

SUPPORTING INFORMATION

Synthesis and use of a new alkene-functionalized SG1-based alkoxyamine

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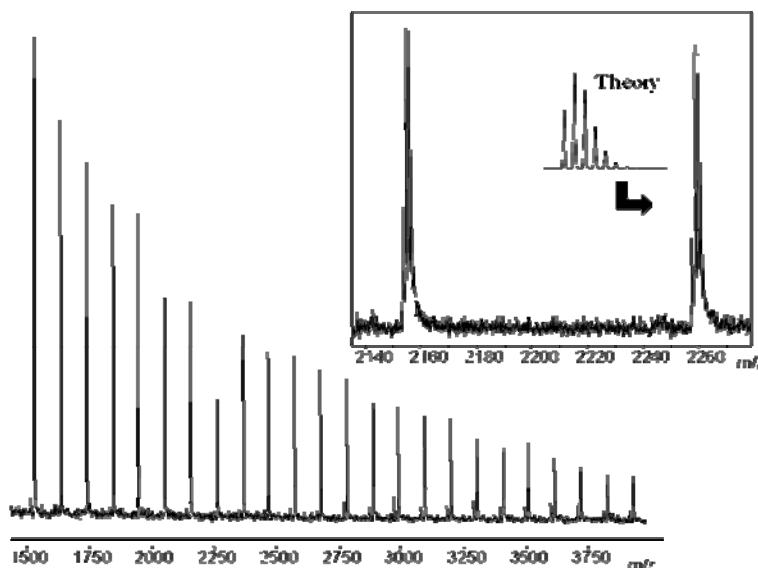


Figure SI-1. MALDI-TOF mass spectra with NaI salt/dithranol matrix in reflector mode of a polystyrene (P1' in Table 1) obtained by NMP initiated by MAMA-ene (sum of 1200 shots, in positive mode and with a laser repetition rate of 10.5 Hz).

Table SI-1. Comparison between the experimental and theoretical molar mass values of the monoisotopic peak of Na^+ -ionized polystyrene (P1' in Table 1) obtained by NMP with MAMA-ene initiator (Dithranol/NaI matrix in reflector mode)

n	Calcd mass	Expt mass	Formula
18	2049.23	2049.49	$\text{CH}_2=\text{CH}-(\text{CH}_2)_2-\text{NHCO-C(CH}_3)_2-$ $(\text{styrene})_{n-1}-\text{CH}_2\text{C}(\text{C}_6\text{H}_5)=\text{CH}_2, \text{Na}^+$
19	2153.29	2153.55	
20	2257.36	2257.62	

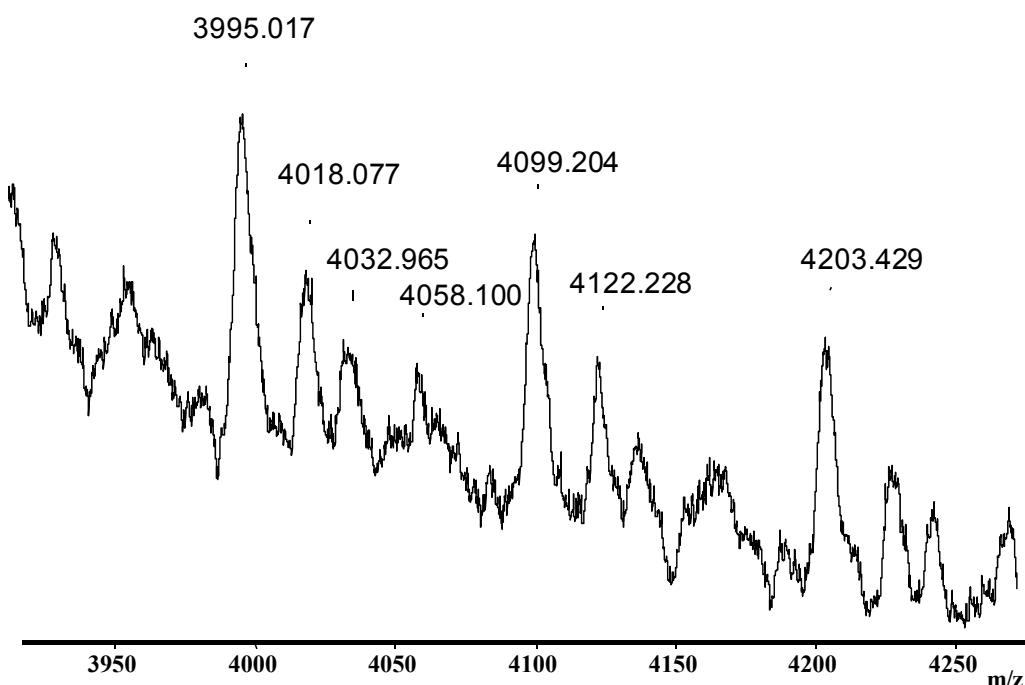


Figure SI-2. MALDI-TOF mass spectrum with DHB matrix in linear mode of a polystyrene (P1' in Table 1) obtained by NMP initiated by MAMA-ene (sum of 2500 shots, in positive mode and with a laser repetition rate of 10.5 Hz).

Table SI-2. Comparison between the experimental and theoretical molar mass values (major series) of the H⁺-ionized polystyrene obtained by NMP with MAMA-ene as the initiator (DHB matrix in linear mode)

n	Calcd mass	Expt mass	Formula
34	3976.74	3995.02	$\text{CH}_2=\text{CH}-(\text{CH}_2)_2-\text{NHCO-C(CH}_3)_2-$ (styrene) _{n-1} -CH ₂ C(C ₆ H ₅)-SG1, H ⁺
35	4080.89	4099.20	
36	4185.04	4203.43	

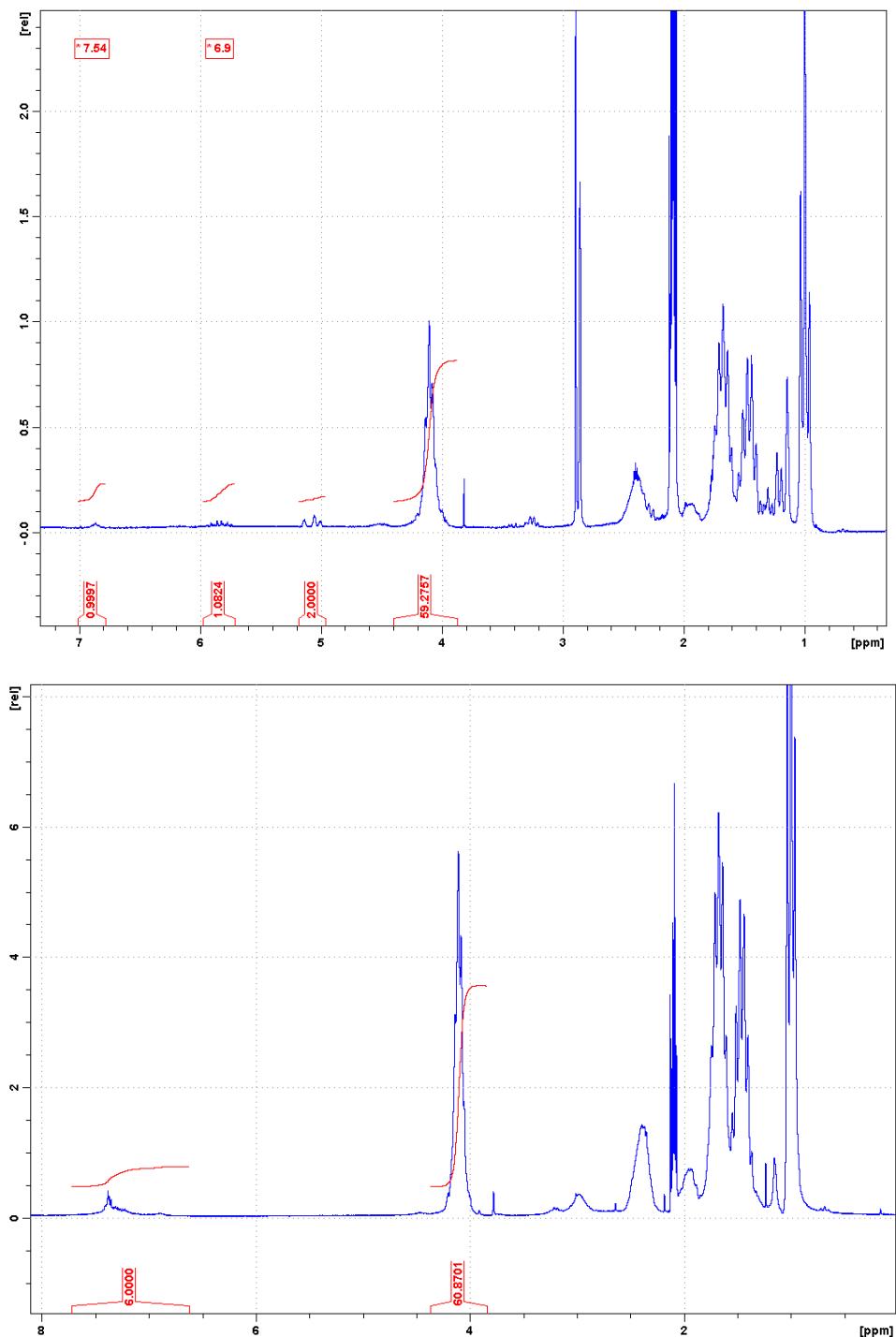


Figure SI-3. ¹H NMR spectra in acetone-d₆ of the alkene chain-end functionalized poly(*n*-butyl acrylate) (P3''', $M_n, SEC = 2391 \text{ g.mol}^{-1}$, PDI = 1.7) (top) and the product after the thiol-ene coupling with benzyl mercaptan and after purification by dialysis (bottom)