

Solvent-Driven Biphasic Architectures in Polymer Gels via Polymerization-Induced Solvent Phase Separation

Yuji Kamiyama* and Ryota Tamate*



Cite This: <https://doi.org/10.1021/jacs.6c03722>



Read Online

ACCESS |



Metrics & More

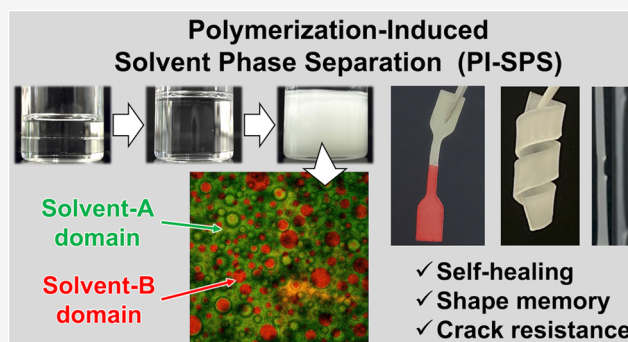


Article Recommendations



Supporting Information

ABSTRACT: Polymer gels with biphasic architectures enable diverse functions, such as enhanced mechanical robustness and programmable drug release. Conventional fabrication of biphasic gels typically relies on the copolymerization of monomers with differing solvent affinities, which constrains structural diversity and tunability. In this study, we introduce “polymerization-induced solvent phase separation” (PI-SPS) as a novel and facile solvent-driven strategy for constructing biphasic gels. Polymerization of a homogeneous precursor solution containing two mutually immiscible solvents and a monomer triggers solvent demixing, yielding a hierarchical structure in which a polymer-rich continuous phase composed of the good solvent encapsulates dispersed droplets of the less favorable solvent-rich phase. We demonstrate the generality of PI-SPS across systems comprising water, organic solvents, and ionic liquids. The resulting biphasic architectures confer emergent properties, including self-healing ability, shape-memory behavior, and enhanced crack resistance, with a fracture energy of 4600 J m^{-2} derived from the spatial organization of solvent domains and polymer networks. Overall, the PI-SPS strategy provides a versatile platform for engineering multiphase soft materials through controlled tuning of solvent affinities.



INTRODUCTION

Polymer gels have emerged as essential components in next-generation technologies, including digital sensors,^{1–3} soft actuators,^{4–6} and flexible electrolytes for energy storage.^{7–10} As these applications become increasingly sophisticated, they require gels with finely tunable mechanical properties—such as stiffness, stretchability, and durability—tailored to specific functional requirements.^{11–13} To meet these demands, the introduction of structural heterogeneity, particularly through phase-separated architectures, has proven to be an effective strategy for imparting mechanical functionalities such as toughness, shape-memory behavior, and crack resistance.^{14–17}

Several approaches have been developed to generate such phase-separated structures in polymer gels, including (1) stimulus-induced phase separation in homopolymers,^{18–21} (2) microphase separation in random or block copolymers,^{16,17,22–25} and (3) incorporation of immiscible fillers.^{26–30} All these strategies leverage variations in polymer–solvent interactions to fabricate separated phases. While effective, their general applicability is constrained by the narrow range of material combinations that simultaneously satisfy solubility requirements and phase-separation criteria, leading to increased molecular design complexity.

In contrast, solvent–solvent phase separation within polymer gels remains an underexplored yet conceptually compelling alternative. Systems featuring solvent phase separation, such as organohydrogels containing dispersed oil droplets stabilized by

surfactants, have primarily been investigated in the context of food science and drug delivery.^{31,32} However, these strategies still face several challenges, including the limited selection of materials capable of forming solvent-phase-separated structures, the complexity of systems and processes arising from the necessity of additives or pretreatments to stabilize the dispersed phase, and the lack of demonstrated mechanical functionalization. In this context, by focusing on tuning solvent–solvent affinity, we leveraged the intrinsically broad and tunable solubility properties of ionic liquids (ILs), which offer a promising opportunity for controlling solvent–solvent phase separation within polymer gels.

In this study, we report a simple and versatile approach for fabricating solvent-phase-separated biphasic gels via polymerization-induced solvent phase separation (PI-SPS). The formation of biphasic structures induced by polymerization has been extensively investigated using the concepts of polymerization-induced phase separation (PIPS)^{33–36} and polymerization-induced self-assembly^{37–40} (PISA). However,

Received: February 18, 2026

Revised: May 19, 2026

Accepted: June 25, 2026

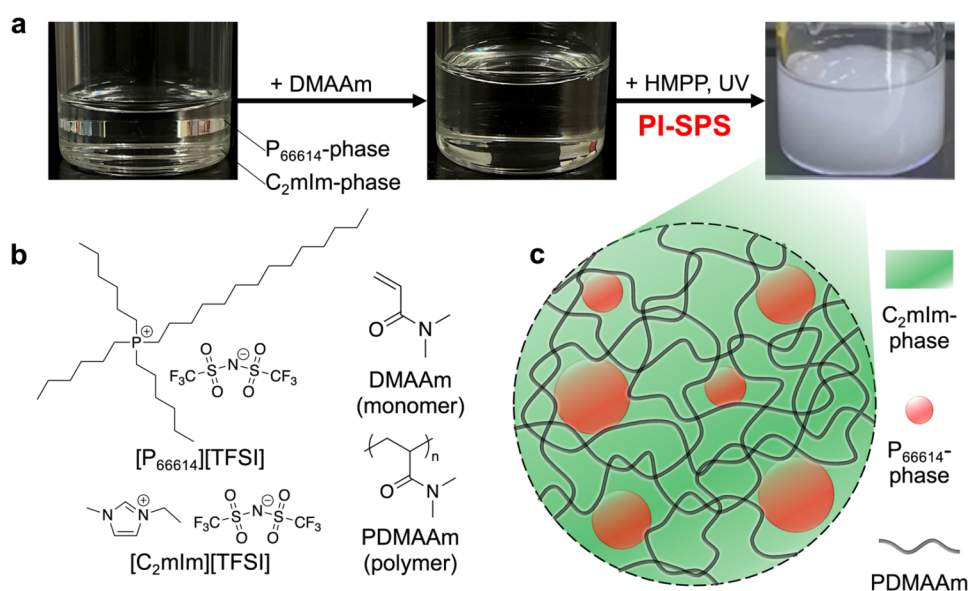


Figure 1. Appearance and structure of a biphasic gel utilizing PI-SPS. (a) Photographs showing phase separation of $[C_2mIm][TFSI]$ and $[P_{66614}][TFSI]$, homogenization upon addition of DMAAm, and solvent phase separation induced by polymerization. (b) Chemical structures of the ILs, monomer, and resulting polymer. (c) Schematic of the internal biphasic structure of PI-SPS gels.

most of these studies have been conducted in single-solvent systems, where phase separation is driven by incompatibility between polymers or between polymers and solvents. In contrast, the present study demonstrates solvent-driven formation of biphasic structures in which two mutually immiscible solvents undergo phase separation triggered by the polymerization reaction itself. Remarkably, the PI-SPS process proceeds in a simple one-pot manner without any additives, enabling the facile fabrication of well-defined biphasic structures through an inherently self-organizing mechanism. We employed a binary IL system consisting of 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($[C_2mIm][TFSI]$) and trihexyltetradecylphosphonium bis(trifluoromethanesulfonyl)imide ($[P_{66614}][TFSI]$), which are mutually immiscible at room temperature.⁴¹ *N,N*-Dimethylacrylamide (DMAAm) was used as the monomer. Upon addition of DMAAm to the phase-separated IL mixture, the pregel solution became temporarily miscible due to the cosolvent effect. However, during polymerization, this cosolvent effect was suppressed, triggering demixing between the two ILs and yielding a gel with a solvent-phase-separated biphasic structure (Figure 1a–c).

Collectively, these findings establish PI-SPS as a simple, robust, and broadly applicable strategy for creating functional biphasic gels based on solvent–solvent interactions, rather than relying on complex polymer architectures. This solvent-driven design paradigm provides a powerful framework for the development of mechanically tunable soft materials, in which the micron-scale morphology and macroscopic mechanical properties can be independently and rationally engineered to meet diverse functional demands.

RESULTS AND DISCUSSION

Polymerization-Induced Solvent Phase Separation

The biphasic gels developed in this study consist of two mutually immiscible solvents and a polymer that remains compatible with at least one solvent-rich phase. Although $[C_2mIm][TFSI]$ and $[P_{66614}][TFSI]$ are immiscible,⁴¹ the addition of DMAAm produces a transparent and homogeneous ternary solution. This

phenomenon arises from a cosolvent effect, whereby the monomer promotes mutual miscibility between the two solvents through both enthalpic and entropic contributions.⁴² Upon initiation of polymerization using 2-hydroxy-2-methylpropio-phenone (HMPP) under UV irradiation, the system undergoes spontaneous solvent–solvent phase separation, yielding an opaque gel, which is a hallmark of PI-SPS. Gel permeation chromatography (GPC) traces and proton nuclear magnetic resonance (¹H NMR) spectra confirm the formation of PDMAAm with a molecular weight of approximately 500 kDa and nearly 100% conversion (Figures S1 and S2). To elucidate the underlying mechanism, we constructed isothermal ternary phase diagrams for the DMAAm/ $[C_2mIm][TFSI]$ / $[P_{66614}][TFSI]$ system before and after polymerization (Figure 2a, b). The gel composition is described by the monomer volume fraction in the precursor solution and the volume fraction of $[P_{66614}][TFSI]$ in the solvent mixture, denoted as x . The binary $[C_2mIm][TFSI]$ – $[P_{66614}][TFSI]$ mixtures formed two-phase systems across a wide composition range ($0.2 < x < 0.8$). However, incorporation of more than 20 vol % DMAAm renders the ternary mixtures fully miscible, yielding clear, homogeneous solutions. In contrast, most of the corresponding systems containing PDMAAm at the same concentration revert to phase-separated states. This phenomenon arises because the unfavorable interactions between the two solvents become dominant again as the cosolvent effect of the monomer is diminished upon polymerization. These observations suggest that PI-SPS occurs specifically in regions where the monomeric state is miscible but the polymeric state is not, highlighting the decisive role of polymerization in triggering solvent demixing. Thus, PI-SPS involves several key processes: the use of at least two mutually immiscible solvents, homogenization of the precursor solution through the cosolvent effect of the monomer, and reinduced solvent–solvent phase separation caused by the reduction of this cosolvent effect during polymerization. In addition, the resulting polymer should remain compatible with at least one solvent-rich phase; otherwise, precipitation of a largely unsolvated polymer would occur, making the system

closer to conventional polymerization-induced phase separation. This compatibility also enables the polymer distribution and local polymer concentration in the polymer-rich phase to be tuned through the solvent mixing ratio, as discussed below. Thermodynamically, PI-SPS can be interpreted by considering the decrease in configurational entropy accompanying polymerization. The Gibbs free energy change, ΔG (normalized by kT) of the ternary mixture is given by⁴³

$$\frac{\Delta G}{kT} = \phi_{\text{sol1}} \ln \phi_{\text{sol1}} + \phi_{\text{sol2}} \ln \phi_{\text{sol2}} + \frac{\phi_{\text{p}}}{N} \ln \phi_{\text{p}} \\ + \chi_{\text{sol1-sol2}} \phi_{\text{sol1}} \phi_{\text{sol2}} + \chi_{\text{sol1-p}} \phi_{\text{sol1}} \phi_{\text{p}} + \chi_{\text{sol2-p}} \phi_{\text{sol2}} \phi_{\text{p}}$$

where ϕ represents the volume fraction of each component, N is the degree of polymerization, and χ denotes the Flory–Huggins interaction parameters. The subscripts “sol” and “p” denote the solvent and the monomer or polymer, respectively. In the binary sol1/sol2 mixture before monomer addition, the combined free-energy contribution from the solvent mixing entropy terms and the unfavorable solvent–solvent interaction term is insufficient to stabilize a homogeneous state, reflecting the intrinsic immiscibility of the two solvents. As polymerization proceeds and N increases, the entropic term decreases, suppressing the mixing entropy of the cosolvent and favoring phase separation. These features distinguish PI-SPS from conventional PIPS, in which phase separation is typically governed by polymer–solvent incompatibility or polymer precipitation. By using polymerization to switch solvent–solvent miscibility, PI-SPS provides a solvent-driven design principle for generating multiphase gel architectures with tunable polymer partitioning and local polymer concentration.

The polymerization products appeared as gel-like materials at monomer concentrations greater than 40 vol %. The resulting biphasic gels formed via PI-SPS exhibited pronounced optical turbidity and tunable mechanical properties, depending on the solvent composition (Figures 2c and S3). These macroscopic features originate from solvent phase separation and the resulting internal architecture, which is highly sensitive to the IL mixing ratio. To visualize these internal structures, confocal laser scanning fluorescence microscopy (CLSM) was performed on PDMAAm/[C₂mIm][TFSI]/[P₆₆₆₁₄][TFSI] gels containing 40 vol % polymer at various solvent mixing ratios x (Figure 2d,e). Nile Red was employed as a fluorescent probe due to its solvatochromic behavior, emitting distinct fluorescence wavelengths depending on the local polarity and thus enabling spatial mapping of the solvent domains.⁴⁴ In control gels prepared using a single IL ($x = 0$ or 1), namely PDMAAm/[C₂mIm][TFSI] and PDMAAm/[P₆₆₆₁₄][TFSI], no phase-separated structures were observed, although differences in fluorescence emission confirmed distinct solvation environments. In contrast, biphasic gels formed via PI-SPS exhibited three-dimensional phase-separated morphologies composed of micron-sized droplets (diameters: 19 ± 3 , 46 ± 16 , and 10 ± 1 μm for $x = 0.25$, 0.5, and 0.75, respectively). The domain structure consistently displayed a sea–island morphology with C₂mIm-rich continuous phases and P₆₆₆₁₄-rich dispersed domains across all compositions examined. During droplet formation and coalescence, the relaxation time of the polymer-rich continuous phase increases markedly as polymerization progresses. As a result, further coalescence and growth of the droplets are kinetically arrested by the viscoelastic nature of the surrounding matrix, leading to a trapped sea–island morphology.

To elucidate the polymer distribution, PDMAAm was covalently labeled via copolymerization with methacryloyl-modified rhodamine B. Fluorescence was predominantly observed in the continuous C₂mIm-rich phase, indicating that PDMAAm preferentially partitioned into this phase (Figure S4). When the solvent composition was skewed toward [P₆₆₆₁₄][TFSI], the C₂mIm-rich phase appeared larger than expected based on feed composition, suggesting partial intermixing among the three components. The preferential partitioning of PDMAAm can be attributed to the distinct stabilization environments provided by the two IL-rich phases. A liquid–liquid partition experiment using dilute PDMAAm revealed that PDMAAm-derived ¹H NMR signals were observed in the C₂mIm-rich phase, whereas no discernible PDMAAm signals were detected in the P₆₆₆₁₄-rich phase, indicating a strong partitioning preference toward the C₂mIm-rich phase (Figure S5).

To clarify the molecular origin of this preference, all-atom molecular dynamics (MD) simulations and density functional theory (DFT) calculations were performed, with detailed analyses presented in the Supporting Information (Table S1, Figures S6–S10). Representative MD snapshots show that the monomer-containing ternary system is homogeneously mixed, whereas the polymerized system develops a phase-separated structure with PDMAAm preferentially located in the C₂mIm-rich region (Figure 2f). This structural transition was further supported by radial distribution function analyses, which showed no pronounced density heterogeneity around DMAAm in the monomer state but clear enrichment of C₂mIm⁺ around PDMAAm in the polymer state, accompanied by segregation of the P₆₆₆₁₄-rich phase at longer distances (Figure S6). Separate simulations of PDMAAm in each ionic liquid revealed a larger first-shell cation coordination number around PDMAAm for C₂mIm⁺ than for P₆₆₆₁₄⁺ ($N_{\text{1st}} \sim 1$ and 0.2, respectively), indicating more effective solvation of PDMAAm by C₂mIm⁺ (Figures 2g and S7–S9). Additionally, DFT calculations using representative DMAAm–cation interaction models demonstrated that the binding energy for the DMAAm–cation interaction (ΔE_{bind}) is more negative for the C₂mIm-based system than for the P₆₆₆₁₄-based system, indicating stronger stabilization of the DMAAm–C₂mIm⁺ interaction (Figures 2g and S10). These results support the preferential stabilization and localization of PDMAAm in the C₂mIm-rich continuous phase formed during PI-SPS. Although the present experiments and simulations clarify the molecular origin of preferential PDMAAm partitioning, the detailed kinetics of solvent demixing and droplet coalescence during polymerization remain an important subject for future investigation.

This facile one-step method for fabricating solvent-phase-separated gels relies on the differential affinities among monomers, polymers, and solvents. To confirm the generality of this phenomenon, we explored a variety of monomer–solvent combinations, revealing that PI-SPS is not limited to specific monomer species or IL systems (Figure S11 and Table S2). Comparable phase separation and turbidity were observed in poly(methyl methacrylate) (PMMA)/[C₂mIm][TFSI]/[P₆₆₆₁₄][TFSI] gels, PDMAAm/water/1-hexyl-3-methylimidazolium ([C₆mIm][BF₄]) hydrogels, and poly(*N,N*-diethyl acrylamide) (PDEAAm)/water/1-butanol organo-hydrogels. In all cases, the polymer was compatible with at least one of the solvent components, suggesting that the turbidity arose from solvent–solvent phase separation rather than from polymer precipitation. The observed universality of PI-SPS across

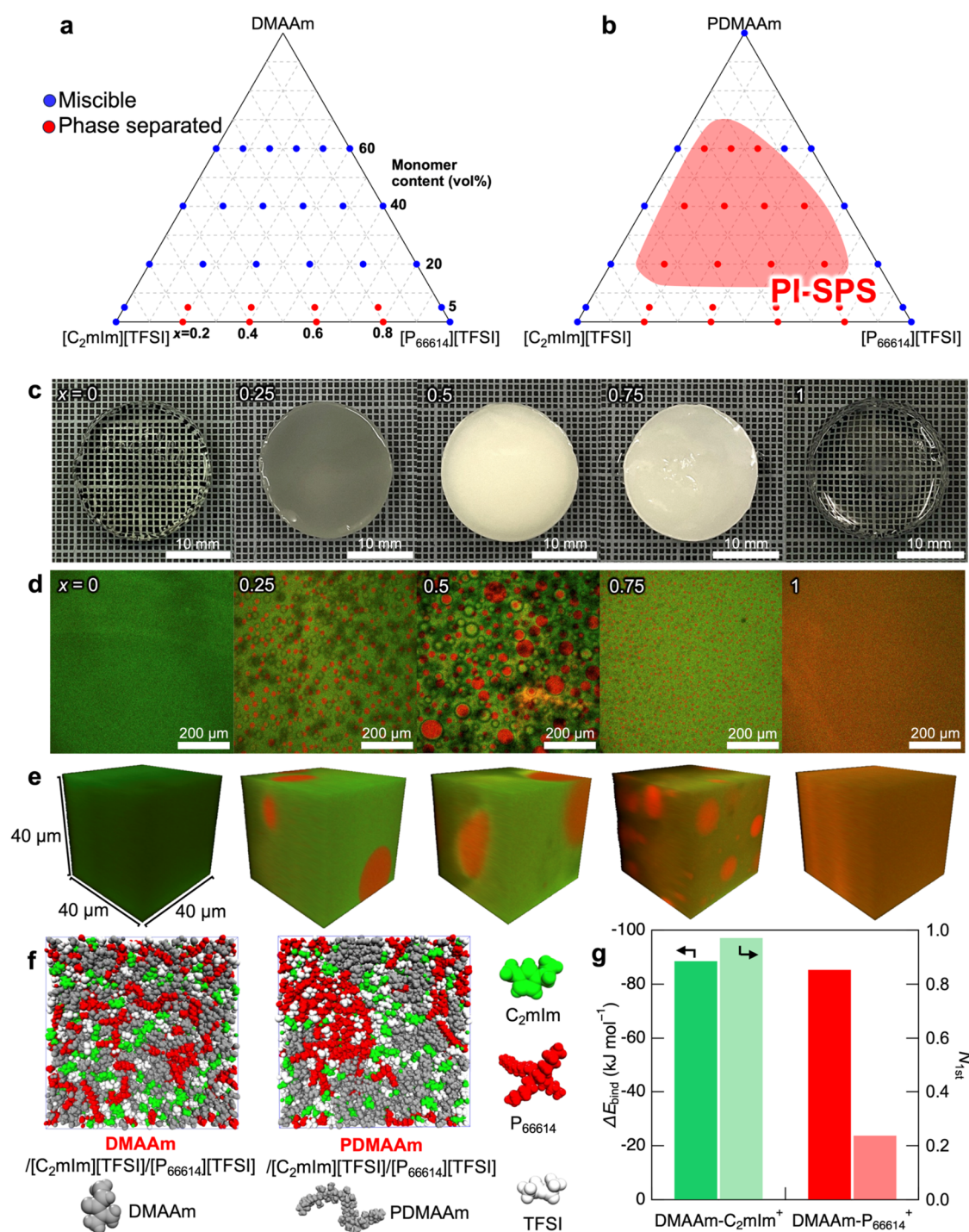


Figure 2. Phase behavior and morphology of PI-SPS gels. (a, b) Ternary isothermal phase diagrams (volume fraction basis) for DMAAm/[C₂mIm][TFSI]/[P₆₆₆₁₄][TFSI] before (a) and after (b) polymerization. (c) Photographs of gels with various solvent mixing ratios x . (d, e) CLSM images for 40 vol % PDMAAm/[C₂mIm][TFSI]/[P₆₆₆₁₄][TFSI] with various x in two-dimensional (d) and three-dimensional (e) views. The green region indicates the low-wavelength range (excitation, 488 nm; detection, 498–537 nm), while the red region indicates the high-wavelength range (excitation, 543 nm; detection, 650–700 nm). The images are merged from measurements taken at each wavelength. (f) Representative snapshots of the simulation boxes for the monomer-containing and polymerized ternary systems. (g) Binding energy (ΔE_{bind}) and first-shell coordination number for DMAAm–cation interactions ($N_{1\text{st}}$).

hydrogels, organogels, and ion gels highlights its broad applicability in diverse fields such as biomaterials and electrochemistry. Moreover, because each solvent system offers distinct solubility parameters and chemical environments, further investigation of their physicochemical properties is critical for rational material design and functional optimization.

Characterization of Thermal and Rheological Behavior in Biphasic Gels

The physical properties of polymer gels, including their viscoelastic behavior, are closely linked to relaxation dynamics, particularly the glass transition temperature (T_g).^{45,46} To examine the relaxation behavior of each phase in biphasic gels

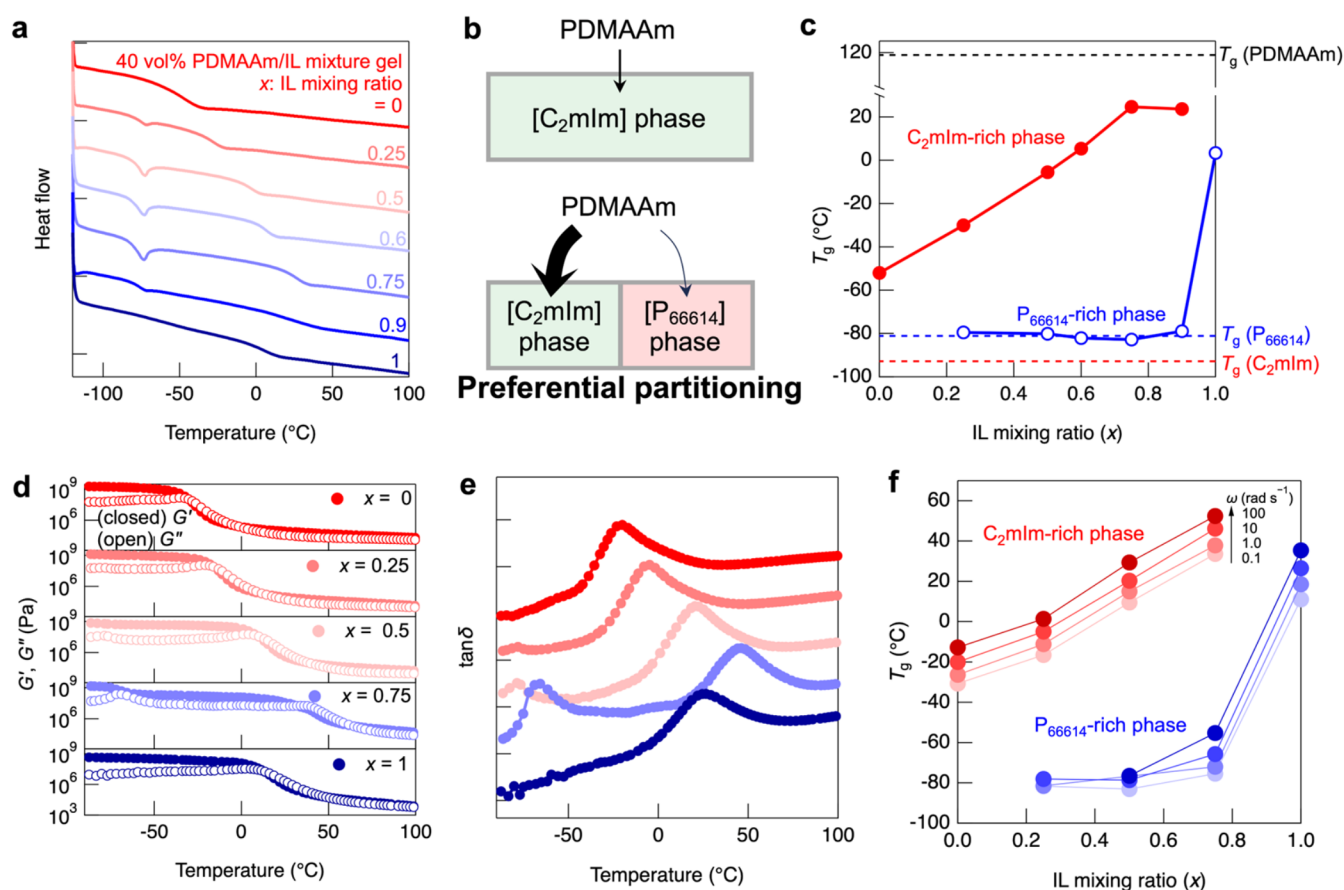


Figure 3. Thermal and rheological behaviors of PI-SPS gels. (a) DSC curves for 40 vol % PDMAAm/[C₂mlm]/[TFSI]/[P₆₆₆₁₄]/[TFSI] gels with various IL mixing ratios, where x denotes the volume fraction of [P₆₆₆₁₄]/[TFSI] in the IL mixture. (b) Schematic of preferential polymer partitioning. (c) Dependence of T_g of each phase on x . (d, e) Temperature dependence of storage modulus (G') and loss modulus (G'') (d) and loss tangent ($\tan \delta$) (e), for various x . (f) Dependence of T_g on x obtained from viscoelastic measurements at different angular frequencies.

produced via PI-SPS, differential scanning calorimetry (DSC) was performed on gels prepared with varying solvent mixing ratios, x , and on the corresponding neat IL mixtures. DSC analysis of the neat ILs revealed that [C₂mlm]/[TFSI] exhibited a T_g at -92.8°C , whereas [P₆₆₆₁₄]/[TFSI] showed a T_g at -81.1°C , followed by crystallization and melting (Figure S12). Upon cooling, an exothermic peak associated with upper critical solution temperature (UCST)-type phase separation was observed, confirming the intrinsic immiscibility of the IL pair at low temperatures (Figure S13). As shown in Figure 3a, the single IL gels exhibited a single T_g reflecting a homogeneous polymer–solvent matrix.⁴⁷ Conversely, the biphasic gels consistently displayed two distinct T_g values. The lower-temperature T_g , associated with P₆₆₆₁₄-rich domains, remained invariant with composition, whereas the higher-temperature T_g , corresponding to C₂mlm-rich domains, increased as the [C₂mlm] fraction decreased. This compositional dependence reflects the preferential partitioning of PDMAAm into the C₂mlm-rich phase (Figure 3b, c). By using the T_g –composition relationships of miscible PDMAAm/IL mixtures, the local polymer concentration in each phase was estimated from the two T_g values observed for the biphasic gels. This analysis indicates that the majority of the introduced PDMAAm is concentrated in the C₂mlm-rich phase, whereas only a minor fraction is estimated to be present in the P₆₆₆₁₄-rich phase, even at high P₆₆₆₁₄ contents (Figure S14). The absence of an additional high-temperature T_g indicated that PDMAAm

remained fully solubilized (Figure S15). This behavior sharply contrasts with precipitation-driven systems, such as conventional polymerization-induced phase separation (PIPS).⁴⁸ In the present system, polymer solubility is maintained in both solvents, and phase separation arises solely from solvent demixing during polymerization. Although a minor fraction of polymer partitions into the dispersed phase at high P₆₆₆₁₄ contents, the majority of PDMAAm remains in the C₂mlm-rich matrix.

To further correlate microscopic structure with mechanical behavior, temperature-dependent rheological measurements were performed (Figure 3d,e). The single-phase gels exhibited a single relaxation, whereas the biphasic gels showed two-step relaxation. Combined frequency–temperature sweep measurements revealed that these relaxations correspond to frequency-dependent glass transitions rather than structural rearrangements induced by temperature changes (Figures S16 and S17). The dependence on the mixing ratio was consistent with the behavior observed in the DSC measurements (Figure 3f). Initial softening associated with the T_g of the P₆₆₆₁₄-rich domains caused only a modest decrease in storage modulus (G'), whereas the glass transition of the C₂mlm-rich continuous phase enriched with PDMAAm resulted in a pronounced drop in G' . This pronounced decrease reflects the fact that the C₂mlm-rich continuous phase forms the percolated load-bearing matrix of the gel.⁴⁹ Because G' is governed mainly by the relaxation of this connected matrix, segmental relaxation in the C₂mlm-rich phase

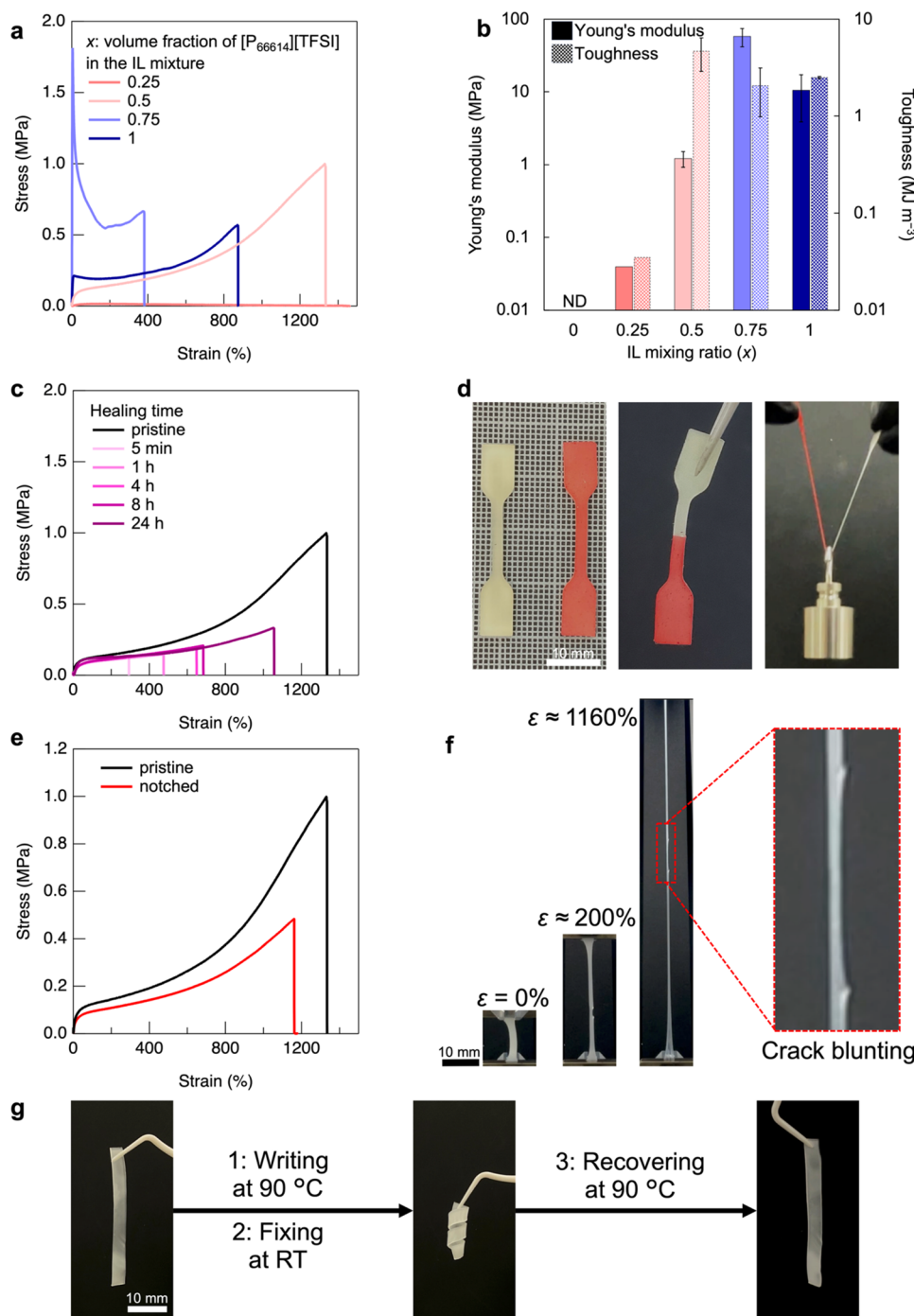


Figure 4. Mechanical properties of PI-SPS gels. (a) Stress–strain curves of gels with different IL mixing ratios, where x denotes the volume fraction of $[P_{66614}][TFSI]$ in the IL mixture. (b) Young's modulus and toughness as a function of x . (c) Stress–strain curve of a self-healed gel ($x = 0.5$) measured at room temperature. (d) Photograph of the self-healed gel. (e) Stress–strain curves of a pristine and a notched sample ($x = 0.5$). (f) Photograph of the notched sample during tensile testing. (g) Demonstration of shape-memory behavior at $x = 0.75$.

causes the dominant modulus drop. In contrast, the P_{66614} -rich domains are dispersed, disconnected, and polymer-poor; therefore, their lower-temperature relaxation contributes only weakly to the bulk modulus.

These results demonstrate that PI-SPS generates a solvent-phase-separated structure, where preferential polymer partitioning produces distinct thermal and mechanical relaxation processes. The pronounced influence of the C_2mIm -rich continuous phase on bulk viscoelasticity suggests that the hierarchical thermal and mechanical architecture established at

the microscale can directly govern the macroscopic response under external deformation. This insight provides a foundation for probing how phase-separated structures control tensile deformation, as explored in the following mechanical tests.

Mechanical Properties of Biphasic Gels

The mechanical properties of the biphasic gels formed via PI-SPS were evaluated by uniaxial tensile testing (Figure 4a). The stress–strain behavior of the gels drastically changed with the mixing ratio x . Gels composed solely of $[C_2mIm][TFSI]$ were

mechanically weak and could not form self-standing samples because of rapid stress relaxation arising from polymer chain disentanglement. In contrast, the single-phase PDMAAm/[P₆₆₆₁₄][TFSI] gel showed enhanced strength, which can be attributed to its T_g being close to room temperature. This higher T_g is mainly explained by the smaller number of ionic liquid molecules per monomer unit in the P₆₆₆₁₄-based gel at the same volume fraction, owing to the larger molecular weight and lower density of [P₆₆₆₁₄][TFSI], which leads to weaker plasticization of PDMAAm. Notably, for all compositions, no liquid exudation or nonuniform fracture were observed during elongation, indicating that the domain structure remained intact even under large deformations. Interestingly, upon mixing the two solvents, the Young's modulus and toughness of the PI-SPS gels did not vary linearly with composition; instead, they exhibited distinct maxima at different mixing ratios (Figure 4b). Among the tested compositions, the gel with $x = 0.5$ showed the highest toughness, whereas that with $x = 0.75$ exhibited an exceptionally high Young's modulus. This nonmonotonic behavior is consistent with the glass transition of the C₂mIm-rich continuous phase, as confirmed by DSC and rheological measurements.

The PI-SPS gel at $x = 0.5$ exhibits a unique combination of three mechanical characteristics: high toughness, self-healing ability, and enhanced crack resistance. The high toughness is attributed to efficient energy dissipation via segmental motion, which corresponds to a T_g near room temperature, as confirmed by DSC and rheological analysis.⁴⁶ The PI-SPS gel exhibited self-healing capability, as illustrated in Figure 4c,d. This behavior is mainly attributed to the C₂mIm-rich continuous phase enriched with PDMAAm, where preferentially partitioned PDMAAm forms reversible physical entanglements that enable reconnection across the cut interface while maintaining high toughness.^{50,51} Furthermore, the biphasic architecture fabricated via the PI-SPS process also plays a critical role in fracture behavior (Figure 4e, f). Previous studies have demonstrated that embedding liquid inclusions within elastomers can impede crack propagation and enhance toughness, as exemplified by liquid metal elastomer composites achieving exceptional fracture resistance.⁵² Similarly, the PI-SPS gel with $x = 0.5$ exhibits outstanding crack resistance, with dispersed P₆₆₆₁₄-rich domains acting as crack stoppers within an elastic and reversible continuous phase, resulting in pronounced crack-blunting behavior. The measured fracture energy reached 4600 J m⁻² despite the high solvent content, and precracked samples retained elongation comparable to pristine gels. To isolate the contribution of the phase-separated architecture, we compared the PI-SPS gel with a single-phase PDMAAm/[C₂mIm][TFSI] gel whose polymer concentration was adjusted to 57 vol %, approximating that of the C₂mIm-rich continuous phase in the PI-SPS gel. The PI-SPS gel exhibited toughness, self-healing performance, and crack resistance comparable to or even superior to those of the single-phase gel, despite its lower overall polymer content (Figure S18). These results indicate that the phase-separated architecture contributes to enhanced mechanical performance, particularly crack resistance, through crack blunting and stress dissipation associated with the polymer-poor liquid droplets.

A dramatic change in mechanical behavior was observed at P₆₆₆₁₄-rich compositions ($x = 0.75$), which is attributed to the continuous phase entering a semiglassy state with a T_g slightly above room temperature.⁵³ Consequently, despite the overall polymer concentration remaining constant, the gel exhibited an

exceptionally high Young's modulus. Remarkably, positioning the T_g above room temperature endowed the PI-SPS gel with a distinct and robust shape-memory capability. As shown in Figure 4g, the gel was rigid at room temperature but became deformable upon heating, and this transition was fully reversible. Shapes programmed at elevated temperatures were fixed upon cooling to room temperature, and subsequently recovered their original geometry upon reheating above T_g , driven by the elasticity of the continuous polymer network. Notably, the overall polymer concentration of this gel remained identical across compositions, highlighting that the shape-memory behavior arises solely from spontaneous, composition-dependent polymer partitioning induced by solvent demixing, a mechanism fundamentally distinct from conventional shape-memory materials.

Collectively, these observations demonstrate that, despite a uniform overall polymer concentration, spontaneous phase separation during polymerization generates localized polymer enrichment and microscale structural heterogeneity. This intrinsic self-organization enables programmable mechanical functionalities, including self-healing, crack resistance, and shape-memory behavior, thereby establishing a new materials design paradigm in which structural and functional diversity emerges solely from solvent-driven self-organization.

CONCLUSION

In this study, polymer gels with well-defined biphasic architectures were successfully developed via PI-SPS. Solvent demixing during polymerization induces spontaneous spatial heterogeneity of polymer distribution, resulting in phase-separated gels originating from solvent immiscibility. Thus, PI-SPS establishes a general solvent-driven strategy for programming multiphase gel architectures through solvent–solvent demixing and polymer partitioning, complementing conventional approaches based on polymer–solvent incompatibility or complex polymer architectures. The two immiscible solvent domains enable a distinct two-step glass transition through preferential partitioning of polymer chains and allow systematic control of the transition behavior by adjusting the solvent mixing ratio. Despite a constant overall polymer concentration, this hierarchical organization leads to pronounced changes in mechanical functionality, including high stretchability, self-healing capability, reversible shape-memory behavior, and enhanced crack resistance. Moreover, the solvent-driven multiphase architecture generated by PI-SPS can be combined synergistically with single-phase toughening strategies, thereby providing an additional design dimension for multifunctional soft materials. Importantly, the PI-SPS concept is not restricted to IL systems and can be readily extended to aqueous or organic solvent systems, demonstrating its broad applicability. By enabling control over mesoscale polymer distribution, PI-SPS offers a versatile platform for creating functional soft materials, from robust biomaterials to adaptive soft actuators. These results highlight how simple solvent interactions coupled with polymerization can generate hierarchical architectures and emergent mechanical functionalities.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.6c03722>.

Materials; experimental procedures for synthesis and characterization; computational methods and detailed results; GPC traces; ^1H NMR spectra; photographs; confocal laser scanning microscopy (CLSM) images; molecular dynamics (MD) simulation snapshots and analyses; density functional theory (DFT) calculation results; differential scanning calorimetry (DSC) curves and corresponding analyses; temperature-dependent rheological measurements; tensile testing data; and additional tables (PDF)

AUTHOR INFORMATION

Corresponding Authors

Yuji Kamiyama — Research Center for Macromolecules & Biomaterials, National Institute for Materials Science, Tsukuba 305-0047, Japan; Email: KAMIYAMA.Yuji@nims.go.jp

Ryota Tamate — Research Center for Macromolecules & Biomaterials, National Institute for Materials Science, Tsukuba 305-0047, Japan; Email: TAMATE.Ryota@nims.go.jp

Complete contact information is available at:
<https://pubs.acs.org/10.1021/jacs.6c03722>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This study was financially supported by JSPS KAKENHI (23K26409 and 26K01248 to R.T.). This work was also supported by the Advanced Research Infrastructure for Materials and Nanotechnology in Japan (ARIM) of the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) (Proposal Number JPMXP1225NMS302).

REFERENCES

- (1) Cui, L.; Lin, Y.; Li, C.; Yang, Z.; Wang, C.-P.; Yin, J.; Zhu, J. Recent progress of 3D-printed polymeric gel sensors for flexible electronics. *Mater. Horiz.* **2025**, *12*, 8802–8831.
- (2) Xiong, J.; Wang, X.; Li, L.; Li, Q.; Zheng, S.; Liu, Z.; Li, W.; Yan, F. Low-Hysteresis and High-Toughness Hydrogels Regulated by Porous Cationic Polymers: the Effect of Counteranions. *Angew. Chem., Int. Ed.* **2024**, *63*, No. e202316375.
- (3) He, Y.; Cheng, Y.; Yang, C.; Guo, C. F. Creep-free polyelectrolyte elastomer for drift-free iontronic sensing. *Nat. Mater.* **2024**, *23*, 1107–1114.
- (4) Zhang, L.; Yan, H.; Zhou, J.; Zhao, Z.; Huang, J.; Chen, L.; Ru, Y.; Liu, M. High-Performance Organohydrogel Artificial Muscle with Compartmentalized Anisotropic Actuation Under Microdomain Confinement. *Adv. Mater.* **2023**, *35*, No. 2202193.
- (5) Na, H.; Kang, Y. W.; Park, C. S.; Jung, S.; Kim, H. Y.; Sun, J. Y. Hydrogel-based strong and fast actuators by electroosmotic turgor pressure. *Science* **2022**, *376*, 301–307.
- (6) Imaizumi, S.; Kokubo, H.; Watanabe, M. Polymer Actuators Using Ion-Gel Electrolytes Prepared by Self-Assembly of ABA-Triblock Copolymers. *Macromolecules* **2012**, *45*, 401–409.
- (7) Li, H.; Xu, F.; Li, Y.; Sun, J. Self-Healing Ionogel-Enabled Self-Healing and Wide-Temperature Flexible Zinc-Air Batteries with Ultra-Long Cycling Lives. *Adv. Sci.* **2024**, *11*, No. e2402193.
- (8) Ma, C.; Cui, W.; Liu, X.; Ding, Y.; Wang, Y. In situ preparation of gel polymer electrolyte for lithium batteries: Progress and perspectives. *InfoMat* **2022**, *4*, No. e12232.
- (9) Mackanic, D. G.; Yan, X.; Zhang, Q.; Matsuhisa, N.; Yu, Z.; Jiang, Y.; Manika, T.; Lopez, J.; Yan, H.; Liu, K.; et al. Decoupling of mechanical properties and ionic conductivity in supramolecular lithium ion conductors. *Nat. Commun.* **2019**, *10*, No. 5384.
- (10) Tamate, R.; Peng, Y.; Kamiyama, Y.; Nishikawa, K. Extremely Tough, Stretchable Gel Electrolytes with Strong Interpolymer Hydrogen Bonding Prepared Using Concentrated Electrolytes to Stabilize Lithium-Metal Anodes. *Adv. Mater.* **2023**, *35*, 2211679.
- (11) Ye, H.; Wu, B.; Sun, S.; Wu, P. Self-compliant ionic skin by leveraging hierarchical hydrogen bond association. *Nat. Commun.* **2024**, *15*, No. 885.
- (12) Wang, Y.; Zanelotti, C. J.; Wang, X.; Kerr, R.; Jin, L.; Kan, W. H.; Dingemans, T. J.; Forsyth, M.; Madsen, L. A. Solid-state rigid-rod polymer composite electrolytes with nanocrystalline lithium ion pathways. *Nat. Mater.* **2021**, *20*, 1255–1263.
- (13) Tamate, R.; Ueki, T. Adaptive Ion-Gel: Stimuli-Responsive, and Self-Healing Ion Gels. *Chem. Rec.* **2023**, *23*, No. e202300043.
- (14) Li, X.; Tsuchibora, H.; Ye, Y. N.; Cui, K.; Kurokawa, T. Mechanical Performance of Polyampholyte Hydrogels Influenced by Ionic Bond Strength under Isochoric Conditions. *Macromolecules* **2025**, *58*, 2984–2995.
- (15) Zhang, L.; Zhao, T.; Liu, M. Bioinspired Multiphase Gels Using Spatial Confinement Strategy. *Acc. Mater. Res.* **2024**, *5*, 48–63.
- (16) Li, X.; Wu, B.; Sun, S.; Wu, P. Making Sticky-Slippery Switchable Fluorogels Through Self-Adaptive Bicontinuous Phase Separation. *Adv. Mater.* **2024**, *36*, No. 2411273.
- (17) Xiang, H.; Li, X.; Wu, B.; Sun, S.; Wu, P. Highly Damping and Self-Healable Ionic Elastomer from Dynamic Phase Separation of Sticky Fluorinated Polymers. *Adv. Mater.* **2023**, *35*, No. e2209581.
- (18) Chai, J.; Ru, Y.; Jia, Y.; Yang, Y.; Zhang, H.; Chen, L.; Zhao, T.; Liu, M. Friction Memory Ionogels With Hysteretic Sticky-Slippery Transition via Thermolocking the Metastable state. *Adv. Mater.* **2025**, *37*, No. e2416250.
- (19) Xie, J.; Li, X.; He, Z.; Fan, L.; Yao, D.; Zheng, Y. Preparation of tough and stiff ionogels via phase separation. *Mater. Horiz.* **2024**, *11*, 238–250.
- (20) Chen, L.; Zhao, C.; Huang, J.; Zhou, J.; Liu, M. Enormous-stiffness-changing polymer networks by glass transition mediated microphase separation. *Nat. Commun.* **2022**, *13*, No. 6821.
- (21) Chen, L.; Lin, C.; Zhao, C.; Duan, X.; Zhao, T.; Liu, M. Ionic Liquids: An Ideal Solvent for Tuning the UCST Phase Behavior of Polymer Gels. *J. Phys. Chem. B* **2023**, *127*, 10903–10911.
- (22) Zhang, C.; Wang, Z.; Zhu, H.; Zhang, Q.; Zhu, S. Dielectric Gels with Microphase Separation for Wide-Range and Self-Damping Pressure Sensing. *Adv. Mater.* **2024**, *36*, No. e2308520.
- (23) Wang, M.; Zhang, P.; Shamsi, M.; Thelen, J. L.; Qian, W.; Truong, V. K.; Ma, J.; Hu, J.; Dicey, M. D. Tough and stretchable ionogels by in situ phase separation. *Nat. Mater.* **2022**, *21*, 359–365.
- (24) Tamate, R.; Hashimoto, K.; Ueki, T.; Watanabe, M. Block copolymer self-assembly in ionic liquids. *Phys. Chem. Chem. Phys.* **2018**, *20*, 25123–25139.
- (25) Tamate, R.; Hashimoto, K.; Horii, T.; Hirasawa, M.; Li, X.; Shibayama, M.; Watanabe, M. Self-Healing Micellar Ion Gels Based on Multiple Hydrogen Bonding. *Adv. Mater.* **2018**, *30*, No. 1802792.
- (26) Wang, H.; Xu, J.; Li, K.; Dong, Y.; Du, Z.; Wang, S. Highly stretchable, self-healable, and self-adhesive ionogels with efficient antibacterial performances for a highly sensitive wearable strain sensor. *J. Mater. Chem. B* **2022**, *10*, 1301–1307.
- (27) Meng, X.; Qiao, Y.; Do, C.; Bras, W.; He, C.; Ke, Y.; Russell, T. P.; Qiu, D. Hysteresis-Free Nanoparticle-Reinforced Hydrogels. *Adv. Mater.* **2022**, *34*, No. e2108243.
- (28) Kamio, E.; Yasui, T.; Iida, Y.; Gong, J. P.; Matsuyama, H. Inorganic/Organic Double-Network Gels Containing Ionic Liquids. *Adv. Mater.* **2017**, *29*, No. 1704118.
- (29) Fukushima, T.; Kosaka, A.; Ishimura, Y.; Yamamoto, T.; Takigawa, T.; Ishii, N.; Aida, T. Molecular Ordering of Organic Molten Salts Triggered by Single-Walled Carbon Nanotubes. *Science* **2003**, *300*, 2072–2074.
- (30) Zhao, Z.; Zhang, K.; Liu, Y.; Zhou, J.; Liu, M. Highly Stretchable, Shape Memory Organohydrogels Using Phase-Transition Micro-inclusions. *Adv. Mater.* **2017**, *29*, No. 1701695.

- (31) Wan, C.; Cheng, Q.; Zeng, M.; Huang, C. Recent progress in emulsion gels: from fundamentals to applications. *Soft Matter* **2023**, *19*, 1282–1292.
- (32) Lu, Y.; Mao, L.; Hou, Z.; Miao, S.; Gao, Y. Development of Emulsion Gels for the Delivery of Functional Food Ingredients: from Structure to Functionality. *Food Eng. Rev.* **2019**, *11*, 245–258.
- (33) Chan, P. K.; Rey, A. D. Polymerization-Induced Phase Separation. 2. Morphological Analysis. *Macromolecules* **1997**, *30*, 2135–2143.
- (34) Szczepanski, C. R.; Pfeifer, C. S.; Stansbury, J. W. A new approach to network heterogeneity: Polymerization induced phase separation in photo-initiated, free-radical methacrylic systems. *Polymer* **2012**, *53*, 4694–4701.
- (35) Schulze, M. W.; McIntosh, L. D.; Hillmyer, M. A.; Lodge, T. P. High-Modulus, High-Conductivity Nanostructured Polymer Electrolyte Membranes via Polymerization-Induced Phase Separation. *Nano Lett.* **2014**, *14*, 122–126.
- (36) McIntosh, L. D.; Schulze, M. W.; Irwin, M. T.; Hillmyer, M. A.; Lodge, T. P. Evolution of Morphology, Modulus, and Conductivity in Polymer Electrolytes Prepared via Polymerization-Induced Phase Separation. *Macromolecules* **2015**, *48*, 1418–1428.
- (37) Foster, J. C.; Varlas, S.; Couturaud, B.; Jones, J. R.; Keogh, R.; Mathers, R. T.; O'Reilly, R. K. Predicting Monomers for Use in Polymerization-Induced Self-Assembly. *Angew. Chem., Int. Ed.* **2018**, *57*, 15733–15737.
- (38) Penfold, N. J. W.; Yeow, J.; Boyer, C.; Armes, S. P. Emerging Trends in Polymerization-Induced Self-Assembly. *ACS Macro Lett.* **2019**, *8*, 1029–1054.
- (39) D'Agosto, F.; Rieger, J.; Lansalot, M. RAFT-Mediated Polymerization-Induced Self-Assembly. *Angew. Chem., Int. Ed.* **2020**, *59*, 8368–8392.
- (40) Morimura, M.; Ida, S.; Oyama, M.; Takeshita, H.; Kanaoka, S. Design of Hydrogels with Thermoresponsive Crosslinked Domain Structures via the Polymerization-Induced Self-Assembly Process and Their Thermoresponsive Toughening in Air. *Macromolecules* **2021**, *54*, 1732–1741.
- (41) Arce, A.; Earle, M. J.; Katdare, S. P.; Rodríguez, H.; Seddon, K. R. Mutually immiscible ionic liquids. *Chem. Commun.* **2006**, 2548–2550.
- (42) Jouyban, A. Review of the cosolvency models for predicting solubility of drugs in water-cosolvent mixtures. *J. Pharm. Pharm. Sci.* **2008**, *11*, 32–58.
- (43) Hsu, C. C.; Prausnitz, J. M. Thermodynamics of Polymer Compatibility in Ternary Systems. *Macromolecules* **1974**, *7*, 320–324.
- (44) Poole, C. F. Chromatographic and spectroscopic methods for the determination of solvent properties of room temperature ionic liquids. *J. Chromatogr. A* **2004**, *1037*, 49–82.
- (45) Kim, Y. M.; Moon, H. C. Ionoskins: Nonvolatile, Highly Transparent, Ultrastretchable Ionic Sensory Platforms for Wearable Electronics. *Adv. Funct. Mater.* **2020**, *30*, No. 1907290, DOI: 10.1002/adfm.201907290.
- (46) Chen, L.; Sun, T. L.; Cui, K.; King, D. R.; Kurokawa, T.; Saruwatari, Y.; Gong, J. P. Facile synthesis of novel elastomers with tunable dynamics for toughness, self-healing and adhesion. *J. Mater. Chem. A* **2019**, *7*, 17334–17344.
- (47) Susan, M. A. B. H.; Kaneko, T.; Noda, A.; Watanabe, M. Ion gels prepared by in situ radical polymerization of vinyl monomers in an ionic liquid and their characterization as polymer electrolytes. *J. Am. Chem. Soc.* **2005**, *127*, 4976–4983.
- (48) Abedin, F.; Ye, Q.; Good, H. J.; Parthasarathy, R.; Spencer, P. Polymerization- and solvent-induced phase separation in hydrophilic-rich dentin adhesive mimic. *Acta Biomater.* **2014**, *10*, 3038–3047.
- (49) Veenstra, H.; Verkooijen, P. C. J.; van Lent, B. J. J.; van Dam, J.; de Boer, A. P.; Nijhof, A. P. H. J. On the mechanical properties of co-continuous polymer blends: experimental and modelling. *Polymer* **2000**, *41*, 1817–1826.
- (50) Kamiyama, Y.; Tamate, R.; Hiroi, T.; Samitsu, S.; Fujii, K.; Ueki, T. Highly stretchable and self-healable polymer gels from physical entanglements of ultrahigh-molecular weight polymers. *Sci. Adv.* **2022**, *8*, No. eadd0226.
- (51) Kamiyama, Y.; Tamate, R.; Fujii, K.; Ueki, T. Controlling mechanical properties of ultrahigh molecular weight ion gels by chemical structure of ionic liquids and monomers. *Soft Matter* **2022**, *18*, 8582–8590.
- (52) Kazem, N.; Bartlett, M. D.; Majidi, C. Extreme Toughening of Soft Materials with Liquid Metal. *Adv. Mater.* **2018**, *30*, No. 1706594.
- (53) Wang, M.; Xiao, X.; Siddika, S.; Shamsi, M.; Frey, E.; Qian, W.; Bai, W.; O'Connor, B. T.; Dickey, M. D. Glassy gels toughened by solvent. *Nature* **2024**, *631*, 313–318.