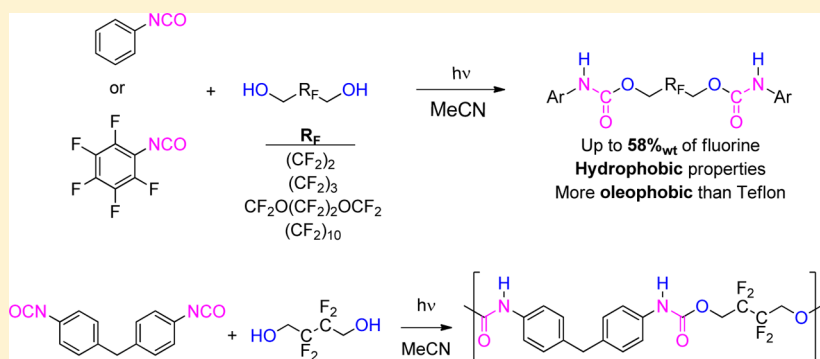


Photochemical Activation of Extremely Weak Nucleophiles: Highly Fluorinated Urethanes and Polyurethanes from Polyfluoro Alcohols

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S Supporting Information



ABSTRACT: An efficient and environmentally friendly photoreaction between phenyl isocyanate or pentafluorophenyl isocyanate and polyfluorinated alcohols and diols is described for the first time. New highly fluorinated urethanes and diurethanes, derived from aromatic isocyanates, are produced in good yields in a photoreaction that is apparently governed by the acidic properties of the polyfluoro alcohols and diols. The wettability properties of the new polyfluorinated diurethanes have been tested, some of them showing significantly high values of hydrophobicity and oleophobicity. This new photoreaction has also been tested in the production of a model polyfluorinated polyurethane, establishing the influence of the irradiation power in the outcome of the process, and directly achieving a molecular weight distribution corresponding to a number-average $DP_n = 12$ and a highest $DP_n = 20$ after 4 h of irradiation (DP_n : “number-average degree of polymerization”).

INTRODUCTION

A lot of attention has been given to the synthesis of fluorinated organic materials.¹ Polyfluorinated organic compounds have very interesting properties,² their applications having special significance in the fields of pharmaceuticals, catalysis and materials science.^{3,4} For instance, fluorinated polyurethanes⁵ combine some virtues of polyurethane and fluorinated polymers, such as high thermal and oxidative stability, good chemical resistance, high oxygen permeability, low water absorptivity and attractive surface properties, excellence resistance to ultraviolet radiation and nuclear radiation, excellent flexibility, high weatherability, and good compatibility with blood in biomedical applications.^{6,7} Also recently, polyfluorinated oligourethanes with special applications as alternatives to polydimethylsiloxane in fouling-releasing coatings,⁸ and in microfluidic device fabrication,⁹ have been described. However, polyfluorocarbamates derivatives have not yet developed all their potential, among other reasons, due to the general very low reactivity of fluorine substituted alcohols, the main organofluorine building blocks involved in their synthesis.

The standard approach to produce carbamates consists of the reaction between an isocyanate and an alcohol.¹⁰ However, polyfluorinated alcohols show a very low nucleophilicity in polar reactions. Thus, polyfluorinated alcohols do not react

with alkyl isocyanates and react very slowly with aromatic isocyanates at room temperature, not very “green conditions” such as catalysis with amines¹¹ or with dibutyltin derivatives,¹² or highly electrophilic carbamates (aroxysulfonylcarbamates),¹³ being necessary, with very few exceptions,^{8b} for the reactions to proceed at a synthetically useful rate. Alternative approaches include the catalyzed reaction of fluorinated carbonates with amines¹⁴ or the electrochemically induced Hofmann rearrangement.¹⁵ Most of the mechanistic schemes proposed for the reactions of isocyanates and alcohols include the intermediacy of “complexes” of the ion-pair, and solvent stabilized ion-pair, type, that evolve efficiently to the final carbamate.^{10,16} However, this evolution does not take place easily when acidic weak nucleophiles such as polyfluoro alcohols are used.

Very recently, we have reported a new radical mechanism for the reaction of polyfluorinated alcohols and phenyl isocyanate.¹⁷ Acidity of polyfluoro alcohols seems to be responsible for the new reactivity, and evidence from kinetic studies, electron paramagnetic resonance and cyclic voltammetry, suggest that polyfluoroalkoxy radical is the key intermediate in the chain. In the present work, we worked to develop this reaction from the preparative point of view, finding that it is

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Table 1. Ground-State Reactions of Phenyl Isocyanate with Polyfluorinated Alcohols

entry	alcohol	Product	Solvent	Yield (%)
1 ^a	HOCH ₂ CF ₃		MeCN	0
2 ^a	2a	3a	DMF	93
3 ^a	HOCH ₂ (CF ₂) ₈ CF ₃		MeCN	0
4 ^a	2b	3b	DMF	58
5 ^a			MeCN	0
6 ^a	2c	3c	DMF	80
7 ^b			DMF ^c	74
8 ^b			DMF ^c	57
9 ^b			DMF ^c	61
10 ^b			DMF	0 ^d

^aReported in ref 17. ^bDescribed in this work. Reaction conditions: 0.50 mmol of PhNCO, 1 mmol of fluorinated diol, dry DMF (50 mL), rt under nitrogen (procedure A). ^cIn acetonitrile, recovery of starting materials. ^dNo reaction observed, recovery of materials.

very sensitive to solvent and concentration, and that diols are only reactive at one end, all together hampering its practical use. However, we succeeded in photochemically stimulating the reaction, and these results constitute the main body of the article.

In this paper, we describe the novel photochemical reaction of aromatic isocyanates and polyfluoro alcohols and polyfluoro diols to produce arylcarbamate derivatives. In this way, a series of polyfluoromonoaryl carbamates and dicarbamates with high fluorine content have been synthesized, and their surface properties (hydrophobicity and oleophobicity) tested. This new photochemical procedure constitutes an environmental friendly access to small molecules with a high content of fluorine¹⁸ that could, in principle, have application as stain, grease, and water-repelling chemicals. It also constitutes a new tool for the synthesis of highly fluorinated polyurethanes as we describe in the article.

RESULTS AND DISCUSSION

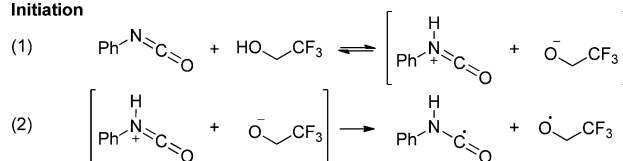
Phenyl isocyanate **1** does not react with 2,2,2-trifluoroethanol **2a**, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-1-octanol **2b**, and 1,1,1,3,3,3-hexafluoro-2-propanol **2c** at room temperature in acetonitrile (Table 1, entries 1, 3, and 5), being the reaction only possible (Table 1, entries 2, 4, and 6) in DMF and under

strict concentration conditions as described in ref 17. Under these conditions, a radical chain mechanism seem to be operating (Scheme 1)¹⁷ with the polyfluoroalkoxy radical as key intermediate.¹⁹

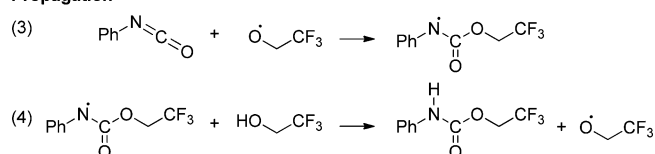
In order to advance toward the aim of producing oligo- and polyurethanes, we explored the reactions of phenylisocyanate

Scheme 1. Mechanism Proposed in ref 17 for the Ground-State Reaction of Phenyl Isocyanate and Polyfluorinated Alcohols in DMF

Initiation



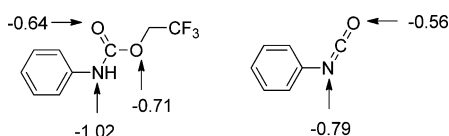
Propagation



with polyfluorodiols, in the same conditions (Table 1, entries 7–10). To our surprise, a rather efficient reaction was observed in three cases (no reaction could be achieved with **2g**), but only clean monocondensation took place (products **3d–f**), with not even traces of the dicondensation products being detected. We were unable to attain a reaction at the second hydroxyl group. The lack of reactivity of the hydroxyl group when a carbamate group is already present in the structure was confirmed by attempting the reaction of the monocondensated products (**3d–f**), previously isolated, with phenyl isocyanate, under the same conditions, that failed completely.

This, in principle, strange behavior could be understood in the framework of the mechanistic proposal described in Scheme 1. A crucial event in the mechanism seems to be the protonation (or hydrogen bond formation) of the isocyanate group by the relatively acidic polyfluoro alcohol. Simple theoretical calculations (Scheme 2, AM1 method, implemented

Scheme 2. Mulliken Charges (AM1) and Preferred Protonation Positions in Carbamates and Isocyanates (Chem3d, ChemBioOffice 2010)



in Chem3D) indicate that the electronic density in the carbamate group is higher than in the isocyanate group. Thus, the presence of a preformed carbamate in the structure would produce a distraction of the proton from the isocyanate and, hence, the quenching of the reaction. The mechanisms probably have short chains and therefore need multiple initiations.

To overcome this obstacle, we turned to photochemistry, expecting that under irradiation the reaction would become more efficient. In Table 2, the photoreactions of simple polyfluoro alcohols with phenyl isocyanate in acetonitrile are

Table 2. Photochemical Reactions of Phenyl Isocyanate with Fluorinated Monoalcohols^a

entry	alcohol	product	yield (%)
1			87
2			36
3			66

^aReaction conditions: 0.5 mmol of PhNCO, 1.0 mmol of fluorinated alcohol, dry CH₃CN, under nitrogen, 60 min irradiation with mercury high pressure lamp Philips HPK 125W (procedure B).

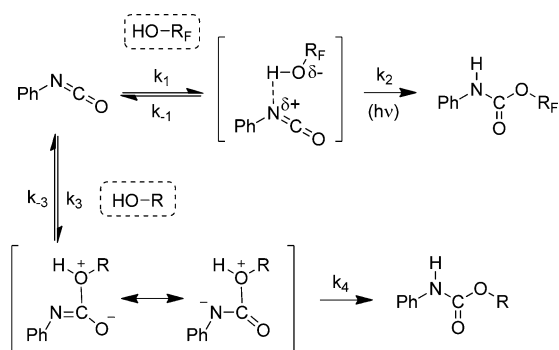
described. Thus, upon irradiation of the solution with a 125 W medium pressure Hg lamp (pyrex filter), the corresponding carbamates were obtained in fair to good yields. It is remarkable that under these new conditions the reaction proceeded in acetonitrile, a useless solvent in the ground state reactions described in Table 1.

In order to obtain some mechanistic insight in this new photoreaction, we have compared the reactivity of trifluoroethanol with that of ethanol. It is remarkable the fact that the reaction with a standard non fluorinated alcohol such as ethanol does not show stimulation by UV irradiation. Thus, the reaction of ethanol with phenylisocyanate (acetonitrile, r.t.) does not show a significant difference in the absence or in the presence of irradiation (25% yield after 15 min in both cases). Comparison of this result with the described in Tables 1 and 2 for trifluoroethanol (acetonitrile), suggests the existence of important differences between the preferred reactivity channels of the two alcohols. This was confirmed by a competition experiment. Thus, when the photoreaction of phenyl isocyanate was carried out with a mixture 1:1 of trifluoroethanol and ethanol, no reaction was observed for ethanol after 15 min, while the trifluoroalkoxycarbamate **3a** was produced in 75% yield as the only product, indicating that under irradiation 2,2,2-trifluoroethanol reacts fast enough to make the reaction of ethanol neglectable.

Having in mind the mechanistic proposal described in Scheme 1 for the ground-state reaction, one question was if we were in the presence of a photoinduced radical-chain process. This was investigated by carrying out the photoreaction between phenyl isocyanate and trifluoroethanol in the presence of different radical scavengers and radical-interacting species such as TEMPO, 1-octene, and acrylonitrile. In no case was any effect observed, thus ruling out the existence of free radicals out of the solvent cage in the photochemical mechanism.

In Scheme 3, an interpretation for these mechanistic experiments is proposed. It is well accepted that in the

Scheme 3. Proposed Mechanisms for the Reaction of Phenyl Isocyanate with 2,2,2-Trifluoroethanol or Ethanol

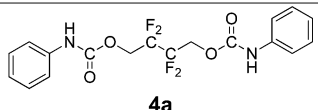
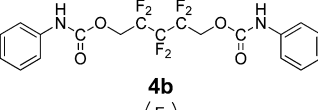
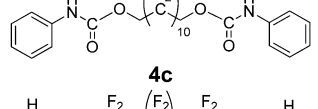
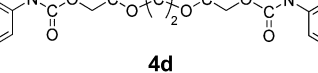


reactions of nonfluorinated alcohols with isocyanates, the nucleophilic center of the alcohol is first added to the electrophilic carbon of the isocyanate group, and then hydrogen atom is transferred to the nitrogen.¹⁰ This would correspond to the reactivity of ethanol with phenyl isocyanate (steps 3 and 4 in Scheme 3). However, 2,2,2-trifluoroethanol is much less nucleophilic but much more acidic than ethanol (ethanol $pK_a = 29.8$ and 2,2,2-trifluoroethanol $pK_a = 23.5$ in DMSO),²⁰ and therefore, the standard order of events seem not to be followed in this case. What we propose here is an opposite order of

events: trifluoroethanol would produce a strong hydrogen bond complex with the isocyanate that upon irradiation would undergo proton transfer followed by nucleophilic addition (steps 1 and 2 in Scheme 3). These hydrogen-bonding complexes between alcohols and isocyanates have been previously proposed in the literature as intermediates in some cases for urethane formation.¹⁶ The results from the competition experiment indicate that the photochemical step is fast ($k_2 \gg k_{-1}$) and that the step 1 is not an equilibrium in the presence of irradiation. These results also indicate that $k_1 \gg k_3$, as expected since step 1 is a fast hydrogen-bond formation process, while step 3 is a slower covalent bond formation.

Next we explored the viability of the new photoreaction, with polyfluorodiols, and the results were remarkable in the photoreactions with phenyl isocyanate (Table 3). Hence, now the dicondensation products **4a–d** could be obtained in good yields (63–77%), thus overcoming the strong limitation found in the ground-state reaction.

Table 3. Photochemical Reaction of Phenyl Isocyanate with Polyfluorinated Diols^a

Entry	Diol	Product	Yield (%)
1	2d		71
2	2e		63
3	2f		68
4	2g		77

^aReaction conditions: 0.5 mmol of PhNCO, 0.5 mmol of fluorinated diol, dry CH₃CN, under nitrogen, 4 h irradiation with mercury high pressure lamp Philips HPK 125W (procedure C).

One of our aims was to build molecules with a high content of fluorine, and therefore, the corresponding photoreactions between the polyfluorodiols and pentafluorophenylisocyanate, **5**, were also tested. The addition products **6a–d** were obtained in good yields (up to 85%, Table 4). It is worth noting that the blank reactions (acetonitrile), in the absence of irradiation, failed completely in all the cases.

Our hypothesis was that this new family of products could show interesting wettability properties. Highly fluorinated compounds normally show hydrophobic and oleophobic properties²¹ that give rise to many potential applications. The wettability of a surface is determined by two factors, the chemical composition and the topographic structure.²² The standard measurement of wettability is the “contact angle” of a droplet of a standard liquid (water and hexadecane in our case) on a surface modified by spin coating with the tested

compounds. The contact angle on a flat surface is referred normally as the “intrinsic contact angle” of the surface. Typically, when the intrinsic contact angle is large enough, a roughening of the surface will result in an increase of the value, that in the ideal situation can give rise to a superhydrophobic and superoleophobic surfaces.²³ We have measured the intrinsic contact angles of water and hexadecane (HD) on surfaces of the products collected in Tables 3 and 4, prepared by spin-coating on glass, and compared the values with the corresponding ones for PTFE (Teflon) measured in the same conditions. The results are gathered in Table 5.

Water sessile drop contact angle measurements (Table 5) gave values over 80° for all compounds except **6c** and **6d**. In this case, the already hydrophobic nature of compounds **4a–d** seems not to be significantly altered by the presence of the perfluorinated phenyl rings. Even on the contrary, the average water sessile drop contact angle for bis(pentafluorophenylcarbamates) **6a–d** is smaller (74°) than the measured average for the nonfluorinated bis(phenylcarbamates) **4a–d** (83°).

A more defined effect is observed in the hexadecane sessile drop contact angle measurements, where a loose relationship can be observed between the contact angle values and the fluorine content in the molecule. Hence, bis(pentafluorophenylcarbamates) **6a–d** show a significantly higher average contact angle value (50°) than the bis(phenylcarbamates) **4a–d** (24°), confirming the effect of the fluorine content on the lipophobicity of a particular molecule.

Remarkable is the behavior of the product **6a** (Table 5, entry 5), containing a short polyfluorodiol moiety, and the pentafluorophenylcarbamate moiety (Figure 1). In this case, the water sessile drop contact angle is 96° and the corresponding hexadecane value is 58° (117° and 48°, respectively, for PTFE in the same conditions), significant values for a nonbranched small molecule.²⁴ Here, it is worth mentioning the prominence that small molecules with a high content of fluorine are gaining recently due to strong environmental concerns over persistent long-chain perfluoroalkyl compounds.¹⁸

Finally, and in order to establish the scope of this simple photochemical procedure, we tested the viability of producing polyurethanes using polyfluorodiols **4a** as a model. Hence, the photoreaction of 2,2,3,3-tetrafluorobutane-1,4-diol, **4a**, with MDI (4,4'-methylenediphenyl diisocyanate)²⁵ under the standard conditions (125 W medium pressure Hg lamp, 4 h) produces a distribution of oligourethanes (Figure 2a, $n = 0, 1, 2$, and 3), with alcohol termination (no isocyanate group absorption was detected by IR). Irradiation for 4 h with a 400 W lamp results in an increase in the average degree of polymerization of the oligomer up to $n = 6$ in Figure 2a representation ($DP_n = 12$, IUPAC definition for “average number degree of polymerization”, DP_n implies $DP_n = 2n$, with “ n ” being the repeating units as indicated in Figure 2a). In Figure 2b, comparison of Gel permeation chromatography (GPC) chromatograms for the two cases is shown. A displacement toward higher molecular weights was observed when a more powerful lamp was used, and in both cases, the limit for the used conditions seems to be around $n = 10–11$ (5000 Da molecular weight, $DP_n = 20–22$).

The evolution of the photopolymerization with time is described in Figure 2c using ¹⁹F{¹H} NMR for the photoreaction with 400 W lamp. Distinct absorptions correspond to fluorine atoms in the monomeric diol and in the polymer, and for the polymer the absorptions are distinct depending if the

Table 4. Photochemical Reaction of Pentafluorophenyl Isocyanate with Polyfluorinated Diols^a

Entry	Diol	Product	Yield (%)
1	2d	6a	79
2	2e	6b	45
3	2f	6c	54
4	2g	6d	85

^aReaction conditions: 0.5 mmol of PhNCO, 0.5 mmol of fluorinated diol, dry CH₃CN, under nitrogen, 4 h irradiation with mercury high-pressure lamp Philips HPK 125W (procedure C).

Table 5. Contact Angle Measurements

entry	compd	%wt F	contact angle ^a (deg)	
			H ₂ O	<i>n</i> -C ₁₆ H ₃₂
1	4a	19.0	86	24
2	4b	25.3	81	19
3	4c	47.5	84	11
4	4d	28.6	82	41
5	6a	45.8	96	58
6	6b	48.2	85	47
7	6c	58.1	44	53
8	6d	48.0	72	40
9	PTFE	76.0	117	48

^aSessile drop contact angle measurement of the corresponding dicarbamate (dissolved in acetone) deposited by spin coating (6.000 rpm) over a 1 × 1 cm surface of cleaned glass.

fluorine atoms are at the end part of the polymer (*terminal* fluorine atoms) or in the inner part of the chain (*inner* fluorine atoms). The different ¹⁹F chemical shifts are indicated in Figure 2a. The use of ¹⁹F NMR allows also establishment of the number-average degree of polymerization through “end group analysis” and complements GPC analysis. Thus, after 1 h of irradiation, the spectrum indicates the presence of monomeric diol 4a and that 30% of polyfluorodiols had reacted by one end but significant poly reaction had not yet occurred. In the spectrum taken after 2 h, there were approximately two

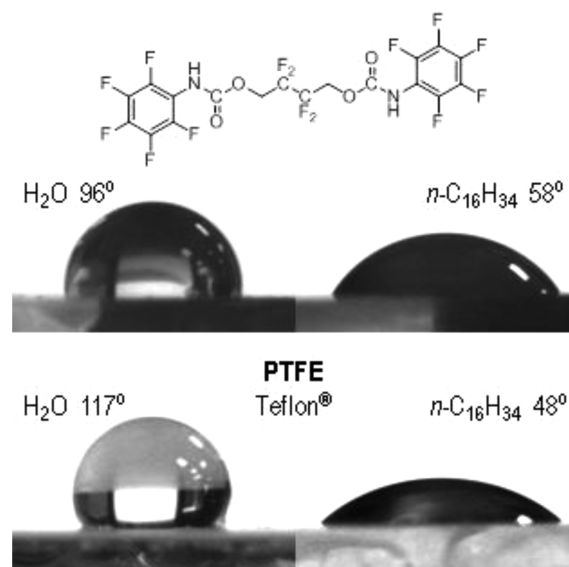


Figure 1. Photographs of sessile drops of water and hexadecane in a surface spin coating modified with 6a and PTFE. Contact angle measurements comparison.

terminal fragments for each inner part, this corresponding to *n* = 1 in the structure of Figure 2a (DP_n = 2). Finally after 4 h, the polyfluorodiols had reacted completely, and three inner parts

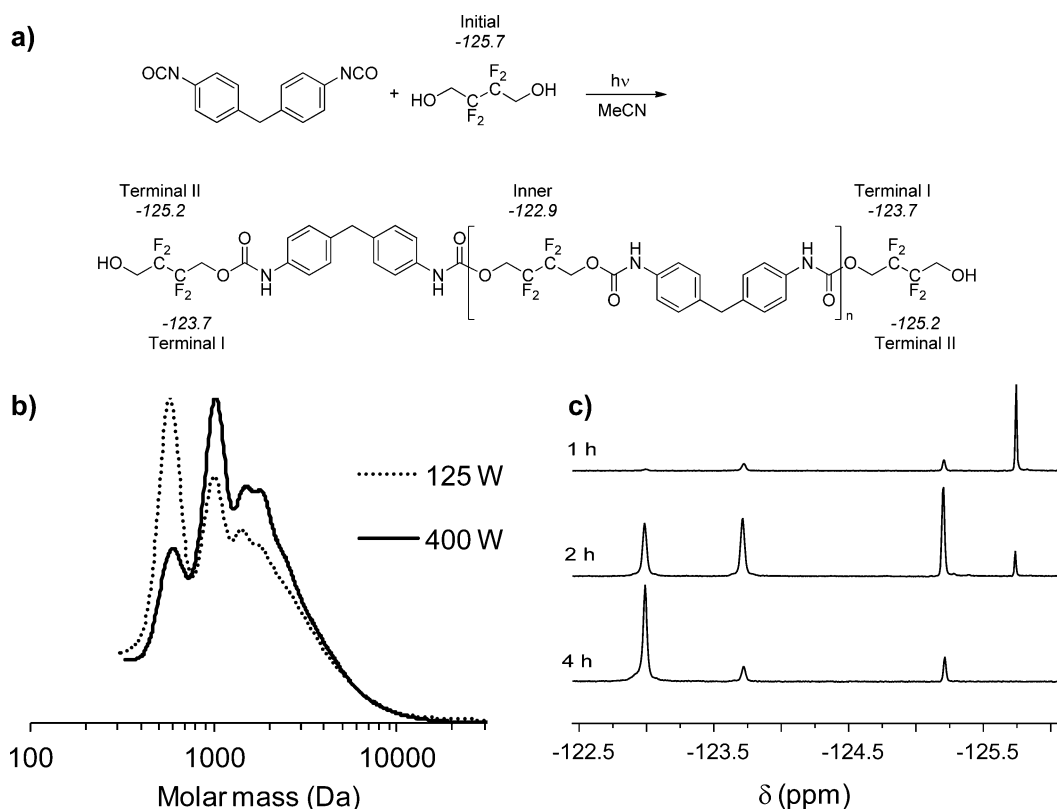


Figure 2. (a) Structure of the polymer and $^{19}\text{F}\{^1\text{H}\}$ NMR chemical shifts in acetone- d_6 . (b) Effect of the irradiation source. Comparison of the GPC chromatograms of photoreaction using a 125 W lamp (1.8×10^{19} photon/s) vs a 400 W lamp (5.0×10^{19} photon/s) (irradiation time 4 h). (c) $^{19}\text{F}\{^1\text{H}\}$ NMR spectra at different reaction times using a 400 W UV–vis light source.

formed for each terminal fragment, which corresponds to $n = 6$ as an average for the structure depicted in Figure 2a ($\text{DP}_n = 12$). This result agrees with the molecular weight distribution obtained from GPC analysis (Figure 2b).

CONCLUSION

We conclude that the attempt to extend the reported ground-state reaction between polyfluoro alcohols and phenyl isocyanate to polyfluoro diols, using the previously described conditions,¹⁷ was not successful. However, a novel photochemical version of the reaction has been successfully tested, allowing the synthesis in good yields of polyfluorinated diurethane small molecules, derived from aromatic isocyanates, with high fluorine content and very interesting wettability properties.

Reactivity studies (comparison with the reactivity of ethanol, radical scavenging, and competence experiments) suggest the operation of a mechanism in the solvent cage, governed by the acidic properties of the polyfluoro alcohols.

This new photochemical reaction has also been preliminary tested successfully in the production of polyfluorinated polyurethanes, this achievement opening a new environmentally friendly avenue for the synthesis of this type of polymers with highly non-nucleophilic alcohols.

EXPERIMENTAL SECTION

General Experimental Methods. Nuclear magnetic resonance: ^1H NMR, ^{13}C NMR, and ^{19}F NMR were recorded at ambient temperature using a 250 MHz spectrometer (250 MHz ^1H NMR; 62.5 MHz ^{13}C NMR; 235.2 MHz ^{19}F NMR) or a 360 MHz spectrometer (360 MHz ^1H NMR; 90.5 MHz ^{13}C NMR). Chemical shifts are in

ppm relative to $\delta(\text{TMS}) = 0$ for ^1H and ^{13}C and $\delta(\text{CFCl}_3) = 0$ for ^{19}F . ^{13}C and ^{19}F NMR spectra were recorded by broadband proton spin decoupling.

Infrared spectra were recorded with a spectrophotometer fitted with a universal ATR (attenuated total reflectance) sampling accessory.

High resolution mass spectra (HRMS) were carried out using MicroTOF-Q with electrospray ionization (ESI).

Solvents were dried and purified using standard procedures from ref 29.

Purifications by flash chromatography were done using silica gel 0.04–0.06 mm, 230–400 mesh eluted using hexanes/ethyl acetate with the appropriate polarity.

Gas chromatography was performed in a chromatograph equipped with column Agilent HP-5 (30 m \times 0.320 mm \times 0.25 μm) and a FID detector. The standard method used is $T_0 = 75^\circ\text{C}$, 0.5 min; $\nu = 25^\circ\text{C}/\text{min}$; $T_1 = 240^\circ\text{C}$.

Melting points have been recorded in a Reichert Kofler block without further correction or alternatively measured using differential scanning calorimetry (DSC) calibrated with indium ($T_m = 429.75\text{ K}$, $\Delta H_m = 3267\text{ kJ/mol}$).

Gel permeation chromatography was performed in an equipment with one column PL Mixed gel C, 5 μm , and another column PL gel, 5 μm , 10.000Å, using THF as solvent and a refractive index detector. The method used injects 40 μL of sample, elutes at a flow of 1 mL/min at an isothermal temperature of 30 $^\circ\text{C}$ and was calibrated using polystyrene standards.

Experimental Procedures and Characterization Data for Products. *General Procedure A.* In a 100 mL Schlenk flask fitted with a magnetic stirring bar under inert atmosphere, phenyl isocyanate (55 μL ; 0.50 mmol) was dissolved in dried DMF (50 mL). Note: Special caution should be employed when handling PhNCO to avoid its tearing vapors. After addition of fluorinated alcohol (1.0 mmol), the mixture was allowed to react for 60 min. After that reaction time, water (20 mL) was added to hydrolyze the remaining isocyanate. The

mixture DMF/water was extracted with ethyl acetate (3 × 20 mL) and the organic phase washed with diluted hydrochloric acid (1 M; 3 × 20 mL) and water (20 mL). The organic phase was dried with anhydrous magnesium sulfate and evaporated in the rotary evaporator. The product after purification by a flash chromatography (initial eluent hexanes/ethyl acetate 5:1) was obtained in yields reported in the description in each case.

General Procedure B. Dry acetonitrile (50 mL) was degassed by three cycles of freeze–pump–thaw and placed in a photochemical reactor equipped with a magnetic stirring, a glass stopper, a stopcock, and a water-flow cooled Pyrex immersion well under nitrogen atmosphere. Phenyl isocyanate (54 μL, 0.5 mmol) was added and the mixture stirred for 5 min. Fluorinated alcohol (1.0 mmol) was added and the mixture stirred for a further 5 min to homogenize the solution. Then, the UV–vis irradiation source, a mercury high-pressure lamp Philips HPK 125 W, was turned on. After 60 min of reaction, the lamp was switched off and the solvent and the alcohol were evaporated in vacuo. The yellowish residue was purified by flash column chromatography using initially hexanes/ethyl acetate 5:1 and then with increasing polarity. Yields are reported in the description in each case.

2,2,2-Trifluoroethyl Phenylcarbamate, 3a.²⁶ Crystalline white solid. Yield: A, 104 mg, 93%; B, 95 mg, 87%. Mp (°C): 57–58. IR (ATR): 3327 (NH st), 2969 (CH st), 1716 (C=O st), 1538 (NH δ), 1226 (NCOO st as), 1160 (C–F st), 1079 cm⁻¹. ¹H NMR (250 MHz, acetone-*d*₆): δ 4.74 (q, ³J_{HF} = 9.3 Hz, 2H), 7.09 (t, ³J_{HH} = 7.5 Hz, 1H), 7.35 (t, ³J_{HH} = 7.5 Hz, 2H), 7.59 (d, ³J_{HH} = 7.9 Hz, 2H), 9.07 (s, 1H). ¹³C NMR (90.5 MHz, acetone-*d*₆): δ 60.1 (q, ²J_{CF} = 35.9 Hz), 118.6 (s), 123.3 (s), 123.7 (q, ¹J_{CF} = 276.9 Hz), 128.9 (s), 138.5 (s), 151.7 (s). ¹⁹F NMR (235.2 MHz, acetone-*d*₆): δ -75.36 (t, ³J_{FF} = 9.3 Hz, 3F). HRMS-ESI⁺: *m/z* calcd for C₉H₉F₃NO₂ [M + H]⁺ 220.0580, found 220.0579; calcd for C₉H₈F₃NNaO₂ [M + Na]⁺ 242.0399, found 242.0395.

2,2,3,3,4,4,5,5,6,6,7,7,8,8-Pentadecafluorooctyl Phenylcarbamate, 3b. White solid. Yield: A, 151 mg, 58%; B, 93 mg, 36%. IR (ATR): 3354 (NH st), 2958, 2935 (CH st), 1728 (C=O st), 1539, 1201 (NCOO st as), 1147, 1101 (CF). ¹H NMR (250 MHz, acetone-*d*₆): δ 4.90 (t, ³J_{HF} = 15 Hz, 1H), 7.10 (t, ³J_{HH} = 7.5 Hz, 1H), 7.35 (t, ³J_{HH} = 7.5 Hz, 2H), 7.60 (d, ³J_{HH} = 7.5 Hz, 2H), 9.13 (bs, 1H). ¹³C NMR (90.5 MHz, acetone-*d*₆): δ 59.3 (t, ²J_{CF} = 26.7 Hz), 106–120 (undefined) 118.6 (s), 123.4 (s), 128.8 (s), 138.4 (s), 151.7 (s). ¹⁹F NMR (235 MHz, acetone-*d*₆): δ -127.18 (bs, 2F), -124.27 (bs, 2F), -123.71 (bs, 2F), -122.98 (bs, 4F), -120.70 (bs, 2F), -82.14 (t, ³J_{FF} = 9.4 Hz, 3F). HRMS-ESI⁺: *m/z* calcd for C₁₅H₉F₁₅NO₂ [M + H]⁺ 520.0388, found 520.0393; calcd for C₁₅H₈F₁₅NNaO₂ [M + Na]⁺ 542.0208, found 542.0220.

1,1,1,3,3,3-Hexafluoropropan-2-yl Phenylcarbamate, 3c.²⁷ White solid. Yield: A, 115 mg, 80%; B, 95 mg, 66%. Mp (°C): 104–105. IR (ATR): 3296 (NH st), 2978 (CH st), 1731 (C=O st), 1537, 1224 (N-CO-O st as), 1193 (C–F st), 1104 cm⁻¹. ¹H NMR (250 MHz, acetone-*d*₆): δ 6.30 (septet, ³J_{HF} = 6.7 Hz, 1H), 7.16 (t, ³J_{HH} = 7.5 Hz, 1H), 7.39 (t, ³J_{HH} = 7.5 Hz, 2H), 7.61 (d, ³J_{HH} = 10.0 Hz, 2H), 9.54 (bs, 1H). ¹³C NMR (90.5 MHz, acetone-*d*₆): δ 67.0 (septet, ²J_{CF} = 34.0 Hz), 118.9 (s), 121.2 (q, ¹J_{CF} = 285.0 Hz), 124.1 (s), 129.0 (s), 137.6 (s), 149.8 (s). ¹⁹F NMR (235 MHz, acetone-*d*₆): δ -74.76 (d, ³J_{HF} = 6.7 Hz). HRMS-ESI⁺: *m/z* calcd for C₁₀H₈F₆NO₂ [M + H]⁺ 288.0454, found 288.0462.

2,2,3,3-Tetrafluoro-4-hydroxybutyl Phenylcarbamate, 3d. White solid. Yield: A, 104 mg, 74%. Mp (°C): 79.3–79.9. IR (ATR): 3323 (NH, OH st), 2955 (CH st), 1721 (C=O st), 1602 (arCC), 1541 (NH δ), 1449, 1264 (NCOO st as), 1116 (CF st), 1101, 930. ¹H NMR (250 MHz, acetone-*d*₆): δ 4.05 (dt, ³J_{HF} = 14.3 Hz, ³J_{HH} = 6.3 Hz, 2H), 4.74 (t, ³J_{HF} = 15.2 Hz, 2H), 5.01 (t, ³J_{HH} = 6.3 Hz, 1H), 7.08 (t, ³J_{HH} = 7.5 Hz, 1H), 7.34 (t, ³J_{HH} = 7.5 Hz, 2H), 7.59 (d, ³J_{HH} = 7.5 Hz, 2H), 9.01 (s, 1H). ¹³C NMR (90.5 MHz, CD₃OD): δ 59.9 (t, ²J_{CF} = 27 Hz), 60.6 (t, ²J_{CF} = 25 Hz), 112–123 (complex absorption), 118.9 (s), 123.6 (s), 129.2 (s), 139.1 (s), 152.6 (s). ¹⁹F{¹H} NMR (235.2 MHz, acetone-*d*₆): δ -125.14 (s, 2F), -123.63 (s, 2F). HRMS-ESI⁺:

m/z calcd for C₁₁H₁₂F₄NO₃ [M + H]⁺ 282.0748, found 282.0786; calcd for C₁₁H₁₂F₄NNaO₃ [M + Na]⁺ 304.0567, found 304.0577.

2,2,3,3,4,4-Hexafluoro-5-hydroxypentyl Phenylcarbamate, 3e. White solid. Yield: A, 94 mg, 57%. IR (ATR): 3331 (NH, OH st), 1719 (C=O st), 1536 (NH δ), 1501, 1445, 1226 (NCOO st as), 1185, 1153 (CF st), 1091, 750, 689. ¹H NMR (360 MHz, acetone-*d*₆): δ 4.11 (dt, ³J_{HF} = 15.1 Hz, ³J_{HH} = 6.7 Hz, 2H), 4.79 (t, ³J_{HF} = 14.9 Hz, 2H), 5.08 (t, ³J_{HH} = 6.9 Hz, 1H), 7.09 (t, ³J_{HH} = 7.5 Hz, 1H), 7.34 (t, ³J_{HH} = 7.5 Hz, 2H), 7.60 (d, ³J_{HH} = 7.5 Hz, 2H), 9.11 (s, 1H). ¹³C NMR (90.5 MHz, acetone-*d*₆): δ 59.5 (m), 59.7 (m), 111–119 (complex absorption), 118.5 (s), 123.2 (s), 128.8 (s), 138.6 (s), 152.0 (s). ¹⁹F{¹H} NMR (235.2 MHz, acetone-*d*₆): δ -127.25 (s, 2F), -123.14 (s, 2F), -121.31 (s, 2F). HRMS-ESI⁺: *m/z* calcd for C₁₂H₁₁F₆NNaO₃ [M + Na]⁺ 354.0535, found 354.0575.

2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11-Icosafluoro-12-hydroxydodecyl Phenylcarbamate, 3f. White-yellowish solid. Yield: A, 208 mg, 61%. ¹H NMR (360 MHz, acetone-*d*₆): δ 3.91 (dt, ³J_{HF} = 14.3 Hz, ³J_{HH} = 6.1 Hz, 2H), 4.59 (t, ³J_{HF} = 15.4 Hz, 2H), 4.87 (t, ³J_{HH} = 6.7 Hz, 1H), 6.93 (t, ³J_{HH} = 7.3 Hz, 1H), 7.19 (t, ³J_{HH} = 7.3 Hz, 2H), 7.45 (d, ³J_{HH} = 7.3 Hz, 2H), 8.87 (s, 1H). ¹³C NMR (90.5 MHz, acetone-*d*₆): δ 60.0 (m), 60.6 (m), 111–119 (complex weak absorption), 119.6 (s), 124.3 (s), 129.8 (s), 139.4 (s), 152.7 (s). ¹⁹F{¹H} NMR (235.2 MHz, acetone-*d*₆): δ -124.44 (bs, 4F), -123.00 (bs, 4F), -122.81 (bs, 6F), -122.76 (bs, 4F), -122.71 (bs, 2F). HRMS-ESI⁺: *m/z* calcd for C₁₉H₁₂F₂₀NO₃ [M + H]⁺ 682.0531, found 682.0492.

General Procedure C. Dry acetonitrile (45 mL) was degassed by three cycles of freeze–pump–thaw and placed under inert atmosphere in a photochemical reactor equipped with a magnetic stirring, a glass stopper, a stopcock, and a water-flow cooled pyrex immersion well. Aromatic isocyanate (1.0 mmol) was added and the mixture stirred for 5 min.

Afterward, a solution of fluorinated diol (0.5 mmol) in dried and degassed acetonitrile (5 mL) was added and stirred for a further 5 min to homogenize the solution. Then, the irradiation source (Philips HPK 125W) was turned on. After 4 h of reaction the lamp was switched off and the solvent and the alcohol were evaporated in vacuo. After flash column chromatography using initially hexanes/ethyl acetate 5:1 the product was obtained with the yield in the description.

2,2,3,3-Tetrafluorobutane-1,4-diyl Bis(phenylcarbamate), 4a. White solid. Yield: C, 141 mg, 71%. Mp (°C): 178.1 (DSC). IR (ATR): 3350 (NH st), 3052 (arom CH st), 2968 (CH st), 1721 (C=O st), 1598 (arom CC), 1532 (NH δ), 1228 (NCOO st as), 1179, 1143 (CF st), 1091, 952, 934, 749 (CF δ) cm⁻¹. ¹H NMR (250 MHz, acetone-*d*₆): δ 4.77 (t, ³J_{HF} = 15.0 Hz, 4H), 7.09 (t, ³J_{HH} = 7.5 Hz, 2H), 7.34 (t, ³J_{HH} = 7.5 Hz, 4H), 7.58 (d, ³J_{HH} = 7.5 Hz, 4H), 9.06 (bs, 2H). ¹³C NMR (90.5 MHz, acetone-*d*₆): δ 59.6 (t, ²J_{CF} = 26.0 Hz), 115.4 (tt, ¹J_{CF} = 252.0 Hz, ²J_{CF} = 31.0 Hz), 118.6 (s), 123.2 (s, 4C), 128.8 (s), 138.6 (s), 152.0 (s). ¹⁹F NMR (235.2 MHz, acetone-*d*₆): δ -122.88 (t, ³J_{HF} = 15 Hz). HRMS-ESI⁺: *m/z* calcd for C₁₈H₁₆F₄N₂O₄ [M + H]⁺ 401.1119, found 401.1126; calcd for C₁₈H₁₆F₄N₂NaO₄ [M + Na]⁺ 423.0938, found 423.0958; calcd for C₁₈H₁₆F₄KN₂O₄ [M + K]⁺ 439.0678, found 439.0680.

2,2,3,3,4,4-Hexafluoropentane-1,5-diyl Bis(phenylcarbamate), 4b. Yield C: 0.139 g, 63%. Mp (°C): 134.5–135.1. IR (ATR): 3336 (NH st), 1705 (C=O st), 1600 (arom CC), 1540 (NH δ), 1448, 1315, 1240 (NCOO st as), 1201, 1150 (CF st), 1088, 963, 937, 885, 763 (C–F δ), 686, 637 cm⁻¹. ¹H NMR (250 MHz, acetone-*d*₆): δ 4.83 (t, ³J_{HF} = 7.5 Hz, 4H), 7.07 (t, ³J_{HH} = 7.5 Hz, 2H), 7.35 (t, ³J_{HH} = 7.5 Hz, 4H), 7.60 (d, ³J_{HH} = 7.5 Hz, 4H), 9.12 (s, 2H). ¹³C NMR (90.5 MHz, CD₃OD): δ 59.5 (t, ²J_{CF} = 28.0 Hz), 111.3 (m), 115.0 (tt, ¹J_{CF} = 257.0 Hz, ²J_{CF} = 30.0 Hz), 118.6 (s), 123.1 (s), 128.5 (s), 138.2 (s), 152.5 (s). ¹⁹F{¹H} NMR (235.2 MHz, acetone-*d*₆): δ -127.31 (s, 2F), -121.15 (s, 4F). HRMS-ESI⁺: *m/z* calcd for C₁₉H₁₇F₆N₂O₄ [M + H]⁺ 451.1087, found 451.1102; calcd for C₁₉H₁₆F₆N₂NaO₄ [M + Na]⁺ 473.0906, found 473.0912; calcd for C₁₉H₁₆F₆KN₂O₄ [M + K]⁺ 489.0646, found 489.0621.

2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11-Icosafluorododecan-1,12-diyl Bis(phenylcarbamate), 4c. Yield C: 0.272 g, 68%. Mp (°C): 146.4 (DSC). IR (ATR): 3351 (NH st), 1722 (C=O st), 1599 (arom CC), 1536 (NH δ), 1447, 1274 (NCOO st as), 1143 (CF st), 988,

953, 806, 759 (CF δ), 689, 622 cm^{-1} . ^1H NMR (360 MHz, acetone- d_6): δ 4.90 (t, $^3J_{\text{HF}} = 10.8$ Hz, 4H), 7.09 (t, $^3J_{\text{HH}} = 7.2$ Hz, 2H), 7.34 (t, $^3J_{\text{HH}} = 7.2$ Hz, 4H), 7.59 (d, $^3J_{\text{HH}} = 7.2$ Hz, 4H), 9.15 (s, 2H). ^{13}C NMR (90.5 MHz, acetone- d_6): δ 59.4 (t, $^2J_{\text{CF}} = 27.2$ Hz), 107–123 (undefined), 118.6 (s), 123.4 (s), 128.9 (s), 138.4 (s), 151.7 (s). ^{19}F NMR (235.2 MHz, acetone- d_6): δ -124.28 (m, 4F), -122.73 (m, 12F), -120.69 (m, 4F). HRMS-ESI⁺: m/z calcd for $\text{C}_{26}\text{H}_{17}\text{F}_{20}\text{N}_2\text{O}_4$ [M + H]⁺ 801.0863, found 801.0889; calcd for $\text{C}_{26}\text{H}_{16}\text{F}_{20}\text{N}_2\text{NaO}_4$ [M + Na]⁺ 823.0683, found 823.0705; calcd for $\text{C}_{26}\text{H}_{16}\text{F}_{20}\text{KN}_2\text{O}_4$ [M + K]⁺ 839.0422, found 839.0439.

2,2,4,4,5,5,7,7-Octafluoro-3,6-dioxaoctane-1,8-diyl Bis(phenylcarbamate), 4d. Yield: C, 0.205 g, 77%. IR (ATR): 3349 (NH st), 1721 (C=O st), 1603 (arom CC), 1538 (NH δ), 1449, 1401, 1276 (NCOO st as), 1151 (C–F st), 1080, 986, 940, 760, 736 (CF δ), 691 cm^{-1} . ^1H NMR (250 MHz, acetone- d_6): δ 4.73 (t, $^3J_{\text{HF}} = 10.0$ Hz, 4H), 7.09 (t, $^3J_{\text{HH}} = 7.5$ Hz, 2H), 7.34 (t, $^3J_{\text{HH}} = 7.5$ Hz, 4H), 7.59 (d, $^3J_{\text{HH}} = 7.5$ Hz, 4H), 9.11 (s, 2H). ^{13}C NMR (62.5 MHz, acetone- d_6): δ 61.8 (t, $^2J_{\text{CF}} = 32.7$ Hz), 119.1 (s), 112–127 (undefined), 123.7 (s), 129.2 (s), 138.8 (s), 152.1 (s). ^{19}F NMR (235.2 MHz, acetone- d_6): -89.81 (t, $^3J_{\text{FF}} = 13.4$ Hz), -78.66 (t, $^3J_{\text{FF}} = 13.4$ Hz). HRMS-ESI⁺: m/z calcd for $\text{C}_{30}\text{H}_{17}\text{F}_8\text{N}_2\text{O}_6$ [M + H]⁺ 533.0953, found 533.0967; calcd for $\text{C}_{20}\text{H}_{16}\text{F}_8\text{N}_2\text{NaO}_6$ [M + Na]⁺ 550.1219, found 550.1222; calcd for $\text{C}_{20}\text{H}_{16}\text{F}_8\text{KN}_2\text{O}_6$ [M + K]⁺ 571.0512, found 571.0529.

2,2,3,3-Tetrafluorobutane-1,4-diyl bis(pentafluorophenylcarbamate), 6a. Yield: C, 0.229 g, 79%. IR (ATR): 3350 (NH st), 1723 (C=O st), 1599 (arom CC), 1535 (NH δ), 1500, 1448, 1274 (NCOO st as), 1144 (CF st), 980, 824, 759 (CF δ), 689, 624 cm^{-1} . ^1H NMR (250 MHz, acetone- d_6): δ 4.81 (t, $^3J_{\text{HF}} = 13.9$ Hz, 2H), 9.03 (bs, 2H). ^{13}C NMR (90.5 MHz, acetone- d_6): 60.6 (t, $^2J_{\text{CF}} = 26.7$ Hz), 112.7 (t, $^2J_{\text{CF}} = 16$ Hz), 116.3 (tt, $^1J_{\text{CF}} = 253.0$ Hz, $^2J_{\text{CF}} = 32$ Hz), 137.7 (dm, $^1J_{\text{CF}} = 249.0$ Hz), 139.3 (dm, $^1J_{\text{CF}} = 251$ Hz), 143.6 (dm, $^1J_{\text{CF}} = 249.0$ Hz), 152.4 (s). ^{19}F NMR (235.2 MHz, acetone- d_6): δ -165.78 (t, $^3J_{\text{FF}} = 18.8$ Hz, 4F), -159.83 (t, $^3J_{\text{FF}} = 19.7$ Hz, 2F), -148.37 (d, $^3J_{\text{FF}} = 17.1$ Hz, 4F), -123.01 (t, $^3J_{\text{HF}} = 13.9$ Hz, 4F). HRMS-ESI⁺: m/z calcd for $\text{C}_{18}\text{H}_7\text{F}_{14}\text{N}_2\text{O}_4$ [M + H]⁺ 581.0177, found 581.0212; calcd for $\text{C}_{18}\text{H}_{10}\text{F}_{14}\text{N}_3\text{O}_4$ [M + NH₄]⁺ 598.0442, found 598.0462; calcd for $\text{C}_{18}\text{H}_6\text{F}_{14}\text{N}_2\text{NaO}_4$ [M + Na]⁺ 602.9996, found 603.0031; calcd for $\text{C}_{18}\text{H}_6\text{F}_{14}\text{KN}_2\text{O}_4$ [M + K]⁺ 618.9736, found 618.9751.

2,2,3,3,4,4-Hexafluoropentane-1,5-diyl Bis(pentafluorophenylcarbamate), 6b. Yield: C, 0.144 g, 45%. IR (ATR): 3349 (NH st), 1722 (C=O st), 1601 (arom CC), 1536 (NH δ), 1448, 1400, 1274 (NCOO st as), 1145 (CF st), 1118, 987, 940, 759 (CF δ), 735, 690, 625 cm^{-1} . ^1H NMR (250 MHz, acetone- d_6): δ 4.88 (t, $^3J_{\text{HF}} = 15.0$ Hz, 4H), 9.11 (bs, 2H). ^{13}C NMR (90.5 MHz, acetone- d_6): 60.7 (t, $^2J_{\text{CF}} = 26.8$ Hz), 108–112 (undefined, central), 112.6 (t, $^2J_{\text{CF}} = 16$ Hz), 115.0 (tt, $^1J_{\text{CF}} = 256$ Hz, $^2J_{\text{CF}} = 32$ Hz), 137.8 (dm, $^1J_{\text{CF}} = 250$ Hz), 140.1 (dm, $^1J_{\text{CF}} = 251$ Hz), 143.6 (dm, $^1J_{\text{CF}} = 248$ Hz), 152.4 (s). ^{19}F { ^1H } NMR (235.2 MHz, acetone- d_6): δ -165.71 (apparent t, $^3J_{\text{FF}} = 18.8$ Hz, 4F), -159.70 (t, $^3J_{\text{FF}} = 19.0$ Hz, 2F), -148.38 (d, $^3J_{\text{FF}} = 16.9$ Hz, 4F), -127.08 (s, 2F), -121.22 (s, 4F). HRMS-ESI⁺: m/z calcd for $\text{C}_{19}\text{H}_6\text{F}_{16}\text{N}_2\text{NaO}_4$ [M + H]⁺ 652.9964, found 652.9969.

2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11-Icosafluorododecan-1,12-diyl Bis(pentafluorophenylcarbamate), 6c. Yield: C, 0.265 g, 54%. IR (ATR): 3349 (NH st), 1722 (C=O st), 1602 (arom CC), 1536 (NH δ), 1448, 1273 (NCOO st as), 1146 (CF st), 940, 759 (CF δ), 735, 690 cm^{-1} . ^1H NMR (250 MHz, acetone- d_6): δ 4.95 (t, $^3J_{\text{HF}} = 13.8$ Hz, 4H), 9.09 (bs, 2H). ^{13}C NMR (90.5 MHz, acetone- d_6): 60.5 (t, $^2J_{\text{CF}} = 26.7$ Hz), 105–120 (complex absorption), 112.6 (t, $^2J_{\text{CF}} = 14.0$ Hz), 138.0 (dm, $^1J_{\text{CF}} = 250$ Hz), 139.7 (dm, $^1J_{\text{CF}} = 251$ Hz), 143.6 (dm, $^1J_{\text{CF}} = 249$ Hz), 152.2 (s). ^{19}F { ^1H } NMR (235.2 MHz, acetone- d_6): δ -165.77 (apparent t, $^3J_{\text{FF}} = 21.1$ Hz, 4F), -159.67 (t, $^3J_{\text{FF}} = 16.0$ Hz, 2F), -148.44 (d, $^3J_{\text{FF}} = 16.5$ Hz, 4F), -124.38 (bs, 4F), -122.35 (bs, F), -120.38 (bs, 4F). HRMS-ESI⁺: m/z calcd for $\text{C}_{26}\text{H}_7\text{F}_{30}\text{N}_2\text{O}_4$ [M + H]⁺ 980.9921, found 980.9909; calcd for $\text{C}_{26}\text{H}_{10}\text{F}_{30}\text{N}_3\text{O}_4$ [M + NH₄]⁺ 998.0187, found 998.0184; calcd for $\text{C}_{26}\text{H}_6\text{F}_{30}\text{N}_2\text{NaO}_4$ [M + Na]⁺ 1002.9741, found 1002.9739; calcd for $\text{C}_{26}\text{H}_6\text{F}_{30}\text{KN}_2\text{O}_4$ [M + K]⁺ 1018.9480, found 1018.9477.

2,2,4,4,5,5,7,7-Octafluoro-3,6-dioxaoctane-1,8-diyl Bis(pentafluorocarbamate), 6d. Yield: C, 0.303 g, 85%. IR (ATR): 3290 (NH st), 1725 (C=O st), 1601 (arom C–C), 1536 (NH δ), 1500, 1449, 1402, 1271 (N–CO–O st as), 1147 (C–F st), 1001, 941, 792, 759 (C–F δ), 689, 624 cm^{-1} . ^1H NMR (360 MHz, acetone- d_6): δ 4.79 (t, $^3J_{\text{HF}} = 10.8$ Hz, 4H), 9.12 (bs, 2H). ^{13}C NMR (90.5 MHz, acetone- d_6): 62.4 (t, $^2J_{\text{CF}} = 33.5$ Hz), 112–122 (undefined), 112.5 (t, $^2J_{\text{CF}} = 22.0$ Hz), 121.7 (t, $^1J_{\text{CF}} = 278$ Hz), 137.2 (dm, $^1J_{\text{CF}} = 251$ Hz), 139.8 (dm, $^1J_{\text{CF}} = 251$ Hz), 143.6 (dm, $^1J_{\text{CF}} = 249$ Hz), 152.1 (s). ^{19}F NMR (235.2 MHz, acetone- d_6): δ -165.74 (t, $^3J_{\text{FF}} = 18.7$ Hz, 4F), -159.74 (t, $^3J_{\text{FF}} = 19.6$ Hz, 2F), -148.42 (d, $^3J_{\text{FF}} = 19.3$ Hz, 4F), -89.92 (t, $^3J_{\text{FF}} = 11.7$ Hz, 4F), -78.88 (t, $^3J_{\text{FF}} = 12.9$ Hz, 4F). HRMS-ESI⁺: m/z calcd for $\text{C}_{20}\text{H}_7\text{F}_{18}\text{N}_2\text{O}_6$ [M + H]⁺ 713.0011, found 713.0042; calcd for $\text{C}_{20}\text{H}_{10}\text{F}_{18}\text{N}_3\text{O}_6$ [M + NH₄]⁺ 730.0277, found 730.0304; calcd for $\text{C}_{20}\text{H}_6\text{F}_{18}\text{N}_2\text{NaO}_6$ [M + Na]⁺ 734.9831, found 734.9869; calcd for $\text{C}_{20}\text{H}_6\text{F}_{18}\text{KN}_2\text{O}_6$ [M + K]⁺ 750.9570, found 750.9589.

Reaction of MDI with 2,2,3,3-Tetrafluorobutan-1,4-diol, 2d. Dry acetonitrile (45 mL) was degassed by three cycles of freeze–pump–thaw and placed under inert atmosphere in a photochemical reactor equipped with a magnetic stirring, a glass stopper, a stopcock, and a water-flow cooled Pyrex immersion well. 4,4'-Methylene diphenyl diisocyanate MDI (63 mg, 0.25 mmol) was added. It was dissolved using vigorous stirring and ultrasound until the solution became clear. Afterward, a solution of 2,2,3,3-tetrafluorobutan-1,4-diol (41 mg, 0.25 mmol) in dried and degassed acetonitrile (5 mL) was added. The mixture was stirred for 5 min to homogenize the solution before the irradiation source was turned on. After 4 h, the lamp was stopped and the solvent evaporated in vacuo to obtain a white-yellowish solid. To perform GPC analysis, 10 mg was solved in 1 mL of THF and filtered with a nylon syringe filter.

Radical Trapping in the Reaction of 2,2,2-Trifluoroethanol 2a with Phenyl Isocyanate 1. Dry acetonitrile (50 mL) was degassed by three cycles of freeze–pump–thaw and placed under inert atmosphere in a photochemical reactor equipped with a magnetic stirring, a glass stopper, a stopcock, and a water-flow cooled Pyrex immersion well.

Phenyl isocyanate (55 μL , 0.5 mmol) was introduced. Afterward, 2,2,2-trifluoroethanol (76 μL , 1 mmol) and 1 mmol of the corresponding additive were added. Immediately, the irradiation source (Philips HPK 125W) was turned on. Additives used: TEMPO (147 mg, 0.94 mmol); 1-octene (156 μL , 1 mmol); acrylonitrile (66 μL , 1 mmol).

In the case of using TEMPO as additive, following the evolution of the reaction of phenyl isocyanate with 2,2,2-trifluoroethanol by GC did not show any appreciable slowing.

In the reactions with 1-octene or acrylonitrile as additive, after 1 h of reaction no polymers or oligomers derived from 1-octene or acrylonitrile were observed by GPC. Moreover signals corresponding to the starting alkenes were observed in ^1H NMR spectra of the reaction mixture at that time.

Effect of Light in the Reaction of Phenyl Isocyanate 1 with Ethanol: This reaction was studied under two conditions: irradiated with UV light and under ground-state conditions.

Irradiated with UV: Dry acetonitrile (50 mL) was degassed by three cycles of freeze–pump–thaw and placed under inert atmosphere in a photochemical reactor equipped with a magnetic stirring, a glass stopper, a stopcock, and a water-flow cooled Pyrex immersion well. Phenyl isocyanate (55 mL, 0.5 mmol) was added, and afterward, dry ethanol (58 mL, 1 mmol) was introduced. Immediately the irradiation source (Philips HPK 125W) was turned on. Ground state: dry acetonitrile (50 mL) was degassed by three cycles of freeze–pump–thaw and placed under inert atmosphere in a Schlenk flask equipped with a magnetic stirring and protected of light with foil. Phenyl isocyanate (55 mL, 0.5 mmol) was added, and afterward, dry ethanol (58 mL, 1 mmol) was introduced. The evolution of both reactions was followed by GC (phenyl isocyanate, $t_{\text{R}} = 1.52$ min; ethyl phenylcarbamate, $t_{\text{R}} = 3.67$ min) without observing any significant difference.

Ethyl Phenylcarbamate: ^1H NMR (360 MHz, CDCl_3): δ 1.32 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3H), 4.24 (q, $^3J_{\text{HH}} = 7.2$ Hz, 2H), 6.89 (bs, 1H), 7.07 (t, $^3J_{\text{HH}} = 7.2$ Hz, 1H), 7.31 (t, $^3J_{\text{HH}} = 7.2$ Hz, 2H), 7.42 (d, $^3J_{\text{HH}} = 7.2$ Hz,

2H). ^{13}C NMR (90.5 MHz, CDCl_3): δ 14.6, 61.2, 118.9, 123.3, 129.0, 138.1, 153.8.

Photochemical Competitive Reaction of PhNCO 1 with 2,2,2-Trifluoroethanol 2a and Ethanol. Dry acetonitrile (50 mL) was degassed by three cycles of freeze–pump–thaw and placed under inert atmosphere in a photochemical reactor equipped with a magnetic stirring, a glass stopper, a stopcock, and a water-flow cooled Pyrex immersion well. Phenyl isocyanate (109 mL, 1 mmol) was introduced, and the concentration checked by GC. Afterward, dry ethanol (58 mL, 1 mmol) and 2,2,2-trifluoroethanol (76 mL, 1 mmol) were added. Immediately the irradiation source (Philips HPK 125W) was turned on. After 15 min of irradiation, an aliquot was analyzed by GC: 2,2,2-trifluoroethyl phenylcarbamate ($t_{\text{R}} = 3.45$ min), 76% conversion; ethyl phenylcarbamate ($t_{\text{R}} = 3.67$ min), no signal was observed.

■ ASSOCIATED CONTENT

■ Supporting Information

Compound characterization spectra (^1H , ^{13}C , ^{19}F NMR, IR, HRMS, and in some cases, DSC thermograms). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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