polymer **3a**. In the case of the polymerization without using HOBt, it went essentially to completion in 15 h, whereas the condensation polymerization using the catalyst was almost complete in 5 h leading to a polyamide with a higher inherent viscosity. A catalytic amount of HOBt (around 20 mole-% based on the diamides) was sufficient to produce a high molecular weight polyamide (Tab. 3). A probable catalysis by HOBt in this condensation polymerization corresponds to the bifunctional, concerted, general acid-base mechanism described previously[9].

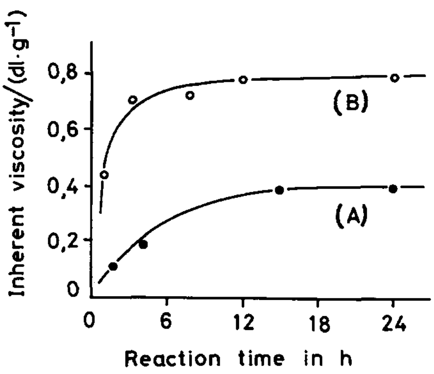


Fig. 1. Time-dependence of the inherent viscosity of the polymer **3a** formed in the condensation polymerization of **1b** with **2a** in 1-methyl-2-pyrrolidone at 70 °C. (A): In the absence of 1-hydroxybenzotriazole (HOBt), and (B): in the presence of HOBt as catalyst (15 mole-%)

Tab. 3. Results of the condensation polymerization of **1b** with **2a**[a] catalyzed by 1-hydroxybenzotriazole (HOBt)

Amount of HOBt in mole-%	Polyamide	
	yield in %	η_{inh}/dl·g^{-1} [b]
0,3	99	0,42
1,5	99	0,60
3	99	0,56
15	99	0,82
22	99	0,91
30	99	0,64

[a] Polymerization was carried out with 2,5 mmol of **1b** and 2,5 mmol of **2a** in 5 ml of 1-methyl-2-pyrrolidone at 70 °C for 1 day.

[b] Measured at a concentration of 0,5 g·dl^{-1} in conc. sulfuric acid at 30 °C.

Experimental Part

Materials

N,N'-Isophthaloyldipyrrolidine-2-thione (**1a**): 2-Pyrrolidinethione (**4a**) was prepared according to the procedure of Tafel and Lawaczeck[10] in 35% yield by the reaction of 2-pyrrolidone with phosphorus pentasulfide in refluxing xylene. Recrystallization from xylene provided white needles; m. p. 114–116 °C (Lit.[10]: m. p. 114–116 °C).

A solution of 10,2 g (0,05 mol) of isophthaloyl dichloride in 100 ml of THF was added dropwise to a stirred solution of 10,1 g (0,10 mol) of **4a** and 10,2 g (0,10 mol) of triethylamine in 200 ml of THF at 0–5 °C, and the mixture was further stirred at room temperature for 6 h. It was then poured into 1,5 l of water. A yellow precipitate formed was collected and dried. Yield of crude product: 15,0 g (90%). Recrystallization from ethyl acetate afforded yellow needles; m. p. 164–165 °C.

IR (KBr): 1680 cm^{-1} (vs; C=O).

$C_{16}H_{16}N_2O_2S_2$ (332,4)	Calc.	C 57,81	H 4,85	N 8,43
	Found	C 57,8	H 4,8	N 8,5

N,N'-Isophthaloyldiperhydroazepine-2-thione (**1b**): Perhydroazepine-2-thione (**4b**) was prepared by the method of Wirth[11] in 45% yield from perhydroazepin-2-one and phosphorus pentasulfide. Recrystallization from water gave white needles; m. p. 108–109 °C (Lit.[11]: m. p. 106–106,6 °C).

Diamide **1b** was synthesized by the reaction of isophthaloyl dichloride (6,09 g, 0,03 mol) with **4b** (7,75 g, 0,06 mol) in the presence of triethylamine (6,1 g, 0,06 mol) in THF. Yield of crude product: 10,9 g (93%). Recrystallization from acetone provided yellow needles; m. p. 152–153 °C.

IR (KBr): 1700 cm^{-1} (vs; C=O).

$C_{20}H_{24}N_2O_2S_2$ (388,5)	Calc.	C 61,83	H 6,23	N 7,21
	Found	C 61,6	H 6,2	N 7,0

Aromatic diamines: Bis(4-aminophenyl) ether (**2a**) and bis(4-aminophenyl)methane (**2b**), both of which were supplied by Sumitomo Chemical Co., were purified by recrystallization from THF and benzene, respectively. *m*-Phenylenediamine (**2c**) was recrystallized from ether before use.

Solvents and reagents: 1-Methyl-2-pyrrolidone (NMP; provided by Mitsubishi Chemical Industries Ltd.) and *N,N*-dimethylacetamide (DMA) were distilled i. vac. and stored over 4 Å molecular sieves. 1-Hydroxybenzotriazole (HOBt) was prepared by the reported procedure[3]. Aniline and other reagents were obtained commercially and used as received.

Model reaction

Isophthalanilide from **1a** *and aniline:* A solution of 0,831 g (2,5 mmol) of **1a** and 0,47 g (5 mmol) of aniline in 5 ml of NMP was stirred at 20 °C for 48 h. The product was isolated by precipitation with 500 ml of water. Yield: 0,696 g (88%); m. p. 291–293 °C (Lit.[3]: m. p. 297–299 °C).

IR (KBr): 3250 (m; N—H) and 1640 cm^{-1} (vs; C=O).

Polymerizations

A typical example of a condensation polymerization is given below.

Polyamide **3a** *from* **1b** *and* **2a**: To a solution of 0,500 g (2,5 mmol) of **2a** and 50 mg (0,37 mmol) of HOBt in 5 ml of NMP, 0,971 g (2,5 mmol) of **1b** was added, and the resulting solution was stirred at 70 °C for 24 h. The polymer was isolated by pouring the solution into 500 ml of water. It was filtered, washed thoroughly with hot methanol, and dried. Yield: 0,817 g (99%). The polymer had an inherent viscosity of 0,82 dl·g^{-1} in conc. sulfuric acid, measured at a concentration of 0,5 g·dl^{-1} at 30 °C.

IR (film): 3280 (m; N—H) and 1650 cm^{-1} (vs; C=O).

$(C_{20}H_{14}N_2O_3)_n$ $(330,3)_n$	Calc.	C 72,72	H 4,27	N 8,48
	Found	C 72,4	H 4,6	N 8,7

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