Polymer 53 (2012) 3861–3877

Contents lists available at SciVerse ScienceDirect

Polymer

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

Controlled synthesis of sulfonated block copolymers having thermoresponsive property by RAFT polymerization of vinyl sulfonate esters

Hideharu Mori [a,*], Yosuke Saito [a], Eri Takahashi [a], Kazuhiro Nakabayashi [a], Atsuhiko Onuma [b], Makoto Morishima [b]

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

ARTICLE INFO

Article history:
Received 1 March 2012
Received in revised form
11 June 2012
Accepted 24 June 2012
Available online 4 July 2012

Keywords:
RAFT polymerization
Thermoresponsive block copolymer
Sulfonic acid-containing polymer

ABSTRACT

Four vinyl sulfonate ester derivatives, methyl ethenesulfonate (MES), ethyl ethenesulfonate (EES), 2,2,2-trifluoroethyl ethenesulfonate (TFES), and 2,2,2-trichloroethyl ethenesulfonate (TCLES), which are protected forms of vinyl sulfonic acids, were polymerized by reversible addition-fragmentation chain transfer (RAFT) polymerization. Polymers having relatively narrow molecular weight distributions and pre-determined molecular weights were obtained by the polymerization of all monomers using a suitable xanthate-type chain transfer agent (CTA). The RAFT polymerizations of EES and TCLES were found to proceed in controlled fashions under suitable conditions, as confirmed by the formation of narrow polydispersity products, molecular weights controlled by the monomer/chain transfer agent ratio, and linear increases in molecular weight with conversion. Deprotection of the ethyl group of poly(EES) by LiBr in refluxing 2-butanone proceeded smoothly to give water-soluble poly(lithium vinyl sulfonate). Poly(potassium vinyl sulfonate) was also obtained by the deprotection of poly(TCLES) using potassium *tert*-butoxide. The syntheses of thermoresponsive block copolymers involving poly(lithium vinyl sulfonate) segments were conducted by RAFT polymerization of *N*-isopropylacrylamide using poly(EES) macro-CTA, followed by deprotection. The thermally-induced phase separation behavior and assembled structures of the block copolymers were also studied in aqueous solution.

1. Introduction

In the past few decades, considerable attention has been given to sulfonic acid-containing block copolymers, which is mainly due to their feasibility to create highly ordered structures as a result of self-organization and their potential applications for proton conductive membranes [1–5] and bio-related materials [6–8]. Recent significant progress in controlled radical polymerization (also known as controlled/"living" radical polymerization or reversible deactivation radical polymerization) has allowed the synthesis of well-defined polymers containing sulfonic acid groups. For example, nitroxide-mediated polymerization and atom transfer radical polymerization of sodium styrenesulfonate have been frequently employed for the synthesis of various sulfonated block copolymers [9–12]. Direct reversible addition-fragmentation chain transfer (RAFT) polymerization of various ionic monomers having sulfonate moieties in the side chains have been reported, including styrene, acrylamide, and (meth)acrylate derivatives [13,14]. Various thermoresponsive block copolymers have also been synthesized by atom transfer radical polymerization of a sulfonic acid-containing acrylamide [6–8]. Other examples involve the synthesis of sulfonic acid-containing block copolymers by controlled radical polymerization of styrene derivatives with protected sulfonic acid groups, followed by deprotection [15–18].

Recently, significant attention has been paid to poly(vinyl sulfonic acid) and its salt forms, which can be regarded as some of the simplest sulfonic acid-containing polymers that have the highest content of sulfonate groups. Since poly(vinyl sulfonic acid) possesses negatively charged sulfonate groups, it represents a class of water-soluble polymers and strong anionic polyelectrolytes. Their potential applications involve blood compatible materials [19], a platform for cationic drug delivery systems [20–22], dye-modifiers [23–25], accelerators for reduction reactions [26,27], polychelatogens to bind metal ions [28], proton conducting solid electrolytes [29], heterogeneous acid catalysts [30], and polymer-enhanced ultrafiltration [31]. In most of these works, salt forms of poly(vinyl sulfonic acid), such as poly(sodium vinyl sulfonate) and

* Corresponding author. 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.2012.06.043

poly(potassium vinyl sulfonate), were employed, because of the difficulties in the purification of the acid form of the monomer, vinyl sulfonic acid, and in the cationic exchange of the sodium form of the polymer, poly(sodium vinyl sulfonate). Recently, free radical polymerization of high-purity vinyl sulfonic acid in water was reported to yield poly(vinyl sulfonic acid) exhibiting a very high acidic proportion (ion-exchange capacity; IEC = 9.2 meq g^{-1}) [30,32].

In a previous study, we reported the synthesis of well-defined polymers with pendant sulfonate esters and lithium sulfonate groups by RAFT polymerization of vinyl sulfonate esters using a xanthate-type chain transfer agent (CTA) [33]. The controlled character of the polymerization of two vinyl sulfonate esters having primary alkyl groups, neopentyl ethenesulfonate (NES) and 1-butyl ethenesulfonate (BES), was confirmed. Deprotection of the neopentyl group of the poly(NES) proceeded smoothly to give water-soluble poly(lithium vinyl sulfonate). Synthesis of well-defined block copolymers involving poly(lithium vinyl sulfonate) segments was conducted by RAFT polymerization of NES using poly(*N*-vinylcarbazole) macro-CTA, followed by deprotection. While successful, this approach suffers from several drawbacks, primarily a time-consuming purification process as well as limited molecular weights and monomer conversion. Since the poly(NES) had good solubility in most organic solvents, almost the same as that of the monomer, the crude poly(NES) obtained after polymerization was purified by dialysis against methanol for 2 days. The good solubility of poly(NES) led to a difficulty recovering the polymers in sufficient yield in some cases of the synthesis of the block copolymers. The molecular weights could be controlled by the monomer/CTA molar ratio with maintaining relatively low polydispersity, while a long reaction time (72 h at 45 °C) was required to achieve the higher molecular weight products with sufficient yields (>60%). Hence, appropriate control of the comonomer composition and chain lengths in the block copolymers was difficult, even if the chain extension from the poly(*N*-vinylcarbazole) macro-CTA to NES could be controlled and provided the block copolymer with a narrow molecular weight distribution.

In this study, we selected four vinyl sulfonate esters having different substituent groups, in order to overcome these drawbacks and enable widespread availability of this class of monomers. Differing from styrene, (meth)acrylate, and (meth)acrylamide-type monomers, the direct linkage of the sulfonate moiety to the vinyl group is an important feature of these monomers, because it may affect not only the polymerization behavior but also various properties of the resulting polymers. First, we compare the RAFT polymerization behavior of four vinyl sulfonate esters, methyl ethenesulfonate (MES), ethyl ethenesulfonate (EES), 2,2,2-trifluoroethyl ethenesulfonate (TFES), and 2,2,2-trichloroethyl ethenesulfonate (TCLES), which are protected forms of vinyl sulfonic acids (Scheme 1). Then, we describe the RAFT polymerization of selected monomers, EES and TCLES, using a suitable chain transfer agent (CTA), and the deprotection of the resulting polymers under various conditions. Thermoresponsive block copolymers involving poly(lithium vinyl sulfonate) segments were synthesized by RAFT polymerization of *N*-isopropylacrylamide (NIPAAm) using poly(EES) macro-CTA, followed by deprotection. Finally, the thermally-induced phase separation behavior and assembled structures of the block copolymers were studied in aqueous solution.

2. Experimental

2.1. Materials

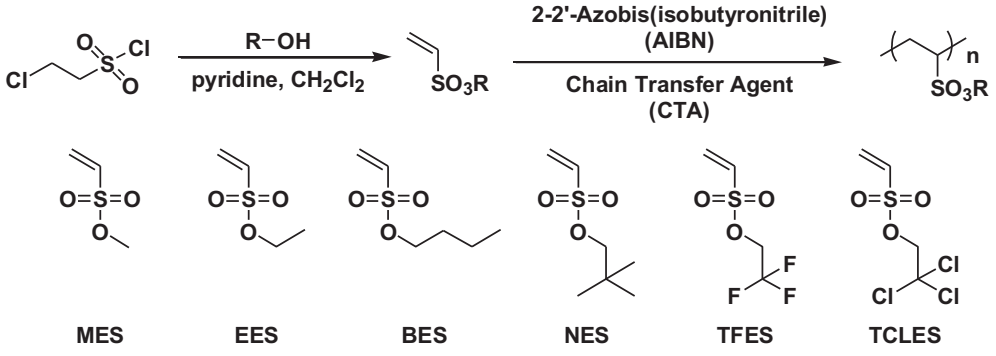
2,2′-Azobis(isobutyronitrile) (AIBN, Kanto Chemical, 97%) was purified by recrystallization from methanol. 2-Chloroethanesulfonyl chloride (Tokyo Kasei Kogyo, >95%), methanol, (Kanto Chemical, >99.5%), ethanol (Kanto Chemical, >99.5%), 2,2,2-trifluoroethanol (Tokyo Kasei, >99%), 2,2,2-trichloroethanol (Tokyo Kasei, >98%), and pyridine (Kanto Chemical, >99.5%) were used as received. *N*-Isopropylacrylamide (NIPAAm, Tokyo Kasei Kogyo, 98%) was purified two times by recrystallization from *n*-hexane. Other materials were used without further purification.

2.2. Synthesis of chain transfer agents (CTA)s

Five different CTAs were employed in this study, as shown in Scheme 2. Benzyl dithiobenzoate (CTA 1) [34,35] and benzyl 1-pyrrolecarbodithioate (CTA 2) [36,37] were synthesized according to the procedures reported previously. *S*-Benzyl-*O*-ethyl dithiocarbonate (CTA 3) [38–40], *O*-ethyl-*S*-(1-methoxycarbonyl) ethyl-dithiocarbonate (CTA 4) [41,42], and *O*-ethyl-*S*-(1-phenylethyl) dithiocarbonate (CTA 5) [38,40,43] were synthesized by the reaction of potassium ethyl xanthogenate with the corresponding bromide (benzyl bromide for CTA 3, methyl 2-bromopropionate for CTA 4, and 1-bromoethyl benzene for CTA 5) according to a procedure reported in the literature. These xanthate-type CTAs were finally purified by column chromatography on silica with *n*-hexane/ethyl acetate (10/1 vol-%) as the eluent.

2.3. Synthesis of vinyl sulfonate esters

Four vinyl sulfonate esters having different substituent groups, methyl ethenesulfonate (MES), ethyl ethenesulfonate (EES), 2,2,2-trifluoroethyl ethenesulfonate (TFES), and 2,2,2-trichloroethyl ethenesulfonate (TCLES), were synthesized by the reaction of 2-chloroethanesulfonyl chloride with the corresponding alcohols according to a previously reported method with slight modifications (Scheme 1) [44–46]. In a typical synthesis of ethyl ethenesulfonate (EES), 4.87 mL of ethanol (5.53 g, 0.12 mol) was added



Scheme 1. Synthesis of vinyl sulfonate esters and reversible addition-fragmentation chain transfer (RAFT) polymerization.