10.1071/CH17570_AC
©CSIRO 2018
Australian Journal of Chemistry 2018, 71(5), 334-340

Supplementary Material

Coordination Initiated – Nitroxide Mediated Polylerization (CI-NMP)

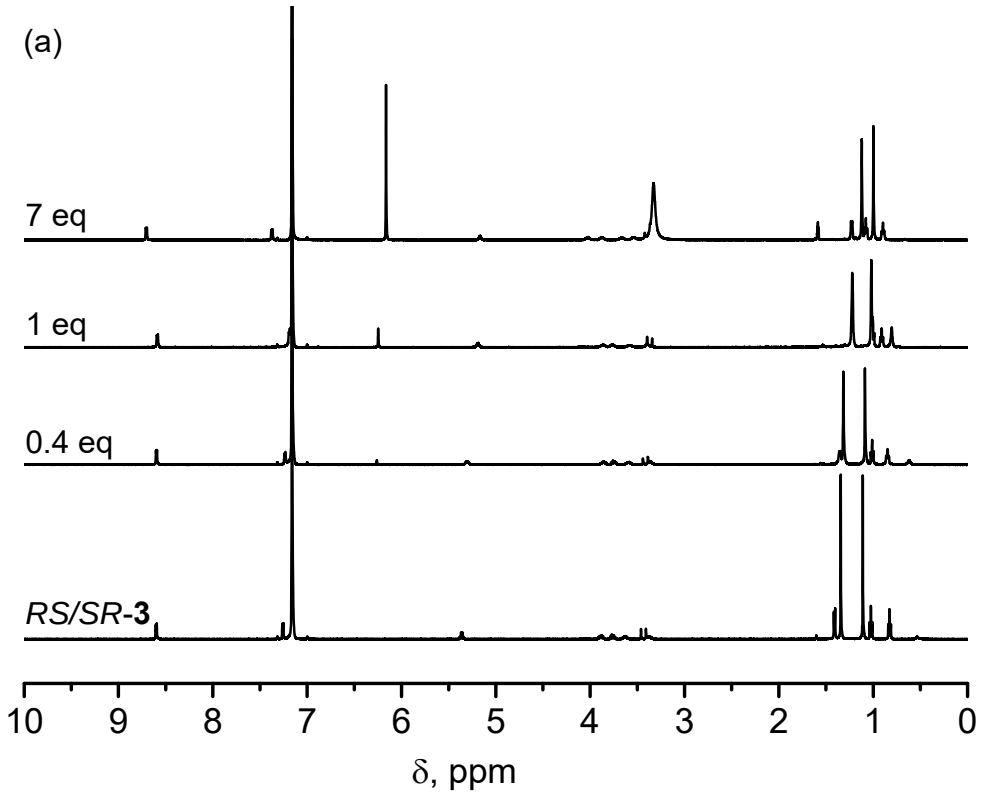
Gérard Audran,[a] Elena Bagryanskaya,[b,c] Mariya Edeleva,[b,c] Sylvain R. A. Marque,[a,b]* Dmitriy Parkhomenko,[b] Evgeny Tretyakov,[b,c] and Svetlana Zhivetyeva[b]

[a] Aix Marseille Univ, CNRS, ICR, UMR 7273, case 551, Avenue Escadrille Normandie-Niemen, 13397 Marseille Cedex 20 France.

[b] N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry SB RAS, Pr. Lavrentjeva 9, 630090 Novosibirsk, Russia.

[c] Novosibirsk State University, 2 Pirogova Str., Novosibirsk, 630090, Russia.

*E-mail: sylvain.marque@univ-amu.fr



(b)

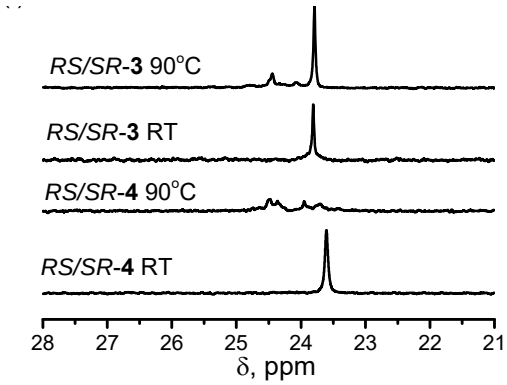


Figure S1. (a) ^{1}H NMR spectra of alkoxyamine *RS/SR*-**3** upon addition of $Zn(hfac)_2$ in C_6D_6; (b) ^{31}P NMR spectra of *RS/SR*- **4** and *RS/SR*-**3** at room temperature and at 90 °C in *n*-butyl acrylate (ABU).

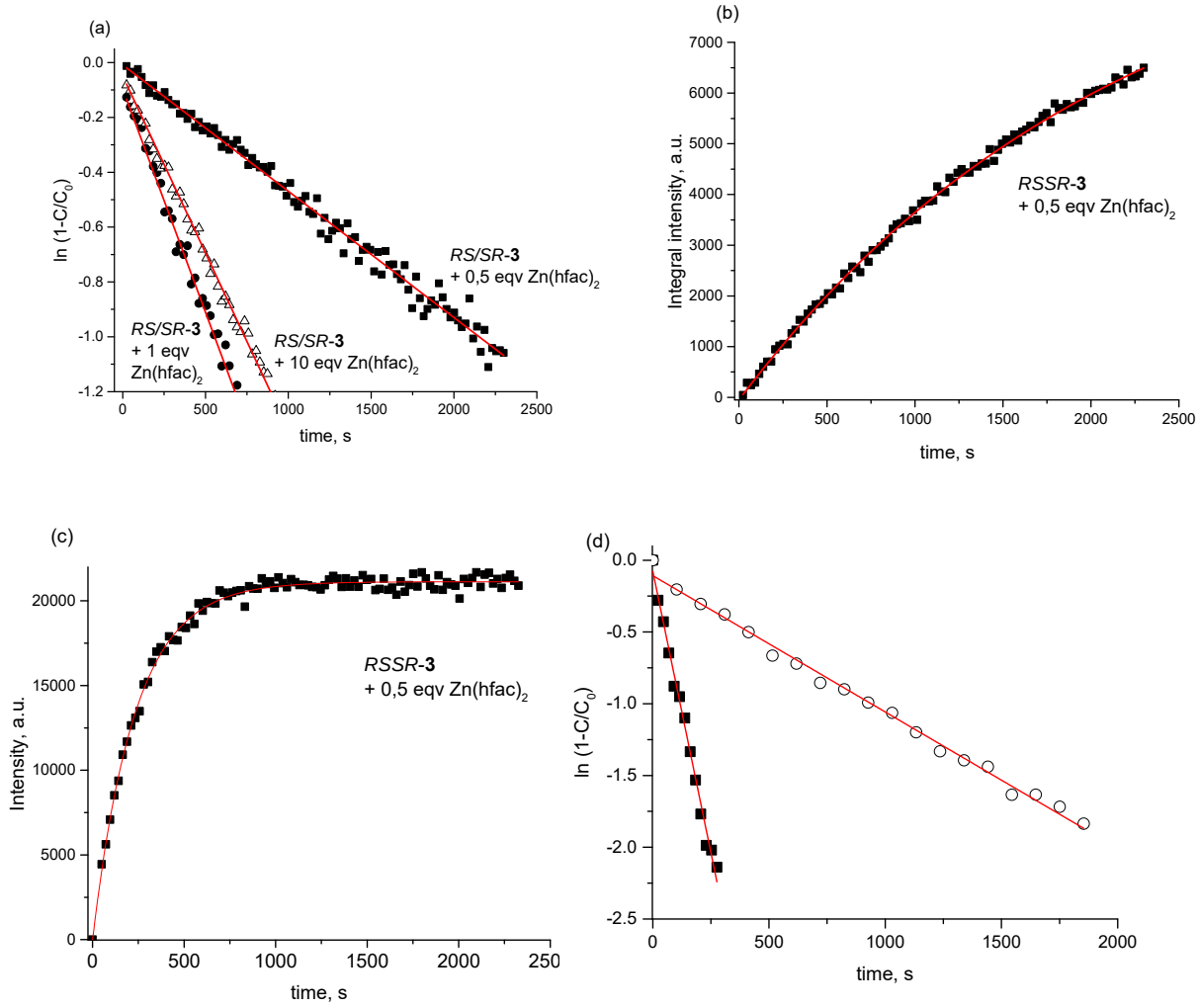


Figure S2. (a) Kinetics of C-ON bound homolysis at 80 °C for *RS/SR*-**3** upon addition of $Zn(hfac)_2$: (■) – 0.5 eq.,(●) – 1 eq, (Δ) – 10 eq, linear fit - (line). Kinetics of C-ON bound homolysis at 80 °C for *RS/SR*-**3** upon addition of 0.5 eq. $Zn(hfac)_2$ at 80 °C (b) and 100 °C (c), (d) *RS/SR*-**3 +** 1 eq of $Zn(hfac)_2$ (■) and *RS/SR*-**3** (○) in ABU at 100 °C.

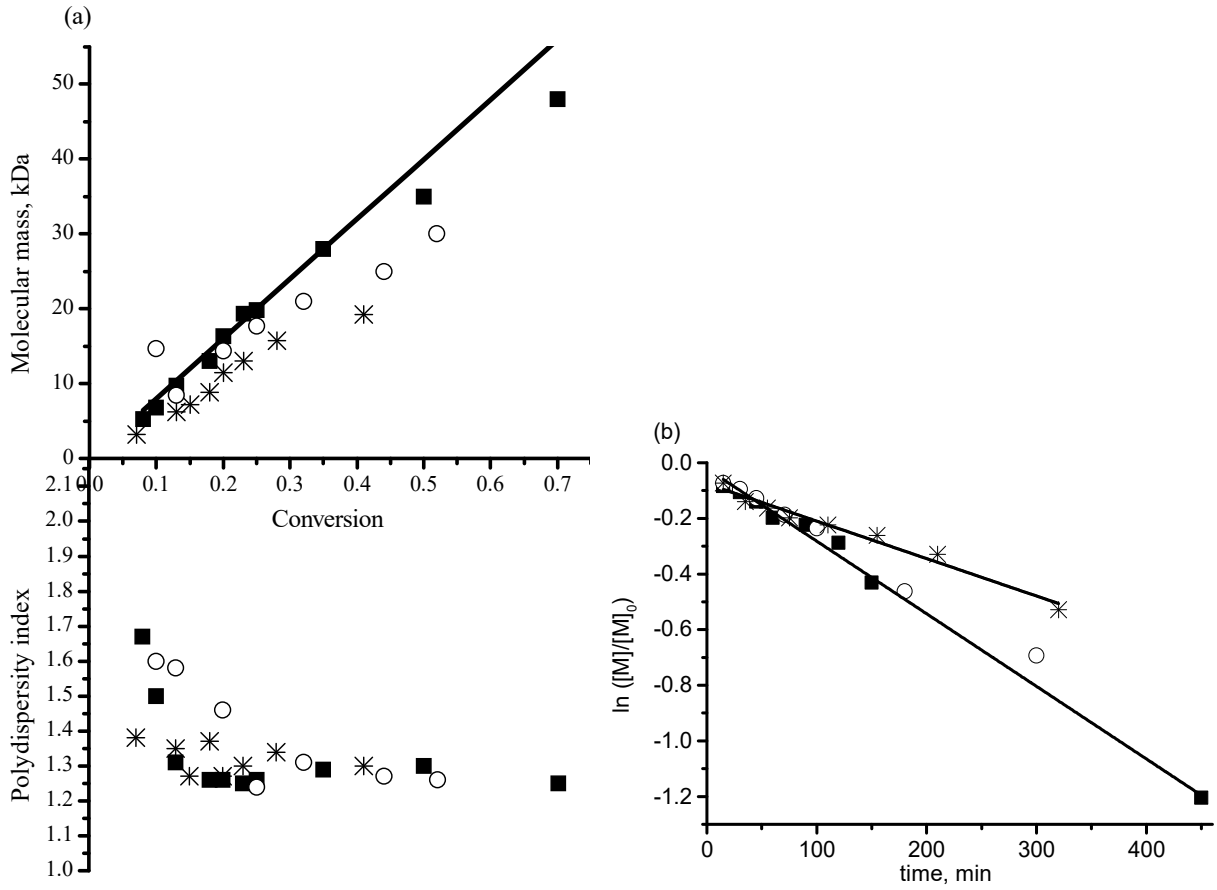


Figure S3. (a) Mn *vs* conversion, PDI *vs* conversion, and (b) ln([M]/[M]$_0$) *vs* time plots for the polymerization of styrene at 110 °C initiated with: *RS/SR*-**3 (*)**, **4** (■), **4** + 1 eq. pyridine (○), monomer to initiator ratio is 800 to 1.

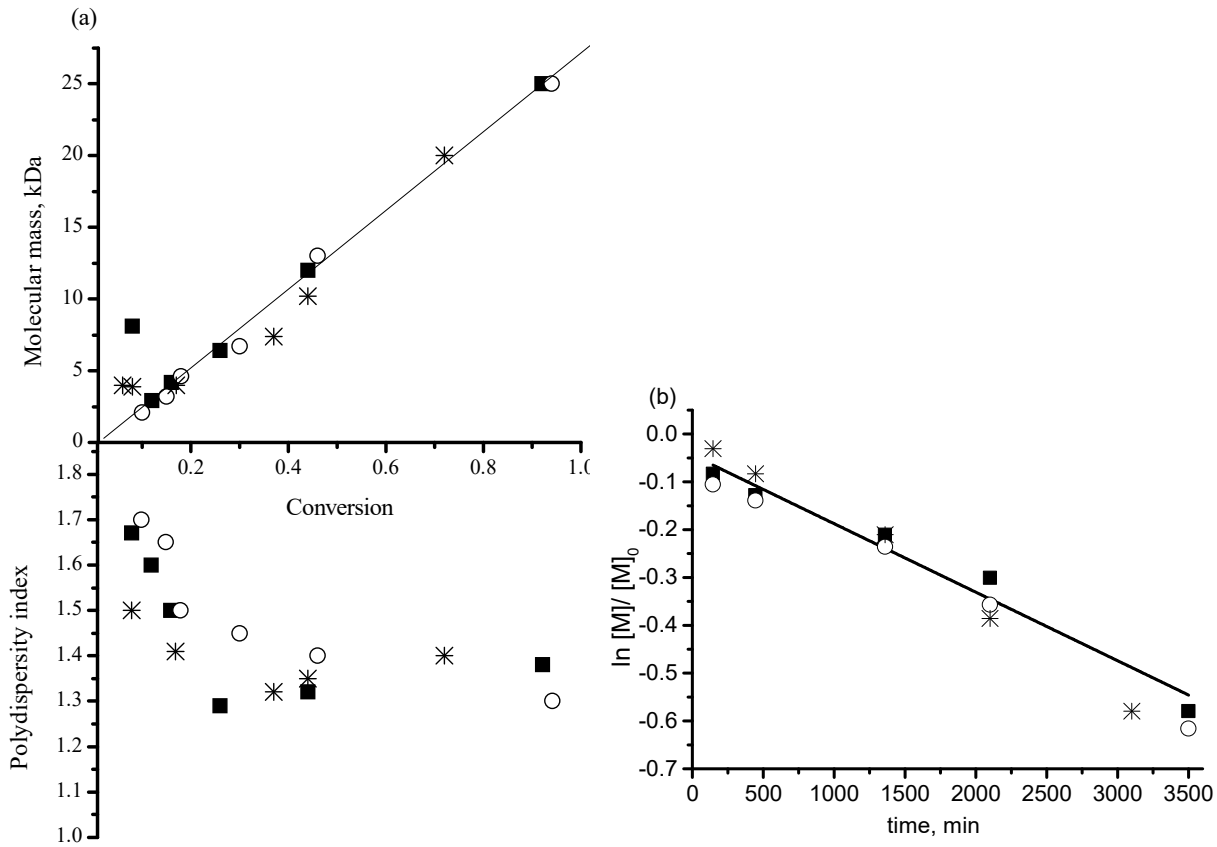


Figure S4. Mn *vs* conversion, PDI *vs* conversion, and ln([M]/[M]$_0$) *vs* time plots for (a) the polymerization of butyl acrylate at 90 °C initiated with: *RS/SR*-**3 (*)**, **4** (■), **4** + 1 eq. Zn(hfac)$_2$ (○), monomer to initiator ratio is 800 to 1.

Table S1. The values of C-ON bound hemolysis rate constants for the compounds under investigation.

Compound	**Conditions**	**k_d x10^3, s^{-1}**	**E_a, kJ/mol**	**Ref**
RS/SR-**3**	Pure[a]	0.15	123.0	1
RS/SR-**4**	Pure[a]	2.1	115.0	2
RS/SR-**3**	0.5 eqv $Zn(hfac)_2$[b]	0.5	119.0	This work
RS/SR-**3**	1 eqv $Zn(hfac)_2$[b]	1.7	116.0	This work
RS/SR-**3**	10 eqv $Zn(hfac)_2$[b]	1.3	116.5	This work
RS/SR-**3**	Pure[c]	0.95	124.0	This work
RS/SR-**3**	1 eqv $Zn(hfac)_2$[c]	8.0	117.5	This work

[a] In *t*-BuPh. k_d estimated at 80 °C. [b] In toluene, measured at 80 °C. [c] In n-butyl acrylate, measured at 100 °C.

Procedure for measurement of k_d

EPR experiments were performed on SpinScan EPR machine (ADANI) equipped with temperature control unit. The values of k_d were measured by recording ESR spectra upon heating of 10^{-4} M toluene solutions of *RS/SR*-**3** in the presence of 3 equivalents of 2,2,6,6-tetramethylpiperidin-*N*-oxyl radical (TEMPO) as alkyl radical scavenger. Solutions were degassed by three cycles of freeze-pump-thaw (residual pressure of 0.1 mbar) and sealed under argon atmosphere prior to measurements to gain narrow ESR signals of SG1 nitroxide generated in the course of heating and to overcome decomposition reaction of SG1 in the presence of oxygen.

Profiles of the relative concentration are obtained by integration of the low field EPR line of **SG1** and the data are fitted linear in semi logarithmic coordinates with eq.

$$ln\frac{[C]_0-[C]}{[C]_0} = -k_d t.$$

The values of k_d are presented in Table 1SI. Activation energies E_a are given by the Arrhenius equation using the value of 2.4 10^{14} s^{-1} as frequency factor A_0.[3]

$$k_d = A_0 \times e^{-\frac{E_a}{RT}}$$

References

[1] Brémond, P.; Koïta, A.; Marque, S. R. A.; Pesce, V.; Roubaud, V.; Siri D. Chemically Trigerred C—ON Bond Homolysis of Alkoxyamines. Quaternization of the Alkyl Fragments. *Org. Lett.* **2012**, *14*, 1, 358-361.

[2] Audran, G.; Bagryanskaya, E.; Bagryanskaya, I.; Edeleva, M.; Marque, S. R. A.; Parkhomenko, D.; Tretyakov, E. Zhivetyeva, S. Zinc(II) Hexafluoroacetylacetonate Complexes of Alkoxyamines: NMR and Kinetic Investigations. First Step for a New Way to Prepare Hybrid Materials *Chem. Select* **2017**, *2*, 3584-3593.

[3] Bagryanskaya, E. G.; Marque, S. R. A. RSC Polymer Chemistry Series, n°=19, Nitroxide Mediated Polymerization: From Fundamentals to Applications in Materials Sciences Gigmes, D., Ed., Royal Society of Chemistry, **2016**, chapter 2, 45-113