

Universal platform for preparation of functional block copolymers

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ABSTRACT

Over the last decade, block co-polymer surfactants have attracted increased interest due to unique physical properties resulting from self-assembly of the polymers into ordered nano-scale structures. To utilize these materials in commercial product development, it is important to be able to establish relationships between polymer structure and product performance. These correlations can be difficult to elucidate due to sample-to-sample variability which arises from variability in the degree of polymerization (DP) and polydispersity (PDI) of each block. Here we describe a synthetic approach which reduces sample-to-sample variability by using atom transfer radical polymerization (ATRP) and yields a universal block copolymer platform which can be used as a precursor for generating systematic libraries of block copolymer surfactants.

Keywords: ATRP, atom transfer radical polymerization, block copolymer, systematic libraries, and surfactant.

1 BACKGROUND AND SIGNIFICANCE

Block copolymers were first synthesized by living anionic polymerization in the 1950s.[1] These materials have become increasingly important for research and development in both academia and industry. Because block copolymers can be designed to contain hydrophilic and hydrophobic segments, they self-assemble to generate a variety of nano-scale structures.[2, 3] The structures range from simple micelles or lamellar to complex gyroid or “plumbers’ nightmare” structures.

Recent studies on block copolymer self assembly have found that nano-scale morphology is highly dependent on block chain length, chain length ratios, polydispersity index, and block composition. Therefore, it is essential to precisely control the degree of polymerization (DP) of each segment in the block copolymer and achieve narrow molecular weight distribution (or low polydispersity index, PDI).

Although living ionic methods achieve this level of control, they suffer from drawbacks including a limited choice of monomers, sensitivity to moisture and carbon

dioxide and side reactions from low level impurities often present in industrial chemicals.

Controlled radical polymerization (CRP) techniques are robust and therefore more suitable for facile synthesis of block copolymers. Atom transfer radical polymerization (ATRP) is particularly suited for block copolymer preparation due to its ability to polymerize a broad range of monomers and its forgiving polymerization requirements.

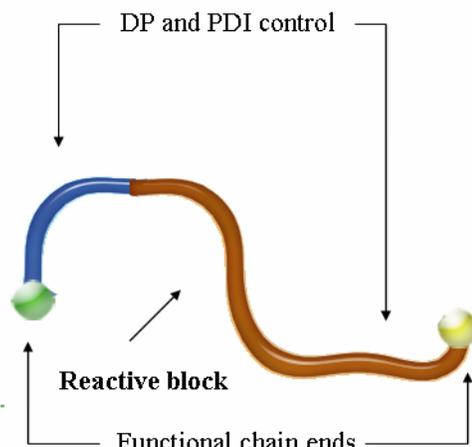


Figure 1: Illustration of the reactive block copolymer prepared by ATRP.

The ATRP process [4, 5] achieves living controlled polymerization by establishing an equilibrium between dormant (alkyl halide, RX) and active (radicals) species. In the presence of monomer, the radicals add across the double bond of the monomer in a process termed propagation. ATRP is ideal for preparation of block copolymers [6] for the following three reasons. First, in ATRP, the DP is pre-determined by setting the monomer-to-initiator ratio prior to starting the polymerization. Therefore, synthetic procedures can be designed to target specific DPs for each block. Second, ATRP results in polymers with narrow molecular weight distribution. Third, polymers prepared by ATRP retain a high level of chain end functionality and few “dead” chains remain upon chain extension from the macroinitiator to the block.

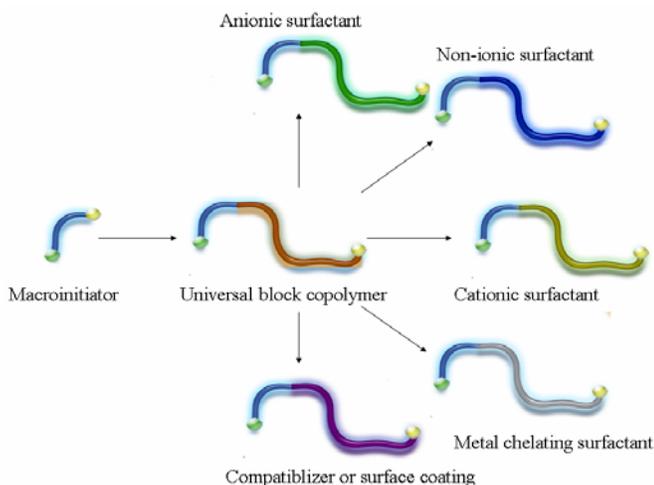
ATRP has proven to be a highly versatile method for preparation of block copolymers due to its compatibility with a wide range of acrylate, methacrylate, styrene, pyridine and acrylonitrile monomers. This wide selection of monomers makes it possible to prepare block polymers with hydrophobic, hydrophilic, fluorescent, metal chelating, reactive, crystalline, non-ionic, anionic or cationic blocks.

It is not surprising that the unique properties exhibited by these types of block copolymers have attracted the interest of scientists in industries across broad market segments. Elucidating correlations between block copolymer structure and product performance, however, is tremendously challenging due to the complexity of block copolymer structure. Within a single block copolymer structure variables include DP of each block and PDI of each block. It is especially challenging when screening the effect of changing functionality within one of the block copolymer segments.

Here we describe a method for producing a universal block copolymer precursor which makes preparation of systematic libraries of block copolymers surfactants with constant DP and PDI for each block and varying functionality possible. This platform makes it possible to customize block copolymers in that the precursor can be converted to a plethora of functionalities. This approach provides researchers with a tool which allows them to quickly design, and prepare, custom block copolymer structures engineered to carry out specific product performance functions.

2 SYNTHETIC APPROACH AND PREPARATION

The universal block copolymer surfactant precursors were synthesized as depicted in Scheme 1. First, we prepared a large lot of macroinitiator by ATRP. Second, the macroinitiator was chain extended with a reactive polymer. Third, the reactive polymer was converted to a variety of functionalities.



Scheme 1: Synthetic approach for preparation of systematic libraries via the universal block copolymer precursor.

The advantage of this systematic approach for preparation of block copolymer libraries is that it allows the scientist to probe the effect of changing polymer functionality while keeping the DP and PDI for each block constant.

2.1 Universal block copolymer platform

For this demonstration, a block copolymer composed of poly(methyl methacrylate) (pMMA) and poly(glycidyl methacrylate) (pGMA) blocks was prepared. The pMMA macroinitiator was prepared by AGRET ATRP.[7, 8] The GPC trace (Figure 2) showed that the macroinitiator had DP = 183 and PDI = 1.15. The pMMA macroinitiator was chain extended by ICAR ATRP [9] with pGMA to form the pMMA-*b*-pGMA block copolymer. The GPC trace of the block copolymer showed that the pGMA block had DP = 50 and the block copolymer has PDI = 1.17. The clean chain extension and the high efficiency of initiation is reflected by the symmetrical GPC curve and the low PDI of the segmented copolymer.

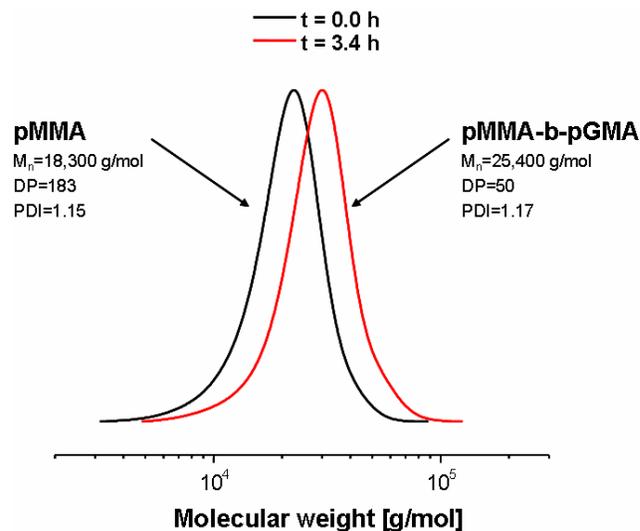


Figure 2: GPC trace of the macroinitiator and the universal block copolymer.

The pGMA block contains a reactive polymer where each monomer unit contains a pendant epoxy group. We chose to utilize epoxy chemistry because it is compatible with ATRP polymerization systems and epoxide chemistry allows for conversion of the segment to a multitude of functionalities.[10-12] Figure 3 shows a selection of reactions which can be performed.

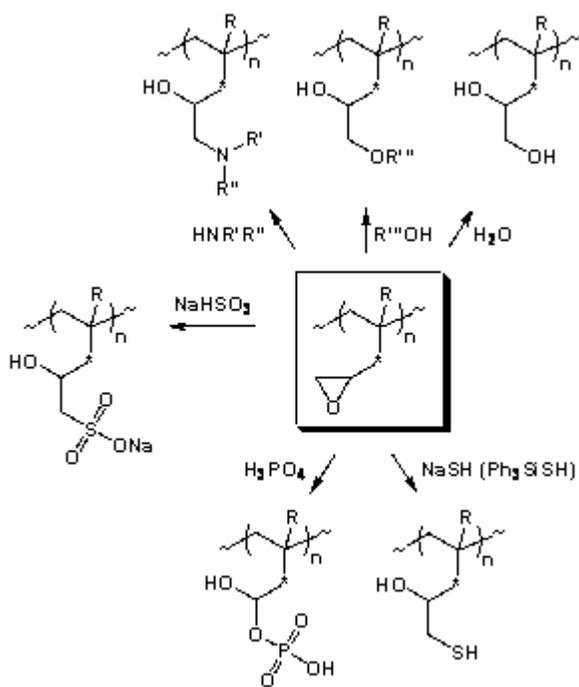


Figure 3: Selected reactions for conversion of epoxide group to functionality.

2.2 Advanced catalysts and purification

The recent discoveries of the novel ATRP initiation techniques ARGET and ICAR make it possible to carry out ATRP with very low catalyst concentrations (in the ppm range). Tris(2-pyridylmethyl)amine (TPMA) and hexamethylated tris(2-aminoethyl)amine (Me_6TREN) have emerged as the two “champion” ligands for ARGET and ICAR ATRP. With 1 gram of TPMA or Me_6TREN ca. 1000 separate ICAR ATRP reactions can be carried out on the 5 gram scale. In addition, the copper (I) complexes of these two ligands broaden the range of monomers and solvents that can be employed in an ATRP. TPMA can be used in various solvent systems including protic and aqueous media.[13]



Figure 4: Image of universal block copolymer precursor before and after purification with ATRPpure resin and after drying as a powder.

Removal of the ATRP catalyst from the polymer is important for commercial applications.[5, 14] The copper catalyst can easily be removed from ARGET and ICAR reactions by stirring the polymer in the presence of ATRPpure catalyst removal resin. Figure 4 shows the polymer before and after purification with ATRPpure resin. The greenish color present in the solution (left) is from the ATRP catalyst. The catalyst is completely removed after treatment with the ATRPpure resin (right). Pure polymer can be decanted easily from the purification resin. The purified sample was dried to give the white polymer powder also shown in Figure 4.

3 CONCLUSIONS

It is clear that block copolymers will play a significant role in improving the performance of tomorrow’s commercial products. This emerging opportunity will be catalyzed by access to both systematic libraries of block copolymers and customizable platforms for tailoring block copolymer properties. Although the advances described in the paper make a significant contribution toward these ends, there are a multitude of polymer compositions and architectures which access to systematic libraries would improve the efficiency of utilization in commercial product development. Our future work will focus on expanding access availability of systematic libraries of well-defined materials.

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