

Doctoral Thesis

Photoresponsive self-assembly/disassembly of thermoresponsive macromolecules in azobenzene functionalized ionic liquids

(アゾベンゼン含有イオン液体中における高分子
の温度および光応答性自己集合)

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**Photoresponsive self-assembly/disassembly of
thermoreponsive macromolecules in azobenzene
functionalized ionic liquids**

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Abstract

Room temperature ionic liquids (ILs) have been attracting increasing interest from various research fields, due to their infinite combinations of attractive physical properties, with feasibly designable chemical structures. These unique properties, such as high chemical and thermal stability, lower volatility and flammability, and desired ionic conductivity, make ILs valuable for use in emerging technologies. However, to process the ILs for these and other applications, it is essential to create more rigid composites, while retaining the desired attributes. A widely-applied method is to add well-designed ABA triblock copolymers into conventional ILs, producing ion gels or ionogels. Generally, A end blocks are immiscible with the IL, consequently self-assembling into micellar cores, while the well-solvated B midblocks serve as bridges among the micelles, resulting in a percolating network. In particular, thermoresponsive sol-gel transitions, enabled by introducing thermoresponsive polymers as A end blocks, have drawn intense attention as affordable materials of interest in 3D printing, patterning, etc. One unique advantage of the thermoresponsive sol-gel transitions is its ability to process materials from the molecular precursor to the product. Prof. Lodge and his coworkers have reported well-designed ABA triblock copolymers and thermoresponsive poly(N-isopropylacrylamide) (NIPAm) as the A end blocks, with poly(ethylene oxide) as the B midblocks, which form gels at low temperature, while being free-flowing liquids above the gelation temperature (T_{gel}). With a further modification of A end blocks by introducing random copolymers comprised of 4-phenylazophenyl methacrylate and NIPAm, photoinduced sol-gel transitions were obtained due to the photoresponsive self-assembly behavior of A end blocks in certain hydrophobic ILs. The photoresponsive sol-gel transitions enable contactless material processing, controlled by selected wavelengths and intensities. In such research, optimizing the azobenzene content is very important, since azobenzene can easily influence the thermoresponsive temperatures. However, the preparation of the azobenzene-functionalized ABA triblock copolymers with the desired content often involves a laborious process. Moreover, azobenzene located on the side chains can make *cis*-azobenzene isomer unstable because of the steric hindrance effect. These undesirable issues greatly constrain the development of photo/thermoresponsive materials. In order to solve these

issues, we have proposed a simple method of constructing a photo/thermo-responsive system, based on an azobenzene-based ionic liquid, inspired by other stimuli located in the solution, such as pH or ionic strength. To the best of our knowledge, no research has been reported on the study of the photoresponsive self-assembling behaviors of block copolymers in a photoswitchable IL.

In this work, by using an azobenzene containing IL, [Azo][NTf₂] ([Azo] = 1-butyl-3-(4-phenylazobenzyl)imidazolium) as a small molecular trigger, diluted by 1-methyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide ([C₁mim][NTf₂]), poly(benzyl methacrylate) (PBnMA) and poly(2-phenylethyl methacrylate) (PPhEtMA) have been reported to show photoresponsive lower critical solution temperature (LCST) behavior for the first time in an IL mixture. In this IL mixture, the cloud temperature point (T_{cp}) of PBnMA is higher under UV than in the dark. However, the T_{cp} of PPhEtMA under UV is lower than that in the dark, even though only a tiny structural difference in alkyl chain (n=1, 2) exists between the ester and aromatic rings. Through temperature dependent ¹H-NMR, the opposite UV responsive chemical shifts of the acidic proton from [C₁mim]⁺ were obtained, resembling the opposite UV responsive solvation interaction changes. It is assumed that the polarity change, induced by azobenzene isomerization, influences the affinities between polymers and IL mixtures, resulting in opposite chemical shifts for this proton from [C₁mim]⁺ cation towards UV, corresponding to opposite photoresponsive LCST behaviors.

Based on photoresponsive LCST behaviors switched by an azobenzene molecular trigger, two well-designed and prepared ABA triblock copolymers, poly(benzyl methacrylate)-b-poly(methyl methacrylate)-b-poly(benzyl methacrylate) (BMB) and poly(2-phenylethyl methacrylate)-b-poly(methyl methacrylate)-b-poly(2-phenylethyl methacrylate) (PMP), underwent a photo/thermo-responsive polymer architecture change in ionic liquid mixtures. Diluted BMB and PMP polymer solutions showed thermo-responsive micellization behaviors in the azobenzene-containing IL mixture, with different micellization temperatures being obtained in the dark and under UV. This range is defined as bi-stable temperature. Under UV, at the bi-stable temperature, the BMB solution underwent a “*micelle to unimer*” transition, while the PMP solution experienced a “*unimer to*

micelle ” transition. In more concentrated polymer solutions, thermoresponsive sol-gel transitions were observed, while different gelation temperatures were obtained under UV and in the dark. At this bi-stable temperature, the PMP solution underwent a UV-responsive “*sol-to-gel*” transition, while the BMB solution underwent a UV-responsive weaker gelation transition, ascribed to the opposite photoresponsive LCST behaviors.

To the best of our knowledge, it is the first time that a photoresponsive system, using the azobenzene ionic liquid as a molecular trigger to drive the self-assembly of thermoresponsive polymers, has been studied. The photoresponsive sol-gel transitions thus achieved are advantageous for processing the polymer materials in a contactless manner. Moreover, the ionic liquid used as a solvent can be easily removed after the polymer materials have been processed into a product. This unique advantage of making materials soft or hard, based on photoresponsive molecular trigger, has potential for application as a novel industrial method to process polymeric materials using light. More importantly, compared with the conventional ways, by adding plasticizers or heating, which are neither environment-friendly, nor economical, using light as stimuli to process materials offers some unique advantages, such as being more environment-friendly, less toxic, with point-to-point operation.

Therefore, this study provides a novel way to develop photo/thermo-responsive “*unimer-micelle*” and “*sol-gel*” transitions through a photoresponsive IL, rather than azobenzene functionalized polymers. More generally, it may create a new path to make polymeric materials soft or hard based on a molecular switch, instead of a photochromic reaction of azobenzene polymers. In short, an outline for the contents of the doctoral thesis is summarized for each chapter as follows.

Chapter 1

General introduction

Progress and challenge of ionic liquids have been introduced in the light of the previous studies and current trends in the fundamental and application perspectives. Then thermoresponsive polymeric IL composites have been summarized in detail in this chapter. Last part is about discussing current photo/thermo-responsive systems.

Chapter 2

Preparation of azobenzene ionic liquids and their physical properties.

Novel azobenzene ionic liquids with various anions or different linkages between cation and azobenzene have been synthesized. Increasing alkyl length of imidazolium cation or increasing anion size can lower the melting points of azobenzene ILs, producing room temperature ILs. Reversible isomerization of azobenzene ILs were observed and it seemed that ionic interaction is beneficial to stabilize *cis*-azobenzene IL, living over 2 days in the dark without any decreasing. In addition, *cis*-azobenzene with bromide anions shows a UV responsive liquification process observed in polar optical microscope, corresponding to tunable melting points based on isomerization of azobenzene molecules.

Chapter 3

Phase transition behaviors for LCST homopolymers

In this section, photo/thermoreponsive phase transition of LCST homopolymers, PBnMA and its derivatives will be discussed. LCST homopolymers were polymerized by atom transfer radical polymerization (ATRP) or reversible addition-fragmentation chain transfer (RAFT). Turbidity measurements of LCST homopolymers in ILs with various azobenzene concentrations were conducted to determine the cloudy temperatures (T_{cp}). Both homopolymers exhibited different T_{cp} s between in the dark (*trans*-ILs, isomerization of azobenzene ionic liquid dominated by *trans*-azobenzene) and under UV (*cis*-IL, isomerization of azobenzene ionic liquid dominated by *cis*-azobenzene). T_{cp} s of PPhEtMA in *cis*-IL are lower than in *trans*-IL, while the T_{cp} s of PPhEtMA in *cis*-IL are higher than that in *trans*-IL. Meanwhile, cycle photoswitchable LCST behaviors were achieved successfully. By $^1\text{H-NMR}$ experiments, different photoresponsive chemical-shifts of one proton belonging to cation were observed, ascribed to different photoresponses.

Chapter 4

Photo/thermoreponsive micellizations and gelations of the PMP solution

After a better understanding of photoresponsive LCST behaviors, well-designed ABA triblock copolymer has been utilized to inducing a percolating network in ILs. Poly(2-phenylethyl methacrylate)-b-

poly(methyl methacrylate)-b-poly(2-phenylethyl methacrylate) (PMP) was designed and synthesized via well-established ATRP using poly(methyl methacrylate) (PMMA) as a macroinitiator, where the A blocks are LCST segment, PPhEtMA, and B midblock is PMMA, which is totally compatible with ILs. In a diluted solution, the hydrodynamic radius R_h value is below 10 nm, unimer state, in consistent with individual PMP polymer chains with a total molecular weight around 10 kDa at lower temperatures. But R_h s increase significantly in *trans*-IL at 65 °C, suggesting that the PMP triblock copolymer self-assembles into micelles with PPhEtMA cores surrounded. Similar behavior has been observed in *cis*-IL and micellization temperature (55 °C) is lower than 65 °C in *trans*-IL. Between these temperature range, photoinduced micellization occurred owing that aggregating behaviors of the A blocks dependent on photoisomerization of azobenzene IL. At a modest concentration of polymer solutions, the A blocks associate into micellar cross-linkers, and the B blocks provide bridging connections between micelles, forming a polymeric network. Meanwhile, photocontrolled sol-gel transitions in a macroscopic was achieved based on photoisomerization of azobenzene IL at a molecular level. To our best knowledge, it is of interest in polymer science that a molecular trigger can evoke a mechanical change of bulk materials.

Chart 5

Photo/thermoreponsive micellizations and gelations of the BMB solution

Another well-designed ABA triblock copolymer with PBnMA as the A endblocks, also has been utilized to induce photoresponsive unimer-micelle systems. Poly(benzyl methacrylate)-b-poly(methyl methacrylate)-b-poly(benzyl methacrylate)(BMB) was synthesized via well-established ATRP using poly(methyl methacrylate) (PMMA) as a macroinitiator. In a diluted polymer solution, micellization temperature in *cis*-IL is higher than that in *trans*-IL, which is just against with result of PPhEtMA. At this temperature difference, UV responsive micelle to unimer transition occurred due to a higher aggregating temperature in *cis*-IL. As expected, two different sol-gel transition temperatures also have been observed at highly concentrated solutions, whose behavior is just against PMP systems. It is found out that UV response of LCST behavior is dependent on azobenzene isomerization as well as polymer structure, which is different

from previously reported azobenzene-based polymer systems.

Chapter 6

Concluding remarks and future directions

Concluding remarks on each chapter have been made individually based on results and discussion to underpin the prime achievements of the chapter. A future prospect of photo/thermo-responsive systems were provided. Also, the improvement of mechanical property while retaining intrinsic ILs property still requires further study to satisfy the practical applications.