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Polymer 46 (2005) 9501–9507

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Synthesis and self-assembly of hyperbranched polyester peripherally modified by touluene-4-sulfonyl groups

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Received 13 December 2004; received in revised form 6 July 2005; accepted 12 July 2005
Available online 8 August 2005

Abstract

In this paper, hyperbranched polyesters (HPs) were synthesized in the molten state from 2,2-bis(hydroxymethyl) propionic acid (bis-MPA) and 2-ethyl-2-hydroxymethyl-1,3-propanediol (TMP) using acid catalysis. The modified hyperbranched polyesters were obtained through the chemical modification of the hyperbranched polyester cores by substituting a controlled fraction of the terminal hydroxyl groups with touluene-4-sulfonyl chloride using triethylamine (TEA) as an acceptor of HCl. The resultant polyesters were characterized by ^{1}H NMR, ^{13}C NMR, FT-IR, UV and GPC and their self-assembly behaviors were investigated. The results revealed that self-assembled structures could be formed in selected solvents (trichloromethane/acetone or trichloromethane/*n*-hexane).

Keywords: Hyperbranched polyesters; Synthesis; Self-assembly

1. Introduction

In the past decades, much attention has been focused on the design and synthesis of molecules in supramolecular network based on non-covalent interactions (such as hydrogen bonding, π–π stacking and/or other weak interactions among molecules) [1], due to their interesting molecular topologies and crystal packing motifs, along with potential applications as functional materials [2–4]. Usually, the reported self-assembled molecules possess well-defined molecular structure, such as small amphiphiles [5], dendrimers [6], linear block copolymers [7] or rodcoil polymers [8]. Simple self-assembly methods can produce a broad rang of intricate self-assembled structures such as nano- or micro-tubes [9], ropes [10], rods [11], rings [7a], vesicles [12], micelles [13]. However, little attention has been paid to the molecular self-assembly of ill-defined polymers such as hyperbranched molecules. Hyperbranched polymers have unique architecture and novel properties, which distinguish them from their linear analogues. The use of hyperbranched polymers for molecular recognition, self-replication, and self-organization based on non-covalent interactions has attracted increasing attention in recent years [14]. Some of works demonstrated that the hyperbranched polymers with amphiphilic core–shell structure conveniently prepared in two synthetic steps exhibit unimolecular reverse micelle properties, i.e. encapsulation and phase transfer of ionic guest molecules in analogy to amphiphilic dendrimers [15, 16]. It has been believed that the intriguing self-assembly properties of hyperbranched polymers are induced by their hydrophobic shell/hydrophilic core structure, and have potential applications as processing modifiers, toughening additives, drug delivery vehicles, synthesis supporting materials, advanced coatings, polymeric electrolytes, and optical wave guide materials [17–19]. Although some significant progresses have been made in the synthesis and applications of hyperbranched polymers, there is still very little detailed information on affect factors for formation of such self-assembly system.

In this contribution, we report on the synthesis of the novel hyperbranched polyesters with touluene-4-sulfonyl terminal branched. The affect factors for self-assembly

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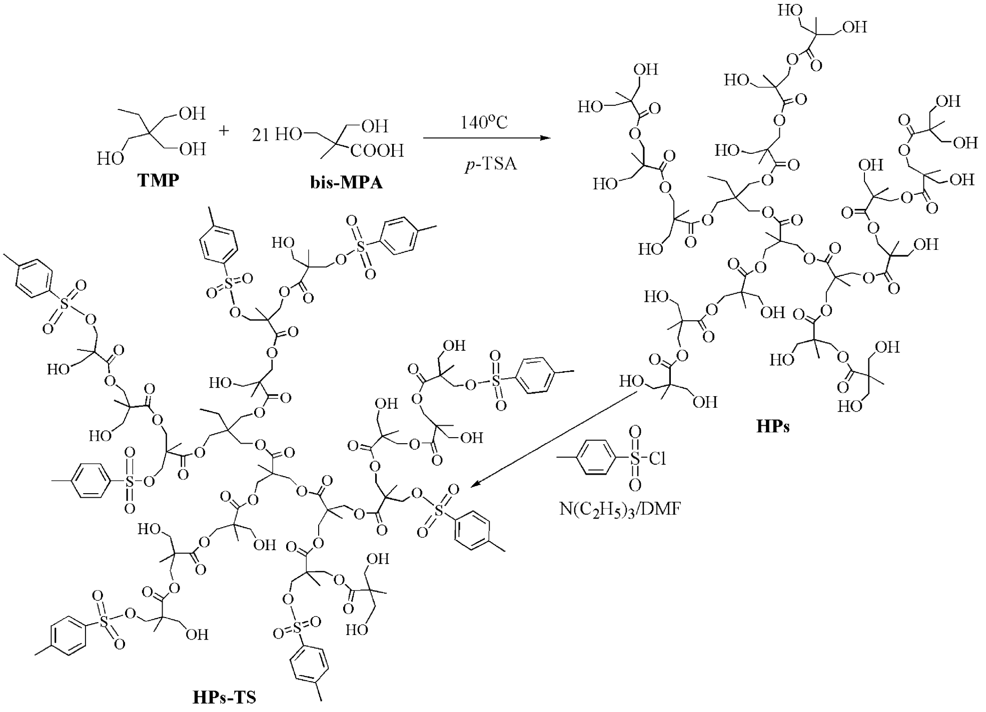
doi:10.1016/j.polymer.2005.07.036



Scheme 1. Reaction scheme for synthesis of hyperbranched polyesters (HPs) and hyperbranched polyesters modified by touluene-4-sulfonyl groups (HPs–TS).

formation are investigated and possible formation mechanism is discussed.

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), dimethyyl sulfoxide (DMSO, reagent grade) and touluene-4-sulfonyl chloride (TS-Cl, analysis 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 across.

2.2. Synthesis of hyperbranched polyesters

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 [20,21]. 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 theoretical 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 (500 MHz, δ, ppm): 1.10–1.31 ($-\mathrm{C}H_3$ and $\mathrm{CH_3C}H_2\mathrm{C}$), 2.04–2.08 ($-\mathrm{CH_2O}H$), 3.63–3.73 ($-\mathrm{C}H_2\mathrm{OH}$), 4.10–4.32 ($-\mathrm{COOC}H_2-$).

2.3. Chemical modification of hyperbranched polymers by touluene-4-sulfonyl groups

Touluene-4-sulfonyl groups were attached by reaction of terminal hydroxyl with touluene-4-sulfonyl chloride in DMF in the presence of TEA as an acceptor of HCl. As the reaction proceeds, triethylamine hydrochloride precipitates from the reaction medium, and its quantity corresponds to consume touluene-4-sulfonyl chloride. The precipitate of triethylamine hydrochloride was filtered off, and the solvent was removed under vacuum from resultant solution. The residue was washed several times with cold DMF. The number of hydroxyl groups consumed by touluene-4-sulfonyl corresponded to 15, 45 and 75% and the corresponding samples were designated as HPs–TS1, HPs–TS2 and HPs–TS3, respectively. All the compounds were low-melting materials and soluble in most organic solvents. The crude product was purified on silica using $\mathrm{CHCl_3}$ as the eluant. ^{1}H NMR (500 MHz, δ, ppm): 1.07–1.37 ($-\mathrm{C}H_3$ and $-\mathrm{CC}H_2\mathrm{CH_3}$), 2.34–2.35 ($-\mathrm{PhC}H_3$), 2.67–2.69 ($-\mathrm{C}H_2\mathrm{OS}$), 2.88–2.95 ($-\mathrm{CH_2O}H$), 3.12–3.17 ($-\mathrm{C}H_2\mathrm{OC}$), 3.60–3.70 ($-\mathrm{C}H_2\mathrm{OH}$), 4.10–4.32 ($-\mathrm{COOC}H_2$), 7.17–7.18 (2,4 positions for $-\mathrm{SO_2Ph}-H$), 7.75–7.76 (3,5 positions for $-\mathrm{SO_2Ph}-H$).

2.4. Characterization

^{1}H NMR and ^{13}C NMR spectra were recorded with an AVANCE DMX-500 NMR spectrometer by using

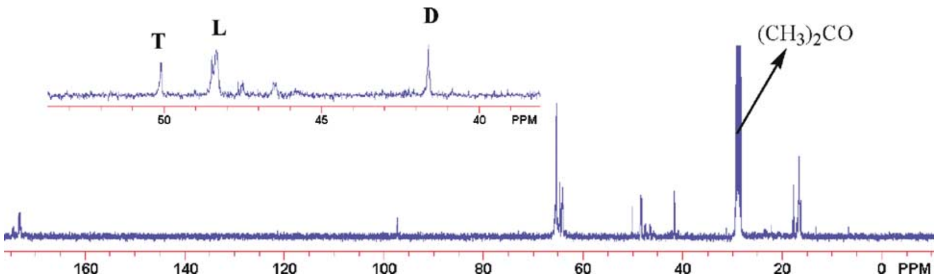


Fig. 1. ^{13}C NMR spectrum of hyperbranched polyesters (HPs) in $(CD_3)_2CO$.

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). Infrared spectra were recorded on Jasco IR-700 infrared spectrophotometer. The UV–visible spectra of the samples were recorded for the wavelength rang 200–700 nm at 25 °C on a Hawlett–Packard 8452A diode array spectrophotometer. Transmission electron micrographs were obtained on a JEOL model 1200EX instrument operated at an accelerating voltage at 160 kV.

3. Results and discussions

3.1. Chemical composition

The synthetic procedure for HPs and HPs–TS is outlined in Scheme 1. Aliphatic (HPs) was firstly synthesized by melt polycondensation of bis-MPA and TMP at a molar ratio of 21/1 using *p*-TSA as catalyst by pseudo one-step synthesis method [20]. The ^{13}C NMR spectrum of HPs 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 [20]. 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), terminal (T) and linear (L) repeating units. For an ideal dendritic substance, the degree of branching (DB) is equal to one. A hyperbranched polymer takes DB values between 0 and 1. According to the Fréchet method [21], the degree of branching (DB) of hyperbranched polymers is given by Eq. (1).

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

A magnified spectrum of hyperbranched polyester (HPs) is shown in Fig. 1. The degree of branching (DB) was calculated from the integral values found for the quaternary carbons and determined to be 0.72, which shows that a highly branched structure is obtained.

After HPs was obtained, a series of HPs–TS with a variable contents of touluene-4-sulfonyl groups at the peripheral of HPs were synthesized through the reaction of the hyperbranched polyesters cores by substituting a controlled fraction of the terminal hydroxyl groups with touluene-4-sulfonyl chloride using triethylamine (TEA) as an acceptor of HCl. The molecular characteristics of synthesized polymers are shown in Table 1. The molecular weight of touluene-4-sulfonyl terminated hyperbranched polyesters shows a gradually increase with substitution content. The experimentally measured molecular weights were systematically lower than the theoretical values obtained from the GPC measurements. The reason for this phenomenon is that PS standard-based GPC measurements

Table 1
Characteristics of hyperbranched polyester and touluene-4-sulfonyl terminated hyperbranched polyester

Compound	M_n[a] theoretical	GPC[b]			[TS]%[c]
		M_n (g/mol)	M_w (g/mol)	M_w/M_n	
HP	2573	1979	3148	1.59	–
HP–TS1	2533	2515	4024	1.60	14.5
HP–TS2	3643	3466	5476	1.58	40.2
HP–TS3	4753	4287	7074	1.65	62.4

[a] As accounted against GPC values for HPs–TS1, HPs–TS2 and HPs–TS3.

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

[c] $[\mathrm{TS}]\% = [M_{\mathrm{HPs-TS}} - M_{\mathrm{HP}}]/[24(190.64 - 36.5)]$, where $M_{\mathrm{HPs-TS}}$ and M_{HP} are the molar weights of HPs–TS*n* ($n = 1$–3) and HP, the number of 190.64 and 36.5 are the molar weights of touluene-4-sulfonyl chloride (TS-Cl) and hydrogen chloride (HCl).

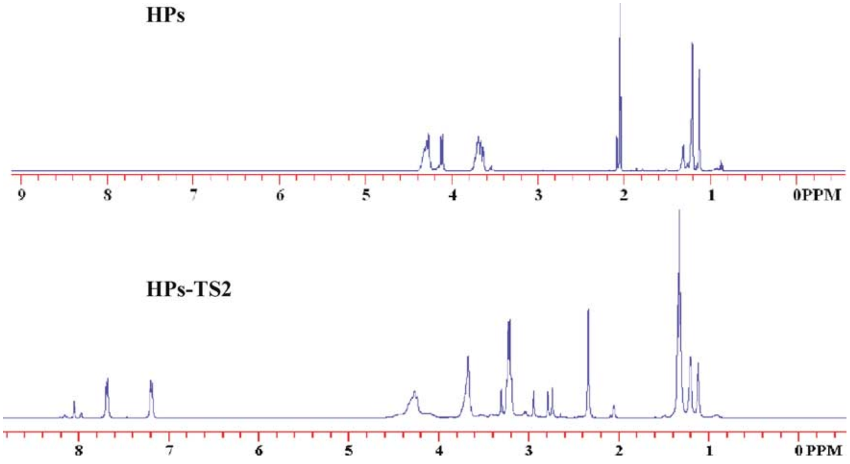


Fig. 2. ^{1}H NMR spectra of hyperbranched polyesters (HPs) and touluene-4-sulfonyl terminated hyperbranched polyesters (HPs–TS2) in $(CD_3)_2CO$.

underestimate the molecular weight of hyperbranched macromolecules because of their different hydrodynamic volumes compared with linear polystyrene having the same molecular weight [19]. The structure of hyperbranched polymers does complicate the determination of the molecular weights of the materials. Therefore, molecular weight obtained by GPC should be used for comparison only [22–24]. Meanwhile, the theoretical content of touluene-4-sulfonyl groups in hyperbranched polyester gradually increases with the substitution content. However, attempts to obtain 100% substituted molecules were not successful.

^{1}H NMR data confirmed the chemical composition of the compounds (Fig. 2). By the reaction of hydroxyl end-groups of HPs and touluene-4-sulfonyl chloride, HPs is further transferred into HPs–TS1, HPs–TS2 and HPs–TS3 with adjusting the amount of the benzoyl chloride. The characteristic resonances originating from touluene-4-sulfonyl moieties at both 7.17–7.18 and 7.75–7.76 ppm in HPs–TS indicated the introduction of aromatic structures.

The FTIR spectra of HPs and touluene-4-sulfonyl terminated hyperbranched polyesters (HPs–TS) are shown in Fig. 3. All four polyester samples show the characteristic peak of the hydroxyl peak around at 3400 cm^{-1} and the touluene-4-sulfonyl terminated hyperbranched polyesters have the benzene rings at 1600 and 750 cm^{-1}. As increase of content of phenyl branches results in systematic reduction of the intensity of hydroxyl peak and a rising intensity of benzene rings peaks. The variation of the peak intensity of hydroxyl and phenyl groups vs a degree of substitution presented shows a gradual increase of phenyl content and corresponding decrease of the amount of the terminal hydroxyl groups.

HPs–TS1, HPs–TS2 and HPs–TS3 have good solubility in common organic solvents, such as $CHCl_3$, THF, DMSO, and DMF. Fig. 4 shows the UV–visible spectra of them in the solution of DMF. A strong absorption maximum of the π–π^* transition of benzene chromophore appeared at about 266 nm, and two absorption maximum appeared at about 415 and 312 nm which contributing to the π–π^* transition of the sulfonyl chromophore. Meanwhile, the intensity of these peaks systematically increased with substitution content.

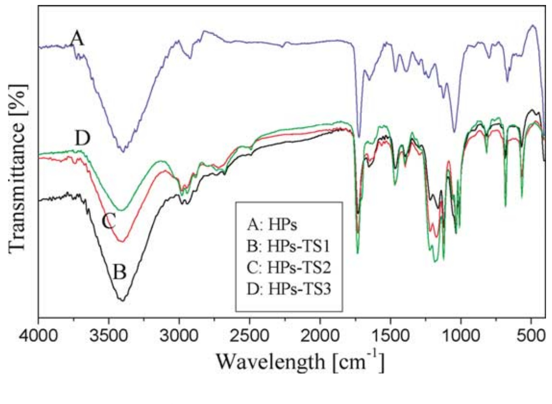


Fig. 3. FTIR spectra of hyperbranched polyesters (A) and touluene-4-sulfonyl terminal hyperbranched polyesters (B: HPs–TS1, C: HPs–TS2 and D: HPs–TS3).

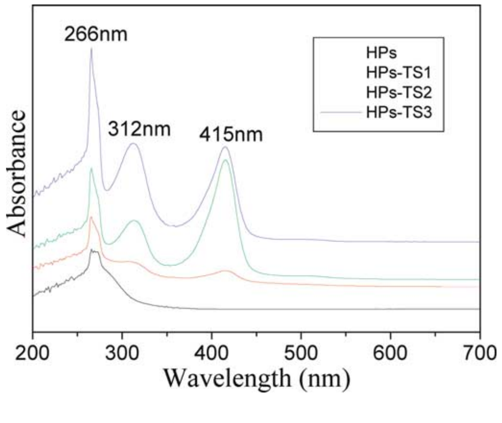


Fig. 4. UV–visible spectra of hyperbranched polyesters (HPs) and touluene-4-sulfonyl terminated hyperbranched polyesters (HPs–TS1, HPs–TS2 and HPs–TS3) with concentration at 15 mg/ml.

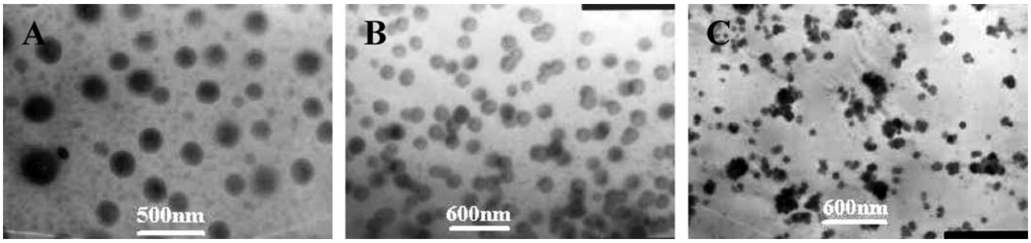


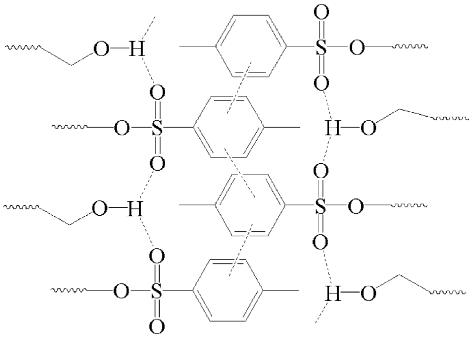
Fig. 5. TEM images of HPs–TS1 (A), HPs–TS2 (B) and HPs–TS3 (C) in the select solvent (trichloromethane/acetone) with the concentration of hyperbranched polyester at 5 mg/ml and the volume ration at 5:1.

3.2. Self-assembly behaviors in selected solvent

In order to observe the self-assembly behaviors, the sample were treated as follow: HPs–TS1, HPs–TS2 and HPs–TS3 were separately dissolved in $CHCl_3$ at room temperature. Into 0.25, 0.5 and 1.5 ml of acetone or *n*-hexane 1 ml of each solution was dropped under whisk. After stirring 10 min, the solutions were placed over night. Then, few drops of the above mixture were poured onto a carbon coated copper grid. The samples were left at room temperature for one night before observation.

The morphologies of HPs–TS1, HPs–TS2 and HPs–TS3 formed from trichloromethane/acetone mixed solution were directly observed by TEM. Self-assembly of the touluene-4-sulfonyl terminated hyperbranched polyester in trichloromethane and acetone mixed solution are shown in Fig. 5. From TEM images we can found that the spherical shape aggregates are formed in these samples. The average diameters of spherical shape aggregates are around at 230 and 220 nm for HPs–TS1 and HPs–TS2, respectively. Meanwhile, the aggregates formed by HPs–TS2 are more uniform than that obtained from HPs–TS1. In the case of HPs–TS3, many little aggregates with diameter less than 100 nm are gained. However, the size and shape of aggregates formed by HPs–TS3 are inhomogeneity and some big ones with diameter more than 300 nm are also obtained.

From these phenomena, we concluded that the content of touluene-4-sulfonyl groups play an important role in controlling the size and shape of self-assembly structures.



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.

Once the touluene-4-sulfonyl terminated polyesters are placed into mixed solvent, the microphase separation induced by the hydrophobic interaction will dramatically shorten the distance not only among hydroxyl groups but also between hydroxyl groups and sulfonyl groups, which facilitates formation of hydrogen bonds in the hyperbranched polyester domains. 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 self-assembly structures (Scheme 2) [25]. In the procedure of self-assembly, the shrinkage of the polyester domains for the strong hydrogen bond interactions among and between the hyperbranched polyester molecules and π–π stacking interactions between the touluene-4-sulfonyl terminated groups, the spherical structures are formed for the smallest surface energy.

When the content of touluene-4-sulfonyl groups at the lower level, the shrinkage of the polyester domains for the strong hydrogen bond interactions among and between the hyperbranched polyester molecules and π–π stacking interactions between the touluene-4-sulfonyl terminated groups in the procedure of self-assembly, the spherical structures are formed for the smallest surface energy [16b]. However, on increasing the level of touluene-4-sulfonyl groups, the interactions among the touluene-4-sulfonyl groups are more prominent, and more and more hyperbranched polyester molecules are aggregation and spherical shape aggregates are formed. Once the content of touluene-4-sulfonyl groups beyond a critical value, the exterior hydroxyls of the polymer are few, and most of residual hydroxyls lie in the center. The H-bonds between H and O atoms are less possible. With the aggregation of HPs cores, the interplay among hydroxyl, sulfonyl, and carboxyl groups increases, and facilitates the formation of irregular aggregation.

Meanwhile, the solvent molecules also affect the self-assembly procedure. They can be easier to penetrate into the self-assembly system in the case of HP-TS1, and bigger aggregates are formed. Contrarily, the solvent molecules are more difficultly to penetrate into the self-assembly system in the case of HP-TS2 for the closer aggregation. And it further facilitates the formation of smaller aggregation. We also investigate that the self-assembly of HPs–TS*n* ($n = 1$–3) in

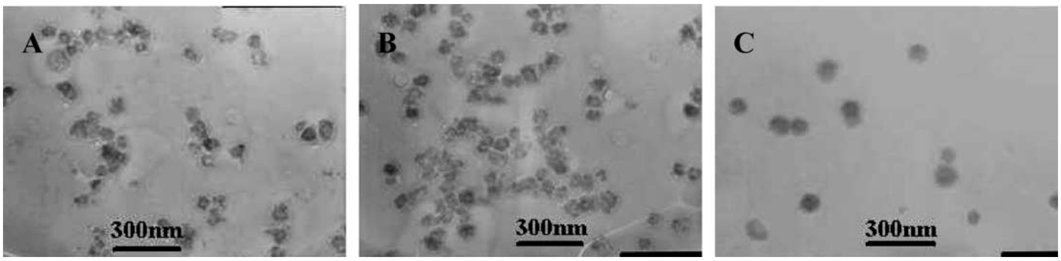
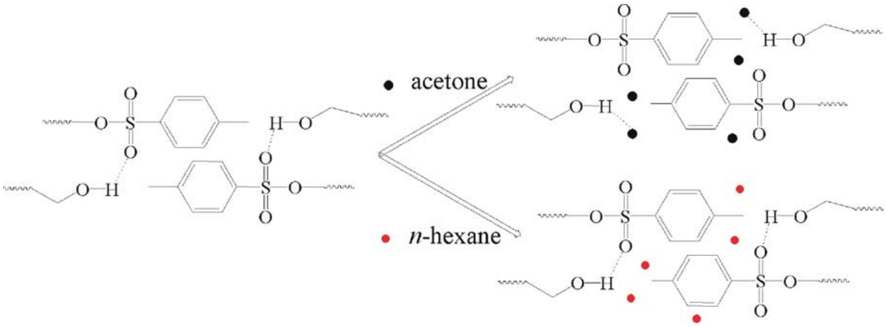


Fig. 6. TEM images of HPs–TS1 (A), HPs–TS2 (B) and HPs–TS3 (C) in the selected solvent (trichloromethane/*n*-hexane) with the concentration of hyperbranched polyester at 5 mg/ml and the volume ration at 2.5:1.



Scheme 3. Schematic image of the effect of solvent in the self-assembly procedure.

the trichloromethane and *n*-hexane mixed solvent for *n*-hexane is a precipitator for HP. Fig. 6 shows the TEM images of the touluene-4-sulfonyl terminated hyperbranched polyester in trichloromethane/*n*-hexane mixed solvent. The average diameters of the aggregates are around at 100 nm for HPs–TS*n* ($n=1$–3) samples. In the cases of HPs–TS1 and HPs–TS2, the aggregates have irregular shapes while spherical shape ones are formed by HPs–TS3.

These phenomena are different from that in trichloromethane/acetone system. It indicates that the composition of the selected solvent also play an important role in controlling the self-assembly structures (Scheme 3). When changing the composition of mixed solvent, the size and shape of aggregates are also changed. The possible reason for that is the solvents penetrate into hyperbranched molecules and affect the formation of driving effects in the self-assembly procedure for their polarity. Because the polarity of acetone is stronger than *n*-hexane, acetone can be easily penetrate into hyperbranched molecules and destroy or weaken the formation of driving effects.

4. Conclusions

Summary, hyperbranched polyesters (HPs) were synthesized in the molten state from 2,2-bis(hydroxymethyl) propionic acid (bis-MPA) and 2-ethyl-2-hydroxymethyl-1, 3-propanediol (TMP) using acid catalysis. The modified hyperbranched polyesters were obtained through the chemical modification of the hyperbranched polyester cores by substituting a controlled fraction of the terminal hydroxyl groups with touluene-4-sulfonyl chloride using triethylamine (TEA) as an acceptor of HCl. Detailed microstructural analysis of the structure revealed that self-assembled structures could be formed in selected solvents (trichloromethane/acetone or trichloromethane/*n*-hexane).

Acknowledgements

This project was financially supported by the Science and Technology Commission of Zhejiang Province (2004C34005) and Ningbo Science and Technology Program.

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