



Amphiphilic azo polymers: Molecular engineering, self-assembly and photoresponsive properties

Dongrui Wang¹, Xiaogong Wang*

Department of Chemical Engineering, Laboratory for Advanced Materials, Tsinghua University, Beijing 100084, PR China

ARTICLE INFO

Article history:

Received 25 April 2010

Received in revised form 26 June 2012

Accepted 28 June 2012

Available online 16 July 2012

Keywords:

Azo polymers

Amphiphilic

Synthesis

Self-assembly

Photoresponsive properties

ABSTRACT

Amphiphilic polymers are well known for their characteristics to form various self-assembling structures under proper conditions. Amphiphilic azo polymers, which are amphiphilic polymers functionalized with aromatic azo moieties, can combine wealthy photoresponsive properties with the self-assembling feature. In recent years, a wide variety of amphiphilic azo polymers have been developed through different molecular design strategies and synthetic routes. This article reviews the background, recent development, current approaches, and outlook of this rapidly developing research area. The emphasis is placed on the synthesis, self-assembly, and photoresponsive properties of amphiphilic azo polymers. According to the molecular architecture, the amphiphilic azo polymers are classified as homopolymers, random copolymers, block copolymers, star-like and dendritic polymers. The polymers show strong tendency to form well-organized structures at surfaces or interfaces, in solutions or dispersion mediums, and through phase-separation in solid thin-films. Colloidal arrays and porous thin films of amphiphilic azo polymers can be obtained through the vertical deposition method and solvent-induced structure inversion. The amphiphilic azo polymers and their self-assembled structures exhibit a variety of photoresponsive properties triggered by the trans–cis photoisomerization of azo chromophores. Some interesting variations caused by the light irradiation, such as the surface wettability change, surface-relief-grating formation, domain orientation, colloid deformation, micelle dissociation, vesicle bursting and fusion, are described in this review in detail. Such properties are promising for applications in areas such as optical devices, sensors, and drug delivery.

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Contents

1. Introduction	272
2. Amphiphilic azo polymers.....	273
2.1. Azo functional groups.....	273
2.2. Polymer architecture and classification	275
3. Synthesis of amphiphilic azo polymers	275
3.1. Homopolymers and random copolymers.....	275

* Corresponding author. Tel.: +86 10 62796171; fax: +86 10 62770304.

E-mail address: wxxg-dce@mail.tsinghua.edu.cn (X. Wang).

¹ Current address: Department of Polymer Science & Engineering, School of Chemistry & Biological Engineering, University of Science & Technology Beijing, Beijing 100083, PR China.

3.1.1.	Direct polymerization	275
3.1.2.	Post-polymerization functionalization	278
3.2.	Amphiphilic block copolymers	280
3.3.	Amphiphilic azo polymers with nonlinear architectures	284
4.	Self-assembly of amphiphilic azo polymers	287
4.1.	Self-assembled monolayers and multilayers	287
4.1.1.	Langmuir–Blodgett approach	287
4.1.2.	Electrostatic layer-by-layer adsorption	288
4.2.	Self-assembly of amphiphilic azo polymers in solutions	290
4.2.1.	Amphiphilic block copolymers	290
4.2.2.	Amphiphilic azo dendrimers	290
4.2.3.	Polydispersed azo homopolymers and random copolymers	292
4.3.	Ordered phase-separation structure in bulk	292
5.	Photoresponsive properties	292
5.1.	Photoresponsive properties of ultrathin films	292
5.2.	Photoinduced domain orientation	293
5.3.	Surface-relief-grating formation	295
5.4.	Photo-induced deformation of colloidal spheres	295
5.5.	Photo-induced micelle dissociation and vesicle fusion	296
6.	Conclusion and outlook	297
	Acknowledgment	298
	References	298

1. Introduction

Aromatic azo compounds have been widely used as dyestuffs, pigments, and pH indicators for a long time [1]. In the past decades, polymers containing azobenzene and its derivatives (azo polymers for short) have aroused considerable research enthusiasm for their interesting properties and applications. Although many azo polymers are brightly colored like their low-molecular-weight counterparts, the current research interest on azo polymers has little to do with their dyeing and coloring applications. In early stage of the contemporary exploration, the research effort was devoted to the use of azo functional groups as molecular probes by incorporating them in the backbones or side-chains of polymers [2]. Through study on photoisomerization kinetics and photostationary states of the azobenzene moieties, the information on the regional arrangement of the polymeric chain, viscosity, glass transition temperature (T_g), and tacticity was obtained. Since then, azobenzenes as “triggers” have been considered by more and more research groups. As a result, a variety of photoresponsive properties of azo polymers have been discovered. The investigations, which have gone far beyond the molecular probes, cover synthesis, structure–property relationship, functions and applications for a variety of new functional materials [3–12]. Azo polymers with different molecular architectures have been synthesized, which contain side-chain or main-chain azo groups and can be classified as linear, branched, crosslinked, star-like, dendritic polymers depending on their topological structure. In addition to the homopolymers and random copolymers, well-defined azo block copolymers and graft copolymers have also been developed.

Azo polymers have been intensively investigated for their properties such as photochemically induced phase transition, optical nonlinearities, photocontrolled

reversible property changes, and photoinduced birefringence and dichroism [3–5]. More recently, photoinduced motion and deformation of azo polymers in meso/macroscale have attracted great research attention [5]. The researches demonstrated that light irradiation can cause diversified variations such as surface-relief-grating (SRG) formation, deformation of liquid crystal elastomeric thin films, deformation of colloidal spheres, formation of self-structured surface patterns [4,5,7–17]. Azo polymers have been actively explored for applications in optical data storage, NLO devices, sensors and actuators, as well as materials suitable for photo-fabrication/processing [3–7]. The photoresponsive properties of azo polymers have been exploited to fabricate various novel surface patterns or other structures such as hexagonal surface structures [13], grating couplers and resonators [14], superhelix-like patterns [15], ellipsoidal colloids [16], and surface-modified microwires [17].

Most of the interesting properties of azo polymers are directly related with the trans–cis photoisomerization of the azobenzene units in the polymeric structures. Trans–cis isomerization of azobenzene and its derivatives has been intensively investigated by different theoretical and experimental methods for several decades [see for example, 18–21]. Azobenzene is a typical example with simplest structure among various azo compounds and has been most intensively investigated. It is well known that azobenzene can exist as trans or cis isomer in the electronic ground state [22]. UV light irradiation can cause the trans isomer to convert to less stable cis isomer and the latter will slowly relax to the trans form in dark environment. Visible light irradiation can accelerate the cis-to-trans isomerization of azobenzene. Two possible mechanisms, isomerization through rotation or inversion, have been proposed to describe the photochemical transition of azobenzene [22,23]. Similar to azobenzene, the

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