Electronic Supplementary Information (ESI)

Using click chemistry to dial up the modulus of doubly crosslinked microgels through precise control of microgel building block functionalisation

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Azidopropyl methacrylate characterisation

The ^{1}H NMR spectrum for azidopropyl methacrylate (AZPMA) is shown in in Fig. S1. The peak positions and integrations match those reported by Sumerlin et al.[1] and are consistent with pure monomer.
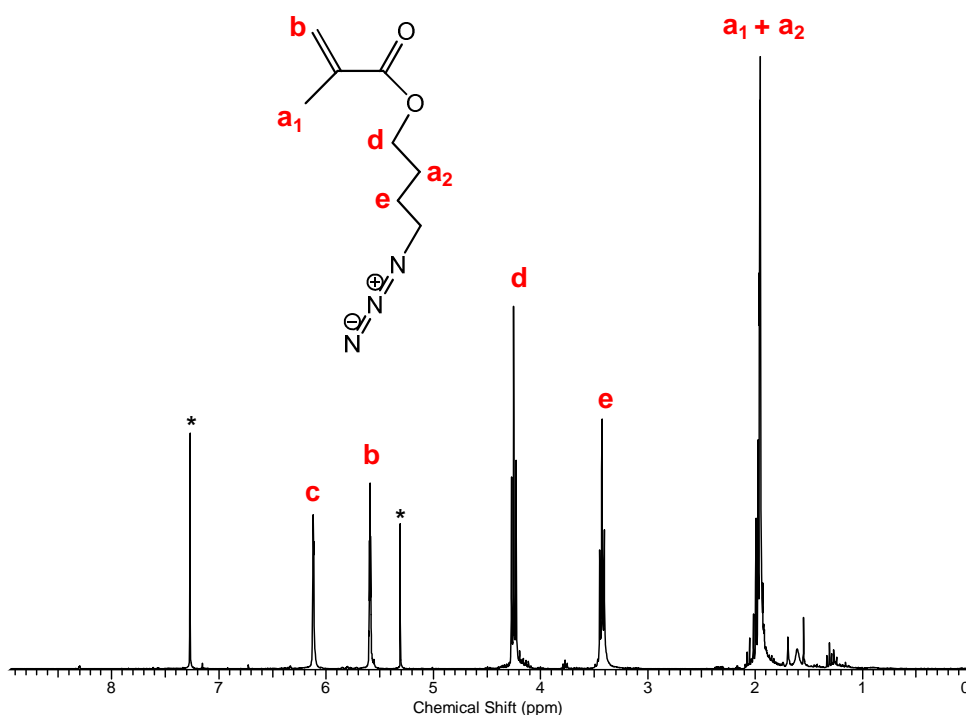

Fig. S1. ^{1}H NMR spectrum for azidopropyl methacrylate

Microgel compositions and elemental analysis data

The approach employed to determine the composition of the microgel (MG) particles followed that reported earlier[2] and used the measured ratios of the %N to %C (= $R_{NC(exp)}$) from elemental analysis data. The structures of the primary polymers used for these calculations are shown in Fig S2. The $R_{NC(exp)}$ values were used to calculate the value of x for PVP-PA$_x$ and also the values of x and y for PVP-PA$_x$-PMA$_y$ as described below.

$(C_7H_7N)_n$
PVP

$(C_7H_7N)_{1-x}(C_6H_6O_2)_x$
PVP-PA$_x$

$(C_7H_7N)_{1-x-y}(C_6H_6O_2)_x(C_{13}H_{17}N_3O_4)_y$
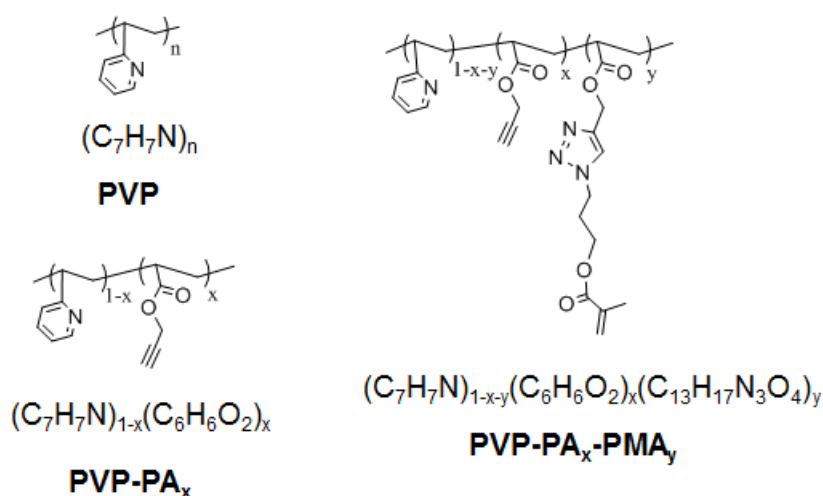**PVP-PA$_x$-PMA$_y$**

Fig. S2. Structures and formulae for the primary polymer chains that comprised the MG particles studied.

Background correction

The value for $R_{NC(exp)}$ underestimated the theoretical value ($R_{NC(thr)}$) based on the composition of the primary structural polymer that comprised the MG particles (Fig. S2) because of the presence of DVB, initiator fragments and residual surfactant. These species were nitrogen-poor and decreased the R_{NC} values. These nitrogen-poor species were assumed to be present at a constant level for all MGs studied. The first step towards using the elemental analysis data to determine composition was to establish a correction for R_{NC}. The %N and %C values for the PVP MG (Table S1) were used obtain a background correction for the elemental analysis data (ΔR_{NC}) using the following equation.

$$\Delta R_{NC} = R_{NC(\text{thr})} - R_{NC(\text{exp})} \qquad \text{(S1)}$$

The value of $R_{NC(thr)}$ for PVP MG was calculated from its structure (Fig. S2) as [(14.007 x 100 x 1) / (12.011 x 100 x 7) =] 0.167. From the latter value and the $R_{NC(exp)}$ value of 0.158 (Table S1) a ΔR_{NC} value of 0.009 was calculated. The latter value was then added to all other $R_{NC(exp)}$ values to give corrected experimental values, i.e., $R_{NC(exp)}{}^{Corr} = R_{NC(exp)} + 0.009$.

Table S1. Elemental analysis data for the MGs studied in this work.

Code	%C	%H	%N	$R_{NC(exp)}{}^{a}$	$R_{NC(exp)}{}^{Corr\ b}$	$y_{exp}{}^{c}$	$x_{exp}{}^{c}$
PVP	74.61 ± 0.97	7.53 ± 0.17	11.78 ± 0.14	0.158 ± 0.001	0.167	-	-
P-0	74.80 ± 0.83	7.27 ± 0.27	10.96 ± 0.25	0.147 ± 0.002	0.156	0	0.073
P-1	73.34 ± 0.82	6.90 ± 0.26	11.18 ± 0.26	0.152 ± 0.002	0.161	0.016	0.057
P-2	72.99 ± 0.81	6.74 ± 0.25	11.45 ± 0.27	0.157 ± 0.002	0.166	0.029	0.044
P-3	71.63 ± 0.80	6.70 ± 0.25	11.80 ± 0.27	0.165 ± 0.002	0.174	0.053	0.020
P-4	68.24 ± 0.76	6.46 ± 0.24	11.58 ± 0.27	0.170 ± 0.002	0.179	0.070	0.003

[a] $R_{NC(exp)}$ = %N / %C. [b] Corrected value – see text. [c] Experimentally determined composition parameters – See text and Fig. S2.

Composition determination for PVP-PA$_x$

The elemental analysis data were used to estimate the composition of PVP-PA$_x$ (P-0 in Table S1) using the following equations, which are based on the structure of the copolymer (Fig. S2).

$$\%C = \left(\frac{12.011x100}{MW}\right)[7(1-x)+6x] \quad (S2)$$

$$\%N = \left(\frac{14.007x100}{MW}\right)(1-x) \quad (S3)$$

Using equations S2 and S3 we obtained:

$$x = \frac{1.1662 - 7R_{NC(exp)}}{1.1662 - R_{NC(exp)}} \quad (S4)$$

The value of $R_{NC(exp)} = 0.147$ (Table S1) was replaced with the corrected value ($R_{NC(exp)}{}^{Corr}$) of 0.156 for PVP-PA$_x$, which gave a value for x of 0.073. Accordingly, the estimated composition of the copolymer that comprised the P-0 MG particles was PVP-PA$_{0.07}$.

Composition determinations for PVP-PA$_x$-PMA$_y$

The composition of PVP-PA$_x$-PMA$_y$ is shown in Fig. S2. The following equations can be written for this copolymer.

$$\%C = \left(\frac{12.011 x 100}{MW}\right)[7(1 - x - y) + 6x + 13y] \quad \text{(S5)}$$

$$\%N = \left(\frac{14.007 x 100}{MW}\right)[(1 - x - y) + 3y] \quad \text{(S6)}$$

$$x + y = 0.073 \quad \text{(S7)}$$

Equation S7 follows from the estimated composition for PVP-PA$_x$ (above). From these equations and $R_{NC(exp)}$ = %N/%C the following expression for the experimentally determined y values were established.

$$y_{exp} = \frac{6.9273 R_{NC(exp)} - 1.0814}{3.4986 - 7 R_{NC(exp)}} \quad \text{(S8)}$$

The values of $R_{NC(exp)}{}^{Corr}$ were used for $R_{NC(exp)}$ as described above which gave the experimentally determined y (and x) values shown in Table S1 and the compositions shown in Table 1.
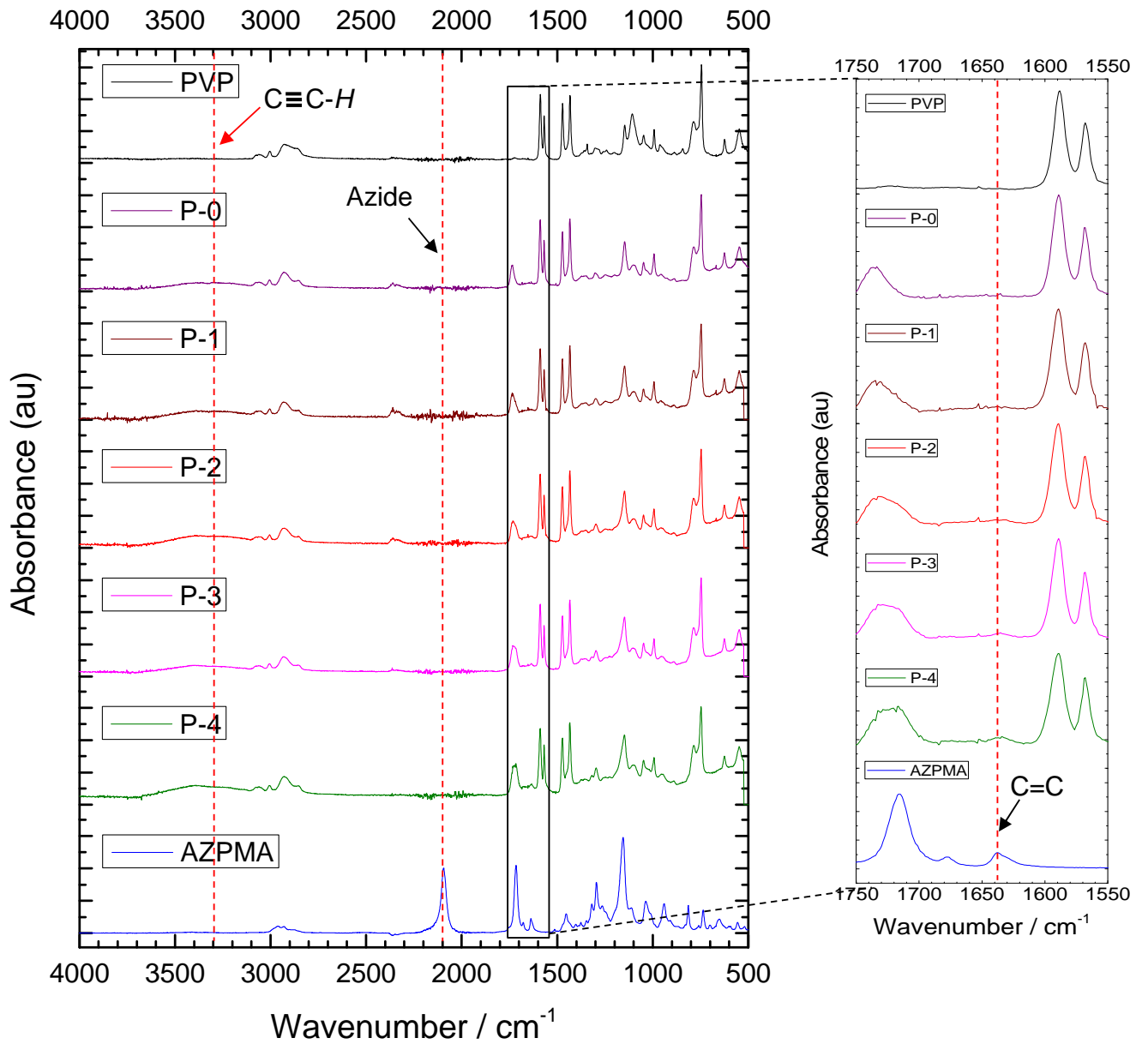
Fig. S3. FTIR spectra for the MG particles studied. The inset shows an expanded view of the 1550 to 1750 cm^{-1} range. Data for AZPMA are also shown for comparison.
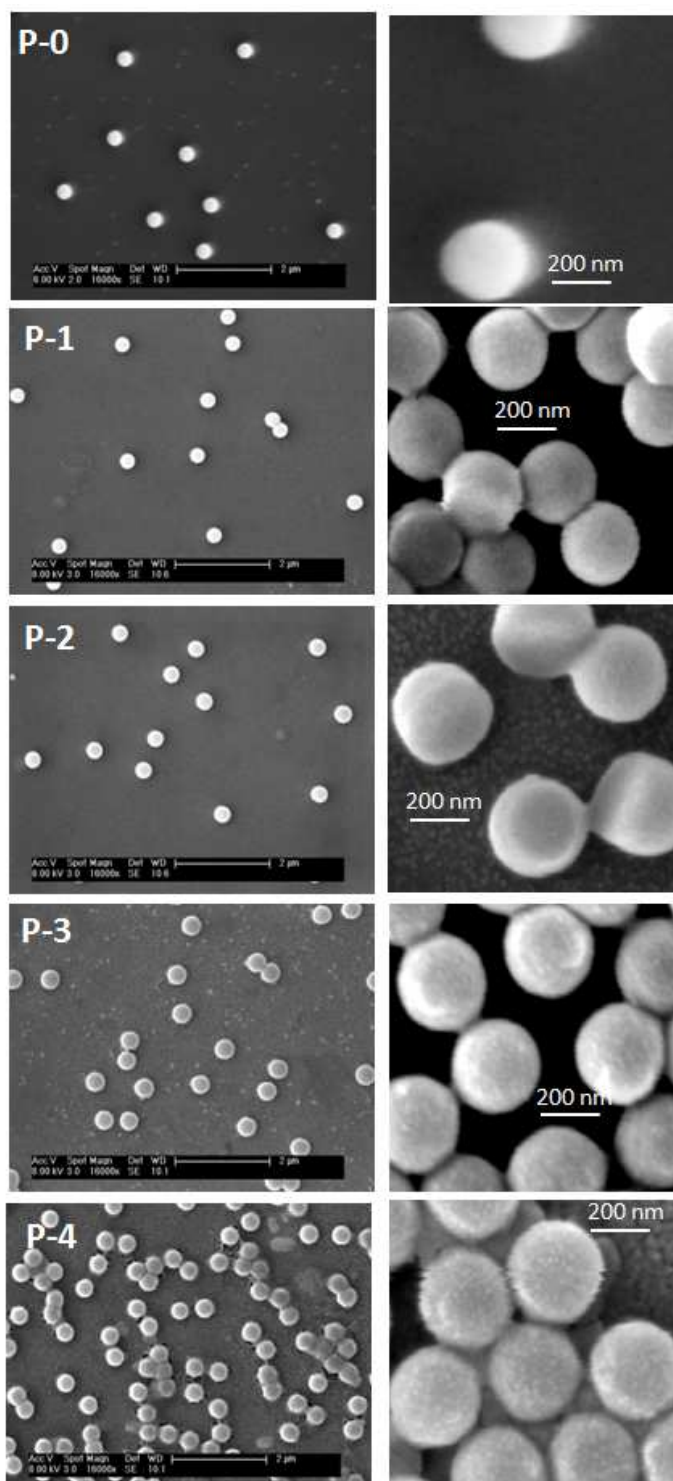
Fig. S4 SEM images for various PVP-PA$_x$-PMA$_y$ MG particles. The compositions for the MGs are shown in Table 1.

References

1.   B. S. Sumerlin, N. V. Tsarevsky, G. Louche, R. Y. Lee, and K. Matyjaszewski. *Macromolecules* 2005, **38**, 7540-7545.
2.   R. Farley, and B. R. Saunders. *Polymer* 2014, **55**, 471-480.