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Controlled emulsion polymerization of styrene and methylmethacrylate in the presence of amphiphilic tertiary amine *N*-oxides

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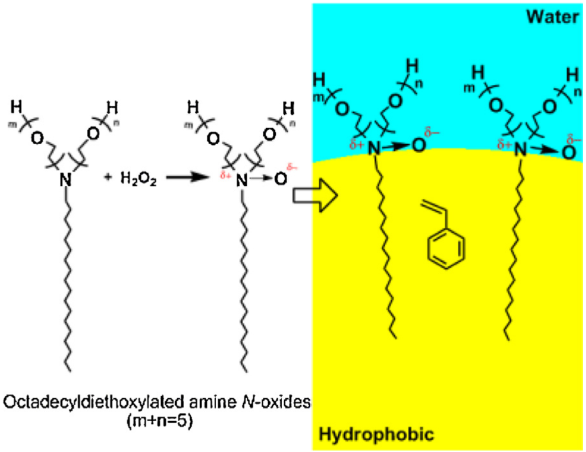
HIGHLIGHTS

- Poly(methylmethacrylate-styrene) block copolymers were synthesized by AO-1805.
- AO-1805 acted both as a surfactant and a mediator simultaneously.
- AO-1805 provides a novel regulation for radicals.

GRAPHICAL ABSTRACT

Synthesis and the interface of styrene micelle with octadecyldiethoxylated amine *N*-oxides (AO1805).



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ABSTRACT

Poly(methylmethacrylate-co-styrene) and poly(methylmethacrylate-styrene) block copolymers were synthesized based on amphiphilic tertiary amine *N*-oxides (AO-1805, EO = 5) with an ultra high molecular weight (Mn > 1800000, PDI = 1.5), in which AO-1805 acted both as a surfactant and a mediator simultaneously. It was found to tailor the different copolymers varied with monomer feeding way, which AO-1805 provides a better mediated performance. Experimental results from DFT calculations and the time-resolved absorption spectroscopy propose the polymerization mechanism and confirm that AO-1805 provides a novel regulation for radicals.

1. Introduction

Block copolymers have received much attention as self-assemble to form various ordered nanostructures, in addition to

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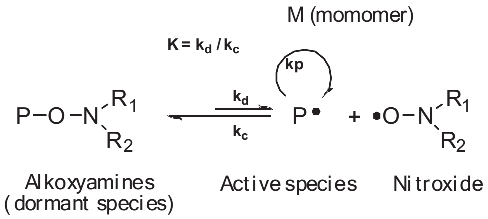
two block chains phase-segregate to yield various nanostructures such as lamellar, hexagonally packed cylinder, spheres arranged in body centered cubic lattice, double gyroid and hexagonally perforated lamellar in bulk as well as in solution [1,2]. A synthetic method of block copolymers is a sequential anionic polymerization with different monomers, however, either rigorous condition or complex process control is required in the polymerization. Emulsion polymerization has been an important and widely used process for the manufacture of polymer products, which is not competent for preparing block copolymers because of the radical performance. In fact, the controlling of the radicals in order has recently been the subject of many investigations and still there is no consensus on controlled radical polymerization (CRP) in water-based systems. Nitroxide-mediated polymerization (NMP) is a very attractive CRP system, in which its process control relies on reversible capture of the propagating species by nitroxides with formation of dormant chains (alkoxyamines) (Scheme 1) during homogeneous polymerization [3].

Since the introduction of 2,2,6,6-tetramethyl-1-piperidinyl-1-oxy (TEMPO) in the controlled polymerization by Julien et al. [4], a great deal of contributions have been made to expand nitroxide-mediated polymerization (NRP) through the employment of miscellaneous nitroxides that a clear picture of the mechanism involved in the polymerization mediated by TEMPO has been shown. Recently many workers have directed their research toward NRP in aqueous dispersed media [5], one of the most difficult obstacles is higher temperature (125–145 °C) for nitroxides in shifting the equilibrium between alkoxyamines and nitroxide [6,7]. As a result, the compatibility of nitroxides with water and the partition coefficients between the various phases is to be of primary criteria. Successful emulsion NRP requires the absence of significant monomer droplet nucleation in emulsion NRP process and nitroxides could be capable to diffuse across the aqueous phase to the particles. The relative progress has been achieved with amino-TEMPO and acetoxy-TEMPO respectively due to their partitioning characteristics between the oil and aqueous phases [8–10], and the appropriate emulsified system and surfactants, such as anionic, nonionic and cationic surfactants have been reported to form the polymer particles in emulsion NRP. Charleux and co-workers have developed an ab initio emulsion NRP system that relies on self-assembly into micelles of SG1-terminated poly(sodium acrylate)-based amphiphilic diblock copolyme [11]. The seeded emulsion NRP of styrene at 125 °C using an oil phase low MW TEMPO-based alkoxyamine and anionic surfactant aerosol MA-80 has reported with considerable control/livingness, though the MWDs would be relatively broad (Mw/Mn ≈1.45) [12].

Recently, we have proposed a mediated emulsion polymerization based on amphiphilic tertiary amine *N*-oxides which acts both as a surfactant and a mediator simultaneously [13]. This paper presents octadecylamine ethoxylates (AO-1805, EO = 5) as a surfactant and a mediator simultaneously for controlling emulsion polymerization of styrene and methylmethacrylate. To examine the nature of emulsion NRP with AO-1805, the prediction program and simulation of the AO-1805 mediated polymerization of styrene have been used to study a stabilizing role of AO-1805. Experimental results indicate that this method takes the advantage of the interfacial characteristics of AO-1805 to form micelles, and show a novel "living" peculiarity based on the characteristics of a weak radical.



Scheme 1. The reversible capture of the propagating species by nitroxides with formation of dormant chains (alkoxyamines).

2. Experimental

2.1. General methods and materials

All reactions were carried out under an oxygen-free argon atmosphere in a stainless steel autoclave. All solvents were purified by a MBraun SPS system. $^{13-}$C NMR spectra of polymer samples were recorded on a Bruker AV400 (FT, 100 MHz for $^{13-}$C) spectrometer in $CDCl_3$. The molecular weight and the molecular weight distribution of polymers were measured by means of gel permeation chromatography (GPC) on a TOSOH HLC-8220 GPC instrument. Tg was measured through differential scanning calorimetry (DSC) analyses, carried out on a Mettler TOPEM TM DSC instrument under a nitrogen atmosphere.

2.2. Computational details

All DFT calculations were performed with the Gaussian 09 program. In the geometry optimizations, the 6-31G* basis set was used for H, C, and N atoms. Geometries of all the species were fully optimized without symmetry constraints. The transition states were ascertained by a single imaginary frequency in the correct mode. The minima on the reaction potential energy surface were verified to have all real frequencies only. Population analysis was carried out by the natural bond orbital (NBO) formalism.

2.3. Emulsion polymerization of methylmethacrylate and styrene with AO-1805

All experiments were carried out under argon using octadecyldiethoxylated amine oxides (AO-1805) both as the mediator and emulsifier simultaneously. AO-1805 was prepared by oxidation of octadecyldiethoxylated amine (A-1805) in the presence of H_2O_2 with control of the molar ratio of H_2O_2 to A-1805, and a subsequent anion nonaqueous titration procedure was used to determine the precursor free amine in the presence of amine oxide. Details of the reaction were conducted as follows: A-1805 (10 g, 0.02 mol) was dissolved in water (25 ml) and heated up to 75 °C to ensure complete dissolution. Then H_2O_2 (27 wt%, 2.77 g, 0.022 mol) was slowly dripped into the solution in half an hour and heated again at 75 °C for 6 h. The further heating process under vacuum was followed to remove the residual H_2O_2, and the conversion of A-1805 was 93-95%. Polystyrene, poly(methylmethacrylate-*co*-styrene) or poly(methyl- methacrylate-styrene) block copolymer were prepared by the AO-1805-mediated emulsion polymerization in a 300 ml stainless steel autoclave. AO-1805 (3.25 g, 0.0065 mol), A-1805 (0.165 g, 0.033 mol), H_2O_2 (27 wt%, 0.045 g, 0.0365 mol), freshly distilled monomers (methylmethacrylate and styrene) (65 g) and deionized water (100 ml) were placed in a deoxygenated reactor with nitrogen and stirred at 350 rpm for 30 min. Then, the system was heated to 55 °C and kept a certain time for finishing the emulsion polymerization, and the final reactant was diluted and purified with ethanol to remove AO-1805 and the residual monomers.