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RAPID COMMUNICATION

Light-switchable LCST windows in an ionic liquid solution of azobenzene copolymers

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Abstract

Photo-induced tuning of lower critical solution temperature (LCST) behavior is an attractive route for reversible phase control, yet the achievable cloud-point shift is often modest in conventional solvent systems. Here, we demonstrate a composition-amplified, light-tunable LCST in ionic liquid polymer solutions using random copolymers of 4-phenylazophenyl methacrylate and phenethyl methacrylate (P(AzoMA-*r*-PhEtMA)) dissolved in 1-ethyl-3-methylimidazolium trifluoromethylsulfonylimide ([C_2mim][TFSI]), a medium in which the azobenzene-containing monomer is readily compatible. Turbidity measurements reveal opposite cloud-point shifts under UV (*cis*-type) and visible-light (*trans*-type) conditions, enabling a bistable temperature window that widens monotonically with azobenzene composition. At 37 °C, the solution is reversibly switched between one-phase and two-phase states by light alone and maintains stable cycling for more than ~40,500 s. These results provide a practical molecular design guideline for targeting ambient-to-physiological light-controlled phase separation in nonvolatile ionic liquid media.

Light offers a uniquely gentle, contactless, and reversible handle to modulate polymer–solvent interactions, enabling "on-demand" shifts of phase boundaries in solution. In thermoresponsive polymers, the photochemical switching of embedded chromophores, such as azobenzenes, can effectively tune the cloud point (T_c) by altering the solvation contrast between two molecular states [1–15]. However, the experimentally observed shift is often not a simple reflection of this intrinsic contrast. Instead, it is constrained by photochemical and physical factors, including the achievable photostationary state composition, thermal back-isomerization, and optical geometry (e.g., limited penetration depth and path-length effects). As a result, even when the underlying solvation difference between the two states is substantial, the macroscopic phase behavior may show only a modest response unless these constraints are explicitly accounted for. Nonvolatile solvents such as ionic liquids (ILs) provide an attractive platform for examining and exploiting phototunable phase behavior because they suppress concentration drift during measurements and offer a designable solvation landscape [16–19]. Moreover, many photoresponsive polymer/IL systems that have been reported to date exhibit phase transitions at elevated temperatures, where thermal back isomerization and optical attenuation can severely limit the effective *cis*-rich population in the bulk [20–23]. This creates a practical and conceptual need for a design strategy that decreases the baseline transition temperature to ambient-to-physiological conditions, thereby allowing the intrinsic *cis*-/*trans*-solvation contrast to be expressed under standard optical path lengths and realistic operating conditions.

Traditionally, photo-induced phase transition temperature modulation has been widely demonstrated for azobenzene-containing thermoresponsive polymers in aqueous media, most notably poly(*N*-isopropylacrylamide) (PNIPAAm)-based copolymers and related backbones [24–27]. These studies established that changing the *cis*-/*trans*-population can shift the phase boundary; however, they also revealed that the observable temperature shift is often limited to a narrow design window; for example, in

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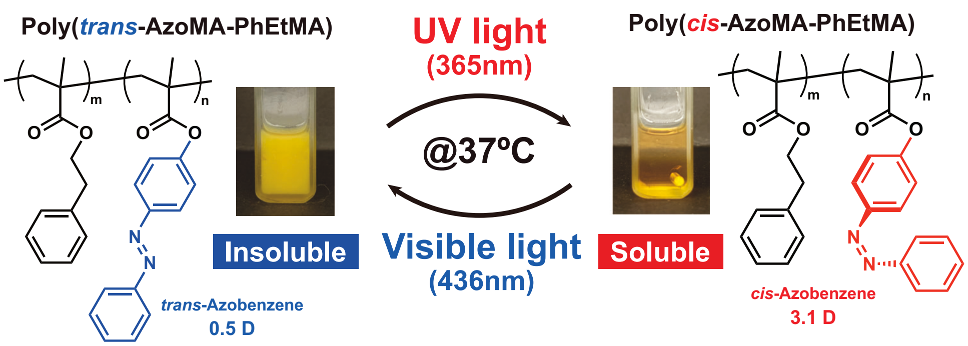

Fig. 1 Conceptual illustration of light-programmable solubility switching of P(AzoMA-*r*-PhEtMA) in the ionic liquid [C_2mim][TFSI] at 37 °C. Visible-light irradiation (436 nm) enriches the *trans*-state, rendering the polymer insoluble and inducing phase separation, whereas UV irradiation (365 nm) enriches the *cis*-state, restoring solubility and yielding a homogeneous solution. The photographs show representative solution states under the two irradiation conditions

P(NIPAAm-*co*-*N*-(4-phenylazophenyl)acrylamide) (P(NIPAAm-*co*-AzoAm), the UV photo stationary state reaches only =60% *cis*-type, and the T_c is maximized only at low azobenzene contents (~2–3 mol%), while higher loadings can suppress solubility and diminish the apparent photo effect [28]. Employing a more hydrophilic backbone can accommodate a larger effective polarity swing; for instance, poly(*N*,*N*-dimethylacrylamide-*co*-4-phyenylazophenyl acrylate) was reported to exhibit a T_c difference of up to ~20 °C between the *cis*- and *trans*-types, which is consistent with a higher attainable *cis* fraction in water [29]. Even when a substantial intrinsic solvation contrast exists, the apparent response can be diminished at elevated temperatures because thermal back-isomerization progressively reduces the *cis*-rich population during the timescale of measurements. In addition, for strongly absorbing chromophores such as azobenzenes, optical attenuation and finite penetration depth can generate spatially inhomogeneous isomer distributions, further reducing the effective *cis* fraction in the bulk and complicating quantitative interpretation [20, 23]. Collectively, the results of prior work indicate that a robust photo-induced T_c shift simultaneously satisfies three practical constraints: (i) a sufficiently high attainable *cis* fraction in the photostationary state, (ii) sufficiently slow thermal back-isomerization on the measurement timescale, and (iii) sufficient optical penetration to avoid strong spatial gradients in isomer composition.

Herein, we address these limitations by combining two complementary design elements in a nonvolatile IL medium. First, we employed poly(phenethyl methacrylate) (PPhEtMA), a polymethacrylate that undergoes LCST-type phase separation at ~40 °C in an IL, 1-ethyl-3-methylimidazolium trifluoromethylsulfonylimide ([C_2mim][TFSI]) [30–34], to establish a low-baseline LCST platform that shifts the phase transition window toward ambient-to-physiological temperatures, thus reducing the impact of thermal back-isomerization and enabling more reliable irradiation of the bulk without relying on specialized optical geometries. Second, we selected a photoswitchable co-monomer, 4-phenylazophenyl methacrylate (AzoMA), whose monomeric form is readily soluble in [C_2mim][TFSI], suggesting strong photoswitch, solvent compatibility and solvation accessibility, conditions expected to amplify the effective *cis*-/*trans*-polarity contrast in solution rather than sequestering the chromophore into poorly solvated microdomains. Using a systematic composition series of P(AzoMA-*r*-PhEtMA), we quantitatively mapped T_c-*trans* and T_c-*cis* in [C_2mim][TFSI], which demonstrate monotonic expansion of the bistable temperature window ΔT_c with the azobenzene fraction and show reversible light-driven switching between one-phase and two-phase states at 37 °C (Fig. 1). Together, these results establish a practical design principle for translating molecular photoisomerization into a robust, quantifiable macroscopic phase response in IL polymer solutions.

Figure 2 highlights a composition-tunable, light-programmable LCST-type phase separation of a series of P(AzoMA-*r*-PhEtMA) in [C_2mim][TFSI]. The preparation, characterization (Supplementary Figs. S1–S12, Supplementary Table S1), photochromism (Supplementary Figs. S13, 14), and thermal relaxation (Supplementary Figs. S15, 16, and Supplementary Tables S2, 3) of P(AzoMA-*r*-PhEtMA) and their protocol are summarized in the *Supporting Information*. Notably, the phase transition window lies near ambient-to-physiological temperatures, reflecting the intrinsically low LCST baseline of the PPhEtMA platform in [C_2mim][TFSI] (Supplementary Fig. S17). To quantify the photostationary-state composition under the present conditions, we performed additional ^{1}H NMR measurements of AzoMA in [C_2mim][TFSI] after UV and visible-light irradiation (Supplementary Fig. S14). Analysis of the photoisomerization-split signals revealed that the *cis* fraction reached 87% under UV irradiation, whereas it was 14% under visible-light irradiation. These

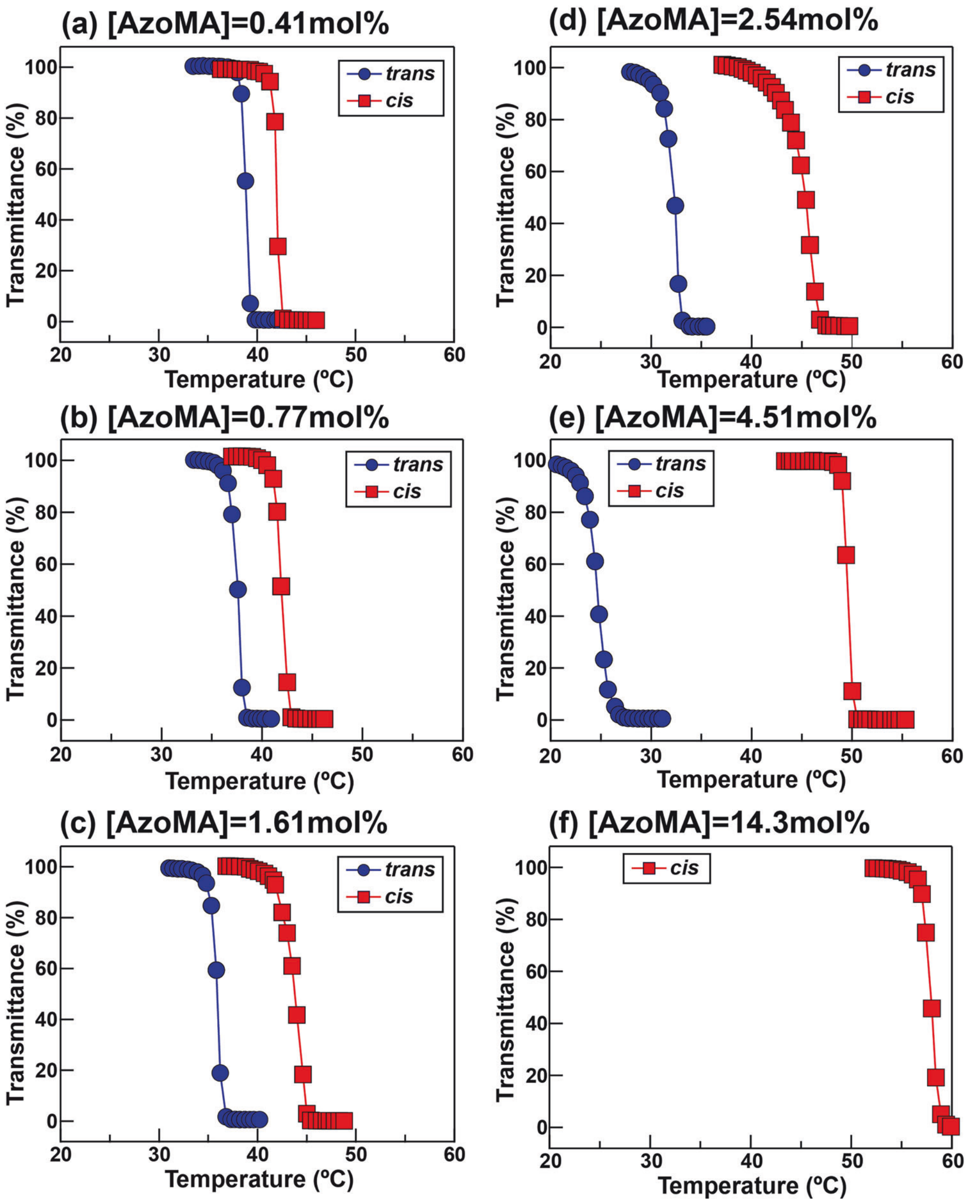

Fig. 2 Temperature-dependent transmittance profiles of P(AzoMA-*r*-PhEtMA) solutions in [C_2mim][TFSI] showing light-tunable LCST-type phase separation. Panels **a**–**f** correspond to copolymers with AzoMA contents of 0.41, 0.77, 1.61, 2.54, 4.51, and 14.3 mol%, respectively. The blue circles and red squares denote the transmittance measured for the *trans*-type (visible light irradiation) and *cis*-type (UV light irradiation) states, respectively. Cloud points were determined from the temperature at 50% transmittance. The polymer concentration = 1 wt%, optical path length = 1 cm, monitoring wavelength = 700 nm, and heating rate = 0.5 °C min^{-1}

results confirm that a sufficiently *cis*-rich state was attained in the present IL medium. Upon UV irradiation, the T_c shifts to higher temperatures (P(*cis*-AzoMA-*r*-PhEtMA)), whereas under visible light, it shifts to lower temperatures (P(*trans*-AzoMA-*r*-PhEtMA)) (Fig. 2, Supplementary Figs. S18–21), demonstrating reversible optical control of the solubility of the IL. This shift direction is consistent with polarity matching. Solvatochromic polarity scales generally place [C_2mim][TFSI] in a moderately high-polarity regime, comparable to that of highly polar organic solvents [35]. In fact, the $E_T(30)$ of [C_2mim][TFSI] is 52.6 kcal/mol [36], indicating that the polarity of the IL is comparable to that of typical polar molecular solvents such as dimethyl sulfoxide (DMSO) (45.1 kcal/mol) and ethanol (51.9 kcal/mol [37]). We therefore interpret the different phase behaviors of the *trans*- and *cis*-rich states not simply in terms of polarity alone but more broadly in terms of differences in solvation compatibility in the IL medium. Moreover, the dipole moment of azobenzene substantially increases upon *trans*-to-*cis* isomerization (from ~0.5 D to ~3.1 D) [38], rendering the *cis*-type polymer more compatible with this solvation environment. A possible molecular origin of this behavior is a change in the local solvation environment in the IL. Previous studies on aromatic methacrylate derivatives in imidazolium-based ILs have suggested preferential cation–π interactions between the imidazolium cation and aromatic side groups, leading to a characteristic solvation structure [39, 40]. By analogy,

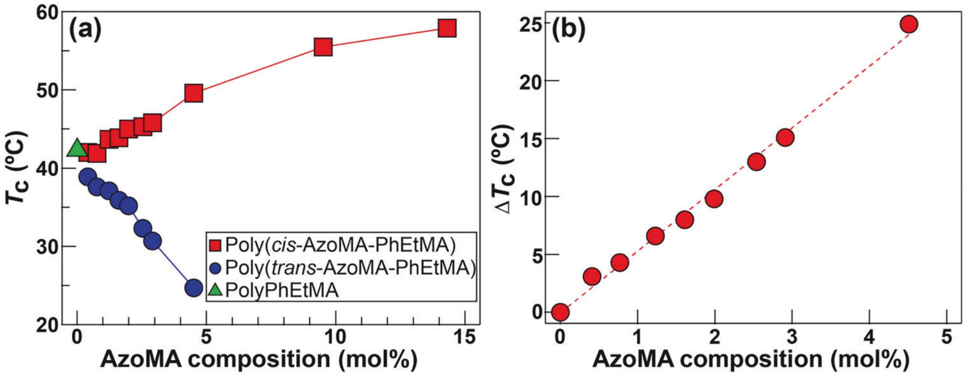

Fig. 3 Composition dependence of the T_cs and bistable temperature window for P(AzoMA-*r*-PhEtMA) in [C_2mim][TFSI]. **a** T_c for *trans*- (blue circles; visible light irradiation) and *cis*- (red square; UV irradiation) states as a function of AzoMA composition. The green triangle denotes the corresponding values for the PPhEtMA homopolymer ([AzoMA] = 0 mol%). **b** Bistable temperature window, $\Delta T_c = T_c$-*cis* – T_c-*trans*, plotted against AzoMA composition, showing monotonic expansion with respect to the azobenzene fraction

similar preferential solvation is plausible for the PhEtMA units in [C_2mim][TFSI]. Photoisomerization of the azobenzene unit is therefore expected to perturb the balance of these polymer–IL interactions and alter the relative stability of the dissolved state, resulting in different phase-transition temperatures for the *trans*-rich and *cis*-rich states. At the highest azobenzene loading examined (P(AzoMA-*r*-PhEtMA) [AzoMA] = 14.3 mol%, Fig. 2f), the *trans*-type polymer becomes sufficiently solvatophobic such that T_c-*trans* shifts below the lower limit of our measurement window**;** thus, only T_c-*cis* (≈56 °C) could be observed within the accessible temperature range.

This composition-dependent divergence of T_c-*trans* and T_c-*cis* is quantified in Fig. 3, which shows that the resulting bistable temperature window, ΔT_c (= T_c-*cis* – T_c-*trans*), can be continuously expanded by increasing the AzoMA fraction. Over the investigated range ([AzoMA] = 0.41 ~ 14.3 mol%), T_c-*trans* decreases monotonically, whereas T_c-*cis* increases monotonically, leading to a systematic widening of ΔT_c up to 24.9 °C at [AzoMA] = 4.51 mol% within the present temperature range. This monotonic widening is particularly notable because in many aqueous azobenzene-polymer systems, the observable T_c separation is confined to a narrow composition window and can become non-monotonic at higher chromophore loadings, reflecting a competitive hydrophilic–hydrophobic balance and limited isomerization contrast under experimental conditions. In the present IL system, by contrast, T_c-*trans* and T_c-*cis* remain well separated and continuously tunable within the studied range, allowing ΔT_c to be treated as a genuine design variable. To assess whether this bistable window is sensitive to polymer loading, we further examined the concentration dependence of T_c for P(AzoMA-*r*-PhEtMA) with [AzoMA] = 0.77, 2.91, and 4.51 mol% (Supplementary Fig. S23). Within the concentration range examined, the T_c-*cis* decreased slightly with increasing polymer concentration for all three copolymers. This trend is consistent with the general behavior of LCST-type phase transitions, in which increasing the polymer volume fraction shifts the phase boundary to lower temperatures [41]. Notably, the two T_cs shift in a largely parallel manner over the investigated range, so ΔT_c remains nearly constant. This concentration-insensitive ΔT_c indicates that the *cis*-/*trans*-solvation contrast is preserved and that the photoprogrammable temperature window is robust against moderate variations in the polymer concentration.

This behavior can be rationalized within the practical constraint framework highlighted in the introduction: the macroscopic T_c shift reflects not only the intrinsic *cis*-/*trans*-solvation contrast but also (i) the attainable *cis* fraction at the photo stationary state, (ii) the timescale of thermal back-isomerization relative to the measurement, and (iii) optical attenuation/penetration that can introduce spatial gradients in isomer composition. In aqueous media, early demonstrations already emphasized that the effective *cis* fraction can be substantially less than unity even under UV irradiation [29] and that thermal relaxation at elevated temperatures can lead to the underestimation of T_c-*cis*. A similar limitation becomes even more consequential in high-temperature LCST platforms employing strongly absorbing chromophores, where optical attenuation and penetration effects can produce a *cis*-rich region only near the illuminated surface, whereas the bulk relaxes toward the *trans*-type, resulting in a reduced apparent T_c-*cis*-/*trans*- and, in extreme cases, a near collapse of the difference [20, 23]. The present "low-baseline LCST" platform mitigates these constraints by operating in an ambient-to-physiological temperature window: the lower transition maintains a meaningful *cis*-enriched population throughout the sample. In this regime, the intrinsic polarity contrast of azobenzene is more faithfully translated into opposite shifts in T_c, thus yielding a robust, composition-amplified ΔT_c under standard optical conditions.

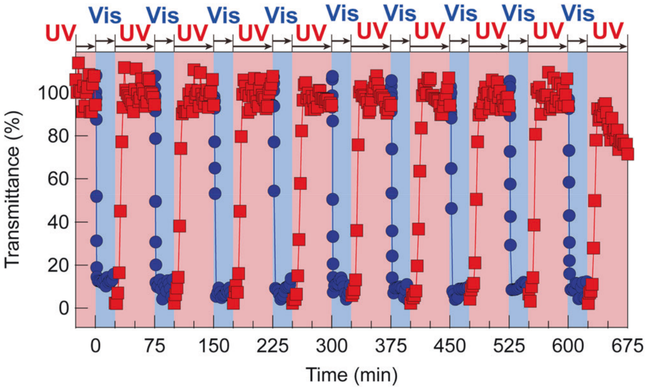

Fig. 4 Reversible, light-triggered solubility switching of P(AzoMA2.91-*r*-PhEtMA) in [C_2mim][TFSI] at 37 °C. The transmittance at 700 nm was monitored over time while the solution was alternately irradiated with UV light and visible light. Red squares and blue circles denote the transmittance values during UV and visible irradiation, respectively. Reversible transmittance switching is maintained over nine cycles spanning ~675 min

Beyond these measurement-level constraints, the magnitude of ΔT_c is expected to depend on whether azobenzene units can effectively participate in the solvent environment rather than be sequestered into strongly aggregated microdomains. Zhao and coworkers demonstrated in mixed-solvent aqueous systems (water/dioxane) that a large photoinduced T_c shift emerges only when the local solvation environment allows azobenzene units to remain sufficiently solvated and responsive, as evidenced by NMR analyses of segment mobility and domain partitioning [6]. Importantly, in our case, the photoswitch unit itself appears highly compatible with the IL medium: the AzoMA monomer is readily soluble in [C_2mim][TFSI] at room temperature (Supplementary Fig. S23), suggesting that azobenzene units remain accessible to solvation in this environment. This differs from the azobenzene acrylamide/acrylate derivatives often used in aqueous LCST systems [25, 26, 28, 42–45], which can exhibit very limited water solubility and may therefore be prone to reduced solvation access. While differences in the *cis*-/*trans*-solubility of the monomer could not be directly quantified because of strong optical absorption at high concentrations, the high baseline solubility of AzoMA in the IL provides a plausible molecular basis for the large ΔT_c achieved here even at low chromophore contents. Consistently, the relatively large ΔT_c observed here, even at low AzoMA contents, is consistent with the efficient solvation of AzoMA units in the IL environment, enabling the *cis*-/*trans*-polarity change to directly modulate the effective polymer–solvent interaction. Sequence-level arrangement can, in principle, further modulate this response: end-group azobenzene designs often display near-additive, composition-proportional shifts because chromophore proximity and cooperative aggregation are minimized [2, 46], whereas side chain azobenzene copolymers can exhibit stronger nonlinearity when chromophore adjacency becomes significant. In our earlier IL upper critical solution temperature (UCST) system [47], we proposed that increased azobenzene adjacency associated with somewhat blocky sequence statistics could promote cooperative chromophore interactions and amplify the transition temperature. In the present P(AzoMA-*r*-PhEtMA) series, sequence distribution analysis indicated a random arrangement within the studied composition range ($r_1 = 1.27$, $r_2 = 2.36$ as [M_1] = PhEtMA, [M_2] = AzoMA; Supplementary Fig. S12), suggesting that strong cooperative chromophore clustering is not required to account for the systematic widening of ΔT_c. Taken together, these considerations support the view that the low-baseline LCST design, combined within an IL solvation environment that effectively “activates” the azobenzene polarity contrast, provides large and tunable bistable temperature windows.

The reversible, light-triggered solubility switching of P(AzoMA-*r*-PhEtMA) [AzoMA] = 2.91 mol% in [C_2mim][TFSI] at a fixed, physiologically relevant temperature (37 °C) is shown in Fig. 4, taking advantage of the bistable window between T_c-*trans* = 30.7 °C and T_c-*cis* = 45.8 °C. The solution was first converted to a homogeneous, transparent, *cis*-type polymer by UV irradiation at 37 °C. Subsequent visible-light irradiation rapidly decreased the transmittance and drove complete phase separation within ~100 s, indicating that the *trans*-type polymer renders the polymer less compatible with the IL solvation environment at this temperature. The transmittance switching is reproducible over 9 cycles spanning ~40,500 s without noticeable loss of contrast, supporting stable operation in a nonvolatile IL medium where concentration drift is negligible. When the turbid, phase-separated sample was irradiated with UV light again, the transmittance recovery was markedly slower: after an induction period of ~300 s, the solution gradually clarified and returned to transparency over ~300 s. This kinetic asymmetry is readily rationalized by optical attenuation in the turbid state, as the polymer-rich domains scatter incident UV light more strongly than the transparent state does, reducing the effective photon flux available for *trans*-to-*cis* conversion in the bulk and thus slowing redissolution. In contrast, the *cis*-to-*trans* switching initiated from a transparent solution proceeds efficiently because light penetration is high and isomerization can occur more uniformly throughout the sample. Importantly, these data provide a direct "operation mode" demonstration: a nonvolatile IL solution can be switched reversibly between one-phase and two-phase states by light alone at constant temperature. The switching timescales are expected to be further tuned through optical intensity, wavelength, and loaded AzoMA, offering a practical route to programmable, ambient-to-physiological photocontrolled phase behavior in IL media. Taken together, the present results suggest a simple design rule for realizing large, reliable photo induced T_c shifts in nonvolatile ILs: (i) choose a host polymer with a sufficiently low baseline LCST to suppress the impact of thermal back-isomerization on the measurement/operation timescale, (ii) ensure that the photoswitch unit is well solvated (or at least not strongly segregated) in the target solvent environment so that *cis*-/*trans*-polarity changes translate into a bulk interaction change, and (iii) operate within an optical regime where irradiation can access the bulk (especially for strongly absorbing chromophores).

In conclusion, we established a practical design framework for robust phototunable LCST phase separation in a nonvolatile IL medium by combining a low-baseline thermoresponsive platform with strong photo switch–solvent compatibility. Using a systematic composition series of P(AzoMA-*r*-PhEtMA) in [C_2mim][TFSI], we achieved a continuous expansion of the ΔT_c and demonstrated reversible, repeatable switching between one-phase and two-phase states at 37 °C over extended operation times. Beyond simply lowering the LCST, our results highlight that large and quantifiable photo-induced shifts require that azobenzene units remain solvation accessible so that the change in the *cis*-/*trans*-polarity can be efficiently translated into a change in macroscopic solubility. Together with optical penetration considerations, these findings identify actionable design levers, baseline transition temperature, photo switch solvation accessibility, and irradiation/geometry conditions that govern both the magnitude and kinetics of switching. Notably, reversible photoswitching is achieved at 37 °C because this temperature is directly relevant to physiological and cell culture conditions [17, 48, 49]. This feature makes the present polymer-IL system a potentially useful platform for future photoresponsive soft materials that operate in biologically relevant environments. We also anticipate that this framework will enable programmable, nonvolatile soft materials in IL media, including photo-addressable ion-gel platforms and dynamic phase-separated systems for responsive transport and actuation.

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Compliance with ethical standards

Conflict of interest The author declares no competing interests.

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