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Synthesis of Polyamides from Active Diacyl Derivatives of 2-Mercaptobenzoxazole and Diamines under Mild Conditions

Mitsuru Ueda,* Kouji Seki, and Yoshio Imai

Department of Polymer Chemistry, Faculty of Engineering, Yamagata University, Yonezawa, Yamagata 992, Japan. *Received June 18, 1981*

ABSTRACT: New active dithioesters and diamides derived from 2-mercaptobenzoxazole were prepared for use in polyamide synthesis. The active thioester and amide reacted readily with amines to give excellent yields of the corresponding amides. The high reactivity of these active thioesters and amides is discussed in relation to the electron-withdrawing effect on the leaving group and intramolecular general-base catalysis. Solution polycondensation of new active dithioesters and amides with aliphatic and aromatic diamines proceeded rapidly under mild conditions to produce polyamides with inherent viscosities up to 1.6 dL/g.

Introduction

The polycondensation of diamines with active dicarboxylic acid derivatives to form polyamides under mild conditions has received considerable attention.[1,2] On the other hand, it is recognized that the increasing reactivity order of carboxylic acid derivatives toward nucleophiles may be roughly correlated with the order of increasing stability of the leaving group anions, that is, pK_a of the leaving group.

From this point of view, we have exploited a series of good leaving groups for the syntheses of active esters and amides and demonstrated that the active ester and amide methods are useful in the preparation of high molecular weight polyamides under mild conditions.[3]

In our foregoing paper,[3e] we described the synthesis of polyamides from active 2-benzothiazolyl dithioesters and diamines. This prompted us to study analogous dithioesters derived from 2-mercaptobenzoxazole, which was expected to be a good leaving group of carboxylic acid derivatives. We have found that the *N*- or *S*-acyl products from the acylation of 2-mercaptobenzoxazole reacted very rapidly with various amines to give excellent yields of the corresponding amides.

This article describes a successful synthesis of polyamides through active dithioesters or diamides obtained from acylation of 2-mercaptobenzoxazole.

Experimental Section

Materials. Solvents and Diamines. *N*-Methyl-2-pyrrolidone (NMP) (supplied by Mitsubishi Chemical Industries Ltd.) and hexamethylphosphoramide (HMPA) were purified by vacuum distillation and stored over 4-Å molecular sieves. Reagent grade hexamethylenediamine (HMDA) was used as received. Bis(4-aminophenyl)methane (MDA) and bis(4-aminophenyl) ether (ODA) (supplied by Sumitomo Chemical Co.) were purified by recrystallization from benzene and tetrahydrofuran (THF), respectively. Other reagents, including 2-mercaptobenzoxazole (MB) and solvents, were obtained commerically and used as received.

***S*-(2-Benzoxazolyl) Thiobenzoate (1).** To a cold solution (−30 °C) of MB (15.1 g, 0.1 mol) and triethylamine (TEA, 14 mL) in THF (300 mL) was added dropwise a solution of benzoyl chloride (14 g, 0.1 mol) in THF (30 mL). The solution was stirred at a temperature lower than −20 °C for 20 min and poured into ice water (100 mL). The precipitate was collected by filtration and dried in vacuo; yield 23 g (90%). Recrystallization from cyclohexane afforded pale yellow needles, mp 83–85 °C. The IR (KBr) spectrum showed an absorption at 1695 cm^{-1} (C=O). Anal. Calcd for $C_{14}H_9NO_2S$: C, 65.87; H, 3.55; N, 5.48. Found: C, 66.0; H, 3.8; N, 5.5.

3-Benzoylbenzoxazoline-2-thione (2). Compound **2** was prepared as described above using acetone as a solvent at 15 °C for 30 min; yield 93%. Recrystallization from ethanol gave yellow needles, mp 117–118 °C (lit.[4] mp 117 °C). The IR (KBr) spectrum showed absorptions at 1695 (C=O) and 1340 cm^{-1} (C=S).

***S,S*′-Bis(2-benzoxazolyl) Dithioisophthalate (3).** A solution of MB (4.0 g, 0.03 mol) and TEA (4.2 mL, 0.03 mol) in THF (80 mL) was cooled in a dry ice–acetone bath. To this solution was added at −30 °C with stirring a solution of isophthaloyl chloride (3.0 g, 0.015 mol) in THF (20 mL). After 20 min of stirring at the above temperature the mixture was poured into water (300 mL). The precipitate formed was collected by filtration, washed with water, and dried in vacuo over P_2O_5. It was thoroughly washed with acetone to give 23 g (77%) of white powder, mp 129–131 °C. The IR (KBr) spectrum showed an absorption at 1700 cm^{-1} (C=O). Anal. Calcd for $C_{22}H_{12}O_4N_2S_2$: C, 61.10; H, 2.80; N, 6.48. Found: C, 61.1; H, 3.0; N, 6.6.

***S,S*′-Bis(2-benzoxazolyl) Dithioadipate (4).** Compound **4** was prepared from adipoyl chloride and MB as previously described. The crude product, which was washed with acetone, was obtained in a yield of 73%. The temperature of thermal rearrangement was 115 °C (by DTA). The IR spectrum (KBr) showed an absorption at 1720 cm^{-1} (C=O). Anal. Calcd for $C_{20}H_{16}N_2O_4S_2$: C, 58.24; H, 3.91; N, 6.79. Found: C, 58.2; H, 4.1; N, 6.8.

***N,N*′-Isophthaloylbis[benzoxazoline-2-thione] (5).** Compound **5** was prepared from isophthaloyl chloride and MB in acetone at room temperature as previously described. The yield was 70%. It was recrystallized from benzene to give yellow needles, mp 201–202 °C. The IR spectrum showed absorptions at 1720 (C=O) and 1380 cm^{-1} (C=S). Anal. Calcd for $C_{22}H_{12}N_2O_4S_2$: C, 61.10; H, 2.80; N, 6.48. Found: C, 61.0; H, 3.0; N, 6.6.

***N,N*′-Adipoylbis[benzoxazoline-2-thione] (6).** Compound **6** was prepared from adipoyl chloride and MB as previously described. The yield was 85%. It was recrystallized from toluene to give white leaflets, mp 242–244 °C. The IR spectrum showed

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Table I
Model Reaction of Active Thioester 1 and Amide 2 with Amines[a]

active acyl derivative	amine	solvent	product	
			type	yield, %
1	benzylamine	THF	7	81
1	benzylamine	NMP	7	83
1	aniline	THF	8	93
1	aniline	NMP	8	95
2	benzylamine	THF	7	82
2	benzylamine	NMP	7	84
2	aniline	THF	8	92
2	aniline	NMP	8	96

[a] Reaction was carried out with 2.5 mmol of each reactant in 5 mL of solvent for 10 min at 15 °C.

absorptions at 1725 (C=O) and 1340 cm^{-1} (C=S). Anal. Calcd for $C_{24}H_{16}N_2O_4S_2$: C, 58.24; H, 3.91; N, 6.79. Found: C, 58.5; H, 4.2; N, 6.6.

Model Reaction. *N*-Benzylbenzamide (7). To a solution of 1 (0.638 g, 2.5 mmol) in NMP (5 mL) was added benzylamine (0.27 mL). The solution was stirred at room temperature for 10 min and poured into 100 mL of 1% aqueous sodium carbonate. The precipitate formed was collected, washed with water, and dried. The yield was 0.440 g (83%); mp 105–106 °C (lit.[5] mp 105–106 °C).

Benzanilide (8). A solution of 2 (0.638 g, 2.5 mmol) and aniline (0.23 mL) in NMP (5 mL) was stirred at room temperature for 10 min. The product was isolated by pouring the solution into aqueous sodium carbonate. It weighed 0.473 g (96%); mp 163–164 °C (lit.[6] mp 165–166 °C).

Polymerization. Two typical examples of the polymerization follow.

Polyamide 9a from 3 and ODA. To a solution of ODA (0.250 g, 1.25 mmol) in NMP (3.2 mL) was added 3 (0.540 g, 1.25 mmol). The mixture was stirred at room temperature for 24 h. The resulting viscous solution was diluted with a small amount of NMP and poured into methanol (500 mL). The product was filtered, washed with methanol, and dried; yield 0.409 g (99%). The inherent viscosity of the polymer in concentrated sulfuric acid was 0.80 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. The IR spectrum (film) showed absorptions at 3280 (NH) and 1650 cm^{-1} (C=O). Anal. Calcd for $C_{20}H_{14}N_2O_3$: C, 72.72; H, 4.27; N, 8.48. Found: C, 72.6; H, 4.3; N, 8.4.

Polyamide 10a from 6 and ODA. A mixture of 6 (0.515 g, 1.25 mmol) and ODA (0.251 g, 1.25 mmol) in HMPA (3.2 mL) was stirred at room temperature for 24 h. The product was isolated by pouring the resulting solution into methanol (300 mL). After the product was thoroughly washed and dried, white polymer weighed 0.384 g (99%). The inherent viscosity was 1.0 dL/g (0.5 g/dL in concentrated sulfuric acid at 30 °C). The IR spectrum (film) exhibited absorptions at 3280 (NH) and 1650 cm^{-1} (C=O). Anal. Calcd for $C_{18}H_{18}N_2O_3$: C, 69.66; H, 5.85; N, 9.03. Found: C, 69.6; H, 5.8; N, 9.0.

Results and Discussion

Model Reaction. Acylation of MB, which may involve reaction at sulfur or nitrogen, has been reported earlier to give *N*-acyl derivatives only.[4,7,8] However, we have successfully synthesized the *S*-benzoyl derivative *S*-(2-benzoxazolyl) thiobenzoate (1) by reaction of benzoyl chloride with MB under carefully controlled reaction conditions. The structure of 1 was assigned on the basis of IR and elemental analysis. The IR spectrum exhibited a strong thioester carbonyl absorption at 1695 cm^{-1}, and no trace of a C=S stretching absorption was detected. Additional proof for the structure of 1 was obtained through the thermal rearrangement of 1 at 90 °C to the isomeric 3-benzoylbenzoxazoline-2-thione (2) quantitatively.

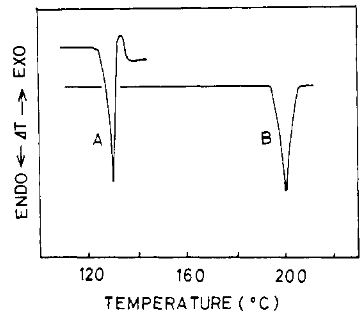
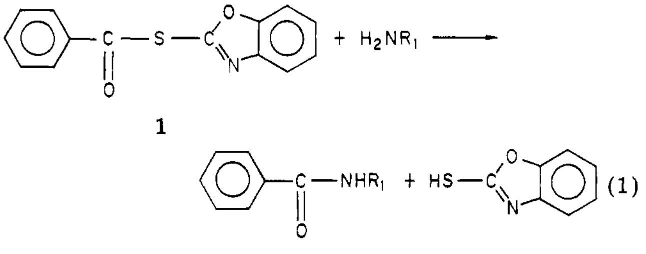


Figure 1. DTA curves for 3.

Hydrolysis and methanolysis of active amide 2, as discussed by Wagner and Leistner,[7,8] mainly occurred at the exocyclic carbonyl group rather than the endo cyclic carbonyl group to give benzoic acid and methyl benzoate, respectively. However, the reactivity toward amines has not been reported. In the present study, the aminolysis of active thioester 1 and amide 2 under mild conditions was studied to demonstrate the feasibility of the reaction for polymer formation.

The reactions with amines were carried out in THF and NMP at room temperature (eq 1 and 2). The results are



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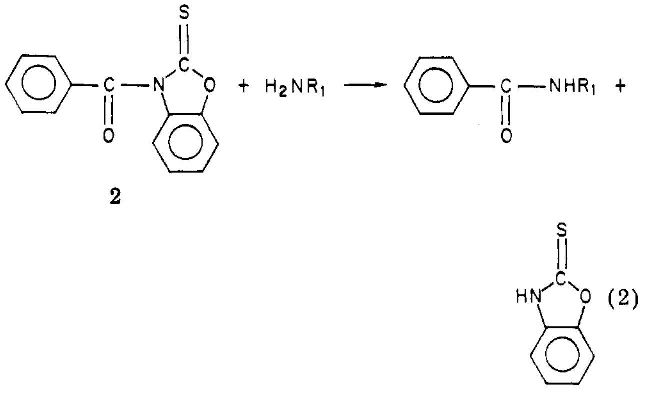
(1)



2

(2)

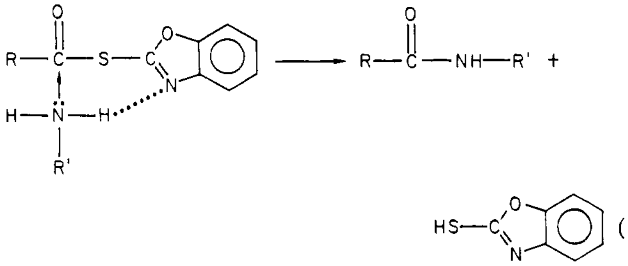
$R_1 = CH_2C_6H_5$ (7) or C_6H_5 (8)

summarized in Table I. Active thioester 1 and amide 2 reacted very rapidly with both aliphatic and aromatic amines. The reactions were almost complete within 10 min, affording excellent yields of the corresponding benzamides. Reactivity of active ester 1 is similar to that of *S*-(2-benzothiazolyl) thiobenzoate, which is one of the most powerful active esters.[3e] On the other hand, active amide 2 is more reactive toward amines than 3-benzoylbenzthiazoline-2-one reported earlier.[3c] This difference in reactivity seems to be ascribable to the different contributions of the pseudoaromatic character.

The high reactivity of active thioester 1 is associated with the pseudoaromatic character of benzoxazole and electron withdrawing by the heterocyclic ring. Meanwhile the high reactivity of active amide 2 is associated with the involvement of the amide nitrogen electron pair in the pseudoaromaticity of the ring; the result is polarization toward nitrogen in the N–(COR) bond. Furthermore, their enhanced aminolysis may be explained by anchimeric assistance (intramolecular general-base catalysis).

8-Hydroxyquinoline esters,[9] catechol esters,[10] 2-mercaptopyridine esters,[11] 2-hydroxypyridine esters,[12] and

1-hydroxybenzotriazole esters,[13] a series of active esters having a similar structural feature, have been reported to undergo anchimerically assisted aminolysis. Therefore, the aminolysis of the active thioester and amide is presumed to proceed by a concerted mechanism, as shown in eq 3 and 4, respectively.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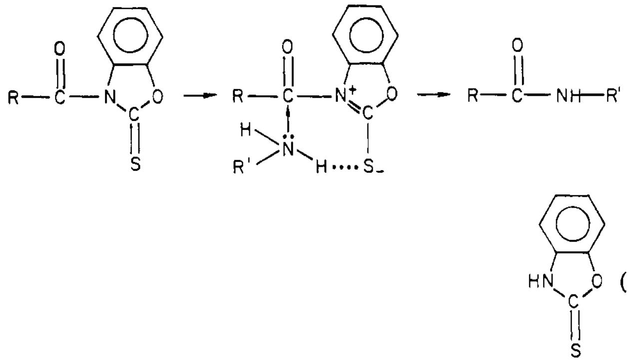
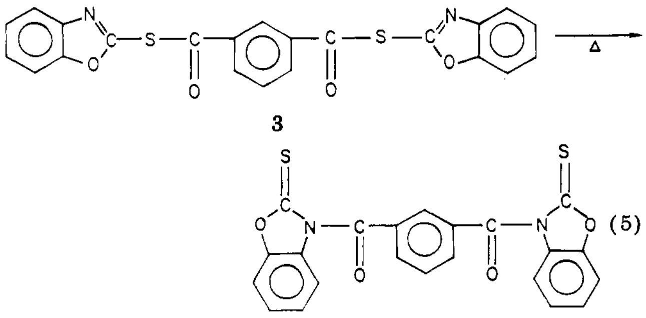

(4)

Monomer Syntheses. In the same manner as with the synthesis of active thioester 1, novel active dithioesters 3 and 4 were synthesized successfully by the reaction of the corresponding diacyl chlorides with MB in tetrahydrofuran at −30 °C in the presence of triethylamine as an acid acceptor. In a similar manner, monomers 5 and 6 were prepared in acetone at room temperature as novel active diamides. All new monomers prepared here were characterized by melting point, elemental analyses, and spectral properties.

Active thioester 1 was observed to undergo a thermal rearrangement at 90 °C to the isomeric active amide 2. Similar thermal rearrangement behavior was observed for the active dithioesters. A typical differential thermal analysis (DTA) is shown for active dithioester 3 in Figure 1. Active dithioester 3 exhibited a sharp exotherm at 130 °C and a endotherm at 135 °C, which reflect the melting point and thermal rearrangement of 3, respectively (curve A). After the sample was cooled, DTA analysis was carried out again. The DTA curve showed a sharp endotherm at 200 °C identical with that of the authentic active diamide 5 (curve B) (eq 5).


3

5

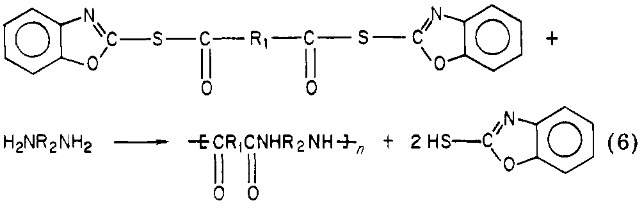
(5)

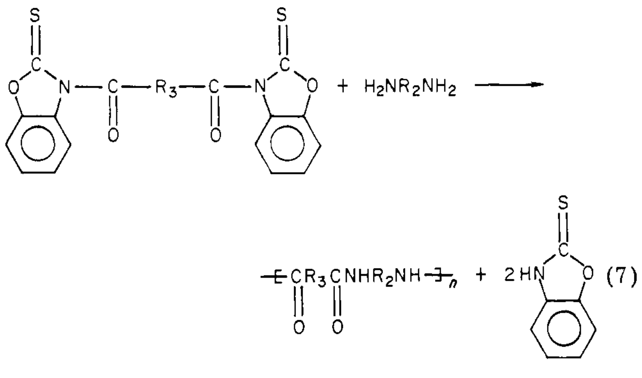
Polymer Synthesis. The polycondensations of the active dithioesters and diamides were carried out by the solution polycondensation technique with diamines that included hexamethylenediamine (HMDA), bis(4-aminophenyl)methane (MDA), and bis(4-aminophenyl)ether (ODA). The polar aprotic solvents NMP and HMPA were used as the polymerization media (eq 6 and 7).

Table II
Polycondensation of Active Dithioesters with Diamines

active dithioester	diamine	reaction conditions[a] solvent	time, days	polymer type	yield, %	η_{inh},[b] dL/g
3	ODA	NMP	1	**9a**	99	0.80
3	ODA	HMPA	1	**9a**	99	0.91
3	MDA	NMP	1	**9b**	99	0.63
3	MDA	HMPA	1	**9b**	98	0.40
3	HMDA	NMP	2	**9c**	76	0.37
3	HMDA	HMPA	1	**9c**	71	0.30
4	ODA	NMP	1	**10a**	99	0.73
4	ODA	HMPA	1	**10a**	98	0.84
4	MDA	NMP	1	**10b**	82	0.74
4	MDA	HMPA	1	**10b**	99	0.68
4	HMDA	NMP	1	**10c**	82	0.34
4	HMDA	HMPA	2	**10c**	93	0.44

[a] Polycondensation was carried out with 1.25 mmol of each monomer in 3 mL of solvent at 15 °C. [b] Measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 30 °C.


(6)


(7)

$R_1 = m\text{-}C_6H_4, -(CH_2)_4-$
$R_2 = -(CH_2)_6-, p\text{-}C_6H_4O\text{-}p\text{-}C_6H_4, p\text{-}C_6H_4CH_2\text{-}p\text{-}C_6H_4$
$R_3 = m\text{-}C_6H_4, -(CH_2)_4-$

The results of polycondensation of active dithioesters with diamines are summarized in Table II. Active dithioesters 3 and 4 reacted rapidly with diamines to produce polyamides. The rate of polycondensation of active dithioester 3 with ODA in NMP in terms of inherent viscosity of the resulting polyamides is given in Figure 2. The polycondensation proceeded very fast and was complete within 10 min in HMPA. Its rate is almost comparable to that of the polycondensation of diacyl chlorides with diamines. High molecular weight polyamides were produced from the aromatic diamines. The polycondensations of active dithioesters 3 and 4 with the aliphatic diamines gave low molecular weight polymers. Because of limited solubility of the resulting polymers the growing chains are terminated through precipitation.

Table III shows the results of polycondensation of active diamides 5 and 6 with diamines. The degree of polycon-

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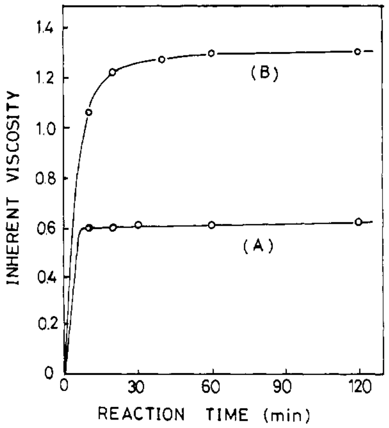

Figure 2. Polycondensation of **3** or **5** with ODA in NMP at 15 °C: (A) reaction of **3**; (B) reaction of **5**.

Table III
Polycondensation of Active Diamides with Diamines

active di-amide	diamine	reaction conditions[a] solvent	time, days	polymer type	yield, %	η_{inh},[b] dL/g
5	ODA	NMP	1	**9a**	99	1.5
5	ODA	HMPA	1	**9a**	99	1.6
5	MDA	NMP	1	**9b**	99	1.2
5	MDA	HMPA	2	**9b**	99	1.2
5	HMDA	NMP	2	**9c**	72	0.44
5	HMDA	HMPA	2	**9c**	95	0.71
6	ODA	NMP	2	**10a**	98	0.67
6	ODA	HMPA	2	**10a**	96	1.0
6	MDA	NMP	1	**10b**	99	0.62
6	MDA	HMPA	2	**10b**	94	0.78
6	HMDA	NMP	1	**10c**	92	0.58
6	HMDA	HMPA	2	**10c**	99	0.54

[a] Polycondensation was carried out with 1.25 mmol of each monomer in 3 mL of solvent at 15 °C. [b] Measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 30 °C.

densation of active diamide **5** with ODA in NMP at room temperature is shown in terms of the inherent viscosity in Figure 2. Surprisingly, polycondensation was almost complete within 30 min and gave polyamide with an inherent viscosity greater than 1.0 dL/g. Table III indicates that polyamides were produced in quantitative yields with inherent viscosities of 0.5–1.7 dL/g.

The polymers obtained were identified as polyamides by comparing their infrared spectra with those of the authentic polyamides. Elemental analyses of the polymers also supported the formation of polyamides.

As expected, new active diesters and diamides derived from MB showed outstanding reactivity toward diamines and produced high molecular weight polyamides under mild conditions.

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Adducts of Polyamides with Perfluoro Diacids

Shaul M. Aharoni* and Edel Wasserman

Corporate Research and Development, Allied Corporation, Morristown, New Jersey 07960.

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ABSTRACT: Perfluoro diacids combine with matched aliphatic or aromatic polyamides to form highly crystalline stoichiometric adducts. Formation is associated with an approximate equivalence between the lengths of the extended diacids and the repeat unit of the polymeric chain. The interaction between the polyamides and diacids appears to be by means of hydrogen bonds. A proposed model suggests that the adducts precipitate out of solution once a sufficient number of intermolecular bonds are formed for the adduct aggregate to surpass a critical size for precipitation. Viscosity data support this model. Fluorinated monoacids and unfluorinated diacids do not form complexes, while excess urea blocks the formation of adducts with perfluoro diacids. Linear oligomers of ϵ-caprolactam of DP $\simeq$ 25 and over combine with perfluoroglutaric acid to yield products similar to that obtained from nylon-6. Shorter linear oligomers did not form crystalline adducts.

Introduction

Synthetic macromolecules rarely interact stoichiometrically with small molecules to form ordered arrays.[1] In contrast, biological systems frequently exhibit specific inter- and intramolecular interactions, often involving hydrogen bonding, leading to well-defined tertiary structures.[2]

We here report the formation of highly crystalline adducts of synthetic aliphatic and aromatic polyamides with perfluoro diacids.

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