

# Preparation and Thermal Stability of New Cellulose-Based Poly(propylene imine) and Poly(amido amine) Hyperbranched Derivatives

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**ABSTRACT:** New cellulose-based hyperbranched derivatives having different degrees of branching were prepared via reaction of cellulose with acrylonitrile followed by reduction of nitrile groups and successive reaction with acrylonitrile or methylacrylate. First- ( $G = 1$ ) and half- ( $G = 0.5$ ) generation cellulose-based hyperbranched poly(propylene imine) or poly(amido amine) derivatives have been prepared with high reaction yield. The structure of the prepared derivatives was confirmed by Fourier transform infrared and  $^{13}\text{C}$  nuclear magnetic resonance ( $^{13}\text{C}$  NMR). Thermal stability of the different cellulose-based hyperbranched de-

derivatives were examined using thermogravimetric analysis to study the effect of branching on the thermal decomposition parameters. The onset degradation temperature and the activation energy of the thermal degradation decreased with increasing the branching of the cellulose-based hyperbranched derivatives. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2079–2087, 2006

**Key words:** cellulose; hyperbranched; cyanoethyl cellulose; poly(propylene imine); poly(amido amine); thermal stability

## INTRODUCTION

Cellulose is the most abundant natural polymer, and it is a polydisperse linear homopolymer consisting of regio- and enantio-selective  $\beta$ -1,4-glycosidic linked D-glucose units. Cellulose has been the subject for enormous modifications to prepare new cellulose derivatives having different supramolecular architectures to be used in a wide range of applications,<sup>1,2</sup> such as in ultra-thin coating,<sup>3–6</sup> host-guest systems,<sup>7–10</sup> biosensors,<sup>11–13</sup> liquid crystalline polymers,<sup>14–16</sup> and biomaterials.<sup>17–24</sup>

Dendrimers and hyperbranched polymers<sup>25</sup> have, in general, a three-dimensional molecular architecture and properties different from their linear counterparts. Dendrimers synthesis is a time consuming step-wise process requiring two or more iterative synthetic and purification steps to produce the final dendrimers. In contrast, hyperbranched polymers can be prepared in a convenient and cheap one-pot synthesis but they possess generally a less defined structure when compared with the perfect dendrimers. The unusual properties of these materials result from their highly branched structure, generally globular shape, multiplicity of chain ends, controlled molecular weight,

versatility in modification of terminal groups, and capability of intermolecular interaction with the immediate environment. These highly functionalized branched materials have found use in many applications.<sup>25–30</sup> Poly(amido amine)<sup>31</sup> (PAMAM) and poly(propylene imine)<sup>32</sup> (PPI) dendrimers are of the first complete dendrimers synthesized, well characterized and commercialized. They have large number of terminal amino, cyano, or ester functional groups. PAMAM dendrimers are prepared by (1) exhaustive Michael addition of acrylate ester to an amine functionality and (2) amidation of the resulting ester moieties with an alkylene diamine (e.g., ethylene diamine). Completion of this sequence gives a full generation ( $G = 1.0$ ) with amines terminal groups, while interruption of this sequence at the first step gives a half generation ( $G = 0.5$ ) with ester terminal groups. Repeating the above sequence leads to self-replication with concurrent introduction of repeating unit multiplicity. On the other hand, PPI dendrimers composed of a 1,4-diaminobutane (DAB) core that is extended with propylene imine units. The first generation ( $G = 1$ ) is obtained by Michael addition of DAB to acrylonitrile and subsequent hydrogenation of the nitrile groups. Repeating these reactions provides the higher generations of PPI dendrimer. These dendrimers, as such or their modified derivatives, have been the subject of many intensive studies as promising materials for potential applications in a variety of fields. For examples, PAMAM and its modified derivatives have

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been used in catalysis,<sup>33,34</sup> gene delivery,<sup>35,36</sup> drug delivery,<sup>37,38</sup> biochemical,<sup>39</sup> biophysical,<sup>40–42</sup> medicinal,<sup>43</sup> hydrogel,<sup>44</sup> biocompatible materials,<sup>45</sup> and selective heavy metal ions removal.<sup>46</sup> Metal-containing PPI were found to have catalytic, electronic, and magnetic properties.<sup>47–50</sup>

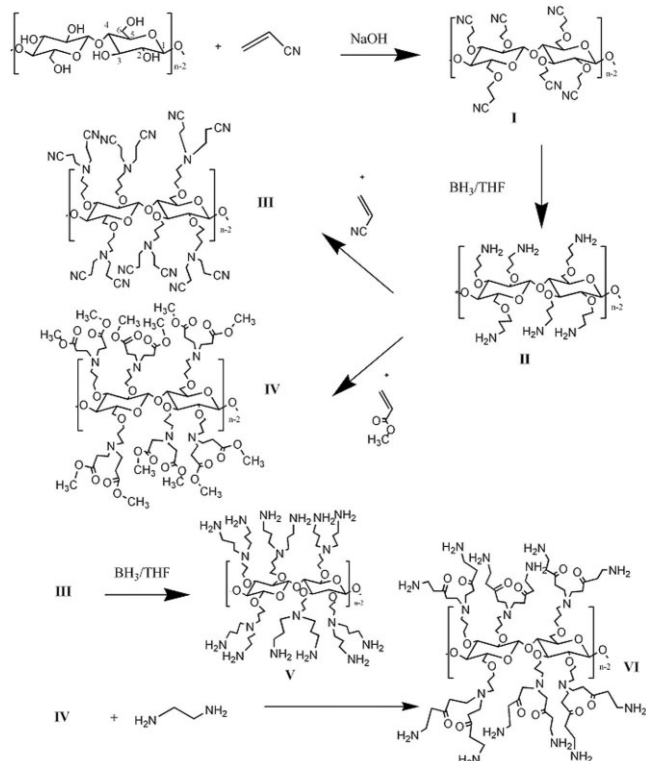
There is an increasing interest in attaching either these dendritic macromolecules or their dendron components to other materials. For example, the attachment of benzyl- or *tert*-butyl-terminated dendrons to silica surface resulted in a new immobilized dendritic silica material, which could be used for enhanced separations in high resolution capillary gas chromatography and capillary microextraction.<sup>51–53</sup> Also, dendrons containing 2,6-di(acylamino)pyridinyl moieties, which are capable of “internal” molecular recognition, were covalently bonded to agarose matrix.<sup>54</sup> Chemical modifications of silica,<sup>55–58</sup> carbon,<sup>59</sup> and chitosan<sup>60,61</sup> with poly(amido amine) hyperbranched constructs having different generations have been reported. Formation of layered thin films and bioactive films either physically adsorbed<sup>62,63</sup> or covalently grafted<sup>64–67</sup> on various substrates using different hyperbranched polymers has been evaluated.

Until now, interaction of cellulose with dendrimers or hyperbranched polymers have been rarely investigated; surface modification of regenerated cellulose film through hydrogen bonding of a hybrid linear-dendritic block copolymer to the cellulose hydroxyl groups was studied.<sup>68</sup> Recently, chemical interaction between cellulose and a series of dendrons having different generations and possessing isocyanate focal substituents have been investigated to prepare novel regioselective dendronized cellulose derivatives.<sup>69</sup> Also, novel regioselective, homo- and heterogeneous cellulose derivatives with dendritic appendages have been prepared via combinatorial-type reaction of cellulose in a *N,N*-dimethyl acetamide/LiCl solvent system with different dendrons possessing an isocyanate focal group.<sup>70</sup> In this work, the ability to prepare new cellulose-based hyperbranched derivatives was investigated with the aim to produce new cellulosic materials with expected wide applications because of the possible synergetic effect of the introduced branched moieties and the cellulose backbone. This would enable a wide variety of molecular designs to new tailored hybrid materials composed of natural polysaccharides and synthetic polymers. Of special importance, the cellulose derivatives having amine functional groups find applications as matrices for enzyme immobilization.<sup>71,72</sup>

## EXPERIMENTAL

### General comments

Reagent-grade fibrous cellulose, acrylonitrile (AN), ethylenediamine (EDA), and methyl acrylate (MA)



**Scheme 1.** Synthetic scheme and theoretical structure of the different cellulose-based hyperbranched derivatives.

were obtained and used without further purification. <sup>13</sup>C NMR spectra of cellulose and the different cellulose-based hyperbranched derivatives were recorded on Varian INOVA 200 MHz CP/MAS spectrometer, samples were packed into 7 mm silicon nitride rotors and spun at 5 KHz. Fourier transform infrared (FTIR) spectra were recorded on an ATI Mattson Benseis Series FTIR spectrophotometer, using the KBr technique. Thermogravimetric analysis was performed with a Mettler-Toledo TG50 thermogravimetric analyzer under nitrogen at a temperature range from 25 to 700°C at a heating rate of 10°C/min, the rate of nitrogen flow was 40 mL/min.

### Preparation of cyanethyl cellulose and aminopropyl cellulose

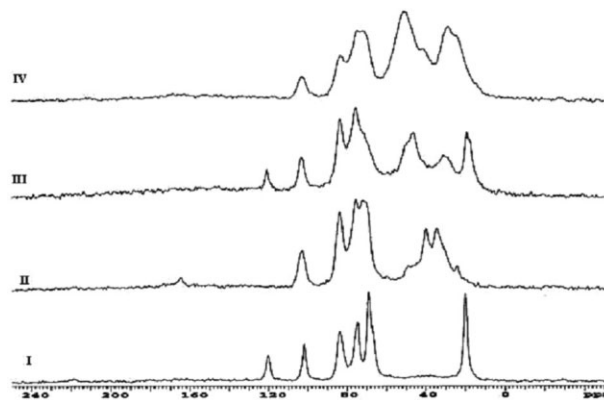
Cyanoethyl cellulose (CEC) I was prepared according to the previously described method,<sup>2</sup> the nitrogen content of the product was 11.4% (DS~2.9). Aminopropyl cellulose (APC) II was prepared by heterogeneous reduction of CEC, using BH<sub>3</sub>/THF solution, for 1 g of CEC I, 15 mL of 1M BH<sub>3</sub>/THF solution were used and the mixture was refluxed for 12 h. The product was then filtered, treated with saturated solution of sodium bicarbonate, washed with water and methanol, and dried at 60°C.

### Preparation of cellulose-based hyperbranched poly(propylene imine) derivatives

Introduction of hyperbranched poly(propylene imine) (PPI) onto cellulose was achieved by repeating Michael addition of AN to APC followed by heterogeneously catalyzed hydrogenation<sup>32</sup> (Scheme 1). Michael addition reaction was carried out as follows: Into 100-mL flask that contained 1 g of APC, 2.5 equivalents of AN per primary amine group were added as an aqueous solution of 0.1M concentration. The first equivalent is added at room temperature and the second equivalent was added at 80°C, the reaction time was 3 h. The produced half-generation ( $G = 0.5$ ) cellulose-based PPI **III** with terminal cyano groups was filtered and washed with methanol. Reduction of **III** was carried out using  $\text{BH}_3/\text{THF}$  mixture to produce first-generation ( $G = 1$ ) cellulose-based PPI **V** with terminal amino groups. The product was then filtered, treated with saturated solution of sodium bicarbonate, washed with water and methanol, and dried at 60°C. The above two reactions were repeated to prepare higher generations of cellulose-based PPI derivatives with different terminal groups. The percent increase in weight (weight percent gain, WPG) due to the reaction was recorded, and the nitrogen content was determined using the micro kjeldhal method.<sup>73</sup>

### Preparation of cellulose-based hyperbranched poly(amido amine) derivatives

Introduction of hyperbranched poly(amido amine) (PAMAM) onto cellulose was achieved by repeating two processes<sup>31</sup> on APC **II** (Scheme 1): (1) Michael addition of MA to APC and (2) amidation of terminal amino groups with EDA. Michael addition was carried out as follows: Into a 100-mL flask that contained 1 g of APC, 20 mL of methanol solution of MA (1.3



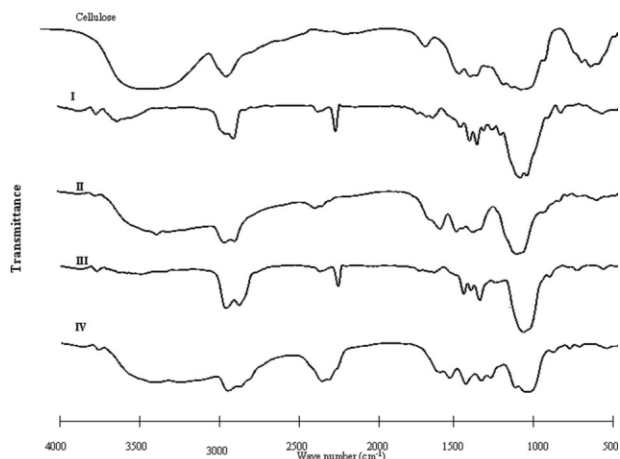
**Figure 2**  $^{13}\text{C}$  NMR spectra of CEC (**I**), APC (**II**), 0.5-generation cellulose-based PPI (**III**), and 1st-generation cellulose-based PPI (**IV**).

equivalent to amino groups) were added. The mixture was stirred under nitrogen atmosphere with a magnetic stirrer at 50°C. After 12 h, the resulting product, half-generation cellulose-based PAMAM **V**, was filtered and washed with methanol. The amidation of terminal ester groups was carried out as follows: Into a 100-mL flask that contained **V**, 20 mL of methanol solution of ethylene diamine (large excess to terminal group) were added and the mixture was stirred with a magnetic stirrer at 50°C for 24 h. The resulting product, first-generation cellulose-based PAMAM **VI** was filtered and washed with methanol. The above two reactions were repeated to prepare higher generations of cellulose-based PAMAM derivatives with different terminal groups. The WPG due to the reaction was recorded, and the nitrogen content was determined.

## RESULTS AND DISCUSSION

### Cellulose-based hyperbranched PPI

CEC is one of the well known cellulose ether that has enhanced thermal stability, an improved rot resistance and also favorable dielectric properties when compared with cellulose.<sup>2</sup> In this work, CEC was used as starting materials for the preparation of the different cellulose-based hyperbranched derivatives. Cyanoethylation of cellulose is a classical example of cellulose etherification by Michael addition of an activated  $\text{C}=\text{C}$  bond to a partially anionized cellulose hydroxyl groups in aqueous medium. The FTIR and  $^{13}\text{C}$  NMR spectra of CEC are shown in Figures 1 and 2, respectively. The degree of substitution (DS) of the prepared CEC was about 2.9. FTIR spectra showed the appearance of the characteristic peak of the introduced nitrile group at  $2254\text{ cm}^{-1}$  and the remarkable reduction of the hydroxyl groups stretching vibration absorption band at  $3400\text{ cm}^{-1}$  and their bending vibration absorption bands at  $610$  and  $666\text{ cm}^{-1}$ .  $^{13}\text{C}$  NMR spectrum of



**Figure 1** FTIR spectra of cellulose, CEC (**I**), APC (**II**), 0.5-generation cellulose-based PPI (**III**), and 1st-generation cellulose-based PPI (**IV**).

**TABLE I**  
**Nitrogen Content and Weight Percent Gain (WPG) of the Different Cellulose-Based Hyperbranched Derivatives**

	Nitrogen content <sup>a</sup> (%)	WPG due to reaction (%)
CEC I	12.64	—
APC II	12.43 (12.5)	—
Half-generation cellulose-based PPI III	7.64 (9.37)	78.3 (93.2)
1st-generation cellulose-based PPI IV	7.60 (9.35)	3.58 (3.5) <sup>b</sup>
Half-generation cellulose-based PAMAM V	3.84 (4.76)	118.2 (150.1)
1st-generation cellulose-based PAMAM VI	14.3 (19.9)	13.7 (19.2) <sup>c</sup>

<sup>a</sup> Values in parentheses are the theoretical values based on DS = 2.9 of the starting CEC.

<sup>b</sup> Theoretical WPG due to reduction of **III**.

<sup>c</sup> Theoretical WPG due to amidation of **VI**.

CEC showed the appearance of new signals at 122 ppm of CN group, at 18 ppm due to methylene carbon adjacent to the cyano group (CH<sub>2</sub>—CH<sub>2</sub>—CN), and another signal due to other methylene carbon of the cyanoethyl group (CH<sub>2</sub>—CH<sub>2</sub>—CN), which almost coincides with the down field-shifted signal of C-1 carbon of the anhydroglucose unit (AGU) of cellulose at 69 ppm. APC was prepared through heterogeneous reduction of CEC using BH<sub>3</sub>/THF solution. FTIR and <sup>13</sup>C NMR spectra (Figs. 1 and 2) show the occurrence of reduction of the nitrile groups. The FTIR spectrum showed the disappearance of the nitrile group absorption band at 2530 cm<sup>-1</sup> and a broad band at about 3400 cm<sup>-1</sup> because of the formation of the amine groups. The appearance of a broad band for the amine groups instead of a double peak at about 3400 and 3500 cm<sup>-1</sup> as usually seen in case of primary amines may be due to extensive hydrogen bonding between the introduced amine groups (propyl amine groups), which causes broadening and shift of the peak to lower wave number. <sup>13</sup>C NMR showed also the disappearance of the nitrile group signal at 122 ppm, new signals at 42 ppm due to carbon atom adjacent to the amine group (O—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—NH<sub>2</sub>), and at

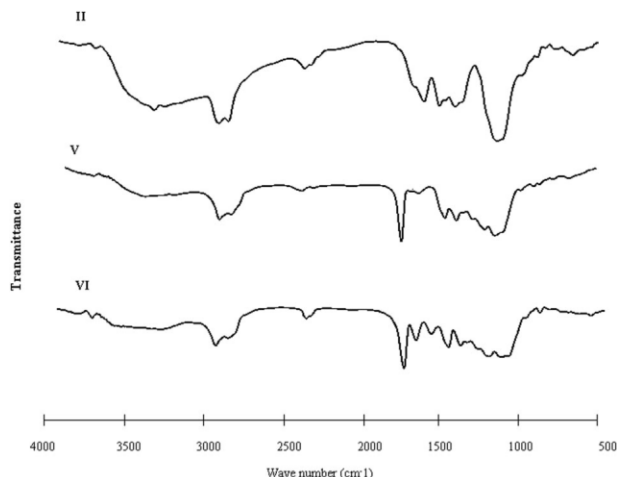
38 ppm due to carbon atom next to the previous one (—O—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—NH<sub>2</sub>).

The preparation of half-generation cellulose-based PPI **III** was successfully achieved via reaction of APC with AN; the nitrogen content and WPG due to the reaction were about 85% of the theoretical values (Table I). FTIR and <sup>13</sup>C NMR spectra (Figs. 1 and 2) confirmed occurrence of the reaction. FTIR spectrum shows the reappearance of the nitrile group absorption at 2250 cm<sup>-1</sup> and disappearance of the broad band amino groups at 3200 cm<sup>-1</sup> as well as increase of the ethylene group absorption band at 2945 cm<sup>-1</sup>. <sup>13</sup>C NMR spectra of **III** showed the appearance of new signals as a result of the introduction of the cyanoethyl groups, <sup>13</sup>C NMR chemical shifts assignment of this derivative and the others are included in Table II. Reduction of **III** using BH<sub>3</sub>/THF solution resulted in preparation of 1st-generation cellulose-based PPI **V**, almost quantitative yield was obtained after the hydrogenation. FTIR spectrum of **V** (Fig. 1) showed similar changes to that noticed in case of reduction of CEC to APC. <sup>13</sup>C NMR spectrum (Fig. 2) showed the new signals correspond to reduction of the nitrile group. Trials to prepare higher generations of the cellulose-

**TABLE II**  
<sup>13</sup>C Chemical Shifts Assignment of Cellulose-Based Poly(propylene imine) and Poly (amids amine)<sup>a</sup>

Derivative	Introduced functional group onto cellulose	Chemical shift (ppm)
CEC I	—[CH <sub>2</sub> —CH <sub>2</sub> —CN] (a) (b) (c)	a: 69, b: 18, c: 120.3
APC II	—[CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —NH <sub>2</sub> ] (a) (b) (c)	a: 70, b: 34, c: 40
Half-generation cellulose-based PPI III	—[CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —N(CH <sub>2</sub> —CH <sub>2</sub> —CN) <sub>2</sub> ] (a) (b) (c) (d) (e) (f)	a: ≈70, b: 30, c: 46, d ≈50, e: 18.4, f: 120.3
1st-generation cellulose-based PPI IV	—[CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —N(CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —NH <sub>2</sub> ) <sub>2</sub> ] (a) (b) (c) (d) (e) (f)	a: ≈71, b: 28, c: ≈52, d ≈46, e: 32, f: ≈40
Half-generation cellulose-based PAMAM V	—[CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —N(CH <sub>2</sub> —CH <sub>2</sub> —COOCH <sub>3</sub> ) <sub>2</sub> ] (a) (b) (c) (d) (e) (f) (g)	a: 70.4, b: 33.1, c: ≈46–50, d ≈46–50, e: 29, f: 172.2, g: 52
1st-generation cellulose-based PAMAM VI	—[CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —N(CH <sub>2</sub> —CH <sub>2</sub> —CONH—CH <sub>2</sub> —CH <sub>2</sub> ) <sub>2</sub> ] (a) (b) (c) (d) (e) (f) (g) (h)	a: 70, b: ≈32, c: ≈46–50, d ≈46–50, e: ≈27, f: 172.2, g: ≈40, h: ≈40

<sup>a</sup> Chemical shifts of AGUs carbons of cellulose are: 102.6 ppm (c-1), ≈75 ppm (c-2 and c-3), 83.7 ppm (c-4), ≈75 ppm (c-5), and 61 ppm (c-6).



**Figure 3** FTIR spectra of cellulose APC (II), 0.5-generation cellulose-based PAMAM (V), and 1st-generation cellulose-based PAMAM (VI).

based PPI derivative with reasonable WPG, i.e., lowest possible imperfection in structure, by repeating the Michael addition and hydrogenation reactions, under the condition used in this work, failed as evident from the little weight gain and the spectral analyses. On reacting first-generation cellulose-based PPI **V** with AN, WPG of about 20 was obtained while the theoretical WPG is about 95. This may be due to heterogeneous system used and the steric hindrance because of the high DS of CEC used as starting material; regioselective cyanoethylation of cellulose at C-6 hydroxyl group through protection and deprotection regime may be a route to prepare higher generations because of the lower predicted steric hindrance in case of the reaction at the C-6 hydroxyl groups due to  $\beta$ -glycosidic structure of the AGUs of cellulose.

### Cellulose-based hyperbranched PMAM

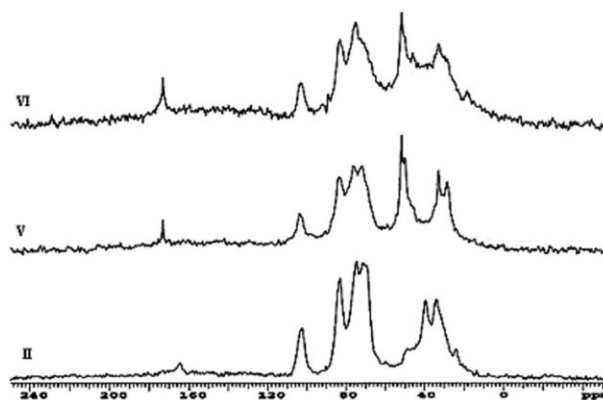
Cellulose-based PAMAM derivatives were prepared via reaction of APC **II** with MA to produce the cellulose-based ester-terminated PAMAM ( $G = 0.5$ ) derivative **V** as shown in Scheme 1. The WPG due to the introduction of the ester-terminated PMAM was about 79% of the theoretical value. Reaction of **V** with EDA resulted in formation of the amine-terminated ( $G = 1$ ) PAMAM cellulose derivative **VI**, the WPG was about 71% of the theoretical value. The lower theoretical WPG values than the actual ones were also observed on grafting of silica, carbon, and chitosan surfaces with different generations of PAMAM, the decrease increased on increasing the generations.<sup>56,57,60,62</sup> Trials to prepare higher generation of cellulose-based PMAM with reasonable WPG failed under the conditions used. On reacting first-generation cellulose-based PAMAM **VI** with MA, WPG of about 16 was

obtained compared to the theoretical WPG of about 99.

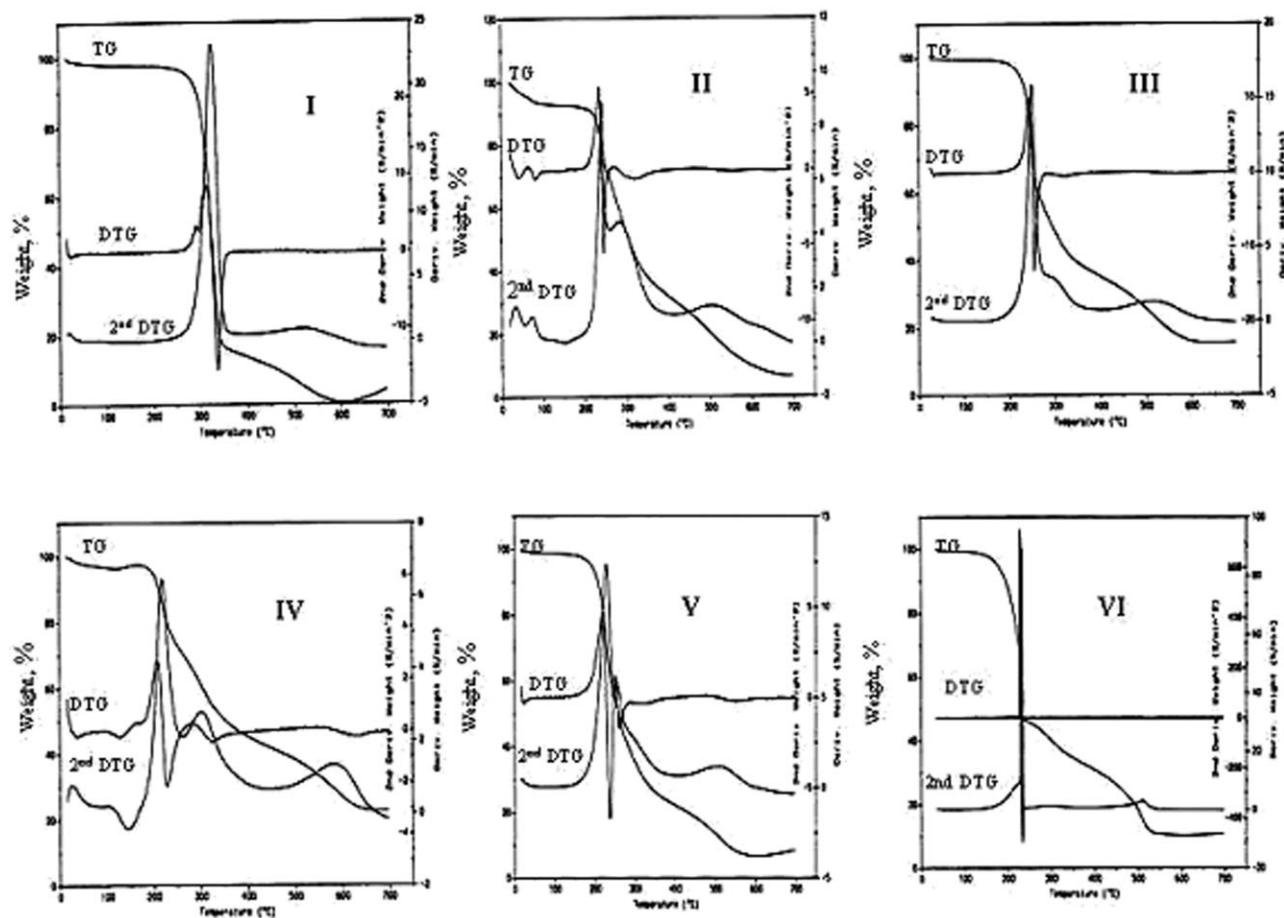
Figures 3 and 4 show FTIR and  $^{13}\text{C}$  NMR of APC **II**, the ester-terminated **V**, and amine terminated **VI** cellulose-based PAMAM derivatives, respectively. FTIR spectrum of **V** showed the appearance of the characteristic peaks of the carbonyl group at  $1735\text{ cm}^{-1}$  and the reduction of the intensity of the  $\text{NH}_2$  band at  $3400\text{ cm}^{-1}$ . Reaction of **V** with EDA resulted in appearance of the characteristic bands of the  $\text{CO-NH}$  group at  $1730$ ,  $1650$ , and  $1530\text{ cm}^{-1}$ ; a very broad band appeared at  $3400\text{ cm}^{-1}$  because of the introduction of terminal amine groups in addition to the increase of ethylene group's band intensity at  $2900\text{ cm}^{-1}$ .  $^{13}\text{C}$  NMR spectrum (Fig. 4) of **V** showed the appearance of the characteristic signal at  $172\text{ ppm}$  because of the presence of  $\text{C=O}$  groups in addition to the other signals of the rest of the PMAM moieties as shown in Table II.  $^{13}\text{C}$  NMR spectrum of **VI** shows the disappearance of the methyl carbon signal ( $\text{CO-O-CH}_3$ ) at  $25\text{ ppm}$  because of formation of the amide bond and elimination of the  $\text{CH}_3\text{-O}$  fragment. Because of the broadening of the signals as a result of the hyperbranching, the signals of the introduced ethylene carbons adjacent to the amino groups [ $-\text{N}-(\text{CH}_2-\text{CH}_2-\text{CO-NH-CH}_2-\text{CH}_2-\text{NH}_2)_2$ ] were merged with the other signals in the area from  $27$  to  $52\text{ ppm}$ .

### Thermal stability and thermal degradation kinetics of the cellulose-based hyperbranched derivatives

Different cellulose derivatives are extensively used as separation membranes, coatings, painting, fibers, plastic films, and functional materials. Cellulose derivatives may encounter elevated temperatures in their use, processing, as well as compounding. So, the thermal stability of cellulose derivatives is important from both practical and academic points of view. Thermal degradation study of these derivatives may determine



**Figure 4**  $^{13}\text{C}$  NMR spectra of APC (II), 0.5-generation cellulose-based PAMAM (V), and 1st-generation cellulose-based PAMAM (VI).



**Figure 5** TG, DTG, and 2nd derivative TG curves of CEC (I), APC (II), 0.5-generation cellulose-based PPI (III), 1st-generation cellulose-based PPI (IV), 0.5-generation cellulose-based PAMAM (V), and 1st-generation cellulose-based PAMAM (VI).

the ultimate life of them at elevated temperatures.<sup>74</sup> In this work, the thermal stability and thermal degradation kinetics of the different cellulose-based hyperbranched derivatives were studied to investigate the thermal degradation characteristics of the prepared cellulose-based hyperbranched derivatives and to

show the effect of hyperbranching on their thermal degradation properties.

Figure 5 shows dynamic thermogravimetric (TG), differential thermogravimetric (DTG), and the 2nd derivative of the thermogravimetric curves of the different cellulose-based hyperbranched derivatives; the

**TABLE III**  
Thermal Decomposition Data of Cellulose and the Different Cellulose-Based Hyperbranched Derivatives

Derivative	$T_d$	$T_{dm}$	Charred yield at 400°C	Activation energy (KJ/mol)	Order ( $n$ )	Ln Z
CEC I	272	326	13.7	176.7	0.92	38.45
APC II	225	250	35.11	166.3	1.41	35.6
Half-generation cellulose-based PPI III (cano-terminated)	230	240	31.84	157.3	0.90	33.13
1st-generation cellulose-based PPI IV (amine-terminated)	204	218	45.18	141.3	0.96	27.05
Half-generation cellulose-based PAMAM V (ester-terminated)	200	228	22.15	110.2	0.32	15.38
1st-generation cellulose-based PAMAM VI (amine-terminated)	184	228	30.1	70.7	0.45	14.59

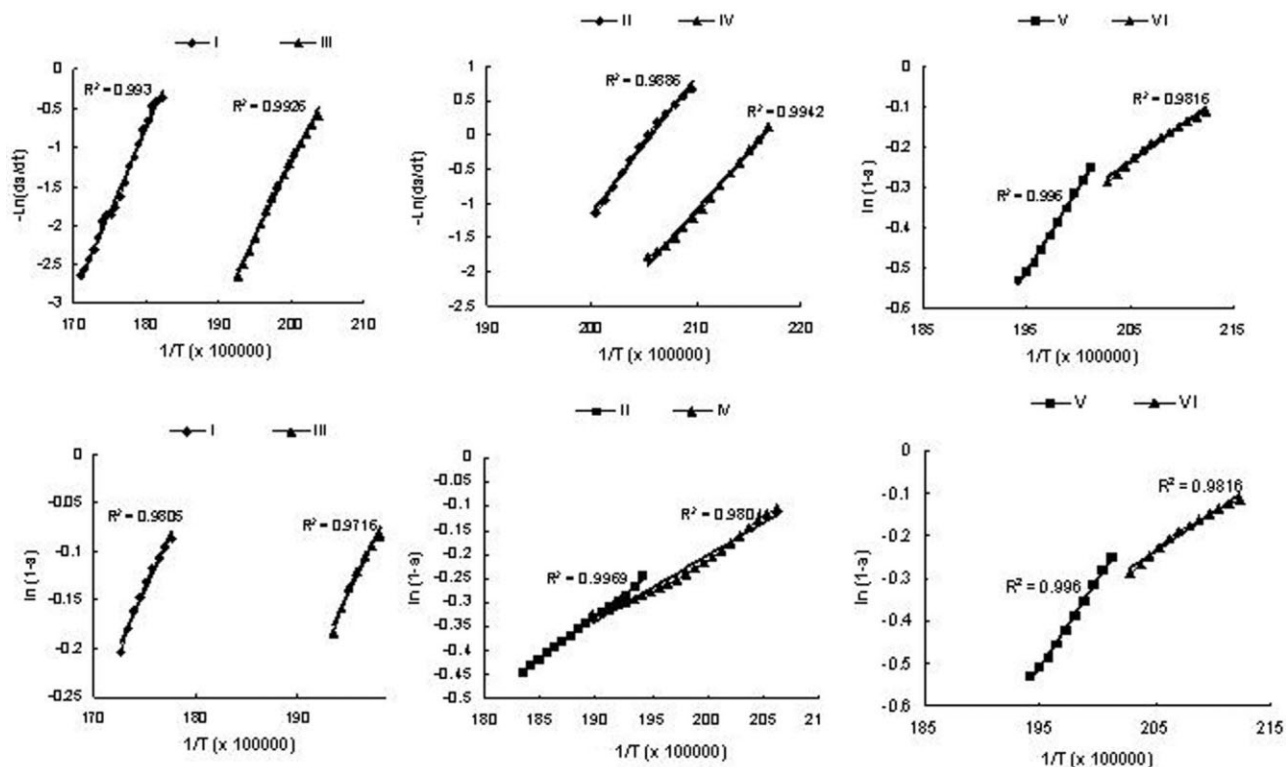
data of these curves are listed in Table III. As shown from the figure, the thermal degradation of the different derivatives consists of a series of degradation reactions after the dehydration step at about 100°C, the degradation became more complicated as the hyperbranching increase as seen from the shape of the curves and the increase of the number of stages of thermal degradation. The thermal stability decreased on increasing the hyperbranching, the half-generation cellulose PPI **III** showed lower onset degradation temperature ( $T_d$ ) and maximum weight loss temperature ( $T_{dm}$ ) than CEC **I** in spite of the larger terminal cyano groups, which was expected to impart higher thermal stability because of the higher possible interaction between the polar cyano groups; the same trend was found for APC **II** and first-generation cellulose-based PPI **V**, and half-generation and first-generation cellulose-based PAMAM (**IV** and **VI**). However, the thermal decomposition was slower as the hyperbranching increased; this is clear from comparing the char yield of the different derivatives at 400°C. This means more complicated reactions occurred during thermal degradation as the hyperbranching increased. The lower thermal stability on increasing the hyperbranching may be attributed to the steric hindrance of these branched derivatives, which under the effect of heat and the increasing mobility of the branches become more labile to thermal degradation. Another possibility is the decrease in crystallinity as the hyperbranching increases. This can be estimated from the FTIR spectra of these derivatives by calculating the ratio of the intensity of some absorption bands. The intensity of certain bands in IR spectra has been found to be sensitive to variations in cellulose crystallinity or crystalline form. Such variation may be determined using the ratio of a band that is affected by cellulose crystallinity to that of a band that is comparatively insensitive to crystallinity changes. The ratio of the absorbency of the peak at 1372  $\text{cm}^{-1}$  to those at 2900  $\text{cm}^{-1}$  ( $A_{1372}/A_{2900}$ ) has been used to measure the relative cellulose crystallinity.<sup>75</sup> This ratio was 0.57, 0.4, 0.43, and 0.4 for CEC **I**, half-generation cellulose PPI **III** (cyano-terminated PPI), APC **II**, and first-generation cellulose PPI **IV**, respectively. In conclusion, the thermal stability of the different cellulose-based hyperbranched derivatives was in the following order; CEC **I** > half-generation cellulose PPI **III** > APC **II** > first-generation cellulose PPI **IV** > half-generation cellulose PMAM **V** > first-generation cellulose PMAM **VI**, while the char yield at 400 C was in the order **IV** > **II** > **III** > **VI** > **V** > **I**. The lower thermal stability of cellulose PMAM derivative is due to the lower thermal stability of the ester bonds when compared with the stronger C—C or C—N bonds. Concerning the mechanism of thermal degradation of the different derivatives, previous work on thermal stability of PPI dendrimers using TGA-MS showed thermally in-

duced retero-Michael addition reaction during thermal degradation.<sup>32</sup> The occurrence of retero-Michael addition during thermal degradation is also possible in case in the PMAM dendrimers since using high temperature during their synthesis was found to increase this reaction and the formation of other degraded products.<sup>33</sup> Thermal degradation of the prepared cellulose-based PPI or PAMAM derivatives is expected to involve these degradation reactions in addition to the known degradation reactions of the cellulose backbone, i.e., pyrolytic fragmentation leading to aromatized entities and finally most probably to a highly crosslinked carbon skeleton.<sup>1</sup>

There are different differential methods used to determine the kinetic parameters of thermal degradation (activation energy  $E$ , order of reaction  $n$ , and frequency factor  $Z$ ) by using the relationship between the weight loss and the absolute temperature  $T$ . Although these methods may give slightly different values but they give the same trend. The Freidman method was used in this work, the method uses the following equation<sup>76</sup>:

$$\ln d\alpha/dt = \ln Z + n(1-\alpha) - E/RT$$

Where  $\alpha$  is the fractional weight loss and  $R$  is the gas constant. The value of  $\ln d\alpha/dt$  can easily obtained from the DTG curve. The value of  $\ln (1-\alpha)$  can be obtained from the TG curve. The values of  $\ln (d\alpha/dt)$  were plotted against  $1/T$ , and then  $E$  can be determined from the slope of the plot. The plot of  $\ln (1-\alpha)$  versus  $1/T$  will give the  $n$  value from the maximum slope of the line. Finally, the  $\ln Z$  can readily be calculated through the equation at a certain temperature. Figure 6 shows the Freidman plots of  $\ln (d\alpha/dt)$  and  $\ln (1-\alpha)$  versus  $1/T$  for the different cellulose-based hyperbranched derivatives, the calculated kinetic degradation parameters ( $E$ ,  $n$ , and  $\ln Z$ ) are shown in Table III. The values of  $E$  and  $\ln Z$  also decreased as the hyperbranching increases, the cellulose-based PAMAM derivatives **V** and **VI** showed a remarkably low activation energy for thermal degradation, the  $E$  value of first-generation cellulose-based PAMAM derivative was about 38% lower than its half-generation analogous while the decrease in the  $E$  values due to increasing the hyperbranching of cellulose-based PPI derivatives (CEC **I** versus half-generation cellulose-based PPI **III** and APC **II** versus first-generation cellulose-based PPI **IV**) was about 7–12%. This means that the introduction of the ester group in case **V** and **VI** of resulted in initiation of faster decomposition even if the ester groups are not the terminal groups as in case of **VI**, which have the lowest  $E$  and  $\ln Z$  values. The cyano-terminated cellulose-based PPI showed the highest activation energy among all the hyperbranched derivatives. From the values of  $n$ , it could be concluded that the decomposition of the



**Figure 6** Friedman plots for the determination of kinetic parameter of the thermal degradation of CEC (I), 0.5-generation cellulose-based PPI (III), APC (II), 1st-generation cellulose-based PPI (IV), 0.5-generation cellulose-based PAMAM (V), and 1st-generation cellulose-based PAMAM (VI). Values on curves are the correlation coefficients of the trend lines.

different cellulose derivatives roughly believed to follow first order reaction during the significant portion of the weight loss, low  $n$  values were obtained for the derivatives V and VI.

## CONCLUSIONS

Cellulose-based hyperbranched derivatives having PMAM and PPI terminal groups could be prepared; however, only the first generation could be obtained in high yield, higher generations gave small yields indicating high degree of imperfection in the structure of the introduced hyperbranched moieties. The low yield obtained in cases of preparation of the higher generations was attributed to the high DS of CEC I used as starting materials and the possible steric hindrance because of introduction of the branched moieties; using CEC regioselectively modified only at C-6 of AGU may be used for the preparation of higher generations' cellulose-based hyperbranched derivatives. The prepared hyperbranched derivatives are expected to have wide application because of the synergistic properties of cellulose backbone and the hyperbranched moieties.

The thermal stability decreased as the hyperbranching increased, the steric hindrance and lower crystallinity as the hyperbranching increased made the pre-

pared derivative more labile to thermal degradation in spite of the larger number of terminal functional groups, which was expected to higher thermal stability due to the possible higher interaction between these terminal groups. However, the increase in hyperbranching resulted in a significant lower rate of thermal decomposition.

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