

SUPPLEMENTARY INFORMATION

**Syndiotactic- and heterotactic-specific radical polymerization of
N-*n*-propylmethacrylamide complexed with alkali metal ions**

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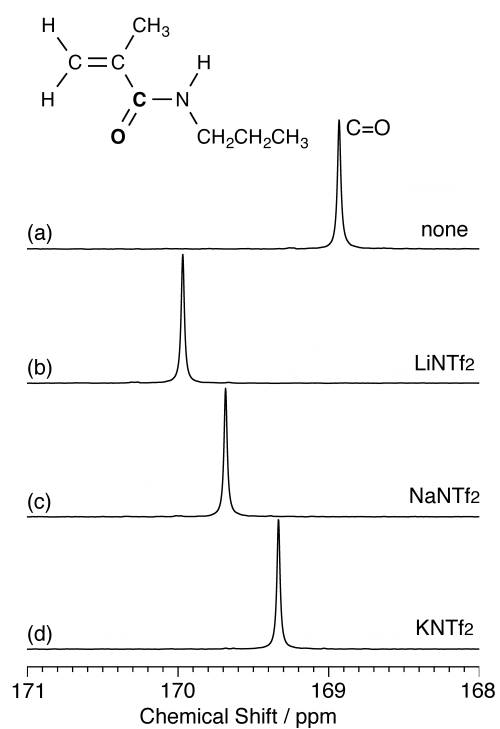


Fig. S1. Expanded ^{13}C NMR spectra of the C=O carbons of NNPMAAm ($2.0 \text{ mol}\cdot\text{L}^{-1}$) in the presence or absence of a 0.5 mole equivalent of MNTf₂ measured in CD₃CN at 0 °C.

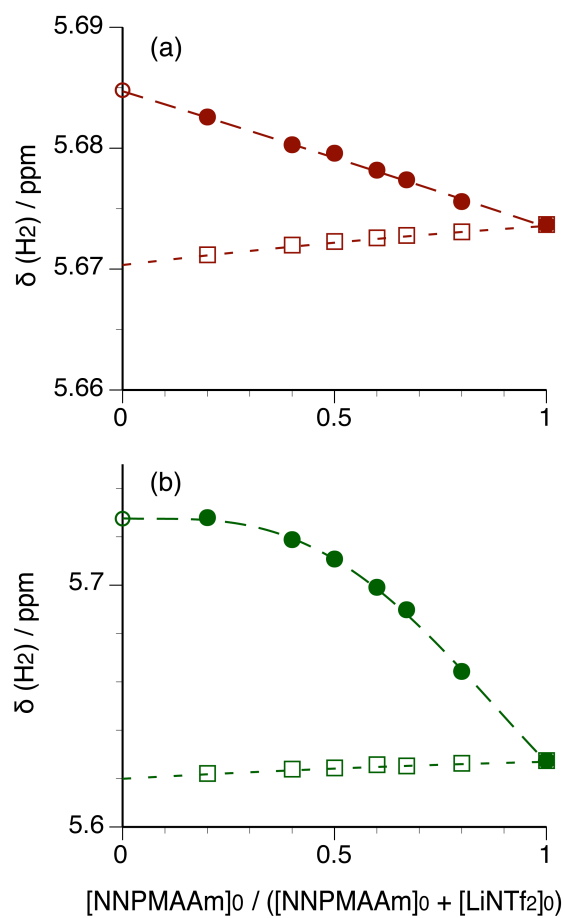


Fig. S2. Changes in the chemical shifts of the H₂ proton in the vinylidene group of NNPMAAm in the presence of LiNTf₂ in (a) CD₃OD and in (b) CD₃CN at 0 °C ($[\text{NNPMAAm}]_0 + [\text{LiNTf}_2]_0 = 0.25 \text{ mol}\cdot\text{L}^{-1}$). The plots marked (□) denote the chemical shifts of DMAAm alone at the corresponding concentration, whereas those marked (●) denote the chemical shifts for the saturated mixtures.

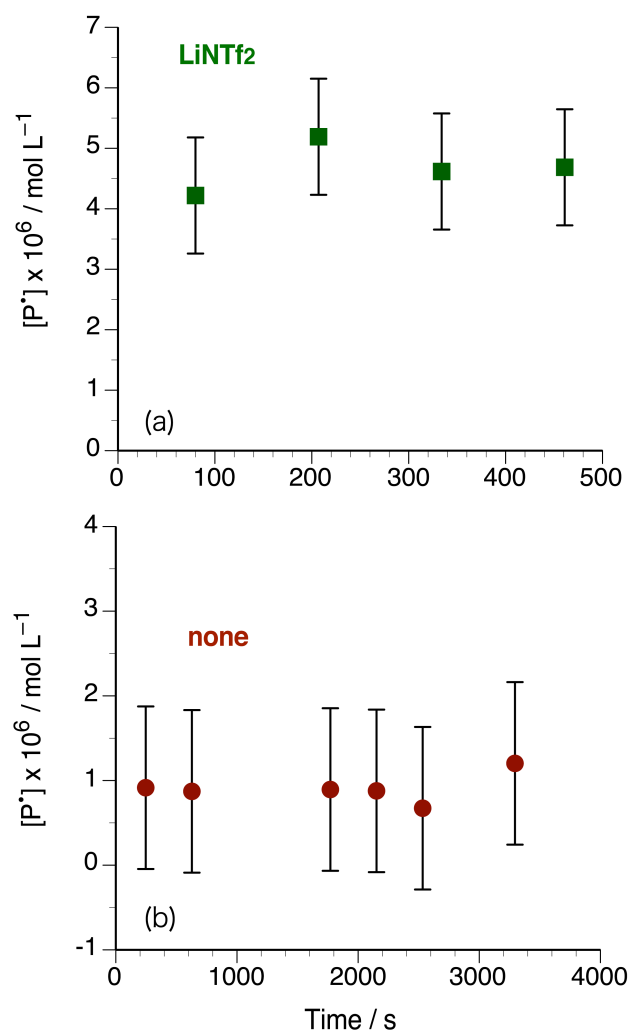


Fig. S3. Relationship between radical concentration and time in the NNPMAAm polymerization in CH_3CN at 0°C in the (a) presence and (b) absence of LiNTf_2 .

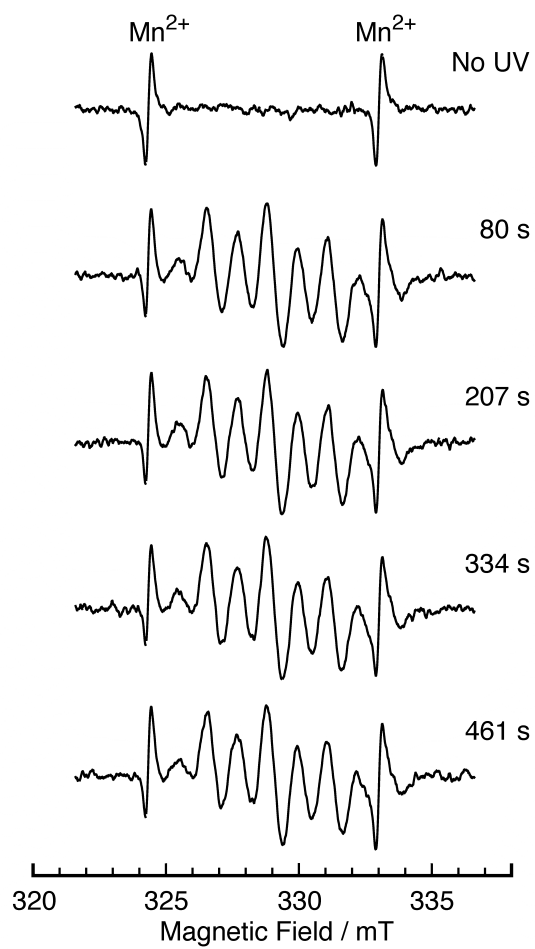


Fig. S4. ESR spectra of the NNPMAM polymerization in CH_3CN at $0\text{ }^\circ\text{C}$ in the presence of LiNTf_2 . Signals from the Mn^{2+} standard are shown at *ca.* 324 and 333 mT.

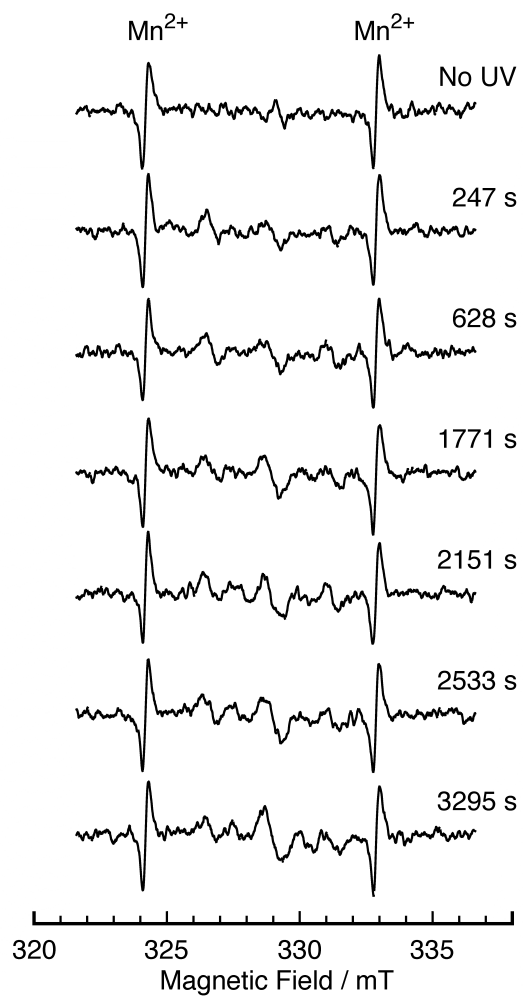


Fig. S5. ESR spectra of the NNPMAAm polymerization in CH_3CN at $0\text{ }^\circ\text{C}$ in the absence of $LiNTf_2$. Signals from the Mn^{2+} standard are shown at *ca.* 324 and 333 mT.

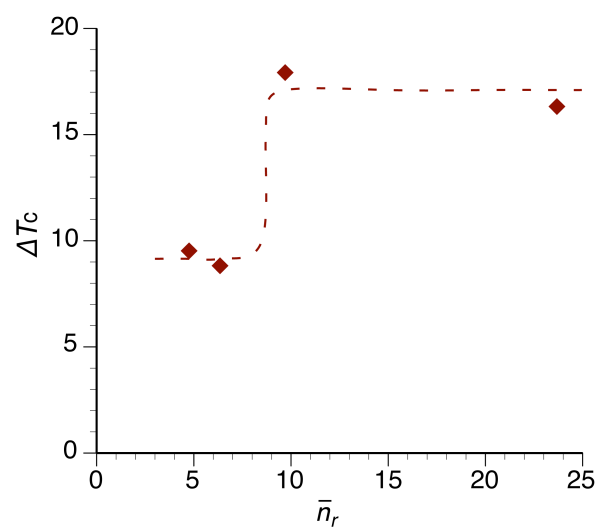


Fig. S6. Relationship between the ΔT_c and \bar{n}_r values in syndiotactic-rich poly(NNPMAAm)s.