Supplementary Information

Dual role for alkali metal cations in enhancing of low-temperature radical polymerization of N,N-dimethylacrylamide

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**Fig. S1** Relationship between the [LiNTf₂]/[DMAAm]₀ ratio and the polymer yield for the polymerization of DMAAm in toluene at −40 °C for 10 sec in the presence of LiNTf₂.
**Fig. S2** $^1$H NMR spectra of the main-chain methylene groups of poly(DMAAm)s obtained in toluene at $-40 \, ^\circ\text{C}$ for 10 sec in the presence of LiNTf$_2$: $[\text{LiNTf}_2]_0 = (\text{a}) \ 0.0 \ \text{mol L}^{-1}, \ (\text{b}) \ 0.1 \ \text{mol L}^{-1}, \ (\text{c}) \ 0.5 \ \text{mol L}^{-1}, \ (\text{d}) \ 1.0 \ \text{mol L}^{-1}$. The peaks marked with an asterisk (*) are impurities.
Fig. S3 $^1$H NMR spectra of the main-chain methylene groups of poly(DMAAm)s obtained at $-40^\circ$C in the presence or absence of LiNTf$_2$. 
Fig. S4 Changes in the $^{13}$C NMR chemical shifts of the C=O group and differences in the $^1$H NMR chemical shift of the $H_1$ and $H_2$ protons of the vinylidene group in DMAAm resulting from variations in the $[\text{LiNTf}_2]_0/\text{[DMAAm]}_0$ ratio.
**Fig. S5** Changes in the chemical shifts of the vinylidene proton \textit{cis} to the C=O group of DMAAm in the presence of LiNTf$_2$ (●), NaNTf$_2$ (▲) and KNTf$_2$ (■) ([DMAAm]$_0$ + [MNTf$_2$]$_0$ = 0.25 mol L$^{-1}$, in CD$_3$CN at 0 °C). The plot marked (×) denotes the chemical shift of DMAAm alone at the corresponding concentration.
Fig. S6 $^1$H NMR spectra of the main-chain methylene groups of poly(DMAAm)s obtained at −40 °C in the presence of LiCl or LiOTf. The peaks marked with an asterisk (*) are impurities.
Fig. S7 $^1$H NMR spectra of the main-chain methylene groups of poly(DMAAm)s obtained at $-40$ °C in the presence of NaNTf$_2$ or KNTf$_2$. 