Supporting Information

Gold nanoparticles supported on dendrimer@resin for the efficient oxidation of styrene using elemental oxygen

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Preparation of Chloroformoyl XAD-4 (XAD-4-COCl)

Synthesis of chloroformoyl XAD-4 from Amberlite XAD-4 was carried out by a method reported by a method reported earlier [1].

Preparation of XAD-4-NH\textsubscript{2} initiator from XAD-4-COCl

Into a 250 mL round bottom flask 5 g of XAD-4-COCl was placed along with ethylenediamine (30 mL) at 70 °C. After 24 hr resin beads were separated by filtration, washed repeatedly with anhydrous methanol and dried overnight under vacuum, generating XAD-4-CO-NH-NH\textsubscript{2}.

Growth of PAMAM dendrimers on the XAD-4 surface initiated by XAD-4

A mixture of methyl acrylate (30 mL) and anhydrous methanol (20 mL) was take in a 250 mL three-necked round-bottom flask. The prepared XAD-4-CO-NH-NH\textsubscript{2} initiator (5 g) carefully dropped into this solution in about 20 min. The reaction mixture was placed in an oil bath for 24 h at 70 °C. At the end of reaction, resin beads were filtered and washed with ethanol in order to ensure that no free reagents were present in the product. The product was dried overnight to give the dendritic polymer grafted XAD-4 generation 0.5 (XAD-4-G\textsubscript{0.5} PAMAM).

Dried XAD-4-G\textsubscript{0.5} PAMAM beads were dropped into 60 mL of 1:1 methanol/ethylenediamine solution and the reaction flask kept in an oil bath for 24 hr at 70
°C. The resin beads were washed repeatedly with methanol and dried to give generation 1.0 dendrimer modified XAD-4-G_{1,0} PAMAM.

Stepwise growth using methyl acrylate and ethylenediamine was repeated thrice in all to generate third generation PAMAM dendrimers [2] as shown in Scheme 1. The dendrimer-modified XAD-4 was stored in methanol till further use.

**Scheme 1** Synthesis of XAD-4-G_{3,0} PAMAM Dendrimer

3.1.1. CHNS Elemental Study
The CHNS elemental analysis data for the each generation of XAD-4-PAMAM dendrimer was carried out by Perkin-Elmer 2400 series and the results are given below:

<table>
<thead>
<tr>
<th>Microspheres</th>
<th>Nitrogen content (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XAD-4-G1.0 PAMAM dendrimer</td>
<td>7.23</td>
</tr>
<tr>
<td>XAD-4-G2.0 PAMAM dendrimer</td>
<td>11.05</td>
</tr>
<tr>
<td>XAD-4-G3.0 PAMAM dendrimer</td>
<td>15.92</td>
</tr>
</tbody>
</table>

From the CHNS elemental study we observed that the N value increased with addition of each generation and thus it was concluded that step by step growth of PAMAM on XAD-4 Surface has taken place. From the nitrogen content of Resin-PAMAM dendrimer, the percentage functionalization of resin was found to be 69.5 %.

3.1.2. FT-IR Spectroscopy Study

This growth of dendrimers on the surface of XAD-4 was also confirmed by the FTIR spectra of various stages and the results are shown in figure 1. The presence of ester group in ester terminated PAMAM dendrimers in each half generation was confirmed by the appearance of characteristic vibrational peaks at 1737 cm\(^{-1}\) (ester C = O stretch) and C–O stretch in the range of 1050–1300 cm\(^{-1}\). The completion of amidation reaction in each full generation was confirmed by the absence of 1737 cm\(^{-1}\) peak and presence of characteristic vibrational peaks at 1646 cm\(^{-1}\) (amide C = O stretch) and 3280 cm\(^{-1}\) (–NH\(_2\) stretch). Thus, the step by step growth of PAMAM Dendron on XAD-4 surface was monitored by using FTIR.
3.1.3. Thermal degradation study

The TGA analysis carried out by TG-DTA-Q 600 SDT instrument. Thermogravimetric studies for XAD-4-G\textsubscript{3.0} PAMAM dendrimer were carried out from room temperature to 800 °C. The sample was heated at a rate of 10 °C/min under nitrogen atmosphere and percentage weight losses as a function of temperature recorded are shown in figure 3. Major losses during thermal decomposition of XAD-4-G\textsubscript{3.0} PAMAM were observed in four stages (i) 60–100 °C (ii) 200–300 °C (iii) 400–
500 °C and (iv) 600–800 °C. In the first stage, 4.04 % weight loss was observed due to loss of adsorbed water. Degradation of dendrimers was observed in two stages. Stage one showed a loss of 15.16 % and stage two showed a weight loss of 39.2 %. A total loss of 66.6 % was observed upto 600 °C and thereafter, the decomposition is linear. The linear degradation is typical of polystyrene resins. The loss of 62.6 % is attributed to the loss of dendrimer functionalization from the resin and is close to value estimated from nitrogen content. No residue was left behind. It can also be concluded that the XAD-4-G₃.₀ PAMAM resin is thermally stable up to 200 °C only.

Fig. 2. TGA of the XAD-4-G₃.₀ PAMAM dendrimer

References
