SUPPORTING INFORMATION

On the effect of using RAFT and FRP for the bulk synthesis of acrylic and methacrylic molecularly imprinted polymers †

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Table S1 Densities, solubility parameters, volume fractions and Flory-Huggins interaction parameters used for estimating the molecular weight between cross-linking points (M_c) in A/M100s and A/M50s.

Table S2 FT-IR data used for calculating the double bond conversion after polymerisation in A/M100s and A/M50s.

Figure S1 (a) Evolution of M_n and PDI versus conversion for RAFT synthesized P(M)MA₁₂₀. (b) Conversion and ln([M₀]/[M]) versus times for RAFT synthesized P(M)MA₁₂₀.

Figure S2 Equilibrium binding experiments on A/M30s and A/M15s.

Flory-Huggins interaction parameters χ applied to the estimation of M_{cs} were calculated according to equation 1¹.

$$\chi = V_{mol} \frac{(\delta_{Tpol} - \delta_{Tsol})^2}{_{RT}}$$
(1)

where V_{mol} is the molar volume of the solvent [i.e. toluene, 106.3 (cm³/mol)], *T* is the temperature (298.15 K), *R* is the ideal gas constant [8.3144 (J/mol K)], and δ_{Tpol} and δ_{Tsol} are the solvent [18.2 (MPa^{1/2})]² and polymer² global solubility parameters.

	d (g/mL)	$\delta_{\rm T} ({\rm MPa}^{1/2})$	Q	$V_{ m p}$	χ	$M_{\rm c}$ (g/mol)
A100 RAFT	1.22	20.77	1.184 ± 0.004	0.457	0.283	2200
A100 FRP	1.22	20.77	1.154 ± 0.035	0.464	0.283	2100
M100 RAFT	1.18	19.34	1.053 ± 0.042	0.505	0.056	900
M100 FRP	1.18	19.34	0.935 ± 0.038	0.500	0.056	800
A50 RAFT	1.22	20.77	0.967 ± 0.061	0.508	0.283	1800
A50 FRP	1.22	20.77	0.718 ± 0.022	0.582	0.283	1500
M50 RAFT	1.18	19.34	0.982 ± 0.068	0.487	0.056	900
M50 FRP	1.18	19.34	1.002 ± 0.015	0.517	0.056	900

Table S1 Density (d), total solubility parameters (δ_T), volume fractions of polymer in the swollen mass (Q, V_p), Flory-Huggins interaction parameters (χ) and M_c s.

Table S2 FT-IR data (v and corresponding heights) used for measuring the double bond conversion upon polymerisation. NPGDMA represents the reference for a 0% conversion.

	C=O		C=C		Height ratio
	$v (cm^{-1})$	Height	$v (cm^{-1})$	Height	
NPGDMA	1724	39.069	1637	11.278	28.86
A100 RAFT	1727	11.662	1650	1.282	10.99
A100 FRP	1728	9.708	1650	0.806	8.3
M100 RAFT	1729	9.996	1644	1.086	10.86
M100 FRP	1726	11.502	1648	0.892	7.75
A50 RAFT	1726	15.212	1648	1.742	11.45
A50 FRP	1727	13.815	1650	1.714	12.4
M50 RAFT	1726	12.375	1650	1.194	9.65
M50 FRP	1727	12.269	1648	1.118	9.11





Figure S1 (a) Average number molecular weight (M_n , filled circles) and PDIs (M_w/M_n , empty circles) versus conversion for RAFT synthesized P(M)MA₁₂₀. (b) Conversion versus time (red circles) and ln([M₀]/[M]) versus time (black symbols) for P(M)MA₁₂₀.



Figure S2 Equilibrium binding experiments on A/M30s and A/M15s. Black and red symbols are respectively RAFT and FRP MIPs (filled spheres) and NIPs (empty circles).

- 1. M. Rubinstein and R. H. Colby, *Polymer Physics*, Oxford University Press, New York, 2003.
- 2. J. Brandrup, E. H. Immergut, E. A. Grulke, A. Abe and D. R. Bloch, *Polymer handbook*, John Wiley & Sons, Inc., 1999.