# A new route to prepare multiresponsive organogels from a block ionomer *via* charge-driven assembly†

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We report a novel route to prepare multiresponsive organogels through charge-driven assembly between a block ionomer and a diblock copolymer. The ionic complex aggregates to form spherical cores, which are connected by the middle block of the block ionomer to form gels. The organogels are responsive to acids, amines and salts.

Multiresponsive organogels have attracted considerable attention recently in both academic and industrial fields for their widespread applications from oil technology to drug delivery,[1] since they are able to respond to external triggers. A promising class of responsive organogels is physically crosslinked polymer networks, including highly stereoregular polystyrene, poly(methyl methacrylate) as well as poly(ester)s obtained through the formation of helical structures,[2] end functional polymers *via* hydrogen bonding,[3] π-conjugated polymers *via* π–π stacking,[4] polymers modified by supramolecular crosslinking agents,[5] polyelectrolyte–surfactant complexes through ionic clustering,[6] and self-assembled triblock copolymers.[7] The transient networks are usually either only responsive to temperature or time-consuming to form. To satisfy a wide range of potential applications, fast formation of multiresponsive organogels from polymers is needed.

Previous studies performed by our group have demonstrated that interaction between acidic and alkaline polymers leads to precipitation in organic solvent.[8] In order to prevent the macroscopic separation, diblock copolymers containing a solvophilic block are used. As a result, microphase separation structure forms with a solvophobic core stabilized by a soluble block.[9] When triblock copolymers containing two acidic/alkaline end blocks are used instead of diblock copolymers and when polymer concentration is high enough, the two end blocks will enter different solvophobic cores stabilized by the middle soluble block. Thus the cores can be connected with each other by the middle block, resulting in formation of gels. Since the ionic interaction between the end blocks of triblock copolymers and the oppositely charged polymers can be affected by external environments, gels formed are usually responsive. Although this idea has been recently applied in preparation of hydrogels,[10] to the best of our knowledge, preparation of organogels has not been reported based on the idea.

Herein we report multiresponsive organogels based on charge-driven assembly between a block ionomer and a diblock copolymer in organic solvents for the first time. The block ionomer sulfonated polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene (SSEBS) consists of two acidic sulfonated polystyrene (SPS) blocks and a neutral solvophilic poly(ethylene-*ran*-butylene) (EB) block, and the diblock copolymer polystyrene-*block*-poly(2-vinylpyridine) (PS-*b*-P2VP) contains an oppositely charged poly(2-vinylpyridine) (P2VP) block. The work demonstrates a novel approach to prepare multiresponsive organogels through charge-driven assembly, and the resultant organogels are responsive to acids, amines and salts.

The organogels formed in 20–30 seconds upon mixing individual solutions of two components, which was confirmed by the tube inversion method[11] (ESI,† movie (a): gel formation). All gels are slightly yellowish without visible heterogeneity, indicating that no macrophase separation occurs. The fast reaction is understandable considering the high reaction rate between $SO_3H$ groups of SPS blocks and pyridine groups of PS-*b*-P2VP.

The formation of gels was further confirmed by rheological measurement. Dynamic frequency measurements of organogels were carried out after mixing SSEBS and PS-*b*-P2VP solutions in 20–30 seconds. The results are shown in Fig. 1. For all organogels with $[SO_3H]/[2VP]$ ratios of 1/1, 1/2 and 1/3, the elastic modulus ($G'$) is higher than the corresponding viscous modulus ($G''$) at all frequencies from 1 to 100 rad s$^{-1}$, indicating the rubber-like behavior in the range.[3] All the elastic moduli increase with increasing amounts of PS-*b*-P2VP. For $[SO_3H]/[2VP]$ = 1/1 gels, the elastic modulus is only about 300 Pa at 1 rad s$^{-1}$, while it increases to over 1400 Pa for gels with $[SO_3H]/[2VP]$ = 1/3. It is also worth noticing that all the SSEBS/PS-*b*-P2VP gels are "viscoelastic gels", since $G'$ and $G''$ do not show a real plateau in the experimental frequency range but a slight increase with frequency. Therefore, they may have a crossover in a certain experimentally inaccessible range and a finite relaxation time is often observed.[12]

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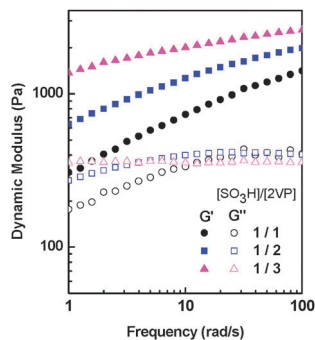
**Fig. 1** Dynamic moduli *G′* (filled) and *G″* (hollow) of organogels with [SO₃H]/[2VP] = 1/1, 1/2 and 1/3 as a function of oscillatory shear frequency.

As a block ionomer containing SO₃H groups on the two end blocks, SSEBS may form gels in certain solvents.[13] Considering this, the control experiment of mixing SSEBS solution with the same amount of toluene shows that SSEBS cannot form gels in the mixed solvents. PS-*b*-P2VP is a diblock copolymer, which may form gels at certain circumstance.[14] So the experiment of blending PS-*b*-P2VP in the same mixed solvents has been carried out, and the result demonstrates that no gel formed. So it is safe to assume that interaction between SSEBS and PS-*b*-P2VP plays a significant role in the formation of organogels.

To reveal the interaction between SSEBS and PS-*b*-P2VP in the gels, Fourier transform infrared (FT-IR) spectroscopy was applied to gels after evaporation of solvent. The results are given in Fig. 2. It is well-known that the characteristic stretching absorptions of pyridine rings on P2VP are at 1590 and 993 cm$^{-1}$, which are also the most affected bands after reaction with acid.[15] According to Fig. 2(a), the intensity of carbon–nitrogen stretching vibration of unprotonated pyridine rings at 1590 cm$^{-1}$ decreases with the addition of SSEBS. Meanwhile, the new absorption bands appear at 1625 and 1637 cm$^{-1}$, which are the characteristic absorptions of protonated pyridine rings on P2VP. The disappearance of pyridine absorption and the appearance of new peaks can be attributed to the formation of pyridium replacing pyridine. This is also confirmed by another characteristic absorption at 993 cm$^{-1}$ (Fig. 2(b)), which becomes less pronounced upon the addition of SO₃H groups. Meanwhile, a peak at 1038 cm$^{-1}$, which can be assigned to symmetric stretching vibration of SO₃H,[16] has been replaced by a peak at 1033 cm$^{-1}$. Therefore the existence of ionic bonding between pyridine groups on PS-*b*-P2VP and SO₃H groups of SPS blocks is evident. The FT-IR control experiment of the mixtures of SSEBS and PS-*b*-P2VP was also
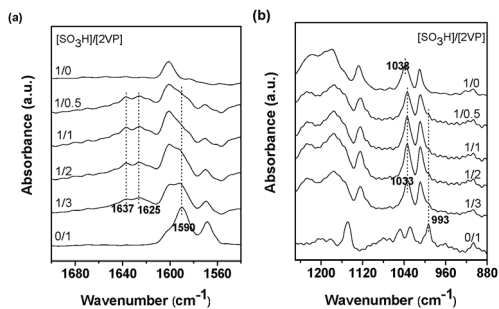
conducted, indicating that there exists ionic interaction in the mixtures as well (see ESI,† 2). So apparently, the gelation should be induced by ionic interaction.

FT-IR results also show that although new peaks at 1625 and 1637 cm$^{-1}$ become more pronounced with the addition of increasing amounts of SSEBS, the absorptions at 1590 cm$^{-1}$ and 993 cm$^{-1}$ can still be observed even when the [SO₃H]/[2VP] ratio reaches 1/0.5, which demonstrates that there are still free pyridine groups in the gel. This reasonably explains the rheological results. As SO₃H groups and pyridine groups cannot react completely according to stoichiometry, the more addition of PS-*b*-P2VP means more ionic bonds formed between SSEBS and PS-*b*-P2VP, and thus elastic modulus increases.

To elicit the structures of the gels, small-angle X-ray scattering (SAXS) measurements were performed for all the samples at room temperature, and their profiles are shown in Fig. 3(a). In order to avoid solvent effects on the morphology, the same solvents were used for all samples, and the SAXS data were corrected for background scattering.

It has been reported that microphase separation occurs in SSEBS in both solid state and swelled in paraffinic oil.[13] While in our experiments, no obvious peak for SSEBS solution was observed, indicating no ordered structures in SSEBS solution. Well-defined peaks are observed for SSEBS/PS-*b*-P2VP gels, and *q* values are dependent on the amount of PS-*b*-P2VP added. The average distance between neighboring domains is 31.2 nm for gels with [SO₃H]/[2VP] = 1/0.5. For the gel with [SO₃H]/[2VP] = 1/1, the peak becomes more obvious and the average distance between two neighboring domains can be estimated to be 27.9 nm. This average distance increases to 29.5 nm when [SO₃H]/[2VP] increases to 1/2, and the peak becomes narrower, indicating more ordered structures in the gel. A further increase in [SO₃H]/[2VP] to 1/3 does not increase the average distance any more, and the peak becomes wider, demonstrating less ordered nanostructures in the gel compared with that for [SO₃H]/[2VP] = 1/2.

Quantitative information on size and distribution of the spherical microdomains was obtained by fitting the SAXS data to a core–shell model using a structure factor of hard spheres and a form factor of star polymers[17] (see ESI,† 3). Fig. 3(b) shows the fitting curve obtained with a hard-sphere radius of 12.5 nm
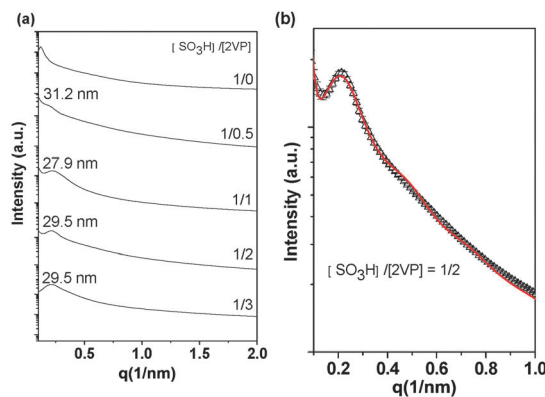


**Fig. 2** FT-IR spectra of SSEBS/PS-*b*-P2VP gels in the range of (a) 1700–1540 cm$^{-1}$ and (b) 1250–880 cm$^{-1}$.



**Fig. 3** (a) SAXS profiles for SSEBS/PS-*b*-P2VP gels with different [SO3H]/[2VP] ratios, (b) SAXS curve for gel with [SO3H]/[VP] = 1/2. The full line in (b) represents the fitting curve according to a core–shell model with a hard-sphere radius of 12.5 nm.
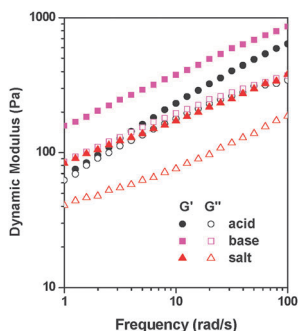
**Fig. 4** Dynamic moduli G' (filled) and G'' (hollow) of organogels with 0.5% of acid, amine and salt as a function of oscillatory shear frequency.

for $[SO_3H]/[2VP] = 1/2$ gels, which is well agreeable with the experimental data. On average about 10 SPS blocks reacted with each P2VP block through ionic interaction between $SO_3H$ groups and pyridine groups. After the reaction, the newly formed ionic complexes become less soluble and tend to form cores, and the radius ($d_c$) of the core is 9 nm. EB blocks and PS blocks form shells to connect and stabilize the solvophobic cores.

The formation of gels is driven by ionic interaction, external stimuli such as pH and salt which can affect the strength of ionic interaction and tune the properties of the gels.[10] However SSEBS/PS-b-P2VP gels formed in nonpolar organic solvent, in which acid, base and salt usually do not dissolve. Thus common acids, bases and salts are not suitable for dissolving the gels. In our experiments, acetic acid, triethylamine and their salts were selected to tune the properties of the gels, since all of them are liquid at room temperature.

The responsiveness of organogels with $[SO_3]/[2VP] = 1$ was investigated by rheological measurements when a very small amount of acid, base or salt was added to pre-formed organogels. Dynamic frequency measurements of organogels with 0.5% (v/v) acid, base or salt were also carried out on a rheometer (ARES, TA), and the measurements were usually carried out after mixing the pre-formed organogels and acid, base or salt in 10–20 seconds. The results are shown in Fig. 4. From the results, it is observed that after addition of 0.5% (v/v) of acid, amine or salt to the gel, though the elastic modulus ($G'$) remains larger than the corresponding viscous modulus ($G''$) in each sample, the corresponding moduli decreased dramatically compared with the pre-formed organogel. Indeed, it is observed that the elastic modulus of the pre-formed organogel is about 300 Pa at 1 rad s$^{-1}$, while the modulus turns to be less than 100 Pa after addition of acid or salt and less than 200 Pa after the addition of triethylamine.

When more acid, base or salt was added to the pre-formed SSEBS/PS-b-P2VP gels, for example, upon addition of 2% (v/v) of acetic acid, triethylamine or their salt, the gels transform into a fluid which can flow freely like water (ESI,† movie (b): response to amines).

As the organogels are stabilized by the less soluble cores formed between $SO_3H$ groups and pyridine groups, any factor changing the strength of the ionic interaction will affect the properties of the organogels. Acetic acid, triethylamine and their salts competitively react with either $SO_3H$ groups or pyridine

groups, which weakens the strength of ionic interaction between SPS and P2VP. As a result, the moduli of gels decrease. When the ionic interaction becomes weak enough, the three-dimensional network lapses, leading to free flow of gels.

In conclusion, we have demonstrated a new approach for preparation of multiresponsive organogels based on charge-driven assembly of two organic solvent-soluble components: a block ionomer consisting of a solvophilic middle block and two acidic end blocks and a diblock copolymer with an alkaline block. The gels form in 20–30 seconds upon mixing the two individual solutions. The reacted SPS blocks and P2VP blocks assemble to form spherical domains which are connected by EB blocks to form organogels. The organogels can respond to acids, amines and salts. The multiresponsiveness and the tunability in the type and length of each of the individual components endow a variety of properties of these novel organogels.

## Notes and references

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