Fluorescent Hyperbranched Polyamine with *s*-Triazine: Synthesis, Characterization and Properties Evaluation

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A hyperbranched polyamine with *s*-triazine unit based on 2,4,6-trichloro-*s*-triazine and 4,4′-oxydianiline has been synthesized by using A_2+B_3 approach. This polyamine was characterized by FT-IR, UV-visible, ^{1}H NMR, ^{13}C NMR spectroscopic, elemental analysis, measurement of solution viscosity, X-ray diffraction and solubility studies. The terminal amino groups of the polymer were dye end capped by methyl red moiety. The hyperbranched polyamine found to display strong fluorescence from 350 nm to 650 nm in DMSO solution. The fluorescence intensity increased significantly by end capping with methyl red. The hyperbranched polyamine also exhibit pH sensitive fluorescence and the intensity increases with the increase of pH of the medium. The Cu^{2+} ion quenched the fluorescence of the polymer solution noticeably. The polymer solution also shows the increase of fluorescence intensity with the decrease in concentration of polymer. The hyperbranched polyamine was soluble only highly polar solvents and exhibits low viscosity ($\eta_{inh} = 0.15$ dL/g). The thermal analyses indicate that the polymer is thermostable upto 300 °C with glass transition (T_g) temperature 238 °C, while by end capping T_g further increased to 271 °C. The polymer also exhibits self-extinguishing characteristic as found by limiting oxygen index (LOI) value measurement.
KEY WORDS: Hyperbranched Polyamine / End Capped / A_2+B_3 Approach / *s*-Triazine / Fluorescence / Thermal Property /

Over the last two decades hyperbranched polymers have attracted considerable attention[1–4] for their unusual properties like low viscosity, high solubility, unique three-dimensional structure and globular shape etc. in different field of applications.[5–7] Among these, fluorescence is one of the most important applications as it has been applied in many areas especially in chemical and biological sciences.[8,9] Further conjugate structures with electron deficient unit such as nitrogen containing heterocyclic moiety are very interesting for this study.[10,11] The design of a polymer with heterocyclic moiety like *s*-triazine unit in the structure has profound effects on the physico-chemical and thermal properties as well as on its processability.[12,13] The incorporation of rigid triazine unit in the hyperbranched polymeric structure is largely due to the case of chemo- and thermo-selective substitution of the chlorine atoms with different nucleophiles to generate a variety of structures. The three chlorine atoms of 2,4,6-trichloro-*s*-triazine (cyanuric chloride) are substituted by the amine nucleophiles consecutively at 0–5 °C, 40–45 °C and 80–90 °C in a single pot reaction, while the reaction is carried out with some precaution.[14,15] There are a large number of reports on the fluorescence studies of hyperbranched polymers with different structures.[16–19] However, the studies on fluorescence of aromatic hyperbranched polyamine with *s*-triazine unit are not known to our knowledge. Again, this type of hyperbranched polymers exhibits many interesting properties like high thermostability, self-extinguishing characteristics, easy of processing etc. Further, three-dimensional structures of hyperbranched polymers help to reduce the aggregation of the conjugated polymer chains and hence improve the luminescent efficiency. Thus in the present investigation *s*-triazine containing hyperbranched polyamine is used for the first time to study the fluorescence behavior in solution state. This 1,3,5-triazine has also two important properties that incline to use this in this study. These are (i) its ionization potential value of 11.67 eV, *i.e.*, it is more electron deficient than pyridine (9.73 eV), pyridazine (10.61 eV), pyrimidine (10.41 eV) and pyrazine (10.2 eV) and (ii) unlike benzene ring connecting three aromatic ring at 2, 4 and 6 positions of 1,3,5-triazine will not create the steric interactions of the ortho hydrogens.[20]

Further end capping with dye molecules or complexation with metal ions influence the fluorescence intensity of hyperbranched polymer by changing the quenching effects of the intra or inter molecular interactions of the different functional groups. For example, fluorescent chemosensors for selective detection of transition metal ions especially Cu^{2+} ion are rather rare,[21,22] although it is a very important metal in human body and plays an important role in various physiological processes. So the effect of end capping and metal ion complexation are very important.[16–18] Similarly the change of pH also affects the fluorescence intensity of the hyperbranched polymers,[15–17,19] hence need to investigate for such study.

Authors, therefore, wish to report the synthesis, characterization and properties evaluation of a fluorescent hyperbranched aromatic polyamine with *s*-triazine unit. The effect of dye end capping is also investigated. The fluorescence of the polymer has also been studied with the variation of concentration, pH of the medium and in the presence of Cu^{2+} ion.

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EXPERIMENTAL

Materials

N,*N*′-Dimethyl acetamide (DMAc, Merck, India) and di-methyl sulphoxide (DMSO, Merck, India) were used after purification by vacuum distillation over calcium oxide and anhydrous calcium sulfate respectively. 2,4,6-Trichloro-1,3,5-triazine (CYC), diisopropyl ethylamine (DIPEA, Merck, Germany), methyl red, cupric acetate and thionyl chloride (Merck, India) were used as received. 4,4′-oxydianiline (ODA, Aldrich Chemie, Germany) were used after purification from aqueous ethanol.

Synthesis of Hyperbranched Polyamine (HBPA)

0.01 mol of CYC in 25 mL DMAc was added very slowly for about 1 h at 0–5 °C in 24 mL solution of 0.015 mol of ODA and 0.01 mol of DIPEA (diisopropyl ethylamine) in DMAc. After 1 h, temperature increased to 40–45 °C and 0.01 mol of DIPEA was added into the reaction mixture. Then the temperature increased to 85–90 °C after 2 h, and 0.01 mol of DIPEA was added again. The mixture was cooled after 5 h and poured slowly in ice cold water. The precipitate was collected and washed several times with methanol and acetone to remove the unreacted reagents. The product was dried under vacuum at temperature 45–50 °C for 3 d to obtain dry powder of the polymer.

Preparation of End Capped Hyperbranched Polyamine (HBPE)

The end capping of hyperbranched polyamine was prepared by the following two step process. At first, 1.8 g (6.7 mmol) of methyl red and 5 mL of thionyl chloride were refluxed together for 6 h. Then the excess thionyl chloride was removed under vacuum and the deep brown solid powered of chloride derivative of methyl red was obtained.

In the next step, 1 g (35×10^{-4} mol) methyl red chloride in 10 mL DMAc and 4.53 g of DIPEA were added dropwise in 1 g (1.75×10^{-4} mol) of DMAc solution of HBPA with constant stirring. The mixture was stirred for 6 h at 80 °C, cooled to room temperature and then poured into ice cold water. The precipitate was filtered, washed with methanol and dried under vacuum at 45 °C for 3 d.
[^{1}H NMR, DMSO-d_6 (δ, ppm): 10.81, 9.12, and 9.22 (-NH), 8.01 (-CONH), 6.68–7.61 (aromatic), 2.85 (aliphatic -CH$_3$). FT-IR (KBr, cm^{-1}) 3350–3370, 1636, 1580–1620.]

Measurements

FT-IR spectra for the compounds were recorded in a Nicolet (Impact 410, Madison, USA) FT-IR spectrophotometer by using KBr pellets. ^{1}H NMR and ^{13}C NMR spectra of the polymer were recorded with 400 MHz NMR spectrometer (Varian, USA) by using d_6-DMSO as the solvent and TMS as the internal standard. The molecular weights of hyperbranched was determined by GPC analysis (Water, USA, Model 515) using DMSO as the solvent. The X-ray diffraction study was made on the powder sample at room temperature (*ca.* 27 °C) on a Rigaku X-ray diffractometer (Miniflex, UK). The scanning rate used was 5.0° min^{-1} over the range of $2\theta = 10$–80° for the above study. UV spectra of samples were recorded in a Hitachi (U-2001, Tokyo, Japan) UV spectrophotometer by using 0.001% solution in DMSO at room temperature (*ca.* 27 °C). The inherent viscosity of the polymer was measured using 0.5% (w/v) solution of the polymer in DMAc at 27 ± 0.1 °C by an Ubbelohde suspended level viscometer. Thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) were carried out in Shimazdu TG 50 and DSC 60 thermal analyzers respectively using the nitrogen flow rate of 30 mL/min and at the heat rate of 10 °C/min. The fluorescence spectra of the compounds were recorded in Perkin Elmer (LS55) spectrophotometer. The density of the polymer was determined by pycnometer in dry toluene at room temperature (*ca.* 27 °C) by the conventional liquid displacement method. The chlorine content of the polymer was determined by the standard Schoniger oxygen combustion method. The elemental analysis (CHN) was carried out in a Perkin Elmer elemental analyzer (model no. 2400 series II).

RESULTS AND DISCUSSION

Synthesis and Characterization of Hyperbranched Polyamine

The *s*-triazine based hyperbranched aromatic polyamine of 4,4′-oxydianiline (ODA) as an A$_2$ monomer and 2,4,6-trichloro 1,3,5-triazine (CYC) as a B$_3$ monomer was synthesized by an A$_2$+B$_3$ approach (Scheme 1). The substitution reaction of CYC by the aromatic diamine is carried out at three different
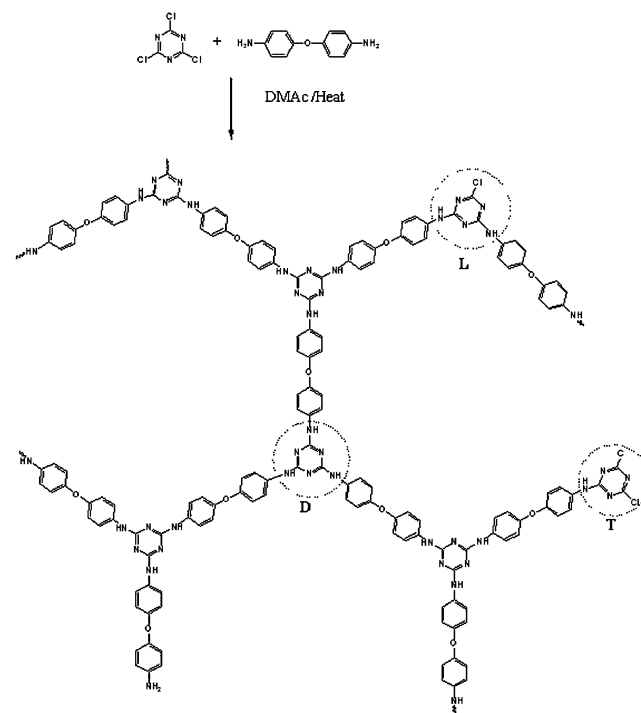
Scheme 1. Synthesis of hyperbranched polyamine.
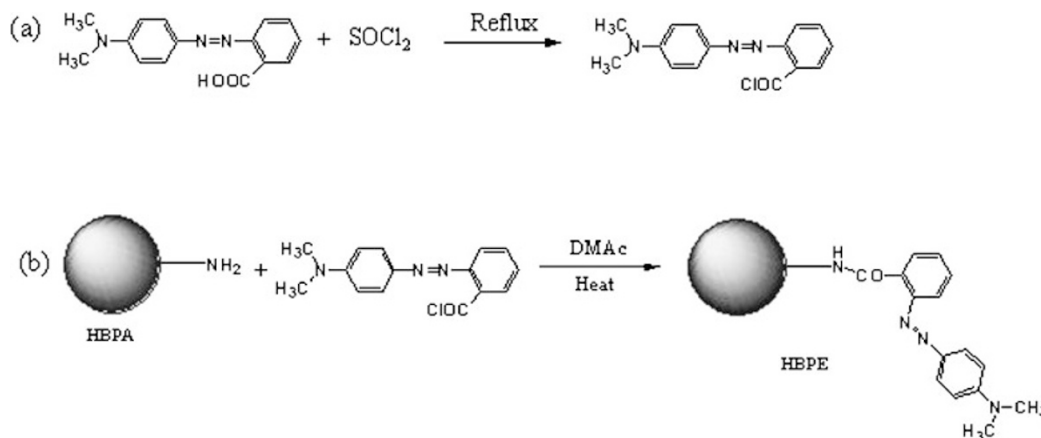
Scheme 2. End capping reaction of methyl red with hyperbranched polyamine.

temperatures as the reactivity of three chlorine atoms in CYC is highly thermoselective.[14] Gelation is a common problem for this type of polymerization reaction. It was avoided by using appropriate ratio (3:2 mole ratio of A_2 and B_3 monomers), concentration ($<10\%$, w/v) and slow addition of the monomers. These reaction conditions not only offered the product without gel but also a good yield (75%). The end capping with methyl red was performed through the reaction of chloride derivative of the methyl red with the active surface primary amine group of the hyperbranched polyamine as shown in Scheme 2. As the acid chloride is more reactive to primary amine than the corresponding acid, so the chloride derivative was prepared first. The amorphous nature of the polymer is confirmed by XRD study. The polymer has moderate density (1.18 g/cc) and light brown color with inherent viscosity (0.15 dL/g). This low viscosity may not only be due to low molecular weight of the polymer but also due to globular type structure. This is also confirmed by the determination of molecular weight (weight average molecular weight, $M_w = 5700$ g/mole and polydispersity index 1.3) of the polymer. From the UV-visible spectra, the λ_{max} values of the polymers, HBPA and HBPE and methyl red dye in DMAc solution were observed at 280 nm and 315 nm, 416 nm respectively, which indicate the presence of aromatic moiety with conjugation and characteristic π-π^* electronic transition in the aromatic 1,3,5-triazine compounds.[23] So a red shift of about 35 nm is observed for end capping with dye molecule. But from the spectra it is difficult to correlate the absorbance values, as their λ_{max} values are different. However, the introduction efficiency of dye molecule in the polymer can be calculated from the elemental analysis data of the polymers by the following procedure. The number average molecular weight of HBPA is 4,384 g/mole (obtained from GPC data) and hence molecular weight of the repeat unit (taking two unit of triazine with three unit of diamine, as the reaction ratio) is 534 g/mole, so the number of such repeat unit is approximately 8. That is approximately 16 triazine units and 25 diamine units are present in the structure. Now by utilizing the DB = 0.58 (obtained from ^{1}H NMR as described below), the number of free amino groups is

Table I. Elemental analysis data (C/H and N/H ratio) of the hyperbranched unmodified and end capped polyamines

polymer		ratio of element	
		C/H	C/N
Pure HBPA	Calculated[a]	9.6	1.71
	Found	9.15	3.91
End capped polymer	Calculated[b1]	10.6	1.8
	Calculated[b2]	12.25	1.87
	Calculated[b3]	13.44	1.94
	Calculated[b6]	18.8	2.13
	Calculated[b9]	26.51	2.28
	Found	19.9	2.1

[a]Calculated using ideal dendritic structure with no chlorine atom.
[bn]Theoretically calculated taking different degree of dye substitution, n = 1, 2, 3, 6 and 9 indicate number of dye molecules per molecule of end capped hyperbranched polyamine.

calculated in the structure and found to be approximately 10. Now, the C/H and C/N ratios of the polymers are calculated taking ideal dendritic structures and experimentally found same values are tabulated in Table I. From this table it is found that the ratios vary continuously with different degree of substitution. So the plot of number of dye molecules per molecule of end capped hyperbranched polymer resulted almost straight line both the cases with varying slope. By fitting the experimentally observed ratio of C/H and C/N of the end capped polymer in this plot in origin software, the number of dye molecules is found to be 6.4–6.8 (6.4 from C/H and 6.8 from C/N ratio). Thus the introduction efficiency is approximately 66%.

The important linkages in FT-IR spectrum like aromatic N-H (primary or secondary) at 3255–3445 cm^{-1}, 1593–1621 cm^{-1} and 1497 cm^{-1}.[24] supported the occurrence of nucleophilic displacement reaction. The marginal shift of these absorption values may be due to the presence of H-bonding.[24] The other linkages like C=N bond of the triazine moiety at 1412 cm^{-1} and aromatic C-Cl bond at 1010 cm^{-1} were also found in the spectrum.[24] The presence of C-Cl bond indicates the displacement reaction was not completed. This was
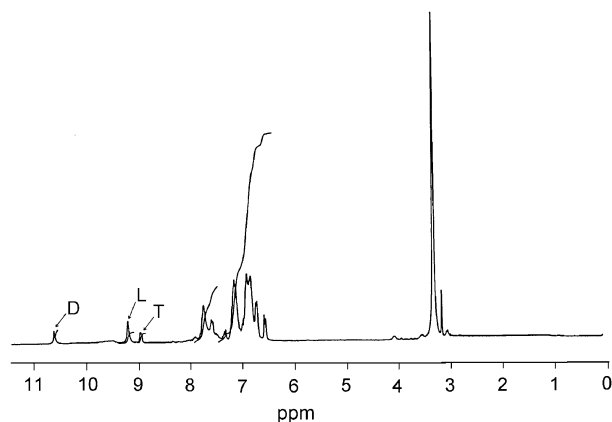
Figure 1. ^{1}H NMR spectrum of hyperbranched polyamine.
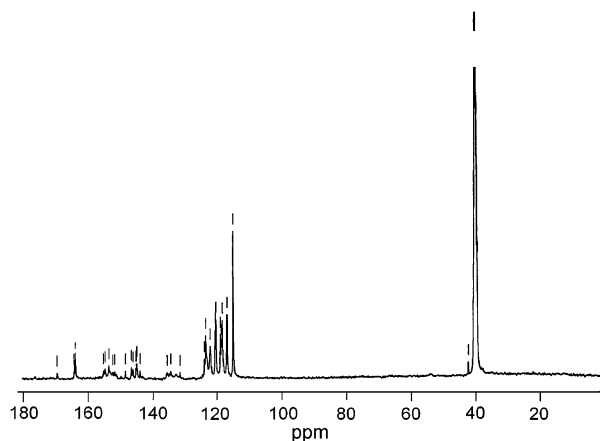

Figure 2. ^{13}C NMR spectrum of hyperbranched polyamine.

confirmed by quantitative measurement of chlorine by Schoniger oxygen combustion method (Table I). The ^{1}H NMR spectrum (Figure 1) of the polymer further indicates the presence of most important peaks for aromatic N-H protons. The dendritic (triazine with no chlorine atom), linear (triazine with one unsubstituted chlorine atom) and terminal units (triazine with two unsubstituted chlorine atoms) in the structure of the polymer are confirmed by the peaks at $\delta = 10.66$ ppm, $\delta = 9.20$ ppm and $\delta = 9.08$ ppm, which are due to above three different >N-H protons.[25] The other protons like -NH$_2$ at $\delta = 3.21$ ppm and aromatic moieties at $\delta = 6.50–7.76$ ppm as multiplate are also observed in the ^{1}H NMR spectrum.[24] The ^{13}C NMR spectrum (Figure 2) indicates the presence of peak at $\delta = 169.57$ ppm is due to unsubstitute chlorine atom in triazine ring, $\delta = 163.98$ ppm (due to the carbon atoms present in the dendritic triazine units),[26] peaks at $\delta = 152.44–143.88$ ppm (due to the carbons directly attached with oxy groups), peaks at $\delta = 135.37–131.37$ ppm (due to the carbon atoms directly attached with –NH groups) and peaks at $\delta = 123.73–114.89$ ppm (for the carbon atoms at ortho and meta to oxy group).[24]

Degree of Branching

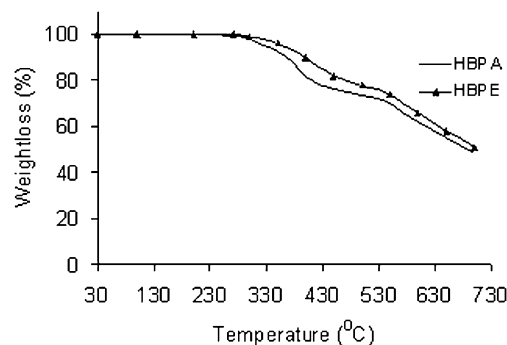The degree of branching (DB) of the polymer is determined

Figure 3. TG thermograms for HBPA and HBPE.

by using Frechet's equation as follow[27] using ^{1}H NMR spectrum.

$$DB = (D + T)/(D + T + L)$$

where D, T, and L refer to the number of dendritic, terminal and linear units in the structure of the polymer respectively. Experimentally, DB was determined from ^{1}H NMR spectroscopy by comparing the integration of the peaks for the respective units in the polymer (Figure 1). The value of DB for the polymer is found to be 0.58. This value indicates that the polymer exhibits near to highly branched structure rather than more linear (DB close to zero for linear, 0.5 for hyperbranched and 1.0 for dendrimer) structure.[28]

Properties of Polymer

From the solubility studies it has been found that the polymer is soluble only in highly polar solvents such as DMAc, DMF, DMSO, NMP, etc., partially soluble in acetone, THF, etc. but insoluble in most of the other solvents like hydrocarbon solvents, water, chlorinated common organic solvents, etc. This may be due to the presence of polar –NH groups, rigid triazine units and aromatic moieties in the polymer structures. This higher solubility not only supported the hyperbranched formation but also confirmed that the polymer is not a crosslinked gel product. Further it has been found that the solubility further enhanced by addition of HCl, which may be due to reduction of inter molecular attraction among the chain molecules.

The thermogravimatric analysis of HBPA and HBPE (Figure 3) showed that the initial degradation temperature, amount degraded at 400 °C, weight residue at 700 °C and overall thermostability of HBPE is better than HBPA, although both the polymers exhibit good thermostability. The initial decomposition temperature of HBPA is 300 °C whereas HBPE has 315 °C. The overall high thermostability of the polymers is due to the presence of thermosatable rigid triazine and aromatic moieties in the structures.[29,30] However, the higher value for HBPE is due incorporation of two more aromatic moieties along with a thermostable. N=N linkage in the structure of the end capped polymer. This is also reflected in the weight loss values at 400 °C and the weight residue at 700 °C (20% and 48% for HBPA and 15% and 52% for HBPE respectively). The
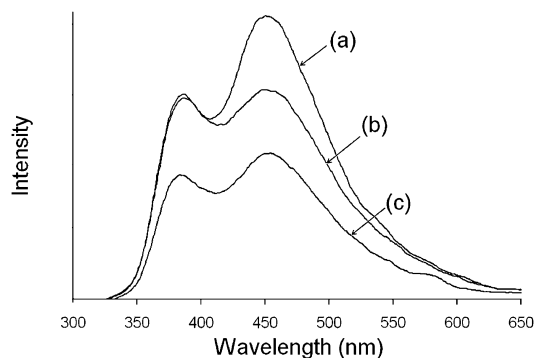
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Figure 4. Fluorescence spectra of (a) HBPE (b) HBPA (c) HBPA-Cu complex.

Figure 5. The fluorescence spectra of HBPA with variation of concentration.

high carbon to hydrogen ratio and the presence of special elements like nitrogen make both the polymer self-extinguishing in nature. The good flame retardancy of the polymers is also supported by high LOI value (36 for HBPA and 38 for HBPE).

In DSC studies no melting or crystallization peak was observed, which indicates that this hyperbranched polymer is amorphous in nature, which supports the XRD result. The polymer has T_g of 238 °C as obtained from DSC and this indicates the rigidity of the structure.[31]

Fluorescence Study

This hyperbranched polyamine containing all three different type of nitrogen linkages, *viz.*, primary at terminal, secondary in main chain and tertiary in triazine unit. The fluorescence emissions of hyperbranched polymer (0.01%, 1.6×10^{-5} mol/L in DMSO), its end-capped derivative with methyl red dye (0.01%) and complex with Cu^{2+} ion (0.015%). were shown in Figure 4. All three samples were excited with a 285 nm wavelength of light and exhibit emission in the yellow to blue region from 350 to 650 nm with maxima at about 455 nm and a shoulder at about 390 nm. From these results it has been observed (Figure 4) that end capping enhanced the intensity of fluorescence significantly. This may be due to the facts that end capping prominently render the quenching process of energy and/or electron transfer processes.[16,17] These processes otherwise could have been occurred between electron donating primary and/or secondary amino groups and electron accepting aromatic and heterocyclic moieties present in the structure of the polymer (Scheme 1). Further the dye molecule also enhances the conjugation and hence increases intensity. The quantum yield was determined by using anthracene with quantum yield 0.27 in ethanol is as the standard compound. The quantum yields of unmodified and end capped polymers are found to be 0.08 and 0.089 respectively. The study of fluorescence of hyperbranched polyamine in the presence of metal ions is very interesting due to its high-branched structure and the presence of different co-ordination sites. In case of Cu^{2+} ion-polymer complex solution, the intensity decreases due to intracomplex quenching effect. Since the hyperbranched polyamine is a 'push pull' system, excitation leads to a
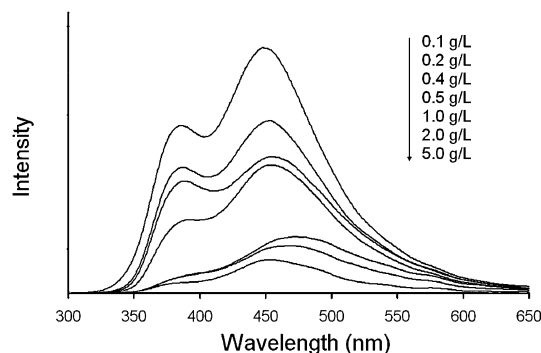
significant redistribution of electron density so that a substantial dipole may be created.[32] This attributed to energy transfer quenching between the complexing elements.

Effect of Concentration

The hyperbranched polyamine exhibit a general concentration 'self-quenching' effect with increasing concentration of polymer in DMSO solvent (Figure 5). Similar results have been reported by other researchers in case hyperbranched poly(sulfone amine) and polyether.[16,17] The decrease of intensity with increase of concentration of the polymer may be attributed by the quenching effect of amino groups present in the structure. Further this decrement *via* the self-association behaviors of polymers would change with concentration and hence the fluorescence behavior would also change with the same.

Effect of pH

Hyperbranched polyamine also exhibits pH dependent fluorescence and shows an increase of fluorescence intensity with the increase of pH (Figure 6). From this figure, it has been found that with the addition of alkali (pH 10.6) the intensity of main peak (455 nm) decreases and the shoulder peak at 390 nm increases. However, the addition of acid (pH 4.1–2.8) merges these two peaks and turns to a broad single peak in the fluorescence spectra. These are due to the following facts. It is well known that concentration of acid or base always has some influences on the polarity, hydrogen bonding ability and
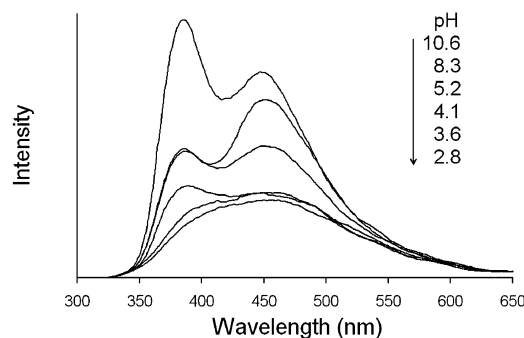

Figure 6. The fluorescence spectra of HBPA with variation of pH.

solubility and hence on association or aggregation state of the polymer.[33,34] As this hyperbranched polyamine exhibits all three types of nitrogen atoms in its structure and they (except the tertiary nitrogen of terminal *s*-triazine unit containing two chlorine atoms, as the basicity of the nitrogen atoms is low but number of such moiety is also less as indicated by elemental chlorine percentage, 2.5%) are protonated under acidic condition, *i.e.*, at low pH, so it is quite obvious that protonation efficiency definitely influenced the fluorescence behavior of the polymer. The increase of fluorescence intensity with the increase of pH by the addition of dilute alkali (NaOH) and decrease of fluorescence intensity with decreasing pH by addition of dilute acid (HCl) respectively may be attributed by at least two factors. The first one is reduction of quenching effect by amino group with decreasing pH, *i.e.*, by addition of HCl solution which makes the polymer as polyelectrolyte.[35] The hydrogen bonds between different bonded molecules at least partly broken as pH decreases resulting steady decrease of association domain, whereas in alkaline pH, the amino groups remain free and increase the hydrophobic association of the polymer, which may be due to formation of hydrogen bonding. But the situation at very high pH (10.6), the primary amino groups may be converted to anionic state though other amino groups may remain as neutral.

CONCLUSIONS

From this study, it can be concluded that hyperbranched aromatic polyamine with *s*-triazine unit was synthesized and well characterized by using different spectroscopic and analytical techniques. The study shows that the fluorescence of the polymer influenced by variation of concentration, pH of the medium, dye end capping and the presence of Cu^{2+} ion. The polymer is also highly thermostable and self-extinguishing. Thus, this hyperbranched polymer may find applications in compact laser devices, light harvesting/light emitting devices, Cu ion and pH sensor and so forth.

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