Electronic Supplementary Material (ESI) for RSC Advances.

Hydrogen-bond-assisted isotactic-specific radical polymerization of *N*-vinyl-2-pyrrolidone with tartrate additives in toluene at low temperatures: high-resolution ^{1}H NMR analysis

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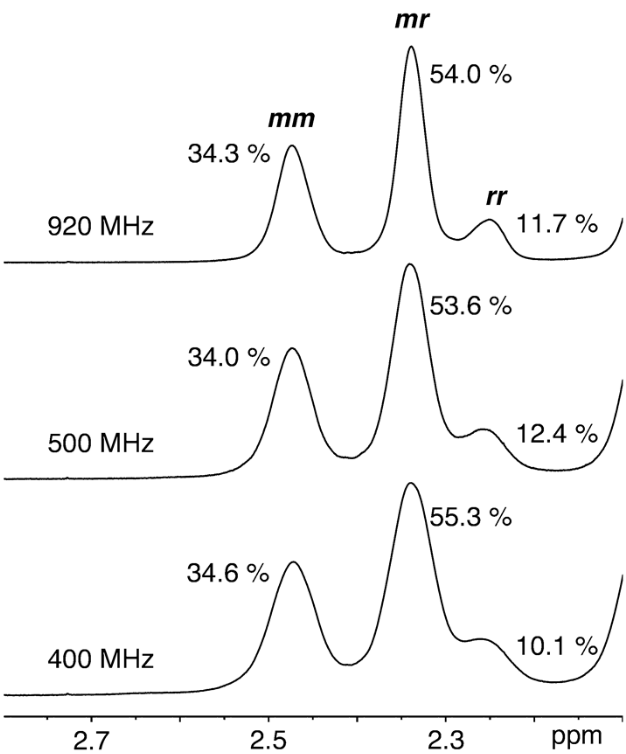


Fig. S1 ^{1}H NMR spectra of the $CH_{2,C=O}$ of PVP measured at different magnetic field strengths.

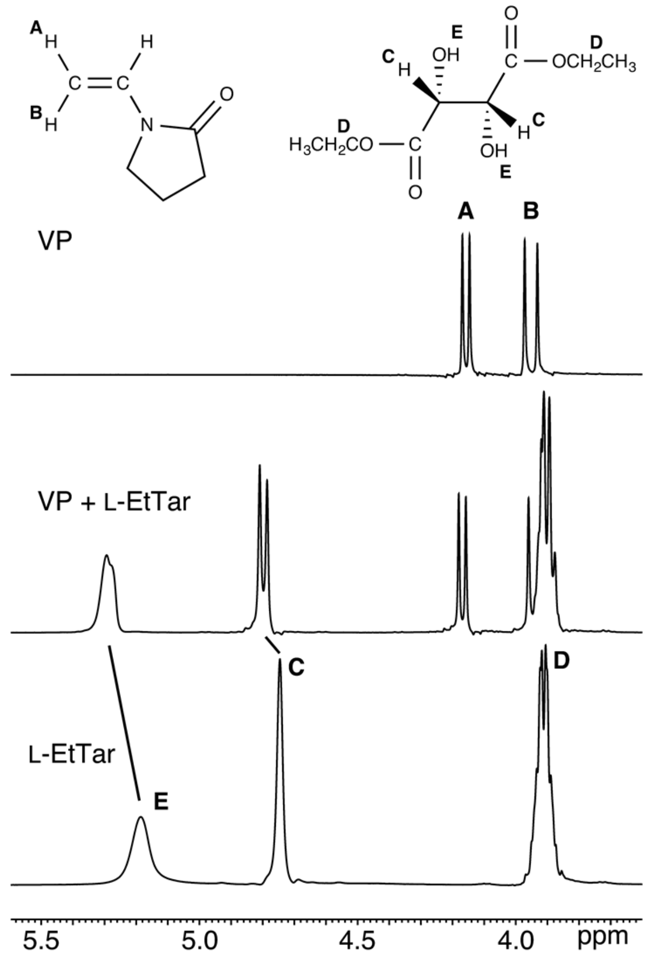


Fig. S2 400 MHz ^{1}H NMR spectra of VP (0.1 mol/L), L-EtTar (0.1 mol/L) and an equimolar mixture of the two components (0.1 mol/L for each) in toluene-d_8 at −60 °C.

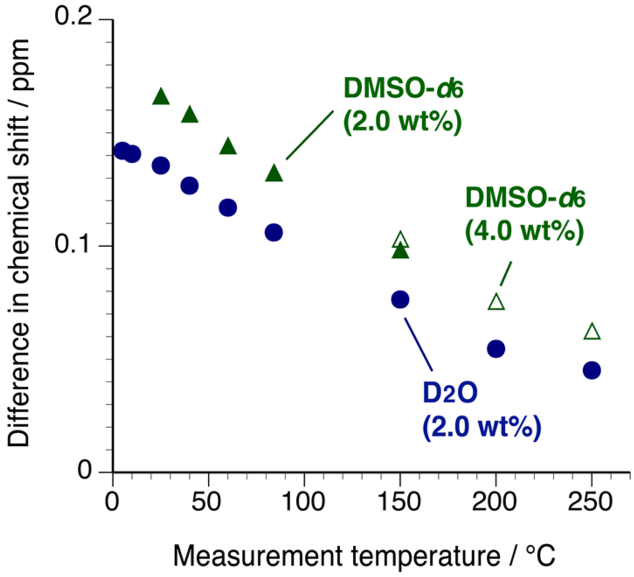


Fig. S3. Temperature dependence of the chemical shift difference between the peaks assignable to the *mm* and *mr* triads in the signals of the $CH_{2,C=O}$ groups of the PVPs (Table 1, run 6) measured in D_2O and DMSO-d_6. The chemical shift difference arising from the polymer concentration (2.0 and 4.0 wt% in DMSO-d_6) was one order of magnitude smaller than that arising from the difference in solvent species (in DMSO-d_6 and D_2O at the fixed polymer concentration of 2.0 wt%).

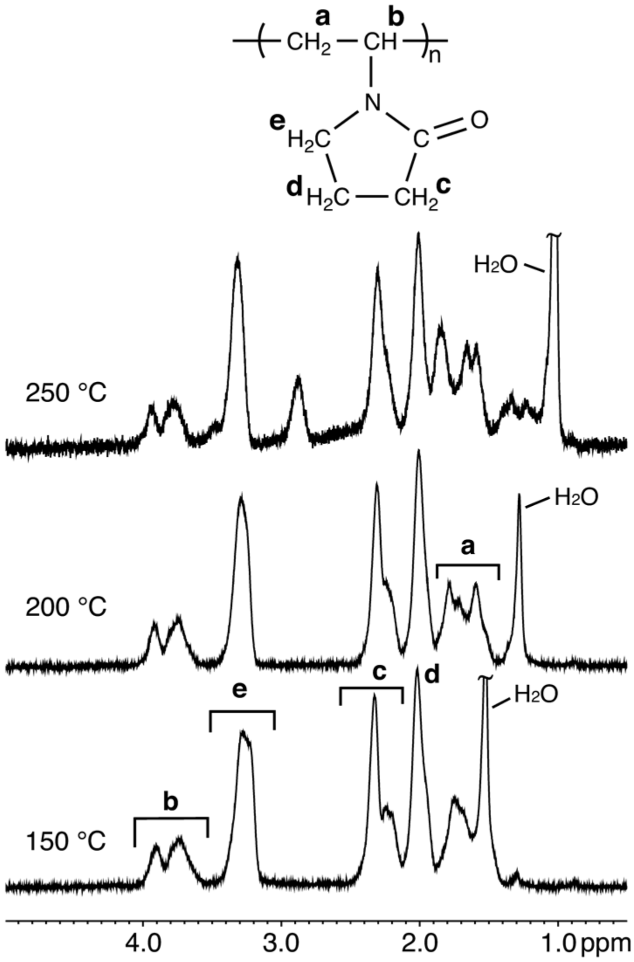


Fig. S4. 500 MHz ^{1}H NMR spectra of PVP in $CDCl_3$ at temperature in the range of 150–250 °C (Table 1, run 6, 4.0 wt%).

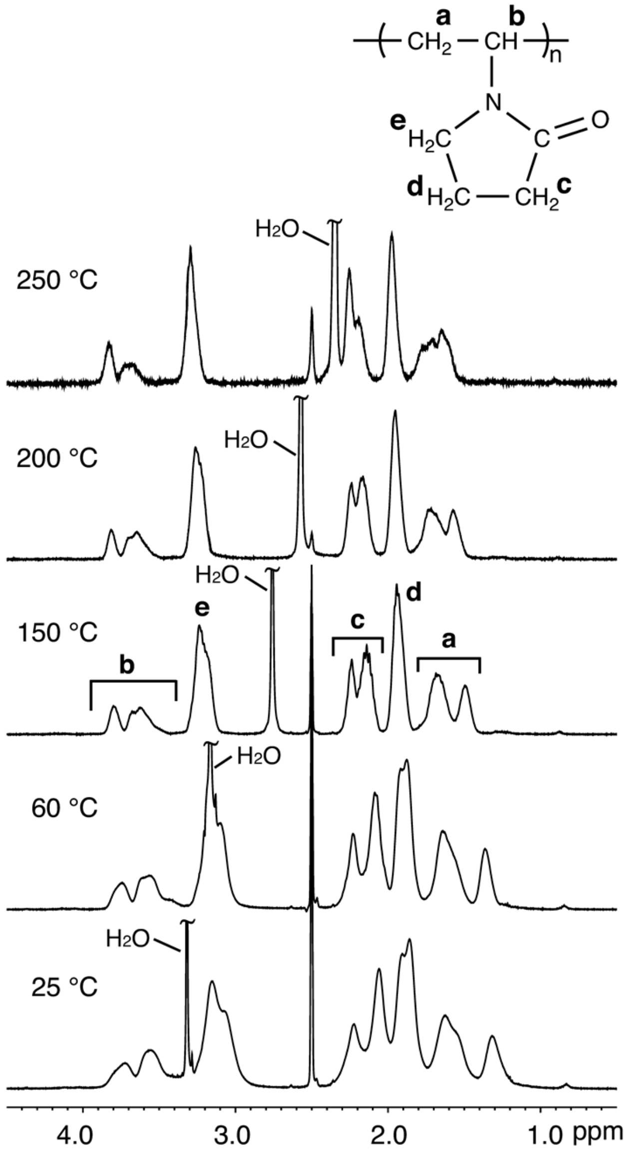


Fig. S5. 500 MHz ^{1}H NMR spectra of PVP in DMSO-d_6 at temperature in the range of 25–250 °C (Table 1, run 6). The spectra at 25–150 °C (2.0 wt%) and 200–250 °C (4.0 wt%) were recorded using standard and high-temperature probes, respectively.

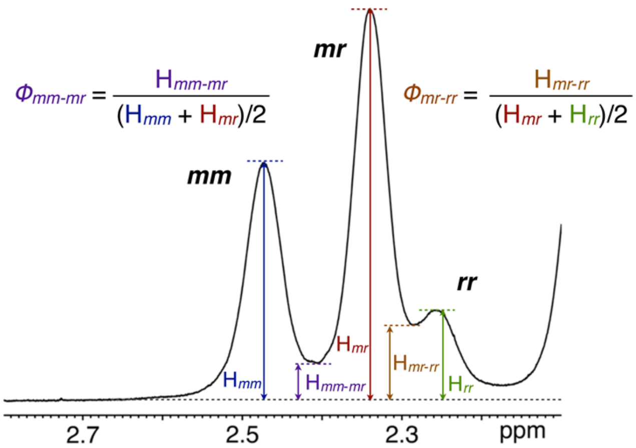


Fig. S6. Definition of the $\Phi_{mm\text{-}mr}$ and $\Phi_{mr\text{-}rr}$ values.

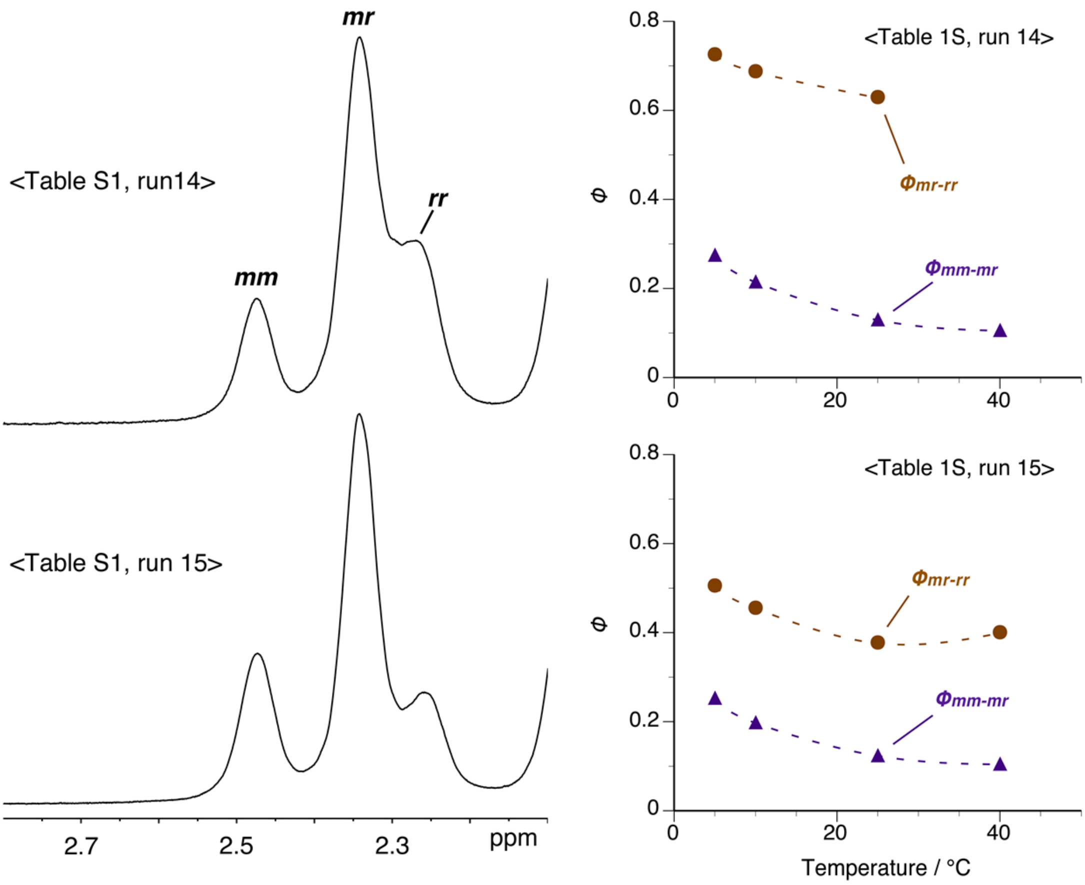
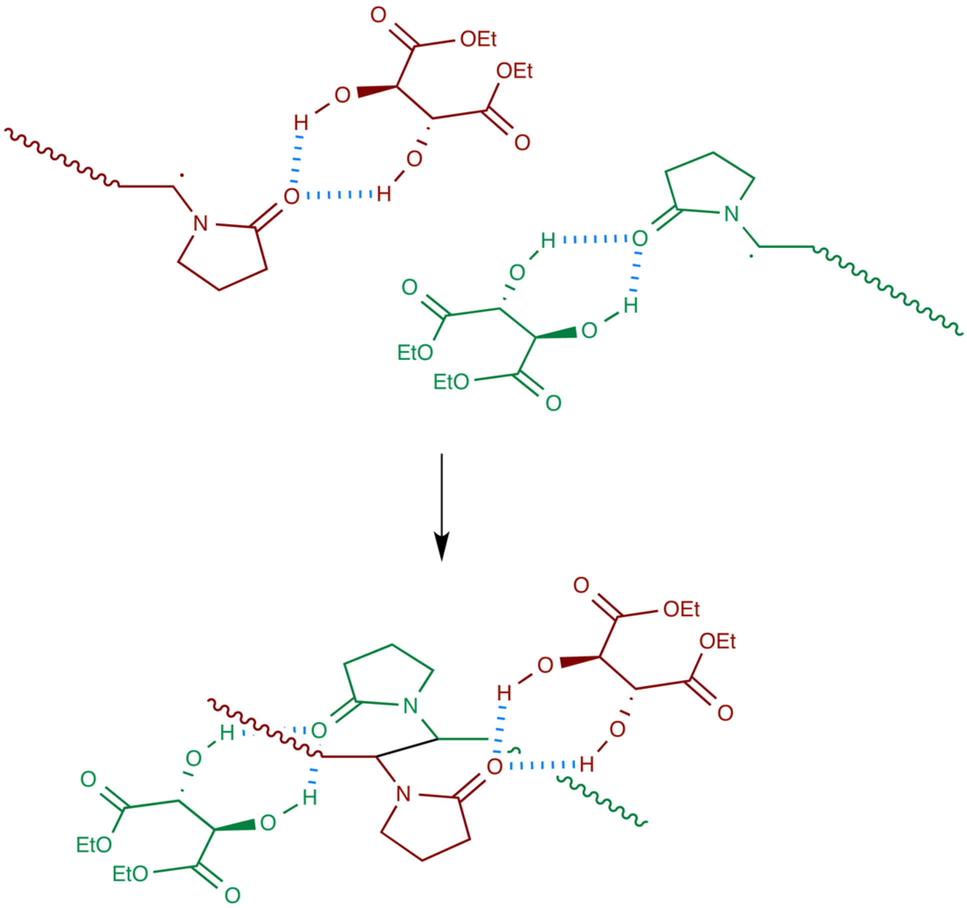


Fig. S7. 500 MHz ^{1}H NMR spectra of the $CH_{2,C=O}$ of PVPs (Table S1, runs 14 & 15) measured in D_2O at 25 °C, and temperature dependence of the $\Phi_{mm\text{-}mr}$ and $\Phi_{mr\text{-}rr}$.



Scheme S1. Proposed configuration for the two polymers during the termination reaction with their propagating ends complexed with L-EtTar.

Table S1. Radical polymerization of VP in water or $(CF_3)_3COH$ at low temperatures for 24 h, average lengths of *m* diad ($\bar{\ }_m$) of the polymers obtained and first order Markovian parameters for the polymerizations.[a]

Run	$[VP]_0$ / mol L^{-1}	Solvent	Temp. / °C	Yield / %	$M_n \times 10^{-3}$ [b]	M_w / M_n [b]	Triad tacticity[c] / %			$\bar{\ }_m$ [d]	Markovian Parameters		
							f_{mm}	f_{mr}	f_{rr}		$P_{m/r}$ [e]	$P_{r/m}$ [f]	$P_{m/r} + P_{r/m}$
14	2.0	water	0	63	52.8	8.6	14.4	57.4	28.2	1.50	0.666	0.504	1.170
15	9.4	$(CF_3)_3COH$	–40	13	14.5	2.8	22.5	61.6	15.9	1.70	0.578	0.660	1.238

[a] $[n\text{-}Bu_3B]_0 = 0.05$ mol L^{-1}. [b] Determined by SEC. [c] Determined by ^1H NMR. [d] $\bar{\ }_m = (f_{mm} + f_{mr}/2) / (f_{mr}/2)$. [e] $P_{m/r} = (f_{mr}/2) / (f_{mm} + f_{mr}/2)$.
[f] $P_{r/m} = (f_{mr}/2) / (f_{rr} + f_{mr}/2)$.