Supporting Information

Non-thermal Microwave Effects in Radical Polymerization of Bio-based Terpenoid (Meth)acrylates

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Figure S1- Temperature (black line), set point (horizontal dashline) and power evolution (bottom dashline) in a microwave assisted free radical polymerization for THGMA at 80 °C (Run 1).

Run	Time (min)	Sampled polymerization		Control polymerization	
	(IIIII)	Conversion	Molar mass (Da)	Conversion	Molar mass
		(%)		(%)	(Da)
6	120	73	165,000	73	165,500
6	210	92	150,000	92	150,400

Table S1 Assessment of the effect of sampling on monomer conversion and molar mass

13	5	86	290,400	86	290,200
13	10	98	278,400	98	278,500
26	5	90	332,900	90	333,100
26	10	99	299,000	99	299,200

Determination of monomer conversion. The conversion was determined by 1H NMR performed at 25°C in CDCl₃ at concentration of 350 mg/ mL (measured precisely)-1 on a DPX-400 or a DPX-500 Spectrometer. 1D ¹H spectra were acquired by use of 32K data points, which were zero-filled to 64K data points prior to Fourier transformation. Deuterated solvents employed were from Sigma-Aldrich. Toluene was introduced as a reaction marker and the CH₃ peak taken as reference. A pre-reaction NMR was performed and the ratio between the CH₃ of toluene at 2.26 ppm and the peak corresponding to one hydrogen on the (meth)acrylic double bound at around 6 ppm. This ratio was set for 0% (*i.e.* 100% of monomer) and then the conversion was obtained by cross product.

Determination of the molar mass distribution. Size Exclusion Chromatography (SEC) which consisted of a guard column (Styragel,Waters) and three columns in series (Styragel HR6, HR4 and HR2 with pore sizes ranging from 10^6 to 10^2 Å, respectively, Waters) was used in combination with a Multiangle Light Scattering detector (MALS, Dawn Heleos II) and a differential refractive index detector (RI, Optilab Rex) both of them from Wyatt Technologies. Before the injection, the samples were dissolved in THF at the desired concentration and afterwards were directly injected without previous filtration. The analysis was performed at 35 °C and at a flow rate of 1 mL.min⁻¹. The refractive index increment (dn/dc) values used for the determination of the absolute molar masses were experimentally measured for each of the polymers: poly(THGA) dn/dc = 0.0678 mL/g, poly(CycA) dn/dc = 0.082 mL/g and poly(NopA) dn/dc = 0.083 mL/g and poly(THGMA) dn/dc = 0.085 mL/g.



Figure S2. Effect of microwave irradiation on Rp and number average molecular weight (\overline{M}_n) on the FRP of THGMA at 90°C (Runs 3 and 4). Solid symbols (microwave irradiation, 300W), open symbols (no irradiation).



Figure S3. Effect of microwave irradiation on Rp and number average molecular weight (\overline{M}_n) on the FRP of CitMA at 80°C (Runs 5 and 6). Solid symbols (microwave irradiation, 300W), open symbols (no irradiation).



Figure S4. Effect of microwave irradiation on Rp and number average molecular weight (\overline{M}_n) on the FRP of CycMA at 80°C (Runs 7 and 8). Solid symbols (microwave irradiation, 300W), open symbols (no irradiation).



Figure S5. Effect of microwave irradiation on Rp and number average molecular weight (\overline{M}_n) on the FRP of NopMA at 80°C (Runs 9 and 10). Solid symbols (microwave irradiation, 300W), open symbols (no irradiation).



Figure S6. Temperatures and power evolution for the free radical polymerization of THGA at 80 °C under microwave irradiation (300 W) and with thermal heating. a) Evolution of the internal temperature of the reactor with thermal heating (triangles) and under microwave irradiation (squares). b) Temperature (black line), set point (top horizontal line) and power evolution (dash line) under microwave irradiation.



Figure S7-Molar mass distributions (replicate measurements) of the last sample of the FRP of THGA carried out at 80°C and 300 W.



Figure S8. FRP of THGA carried out with thermal heating at 80 (triangles) and 90 (circles) °C (Runs 12 and 17). Reaction 11 (80°C under microwave irradiation) is included for comparison (squares). Open symbols (*D*).



Figure S9. Effect of microwave irradiation (300W) on the evolution of conversion, \overline{M}_n and dispersity (*D*) in the FRP of THGA carried out at 60 °C Runs 13 and 14). Squares (300W), triangles (no irradiation). Open symbols (*D*).



Figure S10. Effect of microwave irradiation (300W) on the evolution of conversion, \overline{M}_n and dispersity (D) in the FRP of THGA carried out at 40 °C (Runs 15 and 16). Squares (300W), triangles (no irradiation). Open symbols (D).





Figure S11- Temperature and power evolution in a microwave assisted free radical polymerization for THGA at 80 °C using different irradiation powers (200W, 100W and 50W) (Runs 18-20). The data for 300W are in Figure S6. The lower panel shows the evolution of the internal temperature of the reactor with thermal heating (crosses) and under microwave irradiation with 300 W (squares), 200W (triangles), 100W (circles), 50W (diamonds).



Figure S12. Effect of microwave irradiation on Rp, number average molecular weight (\overline{M}_n) and dispersity (\overline{D}) on the FRP of CitA at 80°C (Runs 21 and 22). Squares (microwave irradiation, 300W), triangles (no irradiation). Open symbols (dispersity).



Figures S13- Effect of microwave irradiation on Rp, number average molecular weight (\overline{M}_n) and dispersity (\mathbb{D}) on the FRP of cyclademol acrylate (CycA) at 80°C (Runs 23 and 24). Squares (microwave irradiation, 300W), triangles (no irradiation). Open symbols (dispersity).



Figures S14- Effect of microwave irradiation on Rp, number average molecular weight (\overline{M}_n) and dispersity (\overline{D}) on the FRP of Nopol Acrylate at 80°C (Runs 25 and 26). Squares (microwave irradiation, 300W), triangles (no irradiation). Open symbols (dispersity).

Factors affecting *Rp* and kinetic chain length

In a homogeneous FRP the equations giving the polymerization rate (Rp) and the kinetic chain length (υ) are

$$Rp = k_p[M][R] = k_p[M] \sqrt{\frac{fk_d[I]}{k_t}}$$
Eq. 1

$$v = \frac{R_p}{R_t} = \frac{k_p[M]}{2\sqrt{fk_d[I]k_t} + k_{tr,M}[M] + k_{tr,S}[S]}}$$
Eq. 2

where k_p , k_t , k_d , $k_{tr,M}$ and $k_{tr,S}$ are the rate coefficients for propagation, termination, initiator decomposition, and chain transfer to monomer and solvent; f is the initiator efficiency factor; and [R], [M], [S] and [I] the concentrations of radicals, monomer, solvent and initiator.