

Article

# Fluorinated Polyurethanes, Synthesis and Properties

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**Abstract:** Fluorinated polyurethanes with a glass transition temperature as low as  $-139\text{ }^{\circ}\text{C}$  and a decomposition onset temperature of  $247\text{--}330\text{ }^{\circ}\text{C}$  were prepared by a reaction of fluorinated alcohols with aromatic and cycloaliphatic diisocyanates in solution or melt.

**Keywords:** aromatic and cycloaliphatic diisocyanates; fluorinated alcohols; fluorinated polyurethanes; glass transition temperature; decomposition temperature

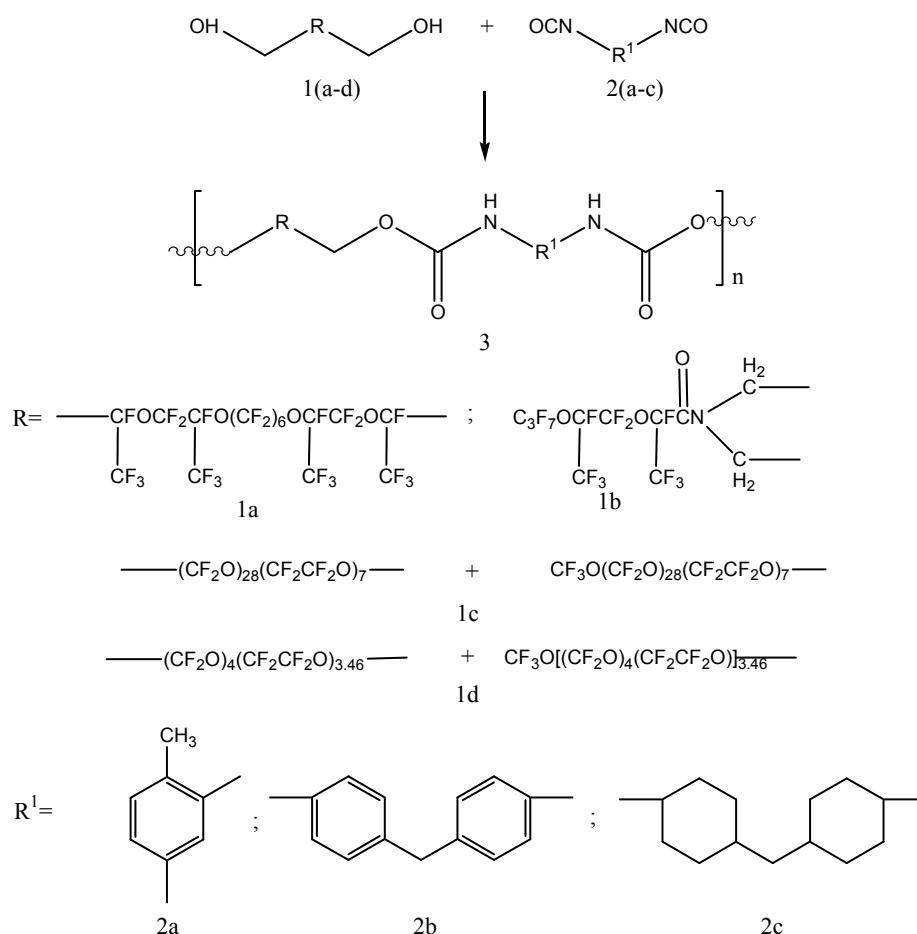
## 1. Introduction

Reactions of aromatic and aliphatic diisocyanates are extensively employed in the synthesis of valuable polymeric materials, viz. polyurethanes (PUs). The preparation of polymers is often assisted by catalysts such as tertiary amines, organotin compounds, etc. [1]. Depending on the starting compounds, plastics or rubberlike products are afforded.

The fluorine incorporation into the polymer backbone or its side chains is the basis for well known methods that lead to great changes in the surface properties [2]. PU is one material that would benefit from the characteristic properties intrinsic to fluorinated polymers. The effect of fluorine-containing PUs on their properties has been described [3–7]. Fluorocarbon chains were incorporated into PUs via fluorine-containing isocyanates [8], chain extenders [3–7] or soft segments [9–11]. The surface and bulk structure of the synthesized PUs were studied. Ge et al. [12] synthesized FPU starting from fluorinated polyether glycol prepared by radical grafting of hexafluoropropylene onto polytetramethylene glycol (PTMG-g-HFP) as a soft segment, 1,6-hexamethylene diisocyanate or toluene diisocyanate as a hard segment and 1,4-butanediol as a chain extender. They studied their mechanical properties and thermal stability in comparison with those of corresponding hydrogenated PUs along with chemical resistance of FPU films through spot tests with different solvents.

It was also shown that introduction of fluorinated fragments to a macromolecule in addition to high hydro- and oleophobic properties considerably contribute towards achievement by the prepared polymers good low temperature parameters in a few cases [13]. 1,4-Butanediol, 2,2,3,3,4,4,5,5-octafluoro-1,6-hexandiol, etc., are often utilized as macromolecule chain extenders [14–18]. Thus, in a number of cases, the glass transition temperature of polymers can be dramatically reduced by the insertion of fluorinated fragments to the macromolecule [19,20].

In this research we endeavored to synthesize new poly- and oligourethanes containing fluoropolyether components of different structure both in the backbone and in the side polymer chain. Aromatic and cycloaliphatic diisocyanates were used as hard segments of FPU. A synthetic route to such FPU is given in Scheme 1.



Scheme 1. FPU synthesis pathway.

## 2. Results and Discussion

Polyaddition of diisocyanates to fluorinated alcohols was performed both in solution (dimethylformamide (DMFA) or perfluorobenzene) and in mass (melt) at temperatures varying from 25 °C to 190 °C. Ethylene glycol was utilized as a chain extender in a number of tests. The synthetic conditions are specified in Table 1.

Analyzing the course of the synthesis of FPUs from aromatic and cycloaliphatic diisocyanates, we established that the polyaddition reaction proceeded quite smoothly without a catalyst both in solvents and in the melt. From technological and environmental points of view, the bulk process applied in this research could have the certain advantage against the process in solution. Meanwhile, a number of researchers explained a need for a catalyst by low basicity of fluorinated diols. Apparently, reactivity of fluorinated diols in such reactions does not merely rely on their basicity.

Figure 1 shows DSC data for fluoropolyurethane 5, which evidence that the prepared low molecular weight polymer has a partially crystalline structure. DSC curve shows temperature interval from −30 °C to 115 °C corresponding to melting procedure with maximum at 40 °C. Phase regularity of polymer chains is likely to be related to interactions between neighboring macromolecules containing urethane groups.

Figure 2 illustrates DSC data for rubberlike high molecular weight FPU 7 obtained from diol 1d and diisocyanate 2c in melt. The glass transition temperature of FPU 7 is −139 °C. An insignificant share of the crystalline phase with the melting point −22 °C was observed herein. It can be concluded that FPU 7 is characterized by a relatively weak intermolecular interaction between C=O and N-H groups of macromolecules. This FPU dissolved only in C<sub>6</sub>F<sub>6</sub>, did not dissolve in DMFA and, to some extent, dissolved in acetone.

**Table 1.** Fluoropolyurethane synthesis conditions and some parameters of the prepared polymers.

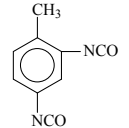
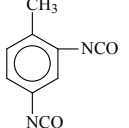
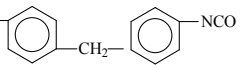
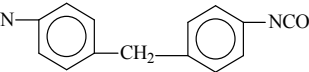
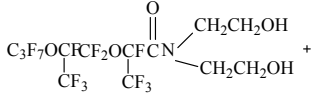
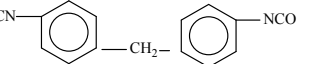
No.	Initial Mixture Composition	Reaction Conditions	Polymer's Appearance	Contact Angle by Water (°)	Parameters of the Polymers
1	$\text{HOCH}_2\text{CFOCF}_2\text{CFO}(\text{CF}_2)_6\text{OCF}_2\text{OCF}_2\text{OCFCH}_2\text{OH} +$ 	60 °C–150 °C 17 h in nitrogen flow DMFA	Solid elastic light-brown	101	( $\eta$ ) = 0.006 dL/g in DMFA
2	$\text{HOCH}_2\text{CFOCF}_2\text{CFO}(\text{CF}_2)_6\text{OCF}_2\text{OCF}_2\text{OCFCH}_2\text{OH} +$ 	190 °C 17 h in nitrogen flow, in melt	Solid elastic light-brown	101	Mp = 20 °C; ( $\eta$ ) = 0.01 dL/g in DMFA T <sub>5% decomp.</sub> = 261 °C
3	$\text{HOCH}_2\text{CFOCF}_2\text{CFO}(\text{CF}_2)_6\text{OCF}_2\text{OCF}_2\text{OCFCH}_2\text{OH} +$ 	190 °C 15 h in nitrogen flow, in melt	Solid yellowish brown	110	T <sub>5% decomp.</sub> = 323 °C
4	$\text{HOCH}_2(\text{CF}_2\text{O})_{28}(\text{CF}_2\text{CF}_2\text{O})_7\text{CH}_2\text{OH} +$ $+ \text{CF}_3\text{O}(\text{CF}_2\text{O})_{28}(\text{CF}_2\text{CF}_2\text{O})_7\text{CH}_2\text{OH} +$ 	190 °C 9 h in nitrogen flow, in melt	Colorless transparent	113	T <sub>5% decomp.</sub> = 247 °C T <sub>g</sub> = -143.6 °C ( $\eta$ ) = 0.13 dL/g in C <sub>6</sub> F <sub>6</sub>
5	 	Room temp., at stirring, in nitrogen flow 1.05:1 DMFA	Brittle yellowish mass	111	Mp = 95–98 °C T <sub>5% decomp.</sub> = 247 °C M <sub>W</sub> = 9667 M <sub>n</sub> = 6062 D = 1.59–1.60

Table 1. Cont.

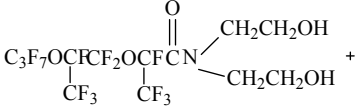
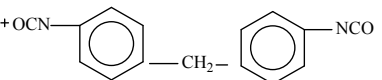
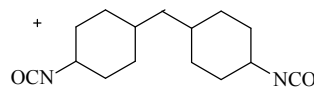
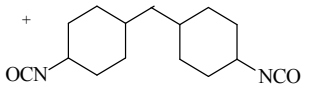
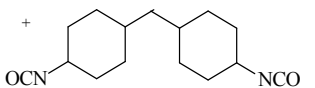
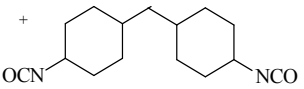
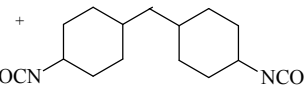
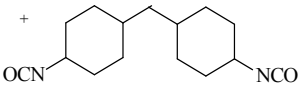
No.	Initial Mixture Composition	Reaction Conditions	Polymer's Appearance	Contact Angle by Water (°)	Parameters of the Polymers
6	 $C_3F_7OCFCF_2OCFCN(CH_2CH_2OH)_2$ + 	Room temp., at stirring, in nitrogen flow, 1:1.1 DMFA	Brittle yellowish-brown mass	114	$M_p = 94-96\text{ }^\circ\text{C}$
7	$HOCH_2(CF_2O)_{28}(CF_2CF_2O)_7CH_2OH$ + $CF_3O(CF_2O)_{28}(CF_2CF_2O)_7CH_2OH$ + 	until 190 °C in nitrogen flow 50 h, 1:1, in melt	Homogenous thick colorless transparent mass	102	$(\eta) = 0.14\text{ dL/g}$ $T_g = -139\text{ }^\circ\text{C}$ $M_p = -22\text{ }^\circ\text{C}$ (contains cryst. polym. segments) $T_{5\% \text{ decomp.}} = 300\text{ }^\circ\text{C}$
8	$HOCH_2[(CF_2O)_4(CF_2CF_2O)]_{3,46}CH_2OH$ + $CF_3O[(CF_2O)_4(CF_2CF_2O)]_{3,46}CH_2OH$ + 	until 190 °C in nitrogen flow 16 h, 1:1, in melt	Homogenous elastic opalescent mass	104	$(\eta) = 0.103\text{ dL/g}$ $T_g = -132\text{ }^\circ\text{C}$ $M_p = -12\text{ }^\circ\text{C}$ (contains cryst. polym. segments) $T_{5\% \text{ decomp.}} = 290\text{ }^\circ\text{C}$
9	$HOCH_2[(CF_2O)_4(CF_2CF_2O)]_{3,46}CH_2OH$ + $CF_3CH_2[(CF_2O)_4(CF_2CF_2O)]_{3,46}CH_2OH$ +  $+ HOCH_2CH_2OH$	60 °C in nitrogen flow, at stirring 10 h 1:3:2 $C_6F_6$	Homogenous white viscous elastic mass	103	$T_g = -132\text{ }^\circ\text{C}$

Table 1. Cont.

No.	Initial Mixture Composition	Reaction Conditions	Polymer's Appearance	Contact Angle by Water (°)	Parameters of the Polymers
10	$\text{HOCH}_2[(\text{CF}_2\text{O})_4(\text{CF}_2\text{CF}_2\text{O})]_{3,46}\text{CH}_2\text{OH} +$ $+ \text{CF}_3\text{CH}_2[(\text{CF}_2\text{O})_4(\text{CF}_2\text{CF}_2\text{O})]_{3,46}\text{CH}_2\text{OH} +$  $+ \text{HOCH}_2\text{CH}_2\text{OH}$	60 °C in nitrogen flow, at stirring 7 h 1:2:1 C <sub>6</sub> F <sub>6</sub>	Homogenous white solid elastic mass	106	T <sub>g</sub> = −136 °C
11	$\text{HOCH}_2[(\text{CF}_2\text{O})_4(\text{CF}_2\text{CF}_2\text{O})]_{3,46}\text{CH}_2\text{OH} +$ $+ \text{CF}_3\text{CH}_2[(\text{CF}_2\text{O})_4(\text{CF}_2\text{CF}_2\text{O})]_{3,46}\text{CH}_2\text{OH} +$  $+ \text{HOCH}_2\text{CH}_2\text{OH}$	60 °C in nitrogen flow, at stirring 12 h 1:2:5 C <sub>6</sub> F <sub>6</sub>	Homogenous white elastic mass	117	(η) = 0.14 dL/g T <sub>g</sub> = −133 °C T <sub>5% decomp.</sub> = 244 °C
12	$\text{HOCH}_2[(\text{CF}_2\text{O})_4(\text{CF}_2\text{CF}_2\text{O})]_{3,46}\text{CH}_2\text{OH} +$ $+ \text{CF}_3\text{CH}_2[(\text{CF}_2\text{O})_4(\text{CF}_2\text{CF}_2\text{O})]_{3,46}\text{CH}_2\text{OH} +$  $+ \text{HOCH}_2\text{CH}_2\text{OH}$	until 190 °C in nitrogen flow 7 h 1:2:5 in melt	Homogenous beige solid elastic mass	106	T <sub>g</sub> = −137 °C T <sub>5% decomp.</sub> = 237 °C

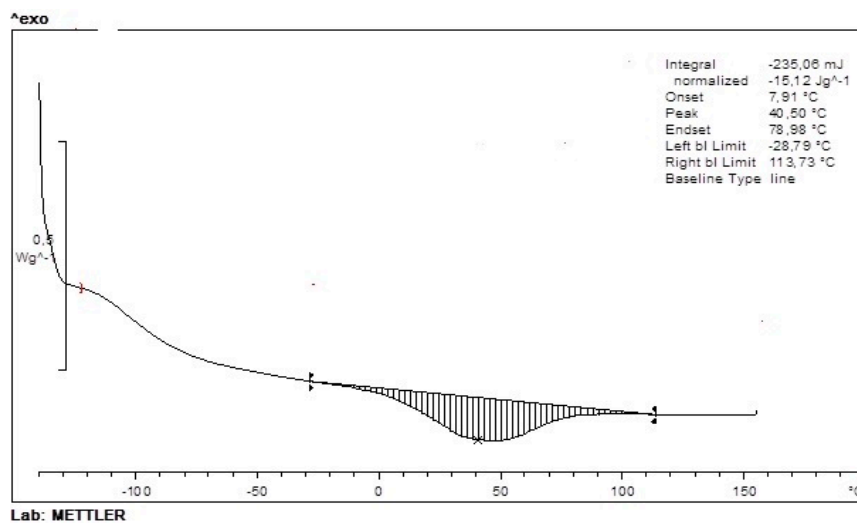


Figure 1. Differential scanning calorimetry (DSC) data for fluoropolyurethane 5.

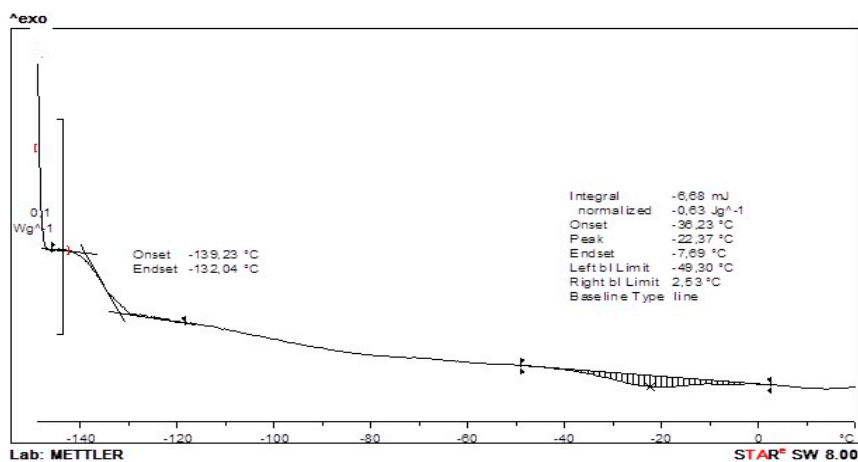


Figure 2. DSC data for fluoropolyurethane 7.

Figure 3 provides thermogravimetric analysis (TGA) data obtained in argon for this polymer. TGA data indicate that the beginning temperature of polymer destruction is close to 300  $^{\circ}C$  and maximum rate of destruction is achieved at 460  $^{\circ}C$ . The TGA results for all other polymers were actually similar and didn't depend on measurement conditions—either in argon or air flow.

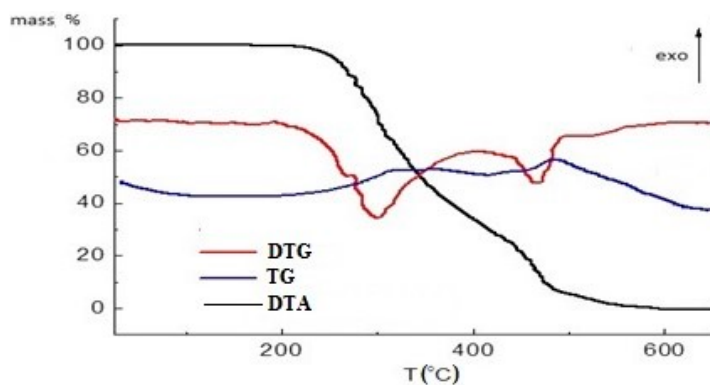


Figure 3. Thermogravimetric analysis (TGA) data for fluoropolyurethane 7.

Summarizing DSC and TGA data for the selected FPU's synthesized in this research (Table 1), it might be concluded that the temperature interval of FPU's performance ( $-139\text{ }^{\circ}\text{C}$  to  $247\text{--}330\text{ }^{\circ}\text{C}$ ) is much broader than that of analogous hydrogenated PUs which is normally within  $-60$  to  $160\text{ }^{\circ}\text{C}$  depending on the structure of glycols and diisocyanates used as starting materials. Thus, the decomposition onset temperature of PUs prepared from alkylendiisocyanates and alkylenglycols is around  $250\text{ }^{\circ}\text{C}$ , of PUs from aromatic diisocyanate-alkylene glycol  $200\text{ }^{\circ}\text{C}$ , and from alkylendiisocyanate-aromatic glycols  $180\text{ }^{\circ}\text{C}$  [21–23]. Glass transition temperature ( $T_g$ ) of these PUs were found to be approximately  $-60\text{ }^{\circ}\text{C}$ .

The measurement of contact angles on the water-wetted surface of the prepared FPU's was performed as follows. The attained FPU melts were applied to glass plates that were then heated to  $90\text{ }^{\circ}\text{C}$  in a desiccator until evaporation of the solvents. Transparent or semitransparent films were prepared. Contact angles of their surface wetting with water were determined. The contact angles achieved  $100^{\circ}\text{--}117^{\circ}$  (Table 1), which was indicative of rather high hydrophobicity of the coatings.

Syntheses of all other tabulated FPU's were performed in the conditions summarized in Table 1. At rather low temperatures FPU's were synthesized in solution. At high temperatures, the polyaddition process was conducted in the melt. Initial mixture composition includes aromatic diisocyanates (rows 1–6) and cycloaliphatic ones (rows 7–12). Depending on the starting materials and reaction conditions used, the oligomers and polymers obtained exhibit different properties. Some of them (like polymer 5, Figure 1) possess crystal segments of polymer chain, others are rubberlike amorphous materials (7–12 samples). Regardless the difference in structure and properties, all of them were shown to possess pronounced hydrophobic properties (surface wetting contact angles found were higher than  $100^{\circ}$ ).

### 3. Materials and Methods

Diisocyanates **2a–c** were commercial products (manufacturer Bayer Material Science) pre-dried in vacuo at  $100\text{--}150\text{ }^{\circ}\text{C}$ : **2a**  $M = 174.2$ ,  $bp = 251\text{ }^{\circ}\text{C}$ ; **2b**  $M = 250.25$ ,  $bp = 152\text{--}154\text{ }^{\circ}\text{C}$  (3 Torr); **2c**  $M = 262.35$ ,  $bp = 358\text{ }^{\circ}\text{C}$ .

Fluorinated alcohols **1a–d** incorporating fluoropolyether units were used as hydroxymethylene derivatives: **1a**  $M = 902$ ,  $bp = 146\text{--}150\text{ }^{\circ}\text{C}$  (0.01 Torr), **1b**  $M = 595$ ,  $bp = 210\text{ }^{\circ}\text{C}$  (0.01 Torr), **1c**  $M = 2442$ , and **1d**  $M = 1418$ .  $Bp$  of the products was above  $200\text{ }^{\circ}\text{C}$  (0.01 Torr). They were prepared according to the procedure reported in [24] and represent fluoropolyether glycols or fluoropolyether amides containing hydroxymethylated terminal groups (**1a–b**) or a mixture of fluoropolyether glycols with alcohols of similar structure (**1c–d**) with ratio 7:1. Molecular weights and compositions of the prepared fluoropolyether diols and alcohols were found from  $^{19}\text{F}$ -NMR and  $^1\text{H}$ -NMR data.  $^1\text{H}$ -NMR and  $^{19}\text{F}$ -NMR were using a Bruker AM 300 SF at 300 MHz ( $^1\text{H}$ ), 282,40 MHz ( $^{19}\text{F}$ ).  $^1\text{H}$ -NMR chemical shifts were referenced to the residual proton signal from  $\text{CDCl}_3$  served as an internal standard.  $^{19}\text{F}$ -NMR spectra (solutions in  $\text{C}_6\text{F}_6$ ,  $-163\text{ ppm}$ ) served as an inside standard. Multiplicities are reported as singlet (s), doublet (d), triplet (t) and some combinations of these, multiplet (m).

The molecular weight characteristics of the polymers were determined using the gel permeation chromatography (GPC) method in DMFA at  $35\text{ }^{\circ}\text{C}$  on a Knauer liquid chromatograph equipped with a refractometer RI-2300 and three columns (Waters Styrogel HT-2, HT-4, and HT-6E). The elution rate 1 mL/min. The calibration was done using the polystyrene standard (PL Polymer Laboratories) in the range from 1250 to 1030000 Da.

The glass transition temperature was determined by the differential scanning calorimetry (DSC) on a DSC-822e instrument (Mettler Toledo, Switzerland) using  $\sim 10\text{ mg}$  samples at the heating rate  $10\text{ }^{\circ}\text{C}/\text{min}$ . IR spectra were registered on a Specord IR-75 spectrometer.

TGA data were determined on the instrument Derivatograph-C (MOM, Hungary) in air and argon flow using  $\sim 15\text{ mg}$  samples at the heating rate  $10\text{ }^{\circ}\text{C}/\text{min}$ .

Inherent viscosity was determined using an Ubbelohde viscometer in DMFA or  $\text{C}_6\text{F}_6$ .

### 3.1. Synthesis of Fluorinated Alcohol **1b**

Pre-distilled diethanolamine (3.32 g, 0.032 mol), bp = 122–125 °C (3 Torr) was placed in a round bottomed flask fitted with a stirrer, thermometer and drop funnel and then 16.2 g (0.032 mol) methyl ester of the hexafluoropropylene oxide trimer was added dropwise from the funnel. The reaction mixture was stirred for 2 h at 65 °C until homogeneity. In the IR spectrum of the products, a signal in the region of 1780 cm<sup>-1</sup> disappeared (C=O in ester) and a signal in the region of 1740 cm<sup>-1</sup> emerged (C=O in amide). <sup>1</sup>H-NMR, (CDCl<sub>3</sub>) δ: 4.38 (2H, s, OH); 2.26 (4H, t, O=C-CH<sub>2</sub>CH<sub>2</sub>); 3.18 (t, 4H, CH<sub>2</sub>OH); <sup>19</sup>F-NMR, (C<sub>6</sub>F<sub>6</sub>) δ: -80.0 to -88.0 (m, 13F CF<sub>2</sub>O + CF<sub>3</sub>); -126.0 to -127.4 (s, 1F OCF(CF<sub>3</sub>)C); -132.0 (m, 2F CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>); -147.0 (m, 1F CF<sub>2</sub>CF(CF<sub>3</sub>)C=O).

### 3.2. Synthesis of Fluoropolyurethanes

#### 3.2.1. Synthesis of Fluoropolyurethane **5**

Diol **1b** (1.88 g, 0.032 mol) in 10 mL DMFA was placed in a four-neck flask fitted with a stirrer, drop funnel, thermometer, and dry nitrogen feeder and then 0.76 g (0.03 mol) of diisocyanate **2b** was added. The process was conducted with intensive stirring in the dry nitrogen flow during 10 h. After DMFA evaporation, in the waterjet pump vacuum was prepared a solid, brittle and transparent mass  $M_w = 9667$ ;  $M_n = 6062$ ,  $D = 1.59$ – $1.60$  (Figure 1), mp = 95–98 °C (Figure 2),  $T_{5\% \text{ decomp.}} = 247$  °C.

The IR spectrum, (KBr), cm<sup>-1</sup>, ν: 3338 (NH), 3032 (ArH), 2923 (CH), 1719 (C=O), 1601 (C-C arom.), 1541 (NH), 1226, 1046 (CF). <sup>1</sup>H-NMR, (CDCl<sub>3</sub>) δ: 6.04 (8H-arom. s.); 3.83–3.74 (4H, t, CH<sub>2</sub>); 2H (Ar-CH<sub>2</sub> Ar, s.). <sup>19</sup>F-NMR, (C<sub>6</sub>F<sub>6</sub>) δ: -80.0 to -88.0 (13F, m, CF<sub>2</sub>O+CF<sub>3</sub>); -126.0 to -127.4 (1F, s, OCF(CF<sub>3</sub>)C=O); -132.0 (2F, m, CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>); -147.0 (1F, s, OCF<sub>2</sub>CF(CF<sub>3</sub>)O).

#### 3.2.2. Synthesis of Fluoropolyurethane **7**

Diol **1c** (2.46 g, 0.001 mol) pre-heated at 110 °C (18 Torr) during 2 h was placed in a four-neck flask fitted with a stirrer, drop funnel, thermometer, and dry nitrogen feeder and then 0.27 g (0.001 mol) of diisocyanate **2c** was added. The process was conducted with intensive stirring in the dry nitrogen flow, gradually increasing the temperature from 25 °C to 190 °C, during 50 h. A homogeneous, thick, colorless and transparent mass was prepared. The reaction completion was monitored against the absence of the free NCO group absorption band in the region of 2270 cm<sup>-1</sup>,  $T_g = -139$  °C (Figure 2),  $T_{5\% \text{ decomp.}} = 300$  °C. Maximum decomposition rate was ≈ 450 °C (Figure 3).

The IR spectrum of fluoropolyurethane **7**, (KBr), cm<sup>-1</sup>, ν: 3337 (NH); 3032 (CH arom.), 2923 (CH); 1719 (C=O, uretane); 1534 (NH); 1226, 1046 (C-F). <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ: 1.32 (8H, m, CH<sub>2</sub>-CH<sub>2</sub>); 1.70 (8H, t, CH<sub>2</sub>-N); 4.47 (4H d, R<sub>F</sub>CH<sub>2</sub>O); 5.55 (2H s, NH). <sup>19</sup>F NMR (C<sub>6</sub>F<sub>6</sub>) δ: -52.16 (3F, s, CF<sub>3</sub>O); -52.76 to -54.71 (2F, s, (CF<sub>2</sub>O)<sub>n</sub>); -88.0 to -89.7 (4F, d, (CF<sub>2</sub>CF<sub>2</sub>O)<sub>n</sub>).

## 4. Conclusions

Novel FPU's possessing promising performance properties have been synthesized starting from fluorinated diols as soft segments and both aromatic and cycloaliphatic diisocyanates as hard segments. Values of their glass transition temperature and the beginning temperature of thermal decomposition achieve -139 °C and 247–330 °C, correspondingly, showing their performance in quite wide temperature intervals in comparison to non-fluorinated analogs. According to literature data, the temperature interval of hydrogenated PUs performance is predominately in the range from -60 °C to 160 °C.

Contact angles of surface wetting with water for FPU's obtained reach 100–117°, providing evidence of quite favorable hydrophobic properties of fluorinated polyurethanes. Potentially, novel fluorinated polyurethanes can be used for production of materials exploited under extreme conditions and in compositions of complex organic and hybrid molecular systems [25,26].



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**Author Contributions:** O.S. performed synthesis of fluorinated polymers; A.G. performed synthesis of fluorinated alcohols; A.Y. performed analysis and interpretation of experiments and results thereof; A.S. conceived and designed the experiments and wrote the paper.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Wang, X.; Hu, J.; Li, Y.; Zhang, J.; Ding, Y. The surface properties and corrosion resistance of fluorinated polyurethane coatings. *J. Fluorine Chem.* **2015**, *176*, 14–19. [[CrossRef](#)]
2. Chattopadhyay, D.K.; Raju, K.V.S.N. Structural engineering of polyurethane coatings for high performance applications. *Prog. Polym. Sci.* **2007**, *32*, 352–418. [[CrossRef](#)]
3. Yoon, S.C.; Ratner, B.D. Surface structure of segmented poly (ether urethanes) and poly (ether urethane ureas) with various perfluoro chain extenders. An X-ray photoelectron spectroscopic investigation. *Macromolecules* **1986**, *19*, 1068–1079. [[CrossRef](#)]
4. Yoon, S.C.; Ratner, B.D. Surface and bulk structure of segmented poly (ether urethanes) with perfluoro chain extenders. 2. FTIR, DSC, and X-ray photoelectron spectroscopic studies. *Macromolecules* **1988**, *21*, 2392–2400. [[CrossRef](#)]
5. Yoon, S.C.; Ratner, B.D. Surface and bulk structure of segmented poly (ether urethanes) with perfluoro chain extenders. 3. Effects of annealing, casting solvent, and casting conditions. *Macromolecules* **1988**, *2*, 2401–2404. [[CrossRef](#)]
6. Yoon, S.C.; Sung, Y.K.; Ratner, B.D. Surface and bulk structure of segmented poly (ether urethanes) with perfluoro chain extenders. 4. Role of hydrogen bonding on thermal transitions. *Macromolecules* **1990**, *2*, 4351–4356. [[CrossRef](#)]
7. Yoon, S.C.; Ratner, B.D.; Ivan, B.; Kennedy, J.P. Surface and bulk structure of segmented poly (ether urethanes) with perfluoro chain extenders. 5. Incorporation of poly(dimethylsiloxane) and polyisobutylene macroglycols. *Macromolecules* **1994**, *27*, 1548–1554. [[CrossRef](#)]
8. Eberhard, K.; Beate, B.; Christian, F.; Juan, G.B. Fluorine-Containing Blocked Isocyanates. US Patent 6509433, 21 January 2003.
9. Ho, T.; Wynne, K.J. A new fluorinated polyurethane: Polymerization, characterization, and mechanical properties. *Macromolecules* **1992**, *25*, 3521–3527. [[CrossRef](#)]
10. Honeychuck, R.V.; Ho, T.; Wynne, K.J.; Nissan, R.A. Preparation and characterization of polyurethanes based on a series of fluorinated diols. *Chem. Mater* **1993**, *5*, 1299–1306. [[CrossRef](#)]
11. Yu, X.H.; Okkema, A.Z.; Cooper, S.L. Synthesis and physical properties of poly(fluoroalkylether) urethanes. *J. Appl. Polym. Sci.* **1990**, *41*, 1777–1795. [[CrossRef](#)]
12. Ge, Z.; Zhang, X.; Dai, J.; Li, W.; Luo, Y. Synthesis, characterization and properties of a novel fluorinated polyurethane. *Eur. Polym. J.* **2009**, *45*, 530–536. [[CrossRef](#)]
13. Nobuo, T. Low Refractive Index Resin Composition and Cured Product Thereof. JP Patent 2007023175 (A), 1 February 2007.
14. Bradly, M.; Oreffo, R.; Tare, R.; Tourniaire, Y. Selective Cellular Adhesion on Polymer Microarrays. GB 2425074 A, 18 October 2006.
15. Chen, K.-Y.; Kuo, J.-F. Synthesis and properties of novel fluorinated aliphatic polyurethanes with fluoro chain extenders. *Macromol. Chem. Phys.* **2000**, *201*, 2676–2686. [[CrossRef](#)]
16. Król, P.; Król, B.; Stagraczyński, R.; Skrzypiec, K. Waterborne cationomer polyurethane coatings with improved hydrophobic properties. *J. Appl. Polym. Sci.* **2013**, *10*, 2508–2519. [[CrossRef](#)]
17. Król, P.; Król, B. Surface free energy of polyurethane coatings with improves hydrophobicity. *Colloid Polym. Sci.* **2012**, *290*, 879–893. [[CrossRef](#)] [[PubMed](#)]
18. Lin, Y.H.; Chou, N.K.; Chang, C.H.; Wang, S.S.; Chu, S.H.; Hsieh, K.H. Blood compatibility of fluorodiols-containing polyurethanes. *J. Polym. Sci. Polym. Chem.* **2007**, *45*, 3231–3242. [[CrossRef](#)]
19. Mashinskaya, S.G.; Menshov, V.M.; Kiseleva, L.A.; Ponomarenko, V.A. Super-flexibility of some fluoropolymeric chains. *Abstr. Pap. Am. Chem. Soc.* **1995**, *210*, 171.

20. Krukovsky, S.P.; Yarosh, A.A.; Glazkov, A.A. Synthesis of cross-linked perfluoroalkylene oxides. In Proceedings of the Advanced Technologies and Production of Organic and Inorganic Chemistry-95, Moscow, Russia, 25–28 April 1995.
21. Dombrow, B.A. Chemistry. In *Polyurethanes*, 2nd ed.; Simonds, H.R., Ed.; Reinhold Publishing Corp: New York, NY, USA, 1965; pp. 12–33.
22. Fergusson, J.; Petrovic, Z. Thermal stability of segmented polyurethanes. *Eur. Polym. J.* **1976**, *12*, 177–181. [[CrossRef](#)]
23. Simon, J.; Barla, F.; Haller, A.K.; Farkas, F.; Kraxner, M. Thermal stability of polyurethanes. *Chromatographia* **1988**, *25*, 99–106.
24. Ushakova, E.N.; Konyushko, O.V.; Glazkov, A.A.; Krukovsky, S.P. Synthesis of 1,1-dihydroperfluorooxaalkan-1-ols and their interaction with terephthaloyl chloride. *Russ. Chem. Bull.* **1996**, *45*, 1573–1576. [[CrossRef](#)]
25. Zhao, Z.; Li, X.; Li, P.; Wang, C.; Luo, Q. Study on properties of waterborne fluorinated polyurethane/acrylate hybrid emulsion and films. *J. Polym. Res.* **2014**, *21*, 460. [[CrossRef](#)]
26. Ananikov, V.P.; Galkin, K.I.; Egorov, M.P.; Sakharov, A.M.; Zlotin, S.G.; Redina, E.A.; Isaeva, V.I.; Kustov, L.M.; Gening, M.L.; Nifantiev, N.E. Challenges in the Development of Organic and Hybrid Molecular Systems. *Mendeleev Commun.* **2016**, *26*. [[CrossRef](#)]

**Sample Availability:** Samples of the compounds **3** are available from the authors.



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