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Macroscopic self-assembly of hyperbranched polyesters

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Abstract

We utilized melt polycondensation of 2,2-bis(hydroxymethyl) propionic acid (bis-MPA) and 2-ethyl-2-hydroxymethyl-1,3-propanediol (TMP) to synthesize a hyperbranched polyester core and subsequent substitution by reaction of terminal hydroxyl with benzoyl chloride in DMF in the presence of TEA as the acceptors of HCl. It has been found that well-defined macroscopic structures can be formed via hydrogen bonding and π–π stacking interactions. Meanwhile, the molecular structures, the nature of the solvent, the molecular concentration, the volatilizing ratio of solvent, and self-assembly temperature also affected the self-assembly structures. The type of self-assembly method offers a synthetic route to well-defined one-dimensional organic macrostructures.

Keywords: Hyperbranched polyesters; Synthesis; Self-assembly

1. Introduction

Inspired by nature's ability to create extraordinarily well-defined objects from comparatively simple molecules, chemists have sought to synthesize molecules capable of self-assembling into macroscopic self-assembly structures that have great potential application in biomimetic materials which are formed by organic molecules through a self-assembly procedure in the nature [1,2]. Molecular self-assembly is an aggregating process of molecules in which molecules or parts of molecules spontaneously organize into highly ordered objects and no human intervention is involved. The interactions among self-assembled molecules are weak and non-covalent ones, including van der Waals interaction and Coulomb interaction, hydrophobic interactions and π–π stack, etc. [3–6]. The design and synthesis of new molecules with special self-assembly driving forces is one of the key goals for construction of self-assembly materials. Many efforts have been exerted in exploring the strategies to utilize different self-assembly methods to produce a broad range of intricate self-assembled nano- or micro-structures [7–24]. Yan et al. [25] first reported that the macroscopic molecular self-assembly of an amphiphilic hyperbranched copolymer (HBPO-star-PEO) with a hydrophobic hyperbranched poly(3-ethyl-3-oxetanemethanol) core (HBPO) and many hydrophilic poly(ethylene glycol) arms (PEO) in acetone generated multiwalled tubes millimeters in diameter and centimeters in length. Thus, macroscopic self-assembly offers one of the most general strategies for generating well-defined objects with macroscopic scale. Nevertheless, the details of the events that induce are still not known at the molecular level. Thus, there is a need for design the new molecules to gain insight internal drives into macroscopic structures. Recently, we have synthesized the benzoyl-modified hyperbranched poly(3-ethyl-3-oxetanethanol) (HBPO-B) by reaction of terminal hydroxyl with benzoyl chloride. The macroscopic self-assembly structures of hyperbranched benzoyl-modified poly(3-ethyl-3-oxetanethanol) can be obtained via a simple solvent volatilizing route and generated multiwalled structures with millimeters in diameter and centimeters in length. Besides the molecular structures, the macroscopic self-assembly of hyperbranched benzoyl-modified poly(3-ethyl-3-oxetanethanol) is also affected by other factors, such as the nature of the solvent, the molecular concentration, the volatilizing ratio of solvent, and self-assembly temperature [4]. In this communication, we designed a new hyperbranched polyester (HPE) (as shown in Scheme 1), which has benzoyl-termined groups, from which we investigate the macroscopic self-assembly of HPE-B by a simple solvent volatilizing route.

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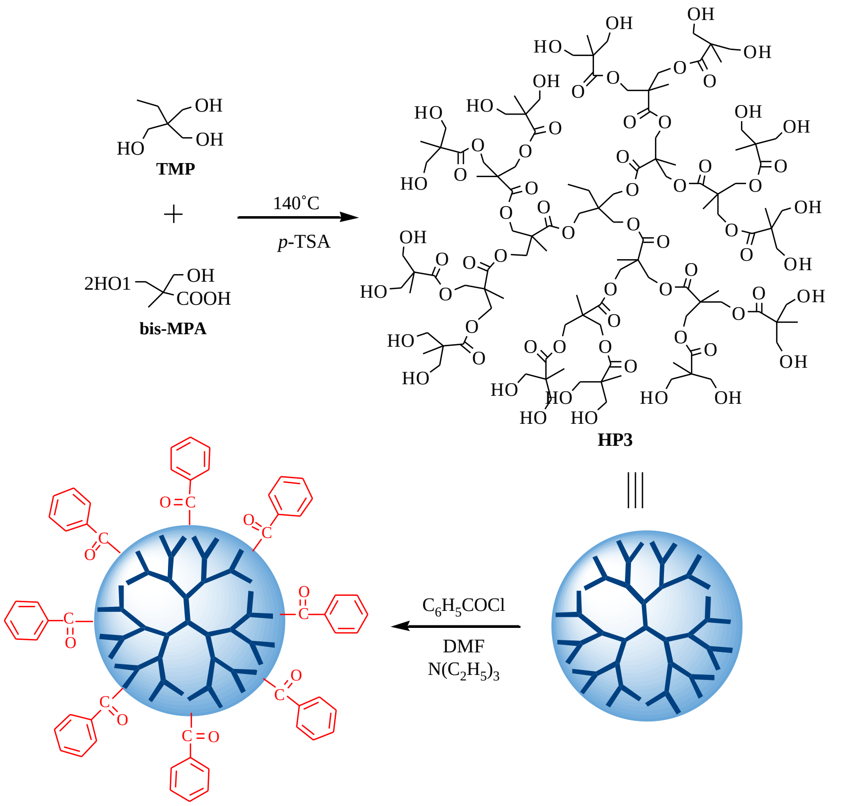


Scheme 1. Reaction scheme for synthesis of hyperbranched polymer and benzoyl-modified hyperbranched polymer (HPE-B).

2. Experimental section

2.1. Materials

Chloroform (reagent grade and analysis grade), acetone (analysis grade), *n*-hexane (analysis grade), dimethylformamide (DMF, analysis grade), triethylamine (TEA, analysis grade) and dimethyl sulfoxide (DMSO, reagent grade) were purchased from East China Chem, Ltd Co. and used as received. 2-Ethyl-2-hydroxymethyl-1,3-propanediol (TMP, 99%), 2,2-bis(hydroxymethyl) propionic acid (bis-MPA), *p*-toluene sulfonic acid (*p*-TSA) were used as received from Acros.

2.2. Synthesis of hyperbranched polyesters (HPE)

All synthetic procedures were made under a dry nitrogen atmosphere. Hyperbranched polyesters–polyol with TMP as a core was prepared by a procedure described in the literature [26,27]. Esterfication was carried out at 140 °C with *p*-TSA as an acid catalyst. The chosen molar ratio of TMP to bis-MPA is 1:21 corresponding to the theortical molecular weight of 2573 g/mol and a hyperbranched polyester with 24 terminal hydroxyl groups. The crude polymer was precipitated from acetone in *n*-hexane and dried under vacuum. FTIR showed no remaining carboxylic acid. ^{1}H NMR ($(CD_3)_2CO$, δ, ppm): 1.10–1.31 ($-CH_3$ and CH_3CH_2C), 2.04–2.08 ($-CH_2OH$), 3.63–3.73 ($-CH_2OH$), 4.10–4.32 ($-COOCH_2-$).

2.3. Synthesis of benzoyls modified hyperbranched polyesters (HPE-B)

Benzoyl groups were attached by reaction of terminal hydroxyl with benzoyl chloride in dimethylformamide (DMF) in the presence of triethylamine (TEA) as an acceptor of HCl. As the reaction proceeds, TEA hydrochloride precipitates from the reaction medium, and its quantity corresponds to consume benzoyl chloride. A precipitate of triethylamine hydrochloride was filtered off, and the solvent was removed under vacuum. A residue was washed several times with cold hexane. The number of hydroxyl groups consumed by benzoyl corresponded to 15, 45 and 75% and the corresponding specimens were designated as HPE-B1, HPE-B2 and HPE-B3, respectively. All the compounds were low-melting materials and soluble in most organic solvents. ^{1}H NMR ($(CD_3)_2CO$, δ, ppm): 1.0–1.3 ($-CH_3$), 2.0–2.1 ($-CH_2OH$), 3.1–3.2 ($-COOCH_2-$), 3.6–3.7 ($-CH_2OH$), 4.10–4.32 ($PhCOOCH_2-$), 7.38–8.17 ($Ph-H$).

2.4. Macroscopic self-assembly of benzoyls modified hyperbranched polyesters (HPE-B)

The macroscopic self-assembly were formed by mixture of benzoyls modified hyperbranched polyesters (HPE-B) and

Table 1
Characteristics of hyperbranched polyester and benzoyl-modified hyperbranched polyester

Compound	M_n (theoretical)	GPC[a]	
		M_n (g/mol)	M_w/M_n
HPE	2573	1979	1.59
HPE-B1	2947	2146	1.61
HPE-B2	3696	2365	1.56
HPE-B3	5094	2595	1.59

[a] As calibrated against linear polystyrene stands with low polydispersity index.

acetone. The concentration of HPE-B controlled in range of 1–150 mg/ml. The solution dropped on a cleared glass with a burette. Then, the glass with HPE on its surface was placed on the bottom of sample bottle that was covered by a plastic membrane with some holes on it to make the solvent volatilize slowly. After several days, the macroscopic self-assembly structures can been seen by naked eyes. The macroscopic self-assembly structures were stable reproducible.

2.5. Analytical equipment

^{1}H NMR and ^{13}C NMR spectra were recorded with an AVANCE DMX-500 NMR spectrometer by using tetramethylsilane (TMS) as internal standard at room temperature. The gel permeation chromatography (GPC) measurements were carried out on a Waters 201 with a µ-styragel column and dimethylformamide (DMF) as an eluent, and the molecular weight was calibrated with standard polystyrene (PS). The microspectroscopy was performed by an optical microscope (type Optiphoto, Nikon Co., Tokyo, Japan).

3. Results and discussion

The synthetic procedure for various polymers is outlined in Scheme 1. Aliphatic hyperbranched polymer (HPE) was firstly synthesized by melt polycondensation of bis-MPA and TMP at a molar ratio of 21/1 using *p*-TSA as catalysis by pseudo one-step synthesis method [26]. The molecular characteristics of synthesized compounds are shown in Table 1. The molecular weight of benzoyl-modified hyperbranched polymers (HPE-B) shows a virtually increase with substitution content, and the experimentally measured molecular weights were systematically lower than the theoretical values obtained from the GPC measurements. However, attempts to obtain 100% substituted molecules were not successful.

The ^{13}C NMR spectrum of HPE is given in Fig. 1. The ^{13}C NMR spectrum exhibits four distinct groups of peaks. The distinct peak at 98 ppm originates from methylene units adjacent to ether bonds. The methylene peak found at 63–70 ppm contains much fine structure due to the fact that carbons with the same chemical surrounding might be situated in different conforms. The quaternary carbons give rise to signals in the region 40–52 ppm. Methyl groups are found at the lowest chemical shifts, around at 15–20 ppm. The repeating unit, bis-MPA, in the hyperbranched polyester can be incorporated into the polymer in three major ways: dendritic (D: 41.8), terminal (T: 50.2) and linear (L: 48.4) repeating units [26]. For an ideal dendritic substance, the degree of branching (DB) is equal to 1. A hyperbranched polymer takes DB values between 0 and 1. According to the Fréchet method [28], the degree of branching (DB) of hyperbranched polymers is given by Eq. (1).

$$\mathrm{DB} = \frac{\Sigma\ \text{dendritic units} + \Sigma\ \text{terminal units}}{\Sigma\ \text{dendritic units} + \Sigma\ \text{linear units} + \Sigma\ \text{terminal units}} \tag{1}$$

The degree of branching (DB) was calculated from the integral values found for the quaternary carbons and determined to be 0.45.

By the reaction between hydroxyl end-groups of HPE and benzoyl chloride, HPE is further transferred into HPE-B1, HPE-B2 and HPE-B3 with adjusting the amount of the benzoyl chloride. ^{1}H NMR data confirmed the chemical

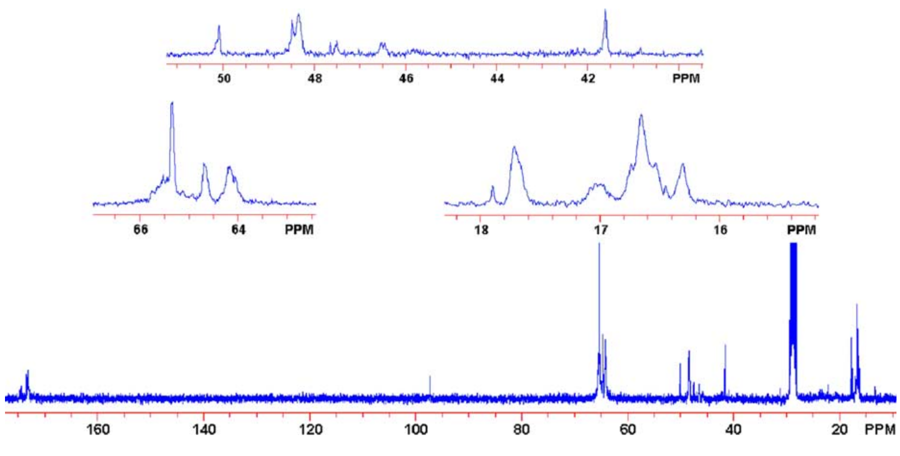


Fig. 1. ^{13}C NMR spectrum of hyperbranched polyesters (HPE) in $(CD_3)_2CO$.

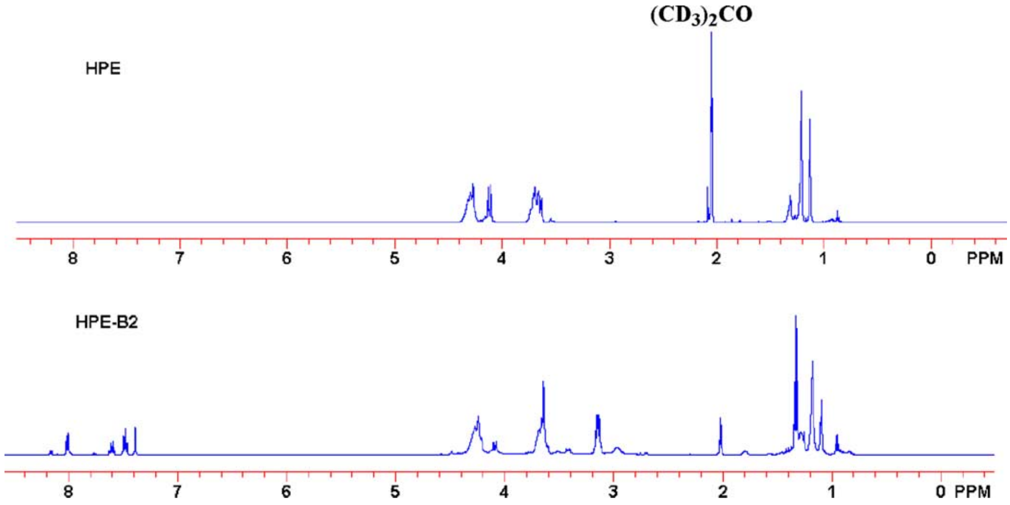


Fig. 2. ^1H NMR spectra of hyperbranched polyesters (HPE) and benzoyl terminal hyperbranched polymer (HPE-B2) ($(CD_3)_2CO$, 25 °C).

composition of the compounds. Fig. 2 shows the typical ^1H NMR spectra for HPE and HPE-B2, which were very similar to each other at the chemical shift from 0 to 5 ppm. The peaks at 7.30–8.20 ppm for HPE-B2 ^1H NMR data indicated the introduction of aromatic structures.

We have combined synthetic hyperbranched molecules (HPE-B) design with solution conditions that favor self-assembly with the solvent volatilizing to produce multi-walled structures with millimeters in diameter and centimeters in length. The macroscopic self-assembly structures are stable reproducible. The assemblies are formed by mixture of HPE-B and acetone. Then, the mixture placed on a glass and making the solvent volatilize slowly. Under optimized conditions, the macroscopic self-assembly structures are the predominant structure of the HPE-B2 and HPE-B3, as seen from the photo of Fig. 3 that obtained by a digital camera. The resultant self-assembly objects can be seen with the naked eye. The diameter of the self-assembly objects approached 0.1 mm, and the average length is about 1 mm. However, in the case of HPE-B1, no obvious self-assembly structures are observed (Fig. 3).

The macroscopic morphology of the self-assembly objects are also observed by optical microscopy. In the case of HPE-B1, a film with many holes on its surface can be observed (Fig. 4(A)), which can be contributed to results of the solvent volatilize. However, tube-like structures can be observed for HPE-B2 and HPE-B3 (Fig. 4(B)). The self-assembly structures can be formed in a wide concentration range from 1 to 1000 mg/ml. Magnification of the self-assembly objects, multiwalled structure can be observed (Fig. 4(C)). To investigate the role of benzoyl groups in the self-assembly procedure and the formation mechanism under which the macroscopic self-assembly structures are formed, we also made some contrastive experiments. First, the hyperbranched molecules (HPE) were used to investigate whether the HPE could self-organize into highly ordered structures or not? It was found that no any self-assembly structures were observed for HPE at same conditions. From these phenomena, we concluded that the benzoyl groups play an important role in the self-assembly procedure. Besides the molecular structures, the macroscopic self-assembly of HPE-B was also affected by other factors, such as the nature of the solvent, the molecular concentration, the volatilizing ratio of solvent, and self-assembly temperature. The further researches on the detail reasons are still proceeding.

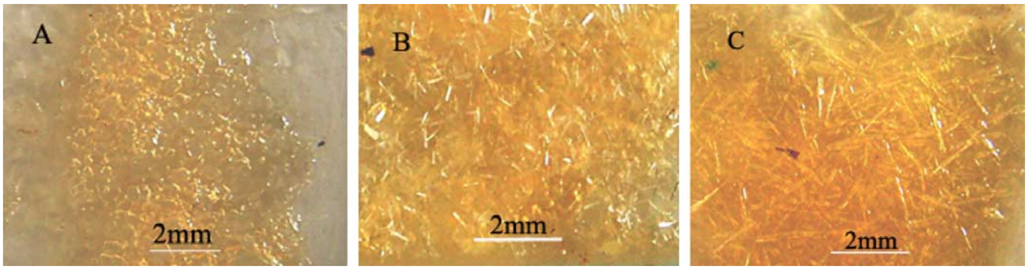


Fig. 3. Macroscopic molecular self-assembly structures obtained from the hyperbranched polyethers (left: HPE-B1, middle: HPE-B2, right: HPE-B3) $CHCl_3$ solution with the concentration at 80 mg/ml (25 °C). The photo was recorded with a digital camera from the bottom of a glass beaker, with white paper as the blackbround. Scale bar, 2 mm.

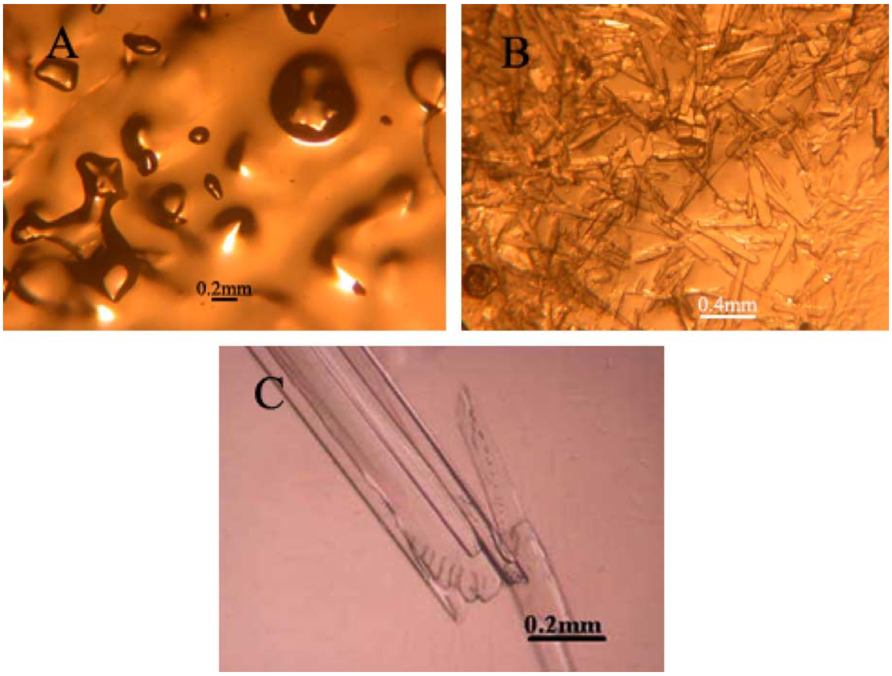
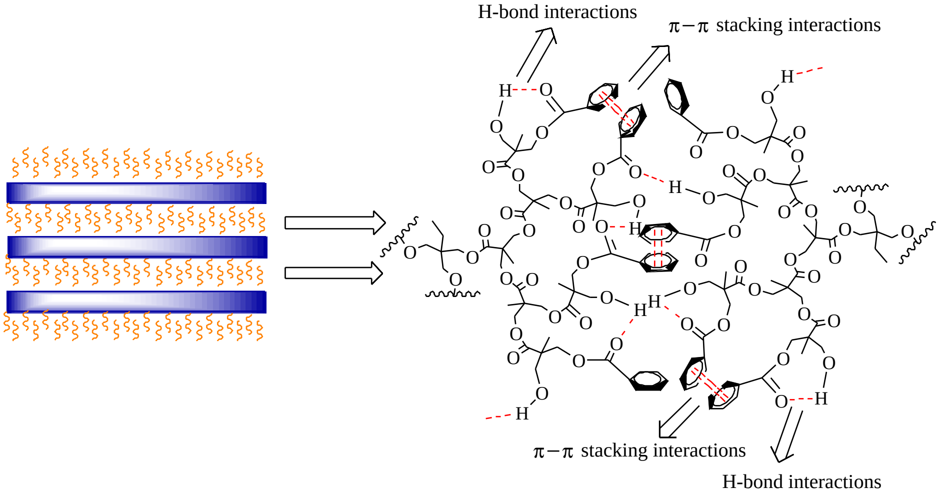


Fig. 4. Optical microspectroscopy image of the self-assembly structures from $(CH_3)_2CO$ with the concentration of HPE-B1 (A) and HPE-B2 at 95 mg/ml. (C) An external screw end of the self-assembly structure from HPE-B2.

To gain insight into the internal structure of the self-assembly structures, we utilize the Scheme 2 to indicate the formation procedure of macroscopic self-assembly structures. During the solvent volatilizing, the HPE cores and benzoyl groups on the external of hyperbranched molecules lead to a spinodal microphase separation for their difference hydrophilic properties. With the aggregation of HPE cores, the distance among hydroxyl to ester groups, hydroxyl groups in HPE, and hydroxyl to carboxyl groups decreases, and facilitates the formation of hydrogen bonds. The hydrogen bonds from OH···O–C and OH···O=C drive the molecular self-assembly process. When the phenyl units are stacked with a certain direction and have an enough short distance, π–π stacking interactions can be formed among them. The π–π stacking interactions can further drive the molecular self-assembly process and strengthen the macroscopic self-assembly structures [4–6,23]. The type of self-assembly structures described here offers a new synthetic route to well-defined organic macrostructures.



Scheme 2. The possible mechanism of formation the macroscopic self-assembly structures driving by hydrogen bonds between H and O atoms and π–π stacking interactions among the phenyl groups.

4. Conclusions

To obtain benzoyl-terminated hyperbranched polymers (HBPO-B), we utilized cation ring-opening polymerization to synthesize a hyperbranched poly(3-ethyl-3-oxetanemethanol) core and subsequent substitution by reaction of terminal hydroxyl with benzoyl chloride in DMF in the presence of TEA as the acceptors of HCl. It has been found that well-defined macroscopic structures can be formed via hydrogen bonding and π–π stacking interactions. These structures can be formed in acetone with a wide concentration range. Meanwhile, the molecular structures, the nature of the solvent, the molecular concentration, the volatilizing ratio of solvent, and self-assembly temperature are also affected the self-assembly structures. The type of self-assembly described here offers a synthetic route to well-defined one-dimensional organic macrostructures.

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