Supporting information for:

Facile synthesis of well-controlled poly(1-vinyl imidazole) by RAFT process

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Additional synthesis procedures.

**Synthesis of methyl 2-((ethoxycarbonothioyl)thio)propanoate (Xanthate 1)**

2-Bromopropionic acid (20.0 g, 130.7 mmol, 1 equiv.), methanol (9.5 g, 296.9 mmol, 2.3 equiv.) and methanesulfonic acid (0.89 g, 9.3 mmol, 0.07 equiv.) were dissolved in 100 mL toluene in a round bottom flask equipped with a stirring bar. The solution was refluxed at 120 °C for 2 hours, it was then transferred to a separatory funnel and washed with saturated Na$_2$CO$_3$ solution (100 mL) for two times and brine (100 mL) for 1 time. The residual water in the organic solution was removed by anhydrous MgSO$_4$, and then the solvent was removed under reduced pressure to yield methyl 2-bromopropanoate as clear liquid in 46% yield. $^1$H NMR (400 MHz, CDCl$_3$): δ 4.38 (q, J=6.9 Hz, 1H), 3.78 (s, 3H), 1.83 (d, J=6.9 Hz, 3H). The spectrum is consistent with previous published value.$^1$

The obtained methyl 2-bromopropanoate (8.0 g, 47.9 mmol, 1 equiv.) was dissolved in 120 mL ethanol in a round bottom flask equipped with a stirring bar. The flask was then immersed in an ice-water-bath, and potassium ethyl xanthogenate (8.1 g, 50.3 mmol, 1.05 equiv.) was added slowly to reaction over 10 minutes. The flask was then removed from the ice-water-bath and stirred at room temperature for 4 hours. The formed precipitate was removed by gravity filtration, and the solvent was removed under reduced pressure. The residue was re-dissolved in 300 mL dichloromethane and washed with DI water (4x100 mL), brine (1x100 mL), and dry over MgSO$_4$. The dichloromethane was then removed under reduced pressure to yield product **Xanthate 1** as pale-yellow liquid (95%). $^1$H NMR (400 MHz, CDCl$_3$): δ 4.64 (q, J=7.3
Hz, 2H), 4.40 (q, J=7.3 Hz, 1H), 3.75 (s, 3H), 1.58 (d, J=7.3 Hz, 3H), 1.41 (t, J=7.3 Hz, 3H). The spectrum is consistent with previous published value.²

**Synthesis of O-ethyl S-(1-phenylethyl) carbonodithioate (Xanthate 2)**

Potassium ethyl xanthogenate (6.5 g, 40.4 mmol, 1.1 equiv.) was dissolved in 40 mL ethanol in a round bottom flask equipped with a stirring bar. (1-Bromoethyl)benzene (6.8 g, 36.7 mmol, 1.0 equiv.) was added dropwise to the flask over 10 minutes. The reaction was stirred at room temperature for 6 hours. The formed precipitate was removed by vacuum filtration, and the solvent was removed under reduced pressure. The residue was re-dissolved in 200 mL diethyl ether and washed with DI water (4x50 mL), brine (1x100 mL), and dry over MgSO₄. The diethyl ether was then removed under reduced pressure to yield product **Xanthate 2** as pale-yellow liquid (90%). ¹H NMR (400 MHz, CDCl₃): δ 7.25-7.44 (m, 5H), 4.91 (q, J=7.3 Hz, 1H), 4.63 (q, J=7.3 Hz, 2H), 1.75 (d, J=7.3 Hz, 3H), 1.41 (t, J=7.3 Hz, 3H). The spectrum is consistent with previous published value.³

**Synthesis of MacroCTA (poly(1VIM)-CDPA)**

CDPA (51.4 mg, 127.6 μmol, 1.0 equiv.), 1VIM (1.2 g, 12.8 mmol, 100.0 equiv.) and AIBN (21.0 mg, 127.6 μmol, 1.0 equiv.) were dissolved in 5.2 mL acetic acid and transferred to a Schlenk flask. The oxygen inside the flask was removed by 3 cycles of freeze-pump-thaw and refilled with argon at the end of third cycle. The reaction was stopped by cooling down to room temperature after being immersed in 70 °C oil bath for 4 hours. The polymerization conversion (~53.0% conversion) was determined by ¹H NMR by dissolving crude polymer solution in DMSO-d₆. The poly(1VIM)-CDPA was purified by precipitation in diethyl ether twice and then dried under reduced pressure until constant weight. ¹H NMR (400 MHz, DMSO-d₆): δ 6.64-7.48 (b, 153H), 2.79-3.18 (b, 51H), 1.90-2.23 (b, 108H), 1.17-1.38 (b, 18H), 0.80-0.89 (b, 3H). SEC (DMF, PMMA standards): $M_n = 10,300$ g/mol, $D = 1.07$. 

³
Additional $^1$H NMR spectra and SEC traces.

**Figure S1.** $^1$H NMR (400 MHz, CDCl$_3$) spectrum of methyl 2-bromopropanoate. The analyte contains a small amount of toluene.

**Figure S2.** $^1$H NMR (400 MHz, CDCl$_3$) spectrum of Xanthate 1. The analyte contains a small amount of dichloromethane.
Figure S3. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of Xanthate 2.

Figure S4. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of poly(1VIM) synthesized by radical polymerization in DMF. The analyte contains a small amount of DMF and diethyl ether.
Figure S5. SEC trace of poly(1VIM) obtained by CDPA controlled polymerization in DMF, a bimodal distribution was observed. ($M_n=14,200$ g/mol, $\bar{D} = 1.41$, PMMA standards)

Figure S6. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of poly(1VIM) synthesized by polymerization in DMF in the presence of CDPA. The analyte contains small amount of DMF and residual monomer. The peaks at 1.24 ppm and 0.86 ppm indicated the presence of RAFT end group.
Figure S7. $^1$H NMR (400 MHz, D$_2$O) spectrum comparison of 1VIM in D$_2$O (10 mg/mL) and 1VIM with different molar ratio of acetic acid in D$_2$O. The shifting of the aromatic regions indicates that 1VIM can effectively react with acetic acid to form ionic monomer.
Figure S8. $^1$H NMR (400 MHz, D$_2$O) spectrum comparison of poly(1VIM) and poly(1VIM-Ac) in D$_2$O. The shifting of the aromatic regions indicates the imidazole rings can effectively react with acetic acid, and the successful removal of acetic acid by dialysis.
Figure S9. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of poly(1VIM) obtained by Xanthate 1 mediated polymerization in acetic acid. The peaks of xanthate end group are not visible (For example, the methylene group at ~4.6 ppm is missing), which indicates the xanthate is not attached on the polymer terminus.

Figure S10. SEC trace of poly(1VIM) obtained by Xanthate 1 mediated polymerization in acetic acid, a small shoulder and broad distribution were observed. ($M_n=9,400$ g/mol, $\bar{D}=1.37$, PMMA standards)
Figure S11. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of poly(1VIM) obtained by Xanthate 2 mediated polymerization in acetic acid. The peaks of xanthate end group are not visible (For example, the methylene group at ~4.6 ppm is missing), which indicates the xanthate is not attached on the polymer terminus.

Figure S12. SEC trace of poly(1VIM) obtained by Xanthate 2 mediated polymerization in acetic acid, a relatively broad distribution was observed. ($M_n=5,800$ g/mol, $D=1.26$, PMMA standards)
**Figure S13.** $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of poly(1VIM)-BTPA. The analyte contains small amount of acetic acid.

**Figure S14.** SEC trace of poly(1VIM-Ac)-BTPA obtained by BTPA controlled polymerization in acetic acid, a relatively narrow distribution was observed. ($M_n = 14,800$ g/mol, $D = 1.08$, PMMA standards)
Figure S15. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of the crude solution of CTPA mediated polymerization of 1VIM in acetic acid after 24 hours reaction. Almost no conversion was observed.

Figure S16. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of the crude solution of BDTB mediated polymerization of 1VIM in acetic acid after 24 hours reaction. Only 2.6% conversion was observed.
Figure S17. SEC traces of poly(1VIM-Ac)s obtained at different reaction time via CDPA controlled polymerization in acetic acid at 70 °C with [1VIM]:[CDPA]:[AIBN]=100:1:0.5;

Figure S18. SEC traces of poly(1VIM-Ac)s obtained at different reaction time via CDPA controlled polymerization in acetic acid at 70 °C with [1VIM]:[CDPA]:[AIBN]=200:1:0.5;
Figure S19. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of poly(1VIM-Ac)-CDPA. The analyte contains small amount of acetic acid.

Figure S20. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of poly(1VIM-b-nBA). The polymerization time was 1.5 hours.
**Figure S21.** $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of poly(1VIM-$b$-nBA). The polymerization time was 2.5 hours.

**Figure S22.** $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of poly(1VIM-$b$-nBA). The polymerization time was 3.0 hours.
Figure S23. $^1$H DOSY spectrum (DMSO-$d_6$, 400 MHz) for poly(1VIM)-CDPA.
Table S1. Summary of block copolymer synthesis with poly(1VIM-Ac)-CDPA as macroCTA.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Second block monomers</th>
<th>Equivalent to MacroCTA</th>
<th>Reaction time (h)</th>
<th>Conversion (%)</th>
<th>( M_n, \text{NMR}^a ) (g/mol)</th>
<th>( M_n, \text{theo.}^b ) (g/mol)</th>
<th>( M_n, \text{SEC}^c ) (g/mol)</th>
<th>( Đ )</th>
<th>SEC unimodal distribution (Y/N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( n )-Butyl acrylate (nBA)</td>
<td>160</td>
<td>1.5</td>
<td>24.1</td>
<td>10,388</td>
<td>10,145</td>
<td>12,600</td>
<td>1.09</td>
<td>Y</td>
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<tr>
<td>2</td>
<td>( n )-Butyl acrylate (nBA)</td>
<td>160</td>
<td>2.5</td>
<td>38.5</td>
<td>13,573</td>
<td>13,099</td>
<td>14,200</td>
<td>1.10</td>
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</tr>
<tr>
<td>3</td>
<td>( n )-Butyl acrylate (nBA)</td>
<td>160</td>
<td>3.0</td>
<td>56.8</td>
<td>17,304</td>
<td>16,852</td>
<td>18,700</td>
<td>1.13</td>
<td>Y</td>
</tr>
<tr>
<td>4</td>
<td>( N,N )-Dimethylacrylamide (DMA)</td>
<td>160</td>
<td>3.0</td>
<td>77.8</td>
<td>19,606</td>
<td>18,663</td>
<td>29,300</td>
<td>1.17</td>
<td>Y</td>
</tr>
<tr>
<td>5</td>
<td>Styrene (S)</td>
<td>100</td>
<td>24</td>
<td>31.6</td>
<td>7,191</td>
<td>9,152</td>
<td>12,100</td>
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<tr>
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<td>( N )-Vinylpyrrolidone (NVP)</td>
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<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

All reactions were carried out in DMF with monomer concentration at 2 mol/L, the initiator AIBN were 0.2 equivalent to macroCTA. \(^a\) Calculated by comparing the integration of the polymer imidazole rings and second block from \(^1\)H NMR spectra in DMSO-d_6. \(^b\) theoretical molecular weight as calculated by conversion, \(^c\) number average molecular weight relative to PMMA standards as determined by DMF SEC.
Figure S24. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of poly(1VIM-b-DMA).

Figure S25. SEC traces of poly(1VIM-b-DMA), ($M_n=29,300$ g/mol, $D=1.17$) and macroCTA poly(1VIM-Ac).
**Figure S26.** $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of poly(1VIM) and PS after purification by precipitation in diethyl ether and following dialysis. *The aromatic regions of PS are visible around 6.52 ppm and 7.09 ppm, which indicates the presence of PS block.*

**Figure S27.** SEC traces of poly(1VIM) and PS, ($M_n=12,100$ g/mol, $D=1.14$) and macroCTA poly(1VIM-Ac).
**Figure S28.** $^1$H DOSY spectrum (DMSO-$d_6$, 400 MHz) for poly(1VIM) and PS after purification by precipitation in diethyl ether and following dialysis.
Figure S29. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of poly(1VIM) and PNVP after purification by precipitation in diethyl ether and following dialysis. The PNVP block is not visible in the spectrum, which indicates the PNVP was not successfully coupled with poly(1VIM).

References