Synthesis and Characterization of ABA-Type Amphiphilic Tri-Block Copolymers Through Anionic Polymerization Using End Functionalized Poly(ethylene oxide) Oligomers

PALASH JYOTI DAS,¹ ANIL BARAK,¹ YUSUKE KAWAKAMI,² THARANIKKARASU KANNAN³

¹Department of Chemistry, North Campus, University of Delhi, Delhi 110007, India

²Graduate School of Materials Science, Japan Advanced Institute of Science and Technology, Asahidai 1-1, Tatsunokuchi, Ishikawa 9231292, Japan

³Department of Chemistry, Pondicherry University, R.V. Nagar, Kalapet, Puducherry 605014, India

Received 10 October 2010; accepted 21 December 2010 DOI: 10.1002/pola.24558 Published online 2 February 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: ABA-type amphiphilic tri-block copolymers were successfully synthesized from poly(ethylene oxide) derivatives through anionic polymerization. When poly(styrene) anions were reacted with telechelic bromine-terminated poly(ethylene oxide) (1) in 2:1 mole ratio, poly(styrene)-b-poly(ethylene oxide)-b-poly(styrene) tri-block copolymers were formed. Similarly, stable telechelic carbanion-terminated poly(ethylene oxide), prepared from 1,1-diphenylethylene-terminated poly (ethylene oxide) (2) and sec-BuLi, was also used to polymerize styrene and methyl methacrylate separately, as a result, poly (styrene)-b-poly(ethylene oxide)-b-poly(styrene) and poly (methyl methacrylate)-b-poly(ethylene oxide)-b-poly(methyl methacrylate) tri-block copolymers were formed respectively. All these tri-block copolymers and poly(ethylene oxide) derivatives, 1 and 2, were characterized by spectroscopic, calorimetric, and chromatographic techniques. Theoretical molecular weights of the tri-block copolymers were found to be similar to

INTRODUCTION Amphiphilic block copolymers show unique properties due to the presence of both hydrophobic and hydrophilic blocks in their structure. These properties have been effectively used to prepare novel materials such as nanoscale materials, drug delivery agents, emulsifiers, and surface modifying agents.¹⁻⁶ Poly(ethylene oxide) (PEO) has been widely used as a hydrophilic block in these amphiphilic block copolymers due to its biocompatibility and ion transporting ability.^{7,8} The precise control of molecular weight and polydispersity index plays a major role in controlling the properties of these block copolymers.⁹ Since the concept of living anionic polymerization was established by Szwarc in 1956,¹⁰ it emerged as a very useful technique to synthesize polymers with desired molecular weight and narrow polydispersity index.¹¹ Synthesis of different types of amphiphilic block copolymers through anionic polymerization has been carried out by various research groups¹² and these amphiphilic block copolymers have been tested for different types of applications.^{13,14}

the experimental molecular weights, and narrow polydispersity index was observed for all the tri-block copolymers. Differential scanning calorimetric studies confirmed the presence of glass transition temperatures of poly(ethylene oxide), poly(styrene), and poly(methyl methacrylate) blocks in the tri-block copolymers. Poly(styrene)-*b*-poly(ethylene oxide)-*b*-poly(styrene) triblock copolymers, prepared from polystyryl anion and **1**, were successfully used to prepare micelles, and according to the transmission electron microscopy and dynamic light scattering results, the micelles were spherical in shape with mean average diameter of 106 \pm 5 nm. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 1376–1386, 2011

KEYWORDS: amphiphiles; amphiphilic; anionic polymerization; block copolymers; poly(ethylene oxide); poly(methyl methacry-late); polystyrene; tri-block copolymers

The utilization of the living anionic polymerization for the synthesis of block copolymers through sequential monomer addition depends upon the nucleophilic reactivity of the living polymeric anion, prepared from the first monomer, with the freshly added second monomer.15,16 For instance, polvstyrene dianion can initiate ethylene oxide to get poly(ethylene oxide)-b-poly(styrene)-b-poly(ethylene oxide) tri-block copolymers,¹⁷ but PEO dianion cannot initiate styrene,¹⁸ as a result, polystyrene-b-poly(ethylene oxide)-b-polystyrene (PSb-PEO-b-PS) tri-block copolymers cannot be synthesized by anionic polymerization. This is due to the low reactivity of PEO anion toward styrene.¹⁹ To overcome this drawback, reactivity boosting process was proposed by Teyssie and coworkers,²⁰ and through this process, oxyanion was reacted with disilacyclopentane, and the resulting silyl anion was used to polymerize styrene and methyl methacrylate (MMA).²⁰ But, all oxyanions could not be converted into silyl anions. In contrast, some of the oxyanions initiated

Additional Supporting Information may be found in the online version of this article. Correspondence to: T. Kannan (E-mail: thavasu@gmail.com) Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 49, 1376–1386 (2011) © 2011 Wiley Periodicals, Inc.



SCHEME 1 Synthesis of amphiphilic triblock copolymers using telechelic poly (ethylene oxide) derivatives.

disilylcyclopentane polymerization, and as a result, along with the silyl anion formation, oligomers of disilacyclopentane were also formed. Due to this, the initiator efficiency of this route was found to be 35% only.²⁰ In another attempt, oxyanion was directly converted into carbanion by reacting with silacyclobutane and the resulting carbanion was used to polymerize styrene.²¹ But, in this case also, oligomerization of silacyclobutane was occurred along with the conversion of oxyanion into carbanion. As a result, in this case also, the initiator efficiency was 11% only.²¹ To improve the initiator efficiency, stable 1,1-diphenlyethylene anion was prepared in situ by reacting 1,1-diphenlyethylene and the carbanion generated from potassium tert-butoxide (t-BuOK) and dimethylsilacyclobutane.¹⁸ The resulting stable carbanion was used to polymerize MMA, and through this route, the initiator efficiency was improved up to 76%.¹⁸ As this route has improved the initiator efficiency, it was used to prepare PS-b-PEO-b-PS and poly(methyl methacrylate)-bpoly(ethylene oxide)-b-poly(methyl methacrylate) (PMMA-b-PEO-b-PMMA) tri-block copolymers,²² but the yield of the block copolymers was very low.

As it is difficult to synthesize these tri-block copolymers through living anionic polymerization, controlled radical polymerization was effectively used to synthesize these block copolymers.^{8,19} But ability to achieve desired molecular weight and narrow polydispersity index is always difficult in controlled radical polymerization when compared with living anionic polymerization. Hence, oxyanion itself was directly used to polymerize methacrylate monomers. Nagasaki et al.²³ reported the polymerization of 2-(dimethylamino)ethyl methacrylate (DMAEMA) by oxyanionic polymerization using potassium 4-vinylbenzylalcoholate, and the same route was used by Armes and coworkers to obtain PEO-bpoly(DMAEMA) di-block copolymers²⁴ and tertiary amine methacrylate-based amphiphilic block copolymers.²⁵ As there is no efficient method to synthesize PS-b-PEO-b-PS and PMMA-b-PEO-b-PMMA tri-block copolymers through living anionic polymerization, in this report, two synthetic routes are proposed for the synthesis of these tri-block copolymers as depicted in Scheme 1. PS-b-PEO-b-PS tri-block copolymers can be synthesized by reacting telechelic bromine-terminated PEO (1) and poly(styrene) anion. Similarly, telechelic 1,1diphenylethylene-terminated PEO (2) can be reacted with *sec*-BuLi to get telechelic carbanion terminated poly(ethylene oxide) and this dianion-terminated PEO can be used to polymerize styrene and MMA to obtain PS-*b*-PEO-*b*-PS and PMMA-*b*-PEO-*b*-PMMA tri-block copolymers respectively. In addition, micelles from PS-*b*-PEO-*b*-PS tri-block copolymers have been successfully prepared and reported in this article.

EXPERIMENTAL

Materials

Poly(ethylene glycol) (PEG; Aldrich) of molecular weight 1000 was purified by azeotropic distillation using toluene and dried under vacuum just prior to use. Styrene (Aldrich) was washed with 10% (w/v) of aqueous NaOH solution to remove the inhibitor followed by washing with distilled water. The resulting styrene was stirred over CaH₂ overnight. In the next day, styrene was distilled under reduced pressure and the middle portion was stored under argon atmosphere until use. Similar to styrene, MMA (CDH, India) was also purified, distilled and stored under argon atmosphere. Tetrahydrofuran (THF, Spectrochem, India) was first distilled, and before using in the anionic polymerization, the middle portion was refluxed over Na-benzophenone complex until color persisted. Hexamethylphosphorictriamide purple (HMPA, Spectrochem, India) was purified by stirring over CaH₂ for overnight and vacuum distilled just before use. Copper (I) bromide (Aldrich) was washed, first with glacial acetic acid, then with methanol and diethyl ether, and finally dried under vacuum. t-BuOK (Aldrich) was purified by sublimation under vacuum and stored under inert atmosphere until use. Magnesium turnings (CDH, India) were washed with 0.1 N HCl followed by distilled water, acetone, and finally dried under vacuum just before use. Lithium perchlorate (Aldrich) was dried by heating at 80 °C under vacuum for 6 h and used. Phosphorous tribromide (Spectrochem, India), methyltriphenylphosphonium bromide (Spectrochem, India), p-bromobenzophenone (CDH, India) and sec-butyllithium (sec-BuLi) in hexane (1.4 M; Aldrich) were used as received. N,N'-Dimethyformamide (DMF, Spectrochem, India) was distilled under reduced pressure and stored over type 4 Å molecular sieves under argon atmosphere. Holey Formvar and pre-carbon coated copper grids were purchased