



# A simple route to vinyl-functionalized hyperbranched polymers: Self-condensing anionic copolymerization of allyl methacrylate and hydroxyethyl methacrylate



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## ARTICLE INFO

### Article history:

Received 13 February 2015

Received in revised form

20 June 2015

Accepted 24 June 2015

Available online 26 June 2015

### Keywords:

Hyperbranched polymer

Anionic copolymerization

Self-condensing vinyl polymerization

## ABSTRACT

Vinyl-functionalized hyperbranched polymers (HBPs) have attracted much attraction because their pendant vinyl groups can be further modified for a required application. However, the syntheses of these polymers are difficult, because the cross-linking is inevitable during the polymerization reaction. The present work reports a new, facile, one-step strategy for the synthesis of vinyl-functionalized HBPs via the self-condensing anionic copolymerization of commercially available allyl methacrylate and hydroxyethyl methacrylate with a monomer conversion approaching 100% at room temperature. The hyperbranched structures were confirmed by triple-detection size exclusion chromatography. The pendant vinyl groups of the resulting polymer were successfully modified by a “thiol-ene” reaction. This method provides a facile approach for preparing vinyl-functionalized HBPs with excellent monomer conversions under mild conditions, and will be useful in materials chemistry.

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## 1. Introduction

Hyperbranched polymers (HBPs) have received significant attention because of their intrinsic globular structures and unique properties, which include greater solubility, lower viscosity, non-/low entanglement, and large numbers of terminal functional groups compared to their linear analogues [1–8]. Increasing efforts have been focused on the synthesis of vinyl-functionalized HBPs because their vinyl groups provide a reactive handle in subsequent modification for the required application [9–14]. Conventionally, vinyl-functionalized HBPs have been directly synthesized via the polymerization of divinyl monomers. However, undesired cross-linking is inevitable during the polymerization reaction, and soluble polymers are only obtained at low monomer conversions, typically no more than 20% in the case of free-radical polymerization. Even by living radical polymerization, such as atom-transfer radical polymerization (ATRP) or addition–fragmentation chain

transfer (RAFT) polymerization, the monomer conversions are 70% or less [14–16]. Another creative approach is catalytic chain transfer polymerization (CCTP) of divinyl monomers, as reported by Guan et al., who polymerized ethylene glycol dimethacrylate (EGDMA) to prepare HBPs in the presence of an efficient cobalt chain-transfer catalyst [13]. However, this method is limited because the monomer conversions must be maintained at a lower value to prevent the formation of insoluble gels. The most reliable synthetic strategy for vinyl-functionalized HBPs is the selective polymerization of asymmetrical divinyl monomers (ADMs) [17,18]. However, the selective polymerization of ADMs is also challenging because it is impossible to avoid radical addition to the less reactive vinyl functionality [16,19,20]. Moreover, the types of commercially available ADMs are very limited. The development of more efficient methods for the synthesis of vinyl-functionalized HBPs is undoubtedly warranted.

Self-condensing vinyl polymerization (SCVP) is well known to be one of the most efficient approaches for the synthesis of HBPs [21–23]. Unfortunately, this method cannot be applied to the synthesis of vinyl-functionalized HBPs, because no suitable monomer, also referred to as an “inimer,” is available. Herein, we

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overcame these limitations, and first applied the concept of SCVP for the synthesis of vinyl-functionalized HBPs by self-condensing anionic copolymerization (SCACP) of the commercially available monomers hydroxyethyl methacrylate (HEMA) and allyl methacrylate (AMA) (Scheme 1). By this method, vinyl-functionalized HBPs were successfully prepared at very high monomer conversions (approaching 100%). We believe this method offers innovation and insights into the synthesis of functional HBPs.

## 2. Experimental section

### 2.1. Materials

AMA from Aldrich was dried over calcium hydride ( $\text{CaH}_2$ ) and distilled under reduced pressure prior to use. Benzyl alcohol (BA) and allyl methyl ether (AME) from Sinopharm were distilled from  $\text{CaH}_2$  prior to use. HEMA from Aldrich was washed with hexanes ( $3 \times 100 \text{ mL}$ ), salted by addition of  $\text{NaCl}$ , dried over  $\text{MgSO}_4$ , and finally distilled under reduced pressure prior to use. (1-tert-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris-(dimethylamino)-phosphoranylideneamino]-2 $\Lambda^5$ , 4 $\Lambda^5$ -catenadi(phosphazene) ( $t\text{-BuP}_4$ ) from Aldrich was used as received. Toluene from Sinopharm was freshly distilled from sodium/benzophenone, and stored under an argon atmosphere. Other reagents from Sinopharm were used as received.

### 2.2. Characterization

#### 2.2.1. Proton nuclear magnetic resonance ( $^1\text{H}$ NMR)

Nuclear magnetic resonance (NMR) spectra were recorded using a Bruker AR $\times$ 400 NMR spectrometer, deuterated chloroform ( $\text{CDCl}_3$ ) as the solvent, and tetramethylsilane (TMS) as the internal standard.

#### 2.2.2. Triple detection size exclusion chromatography (TD-SEC)

The molecular weight and polydispersity of the samples were obtained by size-exclusion chromatography equipped with online light scattering and viscosity detectors (TD-SEC) at  $35^\circ\text{C}$ . The instrumentation consists of a Waters 1515 Isocratic HPLC pump with 5 mm Waters Styragel columns (guard, HR3, HR4, HR5, and HR6; the molecular weight ranges of the four HR columns are 500–30000, 5000–600000, 50000–4000000, and 200000–10000000  $\text{g mol}^{-1}$ , respectively), a Waters 717 PLUS Autosampler, a Waters 2414 Differential Refractive Index (DRI) detector with a wavelength of 880 nm, a multiangle laser light scattering (MALLS) detector (Wyatt mini-DAWN HELEOS-II) with an 18-angle light scattering detector at a wavelength of 690 nm and 220 W power, a Wyatt Visco Star viscometer detector, and a Waters

Breeze data manager. The eluent was HPLC-grade THF with a flow rate of 1.0 mL/min. The refractive index increments ( $\text{dn}/\text{dC}$ ) determined using a Wyatt Optilab REX ( $\lambda = 640 \text{ nm}$ ) interferometric differential refractometer in batch mode at  $25^\circ\text{C}$  for PAMA is 0.093 mL/g.

### 2.3. Polymerization

#### 2.3.1. Synthesis of linear polymers using BA as the initiator

A typical polymerization procedure was performed as follows: AMA (0.22 g, 1.74 mmol, 40 equiv), BA (4.60  $\mu\text{L}$ , 0.043 mmol, 1.0 equiv), and toluene (0.43 g) were added to a flame-dried and nitrogen-purged round-bottom flask equipped with a magnetic stirrer.  $t\text{-BuP}_4$  (55  $\mu\text{L}$ , 0.043 mmol, 0.8 equiv) was added by a rubber septum with a syringe to start the polymerization at  $25^\circ\text{C}$ . After polymerization, the reaction was terminated with hydrochloric acid/methanol (1/20 v/v). The product was dissolved in THF and precipitated into a large excess of hexane. After the filtration, the polymer was dried under vacuum and stored at  $0^\circ\text{C}$ .

#### 2.3.2. Synthesis of h-PAMA using HEMA as inimer

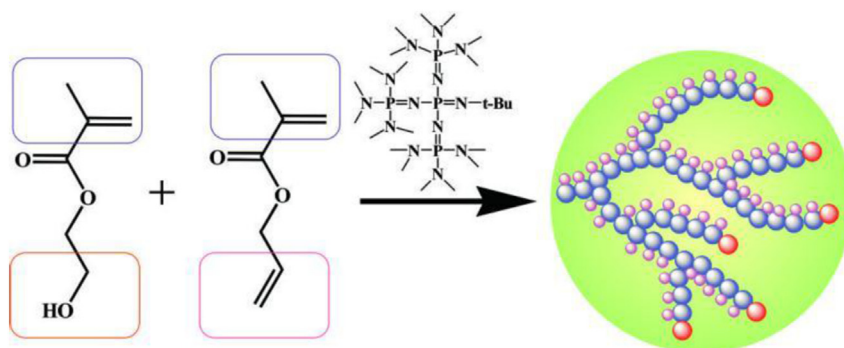
A typical polymerization procedure was performed as follows: AMA (0.24 g, 1.96 mmol, 50 equiv), HEMA (4.6  $\mu\text{L}$ , 0.038 mmol, 1.0 equiv), and toluene (0.50 g) were added to a flame-dried and nitrogen-purged round-bottom flask equipped with a magnetic stirrer.  $t\text{-BuP}_4$  (60  $\mu\text{L}$ , 0.048 mmol, 0.8 equiv in hexane) was added through a rubber septum by a syringe to start the polymerization at  $25^\circ\text{C}$ . After polymerization, the reaction was terminated with hydrochloric acid/methanol (1/20 v/v). The product was dissolved in THF and precipitated into a large excess of hexane. After the filtration, the polymer was dried under vacuum and stored at  $0^\circ\text{C}$ .

#### 2.3.3. Modification of ene-functionalized polymers

0.073 g of poly(allyl methacrylate) (containing 0.58 mmol -ene groups), 0.048 g of AIBN (0.5 equiv. to -ene groups), and 40 equiv. of 2-mercaptoethanol were added into 8.0 g of THF. The mixture was then degassed via three freeze–pump–thaw cycles and subsequently flame-sealed. The ampule was heated for 24 h at  $75^\circ\text{C}$ . The reaction products were poured into diethyl ether. The precipitate was filtered, washed with diethyl ether and dried under vacuum at room temperature.

## 3. Results and discussion

AMA, containing a conjugated methacrylate group and an unconjugated allylic group, is one of the most studied commercial ADMs [14]. It is commonly used as a cross-linking agent in the preparation of coatings, resin foams, and high-water-absorption



Scheme 1. Synthesis of hyperbranched PAMA.

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