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Synthesis, characterization and metal ion uptake studies of PAMAM dendrimers on solid support

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ABSTRACT

Polyamidoamine (PAMAM) dendrimers were synthesized by a novel route involving solid support holding the ester for reaction with the amine moiety of diethylenetriamine. The solid support, PE-g-poly (MA), was synthesized by chemical method induced grafting of methylacrylate (MA) onto polyethylene (PE) on which dendrimer moiety was synthesized. Dendrimer synthesis was carried out by divergent method in methanol using methylacrylate and diethylenetriamine up to 1.5 generations beyond which the viscosity of the reaction mixture increases which inhibited further reactions on the support. Characterization of solid support based PAMAM dendrimer was carried out by FTIR and ES-MS spectral methods. Solid support dendrimers (G1.5) have also been used for metal ion uptake studies.

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KEYWORDS

Solid support;
PE;
Methyl acrylate;
Grafting, dendrimer;
PAMAM;
Metal uptake.

INTRODUCTION

Dendrimers are a class of highly ordered branched oligomers, assembled in a modular fashion from polyfunctional building blocks.^[1-3] Since the pioneering studies done and published in late 1970s and early 1980s by group of Vogtle,^[4] Denekwalter,^[5] Tomalia^[6] and Newkome^[7] numerous advances in the synthesis, analysis and applications of these polymers have been reported by hundreds of research groups^[8]. Frechet-type polyether compositions and Tomalia-type polyamidoamine (PAMAM) dendrimers are the two most widely studied dendrimer families. Out of these, the most common dendrimer scaffold is that of the PAMAM dendrimers, which are available commercially with a wide variety of generations and peripheral

functionalities. Highly branched PAMAM series called 'starburst dendrimers'^[9,10] with extremely low polydispersity by stepwise polymerizations have been synthesized by Tomalia et al.^[6] and Denekwalter et al.^[11]

Majority of dendrimeric structures are prepared using conventional methods involving divergent and convergent synthetic methods. This leads to high generation dendrimers with large number of terminal functional groups that pose problems of purification, heterogeneity and also harmful effects. Increasing attention has, therefore, been diverted to dendrimer preparation on solid support which can provide solutions to all such problems such as marked improvement in the yield and homogeneity of the formed dendrimer. Solid support synthesis of dendrimers involves large number of simultaneous

reactions during the building up of each generation posing a challenge to polymer chemists. Nevertheless, purification of intermediates is easier, which is the most painstaking and time consuming process in solution phase synthesis of dendrimers. Therefore, over the past decade, a number of dendrimers have been prepared on solid support. Divergent synthesis is more suitable and widely employed for solid phase synthesis of dendrimers with few exceptions. The first example of solid support dendrimers synthesis was reported by Tam and Posnett et al.^[13]

The most widely studied dendrimers attached to insoluble solid support are PAMAM dendrimers. Swali et al.^[14] introduced the solid phase synthesis of PAMAM dendrimers on organic polymer support. Initially these dendrons were prepared on TentaGel up to fourth generation. Later PAMAM dendrons were synthesized on polystyrene beads equipped with a short PEG spacer.^[15, 16] The reaction proceeded smoothly up to second generation but the third and fourth generation dendrimers showed defected structure due to the steric hindrance which resulted increased and incomplete propagation reactions.

PAMAM dendrons were also prepared from other polymer particle cores, such as Chitosan, zirconia-urea-formaldehyde resin, silica coated magnetite and carbon nanotubes.^[17-20] Triply branched polyamidourea dendrons were developed on polystyrene aminomethyl resins by Bradely et al.^[21, 22] Heterogeneous diphosphonated polyamidoamine (PAMAM) derivatives, synthesized on a silica gel support, when complexed to rhodium (I) act as excellent catalysts for the hydroformylation of aryl olefins and vinyl esters.^[23] Using the standard method developed by Tomalia et al.^[24] the PAMAM dendrimers up to generation-4 were synthesized from aminopropyl groups on the silica gel particles. Alper et al.^[25] extended the application of silica supported phosphine-rhodium terminated PAMAM dendrimers, to the use of palladium complexes for the catalysis of the Heck reaction.

It is thus observed that the synthesis of dendrimers on the solid support generally uses silica gel or resins as supports, however, in the present

work, attempts have been made to synthesize PAMAM dendrimers on the polyethylene (PE) based graft copolymer. Grafting of methyl acrylate (MA) carrying the ester moiety was carried out by chemical method using benzoylperoxide (BPO) as the radical initiator. The pendent ester groups offered the sites for nucleophilic reaction of the amine precursor used for the dendrimer synthesis. The dendrimers have further been used for metal ion uptake studies.

EXPERIMENTAL

Materials and methods

Polyethylene (PE), in the form of beads, was reprecipitated from xylene and used as a powder. Diethylenetriamine, (DETA) (Merck), methylacrylate, (MA) (Merck), were used as received. Methanol was used as reaction solvent; benzene was used as a solvent for distillation of diethylenetriamine and methanol under reduced pressure.

Synthesis of PAMAM dendrimer on solid support

Divergent synthesis of PAMAM dendrimer was carried out via excess reagent method. PAMAM dendrimer was synthesized on a solid PE graft support. The solid support was synthesized by grafting methylacrylate onto polyethylene by the following method.

Synthesis of polymer support

Graft copolymerization of methylacrylate onto polyethylene was carried out by chemical method using benzoyl peroxide as the radical initiator. Polyethylene (PE) (2.500g) was suspended in a 30 mL of water in a round bottomed flask. To this was added a known amount of the initiator, BPO (0.344 mol/L) and monomer, MA (3.64 mol/L). The reaction mixture was refluxed for three hour at 60°C. After the specified time period the product was filtered and washed thoroughly with benzene to remove the homopolymer and the unreacted BPO. Percent grafting was determined gravimetrically from the increase in weight of polyethylene and was found to be 133.2%.

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Solid support synthesis of PAMAM (G0.5) dendrimer

PE-g- (MA) (0.500g) was slowly suspended in a solution of excess of DETA in methanol, kept at 0°C for one hour. The reaction was then allowed to slowly accomplish room temperature and was kept under stirring for 150h at room temperature. After the specified time period, solid was removed from the reaction mixture and thoroughly washed with methanol to remove unreacted DETA to give PE graft supported PAMAM (G0.5).

Solid support synthesis of PAMAM (G1) dendrimer

Polymer supported PAMAM (G0.5) dendrimer was treated with 20 mL of methyl acrylate in 50 mL of methanol. The mixture was kept under stirring for 236h at room temperature. After the specified time period the solvent methanol was removed by vacuum distillation below 55°C. This results in the formation of PE graft supported PAMAM (G1) dendrimer with ester endings.

Solid support synthesis of PAMAM (G1.5) dendrimer

Polymer supported PAMAM (G1) dendrimer was treated with 30 mL of DETA in methanol (20 mL). The mixture was kept under stirring for 240h at room temperature. After the specified time period the solvent methanol was removed by vacuum distillation below 55°C. The excess of DETA was later removed using benzene as solvent for distillation and finally the residual methanol was removed under reduced pressure below 55°C. This results in the formation of PE graft supported PAMAM (G1.5) dendrimers with amine endings.

Preparation of poly (vinyl alcohol)-acrylamide, (PVA-AAm) cross-linked hydrogel

In order to study metal uptake behavior of the solid support dendrimers, poly (vinyl alcohol) (PVA) grafted and cross-linked with acryl amide (AAm) was prepared. PVA (5gm); AAm (2.5 gm) and 0.5 gm of N,N-methylene-bis-acrylamide were dissolved in 20 ml of water and irradiated with α -rays from Co⁶⁰ source (2.94 kGy/h) for 24h. The

white highly swollen gel was obtained which was dried and weighed.

Formulation of standard curve

Standard solutions of 0.1M NiSO₄·7H₂O, 0.1M CuSO₄·5H₂O, 0.1M CoCl₂·6H₂O and 0.1M FeSO₄·7H₂O were prepared and their optical density (OD) were measured for varying concentration at wavelength that gave the maximum absorption (ϵ_{max} .656nm, 227nm, 510nm 699nm respectively) for each respective solution measured on UV Spectrophotometer. A plot of OD against concentration form standard curve for each respective metal ion solution.

Adsorption of Solid support dendrimer onto

(1) Molecular sieves: Dried and weighed molecular sieves (0.500g) were immersed in 1mL of the G1.5 solid support dendrimers for 24h at room temperature for maximum adsorption.

(2) PVA-g- Poly (AAm) cross linked hydrogel:

The solid support dendrimer i.e. G1.5 with amine endings was used for metal ion uptake studies. The dendrimer was adsorbed on the solid support for effective adsorption of metal ions (Ni²⁺, Cu²⁺, Co²⁺ and Fe²⁺) from their respective salt solutions. The adsorption of the dendrimer was carried out as follows:

(a) Dried and weighed hydrogel (0.500g) was immersed in 1mL of G1.5 solid support dendrimers for 24h at room temperature for maximum adsorption.

(b) Pre-swollen hydrogel (0.500g swollen in 50 mL H₂O) was placed in 1mL of G1.5 solid support dendrimer at room temperature for 24h.

(c) Dried and weighed hydrogel (0.500g) was immersed in 1:1 (v/v) solution of G1.5 solid support dendrimer in water for 24h at room temperature.

After the specified time period of immersion, molecular sieves/hydrogel adsorbed with the dendrimers was placed in the metal ion solution and left at room temperature for 24h. After stipulated time, molecular sieves/hydrogel was removed from the metal ion solution. The OD of the residual solution was measured and the concentration of the metal ion adsorbed was determined from the standard curve. The results are presented in TABLE 1.

TABLE 1 : Metal uptake data of solid support dendrimers

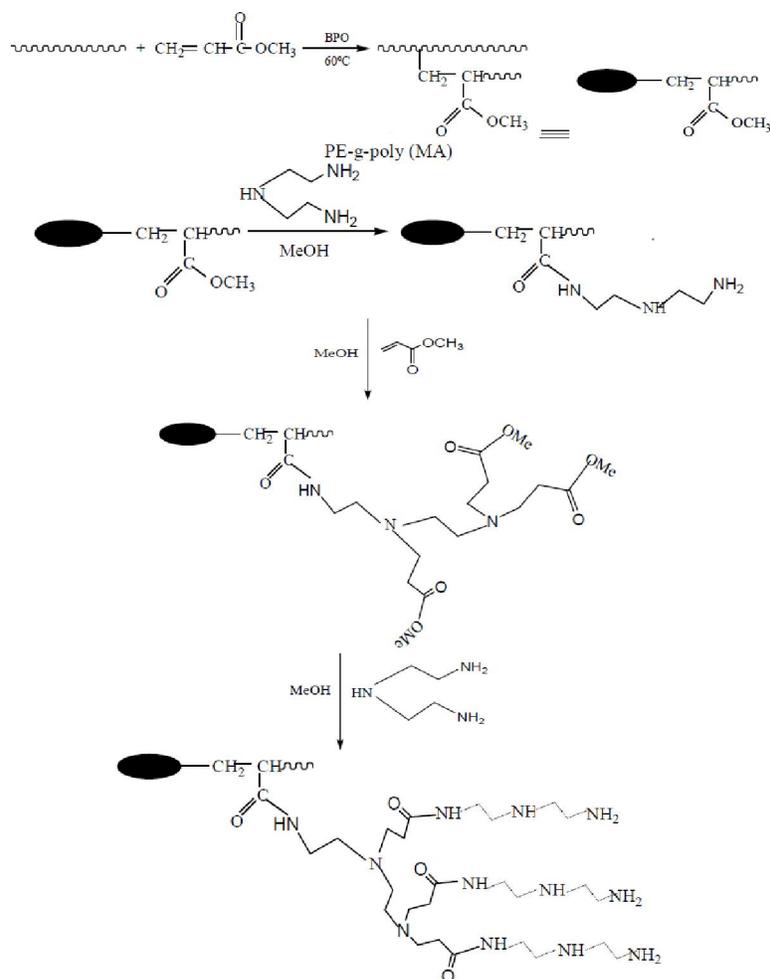
solid base for adsorption	λ_{\max}	Maximum adsorption (OD)	Conc. Of m^{n+} before Adsorption	Conc. Of m^{n+} after Adsorption	Conc. Of m^{n+} adsorbed	% ion adsorption	Color change
Solid support G1.5 dend on Molecular sieves	656	0.344	0.1 M Ni^{2+} (aq)	0.0769	.0231	23.1	
Solid support G1.5 dend on unswelled HYDROGEL	656	0.344	0.1 M Ni^{2+} (aq)	.00288	0.0712	71.2	
Solid support G1.5 dend on pre swollen HYDROGEL	656	0.344	0.1 M Ni^{2+} (aq)	OD increased to maximum		COMPLEX FORMED	Green to pink
Amine term. Solid support dend G1.5 (1:1 G1.5: water) on unswelled HYDROGEL	393	0.472	0.1 M Ni^{2+} (aq)	0.0382	0.06180	61.8	
Ester term. Solid support dend G-1 (1:1 G1: water) on unswelled HYDROGEL	393	0.472	0.1 M Ni^{2+} (aq)	0.053	0.0470	47.0	
Amine term. Solid support dend G1.5 (1 mL)	656	0.344	0.1 M Ni^{2+} (aq)	OD increased to maximum		COMPLEX FORMED	Green to pink
Amine term. Solid support dend G1.5 (1 mL)	227	4.351	0.1 M Cu^{2+} (aq)	OD increased to maximum		COMPLEX FORMED	Blue to deep black blue
Amine term. Solid support dend G1.5 (1 mL)	510	0.446	0.1 M Co^{2+} (aq)	OD increased to maximum		COMPLEX FORMED	Purple to deep red
Amine term. Solid support dend G1.5 (1 mL)	699	1.799	0.1 M Fe^{2+} (aq)	OD increased to maximum		COMPLEX FORMED	Brown to dark brown

It is observed from the Table that between the molecular sieve and hydrogel, uptake of Ni^{2+} ions is higher by the hydrogel (71.2%) in comparison to molecular sieves (23.1%) therefore all other studies were made with the solid support dendrimer (G1.5) on the hydrogel. When solid support dendrimer G1.5 was adsorbed on hydrogel from the aqueous solution (1:1 v/v H_2O : G1.5) and used for Ni^{2+} uptake studies, % uptake decreases to 61.8%, which may be due to decreased concentration of solid support dendrimer (G1.5). Similarly solid support dendrimer G-1 with ester endings adsorbed on hydrogel also gave the lower % uptake of Ni^{2+} ions (47%).

In another experiment, the hydrogel was swollen in water and was then loaded with G1.5 solid support dendrimer. In case of absorption of Cu^{2+} , Co^{2+} and

Fe^{2+} , the studies were made with (1:1 v/v H_2O : G1.5) solid support dendrimer adsorbed on PVA-AAm cross-linked hydrogel. In all these experiment different observations were made. The OD of the residual metal solution increased than the original OD of the metal solution with drastic change in color. Increase in OD indicates the formation of charge transfer complexes which is possible because the number of amines groups with lone pair of electrons interacting with the transition metals i.e., Co^{2+} , Cu^{2+} and Fe^{2+} . Increase in OD and appearance of colors upon formation of charge transfer complexes is well known. A deep blue complex between aniline with $\lambda_{\max}=280\text{nm}$ and tetra cyano-ethylene with $\lambda_{\max}=380\text{nm}$ appears at a much higher, $\lambda_{\max}=610\text{nm}$ in the visible region.^[26]

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Scheme 1: Synthesis of PE graft supported PAMAM (G1.5) Dendrimer

Solid support dendrimer 1.5 generation (1mL) was suspended in 0.1M solutions of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ separately. It was observed that as soon as solid support dendrimer was added to the respective solution of metal ions, the color of the solution instantaneously changes to intensive dark colors and the optical density on the U.V. spectrophotometer exceeds the maximum measured value of the instrument i.e. 10.000. From these observations it can be concluded that the amine endings of dendrimers strongly complexes with the metal ions to give charge transfer complexes with higher absorption wavelength.

In a separate study, solid support dendrimer (1mL) was added to the metal ion solution (0.1 gm of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ dissolved in 6 ml of water) and noted the O.D. To this solution another 0.1 gm $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ was added and noted the O.D. This was continued

till addition of 0.3 gm of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ where O.D. was found to increase continuously. But as soon the next 0.1 gm of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ was added, the O.D. value exceeds the limit. The solution was diluted 10 times and recorded the O.D. The conc. corresponding to this O.D. from standard curve indicates that about 0.8 gm of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ / molecule of dendrimer were adsorbed.

CHARACTERIZATION

FTIR Spectroscopy: FTIR spectra of all the products obtained after each step have been obtained by Thermo 5700 Spectrophotometer.

Mass Spectrometry: Mass spectra of all the products obtained after each step have been obtained by TOF ES-MS.

Optical Density Measurements: Optical density measurements of the metal ion solutions were made

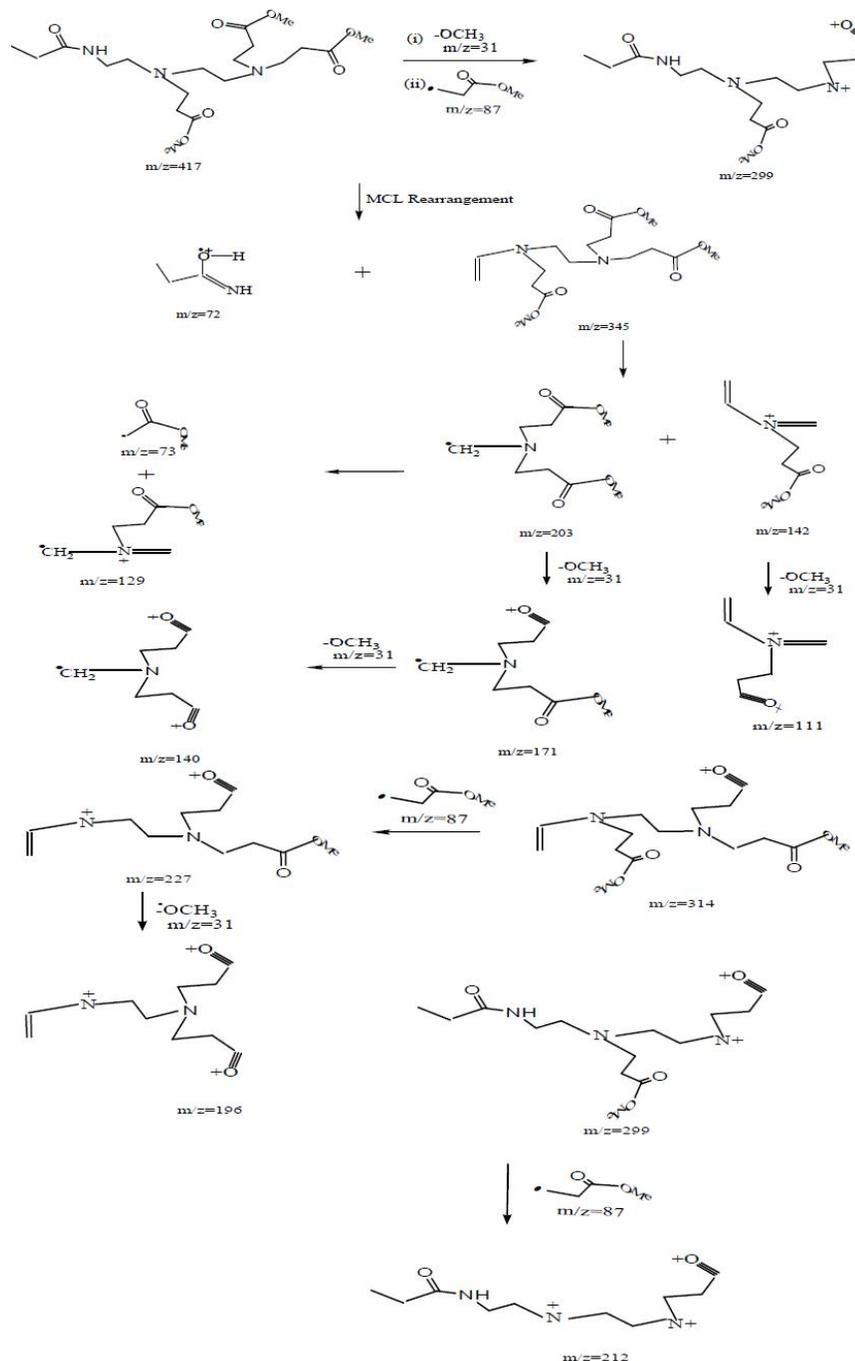
on CARY 100 Bio UV- Visible Spectrophotometer.

RESULTS AND DISCUSSION

PE was grafted with methyl acrylate to give PE-g-poly (MA) graft copolymer, which has been used as the solid support for the dendrimer synthesis. Benzoylperoxide is a well known radical initiator for polymerization and graft copolymerization reactions.

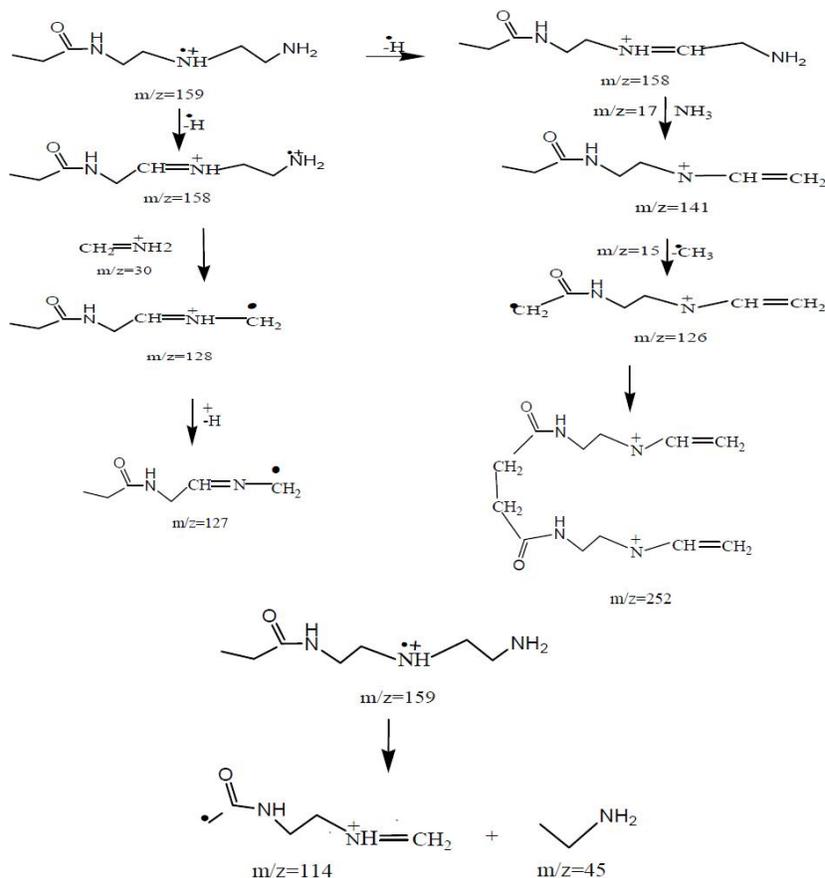
The phenyl radical from BPO initiates the monomer and also activates the polymer backbone. The interaction between the growing polymeric chains of MA and the active sites on PE leads to the formation of the graft copolymer.

As DETA is nucleophilic and MA is electrophilic in nature therefore, all the steps are basically electrophilic-nucleophilic interactions. The first step in the present case is, therefore, amidation (or



Mass fragmentation of solid support G1 PAMAM dendrimer

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substitution) reaction through condensation between pendent ester groups of PE-g- poly (MA) and NH_2 ending group of the DETA resulting in the solid support dendrimers with amine ($-NH_2$) endings. The second step is Michael addition across the double bonds of methyl acrylate. These two steps have been performed alternately to give the final product. However, the last step has been stirred for 240h since DETA being a large molecule and dendrimer has grown in size, steric hindrance decreases the rate of

the Michael addition reaction.

Different steps involved in the synthesis of solid support G1.5 PAMAM dendrimers are presented in Scheme I.

CHARACTERIZATION

All the products have been characterized by FTIR and ES-MS methods. Both the spectra are in accordance with the expected data, although some

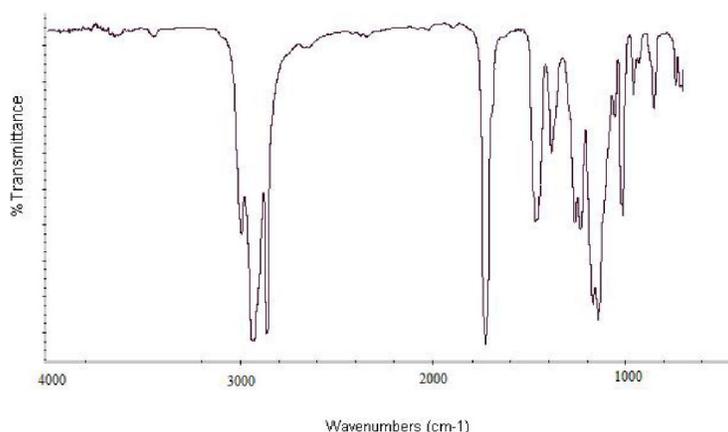


Figure 1 : IR spectrum of PE-g-poly (MA)

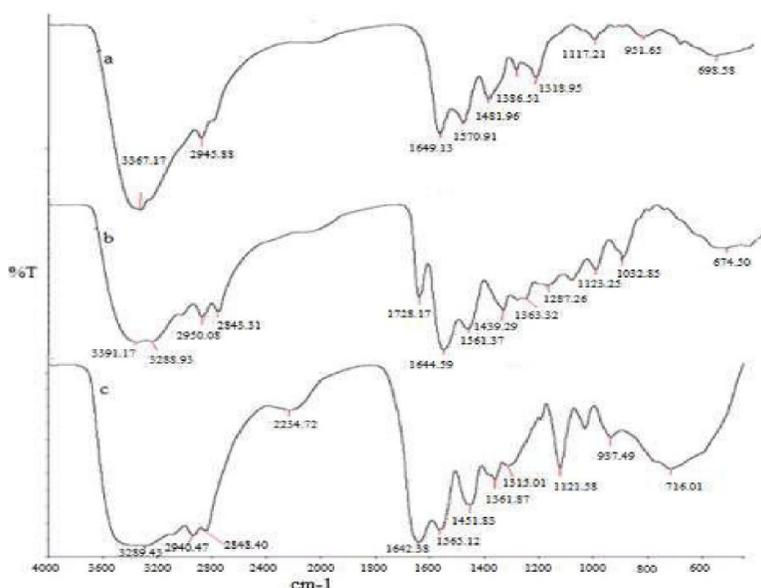


Figure 2 : IR spectra of PE graft supported PAMAM (a) (G0.5), (b) (G1), (c) (G1.5) dendrimers

extra peaks were obtained in case of mass spectra, which might be due to presence of the product from incomplete reaction where one of the reactive sites remained unreacted.

FTIR spectroscopy

The IR spectra at each step have been taken and peaks identified. The IR spectrum of PE-g-poly (MA) shows an additional peak at 1725cm^{-1} due to the $>\text{C}=\text{O}$ of the ester moiety of MA in addition to the peaks observed in the IR spectrum of PE.

PE graft supported PAMAM (G0.5) dendrimer

Nucleophilic substitution, in the first step, gives amide linkages (Figure 2a). A peak due to the ester moiety (1725cm^{-1}) disappears while peaks due to the amide I and amide II appear at 1649.13cm^{-1} and 1570.91cm^{-1} respectively. In addition a small peak at 3367.17cm^{-1} due to the N-H stretching of amine groups is also observed.

PE graft supported PAMAM (G1) dendrimer

A peak at 1728.17cm^{-1} due to carbonyl group of ester is observed (Figure 2b). Peaks at 2950.8cm^{-1} and 1439.29cm^{-1} respectively due to $^i\text{C}-\text{H}$ symmetric stretching and asymmetric stretching were observed. The peaks at 1644.59cm^{-1} and 1561.37cm^{-1} due to amide groups of half generation are also observed.

PE graft supported PAMAM (G1.5) dendrimer

In the third step, nucleophilic attack by amino group of DETA on the carbonyl of the ester ending of G1 dendrimer forms amide linkages (Figure 2c). A peak due to the ester moiety disappears completely while peaks due to the amide groups at 1642.38cm^{-1} and 1565.12cm^{-1} and the peak at 3289.43cm^{-1} due to the N-H stretching of amine groups become larger and broader.

In going further to synthesize the higher generations, i.e. G2, it was observed that after a reaction of 240 h, the IR spectrum was similar to that of spectra of previous generation indicating that further reactions becomes difficult because of the steric hindrance. Similar observations have been made during synthesis of dendrimers on solid support.^{18,19}

Mass spectroscopy

The mass spectra of each step have been taken and peaks identified.

PE graft supported PAMAM (G0.5) dendrimer

Mass spectra of PE graft supported PAMAM (G0.5) dendrimer (Figure 3a) shows peaks at $m/z=163.1$ and $m/z=164.1$ due to $[\text{M}+4\text{H}]^+$ and $[\text{M}+5\text{H}]^+$ respectively. Peaks at $m/z=128.1$ represent $[\text{M}-32]^+$ i.e by the removal of hydrogen free radical ($m/z=1$) and carbonium ion ($m/z=30$) respectively. Peak observed at $m/z=114.1$ represents $[\text{M}-45]^+$, which is obtained by the loss of ethyl amine from

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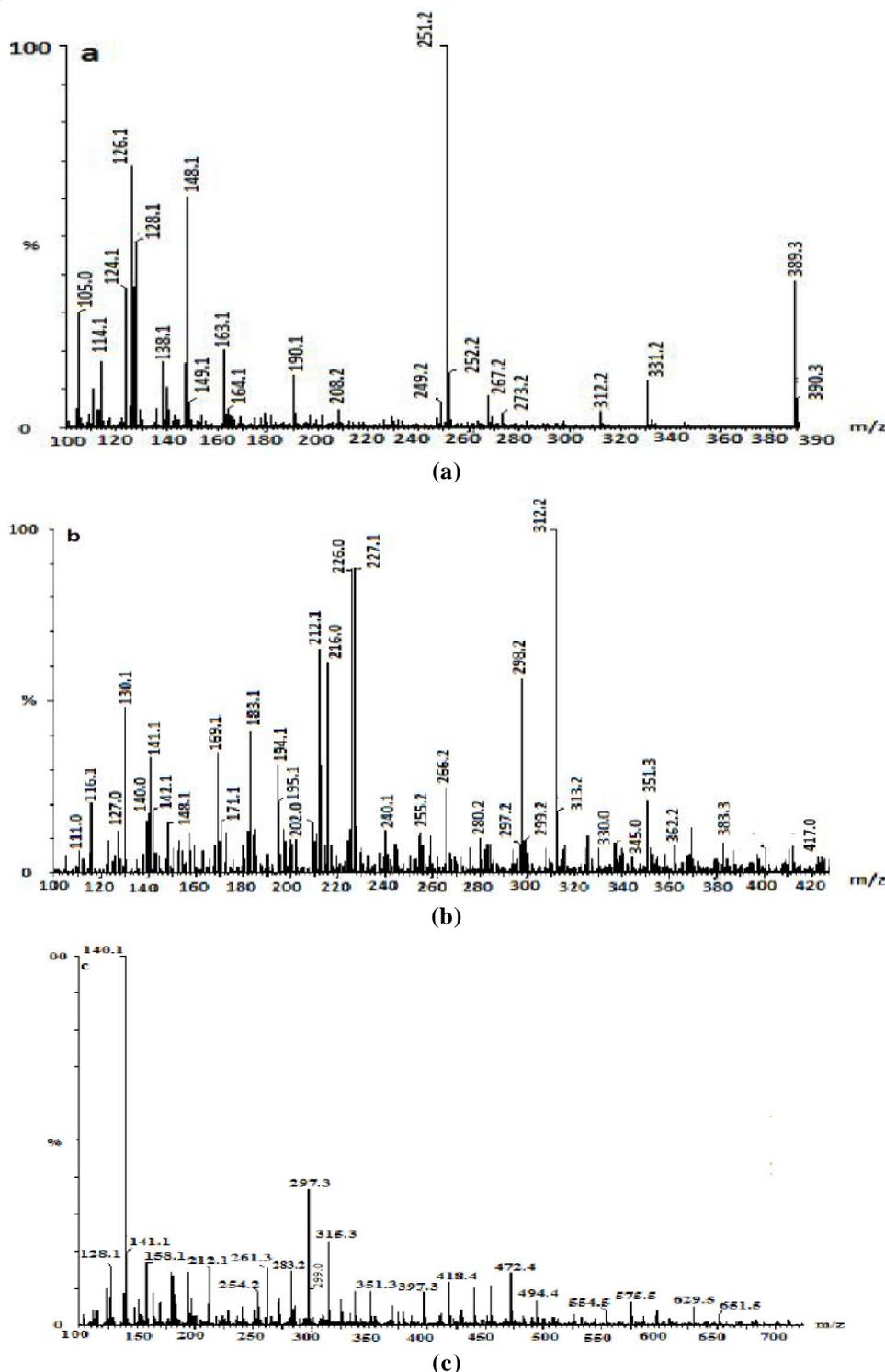


Figure 3 : Mass spectra of PE graft supported PAMAM (a) (G0.5), (b) (G1), (c) (G1.5) dendrimers

$[M]^+$, $m/z=159$.

PE graft supported PAMAM (G1) dendrimer

PE graft supported PAMAM (G1) dendrimer shows peak $[M]^+$ at $m/z=417$, peak at $m/z=344$

represent the McLafferty rearrangement product, peaks at $m/z=142$ and $m/z=202$ represent the fragments of McLafferty rearrangement product (Figure 3b). Peak at $m/z=111$ was observed due to the loss of $m/z=31$ from $m/z=142$, Peak at $m/z=171.1$

and $m/z=140$ represent loss of OCH_3 group from $m/z=202$. Mass peaks at $m/z=330, 313, 299, 226, 212, 195.1$ represents the mass of different fragments of $[\text{M}]^+$.

PE graft supported PAMAM (G1.5) dendrimer

In mass spectra of PE graft supported PAMAM (G1.5) dendrimer (Figure 3c), the molecular ion peak, $[\text{M}]^+$ is observed at $m/z=629.50$. Mass peaks at $m/z=472.4, 375.3, 315.3, 158.1, 128.1$ represent the different fragments mass of $[\text{M}]^+$.

CONCLUSION

Synthesis of PAMAM dendrimer by divergent method on a novel PE graft copolymer has been successfully achieved. MA bearing ester moieties is grafted onto PE which are the reactive sites for the nucleophilic attack by the amine endings of the amine, thus eliminating the first Michael addition step. The product at each step has been characterized by IR and Mass spectral methods. Metal ion uptake studies by the dendrimers show good absorption for Ni^{2+} ions but in general forms charge transfer complex with metal ions with high absorption in UV. Thus from the above studies it can be concluded that the amine terminated dendrimers can be effectively used for metal uptake studies and thus can be useful in various separation from the industrial effluents.

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