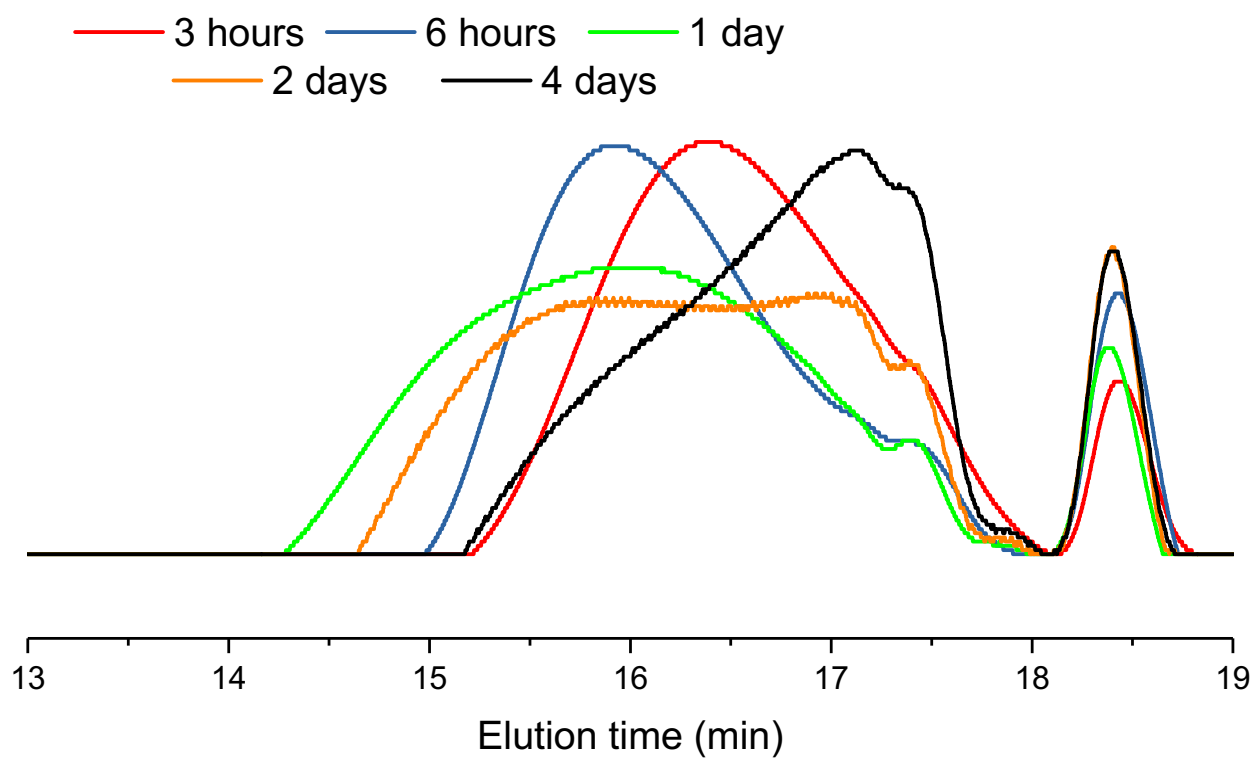
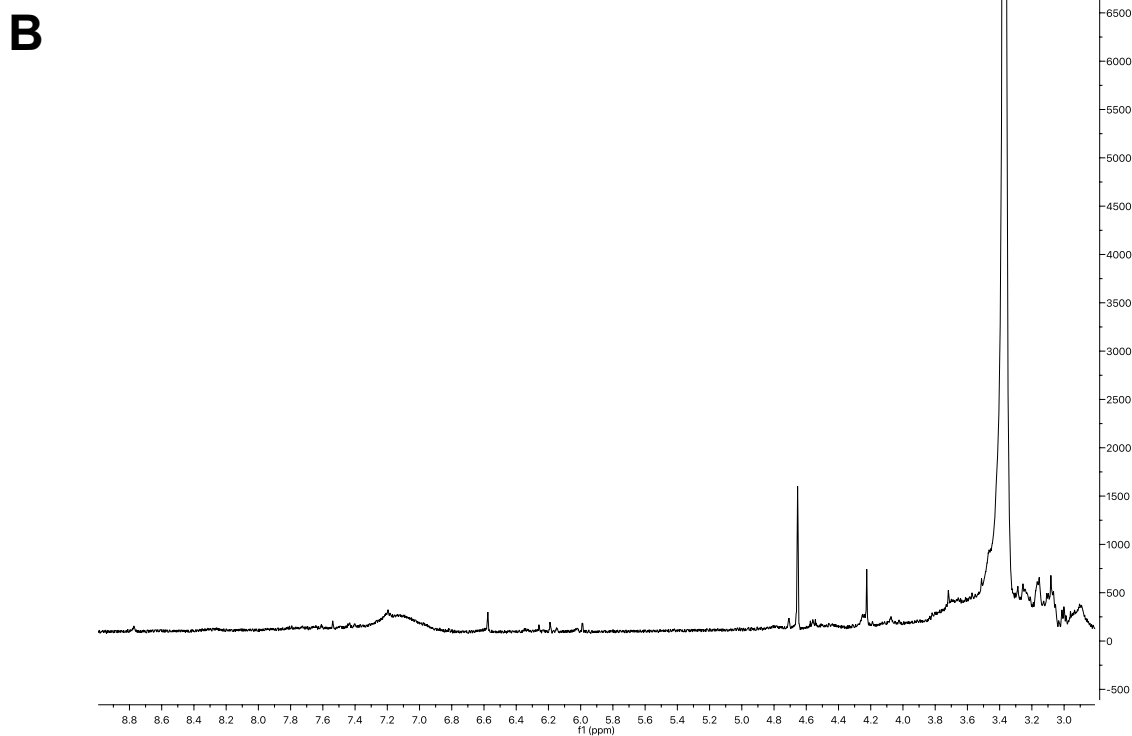
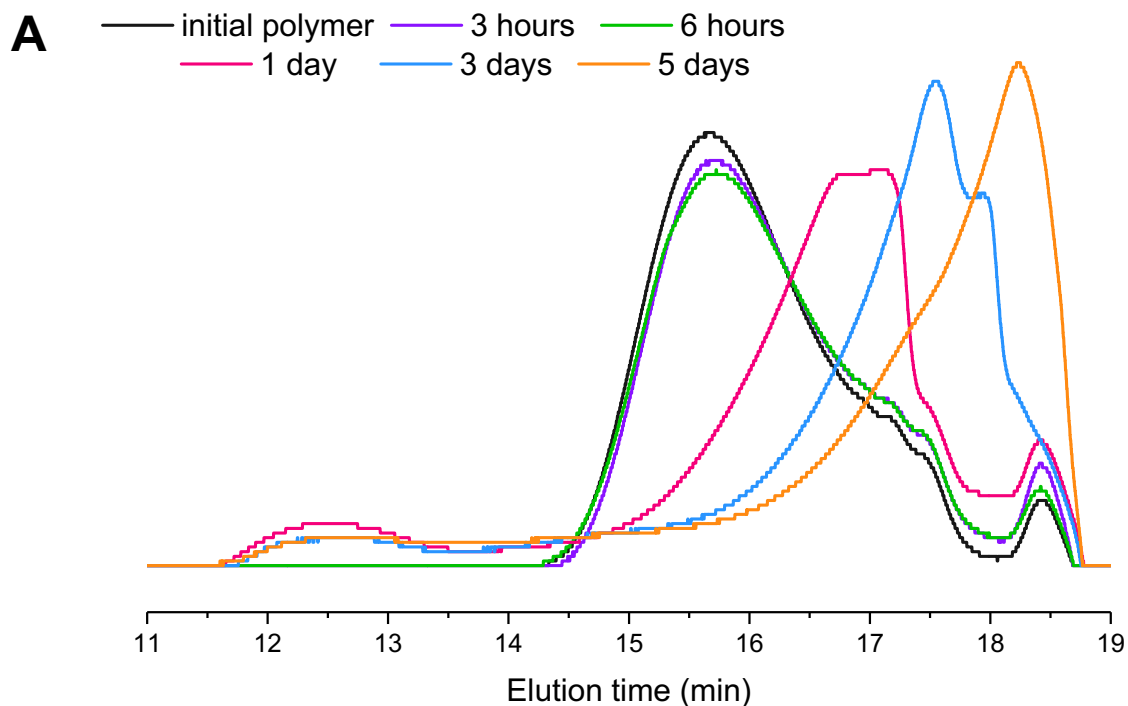


## Supporting Information

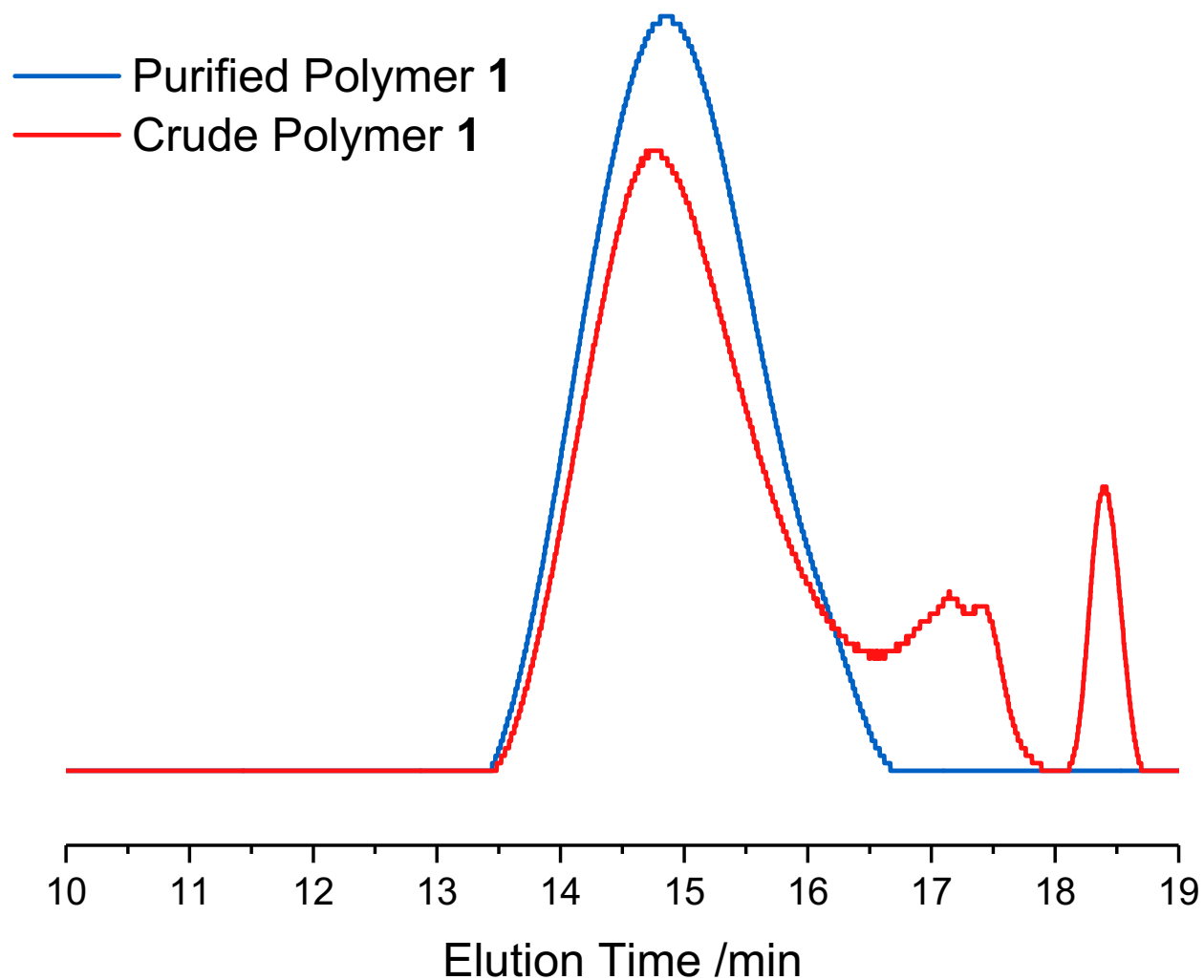
**SI Figure 1.** Time-course evolution of polymer **1** at 100°C arising from the reaction of 2.0 M DVS and 2.0 M TBC in DMSO.



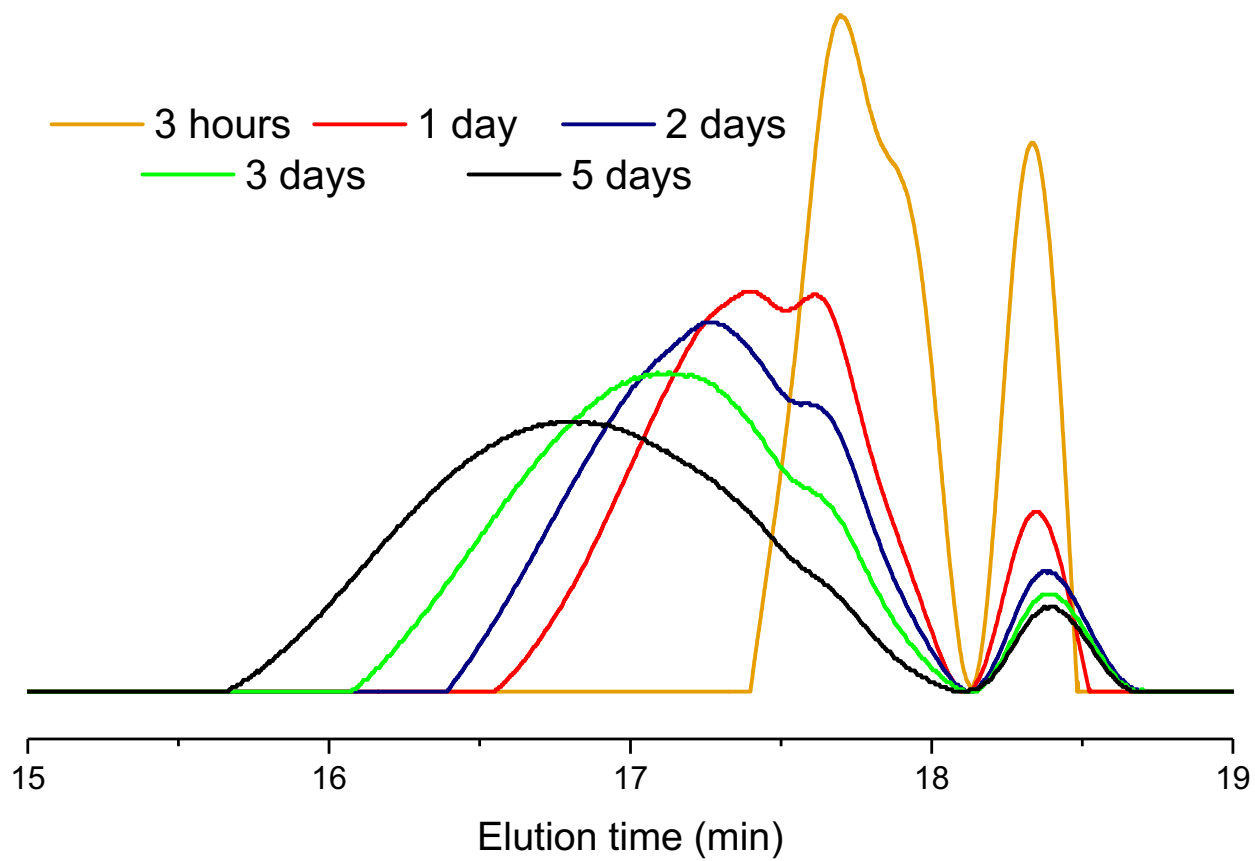
**SI Figure 2.** Non-specific degradation of polymer **2** is observed at 100°C, which corroborates the shift to lower  $M_n$  as a function of time in SI Figure 1. (A) GPC analysis of polymer **2** degradation. (B)  $^1\text{H}$  NMR of polymer **2** after heating for 5 d at 100°C.



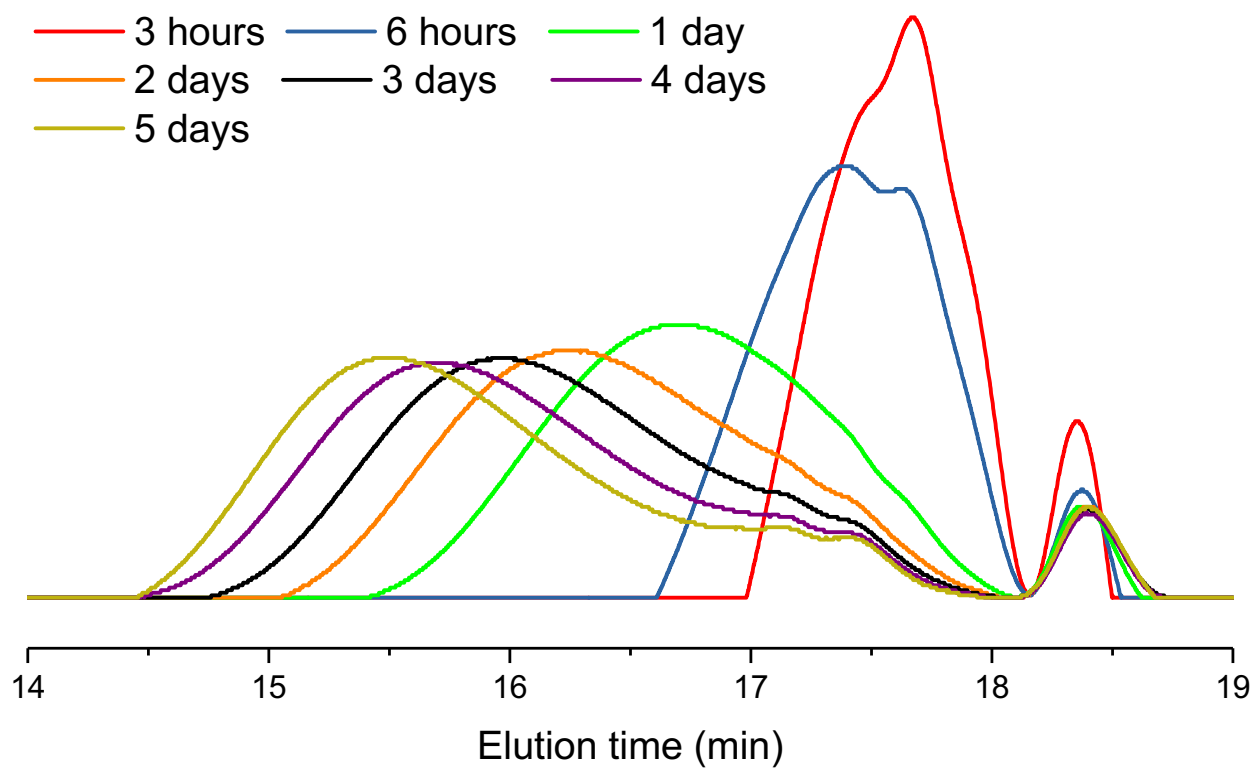
**SI Figure 3.** GPC traces of the 85 mmol scale of **1** showing the crude reaction mixture and removal of low-molecular weight cycles and impurities after washing.



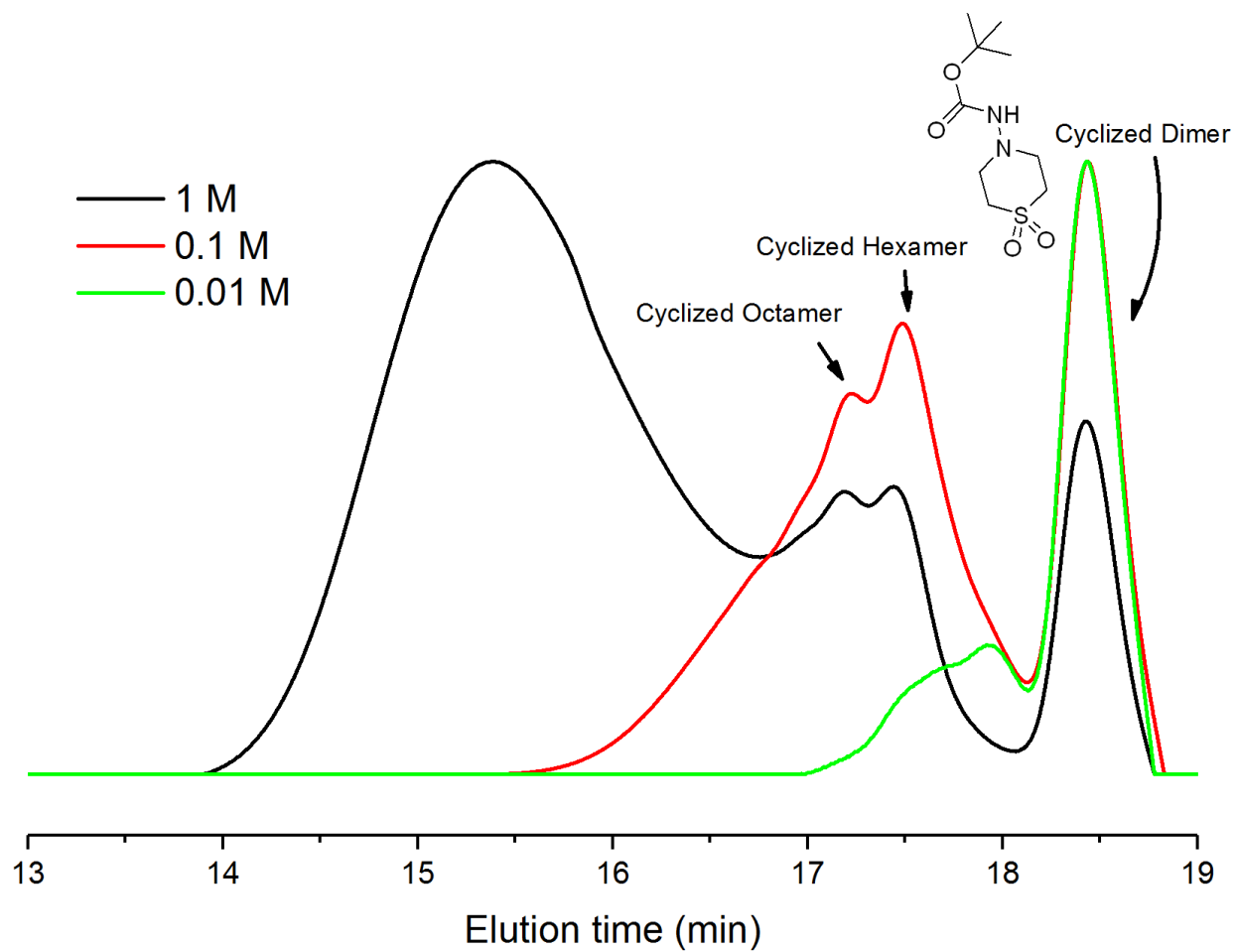
**SI Figure 4.** Time-course evolution of polymer **1** at 25 °C arising from the reaction of 2.0 M DVS and 2.0 M TBC in DMSO.



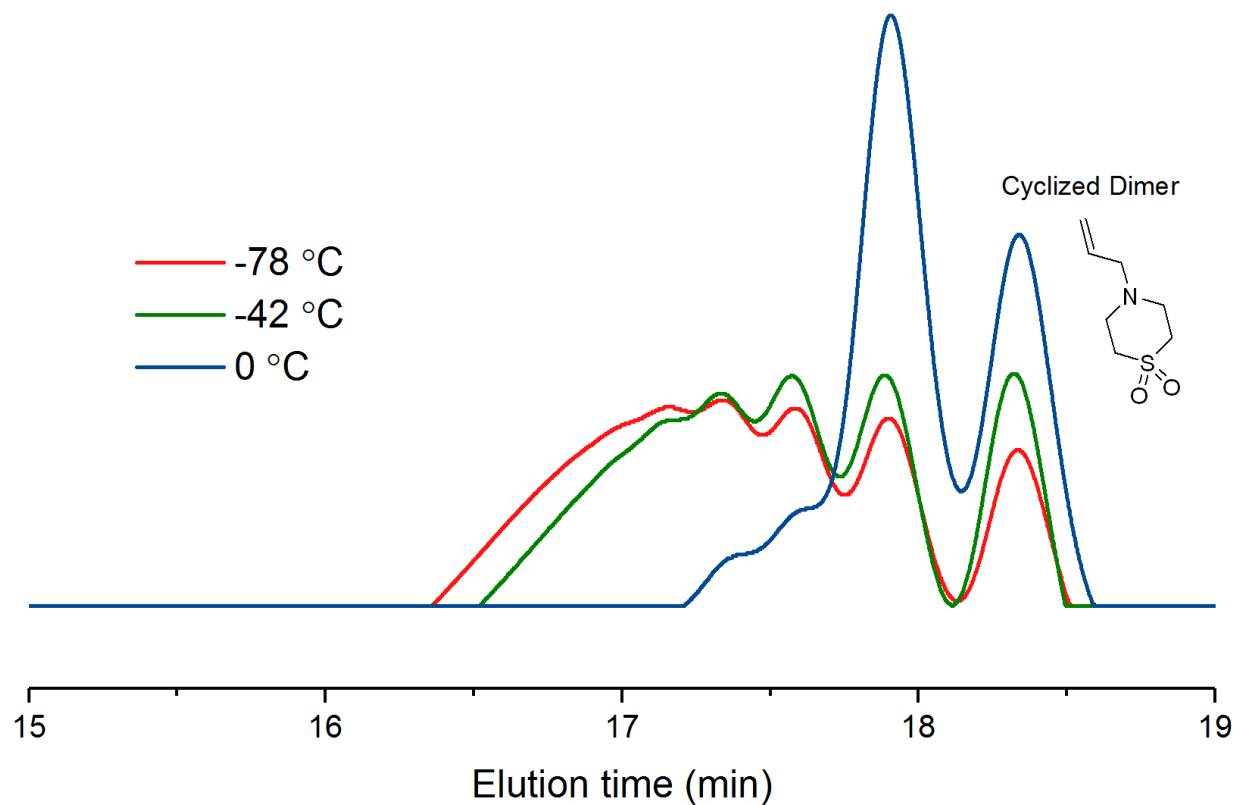
**SI Figure 5.** Time-course evolution of polymer **1** at 50°C arising from the reaction of 2.0 M DVS and 2.0 M TBC in DMSO.



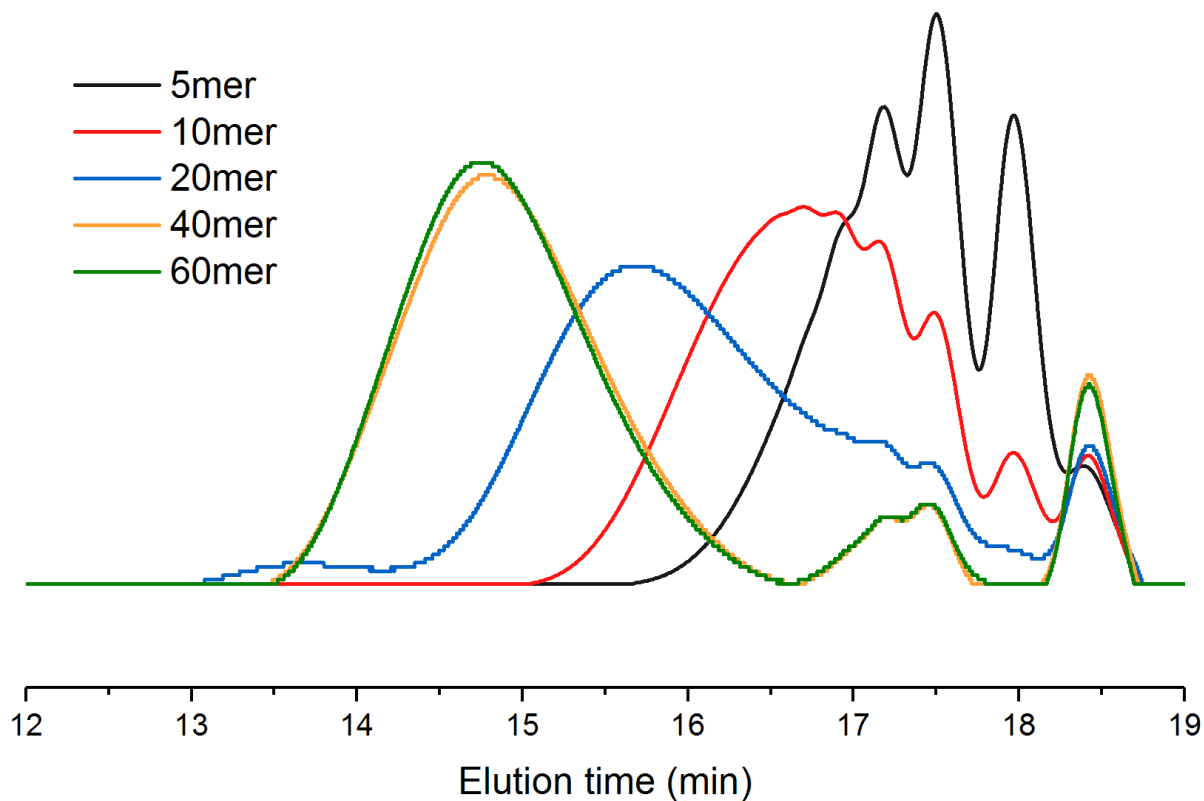
**SI Figure 6.** Polymer arising from the reaction of DVS and TBC at 1.0 M, 0.1 M, and 0.01 M in DMSO at 75°C after 5 days. Only cyclized species are observed at concentrations  $\leq 0.1$  M.



**SI Figure 7.** GPC traces of the reaction of allyl amine (1 mmol, neat) added dropwise to a solution of DVS (2.0 M in DMSO) over the course of an hour at  $-78^{\circ}\text{C}$ ,  $-42^{\circ}\text{C}$ , and  $0^{\circ}\text{C}$ . The reactions were warmed to ambient and stirred for 5 days until all vinyl sulfone functionalities were consumed. Only low molecular weight cyclized species are observed.

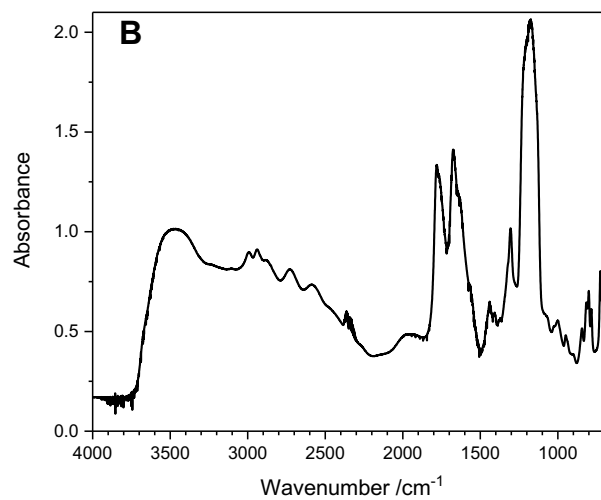
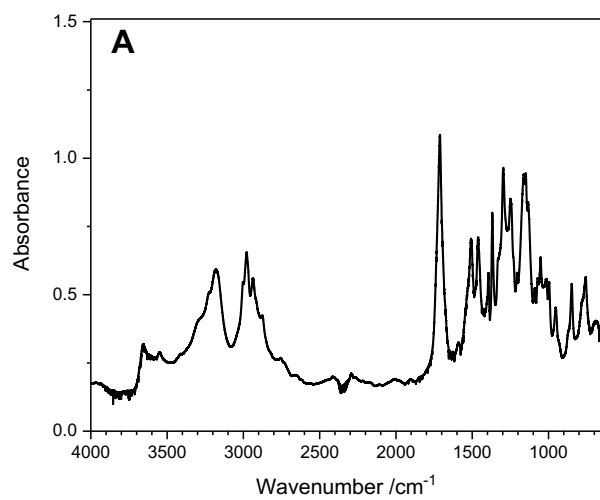


**SI Figure 8.** Tailoring polymer length with stoichiometry control. GPC traces of reactions at 2.0 M TBC and excess DVS in DMSO at 75 °C for 5 days. DVS at 3% excess gave 60-mers; 5% excess gave 40-mers; 11% excess gave 20-mers; 25% excess gave 10-mers; and 50% excess gave 5-mers.

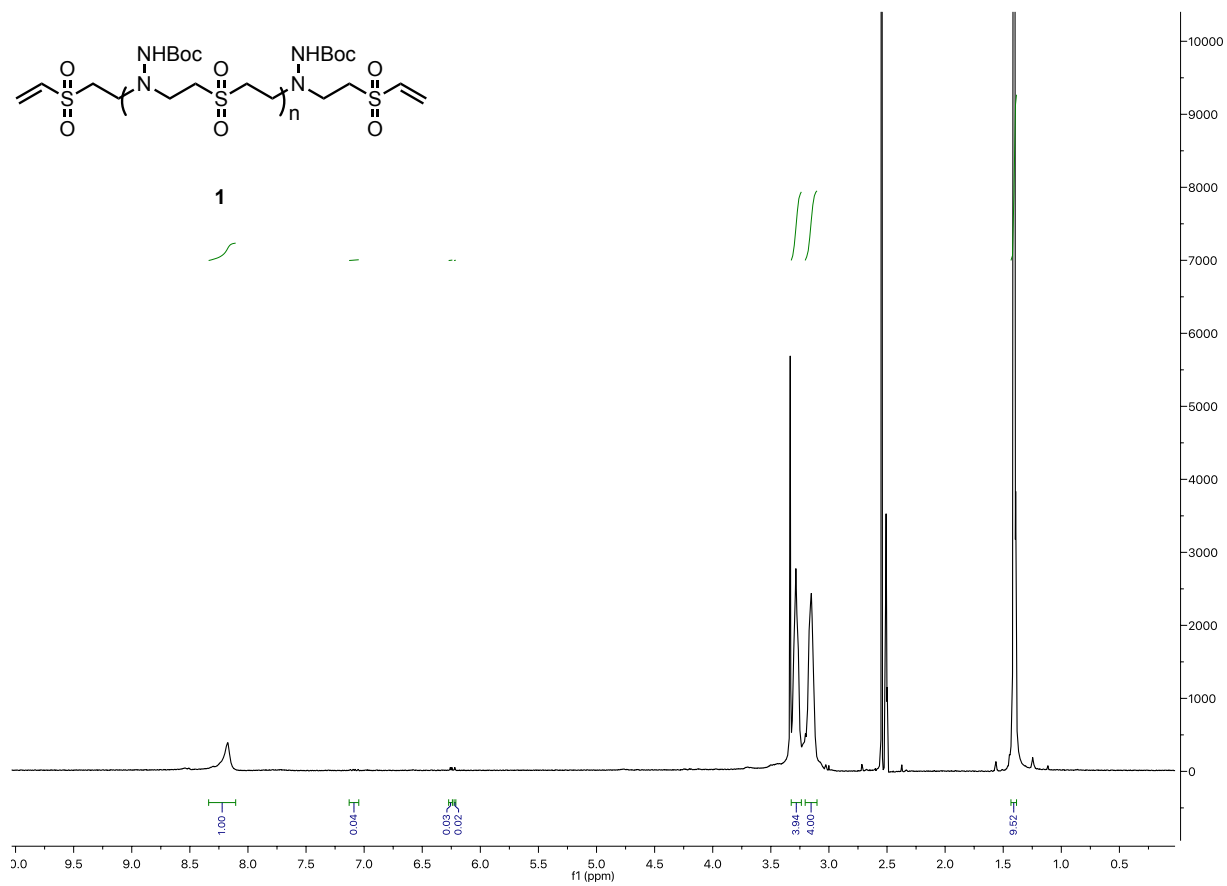




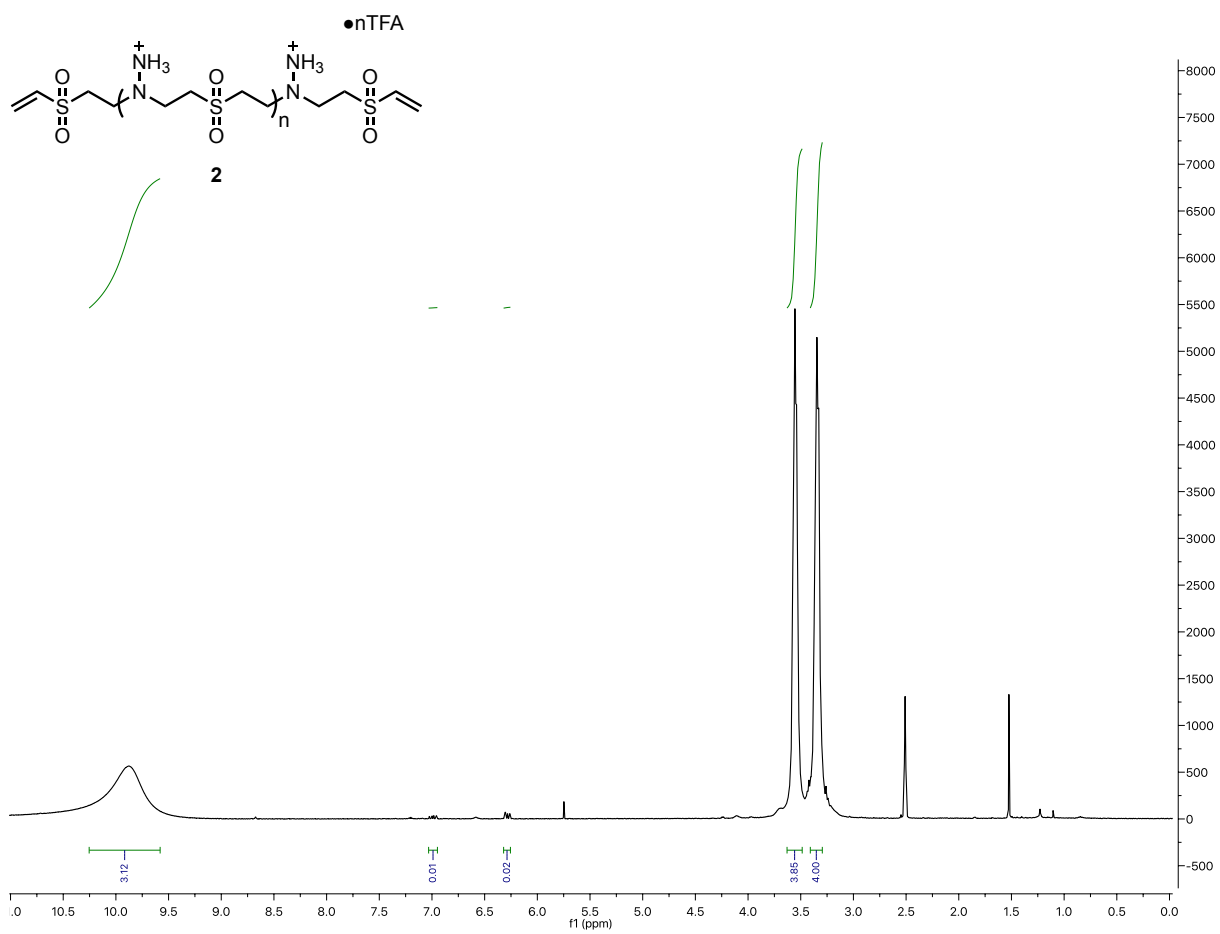
**SI Figure 9.** (A) FTIR spectrum of **1** and (B) FTIR spectrum of **2**.



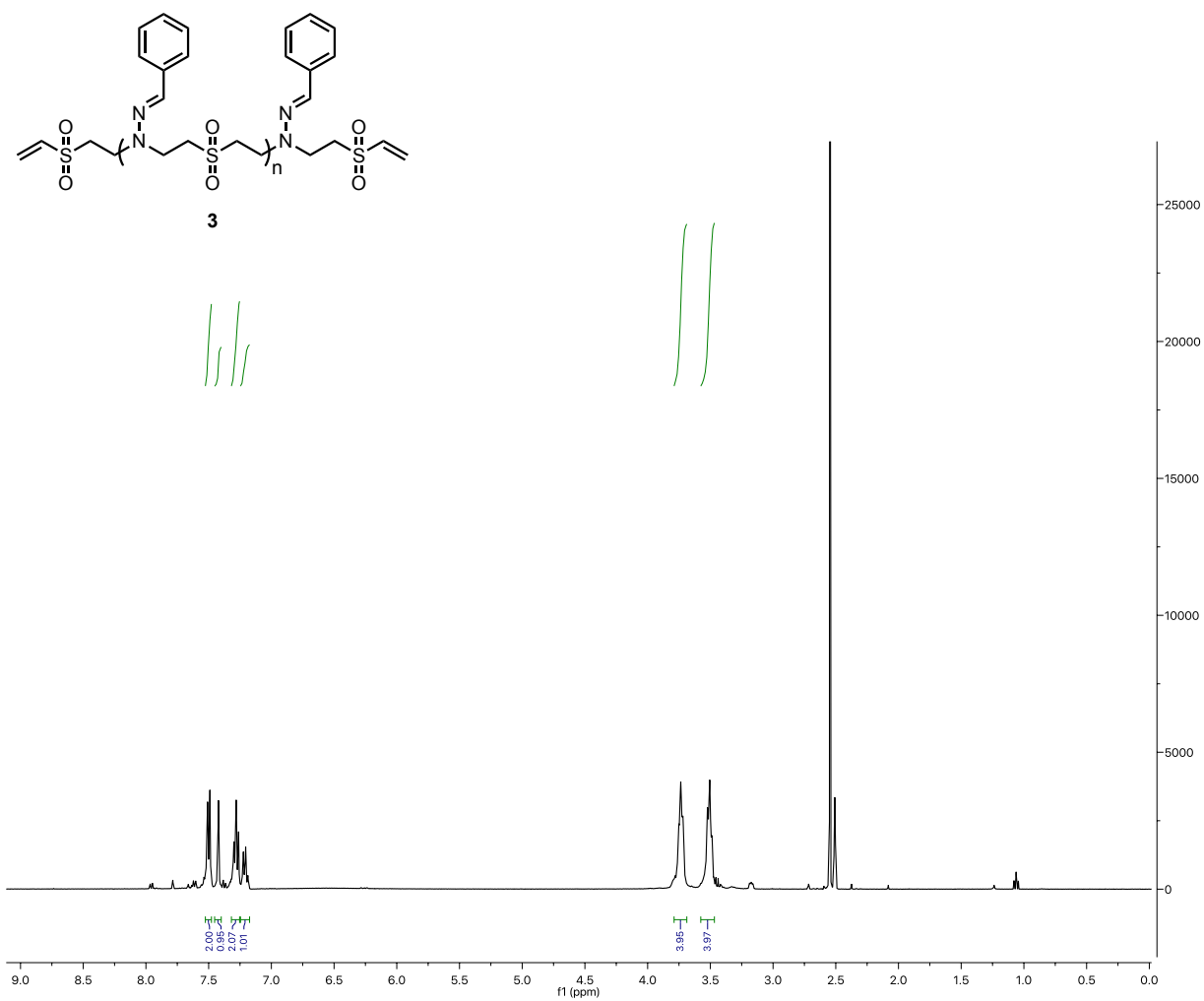
**SI Figure 10.**  $^1\text{H}$  NMR of polymer **1**. Peaks at 3.33, 2.54, and 2.50 ppm are  $\text{H}_2\text{O}$ , DMSO, and  $\text{DMSO-}d_5$ , respectively.



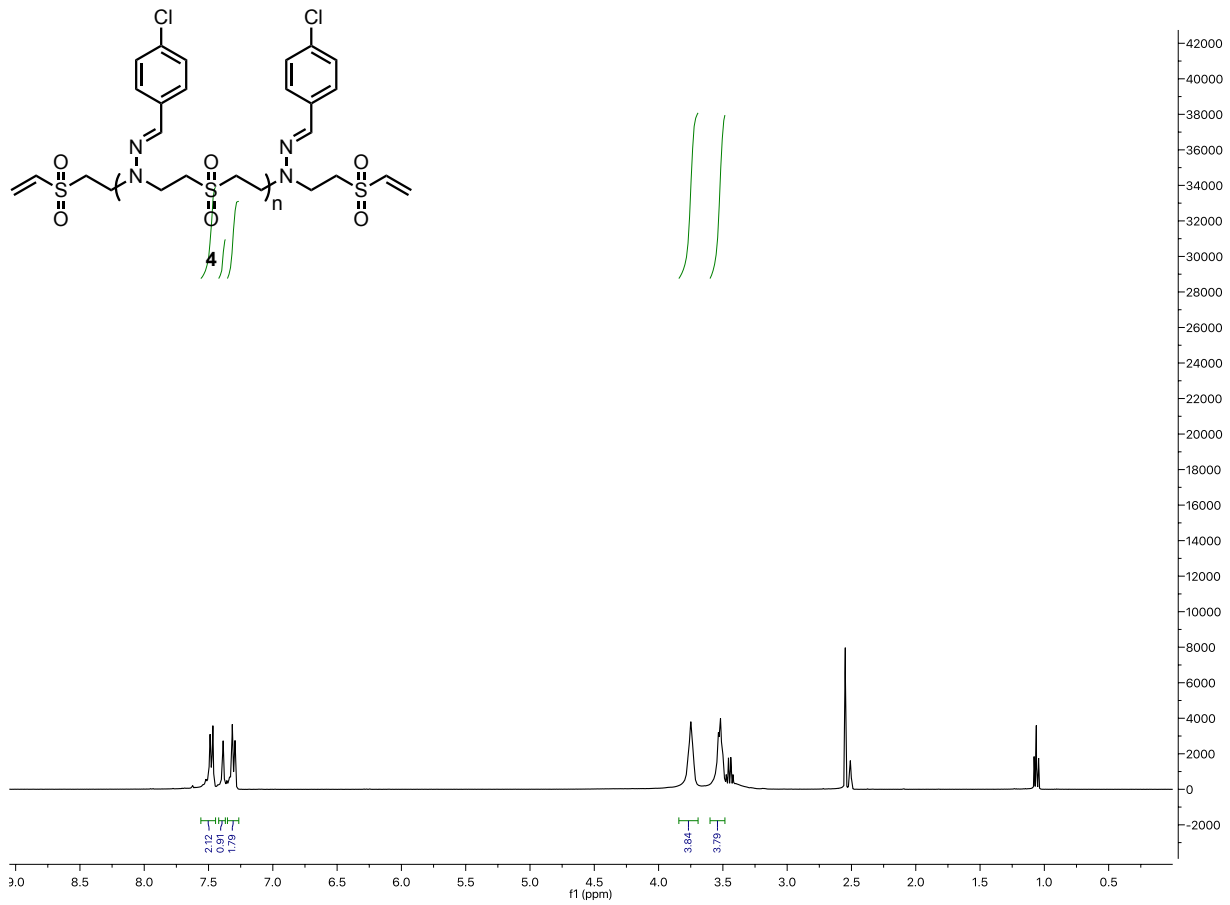
SI Figure 11.  $^1\text{H}$  NMR of polymer **2**.



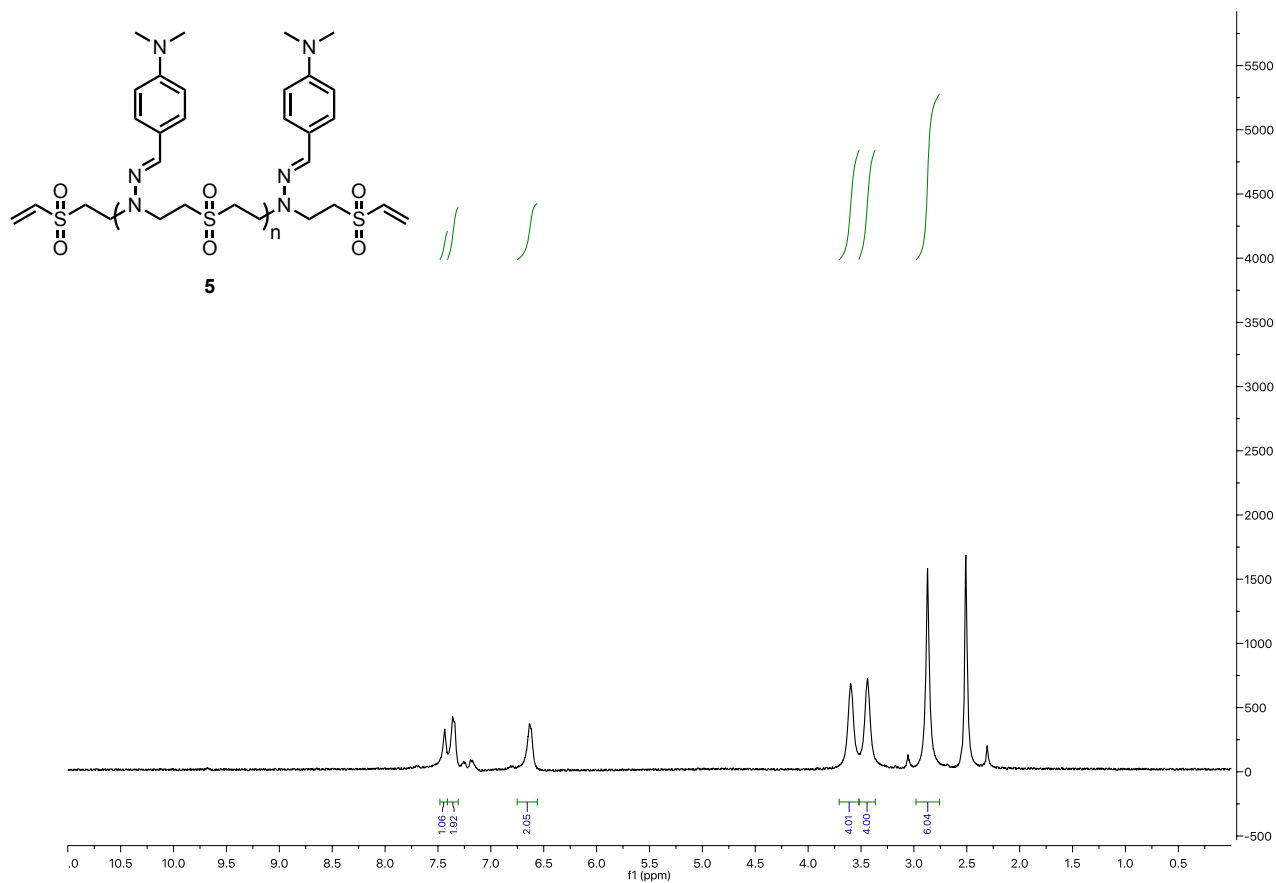
SI Figure 12.  $^1\text{H}$  NMR of polymer **3**.



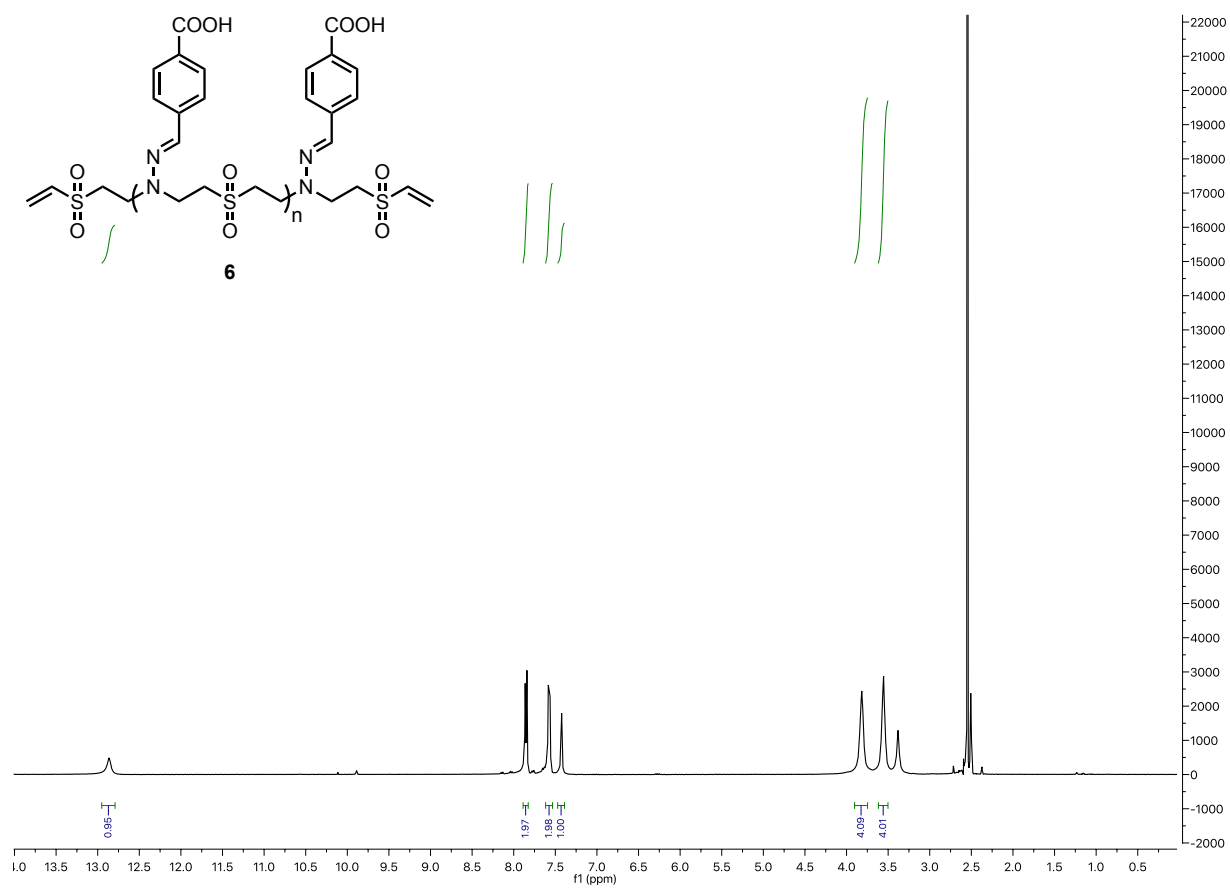
**SI Figure 13.**  $^1\text{H}$  NMR of polymer **4**. Quartet at 3.45 and triplet at 1.25 correspond to residual ethanol.



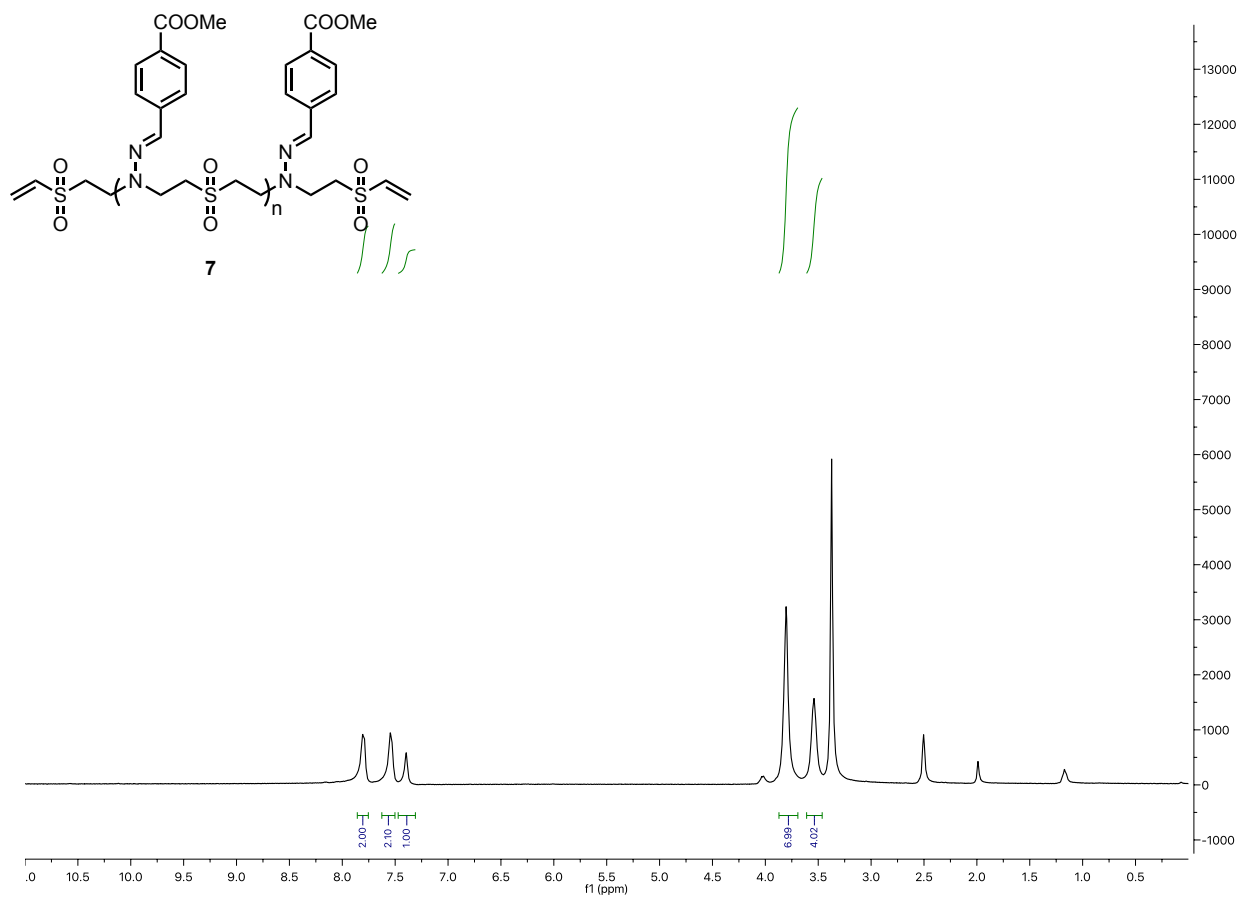
SI Figure 14.  $^1\text{H}$  NMR of polymer **5**.



SI Figure 15.  $^1\text{H}$  NMR of polymer **6**. Singlet at 3.33 ppm corresponds to residual  $\text{H}_2\text{O}$ .

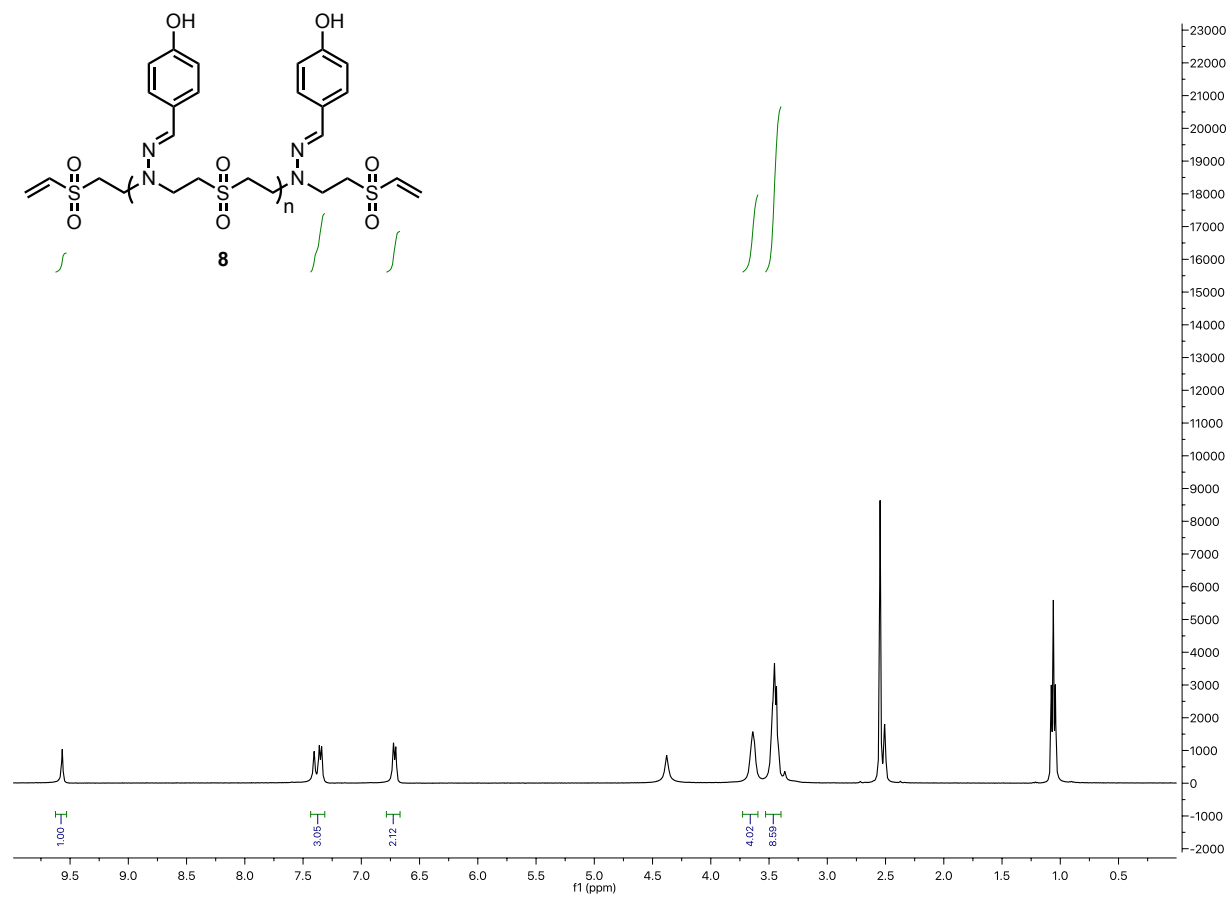


**SI Figure 16.**  $^1\text{H}$  NMR of polymer **6**. Backbone resonances and methyl ester singlet overlap at 3.8 ppm. Singlet at 3.33 ppm corresponds to residual  $\text{H}_2\text{O}$ .

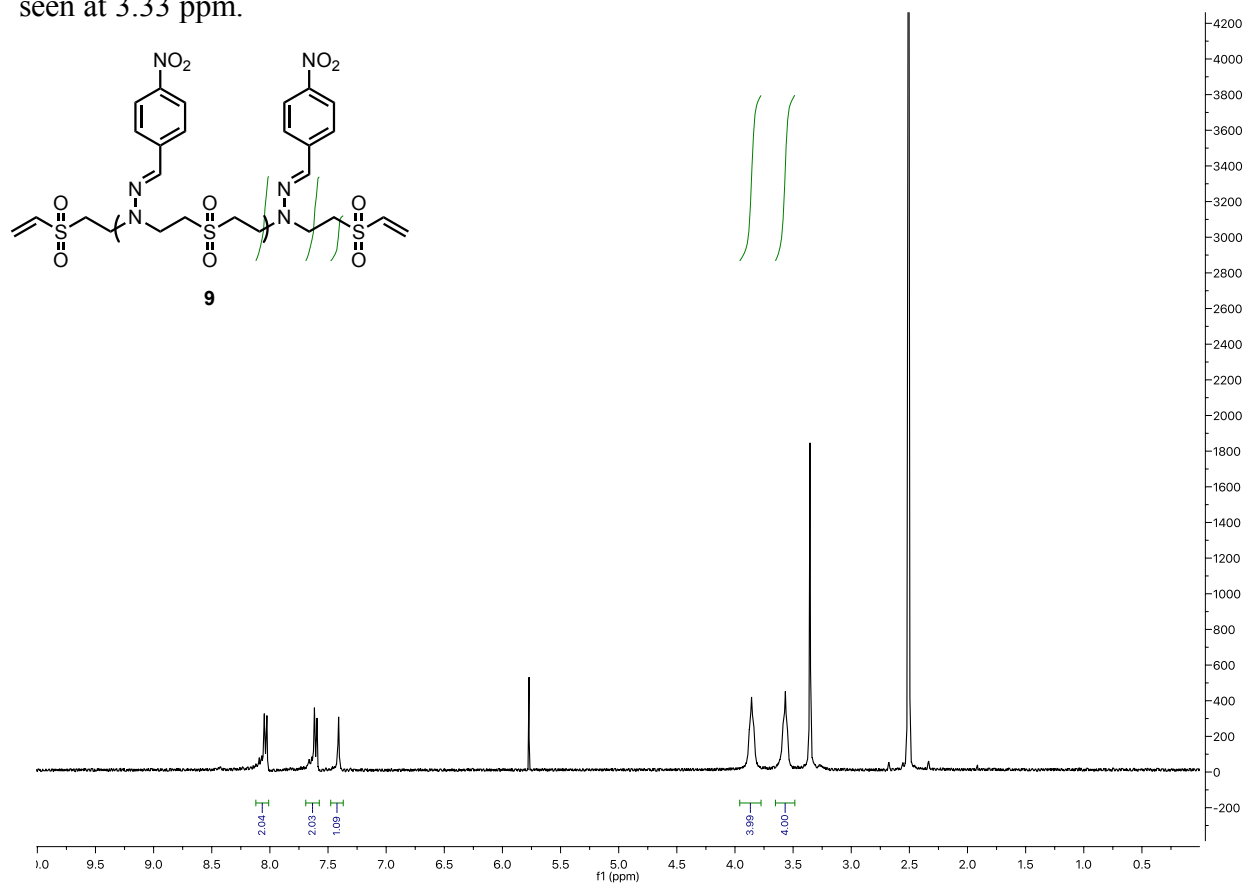




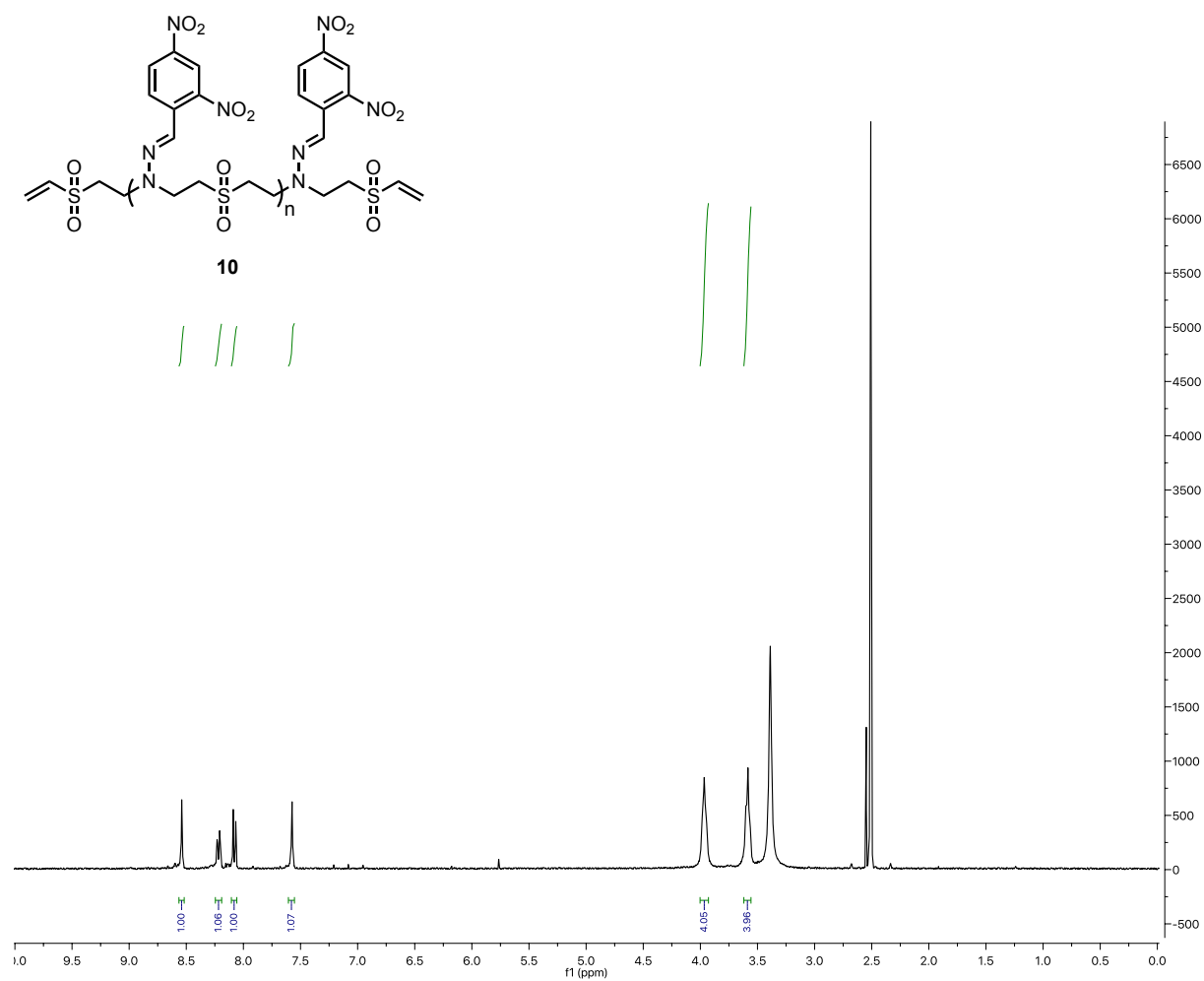
**SI Figure 17.**  $^1\text{H}$  NMR of polymer **8**. Residual ethanol is observed at 4.38, 3.45 (overlaps with backbone resonances), and 1.25 ppm.



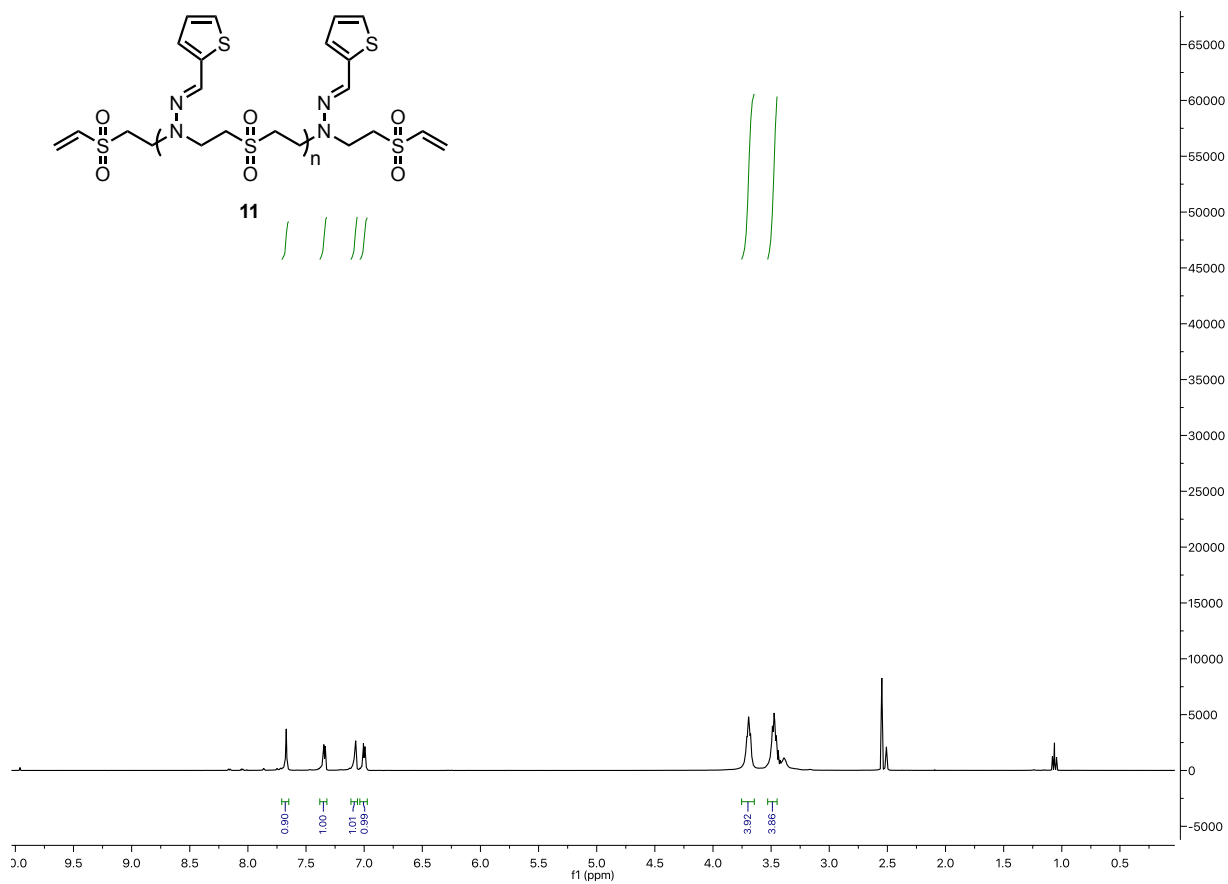
**SI Figure 18.**  $^1\text{H}$  NMR of polymer **9**. Residual  $\text{CH}_2\text{Cl}_2$  is seen at 5.78 ppm, and residual  $\text{H}_2\text{O}$  is seen at 3.33 ppm.



SI Figure 19.  $^1\text{H}$  NMR of polymer **10**. Residual  $\text{H}_2\text{O}$  is seen at 3.33 ppm



SI Figure 20.  $^1\text{H}$  NMR of polymer **11**. Residual ethanol is seen at 3.45 and 1.25 ppm.



**SI Figure 21.**  $^1\text{H}$  NMR of polymer **12**. Peaks at 5.78 and 3.33 ppm correspond to residual  $\text{CH}_2\text{Cl}_2$  and  $\text{H}_2\text{O}$ , respectively.

