Electronic Supplementary Information

for

Highly reactive α-bromoacrylate monomers and Michael acceptors by Cu(II)Br_2-dibromination of acrylates and instantaneous E2 by ligand

Adrian Moreno,[a,b] Jãnis Lejnieks,[a] Liang Ding,[a] Silvia Grama,[a] Marina Galià,[b] Gerard Lligadas,[a,b] and Virgil Percec[a]

[a]Roy & Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323, United States
[b]Laboratory of Sustainable Polymers, Department of Analytical Chemistry and Organic Chemistry, University Rovira i Virgili, Tarragona, Spain

*Correspondence to: V. Percec (E-mail: percec@sas.upenn.edu)

Experimental

Materials

Methyl acrylate (MA) (99%) and butyl acrylate (BA) (99+%) both from Acros were passed over a short column of basic Al_2O_3 before use to remove the radical inhibitor. Cu(II)Br_2 (99%, Alfa Aesar), Cu(II)Cl_2 (98%, Fluka), tris(2-aminoethyl)amine (TREN, 99%, Acros) and $CDCl_3$ (99.8%, Cambridge Isotope Laboratories Inc) were used as received. Acetonitrile (99.5+%, EMD Chemicals Inc) was distilled before use. Hexamethylated tris(2-aminoethyl)amine (Me_6-TREN) was synthesized following a literature procedure.[1]

Techniques

500 MHz ^{1}H-NMR spectra were recorded on a Bruker DRX500 NMR instrument at 28 °C in $CDCl_3$ containing tetramethylsilane (TMS) as internal standard.

Typical procedure for the Cu(II)Br_2-promoted dibromination of MA or BA in acetonitrile

Cu(II)Br_2 (0.1 g, 0.448 mmol) was weighted in a vial containing a magnetic stirring bar, both dried overnight in an oven, and deoxygenized by purging with N_2 for 10 min at 25 ºC. In another vial acetonitrile (1 mL) and monomer (MA 21 µL, or BA 32 µL, 0.224 mmol) were added and the mixture was deoxygenized by bubbling with N_2 for 30 min at 0 ºC. Then, the deoxygenized mixture of monomer and acetonitrile was transferred via a degassed syringe and added under N_2 on top of the Cu(II)Br_2, to start the reaction. Samples of 0.1 mL were periodically withdrawn from the reaction mixture, diluted in $CDCl_3$, filtered over cotton to immediately record the ^{1}H-NMR spectra. Further experiments showed that this reaction can be carried out in the presence of oxygen. The conversion of MA or BA onto methyl 2,3-dibromopropionate or butyl 2,3-dibromopropionate was calculated by comparison of integrals (∫) from the ^{1}H-NMR spectra as follows:

$$\text{Conversion (\%)} = \left(\frac{\int Ha'}{\int Ha' + \int Ha} \right) * 100 .$$

Typical procedure for the base-promoted dehydrobromination of methyl 2,3-dibromopropionate mediated by Me_6-TREN or TREN

Methyl 2,3-dibromopropionate (1.89 µL, 0.015 mmol), 0.6 mL $CDCl_3$ and ligand (TREN 0.74 µL, or Me_6-TREN 1.33 µL, 0.005 mmol) were placed in an NMR tube. The reactions were monitored by ^{1}H-NMR.

References

[1] M. Ciampolini and N. Nardi, *Inorg. Chem*. 1966, **5**, 41–44.