# A New Class of Polymer Having the −CO−NH−CO−NH−CO− Structure: Poly(*N,N'*-diacylurea)s Synthesized by Polyaddition of Diamides to Bis(*N*-acyl isocyanate)s

**Masami Kanamaru, Toshikazu Takata,† and Takeshi Endo***

*Research Laboratory of Resources Utilization,*
*Tokyo Institute of Technology, Nagatsuta-cho,*
*Midori-ku, Yokohama 227, Japan*

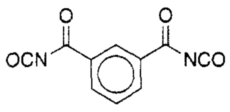
*Received June 1, 1994*
*Revised Manuscript Received September 6, 1994*

## Introduction

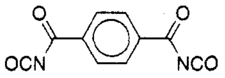
Isocyanates having electron-withdrawing groups on the nitrogen atoms are much more reactive than common isocyanates toward nucleophiles such as alcohols. We have utilized the reactivity of *N*-acyl isocyanates for the synthesis of new polymers. For example, poly(*N*-acyl carbamate)s and poly(*N*-acylurea)s have been synthesized.[1−3] It has been reported that benzoyl isocyanate (**1**) spontaneously reacts with benzamide at room temperature in ca. 30% yield to give *N,N'*-dibenzoylurea (**2**), which has an interesting functional group consisting of two NH and three CO moieties (Scheme 1).[4] Polymers having the −CO−NH−CO−NH−CO− unit as the main-chain structure[5] are called poly(*N,N'*-diacylurea)s and are expected to exhibit some unique properties based on their structural characteristics such as reinforced hydrogen bonding. This paper describes the synthesis of poly(*N,N'*-diacylurea)s as a new class of polymers.

## Results and Discussion

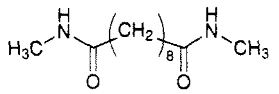
Although the reaction of 1 with benzamide has been reported[4] (Scheme 1), it has not been studied in detail. The reaction of benzoyl isocyanate (1) with 4-*tert*-butylbenzamide was carried out in tetrahydrofuran (THF) at 65 °C for 20 min to afford **4** in a quantitative yield (Scheme 2).



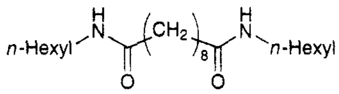
**5a**



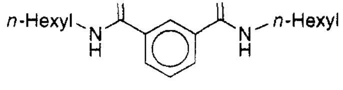
**5b**



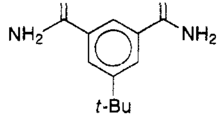
**6a**



**6b**



**6c**



**6d**

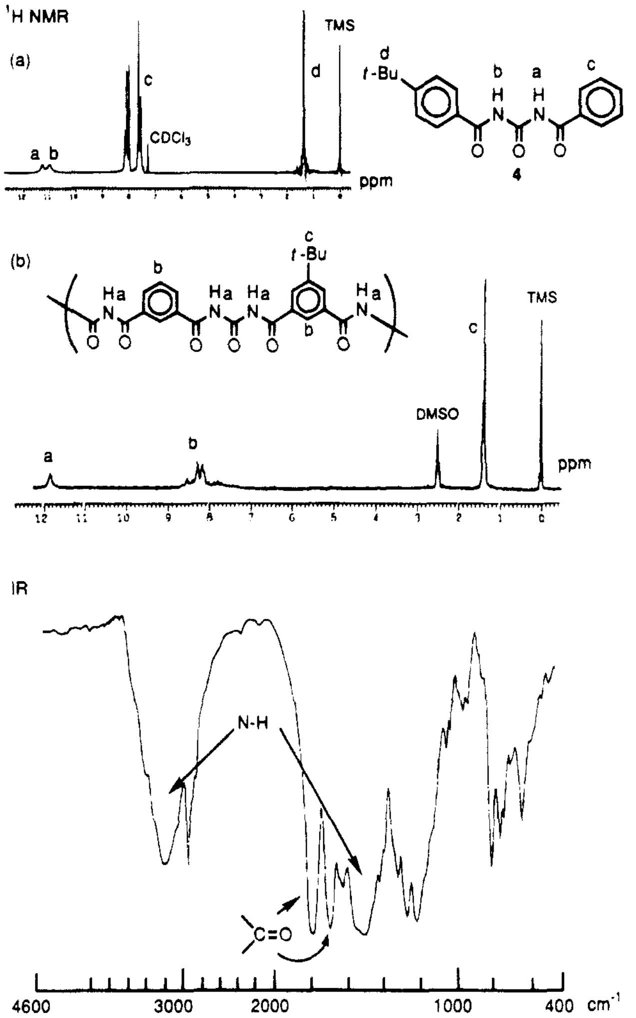
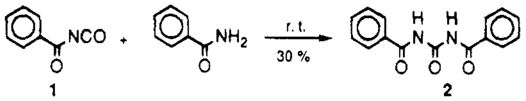
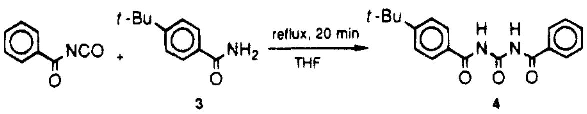


**Figure 1.** $^1$H NMR ((a) solvent, CDCl$_3$) spectrum of **4** and $^1$H NMR ((b) solvent, DMSO-$d_6$) and IR (KBr) spectra of poly(*N,N'*-diacylurea) (**7ad-1**).

**Scheme 1**



**Scheme 2**



An equimolar mixture of bis(*N*-acyl isocyanate) (**5a**)[7,8] and diamide (**6d**) was heated for 20 min at 65 °C in dimethylacetamide (DMAc) under an argon atmosphere to give an ether-insoluble polymer ($\bar{M}_n$, 1600); $\bar{M}_w/\bar{M}_n$, 2.00) in 96% yield (run 8). The structure of the resultant polymer was confirmed as the corresponding poly(*N,N'*-diacylurea) by IR and $^1$H NMR spectra (Figure 1). The proton signal of the NH group shifted to low magnetic field presumably due to the electron-withdrawing character of the *N*-acyl group, which was in good agreement with the $^1$H NMR spectrum of the model compound (**4**). The IR spectrum (Figure 1) displays typical carbonyl absorptions attributable to the *N*-acyl group at 1674 cm$^{-1}$ and the central carbonyl group of the urea group at 1771 cm$^{-1}$. In a similar manner, several poly(*N,N'*-diacylurea)s (**7aa, 7ab, 7ac, 7ad, 7ba, 7bb, 7bc,** and **7be**) were prepared by polymerizations in DMAc or tetrahydrofuran (THF) (Scheme 3). The results are summarized in Table 1. Because the solubility of **6a** in THF was very low, the polyaddition of **6a** to **5** was carried out in DMAc. In the cases of runs 10, 13, and 14, polymer **7** was precipitated

---

† JAIST (Japan Advanced Institute of Science and Technology), Tatsunokuchi, Ishikawa 923-12, Japan.

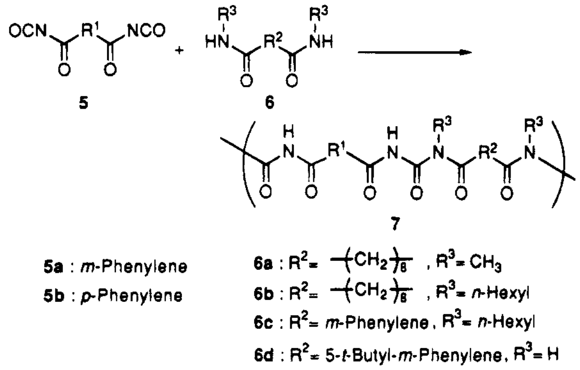
0024-9297/94/2227-7492$04.50/0

**Table 1. Synthesis of Poly(*N,N'*-diacylurea)s (7) by Polyaddition of Diamides (6) to Bis(*N*-acyl isocyanate)s (5)**

| run | bis(*N*-acyl isocyanate) | diamide | solvent (M) | temp (°C) | time (min) | polymer | yield[a] (%) | $\bar{M}_n$[b] ($\bar{M}_w/\bar{M}_n$) |
|---|---|---|---|---|---|---|---|---|
| 1 | **5a** | **6a** | DMAc (1) | 65 | 20 | **7aa-1** | 88 | 4300 (1.70) |
| 2 | **5a** | **6a** | DMAc (1) | 65 | 180 | **7aa-2** | 91 | 4700 (1.57) |
| 3 | **5a** | **6b** | DMAc (1) | 65 | 20 | **7ab-1** | 45 | 1800 (1.42) |
| 4 | **5a** | **6b** | DMAc (1) | 65 | 180 | **7ab-2**[c] | 67 | 2500 (1.76) |
| 5 | **5a** | **6b** | THF (1) | reflux | 20 | **7ab-3** | 95 | 4000 (1.42) |
| 6 | **5a** | **6c** | DMAc (1) | 65 | 180 | **7ac-1** | 96 | 3000 (1.52) |
| 7 | **5a** | **6c** | THF (1) | reflux | 20 | **7ac-2** | 48 | 3000 (1.32) |
| 8 | **5a** | **6d** | DMAc (2) | 65 | 20 | **7ad-1** | 96 | 1600 (2.00) |
| 9 | **5a** | **6d** | DMAc (1) | 65 | 180 | **7ad-2**[d] | 96 | 3400 (1.24) |
| 10 | **5a** | **6d** | THF (1) | reflux | 10 | **7ad-3** | 99[e] | 2700 (1.16) |
| 11 | **5b** | **6a** | DMAc (1) | 65 | 180 | **7ba** | 84 | 3000 (1.37) |
| 12 | **5b** | **6b** | DMAc (1) | 65 | 180 | **7bb** | 72 | 2500 (1.50) |
| 13 | **5b** | **6c** | DMAc (1) | 65 | 180 | **7bc** | 33[e] | 2500 (1.47) |
| 14 | **5b** | **6d** | DMAc (1) | 65 | 180 | **7bd** | 97[e] | 2500 (1.37) |

[a] Ether-insoluble part. [b] Estimated by GPC (eluent: DMF). [c] $\eta_{inh}$ was 0.11 dL/g (DMAc, 0.5 g/dL, 30 °C). [d] $\eta_{inh}$ was 0.09 dL/g (DMAc, 0.5 g/dL, 30 °C). [e] Polymer was precipitated during polymerization.

**Scheme 3**



during the polymerization. This resulted from the strong intermolecular hydrogen bonding of the diacylurea groups. Polymer yield increased with an increase of the polymerization time. **7aa**, **7ad**, **7ba**, and **7bd** were soluble in polar solvents such as DMAc and dimethyl sulfoxide (DMSO), but **7ab**, **7ac**, **7bb**, and **7bc** were soluble in less polar solvents such as THF and dichloromethane, undoubtedly due to the effect of the long alkyl chain on the diamide moieties. Number-average molecular weights ($\bar{M}_n$'s) of poly(*N,N'*-diacylurea)s from the aromatic diamides (**7ac**, **7bc**, **7ad**, **7bd**) were smaller than those from the aliphatic diamides. This would be explained by lower reactivity of the aromatic amides toward the isocyanate group.

For comparison of reactivity of the *N*-acyl isocyanate with the corresponding isocyanate under similar reaction conditions, polyaddition of diamide (**6b**) to *m*-phenylene diisocyanate was carried out at 65 °C for 20 min in THF (1 M). None of the corresponding polymer was obtained, thus confirming the extremely enhanced reactivity of the *N*-acyl isocyanate.

Results of thermal analysis of poly(*N,N'*-diacylurea)s (**7**) are shown in Table 2. $T_g$ of **7bc** was higher than that of **7ac-1** and $T_g$ of **7ac-1** was lower than that of **7ad-2**, presumably because of an increase of the thermal mobility of the polymer segment based on an *n*-hexyl group. Two $T_m$'s were observed for each of **7ab-2** and **7bb** derived from *N,N'*-di-*n*-hexylsebacoamide, and the lower $T_m$ would be attributed to their hexyl side chain. 10% weight loss temperatures ($T_{d_{10}}$) of **7** derived from aromatic diamides were lower than those derived from aliphatic diamides presumably because of the low thermal stability of diacylurea bonding derived from aromatic diamides, which attribute to the higher leaving ability of the aromatic amide than the aliphatic one.

**Table 2. Thermal Properties of Poly(*N,N'*-diacylurea)s (7)**

| polymer[a] | $T_g$ (°C)[b] | $T_{m_1}$ (°C)[b] | $T_{m_2}$ (°C)[b] | $T_{d_{10}}$ (°C)[c] |
|---|---|---|---|---|
| **7aa-2** | 54 | 124 | | 255 |
| **7ba** | 40 | 133 | | 255 |
| **7ab-2** | | 50 | 139 | 269 |
| **7bb** | | 49 | 131 | 263 |
| **7ac-1** | 36 | | | 224 |
| **7bc** | 86 | | | 218 |
| **7ad-2** | 141 | | | 224 |
| **7bd** | | | | 248 |

[a] Polymers obtained under the conditions shown in Table 1. [b] Determined by differential scanning calorimetry. [c] Determined by thermogravimetric analysis.

## References and Notes

(1) Kanamaru, M.; Takata, T.; Endo, T. *Polym. Prepr. Jpn.* **1993**, *42*, 464.
(2) Kanamaru, M.; Takata, T.; Endo, T. *Polym. Prepr. Jpn.* **1993**, *42*, 1922.
(3) Kanamaru, M.; Takata, T.; Endo, T. *Macromolecules* **1994**, *27*, 3694.
(4) Billeter, O. C. *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 3218.
(5) Synthesis of polymers having –NH–CO–NH–CO–NH– structure by polycondensation of *N,N'*-disilylated diamides with chloroformyl isocyanate has already been reported by Kricheldorf et al.[6]
(6) Kricheldorf, H. R.; Haack, M.-J. *Makromol. Chem.* **1992**, *193*, 2631.
(7) Tsuge, O.; Itoh, T.; Tashiro, M. *Tetrahedron* **1968**, *24*, 2583.
(8) Neidlein, R.; Bottler, R. *Chem. Ber.* **1967**, *100*, 698.