

Supporting Information

***Absolut* “copper catalyzation perfected”; robust living polymerization of NIPAM: *Guinness* is good for SET-LRP**

Christopher Waldron, Qiang Zhang, Zaidong Li, Vasiliki Nikolaou, Gabit Nurumbetov, Jamie Godfrey, Ronan McHale, Gokhan Yilmaz, Rajan K. Randev, Mony Girault, Kayleigh McEwan, David M. Haddleton*, Martijn Droesbeke, Alice J. Haddleton, Paul Wilson, Alexandre Simula, Jennifer Collins, Danielle J. Lloyd, James A. Burns, Christopher Summers, Claudia Houben, Athina Anastasaki, Muxiu Li, C. Remzi Becer, Jenny K. Kiviaho, and Nuttapol Risangud, †

*Corresponding author

Email: D.M.Haddleton@warwick.ac.uk

† Order of authors was picked from a hat

Dept. of Chemistry, Library Road, University of Warwick, Coventry, UK, CV4 7AL

Experimental

Materials and Methods

Alcoholic “solvents” were purchased in various supermarkets, bars, airports *etc.* around the world and used as received, apart from the homemade Romanian brandy which was kindly donated by Prof. Virgil Perced, University of Pennsylvania and the Verveine Verte which was donated by Prof. Sébastien Perrier, University of Sydney.

Tris(2-(dimethylamino)ethyl)amine (Me_6TREN) was synthesized according to literature procedure and stored under a nitrogen atmosphere prior to use.^{1,2} Beer soluble initiator 2, 3-dihydroxypropyl 2-bromo-2-methylpropanoate was synthesized according to literature procedure.³ Copper (I) bromide (CuBr , 98%, Sigma-Aldrich) was washed sequentially with acetic acid and ethanol and dried under vacuum. *N*-Isopropylacrylamide (NIPAM, 97%) was obtained from Sigma-Aldrich and used without further purification.

^1H NMR spectra were recorded on either Bruker DPX-300 or DPX-400 spectrometers using D_2O obtained from Aldrich as solvent. Monomer conversion was calculated for NIPAM polymerization by comparing the integral of vinyl protons with isopropyl protons. SEC was conducted on Varian 390-LC system in DMF (5 mM NH_4BF_4) at 50 °C, equipped with refractive index, UV and viscometry detectors, 2 × PLgel 5 mm mixed-D columns (300 × 7.5 mm), 1 × PLgel 5 mm guard column (50 × 7.5 mm) and autosampler. Narrow linear poly (methyl methacrylate) standards in the range 200 to 1.0×10^6 $\text{g}\cdot\text{mol}^{-1}$ were used to calibrate the system. GPC samples (crude final polymerization mixture diluted in DMF) were passed through both an alumina plug and a 0.45 μm Nylon filter prior to analysis.

Typical Polymerization Procedure

All beers were subjected to three freeze-thaw degas procedures prior to polymerization to remove dissolved gases. Other alcoholic beverages were degassed by bubbling with nitrogen for a minimum of 15 minutes. While primary solvent analysis was conducted by a taste test post-experiment, ^1H NMR analysis in D_2O was also done to ascertain differences between the beverages (see below). Polymerizations were conducted at a relatively small-scale (4.5 ml of solvent) to ensure sufficient beverage remained for the crucial taste tests.

CuBr (14.3 mg; 0.4 equivalents relative to bromide initiator) and Me_6TREN (27 μL ; 0.4 eq.) were added to 2.5 ml of the alcoholic beverage (beers previously degassed by freeze-thaw cycles) in a schlenk tube equipped with a stir bar and sealed with a rubber septum. N_2 gas was bubbled through the stirred mixture for approx. 15 mins while the schlenk tube was immersed in an ice bath. Metallic Cu particles were observed on the side of the schlenk tube as disproportionation proceeded. A green or turquoise colour was observed in solution. Separately, a solution of NIPAM (0.563 g; 20 eq.) and the beer soluble initiator (60 mg; 1 eq.) in 2 ml of the alcoholic beverage was degassed by the same N_2 bubbling procedure in an ice bath. After both solutions were degassed, the monomer/initiator solution was added quickly to the catalytic solution using a canula procedure to ensure no exposure to oxygen, whilst maintaining the polymerization mixture in an ice bath. The metallic copper is observed to disappear quickly on mixing the solutions. Time zero was taken at this point, with regular samples taken thereafter to monitor monomer conversion.

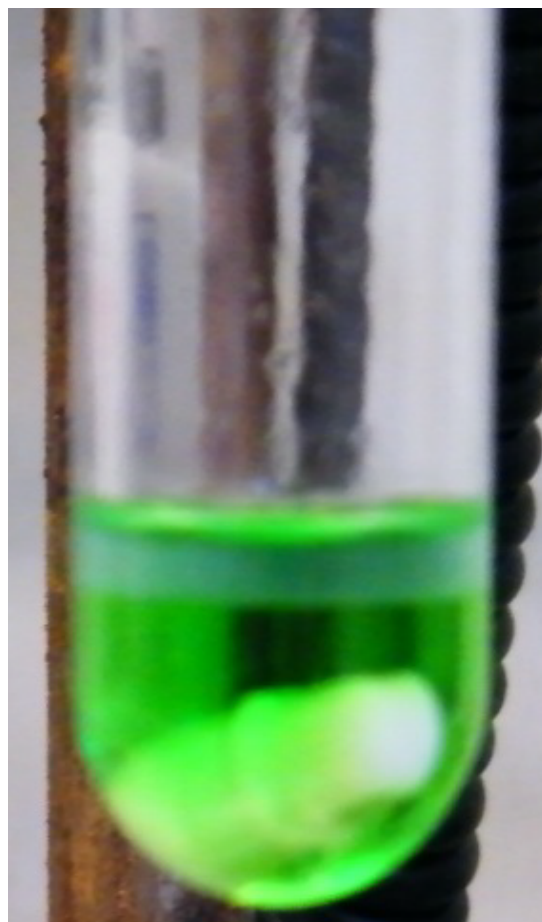


Figure S1: Phase separation of poly(NIPAM) from Verveine Verte (55% alc. content). Final conversion 62%; $M_n = 1600$; PDI = 1.05.

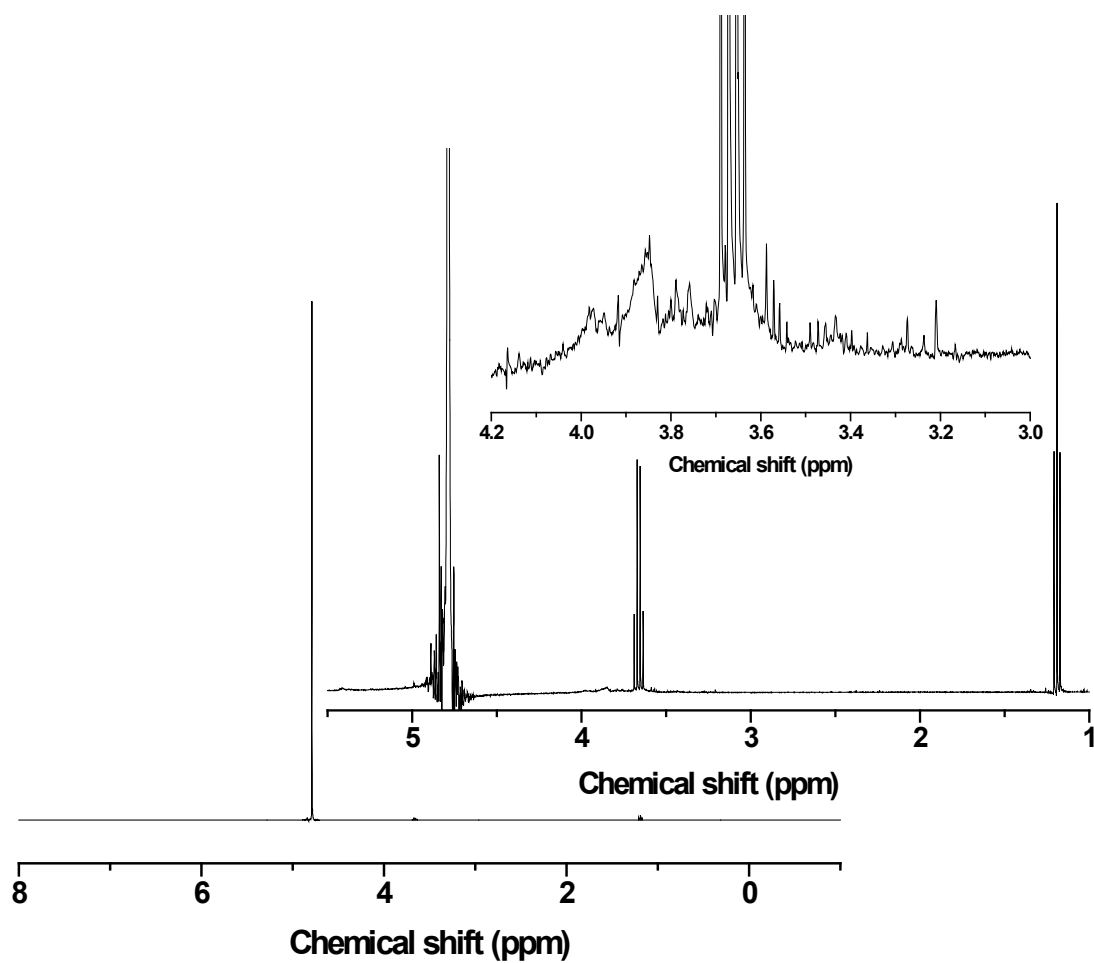


Figure S2a: ¹H NMR of GUINNESS in D₂O. Residual solvent peak (@ 4.79 ppm) is strongest in main image. First zoom reveals ethanol peaks at 3.66 (q) and 1.18 (t) ppm. Next zoom in reveals likely sugar/carbohydrate peaks between 3.2 and 4.2 ppm.

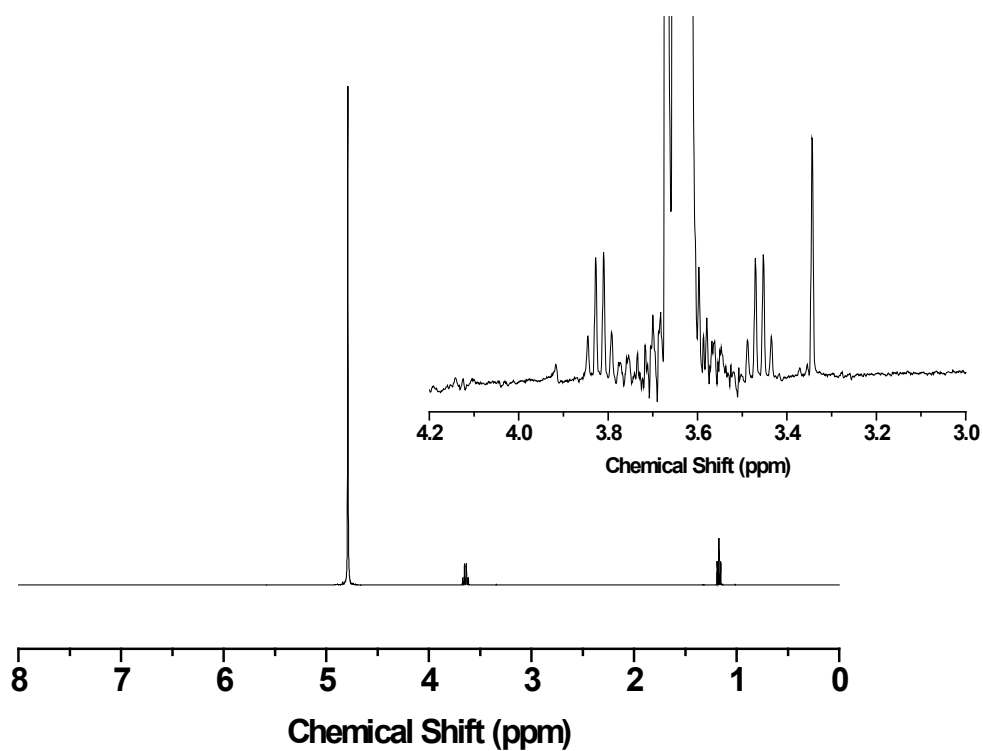


Figure S2b: ¹H NMR of Tsipouro in D₂O. Residual solvent peak (@ 4.79 ppm) and ethanol peaks visible in main image. Zoom in reveals little if any sugar/carbohydrate peaks; visible quartets are satellite peaks of ethanol.

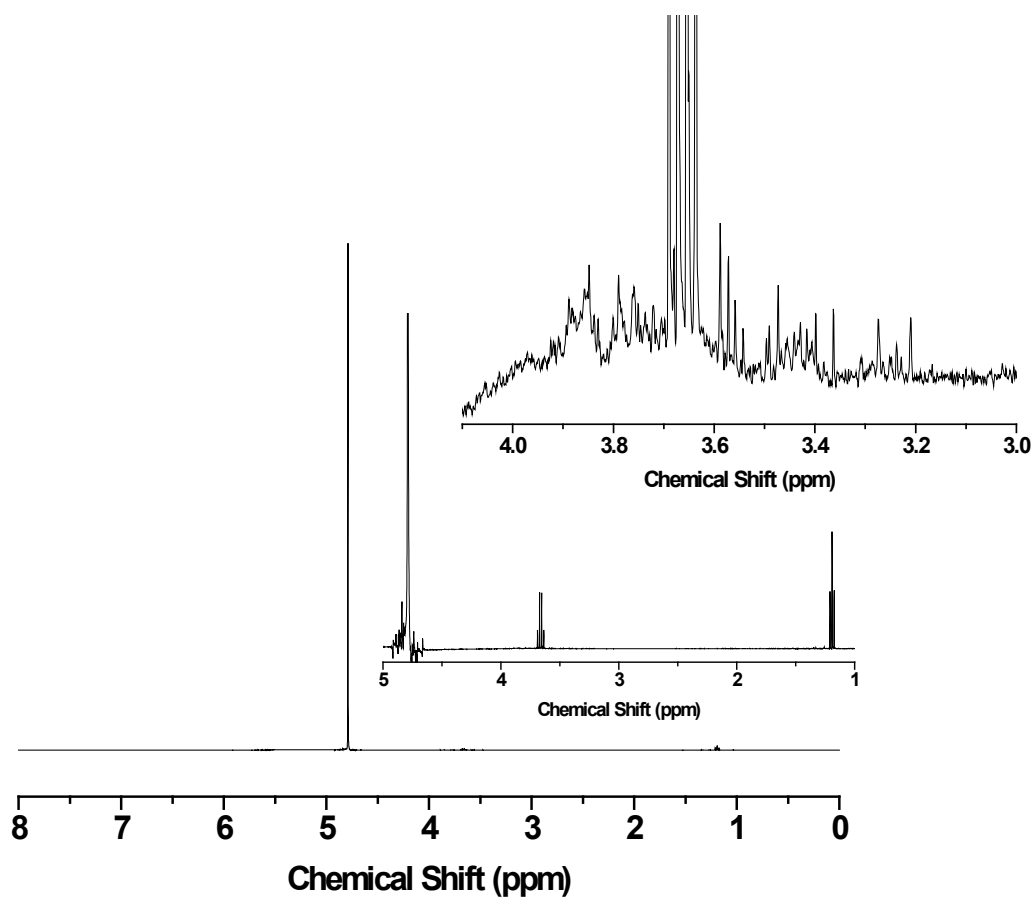


Figure S2c: ¹H NMR of Singha in D₂O. Residual solvent peak (@ 4.79 ppm) is strongest in main image. First zoom reveals ethanol peaks at 3.66 (q) and 1.18 (t) ppm. Next zoom in reveals likely sugar/carbohydrate peaks between 3.2 and 4.1 ppm.

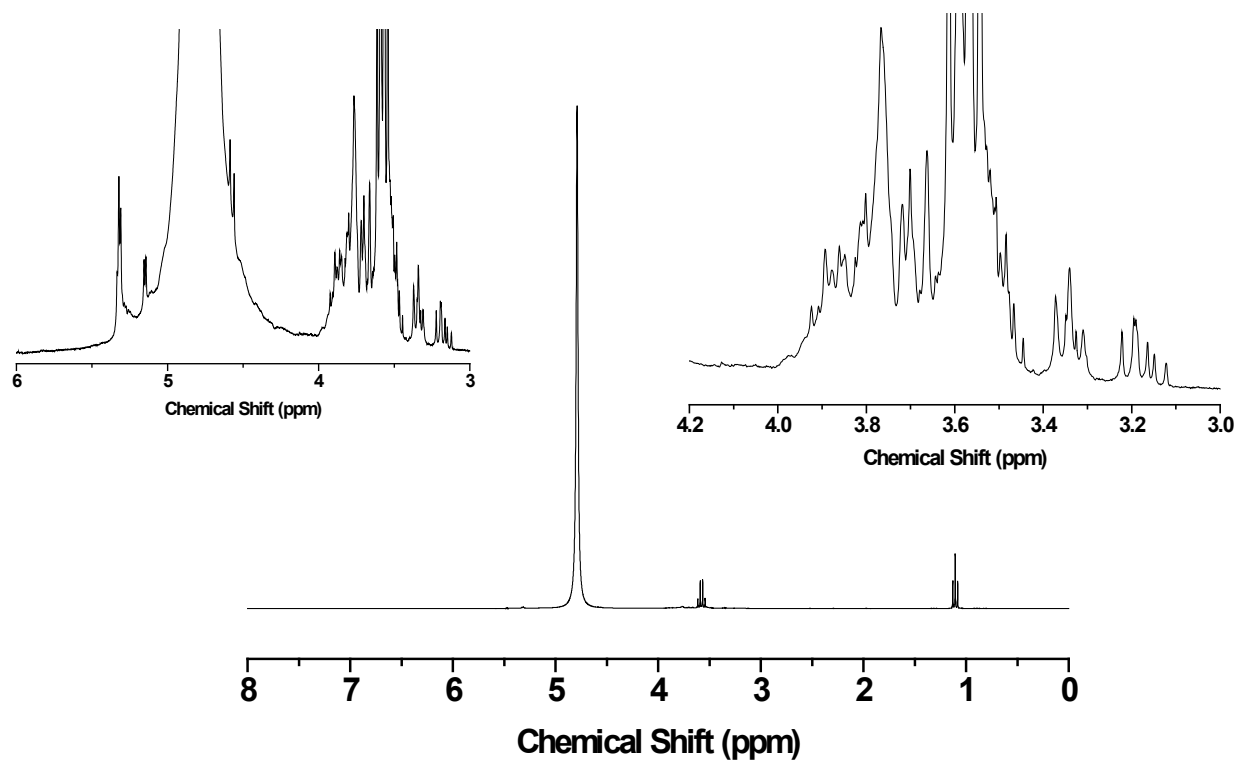


Figure S2d: ^1H NMR of McEwan's Champion in D_2O .

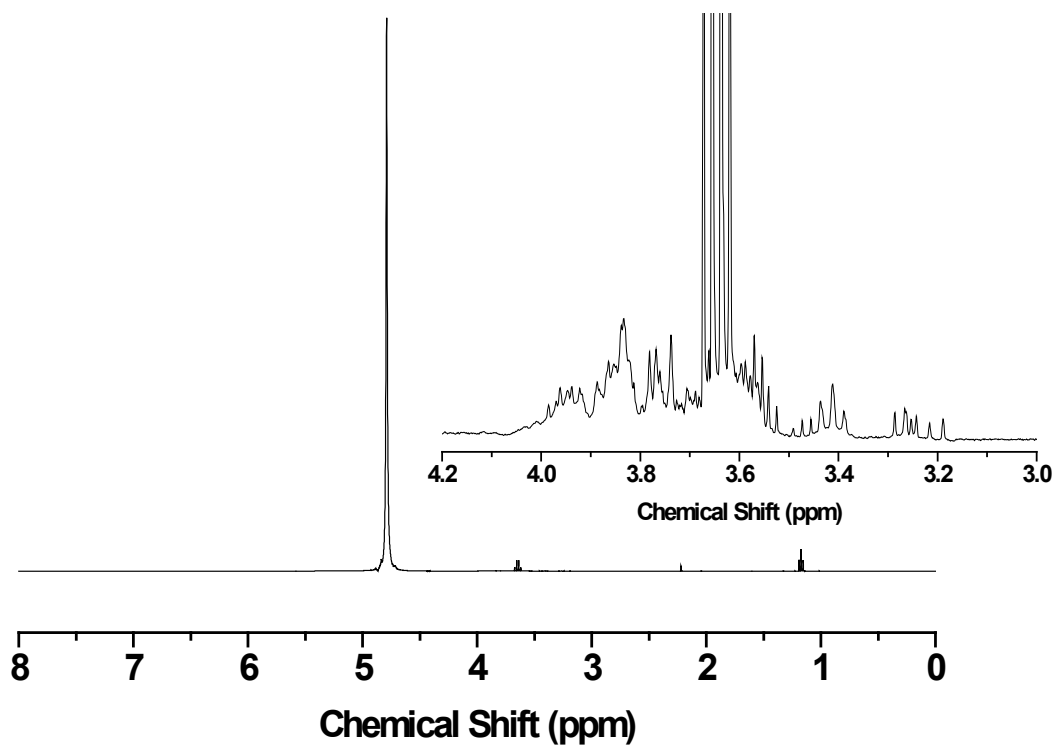


Figure S2e: ^1H NMR of Banks' Mild in D_2O .

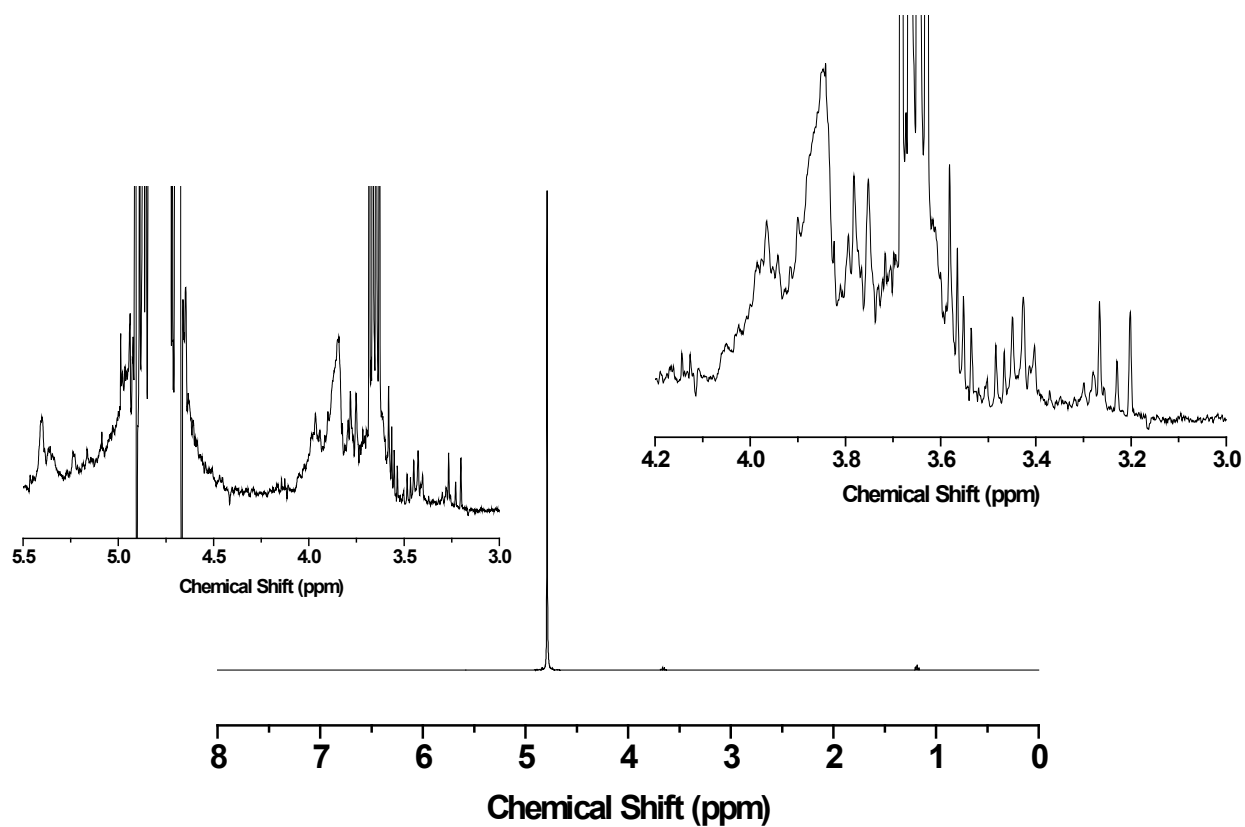


Figure S2f: ^1H NMR of Alpha beer in D_2O .

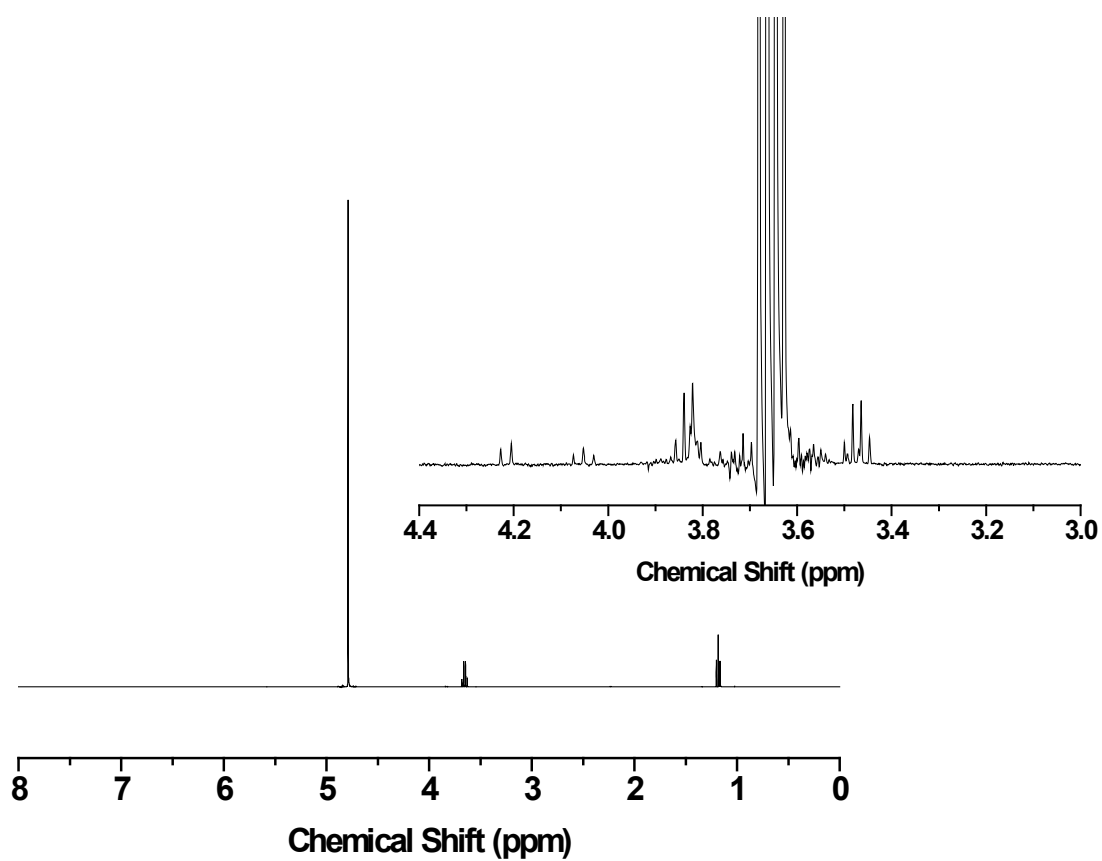


Figure S2g: ^1H NMR of Ouzo in D_2O .

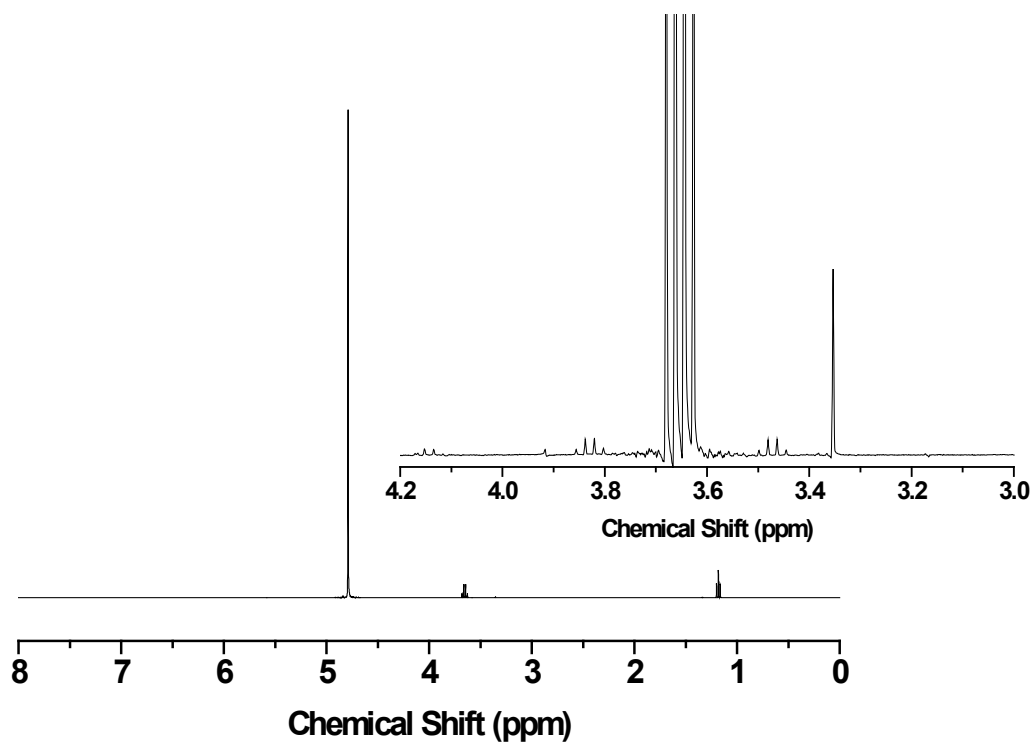


Figure S2h: ^1H NMR of homemade Romanian brandy in D_2O .

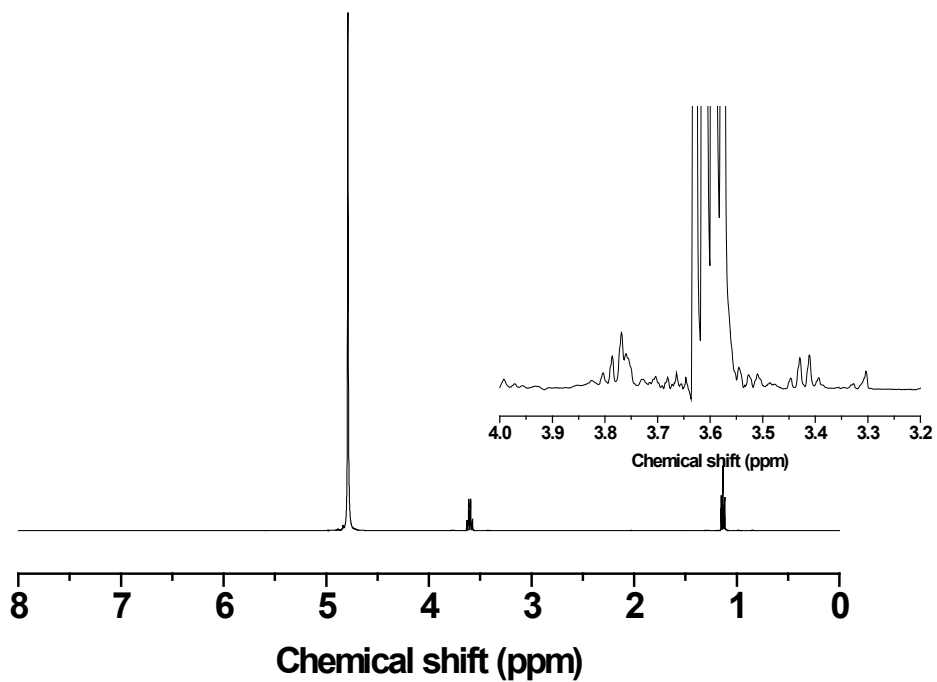


Figure S2i: ^1H NMR of Napoleon brandy in D_2O .

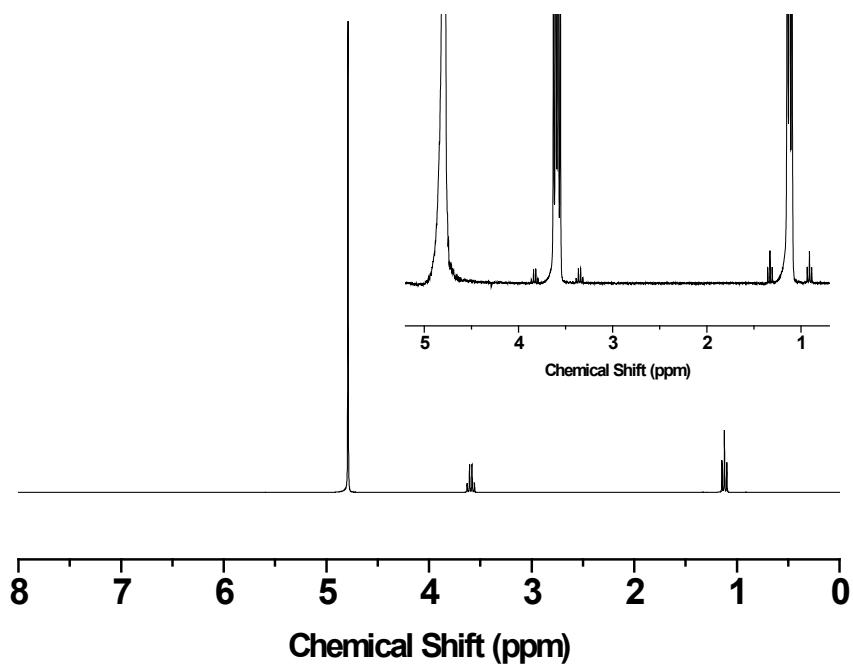


Figure S2j: ^1H NMR of Imperial vodka in D_2O .

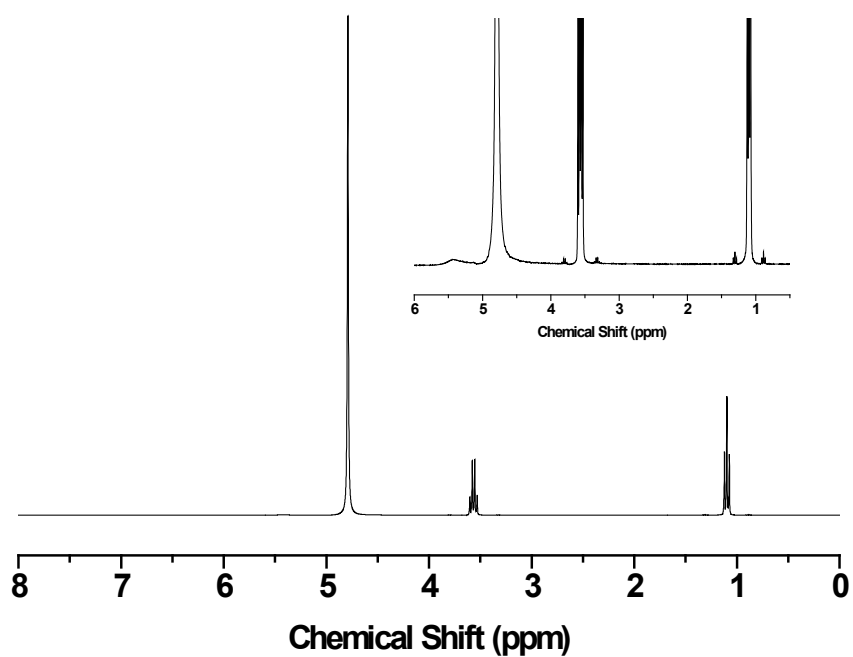


Figure S2k: ^1H NMR of Absolut Elyx vodka in D_2O

References

1. M. Ciampolini and N. Nardi, *Inorg. Chem.* 1966, **5**, 41-44.
2. J. Queffelec, S. G. Gaynor and K. Matyjaszewski, *Macromolecules*, 2000, **33**, 8629-8639.
3. S. Perrier, S. P. Armes, X. S. Wang, F. Malet and D. M. Haddleton, *J. Polym. Sci., Part A: Polym. Chem.*, 2001, **39**, 1696-1707.