LOW REFRACTIVE INDEX MATERIALS FOR MICROFLUIDIC APPLICATIONS IN OPTOFLUIDIC CHIPS

Lisa De Toni, Elmina Kabouraki, Maria Farsari and Kelly Velonia

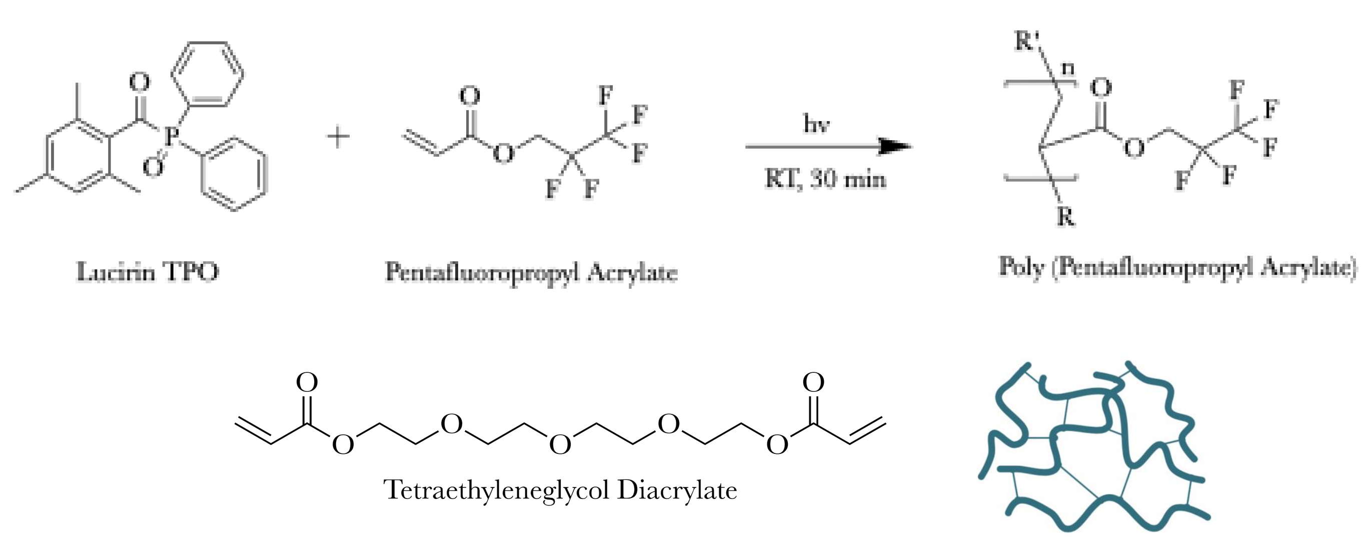
Department of Material Science and Technology, University of Crete, 70013, Heraklion, Crete, Greece
Foundation for Research and Technology, 70013, Heraklion, Crete, Greece
e-mail: lisadetoni@materials.uoc.gr

Imaging flow cytometry stands out as a highly effective approach for high resolution single cell analysis, with its performance being primarily limited by optical distortions and material incompatibilities in current microfluidic platforms. The NEXTSCREEN network addresses these issues by developing advanced, cost-effective microfluidic tools for diagnostics and personalized medicine.
In this context, the NEXTSCREEN project places significant focus on synthesizing and characterizing low refractive index polymers tailored for lab on chip devices, with optimized optical properties for microfluidic integration. Moreover, the compatibility of the selected monomers with Two Photon Polymerization (2PP)[1] is also explored to enable precise 3D microstructuring. These efforts aim to overcome material limitations and advance next generation optofluidic technologies for more accurate analysis.

1. Introduction

Fluorinated polymers were selected for their intrinsically low refractive index, stemming from the high electronegativity and low polarizability of fluorinated compounds - which also correlate with high ionization potential- making them ideal candidates for optofluidic applications. In this context, pentafluoropropyl acrylate was specifically chosen as the starting monomer due to its optical performance and commercial availability.
Polymerization was optimized using Lucirin TPO as the photoinitiator in both bulk and solution polymerizations[3]. Additionally, the role of a crosslinker (tetraethyleneglycol acrylate) was also evaluated to access its impact in the overall properties of the resulting polymers. Finally, all materials underwent characterization to evaluate their suitability for integration into microfluidic devices.

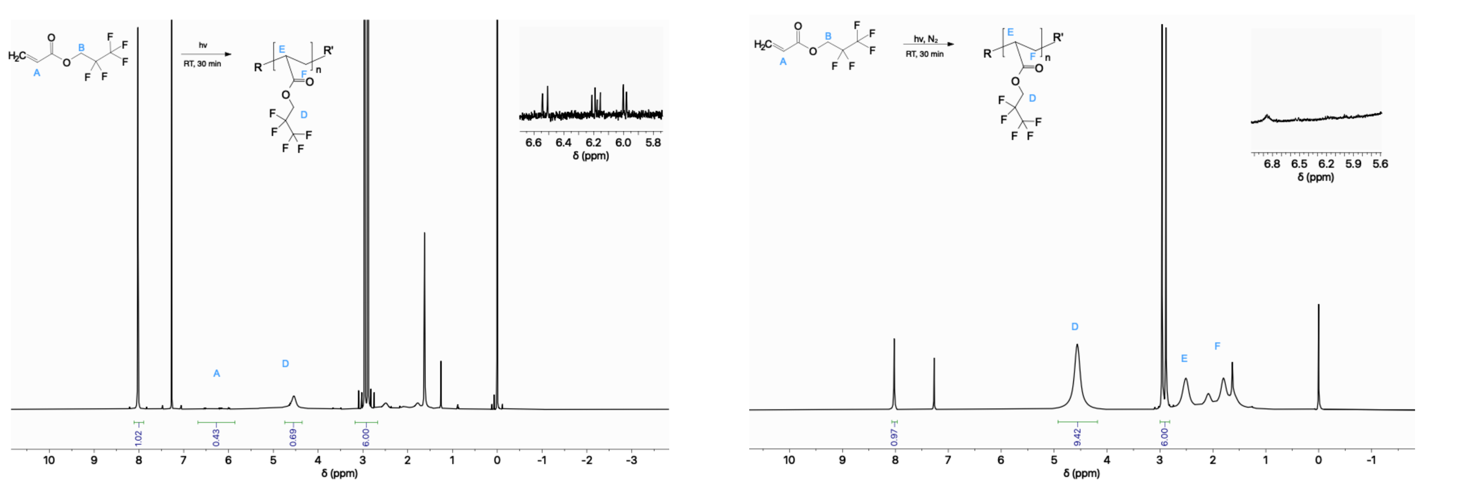
MONOMER	RI
(1,1,1,3,3,3-hexafluoroisopropyl acrylate)	1.319
(1,1,1,3,3,3-hexafluoroisopropyl methacrylate)	1.331
(2,2,3,4,4,4-hexafluorobutyl acrylate)	1.352
(2,2,3,4,4,4-hexafluorobutyl methacrylate)	1.361
(2,2,3,3,3-pentafluoropropyl acrylate)	1.336
(2,2,3,3,3-pentafluoropropyl methacrylate)	1.347
(2,2,3,3,4,4,4-heptafluorobutyl acrylate)	1.331
(2,2,3,3,4,4,4-heptafluorobutyl methacrylate)	1.341



2. Results and Discussion

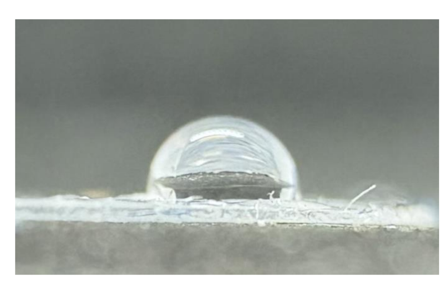
STRUCTURAL ANALYSIS

Photopolymerization of pentafluoropropyl acrylate using TPO as the initiator was investigated under varied conditions. The effect of oxygen inhibition was assessed, revealing that nitrogen saturated environments significantly improve polymerization efficiency and material quality.



NMR analysis confirmed the impact of oxygen inhibition. Left – Polymerization without prior N_2 atmosphere: a reduced polymer backbone signal (D) and a clear peak corresponding to the unreacted monomer (A). Right – Same polymerization under N_2 atmosphere: a strong polymer backbone signal and no detectable monomer peak, indicating improved polymerization efficiency.

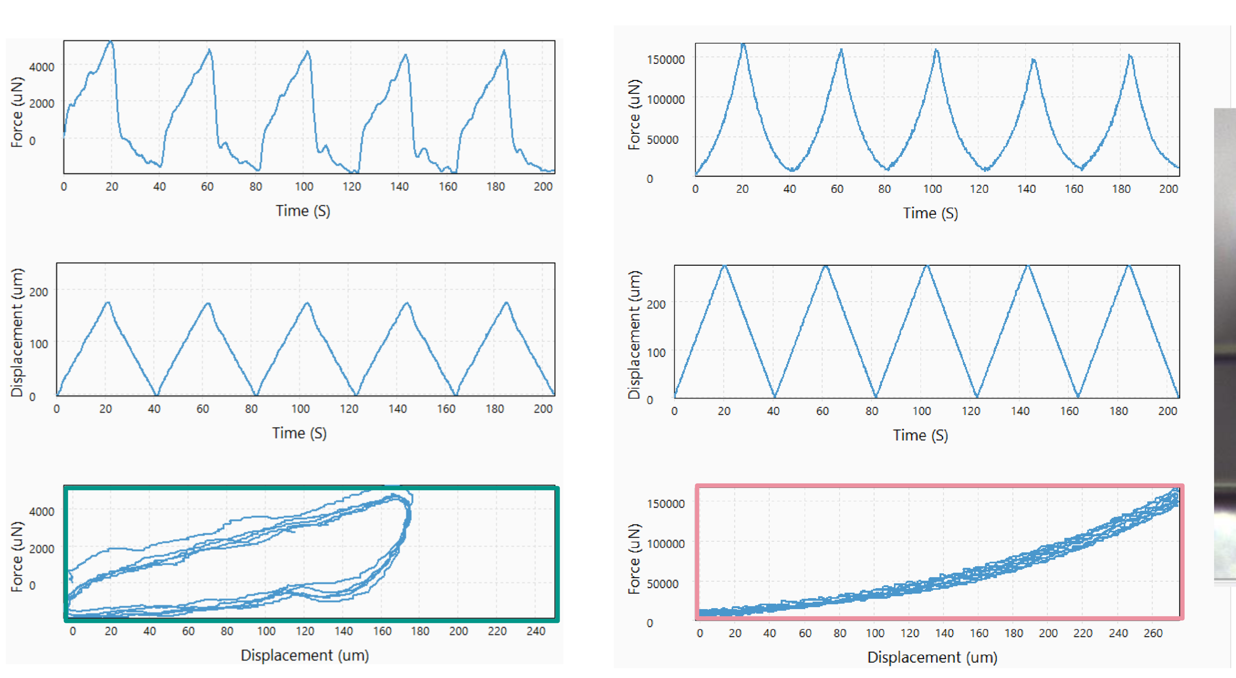
CONTACT ANGLE MEASUREMENTS

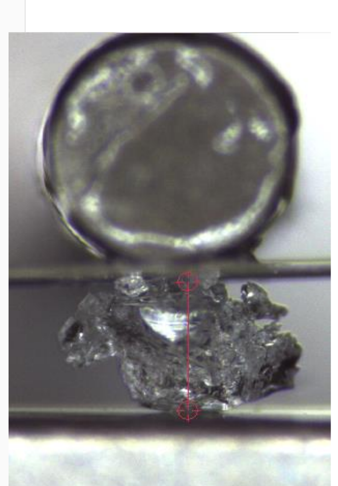


MONOMER	Crosslinker (%)	Contact angle	Error
Pentafluoropropyl Acrylate	0%	108.795	±0.959
Pentafluoropropyl Acrylate	5%	108.782	±1.094
Pentafluoropropyl Acrylate	10%	108.780	±0.834
Pentafluoropropyl Acrylate	15%	105.637	±1.152
Pentafluoropropyl Acrylate	20%	99.400	±1.792
Pentafluoropropyl Acrylate	25%	92.806	±2.139

MECHANICAL PROPERTIES MEASUREMENTS

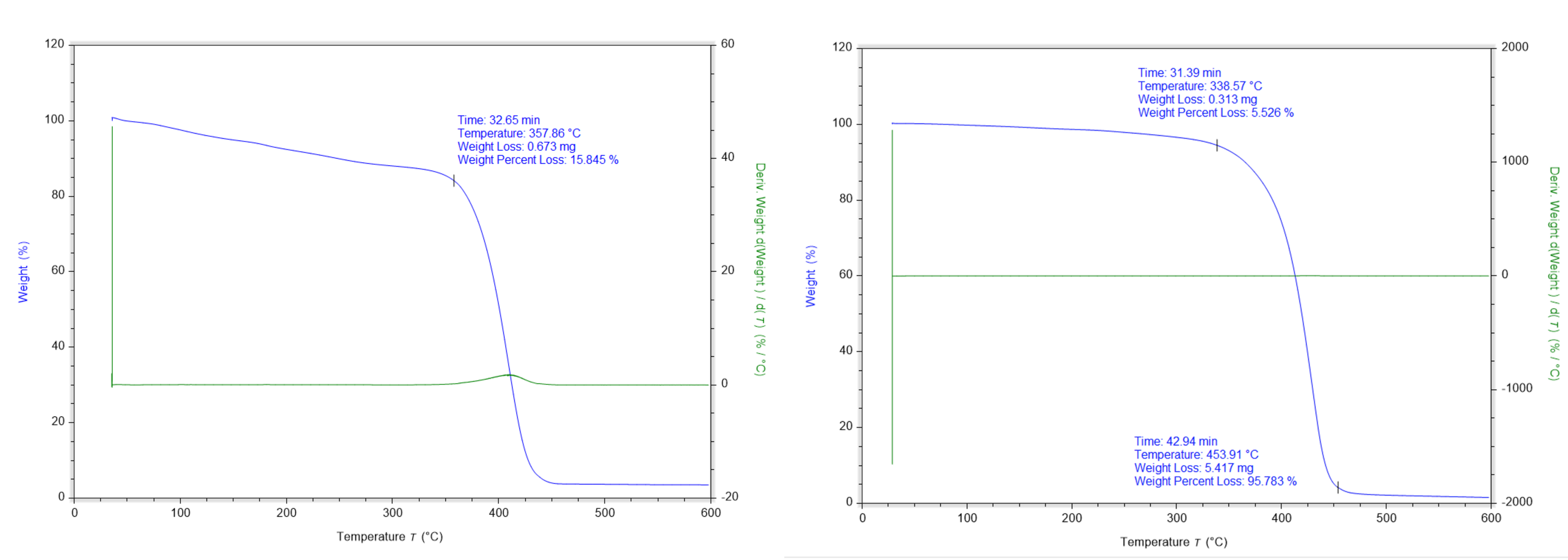
Mechanical tests were performed using a Microtester LT (CellScale, Canada) in compression. The 0% crosslinker sample exhibited typical elastomeric behavior with a pronounced viscoelastic response (left), whereas the 5% crosslinker sample showed a noticeably more resilient response (right), as indicated by the reduced hysteresis area.





THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis revealed a typical polymer profile further indicating a successful polymerization. The analysis was performed with a ramp of 600°C and a heating rate of 10°C/min.



TGA confirmed oxygen inhibition. Left – Polymerization without N_2 atmosphere: a more pronounced mass loss before the main degradation event, indicating lower polymerization efficiency. Right – Same polymerization under N_2 atmosphere: no early mass loss observed, suggesting higher polymerization efficiency.

3. Conclusions

The synthesized fluorinated polymers exhibit well defined chemical and physical properties, confirming both the efficiency and reproducibility of the optimized photopolymerization protocol. Ongoing work is dedicated to more in depth material characterization and the development of functionalization strategies that yield polymers with tailored properties. In parallel, particular attention is being given to the integration of Two Photon Polymerization techniques into the preparation of low refractive index materials, aiming to enable high resolution structuring and the fabrication of increasingly complex 3D architectures. These efforts are expected to broaden the applicability of the developed materials in emerging microscale technologies.

4. References

[1] De Marco, C., Gaidukeviciute, A., Kiyan, R., Eaton, S. M., Levi, M., Osellame, R., Chichkov, B. N., & Turri, S. (2013). A new perfluoropolyether-based hydrophobic and chemically resistant photoresist structured by two-photon polymerization. *Langmuir*, *29*(1), 426–431. https://doi.org/10.1021/la303799u
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[3] Yaseen, W. K., Marpu, S. B., Golden, T. D., & Omary, M. A. (2020). Synthesis and evaluation of a novel fluorinated poly(hexafluoroisopropyl methacrylate) polymer coating for corrosion protection on aluminum alloy. *Surface and Coatings Technology*, *404*. https://doi.org/10.1016/j.surfcoat.2020.126444

NEXTSCREEN
DOCTORAL NETWORK