

SUPPLEMENTARY INFORMATION

Poly(vinylamine) Microgels: pH-Responsive Particles with High Primary Amine Contents

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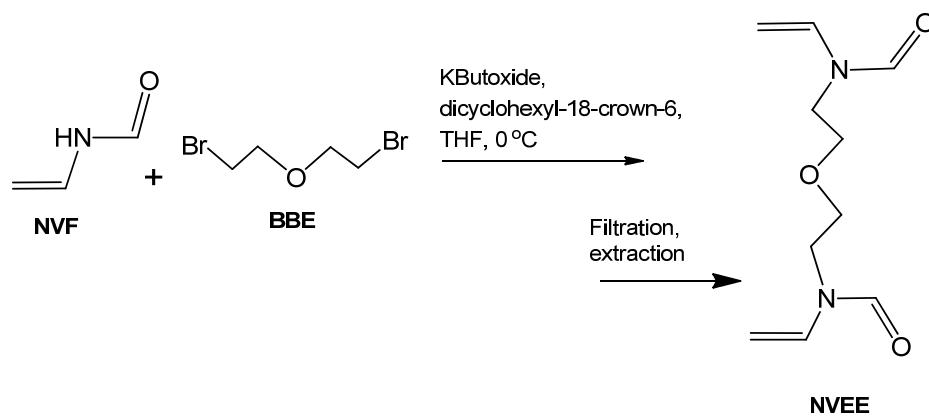
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NVEE synthesis and characterisation

NVEE is a potentially important difunctional monomer because it can be alkali-hydrolysed without cleaving the ether linkage between crosslinking junctions¹. The product was conveniently prepared in multigram quantities (See Experimental Section). The synthetic method employed is depicted in Scheme S1.



Scheme S1. Depiction of method used to synthesize NVEE.

The measured (and expected) %C, %H and %N values from elemental analysis for NVEE were 56.2 % (56.6 %), 8.2 % (7.6 %) and 13.4 % (13.2 %), respectively. This agreement shows the product can be considered compositionally pure. The ¹H NMR spectrum of NVEE is shown in Fig.

S1(a). The peak positions match those reported earlier by Shi et al.² For comparison, the spectrum for as-supplied NVF is shown in Fig. S1(b). For NVF there are two environments for the hydrogen attached to the amide (e_{cis} and e_{tr}) and the vinyl hydrogen closest to the nitrogen atom (c_{cis} and c_{tr}) (Fig. S1(b)). These are ascribed to³⁻⁴ *trans* and *cis* isomers. From our spectral integrations for NVF the *trans*-to-*cis* molar ratio was 3:1. This is the same ratio reported by White et al.⁴ for NVF.

In the case of NVEE (Fig. S1(a)) there are also two environments for the hydrogen attached to the amide (e_{cis} and e_{tr}) and the vinyl hydrogen closest to the nitrogen atom (c_{cis} and c_{tr}). The ratio of the integrated areas for e_{trans} / e_{cis} and c_{trans} / c_{cis} are *both* 1 to 2. Accordingly, the ¹H NMR data show that the proportion of *trans*-to-*cis* species for as made NVEE is 1:2. The ratio of *trans* to *cis* was significantly smaller for NVEE compared to NVF. We speculate that the *cis* isomer is favoured because it maximises separation of the unpaired oxygen electrons (from C=O) and the hydrogen atoms (labelled as f) in the CH₂ groups from the ether linkage.

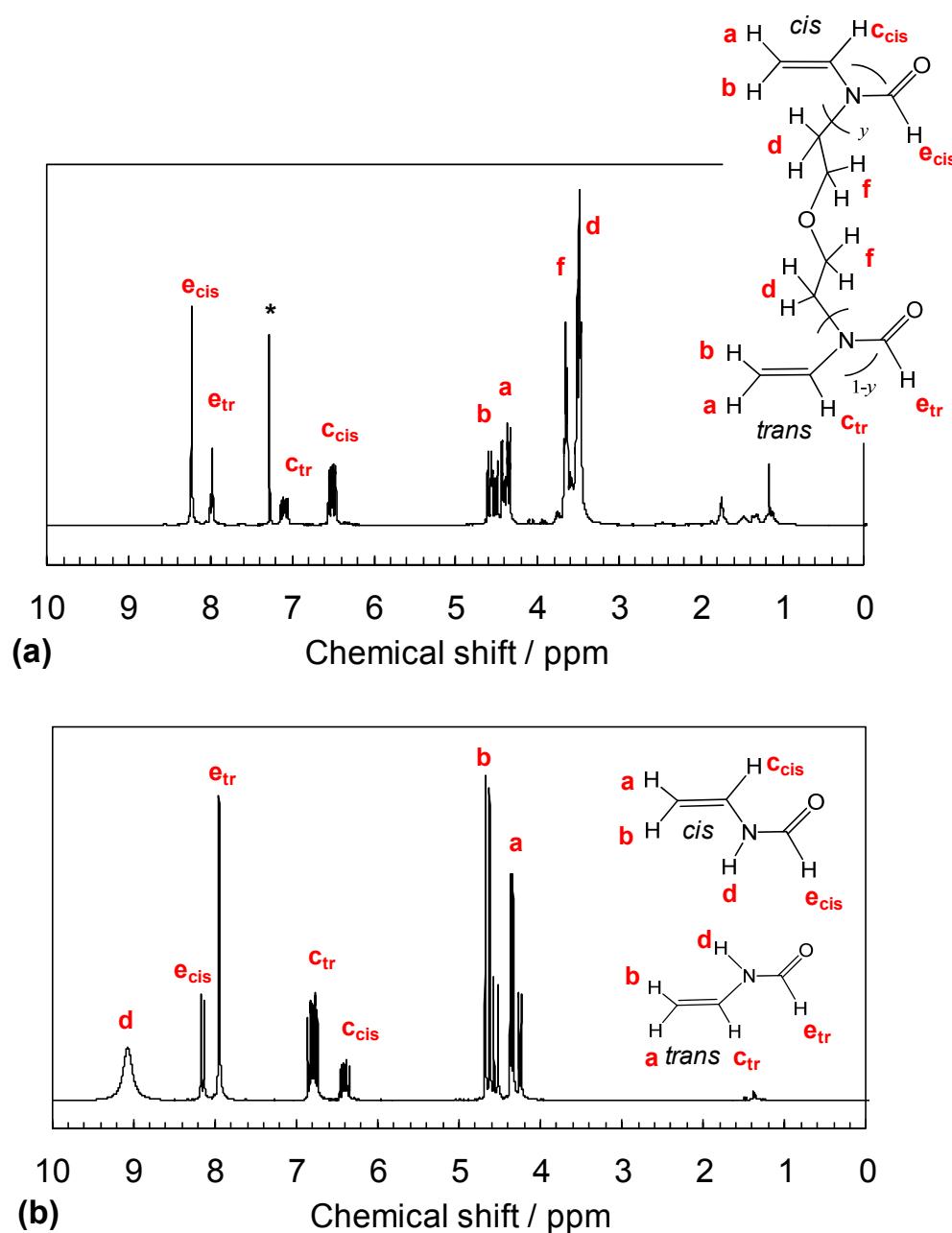


Fig. S1. ¹H NMR spectrum of (a) NVEE and (b) NVF. The asterisk indicates a solvent (CHCl_3) peak. NVEE and NVF exist as mixtures of *cis* and *trans* isomers.

The FTIR spectrum for NVEE is shown in Fig. S2. The spectrum for NVF is shown for comparison. The spectra show that relative heights of the bands due to the vinyl groups⁵ (1632 cm^{-1}) and that of the $-\text{NHC}(=\text{O})\text{H}$ stretch² (1680 cm^{-1}) are similar for NVEE and NVF. The key difference between the spectra is the loss of stretches associated with NH groups for the NVEE system. The NVEE spectrum does not have the amide II band (1510 cm^{-1}), the N-C-H bending mode at⁶ 1380 cm^{-1} , and the N-H band at 3260 cm^{-1} . Our product did not contain residual NVF. Furthermore, there is a new peak for NVEE at 1090 cm^{-1} . This is ascribed to an ether-type band⁷ ($\text{CH}_2\text{-O-CH}_2$).

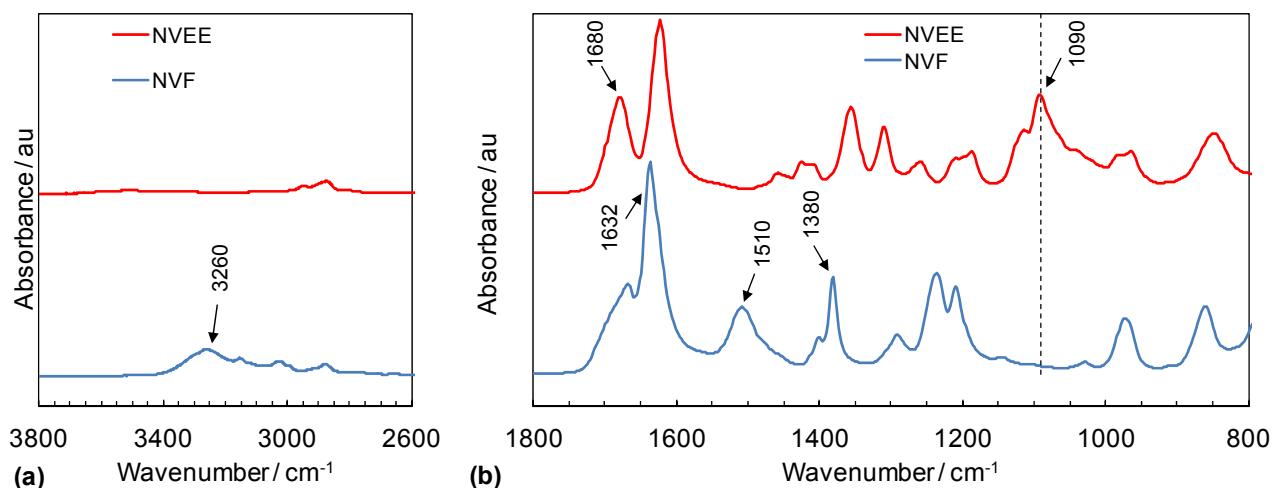


Fig. S2 FTIR spectra of NVEE and NVF. Key positions for the spectra are indicated.

Table S1. Elemental data for the microgels.

Code	%C	%H	%N
PNVF	45.2	7.9	17.2
PNVF-4NVEE	47.2	7.9	17.0
PNVF-9NVEE	48.6	7.8	17.1
PNVF-13NVEE	46.9	7.6	16.1
PVAM ^a	45.2	11.0	24.3
PVAM-4BEVAME	41.7	9.4	19.9
PVAM-9BEVAME	43.2	10.4	21.6
PVAM-13BEVAME	43.1	10.3	20.3

^a From ref.8.

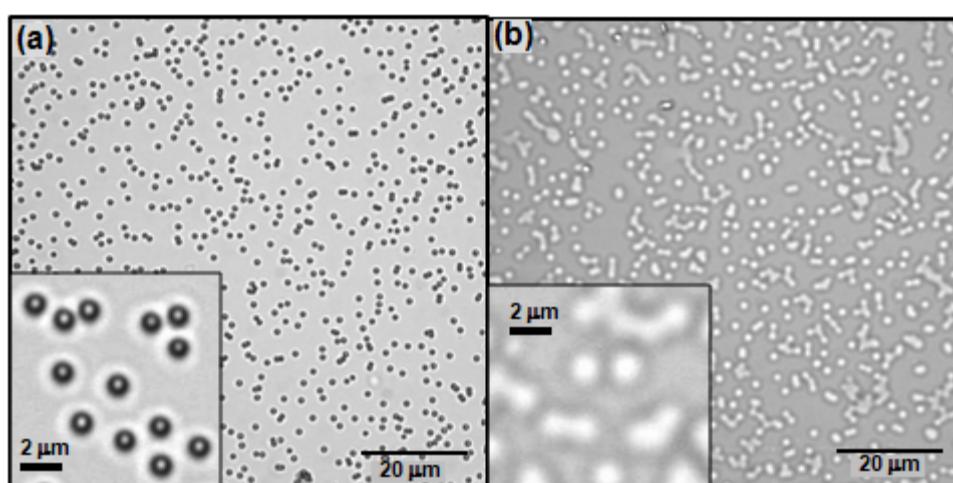


Fig. S3. Optical microscopy images of PNVF particles (a) deposited on a glass microscope slide from ethanol and (b) 5 minutes after ethanol had evaporated. The particles had begun to spread and coalesce in air.

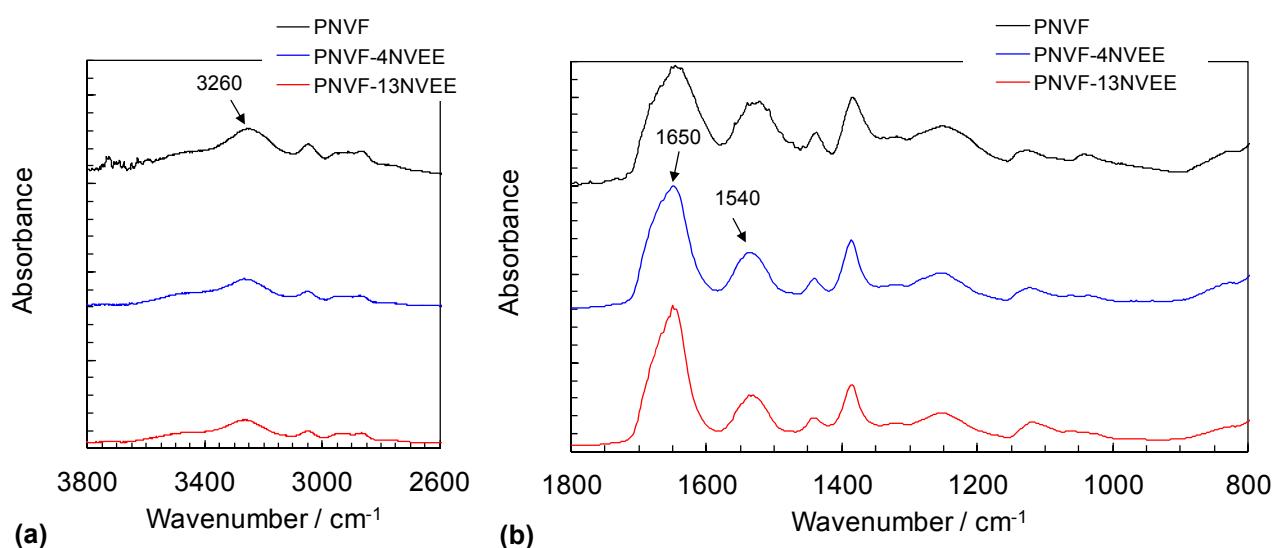


Fig. S4 FTIR spectra of PNVF and PNVF- x NVEE particles.

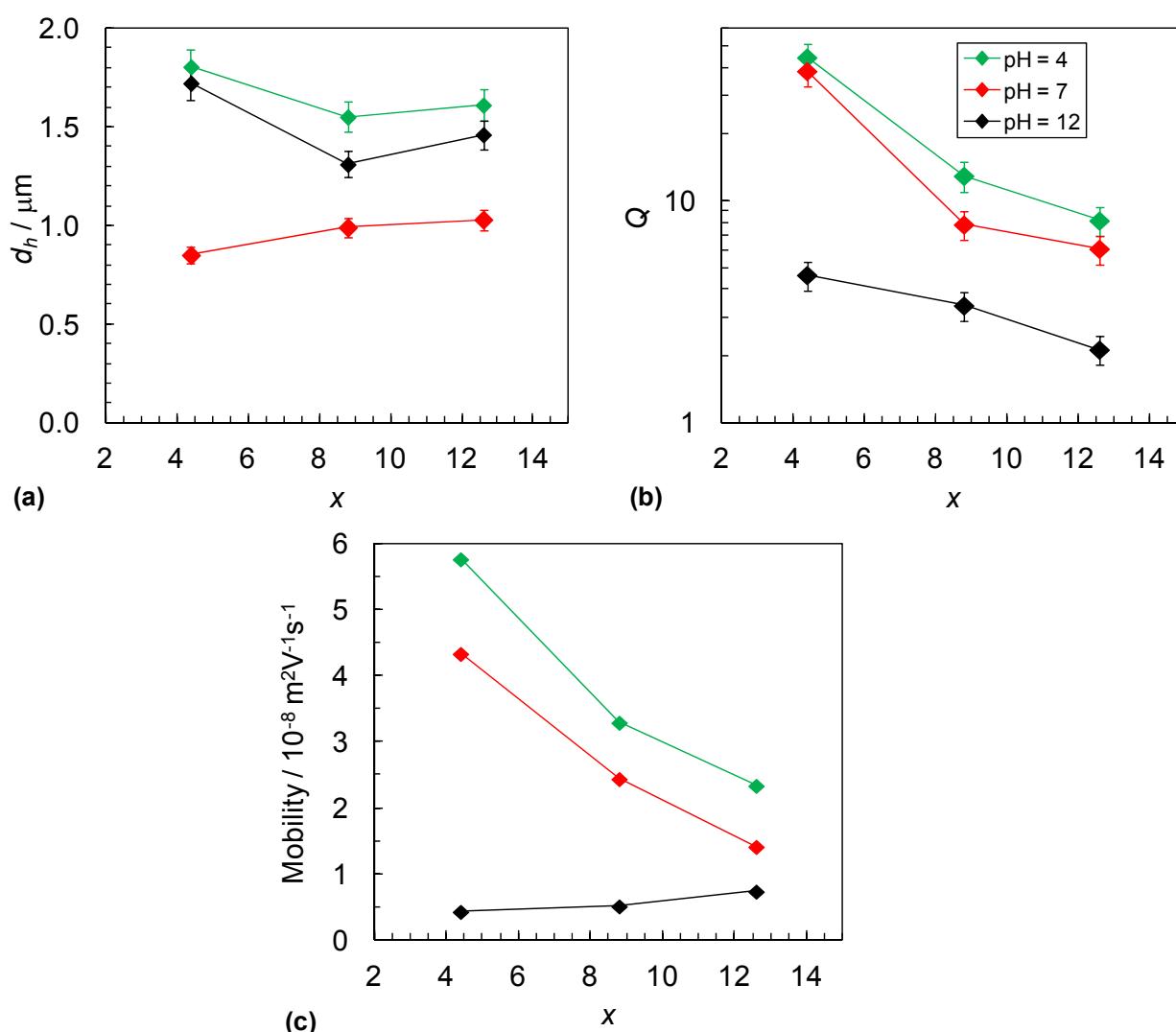


Fig. S5 Variation of (a) hydrodynamic diameter, (b) nominal swelling ratio and (c) electrophoretic mobility for PVAM- x BEVAME microgels with x . The lines are guides for the eye.

References

1. Z. Mohammadi, A. Cole, and C. Berkland. *J. Phys. Chem. C*. 2009, **113**, 7652.
2. L. Shi, and C. Berkland. *Macromolecules* 2007, **40**, 4635.
3. L. Shi, K. A. Boduch-Lee, J. T. Henssler, E. J. Beckman, and T. M. Chapman. *J. Polym. Sci. A., Polym. Chem.* 2004, **42**, 4994.
4. L. A. White, C. E. Hoyle, S. Jonsson, and L. J. Mathias. *Designed Mon. Polym.* 2005, **8**, 297.
5. M. Yang, C. Liu, Z. Li, G. Gao, and F. Liu. *Macromolecules* 2010, **43**, 10645.
6. J. S. Kwiatkowski, and J. Leszczynski. *J. Molec. Struct.* 1993, **297**, 277.
7. R. C. Weast, M. J. Astle, and W. H. Beyer (1985) *CRC Handbook of Chemistry and Physics*, 65 ed., CRC, Boca Raton.
8. S. Thaiboonrod, F. Cellesi, R. V. Ulijn, and B. R. Saunders. *Langmuir* 2012, **28**, 5227.