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RAFT ab initio emulsion copolymerization of γ-methyl-α-methylene-γ-butyrolactone and styrene

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ABSTRACT

RAFT ab initio emulsion copolymerization of γ-methyl-α-methylene-γ-butyrolactone (MeMBL) and styrene with various monomer ratios was investigated with PAA_{20}-PS_5 trithiocarbonate being mediator and surfactant at 70 °C. The polymerization was fully controlled as evidenced by stable latexes, well predicted molecular weights and low PDIs about 1.2 when [MeMBL]:[St] $\leq$ 1:2. However, in the case of [MeMBL]:[St] = 1:1, the molecular weight became out of control due to gel effect of RAFT reactions. The relatively water-soluble MeMBL was found to dramatically influence the polymerization kinetics and copolymer properties, as evidenced by (1) No inhibition period was observed; (2) The copolymer compositions in the early stage of polymerization were much higher than those predicted by the Mayo-Lewis equation in the case of [MeMBL]:[St] = 1:2, leading to the formation of linear gradient copolymer. (3) T_gs of the copolymers from emulsion copolymerization were higher than those from bulk copolymerization. It was concluded that we could synthesize the gradient copolymer with preset molecular weight and low PDI in RAFT emulsion polymerization, T_g of which should be much higher than 100 °C.

1. Introduction

Chemical compound derived from biomass is becoming increasingly important in terms of sustaining development strategies. γ-Methyl-α-methylene-γ-butyrolactone (MeMBL), being a cyclic analog of ethyl methacrylate, was reported 50 years ago [1]. However, a commercially attractive synthesis process had not been available until DuPont recently developed a two-step catalytic process for MeMBL synthesis from levulinic acid, a chemical intermediate readily derived from biomass [2,3]. This process allows manufacturing MeMBL on an industrial scale from renewable sources. MeMBL possesses structural features similar to those of MMA and is able to polymerize in a similar manner, thus it is potentially a good substitute for MMA. For example, poly(MeMBL) exhibits excellent solvent resistance to common organic solvents [4]. More interestingly, poly(MeMBL) has a significantly higher glass transition temperature than PMMA (210–227 °C [5,6] vs. 104 °C [7]). Theoretically, incorporation MeMBL into PS, PMMA, or PVC via copolymerization could effectively increase their T_gs and thus improve the thermal properties.

The polymerization of MeMBL receives more and more attentions. Suenaga et al. [4] undertook a study of radical, anionic, and group-transfer polymerization of MeMBL and solubility properties of the resulted polymers but without polymerization and molecular weight data. Cockburn et al. [8,9] systematically investigated the free radical bulk copolymerization kinetics of MeMBL with styrene, methyl methacrylate and *n*-butyl acrylate by the pulsed laser polymerization (PLP)-size exclusion chromatography (SEC) technique, and the results showed that the propagation kinetics of MeMBL and MMA were very similar. The dispersion copolymerization of MeMBL and MMA was also investigated, which offered some insight into the nature of nucleation and particle growth in dispersed systems [10]. Chen at el. polymerized MeMBL via metal-mediated coordination polymerization [6], silylium-catalyzed polymerization [5], Lewis pair polymerization (LPP) [11], anionic polymerization [12], and conjugate-addition organopolymerization [13].

Controlled/living radical polymerization (CLRP), including nitroxide mediated polymerization (NMP) [14], atom transfer radical polymerization (ATRP) [15] and reversible additio–fragmentation chain transfer (RAFT) [16] has been a powerful tool to precisely synthesize (co)polymer with predicted molecular weight, narrow molecular weight distribution and well-defined complex chain microstructures like block and gradient copolymer in mild conditions. RAFT emulsion polymerization not only is more desirable in a commercial application but also offers an effective method to suppress the irreversible termination with little cost of the polymerization rate due to the radical segregation effect [17–22], which is particularly crucial in the synthesis of high molecular weight polymer

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[23,24]. Qi et al. [25] studied the miniemulsion homopolymerization of MeMBL and RAFT miniemulsion copolymerization of MeMBL with styrene. It was evidenced that the homogenous nucleation occurred in the miniemulsion homopolymerization of MeMBL, as MeMBL is a monomer with rather high water solubility ($\sim$9 wt% based on water, at room temperature). To suppress the homogeneous nucleation of MeMBL, the RAFT miniemulsion copolymerization of styrene and MeMBL was carried out with the oil-soluble initiator. The polymerization rate was found to be lower than that of the bulk polymerization. Large deviation in molecular weight from theoretical predictions was observed and was ascribed to the employment of PS standards of GPC method. After an extensive investigation for over one decade, RAFT polymerization has been able to be successfully employed in ab initio emulsion polymerization [24,26–36]. Using a carefully designed amphiphilic macroRAFT agent, which served as both surfactant and RAFT agent, and tuning the self assembling properties of the amphiphilic macroRAFT agent turned out to be crucial to remain a stable colloidal system and to obtain the well-defined structures of the resulted polymer in the polymerization of styrene [24] and *n*-butyl acrylate [32].

In this work, we explored the RAFT ab initio emulsion copolymerization of MeMBL and styrene. Particularly, the effect of MeMBL, being a monomer with rather high water solubility, on the RAFT ab initio emulsion polymerization and T_gs of the products were investigated.

2. Experimental section

2.1. Materials

Acrylic acid and styrene were distilled under reduced pressure prior to polymerization. MeMBL was purchased from TCI Japan and the inhibitor was removed by passing it through an alumina column. Potassium persulfate (KPS, >99%), 4,4′-azobis-(4-cyanopentaoic acid) (V501, >99%), 2,2′-azobis-(isobutyronitrile) (AIBN, >99%), sodium hydroxide (NaOH, >99%), 1,4-dioxane (>99%), cyclohexane (>99%) and methanol (>99%) were directly used without further purification. The small RAFT agent, 2-(((dodecylsulfanyl) carbonothioyl)sulfanyl)propanoic acid (>98%), was synthesized and purified according to the literature procedures [30].

2.2. Synthesis of poly(acrylic acid)$_{20}$-b-poly(styrene)$_5$ trithiocarbonate macroRAFT agent

The poly(acrylic acid-*b*-styrene) trithiocarbonate macroRAFT agent was synthesized by a two-step solution polymerization. First, a solution containing 3.01 g (8.6×10^{-3} mol) of the small RAFT agent, 0.20 g (7.1×10^{-4} mol) of V501, 12.51 g (0.17 mol) of acrylic acid, and 86 g of 1,4-dioxane was introduced to a three-neck round flask, and the reaction proceeded with stirring at 80 °C for 2 h after deoxygenization. The monomer conversion was almost 100%. The flask was then cooled to room temperature, and another solution containing 10.32 g (9.9×10^{-2} mol) of styrene, 0.20 g (7.1×10^{-4} mol) of V501, and 32 g of 1,4-dioxane was added. The polymerization was started at 80 °C after deoxygenization and carried on for 12 h. The conversion of styrene was about 50%. The resulted macroRAFT was collected by precipitation of the mixture in cyclohexane and then dried under vacuum at 45 °C.

2.3. Synthesis of poly(MeMBL-co-St) via RAFT ab initio emulsion copolymerization

Taking the experiment of [MeMBL]:[St] = 1:2 as an example, 0.93 g (4×10^{-4} mol) of the macroRAFT agent was dissolved in 45.44 g of deionized water without neutralization, the aqueous pH value was about 3.0. Then 8.05 g (7.7×10^{-2} mol) of styrene and 4.34 g (3.9×10^{-2} mol) of MeMBL (20% solid content based on total latex) were mixed with the aqueous solution in a 100 mL four-neck round flask. The emulsion was stirred at room temperature with highly pure nitrogen purged for 30 min and then immersed in a thermostatic water bath at 70 °C. The initiator potassium persulfate (KPS, 0.02 g, 8×10^{-5} mol, in 3.12 g of deionized water) was injected to start the polymerization. After 20 min, sodium hydroxide (NaOH, 0.06 g, 1.6×10^{-3} mol, in 3.01 g of deionized water) was injected slowly to partly neutralize the macroRAFT (the molar ratio of added NaOH over acrylic acid of macroRFAT was 4:20) to suppress the possible particle coalescence [24,36]. Samples were withdrawn during the process for gravimetric, GPC, and Malvern ZETASIZER analysis. During the polymerization, the stirring rate was remained to be 350 rpm.

2.4. Synthesis of poly(MeMBL-co-St) via RAFT bulk copolymerization

8.33 g (8×10^{-2} mol) of styrene, 8.97 g (8×10^{-2} mol) of MeMBL, 0.03 g (1.8×10^{-4} mol) of AIBN, and 0.22 g (6.3×10^{-4} mol) of the small RAFT agent were mixed, then dispensed to glass tubes (diameter of 4 mm, thick of 1 mm) and deoxygenated. The tubes, sealed with septa, were bathed in 70 °C water and removed at the preset time intervals. The reactions were quenched by cooling the tubes in an ice bath and then adding hydroquinone/tetrahydrofuran (THF) solution. The resulted samples were precipitated in methanol and solid polymers were collected by removing the solvent and residual monomers.

2.5. Measurements

2.5.1. NMR analysis

The structure of the macroRAFT agent was determined by ^{1}H-NMR 500 MHz using DMSO-d$_6$ as solvent on a BRUKER Avance DMX 500 spectrometer. ^{1}H-NMR signals were assigned as follows (in ppm): 0.85 (3H, $-CH_3$ of $-C_{12}H_{25}$ chain moiety), 1.04 (3H, $-CH_3$ of $-CHCH_3(COOH)$ chain moiety), 1.23 (18H, $-CH_2(CH_2)_9CH_3$ of $-C_{12}H_{25}$ chain), 1.52 ($-C-CH_2-C-$ of PAA-PSt chain), 2.21 ($-CH(COOH)-$ of PAA chain), 7.01 (25H, -Ph-H of PSt chain), 12.24 (21H, $-COOH$ of PAA chain), 1.76, 3.58 (H of impurities 1,4-dioxane). The signal at 0.85 ppm (3H, $-CH_3$ of $-C_{12}H_{25}$ chain moiety) was used to estimate the composition. The poly(acrylic acid-*b*-styrene) trithiocarbonate macroRAFT agent had 20 acrylic acid units (12.24 ppm, 21 H, which contain one H from the small RAFT agent) and 5 styrene units (7.01 ppm, 25 H). The composition of poly(MeMBL-*co*-St) was determined by ^{1}H-NMR using DMSO-d$_6$ or THF-d$_8$ as solvent with tetramethylsilane (TMS) as a reference. Chemical shift from the proton at the gamma carbon (attached to the exocyolic methyl group) of MeMBL was in the region of 3.8–4.6 ppm, and which from the phenyl protons of St were in the region of 6.3–7.5 ppm.

2.5.2. Monomer conversion

Monomer conversion was measured by gravimetry.

2.5.3. pH value measurement

The initial pH value of aqueous phase was detected by a pH-meter (LEICI PHS-2C). The electrode type was E201-4.

2.5.4. GPC analysis

After removing the residual monomers and solvent, the dried polymer samples were dissolved in THF, which contained 2 wt % 1 mol/L hydrochloric acid aqueous solution to mask $-COOH$ group interactions with GPC columns [37]. Most polymers formed at different conversions in the case of [MeMBL]:[St] = 1:1 and 2:1 are