

# Synthesis of Morphologically Different, Metal Absorbing Aniline-Formaldehyde Polymers Including Micron-Sized Sphere Using Simple Alcohols as Morphology Modifier

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**ABSTRACT:** Aniline-formaldehyde condensate (AFC) is an amine functional group containing polymer. The sticky resinous nature of the polymer limits its usefulness. Synthesis of AFC in presence of methanol, isopropanol, *t*-butanol, *n*-octanol or glycerine formed solid cakes instead of resinous material. The scanning electron microscopic (SEM) picture of the polymer synthesized in presence of *t*-butanol shows the formation of micron sized spheroids while the presence of methanol, isopropanol, *n*-octanol and glycerine leads to amorphous polymer. The polymers were characterized with IR, MALDI-TOF mass and Energy Dispersive X-ray (EDAX) analysis. To probe the accessibility of the amine

functional groups by external reagents and as an application, metal removal property of the polymers were tested using aqueous Cr(VI) solution. All the polymers remove Cr(VI) efficiently at pH 3 with extent of metal removal depends on their morphology. Polymer synthesized in presence of isopropanol removes ~ 66% Cr(VI) removal from an initial concentration of 9 mg/L. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1158–1164, 2008

**Key words:** AFC; aniline formaldehyde condensate; polymer spheroids; chromium removal; polymer morphology; MALDI mass; SEM

## INTRODUCTION

The addition of formaldehyde to aniline in acidic media spontaneously forms a rubbery thermoplastic resin, also known as Aniline Formaldehyde Condensate (AFC), is used in the adhesive industry.<sup>1</sup> The reaction involves electrophilic addition of protonated formaldehyde to the *ortho* and/or *para* position of aniline depending on the formaldehyde to aniline ratio.<sup>1</sup> Despite the presence of large number of functional amine group similar to chitosan,<sup>2,3</sup> the AFC has limited number of application presumably because of its resinous nature. This paper presents our finding that addition of simple alcohols during synthesis and controlled temperature produces solid AFC instead of sticky resin with wide ranging morphology. Interestingly, addition of *t*-Butanol without

any surfactant leads to the formation of submicron (700 nm to 2  $\mu$ m) sized spheroids. Nanometer to micrometer sized regular shaped polymer spheres with high surface area has been of interest because of their potential in biomedical applications.<sup>4</sup> The common method of polymer sphere preparation involves formation of polymers around a micelle or vesicle using surfactants.<sup>4–7</sup>

To test the usefulness of the polymers as well as to probe the accessibility of the amine functional groups by external reagents, we measured metal removal property of the polymers using Cr(VI) as a test case. Removal of Cr(VI), a pollutant in various industrial waste, has been studied by several groups using natural or synthetic adsorbent.<sup>8–14</sup> AFC was used for removal of Hg<sup>2+</sup> from the aqueous solution.<sup>15,16</sup> Earlier, we have demonstrated that AFC coated on silica gel effectively remove Cr(VI) from acidic solution<sup>8</sup> by acting as anion-exchanger in the acidic medium or Cu(II) in pH 6<sup>9</sup> similar to other amine rich natural adsorbent.<sup>10–14</sup> The resinous nature of AFC specially in acidic medium, oxidation of amines upon long term (months) storage and larger weight of support material put several hurdles for its effective use. The result showing improved processibility, stability, and Cr(VI) removal property of the present polymers over other synthetic<sup>13,14</sup> and natural polymers<sup>10–12</sup> has been presented in this paper.

Additional Supporting Information may be found in the online version of this article.

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## EXPERIMENTAL

FTIR spectra were recorded on Perkin–Elmer Spectrum one spectrophotometer. SEM photographs were recorded using a Leo-1430 VP instrument with Energy Dispersive X-ray (EDAX) analysis attachment and the polymer samples were coated with gold vapor before measurements to reduce charging. Total chromium concentration of the aqueous solution before and after adsorption with polymers were measured using a Varian model 55B Atomic Absorption Spectrometer using air-acetylene flame at wavelength of 429 nm with slit width of 0.5 nm. Elemental analyses were done on Carlo Erba 1108. MALDI-TOF mass measurements were recorded on Micromass TOF Spec 2E instrument using a nitrogen 337 nm laser (4 nm pulses). At least 40–50 shots are summed up. The matrix used is 2,5-dihydroxy benzoic acid dissolved in methanol. The sample and the matrix spotted on MALDI target and allowed to dry before introducing into the mass spectrometer.

### General synthesis of the polymers

In a typical synthesis, alcoholic solution of aniline and conc. HCl was precooled to 0–5°C before mixing. Upon addition of a cold alcoholic solution of formaldehyde to the unstirred aniline solution, the solution turns turbid and slowly thickened over few minutes, changing from white to pale yellow color. Over time the polymer solidifies and turned light yellow. If the reaction is performed at room temperature, the exothermic reaction resulted in a fragile and dark red polymer. The polymer formed in room temperature is not uniform in texture. The reported procedure for resinous AFC uses higher temperature and longer duration in the synthesis.<sup>1</sup> The solid polymers formed in shape of the reaction vessel were washed sequentially with 1M HCl, 1M NaOH, and distilled water to remove unreacted reagents and to form the polymers in the amine form. The light yellow polymers were dried in vacuum desiccator for 1–3 days (depending on alcohol used) over anhydrous calcium chloride to remove water and any traces of alcohols remain trapped in the polymer. Quantitative details of one synthesis is given below

### Synthesis of polymer in presence of *t*-butanol

Aniline (9 g, 0.096 mol) and *t*-butanol (3.5 mL) were dissolved in 2.25 mL of conc. HCl (0.025 mol). The solution was cooled to below 5°C with an ice bath. A solution of 37% (w/v) formaldehyde (7.5 mL, 0.094 mol) in 3.5 mL of precooled *t*-butanol was added drop wise into the aniline-acid solution with vigorous stirring to obtain a uniform homogeneous solution. The temperature was maintained at 0–5°C

for 25 min and then allowed to warm up to the room temperature. The solid polymer was cut into pieces and washed with 1M HCl solution followed by 1M NaOH solution and finally with distilled water and dried under vacuum desiccator.

### Analysis of polymers

*t*-Butanol: C% 72.52, H% 6.37, N% 11.40; C : N mol ratio 7.5 : 1. *Iso*-propanol: C% 58.37, H% 7.07, N% 9.65; C : N mol ratio 7 : 1. Methanol: C% 58.03, H% 6.49, N% 9.06; C : N mol ratio 7.5 : 1. Glycerol: C% 70.16, H% 6.05, N% 10.15; C : N mol ratio 8 : 1.

## RESULTS AND DISCUSSION

### Synthesis and characterization

The IR spectra of all the polymers show peaks at 3400 cm<sup>-1</sup> (primary amine), sharp peaks at ~ 1650 and 1610 (amine bending), 1515 and at 808 cm<sup>-1</sup>. The peaks are similar to the polymer prepared following the reported procedure without the use of alcohols.<sup>8,9</sup> The polymers are insoluble in common organic solvent including DMF and DMSO. Thus <sup>1</sup>H-NMR could not be performed.

Elemental analysis (Carbon, Hydrogen and Nitrogen) data in terms of percentage on the polymers were varied widely (section “Analysis of polymers”) as it is difficult to control the amount of residual acid attached to amines and salts trapped within the solid. The EDAX analysis on the polymers during SEM measurements shows the presence of significant amount of chloride in the polymers. Thus washing the polymers with NaOH and water did not convert all the anilinium hydrochloride sites to free amine form or in other words, some anilinium sites remain inaccessible to acids and water. As the source of C and N in the polymer is determined by the *o*-methylene aniline unit (C : N is 7 : 1) the ratio of C : N determined from elemental analysis, lies between 7 : 1 to 8 : 1 are close considering the variation possible due to small amount of entrapped alcohols.

### Maldi-TOF mass spectral analysis

Matrix assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS) is a soft ionization technique developed by Karas and Hillenkamp and has been found to be a valuable tool for the characterization of polymers.<sup>17</sup> The spectrum for polymer from *t*-Butanol (Fig. 1) shows at least four series of oligomers. The  $\Delta_m$  calculated from MALDI-TOF Mass spectra (Fig. 1) 105, equivalent to *o*-methylene aniline unit (C<sub>7</sub>H<sub>7</sub>N, calcd as 105.13). MALDI-TOF has been used to determine molecular weight distribution for polymer isolated from *para*-

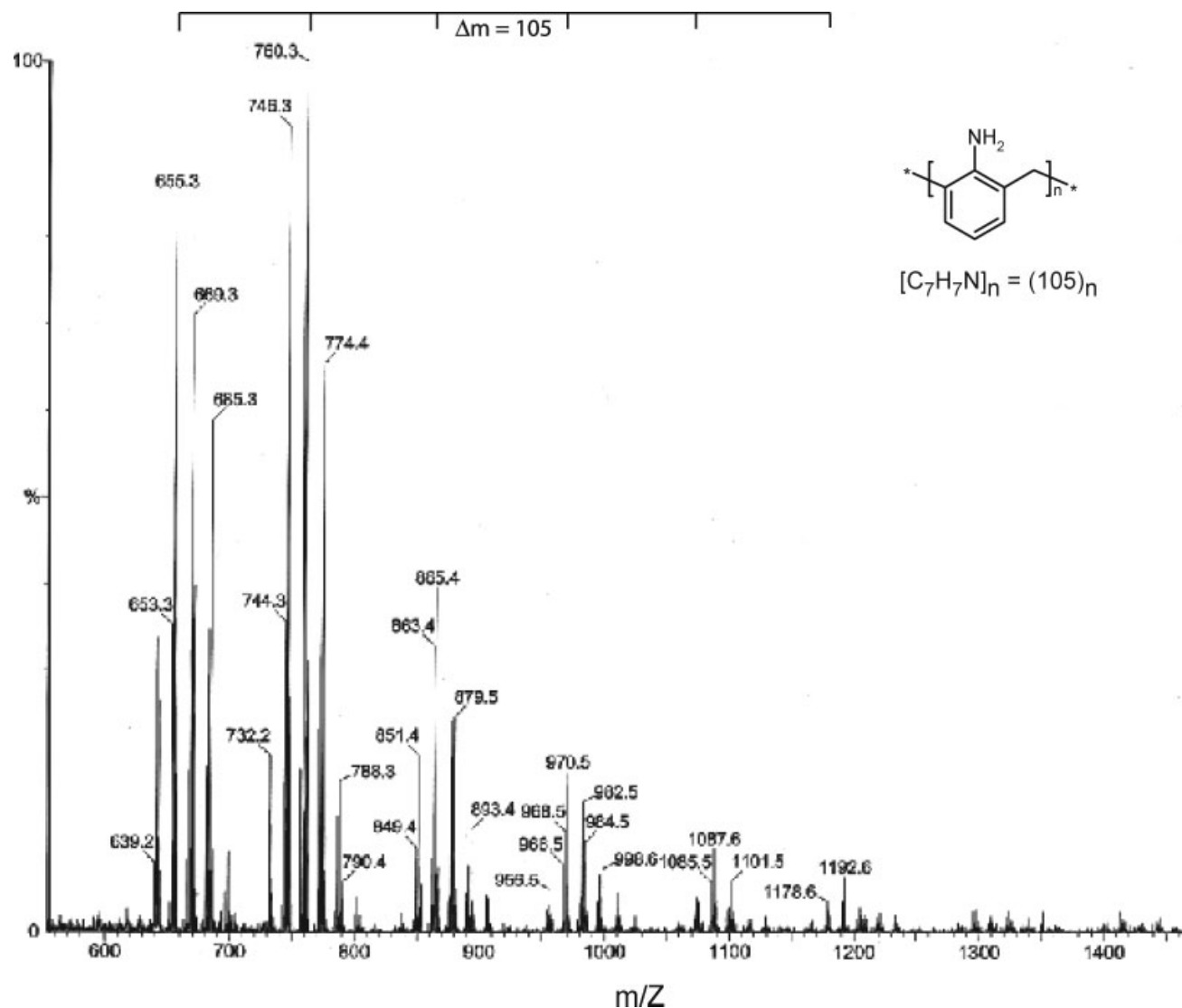


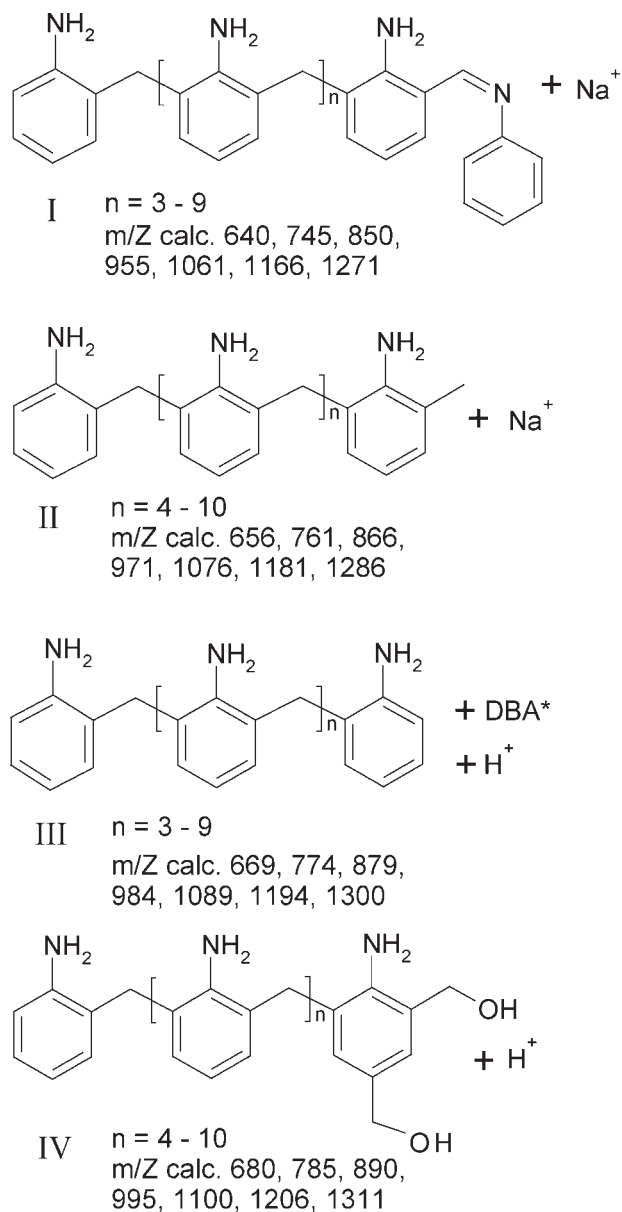
Figure 1 The MALDI-TOF mass spectrum of the AFC polymer synthesized in presence of *t*-butanol.

substituted phenol and formaldehyde.<sup>18</sup> However, the presence of multiple positively charged center (ammonium or amine+Na<sup>+</sup>) and possibility of branching at the *para* position of the aniline moiety generate several structure with nearly same mass value and thus predicting structure of the oligomer series based only on mass spectrum with certainty is difficult. In Scheme 1 we have presented a set of probable series with calculated mass values which comes close to the mass values observed in the MALDI-Mass. The structure I, II, and IV are based on the products proposed in the formaldehyde phenol polymerization.<sup>19</sup> Some of the structures presented in (Scheme 1) can very well be branched at the *para* position as such branching only changes the value of *n* preserving the mass of the molecule nearly same. The polymer from isopropanol shows a similar spectrum (Supplementary Materials). The identical  $\Delta m$  value for both the polymer confirmed

that these are polymers with multiple units of *o*-methylene aniline as expected for AFC. Thus chemically the polymers are not very different.

#### Stability of the polymers

All the polymers were thermally stable up to 240°C with charring occurs above 240°C. The polymer from *t*-butanol remains unchanged even at 250°C. The stability of the polymers in air varies and the polymer from methanol has a tendency to get darker in air with time due to aerobic oxidation of amines over 4–6 weeks. Rests of the polymers are air stable for over 6 months without any coloration due to aerobic amine oxidation. The lower initial reaction temperature and the presence of alcohols possibly allowed formation of few large molecular weight oligomer series where free amine groups remain protected because of the dense nature of the polymer. The well defined



**Scheme 1** The series of oligomers with calculated mass values proposed on the basis of MALDI-TOF Mass spectrum. DBA is 2,5-dihydroxy benzoic acid used in the matrix preparation.

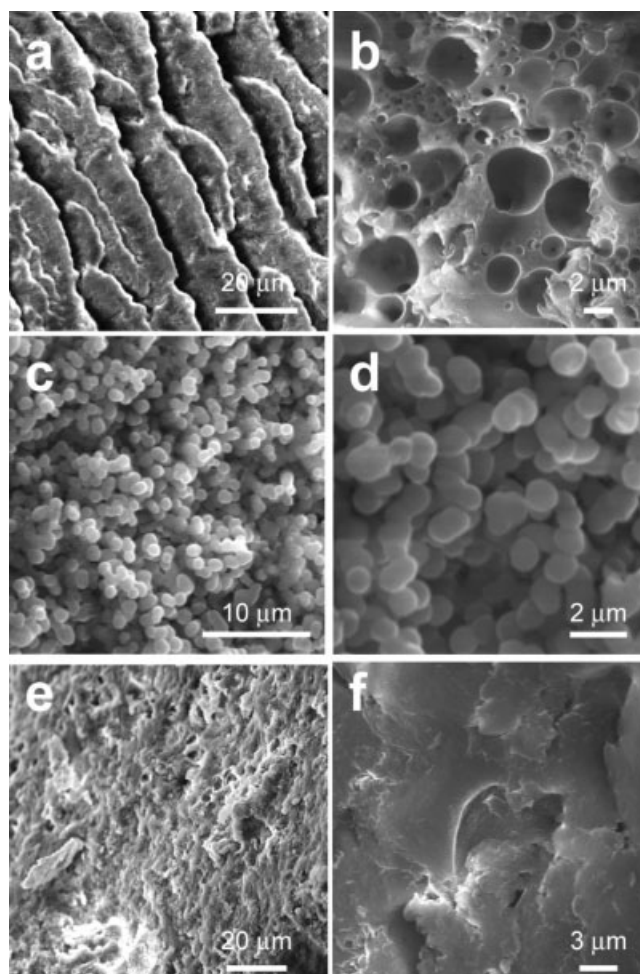
nature of the mass spectra (Fig. 1) suggests the formation of fewer oligomeric series with narrow mass distribution. The multiple charge centers prevented precise molecular weight determination (section "Synthesis and characterization").

### Scanning electron microscopy

The scanning electron microscope (SEM) images (Fig. 2) revealed the formation of spheroids of polymers in presence of *t*-butanol but morphologically different solid polymer in case of other alcohols. The SEM photographs of different batches as well as from different parts of the polymer block prepared from *t*-butanol

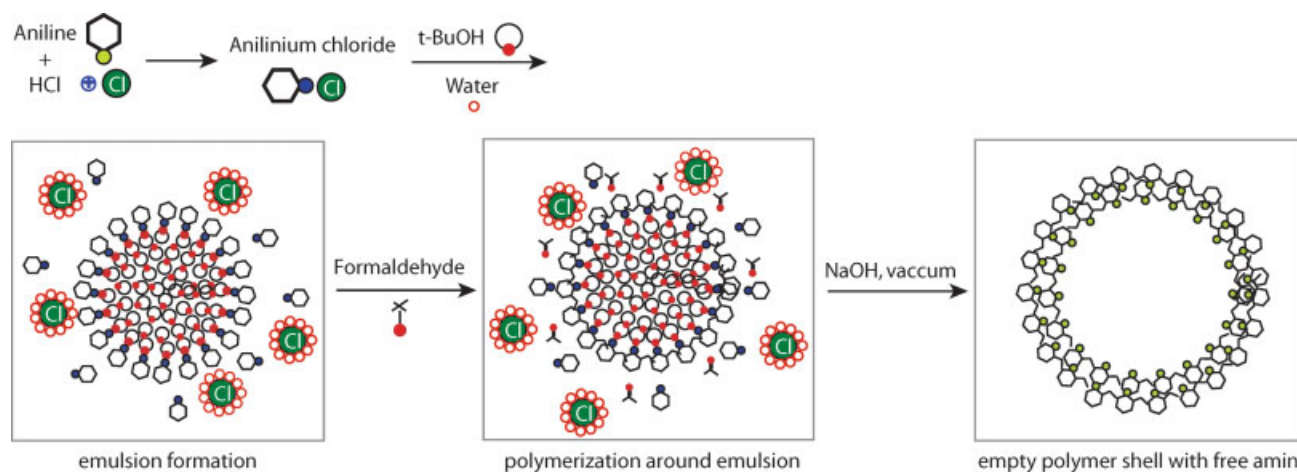
shows the spheroids size and distribution is almost uniform (almost uniformly 750 nm to 2  $\mu\text{m}$  in size). In case of polyalcohol such as glycerine the polymer formed as a semi transparent gel which once dried breaks in to flakes/layers consistent with its SEM image.

Although the exact reason for spherical formation in case of *t*-butanol is not known or observed in any other reports, theoretical studies on effect of salt addition to *t*-butanol/water mixture has been shown to form ring like distribution of hydrophobic *t*-butanol molecules with salts surrounding the *t*-butanol molecules which is unique for *t*-butanol.<sup>20</sup> Thus, *t*-butanol/water mixture in presence of ionic aniline HCl might have arranged in a nano sized ring like distribution or droplets of *t*-BuOH acting as the core for polymerization on the surface of the ring, leading to the spheroid shape observed (Scheme 2). We expected that *n*-octanol with its ability to form micelle would give rise to spheroid polymer but phase separation between *n*-octanol and water due to the higher concentration of *n*-octanol and higher hydrophobicity of *n*-octanol prevented that.



**Figure 2** SEM images of the polymers formed in presence of (a) methanol, (b) isopropanol, (c,d) *t*-butanol, (e) *n*-octanol and (f) glycerine.

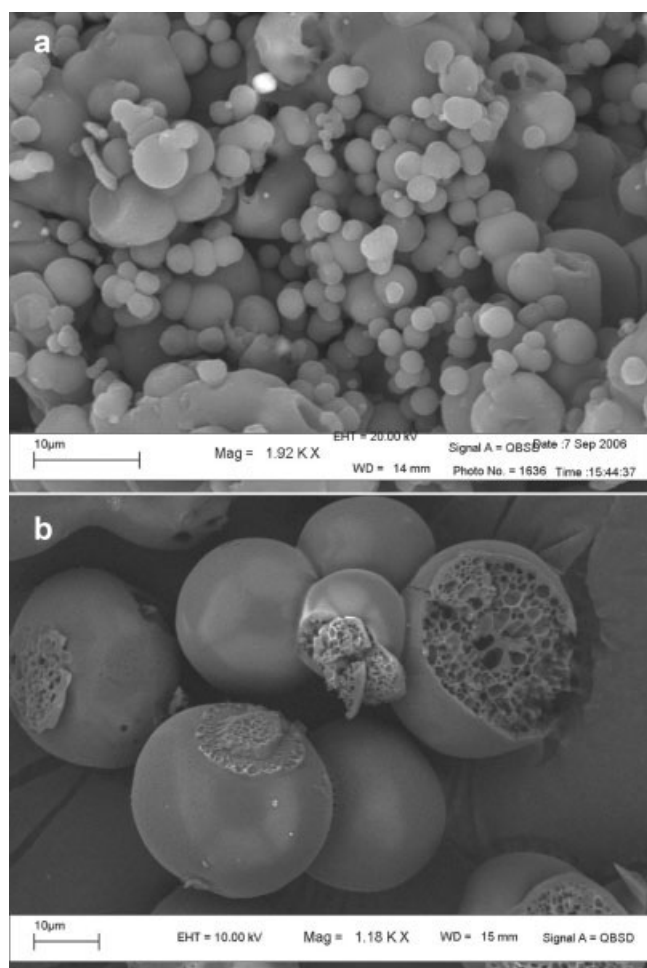




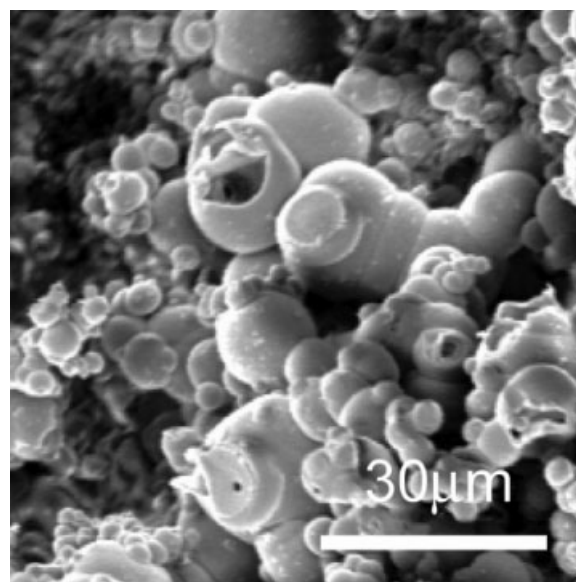
**Scheme 2** The proposed path of formation of polymer spheres in *t*-BuOH water mixture. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

Both amount of solvent and temperature plays important role in determining the size of the spheroids. A 10-fold increase in amount of water, keeping the

temperature constant ( $<0^{\circ}\text{C}$ ), the spheroid size increases to 2–3  $\mu\text{m}$  with wider distribution of size but the yield is poor. This accompanies formation of large amount of soluble AFC which precipitates in alkaline medium. This observation indicates that at low temperature the polymer formation initiated around the *t*-butanol core (Scheme 2) which slowly grows in size and molecular weight over time forming spheroids until the space between spheroids diminished leading to solid formed out of partially fused spheroids [Fig. 2(c)]. Upon dilution some of the spheroids grow further until reagent concentration diminished. The dilution also causes formation of more seed which does not grow further leading to formation of smaller soluble form of AFC. On the other hand, in concentrated medium, several of the droplets of *t*-BuOH fuses together and large lump



**Figure 3** SEM images of the *t*-BuOH-AFC polymer from concentrated medium (a) and *i*-PrOH-AFC from temperature controlled medium (b).



**Figure 4** SEM images of the AFC polymer after chromium binding.

TABLE I  
Binding Properties of the Grinded Polymers for  $\text{HCrO}_4^-$  in Different Initial Concentration at pH 3<sup>a</sup>

Initial conc. Polymer Prepared from	100 (mg/L)		50 (mg/L)		9 (mg/L)	
	Cr(VI) removal (%)	$q_e$ (mg/g)	Cr(VI) removal (%)	$q_e$ (mg/g)	Cr(VI) removal (%)	$q_e$ (mg/g)
Methanol	68	68	66	33	61	2.7
Isopropanol	39	39	50	25	70	3.1
<i>t</i> -butanol	13	13	28	14	50	2.2
<i>n</i> -Octanol	66	66	76	38	49	2.2
Glycerine	44	44	66	33	69	3.1

<sup>a</sup> Quantity of polymer used: 1g/L for initial conc. of 100 mg/L and 50 mg/L, and 2 g/L for 9 mg/L. Each set was allowed to equilibrate for 3 h. Results are average of three sets.

formation is observed along with spheroids [Fig. 3(a)]. The rapid rate of reaction at room temperature causes partial evaporation of *t*-butanol and formation of significant amount of oxidized bright red irregular shaped polymer. If the temperature is maintained strictly at or below 0°C, spheroid shaped formation is also observed in isopropanol [Fig. 3(b)]. However, spheroid formed in isopropanol are much larger (~ 20 micron) and unlike spheroids from *t*-BuOH (Fig. 4) inside [Fig. 3(b)] is not empty. Overall, symmetrical shape of *t*-BuOH influences the formation of 700–2 micron spheroid and reproducibility possibly through a regular shaped solvent core (Scheme 2).

### Chromium removal property

We chose to study the binding properties of these polymers with Cr(VI) because it will allow us (a) to probe the accessibility of the amine functional groups to aqueous reagents and (b) to check the probable application for these polymers. In acidic pH, AFC and other amine containing polymers or natural adsorbent has been used by us and other investigators to remove toxic Cr(VI) from aqueous solutions.<sup>10–14</sup> Usually at acidic pH, amines in the polymer exist as  $-\text{NH}_3^+\text{Cl}^-$  which acting as anion exchanger absorbs  $\text{HCrO}_4^-$ . This has been confirmed by (a) presence of  $\nu_{\text{Cr=O}}$  stretch at  $932\text{ cm}^{-1}$  in the FTIR spectrum of Cr(VI) treated polymer<sup>21</sup> and (b) testing Cr(VI) treated polymer for presence of chromate with KI in presence of acid and subsequent iodine liberation.<sup>22</sup> The results of the Cr(VI) binding for the polymers is shown in (Table I). All the polymers, except spheroids from *t*-butanol show effective removal of Cr(VI) with high  $q_e$  (mg of Cr removed by 1 g of polymer). In comparison, reported amine containing polymers have  $q_e$  values between 16 and 23.\* The present poly-

mers are effective even at a low concentration of 9 mg/L (9 ppm) and reduces Cr(VI) level by 70% (~ 3 mg/L) in case of polymer synthesized from isopropanol (Table I).

The variation of  $q_e$  values for a particular initial concentration of Cr(VI) from polymer to polymer might be due to the differences in accessibility of the  $-\text{NH}_3^+$  exchange sites. The removal is highest for polymers from MeOH and isopropanol. The polymer from *t*-butanol shows considerably less removal of Cr(VI) compared to polymers synthesized from other alcohol. The EDAX spot analysis of Cr(VI) absorbed polymers from isopropanol shows presence of chromium on the surface but the spheroids from *t*-butanol indicate significantly less chromium on the surface. We think that in *t*-butanol, most of the amine sites are either in the inner surface of the spheroids or too much crowded to be accessible (Scheme 2). On the other hand, polymers from methanol, isopropanol or *n*-octanol due to their lack of seeding during formation yields exchange sites are more open for access to Cr(VI). The SEM photograph of the *t*-butanol sample after it was soaked in Cr(VI) solution for several hours followed by washing and vacuum drying (Fig. 4) shows that some of the spheroids have been swollen to 2–3  $\mu\text{m}$  size and burst open showing interiors as empty hollow sphere.

Cr(VI) removal experiments were tested for both grinded and ungrinded form to check the effect of surface area (Table II). Decreasing the surface area with large particle size (~ 100  $\mu\text{m}^3$  cubic blocks), the polymers remain effective in removing Cr(VI) (Table II). Thus the polymers are porous enough to enable the solvent penetration through the matrix.

### CONCLUSIONS

Thus we are able to modify AFC polymerization reaction by controlling reaction temperature and addition of simple alcohols to produce stable solid polymers instead of sticky resin which increases the usefulness of AFC, a polymer with high amine content similar to chitosan. We have also characterized ~ 1  $\mu\text{m}$  sized

\*Cr(VI) removal  $q_e$  (mg/g) value 20.7 for acrylonitrile fibre at pH 2.4 with initial conc. 50mg/L (Ref. 14); 23 for crosslink polymer at pH 2 with initial conc. 100 mg/L (Ref. 13); 16 for Xanthated chitosan at pH 3 with initial conc. 50 mg/L (Ref. 12).

**TABLE II**  
**Binding Properties of the Large Particles of Polymers ( $\sim 100 \text{ mm}^3$  Cubic Blocks) for  $\text{HCrO}_4^-$  in Different Initial Concentration at pH 3<sup>a</sup>**

Initial conc. Polymer prepared from	100 (mg/L)		50 (mg/L)	
	Cr(VI) removal (%)	$q_e$ (mg/g)	Cr(VI) removal (%)	$q_e$ (mg/g)
Methanol	40	40	52	26
Isopropanol	40	40	60	30
<i>t</i> -butanol	30	30	24	12
<i>n</i> -Octanol	27	27	22	11
Glycerine	31	31	44	22

<sup>a</sup> Quantity of polymer used: 1 g/L. Polymers used are  $\sim 3\text{--}5$  mm square blocks. Each set was allowed to equilibrate for 3 h.

polymer spheres in bulk quantity (multi gram) by adding *t*-butanol. All the polymers remove Cr(VI) from aqueous solution efficiently. Variation in metal removal capacity among the polymers also demonstrate that (a) the amine groups are accessible to outside reagent (b) the morphology plays a major role in the metal binding property (c) the template effect of *t*-butanol made the spheroids with free amine groups mostly in the inner surface. To the best of our knowledge, synthesis of submicron size polymer sphere using only alcohol template without using surfactants or micelles has not been reported before.

All the polymers except the spheroids are useful in removing Cr(VI), an industrial pollutant, from acidic aqueous solution. Compared to AFC coated on silica gel under the similar condition, removal efficiency showed 2.5 times increase in efficiency [Ref at Cr(VI) conc. of 100 mg/L with 1 g polymer/L,  $q_e$  value for AFC coated on silica gel 28].<sup>8</sup> All the polymers show significantly better removal of Cr(VI) compared to other known adsorbent in the similar concentration and pH range and it is effective even at very low concentration of  $\sim 10$  ppm (70% removal).\*

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