

Furandiacylazide: A Biomass-Derived Versatile Polymer Platform toward Photodegradable and Nonflammable Polyurethanes

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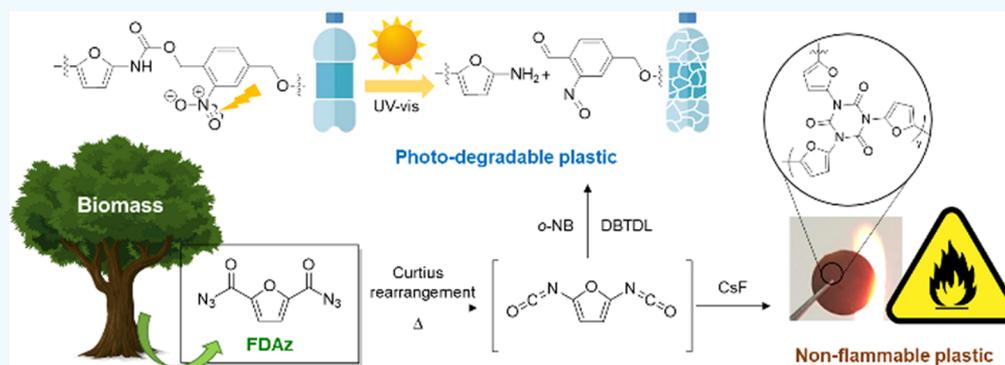
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ABSTRACT: The development of a biomass-based polymer platform has become increasingly important to address environmental problems. In the present study, we present a furan-based polymer platform, furandiacylazide (FDAz), which can undergo a thermal Curtius rearrangement to produce a diisocyanate intermediate. Poly(furanyl-urethane-isocyanurate)s (PFUIs) were successfully formed via in situ polymerization of FDAz with various diols. Interestingly, by introducing an *ortho*-nitro group containing phenylene, a photodegradable polyurethane was easily synthesized. Tuning the polymerization conditions enabled control of the relative ratios of the urethane and isocyanurate moieties. Remarkably, a fully isocyanurate-containing polymer of isocyanates was successfully prepared through trimerization and was found to exhibit good heat resistance. FDAz is indeed a versatile polymer platform that can be applied to the synthesis of various eco-friendly functional polymers, potentially useful for the development of degradable plastics and nonflammable polymers.

KEYWORDS: biomass, Curtius rearrangement, polyurethane, photodegradability, nonflammability

1. INTRODUCTION

Driven by the depletion of fossil fuels, extensive research has been conducted on the development of alternatives to petroleum resources for polymer feedstocks. In addition, the use of recyclable plastics has become essential in reducing waste and addressing the related environmental problems. In this regard, biomass is an eco-friendly alternative that originates from plant or agricultural resources such as sugar cane, corn, straw, and wood.¹ After they have been extracted in the form of five- or six-membered ring sugars, various eco-friendly polymer feedstocks such as 5-hydroxymethylfurfural (5-HMF), 2,5-furandicarboxylic acid (FDCA), and isosorbide can be obtained using chemical processes.^{2,3} Among these feedstocks, FDCA can be obtained from 5-HMF via oxidation reactions and can be used as a monomer for polymerization via its diacid functional group.^{4,5} Most studies involving FDCA have produced furan polyesters (e.g., poly(*n*-methylene-2,5-furandicarboxylate)) by reacting FDCA with specific diols, usually either through direct esterification or transesterification.⁶ Only a few examples of polymerization pathways have

been found, such as the pathway for poly(hydroxyurethane) via bis(cyclic carbonate) from FDCA.⁷ That is, the development of new polymerization methods is rare and has been mostly limited to (trans)esterification reactions,^{8–12} potentially hindering further expansion of biomass-derived feedstocks such as FDCA into various functional polymers. In the present paper, we propose a polymerization method in which furandiacylazide (FDAz), which is easily prepared from FDCA, is used to prepare eco-friendly furan-based polyurethane copolymers. With effective thermal Curtius rearrangement, FDAz can be a useful polymer platform that reacts well with various diols, including those biomass-derived. Although FDAz has been synthesized before, there has been no case of

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synthesizing polymers from FDAz. Only a few examples of its application to prepare small molecule carbamates have been reported.¹³

The Curtius rearrangement refers to the process of converting an acyl azide into an isocyanate under an external stimulus such as heat or light (Figure 1a).^{14–17} After a N₂

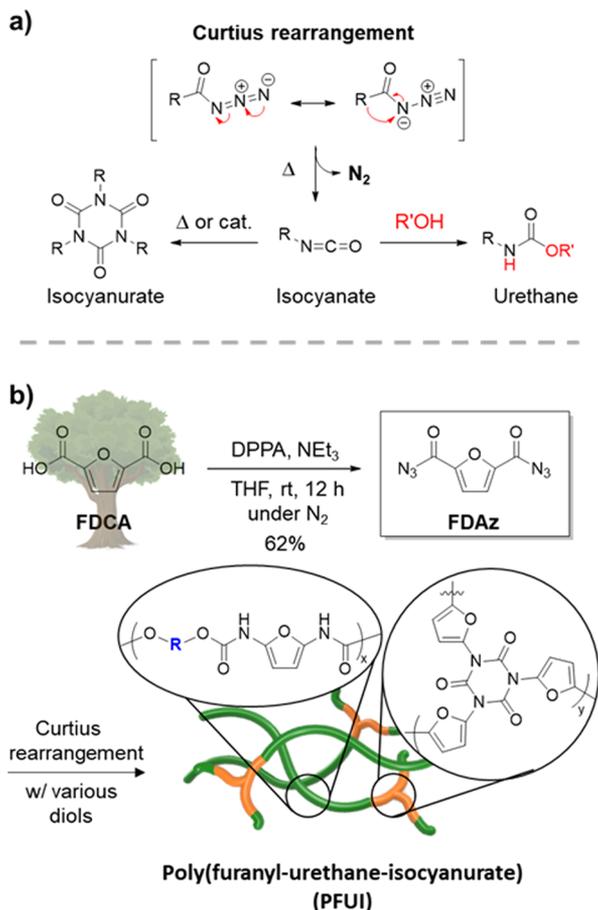


Figure 1. (a) Concerted thermal Curtius rearrangement for an acyl azide compound and the route to several materials, such as isocyanurates and urethanes. (b) Synthesis of FDAz and a scheme for the furan-derived polyurethane copolymer PFUI using Curtius rearrangement.

molecule is released, the R group of the nitrene intermediate migrates to the electron-deficient N to form an isocyanate.^{18–20} Alternatively, the migration of the R group and the N₂ release can occur in concert. The resultant isocyanates can be used to synthesize various functional groups, including amines, urethanes, and isocyanurates,^{21–24} through nucleophilic addition reactions.^{25,26} Although the Curtius rearrangement has been widely used in organic syntheses,^{27–29} it has seldom been applied to polymer preparations.³⁰ Only a few previous studies have reported the preparation of dendritic or hyperbranched polymers using azide chemistry (i.e., the Curtius rearrangement), such as dendritic aromatic poly(urea-amide)s and hyperbranched polyureas.^{31–33} In fact, Klein and co-workers reported 5-HMF-based bisazide (bis(5-azidocarbonylfurfuryl)ether) for the preparations of thermoplastic and cross-linked polyurethanes.³⁴ However, the bisazide required several steps from 5-HMF (etherification, oxidation, and azidation), and thermoplastic polyurethanes were prepared

by urethane exchange, not by the direct, one-pot addition reaction between alcohol and isocyanate. In addition, the structure of 2-oxymethylene furan would suffer from thermal instability.^{35,36} Furthermore, extensibility as a platform monomer that can be extended to other functional polymers has not been reported. To the best of our knowledge, the present study is the first reported attempt to show FDAz as a biomass-derived polymer platform for synthesizing polyurethane copolymers with various functionalities via Curtius rearrangement in “one pot.”^{28,37}

More importantly, the Curtius polymerization method can be easily extended to the preparations of eco-friendly functional polymers. One of these preparations is the development of photodegradable polymers by introducing an *ortho*-nitro group.^{38–44} The *o*-nitro-substituted aryl structure is a photolabile precursor widely used as a photocleavable linker. For example, Zhao and co-workers demonstrated the potential application of *o*-nitrobenzyl (*o*-NB) linkers in drug delivery and phototherapeutics by synthesizing an amphiphilic block copolymer based on *o*-NB.⁴⁵ When an *o*-NB group is introduced into a furan-based polyurethane copolymer using azide chemistry, the polymer may be degraded by photolysis under ultraviolet (UV) irradiation. The other interesting feature of the one-pot Curtius polymerization of isocyanates to form isocyanurate moieties (Figure 1a).^{16,24,46} Isocyanurates are known to exhibit substantial thermal stability or heat resistance,^{22,47,48} making it possible to impart biomass-derived polyurethane copolymers with nonflammability.⁴⁹

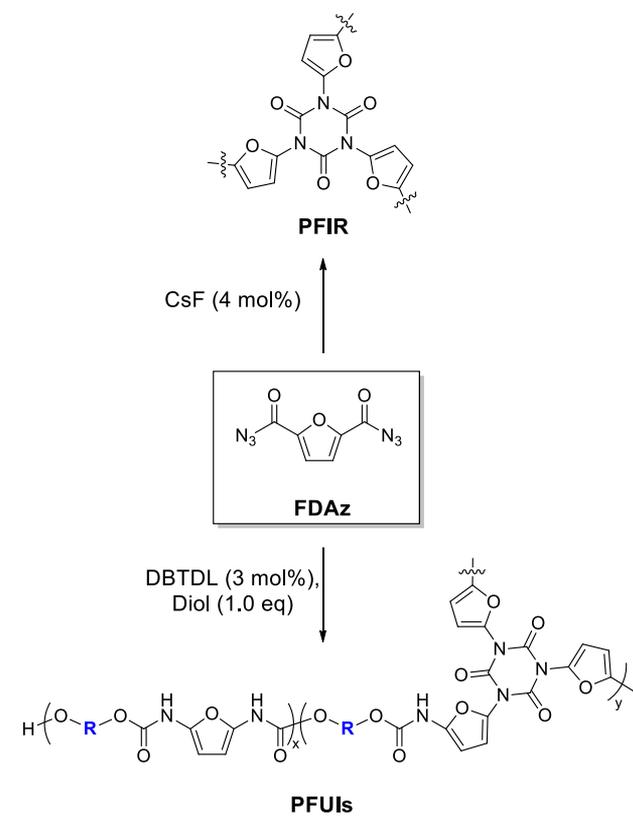
In the present work, several poly(furanyl-urethane-isocyanurate) copolymers were synthesized from a new biomass-derived polymer platform, FDAz (Scheme 1). The ratios of urethane and isocyanurate moieties were reasonably controlled via the choice of the reagent and catalytic conditions, up to entirely polyisocyanurate in the absence of a diol comonomer. In addition, new functionality was imparted to the biomass-derived copolymers. The photodegradable poly(urethane-isocyanurate) copolymer was synthesized by introducing an *o*-NB group. In addition, polymers with higher proportions of isocyanurates were prepared and their high heat-resistance was demonstrated. We believe FDAz is a versatile polymer platform that can be applied to the synthesis of various eco-friendly functional polymers, which will be potentially useful for the development of environmental friendly polymer materials such as degradable plastics and nonflammable polymers.

2. EXPERIMENTAL SECTION

2.1. Materials and Reagents. All chemicals used in the experiments were purchased from commercial sources: Sigma-Aldrich (Seoul, Korea), Alfa Aesar (Seoul, Korea), Tokyo Chemical Industry Co. (Tokyo, Japan), Acros Organics (Geel, Belgium), or Samchun Chemical (Seoul, Korea). The chemicals were used as received without further purification. Deuterated solvents for nuclear magnetic resonance (NMR) were purchased from Cambridge Isotope Laboratories (Tewksbury, MA, USA).

2.2. Measurements. ¹H NMR spectra were recorded using a Bruker 500 MHz spectrometer. ¹³C NMR spectra were recorded using a 125 MHz spectrometer with complete proton decoupling. The chemical shifts are reported in ppm (δ) with trimethylsilane (TMS) as an internal standard, and the coupling constants (*J*) are expressed in Hz. Solid-state ¹³C NMR spectra were recorded using a 400 MHz(C) solid-state NMR spectrometer. Column chromatography was carried out using 100–200 mesh silica gel. Thin-layer chromatography was performed on precoated silica gel 60 F₂₅₄ slides and visualized by UV

Scheme 1. Synthesis of Network Polymer Poly(furanyl-isocyanurate) (PFIR) and Poly(furanyl-urethane-isocyanurate) Copolymer Series (PFUIs)



irradiation. Fourier transform infrared (FT-IR) spectra were recorded using a spectrometer (Bruker Optik, Vertex70) equipped with a diamond attenuated total reflectance (ATR) unit. UV-vis absorption measurements were carried out using a UV-1800 (Shimadzu) spectrophotometer under ambient conditions (room temperature (rt), air) with a 1.0 cm quartz cell. High-resolution mass spectrometry (HRMS) was carried out using a Bruker Daltonics APEX II 3 T FT-ICR-MS. The average molecular weight and polydispersity index (PDI) of the polymers were determined through gel-permeation chromatography (GPC) using a detection wavelength of 254 nm through VWD analysis with dimethylformamide (DMF) as the eluent and polystyrene as the standard using an Agilent Technology 1260 Infinity chromatograph. Differential scanning calorimetry (DSC) tests were carried out on the Seiko Exstar 6000 DSC 7020 (DSC; Chiba, Japan) under N₂ conditions. The sample was prepared as a powder form. The glass transition temperature was measured as a function of temperature from -30 to 150 °C at 10 °C/min heating rate. For the photodegradability test, the light source was lased with a 200 W UV lamp (Lumatec), 200–300 nm LED source. The decomposition temperature of the polymer was determined by thermogravimetric analysis (TGA) using a Hitachi simultaneous thermogravimetric analyzer (STA7200). The measurements were carried out from 0 to 700 °C at a heating rate of 10 °C min⁻¹ under a flow of 100% N₂. The Brunauer-Emmett-Teller (BET) was obtained from BET N₂ adsorption-desorption isotherms recorded using a Micromeritics surface area and pore size analyzer (3Flex). Scanning electron microscopy (SEM) images were captured on a JEOL 7100 field-emission SEM (FE-SEM) operated at an accelerating voltage of 15 kV.

2.3. Synthesis of Furan-acyl azide (FAz). 2-Furoyl chloride (2.0 g, 0.015 mol) was dissolved in dry tetrahydrofuran (THF) (15 mL, 1.0 M) in a 25 mL flask under a N₂ atmosphere. To the resultant solution at 0 °C was added dropwise a solution containing 3.0 g (0.046 mol) of sodium azide in 7 mL of water. The mixture was

stirred at 0 °C for 30 min, then warmed to room temperature, and stirred for 12 h. The solvent was removed under reduced pressure, and the product was extracted with ethyl acetate, H₂O, and brine. The organic layer was dried over Na₂SO₄, filtered, and evaporated under vacuum. The residue was subjected to flash column chromatography (hexane/ethyl acetate = 1/1 v/v), and FAz was obtained (1.7 g, 83%). ¹H NMR (500 MHz, CDCl₃) δ 7.66 (d, *J* = 1.7 Hz, 1H), 7.27 (d, *J* = 3.7 Hz, 1H), 6.55 (dd, *J* = 3.6, 1.7 Hz, 1H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ 162.55, 148.07, 145.65, 120.04, 112.55 ppm.

2.4. Synthesis of the Phenylfuran-Based Isocyanurate Model Compound (Ph-FAz). 5-Phenylfuran-2-carboxylic acid (0.15 g, 0.80 mmol) was dissolved in dry THF (4.0 mL, 0.2 M) in a 10 mL flask under a N₂ atmosphere, and Et₃N (0.14 mL, 0.96 mmol) was added to the resultant mixture. Diphenyl phosphoryl azide (0.21 mL, 0.96 mmol) was then added dropwise, and the resultant mixture was stirred at room temperature for 12 h. The solvent was removed under reduced pressure, and the product was extracted with ethyl acetate, H₂O, and brine. The organic layer was dried over Na₂SO₄ and filtered, and the solvent was evaporated under vacuum. The residue was subjected to flash column chromatography (hexane/ethyl acetate = 3/1 v/v), and Ph-FAz was obtained (0.15 g, 91%). ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.88 (dd, *J* = 7.5, 1.3 Hz, 2H), 7.59 (d, *J* = 3.8 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.47 (tt, *J* = 7.5, 1.3 Hz, 1H), 7.30 (d, *J* = 3.8 Hz, 1H) ppm. ¹³C NMR (125 MHz, DMSO-*d*₆) δ 161.98, 159.14, 144.42, 130.23, 129.71, 128.96, 125.32, 123.52, 109.41 ppm.

2.5. Synthesis of the 2-Nitrobenzyl furan carbamate Model (FPU3-M). Furan-2-carbonyl azide (0.10 g, 0.73 mmol) and 4,5-dimethoxy-2-nitrobenzyl alcohol (1.0 equiv, 0.73 mmol) were dissolved in dry THF (1.5 mL, 0.50 M) in a Schlenk flask under a N₂ atmosphere. The reaction mixture was refluxed and stirred for 12 h. The solvent was removed under reduced pressure, the residue was subjected to flash column chromatography (hexane/ethyl acetate = 3/1 v/v), and FPU3-M was obtained (0.16 g, 68%). ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.46 (br, 1H), 7.72 (s, 1H), 7.34 (s, 1H), 7.28 (s, 1H), 6.43 (dd, *J* = 2.7, 2.2 Hz, 1H), 6.02 (d, *J* = 2.7 Hz, 1H), 5.45 (s, 2H), 3.92 (s, 3H), 3.88 (s, 3H) ppm. ¹³C NMR (125 MHz, DMSO-*d*₆) δ 153.82, 152.42, 148.38, 140.08, 139.90, 135.80, 127.22, 111.70, 108.71, 63.81, 56.79, 56.60 ppm. MS (HRMS): *m/z* calculated for C₁₄H₁₃N₂O₇ [*M* + *H*]⁺: 323.0801; found: 323.0883.

2.6. Synthesis of the Furan-Based Isocyanurate Model Compound (FIR-M). Cesium fluoride (CsF, 5.7 mg, 4.0 mol %) was charged in a 15 mL pressure-tube vessel, then placed under vacuum, and heated with a heat gun. The flask was refilled with N₂ after cooling to room temperature. Ph-FAz (0.20 g, 0.94 mmol) was added to the flask under a N₂ atmosphere. Dry THF (1.0 mL, 1.0 M) was added using a syringe. The mixture was heated to 100 °C and stirred for 12 h. The orange precipitate was filtered, washed with THF, and dried under vacuum. The residue was subjected to flash column chromatography (hexane/ethyl acetate = 3/1 v/v), and FIR-M was obtained (95 mg, 20%). A reaction under different conditions was carried out via the same procedure, as detailed in Table S2. ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.73 (dd, *J* = 8, 1.3 Hz, 6H), 7.47 (t, *J* = 8 Hz, 6H), 7.36 (tt, *J* = 8, 1.3 Hz, 3H), 7.13 (d, *J* = 3.5 Hz, 3H), 6.75 (d, *J* = 3.5 Hz, 3H) ppm. ¹³C NMR (125 MHz, DMSO-*d*₆) δ 152.62, 147.91, 138.30, 129.90, 129.51, 128.69, 124.02, 111.32, 107.92 ppm. MS (HRMS): *m/z* calculated for C₃₃H₂₁N₃O₆ [*M*]⁺: 555.1430; found: 555.1432.

2.7. Synthesis of Furan-2,5-diacyl azide (FDAz). 2,5-Furandicarboxylic acid (2.0 g, 0.013 mol) was dissolved in dry THF (64 mL, 0.20 M) in a 250 mL flask under a N₂ atmosphere, and Et₃N (4.3 mL, 0.038 mol) was added to the reaction mixture. Diphenyl phosphoryl azide (8.1 mL, 0.038 mol) was then added dropwise, and the resultant solution was stirred at room temperature for 12 h. The solvent was removed under reduced pressure, and the product was extracted with ethyl acetate, H₂O, and brine. The organic layer was dried over Na₂SO₄ and filtered, and the solvent was evaporated under vacuum. The residue was subjected to flash column chromatography (hexane/ethyl acetate = 9/1 v/v), and FDAz was obtained (1.5 g, 57%). ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.57 (s, 1H) ppm. ¹³C

NMR (125 MHz, DMSO- d_6) δ 162.53, 148.38, 121.37 ppm. MS (HRMS): m/z calculated for $C_6H_2N_6O_3$ [M] $^+$: 206.0188; found: 206.0215.

2.8. Synthesis of Dihexyl Furan-2,5-diylidicarbamate (D-FU). FDAz (0.10 g, 0.49 mmol) and 1-hexanol (2.0 equiv, 0.97 mmol) was dissolved in dry THF (1.0 mL, 0.5 M) in a Schlenk flask under a N_2 atmosphere, and dibutyltin dilaurate (DBTDL, 0.1 M stock in THF) (0.15 mL, 3.0 mol %) was added to the reaction mixture. The resultant mixture was refluxed and stirred for 12 h. The solvent was removed under reduced pressure, the residue was subjected to flash column chromatography (hexane/ethyl acetate = 3/1 v/v), and D-FU was obtained (0.11 g, 63%). 1H NMR (500 MHz, DMSO- d_6) δ 7.41 (s, 2H), 4.29 (t, J = 6.7 Hz, 4H), 1.69 (q, J = 7.1 Hz, 4H), 1.37 (m, 4H), 1.30 (m, 8H), 0.88 (m, 6H) ppm. ^{13}C NMR (125 MHz, DMSO- d_6) δ 157.94, 146.67, 119.43, 65.69, 31.29, 28.48, 25.42, 22.44, 14.32 ppm. MS (HRMS): m/z calculated for $C_{18}H_{31}N_2O_5$ [$M + H$] $^+$: 355.2155; found: 355.2211.

2.9. Synthesis of Poly(furanyl-urethane-isocyanurate) (PFUI). The polycondensation reaction was used to prepare PFUI-1, PFUI-2, PFUI-3, PFUI-4, PFUI-5, and PFUI-6 from diols 1,6-hexanediol, 1,4-benzenedimethanol, 2-nitro-*p*-xylene glycol, 2,5-bis-(hydroxymethyl)furan, isosorbide, and bisphenol-*A*, respectively; the FDAz/diol molar ratio was 1/1. All polymerizations were conducted as a one-pot reaction in a pressure-tube vessel with a strong magnetic stirrer. FDAz (50 mg, 0.24 mmol) and diol (1.0 equiv, 0.24 mmol) were dissolved in dry THF (0.3 mL, 1.0 M) in a 15 mL pressure tube under a N_2 atmosphere. DBTDL (0.10 M stock in THF) (73 μ L, 3.0 mol %) was added to the solution, and the lid was quickly changed to a pressure lid to maintain the N_2 condition. The reaction mixture was then refluxed and stirred for 12 h. The mixture was precipitated in methanol. The optimization of PFUI-1 was carried out by catalyst screenings, as described in Table 1. The synthesis conditions for PFUI-2, PFUI-3, PFUI-4, PFUI-5, and PFUI-6 are detailed in Table 2.

Table 1. Optimizations of the Synthesis of the Poly(furanyl-urethane-isocyanurate) Copolymer (PFUI-1) Using 1,6-Hexanediol^a

entry	catalyst (mol %)	diol (equiv)	yield ^b (%)	$x:y$ ^c	M_n ^d (kDa)	PDI ^d
1	none	1	94	n/d	n/d	
2	DBACO (3)	1	49 ^e	7:3	16	1.3
3	DBU (3)	1	31 ^e	5:5	14	1.3
4	TBD (3)	1	41 ^e	7:3	14	1.3
5	DBTDL (3)	1	73	7:3	24	1.2
6	DBTDL (1)	1	41	7:3	24	1.2
7	DBTDL (5)	1	51	7:3	26	1.2
8	DBTDL (3)	2	85 ^f	~10:0	12	1.2
9	CsF (4)	1	98	2:8	n/d	
10	CsF (4)	none	99	n/d	n/d	

^aReaction and conditions: FDAz (0.24 mmol), 1,6-hexanediol (1.0 equiv), THF (1.0 M), reflux, 12 h, using a pressure tube and under an N_2 atmosphere (for details see the Supporting Information). ^bIsolated yield. ^cCalculated by NMR. ^dPolydispersity index determined by GPC using a polystyrene standard calibration and *N,N*-dimethylformamide (DMF) as an eluent. ^eYield by 1H NMR analysis of the crude reaction mixture using imidazole as an internal standard. ^fCrude yield.

PFUI-1. (62 mg, 95%) 1H NMR (500 MHz, DMSO- d_6) δ 11.04 (br, 4H), 7.39 (s, 14H), 7.26 (s, 4H), 6.88 (s, 1H), 6.65 (s, 1H), 6.15 (s, 4H), 4.29 (s, 28H), 4.20–4.11 (m, 16H), 1.76–1.64 (m, 44H), 1.42–1.37 (m, 44H) ppm. FT-IR (ν/cm^{-1}): 1720 (urethane and ester C=O), 1553 (C=C), 1392 (isocyanurate -C-N-), 1278 (urethane -C-N-), 1226 (furan ring -C-O-), 1140, 1017, 981, 770 (=CH).

PFUI-2. (55 mg, 78%) 1H NMR (500 MHz, DMSO- d_6) δ 11.26 (br, 12H), 7.49–7.41 (m, 28H), 7.36–7.34 (m, 8H), 6.89 (s, 2H), 6.66 (s, 2H), 6.20 (s, 6H), 5.37–5.35 (m, 12H), 5.28–5.17 (m, 16H)

ppm. FT-IR (ν/cm^{-1}) 1724 (urethane and ester C=O), 1555 (C=C), 1375 (isocyanurate -C-N-), 1273 (urethane -C-N-), 1226 (furan ring -C-O-), 1130, 1009, 971, 764 (=CH).

PFUI-3. (63 mg, 77%) 1H NMR (500 MHz, DMSO- d_6) δ 11.46 (br, 13H), 8.27–8.11 (m, 9H), 7.97–7.75 (m, 12H), 7.56–7.41 (m, 10H), 6.89 (s, 2H), 6.66 (s, 2H), 6.22 (s, 4H), 5.71–5.22 (m, 28H) ppm. FT-IR (ν/cm^{-1}): 1724 (urethane and ester C=O), 1536 (C=C), 1347 (isocyanurate -C-N-), 1273 (urethane -C-N-), 1216 (furan ring -C-O-), 1130, 1056, 981, 754 (=CH).

PFUI-4. (46 mg, 68%) 1H NMR (500 MHz, DMSO- d_6) δ 11.26 (s, 6H), 7.44 (s, 13H), 7.33 (s, 4H), 6.89 (s, 2H), 6.65 (s, 13H), 6.59 (s, 8H), 6.19 (s, 4H), 5.77 (s, 4H), 5.34 (s, 16H), 5.24–5.15 (m, 26H) ppm. FT-IR (ν/cm^{-1}): 1724 (urethane and ester C=O), 1565 (C=C), 1375 (isocyanurate -C-N-), 1273 (urethane -C-N-), 1216 (furan ring -C-O-), 1130, 1028, 961, 764 (=CH).

PFUI-5. (52 mg, 72%) FT-IR (ν/cm^{-1}): 2927 (C-H), 1721 (urethane and ester C=O), 1519 (C=C), 1361 (isocyanurate -C-N-), 1216 (urethane -C-N-), 1014 (furan ring -C-O-).

PFUI-6. (39 mg, 44%) FT-IR (ν/cm^{-1}): 3256 (urethane -NH-), 2944 (C-H), 1750, 1659 (urethane and ester C=O), 1498 (C=C), 1381 (isocyanurate -C-N-), 1026 (furan ring -C-O-).

2.10. Synthesis of Furan-Based Polyisocyanurate (PFIR). Cesium fluoride (CsF, 15 mg, 4.0 mol %) was charged in a 15 mL pressure-tube vessel, then placed under vacuum, and heated with a heat gun. The flask was then refilled with N_2 after cooling to room temperature. FDAz (0.50 g, 2.4 mmol) was added to the flask under a N_2 atmosphere. Dry THF (2.5 mL, 1.0 M) was then added using a syringe. The mixture was heated to 100 $^{\circ}C$ and stirred for 12 h. The orange precipitate was filtered, washed with THF, and dried under vacuum. The product was an orange solid (0.37 g, 99%). The reaction was conducted under another set of reaction conditions using the same procedure, as detailed in Table 1, entry 9. 1H NMR (400 MHz, solid state) δ 6.44, 3.39, 1.68 ppm. ^{13}C NMR (400 MHz, solid state) δ 159.07, 147.07, 137.15, 111.93, 95.39, 81.33 ppm. FT-IR (ν/cm^{-1}): 1736 (urethane and ester C=O), 1406 (isocyanurate -C-N-), 1206 (furan ring -C-O-), 1018, 975, 747 (=CH).

2.11. Fabrication of the Film for the Photodegradability Test. In the case of a PFUI-3 film, PFUI-3 (25 mg, 33 wt %) and polyethyleneglycol (PEG M_n 20 kDa, 50 mg, 67 wt %) were dissolved in DMSO (0.35 mL) and the resultant solution was dropped into a Teflon mold and dried at 80 $^{\circ}C$. The film was irradiated with a 200 W UV light for 36 h.

2.12. Fabrication of the Film for the Flammability Test. As a commercial film, polyacrylonitrile (PAN M_w 150 kDa, 50 mg) was dissolved in DMSO (0.50 mL). For the PFUI-1 film, PFUI-1 (20 mg, 29 wt %) and PAN (50 mg, 71 wt %) were dissolved in DMSO (0.60 mL) and the resultant solution was dropped into a Teflon mold and vacuum-dried. For the PFIR film, because PFIR did not dissolve in any solvent, the film was produced by compressing it in the form of a pellet. Each film was directly ignited to perform the flammability test.

2.13. Photodegradation Kinetics Measurements. The photodegradation kinetics of FPU3-M was investigated using UV-vis spectroscopy for various UV irradiation times (0, 1, 3, 5, 10, and 20 min). The objective of this study was to determine the degradation constants (k_d s) of FGM under UV irradiation (200 W and 17 mW) and at several concentrations (200, 100, 50, and 10 μ M in dimethyl sulfoxide (DMSO)). The wavelength (λ) of the 17 mW UV light source was 343 nm (Figure S13). The decrease in FPU3-M absorption at $\lambda_{max} = 343$ nm during the UV irradiation could be modeled as a first-order reaction, enabling calculation of the k_d values via nonlinear curve fitting according to eq 1:

$$[A]_t = [A]_0 \times \exp(-k_d t) \quad (1)$$

where $[A]_0$ and $[A]_t$ are the concentration of FPU3-M initially and at time t , respectively.

3. RESULTS AND DISCUSSION

3.1. Preparation of FDAz and Its Curtius Rearrangement. The new azide-containing polymer platform, FDAz,

Table 2. Synthesis of Poly(urethane-isocyanurate) Copolymers (PFUI x) Using Various Diols^a

entry	polymer	diol	yield ^b (%)	$x:y$ ^c	T_g ^d (°C)	M_n ^e (kDa)	PDI ^e
1	PFUI-1	1,6-hexanediol	73	7:3	78	24	1.2
2	PFUI-2	1,4-benzenedimethanol	79	6:4	52	31	1.2
3	PFUI-3	2-nitro- <i>p</i> -xylene glycol	78	7:3	67	65	1.5
4	PFUI-4	2,5-bis(hydroxymethyl)furan	68	7:3	73	51	1.3
5	PFUI-5	isosorbide	72	n/d	79	n/d	
6	PFUI-6	bisphenol-A	41	n/d	n/d	n/d	

^aReaction and conditions: FDAz (0.24 mmol), diol (1.0 equiv), DBTDL (3.0 mol %), solvent (THF, 1.0 M), reflux, 12 h, using a pressure tube and under a N₂ atmosphere (for details, see the Supporting Information). ^bIsolated yield. ^cCalculated values by NMR. ^dDetermined by the inflection of the second heating curves. ^eDetermined by GPC using polystyrene standards and DMF as an eluent.

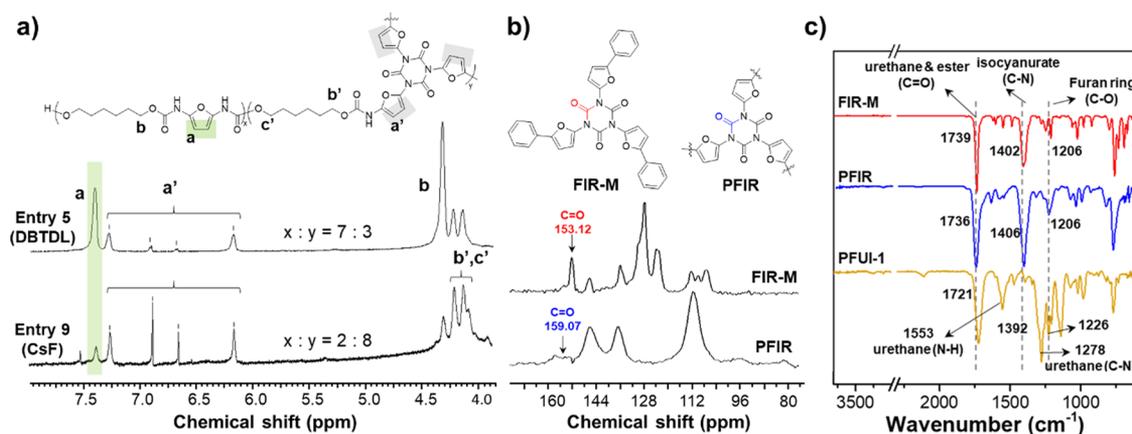


Figure 2. (a) ¹H NMR spectra (DMSO-*d*₆) of PFUI-1, showing the difference between DBTDL and CsF catalysts. (b) Solid-state ¹³C NMR spectra of the polyisocyanurate (PFIR) model compound (FIR-M) and the PFIR. (c) FT-IR analysis of the poly(furanyl-urethane-isocyanurate) series (PFUIs), FIR-M, and PFIR.

could be easily synthesized in reasonable yields using an eco-friendly azidation reagent, diphenyl phosphoryl azide (DPPA) (Figure 1b).^{50,51} Briefly, the diacyl azide in FDAz was obtained in 62% yield when 2,5-furandicarboxylic acid (FDCA) was subjected to DPPA and Et₃N in THF (0.20 M) at room temperature. In the conventional synthesis method in the literature,^{52,53} a nucleophilic acyl substitution with sodium azide (NaN₃) was carried out after a chlorination reagent such as thionyl chloride was used, which is a somewhat harsher method than the DPPA method.

FDAz was converted to an isocyanate (–NCO) structure through a thermal Curtius rearrangement and was used in the subsequent reaction without further isolation (Scheme 1). When the toluene solution of FDAz was heated to 100 °C, bubbles were generated, which strongly indicated that N₂ was produced to give furan diisocyanate (FDI). Despite numerous attempts, FDI could not be isolated. The existence of FDI was therefore verified through the formation of carbamate materials (D-FU) in the presence of 1-hexanol (Scheme S1), which was confirmed by ¹H and ¹³C NMR and FT-IR spectroscopic analyses (refer to the experimental procedures of the Supporting Information). It was confirmed that all FDAz disappeared in 3 h under THF reflux (70 °C) according to ¹H NMR analysis (Figure S1). The degradation of the acyl azide group was estimated from the integration of the peak at 7.58 ppm, the furanyl protons of FDAz. It was also observed that after FDAz was rapidly degraded, monocarbamate (M-FU) was formed first, followed by conversion to dicarbamate (D-FU). Assuming the first-order kinetics (rate = $-k$ [FDAz]), the rate constant k for FDAz degradation was estimated to $5.88 \times 10^{-4} \text{ s}^{-1}$. The results show that the Curtius rearrangement to

diisocyanate was effective when FDAz was used and that carbamates could be easily synthesized in one-pot. Activation of the acyl azide required a temperature of at least 60 °C,⁵⁴ and THF was found to be a more effective solvent than toluene for carbamate synthesis.

3.2. One-Pot Polymerization of FDAz to Poly(furanyl-urethane-isocyanurate) (PFUI) and Structural Characterizations. Having the successful Curtius rearrangement of FDAz to diisocyanate available, we attempted the one-pot polymerization with 1,6-hexanediol. The reaction mixture of FDAz (1.0 equiv) and 1,6-hexanediol (1.0 equiv) was refluxed in a pressure tube with THF (1.0 M) as the solvent without any catalyst (Table 1, entry 1). The solution turned orange over time; after the reaction was completed, insoluble powders were generated. Although the majority of the mass was recovered (~94%), the structure could not be determined through ¹H NMR analysis or GPC. The isocyanurate (Figure 1a) was significantly generated through the trimerization of isocyanate (see below), limiting the polymer's solubility because of its cross-linked structure.

To optimize the polymerization conditions,⁵⁵ organic/organometallic catalysts were screened using 1,4-diazabicyclo[2.2.2]octane (DABCO), 1,8-diazabicyclo(5.4.0)-undec-7-ene (DBU), 1,5,7-triazabicyclodec-5-ene (TBD), and dibutyltin dilaurate (DBTDL) under conditions similar to those previously described (3 mol %, entries 2–5). Fortunately, the catalysts enabled the production of soluble polymers, which were subsequently characterized by ¹H NMR, GPC, and FT-IR analyses. The isolated yields of the polymers were generally low or moderate (31–73%), and the highest yield was obtained with DBTDL (entry 5). We attributed this

high yield to the polymer's relatively high molecular weight with DBTDL (M_n 24 vs 14–16 kDa with other catalysts). Notably, in the elution profiles of the GPC, aggregation peaks were also observed in front of the main peak, as shown in Table 1 (Figure S2). The narrow polydispersity indices (PDIs, 1.2–1.3), which were far narrower than the most probable distribution (i.e., PDI = 2.0) in the step polymerizations, also suggested that certain portions of the product polymers were characterized. Even when the catalysts were present, cross-linking via isocyanurate apparently occurred, albeit to a lesser extent. To estimate the relative amounts of linear urethane (x) and isocyanurate (y) moieties, ^1H NMR analysis was conducted for DMSO- d_6 solutions of the polymers (Figure 2a). At least ~25 and ~32% of FDAz was transformed into linear urethane linkages with DBU ($x:y = 5:5$) and DBTDL ($x:y = 7:3$), respectively; the rest of the FDAz was incorporated into isocyanurate via trimerization. Under thermal conditions for Curtius rearrangement, the trimerization reactions of the resultant isocyanates appeared to proceed relatively rapidly; substantial proportions of isocyanurates were generated, even in the presence of the catalysts for the urethane reactions. When we varied the catalyst loading from 1.0 to 5.0 mol %, the polymerization reaction was not substantially affected (entries 5–7 and Figure S3) and the loading of 3 mol % was chosen as the optimal loading amount because of the slightly higher yield. When we tried to synthesize copolymers PFUIs by increasing the equivalence of FDAz, the resulting molecular weights were not satisfactory. The synthesis was carried out for 1, 1.2, 1.3, and 1.5 equiv of FDAz compared to 1,6-hexanediol, and all other conditions were the same. As shown in Table S1, the increasing equivalence of FDAz did not improve the number-average molecular weight (M_n) (19–20 kDa). Thus, we suspect that increasing equivalence of FDAz leads to the formation of more trimer moieties, resulting in aggregation and solubility issues. Therefore, we concluded that it is best to fix the ratio of diacylazide to diol at 1:1 despite slight off-stoichiometry. When the reaction was subjected to excess diol (2.0 equiv), only the linear polymer (M_n 12 kDa with DBTDL 3.0 mol %) was generated (85% yield; entry 8 and Figure S4).

To confirm our hypothesis of isocyanurate formation, we used CsF as a catalyst because it is well known to promote the trimerization of isocyanate (Table 1, entry 9).^{56–58} Indeed, a mostly insoluble product was obtained and the proportion of isocyanurate was substantially increased ($x:y = 2:8$), as analyzed by ^1H NMR, from its sparingly soluble solution (Figure S4). We therefore speculated that if we conducted the reaction with only FDAz (i.e., without the diol), a fully isocyanurate-based network polymer would be obtained. To optimize the conditions for the network polymer (poly(furanyl-isocyanurate), PFIR), we first tested the reactions on the model compound, 5-phenylfuran-2-carbonyl azide, which had been prepared from the corresponding acid using DPPA. The most suitable catalyst for trimerization of furanyl isocyanate was found to be CsF (Table S2). The chemical structure of the model trimer FIR-M was confirmed through ^1H and ^{13}C NMR analyses, in conjunction with high-resolution mass spectrometric analysis. In the FT-IR spectra, the azide vibration peak at 2164 cm^{-1} disappeared completely and the carbonyl vibration peak appeared to shift from 1683 to 1739 cm^{-1} . A strong vibration peak was generated at 1406 cm^{-1} and was assigned to the specific C–N bond of the isocyanurate (Figure S5).^{59–62}

When FDAz was subjected to the CsF conditions, the trimerization of the isocyanates gave PFIR in 99% yield (entry 10). In the absence of the catalyst, the yield of the PFIR was as low as 33% (Table S3, entry S7a). Because of the network structure of the PFIR, we recorded its BET N_2 adsorption–desorption isotherms; however, the results showed only the presence of pore size, as indicated by the small specific surface areas (α_{SAS}) of 1.9 – $4.4\text{ m}^2\text{ g}^{-1}$ (Figure S6). The isocyanurate structure of the PFIR was confirmed through comparison with the structure of the model FIR-M determined via solid-state NMR analysis (Figure 2b). In the solution ^{13}C NMR spectrum of FIR-M, the carbonyl peak was observed at 153 ppm; in the solid-state ^{13}C NMR spectrum, it appeared at the same position, 153 ppm.⁶³ On the basis of these results, we assigned the peak at ~159 ppm in the solid-state ^{13}C NMR spectrum of the PFIR to the carbonyl group of the furan-based isocyanurate. In the FT-IR analysis, we observed the C–N vibration peak of the isocyanurate moiety of the PFIR at 1406 cm^{-1} , which is similar to the frequency of the corresponding peak in the spectrum of FIR-M (1402 cm^{-1}). Interestingly, in the spectrum of copolymer PFUI-1, the isocyanurate vibration peak (C–N) was observed at 1392 cm^{-1} , supporting the formation of the poly(furanyl-urethane-isocyanurate) copolymers (Figure 2c).

3.3. Synthesis of Biomass-Derived Furanyl Copolymers PFUIs Using Various Diols. Under the optimized polymerization conditions, several copolymers were synthesized using various diols (Table 2). For comparison with the aliphatic diol in entry 1, the aromatic group containing diols were tested, including xylenyl, nitro-xylenyl, and biomass-derived furan diols (entries 2, 3, and 4, respectively; Figures S7 and S8). The polymerization yields were similar to that achieved with 1,6-hexanediol (entry 1), and only a slight increase of the isocyanurate portion (y) for xylenyl was observed ($x:y = 6:4$). Although the diols had an aromatic moiety, they were still primary alcohols and thus exhibited similar rates of nucleophilic addition to isocyanate. When the secondary alcohol isosorbide (entry 5) was used, the nucleophilic addition to isocyanate (urethane formation) did not occur efficiently, leading to a high proportion of isocyanurate (Figure S9). As the isocyanurate structure was produced in a large amount, the polymers were likely to be insoluble, similar to the full-network PFIR. Interestingly, the phenolic diol (bisphenol-A) produced completely insoluble powders (entry 6), presumably because of its rigid structure and diminished nucleophilicity. These results show that if a diol has sufficient nucleophilicity, the copolymer PFUI can be efficiently prepared in a sufficiently soluble form. All polyurethanes exhibit a similar glass transition temperature (T_g , 50–80 °C) when compared to various furan-based polymers or polyurethane elastomers as shown in Table 2 and Figure S10.^{36,64}

3.4. Photocleavage Reaction of the *o*-NB-Substituted Copolymer PFUI-3. In the process of polymerization of FDAz through Curtius rearrangement, useful functionalities could be easily incorporated. To demonstrate this concept, we prepared a photodegradable copolymer using 2-nitro-*p*-xylene glycol as a diol (PFUI-3; entry 3 in Table 2). The photolysis was based on the photocleavage reaction of the *o*-NB groups, which are frequently used in photolabile linkers.^{42,65,66} A DMF solution of PFUI-3 (25 mM) was irradiated with UV light (320–400 nm, 4.50 W), and the decomposition behavior was investigated through GPC analysis. As shown in Figure 3a, the

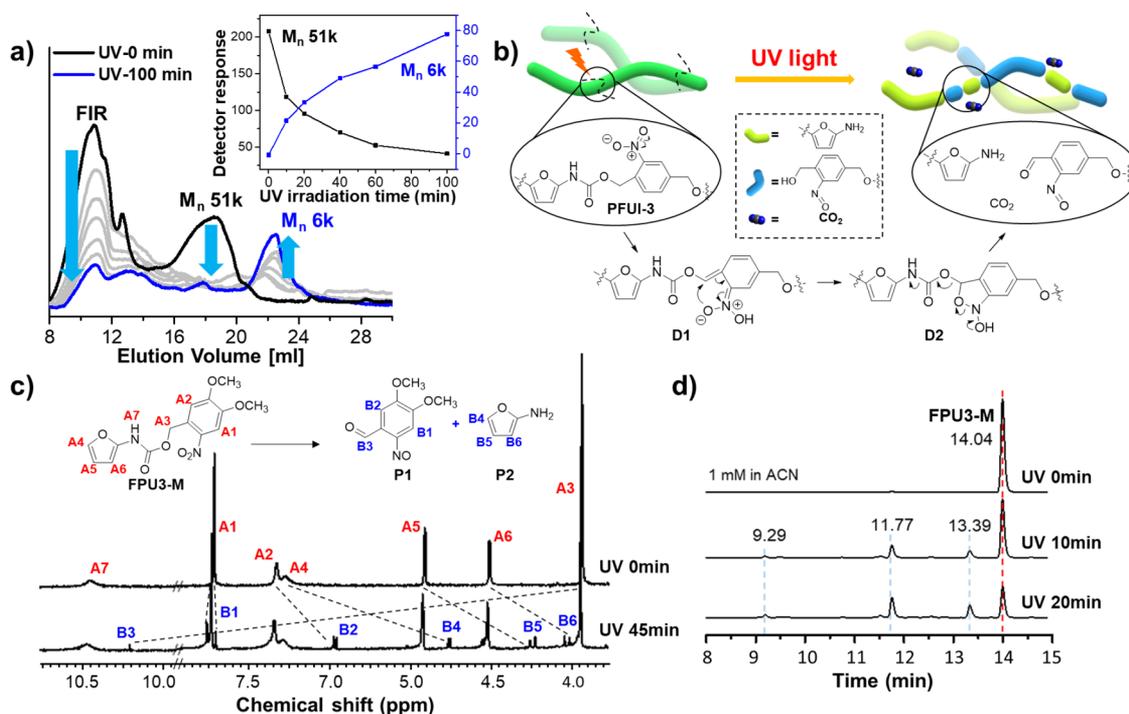


Figure 3. (a) GPC traces (detected at 254 nm, 25 mM) of PFUI-3 depending on the UV light irradiation time (320–400 nm, 200 W). (b) Schematic and mechanism for the photodegradation of PFUI-3 by UV light (320–400 nm, 200 W). (c) ^1H NMR analysis (5.0 mM in $\text{DMSO}-d_6$) of photodegradation of FPU3-M by UV irradiation (343 nm, 17 mW). (d) High-performance liquid chromatographic analysis of the photodegradation of FPU3-M by UV irradiation (343 nm, 17 mW).

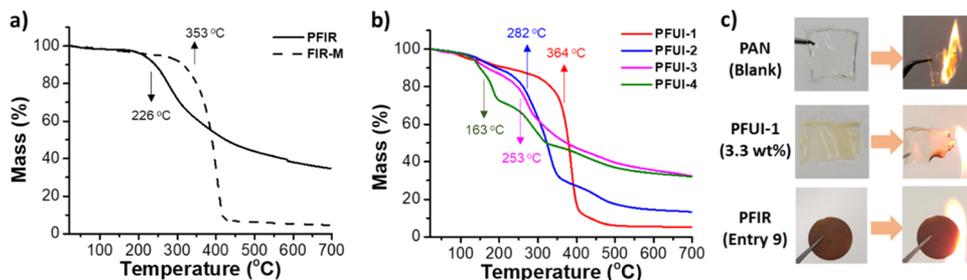


Figure 4. (a) TGA curves of FIR-M and PFIR. (b) TGA curves of PFUI-1, PFUI-2, PFUI-3, and PFUI-4. (c) Photographs of the nonflammable polymer films after the burning tests.

GPC profile of the pristine polymer PFIR-3 presented two peaks: the aggregated peak at an elution time of ~ 11 min, presumably due to furanyl isocyanurate (FIR) and the linear furanyl urethane (FU) portions at an elution time of ~ 18 min ($M_n \sim 51$ kDa). As the UV light was irradiated, the peak at ~ 18 min (FU) decreased in intensity immediately and that at approximately 11 min (FIR) decreased in intensity slowly. The peak at ~ 22 min simultaneously increased in intensity over time, which we attributed to the photodecomposed debris ($M_n \sim 6$ kDa) from PFUI-3. On the basis of the previously reported photolysis mechanism of *o*-NB,⁶⁷ we propose a plausible photodecomposition pathway for furanyl *o*-NB moieties in PFUI-3 (Figure 3b). Under UV light irradiation, the nitro group can undergo photoinduced charge transfer; the neutral aci-moiety (D1) is then formed through radical degradation or tautomerisation,^{43,68} followed by irreversible cyclisation to the 1,3-dihydrobenz-[c]isoxazol-1-ol intermediate (D2). Thereafter, the ring-opening resulted in several charge transfers and CO_2 was released, a process expected to be the rate-determining step and that may be dependent on the leaving

group.^{65,66,68} For the photodegradation tests, the film containing 33 wt % of copolymer PFUI-3 was prepared in polyethyleneglycol (PEG) using DMSO. Under UV irradiation (320–400 nm, 4.50 W) for 36 h, the crack in the film was generated by the degradation mechanism of the *o*-NB linker, producing carbon dioxide and several byproducts (Figure S11).^{41,69}

To support our hypothesis for the photolysis of *o*-NB-incorporated PFUI-3, the photodecomposition was investigated with a model compound FPU3-M through ^1H -NMR analysis (Figures 3c and S12). The $\text{DMSO}-d_6$ solution of FPU3-M (5 mM) was subjected to irradiation with UV light (343 nm, 17 mW). The benzylic proton signal (A3, 5.45 ppm) of FPU3-M decreased in intensity when the sample was irradiated with UV light, and the signal of the aldehyde proton (B3, 10.20 ppm) of byproduct P1 appeared.⁷⁰ In addition, the new proton peaks appear to match those of byproducts benzaldehyde P1 and amino-furan P2, along with those of a possible imine product from P1 and P2.⁷¹ The high-resolution mass spectrometry (HPLC) traces corresponding to the

photoirradiated mixture of FPU3-M (Figure 3d) show that as the peak of the starting FPU3-M decreased in intensity, three new peaks appeared, matching the results of the NMR analysis. In the UV-vis analysis using acetonitrile solutions of FPU3-M (200, 100, 50, and 10 μM), photoinduced decomposition was investigated through the decrease in absorbance at $\lambda_{\text{max}} = 343$ nm (Figure S13).⁷² We found that the half-life τ was approximately 17 min for the decomposition of FPU3-M, resulting in an average k_d of 0.039 with pseudo-first-order kinetics.⁷³

3.5. Thermal Stability of Biomass-Derived PFIR and PFUIs with the Flame Resistance Test. Because isocyanurate groups are well known to exhibit good heat resistance, the biomass-derived (co)polymers from FDAz were tested for flame retardancy.^{24,46–48,62} The thermal decomposition behaviors were investigated by TGA (Figure 4a,b), which was performed under N_2 at a temperature ramp rate of $10\text{ }^\circ\text{C min}^{-1}$ in the range from 0 to $700\text{ }^\circ\text{C}$. In the case of the fully isocyanurate PFIR (Figure 4a), a large weight loss occurred at approximately $226\text{ }^\circ\text{C}$, which is slightly lower than the temperature of the weight loss of the model compound, FIR-M ($353\text{ }^\circ\text{C}$). This temperature, which was determined on the basis of the onset temperature, was assigned to the decomposition of the furanyl isocyanurate groups. According to the TGA profiles of copolymer PFUIs under the same conditions (Figure 4b), the thermal decomposition involved several steps. The onset temperature was observed at approximately $163\text{ }^\circ\text{C}$, which we assigned to the decomposition of the linear urethane moieties. The decomposition at this stage was most prominent in PFUI-4 with 2,5-oxy-methylfuran moieties, which were very unstable compared with the 2,5-carbonyl-furans.³⁵ The secondary decomposition of all four copolymers occurred at approximately $253\text{--}364\text{ }^\circ\text{C}$, which was assigned to the decomposition of the isocyanurate moieties. Interestingly, the aliphatic copolymer PFUI-1 exhibited the highest thermal stability among the investigated materials better than the stability of the benzyl or nitrobenzyl derivatives.

For the flame-retardant tests, a film containing 29 wt % of copolymer PFUI-1 was prepared in PAN. In the case of the fully isocyanurate PFIR, a pelletized film (thickness of $53\text{ }\mu\text{m}$) was fabricated because the sample was not soluble in any solvent. A control PAN film that did not contain any flame-retardant polymer appeared to catch fire quickly and was transformed into charred chunks. By contrast, the PFUI-1-containing PAN film was only slightly burnt. The PFIR did not catch fire at all; it was only slightly deformed by the heat. To determine how much the furan or isocyanurate moieties can contribute to the flame-retardant property, we additionally performed a flame retardancy test using a film of a furan-containing linear PU (FR-co-PU1a), which was reported in our previous study (Figure S14).³⁶ Note that FR-co-PU1a contains furan moieties but without isocyanurate moieties. The film of FR-co-PU1a was prepared with the same conditions as those with PFUI-1 (Figure 4c) (i.e., PAN 50 mg and FR-co-PU1a 20 mg). It was clearly observed that the film of linear PU without isocyanurate structures burnt much faster than the film with isocyanurate moieties (Figure S14). These results strongly suggest that the flame-retardant properties of PFUI-1 originate from the thermally stable isocyanurate moieties of the polymer. In TGA, the decomposition temperature of FR-co-PU1a was measured to be about $200\text{ }^\circ\text{C}$, which is much lower than that of PFUI-1 ($364\text{ }^\circ\text{C}$). Although the flame retardancy has only

been demonstrated at the proof-of-concept level here, the preparation of flame-retardant materials using isocyanurate-containing polymers synthesized from a biomass-derived monomer, FDAz, appears to be feasible.

4. CONCLUSIONS

Using the versatile polymer platform FDAz, we synthesized various biomass-derived furan copolymers of PFUIs and the PFIR network via thermal Curtius rearrangement. The synthesized (co)polymers were thoroughly characterized by solution/solid-state NMR and FT-IR analyses, with the aid of a model isocyanurate. In the copolymer PFUIs, the relative proportions of linear urethane and branched isocyanurate moieties were roughly controlled by the diol ratio and the choice of the catalyst. The designed functional properties of the biomass-derived PFUIs and PFIR were investigated in terms of photodegradability and thermal stability (flame retardancy). The eco-friendly and photodegradable polymer PFUI-3 was prepared by the introduction of an *o*-nitro functional group; its photoinduced decomposition was demonstrated in GPC traces, along with the generation of byproducts detected in the NMR and HPLC analyses. TGA studies confirmed the thermal stability of the cyclic polyisocyanurate component as two inflection points at approximately $300\text{ }^\circ\text{C}$. Interestingly, PFIR exhibited effective nonflammability, and the inclusion of a PFUI copolymer in a PAN matrix led to flame retardancy because of the isocyanurate structure. We believe that FDAz is a versatile polymer platform that can be applied to the synthesis of various eco-friendly functional polymers and is expected to be useful in the development of eco-friendly polymer materials such as degradable plastics and nonflammable polymers.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsapm.1c01005>.

GPC traces for catalyst screening of synthesis of PFUI-1 and synthesis of PFUI-1 (with diol (2.0 equiv) and with only the CsF catalyst); decomposition kinetics of FDAz through ^1H NMR; synthesis of PFUI-1 from various equivalents of FDAz; optimization of synthesis of FIR-M and PFIR; FT-IR spectra of FIR-M and poly(furanyl-urethane-isocyanurate) copolymers (PFUIs); ^1H NMR spectra of poly(furanyl-urethane-isocyanurate) copolymers (PFUIs); ^1H NMR spectra for byproducts of degradation of a photodegradable model compound (FPU3-M); absorption spectra for the photodegradation of FPU3-M using UV irradiation (343 nm); nonlinear curve fitting analysis of FPU3-M depending on concentration; photographs of the furan-containing polymer film comparison with FR-co-PU1a and PFUI-1 in the burning test; and ^1H NMR and ^{13}C NMR spectra of all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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