



# The synthesis of dendrimer based on the dielectric barrier discharge plasma grafting amino group film<sup>☆</sup>

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## ABSTRACT

In this paper polyamidoamino (PAMAM) dendrimer synthesized on the solid surface of poly ethylene terephthalate (PET) film through repetitive Michael addition and amidation reactions is reported. Before the synthesis, the amino groups were grafted on the PET surfaces using a dielectric barrier discharges (DBD) at atmospheric pressure with ammonia as a monomer. Then with the grafted amine as core the polyamido amino was synthesized on organic PET solid film surface. The dendrimer structures were then characterized by Fourier transform spectroscopy (FTIR) and <sup>1</sup>H nuclear magnetic resonance (NMR), and the surface morphology was scanned by atomic force microscopy (AFM). This strategy provides a novel way to modify the film surface by combining plasma technology and chemical reaction. It shall be benefit for biosensor, biomedical, catalyst, photonic crystal, plasmonic crystal, and magnetic domain applications and so on.

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## 1. Introduction

Dendrimers are a novel macromolecule with highly branched dendritic molecules which possess unique properties including relatively large molecular size, narrow size distribution, well-defined globular structure, and ease of derivatization via the peripheral functional groups. These properties have attracted a great interest in exploring their potential applications such as macromolecular catalysis [1], drug delivery [2,3], gene transfection, and imaging [4], magnetic resonance imaging (MRI) contrast agents [5,6], and metal ion extraction [7–9]. Dendrimer polyamidoamine (PAMAM) as one of commercial ones [10] due to the controllable mass, the water solubility, and the possibility of surface functionality, has been widely used in the biomedical and genetics [11]. Fan [12] even built a model for the self-assembly of the dendrimer–DNA system proposed on the basis of the experimental data achievement: the PAMAM dendrimer-induced condensation of the DNA strongly attenuated transcription.

The PAMAM dendrimer-encapsulated nanoparticles (DENS) is also one of the highlight areas due to the potential application in the field of catalysis. DENS is prepared by using the dendrimers as a template to synthesize nanoparticles [13]. The first DENS were Cu nanoparticles [14–16]. However the Cu DENS was synthesized by PAMAM and poly (propylene imine) (PPI) dendrimers as templates adsorbed on the

solid surface from aqueous solutions in [17–19]. Cahill et al. [20] explored in detail the adsorption behavior of PAMAM dendrimer to the silica interface. But, the directly PAMAM synthesis on solid face, in particular on an organic surface, is not reported yet.

The dielectric barrier discharge (DBD) plasma sources recently received increasing attention due to their many advantages, such as simplification in experimental set-up, no need for expensive vacuum equipment, and easy operation. It is well known that [22] the DBD demonstrates a widely potential application in surface modifications, especially in organic surface modification due to no-damage in the inherent bulk properties of the materials at an atmospheric pressure. Then the atmospheric pressure DBD plasmas have been employed as alternatives for amino group film polymerizations and modifications in many areas by researchers [23–25].

In this work, the plasma technology was combined with chemosynthesis. The different generations of dendrimer PAMAM were synthesized directly on the PET solid films after the amino groups were grafted on the surfaces through DBD treatment at atmospheric pressure ammonia plasma. This paper stressed the dendrimer structure, which was then characterized by Fourier transform spectroscopy (FTIR) and <sup>1</sup>H nuclear magnetic resonance (NMR). The surface morphology was also scanned by atomic force microscopy (AFM).

## 2. Experimental

### 2.1. Materials and equipments

A 50 KHz power source driven DBD plasma was used to graft amine-containing functional films in mixture gases of Ar and NH<sub>3</sub>.

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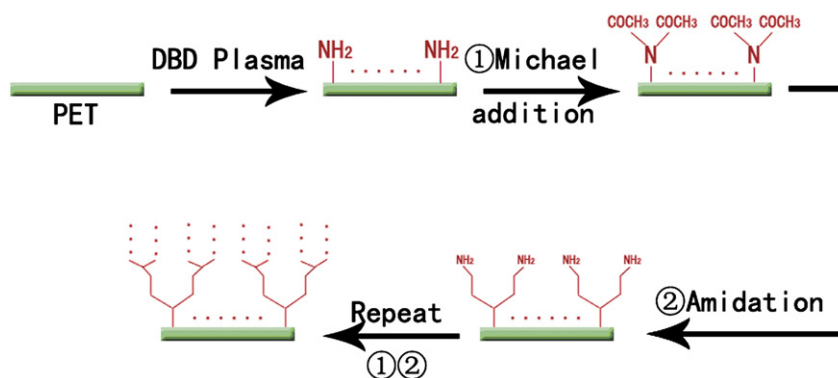


Fig. 1. Schematic diagram of the PAMAM synthesized on the PET surface.

The detailed description of the plasma setup was reported in previous work [21], in which the grafted film properties and structures, the influence of discharge parameters, in particular applied power, on amine density were emphasized. With the same processing protocol, the poly ethylene terephthalate (PET) film (5 cm\*5 cm in area, 80  $\mu\text{m}$  in thickness) was used as substrate treated in plasma. Ethylene dimine, methyl acrylate and methanol (all are in the analysis purity level) were used as reagents for the PAMAM synthesis.

## 2.2. Experimental process

Fig. 1 is the schematic diagram of the experimental protocol. Firstly, the PET film was treated under the DBD plasma. The density of amine groups on the surface was estimated using fluorescent labeled techniques and x-ray photo spectroscopy. It is noticed that the maximum density was about 9.97  $\text{NH}_2/\text{nm}^2$  in the optimal discharge parameters [26] when the discharge gap was 2 mm, the exposure time was 40 s. In our experiment the modification conditions were following these parameters. Secondly, 2.0–5.0 generation (G) dendrimers PAMAM were synthesized with these grafted amine groups as cores through repetitive Michael addition and amidation reactions. The reactions took place in the three-necked flasks under the water warm bath at temperature of  $25 \pm 0.2^\circ\text{C}$ . It is worth noting that after DBD plasma treatment the films were put quickly into a three-neck flask in sequence. Then protocol of the PAMAM synthesis was same as in [27].

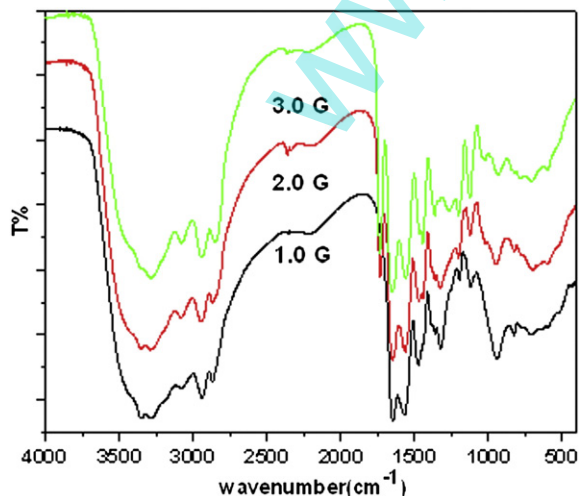


Fig. 2. FTIR spectrum of the PET film with 1.0, 2.0 and 3.0 G PAMAM.

## 2.3. Measurements

FT-IR spectra were obtained on KBr pellet for the chemical structure (Shimadzu, FTIR-8400,  $\pm 4 \text{ cm}^{-1}$ , Japan). The concentration of the PAMAM for FTIR measurement is 3 mg/500 mg KBr. NMR is a useful tool for chemical structure analysis based on the magnetic nuclei in a magnetic field with applied electromagnetic (EM) pulse shall cause the nuclei absorbing energy from the EM pulse and radiating the energy back out for measurement. By analysis of the peaks of NMR spectra, the chemical structure of compounds can be deduced. In here  $\text{CDCl}_3$  was used as solvent, and the observation frequency was 399.716 MHz. For surface morphology, AFM (CSPM-4000, Benyuan, China) in tapping mode was utilized to scan the surface morphology of control PET and PAMAM modified PET films.

## 3. Results and discussion

### 3.1. FT-IR spectra

Fig. 2 is FTIR spectroscopy analyzing the chemical component of PAMAM. The peak between  $3100 \text{ cm}^{-1}$  and  $3600 \text{ cm}^{-1}$  is attributed to stretching vibrations of  $-\text{NH}$  and  $-\text{OH}$  groups [28]. The  $-\text{OH}$  group might be contribution of the adsorption from air on the surface. The peak at  $3285 \text{ cm}^{-1}$  is stretching vibrations of  $-\text{NH}$  group, the peaks at  $1648 \text{ cm}^{-1}$  (amide I) and  $1558 \text{ cm}^{-1}$  (amide II) are assigned to the N–H bending vibrations are assigned to the peaks at  $1648 \text{ cm}^{-1}$  for amide I and  $1558 \text{ cm}^{-1}$  for amide II in amide group, respectively (Table 1). The results were consistent with previous data [29,30]. The peaks at 2952 and  $2850 \text{ cm}^{-1}$  are contribution of the C–H stretching vibrations of methyl and methylene groups, respectively [31]. The peak at  $1726 \text{ cm}^{-1}$  for C = O stretching in 2.0 G PAMAM and 3.0 G PAMAM synthesized on the PET surface in Fig. 2 might be caused from the remaining methyl acrylate.

Table 1  
Spectral mode assignment for different generations of PAMAM.

Wave number ( $\text{cm}^{-1}$ )	Assignment
3285	Stretching vibrations of free NH groups
3078	Aromatic C–H stretch
$2950 \pm 5$	Anti-symmetrical stretching vibrations of $\text{CH}_2$ groups
$2860 \pm 5$	Symmetrical stretching vibrations of $\text{CH}_2$ groups
1726	Stretching vibrations of ester C = O groups
1648	Amide I mode
1558	Amide II mode
1454	Stretching vibrations of C–H groups
1331	C–N stretching vibration

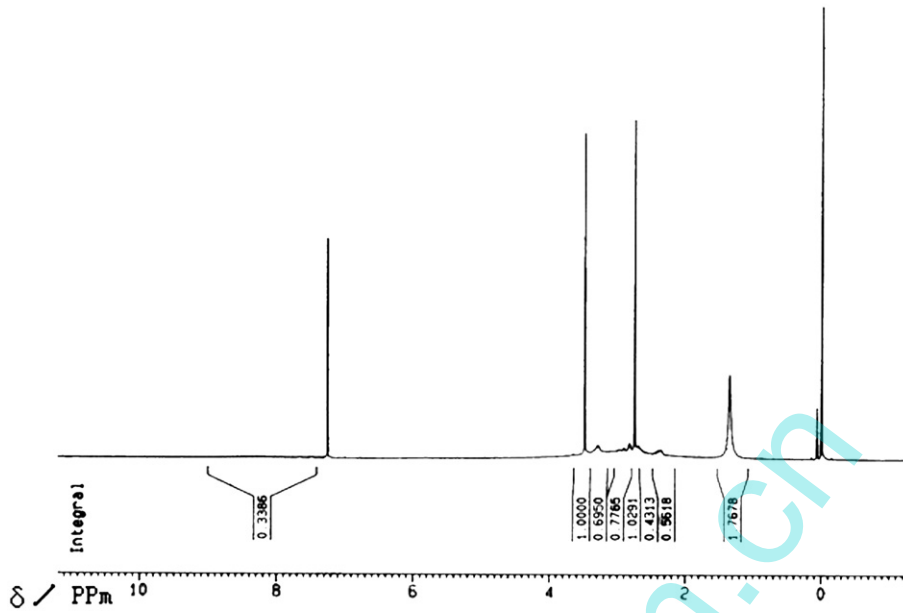


Fig. 3. <sup>1</sup>H NMR spectra (ppm) of 3.0 G PAMAM synthesized on the PET in CDCl<sub>3</sub>.

3.2. <sup>1</sup>H NMR

The results of FTIR were proofed by the <sup>1</sup>H NMR spectra as shown in Fig. 3. The peaks at 3.48 ppm for NCH<sub>2</sub>CH<sub>2</sub>N, 3.29~3.25 ppm for CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, 2.79~2.75 ppm for CH<sub>2</sub>N, 2.70 ppm for CH<sub>2</sub>NH<sub>2</sub>, and 2.36 ppm for NH<sub>2</sub> all confirm the formation of PAMAM. Due to the terminal group of the 3 G PAMAM was amino, it is noticed that the chemical shift was relatively small in the range of 1.23~1.37 ppm.

And the relatively small value of  $\sigma$  is due to N element directly bonding to H element, a not strong electron withdrawing group in the chain.

3.3. AFM analysis

Fig. 4 shows the AFM images of control PET, plasma modified PET, and 2.0 G and 3.0 G PAMAM modified PET films, respectively. For

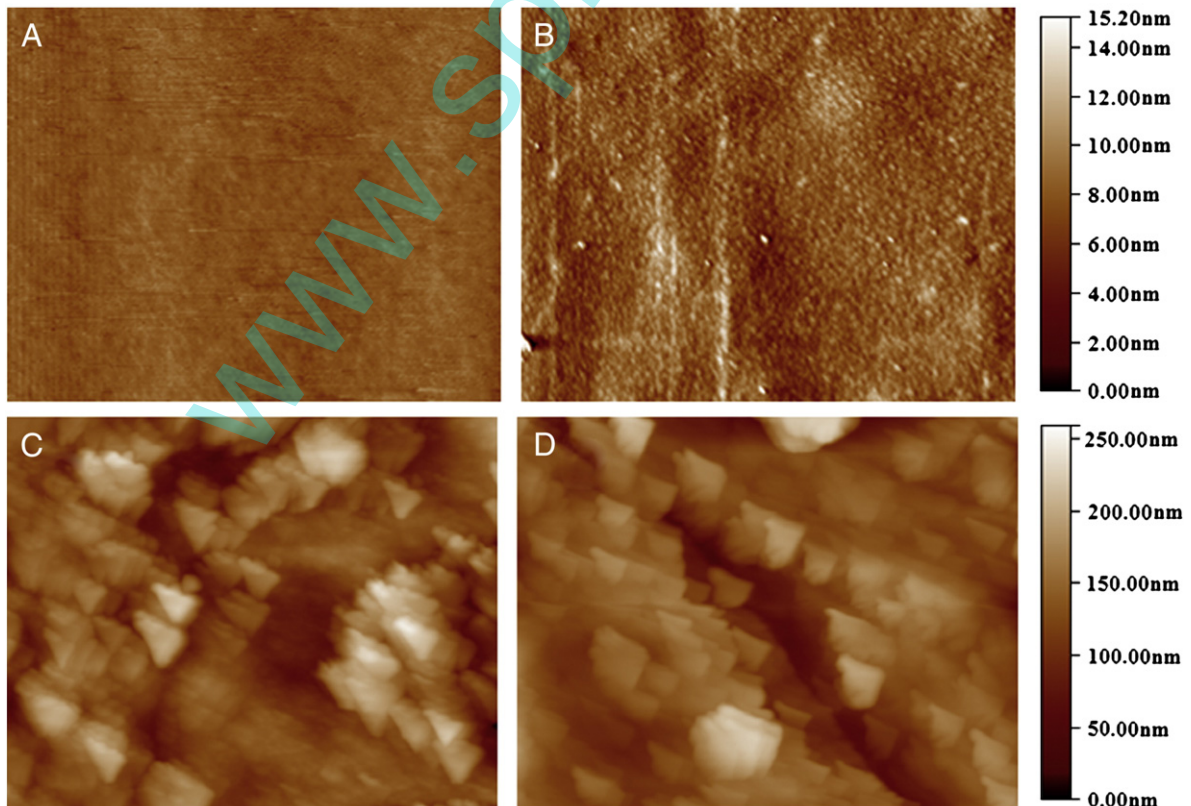


Fig. 4. AFM images for A-control PET, B-plasma treatment PET, C-and PET modified by 2.0G and D-3.0G PAMAM (scan area is 10  $\mu$ m  $\times$  10  $\mu$ m).

**Table 2**  
RMS of the samples measured by AFM.

Samples	Control PET	Amine grafted PET	Modified by 2.0 G PAMAM	Modified by 3.0 G PAMAM
RMS (nm)	0.23	1.16	24.96	25.34

control PET film the surface is relatively smooth, whereas the PET film after plasma grafted amine groups exhibits the micro scale holes and vales. It was explained due to the grafted amino groups changing the surface morphology [26]. After PET modified with 2.0 G and 3.0G PAMAM, moreover, the film surfaces demonstrate the large-scale holes and vales. The repeating patterns in images Fig. 4C and D are caused from the pattern PAMAM dendrimer, which is in the regular chemical structure.

The surface topography is then quantified by surface roughness analysis based on the height-to-height correlation function,  $H(r)$  [32]. Table 2 shows the roughness of samples. One can see that the roughness is remarkably larger after the PAMAM was synthesis on the PET surface, which reached up to 24.96 nm modified by 2.0 G PAMAM while 25.34 nm by 3.0 G PAMAM.

#### 4. Conclusions

In this paper, 2.0~3.0 G dendrimers PAMAM were synthesized on the DBD plasma modification PET surface through repetitive Michael addition and amidation reactions. FTIR,  $^1\text{H}$  NMR and AFM were used to characterize samples. The results of FTIR and  $^1\text{H}$  NMR confirm the formation of PAMAM on the PET surface. AFM images certify the PAMAM synthesis on PET surface through the micro scale structures of macromolecule. It indicates that a strategy is funded to modify the plastic film surface by combining plasma technology with the chemical reaction, which shall be benefit for biosensor, biomedical, catalyst, photonic crystal, plasmonic crystal, and magnetic domain applications. The applications shall be reported later.

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