Photo-on-Demand Phosgenation Reactions with Chloroform for Selective Syntheses of N-Substituted Ureas and Isocyanates

Muranaka, Ryo

Liu, Yue

Okada, Itsuumi

Okazoe, Takashi

Tsuda, Akihiko

(Rights)

(URL)
https://hdl.handle.net/20.500.14094/90009121

Photo-on-Demand Phosgenation Reactions with Chloroform for Selective Syntheses of N-Substituted Ureas and Isocyanates

Ryo Muranaka, Yue Liu, Itsuumi Okada, Takashi Okazoe, and Akihiko Tsuda*

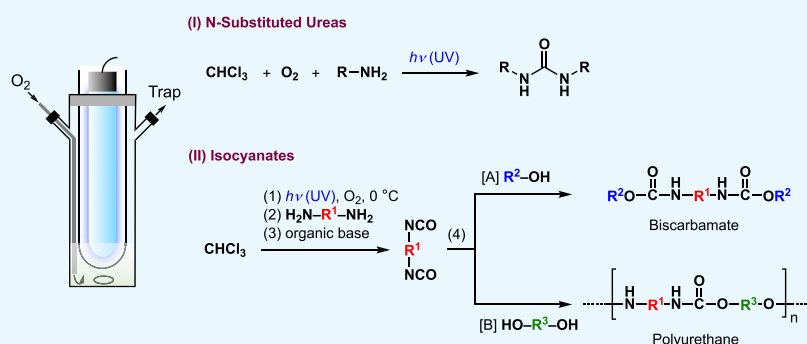Cite This: *ACS Omega* 2022, 7, 5584−5594

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

(I) N-Substituted Ureas

(II) Isocyanates

ABSTRACT: Two new reaction processes involving the *in situ* oxidative photochemical conversion of $CHCl_3$ to $COCl_2$ allowed selective syntheses of N-substituted ureas and isocyanates from amines. (I) A $CHCl_3$ solution containing an amine and an organic base under O_2 bubbling provided the urea derivative under exposure to UV light generated from a low-pressure mercury lamp at 20−40 °C. (II) A two-step reaction involving the oxidative photodecomposition of $CHCl_3$ at lower temperatures and subsequent sequential injections of an amine and organic base into the sample solution provided the isocyanate in high yield. The reaction processes of (I) and (II) capitalize on the solution conditions of $[COCl_2] < [amine]$ and $[COCl_2] > [amine]$, respectively, to result in 1:2 and 1:1 reactions. In general, isocyanates, especially aromatic and haloalkyl ones, readily undergo hydrolysis in the presence of an organic base. However, with the advantage of synthesizing the isocyanates in $CHCl_3$ solvent, direct addition of monoalcohols and diols to the as-prepared sample solution containing the diisocyanate allowed the one-pot syntheses of biscarbamates and polyurethanes, respectively. The reactions developed in this study are simple, safe, and inexpensive methods of synthesizing N-substituted ureas and isocyanates, and derivatives of isocyanates such as carbamates and polyurethanes. The present new methods can replace current synthetic methods using $COCl_2$ in both academia and industry.

INTRODUCTION

Isocyanates, having a −N═C═O group, are typically synthesized from amines and phosgene ($COCl_2$) in industry (Scheme 1, reaction a).[1−3] This chemical reaction was first reported by Hentschel in 1884[4] and has been used widely in manufacturing isocyanate derivatives. N-Substituted ureas are also formed through the reaction of isocyanates and amines, but they can be reconverted to the isocyanates upon heating with $COCl_2$ (reaction b).[5,6] Although these reactions use $COCl_2$, a highly toxic gaseous compound at room temperature, they have enormous advantages in terms of reactivity, product quality, and cost in comparison with other developed methods.[7] Hence, this method has been used for a century without major modifications. For safe use of $COCl_2$, bis(trichloromethyl)carbonate (BTC), generally called triphosgene, a solid under standard conditions, is preferred for synthesizing isocyanates in laboratory-scale experiments and small-scale industrial production.[8] BTC generates $COCl_2$ *in situ* upon mixing with an organic base in the solution, and its subsequent rapid reaction with an amine gives the isocyanate

(reaction c). However, Cotarca and co-workers recently reported that BTC is also a highly toxic compound, whose vapor pressure is sufficiently high to reach toxic concentrations at room temperature.[9] This background motivated us to develop safe, convenient, and inexpensive phosgenation reactions for synthesizing N-substituted ureas and isocyanates without the use of highly toxic corrosive reagents, expensive reagents, or a complicated special apparatus. We herein report two novel reaction methods that allow their selective syntheses by applying the *in situ* photochemical conversion of $CHCl_3$ to $COCl_2$. In these reactions, $CHCl_3$ bifunctionally serves as a solvent and a $COCl_2$ precursor (reactions d and e).
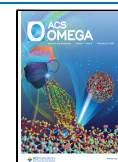
Scheme 1. Syntheses of N-Substituted Ureas and Isocyanates[a]
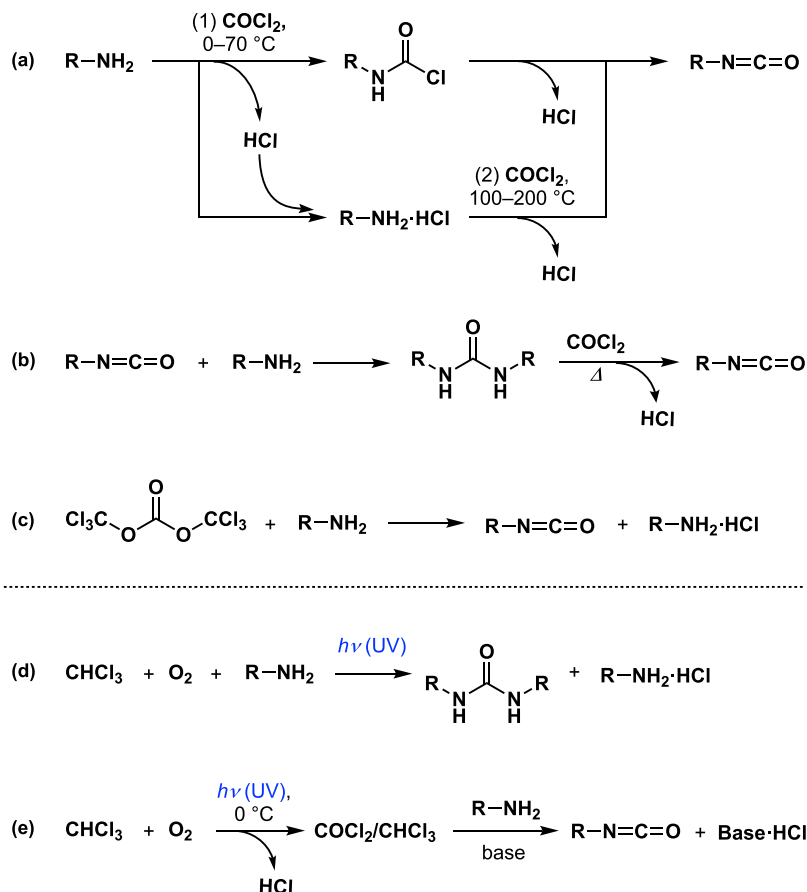
[a](a–c) Conventional reactions. (d, e) New reactions developed in this study.

We previously reported that CHCl₃ undergoes oxidative photodecomposition under exposure to UV light to efficiently produce COCl₂ (Scheme 2).[10] Recently, we then successfully
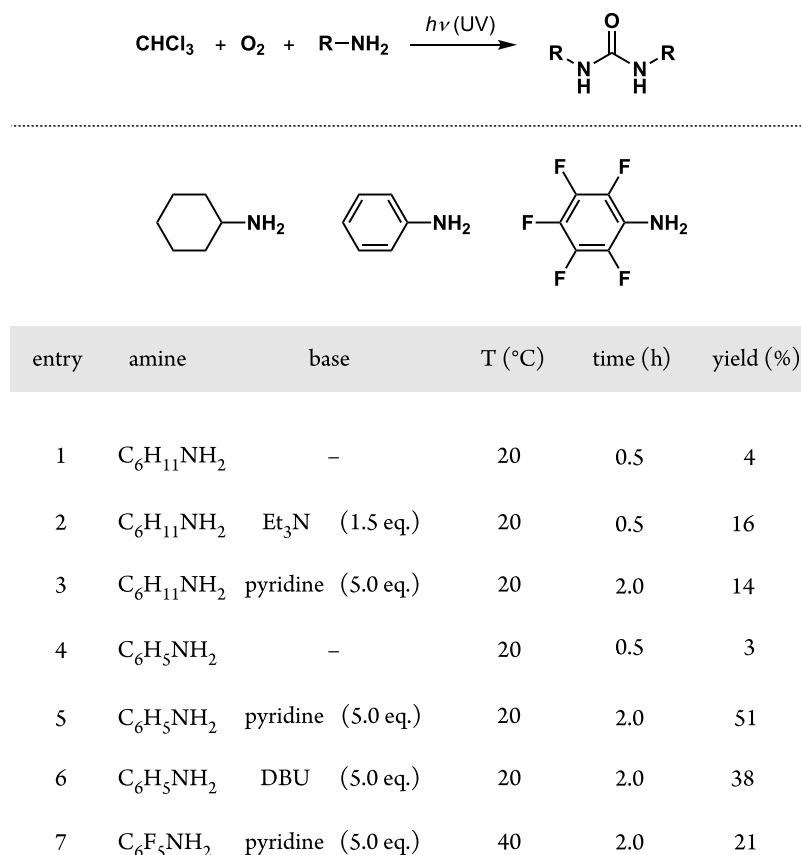
Scheme 2. Photo-on-Demand Syntheses of (a) Phosgene, (b) Chloroformate, and (c) Carbonate Ester with CHCl₃ as Reported Previously by Our Group
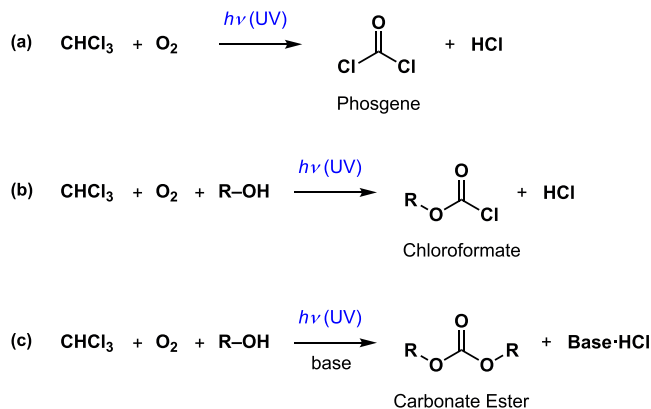
developed *in situ* photo-on-demand phosgenation reactions.[11–13] As a representative example, a CHCl₃ solution containing a mixture of an alcohol and an organic base such as pyridine upon exposure to UV-C light provided carbonate esters in high yield *via* the chloroformate as an intermediate.[13] Although it is known that the alcohol serves as a stabilizer to

decelerate the decomposition of CHCl₃, and further, that the organic base absorbs UV light,[14,15] the phosgenation reaction occurred to give the product through an *in situ* base-catalyzed reaction of the alcohol and COCl₂ generated by the oxidative photodecomposition of CHCl₃. In this study, with the same procedures, we succeeded in synthesizing N-substituted ureas through an *in situ* photo-on-demand phosgenation reaction of amines with CHCl₃.[16] Furthermore, we found that a two-step reaction, involving oxidative photodecomposition of CHCl₃ at low temperatures and subsequent sequential injections of the amine and base into the solution, allowed the practical synthesis of isocyanates.[17] The reaction facilitated one-pot conversions of the isocyanates to carbamates and polyurethanes (PU) upon mixing with alcohols.

■ RESULTS AND DISCUSSION

Photochemical Reaction System. A low-pressure mercury lamp generates UV light mainly at wavelengths of 184.9 and 253.7 nm, which cover the electronic absorption bands of CHCl₃, originating from σ−σ* and/or n−σ* transitions. The lamp has an advantage in terms of its relatively low electric power consumption compared with other light sources including light-emitting diodes (LEDs) capable of emitting short-wavelength UV-C light.[10a,18] The lamp (20 W, ⌀24 mm × 120 mm), whose illuminance at 185 and 254 nm is 2.00− 2.33 and 5.96−8.09 mW/cm², respectively, at 5 mm from the lamp, was inserted into the solution *via* a quartz glass jacket (⌀28 mm) fixed in the center of a cylindrical flask (⌀42 mm).

Scheme 3. Photochemical Syntheses of N-Substituted Ureas with CHCl₃ Solutions Containing an Amine and an Organic Base[a]

entry	amine	base		T (°C)	time (h)	yield (%)
1	$C_6H_{11}NH_2$	–		20	0.5	4
2	$C_6H_{11}NH_2$	Et₃N	(1.5 eq.)	20	0.5	16
3	$C_6H_{11}NH_2$	pyridine	(5.0 eq.)	20	2.0	14
4	$C_6H_5NH_2$	–		20	0.5	3
5	$C_6H_5NH_2$	pyridine	(5.0 eq.)	20	2.0	51
6	$C_6H_5NH_2$	DBU	(5.0 eq.)	20	2.0	38
7	$C_6F_5NH_2$	pyridine	(5.0 eq.)	40	2.0	21

[a]Reaction procedures and conditions: Irradiation by UV light of 20 mL of CHCl₃ containing 10 mmol of amine and 0–5 equiv of base under O₂ bubbling (0.1 L/min) with a 20 W low-pressure mercury lamp.

Scheme 4. Photochemical Synthesis of CDI with CHCl₃ Solutions Containing Imidazole and 2,6-Lutidine[a]
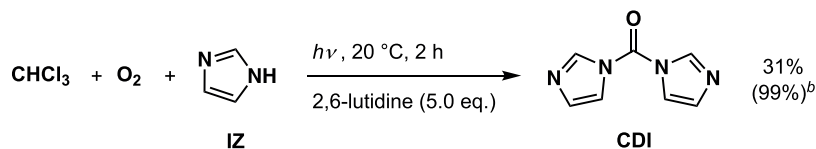
[b]Yield was determined by ¹H NMR analysis. [a]Reaction procedures and conditions: Irradiation by UV light of 20 mL of CHCl₃ containing 10 mmol of IZ and 5 equiv of 2,6-lutidine under O₂ bubbling (0.1 L/min) with a 20 W low-pressure mercury lamp.

This setup allows for transmission of UV-C light, while protecting the lamp from corrosive gases such as HCl and COCl₂, which are generated by photochemical reactions. The photoreactor is further connected to a gas trap system containing alkaline water such as NaHCO₃ aq. and NaOH aq., which can decompose unreacted COCl₂ and HCl.

Photo-on-Demand Synthesis of N-Substituted Ureas. With this reaction system, we initially demonstrated the *in situ* photo-on-demand phosgenation reaction with cyclohexylamine, an aliphatic amine, by reference to the procedures developed in our previous study.[13] When a CHCl₃ solution (20 mL) containing 10 mmol of amine was exposed to UV light under O₂ bubbling (0.1 L/min) with vigorous stirring at 20 °C, the sample solution immediately became a white suspension due to the formation of the HCl salt of the amine (Scheme 3, entry 1). The resulting sample solution contained 1,3-dicyclohexylurea, which is expected from the reaction of the amine and COCl₂, but it was obtained only in 4% yield. To trap the generated HCl, which most likely decelerates the

nucleophilic substitution of the amine to COCl₂, the photochemical reaction was then carried out upon mixing with triethylamine (TEA). Although the urea yield was slightly increased to 16%, the reaction stopped in a short time, probably due to the decomposition of TEA that resulted in dark coloration of the sample solution (entry 2). The yield was also increased slightly when using pyridine, whose UV light resistance and basicity are relatively higher and lower, respectively, than those of TEA (entry 3). Based on the hypothesis that aliphatic amines having higher basicity dominantly react with HCl rather than COCl₂, we next performed the photochemical reaction with aniline, an aromatic amine, having lower basicity. The reaction of aniline without a base also mainly provided the HCl salt of aniline with the corresponding urea only in 3% yield (entry 4). However, the reaction with a CHCl₃ solution containing a mixture of aniline and 5 equiv amounts of pyridine provided 1,3-diphenylurea in 51% isolated yield (entry 5). 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), having higher basicity

than pyridine, also allowed the formation of urea but caused its photodecomposition, decreasing the yield to 38% (entry 6). Pentafluoroaniline, having lower basicity than aniline, in the presence of pyridine provided the corresponding urea in 21% yield (entry 7). When this reaction was applied to the synthesis of 1,1′-carbonyldiimidazole (CDI),[19] which is widely used as a phosgene substitute in organic syntheses, it was obtained in 31% yield (>99% in ^{1}H NMR yield) from a $CHCl_3$ solution of imidazole (IZ) and 2,6-lutidine (Scheme 4). The lower isolated yield than that estimated by ^{1}H NMR analysis (>99%) may be responsible to that CDI readily undergoes hydrolysis under air in the presence of base.

Synthesis of Isocyanates by a Two-Step Procedure. The N-substituted ureas described above might form under the condition of [amine] > [$COCl_2$], which allows an immediate reaction of $COCl_2$ with two molecules of the amine via the formation of an isocyanate. Thus, it can be expected that the condition of [amine] < [$COCl_2$], which allows a preferential reaction of the amine with $COCl_2$ rather than the isocyanate formed in the reaction, would provide mainly the corresponding isocyanate through a 1:1 reaction. Considering the low boiling point of $COCl_2$ (8.3 °C), a two-step procedure by preparation of a $CHCl_3$ solution containing $COCl_2$ was conducted at low temperatures, with subsequent injection of the amine into the solution. Prior to performing this experiment, we first examined whether $CHCl_3$ undergoes oxidative photodecomposition at 0 °C to give a $CHCl_3$ solution of $COCl_2$. With the same reaction system as that for the preparation of N-substituted ureas, 20 mL of $CHCl_3$ after exposure to UV light at 0 °C for 1 h under O_2 bubbling at a flow rate of 0.1 L/min was found to contain 18.5 mmol of $COCl_2$, which could be estimated from the amounts of the products formed upon addition of ethanol (chloroformate and carbonate ester). By reference to this result, 10 mmol of aniline was added to 50 mL of a $CHCl_3$ solution containing $COCl_2$, as prepared upon photoirradiation at 0 °C for 3 h. The aniline was slightly converted to the corresponding isocyanate but was mainly obtained as its HCl salt. The HCl originated from what remained in the $CHCl_3$ solution and what was generated by the reaction of aniline with $COCl_2$. However, the HCl salt of aniline could be further reacted with unreacted $COCl_2$ upon elevating the temperature to 60 °C to give the isocyanate in 80% yield (Scheme 5, entry 1). The HCl salts of amines are known to react with $COCl_2$ at high temperatures (vide ante) to give isocyanates,[2b] and this method has actually been used for industrial production. However, one may expect under these conditions that $COCl_2$ would not be retained in the sample solution but would vaporize to the gas phase. This may reduce the yield of the product and is also unfavorable in terms of the safe handling of the reaction, especially in laboratory-scale experiments. To achieve the synthesis of the isocyanate at low temperatures, preferably below the boiling point of $COCl_2$, we then added an organic base such as pyridine or 2,6-lutidine to the above $CHCl_3$ solution containing the HCl salt of aniline and $COCl_2$ without elevating the temperature. The corresponding isocyanate was obtained in >99 and 97% yields, respectively (entries 2 and 3).

The reaction was further available for the synthesis of a variety of isocyanates (Scheme 6). Hexylamine, having higher basicity than aniline, also provided the corresponding isocyanate in >99% yield. Fluorine-substituted aniline and an alkyl amine, having lower basicity, provided the corresponding isocyanates in 62 and 66% yields, respectively. 3-
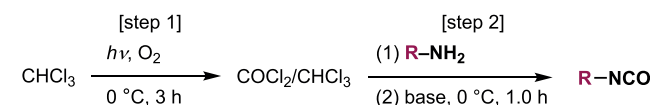
Scheme 5. Two-Step Procedure for Synthesizing Phenyl Isocyanate through the Photochemical Conversion of $CHCl_3$ to $COCl_2$ and Subsequent Addition of Aniline[a]
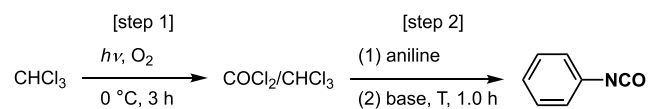
entry	base	T (°C)	yield (%)[b]
1	–	60	80
2	pyridine (5.0 eq.)	0	>99
3	2,6-lutidine (5.0 eq.)	0	97

[b]Yields were determined by ^{1}H NMR analysis. [a]Reaction procedures and conditions: [Step 1] irradiation by UV light of 50 mL of $CHCl_3$ under O_2 bubbling (0.1 L/min) at 0 °C for 3 h. [Step 2] (1) Addition of 10 mmol of amine. (2) Addition of 5 equiv of base.

Scheme 6. Two-Step Procedure for Synthesizing Monoisocyanates through the Photochemical Conversion of $CHCl_3$ to $COCl_2$ and Subsequent Addition of Amine[a]
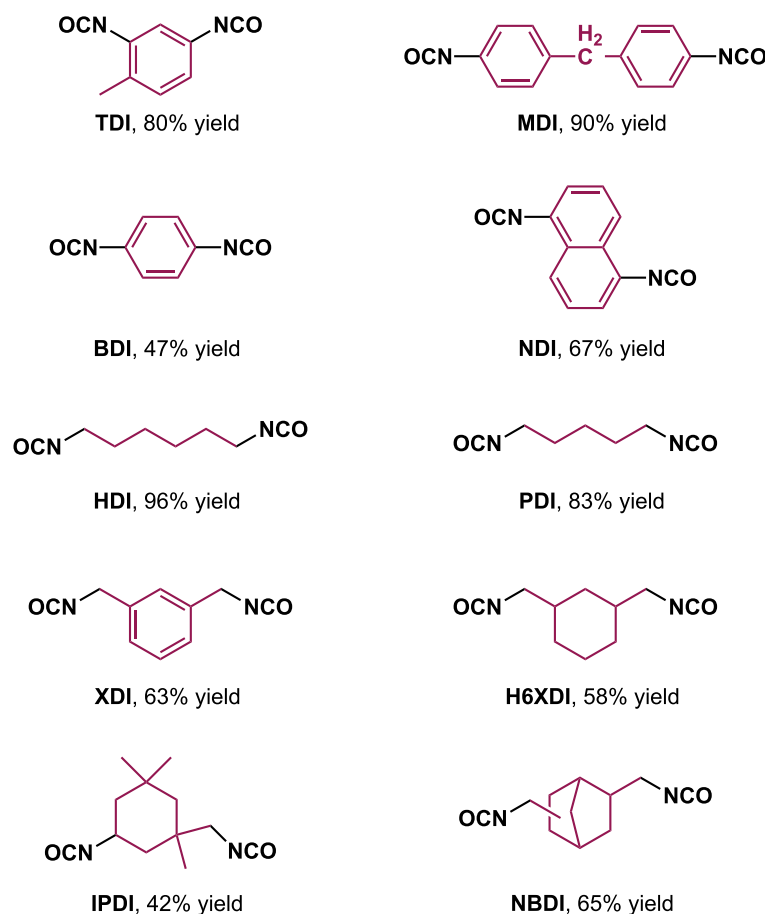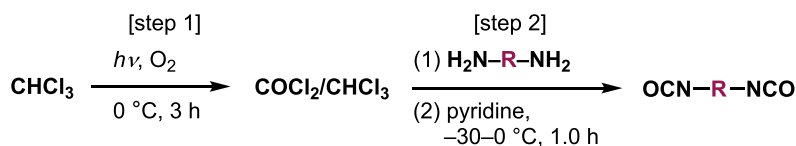

[a]Reaction procedures and conditions: [Step 1] Irradiation by UV light of 50 mL of $CHCl_3$ under O_2 bubbling (0.1 L/min) at 0 °C for 3 h. [Step 2] (1) Addition of 10 mmol of amine. (2) Addition of 5 equiv of base. Yields were determined by ^{1}H NMR analysis.

(Triethoxysilyl)propylamine and 3-(trimethoxysilyl)-propylamine, which readily undergo hydrolysis condensations with water under acidic conditions, also provided the corresponding isocyanates in 62 and 56% yields, respectively. This reaction was further applicable to the synthesis of a series of diisocyanates that are used in the manufacturing of polyurethanes in industry (Scheme 7).[6] Aromatic diisocyanates such as toluene diisocyanate (TDI), methylenediphenyl diisocyanate (MDI), benzene diisocyanate (BDI), and naphthalene diisocyanate (NDI) were successfully synthesized in 80, 90, 47, and 67% yields, respectively. Alkyl diisocyanates such as hexamethylene diisocyanate (HDI) and pentam-ethylene diisocyanate (PDI) were also obtained in 96 and 83% yields, respectively. Aliphatic diisocyanates including a

Scheme 7. Two-Step Procedure for Synthesizing Diisocyanates through the Photochemical Conversion of CHCl$_3$ to COCl$_2$ and Subsequent Addition of Diamines[a]

[a]Reaction procedures and conditions: [Step 1] Irradiation by UV light of 50 mL of CHCl$_3$ under O$_2$ bubbling (0.1 L/min) at 0 °C for 3 h. [Step 2] (1) Addition of 10 mmol of diamine. (2) Addition of 5 equiv of base. Yields were determined by ^{1}H NMR analysis.

cyclic component such as *m*-xylylene diisocyanate (XDI), 1,4-bis(isocyanatomethyl) cyclohexane (H6XDI), isophorone diisocyanate (IPDI), and norbornanediisocyanate (NBDI) were obtained in 63, 58, 42, and 65% yields, respectively.

One-Pot Syntheses of Biscarbamates and Polyurethanes. These isocyanates and diisocyanates can be isolated by vacuum distillation, and the HCl salt of pyridine remaining as a byproduct can also be reused by treating it with an inorganic base such as aqueous NaOH. However, since isocyanates are generally moisture sensitive, especially in the presence of organic bases, the isocyanates produced using this method readily undergo hydrolysis under air to give the corresponding amines. The amine then further reacts with isocyanate to give the corresponding urea derivative. With the advantage of preparing the isocyanates in CHCl$_3$ solvent, we further demonstrated the one-pot synthesis of carbamates without their isolation (Scheme 8). When EtOH was added to the CHCl$_3$ solution containing MDI, as prepared by the above

two-step procedure, the corresponding biscarbamate was obtained in 78% yield (91% by ^{1}H NMR). 1,1,1,3,3,3,-Hexafluoro-2-propanol (HFIP), whose nucleophilicity is lower than that of EtOH, also allowed the reaction upon mixing with additional pyridine to give the corresponding biscarbamate in 71% yield (76% in ^{1}H NMR yield). The pyridine might allow the catalytic substitution of HFIP to MDI. HDI, whose reactivity is relatively low compared with MDI, also provided the corresponding biscarbamate through the reaction with HFIP, but the yield was reduced to 37% (47% by ^{1}H NMR). We further demonstrated the one-pot synthesis of polyurethane upon addition of 1,6-hexanediol (HD) to the CHCl$_3$ solution containing MDI. The corresponding polyurethane [poly(MDI-HD)] was obtained in 50% yield and had an average molecular weight of $M_w = 4100$ and $M_n = 2200$ ($M_w/M_n = 1.87$). This observed low yield and relatively low average molecular weight most likely originated from the poor solubility of the PU formed in the reaction. Poly(propylene
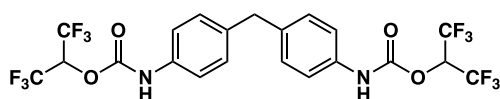
Scheme 8. One-Pot Syntheses of Biscarbamates and Polyurethanes from Diamines through Their Photochemical Conversions to the Diisocyanates[a]
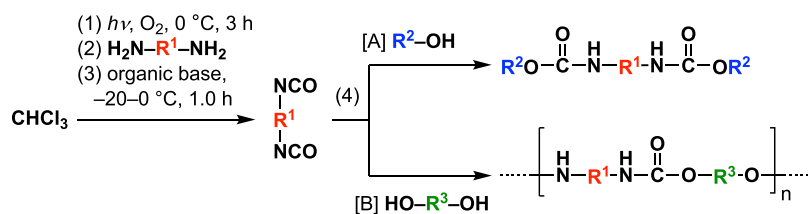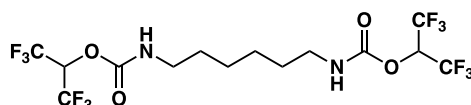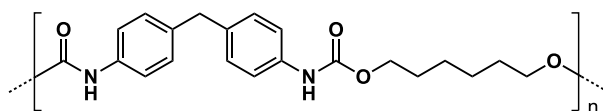

[A] Biscarbamate
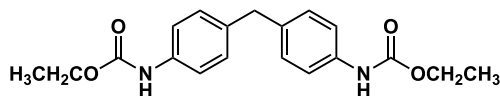
MDI-2EtOH, 78% (91%)[b] yield

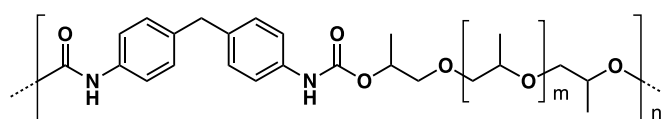**MDI-2HFIP**, 71% (76%)[b] yield

HDI-2HFIP, 37% (47%)[b] yield

[B] Polyurethane

Poly(MDI-HD), 50% yield

$M_w = 4100$
$M_n = 2200$
$M_w/M_n = 1.87$

Poly(MDI-PPG), 89% yield

$M_w = 6200$
$M_n = 3600$
$M_w/M_n = 1.72$

[b]Yields were determined by ^{1}H NMR analysis. [a]Reaction procedures and conditions: (1) irradiation by UV light of 50 mL of CHCl$_3$ under O$_2$ bubbling (0.1 L/min) at 0 °C for 3 h. (2) Addition of 5 mmol of diamine. (3) Addition of 10 equiv of base. (4) Addition of [A] 20 mmol of alcohol with or without 25 mmol of base or [B] 5 mmol of diol.

glycol) (PPG) with an average molecular weight of 400 that can increase the solubility of PU provided poly(MDI-PPG) in 89% yield with $M_w = 6200$ and $M_n = 3600$ ($M_w/M_n = 1.72$).

With similar procedures, we next demonstrated the one-pot syntheses of a biscarbonate and a polyurethane, including a fluoroalkyl backbone, from the HCl salt of 2,2,3,3,4,4,5,5-octafluorohexane-1,6-diamine (8FHDA·2HCl) (Scheme 9). Photoirradiation of a CHCl$_3$ solution containing insoluble 8FHDA·2HCl at 0 °C, and subsequent slow injection of 2,6-lutidine into the sample solution, quantitatively provided the corresponding diisocyanate (8FHDI), which was characterized by ^{1}H NMR analysis. Although 8FHDI formed in the solution

was highly moisture sensitive, which would cause its hydration, the one-pot procedure upon addition of HFIP to the sample solution afforded the corresponding biscarbamate in 37% yield (68% by ^{1}H NMR). The addition of HD and PPG provided the corresponding polyurethanes in 91% yield with $M_w = 4000$ and $M_n = 2400$ ($M_w/M_n = 1.66$) and 86% yield with $M_w = 8800$ and $M_n = 3400$ ($M_w/M_n = 2.59$), respectively.

■ CONCLUSIONS

In this study, N-substituted ureas and isocyanates were selectively synthesized from amines by two new reaction processes, involving photo-on-demand phosgenation reactions
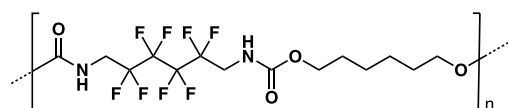
Scheme 9. One-Pot Syntheses of Biscarbamates and Polyurethane from a HCl Salt of Fluoroalkylene Diamine through Photochemical Conversion to Diisocyanate[a]
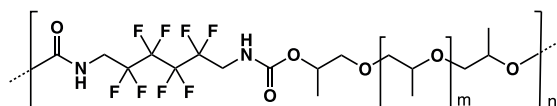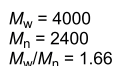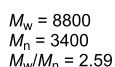

8FHDI, >99%

[A] R¹–OH

[B] HO–R²–OH

[A] Biscarbamate

8FHDI-2HFIP, 37% (68%)[b] yield
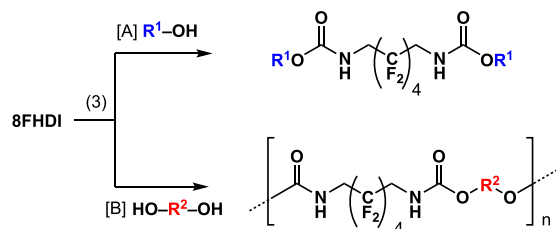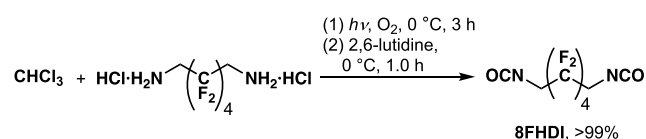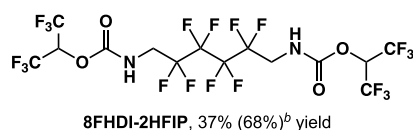
[B] Polyurethane

Poly(8FHDI-HD), 91% yield
$M_w = 4000$
$M_n = 2400$
$M_w/M_n = 1.66$

Poly(8FHDI-PPG), 86% yield
$M_w = 8800$
$M_n = 3400$
$M_w/M_n = 2.59$

[b]Yields were determined by ¹H NMR analysis. [a]Reaction procedures and conditions: (1) irradiation by UV light of 30 mL of CHCl₃ containing 2 mmol of 8FHDA·2HCl under O₂ bubbling (0.1 L/min) at 0 °C for 3 h. (2) Addition of 10 equiv of 2,6-lutidine. (3) Addition of [A] 8 mmol of HFIP with 8 mmol of 2,6-lutidine or [B] 2 mmol of diol.

with CHCl₃. Direct UV irradiation of a CHCl₃ solution containing an amine under O₂ bubbling provided N-substituted ureas. This reaction allowed for a higher concentration of the amine than that of COCl₂, which was constantly generated from the CHCl₃ solution, resulting in a 2:1 reaction. A two-step reaction, involving oxidative photo-decomposition of CHCl₃ at low temperatures and subsequent slow injection of an amine and organic base into the sample solution, resulted in dominant formation of the isocyanate through the base-catalyzed 1:1 reaction of amine and COCl₂. This process allowed a lower concentration of the amine than that of COCl₂. The isocyanates formed under these conditions readily underwent hydrolysis under air. However, with the advantage of synthesizing isocyanates in CHCl₃ solvent, this reaction system allowed for one-pot syntheses of biscarbamates and polyurethanes upon direct addition of monoalcohols and diols, respectively, to the as-prepared CHCl₃ solution of the

diisocyanate. The obtained biscarbamates bearing electron-withdrawing fluoroalkyl groups are also interesting as blocked isocyanates applicable for synthesizing polyurethanes.[20] The photochemical reactions reported herein are simple and safe methods of synthesizing N-substituted ureas and isocyanates and are expected to be an innovative method that can replace current phosgenation reactions.

■ EXPERIMENTAL SECTION

General Information. Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. 2,2,3,3,4,4,5,5-Octafluoro-1,6-diaminohexane hydrochloride (8FHDA·2HCl) was synthesized according to the literature method.[21] For vacuum distillation, a glass tube oven (Sibata Scientific Technology, model GTO-1000) was used with an oil rotary vacuum pump. ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE 400 spectrometer or Bruker AVANCE 500 spectrometer, where chemical shifts (δ in ppm) were determined with respect to tetramethylsilane as an internal standard. ¹⁹F NMR spectra were recorded on a Bruker AVANCE 400 spectrometer, where chemical shifts (δ in ppm) were determined with respect to hexafluorobenzene as an external standard. Fourier transform infrared (FTIR) spectroscopy was performed on a JASCO FT/IR 4200. Fourier transform mass spectrometry was performed on a Thermo Fisher Scientific LTQ Orbitrap. Elemental analysis was carried out on a Yanaco CHN corder MT-5 analyzer. Size-exclusion chromatography (SEC) measurements were performed at 40 °C on TOHSOH TSKgel G5000H$_{HR}$ and TSKgel G4000H$_{HR}$ columns using a JASCO Type PU-2089 quaternary gradient pump, equipped with a JASCO type RI-4030 refractive index detector with tetrahydrofuran (THF) as an eluent. Polystyrene standards (123 000, 50 000, 25 000, 13 502, 4000, 1300 Da, 0.56% w/v) were used for calibration of the molecular weights of the polymers.

General Procedure for the Synthesis of N-Substituted Ureas. A cylindrical flask ($\varnothing 42 \times 120$ mm²), equipped with a low-pressure mercury lamp (Sen Light Co., UVL20PH-6, 20 W, $\varnothing 24 \times 120$ mm²) and a magnetic stirring bar, was charged with a CHCl₃ solution (20 mL) containing an amine (10 mmol) and an organic base (1.5 or 5.0 equiv). If necessary, an aluminum block bath or water bath was used to heat the sample solution. The sample solution was vigorously stirred upon bubbling with O₂ (0.1 L/min) under exposure to UV light for 0.5–2.0 h. After the photochemical reaction, the lamp was turned off, and the sample solution was stirred at 50 °C for 0.5–1.0 h to remove the unreacted COCl₂ and generated HCl dissolved in the solution. The resulting sample solution was washed with water and extracted with CH₂Cl₂. The combined organic layer was dried over anhydrous Na₂SO₄ and evaporated to dryness. The residue was recrystallized to give the N-substituted urea.

1,3-Dicyclohexylurea. CHCl₃ (20 mL), cyclohexylamine (10 mmol, 1.15 mL), and triethylamine (15 mmol, 2.1 mL) were mixed in a cylindrical flask. The sample solution was vigorously stirred under O₂ bubbling (0.1 L/min) and exposed to UV light at 20 °C for 0.5 h. After the photochemical reaction, the lamp was turned off, and the sample solution was stirred at 50 °C for 1 h. It was then washed with water and extracted with CH₂Cl₂. The combined organic layer was dried over anhydrous Na₂SO₄ and evaporated to dryness. 1,3-Dicyclohexylurea was obtained through recrystallization with CHCl₃/n-hexane as a white solid in 16% yield (0.18 g, 0.8

mmol). ^{1}H NMR (400 MHz, dimethyl sulfoxide (DMSO)-d_6, 293 K) δ/ppm: 5.56 (d, 2H, J = 8.0 Hz), 1.70−1.74 (m, 4H), 1.61 (dt, 4H, J = 3.6, 13.2 Hz), 1.50 (dt, 2H, J = 3.2, 12.0 Hz), 1.03−1.27 (m, 10H); ^{13}C NMR (100 MHz, DMSO-d_6, 293 K) δ/ppm: 47.4, 33.2, 25.2, 24.4.

1,3-Diphenylurea. CHCl$_3$ (20 mL), aniline (10 mmol, 0.91 mL), and pyridine (50 mmol, 4.0 mL) were mixed in a cylindrical flask. The sample solution was vigorously stirred under O$_2$ bubbling (0.1 L/min) and exposed to UV light at 20 °C for 2 h. After the photochemical reaction, the lamp was turned off, and the sample solution was stirred at 50 °C for 1 h. It was then washed with water and extracted with CH$_2$Cl$_2$. The combined organic layer was dried over anhydrous Na$_2$SO$_4$ and evaporated to dryness. 1,3-Diphenylurea was obtained through recrystallization with EtOAc/n-hexane as a white solid in 51% yield (0.54 g, 2.5 mmol). ^{1}H NMR (400 MHz, DMSO-d_6, 293 K) δ/ppm: 7.45 (d, 4H, J = 7.6 Hz), 7.28 (t, 4H, J = 7.8 Hz), 6.97 (t, 2H, J = 7.4 Hz); ^{13}C NMR (100 MHz, DMSO-d_6, 293 K) δ/ppm: 152.5, 139.6, 128.7, 121.7, 118.1.

1,3-Bis(perfluorophenyl)urea. CHCl$_3$ (20 mL), 2,3,4,5,6-pentafluoroaniline (10 mmol, 1.83 g), and pyridine (50 mmol, 4.0 mL) were mixed in a cylindrical flask. The sample solution was vigorously stirred under O$_2$ bubbling (0.1 L/min) and exposed to UV light at 40 °C for 2 h. After the photochemical reaction, the lamp was turned off, and the sample solution was stirred at 50 °C for 1 h. It was then washed with water and extracted with CH$_2$Cl$_2$. The combined organic layer was dried over anhydrous Na$_2$SO$_4$ and evaporated to dryness. 1,3-Bis(perfluorophenyl)urea was obtained through recrystallization with EtOAc/n-hexane as a white solid in 21% yield (0.41 g, 1.0 mmol). ^{1}H NMR (400 MHz, DMSO-d_6, 293 K) δ/ppm: 9.04 (br, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, 293 K) δ/ppm: 152.1, 114.3, 141.9, 140.1, 138.5, 137.6, 136.0, 113.6; ^{19}F NMR (376 MHz, DMSO-d_6, 293 K) δ/ppm = −146.4 (d, 4F, J = 20.3 Hz), −158.8 (br, 2F), −163.9 (t, 4F, J = 21.8 Hz).

1,1-Carbonyldiimidazole. CHCl$_3$ (20 mL), imidazole (10 mmol, 0.68 g), and 2,6-lutidine (50 mmol, 5.80 mL) were mixed in a cylindrical flask. The sample solution was vigorously stirred under O$_2$ bubbling (0.1 L/min) and exposed to UV light at 20 °C for 2 h. After the photochemical reaction, the lamp was turned off, and the sample solution was stirred at 50 °C for 0.5 h. 1,2-Dichloroethane (5 mmol, 0.40 mL) was then added to the sample solution as an internal standard, and the yield of 1,1-carbonyldiimidazole produced was estimated to be 99% in the ^{1}H NMR analysis. The solvent was evaporated to dryness under reduced pressure. The residue was recrystallized with THF to give a white solid in 31% yield (0.25 g, 1.5 mmol). ^{1}H NMR (400 MHz, CDCl$_3$, 293 K) δ/ppm: 8.20 (s, 2H), 7.53 (t, 2H, J = 1.6 Hz), 7.26 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$, 293 K) δ/ppm: 138.3, 132.3, 118.9.

General Procedure for the Synthesis of Monoisocyanates. A cylindrical flask (ø42 × 120 mm^2), equipped with a low-pressure mercury lamp (Sen Light Co., UVL20PH-6, 20 W, ø24 × 120 mm^2) and a magnetic stirring bar, was charged with CHCl$_3$ (20 mL). The sample was cooled at 0 °C with an ice bath and vigorously stirred upon bubbling with O$_2$ (0.1 L/min) under exposure to UV light for 3 h. After the photochemical reaction, the lamp was turned off, and amine (10 mmol) and organic base (5 equiv) were sequentially added to the sample solution with a syringe pump. The sample solution was stirred at 0 °C for 1 h and then further stirred at 60 °C for 1.5 h to remove the unreacted COCl$_2$ dissolved in the solution. C$_2$H$_4$Cl$_2$ or CH$_2$Cl$_2$ was then added to the sample

solution as an internal standard, and the yield of the isocyanate produced was determined by ^{1}H NMR analysis.

General Procedure for the Synthesis of Diisocyanates. A cylindrical flask (ø42 × 120 mm^2), equipped with a low-pressure mercury lamp (Sen Light Co., UVL20PH-6, 20 W, ø24 × 120 mm^2) and a magnetic stirring bar, was charged with CHCl$_3$ (50 mL). The sample was cooled at 0 °C with an ice bath and vigorously stirred upon bubbling with O$_2$ (0.1 L/min) under exposure to UV light for 3 h. After the photochemical reaction, the lamp was turned off, and diamine (5 mmol) and organic base (10 equiv) were sequentially added to the sample solution with a syringe pump at −20 to 0 °C. The sample solution was further stirred for 1.5 h at 60 °C or subjected to vacuum distillation to remove the unreacted COCl$_2$ dissolved in the solution. The yields of the diisocyanates were then determined by ^{1}H NMR analysis with CH$_2$Cl$_2$ or C$_2$H$_4$Cl$_2$ as an internal standard.

Synthesis of Biscarbamates and Polyurethane. *MDI-2EtOH.* A cylindrical flask, equipped with a low-pressure mercury lamp and a magnetic stirring bar, was charged with CHCl$_3$ (50 mL). The sample was cooled at 0 °C with an ice bath and vigorously stirred upon bubbling with O$_2$ (0.1 L/min) under exposure to UV light for 3 h. After the photochemical reaction, the lamp was turned off, and the sample solution was cooled to −20 °C. 4,4′-Diaminodiphenylmethane (5.0 mmol, 1.00 g) dissolved in CHCl$_3$ (10 mL) and pyridine (50 mmol, 4.0 mL) was sequentially added to the sample solution with a syringe pump at this temperature. The sample solution was then evaporated at 100 °C to remove the solvent. Ethanol (20 mmol, 1.17 mL) was injected into the sample with a syringe pump, and the sample solution was stirred at 30 °C for 2 h. The sample was washed with water and extracted with CH$_2$Cl$_2$. The combined organic layer was dried over anhydrous Na$_2$SO$_4$ and evaporated to dryness under reduced pressure. The residue was dried under vacuum at 50 °C for 2 h to give MDI-2EtOH in 78% yield (1.33 g) as a dark brown colloidal solid. ^{1}H NMR (400 MHz, DMSO-d_6, 293 K) δ/ppm: 9.52 (s, NH), 7.37 (d, 4H, J = 8.4 Hz), 7.09 (d, 4H, J = 8.4 Hz), 4.11 (q, 4H, J = 7.2 Hz), 3.79 (s, 2H), 1.23 (t, 6H, J = 7.2 Hz); ^{13}C NMR (100 MHz, DMSO-d_6, 293 K) δ/ppm: 153.5, 137.1, 135.3, 128.7, 118.3, 59.9, 14.5. IR (attenuated total reflectance (ATR)) ν (cm^{-1}): 3320, 3123, 3045, 2979, 2931, 1697, 1595, 1525, 1478, 1443, 1414, 1390, 1365, 1315, 1230, 1067, 922, 858, 815, 758, 668. High-resolution mass spectrometry (HRMS) (electrospray ionization (ESI) orbitrap) m/z: [M + Na]$^+$ calcd for C$_{19}$H$_{22}$N$_2$O$_4$Na 365.1477; found 365.1475.

MDI-2HFIP. A cylindrical flask, equipped with a low-pressure mercury lamp and a magnetic stirring bar, was charged with CHCl$_3$ (50 mL). The sample was cooled at 0 °C with an ice bath and vigorously stirred upon bubbling with O$_2$ (0.1 L/min) under exposure to UV light for 3 h. After the photochemical reaction, the lamp was turned off, and the sample solution was cooled to −20 °C. 4,4′-Diaminodiphenylmethane (5.0 mmol, 1.00 g) dissolved in CHCl$_3$ (10 mL) and pyridine (50 mmol, 4.0 mL) was sequentially added to the sample solution with a syringe pump at this temperature. The sample solution was then evaporated at 100 °C to remove the solvent. A mixture of 1,1,1,3,3,3-hexafluoro-2-propanol (20 mmol, 2.31 mL) and pyridine (25 mmol, 2.0 mL) was injected into the sample with a syringe pump, and the sample solution was stirred at 30 °C for 2 h. The sample was washed with water and extracted with CH$_2$Cl$_2$. The combined organic layer was

dried over anhydrous Na_2SO_4 and evaporated to dryness under reduced pressure. The residue was dried under vacuum at 50 °C for 2 h to give MDI-2HFIP in 71% yield (2.07 g) as light brown powder. ^{1}H NMR (400 MHz, CDCl$_3$, 293 K) δ/ppm: 7.33 (d, 4H, J = 8.0 Hz), 7.16 (d, 4H, J = 7.6 Hz), 5.75 (sep, 2H, J = 3.6 Hz), 3.94 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, 293 K) δ/ppm: 149.6, 136.8, 135.4, 139.1, 120.1 (q, J = 278.5 Hz), 119.0, 116.7, 66.4 (m); ^{19}F NMR (376 MHz, DMSO-d_6, 293 K) δ/ppm: −72.5 (d, J = 6.8 Hz). IR (ATR) ν (cm^{-1}): 3308, 3126, 3045, 2977, 1736, 1597, 1539, 1414, 1382, 1357, 1247, 1222, 1190, 1105, 1005, 906, 888, 848, 809, 781, 757, 688, 658. HRMS (ESI orbitrap) m/z: [M + Na]$^+$ calcd for $C_{21}H_{14}F_{12}N_2O_4Na$ 609.0660; found 609.0639.

HDI-2HFIP. A cylindrical flask, equipped with a low-pressure mercury lamp and a magnetic stirring bar, was charged with CHCl$_3$ (50 mL). The sample was cooled at 0 °C with an ice bath and vigorously stirred upon bubbling with O$_2$ (0.1 L/min) under exposure to UV light for 3 h. After the photochemical reaction, the lamp was turned off, and the sample solution was cooled to −20 °C. 1,6-Hexanediamine (5.0 mmol, 0.58 g) dissolved in CHCl$_3$ (10 mL) and pyridine (50 mmol, 4.0 mL) was sequentially added to the sample solution with a syringe pump at this temperature. The sample solution was then evaporated at 100 °C to remove the solvent. A mixture of 1,1,1,3,3,3-hexafluoro-2-propanol (20 mmol, 2.31 mL) and 2,6-lutidine (25 mmol, 2.9 mL) was injected into the sample with a syringe pump, and the sample solution was stirred at 40 °C for 65 h. The sample was washed with water and extracted with CH$_2$Cl$_2$. The combined organic layer was dried over anhydrous Na$_2$SO$_4$, and evaporated to dryness under reduced pressure. The residue was dried under vacuum at 50 °C for 2 h to give HDI-2HFIP in 37% yield (0.86 g) as white powder. ^{1}H NMR (400 MHz, CDCl$_3$, 293 K) δ/ppm: 5.67 (sep, 2H, J = 6.0 Hz), 5.12 (br, NH), 3.27 (q, 4H, J = 8.8 Hz), 1.57 (t, 4H, J = 6.8 Hz), 1.37 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6, 293 K) δ/ppm: 152.4, 121.1 (q, J = 282.9 Hz), 66.5 (m), 40.8, 28.8, 25.7; ^{19}F NMR (376 MHz, CDCl$_3$, 293 K) δ/ppm: −73.6 (d, J = 5.3 Hz). IR (ATR) ν (cm^{-1}): 3336, 3072, 2971, 2937, 2865, 1731, 1548, 1383, 1355, 1252, 1193, 1145, 1102, 1066, 1007, 944, 905, 878, 747, 691, 652. ESI HRMS m/z: [M + Na]$^+$ calcd for $C_{14}H_{16}F_{12}N_2O_4Na$ 527.0816; found 527.0812.

Poly(MDI-HD). A cylindrical flask, equipped with a low-pressure mercury lamp and a magnetic stirring bar, was charged with CHCl$_3$ (50 mL). The sample was cooled at 0 °C with an ice bath and vigorously stirred upon bubbling with O$_2$ (0.1 L/min) under exposure to UV light for 3 h. After the photochemical reaction, the lamp was turned off, and the sample solution was cooled to −20 °C. 4,4′-Diaminodiphenyl-methane (5.0 mmol, 1.00 g) dissolved in CHCl$_3$ (10 mL) and pyridine (50 mmol, 4.0 mL) was sequentially added to the sample solution with a syringe pump at this temperature. The sample solution was then evaporated at 90 °C to remove the solvent. 1,6-Hexanediol (5 mmol, 0.59 g) dissolved in CHCl$_3$ (7 mL) was injected into the sample with a syringe pump, and the sample solution was stirred at −20 °C for 12 h. The sample was washed with water and extracted with CH$_2$Cl$_2$. The combined organic layer was dried over anhydrous Na$_2$SO$_4$ and evaporated to dryness under reduced pressure. The residue was dried under vacuum at 50 °C for 2 h to give poly(MDI-HD) in 50% yield (0.92 g) as brown powder. The average molecular weight was estimated by gel permeation chromatography (GPC) in comparison with the polystyrene standard: M_w =

4100, M_n = 2200, M_w/M_n = 1.87. ^{1}H NMR (400 MHz, DMSO-d_6, 293 K) δ/ppm: 9.50 (s, NH), 7.35 (d, 4H, J = 8.0 Hz), 7.08 (d, 4H, J = 8.0 Hz), 4.05 (s, 4H), 3.78 (s, 2H), 3.39 (t, 4H, J = 6.4 Hz), 1.62−1.21 (m, 9H). ^{13}C NMR (100 MHz, DMSO-d_6, 293 K) δ/ppm: 153.5, 137.0, 135.3, 128.7, 118.2, 63.9, 60.5, 32.3, 28.4, 25.1. IR (ATR) ν (cm^{-1}): 3308, 3120, 3045, 2934, 2857, 1698, 1596, 1530, 1413, 1310, 1230, 1069, 815, 769, 678.

Poly(MDI-PPG). A cylindrical flask, equipped with a low-pressure mercury lamp and a magnetic stirring bar, was charged with CHCl$_3$ (50 mL). The sample was cooled at 0 °C with an ice bath, and vigorously stirred upon bubbling with O$_2$ (0.1 L/min) under exposure to UV light for 3 h. After the photochemical reaction, the lamp was turned off, and the sample solution was cooled to −20 °C. 4,4′-Diaminodiphenyl-methane (5.0 mmol, 1.00 g) dissolved in CHCl$_3$ (10 mL) and pyridine (50 mmol, 4.0 mL) was sequentially added to the sample solution with a syringe pump at this temperature. The sample solution was then evaporated at 90 °C to remove the solvent. PPG with the average molecular weight of 400 (5 mmol, 2.00 g) was injected into the sample with a syringe pump, and the sample was stirred at 50 °C for 13 h. The sample was washed with water and extracted with CH$_2$Cl$_2$. The combined organic layer was dried over anhydrous Na$_2$SO$_4$ and evaporated to dryness under reduced pressure. The residue was dried under vacuum at 60 °C for 2 h to give poly(MDI-PPG) in 89% yield (2.91 g) as dark brown solid. The average molecular weight was estimated by GPC in comparison with the polystyrene standard: M_w = 6200, M_n = 3600, M_w/M_n = 1.72. ^{1}H NMR (400 MHz, CDCl$_3$, 293 K) δ/ppm: 7.37 (m, 4H), 7.08 (m, 4H), 4.87 (s, 1H), 3.53−3.31 (m, 29H), 1.91−1.02 (m, 24H); ^{13}C NMR (100 MHz, DMSO-d_6, 293 K) δ/ppm: 153.2, 137.8, 137.2, 135.4, 135.3, 129.2, 118.3, 79.2, 74.6, 72.4, 72.2, 71.2, 65.4, 20.2, 17.4. IR (ATR) ν (cm^{-1}): 3275, 3188, 3114, 3059, 2970, 2923, 1723, 1597, 1533, 1509, 1456, 1411, 1374, 1308, 1224, 1079, 927, 817, 754, 681.

8FHDI-2FIP. A cylindrical flask, equipped with a low-pressure mercury lamp and a magnetic stirring bar, was charged with CHCl$_3$ (20 mL) and 8FHDA·2HCl (2 mmol, 0.68 g). The sample was cooled at 0 °C with an ice bath and vigorously stirred upon bubbling with O$_2$ (0.1 L/min) under exposure to UV light for 3 h. After the photochemical reaction, the lamp was turned off, and 2,6-lutidine (20 mmol, 2.3 mL) was slowly added to the sample solution with a syringe pump. The sample solution was then evaporated at 100 °C to remove the solvent. A mixture of 1,1,1,3,3,3-hexafluoro-2-propanol (8 mmol, 0.92 mL) and 2,6-lutidine (8 mmol, 0.92 mL) was injected into the sample with a syringe pump, and the sample solution was stirred at 50 °C for 20 h. The sample was washed with water and extracted with CH$_2$Cl$_2$. The combined organic layer was dried over anhydrous Na$_2$SO$_4$ and evaporated to dryness under reduced pressure. The residue was dried under vacuum at 30 °C for 16 h to give 8FHDI-2HFIP in 37% yield (0.48 g) as white powder. ^{1}H NMR (400 MHz, CDCl$_3$, 293 K) δ/ppm: 5.68 (sep, 2H, J = 6.0 Hz), 5.40 (t, NH), 3.98 (td, 4H, J = 15.2, 6.4 Hz); ^{13}C NMR (100 MHz, DMSO-d_6, 293 K) δ/ppm: 153.3, 121.0 (q, J = 282.8 Hz), 115.6 (m), 111.0 (m), 67.1 (m), 41.1 (m); ^{19}F NMR (376 MHz, CDCl$_3$, 293 K) δ/ppm: −73.6 (d, J = 5.3 Hz), −118.8, −123.5 (m). IR (ATR) ν (cm^{-1}): 3342, 3094, 2981, 1736, 1560, 1438, 1382, 1360, 1257, 1201, 1155, 1106, 1081, 1014, 924, 906, 872, 751, 734, 691, 650. HRMS (ESI orbitrap) m/z: [M − H]$^-$ calcd for $C_{14}H_7F_{20}N_2O_4$ 647.0092; found 647.0083.

Poly(8FHDI-HD). A cylindrical flask, equipped with a low-pressure mercury lamp and a magnetic stirring bar, was charged with $CHCl_3$ (30 mL) and 8FHDA·2HCl (2 mmol, 0.68 g). The sample was cooled at 0 °C with an ice bath and vigorously stirred upon bubbling with O_2 (0.1 L/min) under exposure to UV light for 2 h. After the photochemical reaction, the lamp was turned off, and 2,6-lutidine (20 mmol, 2.3 mL) was slowly added to the sample solution with a syringe pump. The sample solution was then evaporated at 90 °C to remove the solvent. 1,6-Hexanediol (2 mmol, 0.24 g) dissolved in $CHCl_3$ (10 mL) was injected into the sample with a syringe pump, and the sample solution was stirred at 50 °C for 110 h. The sample was washed with water and extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness under reduced pressure. The residue was dried under vacuum at 60 °C for 2 h to give poly(8FHDI-HD) in 91% yield (0.81 g) as brown powder. The average molecular weight was estimated by GPC in comparison with the polystyrene standard: $M_w = 4000$, $M_n = 2400$, $M_w/M_n = 1.66$. ^1H NMR (400 MHz, DMSO-d_6, 293 K) δ/ppm: 3.99 (t, 4H, $J = 6.4$ Hz), 3.91 (td, $J = 18.0$, 6.4 Hz), 3.79 (td, $J = 16.4$, 6.0 Hz), 1.40−1.55 (m, 4H), 1.32 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6, 293 K) δ/ppm: 156.7, 154.7, 124.6, 106.9, 67.0, 64.4, 60.6, 45.2, 32.4, 32.4, 31.9, 27.9, 25.1; ^{19}F NMR (376 MHz, DMSO-d_6, 293 K) δ/ppm: −118.1, −123.4. IR (ATR) ν (cm^{-1}): 3322, 3072, 2944, 2868, 1698, 1543, 1474, 1425, 1267, 1221, 1155, 1125, 979, 862, 781, 734. Anal. calcd for $[C_{14}H_{18}F_8N_2O_4]_n$: C, 39.08; H, 4.22; N, 6.51. Found: C, 39.53; H, 4.39; N, 6.23.

Poly(8FHDI-PPG). A cylindrical flask, equipped with a low-pressure mercury lamp and a magnetic stirring bar, was charged with $CHCl_3$ (30 mL) and 8FHDA·2HCl (2 mmol, 0.68 g). The sample was cooled at 0 °C with an ice bath and vigorously stirred upon bubbling with O_2 (0.1 L/min) under exposure to UV light for 2 h. After the photochemical reaction, the lamp was turned off, and 2,6-lutidine (20 mmol, 2.3 mL) was slowly added to the sample solution with a syringe pump. The sample solution was then evaporated at 100 °C to remove the solvent. PPG with the average molecular weight of 400 (2 mmol, 0.8 g) was injected into the sample with a syringe pump, and the sample was stirred at 50 °C for 20 h. The sample was washed with water and extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness under reduced pressure. The residue was dried under vacuum at 60 °C for 2 h to give poly(8FHDI-PPG) in 86% yield (1.18 g) as a light brown solid. The average molecular weight was estimated by GPC in comparison with the polystyrene standard: $M_w = 8800$, $M_n = 3400$, $M_w/M_n = 2.59$. ^1H NMR (400 MHz, CDCl_3, 293 K) δ/ppm: 4.96 (br, 1H), 3.91 (br, 2H), 3.49 (m, 22H), 1.13−1.25 (m, 26H); ^{13}C NMR (100 MHz, DMSO-d_6, 293 K) δ/ppm: 156.1, 79.1, 74.7, 72.3, 71.0, 70.8, 70.2, 70.0, 65.2, 20.2, 17.0; ^{19}F NMR (376 MHz, DMSO-d_6, 293 K) δ/ppm: −119.0, −123.7. IR (ATR) ν (cm^{-1}): 3314, 2973, 2933, 2873, 1723, 1541, 1453, 1375, 1256, 1161, 1119, 942, 863, 827, 753, 680. Anal. calcd for $[C_{14}H_{18}F_8N_2O_5(C_3H_6O)_5]_n$: C, 47.24; H, 6.52; N, 3.80. Found: C, 46.86; H, 6.51; N, 3.89.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c07132.

^1H, ^{13}C, and ^{19}F NMR spectra; GPC profiles (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Akihiko Tsuda − *Department of Chemistry, Graduate School of Science, Kobe University, Kobe 657-8501, Japan;* ⓞ orcid.org/0000-0002-9232-1455; Email: tsuda@harbor.kobe-u.ac.jp

Authors

Ryo Muranaka − *Department of Chemistry, Graduate School of Science, Kobe University, Kobe 657-8501, Japan*

Yue Liu − *Department of Chemistry, Graduate School of Science, Kobe University, Kobe 657-8501, Japan*

Itsuumi Okada − *Department of Chemistry, Graduate School of Science, Kobe University, Kobe 657-8501, Japan*

Takashi Okazoe − *Materials Integration Laboratories, AGC Inc., Yokohama City, Kanagawa 230-0045, Japan*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.1c07132

Notes

The authors declare the following competing financial interest(s): This research was funded by AGC Inc.

■ REFERENCES

(1) (a) Saunders, J. H.; Slocombe, R. J. The Chemistry of the Organic Isocyanates. *Chem. Rev.* **1948**, *43*, 203−2018. (b) Arnold, R. G.; Nelson, J. A.; Verbanc, J. J. Recent Advances in Isocyanate Chemistry. *Chem. Rev.* **1957**, *57*, 47−76. (c) Ozaki, S. Recent Advances in Isocyanate Chemistry. *Chem. Rev.* **1972**, *72*, 457−496.

(2) (a) Shriner, R. L.; Horne, W. H.; Cox, R. F. B. *p*-Nitrophenyl Isocyanate. *Organic Syntheses*; Wiley, 1943; Vol, 2, p 453. (b) Farlow, M. W. Hexamethylene Diicocyanate. *Organic Syntheses*; Wiley, 1963; Vol. 4, p 521.

(3) (a) Hardy, D. V. N. Preparation of Aryl Carbimides. *J. Chem. Soc.* **1934**, 2011. (b) Gill, J. E.; MacGillivray, R.; Munro, J. Preparation of Symmetrical Aromatic Triamines and Triisocyanates. *J. Chem. Soc.* **1949**, 1753−1754. (c) Slocombe, R. J.; Hardy, E. E.; Saunders, J. H.; Jenkins, R. L. Phosgene Derivatives. The Preparation of Isocyanates, Carbamyl Chlorides and Cyanuric Acid. *J. Am. Chem. Soc.* **1950**, *72*, 1888−1891.

(4) Hentschel, W. Notizen. *Ber. Dtsch. Chem. Ges.* **1884**, *17*, 1284−1289.

(5) (a) Busschaert, N.; Kirby, I. L.; Young, S.; Coles, S. J.; Horton, P. N.; Light, M. E.; Gale, P. A. Squaramides as Potent Transmembrane Anion Transporters. *Angew. Chem., Int. Ed.* **2012**, *51*, 4426−4430. (b) Chen, Y.; Su, L.; Yang, X.; Pan, W.; Fang, H. Enantioselective Synthesis of 3,5-Disubstituted Thiohydantoins and Hydantoins. *Tetrahedron* **2015**, *71*, 9234−9239. (c) Blain, M.; Yau, H.; Jean-Gerard, L.; Auvergne, R.; Benazet, D.; Schreiner, P. R.; Caillol, S.; Andrioletti, B. Urea- and Thiourea-Catalyzed Aminolysis of Carbonates. *ChemSusChem* **2016**, *9*, 2269−2272.

(6) Ozaki, S. Isocyanates. *Nippon Gomu Kyokaishi* **1972**, *45*, 435−443.

(7) Babad, H.; Zeiler, A. G. The Chemistry of Phosgene. *Chem. Rev.* **1973**, *73*, 75−91.

(8) (a) Eckert, H.; Forster, B. Triphosgene, a Crystalline Phosgene Substitute. *Angew. Chem., Int. Ed.* **1987**, *26*, 894−895. (b) Cotarca, L.;

Eckert, H. *Phosgenations—A Handbook*; Wiley-VCH: Weinheim, 2003. (c) Tsai, J. H.; Takaoka, L. R.; Powell, N. A.; Nowick, J. S. Synthesis of Amino Acid Ester Isocyanates: Methyl (*S*)-2-Isocyanato-3-Phenylpropanoate. *Organic Syntheses*; Wiley, 2004; Vol. 10, p 544.

(9) Cotarca, L.; Geller, T.; Répási, J. Bis(trichloromethyl)carbonate (BTC, Triphosgene): A Safer Alternative to Phosgene? *Org. Process Res. Dev.* **2017**, *21*, 1439−1446.

(10) (a) Kuwahara, Y.; Zhang, A.; Soma, H.; Tsuda, A. Photochemical Molecular Storage of Cl_2, HCl, and $COCl_2$: Synthesis of Organochlorine Compounds, Salts, Ureas, and Polycarbonate with Photodecomposed Chloroform. *Org. Lett.* **2012**, *14*, 3376−3379. (b) Tsuda, A. Preparation of Halogenated Carboxylate Esters by Irradiating Light to Halocarbons and Alcohols in the Presence of Oxygen. JP5900920B2, 2016.

(11) Liang, F.; Yanai, M.; Suzuki, Y.; Tsuda, A. Photo-on-Demand Synthesis of Chloroformates with a Chloroform Solution Containing an Alcohol and Its One-Pot Conversion to Carbonates and Carbamates. *Org. Lett.* **2020**, *22*, 3566−3569.

(12) Liang, F.; Eda, K.; Okazoe, T.; Wada, A.; Mori, N.; Konishi, K.; Tsuda, A. Photo-on-demand Synthesis of Vilsmeier Reagents with Chloroform and their Applications to One-pot Organic Syntheses. *J. Org. Chem.* **2021**, *86*, 6504−6517.

(13) Hashimoto, Y.; Hosokawa, S.; Liang, F.; Suzuki, Y.; Dai, N.; Tana, G.; Eda, K.; Kakiuchi, T.; Okazoe, T.; Harada, H.; Tsuda, A. Photo-on-Demand Base-Catalyzed Phosgenation Reactions with Chloroform: Synthesis of Arylcarbonate and Halocarbonate Esters. *J. Org. Chem.* **2021**, *86*, 9811−9819.

(14) (a) Riddick, J. A.; Bunger, W. B. *Techniques of Chemistry, Volume II, Organic Solvents*; Wiley: New York, 1970; pp 771−773. (b) Kawai, S. Discussion on Decomposition of Chloroform. *Yakugaku Zasshi* **1966**, *86*, 1125−1132.

(15) (a) Ohkuma, S.; Sakai, I. Detection of Aromatic Primary Amines by a Photochemical Reaction with Pyridine. *Bunseki Kagaku.* **1975**, *24*, 385−387. (b) Mercier, P.; Dupuis, P.; Sauvageau, P.; Sandorfy, C. The Electronic Spectrum of the Triethylamine-Perfluoro-tert-Butanol Complex. *Chem. Phys. Lett.* **1979**, *68*, 1−4. (c) Prather, K. A.; Lee, Y. T. The Photodissociation of Pyridine at 193 nm. *Isr. J. Chem.* **1994**, *34*, 43−53. (d) Errami, M.; El Dib, G.; Cazaunau, M.; Roth, E.; Salghi, R.; Mellouki, A.; Chakir, A. Atmospheric Degradation of Pyridine: UV Absorption Spectrum and Reaction with OH Radicals and O_3. *Chem. Phys. Lett.* **2016**, *662*, 141−145.

(16) Tsuda, A. Carbonate Derivative Production Method. WO2018211952A1, Nov 22, 2018.

(17) Tsuda, A.; Okazoe, T. Production Method for Isocyanate Compound. WO2020100971A1, May 22, 2020.

(18) (a) Russell, B. R.; Edwards, L. O.; Raymonda, J. W. Vacuum Ultraviolet Absorption Spectra of the Chloromethanes. *J. Am. Chem. Soc.* **1973**, *95*, 2129−2133. (b) Ogita, T.; Hatta, H.; Kagiya, T. Photoinduced Decomposition of Trihalomethanes in Aqueous Solution by UV Irradiation. *Nippon Kagaku Kaishi* **1983**, *11*, 1664−1669.

(19) (a) Paul, R.; Anderson, G. W. N,N'-Carbonyldiimidazole, a New Peptide Forming Reagent. *J. Am. Chem. Soc.* **1960**, *82*, 4596−4600. (b) Staab, H. A.; Wendel, K. 1,1-Carbonyldiimidazole. *Organic Syntheses*; Wiley, 1973; Vol. 5, p 201.

(20) Tsuda, A.; Okazoe, T.; Wada, H.; Tanaka, H.; Sunayama, T.; Kakiuchi, T. Method for Manufacturing Fluorinated Polyurethane. JP2021-179746, Nov 2, 2021.

(21) (a) Takakura, T.; Yamabe, M.; Kato, M. Synthesis of Fluorinated Dicarboxylic Acids and Their Derivatives. *Nippon Kagaku Kaishi* **1985**, *11*, 2208−2210. (b) Takakura, T.; Yamabe, M.; Kato, M. Synthesis of Fluorinated Difunctional Monomers. *J. Fluorine Chem.* **1988**, *41*, 173−183.