Phase separation of poly(amic acid) : phase diagrams and kinetics followed by small-angle neutron scattering

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Poly(amic acids) (PAA) are interesting precursors of polyimides. The latter polymers, due to their excellent thermal, mechanical, and chemical properties, are extremely useful for applications such as porous membranes for gas separation and nanofiltration. [1,2] We recently discovered that poly(amic acid) salts (Fig.1a) undergo liquid-liquid phase separation (PS) by adding salt (monovalent or divalent) and lowering temperature enough. PS is precisely a key process in making porous membranes [3] through the formation of interconnected phases by spinodal-like PS for instance. In that case the polymer-rich phase is stabilized to form the porous membranes matrix. We combine rheological measurements, UV-visible spectroscopy and scattering techniques to investigate the solution behavior of poly(amic acid) salts (PAAS) across a range of conditions in the monophasic domain, including variations in ionic strength, polymer concentration and temperature. Specific viscosity measurements reveal a characteristic polyelectrolyte behavior, following Fuoss's law in salt-free solutions, switching to a neutral polymer-like scaling with added salt. Phase diagrams demonstrate an upper critical solution temperature UCST-type transition (Fig. 1b), characterized by reversible phase transition behavior induced by changes in ionic strength and temperature.
To further elucidate the underlying mechanisms of PS, we have recently investigated the dynamics of phase separation using small-angle neutron scattering (SANS), by performing thermal quenches or ramps from the one-phase region to the two-phase one. The kinetics of growth can be followed in time through the evolution of the scattered intensity at low wavevectors (Fig.1c).

Keywords:
water-soluble poly(amic acid) salt, aqueous phase separation,membrane, phase diagram

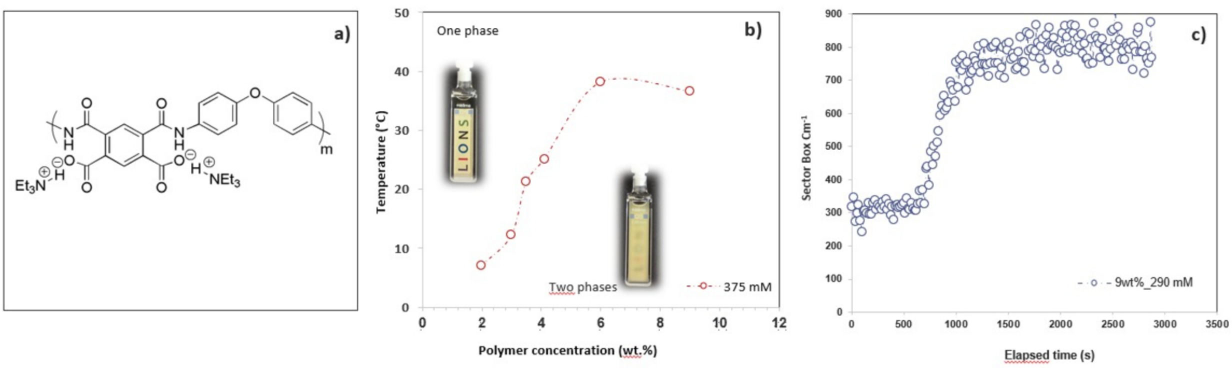

Figure 1. (a) Monomer chemical structure of water-soluble poly(amic acid) salt; (b) Phase diagram for poly(amic acid) salt solution at Cs = 375 mM NaCl; and (c)Time evolution of average intensity from SANS data over a q range 0.001-0.002 Å-1 with a quench temperature from 40°C to 15°C

References:

[1] S.-H.Hsiao, C.-P.Yang & S.-C.Huang, Eur. Polym. J.,2004, 40(6), 1063-1074.
[2] C.Huang, S.Wang, H.Zhang, T.Li, S.Chen, C.Lai, & H.Hou, Eur. Polym. J., 2006, 42(5), 1099-1104.
[3] O. M'barki, A. Hanafia, D. Bouyer, C. Faur, R. Sescousse, U. Delabre, C. Blot, P. Guenoun, A. Deratani, D. Quemener and C. Pochat-Bohatier, J. Memb. Sci., 2014, 458, 225–235.