

Extraction of azo dye molecules from aqueous solution using polyamidoamine dendrimer based polymeric network

Samaresh Ghosh*

Department of Chemistry, Bankura Sammilani College, Kenduadihi, Bankura-722102, WB, India

Synthesis of novel polyamidoamine (PAMAM) dendrimer based network polymer **2** based on the reaction between an amine-terminated PAMAM dendrimer **1** (G = 3, ethylenediamine core) and butanediol diglycidylether has been achieved. The divergent approach has been employed for the synthesis of the PAMAM dendrimer **1**. This polyamidoamine (PAMAM) dendrimer based network polymer **2** has been successfully characterised by means of FT-IR spectroscopy and elemental analyses and the extraction of methyl orange dye molecules from aqueous solution has been investigated.

Keywords: polyamidoamine dendrimer, network polymer, azo-dye extractant, methyl orange dye

In recent years there has been increasing recognition that polymer networks (see refs 1 and 2 and references therein) are materials of outstanding research importance because of their unique cross-linked structures and properties. These cross-linked polymeric materials have a wide range of applications³⁻⁶ in the fields of chemistry, biology and material science. The design and synthesis of polymeric systems for the separation of ions and molecules have attracted considerable attention in the field of separation science and analytical chemistry. Of particular interest is the design and development of polymeric materials for the effective extraction of dye molecules. Among the polymeric extractants reported⁷⁻¹⁰ so far, dendritic polymers are particularly interesting because of their distinct highly branched regular three-dimensional tree-like structures. Polyamidoamine (PAMAM) dendrimers (see refs 10–16 and references in refs 10, 12, 14 and 16) possessing high concentrations of amide, amine functional groups becomes interesting in the field of host-guest chemistry. Taking into account the unique architectural features, a PAMAM dendrimer based network polymer will be suitable for the extraction of azo-dye molecules.

We report here a simple, efficient and novel synthetic approach based on the reaction between an amine-terminated PAMAM dendrimer (G = 3, ethylenediamine core) and butanediol diglycidylether leading to the development of a novel PAMAM dendrimer based network polymer. The potential of the network polymer obtained to serve as an azo-dye extractant has been explored.

Experimental

Materials and characterisation:

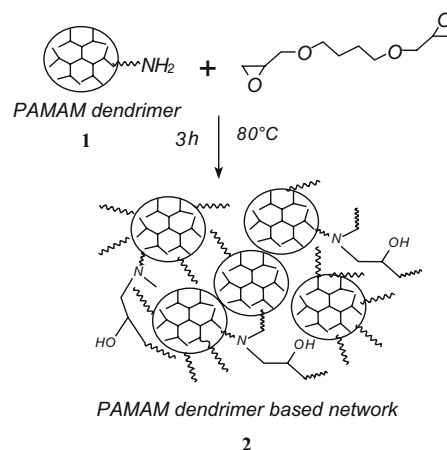
Amine-terminated PAMAM dendrimer **1** was prepared according to the reported procedure.¹¹ Other reagents were used as received without further purification. FT-IR spectroscopic measurement were carried out using a Thermo-Nicolate Nexus-870-FTIR spectrometer. Elemental analysis (C/H/N) was obtained from a 2400 series II CHNS/O analyser (Perkin Elmer) using helium as a driving gas and oxygen as a combustion gas.

Synthesis of standard polyamine network (1a): Amine-terminated PAMAM dendrimer **1** (G = 3, ethylenediamine core; 1 g, 0.3 mmol) was reacted with butanediol diglycidylether (0.5 g; 2.44 mmol) at 80°C for 3 h. The network polymer was then purified by washing with water and dried.

Synthesis of PAMAM based polymeric network (2): Ethylenediamine (0.22 g, 3.7 mmol) was reacted with butanediol diglycidylether (0.6 g; 2.9 mmol) at 80°C for 3 h. The network polymer was then purified by washing with water and dried.

Azo-dye extraction study

The extraction behaviour of polymer **2** was determined by measuring



Scheme 1

the decrease in absorbance in the aqueous phase on a Systronics UV-VIS spectrophotometer-117. All aqueous solutions for extraction study were prepared with deionised water. Different amounts of polymer **2** were mixed with 4 ml of aqueous solution of the azo-dye (methyl orange) in stopped vials that were shaken occasionally (15 min interval) at room temperature for 4 h. The polymer was removed by centrifugation or filtration before measurements. The percentage extraction (E%) was calculated from the decrease in absorbance at $\lambda_{\text{max}} = 440$ nm in aqueous solution according to the following equation.

$$E\% = [100(A_0 - A)/A_0]$$

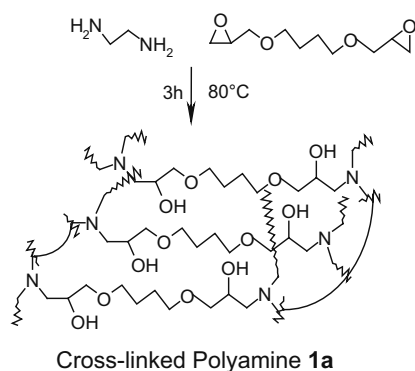
where A_0 and A are the initial and final absorbance at $\lambda_{\text{max}} = 440$ nm of the methyl orange solution before and after extraction respectively. Dye loading into the polymer network in mmol/g was calculated based on the experimental analysis data.

Results and discussion

Synthesis

Amine-terminated polyamidoamine (PAMAM) dendrimers are extremely useful precursors for the preparation of unique dendrimer-based network structures. In this context, Scheme 1 illustrates the synthesis of novel polyamidoamine dendrimer based network polymer **2** based on the reaction between amine-terminated PAMAM dendrimer **1** (G = 3, ethylenediamine core) and butanediol diglycidylether at 80°C. The divergent approach, pioneered by Tomalia *et al.*,¹¹ has been employed for the synthesis of PAMAM dendrimer precursor **1**. This network polymer **2** having high concentrations of amide, amine and hydroxyl functionalities can be advantageously utilised for extraction of azo-dye molecules. For comparison, cross-linked polyamine **1a** was synthesised following a similar synthetic procedure (Scheme 2).

* Correspondent. E-mail: gsamaresh@yahoo.com



Scheme 2

Characterisation

Since the polymer networks obtained were insoluble in water and in common organic solvents, their characterisation by molecular weight determination was not possible. However, polymers **1a** and **2** have been successfully characterised by means of FT-IR spectroscopy and elemental analyses. The FT-IR spectrum of **2**, for instance, shows the absorption band centred at 3424 cm^{-1} that is characteristic of the hydroxyl O–H and amide N–H stretching frequencies.

The broad band occurring between 2847 and 2923 cm^{-1} is associated with the C–H stretching of $-\text{CH}-$ and $-\text{CH}_2-$ groups. Other FT-IR spectroscopic features include amide-I vibrations at 1645 cm^{-1} , amide-II at 1554 cm^{-1} and the fingerprint region below 1500 cm^{-1} . The detailed FT-IR peak assignments are shown in Table 1.

The bands at 1437 – 1362 cm^{-1} manifest the various modes of $-\text{CH}_2-$ vibrations. The band at 1110 cm^{-1} is attributed to the stretching of the ether $-\text{C}-\text{O}-\text{C}-$ group as well as hydroxyl C–O stretching. Elemental analysis data indicate the observed C/H/N percentages for **2** as mentioned in Table 1.

Azo-dye extraction study

PAMAM dendrimers maintain a well-defined structure that creates a highly branched spherical morphology with internal cavities and a high concentration of surface functionalities. The internal cavities of the PAMAM dendritic skeleton thus might be used as a template to host dye molecules. Therefore,

Table 1 Assignments of characteristic FT-IR bands (cm^{-1}) and elemental analysis for **2**

Characteristic FT-IR bands		Elemental analysis
ν/cm^{-1}	Assignment	
3424	OH, NH stretch	C (%) –44.05
2923, 2847	CH stretch	H (%) –9.0
1645	Amide –I	N (%) –11.9
1554	Amide –II	
1110	ether $-\text{C}-\text{O}-\text{C}-$ and hydroxyl C–O stretching	

the main purpose of this approach was to develop this appropriately designed PAMAM dendrimer based network **2** with potential for extraction of dye molecules. Methyl orange, was extracted by the three-dimensional polymer network **2** on keeping it in an aqueous solution of the dye. Upon successive increases in amount of polymer **2**, however, absorbance at 440 nm decreases gradually as evidenced by Fig. 1. We have compared the extraction behaviour of **2** with the modelled cross-linked polyamine **1a**. By this procedure network **2** which swelled in water shows a reasonably high methyl orange azo-dye extraction of 13 mmol/g as compared to modelled polyamine network **1a**, which only shows lower extraction ability of azo dye (6 mmol/g). The azo dye extraction property of **2** is thus considered to be more significant by the genuine advantage of the intrinsic structure of the PAMAM architecture embedded within the polymer network.

A proposed mechanism for the visual colour changes associated with UV-vis spectral changes is shown in Scheme 3. When polymer **2** is immersed in the aqueous solution of methyl orange, the voids of the polymer network possessing amine, amide and hydroxyl functional groups are most likely show the ability to bind dye molecules.

Conclusion

We have thus successfully developed for the first time a strategy to prepare PAMAM-based network material and characterised it. The well-defined structure, shape, size and abundant surface functionalities of the PAMAM dendritic precursor has made it ideal for the development of three-dimensional network polymer **2**. Macromolecular networks of this type capable of extracting azo-dye molecules could thus have potential applications for the removal of some dyes from aqueous solutions. Further studies are under progress.

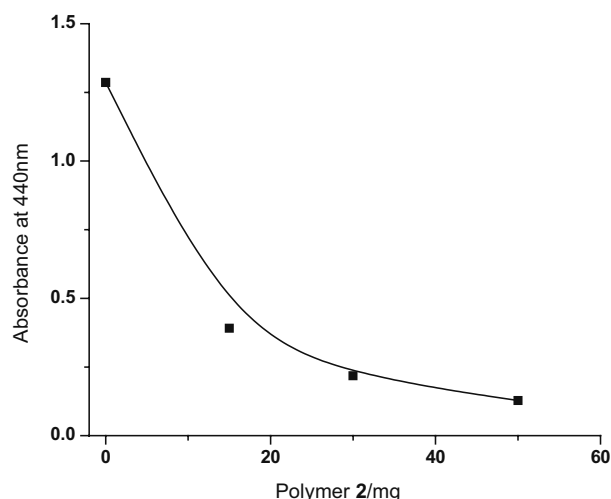
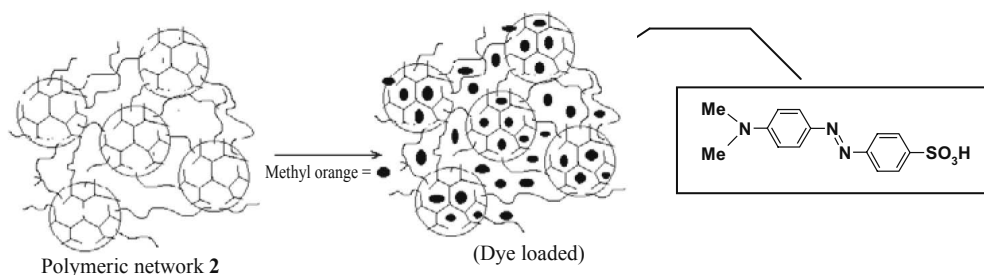


Fig. 1 Variation of absorbance at 440 nm of methyl orange dye ($8.19 \times 10^{-6}\text{ M}$) in aqueous solution (4 ml) as a function of added polymer **2** (in mg).



Scheme 3

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