

Photochemical reaction in azobenzene-containing rigid poly(amide acid) networks



Daichi Kusano¹, Ryota Ohshima¹, Nobuhiko Hosono^{*}, Kenro Totani, Toshiyuki Watanabe^{**}

Department of Applied Chemistry, Graduate School of Engineering, Tokyo University of Agriculture and Technology, 2-24-16, Naka-cho, Koganei-shi, Tokyo 184-8588, Japan

ARTICLE INFO

Article history:

Received 11 July 2014

Received in revised form

3 September 2014

Accepted 12 September 2014

Available online 22 September 2014

Keywords:

Polymer network

Azobenzene

Photomechanical effect

ABSTRACT

Photochemical reaction of azobenzenes embedded into rigid poly(amide acid) (PAA) networks, which undergo reversible photomechanical response upon alternating irradiation of 405 nm and 532 nm lights, was explored. Azobenzene functionalities are incorporated into the PAA backbone that is end-linked with tri- and tetra-armed crosslinkers, 1,3,5-tris(4-aminophenyl)benzene (TAPB) and tetra(4-aminophenyl)methane (TAPM), respectively, to give photoresponsive polymer networks. It was discovered that the *trans*-to-*cis* photoisomerization rate of azobenzene moiety is highly dependent on the network architecture. Before crosslinking, the photoisomerization rate is considerably low and totally independent on molecular weights of the backbone whereas, after crosslinking, the rate is dramatically enhanced and highly dependent on the molecular weights. A crosslinker effect on the photomechanical response is also disclosed. These results are attributed to an inter-chain aggregation of PAA backbones. The bulky structure and superior connectivity of TAPM make the network structure spatially extended with less defects, which not only prevents the aggregation but also contributes to the nano-to-macroscopic propagation of molecular deformation of azobenzene.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Developments of responsive molecular materials affording nano-to-macroscopic mechanical transduction have attracted scientific and technological attentions for creating energy efficient materials, which offers direct energy conversion from lights to macroscopic work [1–5]. Efficient material design for the photo-mechanical energy conversion has been explored by many groups [6–20]. However, in the most cases the photo-actuation of the materials is based on photoinduced phase transitions [8–11], orientational change induced by photoisomerizations [12–14], and other secondary interactions including supramolecular interactions [15] and osmotic effects [16,17]. Also as can be known from the limited successful examples reported particularly in crystalline

materials [18–20], developing rational design to transduce the molecular motion directly to the macroscopic motion still remains challenging. We recently reported azobenzene-containing polymer gels, which undergo macroscopic reversible deformation in response to blue (420 nm) and visible (>490 nm) light irradiation [21,22]. The *trans*-to-*cis* photoisomerization of azobenzene, which is incorporated into the polymer backbone of the network, is directly translated and amplified to the macroscopic motion of the gel. The polymer network consists of “rigid” aromatic poly(amide acid) backbone crosslinked with a symmetric crosslinker, which effectively propagates tiny structural deformation of azobenzene moieties to macroscopic scale and consequently results in a bending motion of centimeter-long gel cantilever (Fig. 1) [22]. Dynamic light scattering study could elucidate that the photoisomerizations directly contribute to the reversible deformation of the network structure [22]. However, the operation mechanism has still not been perfectly understood. Much closer investigation of the operation mechanism with collecting the essence of network design is required for further improvements of the responsive performances and broad applications to other molecular systems.

Here we disclose the influences of network architecture to the photochemical reactions of internal azobenzene moieties. In the

^{*} Corresponding author. Present address: Institute for Integrated Cell-Material Sciences (WPI-iCeMS), Kyoto University, Nishikyo-ku, Katsura, Kyoto 615-8510, Japan. Tel./fax: +81 42 388 7289.

^{**} Corresponding author.

E-mail addresses: nhosono@icems.kyoto-u.ac.jp (N. Hosono), toshi@cc.tuat.ac.jp (T. Watanabe).

¹ These authors contributed equally to work.

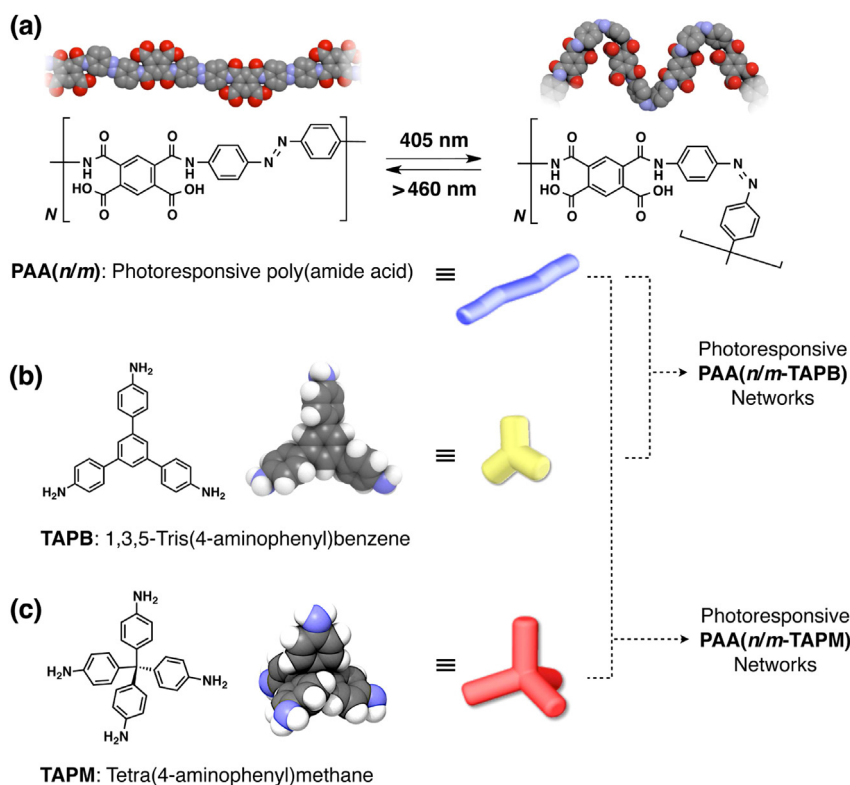


Fig. 1. (a) Schematic representations and chemical structure of photoresponsive PAA backbone. Upon 405-nm light irradiation, the azobenzene-containing backbone adopts so-called stiff zigzag conformation. Chemical structure and three-dimensional molecular structure of (b) TAPB and (c) TAPM optimized using semiempirical calculations (PM5, MOPAC, Fujitsu). **PAA(*n/m*)** precursors with TAPB and TAPM form corresponding TAPB-linked networks, **PAA(*n/m*-TAPB)**, and TAPM-linked network, **PAA(*n/m*-TAPM)**, respectively see also Scheme 1.

previous paper, we proposed that robust polymer frameworks crosslinked with bulky and symmetric crosslinkers could provide an ideal structure leading to the efficient photomechanical transduction [22]. This motivates us to further investigate the effect of network architecture on the photochemical reaction and photo-mechanical response of the gel cantilever.

In the present study, tri- and tetra-functional symmetric amine crosslinkers, 1,3,5-tris(4-aminophenyl)benzene (TAPB) and tetra(4-aminophenyl)methane (TAPM), respectively, were employed to make the photoresponsive networks and compared in the photoresponsive capability of gel cantilevers (Fig. 1). Photoresponsive poly(amide acid) precursors with a variety of molecular weights, **PAA(*n/m*)**, were prepared from pyromellitic dianhydride (PMDA) and 4,4'-diaminoazobenzene (DAA), where *n* and *m* denote composition of PMDA and DAA monomers, respectively (*n* = 3, 5, 7, 9, and 11; *m* = *n* - 1) (Scheme 1). The photoresponsive oligomeric precursors are end-linked with TAPB or TAPM crosslinkers to give **PAA(*n/m*-TAPB)** and **PAA(*n/m*-TAPM)** photoresponsive gels, respectively. Whereas TAPB has three reactive amines at planar threefold symmetric (C_3) positions, TAPM has four amines at tetragonal (S_4) positions. Due to the highly symmetric configuration of TAPM, resultant TAPM-linked networks might have a lattice-like robust framework structure that can be more regular mesh structure than TAPB-linked networks (Fig. 2) [23]. We anticipate that the robust and regular framework contributes to the efficient nano-to-macroscopic mechanical propagation of photoinduced conformational change of azobenzene moieties. In fact, TAPM-linked PAA gel cantilevers showed faster response (ca. two to three times) than TAPB-linked ones.

The *trans*-to-*cis* photoisomerization rate constant of azobenzene moiety was estimated in **PAA(*n/m*)** oligomer solution (before

crosslinking) and crosslinked gel state (after crosslinking), in which an intriguing crosslinking effect on the photoresponsive capability was discovered. The crosslinking treatment dramatically enhances the *trans*-to-*cis* photoisomerization by preventing intermolecular aggregation of the polymer backbones. This effect is more pronounced in the case of the network crosslinked with TAPM, in which the bulky shape of TAPM contributes to less aggregation of the rigid backbones by spreading and extending the robust framework structure.

In order to further investigate the operation mechanism of the PAA gels, the photoinduced volume changes were measured before and after photoirradiation. It was found that the volume contraction ratio between before and after photoirradiation was measured to be ~10% for TAPB-, and ~20% for TAPM-linked gel. These observations could reasonably explain a mechanism of the faster photomechanical response observed in TAPM-linked gels. The present study demonstrates that the networking architecture in molecular size is of much importance in the efficient propagation of the nano-scale azobenzene deformation into the macroscopic photomechanical motion.

2. Experimental

2.1. Materials

All reagents were purchased from Tokyo Kasei Organic Chemicals, Wako Pure Chemical Industries, and Lancaster Chemicals, and were used without further purification unless otherwise noted. Dehydrated *N*-methylpyrrolidone (NMP) was used as received from Wako Pure Chemical Industries. Pyromellitic dianhydride (PMDA) was received from Wako Pure Chemical Industries and used after

Download English Version:

<https://daneshyari.com/en/article/5180699>

Download Persian Version:

<https://daneshyari.com/article/5180699>

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