Polymer 54 (2013) 2001–2010

Contents lists available at SciVerse ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Water-soluble poly(*N*-vinyl-1,2,4-triazole) star and amphiphilic star block copolymers by RAFT polymerization

Hideharu Mori [a,b,*], Kazunori Ishikawa [a], Yohei Abiko [b], Kazuhiro Nakabayashi [a], Atsuhiko Onuma [c], Makoto Morishima [c]

[a] *Department of Polymer Science and Engineering, Graduate School of Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa 992-8510, Japan*
[b] *Department of Organic Device Engineering, Graduate School of Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa 992-8510, Japan*
[c] *Hitachi Research Laboratory, Hitachi Ltd., 7-1-1 Omika, Hitachi 319-1292, Japan*

ARTICLE INFO

Article history:
Received 25 September 2012
Received in revised form
28 November 2012
Accepted 10 December 2012
Available online 17 December 2012

Keywords:
Amphiphilic star block copolymer
Reversible addition-fragmentation chain transfer (RAFT) polymerization
Optoelectronic polymer

ABSTRACT

Water-soluble star polymers were synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization of *N*-vinyl-1,2,4-triazole (NVTri), which is a non-conjugated *N*-vinyl monomer having an aromatic heterocycle. Four-arm poly(NVTri)s having low polydispersities and controlled molecular weights were obtained using a xanthate-type tetrafunctional chain transfer agent (CTA). Amphiphilic star block copolymers having inner water-soluble segments connected to the core were synthesized by RAFT polymerization of *N*-vinylcarbazole (NVC) using poly(NVTri) star as a macro-CTA. In contrast, RAFT polymerization of NVTri using poly(NVC) star afforded star block copolymers with block arms consisting of inner optoelectronic poly(NVC) segment and outer hydrophilic poly(NVTri) segment. Assembled structures of these amphiphilic star block copolymers formed in selective solvents and characteristic optoelectronic properties were evaluated by dynamic light scattering (DLS), UV–vis, and fluorescence spectroscopic methods.

1. Introduction

Recently, there has been considerable interest in the developing of functional polymers derived from vinyl-triazole derivatives, because triazoles are highly stable heterocyclic compounds possessing an electron-rich aromatic ring prone to $\pi-\pi$ interactions, nitrogen atoms available for hydrogen bonding or metal ion coordination, and a strong dipole moment [1,2]. In particular, the synthesis and polymerization of vinyl-1,2,3-triazoles have gained great attention driven by the remarkable development of the copper-catalyzed azide-alkyne cycloaddition, which is recognized as the most widely applied example of the “click” chemistry. Recent significant progress of controlled radical polymerization (also known as controlled/“living” radical polymerization or reversible deactivation radical polymerization) has allowed for the synthesis of well-defined polymers from *C*-vinyl and *N*-vinyl-1,2,3-triazole-based monomers [3–5]. For example, Hawker's group reported that reversible addition-fragmentation chain transfer (RAFT) and nitroxide-mediated polymerizations of 1-vinyl-1,2,3-triazoles derivatives having various substituent groups, which were prepared by the “click” chemistry, were successfully employed for the synthesis of functional polymers and block copolymers [5]. In contrast, we recently focused on *N*-vinyl-1,2,4-triazole (NVTri), which is a non-conjugated *N*-vinyl monomer having basic nitrogen atoms of the pyridine type in the heterocycle [6]. RAFT polymerization of NVTri was found to proceed in a controlled fashion using a suitable xanthate-type chain transfer agent (CTA), resulting in the formation of well-defined water-soluble polymer [6]. The water solubility of nonionogenic poly(vinyl azole)s including poly(NVTri) was reported to be associated with the presence of basic nitrogen atoms of the pyridine type in the heterocycle that tend to form hydrogen bonds with water molecules [2]. Whereas, poly(vinyl azole)s containing sequences of two or a large amount of nitrogen atoms in the heterocycle, such as poly(*N*-vinyl-1,2,3-triazole) and poly(*N*-vinyl-1,3,4-triazole), are insoluble in water.

Carbazole-containing polymers having various architectures have been widely investigated, because of their attractive features, such as their hole-transporting, high charge-carrier, and electroluminescent properties [7]. Star-shaped polymers incorporating carbazole functionality have attracted significant research interest, as they exhibit interesting structures and potential applications in the optoelectronic fields [8–13]. Depending on the location and

---

* Corresponding author. Department of Polymer Science and Engineering, Graduate School of Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa 992-8510, Japan. Tel.: +81 238 26 3765; fax: +81 238 26 3749.
E-mail address: h.mori@yz.yamagata-u.ac.jp (H. Mori).

0032-3861/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymer.2012.12.033

stacking of the carbazole moiety, the three-dimensional hierarchical structures of the carbazole-containing star polymers may lead to unique electronic and photonic functions. In particular, the design and synthesis of novel star copolymers having characteristic architectures, such as star block copolymers and heteroarm or miktoarm (mixed) star polymers, with characteristic carbazole functionality are of interest. For example, amphiphilic star block copolymers were synthesized by the RAFT polymerization of *N*-vinylcarbazole (NVC) using the poly(acrylic acid) star, which was prepared from a tetrafunctional CTA [12]. The absorbance and fluorescence spectra indicated that specific conformations of the amphiphilic stars, like micelles and inverse micelles, affected the characteristic optoelectronic properties. Another example has been the synthesis of amphiphilic A_3B miktoarm star copolymer, in which poly(*N*-isopropylacrylamide)$_3$-poly(NVC) was successfully synthesized by a combination of single-electron transfer living radical polymerization and RAFT polymerization [13]. The amphiphilic A_3B miktoarm star copolymer showed an increase in the fluorescence intensity of micelle with temperature and had good temperature reversibility. In general, amphiphilic star block copolymers and miktoarm star polymers can form a variety of superstructures as a result of self-organization, and the resulting assembled structures should be governed by the branched architecture, as well as the chemical nature of the components, their composition, and molecular weight [14–20].

We now report the controlled synthesis of amphiphilic star block copolymers comprising poly(NVTri) as a hydrophilic segment and a hydrophobic poly(NVC) having characteristic optoelectronic properties by RAFT polymerization. Poly(NVTri) was reported to be a non-toxic, biocompatible, thermally stable and easily soluble in water or polar solvents [21,22]. Poly(NVTri), copolymers, and networks have been exploited to a wide range of applications, such as controlled release [23], dielectric layer for organic field effect transistor [24], polymer matrixes for nanoparticles-based composites [25], proton conducting electrolytes [26–28], polycations to form complexes with anionic polyelectrolytes [26,29], and energetic polymer salts [30]. In the first part, we present RAFT polymerization of NVTri using R-designed tetrafunctional CTA having dithiocarbonate moieties as the Z-groups for the controlled synthesis of water-soluble star polymers (Scheme 1). We then describe the synthesis of amphiphilic star block copolymers by RAFT polymerization of NVC using four-arm poly(NVTri) star as a hydrophilic tetrafunctional CTA (Scheme 2a) and RAFT polymerization of NVTri using poly(NVC) star as a hydrophobic macro-CTA (Scheme 2b). Finally, aggregation behavior and optoelectronic properties of these star block copolymers were evaluated by dynamic light scattering (DLS), UV–vis and fluorescent spectroscopic methods. In addition to the comonomer composition and chain length of each segment, the branched structure and the sequence of each block (location of the poly(NVC) segment) affected characteristic optoelectronic properties and assembled structures of the carbazole-containing star block copolymers.

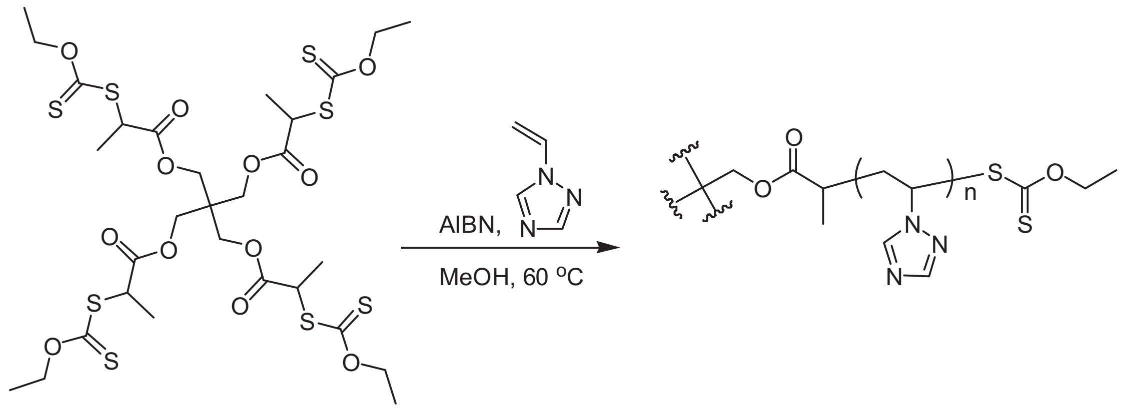
2. Experimental section

2.1. Materials

2,2′-Azobis(isobutyronitrile) (AIBN, Kanto Chemical, 97%) was purified by recrystallization from methanol. Methanol (anhydrous MeOH, Kanto Chemical, 99.8%) and *N*,*N*-dimethylformamide (anhydrous DMF, Kanto Chemical, 99.5%) were used as received. 1,4-Dioxane (Kanto Chemical, 99%) was distilled from sodium wire. *N*-Vinylcarbazole (NVC, Tokyo Kasei, 98%) was recrystallized two times from methanol. *N*-Vinyl-1,2,4-triazole (NVTri) was obtained by the *N*-alkylation of 1,2,4-triazole, followed by the elimination reaction [6,31]. The xanthate-type tetrafunctional CTA was synthesized by a two-step procedure according to a previously reported procedure [12,32]. The first step is the reaction of pentaerythritol with 2-bromopropylbromide in the presence of pyridine to yield a tetrafunctional bromide precursor. The precursor was then reacted with potassium ethyl xanthogenate to afford the tetrafunctional CTA. The CTA was finally purified by column chromatography on silica with hexane/ethyl acetate (7/3 vol%) as the eluent to give a pale yellow viscous oil. Other materials were used without further purification.

2.2. Synthesis of four-arm poly(NVTri) star

All polymerizations were carried out in a degassed sealed tube. A representative example is as follows: NVTri (0.19 g, 2.00 mmol), tetrafunctional CTA (16.8 mg, 0.020 mmol), AIBN (1.6 mg, 0.01 mmol), and methanol (1.0 mL) were placed in a dry glass ampule equipped with a magnetic stirr bar, and then the solution was degassed by three freeze-evacuate-thaw cycles. After the ampule was flame-sealed under vacuum, it was stirred at 60 °C for 3 h. The reaction was stopped by rapid cooling with liquid nitrogen. For the determination of the monomer conversion, the ^{1}H NMR spectrum of the polymerization mixture collected just after the polymerization was measured in DMSO-d_6 at room temperature. The integration of polymer main chain (2H) at 2.6–1.7 ppm was compared with the monomer $CH_2 = CH$- resonance (1H) at around 5.1 ppm. After the crude sample was dissolved in a small amount of DMSO, it was purified by reprecipitation into a large excess of acetone, and the resulting product was dried under vacuum



Scheme 1. Synthesis of water-soluble star polymer by RAFT polymerization of *N*-vinyl-1,2,4-triazole (NVTri) using a tetrafunctional chain transfer agent (CTA).