Ambient temperature rapid SARA ATRP of acrylates and methacrylates in alcohol–water solutions mediated by a mixed sulfite/Cu(II)Br$_2$ catalytic system

Carlos M. R. Abreu,$^a$ Arménio C. Serra,$^a$ Anatoliy V. Popov,$^b$ Krzysztof Matyjaszewski,$^c$ Tamaz Gulishvili$^{*d}$ and Jorge F. J. Coelho$^*$

Author affiliations

Abstract

The new generation of catalytic systems for Controlled/“Living” Radical Polymerization (CLRP) of vinyl monomers should be non-toxic, inexpensive and provide fast polymerizations in environmentally friendly media. Herein, we report the successful ambient temperature ATRP of several vinyl monomers (MA, $n$-BA, MMA and DMAEMA) catalyzed by inorganic sulfites (Na$_2$S$_2$O$_4$ and Na$_2$S$_2$O$_3$) and small amounts of a Cu(II)Br$_2$/Me$_6$TREN system in alcohol–water mixtures. The controlled character of ATRP of acrylates and methacrylates was confirmed by the linear increase of molecular weights with monomer conversion, narrow molecular weight distributions ($M_W/M_N \sim 1.05$) and by reinitiation experiments (copolymerization and chain extension). $^1$H NMR and MALDI-TOF analyses confirmed the molecular structure and chain-end functionality of the obtained polymers. ATRP of MA using this novel catalytic system in alcohol–water mixtures with multifunctional Br-based initiators provides 4 and 6 arm star polyacrylates in a controlled manner without any observable gel formation. The data presented open up the possibility of using fast ATRP catalyzed by inorganic sulfites (approved by FDA as food and beverage additives) in solvents that are inexpensive, eco-friendly and widely used in chemical industrial processes.
Eco-friendly ATRP

Sulfites (Na₂S₂O₅ or Na₂S₂O₇)

ppm Cu(i)Br₂/M₆TREN

Low $M_n/M_w$

MA MMA $\cdot$ BA $\cdot$ DMAEMA

Alcohol/Water r.t.