

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

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### Introduction

Sulfonated polystyrene block copolymers are used in wide range of application such as thermoplastic elastomers, proton exchange membranes, separators for gas and liquid, and additives in composite etc.<sup>1</sup> Synthesis of this block copolymer have usually been synthesized by post sulfonation of polystyrene segment in the block copolymer using a sulfonating 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. Controlled radical polymerization 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 copolymers by the polymerization of sodium styrene sulfonate in nitroxide mediated radical polymerization (NMRP)<sup>2</sup> or atom transfer radical polymerization (ATRP).<sup>3</sup> However, all these 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 sulfonate by NMRP in organic solvent, wherein the styrene sulfonate segments gave sulfonic acid groups by thermal treatment or acidification.<sup>4</sup> We also recently synthesized well-defined such protected polystyrene sulfonate with higher molecular weight ( $M_n = 20,500$ ;  $PDI < 1.12$ ) by CuBr catalyzed ATRP.<sup>5</sup> Since ATRP can control the polymerization of various kinds of monomers such as styrene, acrylate, methacrylate, acrylamide etc.,<sup>6</sup> we here demonstrated synthesis of sulfonated block copolymers by sequential copolymerization of *n*-butyl acrylate and styrenesulfonate via ATRP followed by acidification by thermolysis. 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*-butyl acrylate) (P*n*BA) (A) was first synthesized by CuBr catalyzed living radical polymerization with 2-bromopropionate as the initiator (EBP), *N,N,N',N'*-pentamethyl diethylenetriamine (PMDETA) in bulk at 80 °C ( $M_n = 19,500$ ,  $PDI < 1.09$ ).<sup>7</sup> Obtained P*n*BA was then used as a macroinitiator to polymerize neopentyl sulfonated styrene (NSS) in the presence of CuBr with PMDETA in anisole at 90 °C to give well defined *n*BA-*block*-NSS copolymer (B) ( $M_n = 29,900$ ,  $PDI < 1.15$ ). 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 thermolysis at 150 °C for 30 min to generate sulfonic acid groups in the PNSS segments (C). <sup>1</sup>H NMR and FT-IR analyses of B and C showed quantitative disappearance of the neopentyl groups in PNSS and complete introduction of sulfonic acid groups in the block copolymers after thermolysis.

Studies of the mechanical stability, the morphology and transport properties of this material are currently underway.

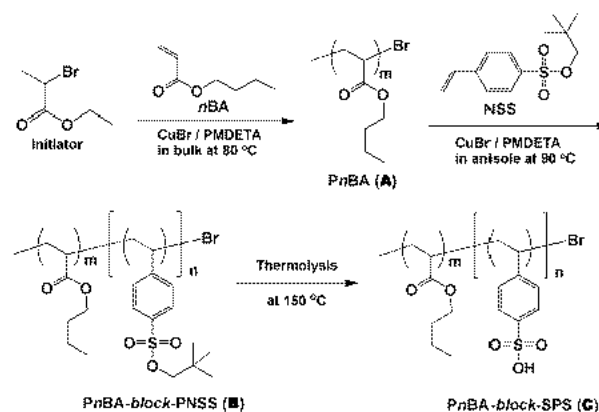
### Experimental

NSS was prepared according to the literature.<sup>5</sup> *n*BA was purified by distillation over CaH<sub>2</sub> before use. Anisole was distilled over CaH<sub>2</sub> and bubbled with N<sub>2</sub> for 15 min before use. Other chemicals were used as received.

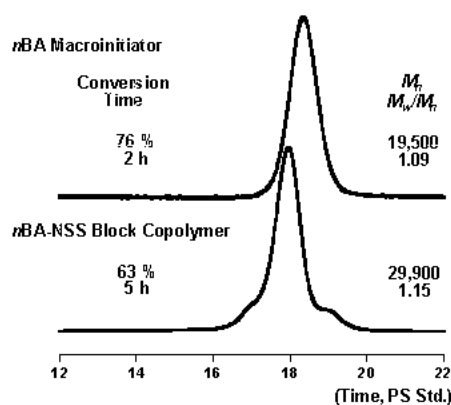
**General Polymerization Procedure.** In a round bottom flask CuBr, *n*BA, PMDETA, and EBP were added sequentially in this order

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 5h, the polymerization was terminated by cooling to -78 °C.

In round bottom flask P*n*BA macroinitiator, CuBr, NSS, anisole and PMDETA was added sequentially in this order under Ar and then placed in oil bath at 90 °C. The polymerization was terminated by cooling to -78 °C.



**Scheme 1.** Synthesis of well defined sulfonated styrene and *n*BA block copolymers by ATRP.



**Figure 1.** GPC curves of P*n*BA precursor and *n*BA-NSS block copolymer.

### References

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