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A Novel Polymerization of Bis(*N*-acyl isocyanate)s and Dicarboxylic Acids—Synthesis of Poly(*N*-acylamide)s

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ABSTRACT: Polycondensation of isophthaloyl diisocyanate (**7b**) and adipic acid (**8b**) was carried out at room temperature in dimethylacetamide (2 M) for 3 h in the presence of triethylamine (TEA, 3.6 mol %) as a catalyst to obtain the corresponding poly(*N*-acylamide) (**9bb**) as an ether-insoluble product in 92% yield ($\bar{M}_n = 5000$) with violent evolution of carbon dioxide. Furthermore, the polycondensation was also carried out by using terephthaloyl diisocyanate (**7a**) and **7b** with 5-*tert*-butylisophthalic acid, adipic acid, sebacic acid, and 1,4-cyclohexanedicarboxylic acid to obtain corresponding poly(*N*-acylamide)s quantitatively. These polycondensations proceeded at 60 °C without the catalyst (TEA). However, dicarboxylic acids such as succinic acid and glutaric acid afforded no polymers because *N*-acyl isocyanate acted as a dehydration agent to eventually give the corresponding amides and cyclic carboxylic anhydrides.

Introduction

High-performance polymers such as polyamides, polyimides, and polysulfones have been extensively studied and nowadays a number of industrial applications of them have been progressed. Poly(*N*-acylamide)s, interesting acyclic analogues of polyimides, have been scarcely investigated so far as we know besides poly(*N*-acylamide) derived from terephthaloyl dichloride and *N,N'*-diphenylterephthalamide[1] and those derived from bis(imidoyl chloride)s and dicarboxylic acids.[2] Synthetic methods for the key unit structure *N*-acylamide involve (i) the reaction of *N*-acyl isocyanate and carboxylic acid, (ii) *N*-acyl isocyanate and Grignard reagent,[3] (iii) amide and carboxylic anhydride,[4] and so on.[5−9] There has been no report of the synthesis of *N*-acylamide by the reaction of *N*-acyl isocyanate with carboxylic acid. Further, aromatic polyamides are in fact prepared by the polycondensation of diisocyanate and dicarboxylic acid at high temperature using phosphoric acid catalyst via the extrusion of carbon dioxide.[10] In addition to our recent studies on the application of *N*-acyl isocyanate to polymer synthesis,[11,12] these results seem to suggest that poly(*N*-acylamide)s can be synthesized from bifunctional *N*-acyl isocyanate with carboxylic acid. This paper describes reaction of monofunctional *N*-acyl isocyanate with carboxylic acid as a model reaction for synthesis of poly(*N*-acylamide) followed by polycondensation of bis(*N*-acyl isocyanate)s and dicarboxylic acids under mild conditions.

Experimental Section

Measurements. IR, ^{1}H NMR, ^{13}C NMR, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA) were performed using a Jasco FT/IR-5300, a JEOL JNM-EX90 (^{1}H NMR, 90 MHz; ^{13}C NMR, 22.5 MHz), JNM-GX-400 (^{13}C NMR, 100 MHz), a SEIKO DSC220C (heating rate, 10 K/min under nitrogen), and a SEIKO TG/DTA220 (heating rate, 10 K/min under nitrogen), respectively.

Number- and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) and molecular weight distribution ($\bar{M}_w/\bar{M}_n$) were estimated by gel permeation chromatography (GPC) on a Tosoh HLC-8020 equipped with polystyrene gel columns (TSKgel G5000HXL, TSKgel G4000HXL, and TSKgel G2500HXL), using dimethylformamide as solvent at a flow rate of 1.0 mL/min, polystyrene calibration, and ultraviolet (UV) detectors.

Materials. Dimethylacetamide (DMAc) and tetrahydrofuran (THF) were purified by distillation after removal of water according to the conventional methods. Benzoic acid, palmitic acid, 5-*tert*-butylisophthalic acid, succinic acid, adipic acid, and sebacic acid were purified by recrystallization from aqueous ethanol. Benzoyl isocyanate was prepared by a reported method.[13] Terephthaloyl diisocyanate and isophthaloyl diisocyanate were synthesized from terephthalamide and isophthalamide, respectively, according to reported methods.[14,15]

Reaction of Benzoyl isocyanate (1) with Benzoic Acid (2). Compound **1** (147 mg, 1.0 mmol) and dry dimethylacetamide (DMAc, 0.5 mL) were placed at room temperature in a 20 mL round-bottomed three-necked flask equipped with an argon inlet tube. To the mxiture was added **2** (122 mg, 1.0 mmol) under an argon atmosphere and the mixture was stirred for 5 min. Triethylamine (TEA, 5 μL) was added to the reaction mixture under an argon atmosphere to evolve carbon dioxide violently. After 30 min stirring the reaction mixture was poured into water (10 mL) to precipitate *N*-benzoylamide (**3**). **3** was collected by filtration and dried at 80 °C under reduced pressure. Yield: 154 mg (69%, white powder). Mp: 143−145 °C. ^{1}H NMR (CDCl$_3$): δ 8.99 (s, 1H), 7.90−7.48 (m, 10H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 166.4, 133.4, 133.1, 128.9, 127.9. IR (KBr): 3449, 3250, 1705, 1676, 1601, 1504, 1476, 1229, 1177, 1119, 1073, 1026, 808, 789, 712, 610 cm^{-1}. Anal. Calcd for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.20; H, 4.62; N, 6.20.

Reaction of 1 with Palmitic Acid (4). Compound **1** (147 mg, 1.0 mmol) and dry tetrahydrofuran (THF, 1.0 mL) were placed at room temperature in a 20 mL round-bottomed three-necked flask equipped with an argon inlet tube. To the solution was added **4** (256 mg, 1.0 mmol) under an argon atmosphere. After 5 min, triethylamine (TEA, 5 μL) was added to the reaction mixture under an argon atmosphere to evolve carbon dioxide violently. The resulting mixture was stirred for 30 min, during which time a white precipitate appeared. The mixture was evapolated, and the resultant residue was purified by recrystallization from ethanol. **5** was collected by filtration and dried at 60 °C under reduced pressure. Yield: 253 mg (63%, white powder) Mp: 76−77 °C. ^{1}H NMR (DMSO-d_6): δ 10.90 (s, 1H), 8.00−7.40 (m, 5H) 2.68 (t, J = 7.1 Hz, 2H), 1.80−1.00 (m, 26H), 0.85 (t, J = 6.3 Hz, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 174.6, 166.3, 133.3, 132.6, 128.4, 128.3, 37.0, 31.3, 29.0, 28.9, 28.8, 28.7, 28.6, 23.4, 22.1, 13.9. IR (CH$_2$Cl$_2$): 2928, 2855, 1746, 1709, 1466, 1418, 1277, 1254, 1142, 1111, 895, 775, 683 cm^{-1}. Anal. Calcd for $C_{23}H_{37}NO_2$: C, 76.83; H, 10.37; N, 3.90. Found: C, 76.69; H, 10.49; N, 4.26.

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Reaction of 1 with Dicarboxylic Acid. A Typical Procedure. To a solution of **1** (147 mg, 1.0 mmol) in dry tetrahydrofuran (THF, 1.0 mL) placed in a 20 mL round-bottomed three-necked flask equipped with an argon inlet tube was added **10** (118 mg, 1.0 mmol) under an argon atmosphere at room temperature. After stirring for 5 min, TEA (5 μL) was added to the reaction mixture under an argon atmosphere to evolve carbon dioxide violently. After 30 min the mixture was evaporated. ^{1}H NMR (DMSO-d_6): δ 8.00–7.80 (m, 2H), 7.60–7.20 (m, 3H) 8.20–7.20 (m, 2H) 2.90 (s, 4H). IR (CH_2Cl_2): 3407, 3181, 1863, 1784, 1699, 1635, 1566, 1453, 1418, 1314, 1281, 1240, 1209, 1184, 1144, 1059, 918, 808, 702 cm^{-1}.

The product obtained by reaction of 1 with glutaric acid was a mixture of benzamide and glutaric anhydride: ^{1}H NMR (DMSO-d_6): δ 8.00–7.80 (m, 2H), 7.60–7.20 (m, 3H), 6.50–6.00 (bs, 2H), 2.76 (t, J = 7.02 Hz, 4H), 2.08 (m, 2H). IR (CH_2Cl_2): 3370, 3179, 1807, 1759, 1663, 1624, 1576, 1451, 1404, 1275, 1238, 1217, 1086, 1028, 939, 706, 635, 557, 530 cm^{-1}.

Polycondensation of Bis(*N*-acyl isocyanate) (7). A Typical Procedure. A mixture of **7b** (108 mg, 0.5 mmol) and **8a** (111 mg, 0.5 mmol) was stirred for 5 min in dry DMAc (0.5 mL) at room temperature in a 20 mL round-bottomed three-necked flask equipped with an argon inlet tube. Triethylamine (TEA, 5 μL) was added to the reaction mixture under an argon atmosphere to evolve carbon dioxide violently. After stirring for 175 min, the mixture was diluted with DMAc (1 mL) and poured into ether (30 mL). The precipitated poly(*N*-acylamide) (**9ba-1**) was collected by filtration and dried at 80 °C under reduced pressure. Yield: 190 mg (96%, white powder). ^{1}H NMR (DMSO-d_6): δ 11.6 (bs, 2H), 8.5–7.4 (m, 7H), 1.3 (s, 9H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 167.5, 151.6, 134.6, 134.2, 134.0, 133.9, 132.8, 131.7, 130.3, 129.3, 129.6, 128.8, 128.4, 127.1, 126.6, 34.9, 31.0. IR (KBr): 3416, 2965, 1730, 1678, 1618, 1495, 1202, 1128, 723, 691, 621 cm^{-1}. $\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$) = 5000 (2.15).

9aa: ^{1}H NMR (DMSO-d_6): δ 11.30 (bs, 2H), 8.5–7.4 (m, 7H), 1.35 (s, 9H). IR (KBr): 3414, 2963, 1762, 1672, 1620, 1481, 1223, 1113, 1015, 737, 691, 629 cm^{-1}.

9ab: ^{1}H NMR (DMSO-d_6): δ 11.09 (s, 2H), 7.98 (s, 4H), 2.73 (bs, 4H), 1.65 (m, 4H). IR (KBr): 3383, 3285, 2944, 1674, 1516, 1474, 1385, 1269, 1171, 1144, 1017, 905, 876, 718, 527 cm^{-1}.

9bb: ^{1}H NMR (DMSO-d_6): δ 11.00 (s, 2H), 8.50–7.40 (m, 4H), 2.75 (m, 4H), 1.65 (m, 4H). IR (KBr): 3420, 3258, 2953, 1744, 1707, 1616, 1501, 1406, 1244, 1186, 1146, 937, 903, 727, 633, 538 cm^{-1}.

9bc-1: ^{1}H NMR (DMSO-d_6): δ 10.97 (s, 2H), 8.43–7.62 (m, 4H), 2.72 (bs, 4H), 1.58 (bs, 4H), 1.19 (m, 8H). IR (KBr): 3416, 3274, 2930, 2855, 1740, 1686, 1616, 1501, 1410, 1383, 1213, 1152, 720, 619, 494 cm^{-1}.

9bd: ^{1}H NMR (DMSO-d_6): δ 11.00 (bs, 2H), 8.50–7.40 (m, 4H), 2.30–1.10 (m, 8H). IR (KBr): 3414, 2944, 1742, 1667, 1618, 1501, 1453, 1400, 1240, 1157, 1022, 916, 725, 623, 530 cm^{-1}.

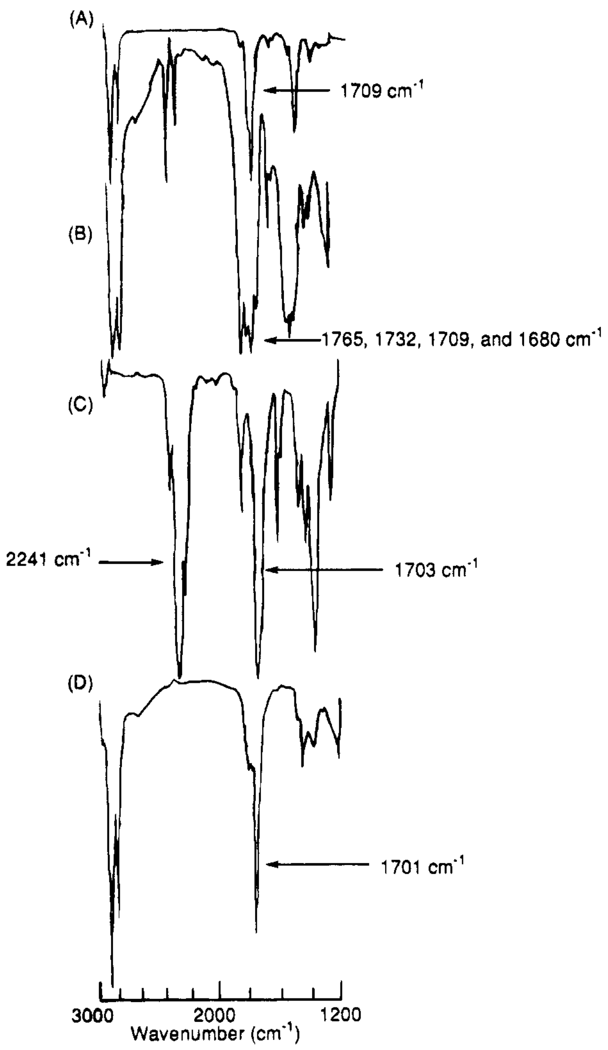
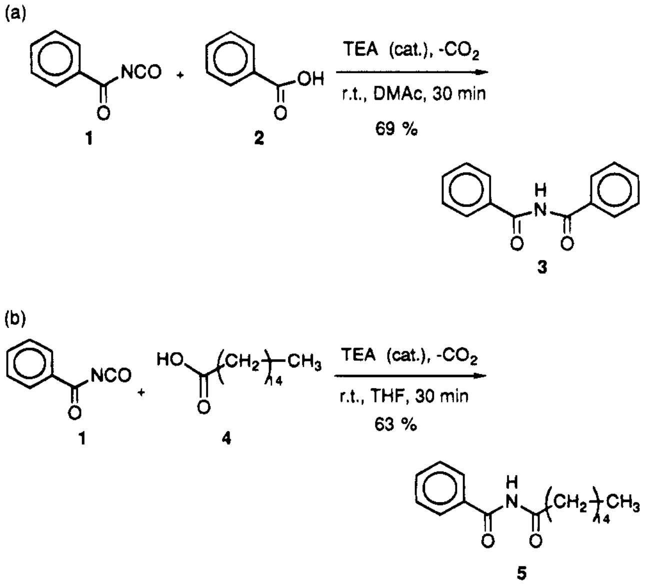


Figure 1. IR spectra of *N*-(pentadecylcarbonyl)benzamide (**5**) (A), a mixture of benzoyl isocyanate (**1**) and palmitic acid (**4**) after 20 min (B), **1** (C), and **4** (D) in CH_2Cl_2.

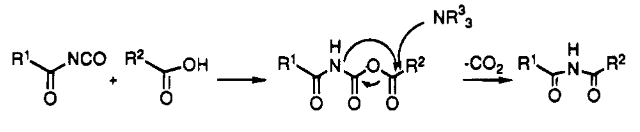
Scheme 1



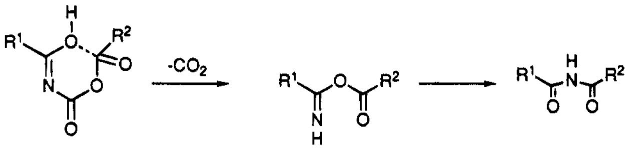
Results and Discussion

To determine the reaction mechanism, i.e. elimination of carbon dioxide, an IR spectral study of the reaction of **1** and **4** was carried out in detail. Figure 1 shows IR spectra of the product **5** (A), a reaction mixture of **1** and **4** (B) obtained after 20 min (before addition of TEA), and **1** (C) and **4** (D) in methylene chloride. The carbonyl absorption of **1**, **4**, and **5** appears at 1709, 1703, and 1701 cm^{-1}, respectively. Absorption of the isocyanate group of **1** (2241 cm^{-1}) almost disappeared and some new carbonyl absorptions (1765, 1732, 1709, and 1680 cm^{-1}) were observed in the reaction mixture. Since the initial reaction of **1** with **4** seems to involve nucleophilic addition of the carboxylic acid group to the isocyanate group, leading to a carboxylic anhydride derivative (**6**), these carbonyl absorptions observed for the reaction mixture before addition of TEA can be assigned as shown in Figure 1. Evolution of carbon dioxide occurred by the addition of TEA is therefore explained by the TEA-catalyzed decomposition of **6** once formed (Scheme 2). In fact, the reaction was too slow to be measured, when TEA was not added. This mechanism involves a concerted decarboxylation–C–N bond formation. Besides this mechanism, general base-catalyzed reaction is also possible (Scheme 3) in which decarboxylation would take place via an enolized form of **6**. However,

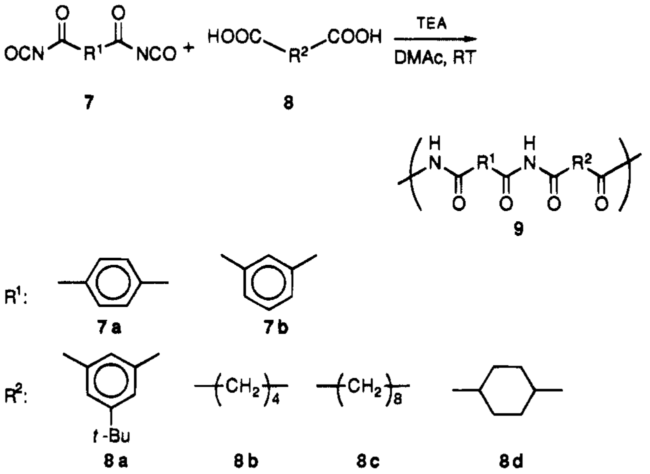
Scheme 2



Scheme 3



Scheme 4



no evolution of carbon dioxide occurred when amine base without nucleophilicity was used as catalyst. Therefore, the reaction was found to proceed along Scheme 2.

In order to clear the reaction course, IR spectra of **5** (Figure 1A), a mixture (Figure 1B) of **1** and **4** after 20 min, **1** (Figure 1C), and **4** (Figure 1D) in methylene chloride were measured with liquid cell instrument. The results are shown in Figure 1. The absorbances of the carbonyl groups of **1**, **4**, and **5** were 1709, 1703, and 1701 cm^{-1}, respectively. The absorbance of the isocyanate group (2241 cm^{-1}) almost disappeared and a new absorbance of a carbonyl group (1765, 1732, 1709, and 1680 cm^{-1}), which would be presumably attributed to the carboxylic anhydride derivative (**6**), could be observed (Figure 1B). These results may indicate that the carboxylic anhydride derivative can be produced at first by the reaction of *N*-acyl isocyanate and carboxylic acid and subsequently the elimination of carbon dioxide proceeded by catalysis with tertiary amine to give *N*-acylamide (Scheme 2).

Reaction of an equimolar mixture of isophthaloyl diisocyanate (**7b**) with adipic acid (**8b**) in DMAc (2 M) at room temperature in the presence of TEA (3.6 mol %) for 3 h gave an ether-insoluble polymer (white powder, $\bar{M}_n$ = 5000, $\bar{M}_w/\bar{M}_n$ = 1.88) in 92% yield (Scheme 4). The structure of the obtained polymer was determined as poly(*N*-acylamide) by its IR and NMR spectra. In addition, several poly(*N*-acylamide)s (**9aa–ab**, **9bb–bd**) were quantitatively obtained using a few bis(*N*-acyl isocyanate)s and dicarboxylic acids (Table 1). Vigorous evolution of carbon dioxide was observed in any case. Typical IR and ^{1}H NMR spectra of the obtained poly(*N*-acylamide) (**9ba-1**) are shown in Figure 2. In the ^{1}H NMR spectrum, the NH proton signal (a) was observed at low magnetic field (11.60 ppm), probably because of the electron-withdrawing character of the *N*-acyl group. Aromatic protons signals (b) were found around 8 ppm, and a *t*-Bu proton signal (c) appeared at 1.33 ppm. The IR spectrum (Figure 2) displayed carbonyl absorptions of the *N*-acyl groups at 1730 and 1678 cm^{-1} besides a broad N–H absorption at 3416 cm^{-1} as representative absorptions. The fact that the experimentally determined carbon content (62.50%) of **9a-1** is lower than the calculated one (68.56%) (see the Experimental Section) seems to suggest that the actual degree of polymerization of **9ba-1** is not high and that terminal structures consist mainly of amide groups probably derived from **7b**. Corresponding poly(*N*-acylamide)s were obtained in the all polymerizations in good yields. In any case, slower elimination of carbon dioxide was observed at room temperature till adding TEA indicating that polycondensation of bis(*N*-acyl isocyanate) and dicarboxylic acid proceeded slowly presumably via are intramolecular mechanism (Scheme 5). Enhancement of concentration gave a slight increase in molecular weight (runs 3 and 4, or runs 8 and 9) that was not high enough to influence the glass transition temperature (T_g) and the 10% weight loss temperature (Td_{10}) of the polymer. Two times the quantity of TEA (7.2 mol %, run 5) also gave a little higher molecular weight polymer relative to the case of run 3 (3.2 mol %).

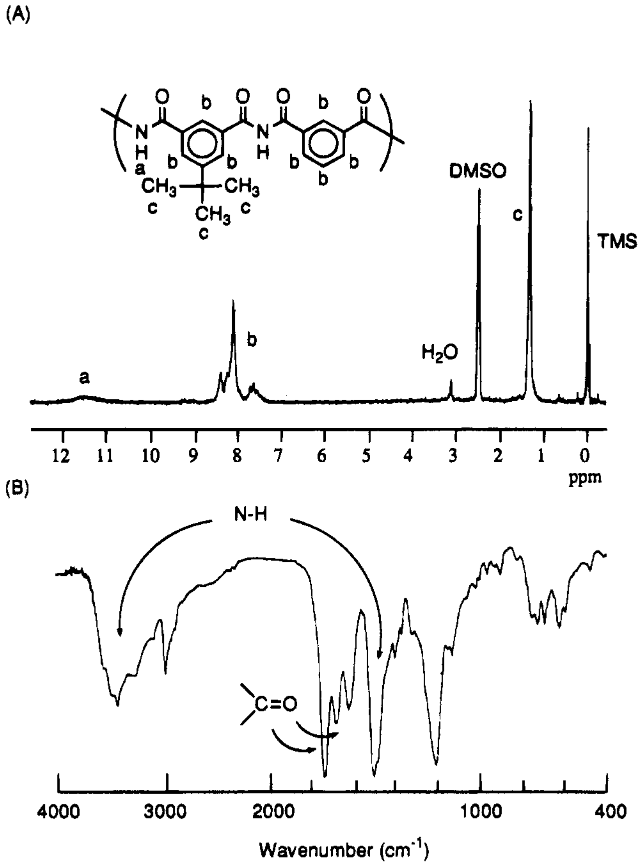


Figure 2. ^{1}H NMR spectrum (90 MHz, in DMSO-d_6) (A) and IR spectrum (B) of poly(*N*-acylamide) (**9ba-1**).

Scheme 5

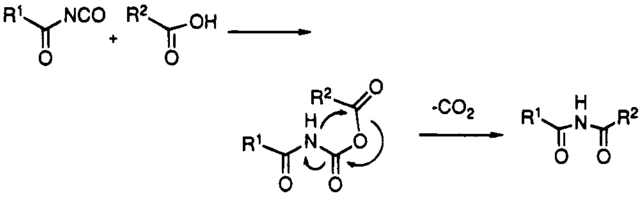
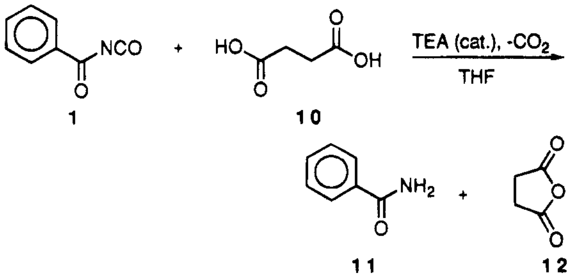


Table 1. Polycondensation of Bis(*N*-acyl isocyanate)s with Dicarboxylic Acid[a]

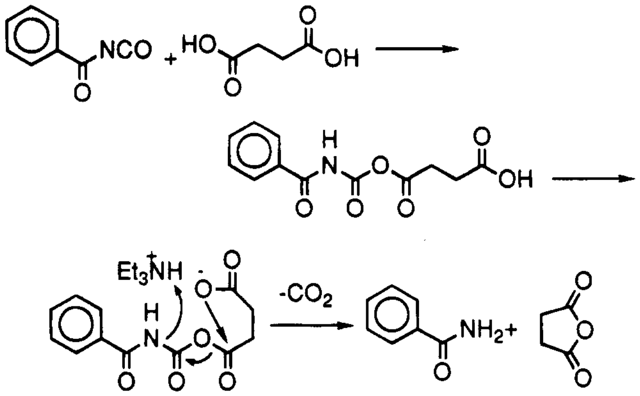
run	bis(acyl isocyanate)	dicarboxylic acid	poly(*N*-acylamide)	concn (M)	yield[b] (%)	$\bar{M}_n$[c] ($\bar{M}_w/\bar{M}_n$)	T_g (°C)	Td_{10}[d] (°C)
1	**7a**	**8a**	**9aa**	2	87	4600 (1.83)	145	207
2	**7a**	**8b**	**9ab**	2	80	7200 (1.63)	86	252
3	**7b**	**8a**	**9ba-1**	2	96	5000 (2.15)	151	248
4	**7b**	**8a**	**9ba-2**	4	91	5900 (2.32)	154	232
5[e]	**7b**	**8a**	**9ba-3**	2	97	6000 (2.13)	166	236
6	**7b**	**8b**	**9bb**	2	92	5000 (1.88)	65	255
7	**7b**	**8c**	**9bc-1**	2	95	6000 (2.02)	63	267
8	**7b**	**8c**	**9bc-2**	1	80	5000 (2.21)	60	259
9	**7b**	**8d**	**9bd**	2	99	2800 (2.20)	62	228

[a] Reaction conditions: room temperature, 3 h, in DMAc, TEA (3.6 mol %). [b] Ether-insoluble part. [c] Estimated by GPC (PSt standard; eluent, DMF). [d] 10% weight loss temperature. [e] TEA (7.2 mol%).

Scheme 6



Scheme 7



Next, when reaction of equimolar of **7b** and **8a** was carried out at 60 °C in DMAc (2 M) for 3 h without catalyst, the reaction proceeded with gradual releasing of carbon dioxide to obtain the corresponding poly(*N*-acylamide) (**9ba-4**: $\bar{M}_n$ = 5800, $\bar{M}_w/\bar{M}_n$ = 2.16) as an ether-insoluble part in 90% yield. Polycondensation of **7b** with **8c** was also carried out in a similar manner as **9ba-4** to give the corresponding poly(*N*-acylamide) (**9bc-3**: $\bar{M}_n$ = 4800, $\bar{M}_w/\bar{M}_n$ = 1.72) in 76% yield. Despite the fact that bis(*N*-acyl isocyanate)s are more reactive than diisocyanate, the molecular weights of the obtained polymers were low presumably because of partial decomposition of the *N*-acyl isocyanate group by humidity and/or reaction of *N*-acylisocyanate with acylamide in the polymer main chain resulting in an imbalance of functional groups.

When a similar polycondensation using **7a** and a succinic acid (**10**) was carried out, no polymeric material like poly(*N*-acylamide) was obtained in spite of evolution of carbon dioxide. Therefore, reaction of **1** with succinic acid was examined to clarify the reaction products. An equimolar mixture of benzamide (**11**) and succinic anhydride (**12**) was the product, and the structures were determined from the ^{1}H NMR and IR spectra and TLC analysis by comparison with those of authentic samples (Scheme 6). A similar result was obtained in the case of **1** and glutaric acid. This means that *N*-acyl isocyanate can behave as a dehydration reagent for succinic and glutaric acids, yielding the corresponding carboxylic anhydride. These carboxylic acids have some advantage in entropy in the ring closure (Scheme 7).

The obtained poly(*N*-acylamide)s were all soluble in polar solvents such as dimethylformamide and dimethyl sulfoxide, but insoluble in less polar solvents such as THF and methylene chloride. As shown in Table 1, the T_g's of all aromatic poly(*N*-acylamide)s (**9aa** and **9ba**) were higher than those of **9ab** and **9bb–bd** derived from aliphatic dicarboxylic acids, because of the high rigidly of the aromatic groups. However, the Td_{10}'s of **9aa** and **9ba** were relatively low compared to those of **9ab** and **9bb–bc**, presumably because of the lower thermal stability of *N*-acylamide bonding derived from aromatic dicarboxylic acids, which might be attributed to the greater leaving ability of an aromatic amide than an aliphatic one. Nucleophiles in a thermal cleavage reaction would be the water in the air and the nitrogen of the polymer main chain. And all Td_{10}'s were low, contrary to the expectation, presumably due to the low molecular weight of the obtained polymers.

In summary, we could demonstrate the facile synthesis of poly(*N*-acylamide)s by polycondensation of bis(*N*-acyl isocyanate)s and dicarboxylic acids with evolution of carbon dioxide under mild conditions. Furthermore, this reaction was found to proceed at 60 °C without catalyst.

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