

# Synthesis of Hyperbranched Aromatic Polyamide–Imide and Its Grafting onto Multiwalled Carbon Nanotubes

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**ABSTRACT:** A flexible hyperbranched aromatic polyamide–imide (PAI) having an amine group in the center and carboxyl groups in the ends was synthesized from a  $AB_2$  type of monomer of 2-(6-aminohexylcarbomoyl) terephthalic acid that was prepared from trimellitic anhydride and 1,6-diaminohexane. Fourier transformed infrared spectra (FTIR), NMR, and ES-MS were used to characterize the structure of the monomer and the synthesized hyperbranched polymer. Then the hyperbranched PAI was grafted onto the multiwalled carbon nanotubes (MWNTs) that was first treated by acid and changed into MWNT-

COCl by  $SOCl_2$  in a tetrahydrofuran solution. By observation with transmission electron microscopy and characterization with FTIR and thermal gravity of analysis, the functionalized MWNTs were terminally enclosed with polymer; it was believed that the MWNTs were linked with a big carboxylic claw at the end and the adsorption ability of the MWNTs to  $NH_2$ -substrate was enhanced. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2413–2421, 2007

**Key words:** MWNTs; polyamide–imide; hyperbranched polymer; graft to

## INTRODUCTION

Compared with similar linear polymers, hyperbranched polymers have an exceptional molecular architecture with a highly branched backbone and a large number of terminal functional groups. Compared with dendrimers, hyperbranched polymers have a less regular structure and a broader molecular weight distribution; therefore it could be prepared by some relatively simple methods, such as one-step polymerization of  $AB_x$ -type multifunctional monomers (where  $x$  is generally 2 or 3) by which gel won't form. Moreover the preparation does not involve tedious isolation and purification procedures, which are required for preparing dendrimers.<sup>1–3</sup> Being a unique type of dendritic polymer, hyperbranched polymers possess interesting properties of the dendritic structures and feasibility for large-scale and inexpensive manufacture at the same time.

Although there have been many researches on hyperbranched and dendritic polyamides, they were generally prepared either by self polymerization of  $AB_2$  type monomers<sup>4–6</sup> or more recently by copoly-

merization methods.<sup>7,8</sup> As to aromatic poly(amide–imide)s, which demonstrates high-performance with the advantages of both polyamides and polyimides, there were few reports regarding preparation of hyperbranched aromatic poly(amide–imide).<sup>9</sup>

Till the present, many research groups have focused on using linear polymer chains<sup>10,11</sup> to modify the surface of multiwalled carbon nanotubes (MWNTs) and single-walled carbon nanotubes (SWNTs) by atom transfer radical polymerization (ATRP), anionic, cationic, and ring-opening polymerizations so that the carbon nanotubes (CNTs) can be easily dispersed in solvent and various matrices. Covalent attachment of polymers to CNTs has been mainly accomplished by “grafting to” and “grafting from” approaches.<sup>12,13</sup> In the former approach, the polymers are first prepared and then reacted with the carboxylic acid functionalities of the CNTs. The “graft to” approach is characterized by low grafting density because of the hindrance of the pregrafted polymer chains, which have reacted with the carboxylic groups of the CNTs so that possibility of further functionalization is reduced. While in the “grafting from” approach, the polymers grow from the surface of nanotubes by first covalently attaching initiators, which involves *in situ* polymerization of monomers from the preformed initiators on the CNT surfaces, and results in higher grafting density and control over polymer growth with the possibility of designable structures.

It is expected that CNTs surfaces functionalized with hyperbranched macromolecules not only provide a new route to highly functionalized CNTs, but also increase the functional complexity of the CNTs,

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protect and stabilize the central conjugated backbone of CNTs, and improve the solubility and processability without altering their electronic characteristics by making use of the abundant reactivity groups of the hyperbranched polymer. Therefore, hyperbranched polymers may be ideal materials to coat MWNTs and enable further functionalization of MWNTs.

It has been reported that star-shaped nanostructures are produced by reaction of the periphery of a multifunctional dendrimer with CNTs.<sup>14</sup> There are other reports about hyperbranched polymer linking to CNTs to improve the solubility of CNTs. For instance, a hyperbranched macromolecule made by self-condensing vinyl polymerization strategy via ATRP was employed to grow on the surfaces of MWNTs.<sup>15</sup> A hyperbranched poly(*m*-phenylenevinylene)-*co*-[(2,5-dioctoxy-*p*-phenylene)vinylene] (PmPV) polymer was used to break up nanotube bundles, wrap bundles of SWNTs, and achieve a sufficient coverage for nanotube dispersion and solubilization.<sup>16</sup> An *in situ* ring-opening polymerization strategy was employed to grow multihydroxyl dendritic macromolecules on the convex surfaces of MWNTs, affording novel one-dimensional molecular nanocomposites.<sup>17</sup> SWNTs and MWNTs functionalized by lipophilic and hydrophilic dendron species under classical amidation and esterification reaction conditions are respectively soluble in hydrocarbon and weakly polar organic solvents or soluble in both organic solvents and water.<sup>18</sup>

In this article, the hyperbranched polyamide-imide (PAI) was made from 2-(6-aminohexylcarbonyl) terephthalic acid, a AB<sub>2</sub> type of monomer, which is synthesized from trimellitic anhydride and 1,6-diaminohexane. A represents —NH<sub>2</sub> and B represents —COOH to ensure that the growing hyperbranched polymer would always end with amide functions and avoid gelation, and also have periphery with carboxyl groups. Then the hyperbranched PAIs were grafted mainly to the ends of the MWNTs to enhance alignment of the functionalized MWNTs on NH<sub>2</sub>-substrate.

## EXPERIMENTAL

### Characterization

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained on a JOEL JNM-ECA 600 NMR spectrometer with DMSO-d<sub>6</sub> and D<sub>2</sub>O as the solvent. Fourier transformed infrared spectra (FTIR) were measured with a Nicolet 560-IR spectrometer by incorporating the sample in a KBr disk. Elemental analysis of C, H, and N was completed through the Heratus CHN-Rapid method. The molecular weights of the monomer and the polymer were determined by ES-MS (Esquire Lc-00136). Thermal gravity of analysis (TGA, TA-60) was utilized to

analyze the weight loss of the oxidized MWNTs and the MWNTs grafted with PAI. Transmission electron microscopy (TEM, Hitachi H-800) and scanning electron microscopy (SEM, JSM-6301F) were utilized to observe the shape of the functionalized MWNTs and the adsorption of MWNTs on NH<sub>2</sub>-substrate, respectively.

### Materials

The MWNTs were obtained from the Tsinghua-Nafine Nano-Powder Commercialization Engineering Centre. Tetrahydrofuran (THF) and *N*-methyl-2-pyrrolodone (NMP) were commercially available and used after being dried over 4 Å molecular sieves. The other reagents were available commercially and used as received.

### Synthesis of AB<sub>2</sub> type monomer

The AB<sub>2</sub> type monomer was prepared from trimellitic anhydride and 1,6-diaminohexane. Trimellitic anhydride (0.01 mol) and 0.10 mol 1,6-diaminohexane were dissolved in 40 mL THF and 150 mL THF, respectively. Then the trimellitic anhydride solution was dripped into 1,6-diaminohexane solution in a 250-mL flask with a mechanical stirrer at 0–5°C. With the occurring of the reaction, the organic salt was made and the solution became whiter and whiter. The organic salt precipitated gradually after the stirrer stopped. The precipitate was filtrated and dissolved in water. Diluted HCl solution was then gradually dripped into transparent water solution. When the pH value was adjusted to be about 5–6, the solution became cloudy and a white sediment appeared. After filtrating the sediment, THF was added into the filtrated solution to extract the AB<sub>2</sub> monomer. The solution was divided into two phases with the addition of THF. The lower phase of solution was separate and THF was added into it until the lower phase of water solution became slimy and finally only a small amount of the AB<sub>2</sub> monomer dissolved in it.

### Thermal polymerization of the AB<sub>2</sub> monomer

The PAI was prepared by direct polycondensation following the general procedures as below: 0.309 g AB<sub>2</sub> was put into a 25 mL round-bottomed flask fitted with a water-cooled condenser and a mechanical stirrer and then 5 mL NMP was added. The mixture was heated under nitrogen atmosphere in an oil bath at 150–160°C for 5 h. After removing the solvent under vacuum, a brown polymer was obtained.

### Preparation of oxidized MWNTs from pristine MWNTs

MWNTs (0.5 g) were added to 50 mL mixture of concentrated sulfuric and nitric acid in 3 : 1 volume ratio

and sonicated in an ultrasonic bath at room temperature for 1 h, then at 75°C for 1.5 h. The solution was diluted with water, then vacuum-filtered through a 0.45  $\mu\text{m}$  Millipore poly(vinylidene fluoride) (PVDF) membrane, and subsequently washed with distilled water until the pH value of the filtrate approached 7. After drying the filtered product for 2 h at 110°C, the oxidized MWNTs, i.e. carboxyl functionalized MWNTs were obtained.

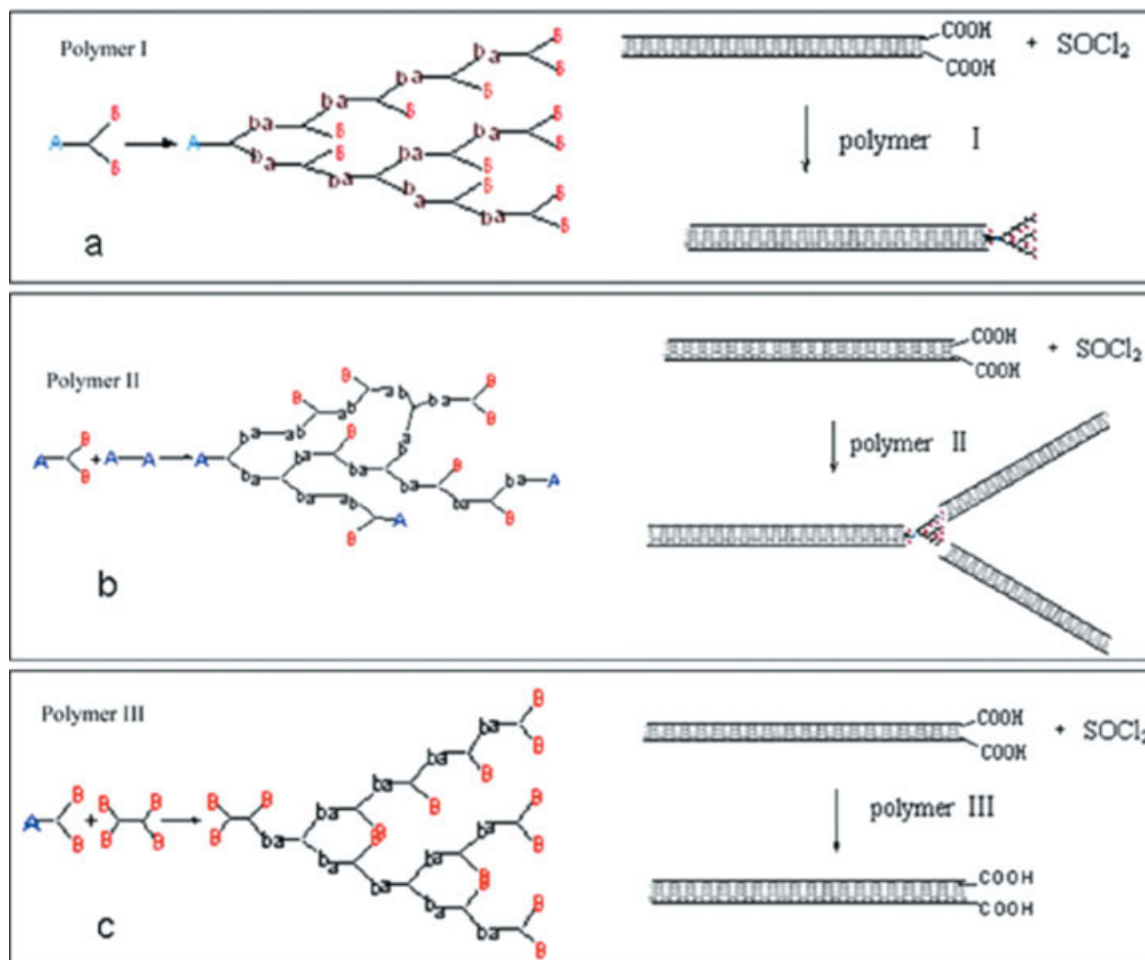
### MWNTs functionalized with hyperbranched PAI and the preparation of samples

The oxidized MWNTs (0.004 g) was first suspended in 15 mL anhydrous THF and 2 mL  $\text{SOCl}_2$  was added. Then the solution was put into 50 mL three-necked round-bottom flask with nitrogen inlet and outlet. After being kept at reflux and at 75°C with magnetic stirrer for 6 h, the carboxyl groups ( $-\text{COOH}$ ) on the MWNTs changed into  $-\text{COCl}$ . When stirring was stopped, the MWNT-COCl was gradually precipitated from the solution. After the MWNT-COCl fully

precipitated, the above solution was sucked out and purified with anhydrous THF several times. Finally, after the MWNT-COCl was dissolved into anhydrous NMP and sonicated in a water bath for 1 h, the hyperbranched PAI/NMP solution was added. Thus the MWNTs were terminated with hyperbranched PAI. The NMP was removed from the solution and the MWNTs solid was rinsed completely with a great amount of THF solvent on a 0.45  $\mu\text{m}$  Millipore PVDF membrane; the PAI that didn't react with MWNTs was removed.

### Adsorption of the functionalized MWNTs on $\text{NH}_2\text{-Si}$ substrate

The MWNTs functionalized with hyperbranched PAI was dispersed in NMP. The  $\text{NH}_2\text{-Si}$  substrate was immersed in the solution. After 30 min the substrate was taken out and put in an oven at 160°C until the solution completely dried. The dried substrate then was put in a THF solvent under sonication for 10 min to remove the nonadsorbed MWNTs.



**Scheme 1** (a) The hyperbranched polymer I synthesized from AB<sub>2</sub> monomers and MWNTs grafted by polymer I. (b) The hyperbranched polymer II synthesized from AB<sub>2</sub> and A<sub>2</sub> monomers and MWNTs crosslinked by polymer II. (c) The hyperbranched polymer III synthesized from AB<sub>2</sub> and B<sub>4</sub> monomers and no reaction between the MWNTs and polymer III. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

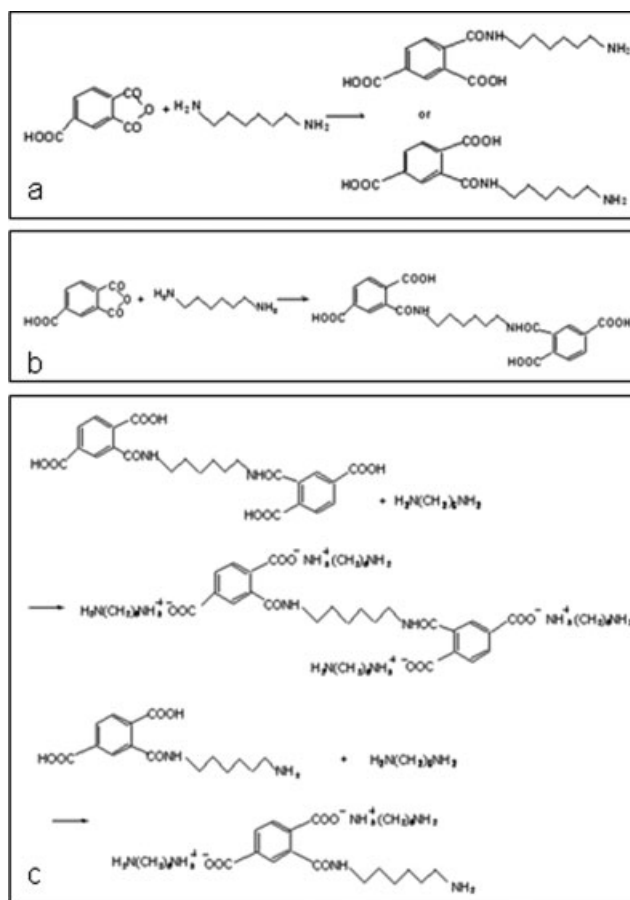
## RESULTS AND DISCUSSION

To functionalize the MWNTs mainly in the ends, to link them with larger end functional groups at the end, and avoid crosslinking between the functionalized MWNTs, a hyperbranched polymer is designed to have terminal carboxyl groups and have only one  $\text{NH}_2$  group, which can link with MWNTs. Among various hyperbranched polymers, the hyperbranched polymer (polymer I) made from  $\text{AB}_2$  monomer mostly fit in with our desire, where A, the  $\text{NH}_2$  group, can easily link with  $\text{MWNT-COCl}$ , and B, the  $-\text{COOH}$  group makes the ends of the MWNTs with thick carboxyl groups, as shown in Scheme 1(a). However, during the synthesis of the hyperbranched polymer, if some  $\text{A}_2$  or  $\text{B}_4$  formed (which are easy to form in the process of the  $\text{AB}_2$  synthesis) the synthesized polymer might have the structure of polymer II and polymer III as shown in Scheme 1(b,c). Polymer II is easy to make the MWNTs crosslink because there are several  $\text{NH}_2$  groups in the structure. On the other hand, there is no  $\text{NH}_2$  group in the structure of polymer III and so MWNTs can't link with it. Therefore it is crucial to synthesize the purified  $\text{AB}_2$  monomer and control the reaction conditions of the synthesis.

### Synthesis of the $\text{AB}_2$ monomer

To avoid highly rigid polymer, the  $\text{AB}_2$  dendron with an aliphatic segment was synthesized. Trimellitic anhydride and 1,6-diaminohexane were chosen to synthesis  $\text{AB}_2$  monomer 2-(6-aminohexylcarbonyl) terephthalic acid for the anhydride, which had a rigid phenyl group and was quite active with the amide. The 1,6-diaminohexane contains a comparatively long aliphatic flexible segment. The desired reaction was shown in Scheme 2(a).

During the synthesis of monomer, some side reactions should also occur. Firstly, the reaction between anhydride and amide must go on quickly. Because the two amide groups in 1,6-diaminohexane had the same reactivity, if the whole or the local concentration of trimellitic anhydride was close to the concentration of 1,6-diaminohexane, the trimellitic anhydride would react with the two amide groups of the 1,6-diaminohexane to bring a large amount of  $\text{B}_4$  type monomer, as shown in Scheme 2(b). To avoid a mass of  $\text{B}_4$ , excess 1,6-diaminohexane was added in this case. And even now, there was still a little side reaction. Secondly, when trimellitic anhydride was dripped into the 1,6-diaminohexane solution, a white organic salt formed suddenly, as shown in Scheme 2(c), which made the local concentration of trimellitic anhydride rise so that the side reaction occurred more easily; the water could easily dissolve the organic salt to prevent it enclose the raw materials. However, the water



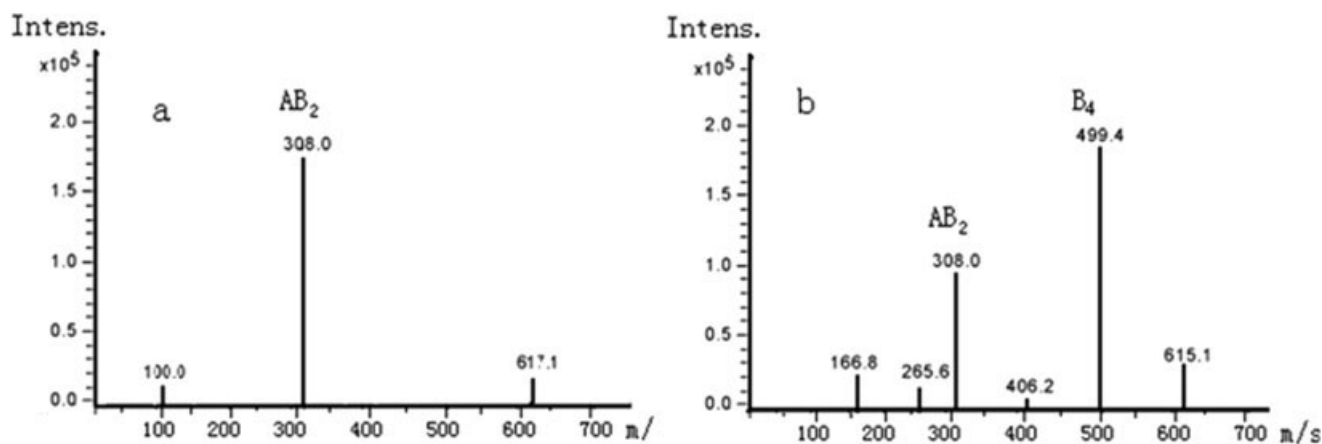
**Scheme 2** The reactions during the synthesis of the  $\text{AB}_2$  dendron. (a) The prepared  $\text{AB}_2$  monomer when the 1,6-diaminohexane reactant was excess. (b) The prepared  $\text{B}_4$  monomer when the local concentration of trimellitic anhydride reactant was high. (c) The formed organic salt.

could hydrolyze trimellitic anhydride, and so the water couldn't be chosen as the solvent.

Figure 1(a) showed ES-MS result that the primary product contained mainly the  $\text{AB}_2$  monomer (the molecular weight was 309) and excess 1,6-diaminohexane reactant, but almost didn't contain any  $\text{B}_4$  monomer when one of the reactants 1,6-diaminohexane was about 10 times more than the other reactant trimellitic anhydride. Figure 1(b) showed ES-MS result that the primary product contained mainly the  $\text{B}_4$  monomer (the molecular weight was 500) and less  $\text{AB}_2$  monomer when the reactants 1,6-diaminohexane had the same mole ratio as trimellitic anhydride.

In fact, the reactants 1,6-diaminohexane was usually about five to ten times more than the trimellitic anhydride reactant and the local concentration of 1,6-diaminohexane reactant was more than trimellitic anhydride reactant. In most of the reactions, the primary products contained  $\text{AB}_2$  monomer, the unwanted excess 1,6-diaminohexane, and the  $\text{B}_4$  monomer. As shown in Scheme 3, when the  $-\text{COO}^-$  anion of the primary product reverted to  $-\text{COOH}$  group and the





**Figure 1** ES-MS of the primary products (a) ES-MS of the mainly prepared AB<sub>2</sub> monomer when the mole of the reactant 1,6-diaminohexane was 10 times more than that of the trimellitic anhydride reactant. (b) ES-MS of the mainly prepared B<sub>4</sub> monomer and less AB<sub>2</sub> monomer when the local concentration of trimellitic anhydride reactant was high.

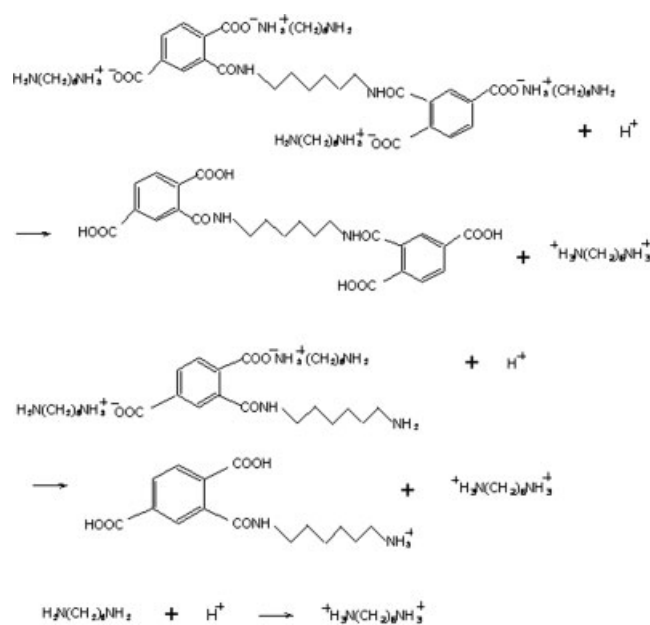
NH<sub>2</sub> group reverted to NH<sub>3</sub><sup>+</sup> cation because of the addition of dilute HCl, the B<sub>4</sub> monomer had four —COOH groups and did not have NH<sub>3</sub><sup>+</sup> cation; the 1,6-diaminohexane had two NH<sub>3</sub><sup>+</sup> cations and did not have —COOH group; the AB<sub>2</sub> monomer had one NH<sub>3</sub><sup>+</sup> cation and two —COOH groups. To obtain the purified AB<sub>2</sub> monomer, the unwanted excess 1,6-diaminohexane and the little B<sub>4</sub> were removed based on their different solubility in water and organic solution.

Firstly, as the white primary product, the organic salt was filtrated from the THF solution. The excess 1,6-diaminohexane dissolved in THF was removed from the primary products, which could be used repeatedly. The salt was dissolved in water to form transparent solution. When dilute HCl solution was gradually dripped into the transparent solution, and the pH value was adjusted to be about 5–6, the solution became cloudy and a white sediment appeared. And the sediment containing more B<sub>4</sub> type side product was first separated from the water solution.

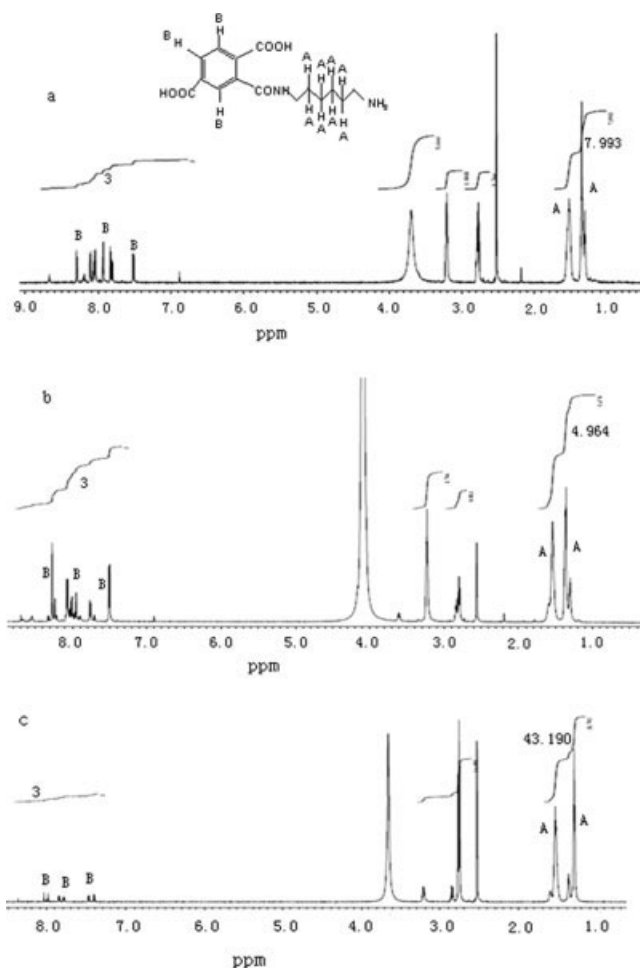
Secondly, about 10 times the volume of THF was put in the water solution to extract the AB<sub>2</sub> monomer. The solution separated into two phases, with the desired product in the upper layer of THF solution and the 1,6-diaminohexane salt in the lower layer of water solution. After collecting the THF solution and getting rid of the THF solvent by vacuum, the desired AB<sub>2</sub> monomer was obtained. Then the operation was repeated until the water layer became white and viscous.

By using <sup>1</sup>H NMR spectroscopy to quantitatively integrate the number of different hydrogen atoms in the monomer, the purification of the monomer was validated by <sup>1</sup>H NMR spectroscopy. The analysis is based on the fact that in the monomer, the chemical shift of three phenyl hydrogen atoms [the B hydrogen atoms as shown in Fig. 2(a)] and the chemical shift of

eight aliphatic hydrogen atoms in the middle of the 1,6-diaminohexane [the A hydrogen atoms as shown in Fig. 2(a)] are stable all the time]. All samples were dissolved in DMSO-d<sub>6</sub>, and two drops of D<sub>2</sub>O were added to eliminate the influence of the active hydrogen of NH<sub>2</sub> and —COOH in the samples. After purification, the AB<sub>2</sub> monomer had three times the hydrogen atoms of the phenyl and 7.993 times hydrogen atoms in the middle of the 1,6-diaminohexane, as shown in Figure 2(a). Besides, in the first departed part containing more B<sub>4</sub> monomer, the <sup>1</sup>H NMR spectroscopy indicated much more phenyl hydrogen atoms, as shown in Figure 2(b). And in the last departed water solution containing more 1,6-diami-



**Scheme 3** Reversion of the —COO<sup>−</sup> and NH<sub>2</sub> of the primary products to —COOH and NH<sub>3</sub><sup>+</sup>.



**Figure 2** The  $^1\text{H}$  NMR spectra of different molecular structure, (a) the purified  $\text{AB}_2$  monomer; the integrating number of phenyl hydrogen atoms was three, corresponding to the chemical shift at 7.0–9.0 ppm; the integrating number of the middle hydrogen atoms of aliphatic segment was 7.993, corresponding to the chemical shift at 1.0–2.0 ppm. (b) The first removed product containing  $\text{B}_4$ , (c) the removed product containing 1,6-diaminohexane.

nohexane salts, there were mainly aliphatic hydrogen atoms of 1,6-diaminohexane and a little phenyl hydrogen atoms, as shown in Figure 2(c). Based on the results of the  $^1\text{H}$  NMR spectroscopy, it was confirmed that the desired  $\text{AB}_2$  monomer was highly purified.

The synthesized  $\text{AB}_2$  monomer was also analyzed by means of elemental analysis: calculated for  $\text{C}_{15}\text{H}_{21}\text{N}_2\text{O}_5$ , C(58.25%), H(6.80%), N(9.06%); found, C(56.50%), H(7.15%), N(8.80%), from the elemental number and by taking into account the trace water in the sample and the instrument system error; it was also affirmed that the obtained  $\text{AB}_2$  monomer was nearly pure.

### Polymerization of the $\text{AB}_2$

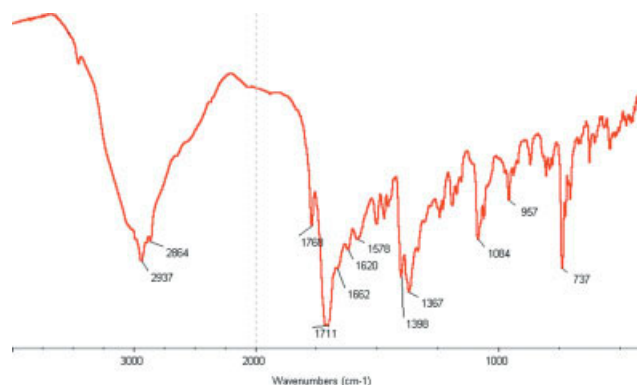
Thermal polymerization is a well-known industrial process for aliphatic polyamides with a high molecular weight because the reaction equilibrium constant

is 400. However, it is very difficult to obtain aromatic polyamides with a high molecular weight by thermal self-polycondensation method because of the lower reactivity of aromatic amines compared with aliphatic amines as to the resonance effect of phenyl groups. And in general higher reaction temperatures easily result in extensive side reactions. In this study, the self-polycondensation of the  $\text{AB}_2$  type monomer was carried out profiting from the aliphatic character of  $\text{AB}_2$  monomer. One-step polymerization of the monomer was carried out in NMP at 150–160°C for 5 h without using condensation agents. After removing the solvent under vacuum, a brown polymer product was obtained, and the polymer I (as shown in Scheme 1a) for the monomer was purified  $\text{AB}_2$  monomer.

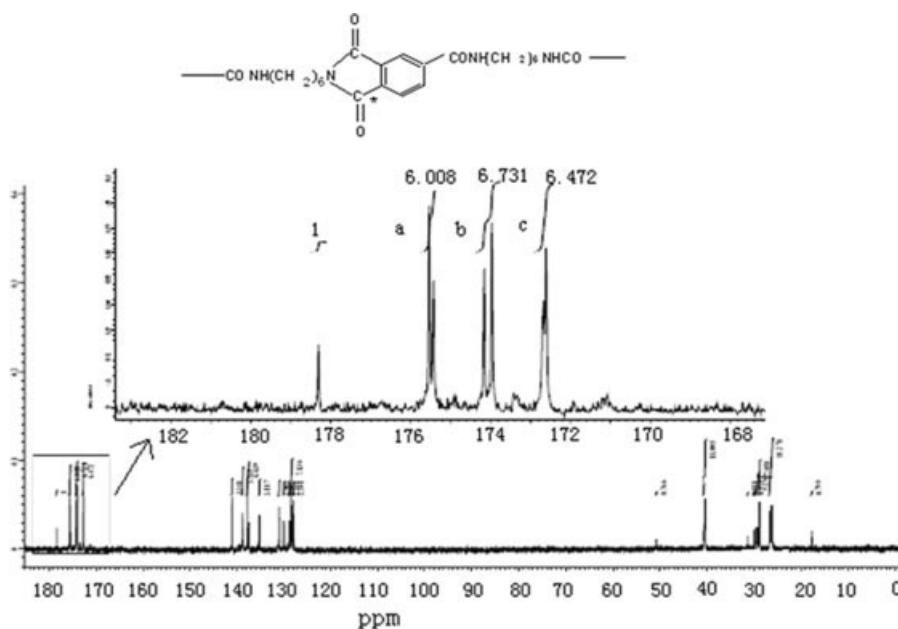
Under the polymerization condition, the imidation reaction between the nearby carboxyl groups of the phenyl and the amide group was hard to avoid completely, and so the resulting hyperbranched polymer was really a mixture of hyperbranched polyamide and polyamidimides. Even now, the ratio of the polyamide and PAI could be controlled, for the reaction activation energy to form polyamide is much lower than that to form polyimides. In addition, it might be beneficial to create part of linear segments of polyimide for the hyperbranched polymer that might have longer branches.

The formation of PAI was characterized by FTIR spectrum and the result was shown in Figure 3. The characteristic absorptions of amide and imide groups in PAI appeared at 3300, 1768, 1711, and 1662  $\text{cm}^{-1}$ , peculiar to N—H stretching and carbonyls stretching of imide and amide, respectively. All of these PAI exhibited strong absorption at 1367 and 737  $\text{cm}^{-1}$ , implying the existence of the imide heterocycle in these polymers.

The ratio of the imide in the structure of PAI was characterized by  $^{13}\text{C}$  NMR. The PAI was dissolved in ammonia, and after adding several droplets of  $\text{D}_2\text{O}$  the solution was put in NMR spectrometer for 48-h



**Figure 3** FTIR spectrum of PAI. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



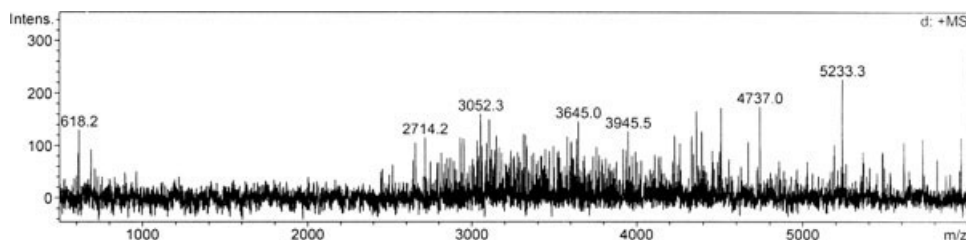
**Figure 4**  $^{13}\text{C}$  NMR spectrum of PAIs. The chemical shift of 178.31 ppm corresponds to the carbonyl group with \* symbol and the integrate number was 1. The chemical shift of 175.5 ppm correspond to carboxyl groups, the chemical shifts of 172.5 ppm to 174 ppm correspond to other carbonyl groups and the integrals were 6.008, 6.731, and 6.472, respectively.

measurement to characterize the structure of the PAI. The result was shown in Figure 4. By integrating ratio of quaternary carbons in the quantitative  $^{13}\text{C}$  NMR measurement, the ratio of polyimide in the whole hyperbranched polymer was determined. From the enlarged spectrum between 170 and 180 ppm, the peaks at 178.31 ppm could be ascribed to the resonance of the carbonyl of the imide groups with integral of 1, and other chemical shifts corresponding to the carbonyl of the imide groups were observed at 172–177 ppm with the whole integral of about 1 too. All the peaks between 172 and 177 ppm corresponded to the resonance of the carbonyl of the imide groups and amide groups, and the integral was 19.211. Therefore the imide segment was about 5%.

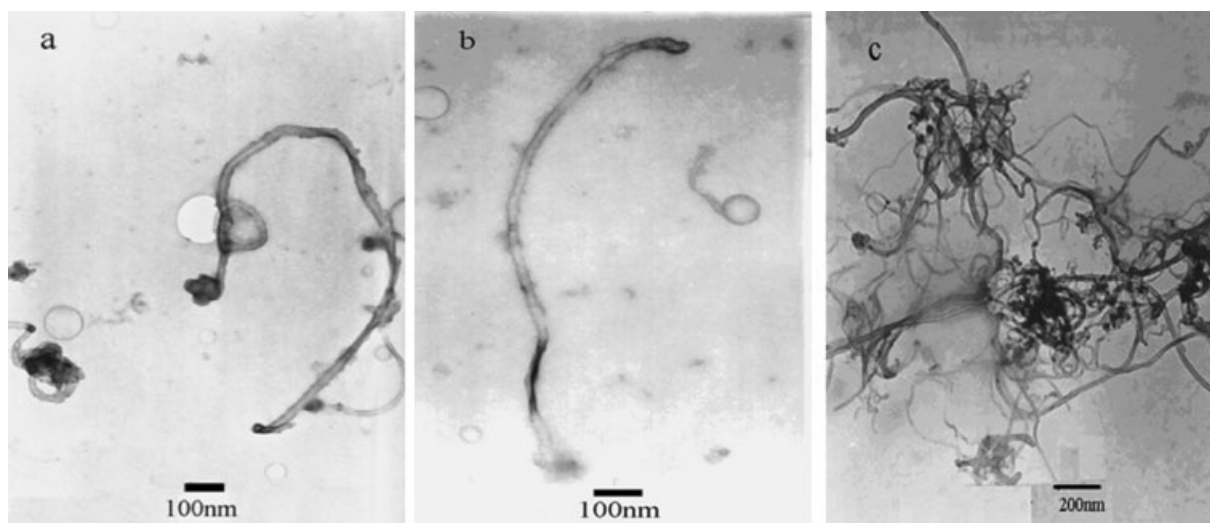
From Figure 4, the PAI could also be confirmed that it had a hyperbranched structure. If the PAI was a linear polymer, every benzene ring in the middle linear polymer must have a carboxyl group (except for the imide segment) and there were two carboxyl groups in every benzene ring of the ends of polymer,

and the integral area of carboxyl group must be more than 31.67% of the integral areas of the whole carbonyl groups. For the integral area of the carboxyl groups (peak of a) that was 6.008 and the whole integral areas of the carbonyl groups (peaks of a, b, and c) that added to 20.211, the carboxyl groups was about 29.73%; there must be some dendritic structure in the PAI, and the PAI was a hyperbranched polymer.

The molecular weight and its distribution were important for the hyperbranched polymer, but the molecular weight and molecular weight distribution of the hyperbranched polymer were difficult to characterize accurately by the usual method. The GPC can characterize the linear polymer, but as to hyperbranched polymer, the  $M_n$  and  $M_w$  were usually lower, and the PAI was not easy to be dissolved in THF solvent, which was a usual solvent in GPC method; so the PAI was not fit to be characterized by GPC. The molecular weight and its distribution of the PAI were characterized by ES-MS. The accurate mo-



**Figure 5** ES-MS spectrum of PAI.



**Figure 6** TEM micrographs of MWNTs functionalized with hyperbranched polymer. (a) and (b): the MWNTs grafted by hyperbranched polymer "polymer I". (c) The MWNTs crosslinked by hyperbranched polymer "polymer II."

lecular weights were obtained, but its distribution couldn't be given, as Figure 5 shown; the molecular weight distribution of PAI was very wide and the molecular weights were mainly from 2700 to 5500.

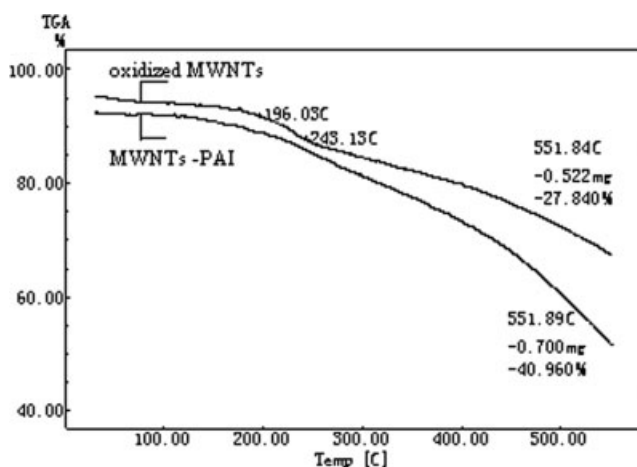
#### The hyperbranched poly(amide-imide) grafted to the MWNTs

In the past studies, hyperbranched polymer was usually linked in the side and at the ends of the MWNTs, for MWNT-COOH was suspended in  $\text{SOCl}_2$  directly. All the carboxyl groups were changed into  $-\text{COCl}$ . In our study, to make the side of the MWNTs linked with polymer as few as possible and the ends as much as possible, the carboxyl MWNTs was suspended in THF solvent. The MWNTs were slightly bundled and most of the ends were exposed in the so-

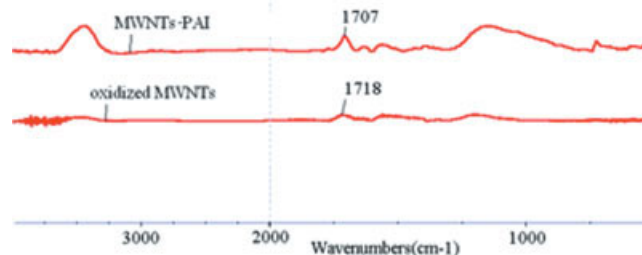
lution. In addition, the ends of MWNTs had much more carboxyl groups than the side. When the concentration of  $\text{SOCl}_2$  was low, the  $-\text{COOH}$  group at the end of MWNTs could be mainly changed into  $-\text{COCl}$  group. So the hyperbranched polymer (polymer I) was mainly grafted onto the ends of the MWNTs, as shown in Figure 6(a,b).

If the product was polymer II in the polymerization process and polymer II was grafted onto MWNT-COCl, the grafted MWNTs should suddenly precipitate and the MWNTs should be crosslinked, as shown in Figure 6(c).

To further verify whether the MWNTs were grafted with PAI, TGA and FTIR were used to characterize the change between the oxidized MWNTs and the MWNTs grafted with PAI. From Figure 7, the oxidized MWNTs lost weight of 27.84% from room temperature to 551°C in nitrogen atmosphere and the MWNTs grafted with PAI lost weight of 40.96% in the same condition. Comparing these results, it could be concluded that the MWNTs were grafted about 13.12% of PAI.



**Figure 7** TGA of the oxidized MWNTs and MWNTs grafted with PAI.



**Figure 8** FTIR spectra of the oxidized MWNTs and MWNTs grafted with PAI. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



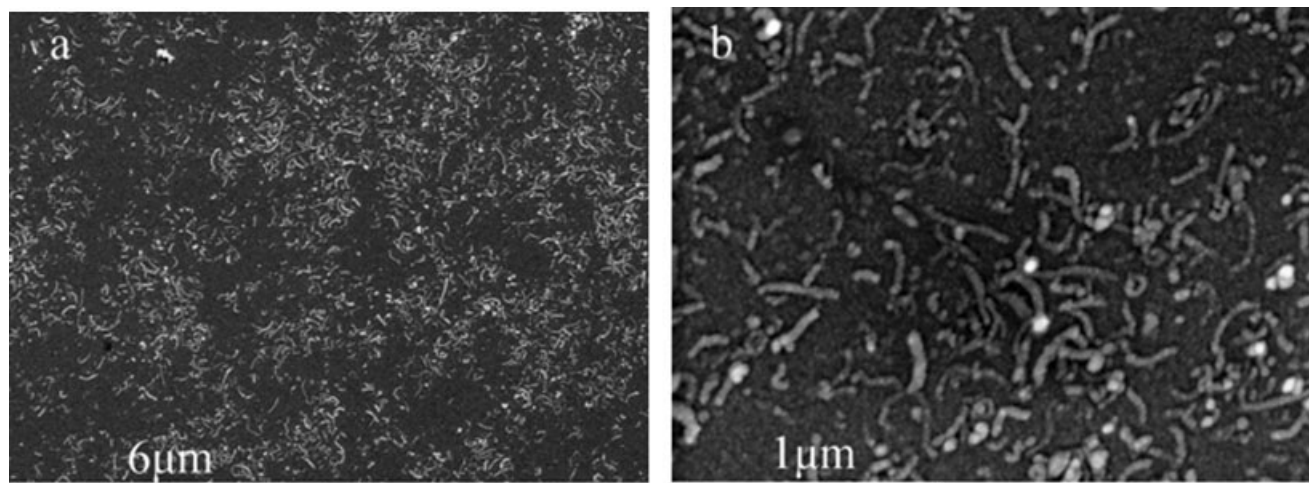


Figure 9 SEM micrographs of MWNTs linking to the  $\text{NH}_2\text{-Si}$  substrate.

From Figure 8, the characteristic absorption peaks of the oxidized MWNTs appeared at  $1718\text{ cm}^{-1}$ . After being grafted with PAI, the absorption band at  $1718\text{ cm}^{-1}$  disappeared and a new absorption band at  $1707\text{ cm}^{-1}$  appeared, which could be ascribed to the absorption of the carboxyl groups in PAI. From the change of the absorption of carboxyl groups, it was also confirmed that the MWNTs were grafted with PAI.

#### Functionalized MWNTs linkage to the $\text{NH}_2\text{-Si}$ substrate

The adsorption of hyperbranched PAI-functionalized MWNTs on the  $\text{NH}_2\text{-Si}$  substrate was characterized by SEM, as shown in Figure 9. A large amount of MWNTs were linked to substrate firmly even under sonication because of the strong interaction between the  $\text{-COOH}$  groups of functionalized MWNTs and the  $\text{NH}_2$  groups on the silicon substrate. It implied that the hyperbranched polymer was grafted on the MWNTs and the adsorption ability of the MWNT to  $\text{NH}_2\text{-substrate}$  was enhanced.

#### CONCLUSION

An  $\text{AB}_2$  monomer with a phenyl ring and a aliphatic linear chain in molecular structure was synthesized by trimellitic anhydride and 1,6-diaminohexane, and purified according to different solubility of the  $\text{AB}_2$  monomer and side products in water and THF. Then the  $\text{AB}_2$  monomer was directly thermal self polycondensated to hyperbranched PAI without condensation agents. The hyperbranched PAI was then grafted onto the MWNT-COCl. By observation with TEM and characterization by TGA and FTIR, it was confirmed that the functionalized MWNTs were terminally

enclosed with the hyperbranched polymer, and by observation with SEM, the linkage ability of the functionalized MWNTs on  $\text{NH}_2\text{-substrate}$  was enhanced.

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