

Electronic Supplementary Information

Copper (0)-Mediated Radical Polymerisation in a Self- Generating Biphasic System

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Characterization

NMR Spectroscopy

¹H NMR spectra were recorded using a Bruker ACF300 (300 MHz) spectrometer employing CDCl₃ as solvent. Monomer conversions were determined via ¹H NMR spectroscopy, comparing the signal areas from the vinyl protons ($\delta \sim 6.50\text{-}6.00$ ppm) 3H/mol to the signal area of OCH₂ signal (at 4.0 ppm) attributed to -CH₂O (*n*-BuA).

Gel Permeation Chromatography (GPC)

Gel permeation chromatography (GPC) was conducted using THF as the mobile phase. GPC analyses were performed at 40 °C (flow rate = 1 mL/min) using a Shimadzu modular system comprising an LC-20AT pump, SIL-10AD auto-injector, CTO-16AC column oven and RID-10A RI detector. Molecular weight separation was achieved via a column set comprising a PL 5.0-mm bead-size guard column (50 × 7.8 mm) followed by four Phenomenex PHENOLGEL GPC columns (300 × 7.8mm; 5 μ m; 10⁻², 10⁻³, 10⁻⁴ and 10⁻⁶Å). A calibration curve was generated with commercial linear polystyrene standards ranging from 500 to 10⁶ g/mol. SEC was conducted on Varian 390-LC system in CHCl₃ at ambient temperature, equipped with refractive index and viscometry detectors, 2 × PLgel 5 μ m mixed-D columns (300 × 7.5 mm), 1 × PLgel 5 μ m guard column (50 × 7.5 mm) and autosampler.

X-ray Photoelectron spectrometer (XPS)

A Kratos Axis ULTRA XPS incorporating a 165 mm hemispherical electron energy was used. The incident radiation was monochromatic Al X-rays (1486.6 eV) at 225 W (15 kV, 15 ma). Survey (wide) scans were taken at an analyzer pass energy of 160 eV and multiplex (narrow) higher resolution scans at 20 eV. Survey scans were carried out over 1200 eV binding energy with 1.0 eV steps and a dwell time of 100 ms. Poly(*n*-butyl acrylate) sample was placed on silica plate and analysed by XPS.

MALDI-TOF Mass Spectrometry

MALDI-TOF MS experiments were carried out on a Bruker UltraFLEX II TOF/TOF-MS instrument equipped with a 337 nm nitrogen laser, ion acceleration voltage of 25 kv and pulse extraction delay time of 90 ns. The instrument was operated in reflectron mode unless otherwise stated and with each spectra being the summation of typically 1000 laser shots in order to maximise the signal to noise ratio.

Sample preparation: Each polymer (0.5 mg/mL) was prepared in THF with sodium iodide (1 mg/mL) and saturated 2,5 dihydroxybenzoic acid (DCTB) matrix in a 1:0.1:1 ratio (sample : salt:matrix). 0.5 μ of the mixture was then spotted onto the target plate and analysed.

Inductively coupled plasma mass spectrometry (ICP-MS)

ICP-MS has been carried out PerkinElmer quadrupole Nexion ICPMS. The instrument has been previously calibrated using copper solution in water. Sample preparation: un-purified poly(n-butyl acrylate) (10 mg) obtained by copper (0) mediated radical polymerization in DMSO has been dissolved in THF (0.200 mL), and then, the solution was drop wise added to water (9.8 mL, 0.1 M of HCl). The solution was mixed for 14 hours before analysis by ICP-MS to determine copper concentration. Each sample was analysed four times, and the average of the four values was calculated.

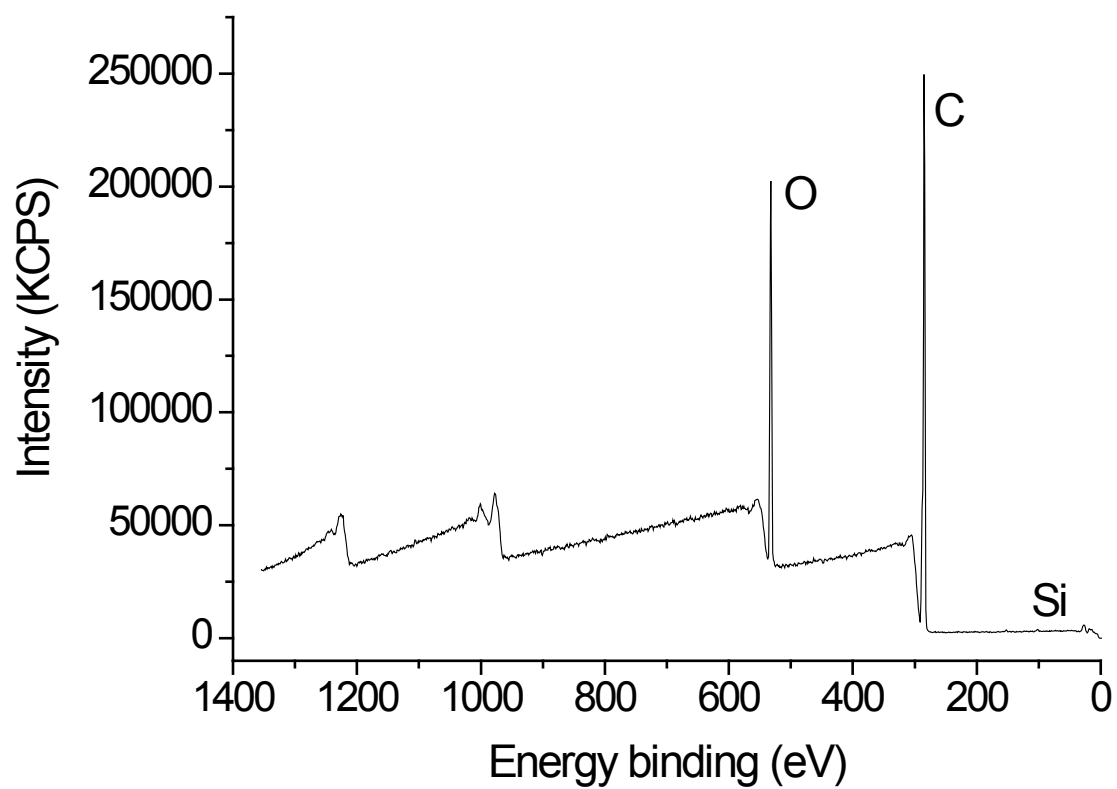


Figure S1. Wide XPS spectrum of crude poly(*n*-butyl acrylate) obtained by copper (0) mediated radical polymerization in biphasic system.

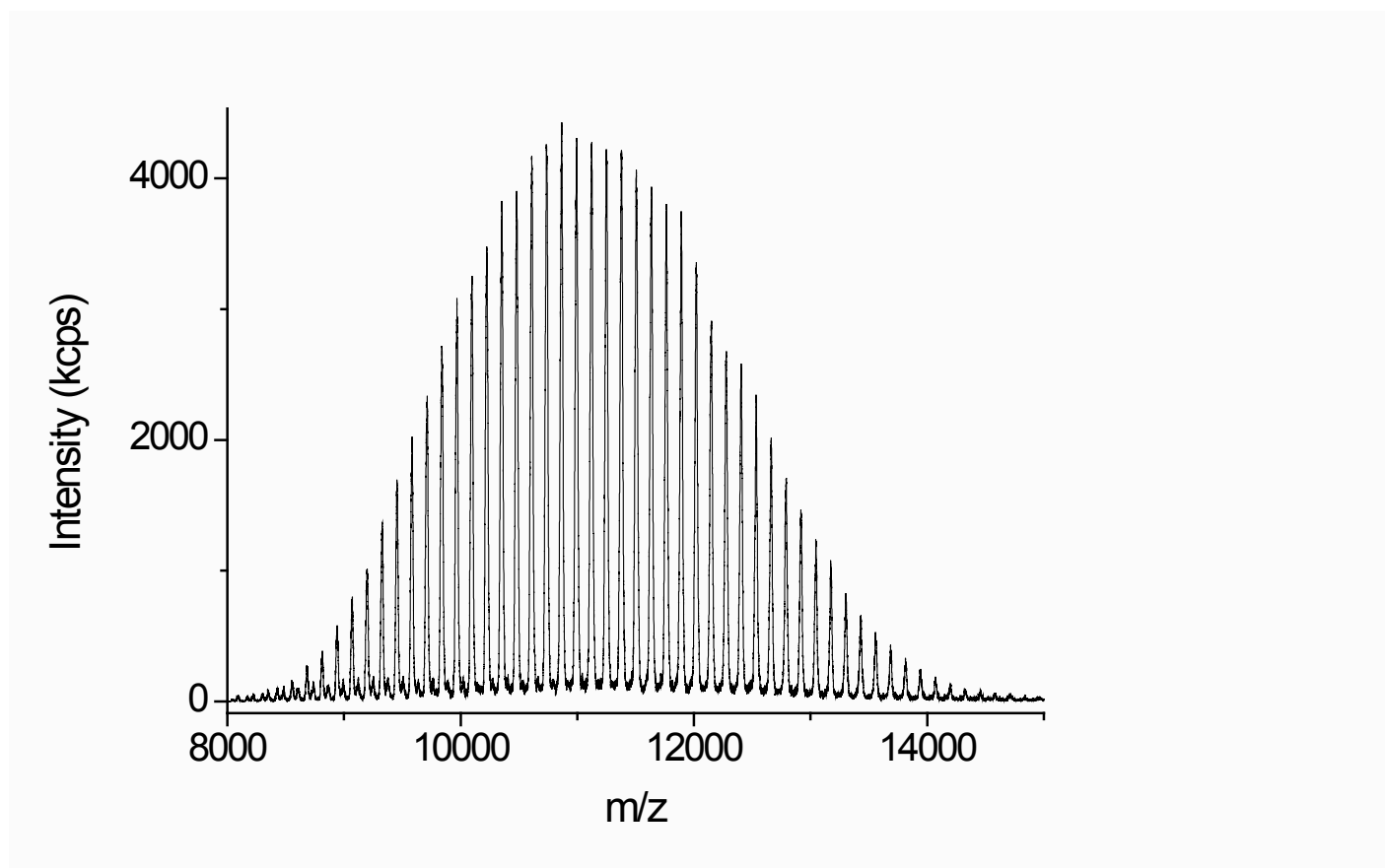
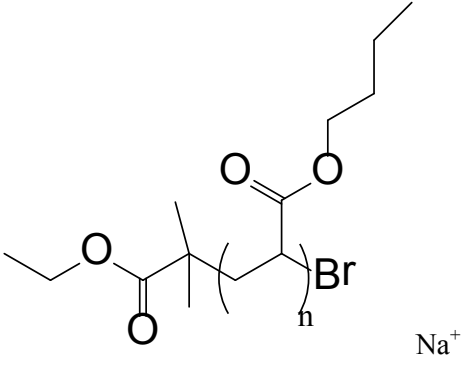
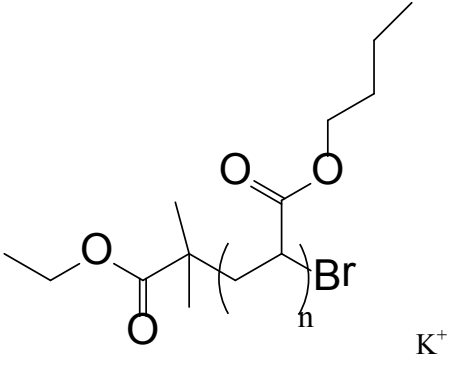
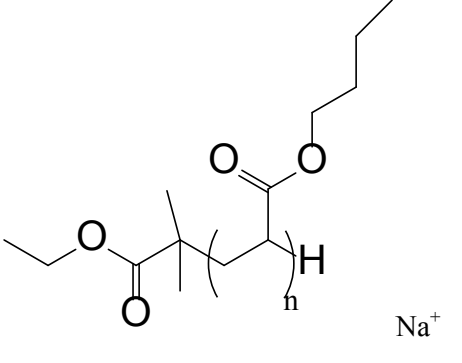
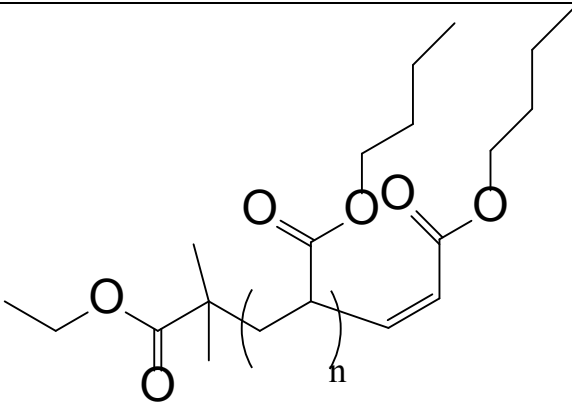


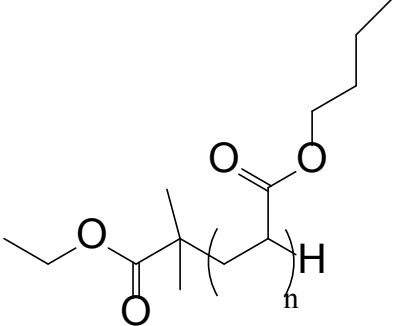
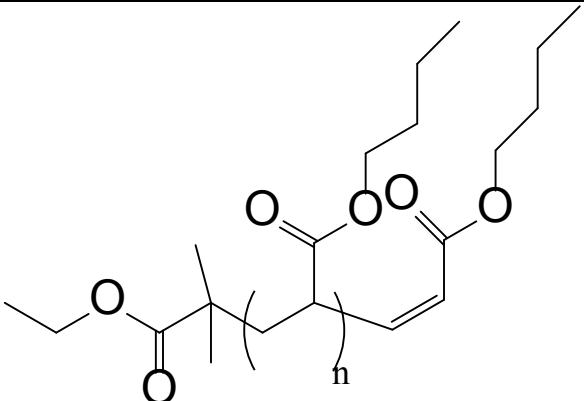
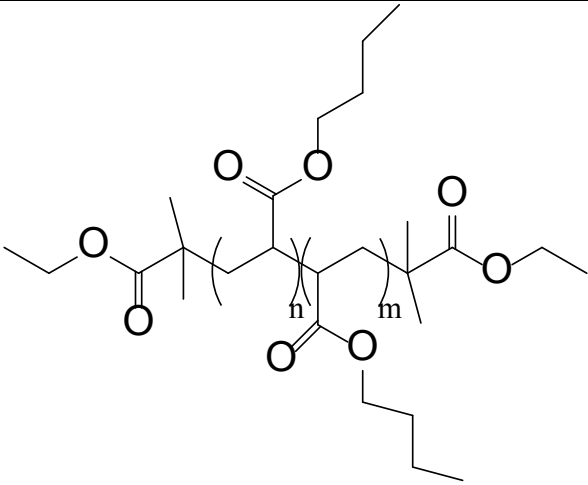
Figure S2. MALDI-TOF spectrum of poly(*n*-butyl acrylate) after chain extension using copper (0) mediated polymerization in the presence of *n*-butyl acrylate in DMSO.

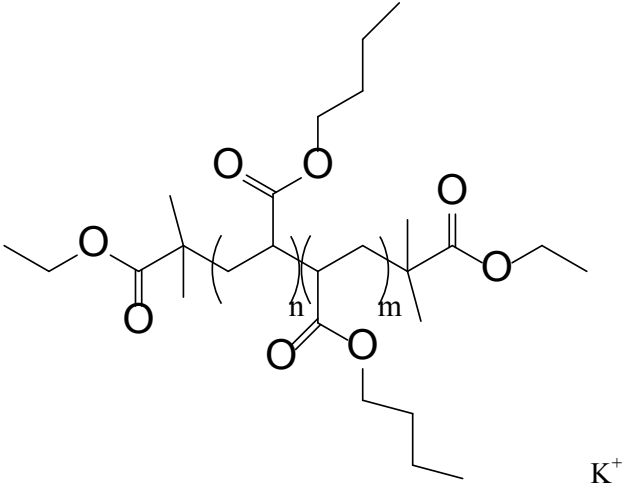
Table S1. Amount of different elements determined by XPS for non-purified poly(*n*-butyl acrylate) obtained by copper (0) mediated radical polymerization in biphasic system.

Type	Energy Binding (eV)	AT-%
C 1s		68.68
O 1s	282-2.89	20.05
Si-O 2p	105.6	0.27
Cu 3s	124-125	Non-detectable
Cu 2p _{1/2}	932-933	Non-detectable
Cu 2p _{3/2}	934-935	Non-detectable

Table S2. Possible populations obtained during the copper(0) mediated radical polymerization.

Species	Theoretical m/z	Experimental m/z
 <p style="text-align: center;">Na^+</p>	3422.48 (n= 24)	3422.3
 <p style="text-align: center;">K^+</p>	3438.54 (n= 24)	3438.7
 <p style="text-align: center;">Na^+</p>	3342.32 (n= 24)	Not observed
 <p style="text-align: center;">Na^+</p>	3340.32 (n= 23)	Not observed

Na^+		
 <p style="text-align: center;">K^+</p>	<p>3358.48 (n= 24)</p>	<p>Not observed</p>
 <p style="text-align: center;">, K^+</p>	<p>3356.48 (n =23)</p>	<p>Not observed</p>
 <p style="text-align: center;">Na^+</p>	<p>3327.20 (n+m= 23)</p>	<p>Not observed</p>

 <p>The image shows a chemical structure of a polymer repeat unit. It consists of two different units, labeled 'n' and 'm', connected by a methylene group. Unit 'n' is a methacrylate derivative with a methyl group and an ethoxy carbonyl group. Unit 'm' is a methacrylate derivative with a methyl group and a butyloxy carbonyl group. The structure is shown with a potassium ion counterion, K⁺, located below the main structure.</p>	3343.38 (n+m=23)	Not observed
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