Electronic Supplementary Information (ESI)

A New Route to Multiresponsive Organogels from Block Ionomer via Charge-Driven Assembly

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1. Experimental Section

Materials. Polystyrene-*block*-poly(2-vinylpyridine) (PS-*b*-P2VP) (PS(57000)-*b*-P2VP(57000), Mw/Mn = 1.08) was purchased from Polymer Source, Inc., while polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene (SEBS, Mn = 118000, 29 mol% polystyrene, Mw/Mn = 1.05) was obtained from Sigma-Aldrich Co.

Synthesis of SSEBS. Sulfonated polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene (SSEBS) was prepared from SEBS according to literature.[1] The sulfonation degree of SSEBS was determined by titration to be 17.9 mol% relative to the polystyrene groups on SEBS.

Preparation of organogels. Organogels were prepared by neutralization of SSEBS with PS-*b*-P2VP. SSEBS was dissolved into mixed solvents of toluene and methanol (98/2, v/v) to obtain 5 % (w/w) SSEBS solution, and then neutralized with 5 % (w/w) PS-*b*-P2VP of toluene solution. After addition of PS-*b*-P2VP solution into SSEBS solution, the mixture was stirred acutely. Gels with different SO_3H groups/2-vinylpyridine ($[SO_3H]/[2VP]$) ratios were prepared by addition of different amount of PS-*b*-P2VP solution into 1 mL of SSEBS solutions.

Rheological measurements. Gels were prepared by mixing together two separate solutions containing either 5 % (w/w) of SSEBS or 5 % (w/w) of PS-*b*-P2VP. After stirred for 25 seconds, the gels were loaded on rheometer, and measured at 25 ^{o}C with a shear strain of 1 %.

Small-angle X-ray scattering (SAXS). SAXS experiments were conducted at the Australian Synchrotron on the small/wide-angle X-ray scattering beamline. The samples were put into 1.0 mm quartz capillaries. The background correction was carried out by measuring the scattering of an empty capillary and correcting for sample absorption.

2. FT-IR Spectra of SSEBS/PS-*b*-P2VP Mixtures

SSEBS was dissolved into THF to obtain 5 % (w/v) SSEBS solution, and then mixed with 5 % (w/v) THF solution of PS-*b*-P2VP. After addition of PS-*b*-P2VP solution into SSEBS solution, the mixture was stirred acutely. After removal of residual solvent *in vacuo*, the sample so obtained was mixed with KBr powder and pressed into thin sheets for FT-IR

measurement. Fig. 1 presents the FT-IR spectra of SSEBS/PS-*b*-P2VP mixtures in the range of 1700 - 1560 cm^{-1} which are the same as those for SSEBS/PS-*b*-P2VP organogels. The results confirm the existence of ionic interaction between SSEBS and PS-*b*-P2VP in the mixtures.
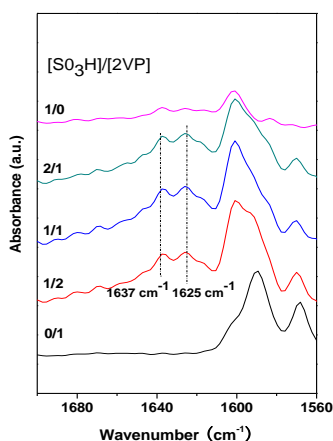

Fig. 1 FT-IR spectra of SSEBS/PS-*b*-P2VP mixtures in the range of 1700 - 1560 cm^{-1} .

3. Quantitative Analysis of SAXS Data

The measured SAXS scattering curves were corrected for background scattering. Fitting was done using the SASfit program downloaded from http://kur.web.psi.ch/sans1/SANSSoft/sasfit.html. Toluene is good solvent for poly(ethylene-*ran*-butylene) (EB) block and polystyrene blocks, while protonated poly(2-vinylpyridine) (P2VP) becomes less soluble. As a result, protonated P2VP blocks and SPS blocks tend to form cores, EB blocks and PS block forming corona to stabilize solvophobic cores. Each P2VP block in gel with [SO$_3$H]/[2VP] reacting with 10 SPS blocks can be calculated from molecular weights of SPS and P2VP blocks, and sulfonation degree of SEBS. EB blocks on SSEBS are like branches emanating from reacted P2VP block, and with the aggregation of the reacted P2VP blocks, the number of EB branches increases. The structure is similar to that of star polymers. For star polymer, Dozier[2] has developed a scattering function as:

$$I_{DozierStar}(Q, I_0, R_G, \alpha, v, \xi) = I_0 \exp\left(-\frac{Q^2 R_G^2}{3}\right) + \frac{4\pi\alpha}{Q\xi} \Gamma(\mu) \frac{\sin(\mu \arctan(Q\xi))}{(1 + Q^2\xi^2)^{\mu/2}}$$

With $\mu = 1/v - 1$

In which I_0, R_G, α, v and ξ stand for scale parameter, radius of gyration, scale parameter for fractal, exponential damping length in mass fractal and Flory exponent, 3/5 in good solvent, 1/2 in theta solvent (i.e. $\mu = 2/3$ to 1) term respectively.

For gel from charge-driven assembly, hard sphere shapes are always found.[3] So scattering function for hard sphere model is used as:

$$S_{HS}(\mathbf{q}, R_{HS}, f_p) = \cfrac{1}{1 + 24 f_p \cfrac{G(f_p + R_{HS}q)}{R_{HS}q}}$$

Where R_{HS} and f_p stand for radius of hard sphere and volume fraction, respectively.
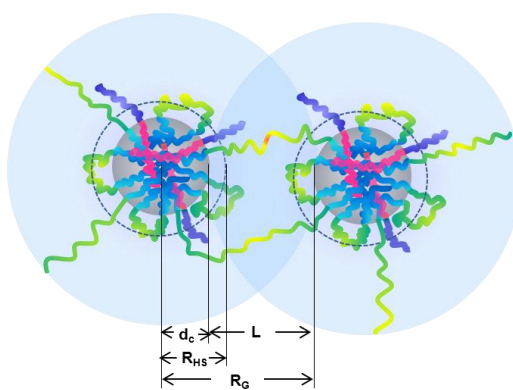
Scheme 1 Scheme of nanoscaled gel based on SAXS fitting, radius of gyration $R_G = 35$ nm, radius of hard sphere $R_{HS} = 12.5$ nm and distance between microdomains $L = 29.5$ nm.

The neighbouring microdomains are symmetrical, and the relationship $2(R_{HS} - d_c) = L - (R_G - R_{HS})$ can be obtained. As a result, radius of core $d_c = 9$ nm can be calculated.

4. Movies

Two short movies are available to show (a) gel formation: the gel formation upon mixing SSEBS and PS-b-P2VP solutions and (b) response to amine: the response of a gel to amine (The responsiveness of gels to acid and melt salt are similar to that to amine.).

5. References

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2 William D. Dozier, J. S. Huang and L. J. Fetters, *Macromolecules* 1991, **24**, 2810-2814.

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