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Morphology, optical, thermal and antimicrobial studies of ibuprofen-based hyperbranched polyester

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Abstract. Herein we report the synthesis of ibuprofen-based hyperbranched polyester ranging from morphological, thermal and fluorescent behaviour. The proposed synthesis of ibuprofen-based hyperbranched polyester was achieved by a simple acid chloride approach. The formation of aromatic ester linkage in the product was confirmed using Fourier transform infrared and nuclear magnetic resonance spectroscopy. The morphology of ibuprofen-based hyperbranched polyester was investigated by using the X-ray diffraction, scanning electron microscopy and differential scanning calorimetry (DSC) analyses. The glass transition temperature (~78°C) and double melting peaks of ibuprofen-based hyperbranched polyester were observed using DSC. The liquid chromatography-mass spectrometry analysis confirmed the chemical structure and the molecular weight of the ibuprofen-based hyperbranched polyester. The presence of broad absorption peak at 301 nm in UV region indicated the fluorescent property of ibuprofen-based hyperbranched polyester. The antimicrobial tests of ibuprofen-based hyperbranched polyester were carried against Gram-negative organisms such as *Escherichia coli* MCIM 2065 and *Salmonella paratyphi* MCIM 2501, Gram-positive organisms such as *Bacillus subtilis* NCIM 2063 and *Staphylococcus aureus* NCIM 2079 and fungi such as *Aspergillus niger* MTCC 1344 and *Candida albicans* MTCC 3100. The result of agar disc diffusion method showed that the polymer had higher antimicrobial potential towards fungi than bacteria.

Keywords. Ibuprofen; hyperbranched polyester; morphological properties; antimicrobial activity.

1. Introduction

Hyperbranched polyesters have attracted widespread attention in recent decades [1,2]. They are extensively studied because of their excellent thermal stability, chemical resistance and mechanical properties [3,4]. They have a highly branched structure, a large number of functional groups and inner cavities, showing low viscosity, excellent solubility and high chemical reactivity, being widely used in many fields [5]. Hyperbranched polyesters can be synthesized from easily available and less expensive raw materials, and have compelled many research groups to investigate them in detail [6]. They can also be prepared by a single-step process avoiding complicated iterative reaction sequences and chromatographic purification [7–10]. The functional groups present at the periphery of the hyperbranched polyesters could be used to modify other materials, so they can be used as polymeric processing agents, toughening components, rheology modifiers, macroscopic tubes and biocompatible polymers [11–13]. The properties of hyperbranched polyesters are often affected by the nature of the backbone, the chain-end functional groups, degree of branching, chain length between branching points and the molecular weight distribution [14]. On account of high solubility and low viscosity, it is possible to prepare modified hyperbranched polyesters by using different agents [15,16]. Hyperbranched polyesters can be easily modified to tailoring their properties for a specific purpose, and it was expected that their modifications would make to obtain nonsteroidal anti-inflammatory drug (NSAID)-based polymers [17,18]. Ibuprofen, a NSAID; however, its solubility in water is poor, which affects pharmaceutical product development in nearly all therapeutic areas [19,20]. Researchers showed interest towards the antimicrobial activity of ibuprofen, both direct and indirect, which has been known for more than 23 years.

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Surprisingly, only about few studies can be found on the subject, while some aspects of the antimicrobial activity of ibuprofen have not been explored at all, such as the mechanisms of the antibacterial action [21].

Ibuprofen is used similar to other NSAIDs because of its analgesic and antipyretic properties [22]. Therefore, it is thought that ibuprofen, as an agent to modify hyperbranched polyester, could be more advantageous in applications [23]. The modification of ibuprofen with certain substances (like silver, polyesters, etc.) has already been reported in the literature. The synthesis of new zinc(II)–ibuprofen, containing complexes with 2-aminopyridine, 2-aminomethyl pyridine, 2,2′-bipy and 2-(methylamino)pyridine and their antimicrobial activity, was evaluated [19]. The synthesis and self-assembling behaviour of well-defined amphiphilic diblock copolymer NSAID prodrugs was evaluated by direct reversible addition–fragmentation transfer polymerization of the acrylamide derivative of ibuprofen [22]. A novel poly(anhydride-ester) using a mannitol-*co*-succinate backbone with four pendant ibuprofen groups per repeat unit as a model bioactive-releasing system [24]. The antibacterial assays over Gram-positive and Gram-negative pathogenic bacterial strains of a silver(I) complex with ibuprofen (Ag–ibu) have been reported [25]. The modifications of ibuprofen with polyester and naproxen-based polyesters have also been reported [18]. In this paper, we incorporated ibuprofen into hyperbranched polyester by a simple condensation route *via* the acid chloride approach and their properties were investigated. The antimicrobial activity of ibuprofen-based hyperbranched polyester was evaluated against the Gram-negative organisms such as *Escherichia coli* and *Salmonella paratyphi*, Gram-positive organisms such as *Bacillus subtilis* and *Staphylococcus aureus* and fungi such as *Aspergillus niger* and *Candida albicans*.

2. Materials and methods

2.1 *Materials*

Hyperbranched bis-MPA polyester-16-hydroxyl generation-2 (hyperbranched polyester) was purchased from Sigma-Aldrich (India). Ibuprofen, tetrahydrofuran (THF), triethylamine, 4-(dimethylamino)pyridine (DMAP) and acyl chloride were purchased from Nice Chemicals Private Limited (India). All other solvents and above chemicals were used with further purification.

2.2 *Synthesis*

Ibuprofen-based hyperbranched polyester was synthesized by two-step reactions: (1) acylation of hyperbranched polyester and (2) terminal modification of acyl chloride-terminated hyperbranched polyester with ibuprofen.

2.2a *Preparation of acyl chloride-terminated hyperbranched polyester:* The preparation of acyl chloride-terminated hyperbranched polyester was carried out according to the reported procedure [26,27]. The details and characterization of acyl chloride-terminated hyperbranched polyester were given in supplementary data.

2.2b *Synthesis of ibuprofen-based hyperbranched polyester:* A total of 1.0 g (13.5 mmol) of acyl chloride-terminated hyperbranched polyester (I) was dissolved in 50 ml of THF to make a clear solution in a three-necked flask equipped with a magnetic stir bar, a thermometer and a condenser. To the clear solution, 0.5 g (16.3 mmol) of DMAP was also added. A total of 1.04 g (30.1 mmol) of ibuprofen, dissolved in THF, was added dropwise into the above solution mixture with constant stirring. The reaction was maintained with constant stirring at room temperature for 2–4 h. The solvent was removed by a rotary evaporator under vacuum. Finally, the solid product (II) was obtained and dried. Yield: 85%. IR (KBr, cm^{-1}): 3341.48 (–NH stretching), 2923.11 ($–CH_2$ stretching), 1719.09 (–C=O stretching), 1063.19 (–CO stretching). ^{1}H NMR (200 MHz, DMSO-d_6, δ/ppm): 7.215 (d, 48H, ArH), 3.6 (d, 16H, C=O), 1.8 (t, 16H, OCH_2CO). ^{13}C NMR (400 MHz, DMSO-d_6, δ/ppm): 174.32, 142.76, 39.42, 16.48. LC-MS: *m*/*z* 5730.70 (M^+) (supplementary figure S1).

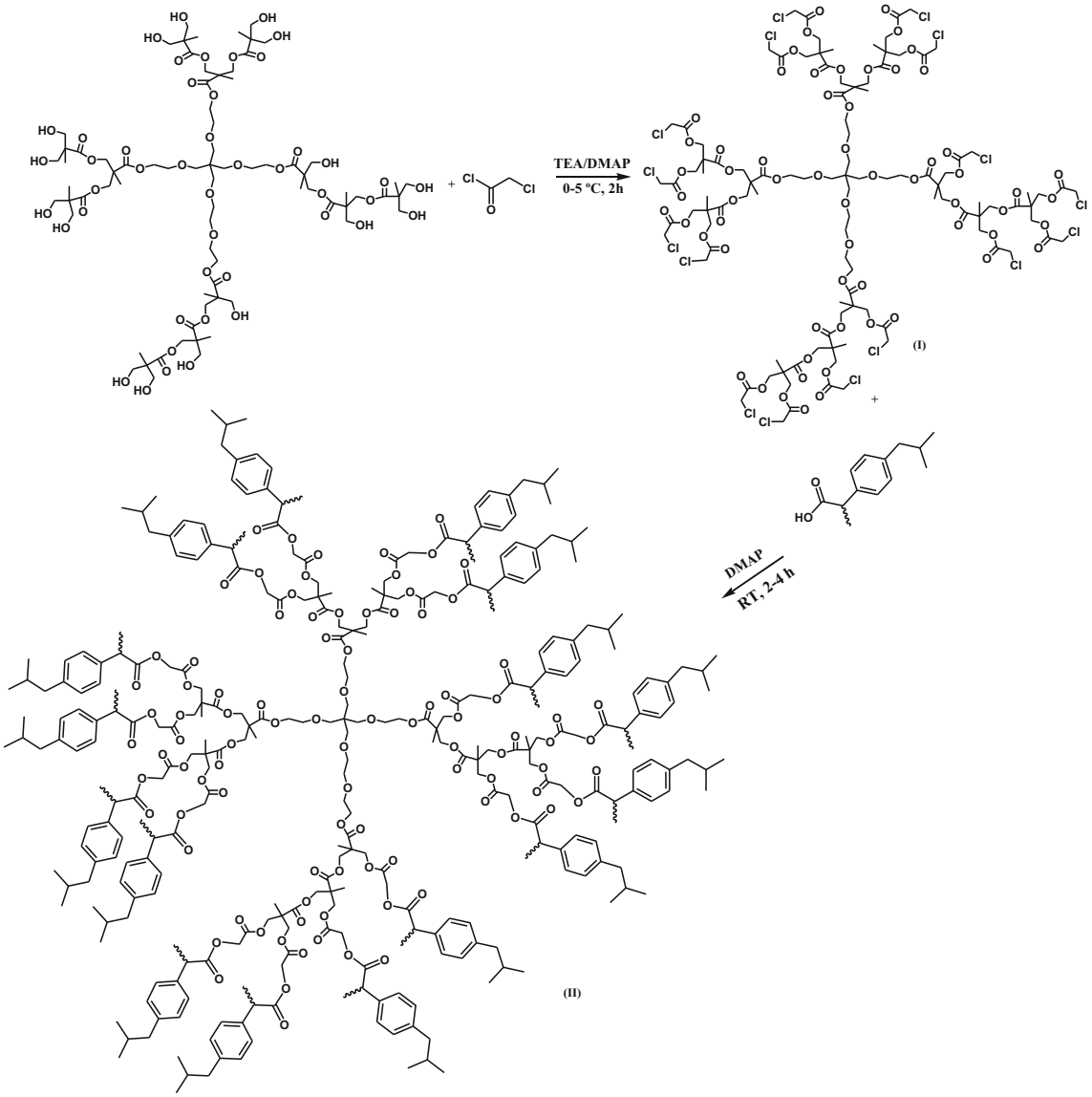
2.3 *Characterization studies*

Fourier transform infrared (FTIR) spectra were obtained using a Shimadzu IR Prestige-21 spectrometer at room temperature in the wavenumber range of 600–4000 cm^{-1}. ^{1}H nuclear magnetic resonance (NMR) spectra were recorded on a Varian 200 MHz spectrometer using DMSO-d_6 as the solvent and internal reference. ^{13}C NMR spectra were measured on JEOL GSX 400 MHz using tetramethylsilane as the internal standard. Molecular weight of the polymer was determined by the liquid chromatography-mass spectrometry (LC-MS) infusion method using LC-MSD-Trap-XCT Plus. X-ray powder diffraction (XRD 6000 Shimadzu model) coupled with Cu-Kα radiation (k = 1.54) was utilized to study the nature of the substance. Scanning electron microscopy (SEM) analysis was utilized to study the morphology and size of the substance using a JEOL JSM-6390 microscope. UV–visible spectra were recorded on a Shimadzu UV-1800 spectrophotometer. The fluorescence spectra were measured on Jasco FP-8200 spectrofluorimeter with a 10 mm quartz cuvette. Thermogravimetric analysis (TGA) (ZETZSCH-STA 409C thermal analyzer) measurements were carried out from 30 to 800°C at a heating rate of 10°C min^{-1} under nitrogen atmosphere with a gas flow rate of 90 ml min^{-1}. Differential scanning calorimetry (DSC) measurements were performed on a ZETZSCH-STA 109C thermal analyzer from 0 to 300°C at a heat range of 10°C min^{-1} under

nitrogen atmosphere. The electrochemical measurements of the polymers were carried out by the cyclic voltammetry technique, using a three-electrode cell electrochemical workstation (CHI6038D, CH Instruments, USA) with a scan rate of 10 mV s^{-1}. Glassy carbon acts as working electrode, the Ag/AgCl in KCl (3 M) solution and an auxiliary platinum wire were used as reference electrode and counter electrode, respectively. 0.1 M of tetrabutylammonium perchlorate mixed with a solution of toluene and acetonitrile (8:2 v/v) was used as the supporting electrolyte (scheme 1).

2.4 *Evaluation of antimicrobial performance*

The agar diffusion method was adopted to evaluate the antibacterial and antifungal activities of the hyperbranched polymers. The test samples were made as tablets with a thickness of 2 mm and a diameter of 9 mm, which were placed on the surface of inoculated agar plates [28]. The antimicrobial activity of the hyperbranched polymers was tested individually against the Gram-negative organisms such as *E. coli* MCIM 2065 and *S. paratyphi* MCIM 2501, Gram-positive organisms such as *B. subtilis* NCIM 2063 and *S. aureus* NCIM 2079 and fungi such as *A. niger* MTCC 1344 and *C. albicans* MTCC 3100. They were standardized with a final cell density of approximately 10^8 CFU ml^{-1} before using the cultures. Here, the following media such as Muller–Hinton agar plate (Merck) and Sabouraud dextrose agar plate (Merck) were used for bacteria and fungi, respectively. The agar plates inoculated from the standardized cultures of the test organisms were spread into the entire media uniformly as far as possible. The prepared tablets were introduced on the upper layer of the seeded agar plate. Sabouraud dextrose agar plate and



Scheme 1. Synthesis route of ibuprofen-based hyperbranched polyester by the condensation method.

Muller–Hinton agar plate were incubated at 37°C for 24 h. The antimicrobial activities of the hyperbranched polymers were compared with standard antibiotics of ciprofloxacin (10 µg per disc) and clotrimazole (10 µg per disc) for bacteria and fungi, respectively. Positive control plates were streaked with test organisms, but no tablet was used. The diameter of inhibition zone (mm) on the surface of the plates was measured on antibiotic scale and the results were reported as mean ± SD after three repeats.

2.5 *Determination of minimum inhibitory concentration by the broth dilution method*

The minimum inhibitory concentration (MIC) of ibuprofen-based hyperbranched polyester was determined by the broth dilution method. The MIC test, specifically carried out only for ibuprofen-based hyperbranched polymer, had greater antimicrobial activity against the organism. Ibuprofen-based hyperbranched polyester was diluted in the order of 1000, 500, 250, 125, 62.5 and 31.25 µg ml^{-1} in Muller–Hinton broth after which a standardized fungal suspension ($1–4 \times 10^6$ CFU ml^{-1}) to be evaluated was added and incubated at 30°C for 24 h. An MIC value is determined by finding the lowest concentration of agent that inhibited the visible growth of bacteria.

3. Results and discussion

3.1 *Characterization of ibuprofen-based hyperbranched polyester*

The synthesis of ibuprofen-based hyperbranched polyester was achieved in two steps from hyperbranched polyester, as shown in the reaction scheme. Initially the hyperbranched polyester was reacted with acyl chloride in the presence of DMAP as a catalyst in a basic medium. The formation of ester linkage between hyperbranched polyester and acyl chloride was detailed in our previous work [26,27]. In the second step, acyl chloride-terminated hyperbranched polyester was allowed to react with ibuprofen in the presence of DMAP as a catalyst. The carboxylic acid groups of ibuprofen were condensed with acyl chloride groups in acyl chloride-terminated hyperbranched polyester (I) to give ibuprofen-based hyperbranched polyester. The formation of ester linkage implies the appearance of aromatic nature in ibuprofen-based hyperbranched polyester.

The FTIR spectra of compound I (acyl chloride-terminated hyperbranched polyester) show the peaks at 1728 and 887.26 cm^{-1} which indicate the presence of the aliphatic ester and acyl chloride, respectively (figure 1). The FTIR analysis of compound II (ibuprofen-based hyperbranched polyester) confirmed the presence of carboxyl stretches of phenyl ester due to the appearance of peak at 1719 cm^{-1} (figure 1).

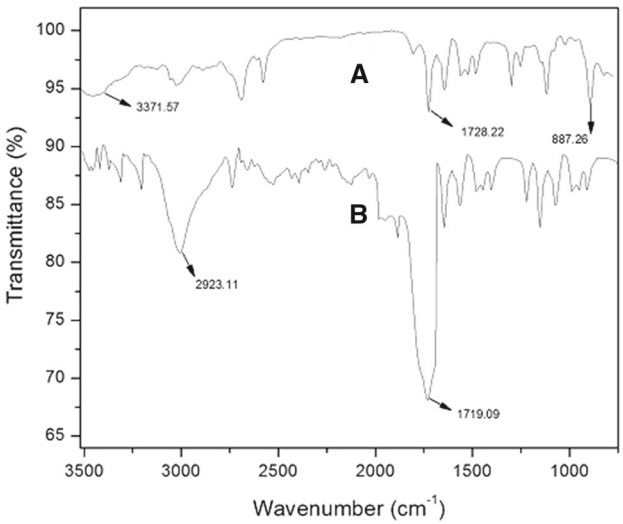


Figure 1. FTIR spectra of (**A**) acyl chloride-terminated hyperbranched polyester and (**B**) ibuprofen-based hyperbranched polyester.

The peak of ^{1}H NMR spectrum of compound I was observed at 3.02 and 1.18 ppm due to the presence of CH_2Cl and alkyl groups, respectively (figure 2A). The formation of phenyl ester and aromatic protons in final product due to the appearance of peaks at 4.2 and 7.2 ppm, respectively (figure 2B).

The appearance of the peak in ^{13}C NMR spectrum for compound I at 42 and 157 ppm confirmed the presence of acyl chloride and ester linkage, respectively (figure 3A). The ^{13}C NMR spectra for compound II showed the peak at 174 ppm which clearly confirmed the presence of ester linkage between ibuprofen and acyl chloride-terminated hyperbranched polyester and the peak at 142 ppm also showed the presence of phenyl group in the product (figure 3B). The above information suggested that the terminal modification on hyperbranched polyester with ibuprofen could be achieved by simple condensation.

3.2 *Morphological studies*

The strong aggregation of polymer enhances the surface area and makes it versatile in many applications. The patterns of the XRD profiles of ibuprofen-based hyperbranched polyester are given in figure 4. XRD patterns of ibuprofen yield typical peaks at 16, 20 and 22° and show the crystalline nature [29]. As the report has already stated, ibuprofen is a clear spherical particle [30]. The SEM image showed that particles of ibuprofen with irregularities were strongly aggregated with hyperbranched polyester layer (supplementary figure S2).

The results obtained from all DSC traces were similar to those of the already reported literature [31]. DSC study showed the glass transition temperature of ibuprofen-based hyperbranched polyester at 78°C and their double melting

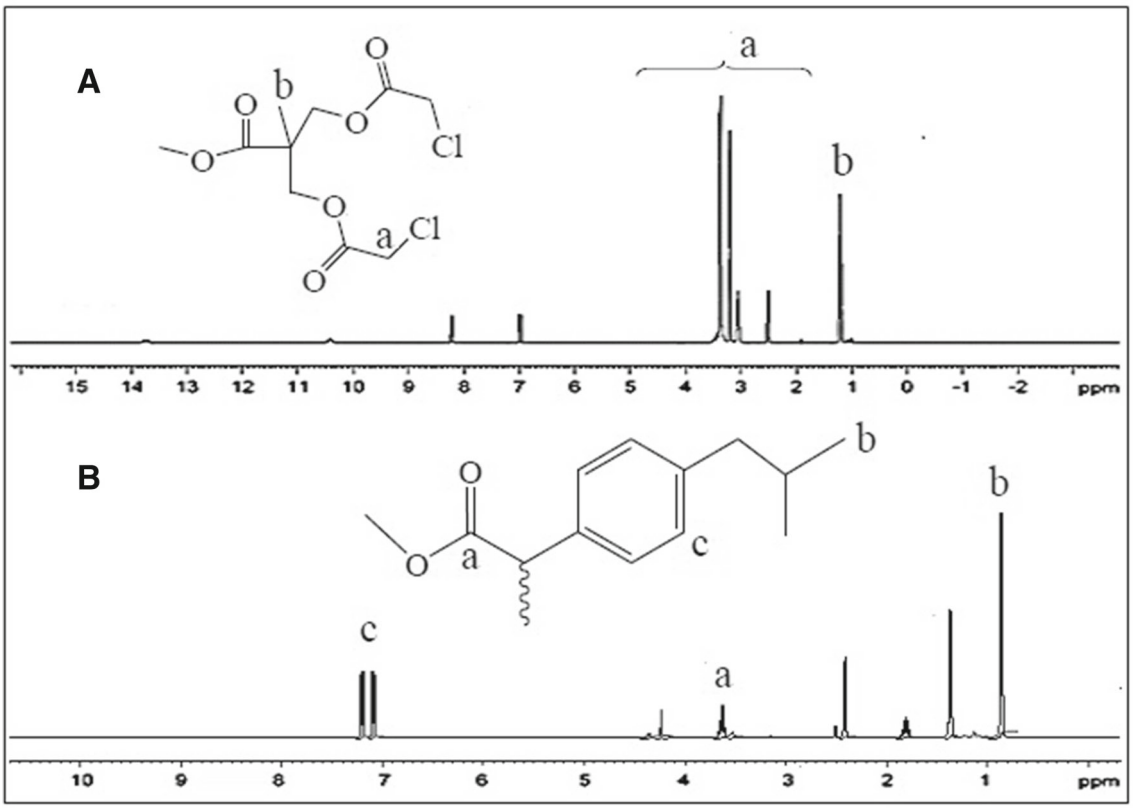


Figure 2. ^{1}H NMR spectra of (**A**) acyl chloride-terminated hyperbranched polyester and (**B**) ibuprofen-based hyperbranched polyester.

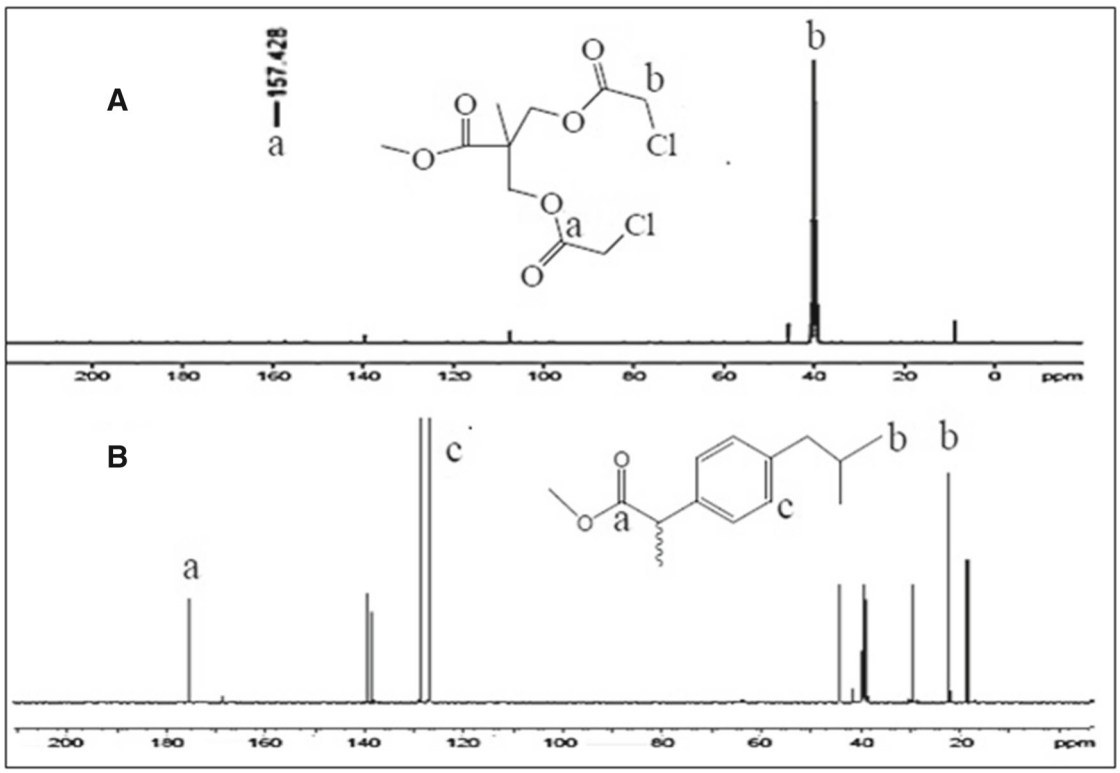


Figure 3. ^{13}C NMR spectra of (**A**) acyl chloride-terminated hyperbranched polyester and (**B**) ibuprofen-based hyperbranched polyester.

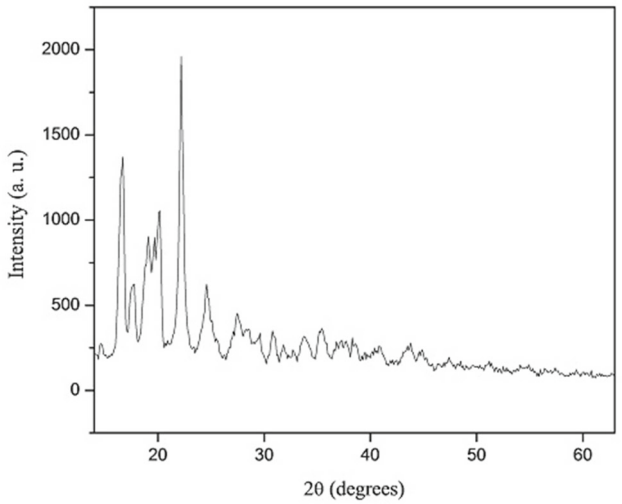


Figure 4. XRD analysis of ibuprofen-based hyperbranched polyester.

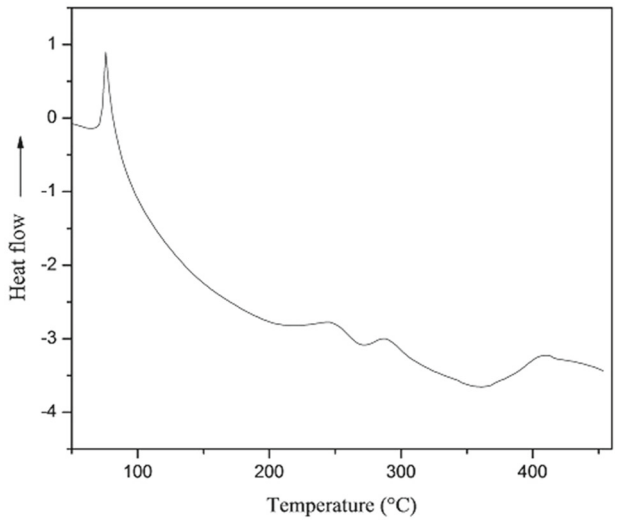


Figure 5. DSC thermogram of ibuprofen-based hyperbranched polyester.

peaks at 244.6 and 281.1°C in figure 5. These double or triple melting peaks of polyesters are usually appeared in a heating scan from DSC [31].

3.3 *Optical properties*

The absorption spectra of the acyl chloride-terminated hyperbranched polyester and ibuprofen-based hyperbranched polyester were recorded in a THF medium using UV–visible spectroscopy. In figure 6A, a broad absorption band displayed at 260 nm in the ultraviolet region for acyl chloride-terminated hyperbranched polyester was attributed to the π–π* transition of the polymer backbone [13]. The UV absorption peak of ibuprofen-based hyperbranched polyester at 301 nm in the ultraviolet region, this red shift occurred due to the association of hyperbranched polyester with ibuprofen [26,27].

The emission spectra of acyl chloride-terminated hyperbranched polyester and ibuprofen-based hyperbranched polyester were recorded (at λ = 260 and 301 nm, respectively) in the THF, as shown in figure 6B. The emission peaks for acyl chloride-terminated hyperbranched polyester were observed at 475, 510 and 565 nm, as shown in figure 6B. By comparing with acyl chloride-terminated hyperbranched polyester, very low intensity peaks were observed at 305, 525 and 570 nm for ibuprofen-based hyperbranched polyester in figure 6B. This intensity effect arises due to the terminal modification on hyperbranched polyester with ibuprofen.

3.4 *Thermal properties*

The thermal studies of ibuprofen-based hyperbranched polyester were carried out using TGA. The decomposition temperature of ibuprofen-based hyperbranched polyester was found at 328°C, as shown in figure 6C. This result showed that the polymer chains of ibuprofen-based hyperbranched polyester were thermally stable up to 328°C. Ibuprofen-based hyperbranched polyester was found to be highly soluble in polar solvents like dimethylformamide (DMF), dimethylacetamide (DMAc), DMSO and THF.

3.5 *Electrochemical properties*

The highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) energy levels of dye properties play a vital role in the material to be used in dye-sensitized solar cells. The above properties and energy gap can be calculated by using the following equations [32]:

$$\text{HOMO} = -\text{e}(E_{\text{ox}} + 4.40)\,(\text{eV}) \quad (1)$$

$$\text{LUMO} = -\text{e}(E_{\text{red}} + 4.40)\,(\text{eV}) \quad (2)$$

$$E_{\text{g}} = \text{HOMO} - \text{LUMO}. \quad (3)$$

From this study, no characteristic peak was observed for ibuprofen-based hyperbranched polyester (supplementary figure S3).

3.6 *Antimicrobial activity*

The antimicrobial measurement of ibuprofen-based hyperbranched polyester against microorganisms was carried out based on the diameter of the inhibition zone. The diameters of the inhibition zone of ibuprofen-based hyperbranched polyester (100 µg per disc) against *E. coli*, *S. paratyphi*, *B. subtilis*, *S. aureus*, *A. niger* and *C. albicans* were 21, 14, 16, 12, 19 and 31 mm, respectively, as shown in a statistical representation in figure 7. The inhibition zone value of

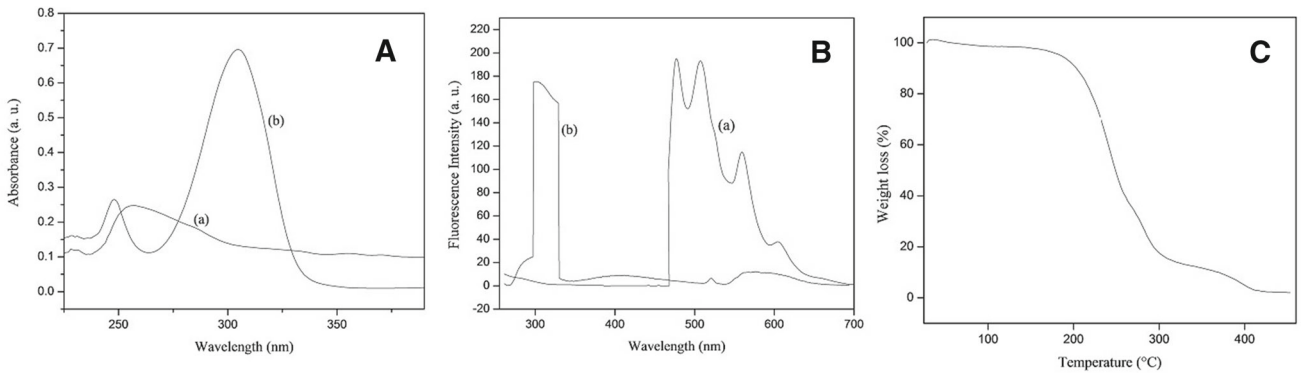


Figure 6. (**A**) UV spectra of (a) acyl chloride-terminated hyperbranched polyester and (b) ibuprofen-based hyperbranched polyester. (**B**) Fluorescence spectra of (a) acyl chloride-terminated hyperbranched polyester and (b) ibuprofen-based hyperbranched polyester. (**C**) TGA thermogram of ibuprofen-based hyperbranched polyester.

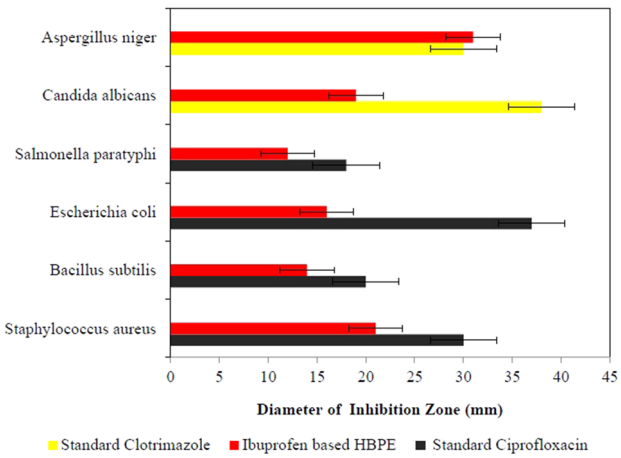


Figure 7. Statistical representation for antimicrobial activity of ibuprofen-based hyperbranched polyester.

ibuprofen-based hyperbranched polyester is correlated with the standard antibiotics, such as ciprofloxacin and clotrimazole. The result revealed that ibuprofen-based hyperbranched polyester showed a great inhibitory effect towards fungi than bacteria. In another view, ibuprofen-based hyperbranched polyester showed more inhibitory effect against Gram-negative bacteria (*E. coli* and *S. paratyphi*) than Gram-positive bacteria (*B. subtilis* and *S. aureus*). Generally, ibuprofen does not have enough potential to show against Gram-negative bacteria [33], but remarkably ibuprofen-based hyperbranched polyester showed the inhibitory effect against Gram-negative bacteria. This is because of the proper amount of ibuprofen (100 μg per disc) and the establishment of ester linkage in ibuprofen-based hyperbranched polyester [23,34]. Ibuprofen-based hyperbranched polyester showed better antimicrobial efficiency than both pure ibuprofen [21] and hyperbranched polyester, as stated in the already reported literature [35]. The improved microbial activities of ibuprofen-based hyperbranched polyester are due to a large number of alkyl chains with a low molecular weight [36]. The greater antimicrobial activity of ibuprofen-based hyperbranched polyester was shown towards fungus *A. niger*. The MIC value of the polymer was tested against *A. niger* and it was found to be 500 μg ml^{-1}.

4. Conclusions

The aromatic ibuprofen-based hyperbranched polyester was successfully synthesized from aliphatic hyperbranched polyester using the acid chloride approach. The particles of ibuprofen strongly aggregated with hyperbranched polyester were displayed in the SEM analysis. The appearance of double melting peaks and glass transition temperature (∼78°C) of ibuprofen-based hyperbranched polyester was studied from DSC thermogram. The crystalline nature of ibuprofen-based hyperbranched polyester was evident from the XRD, SEM and DSC analysis. Ibuprofen-based hyperbranched polyester holds thermal stability up to 330°C, as measured by TGA. The fluorescent behaviour of the polymer was established from UV–visible and fluorescence spectroscopy. The minor current of ibuprofen-based hyperbranched polyester was traced, but no peak potential was observed. Ibuprofen-based hyperbranched polyester was found to be highly soluble in polar solvents like DMF, DMAc, DMSO and THF. Ibuprofen-based hyperbranched polyester showed better inhibitory activity towards fungi than bacteria. Ibuprofen-based hyperbranched polyester is a promising material for pharmaceutical applications. The MIC test was carried out against *A. niger* and the value was found to be 500 μg ml^{-1}.

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