Supplementary information

Thermodynamic and kinetic properties of interpolymer complexes assessed by Isothermal Titration Calorimetry and Surface Plasmon Resonance

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Thermodynamic considerations

$$\Delta G^M = \Delta H^M - T\Delta S^M$$

Spontaneous formation of polymer-polymer complexes in solutions requires Gibbs free energy (ΔG^M) to be negative; this requires the enthalpy of a reaction (ΔH^M) to be negative or entropy (ΔS^M) to be large and positive. [1,2]

The change in enthalpy measured by the ITC (ΔH observed) is the sum of 3 terms:

$$\Delta H\ observed = \Delta H\ binding + \Delta H\ ionization + \Delta H\ conformation$$

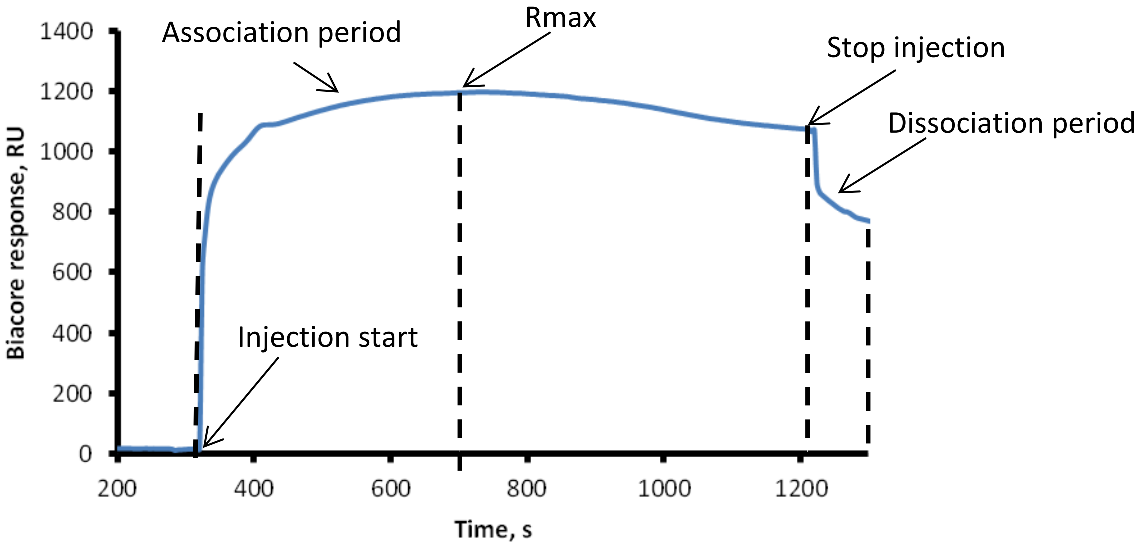

Figure S1. Example Biacore sensorgram, detailing ka determination. Association rate (ka) was calculated via BIAevaluation software. Software fits data to a standard local kinetics model obtained using injection start, association period, Rmax and polymer concentration values. Data was transformed producing ka (see Table 2) as a measure of time and molar concentration ($M^{-1}s^{-1}$).

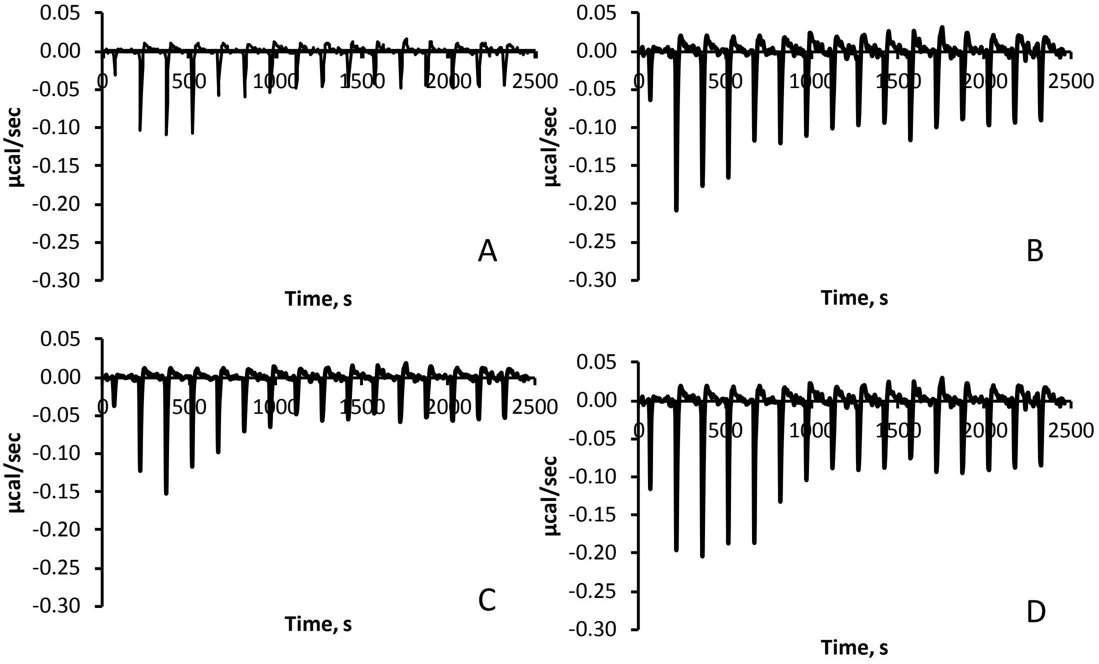

Figure S2. Isothermal titration calorimetry isotherms obtained by titrating (A) water, (B) 0.2 % w/v PAA, (C) 0.2 % w/v PMAA and (D) 0.2 % w/v TA with water at pH 2.0.

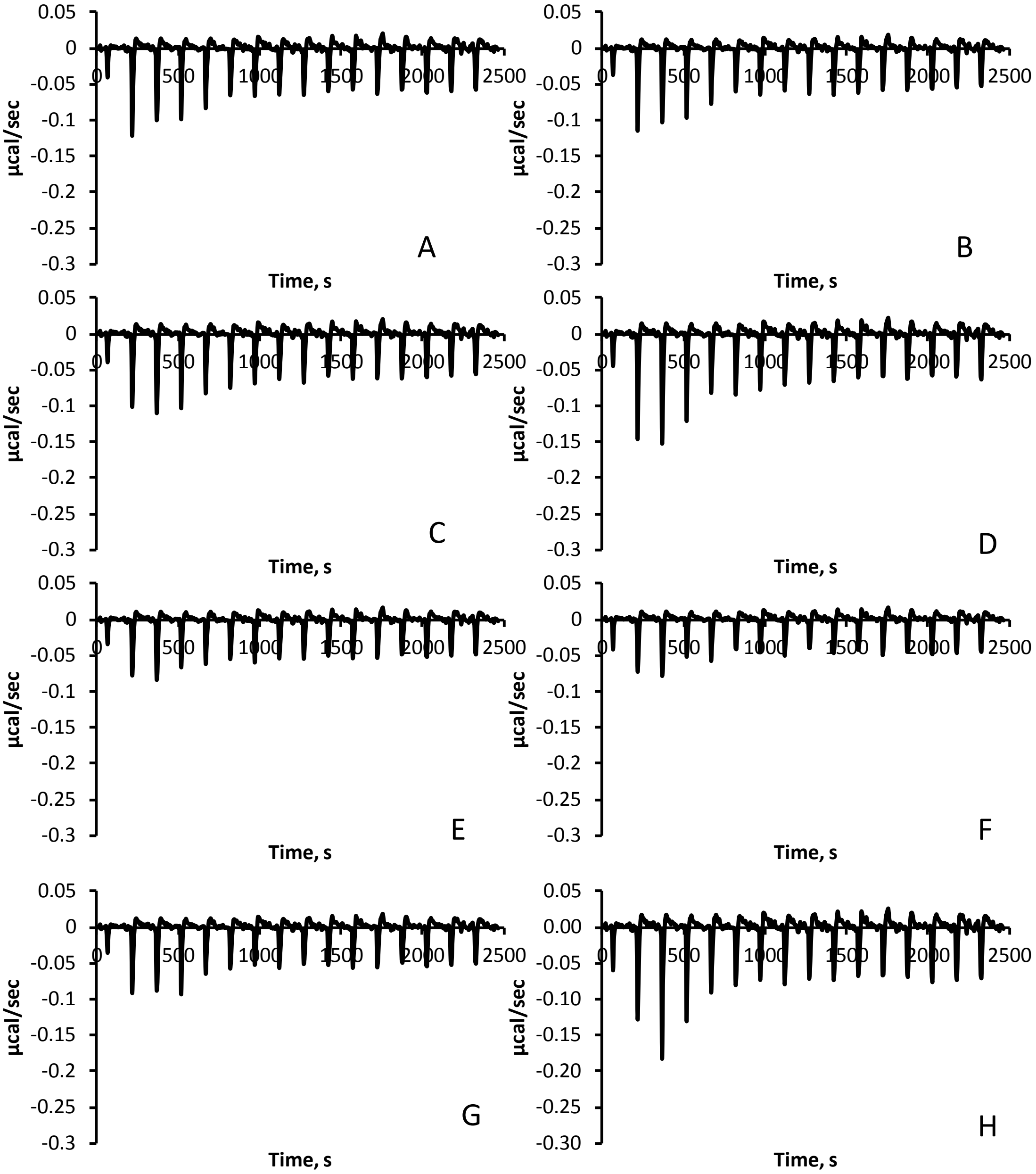

Figure S3. Isothermal titration calorimetry isotherms obtained by titrating (A) 0.2 % w/v DEX, (B) 0.2 % w/v HEC, (C) 0.2 % w/v MC, (D) 0.2 % w/v PAM, (E) 0.2 % w/v PEO, (F) 0.2 % w/v PVA, (G) 0.2% w/v PMVE and (H) 0.2 % w/v PVP with water at pH 2.0.

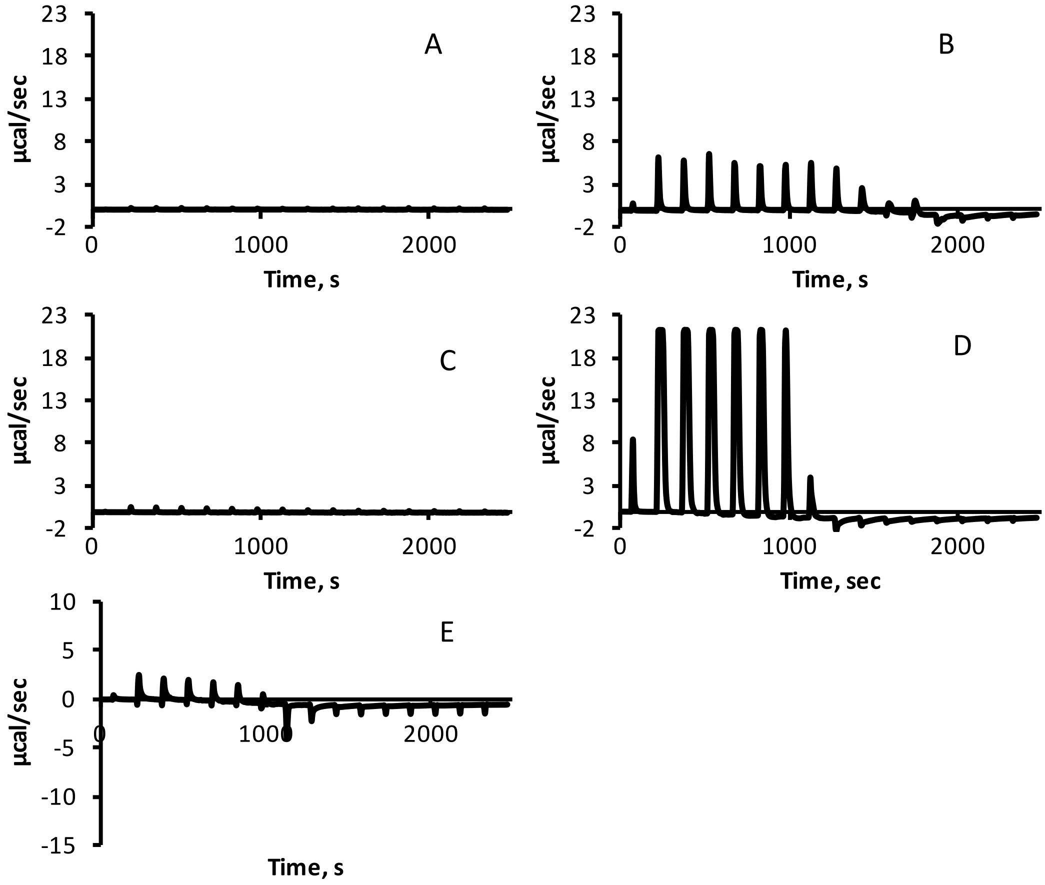

Figure S4. Isothermal titration calorimetry isotherms obtained by titrating (A) 0.2 % w/v HEC, (B) 0.2 % w/v PEO, (C) 0.2 % w/v PVA, (D) 0.2 % w/v PMVE and (E) 0.2 % w/v PVP with 2 % w/v poly (acrylic acid) solutions at pH 2.0.

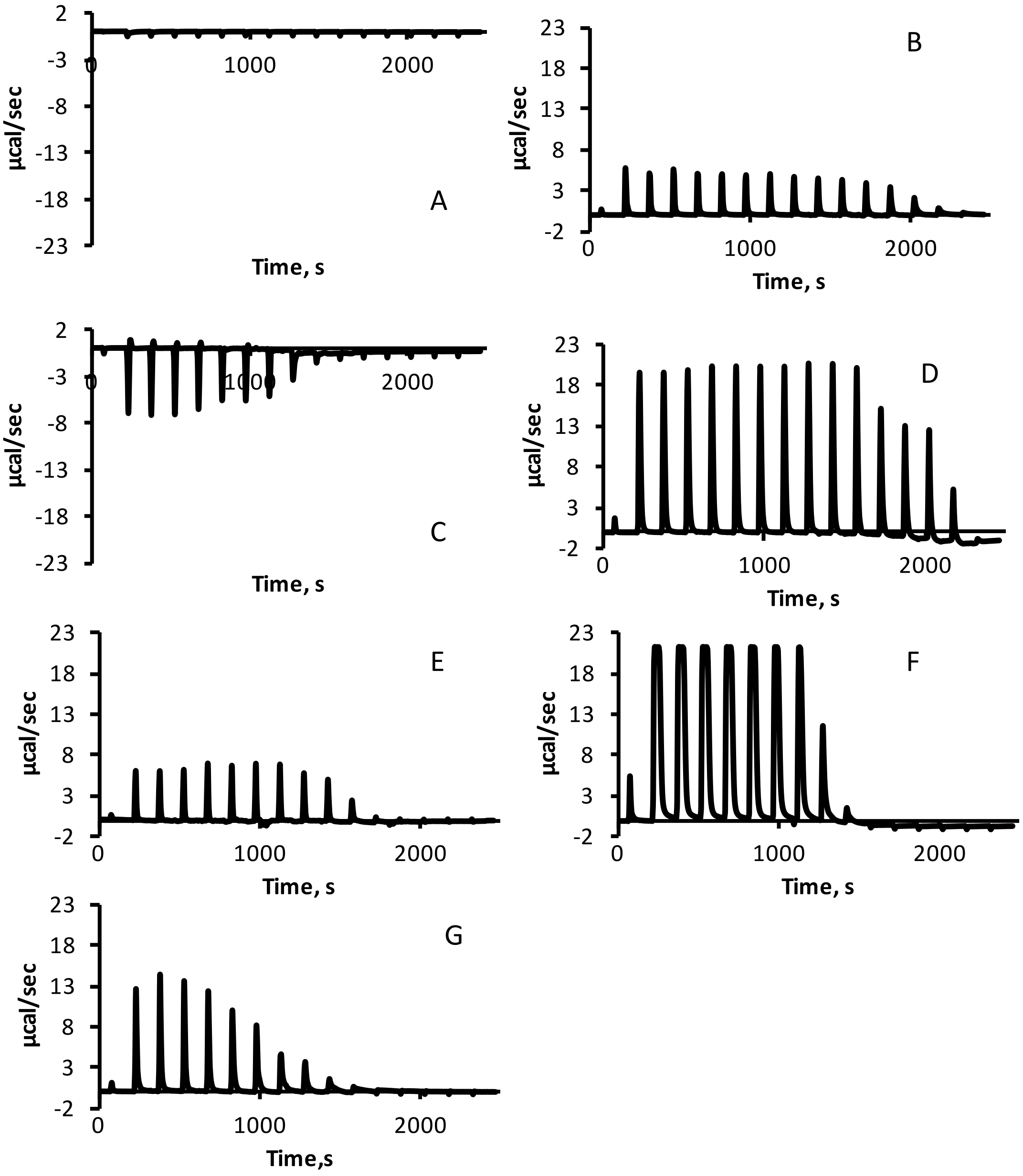

Figure S5. Isothermal titration calorimetry isotherms obtained by titrating (A) 0.2 % w/v DEX, (B) 0.2 % w/v HEC, (C) 0.2 % w/v PAM, (D) 0.2 % w/v PEO, (E) 0.2 % w/v PVA, (F) 0.2 % w/v PMVE and (G) 0.2% w/v PVP with 2 % w/v poly (methacrylic acid) solutions at pH 2.0.

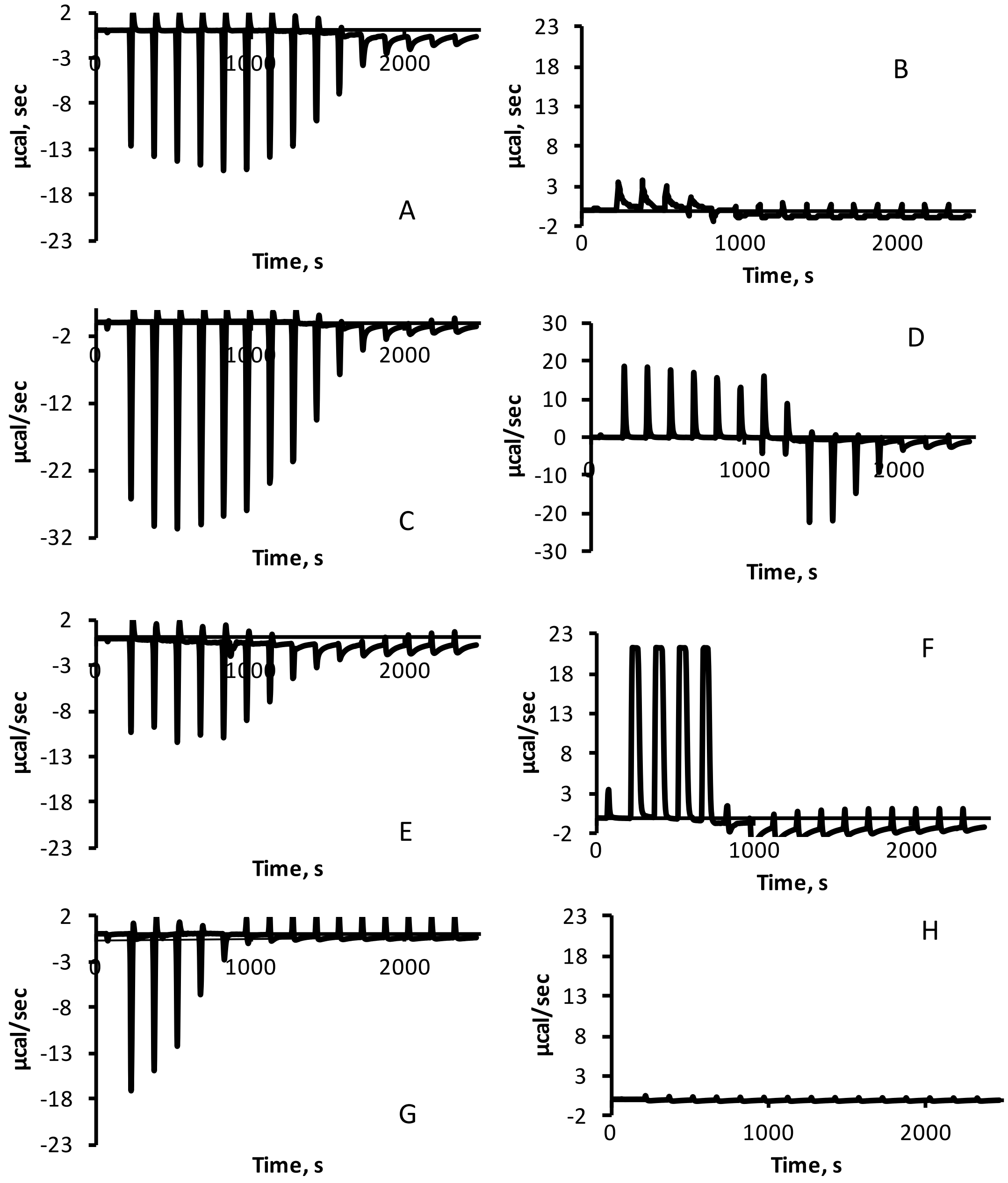

Figure S6. Isothermal titration calorimetry isotherms obtained by titrating (A) 0.2 % w/v HEC, (B) 0.2 % w/v MC, (C) 0.2 % w/v PAM, (D) 0.2 % w/v PEO, (E) 0.2 % w/v PVA, (F) 0.2 % w/v PMVE, (G) 0.2% w/v PVP and (H) 0.2 % w/v DEX with 2 % w/v tannic acid solutions at pH 2.0.

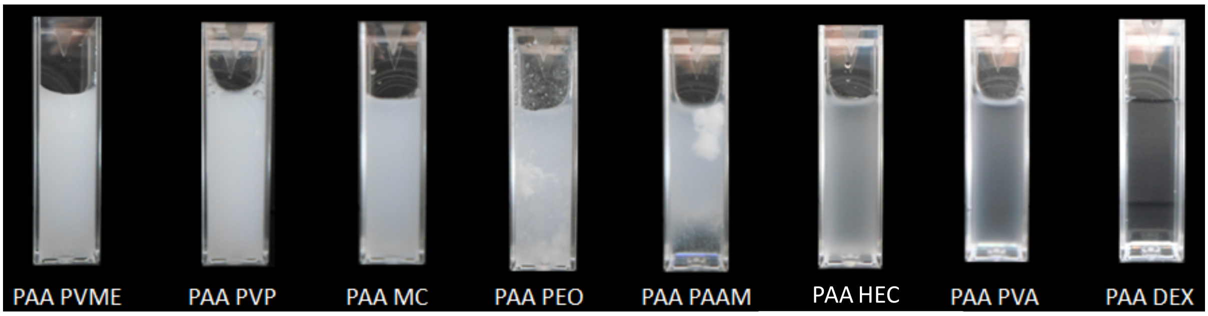

Figure S7. Turbidity of polymer combinations, 0.2 % w/v acidic compound (1.5 mL) was mixed with 0.2 % w/v non-ionic polymer (1.5 mL) at pH 2.0 and stirred for 1 minute.

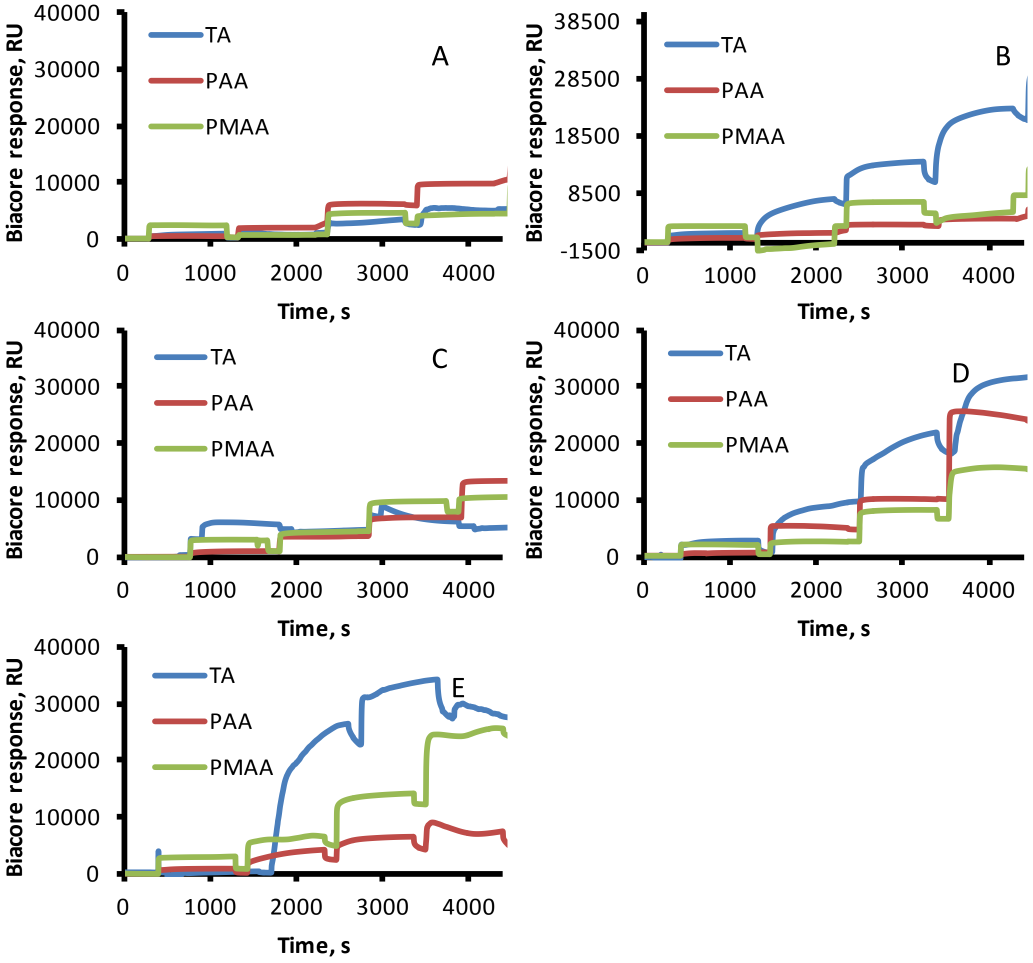

Figure S8. Biacore sensorgrams for the formation of IPCs between acidic compounds and (A) PEO, (B) HEC, (C) PVP, (D) PMVE and (E) PVA. Concentrations are 0.2% w/v for acidic compounds and 0.2% w/v for non-ionic polymer solutions at pH 2.0.

References

1 Ababou and E. J. Ladbury, *Journal of Molecular recognition*. 2007, **21**, 4.
2 M. J. Blandamer, P. M. Cullis and J. B. F. N. Engberts, *Journal of the Chemical Society-Faraday Transactions*. 1998, **94**, 2261.