Electronic Supplementary Material (ESI) for Soft Matter.

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Electronic Supplementary Information for Soft Matter manuscript:

Enhanced stability of complex coacervate core micelles following different core-crosslinking strategies

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^{1}H-NMR spectra of the homopolymer poly(2-vinylpyridine)$_{44}$ (P2VP$_{44}$) before and after quaternization (Fig. S1). These data show that the quaternization and deprotection of the homopolymer were successful, so that the quaternization procedure could also be applied to the diblock copolymer poly(2-vinylpyridine)$_{128}$-*block*-poly(ethylene oxide)$_{477}$ (P2VP$_{128}$-*b*-PEO$_{477}$).

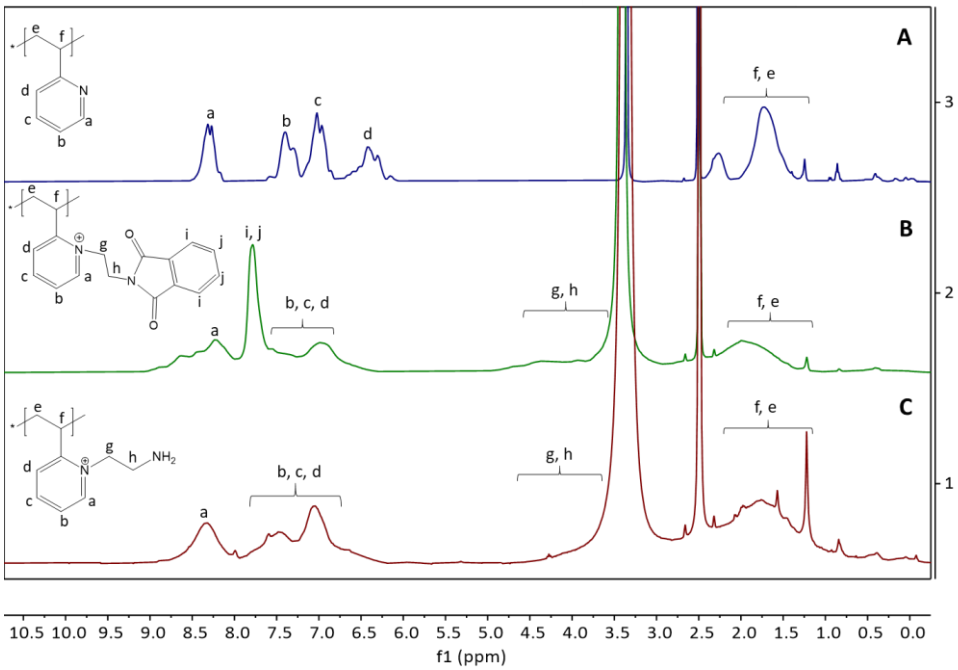

Fig. S1 ^{1}H-NMR spectra of the homopolymer P2VP$_{44}$. (A) Homopolymer before quaternization, (B) homopolymer after quaternization using *N*-(2-bromoethyl)phthalimide, (C) quaternized homopolymer after deprotection using hydrazine hydrate. Spectra A, B, and C were recorded in DMSO-d$_6$.

The quaternization degree of the homopolymer $P2VP_{44}$ was calculated from the ratio of the integral area of the aromatic rings and the integral area of P2VP's backbone, and was about 92% (Fig. S2).

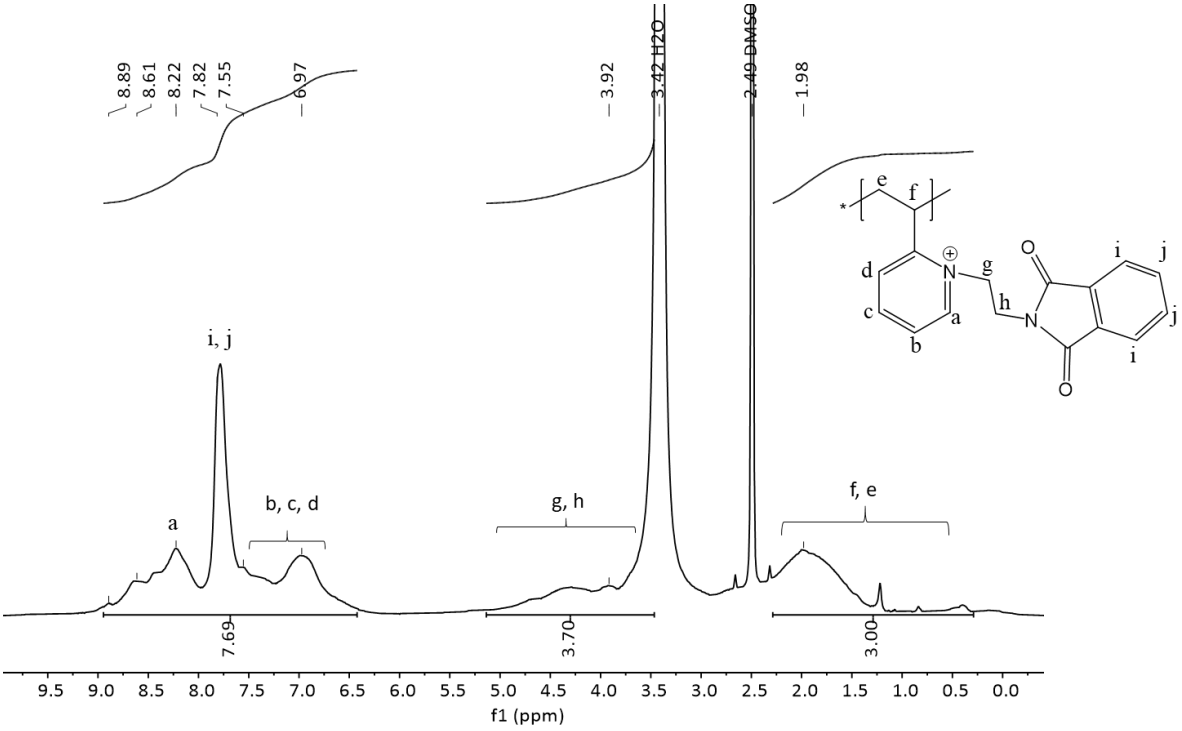

Fig. S2 ^{1}H-NMR spectrum of the homopolymer $P2VP_{44}$ after quaternization using *N*-(2-bromoethyl)phthalimide. The spectrum was recorded in DMSO-d_6. Degree of quaternization (DQ) was calculated from the ratio of the integral area of the aromatic rings and the integral area of P2VP's backbone. DQ = (((7.69 – 4)/4) : (3/3)) * 100% = 92%.

^{1}H-NMR spectrum of the diblock copolymer poly(2-vinylpyridine)$_{128}$-*block*-poly(ethylene oxide)$_{477}$ (P2VP$_{128}$-*b*-PEO$_{477}$) before quaternization in $CDCl_3$, to confirm the composition of P2VP-*b*-PEO before quaternization (Fig. S3).

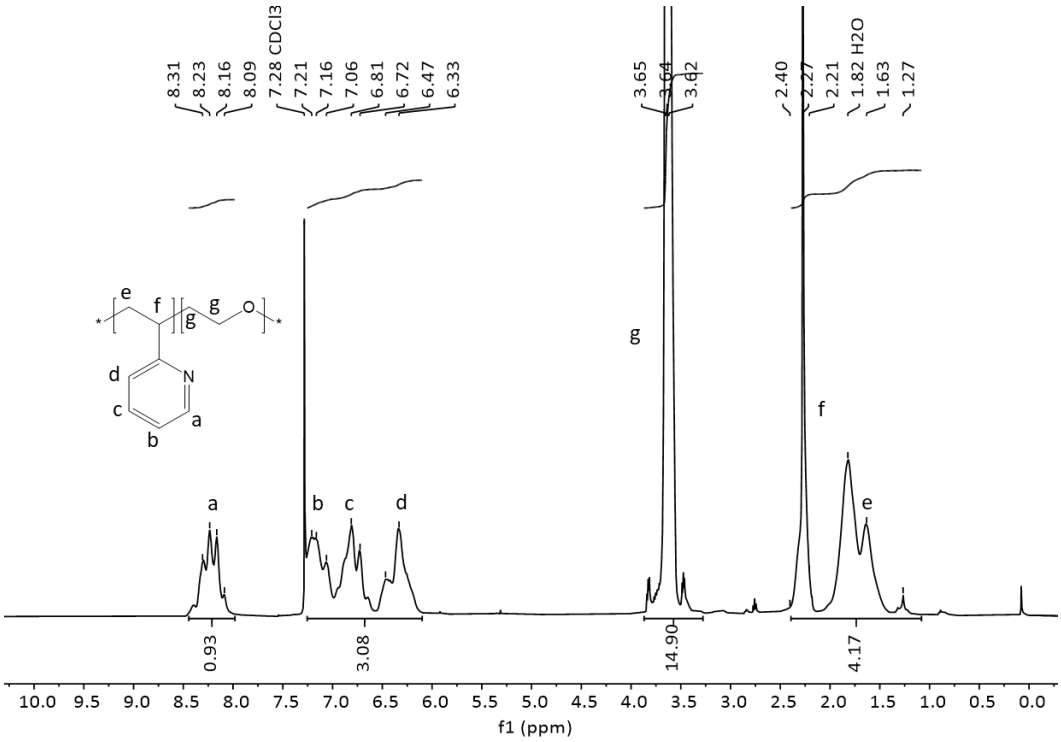

Fig. S3 ^{1}H-NMR spectrum of the neat diblock copolymer P2VP$_{128}$-*b*-PEO$_{477}$ in $CDCl_3$. The block ratio of P2VP and PEO was calculated from the ratio of the integral area of the aromatic rings and the integral area of PEO. Block ratio = (0.93 + 3.08) : 14.9 = 4.0 : 14.9 = 128 : 477.

The quaternization degree of the diblock copolymer $P2VP_{128}$-*b*-PEO_{477} was calculated from the ratio of the integral area of the aromatic region and the integral area of P2VP's backbone, and was about 85% (Fig. S4).

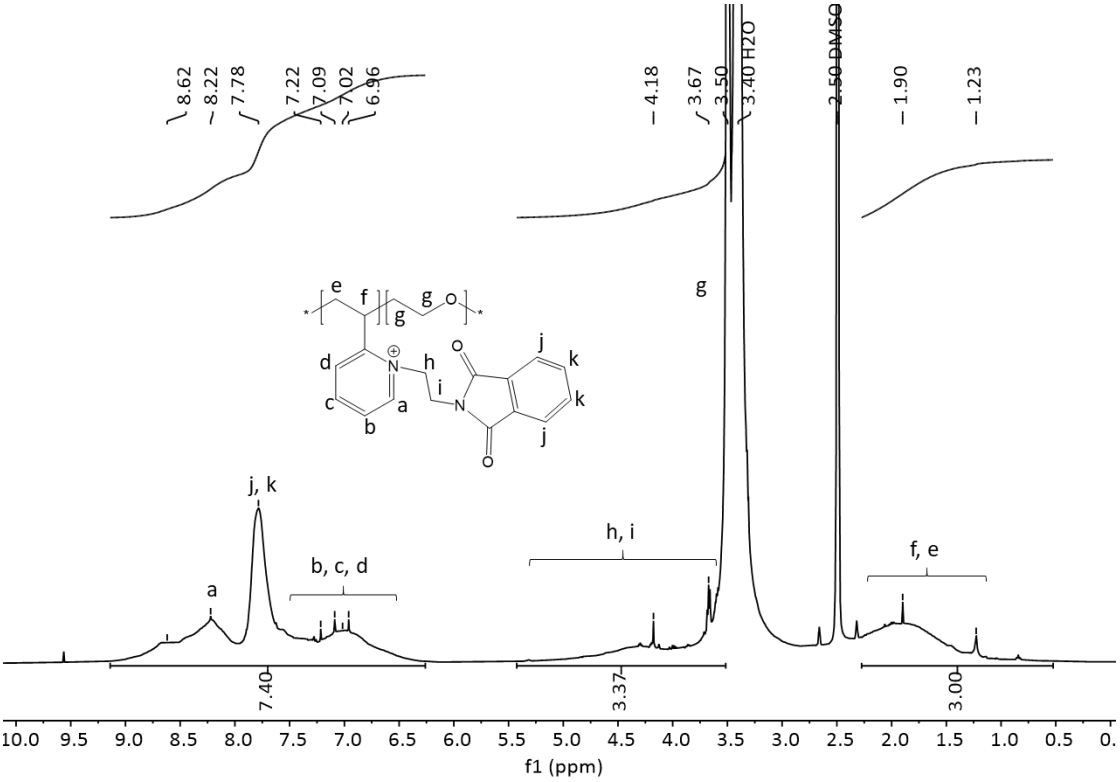

Fig. S4 ^{1}H-NMR spectrum of the diblock copolymer $P2VP_{128}$-*b*-PEO_{477} after quaternization using *N*-(2-bromoethyl)phthalimide. The spectrum was recorded in DMSO-d_6. The degree of quaternization (DQ) was calculated from the ratio of the integral area of the aromatic rings and the integral area of P2VP's backbone. DQ = (((7.4 – 4)/4) : (3/3)) * 100 % = 85%.

For determination of the CMC, a 2.50 µM C3M stock solution was diluted with buffer and analyzed by dynamic light scattering (DLS). From this dilution series, the CMC was estimated to be equal to or lower than 0.59 µM – at even lower polymer concentrations the measurement becomes inaccurate due to relatively strong scattering of the buffer (17 – 20 kHz).

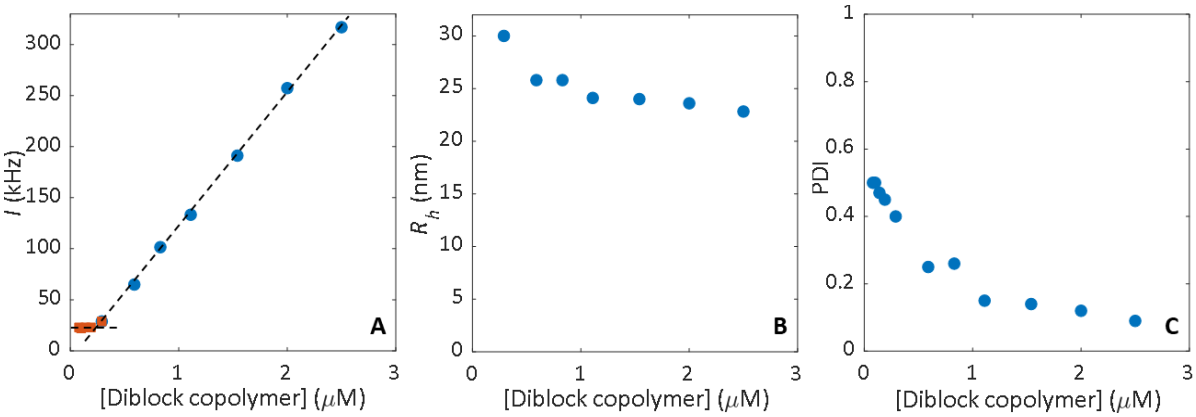

Fig. S5 Determination of the critical micelle concentration (CMC) at the PMC. DLS results are plotted as a function of the quaternized P2VP$_{128}$-*b*-PEO$_{477}$ concentration. (A) Absolute scattering intensity (I), (B) hydrodynamic radius (R_h), and (C) polydispersity index (PDI). Dashed lines indicate the slope of the scattering intensity values during dilution. Orange data points indicate weak scattering below the estimated CMC.