Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

SUPERHYDROPHOBICITY OF NANOSTRUCTURED FLUORINATED ACRYLIC POLYMERS

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Determination of final conversion by DSC

After the polymerization process, in order both to check if the polymerization was completed and to characterize the obtained polymer, in the same aluminum pan two dynamic calorimetric processes, cooling and heating, were carried out as described in experimental section. In Figure S1, as an example the thermograms for the polymer obtained at 90ºC are plotted. As observed in figure only two peaks appear, one in the cooling section, associated to the crystallization of the polymers and the second one, when heating, so associated to the fusion process. Therefore, the thermograms confirm the complete homopolymerization of PFA in the first isothermal process and that the polymer is semicrystalline.

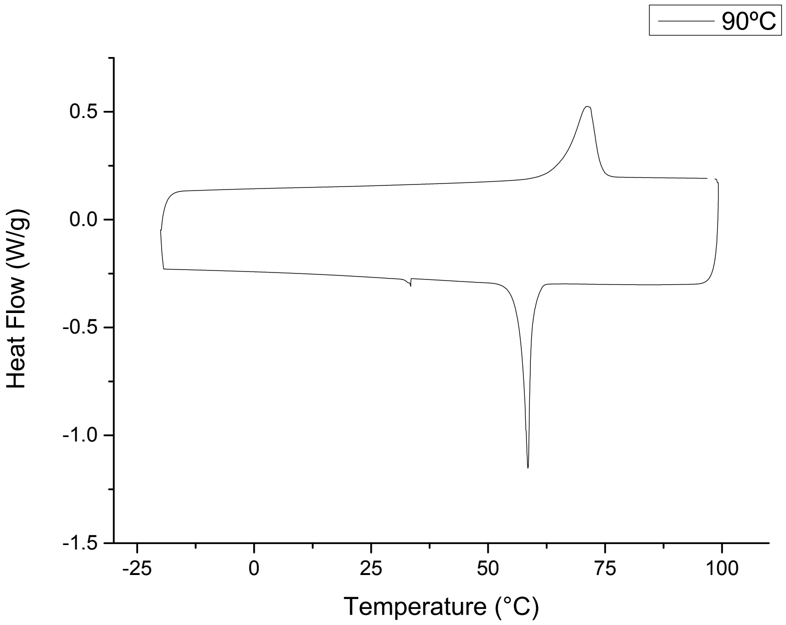


Figure S1 Thermogram of poly(MFA) homopolymer produced at 90°C.

In-situ polymerization. Determination of monomer conversion by Confocal Raman Microscopy

The determination of monomer conversion by Raman Microscopy in AAO template was carried out by a linear regression obtained with different composition (equivalent to monomer conversion) of samples contained MFA and PFA. With these different samples we determine the $I_{C=C}/I_{CF2}$ relationship for each monomer conversion. The signal at ~1640 cm^{-1} corresponds to C=C stretching band, which is present only in the monomer (MA); while the signal at ~725 cm^{-1} corresponds to the skeletal C-C stretching band, present in monomer and polymer, so it represents 100%. The spectrum has been normalized with the signal at 725 cm^{-1}.

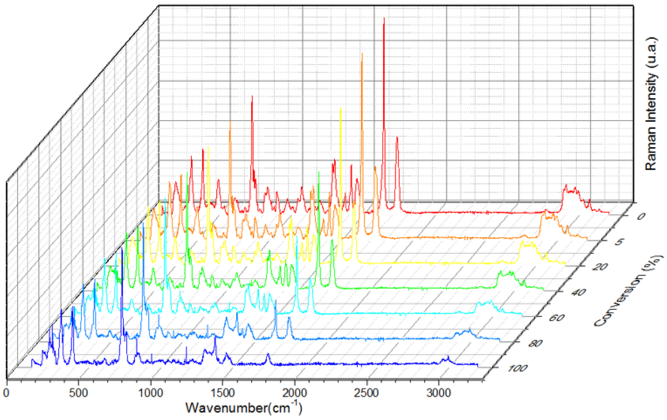
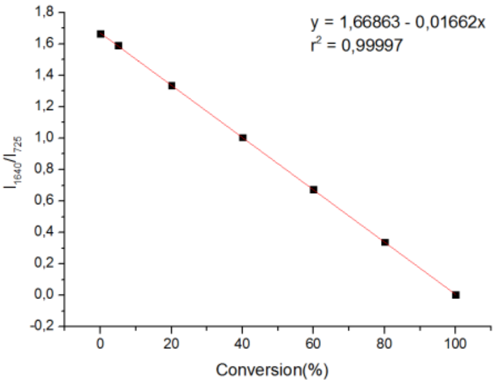


Figure S2 Raman spectra during polymerization of MFA within AAO template.

Time	I_{1641}	Normalized	Conversion (%)
0	2563,43	1,663	0
15	2183,31	1,417	15,1
30	1122,51	0,728	56,6
45	1017,41	0,66	60,7
60	436,15	0,283	83,4
120	303,18	0,197	88,5
165	426,25	0,277	83,7



Derivation of polymerization rate

For the case of a free radical polymerization in bulk media the rate of monomer consumption is given by

$$-\frac{d[M]}{dt} = k_p[M][P^{\cdot}]$$

Where kp is the polymerization rate constant, [M] is monomer concentration and [P•] is the radical concentration. The overall concentration of radicals, equated to 0 by the steady state approximation, in solution is given as the rate of production of radicals by decomposition of the thermal initiator minus the rate of consumption of radicals by termination

$$\frac{d[P^\cdot]}{dt} = 2k_d f[I] - 2k_t[P^\cdot]^2 = 0$$

Where kd is the initiator decomposition constant, f is the initiator efficiency, [I] is the initiator concentration and kt is the termination constant. The radical concentration is therefore given by

$$[P^\cdot] = \sqrt{\frac{k_d f[I]}{k_t}}$$

Substitution of this value back to the original rate equation gives us

$$-\frac{d[M]}{dt} = k_p[M]\sqrt{\frac{k_d f[I]}{k_t}}$$

And subsequent integration gives the time dependence on conversion.

$$-\ln(1 - X_M) = k_p\sqrt{\frac{k_d f[I]}{k_t}}t$$

Kinetic Model for Free Radical Polymerization in Confinement

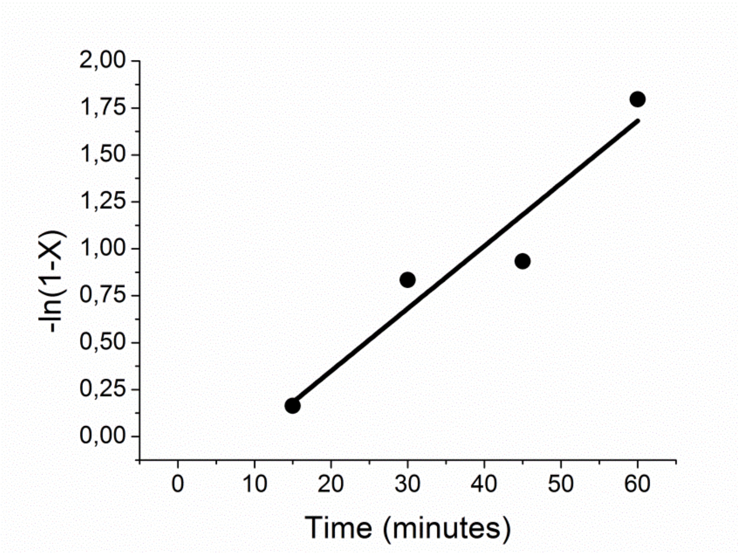


Figure S3. Linear plot of nanoconfined free radical polymerization of MFA at 70 °C. The symbols represent experimental data points and the straight lines correspond to the linear fit of the data in this region.