



Precise insertion of clickable monomer along polymer backbone by dynamic temperature controlled radical polymerization



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ABSTRACT

Styrenic copolymers have been prepared that contain localized areas of high azide functionality by exploiting the unexpected copolymerization behavior of azidomethyl styrene with styrene. Kinetic studies have shown that during the nitroxide-mediated polymerization of styrene and azidomethyl styrene, small equivalents of azidomethyl styrene are consumed at a relatively higher rate. This property was further enhanced by lowering the reaction temperature, leading to a more precisely defined area of azide functionality. Furthermore, by actively controlling the reaction temperature azidomethyl styrene can be inserted into different points along the polymer backbone. This approach was used in combination with previous sequence control techniques, strong donor/acceptor comonomer pairs, to synthesize well-defined copolymers with controlled areas of functional monomers allowing for a wide scope of post-polymerization modification methods.

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1. Introduction

Replicating the high order and sequence controlled nature of biopolymers is an ever present challenge for synthetic polymer chemistry [1]. Controlled polymerization techniques such as living ionic polymerization [2,3] and living radical polymerization [4–7] pave the way for high order control by regulating the chain length, narrowing molecular weight distribution and facilitating the synthesis of macromolecular architectures such as block, graft, star and telechelic polymers [8–14].

In recent years there have been multiple synthetic approaches developed to control the primary sequence of macromolecules, for example bifunctional initiators that firstly polymerize a protected amine monomer to form

part of a template initiator, which is then capable of radically polymerizing acidic monomers with greater selectivity over the methyl ester analogue [15]. Using Cu(0) mediated polymerization, Whittaker and coworkers have demonstrated the synthesis of multiblock copolymers of very short blocks, typically two repeat units, by iterative addition of acrylates [16]. RAFT polymerization has also been utilized to synthesize multiblock copolymers, by sequential monomer additions, containing as many as twenty individual blocks [12] as well as sequence controlled acrylate oligomers [13]. Other methods involve sequential growth on polymer supports that resemble traditional sequential condensation reactions of amino acids on solid supports [17].

Selective reactivity between electron-donor monomers (styrenes) and strongly electron-accepting monomers (*N*-substituted maleimides), has been extensively investigated and successfully used to control polymer sequence [18–20]. Precise insertion of the maleimide along the polystyrene

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backbone can be achieved multiple times and essentially allows one to insert specific information onto the gross properties of polystyrene. This technique is very versatile and easily incorporated into styrenic polymerization systems [21].

The work presented in this article shows the same versatility for styrenic systems, it exploits the unexpected reactivity of azidomethyl styrene (AMS) in copolymerizations of styrene and 2,3,4,5,6-pentafluorostyrene (PFS) (Scheme 1). Furthermore, reactivity can be further tuned towards greater selectivity by lowering reaction temperature, a very simple parameter to control. It has been possible to quickly polymerize small equivalents of AMS, whilst styrene conversion stays low, to synthesize polystyrene with local areas of high azide functionality compared to the gross polymer structure. By taking active control of reaction temperature whilst polymerization is on-going it has been possible to insert this azide function at multiple points along the backbone. Finally this concept was combined with Lutz type control to start quickly and simply building complex polymer structures. All of which was achieved by using typical Nitroxide Mediated Polymerization (NMP) conditions and commercially available monomers, except for AMS, which is readily prepared through a one-step synthesis [22,23].

2. Results and discussion

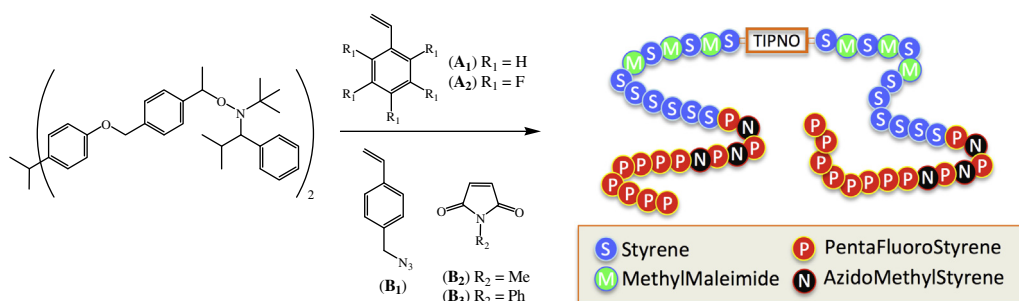
The initial aim of the present work was to copolymerize styrene with small equivalents of AMS via NMP to synthesize copolymers capable of post-polymerization modification, which was successful. However, whilst measuring the kinetics of such copolymerizations it was observed that AMS was being consumed at a faster rate than that of styrene (Fig. 1). To enhance this behavior further the reaction temperature was lowered by 5 °C to 105 °C (Fig. 1), which slowed the rate of polymerization for both monomers as expected, but the reduction was more pronounced for styrene. Similarly, Weck et al. have reported the orthogonal multifunctionalization of random and alternating copolymers based on PFS and styrene derivatives [24]. In their report, it was shown that the nature of the substituent in the para position of the styrene monomer determines the random versus alternating nature of obtained copolymers. Nitrogen containing groups have yielded alternating copolymers.

Apparent rate of polymerization values (k_p^{app}) for styrene and AMS at 110, 105 and 80 °C are listed in Table 1. The most dramatic differences in k_p^{app} are between 110 and 80 °C. For styrene, k_p^{app} decreased from 2.4×10^{-5} to $6.4 \times 10^{-7} \text{ s}^{-1}$, 37.5 times slower at 80 °C, whereas for AMS k_p^{app} decreased from 1.7×10^{-4} to $1.5 \times 10^{-5} \text{ s}^{-1}$, only 11.3 times slower at 80 °C. These observations clearly show that AMS can be more selectively polymerized by simply lowering the reaction temperature, leading to a better defined localization of azide functionality.

Furthermore, GPC analysis (Fig. S2 and S3) showed that molecular weight increased predictably with monomer conversion, with narrow molecular weight distributions maintained throughout. Bimolecular coupling was observed and seemed to become less apparent when reaction temperature was reduced.

These styrenic copolymers contain a localized intensity of azide functionality that can be more defined by lowering the reaction temperature. Therefore, reaction temperature was decreased to 80 °C and the same relative reduction in polymerization rate was observed leading to increasingly defined localized azide functionality. When high conversion of AMS was achieved it was possible to increase the reaction temperature to 110 °C and polymerize styrene at a faster rate (Fig. 1). After a desired conversion of styrene, reaction temperature was reduced back to the starting 80 °C and a second portion of AMS was injected into the reaction mixture. The kinetic plot confirmed the presence of new AMS as well as the behavior for selective polymerization that was previously observed. This shows that AMS insertions can be localized at the start or during the polymerization, as well as showing that multiple insertions can be achieved on the same polymer by actively controlling the reaction temperature. Towards completion of the reaction it appeared as if styrene conversion was decreasing, most likely caused by loss of solvent, which is used as the standard for measuring conversion. This is expected as the reaction runs for several days at high temperature and under a constant flow of N_2 , prompting the use of a solvent that has lower volatility in future investigations. Molecular weight again increased predictably with conversion and low dispersity was maintained throughout (Fig. 1).

As previously mentioned, Lutz and coworkers have achieved sequence control by manipulating donor/acceptor monomer pairs during NMP, making this an attractive concept to try and incorporate into our system. Phenyl



Scheme 1. Schematic representation of the sequence controlled polymer structure based on styrenic and maleimide monomers.

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