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Synthesis of hydroxyl-terminated polybutadiene bearing pendant carboxyl groups by combination of anionic polymerization and blue light photocatalytic thiol-ene reaction and its pH-triggered self-assemble behavior

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ABSTRACT

Polybutadiene with the simultaneous presence of hydroxyl end-groups and pendant carboxyl side groups was successfully synthesized by combination of living anionic polymerization and blue light photocatalytic thiol-ene "click" reaction. Firstly, hydroxyl-terminated polybutadiene (HTPB) with high content of 1,4-butadiene unit was synthesized by living anionic polymerization using hydroxy-protected initiator, and followed by de-protection. Then, double bonds in backbone of HTPB were modified into pendant carboxyl side groups by blue light photocatalytic thiol-ene "click" reaction using $Ru(bpy)_3Cl_2$ and *p*-toluidine as photoredox catalysts. The blue light photocatalytic thiol-ene reaction exhibit high-efficiency, and all the unsaturated bonds were modified after reacting for 5 h, in spite of that in-chain double bonds in 1,4-butadiene units are much less reactive than vinyl groups in 1,2-butadiene units. When all the double bonds were modified, the structure of resulting polymer can be deemed as carboxyl functionalized hydroxyl-terminated polyethylene. Furthermore, the solution properties of resulting polymer have been investigated by various technologies. The results showed carboxyl functionalized hydroxyl-terminated polyethylene experience a dissolution-assembly-aggregation transition process with pH value of solution decreased from 12.0 to 2.0. The mechanism of this pH-triggered phase transition behavior was supposed to depend on the ionization of carboxyl side groups at varying pH values.

1. Introduction

Hydroxyl-terminated polyolefins are widespread used in various fields, as their properties can be tailored in a wide range by tuning the molecular weight, microstructure, and functional groups [1–3]. Among them, hydroxyl-terminated polybutadiene (HTPB) attracted growing interest, due to their fascinating chemical and physical properties, such as low surface energy and low-temperature flexibility. Up to now, HTPB has found range of usability in various fields, such as adhesives, polyurethanes, and fuel binder in solid propellants [4–10]. However, the major drawback of HTPB is its poor compatibility with polar components, which is attribute to its weak polar backbone, where nearly all the groups are nonpolar except for the end groups [11,12]. Predictably, such inherent shortcoming severely limits their practical applications in industry.

To date, several modification strategies have been proposed to endow HTPB with polarity, because of their larger breadth of applications in comparison with the nonpolar HTPB [13]. One strategy is using hydroxyl end-groups as reactive groups, to initiate polymerization of polar functional monomers, and form block copolymers with polar segments. For instance, the synthesis of PCL-*b*-PB-*b*-PCL, PEO-*b*-PB-*b*-PEO, as well as P(THF-*co*-PO)-*b*-PB-*b*-P(THF-*co*-PO) reported by our group recently [5,14,15]. Drawbacks of this strategy are limited range of polar monomers can undergo polymerization and require rigor react conditions, for example oxygen and moisture free. The other strategy is using double bonds as reactive groups. This strategy provided a facile platform for the preparation of functional polybutadiene, and received growing interesting during the past years, for instance, the epoxidation of HTPB. Unfortunately, epoxidation need precision control of reaction conditions in order to obtain high epoxidation degree [16].

In recent years, thiol-ene "click" reaction was recognized as a powerful approach for the post-functionalization of unsaturated polyolefins with functional groups, due to its high efficiency and

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compatibility with polar functional groups [17]. Various of thiol containing compounds were used to functionalize unsaturated polyolefins, e.g. mercaptoethanol, mercaptoacetic acid, as well as cysteine derivatives [18–22]. In general, thermal or UV light was required to induce thiol-ene "click" reaction by using corresponding radical initiator [23–28]. Unfortunately, both thermal and UV light are harsh and uneconomic conditions for the functionalization of polymers. Recently, thiol-ene reaction was reported can be initiated at room temperature by visible light using novel visible light absorbing transition metal photocatalysts, and has become widely available for the synthesis of small molecular compounds [17,29]. As for polymers, Cyrille Boyer and Helmut Schlaad reported the thiol-ene modification of poly(1,2-butadiene) using visible light, and the results showed that all double bonds were converted in a short time [30,31]. Considering that the pendant vinyl groups in poly(1,2-butadiene) are 10 times more reactive to thiol than in-chain double bonds, it is very necessary and significant to investigate the modification of polybutadiene with high content of 1,4-butadiene unit via visible light photocatalytic thiol-ene reaction [32]. Moreover, compared to the tremendous researches on the functionalization of polybutadiene with polar side groups, relatively few studies were focusing on the synthesis of polybutadiene with the simultaneous presence of active terminal and polar side groups [13].

Considering that carboxyl functionalized polyolefins were reported exhibit the advantages such as enhanced compatibility with polar additives and improved electromechanical properties [33,34]. In this article, inspired by pervious researches, carboxyl functionalized hydroxyl-terminated polybutadiene was synthesized by combination of living anionic polymerization and blue light photocatalytic thiol-ene reaction. Firstly, HTPB with high content of 1,4-butadiene unit was synthesized by living anionic polymerization. Afterwards, blue light was used to induce thiol-ene reaction between HTPB and 3-mercaptopropionic acid. After a well-defined characterization for the structures by using of FTIR, ^{1}H NMR, ^{13}C NMR and SEC/MALLS, the pH-triggered self-assemble behaviors of polymer was investigated by various technologies, such as DLS, TEM, UV–Vis spectroscopy as well as fluorescence spectrophotometer.

2. Experimental

2.1. Materials

Butyldimethylsilyl chloride (97%), 3-chloro-1-propanol (98%) and imidazole (99%) were obtained from Aladdin. 1,3-Butadiene (15 wt% solution in *n*-hexane) was purchased from TCI, and was bubbled with argon before used. Lithium (Li, 98%) was purchased from Acros and stored in sealed preserving condition in glovebox. Epoxyethane (EO) was purchased from Sinopharm Chemical Reagent Co., Ltd. (SCRC) and stored with 3 Å molecular sieves in sealed preserving condition at −30 °C. Tetrabutylammonium fluoride (TBAF) was obtained from Alfa. $Ru(bpy)_3Cl_2$ (98%) and *p*-toluidine (99%) were purchased from Adamas and used as received. 3-Mercaptopropionic acid (98%) was purchased from Macklin. Methanol, *N*-methyl-2-pyrrolidone (NMP, 99%) and other organic solvents were all purchased from SCRC and used without any purification.

2.2. Synthesis of anionic polymerization initiator bearing hydroxy-protecting group

Anionic polymerization initiator 3-*tert*-butyldimethylsilyloxy-1-propyllithium (*t*BDMSOPrLi) was synthesized in two steps according to literature with a few modifications [35]. *t*-Butyldimethylsilyloxy propyl chloride (*t*BDMSOPrCl) was first synthesized by the reaction between 3-chloro-1-propanol and *t*-butyldimethylsilyl chloride in the presence of imidazole. Briefly, 3-chloro-1-propanol (11.34 g, 0.12 mol) was added dropwise to a solution of *t*-butyldimethylsilyl chloride (15.07 g, 0.1 mol) and imidazole (8.17 g, 0.12 mol) in 80 mL DMF at 50 °C. After addition, the mixture was allowed to react for 5 h under stir. Then, the mixture was extracted by *n*-hexane. The *n*-hexane solution was washed with distilled water, and further purified by passing column chromatography on silica using cyclohexane as eluent. ^{1}H NMR ($CDCl_3$, δ): 0.08 (6H, $-Si-(C\boldsymbol{H}_3)_2$), 0.92 (9H, $-Si-C-(C\boldsymbol{H}_3)_3$), 3.77 (2H, $-O-C\boldsymbol{H}_2-$), 3.67 (2H, $-CH_2-C\boldsymbol{H}_2-Cl$), 1.97 (2H, $-CH_2-C\boldsymbol{H}_2-Cl$).

In the following step, anionic polymerization initiator *t*BDMSOPrLi was synthesized by the substitution reaction between *t*BDMSOPrCl and metallic lithium. Prior to reaction, all the glasswares were carefully dried to ensure a waterless system. Then, *t*BDMSOPrCl (10 g, 48 mmol) solution in anhydrous cyclohexane was added dropwise to a suspension of Li (3.33 g, 480 mmol) in 50 mL cyclohexane within 60 mins under argon atmosphere at 60 °C. Then, the mixture was allowed to react for another 5 h. After reaction, the supernatant was transferred to a pretreated receiver by internal transfer under argon protection. And a solution of *t*BDMSOPrLi in cyclohexane was obtained and stored in sealed preserving condition in glovebox. The concentration of initiator solution was determined by double titration analyses.

2.3. Synthesis of HTPB via living anionic polymerization

HTPB owning two hydroxyl groups at both ends of chain was synthesized in two steps. Firstly, polybutadiene with one hydroxy end group and another silyl hydroxy-protecting end group (*t*BDMSO-PB-OH) was synthesized by living anionic polymerization using 1,3-butadiene as monomer and *t*BDMSOPrLi as initiator. Prior to polymerization, all the glasswares were carefully dried and charged with argon. Into a Schlenk tube, 1 mL (0.5 mmol) *t*BDMSOPrLi solution (0.5 mol/L) and 13.33 g (36.97 mmol) 1,3-butadiene solution (15 wt% solution in *n*-hexane) were added under argon atmosphere. The polymerization was carried out at 50 °C for 5 h. Then, EO (0.55 g, 12.5 mmol) was introduced, the mixture was sealed off and allowed to react for another 2 h. Finally, the reaction was terminated by the addition of methanol to form hydroxy end group in polybutadiene. The solution was concentrated and precipitated into an excess of methanol to obtain polybutadiene with one hydroxy end group as a white viscous liquid.

In the next step, α,ω-hydroxyl polybutadiene (HO-PB-OH, HTPB) with two hydroxyl groups at both ends of chain was synthesized by the de-protection of above intermediate product. An excess of TBAF was added to a solution of above intermediate product in THF, and the mixture was allowed to react for 24 h at room temperature. After concentrated and precipitated into an excess of methanol, HTPB was obtained as a slight yellow viscous liquid. $M_{n,SEC} = 3240\ g\ mol^{-1}$, $M_w/M_n = 1.06$. FTIR (cm^{-1}): 961 ($-C{=}C-$ in trans 1,4-butadiene units), 915 ($-C{=}C-$ in 1,2-butadiene units), 720 ($-C{=}C-$ in cis 1,4-butadiene units). ^{1}H NMR ($CDCl_3$, δ): 5.41–5.61 ($-C\boldsymbol{H}{=}C\boldsymbol{H}-$ and $-C\boldsymbol{H}{=}CH_2$), 5.02 ($-CH{=}C\boldsymbol{H}_2$), 2.07–2.11 ($-C\boldsymbol{H}_2-$ in 1,4-butadiene units, and $-C\boldsymbol{H}-$ in 1,2-butadiene units), 1.31–1.46 ($-C\boldsymbol{H}_2-$ in 1,2-butadiene units). ^{13}C NMR ($CDCl_3$, δ): 114 ($-CH{=}\boldsymbol{C}H_2$), 128–131 ($-\boldsymbol{C}H{=}\boldsymbol{C}H-$), 143 ($-\boldsymbol{C}H{=}CH_2$), 63 ($-\boldsymbol{C}H_2-OH$).

2.4. Synthesis of carboxyl functionalized hydroxyl-terminated polybutadiene

Carboxyl functionalized hydroxyl-terminated polybutadiene was synthesized by blue light photocatalytic thiol-ene reaction between HTPB and 3-mercaptopropionic acid. HTPB (486 mg, 0.15 mmol, 9 mmol olefin), 3-mercaptopropionic acid (3.92 mL, 45 mmol), $Ru(bpy)_3Cl_2$ (3.40 mg, 4.5×10^{-3} mmol) and *p*-toluidine (30 mg, 0.28 mmol) were dissolved in 6 mL NMP and irradiated by a household blue LED lights bulb (7 W) for a certain time at room temperature. After reaction, unreacted 3-mercaptopropionic acid and NMP were isolated by dialyzed (molecular weight cut off: 1000) against distilled water for 72 h, and final product was obtained by freeze drying. FTIR (cm^{-1}): 1730 ($-C{=}O$ in carbonyl groups). ^{1}H NMR (DMSO-d_6, δ): 12.20 ($-COO\boldsymbol{H}$), 2.49 ($-C\boldsymbol{H}_2-COOH$), 2.66 ($-C\boldsymbol{H}_2-S-$), 1.50 (saturation