SUPPORTING INFORMATION

The role of acrylonitrile in controlling the structure and properties of nanostructured ionomer films

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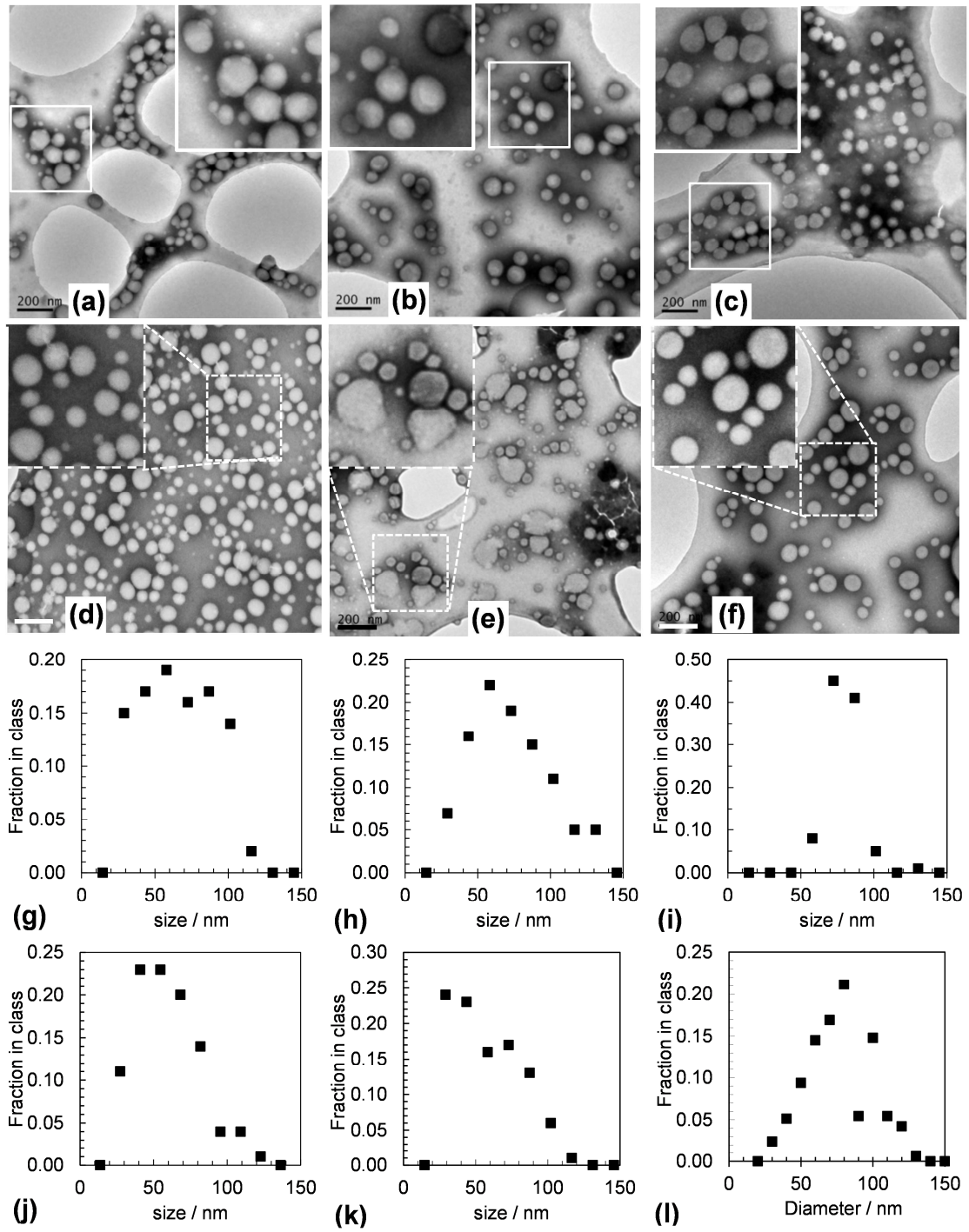

Fig. S1. TEM images (upper) and histograms (lower) for NC50(0.5)S(1) ((a) and (g)), NC50(4)S(1) ((b) and (h)), NS100S(1) ((c) and (i)), C100(0.5) (d) and (j)), (e) C100(4) ((e) and (k)) and C50(0.5)S(1) ((f) and (l)). The scale bars represent 200 nm.

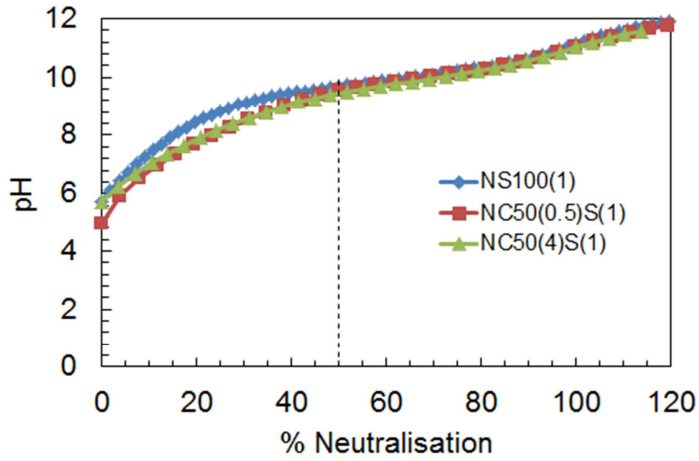

Fig. S2. Titration data for various nanoparticles. The apparent pK_a values were determined from the pH values corresponding to 50% neutralisation.

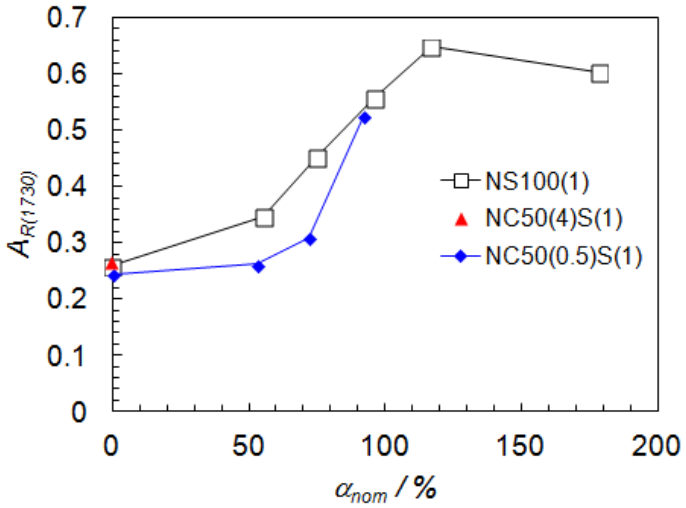

Fig. S3. The area fraction of the band at 1730 cm^{-1} as a function of neutralisation (see text).

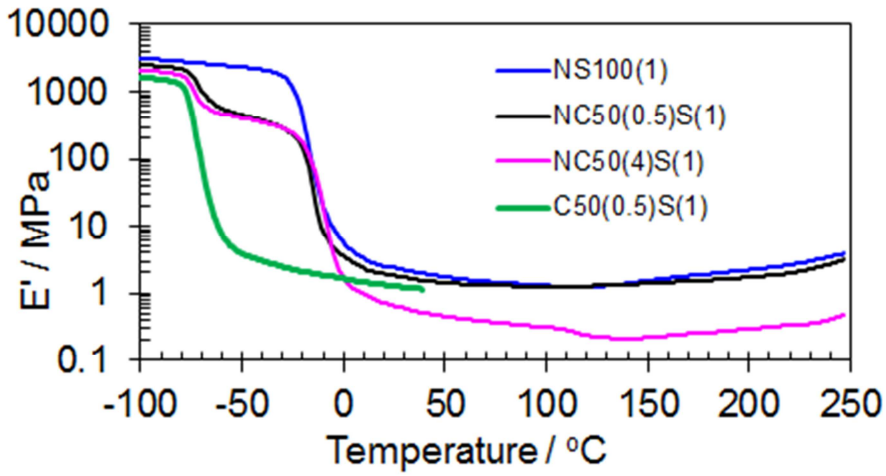

Fig. S4. Temperature-dependence of *E'* from DMTA data for various polyacid films (α_{nom} = 0%).

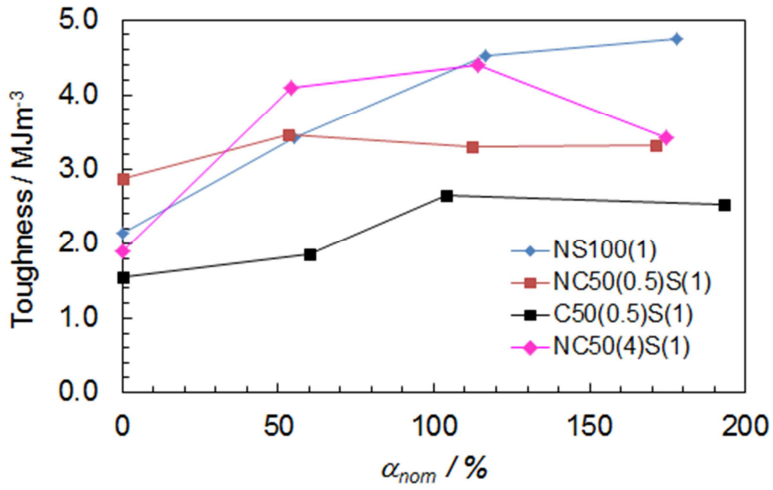

Fig. S5. The effect of toughness as a function of neutralisation for various nanostructured films.

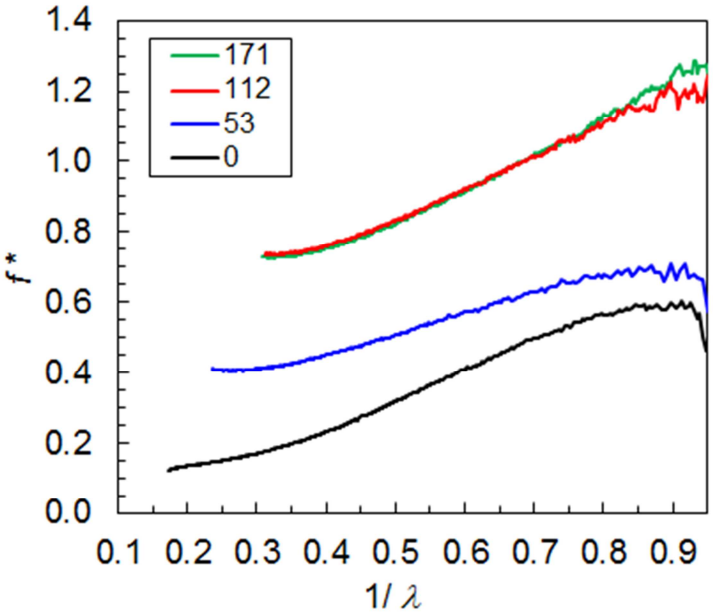

Fig. S6. Variation of reduced stress with the reciprocal of the extension ratio as a function of neutralisation for NC50(0.5)S(1) films. The values for α_{nom} appear in the legend.

Estimation of the number of AN groups per elastically effective chain

The modulus (E_i) of the nanostructured films comprising core-shell nanoparticles of type *i* is related to the number-density of elastically effective chains for the whole film ($\nu_{e(i)}$) is given by:

$$E_i = 3\upsilon_{e(i)}kT \qquad \text{(S1)}$$

The nanostructured morphologies for the NC50(0.5)S(1) NC50(0.5)S(4) and C50(0.5)S(1) films is depicted in Fig. S7. The shells overlap to form a matrix (and hence continuous phase) which contains dispersed core particles which are covalently linked to the matrix. The shells form the matrix (with a modulus, $E_{Shell(i)}$) that the cores are dispersed within (with a modulus, $E_{Core(i)}$). We assume that the isostrain model[1] applies to these films. This assumption is reasonable because the PBd cores will have lower elasticity than the shells that contain AN and MAA. Consequently, the PBd cores should experience the same strain as that of the matrix.

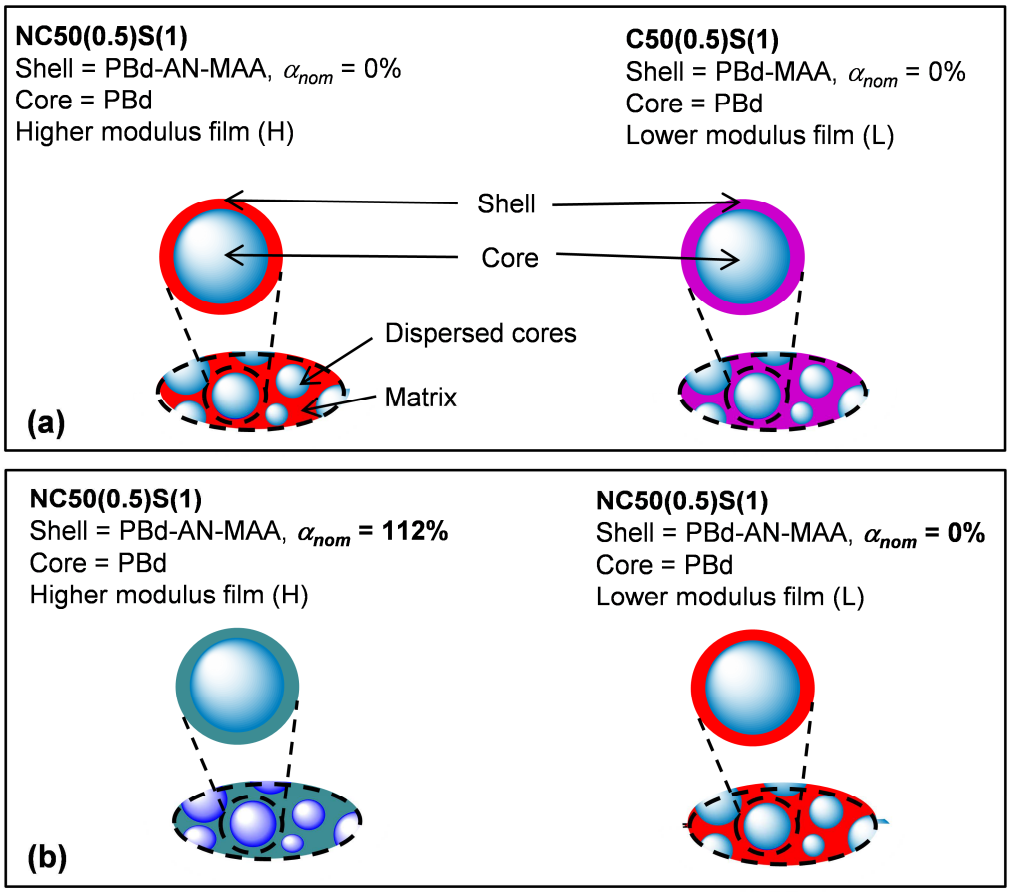

Fig. S7. Depictions of structural elements within nanostructured films. The higher modulus (H) and lower modulus (L) films are on the left and right hand sides of the figure. (a) and (b) show the two cases considered in the text.

The following expression describes E_i according to the isostrain model[1]:

$$E_i = E_{Core(i)}\phi_{Core(i)} + E_{Shell(i)}\phi_{Shell(i)} \qquad \text{(S2)}$$

For the core-shell nanoparticles considered here the nominal volume fractions of core ($\phi_{Core(i)}$) and shells ($\phi_{Shell(i)}$) for the particles are 0.5. It follows from equations (S1) and (S2) that:

$$\upsilon_{e(i)} = \frac{\upsilon_{e(Core(i))}}{2} + \frac{\upsilon_{e(Shell(i))}}{2} \qquad \text{(S3)}$$

Using equation (S3) we next determine the difference in the number-densities of elastically effective chains for the more highly crosslinked AN-containing films of NC50(0.5)S(1) (Film H) and the more lightly crosslinked AN-free films of C50(0.5)S(1) (Film L).

$$\upsilon_{e(H)} - \upsilon_{e(L)} = \frac{\upsilon_{e(Core(H))} - \upsilon_{e(Core(L))}}{2} + \frac{\upsilon_{e(Shell(H))} - \upsilon_{e(Shell(L))}}{2} \qquad \text{(S4)}$$

We define the difference in the number-density of elastically effective chains in the shell due to AN by:

$$\Delta\upsilon_{e(Shell(AN))} = \upsilon_{e(Shell(H))} - \upsilon_{e(Shell(L))} \qquad \text{(S5)}$$

It is assumed that $\nu_{e(Core(H))} = \nu_{e(Core(L))}$ because the core particles for both systems were obtained from the seed same latex (C100(0.5)). Hence, equations (S4) and (S5) simplify to:

$$\Delta\upsilon_{e(Shell(AN))} = 2(\upsilon_{e(H)} - \upsilon_{e(L)}) \qquad \text{(S6)}$$

Equation (S6) can be expressed in terms of modulus values using equation (S1):

$$\Delta\upsilon_{e(Shell(AN))} = \frac{2}{3kT}(E_{(H)} - E_{(L)}) \qquad \text{(S7)}$$

Equation (S7) enables estimation of the increase in the number-density of elastically effective chains in the NC50(0.5)S(1) matrix caused by replacing Bd units in C50(0.5)S(1) with AN units. The morphologies are depicted in Fig. S7(a).

Using $E_{(H)} = E_{NC50(0.5)S(1)}$ and $E_{(L)} = E_{C50(0.5)S(1)}$ values of 1.72 and 1.19 MPa, respectively, for these films (at α_{nom} = 0%) it follows that $\Delta\nu_{e,Shell(AN)}$ = 8.6 x 10^{25} m^{-3}.

Estimation of the number of $RCOO^-$ groups per elastically effective chain

We apply the same general approach described above to the NC50(0.5)S(1) films with α_{nom} = 0% (lower modulus, L) and approximately 112% (higher modulus, H). Fig. S7(b) depicts the structural elements. The difference in modulus should be directly proportional to the number of elastically-

effective chains created by ionically crosslinked $RCOO^-$ groups. The difference in the number-densities of elastically effective chains for the H and L films is given by equation (S4). We define the difference in the number-density of elastically-effective chains in the shell due to neutralisation by:

$$\Delta\upsilon_{e(Shell(Neut))} = \upsilon_{e(Shell(H))} - \upsilon_{e(Shell(L))} \qquad \text{(S8)}$$

It is assumed that $\nu_{e(Core(H))} = \nu_{e(Core(L))}$ because the core particles for both systems were obtained from the seed same latex (C100(0.5)). The values for $\phi_{Core(i)}$) and $\phi_{Shell(i)}$ for these particles are 0.5 and equation (S4) applies. Because the cores were MAA-free, neutralisation should not affect their modulus values. Hence, equations (S4) and (S8) can be rearranged to:

$$\Delta\upsilon_{e(Shell(Neut))} = 2(\upsilon_{e(H)} - \upsilon_{e(L)}) \qquad \text{(S9)}$$

Equation (S9) can be expressed in terms of modulus values using equation (S1):

$$\Delta\upsilon_{e(Shell(Neut))} = \frac{2}{3kT}(E_{(H)} - E_{(L)}) \qquad \text{(S10)}$$

Equation (S10) enables estimation of the increase in the number-density of elastically effective chains in the NC50(0.5)S(1) matrix caused by replacing RCOOH units in polyacid NC50(0.5)S(1) with $(Zn^{2+})(RCOO^-)_2$ units. The morphology is depicted in Fig. S7(b). Using *E* values of 3.41 and 1.72 MPa for the NC50(0.5)S(1) α_{nom} = 112 and 0% films, respectively, it follows that $\Delta\nu_{e(Shell(Neut))}$ = 2.7 x 10^{26} m^{-3} (from equation (S10)).

References

1. Morris, E. R. *Carbohyd. Polym.*, 17, 65, 1992.