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## Viscoelastic change of block copolymer ion gels in a photo-switchable azobenzene ionic liquid triggered by light

Caihong Wang, Kei Hashimoto, Ryota Tamate, Hisashi Kokubo, Ken Morishima, Xiang Li, Mitsuhiro Shibayama, Fengniu Lu, Takashi Nakanishi and Masayoshi Watanabe*

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## COMMUNICATION

# Viscoelastic change of block copolymer ion gels in a photo-switchable azobenzene ionic liquid triggered by light†

Caihong Wang,‡[ab] Kei Hashimoto,‡[b] Ryota Tamate, [ID][b] Hisashi Kokubo,[b] Ken Morishima,[c] Xiang Li, [ID][d] Mitsuhiro Shibayama, [ID][d] Fengniu Lu, [ID][e] Takashi Nakanishi [ID][e] and Masayoshi Watanabe [ID]*[b]

A photo-switchable ionic liquid solvent bearing an azobenzene moiety induced a viscoelastic change of block copolymer ion gels by light. ABA triblock copolymers having poly(phenethyl methacrylate) and poly(benzyl methacrylate) as A blocks exhibited opposite photoinduced rheological responses although they had only a tiny structural difference in the alkyl chain length.

Ion gels formed by polymeric networks containing ionic liquids (ILs) have received growing interest for their solid-like mechanical properties while retaining the intrinsic properties of ILs. Key attributes of these ion gels include thermal stability, negligible volatility, high ionic conductivity, a tunable modulus, and processability, which can be widely applied in electrochemical devices, separation membranes, and so forth.[1–3] Among the various formation methods of ion gels, the self-assembly of ABA triblock copolymers in ILs has been proven to be particularly versatile with reversible cross-linking points and tunable mechanical strength.[4–6] Incorporating a thermoresponsive segment showing an upper or lower critical solution temperature (UCST or LCST, respectively) into A endblocks could result in a thermoresponsive sol–gel transition, ascribed to the dissociation and association of cross-linking points in the ILs in response to temperature. By selecting appropriate polymer compositions and ILs, the sol–gel transition temperatures can be tailored. We previously reported that

poly(phenethyl methacrylate)-b-poly(methyl methacrylate)-b-poly(phenethyl methacrylate) (PPhEtMA-b-PMMA-b-PPhEtMA, denoted as PMP) underwent sol–gel transitions with tunable gelation temperatures ranging from 20 °C to 140 °C by mixing [C$_2$mim][NTf$_2$] and [C$_4$mim][NTf$_2$] ([C$_2$mim]: 1-ethyl-3-methylimidazolium; [C$_4$mim]: 1-butyl-3-methylimidazolium; [NTf$_2$]: bis(trifluoromethanesulfonyl)amide) in different ratios.[7] Importantly, these noncovalent network structures can be reversibly processed from liquids, then solidified in situ using temperature control, enabling rapid and cost-efficient processing methods such as aerosol jet printing and transfer printing.[8] Nevertheless, a limited spatial resolution and operating temperature are noticeable disadvantages of thermoresponsive systems.

Azobenzene, a well-known photochromic molecule, could have significant potential as a reversible processing trigger that makes materials soft or hard in a contactless manner by light irradiation at a selected intensity and wavelength, if the glass transition temperatures ($T_g$s) of the materials are substantially changed by photochromism.[9,10] In a previous study, we demonstrated the light-switchable sol–gel transitions of thermoresponsive PMP triblock copolymers in ILs at constant temperature by using a small amount of azobenzene functionalized ionic liquid (Azo-IL) as a molecular trigger.[11] Meanwhile, in Azo-IL systems, we found that a tiny structural change of the polymers could induce drastic changes in photoresponsive phase transition behaviors.[12] By changing the number of methylene spacers between the ester and aromatic ring from 2 (poly(phenethyl methacrylate), PPhEtMA) to 1 (poly(benzyl methacrylate), PBnMA), the opposite photoresponsive phase separation behaviors were obtained: the LCST of PBnMA in ILs containing the cis Azo-IL was higher than that containing the trans Azo-IL, whereas PPhEtMA showed the opposite trend. In this study, we prepared two ABA triblock copolymers with PBnMA and PPhEtMA as A blocks, i.e., PBnMA-b-PMMA-b-PBnMA (BMB) and PPhEtMA-b-PMMA-b-PPhEtMA (PMP) to investigate their opposite viscoelastic transitions switched by

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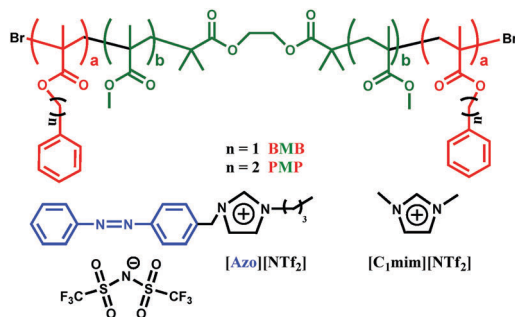
Fig. 1 Chemical structures of triblock copolymers and ILs.

a molecular trigger. Those unique photoresponsive behaviors presented here originate from the photoisomerization reaction of a small amount of an azobenzene containing ionic liquid, different from reported photoresponsive polymer systems.[13,14]

Well-defined BMB and PMP triblock copolymers with similar molecular weights were synthesized by atom transfer radical polymerization based on a PMMA macroinitiator.[12] The detailed procedure and characterization results are summarized in the ESI† (Table S1 and Fig. S1, S2). Azobenzene functionalized IL, 1-butyl-3-(4-phenylazobenzyl)imidazolium bis(trifluoromethanesulfonyl)amide ([Azo][NTf$_2$]), was synthesized according to a previously reported procedure.[12] The structures of the synthesized polymers and ILs are shown in Fig. 1. In this study, a mixture of [Azo][NTf$_2$] and [C$_1$mim][NTf$_2$] ([C$_1$mim]: 1,3-dimethylimidazolium) was used as the solvent IL ([Azo][NTf$_2$]: [C$_1$mim][NTf$_2$] = 5 : 95 wt/wt). The quick isomerization response of [Azo][NTf$_2$] to UV light within 1 min was confirmed in our previous study.[12] After isomerization, the ratio of the cis Azo-IL in mixed ILs was 40% at 25 °C and the value was constant even at 65 °C (Fig. S3, ESI†), indicating slow kinetics of thermal relaxation. All rheological and SAXS experiments were conducted at temperatures below 140 °C, where the thermal stability of ion gels was maintained (Fig. S4, ESI†). All SAXS measurements were conducted in the dark due to the hermetic experimental setup.

Dynamic temperature sweeps demonstrate the thermoresponsive gelation of BMB and PMP ion gels upon heating processes in the dark and under UV (Fig. 2). When the polymer concentration (20 wt%) is higher than the chain overlap concentration at temperatures above the LCST, the PBnMA or

PPhEtMA chains aggregate to form micellar cores and the outer PMMA chains connect those cores together as a bridge, producing a three-dimensional polymer network. At 80 °C, the BMB triblock copolymer solution behaved as a viscoelastic fluid (i.e., $G' < G''$). After heating, $G'$ and $G''$ sharply increased, which is attributed to the LCST phase transition behavior of the PBnMA endblock, leading to ion gel formation ($G' > G''$). The temperature at which $G'$ and $G''$ intersected is defined as the sol–gel transition temperature ($T_{gel}$). For the BMB solution, $T_{gel}$ was 88 °C in the dark, denoted as trans-$T_{gel}$ and 97 °C under UV, denoted as cis-$T_{gel}$ (Fig. 2(a)). The PMP solution shows relatively lower gelation temperatures, trans-$T_{gel}$ at 61 °C and cis-$T_{gel}$ 56 °C (Fig. 2(b)). As shown in strain sweep measurements (Fig. S5, ESI†), the PMP ion gel above $T_{gel}$ (in the dark) exhibited clear critical strain at approximately 20% strain, which is indicative of the existence of a percolated network. The gaps between $T_{gel}$s in the dark and under UV are ascribed to their different phase transition temperatures under UV and in the dark. Remarkably, cis-$T_{gel}$ was higher than trans-$T_{gel}$ for the BMB, whereas the opposite behavior was confirmed for the PMP, that cis-$T_{gel}$ was lower than trans-$T_{gel}$. Consequently, a bistable temperature region emerged where the material states, i.e., whether in a sol state or in a gel state, depend on the presence or absence of light irradiation.

Photoinduced reversible rheological changes of the BMB and PMP triblock copolymer solutions can be achieved by exploiting the photoisomerization of [Azo][NTf$_2$] as a molecular trigger, as shown in Fig. 3(a) and (b). A sharp decrease of $G'$ was observed for the BMB solution after switching from visible to UV light irradiation. Although softening of the ion gel was confirmed, under UV light the BMB solution maintained its gel state rather than sol state. Even when the irradiation time was prolonged for 8 h, no change in either $G'$ or $G''$ values occurred, indicating a stable soft gel state. This could be explained by the fact that the higher incompatibility of PBnMA with the ILs might contribute to the higher energy barrier for the complete disassembly of the micelle core in the BMB ion gel. We performed dynamic frequency sweep measurements for the BMB solution in the dark (Fig. S6, ESI†). At 140 °C, a plateau region without frequency dependence of $G'$ was clearly observed, which is indicative of the frozen physical cross-linking point. Meanwhile, dynamic frequency sweep
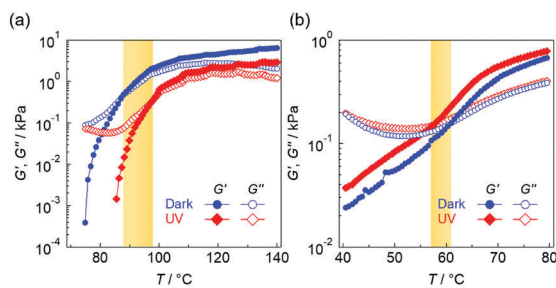


Fig. 2 Dynamic temperature sweeps for 20 wt% BMB (a) and PMP (b)/IL solutions in the dark and under UV light irradiation.
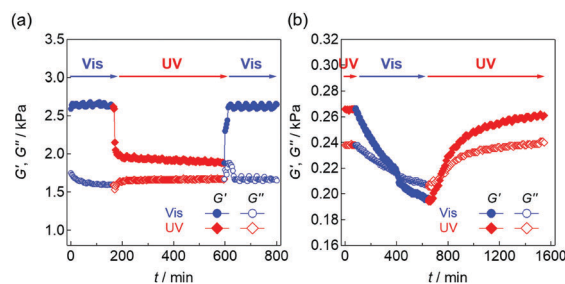


Fig. 3 Photoreversible gelation behaviors for 20 wt% BMB solution at 95 °C (a) and 20 wt% PMP solution at 58 °C (b) under cyclic switching of UV and visible light sources.

measurements for the PMP solution in the dark showed clear dependence on frequency even at much higher temperatures than $T_{gel}$ (Fig. S7, ESI†), indicating that the PMP ion gel has more "dynamic" cores than the BMB ion gel.[15] Thus, contrary to the BMB solution, the PMP ion gel underwent a gel-to-sol transition under visible light irradiation. However, changes in the $G'$ and $G''$ values of the PMP solution were slower than those of the BMB solution. The lower experimental temperature for the PMP solution is likely to result in slower kinetics of the transition. These results demonstrate that, by combining structurally different triblock copolymers and a small amount of Azo-IL as a molecular trigger, versatile photoresponsive ion gels with significantly different rheological transitions can be obtained.

Fig. 4(a) shows the SAXS profiles for the thermoresponsive gelation process of 20 wt% PMP solution in the dark. The measurements were performed in BL-10C, Photon Factory, Japan. In the temperature range of 25–33 °C, no significant peak was observed, and the scattering intensity was practically unchanged with increasing temperature, indicating that the solvent acts as a good solvent for the polymer. At 34 °C, the intensity suddenly increased. This change in intensity is likely attributable to the microphase separation induced by the solubility change of PPhEtMA endblocks. At temperatures higher than 34 °C, the first and second peaks were clearly observed at approximately 0.1 and 0.3 $nm^{-1}$, respectively



(Fig. 4(b)). Thus, these peaks can be ascribed to the microdomains of PPhEtMA blocks. According to rheological measurements (*vide supra*), the $G'$ value for 20 wt% PMP solution in the dark increased from 35 °C, which is in good agreement with the structural transition behavior. To discuss the microphase separation structures in detail, we fitted the profiles at 60, 70, and 80 °C using the Percus–Yevick hard sphere model (solid lines in Fig. 4(b))[16–18] In the model, the structure factor assumes a hard sphere with a hypothetical radius ($R_{HS}$), which only counts the excluded volume interaction potential. That is, the direct correlation function, $c(r)$, where $r$ is the inter-particle distance, is 0 at $r > 2R_{HS}$ and $c(r)$ is defined as a function of the number density of the hard sphere ($N_{HS}$) and $r/R_{HS}$ at $r \leq 2R_{HS}$. Thus, the structure factor, $S(q)$, can be defined as a function of $q$, $R_{HS}$, and $N_{HS}$. In this system, $R_{HS}$ can be regarded as a hypothetical radius of the effective excluded volume of the particle, including the hard sphere core and soft corona. Meanwhile, the form factor, $P(q)$, is a function of the radius of the spherical core ($R_c$). In addition, we assumed the Gaussian distribution in the $R_c$ and estimated its mean ($\langle R_c \rangle$) and standard deviation ($\sigma_R$). Details of the fitting function are described in the ESI.† The fitting parameters are summarized in Table 1. The fitting curves reproduced the profiles well for all three temperatures (Fig. 4(b)), indicating very similar microphase structures to those previously reported;[18] *i.e.*, thermoresponsive PPhEtMA blocks aggregated over the LCST to form spherical cores, and the cores containing PMMA chains as corona were randomly packed. In Table 1, $\langle R_c \rangle$ increased while the relative standard deviation ($\sigma_R/\langle R_c \rangle$) decreased with elevating temperature. This indicates that phase separation proceeded during the heating process, resulting in the formation of more monodispersed cores with a larger radius. In contrast, $R_{HS}$ slightly decreased while $N_{HS}$ largely increased with increasing temperature, indicating the formation of additional micellar structures due to continuous thermoresponsive self-assembly. That is to say, the increase in the number of micelle cores is driven by the increase in solvophobicity of the PPhEtMA block at elevated temperatures, resulting in the more densely packed hypothetical hard spheres in the PMP ion gel. Thus, the increase in $G'$ values in the rheological measurement (Fig. 3(b)) can be ascribed to the increase of spherical cross-linking points with increasing temperature.

Fig. 4(c) shows SAXS profiles for 20 wt% BMB solution in the dark. The measurements were performed using SAXSess mc²
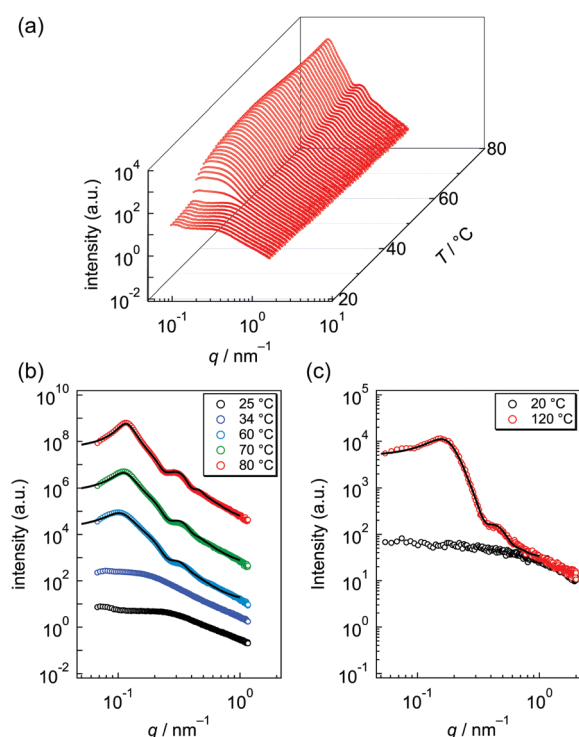
**Fig. 4** (a) Temperature variation of SAXS profiles for 20 wt% PMP solution in the dark from 25 to 80 °C, (b) profiles for 20 wt% PMP at 25, 34, 60, 70, and 80 °C in the dark, and (c) SAXS profiles for 20 wt% BMB at 20 and 120 °C in the dark. The solid lines correspond to the fitting lines based on the Percus–Yevick hard sphere model.

**Table 1** Fitting parameters for 20 wt% PMP solution at 60, 70, and 80 °C and 20 wt% BMB solution at 120 °C

| Polymer temperature | PMP 60 °C | PMP 70 °C | PMP 80 °C | BMB 120 °C |
|---|---|---|---|---|
| $\langle R_c \rangle^a$ [nm] | 16.6 | 16.9 | 18.3 | 11.8 |
| $\sigma_R/\langle R_c \rangle^a$ | 0.18 | 0.16 | 0.13 | 0.15 |
| $R_{HS}{}^a$ [nm] | 28.6 | 27.4 | 27.4 | 16.7 |
| $N_{HS}$ [$\times 10^{15}$ $cm^{-1}$]$^a$ | 2.7 | 3.7 | 4.4 | 11.0 |
| $N_{agg}{}^b$ | 376 | 396 | 503 | 113 |

$^a$ Obtained by the fitting results for SAXS profiles. $^b$ Calculated from $N_{agg} = (4\pi/3)\langle R_c \rangle^3/V_P$, where $V_P$ is the molecular volume of A segment per block.

(Anton Paar). There was no peak at 20 °C while the first and second peaks were observed at 120 °C, which is analogous behavior to the PMP system. The fitting parameters for the data at 120 °C are listed in Table 1. $N_{HS}$ is higher than PMP, implying more crosslinking points, which explains the one order higher values of $G'$ for BMB than for PMP (Fig. 2). On the other hand, $\langle R_c \rangle$, $\sigma_R/\langle R_c \rangle$, and $R_{HS}$ values were significantly smaller than those in the PMP system. This indicates that the BMB forms smaller micelle structures than PMP, although the molecular weight (Table S1, ESI†) and volume fraction (Table S2, ESI†) of the BnMA blocks ($f_B = 0.163$) were almost the same as those of the PhEtMA blocks ($f_P = 0.167$). The size of the micellar core can be approximately estimated from the end-to-end distance of the A endblock, $R_0$. If we assume globular polymer chains ($R_0 = bN^{1/3}$, where $N$ is the degree of polymerization and $b$ is a Kuhn monomer length of 1.8 nm [the literature value for polystyrene][19]), $R_0$ was estimated as approximately 10 nm. We found that the $\langle R_c \rangle$ for PMP ($\sim$18 nm) was significantly larger than this value. This result implies that the A endblock is not in the globular state, that is, swollen by the solvent. Therefore, the large $\langle R_c \rangle$ and $N_{agg}$ (aggregation numbers of the polymer in a core) can be ascribed to the swollen cores containing both solvent and polymer, and it should be noted that these parameters are apparent values. $\langle R_c \rangle$ for the BMB (= 11.76 nm) was of the same magnitude as $R_0$ (= 10 nm), implying that the amount of IL in the cores was minimal. $N_{agg}$ was estimated to be 133, which was notably smaller than that of the PMP system. Lodge et al.[20] reported that a block copolymer containing poly(ethylene-alt-propylene) (3 kDa), which forms a rigid core in IL, self-assembles into micelles with $N_{agg} = 95$, as estimated by SAXS. We cannot directly compare this value with our system due to the difference in chain length; however, the lower $N_{agg}$ value implies a more rigid core for the PMP system than for the BMB system. That is, the amount of solvent in the core is less than that in the PMP system, resulting in harder cores. In this study, the photo-responsive moiety was attached to the solvent IL; thus, it is plausible that the rigidity of the cores limits the effect of the solubility change induced by photo-isomerization. This might be one reason why the sol–gel transition was not observed in the BMB system.

Based on the photoisomerization of the azobenzene molecular trigger in the IL solvent, the rheological properties of thermoresponsive ion gels can be tuned using light, and opposite photoresponsive changes of the storage modulus were obtained by slightly modifying the polymer structures. The gelation processes were evaluated using rheological and SAXS measurements. UV light made the BMB gel softer and the PMP system harder with the sol-to-gel transition, which is ascribed to their different photoresponsive phase transition behaviors. The fitting result of the SAXS profiles indicates that the amount of ILs in the cores of the BMB systems was substantially lower than that of the PMP systems. The absence of photoresponsive gel-to-sol transitions in the BMB system can be ascribed to the less swollen cores. This is the first study to demonstrate that UV light can either harden or soften ion gels that contain the same photoresponsive IL mixture.

## Conflicts of interest

There are no conflicts to declare.

## References

1 P. C. Marr and A. C. Marr, *Green Chem.*, 2016, **18**, 105–128.
2 J. Pu, Y. Yomogida, K. K. Liu, L. J. Li, Y. Iwasa and T. Takenobu, *Nano Lett.*, 2012, **12**, 4013–4017.
3 F. Moghadam, E. Kamio, A. Yoshizumi and H. Matsuyama, *Chem. Commun.*, 2015, **51**, 13658.
4 R. Tamate, K. Hashimoto, T. Ueki and M. Watanabe, *Phys. Chem. Chem. Phys.*, 2018, **20**, 25123–25139.
5 T. P. Lodge, *Science*, 2008, **321**, 50–51.
6 T. P. Lodge and T. Ueki, *Acc. Chem. Res.*, 2016, **19**, 2107–2114.
7 Y. Kitazawa, T. Ueki, S. Imaizumi, T. P. Lodge and M. Watanabe, *Chem. Lett.*, 2014, **43**, 204–206.
8 K. H. Lee, M. S. Kang, S. Zhang, Y. Gu, T. P. Lodge and C. D. Frisbie, *Adv. Mater.*, 2012, **24**, 4457–4462.
9 H. Akiyama and M. Yoshida, *Adv. Mater.*, 2012, **24**, 2353–2356.
10 H. Zhou, C. Xue, P. Weis, Y. Suzuki, S. Huang, K. Koynov, G. K. Auernhammer, R. Berger, H. J. Butt and S. Wu, *Nat. Chem.*, 2017, **9**, 145–151.
11 C. Wang, K. Hashimoto, R. Tamate, H. Kokubo and M. Watanabe, *Angew. Chem., Int. Ed. Engl.*, 2018, **57**, 227–230.
12 C. Wang, X. Ma, Y. Kitazawa, Y. Kobayashi, S. Zhang, H. Kokubo and M. Watanabe, *Macromol. Rapid Commun.*, 2016, **37**, 1960–1965.
13 T. Ueki, R. Usui, Y. Kitazawa, T. P. Lodge and M. Watanabe, *Macromolecules*, 2015, **48**, 5928–5933.
14 R. Tamate, R. Usui, K. Hashimoto, Y. Kitazawa, H. Kokubo and M. Watanabe, *Soft Matter*, 2018, **14**, 9088–9095.
15 C. Tsitsilianis, G. Serras, C.-H. Ko, F. Jung, C. M. Papadakis, M. Rikkou-Kalourkoti, C. S. Patrickios, R. Schweins and C. Chassenieux, *Macromolecules*, 2018, **51**, 2169–2179.
16 J. K. Percus and G. J. Yevick, *Phys. Rev.*, 1958, **110**, 1–13.
17 D. J. Kinning and E. L. Thomas, *Macromolecules*, 1984, **17**, 1712–1718.
18 Y. Kitazawa, T. Ueki, L. D. McIntosh, S. Tamura, K. Niitsuma, S. Imaizumi, T. P. Lodge and M. Watanabe, *Macromolecules*, 2016, **49**, 1414–1423.
19 M. Rubinstein and R. H. Colby, *Polymer physics*, Oxford University, New-York, 2003.
20 C. C. Hall, C. Zhou, S. P. O. Danielsen and T. P. Lodge, *Macromolecules*, 2016, **49**, 2298–2306.