

## Supporting Information for

# ***Deep Eutectic Solvents* for Cu-catalysed ARGET ATRP under Air Atmosphere: a Sustainable and Efficient Route to Poly(methyl methacrylate) using Recyclable Cu(II) Metal-Organic Framework.**

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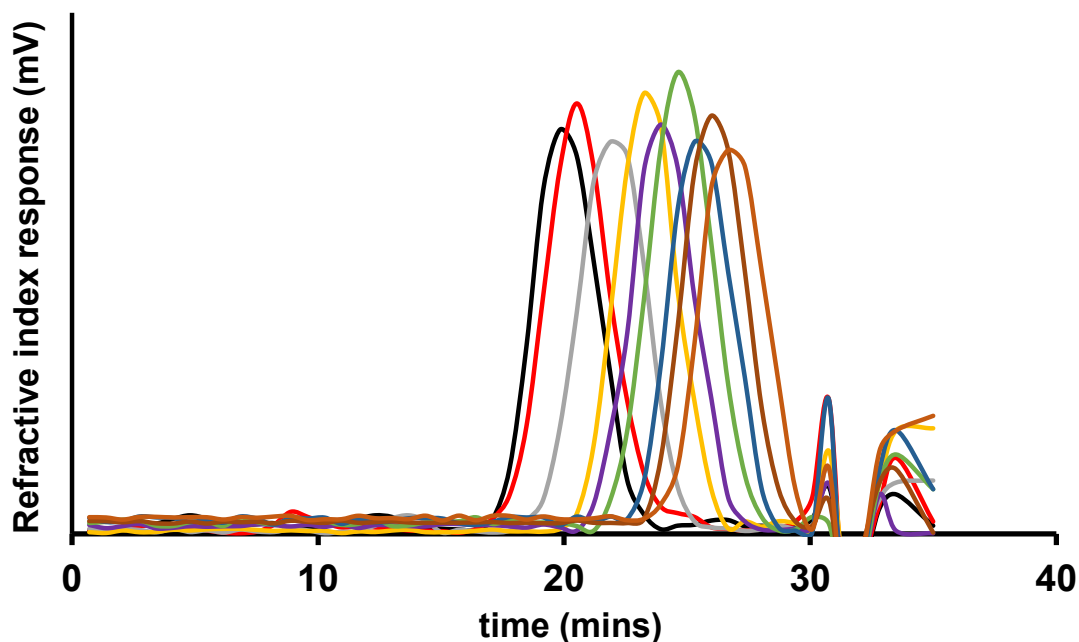
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**Table S1.** Molecular weight parameters at different reaction times for PMMAs prepared by homogeneous CuCl<sub>2</sub>-catalysed ARGET ATRP in DES (1*ChCl*/2*Gly*).

Entry <sup>[a]</sup>	t (mins)	Conv. (%) <sup>[b]</sup>	$M_n^{\text{th}}$ Kg/mol <sup>[c]</sup>	$M_n^{\text{SEC}}$ Kg/mol <sup>[d]</sup>	$\bar{D}$ <sup>[e]</sup>
1	10	13	6.12	6.48	1.17
2	20	16	7.53	7.10	1.19
3	30	20	9.41	9.50	1.23
4	40	23	10.8	12.0	1.28
5	50	30	14.1	15.8	1.19
6	60	40	18.8	19.0	1.17
7	80	57	26.8	27.5	1.29
8	100	85	39.9	42.2	1.22
9	120	94	44.2	46.8	1.20

[a] General conditions: [MMA]<sub>0</sub>/[EBiB]<sub>0</sub>/[Sn(EH)<sub>2</sub>]<sub>0</sub>/[CuCl<sub>2</sub>]<sub>0</sub>/[PMDETA]<sub>0</sub> = 470/1/48/0.23/0.56; T = 70° C; [MMA]<sub>0</sub>/[DES]<sub>0</sub> = 4.2 (v/v). [b] Conversions of the monomer (MMA) were determined by relative integration of MMA and PMMA characteristic peaks in the <sup>1</sup>H-NMR spectra of the reaction crudes. [c]  $M_n^{\text{th}}$  = Theoretical molecular weight = [MMA]<sub>0</sub>/[Initiator]<sub>0</sub> ×  $M_{\text{MMA}}$  × conversion ( $M_{\text{MMA}}$  = molecular weight of MMA = 100.12 g/mol). [d]  $M_n^{\text{SEC}}$ : Molecular weight determined by size exclusion chromatography. [e] Polydispersity index ( $M_w/M_n$ ) determined by size exclusion chromatography.

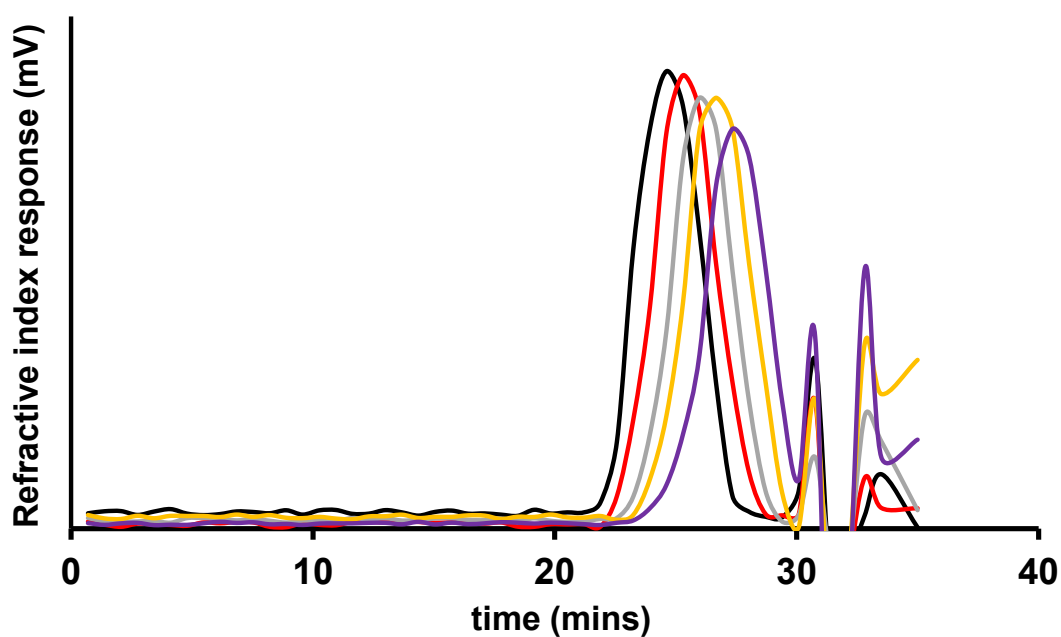


**Figure S1.** GPC traces of PMMAs prepared in Table S1. Color code corresponds to colors in Table S1.

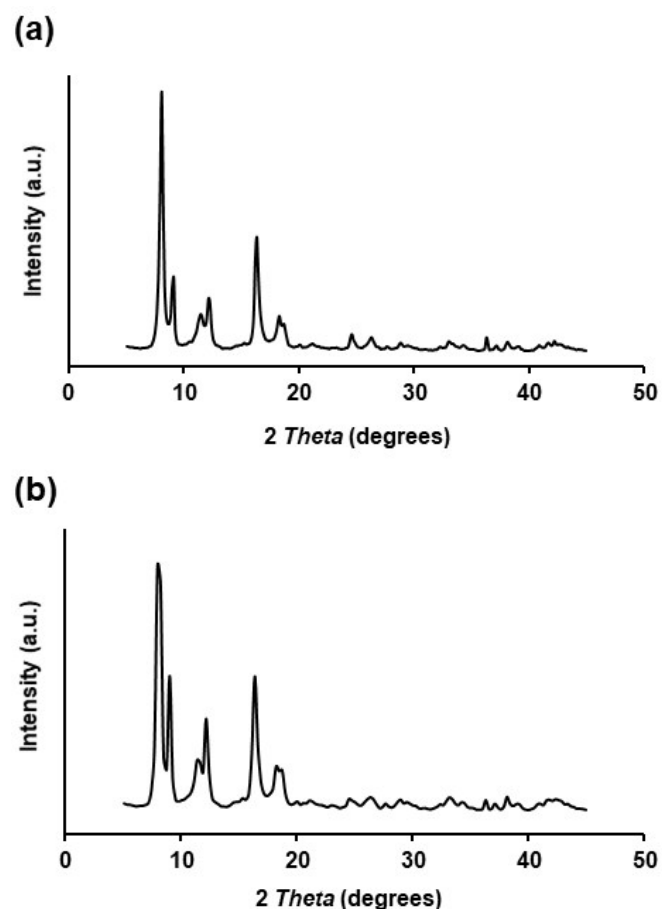
**Table S2.** Molecular weight parameters at different reaction times for PMMAs prepared by heterogeneous Cu(II) MOF-catalysed ARGET ATRP in DES (1*ChCl*/2*Gly*).

Entry <sup>[a]</sup>	t (mins)	Conv. (%) <sup>[b]</sup>	$M_n^{\text{th}}$ Kg/mol <sup>[c]</sup>	$M_n^{\text{SEC}}$ Kg/mol <sup>[d]</sup>	$\bar{D}$ <sup>[e]</sup>
<b>1</b>	<b>20</b>	<b>3.6</b>	<b>1.69</b>	<b>1.75</b>	<b>1.23</b>
<b>2</b>	<b>45</b>	<b>7.1</b>	<b>3.35</b>	<b>3.55</b>	<b>1.14</b>
3	75	13.7	6.44	7.12	1.14
<b>4</b>	<b>105</b>	<b>17.7</b>	<b>8.33</b>	<b>9.25</b>	<b>1.12</b>
<b>5</b>	<b>120</b>	<b>23.0</b>	<b>10.8</b>	<b>11.9</b>	<b>1.13</b>

[a] General conditions:  $[\text{MMA}]_0/[\text{EBiB}]_0/[\text{Sn}(\text{EH})_2]_0/[\text{Cu}_2(\text{bdc})_2(\text{DABCO})]_0 = 470/1/96/0.48$ ;  $T = 70^\circ \text{C}$ ;  $[\text{MMA}]_0/[\text{DES}]_0 = 1.0$  (v/v). [b] Conversions of the monomer (MMA) were determined by relative integration of MMA and PMMA characteristic peaks in the  $^1\text{H-NMR}$  spectra of the reaction crudes. [c]  $M_n^{\text{th}}$  = Theoretical molecular weight =  $[\text{MMA}]_0/[\text{Initiator}]_0 \times M_{\text{MMA}} \times \text{conversion}$  ( $M_{\text{MMA}}$  = molecular weight of MMA = 100.12 g/mol). [d]  $M_n^{\text{SEC}}$ : Molecular weight determined by size exclusion chromatography. [e] Polydispersity index ( $M_w/M_n$ ) determined by size exclusion chromatography.



**Figure S2.** GPC traces of PMMAs prepared in Table S2. Color code corresponds to colors in Table S2.



**Figure S3.** XRD profiles of  $\text{Cu}_2(\text{bdc})_2(\text{DABCO})$  MOF before (a) and after (b) ARGET ATRP with MMA.