Electronic Supplementary Material (ESI) for Polymer Chemistry.


**Supplementary Information**

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

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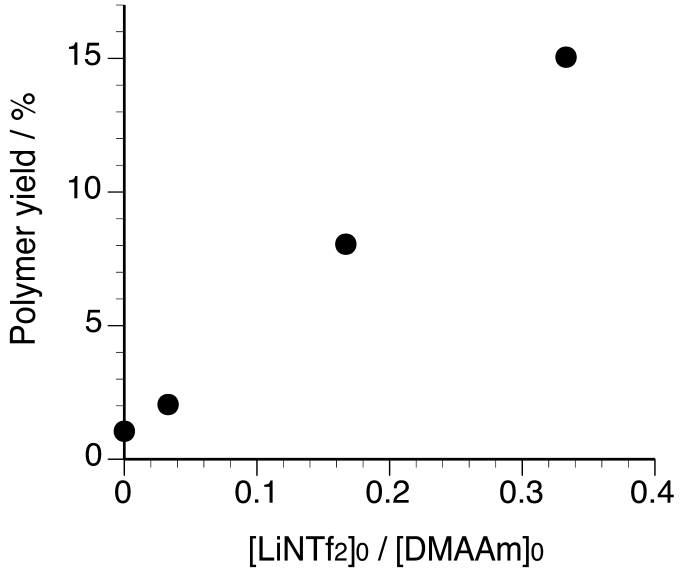


**Fig. S1** Relationship between the $[LiNTf_2]_0/[DMAAm]_0$ ratio and the polymer yield for the polymerization of DMAAm in toluene at −40 °C for 10 sec in the presence of $LiNTf_2$.

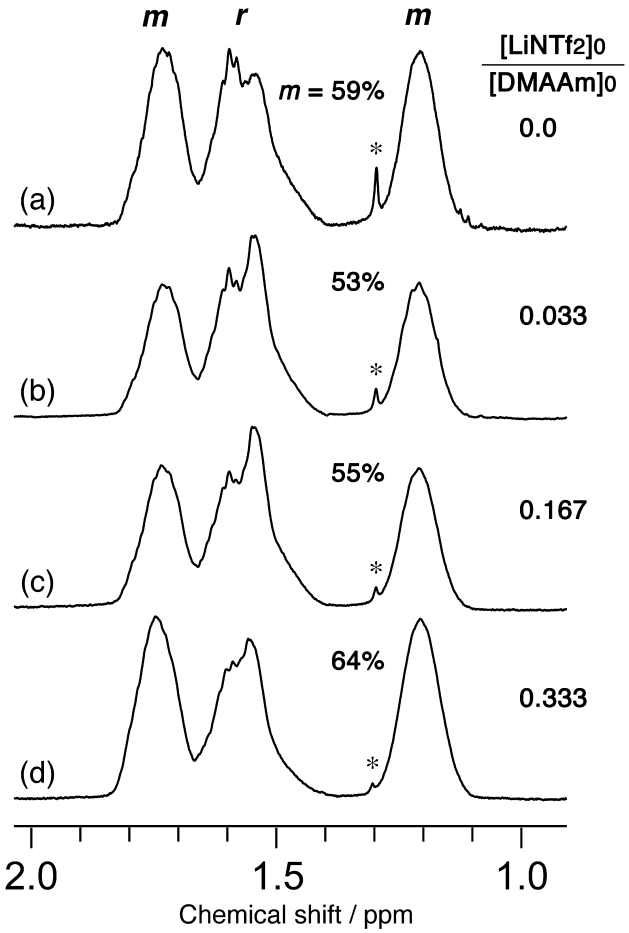


**Fig. S2** $^{1}$H NMR spectra of the main-chain methylene groups of poly(DMAAm)s obtained in toluene at −40 °C for 10 sec in the presence of $LiNTf_2$: $[LiNTf_2]_0$ = (a) 0.0 mol $L^{-1}$, (b) 0.1 mol $L^{-1}$ (c) 0.5 mol $L^{-1}$, and (d) 1.0 mol $L^{-1}$. The peaks marked with an asterisk (*) are impurities.

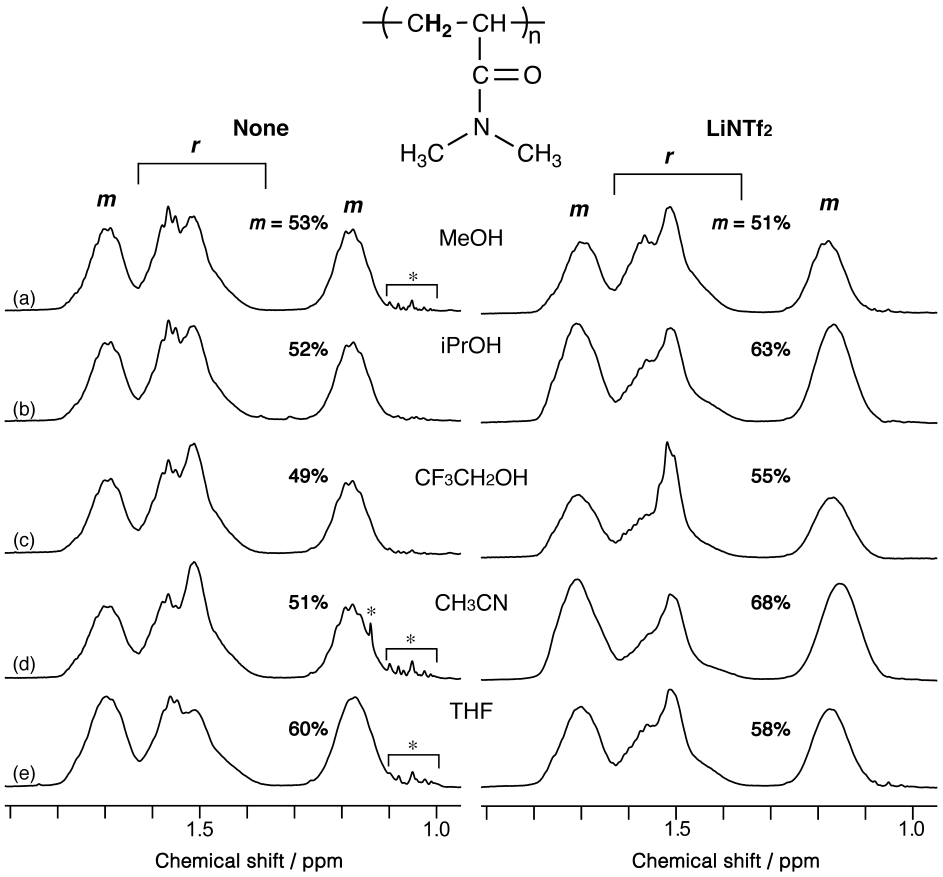


**Fig. S3** $^{1}$H NMR spectra of the main-chain methylene groups of poly(DMAAm)s obtained at −40 °C in the presence or absence of $LiNTf_2$.

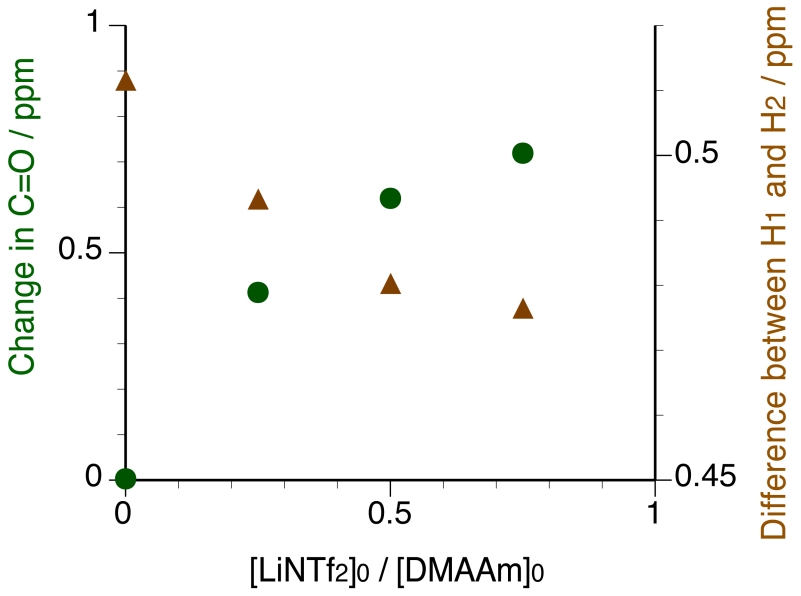


**Fig. S4** Changes in the $^{13}C$ NMR chemical shifts of the C=O group and differences in the $^{1}H$ NMR chemical shift of the $H_1$ and $H_2$ protons of the vinylidene group in DMAAm resulting from variations in the $[LiNTf_2]_0/[DMAAm]_0$ ratio.

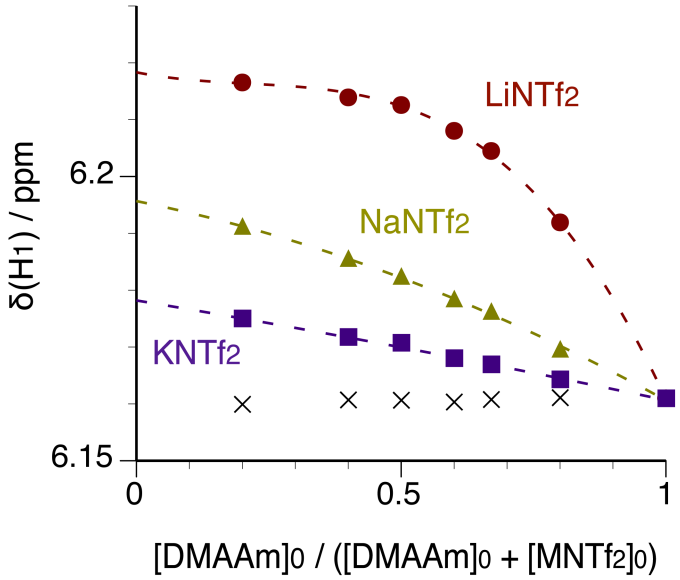


**Fig. S5** Changes in the chemical shifts of the vinylidene proton *cis* to the C=O group of DMAAm in the presence of $LiNTf_2$ (●), $NaNTf_2$ (▲) and $KNTf_2$ (■) ($[DMAAm]_0 + [MNTf_2]_0$ = 0.25 mol $L^{-1}$, in $CD_3CN$ at 0 °C). The plot marked (×) denotes the chemical shift of DMAAm alone at the corresponding concentration.

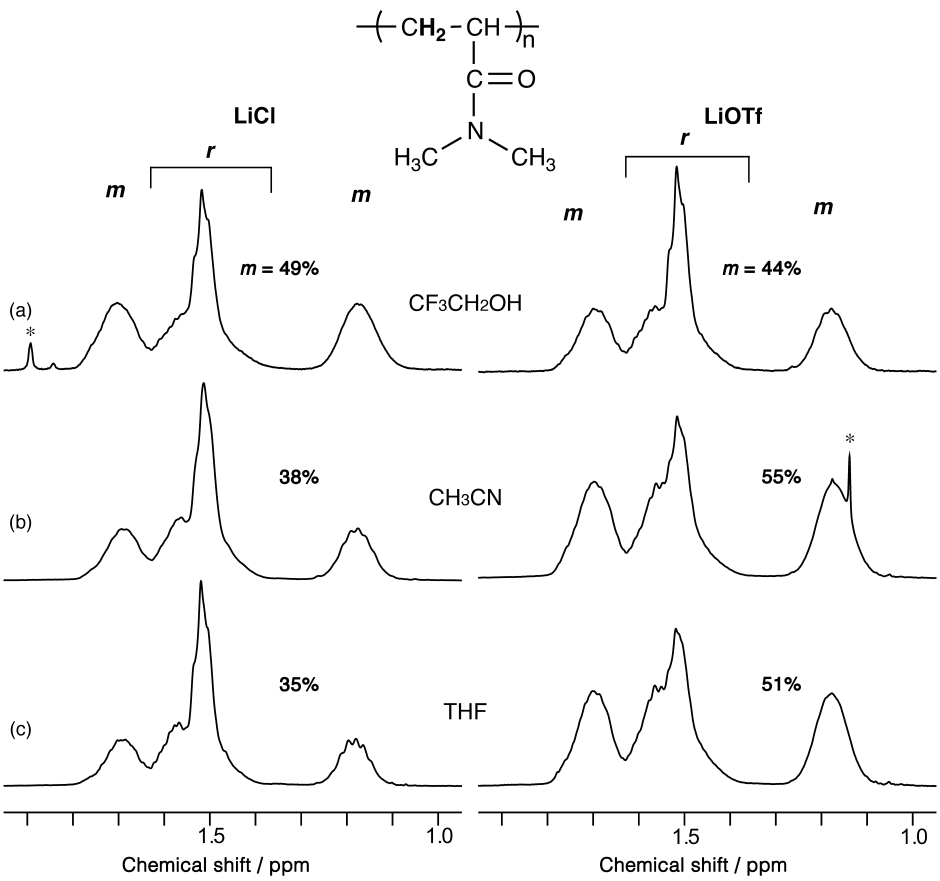


**Fig. S6** $^{1}$H NMR spectra of the main-chain methylene groups of poly(DMAAm)s obtained at −40 °C in the presence of LiCl or LiOTf. The peaks marked with an asterisk (*) are impurities.

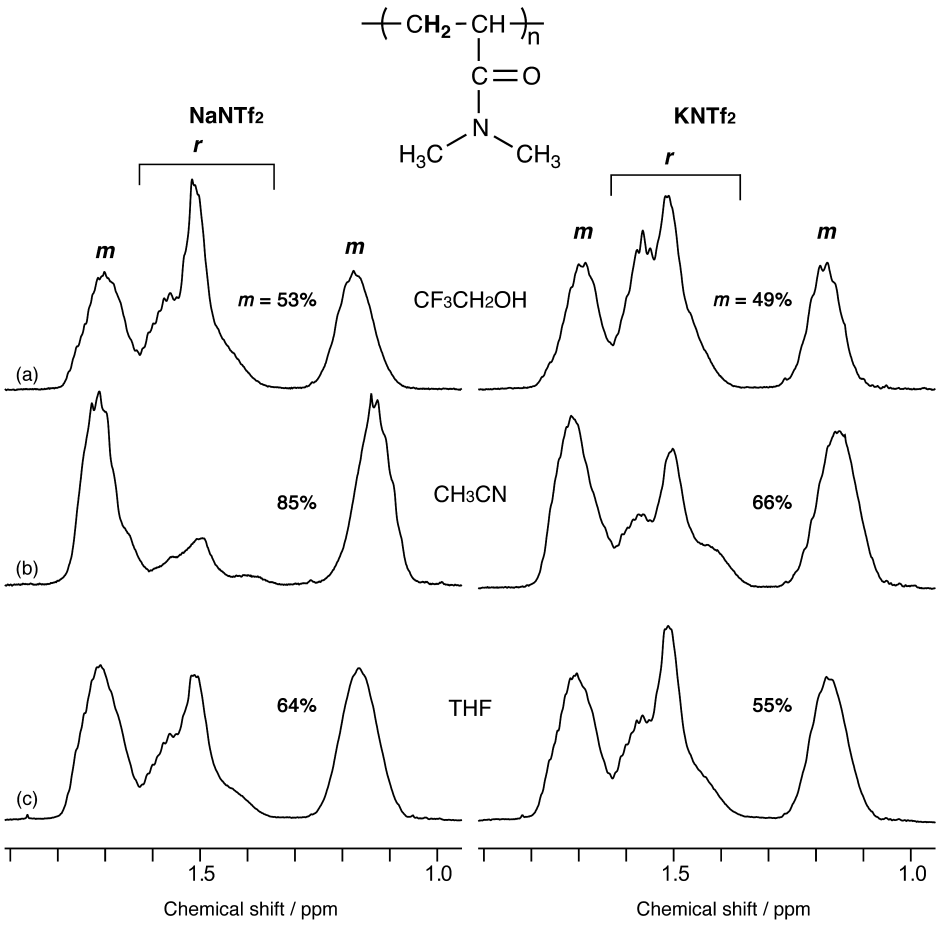


**Fig. S7** $^{1}$H NMR spectra of the main-chain methylene groups of poly(DMAAm)s obtained at −40 °C in the presence of $NaNTf_2$ or $KNTf_2$.