



Light-tunable thermoresponsive behavior of branched polyethylenimine derivatives in water



Yeongbong Mok^a, Minwoo Noh^a, Gyu Chan Kim^a, Youngjun Song^a, Heejin Kim^a, Seulah Kim^a, Sihyeong Yi^a, Ji-Hun Seo^b, Yan Lee^{a,*}

^a Department of Chemistry, College of Natural Sciences, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul, 151-747, Republic of Korea

^b Department of Materials Science and Engineering, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul, 136-701, Republic of Korea

ARTICLE INFO

Article history:

Received 23 August 2016

Received in revised form

1 November 2016

Accepted 8 November 2016

Available online 9 November 2016

Keywords:

Stimuli-responsive polymers

LCST

UCST

Polyethylenimine

Azobenzene

ABSTRACTS

Combinatorial introduction of acyl, alkylsulfonyl and azobenzene (Ab) functionalities into amine-rich branched polyethylenimine produces dual-signal-responsive polymers with both temperature- and light-responsiveness in aqueous solutions. Light-tunable L/UCST polymers were synthesized by simple introduction of acyl and Ab groups or alkylsulfonyl and Ab groups, respectively. The phase transition temperatures of the polymers were dependent upon the ratios of the functionalities and reversibly controlled by light irradiation. More than 35°C-shift of the LCST was obtained by UV-irradiation, which is the largest shift reported in water. Moreover, 19°C-shift of the UCST was obtained by UV-irradiation, which is the first UCST shift reported in polymer–water binary systems.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Stimuli-responsive smart polymers have attracted great interest in various fields including polymer, materials, and biomedical sciences [1–3]. Smart polymers that respond to temperature changes, light irradiation, pH changes, ultrasound, a reductive potential, and so on have been actively studied; furthermore, two or more stimuli-responsive characteristics have been combined for more delicate control of the responsiveness [4–6].

Among such materials, a water-soluble polymer responding to both temperature and light stimuli was first reported three decades ago [7]. In Menzel and co-workers' report, a copolymer based on *N,N*-dimethylacrylamide and 4-phenylazophenyl acrylate showed a shift of the phase transition temperature under UV irradiation [8]. The polymer was miscible with water below the lower critical solution temperature (LCST) phase transition temperature and separated from water above this temperature. UV irradiation elevated the phase transition temperature by 20 °C. Subsequently,

there has been intensive research to develop dual-responsive polymers that combined responsiveness to these two representative physical stimuli, temperature and light [9–15]. However, the LCST shift upon irradiation in later reports was only several degrees Celsius, which is smaller than the 20°C-shift reported by Menzel et al. [8] Dual-responsive polymers with larger LCST shift would be preferred for better understanding of the molecular basis of phase transition as well as practical application of smart materials.

Further, photocontrol of the upper critical solution temperature (UCST) phase transition behavior has also been investigated in the past five years [16–18]. Unlike LCST polymers, UCST polymers show phase separation below a certain temperature. In Watanabe and co-workers' report, a copolymer-based *N*-isopropylacrylamide and 4-phenylazophenyl methacrylate showed a 43°C-shift of the UCST phase transition temperature under UV irradiation in an ionic liquid [16]. Although a few studies have demonstrated a photo-tunable UCST of polymers in alcohol [17] and ethanol–water mixtures [18], this feature has not yet been realized in polymer–water binary systems. Photo-controllable UCST polymers in polymer–water binary systems would be more difficult to be obtained due to the strong water–polymer interactions, but welcomed in various applications such as biosystems.

* Corresponding author.

E-mail address: gacn@snu.ac.kr (Y. Lee).

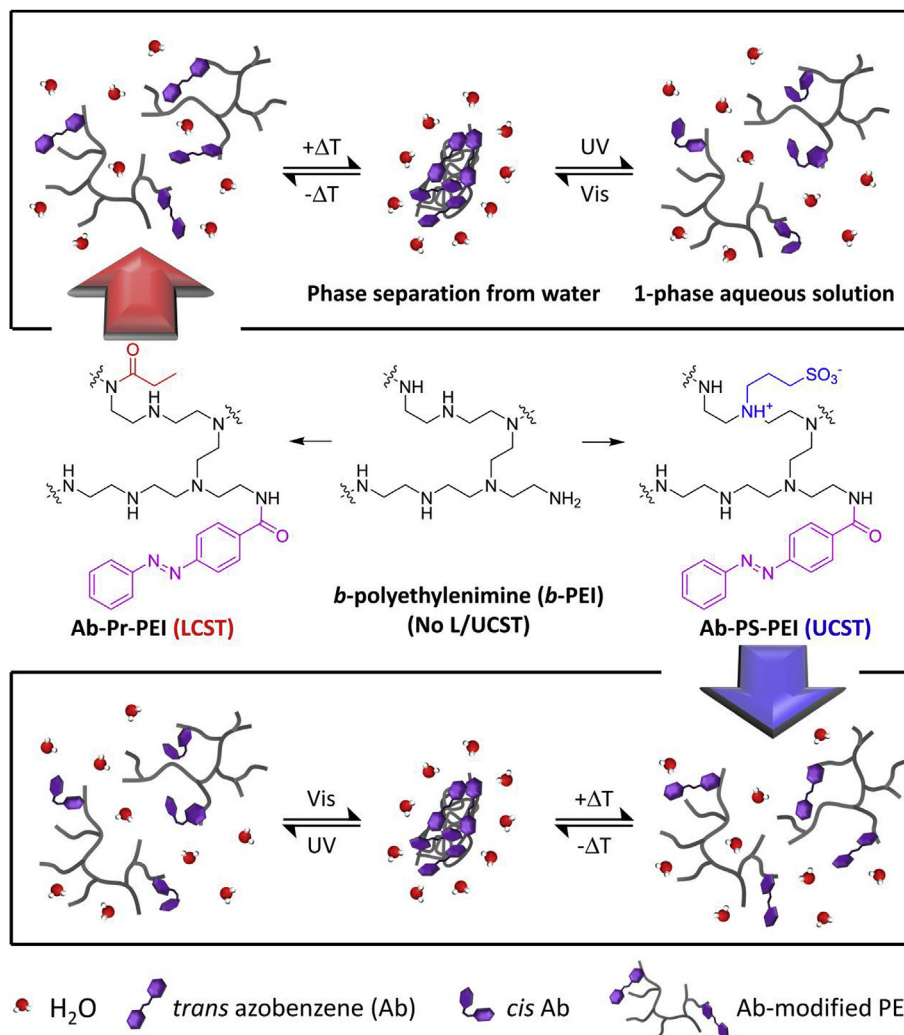


Fig. 1. Chemical structures of *b*-PEI derivatives and schematic illustration of light-tunable L/UCST-type phase transition.

Herein, we report that both the LCST and UCST of branched polyethylenimine (*b*-PEI) derivatives can be reversibly controlled in the polymer–water binary system by UV–vis irradiation (Fig. 1). *b*-PEIs possess many amine residues (one amine residue per two carbon atoms) that are capable of reaction with various electrophiles. In our previous report, acylation of *b*-PEI yielded LCST-type polymers by introducing hydrophobic residues with strong polymer–water interactions [19]. On the other hand, sulfopropylation of *b*-PEI produces UCST-type polymers by increasing the intra- and inter-polymeric electrostatic interaction between zwitterionic residues [20]. The LCST and UCST behavior of aqueous polymeric solutions depends upon a delicate balance of polymer–water interactions and polymer–polymer interactions [21,22]. Therefore, if the hydrophobicity of polymers or polymer–polymer interaction can be tuned by light, the phase transition temperature can also be controlled. Azobenzene (Ab) shows reversible *trans*–*cis* isomerization accompanied by alteration of the dipole moment from 0 Debye for the *trans*-isomer to 3 Debye for the *cis*-isomer [23]. Thus, we expected that Ab moieties could be introduced for the control of both the LCST and UCST by light irradiation. On the basis of our previous results about temperature-responsive *b*-PEI derivatives [19,20], we would carefully introduce Ab moieties along with acyl or alkylsulfonyle moieties to *b*-PEI for generating new polymers responding to both temperature and light.

2. Experimental section

2.1. Materials

Branched polyethylenimine (*b*-PEI, $M_n = 10,000$, PDI = 2.5) and 1,3-propanesultone were purchased from Sigma-Aldrich (US). 4-phenylazobenzoyl chloride and propionyl chloride were purchased from TCI chemicals (Japan). Methanol and triethylamine (TEA) were purchased from Daejung (South Korea). Dichloromethane (DCM) was purchased from Samchun (South Korea). All reagents were used as received unless specified.

2.2. Synthesis of light-tunable LCST polymers

Azobenzene (Ab)-containing propionylated *b*-PEI (Ab-Pr-PEI) was synthesized as below. 1.20 g *b*-PEI (27.9 mmol amine residues) and 4 mL of TEA (28.7 mmol) were dissolved in 30 mL of DCM and then chilled on 0 °C 1 mL of a DCM solution dissolving 307 mg 4-phenylazobenzoyl chloride (1.25 mmol; 0.0600 eq. to reactive amine residues and 0.0450 eq. to total amine residues) and 0.913 mL propionyl chloride (10.5 mmol; 0.375 eq. to total amine residues) was added dropwise to the solution. After 30 min-stirring on ice, the reaction temperature was adjusted to room temperature and the reaction proceeded overnight. After evaporation of most of

Download English Version:

<https://daneshyari.com/en/article/5178782>

Download Persian Version:

<https://daneshyari.com/article/5178782>

[Daneshyari.com](https://daneshyari.com)