

Electronic Supplementary Information (ESI)

Solvent-Resistant and Fully Recyclable Perfluoropolyether-Based Elastomer for Microfluidic Chip Fabrication

*Shenglong Liao, Yonglin He, Yanji Chu, Hongguang Liao and Yapei Wang**

Department of Chemistry, Renmin University of China, Beijing, 100872, China

Corresponding author: Yapei Wang. Email: yapeiwan@ruc.edu.cn

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Experimental section

1. Synthesis and characterization of perfluoropolyether (PFPE)-based elastomer.

The PFPE-based thermoset elastomer was synthesized via one-pot reaction among PFPE-diol (Fomblin® ZDOL 4000 ($M_w=4000$ g/mol) or Fluorolink D10-H ($M_w=1500$ g/mol), Solvay Solexis), *N, N'*-di-*tert*-butyl-ethylenediamine (TBEA, Aladdin Bio-chem), and a tri-functional homopolymer of hexamethylene diisocyanate (THDI, Desmodur® N 3900, Covestro). The PFPE-diol (2.0 g, *ca.* 1 mmol hydroxyl group) was dissolved in 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113, 2.0 mL, Aladdin Bio-chem). Then, the TBEA (0.1 mmol) and 2 drops of dibutyltin dilaurate (DBDTL, Aladdin Bio-chem) was added into the above solution. Another component, THDI (0.33 mmol), was dissolved in the mixture of CFC-113 (1.0 mL) and dichloromethane (1.0 mL). At last, the above two types of solutions were mixed and the reaction was carried out in a glass vessel at 45 °C for 6 hours. The whole product was cut into small pieces after solvent evaporation in vacuum oven at 60 °C. Then the small pieces were filled into a customized metal chamber and molded with a pressure about 1.0 MPa at 130 °C for 12 hours. Finally, the PFU-2 product was processed into pre-designed shapes.

The PFU-2 product was characterized via solid-state ^{13}C -NMR and FT-IR spectroscopy. The solid-state ^{13}C -NMR was recorded on a JEOL JNM-ECZ600R/M1 spectrometer with a field strength of 14 T (600 MHz) at ambient temperature. Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectrum was obtained from VERTEX 70 Bruker with a resolution of 4.0 cm^{-1} . Detailed analysis of these spectra is provided in Fig. S1 and Fig. S2.

2. Measurement of swelling ratio of PFU-2 and PDMS.

In this work, mass swelling ratio (S_w) and size swelling ratio (S_l) were measured independently. PDMS (base: curing agent=15: 1 w/w, Sylgard 184, Dow Corning) was cured at 80 °C for 12 hours. The sample mass was recorded before (m_0) and after

immersion in a specific solvent (m_s) for certain time. And the mass swelling ratio is calculated according to the following equation (eq. S1):

$$S_w = (m_s/m_0 - 1) \times 100\% \quad (\text{eq. S1})$$

The size swelling ratio was measured based on the swelling ratio of micropatterns (*ca.* $200 \times 200 \mu\text{m}$) on the surfaces of PDMS or PFU-2. The sizes of the micropatterns before (l_0) and after immersed in a specific solvent (l_s) were measured on an invert microscope (Leica DMI8). Similarly, the size swelling ratio is calculated according to the following equation (eq. S2):

$$S_l = (l_s/l_0 - 1) \times 100\% \quad (\text{eq. S2})$$

3. Micro-molding and dynamic mechanical analysis of PFU-2.

In terms of thermoplasticity, the PFU-2 elastomer was applied to micropattern fabrication via hot pressing approach. Several types of micropatterns including the logo and Quick Respond (QR) code of Renmin University of China and our research group were fabricated via standard photolithography. Typically, SU-8 2025 (MicroChem) was firstly spin-coated onto a 3-inch silicon wafer at a speed of 2000 rpm for 45 seconds. Then the wafer was conducted with two successive soft bake processes on heating stage (65 °C for 3 minutes and 95 °C for 6 minutes). Immediately, the silicon wafer was exposed to patterned UV light with the assistance of a photomask on a photolithography machine (H94-25C, Nanguang Vacuum Technology). After post exposure bake process (65 °C for 1 minute and 95 °C for 10 minutes), the wafer was immersed into propylene glycol monomethyl ether acetate (PGMEA, Aladdin Bio-chem) to remove the excess photoresist. The micropatterns were transferred onto PFU-2 surface via hot pressing on thermal plate or vacuum oven at 130 °C for 2 hours. The micropatterns on PFU-2 were imaged on a field-emission scanning electron microscope (FE-SEM, Hitachi SU8010).

Mechanical properties of PFU-2 were fully characterized on a dynamic mechanical analyzer (DMA Q800, TA Instruments). All tests were conducted with the film tension clamp and the typical sample is rectangular film with size of *ca.* $15 \times 5 \times 1 \text{ mm}$. To investigate the principle of thermoplasticity and reprocessability,

stress-relaxation tests were carried out at a constant strain of 2% and different temperatures from 100 °C to 150 °C with an interval of 10 °C. The elasticity of the PFU-2 sample was presented via the cyclic tensile test and relaxation-recovery test. The tensile test was carried out via two cyclic stress-ramp processes including ramping from 5 kPa to 250 kPa at rate of 150 kPa/min and ramping from 250 kPa to 5 kPa at the same rate. The cyclic relaxation-recovery test (relaxation at 50% strain for 30 seconds and recovery for 30 seconds) was carried out successively for 100 times. Besides, the stress-strain curves of original PFU-2, reprocessed PFU-2, and PDMS were also measured with the force-ramp method (0.5 N/min). The storage and loss modules of original and reprocessed PFU-2 were recorded with the temperature-ramp method (temperature ramp rate: 3 °C/min; amplitude 15 µm; frequency: 1 Hz).

4. Fabrication and reprocessing of PFU-2 microfluidic chips.

The PFU-2 microfluidic chips were prepared via a hot pressing process and a reversible sealing method. Typically, a PFU-2 block was replicated with microfluidic channels as the same as above method for replication of micropatterns. Then inlet and outlet holes were punched with the assistance of an 18-Gauge blunt syringe needle. The as-prepared PFU-2 block along with a bare glass plate was inserted into the gap between two poly(methyl methacrylate) (PMMA) plates, and the four components were fixed by screws. For reprocessing of PFU-2 microfluidic chip, the procedure is similar to the fabrication processing of the first microfluidic chip as stated above. In details, the original PFU-2 chip was disassembled. The PFU-2 block with original micro-channels was chopped into small pieces and reprocessed into another bare block. Then micropattern of another microfluidic channel was transferred onto this reprocessed PFU-2 block and a new microfluidic chip was setup by laminating the PFU-2 block with the glass and PMMA plates.

5. Dye diffusion experiments within PFU-2 and PDMS microfluidic chips.

Organic fluid was injected into the microfluidic channel and the fluorescent images at different times were captured on an invert fluorescence microscope (Leica DMi8). The analysis of these images including the fluorescence intensity and lateral

distribution was performed on Image J (available from NIH). For the single-channel diffusion test, the organic fluid is toluene dissolving petroleum fluorescent tracing dye (green fluorescence, 400 $\mu\text{g}/\text{mL}$; flow rate: 2.5 $\mu\text{L}/\text{min}$). For cross-contamination, there were two kinds of dyed solution of toluene, including petroleum fluorescent tracing dye in toluene (green fluorescence, 400 $\mu\text{g}/\text{mL}$; flow rate: 2.5 $\mu\text{L}/\text{min}$) and Nile Red in toluene (red fluorescence, 50 $\mu\text{g}/\text{mL}$; flow rate: 2.5 $\mu\text{L}/\text{min}$).

6. Degradation of PFU-2 and characterization of the degraded product.

The degradation of PFU-2 was accomplished in diethylene glycol (DEG) with potassium acetate as catalyst at temperature above 150 $^{\circ}\text{C}$. Typically, PFU-2 (10.0 g) and potassium acetate (1.0 g) were added into a 100 mL round-bottom flask with 25.0 g DEG. Then the flask was heated in oil bath under steady stirring at 150 $^{\circ}\text{C}$ for 6 hours. After degradation, liquids in flask separated into two phases. Due to the high mass density of PFPE-diol, the bottom phase was sucked out and washed with ethanol for several times to remove the potassium acetate, DEG, and other by-products. To remove the small amount of mixed ethanol, the final product was heated in vacuum oven at 80 $^{\circ}\text{C}$ for 12 hours. Finally, a bottle of colorless and transparent liquid product was achieved.

The recycled product was characterized with different tools, including ^{13}C -NMR, ^{19}F -NMR, FT-IR, thermogravimetric analysis (TGA), surface energy measurement, mass density and viscosity measurement. ^{13}C -NMR and ^{19}F -NMR spectra were directly recorded on a Bruker Avance 600 MHz NMR spectrometer without adding solvent. The FT-IR spectra were measured on an infrared spectrometer (Tensor 27, Bruker) through CaF_2 plate method. Typically, small amount of liquid ($\sim 1.0 \mu\text{L}$) was dipped onto one CaF_2 plate and then covered by the other plate. TGA was carried out on a TA Q500 thermogravimetric analyzer at temperature ramp rate of 10 $^{\circ}\text{C}/\text{min}$ under nitrogen atmosphere. The mass density and viscosity were measured via a density meter (DMA 4500 M, Anton Paar) and a rolling-ball microviscometer (Lovis 2000 M, Anton Paar). Surface tensions were tested with pendant drop method on a drop shape analyzer (DSA30, KRÜSS GmbH).

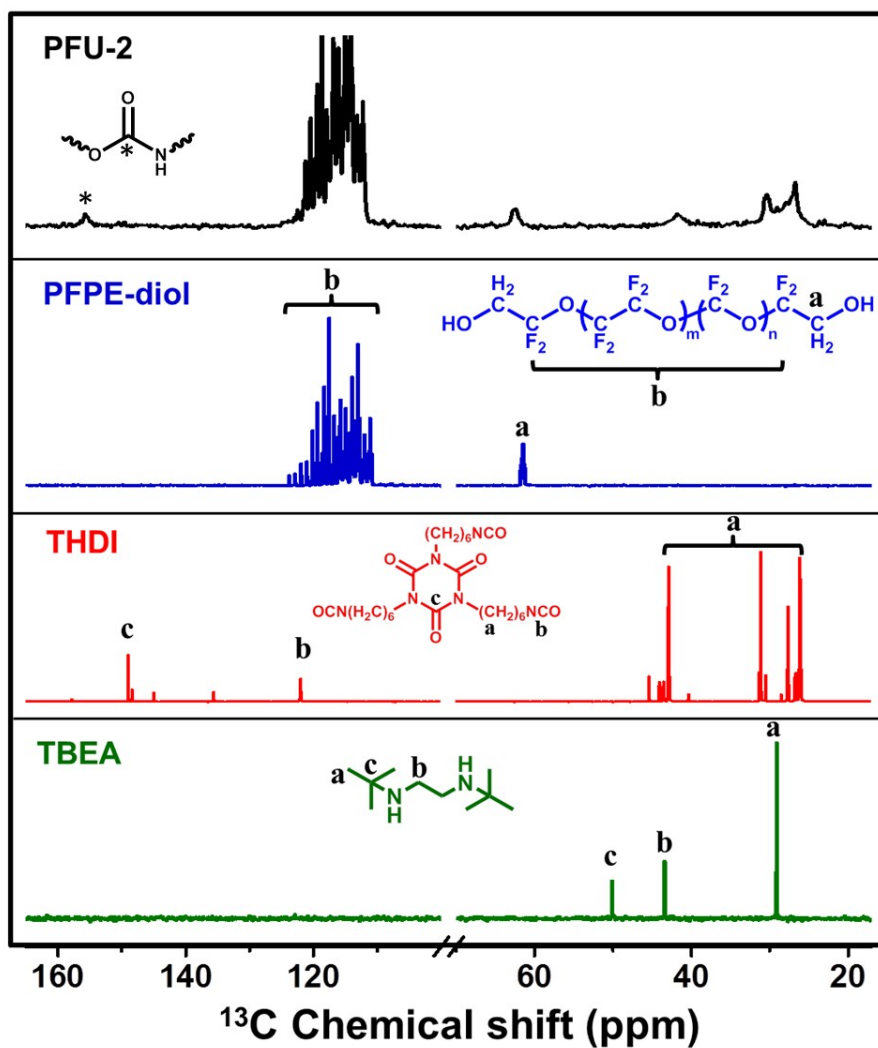


Fig. S1. ^{13}C -NMR spectra of PFU-2 and its raw materials. The disappearance of isocyanate group (*ca.* 122 ppm) and the appearance of urethane group (*ca.* 156 ppm) suggest the formation of urethane bond. The formation of urea bond is difficult to be observed via NMR spectrum because of the limited amount of TBEA content in PFU-2 network.

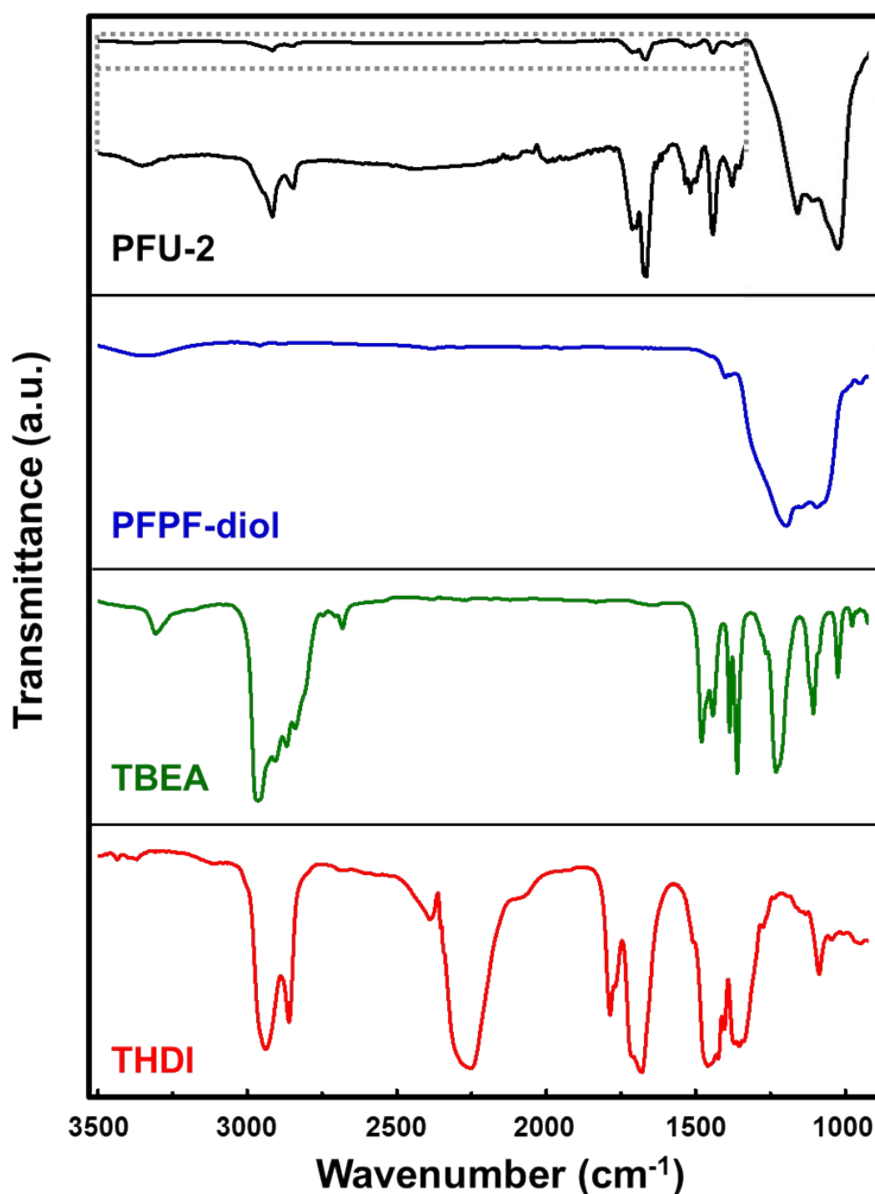


Fig. S2. FT-IR spectra of PFU-2 and its raw materials. Typical absorption peaks are listed as below. THDI: 2940 cm^{-1} and 2860 cm^{-1} (*C-H*, stretching); 2250 cm^{-1} (*N=C=O*, stretching); 1460 cm^{-1} (*C-H*, bending). TBEA: 3305 cm^{-1} (*N-H*, stretching); 2960, 2908, 2866, and 2840 cm^{-1} (*C-H*, stretching). PFPE-diol: 3340 cm^{-1} (*O-H*, stretching); 1200 cm^{-1} (*C-F*, stretching); 1090 cm^{-1} (*C-O*, stretching). PFU-2: 3350 cm^{-1} (*O-H*, stretching); 2920, 2852 cm^{-1} (*C-H*, stretching); 1468 cm^{-1} (*C-H*, bending); 1730 and 1688 cm^{-1} (*C=O*, stretching); 1186 cm^{-1} (*C-F*, stretching); 1060 cm^{-1} (*C-O*, stretching).

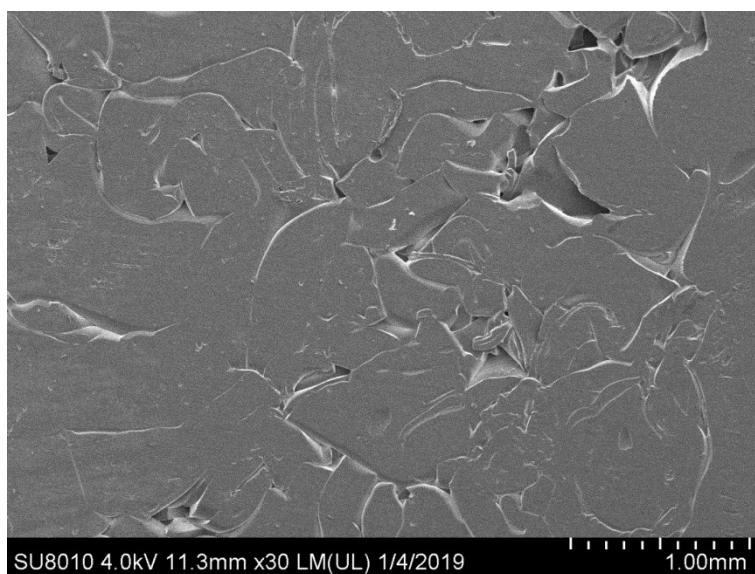


Fig. S3. Scanning electron microscope image of PFU-1 surface after reprocessing.

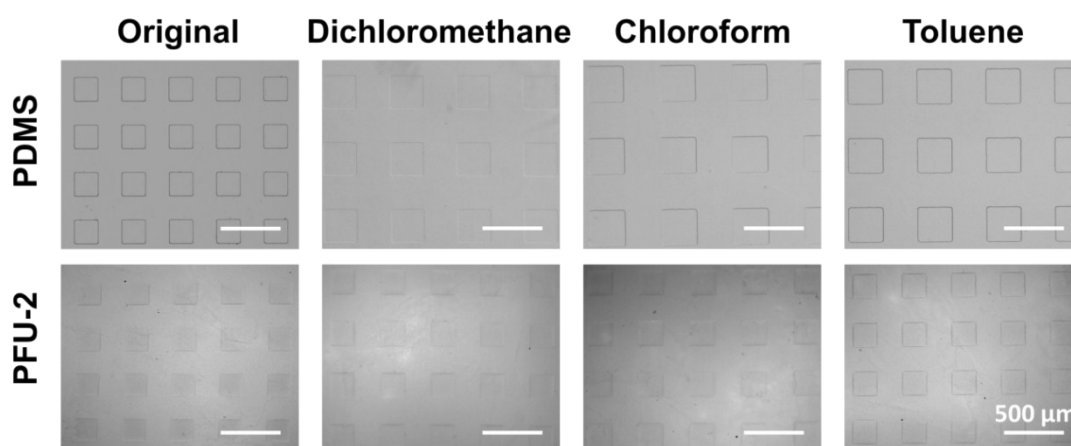


Fig. S4. Microscopic images of PDMS and PFU-2 with $200 \times 200 \mu\text{m}$ square patterns on PDMS or PFU-2 surfaces before and after swollen in dichloromethane, chloroform or toluene for 24 hours.

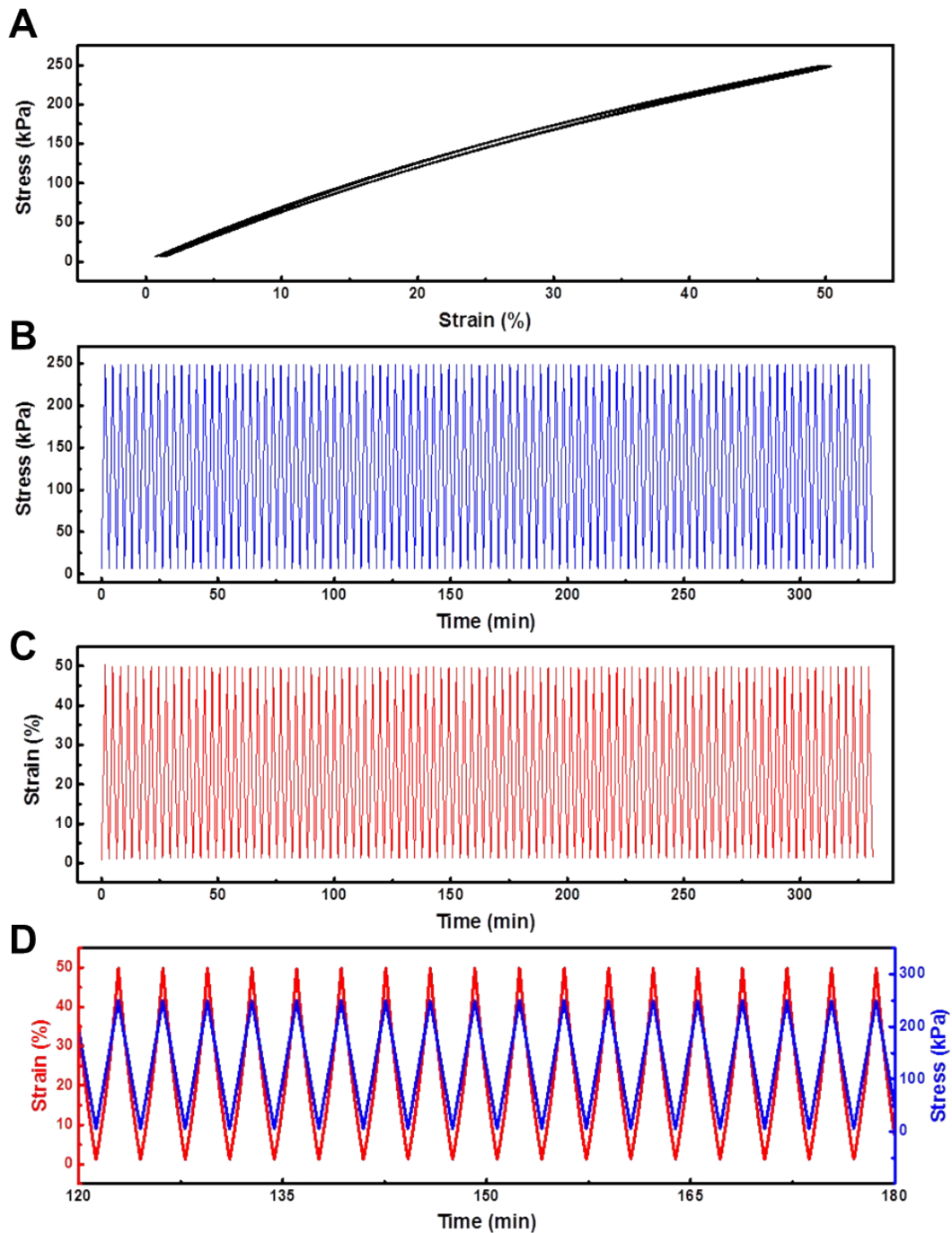


Fig. S5. Cyclic tensile tests of PFU-2. (A) Stress-strain curve within 100 continuous cycles. (B) The program-controlled stress curve that is applied to the PFU-2 sample. (C) The measured strain curve of PFU-2 responded to the program-controlled stress. (D) Enlarged view and overlay of the stress and strain changes along with time.

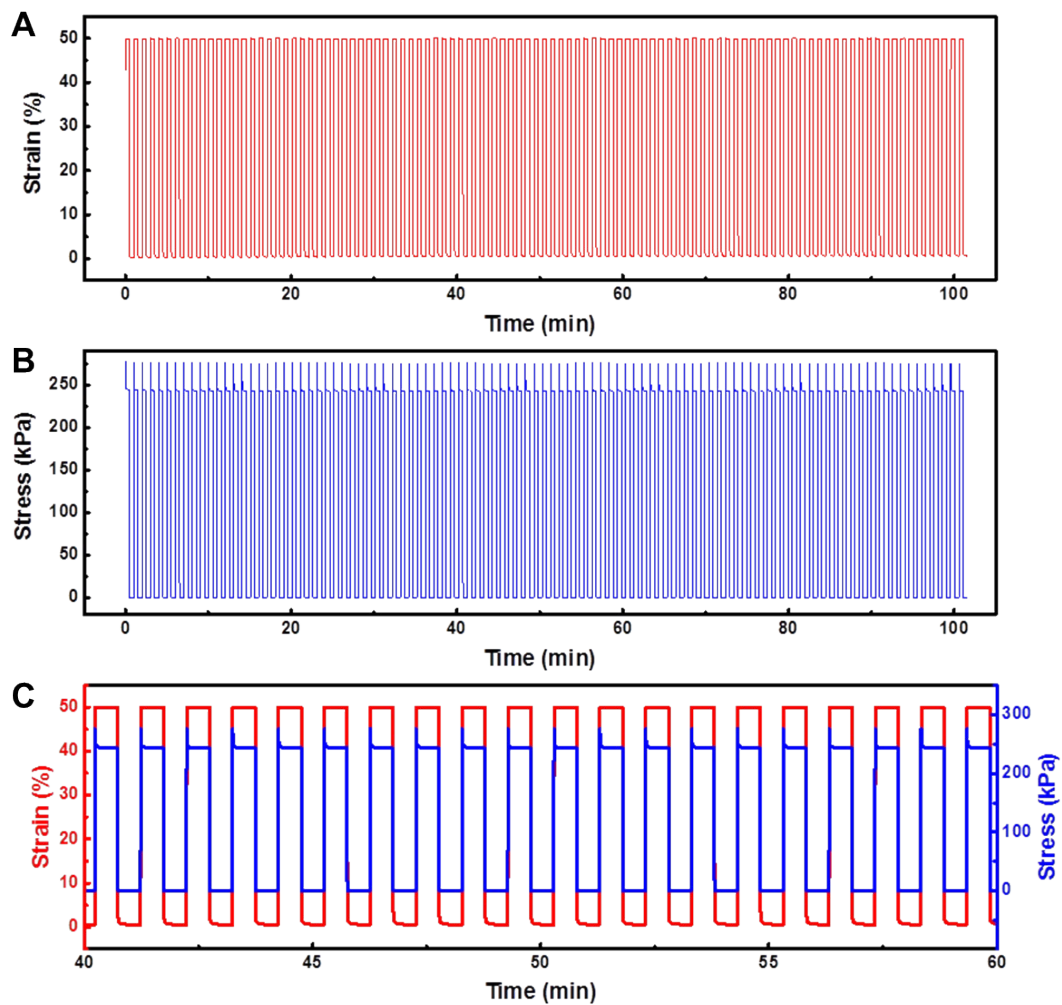


Fig. S6. Continuous strain-controlled relaxation-recovery cycles of PFU-2. One cycle is composed with relaxation process at 50% strain for 30 seconds and recovery process for 30 seconds. (A) Strain curve within 100 continuous cycles. (B) Stress curve within 100 continuous cycles. (C) Enlarged view and overlay of the stress and strain changes along with time.

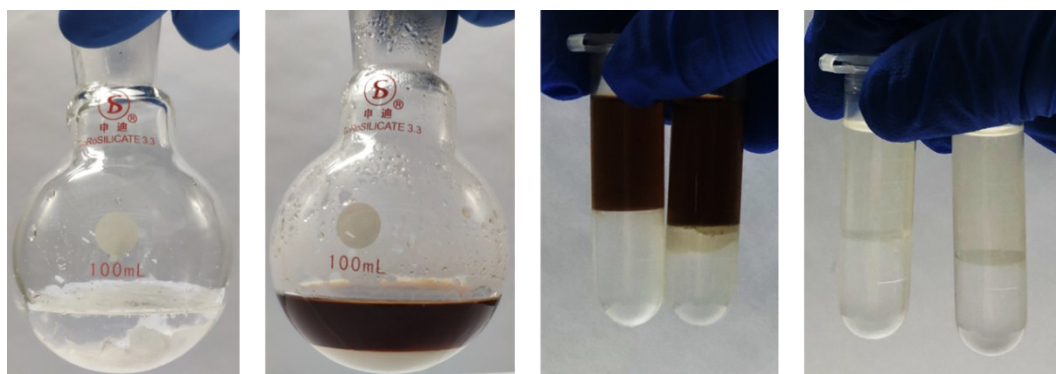


Fig. S7. Optical images of the degradation and recycling process of PFU-2. From left to right: PFU-2 immersed in diethylene glycol before degradation; Degradation at 180 °C for 1h; Separated product (bottom part) after centrifugation at 2000rpm for 3 minutes; Clear product (bottom part) after rinsed with ethanol and centrifuging at 2000rpm for 3 minutes.

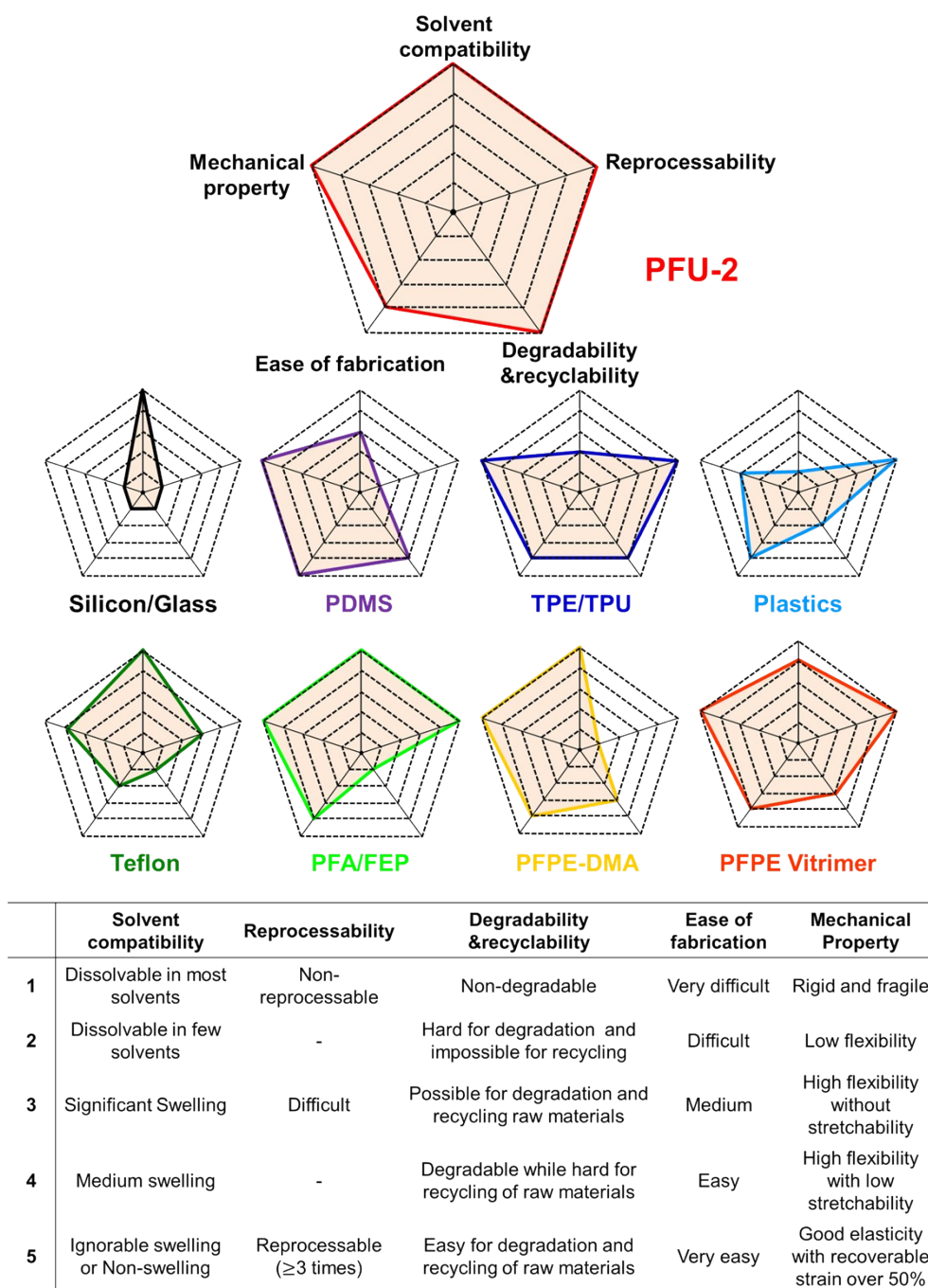


Fig. S8. Radar plots and criteria for qualitatively comparing the PFU-2 with other microfluidic materials from five viewpoints.^[1-8] Three or five grades are divided from inner part to outer part for each viewpoint. TPE: thermoplastic elastomer. TPU: thermoplastic polyurethane. Plastics include polystyrene, polycarbonate, poly(methyl methacrylate), and etc. PFA: perfluoroalkoxy alkanes. FEP: fluorinated ethylene propylene. PFPE-DMA: PFPE dimethacrylate. PFPE vitriimer is summarized from a recently published work.^[8]

Table S1. Quantitative analysis of ^{19}F -NMR spectra of original PFPE-diol and recycled PFPE-diol

Responding signal	Original PFPE-diol		Recycled PFPE-diol	
	δ_{peak} (ppm)	Peak area	δ_{peak} (ppm)	Peak area
$-\text{CF}_2\text{O}-$	-53.85	6.06	-53.86	6.22
	-55.44	11.06	-55.45	11.39
	-57.17	5.03	-57.17	5.20
$-\text{CF}_2\text{CF}_2\text{O}-$	-90.84	20.46	-90.84	21.17
	-92.46	23.37	-92.47	24.24
$-\text{CF}_2-$ (Terminus)	-83.08	1.00	-83.11	1.00
	-85.10	1.08	-85.13	1.05
M_w (kg/mol) #	3.9		4.1	

#: The molecular weights are calculated according to above peak area as well as the integral of ^{19}F -NMR spectrum.

Captions for movies S1 to S2

Movie S1. One hour time-lapse video of dye diffusion process in single channel within PDMS and PFU-2 microfluidic chips.

Movie S2. One hour time-lapse video of cross-contamination test between two parallel channels within PDMS and PFU-2 microfluidic chips.

References

- [1] K. Ren, J. Zhou and H. Wu, *Acc. Chem. Res.*, **2013**, *46*, 2396-2406.
- [2] K. Ren, W. Dai, J. Zhou, J. Su and H. Wu, *Proc. Natl. Acad. Sci. USA*, **2011**, *108*, 8162-8166.
- [3] C.-W. Tsao, *Micromachines*, **2016**, *7*, 225-235.
- [4] Materials for microfluidic device fabrication: a review 2017, Elveflow, <https://www.elveflow.com/microfluidic-tutorials/microfluidic-reviews-and-tutorials/materials-for-microfluidic-chips-fabrication-a-review-2017/>
- [5] J. N. Lee, C. Park and G. M. Whitesides, *Anal. Chem.*, **2003**, *75*, 6544-6554.
- [6] J. P. Rolland, R. M. Van Dam, D. A. Schorzman, S. R. Quake and J. M. DeSimone, *J. Am. Chem. Soc.*, **2004**, *126*, 2322-2323.
- [7] S. Begolo, G. Colas, J.-L. Viovy and Laurent Malaquin, *Lab Chip*, **2011**, *11*, 508-512
- [8] M. Guerre, C. Taplan, R. Nicolaÿ, J. M. Winne and F. E. Du Prez, *J. Am. Chem. Soc.*, **2018**, *140*, 13272-13284.