Synthesis of Well Defined Sulfonated Block Copolymers by Atom Transfer Radical Polymerization

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Introduction

Sulfonated poly styrene block copolymers are used in wide range of applications such as thermoplastic elastomers, proton exchange membranes, separators for gas and liquid, and additives in composite. Synthesis of this block copolymer have usually been synthesized by post sulfonation of polystyrene segment in the block copolymer using a sulfating reagent such as sulfur trioxide for high sulfonation and acetyl sulfate for mild sulfonation. However, it was not easy to introduce high amounts of sulfonic acid groups onto polystyrene segments, because the solubility of the block copolymer was changed during the sulfonation. Controlling the polydispersity is one of the methods to overcome this limitation because it enables direct polymerization of sulfonated styrene. Several researchers have reported synthesis of well defined sulfonated polystyrene and its block copolymer by the polymerization of sodium styrene sulfinate in microwaves mediated radical polymerization (OMDRP) or atom transfer radical polymerization (ATRP). However, all those polymers were water soluble homo or block copolymers, which were only achieved in aqueous media. Okamura et al. reported synthesis of well defined random and block copolymers of styrene and styrene sulfinate by ATRP in organic solvent, whereas the styrene sulfinate segments gave sulfonic acid groups by thermal treatment or acidification. We also recently synthesized well defined protected polystyrene sulfinate with higher molecular weight (Mn = 20,500, PDI < 1.12) by CuBr catalyzed ATRP. Since ATRP can control the polymerization of various kinds of monomers such as styrene, acrylate, methacrylate, acrylic acid etc., we have demonstrated synthesis of sulfonated block copolymer by sequential copolymerization of p-buty acrylate and styrene sulfinate via ATRP followed by acidification by thermal treatment. We have thus obtained novel ionomeric block copolymers with soft and hard segments.

Results and discussion

Well defined sulfonated block copolymers were synthesized as shown in Scheme 1. Thus, poly(N-buty acrylate) (PnBA) (A) was first synthesized by CuBr catalyzed living radical polymerization with 2-bromopropionate as the initiator (CEP). HMPA N,N,N -dimethylacetamide (DMC) in toluene at 50 °C (Mn = 12,700, PDI < 1.09). Obtained PnBA was then used as a macroinitiator to polymerize neopentyl sulfonated styrene (N-S) in the presence of CuBr with PMDETA in toluene at 50 °C to give well defined nBA-block-NSS copolymer (B) (Mn = 29,000, PDI < 1.15). Figure 1 shows GPC curves of the block copolymer which is clearly shifted to high molecular weight, indicating the success of the block copolymer.

These block copolymers were then acidified by thermal treatment at 150 °C for 30 min to generate sulfonic acid groups in the PnBA segments (C). 1H NMR and FT-IR analysis of B and C showed quantitative disappearance of the neopentyl groups in PnBA and complete introduction of sulfonic acid groups in the block copolymers after thermal treatment. Studies of the mechanical stability, the morphology and transport properties of this material are currently underway.

Experimental

N-S was prepared according to the literature. PBA was purified by distillation over CaH2 before use. Ammonia was distilled over CaH2 and bubbled with N2 for 15 min before use. Other chemicals were used as received.

General Polymerization Procedure. In a round bottom flask, CuBr, nBA, PMDETA, and BPB were added sequentially in this order under Ar. After 20 min of mixing, the solution was then sealed in baked glass tubes and placed in an oil bath at 80 °C. After 5 h, the polymerization was terminated by cooling to 78 °C.

In a round bottom flask, PnBA macroinitiator, CuBr, N-S, amine and PMDETA was added sequentially in this order under Ar and then placed in an oil bath at 80 °C. The polymerization was terminated by cooling to 78 °C.

Scheme 1. Synthesis of well defined sulfonated styrene and nBA block copolymers by ATRP.

Figure 1. GPC curves of PnBA precursor and nBA-NSS block copolymer.

References