Electronic supplementary information 1

Addressing sustainability in photopolymerization: comparative LCA study of six synthetic routes of 1-hydroxycyclohexyl phenyl ketone as photoinitiator for copolymer applications

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S1 - General.

All reagents, solvents and chemicals used in this study were of analytical grade and purchased from various commercial suppliers. Crotonic acid (CA) and vinyl acetate (VA) were purchased from Sigma-Aldrich. The acid was used without further purification, VA was distilled prior to use and stored in the freezer. Polyvinyl alcohol (PVOH 25-88) was supplied by Vinavil (Italy). The photoinitiators 1-hydroxycyclohexyl phenyl ketone (HCPK, commercial name: IRGACURE 184), bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (BAPO, commercial name: OMNIRAD 819), 2,2-dimethoxy-1,2-diphenylethan-1-one (DMPA) and camphorquinone (CQ) were purchased from commercial sources. Photochemical reactions were carried out by means of Kessil PR-160L LED lamps (40 W) with emission centred at different wavelengths (370, 390 and 427 nm; for emission spectra, see: https://kessil.com/products/science_PR160L.php) or EvoluChem LED lamps (18 W) with emission centred at 405 nm (for emission spectrum, see: https://hepatochem.com/photoreactors-leds-accessories/photoreactor-leds-evoluchem/) as the light source.

NMR analyses on the polymers were carried out in the deuterated solvent of choice. Proton ^{1}H NMR spectra were recorded on a Bruker Avance Neo 400 MHz. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual solvent as the internal reference.

The determination of PDI, Mn and Mw was carried out by processing chromatographic traces obtained from GPC analysis, carried out on the polymer dissolved in solvent (THF) and appropriately diluted. Experimental conditions: Eluant: non stabilized THF, Column: STYRAGEL 5 μm, 50-100-1000-10000 Å porosity, placed in a thermostatic oven, 1515 Waters pump, Waters 2707 Autosampler, loop volume 100 μL, 1 mL/min flux, Detector: Refractive Index Waters 2414.

S2 - General procedure for the photochemical synthesis of poly(vinyl acetate-co-crotonic acid). In a flame-dried 10 mL round-bottom flask, 2 mL of freshly distilled vinyl acetate VA (ρ = 0.93 g/mL, 1.86 g; 0.01 mol), 28 mg of crotonic acid CA (1.5 wt%; bio-based or commercial origin) and 4 mL of water with polyvinyl alcohol as emulsifier (2.5 wt%) were mixed together. The selected amount of the chosen photoinitiator (1-12 mg) was then added, and the round-bottom flask (25 mL) was sealed with a septum. Finally, the so-formed mixture was purged with nitrogen for 5 min and irradiated at the indicated wavelength under vigorous stirring (Figure S1). The polymer was obtained by precipitation in cyclohexane and subsequently dried at room temperature prior to characterization (Figure S2).

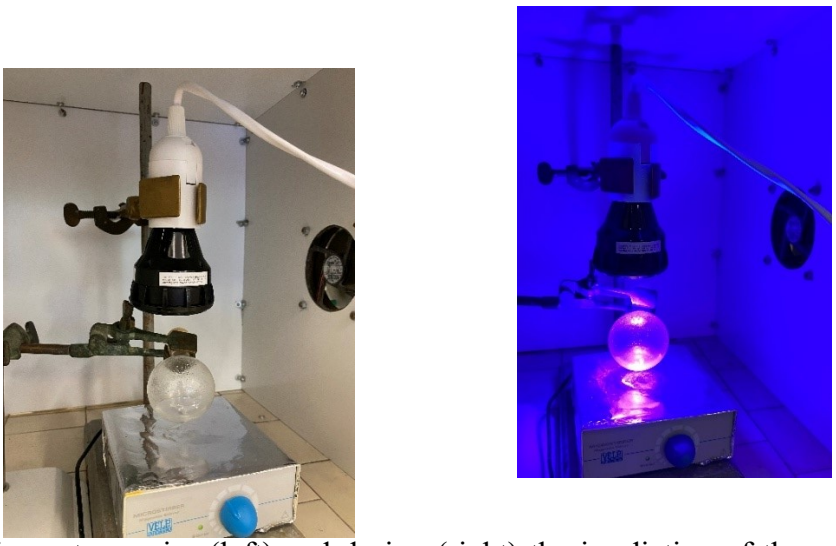


Figure S1. Irradiation set-up prior (left) and during (right) the irradiation of the mixture with the Evoluchem Lamp (18 W, emission centered at 405 nm).

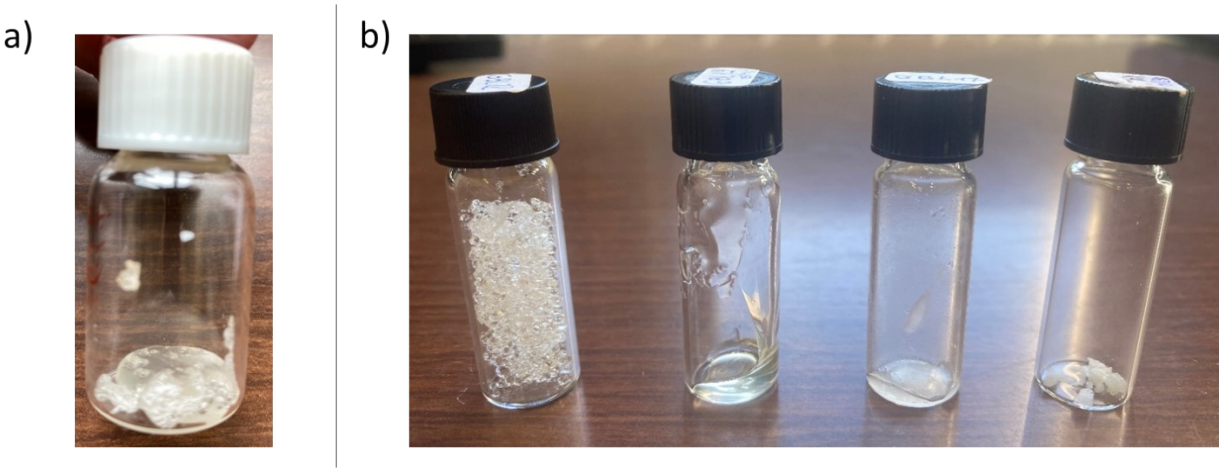
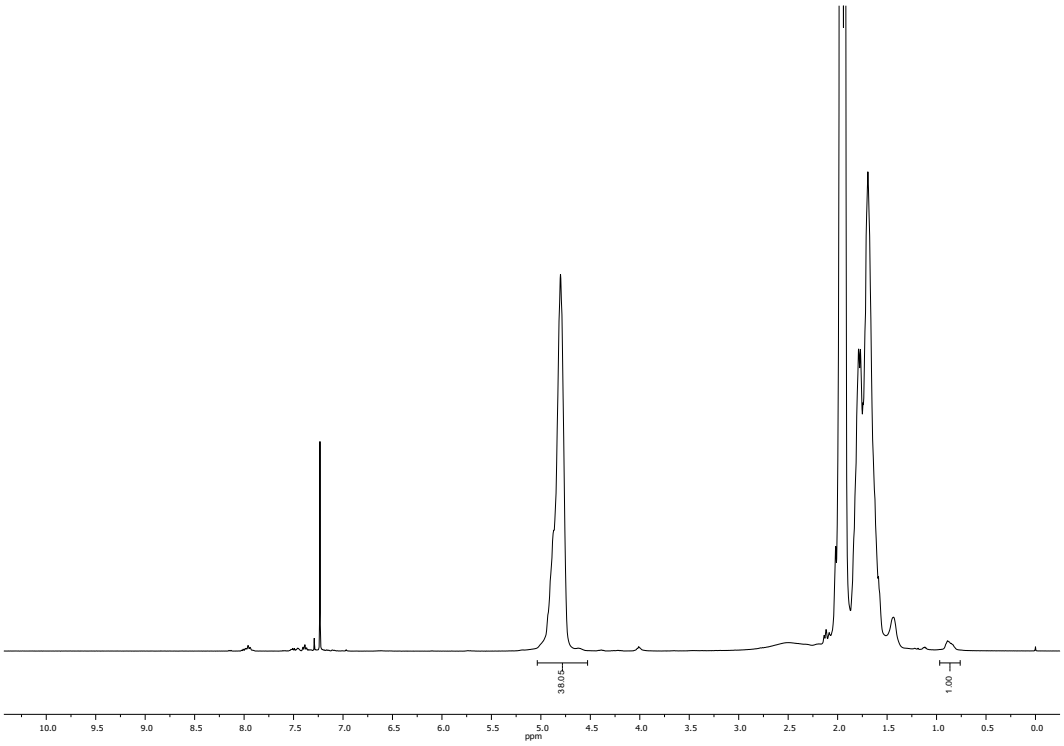


Figure S2. a) Typical appearance of the poly(vinyl acetate-*co*-crotonic acid) polymer obtained from the raw product after precipitation in cyclohexane; b) Poly(vinyl acetate-*co*-crotonic acid) polymer obtained upon irradiation of the mixture of monomers in the presence of different PIs. From left to right: with HCPK, BAPO, DMPA and CQ.

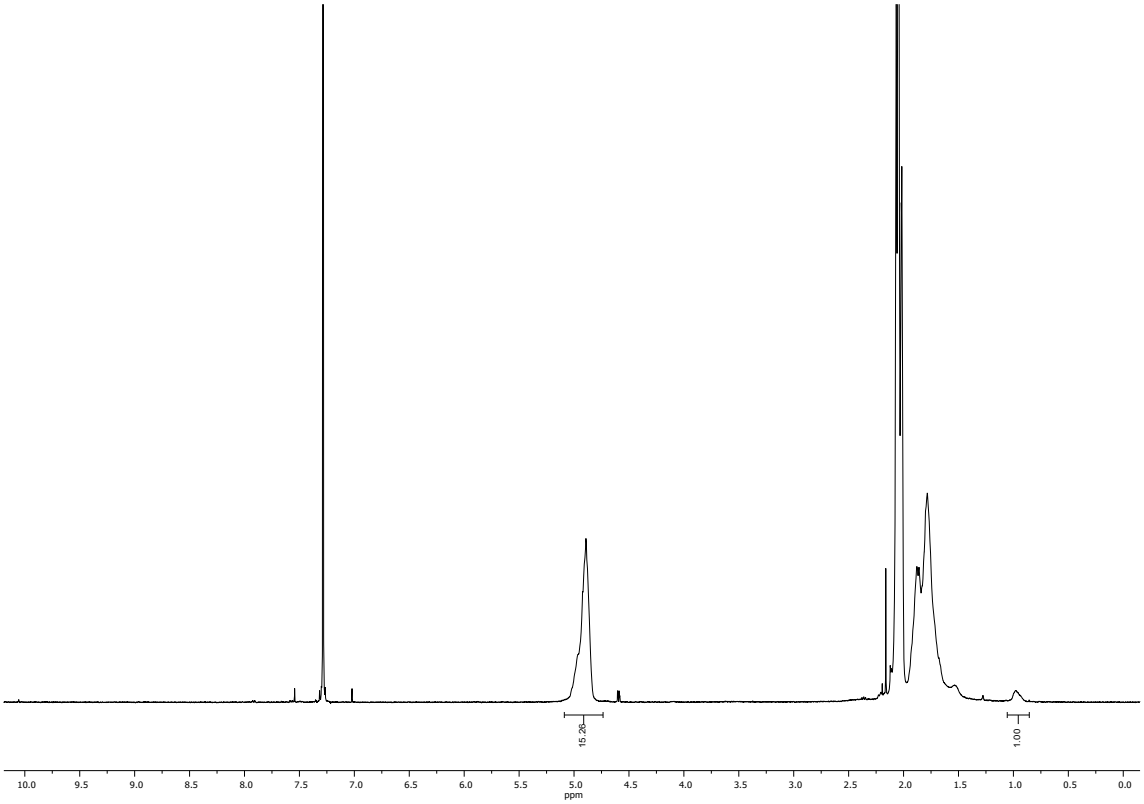
S3 - NMR analysis of the poly(vinyl acetate-co-crotonic acid) polymer

The prepared polymers have been characterized by ^{1}H-NMR spectroscopy. Their spectra have been likewise compared with that obtained for the commercially available polymer (Figure S3). From the ^{1}H-NMR spectrum, it is possible to estimate the ratio between the amount of VA *vs* CA incorporated into the polymer. The molar ratio of the monomers incorporating in the polymer was calculated based on the ratio between the integration of the signal at *ca* 0.9 ppm (terminal methyl group (accounting for 3 protons) from CA) and the signal at *ca* 4.8 ppm (a single proton from VA).



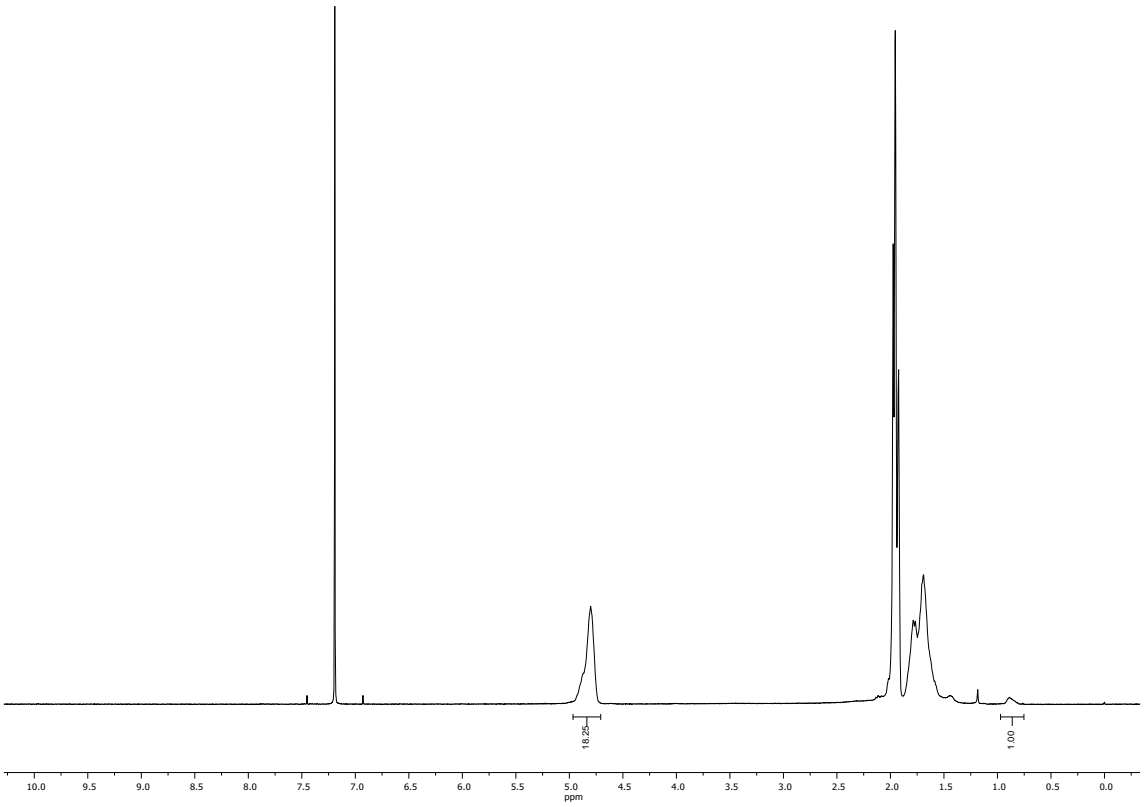
Molar ratio (mol%)	
CA	**VA**
0.9	99.1

Figure S3. ^{1}H NMR ($CDCl_3$, 400 MHz) of the commercial poly(vinyl acetate-co-crotonic acid) polymer.



Molar ratio (mol%)	
CA	**VA**
2.15	97.85

Figure S4. ^{1}H NMR ($CDCl_3$, 400 MHz) of the poly(vinyl acetate-co-crotonic acid) polymer sample obtained in entry 9 (Table 1, see main text).



Molar ratio (mol%)	
CA	**VA**
1.8	98.2

Figure S5. ^{1}H NMR ($CDCl_3$, 400 MHz) of the poly(vinyl acetate-co-crotonic acid) polymer sample obtained in entry 10 (Table 1, see main text).

Table S1. Physical and chemical characteristic of commercially available polymer and the polymers obtained by adopting the conditions in entries 9 and 10 (Table 1, see main text).

	Commercially available polymer	Polymer from entry 9	Polymer from entry 10
Molar ratio (mol%) of **CA**	0.90	2.15	1.80
PDI	2.97	2.84	2.57
Mn	69,373	133,853	232,907
Mw	206,399	379,956	597,601