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.

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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 $-60 \, ^\circ$C.
Fig. S3. Temperature dependence of the chemical shift difference between the peaks assignable to the $nm$ and $mr$ triads in the signals of the CH$_2$C=O groups of the PVPs (Table 1, run 6) measured in D$_2$O 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$_2$O 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 $\Phi_{\text{mm-mr}}$ and $\Phi_{\text{mr-rr}}$ 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$_2$O at 25 °C, and temperature dependence of the $\phi_{mm-mr}$ and $\phi_{mr-rr}$. 
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$_3$)$_3$COH at low temperatures for 24 h, average lengths of $n$ diad ($\overline{n}$) of the polymers obtained and first order Markovian parameters for the polymerizations.*

<table>
<thead>
<tr>
<th>Run</th>
<th>[VP]$_0$ mol L$^{-1}$</th>
<th>Solvent</th>
<th>Temp. °C</th>
<th>Yield %</th>
<th>$M_\alpha \times 10^{-3}$</th>
<th>$M_\alpha / M_\beta$</th>
<th>$f_m$</th>
<th>$f_m$</th>
<th>$f_m$</th>
<th>$f_m$</th>
<th>$f_m$</th>
<th>$f_m$</th>
<th>$f_m$</th>
<th>$f_m$</th>
<th>Markovian Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>2.0</td>
<td>water</td>
<td>0</td>
<td>63</td>
<td>52.8</td>
<td>8.6</td>
<td>14.4</td>
<td>57.4</td>
<td>28.2</td>
<td>1.50</td>
<td>0.666</td>
<td>0.504</td>
<td>1.170</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>9.4</td>
<td>(CF$_3$)$_3$COH</td>
<td>−40</td>
<td>13</td>
<td>14.5</td>
<td>2.8</td>
<td>22.5</td>
<td>61.6</td>
<td>15.9</td>
<td>1.70</td>
<td>0.578</td>
<td>0.660</td>
<td>1.238</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* [n-Bu$_3$B]$_0$ = 0.05 mol L$^{-1}$.  
* Determined by SEC.  
* Determined by $^1$H NMR.  
* $\overline{n} = (f_m + f_m') / 2$.  
* $P_{mm} = (f_m') / (f_m + f_m')$.  
* $P_{rr} = (f_r') / (f_r + f_r')$.  
* $P_{mr} = (f_m') / (f_r + f_r')$.  

$\overline{m} = \frac{(f_m + f_m')/2}{(f_r + f_m')/2}$. 

$P_{mr} = (f_m') / (f_r + f_m')$.  

$P_{mm} = (f_m') / (f_m + f_m')$.  

$P_{rr} = (f_r') / (f_r + f_r')$.