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Synthesis and macroscopic self-assembly of multiarm hyperbranched polyethers with benzoyl-terminated groups

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Abstract

The benzoyl-terminated multiarm hyperbranched poly(3-ethyl-3-oxetanethanol) (HBPO-B) was synthesized by reaction of terminal hydroxyl with benzoyl chloride in CH_2Cl_2 in the presence of pyridine and triethylamine (TEA) as the acceptors of HCl. The macroscopic self-assembly structures of hyperbranched benzoyl-terminated 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-terminated 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.

Keywords: Macroscopic self-assembly; Solvent volatilizing; Hyperbranched polyethers

1. Introduction

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 and Coulomb interactions, hydrophobic interactions and π–π stack etc. [1]. 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 effectors 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 [2–14]. Inspired by nature's ability to create extraordinarily well-defined objects from comparatively simple molecules, and with an eye toward creating nanoscale devices, chemists have sought to develop molecules capable of self-assembling into macroscopic self-assembly structures that has great potential application in biomimetic materials, which are formed by organic molecules through a self-assembly procedure in the nature [15,16]. Yan et al. [17] first reported the macroscopic molecular self-assembly of an amphiphilic hyper-branched copolymer (HBPO-star-PEO) with a hydrophobic hyperbranched poly(3-ethyl-3-oxetane-methanol) 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. For this reason, we designed a new hyperbranched polyether (as shown in Scheme 1), which has benzoyl-termined groups, from which we investigate the macroscopic self-assembly of HBPO-B by a simple solvent volatilizing route.

2. Experimental section

2.1. Materials

Chloroform (Reagent grade), acetone (Analysis grade), tetrahydrofuran (THF) (Analysis grade), dichloromethane

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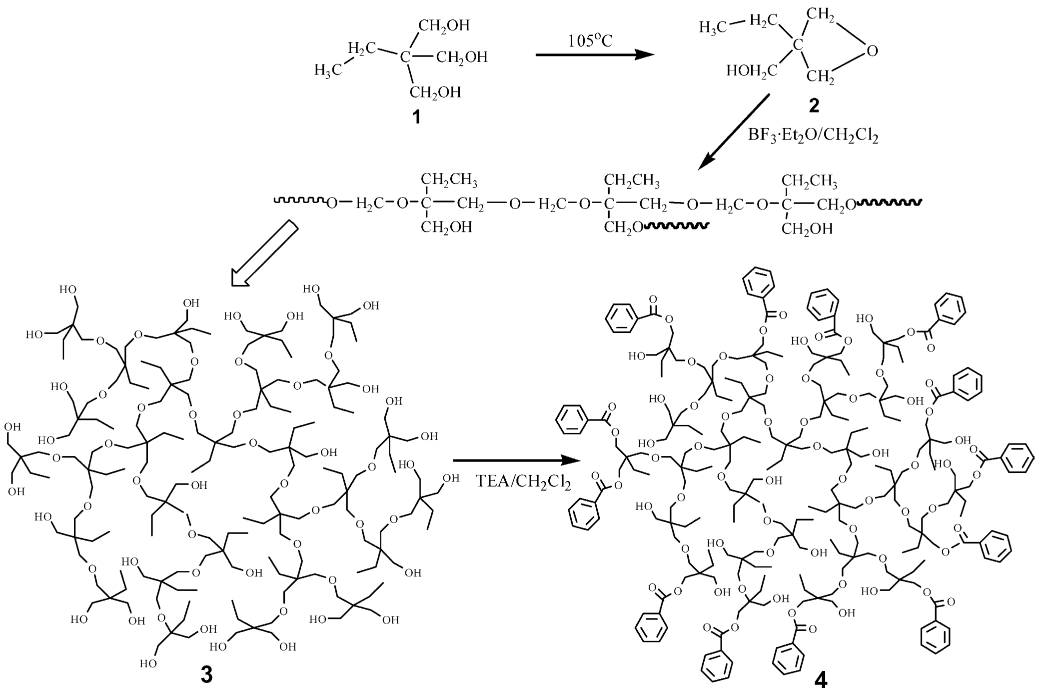


Scheme 1. Reaction scheme for synthesis of hyperbranched polymer and benzoyl-terminated hyperbranched polymer.

(CH_2Cl_2, Analysis grade), trichloromethane ($CHCl_3$, Analysis grade), ethyl alcohol (EtOH, Analysis grade), pyridine (PyD, Analysis) and triethylamine (TEA, Analysis grade), diethyl carbonate (99%), potassium hydroxide (KOH, 99%) and benzoyl chloride (Analysis grade) were purchased from East of China Chem. Ltd Co. and used as received. Trimethylopropane (TMP, 99%) was used as received from Acros.

2.2. Synthesis of 3-ethyl-3-oxetanethanol (**2**)

3-Ethyl-3-oxetanethanol was prepared by a modified procedure described in the literature [18]. A mixture of trimethylopropane (**1**, 26.8 g, 0.2 mol), diethyl carbonate (23.6 g, 0.2 mol), potassium hydroxide (0.1 g, 1.8 mmol) in 2 ml of absolute ethyl alcohol was refluxed in oil bath at 110 °C for 1 h. Then, the mixture was distilled at 110 °C for 1 h. Distillation was continued until the oil bath was 140 °C. After the distillation, the vacuum was supplied for 1 h to remove the excess solvent. Upon heating above 185 °C, the distilled materials were collected in the cold trap under vacuum and obtained with more than 85% of the theoretical yield.

2.3. Cationic ring-opening polymerization of 3-ethyl-3-oxetanethanol (**2**) using $BF_3 \cdot OEt_2$ [19]

The cationic polymerization of 3-ethyl-3-oxetanemethanol directly initiated by $BF_3 \cdot OEt_2$, polymerization was carried out at under a dry nitrogen atmosphere in a three-necked round-bottomed flask with a PTEE stirrer and a funnel. The reaction temperature was controlled at 0 °C and after 24 h the polymerization was quenched with water. The poly(3-ethyl-3-oxetanemethanol) (HBPO, **3**) was precipitated in distilled water and dried at 100 °C under vacuum. ^1H NMR (δ, ppm): 0.82–0.85 (–CH_3), 1.16–1.29 (–CH_2CH_3), 2.85–3.10 (–OCH_2–), 3.35–3.68 (–CH_2OH).

2.4. Synthesis of hyperbranched benzoyl-terminated polymers (**4**)

Benzoyl groups were attached by reaction of terminal hydroxyl with benzoyl chloride in CH_2Cl_2 in the presence of TEA and PyD as the acceptors 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 HBPO-B1, HBPO-B2 and HBPO-B3, respectively. All the compounds were soluble in most organic solvents. ^1H NMR (δ, ppm): 0.77–0.93 (–CH_3), 1.20–1.47 (–CH_2CH_3), 3.10–3.50 (–OCH_2– and –CH_2OH), 4.20–4.37 (–OCH_2COOPh), 7.38–7.42 (3, 5 positions of –$COOPhH$), 7.42–7.54 (4 position of –$COOPhH$), 7.96–8.10 (2, 6 positions of –$COOPhH$).

2.5. Characterization

^1H 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 tetrahydronfuran (THF) 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–vis spectra of the samples were recorded for the wavelength range 200–700 nm at 25 °C on a Hewlett-Packard 8452A diode array spectrophotometer. The microspectroscopy was performed by using an optical microscope (type Optiphoto, Nikon Co., Tokyo, Japan).

3. Results and discussions

3.1. Chemical composition

Three different hyperbranched polyethers with various amounts of benzoyl groups were involved in this study. The synthetic procedure for various polymers is outlined in Scheme 1. First, we tried to synthesize hyperbranched polyethers by cationic ring-opening polymerization of 3-ethyl-3-oxetanethanol (**2**) using $BF_3 \cdot OEt_2$ and subsequent substitution by reaction of terminal hydroxyl with benzoyl chloride in CH_2Cl_2 in the presence of TEA and PyD as the acceptors of HCl. The products were purified by redeposition or column chromatography. Attempts to obtain 100% substituted molecules were not successful. The molecular characteristics of synthesized compounds are shown in Table 1.

The FT-IR spectra of hyperbranched poly(3-ethyl-3-oxetanemethanol) and benzoyl-terminated hyperbranched poly(3-ethyl-3-oxetanemethanol) are shown in Fig. 1. The two samples show the characteristic peak of the hydroxyl at 3400 cm^{-1} and the benzoyl-terminated hyperbranched polymer has the new peaks at 1715 and 708 cm^{-1} which are ascribed to the characteristic stretching of carboxylic and benzene rings. As increase of content of benzoyl groups results in the 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 in HBPO and HBPO-B3 presented shows the benzoyl groups have been successfully grafted in HBPO.

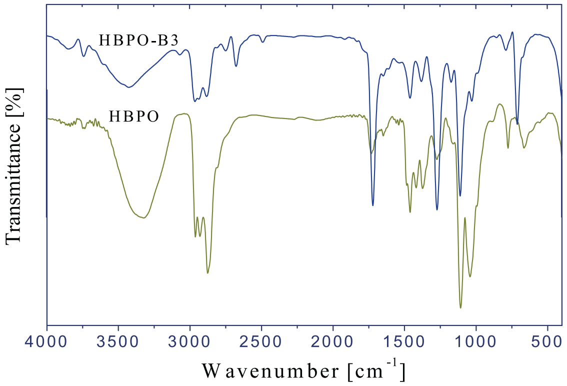


Fig. 1. FT-IR spectra of hyperbranched polyether (HBPO) and benzoyl-terminated hyperbranched polyether (HBPO-B3).

Table 1
Characteristics of hyperbranched polyether and benzoyl-terminated hyperbranched polyether

Compound	$M_n \times 10^{-3}$ [a] theoretical	GPC[b]		
		$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n
HBPO	–	4.88	7.61	1.56
HBPO-B1	5.60	5.25	8.45	1.61
HBPO-B2	7.12	6.54	11.77	1.58
HBPO-B3	8.62	8.10	12.72	1.57

[a] As calculated against GPC results.
[b] As calibrated against linear polystyrene stands with low polydispersity index.

By the reaction between hydroxyl end-groups of HBPO and benzoyl chloride, HBPO is further transferred into HBPO-B1, HBPO-B2 and HBPO-B3 by adjusting the amount of the benzoyl chloride. ^1H NMR data further confirmed the chemical composition of the compounds. Fig. 2 shows the typical ^1H NMR spectra for HBPO and HBPO-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 HBPO-B2 ^1H NMR data indicated the introduction of aromatic structures.

HBPO-B1, HBPO-B2 and HBPO-B3 have good solubility in common organic solvents, such as $CHCl_3$, THF, DMSO, and DMF. Fig. 3 shows the UV–vis spectra of them in the solution of DMF. A strong absorption maximum of the π–π^* transition of benzene chromophore appeared at about 272 nm. Meanwhile, the intensity of these peaks systematically increased with substitution content.

3.2. Macroscopic self-assembly of hyperbranched benzoyl-terminated polymers

We have combined synthetic hyperbranched molecules (HBPO-B) design with solution conditions that favor self-assembly with the solvent volatilizing to produce multiwalled structures with millimeters in diameter and centimeters in length. The macroscopic self-assembly structures are stable reproducible. The assemblies are formed by mixture of HBPO-B and solvent such as CH_2Cl_2, $CHCl_3$, THF and EtOH. Then, the mixture placed in a weighing bottle with 4 cm in diameter and making the solvent volatilizing completely for more than 12 h.

Under optimized conditions, the macroscopic self-assembly structures is the predominant structure of the HBPO-B3, as seen from the photo of Fig. 4(A) 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 (Fig. 4(B)), and the average length is about 1.5 cm. In addition, there are a

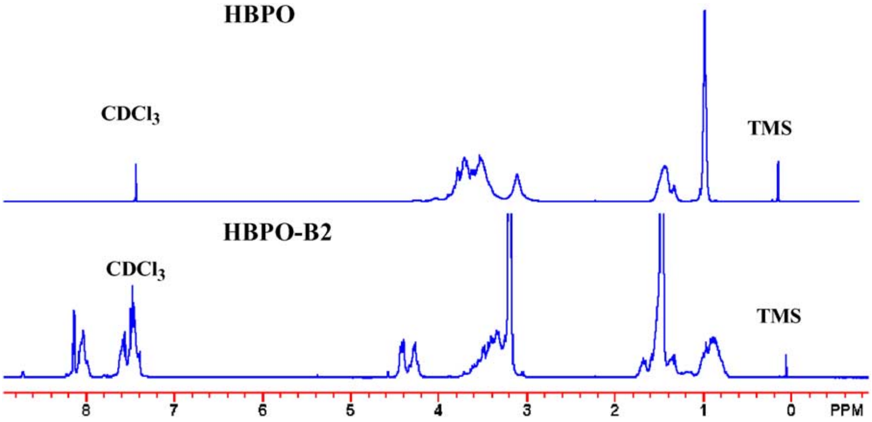


Fig. 2. ^{1}H NMR spectra of hyperbranched polyether (HBPO, top) and benzoyl-terminated hyperbranched polyether (HBPO-B2, bottom) in $CDCl_3$.

number of imperfect objects around the margin of the bottom of beaker. The macroscopic morphology of the self-assembly objects are also observed by optical microscopy. A multiwalled line-like structures can be observed from Fig. 4(C) and (D). The self-assembly structures can be formed in a wide concentration range from 1 to 1000 mg/ml. The dissolution of the self-assembly structures in CH_2Cl_2, the self-assembly structures can be reproduced after the volatilizing of solvent.

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 HBPO 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 HBPO cores, the distance among hydroxyl to ether groups, hydroxyl groups in HBPO, 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. The type of self-assembly structures describes here offers a new synthetic route to well-defined organic macrostructures.

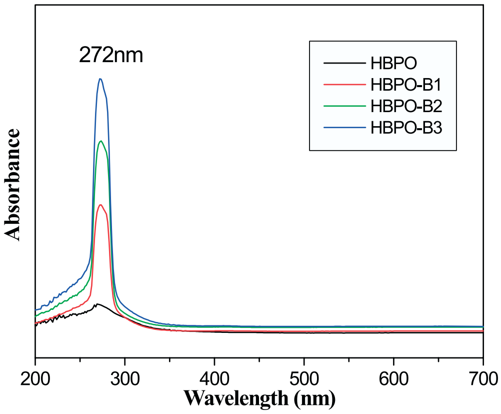


Fig. 3. UV–vis spectra of hyperbranched polyether (HBPO) and benzoyl-terminated hyperbranched polyether (HBPO-B1, HBPO-B2 and HBPO-B3).

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 (HBPO) were used to investigate whether the HBPO could self-organize into highly ordered structures or not? It was found that no any self-assembly structures were observed (Fig. 5(A)) for HBPO at same conditions, and the higher content of benzoyl groups in HBPO-B, the more prominent of the macroscopic self-assembly structures can be obtained (Fig. 5(B)–(D)). From these phenomena, we concluded that the benzoyl groups play an important role in the self-assembly procedure. When the solution of HBPO-B in CH_2Cl_2 dropped on the glass, the resulting objects also can be seen with the naked eyes. However, the degree of regular is lower than that obtained from the solution. Many concave regions could be seen from the optical microspectroscopy images. The reason for that was the volatilizing ratio of solvent is too quick to assemble the regular structures in a short time. The self-assembly structures could be dissoluble in H_2O for the hydrolyzing of benzoyl groups, and the macroscopic self-assembly structures can not be reproduce after the volatilizing of H_2O, which further verified the important effect of benzoyl groups on the molecular self-assembly.

Besides the molecular structures, the macroscopic self-assembly of HBPO-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. Fig. 6 showed the self-assembly structures that formed in the different solvent. As can been seen in Fig. 6(A), the specific structures that were similar to spherulites were formed in the $CHCl_3$ solution. However, using THF or EtOH as solvent, the optical microspectroscopy images were shown in Fig. 6(B) and (C). No regular

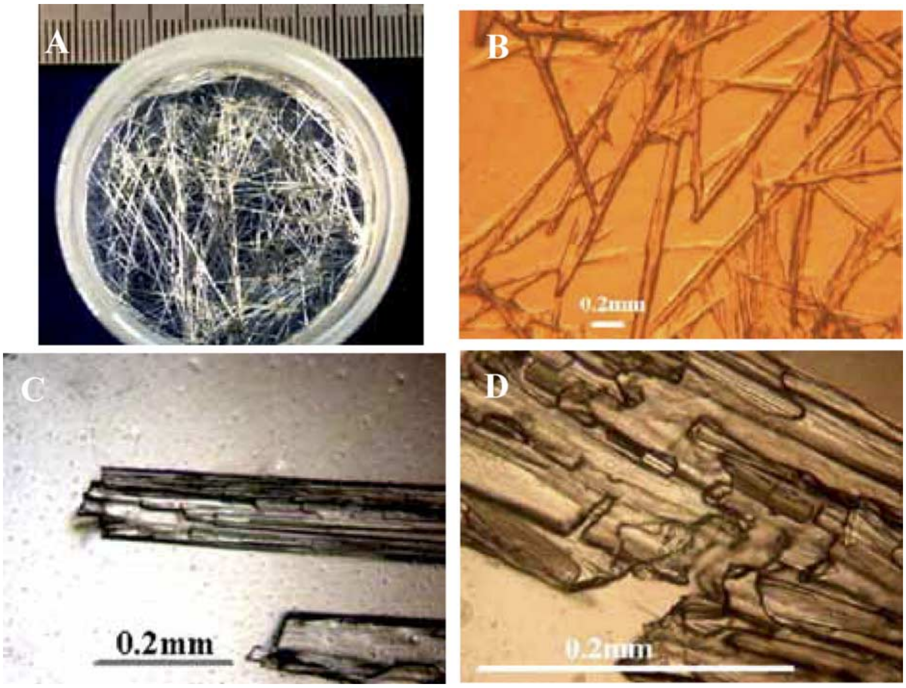
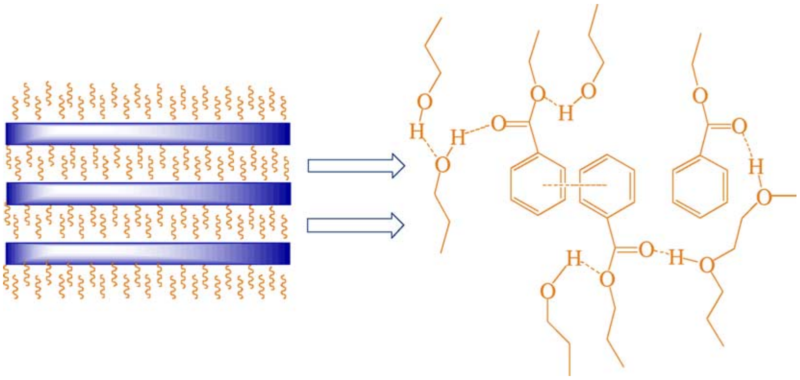


Fig. 4. (A) Macroscopic molecular self-assembly structures from the benzoyl-terminated hyperbranched polyethers (HBPO-B3) CH_2Cl_2 solution with the concentration at 80 mg/ml (25 °C). The photo was recorded with a digital camera from the bottom of a glass beaker, with blue paper as the background. Scale bar, 1 mm. (B) Optical microspectroscopy image of the self-assembly structures from CH_2Cl_2 with the concentration of HBPO-B3 at 95 mg/ml. (C) An external screw end of the self-assembly structure. (D) A middle rupture of the self-assembly structure.

macroscopic self-assembly structures are observed. The possible reason for that was the solvents penetrate into hyperbranched molecules and affect the formation of driving effects in the self-assembly procedure for their strong polarity. The temperature also play an important role in the self-assembly procedure. No self-assembly structures were obtained under 20 °C.

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 CH_2Cl_2 in the presence of TEA and PyD 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 CH_2Cl_2 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



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.

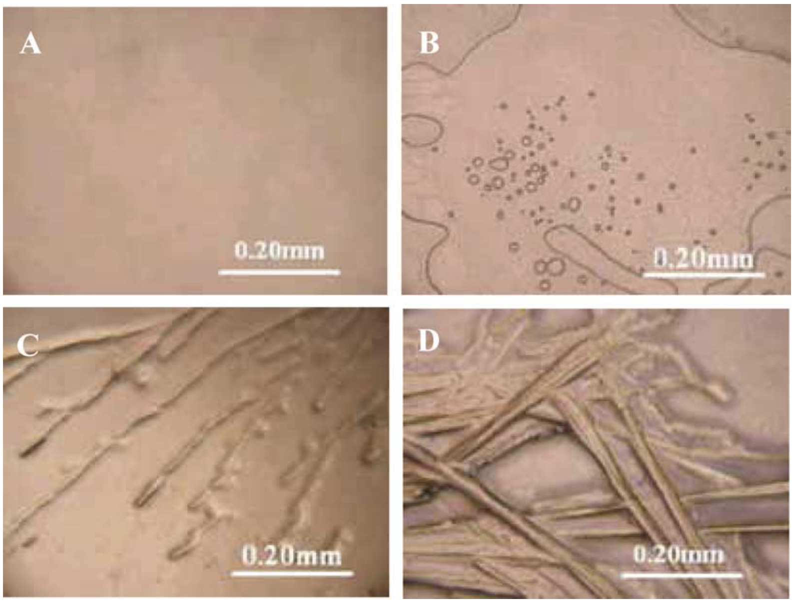


Fig. 5. Optical micro spectroscopy images of hyper branched HBPO-B from CH_2Cl_2 solution with the different content benzoyl groups (A) 0%, (B) 15%, (C) 45% and (D) 75% in the terminal of HBPO with the concentration of HBPO at 20 mg/ml.

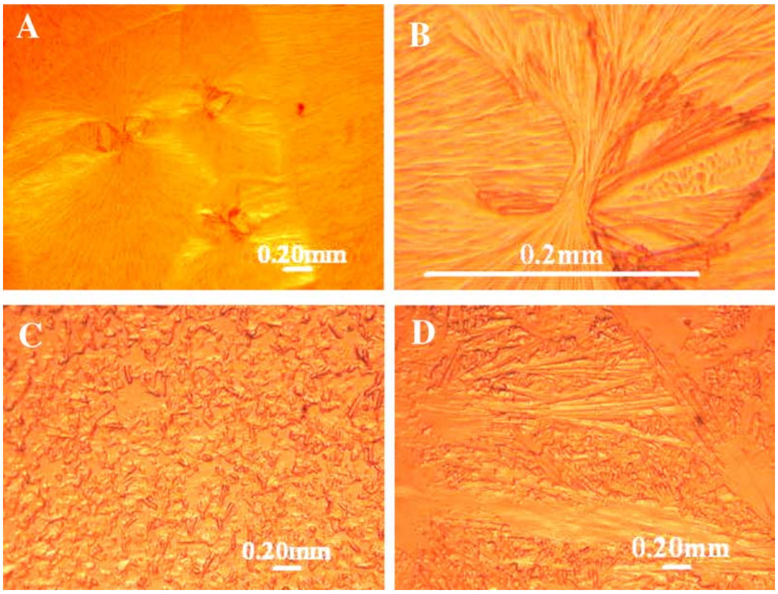


Fig. 6. Optical microspectroscopy image of hyperbranched HBPO-B3 from $CHCl_3$ (A), THF (B) and EtOH (C) solution with the concentration of HBPO-B at 80 mg/ml.

are also affected the self-assembly structures. The type of self-assembly describes here offers a synthetic route to well-defined one-dimensional organic macrostructures.

Acknowledgements

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