# One-Pot Synthesis of Polymeric Bead Bearing Surface Charge

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**ABSTRACT:** Preparation of polymeric bead bearing surface charge was carried out by using one-pot suspension polymerization of styrene and divinylbenzene (DVB) in the presence of cationic functional monomer, 3-methacryloylamino) propyl trimethyl ammonium chloride (MAPTAC), by using $K_2S_2O_8$ and AIBN as initiators. First, polymerization of MAPTAC in aqueous solution using $K_2S_2O_8$ initiator was performed for the determined time to generate a PMAPTAC radical. Second, the mixture of styrene, DVB, and AIBN initiator was fed into the solution of PMAPTAC radicals and then allowed the polymerization to proceed for another specified time. During the stage of polymerization of styrene and DVB, incorporation of PMAPTAC radicals onto the bead surface took place, resulting in the final bead particle comprising two layers (from SEM results): the inner core of the poly(styrene-*co*-DVB) support and the outer layer of copolymerization adduct of styrene, DVB, and PMAPTAC radical revealed by FTIR analysis. Factors affecting particle size, size distribution, and surface functionality (PMAPTAC segment) were investigated. Of all synthetic parameters, types of surfactants and amounts of DVB were found to play an important role in controlling the particle size and the surface functionality, respectively. Nonionic surfactant (cetyl alcohol) tended to produce large particle size with a majority of the population falling in the range of 500-1800 $\mu$m. Replacement of nonionic surfactant with cationic surfactant (CTAB) resulted in better control of particle size and size distribution because of its effective electrostatic stabilizer. An increase in the amount of DVB led to smoother bead surface as a result of less availability of styrene on bead surface, reducing surface charge density. The results of dye adsorption isotherm further confirmed that the cationic functional group was incorporated into the outer shell of the polymer bead. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1375–1387, 2004

**Key words:** one-pot suspension polymerization; polymer bead; surface charge; anion exchange; dye adsorption

## INTRODUCTION

Adsorption is one treatment technique for removal of textile dye waste commonly containing anionic dyes such as unfixed reactive dyes. Typical dye adsorbents include agricultural by-products,[1,2] activated carbon,[3,4] and metal sludge.[5,6,7] Agriculture-based adsorbents usually contain a negative charge, which repels anionic dyes. They can be modified in low pH conditions to reduced coulombic repulsion but this means a higher cost of pH adjustment and COD increase. Activated carbon is an expensive material, while metal sludge is cheap but leachable to release toxic heavy metal ions. Adsorbents based on synthetic polymers are commercially available and have mostly found application in areas of chromatography,[8,9] water softening, and small ionic species,[10] such as counter anions[11,12] and cations.[13] Their adsorption capacity of very large molecules such as most synthetic dyes is extremely low and costly to be applied.

Most ion exchange bead resins are manufactured by a suspension polymerization using styrene and divinylbenzene (DVB).[14,15,16] The DVB is a crosslinking agent which gives the beads their physical strength. The polymeric bead needs to be chemically activated to make it capable of exchanging ions. Functional groups are attached chemically to the bead as a source of charge. Each active group has a fixed electrical charge, which is balanced by the equivalent number of oppositely charged ions. Strong base exchangers are based upon quaternary ammonium groups ($-NR_3^+$), where R may be a methyl, ethyl, or other organic substituents. Activation of polystyrene/DVB bead involves a two-step process: chloroethylation and subsequent treatment with ammonia or primary, secondary, or tertiary alkyl amine.[17] It can be seen that several involved reaction steps with a requirement of toxic chemicals contribute to the high cost of the final resins, which makes them too expensive for treatment of textile dye wastewater.

It is of interest to prepare anion exchange resin by a single-batch process at the ultimate aim of resins suitable for textile dye adsorption. In this work, suspension polymerization of styrene and DVB was carried out in the aqueous solution of functional monomer [3-methacryloylamino) propyl trimethyl ammonium chloride (MAPTAC, a cationic monomer)]. The functional monomer is first initiated by potassium persul-

### TABLE I
### Experimental Conditions

| Reagents and conditions | Conditions | wt % (based on styrene) |
|---|---|---|
| MAPTAC | 2.25 g | 55.15 |
| $K_2S_2O_8$ | 0.09 g | 4.00[a] |
| 0.1 wt % PVA solution | 90 ml | — |
| Polymerization time of MAPTAC | 15–45 min | — |
| Styrene | 4.08 g | — |
| DVB | 0.46–1.84 g | 11.27–45.10 |
| Surfactant | | |
|   Cetyl alcohol or CTAB | 0–0.03 or 0–0.005 g | 0–0.74 or 0–0.12 |
| AIBN | 0.10–0.13 g | 2.20[b] |
| Polymerization time of Styrene and PMAPTAC radical | 1 h | — |
| Polymerization temperature | 60–80°C | — |
| Stirring speed | 200–400 rpm | — |

[a] Based on MAPTAC.
[b] Based on styrene and DVB.

fate to generate a short chain length of PMAPTAC radical (the functional group). Styrene and DVB mixture containing AIBN initiator are fed after a certain time. It is expected that the surface of poly(styrene-*co*-DVB) bead would be functionalized by the graft reaction of PMAPTAC radical with available surface monomer. Effects of synthetic parameters such as polymerization time of MAPTAC, polymerization temperature, and surfactants on the particle size and size distribution are investigated. Dye adsorption isotherm is also presented to elucidate the dye adsorption capacity of the prepared beads.

## EXPERIMENTAL

### Materials

MAPTAC (50 wt % solution) was purchased from Aldrich Co. DVB crosslinking monomer (Fluka) was used as received. Styrene (Fluka) was used without further purification. 2,2′-Azobis(isobutyronitrile) (AIBN), kindly supplied by Siam Chemical Industry Co., Ltd., and potassium persulfate, from M&B Laboratory Chemical, were used as received (purity not less than 98%). Poly(vinyl alcohol) [molecular weight (MW) 115,000] used in the suspension polymerization as a suspending agent was supplied by BDH Laboratory Reagent. Surfactants, such as cetyl alcohol and hexadecyltrimethylammonium bromide (CTAB), were used and supplied by Union Chemical and Fluka, respectively. Nonylphenol ethoxylate (Tergitol NP-15, Union Carbide) was used as wetting agent. The three commercial reactive dyes (from Modern Dyestuffs and Pigment, Co., Ltd.) chosen for this study were C.I. Reactive Blue 171, C.I. Reactive Red 195, and C.I. Reactive Yellow 84.

### Synthesis of poly(styrene-*co*-DVB) beads bearing surface charge

Synthesis of poly(styrene-*co*-DVB) beads was conducted in two steps: the polymerization of MAP-

TAC in aqueous continuous phase and the surface functionalization of styrene and DVB droplet with the PMAPTAC radicals. In the first step, 90 mL of 0.1 wt % poly(vinyl alcohol) (PVA) aqueous solution was added into a 500-mL four-necked round-bottomed flask which was immersed in a thermostat oil bath as a source of constant heat supply. The reaction flask was equipped with a mechanical stirrer, a thermometer, a reflux condenser, and a nitrogen gas inlet tube. The suspending agent solution was preheated to the desired temperature and kept constant for 30 min. MAPTAC and $K_2S_2O_8$ initiator were well mixed before adding to the reaction flask in which the suspending agent was stirred at a constant speed. The reaction was allowed to proceed for a determined time. In the second step, the mixture solution of styrene, DVB, surfactant, and AIBN initiator were added into the reaction flask and the copolymerization reaction was continued for a set period of time. At the end of the reaction, the polymeric particles were formed. After that, the polymeric beads were washed with distilled water and then acetone and dried at room temperature. The product yield was calculated. The experimental conditions were varied as shown in Table I.

### Characterizations

Particle size measurement

The final polymer beads were sieved into discrete particle size ranges by using Laboratory Test Sieve (mesh number 6-140; Endecotts Ltd., London, UK).

Gel permeation chromatography (GPC) experiment

A GPC experiment was carried out to obtain the information of the molecular weight distribution of PMAPTAC radicals. Separate polymerization of
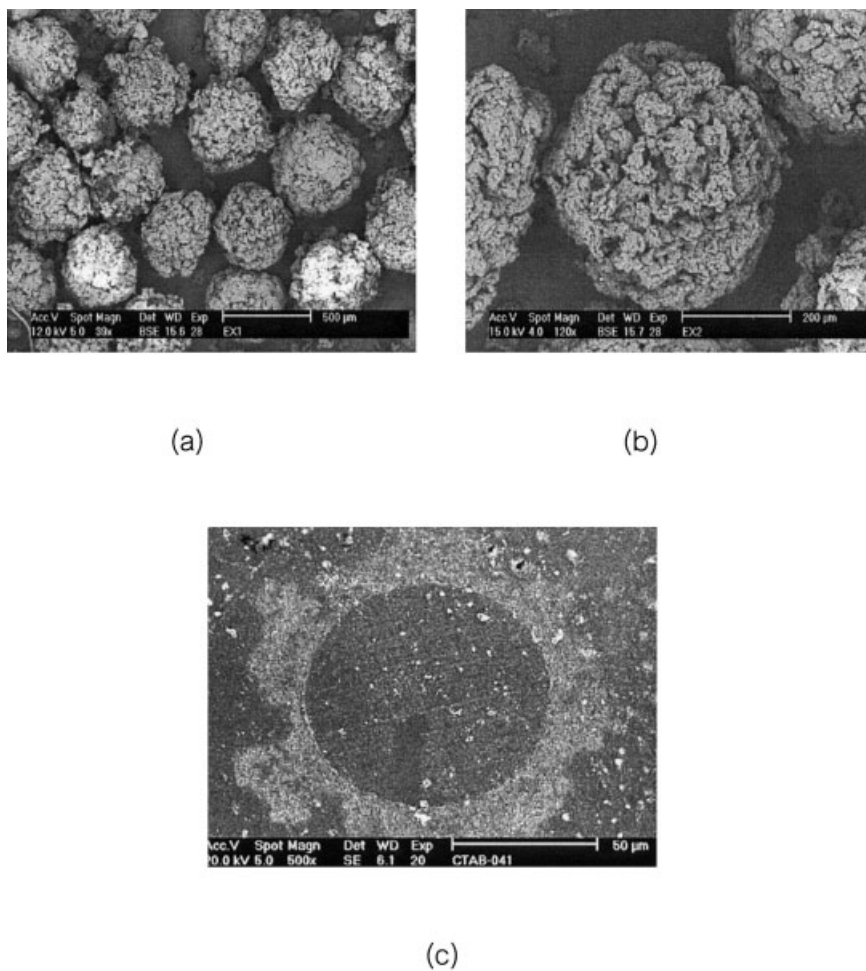
(a)

(b)

(c)

**Figure 1** SEM micrographs of the bead morphology and the cross-sectional view of the polymer bead: (a, b) surface morphology of the polymer bead; (c) cross section of the polymer bead.

MAPTAC was conducted at a temperature of 70°C under nitrogen atmosphere in a four-necked round-bottom flask. After proceeding for a determined amount of time, the polymerization was stopped by the addition of hydroquinone. The products obtained were dried and MW of PMAPTAC was determined. The MW of PMAPTAC was obtained by GPC analysis by using $0.1M$ sodium nitrate : acetonitrile $(80:20)$ as an eluant at a temperature of 30°C. The column was
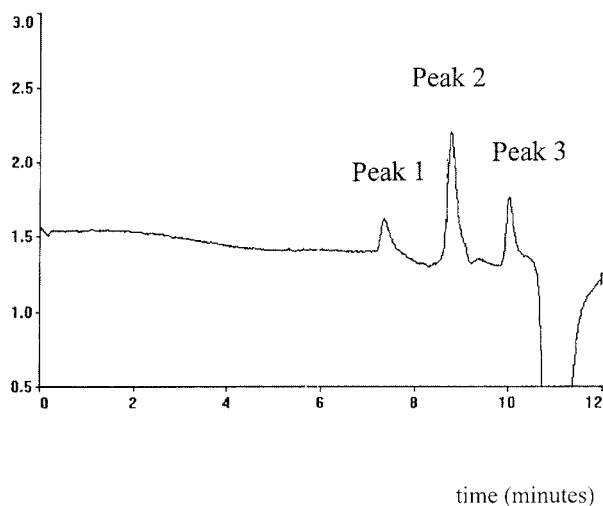


**Figure 2** GPC chromatogram of the PMAPTAC at polymerization time of 15 min.

**TABLE II**
**Molecular Weight of PMAPTAC Determined by Gel Permeation Chromatography (GPC)**

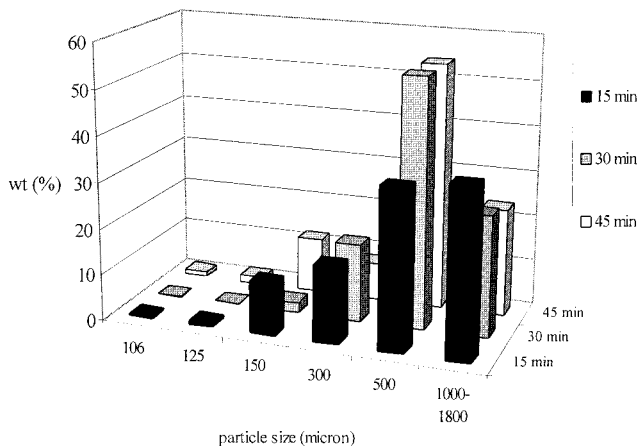| Polymerization time of MAPTAC (min) | Peak number | $M_n$ | $M_w$ | $M_v$ | Polydispersity |
|---|---|---|---|---|---|
| 15 | 1 | 2191 | 2239 | 2233 | 1.02 |
| | 2 | 659 | 667 | 666 | 1.01 |
| | 3 | 218 | 220 | 220 | 1.01 |
| 30 | 1 | 2126 | 2194 | 2184 | 1.03 |
| | 2 | 661 | 667 | 666 | 1.01 |
| | 3 | 234 | 235 | 234 | 1.00 |
| 45 | 1 | 2256 | 2292 | 2287 | 1.02 |
| | 2 | 648 | 653 | 652 | 1.01 |
| | 3 | 221 | 222 | 222 | 1.00 |

**Figure 3** Particle size and distribution obtained from polymerization times of MAPTAC 15–45 min.

packed with Shodex Asahipak GS-220 HQ with MW resolving range 200-3000. Flow rate was 1.0 mL/min. Detection was obtained by a refractive index detector. Polysaccharide standard kits were used as relative standards.

### FTIR measurement

FTIR spectra of polystyrene, PMAPTAC, and polymer beads were recorded in KBr pellets by using an Omnic Nicolet Impact 400 D FTIR spectrophotometer.

### Microscopic studies

The particle structure and the surface morphology of polymer beads were observed with a scanning electron microscope (SEM, XL 30 CP, Philips). The internal

structure of the bead was studied by sectioning the bead previously embedded in epoxy resin and observed by using SEM.

## Dye adsorption characteristics

### Determination of contact time

The contact time measurement of dye adsorption properties of adsorbent beads with particle sizes ranging from 150 and 500 $\mu$m was carried out at a temperature of 80°C. The beads (0.5 g) and the volume of the dye solution at concentrations of 500 and 3500 mg/L (5 mL) and a wetting agent of 1 g/L were stirred with a magnetic stirrer in a test tube at 100 rpm. The concentration of remaining dye was monitored at certain intervals by Specord S 100 UV spectrophotometer at the $\lambda_{max}$ of the absorbance.

### Dye adsorption isotherms study

The equilibrium adsorption isotherm was determined by mixing 0.5 g of 150 $\mu$m adsorbent beads with 5 mL of reactive dyes solution (blue, red, and yellow) and 1 g/L wetting agent in a test tube at room temperature for 24 h. Each isotherm consisted of seven different concentrations varying from 500 to 3500 mg/L of dye. The tubes containing dye solution and adsorbent beads were stirred with a magnetic stirrer at 100 rpm for 1 min. The equilibrium concentrations of different combinations were measured by the UV spectrophotometer and referenced with the calibration curve.
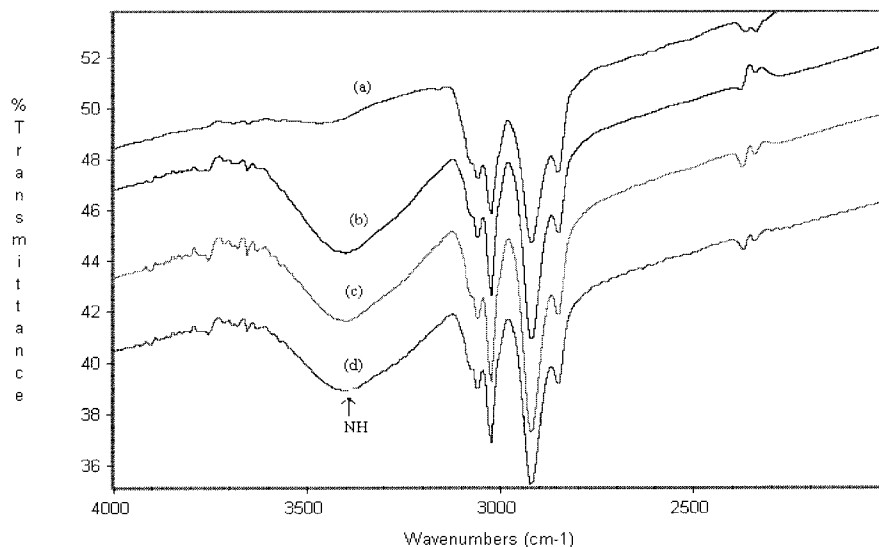


**Figure 4** FTIR spectrum of polymer bead obtained from different polymerization times of MAPTAC: (a) polystyrene; (b) 15 min; (c) 30 min; (d) 45 min.
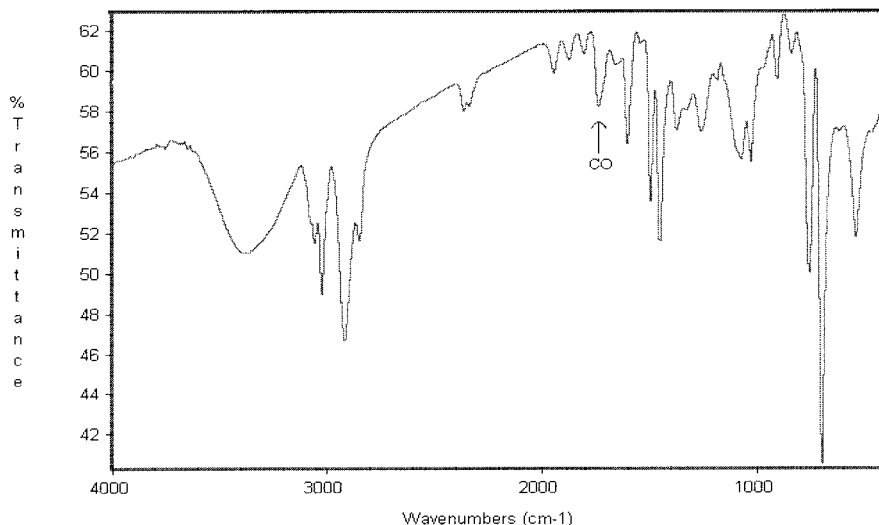
**Figure 5** FTIR spectrum of polymer bead obtained from polymerization time of MAPTAC 30 min.

## RESULTS AND DISCUSSION

### Synthesis of polymeric beads bearing surface charge

One-pot synthesis of poly(styrene-*co*-DVB)-based spherical particle bearing cationically charged surface was carried out by using the suspension polymerization of MAPTAC, styrene, and DVB. The polymerization technique used in this study involved two steps: first, MAPTAC was polymerized in aqueous solution of PVA for desired periods of times by using $K_2S_2O_8$ as an initiator; then the mixture of styrene, DVB, AIBN, and surfactant was fed quickly into the reactor, meanwhile agitating continuously. At this stage, the droplets were formed and uniformly dispersed in the aqueous solution of growing polymeric chain of PMAPTAC radicals. The droplet sizes were dependent on the stirring speed, polymerization temperature, and the presence of surfactants, etc. Furthermore,

at this stage AIBN would begin to initiate the copolymerization of styrene and DVB to transform into gel bead. Meanwhile, it was expected that PMAPTAC radicals would diffuse through the surfactant layer into the gel bead surface to undergo the reaction with available styrene or DVB monomers present at the bead surface. As polymerization proceeded, the gel bead was gradually transformed into a solid particle having cationic charge surface layer. Table I shows the polymerization conditions used in this study. Various polymerization conditions affecting size, shape, and surface charge density were investigated. Typical morphology and the cross section of polymer bead was examined by using SEM analysis and illustrated as shown in Figure 1. The particle revealed by SEM image exhibits a rough-shaped bead which is uniquely different from the smooth spherical particle typically obtained from conventional synthesis.[18] The cross sec-
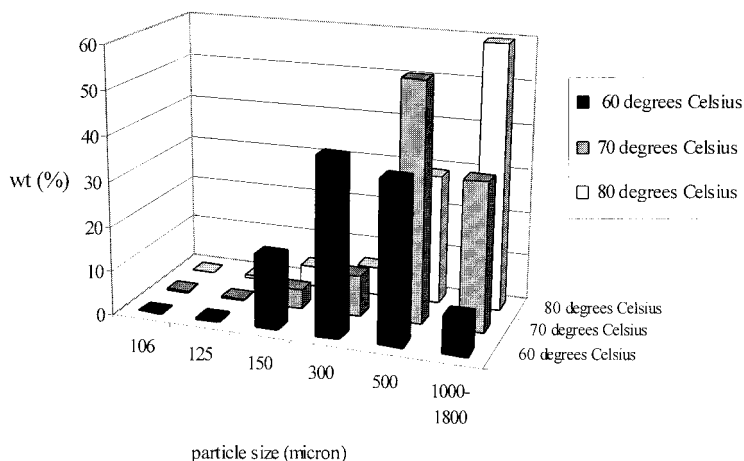


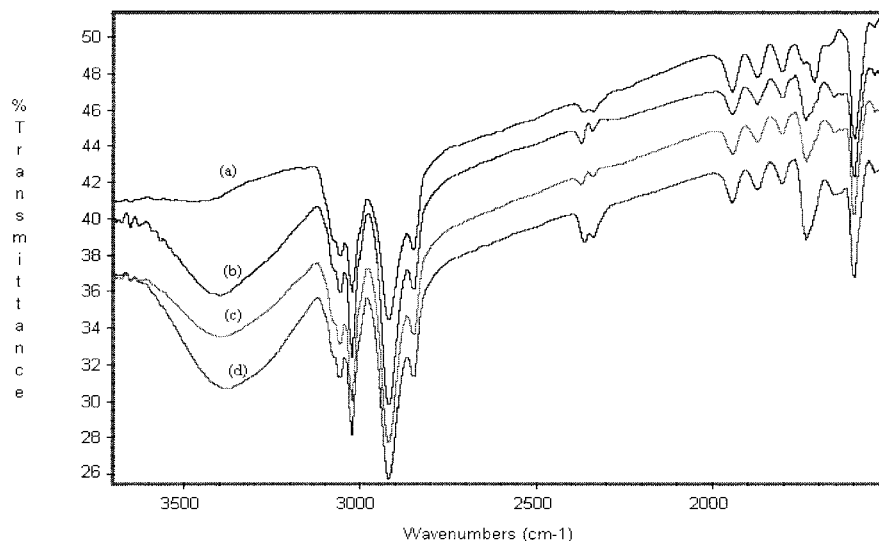**Figure 6** Particle size and distribution at temperatures of polymerization of 60–80°C.

**Figure 7** FTIR spectrum of polymer bead obtained from different polymerization temperatures: (a) polystyrene; (b) 60°C; (c) 70°C; (d) 80°C.

tion view further proves that the bead comprises two layers: the inner core represents the poly(styrene-*co*-DVB) support and the outer layer is the copolymerization product of surface styrene, DVB and PMAPTAC radical capable of diffusing through surfactant layer during the polymerization process. The percentage yield of the products is about 45% on average for all synthesis batches.

The effects of several parameters were investigated in controlling the particle size, size distribution, and surface charge density. The results obtained are reported below.

### Effect of polymerization time of MAPTAC

To study the effect of polymerization time of MAPTAC on particle size and size distribution, the polymerization time of MAPTAC in the first stage was varied from 15 to 45 min to generate the PMAPTAC radicals. Characterization of quenched PMAPTAC oligomer by GPC analysis was separately performed to get information of its molecular weight and weight distribution. The typical GPC chromatogram (Fig. 2) shows peaks corresponding to the molecular weights of $2 \times 10^3$ and $6 \times 10^2$. Another peak with a molecular weight of $2 \times 10^2$ probably represents the unreacted monomer. The molecular weights obtained from different polymerization times are given in Table II. It shows that the molecular weight of PMAPTAC oligomers obtained from various polymerization times are not different, reflecting the characteristic of free-radical chain polymerization. The short-chain PMAPTAC radical of MW of ~ 600 was the major reaction product. Because generated PMAPTAC radi-
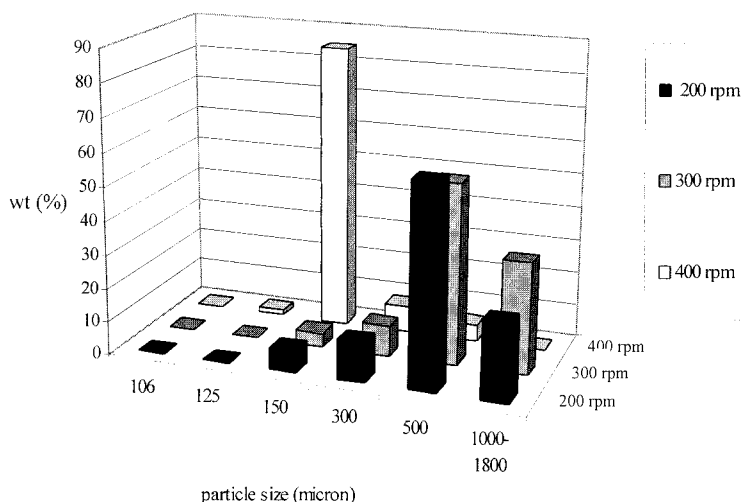


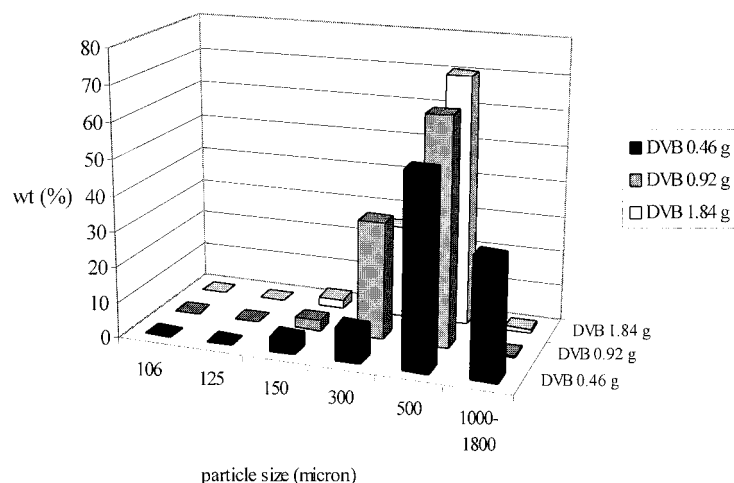**Figure 8** Particle size and distribution at stirring speeds of 200–400 rpm.

**Figure 9** Particle size and distribution at DVB of 0.46–1.84 g.

cal was a polyelectrolyte, it was capable of enhancing the stabilization of styrene droplets by the electrostatic effect.[19,20] Figure 3 shows the particle sizes and size distributions of resulting polymer beads achieved as a function of polymerization time of MAPTAC. The particle size found ranges widely from 100 to $\sim$ 2000 $\mu$m with a mean size of 500 $\mu$m. These results suggest that the polymerization time of MAPTAC in the studied range did not cause the difference in the final particle size. It should be noted that where the applications of the bead are concerned the small particle size with large surface as well as high surface charge density is preferable. Effects on particle size will be discussed later. In this work, an attempt to incorporate the surface charge density onto bead surface was carried out during the polymerization process. Hence, the surface charge density was greatly dependent on the PMAPTAC radical capability of attaching to bead surface. The reason for varying polymerization times of MAPTAC was to generate the different chain length radicals with various reactivities to optimize the bead surface charge density. Unfortunately, based on the results of molecular weight determination, nearly identical molecular weight was found in all cases of polymerization times. FTIR spectroscopy was chosen to identify the functional group (cationic charge) on the bead surface; the results are shown in Figures 4 and 5. The absorption bands at 3400 and 1700 cm$^{-1}$ corresponding to the absorbance of NH and C=O functional groups are indicative of the attachment of PMAPTAC segment on the bead particle. The results show that the peak intensities of bead functional groups obtained from various polymerization times of MAPTAC are not significantly different. This implies that the effect of varying polymerization times of MAPTAC from 15 to 45 min brought about indifference in the surface charge density as a result of indifference in chain length of PMAPTAC radicals. For the

further experiments throughout, the constant polymerization time of MAPTAC of 30 min was chosen.

**Effect of polymerization temperature**

Effect of polymerization temperature on the particle size and its morphology was investigated. The reaction temperatures ranging from 60 to 80°C, which are the dissociation temperatures of both initiators, persulfate and AIBN, were performed. The other parameters were kept constant as follows: the polymerization time of MAPTAC was 30 min at fixed stirring speed of 300 rpm. DVB and cetyl alcohol content were 11.27 and 0.25 wt % (based on styrene), respectively. Figure 6 shows the relationship between the particle size and size distribution with the reaction temperature. The results show that the reaction temperatures of 60°C tended to produce the small particle size with broad size distribution in the range of 106 to 1000 $\mu$m. At a temperature of 70°C, the particle size tended to increase from 150 to 300 to 500 $\mu$m, while the reaction temperature of 80°C yielded most of large particle size of 1000 $\mu$m with narrow size distribution. A similar observation was reported by Shen et al.[21] Increasing the reaction temperature normally causes the decrease in the adsorption rate of PVA due to its increasing solubility in water,[22] leading to coalescence of styrene–DVB droplets. Moreover, higher temperatures resulted in a faster polymerization rate, further accelerating the conversion of coalesced droplet into stable particle. Figure 7 shows FTIR spectra of bead functional groups obtained from different polymerization temperatures. The results show that by comparison with unchanged intensity (aromatic C—H stretching at 695 cm$^{-1}$, not shown in the figure) the peak intensities of carbonyl group increases with an increase in polymerization temperature, implying the increase in the agglomerate outer layer. As a result, this effect
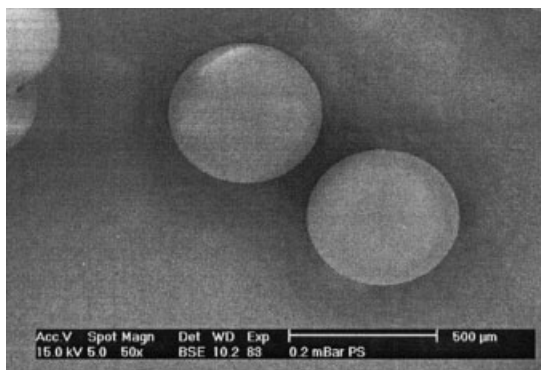
(a)
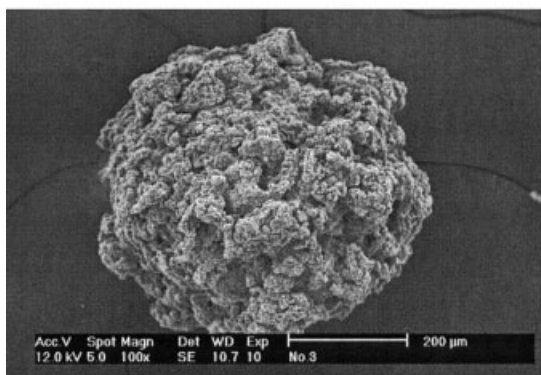


(b)
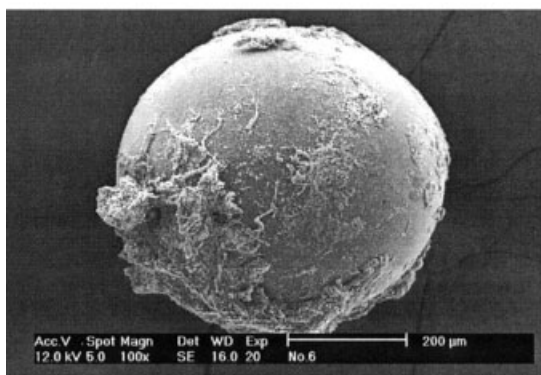


(c)

**Figure 10** Comparison of SEM micrographs of polymer bead with different amounts of DVB: (a) polystyrene beads; (b) polymer bead at DVB content 0.46 g; (c) polymer bead at DVB content 1.84 g.

further contributed to the increase in final particle size with relation to polymerization temperature.

## Effect of stirring speed

In suspension polymerization, stirring speed during polymerization is necessary to keep the oil phase properly dispersed. Three stirring speeds of 200, 300, and 400 rpm were employed at the constant polymerization temperature of 70°C. The results shown in Figure 8 indicate that the particle size is closely dependent on the stirring speed: the higher the stirring speed, the smaller the particle size with a tendency of narrower size distribution. Basically, the two-phase system in suspension polymerization cannot be maintained without agitation which controls the balance between droplet breakage and coalescence. At higher stirring speed, the balance is shifted toward the rate of drop breakage, resulting in smaller drop size. As can be seen from the figure, an increase in the rate of stirring speed tended to produce an increase in the population of the final particle with smaller size.

## Effect of DVB

DVB is commonly employed as a crosslinking agent to achieve a polymeric bead with good mechanical properties. To study the effect of DVB, other synthesis parameters such as polymerization time and temperature as well as stirring speed were controlled. Amounts of DVB were varied from 11.27 to 45.10 wt % (based on styrene). The average final particle size obtained is found in the range of 500 $\mu$m for all conditions as shown in Figure 9. Figure 10 compares SEM micrographs of polymer bead with different amounts of DVB. It can be seen that the morphology of obtained beads exhibit a coarse surface with various degrees of surface irregularity, which increases with the increased amount of DVB. As the DVB content increased, the polymer bead gave rise to smoother surface particle. From the study of Kangwansupamonkon et al.,[23] the presence of DVB enhanced the copolymerization rate of styrene and DVB in droplet phase, leading to a rapid conversion of droplet with subsequent reduced reactivity of growing polymeric radicals on the droplet surface. Due to less availability of reactive species at the interface, incorporation capability of PMAPTAC radicals would be successively reduced when the amount of DVB rose, evidenced by a smoother bead surface with an increased amount of DVB observed from SEM micrographs.

## Effect of surfactants

The role of surfactants in suspension polymerization is to stabilize the droplet phase during polymerization. In this work, it was found that the pres-
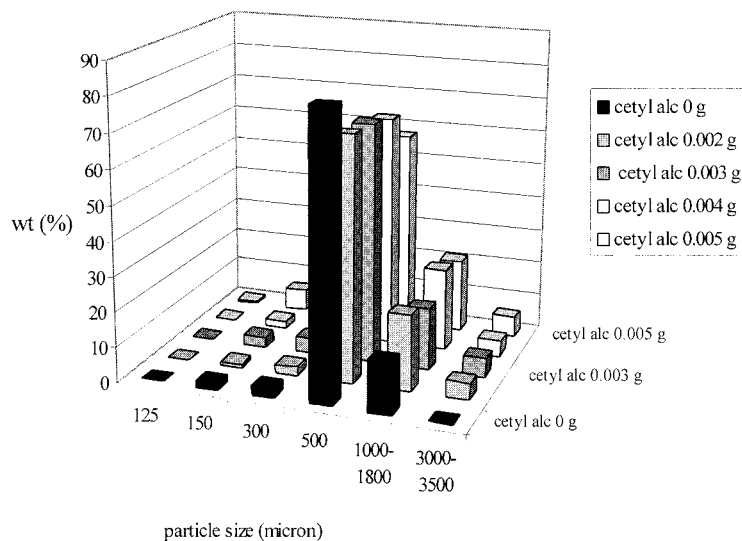
(a)
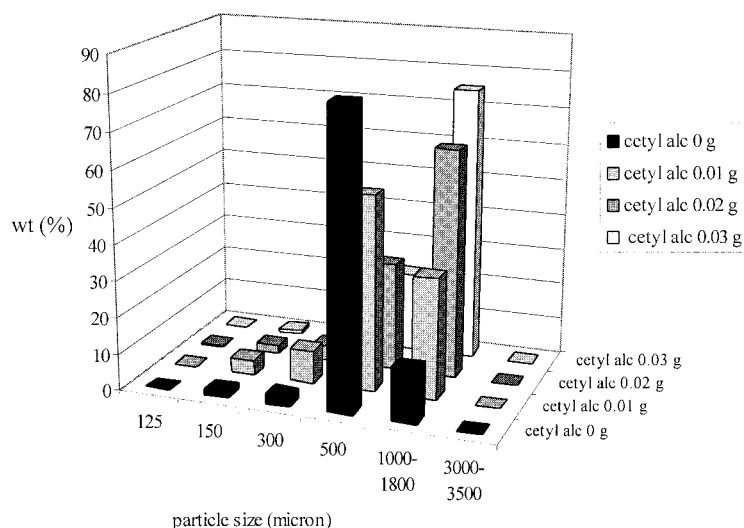


(b)

**Figure 11** Particle size and distribution at various cetyl alcohol contents: (a) cetyl alcohol 0–0.005 g; (b) cetyl alcohol 0.01–0.03 g.

ence of surfactant enhanced the incorporation capability of PMAPTAC radicals into the bead surface by decreasing the surface tension at the interphase. Two types of surfactants were investigated: nonionic surfactant (cetyl alcohol) and cationic surfactant (CTAB).

**Effect of nonionic surfactant**

Cetyl alcohol was added into the system prior to the addition of styrene and DVB. The amount of cetyl alcohol was varied from 0 to 0.74 wt % (based on

styrene). Figure 11 shows the effect of cetyl alcohol content on the particle size and size distribution. The use of cetyl alcohol tended to produce large particle size with the majority of population falling in the range of 500-1800 $\mu$m. Broad size distribution was also observed when compared with the case of without cetyl alcohol. It is well documented that, in suspension polymerization, a suspending agent such as PVA is a dominant factor, providing the protective layer resulting from the surface adsorption.[24] The suspending agent molecules adsorbed by monomer droplets locate at the monomer/water interface, which would give
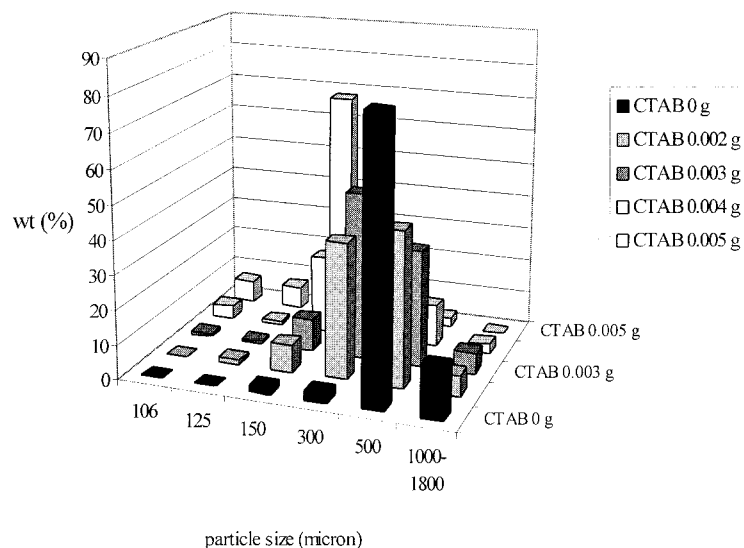
**Figure 12**   Particle size and distribution at CTAB content of 0−0.005 g.

coalescence resistance to droplets. The solubility of cetyl alcohol in styrene droplet is better than PVA, which is a suspending agent used in this work. Therefore, it would be adsorbed faster on the styrene/water interface. As a result, the coalescence resistance from PVA would decrease, leading to large particle size formed with an increase in the amount of cetyl alcohol. The results reported by Tseng et al. also indicated that the presence of cetyl alcohol led to the production of large particle size.[25]

**Effect of cationic surfactant**

In the field of dye adsorbents, large particle size is not desirable because of small surface area which, consequently, reduces dye adsorption capability. To achieve better control of particle size, cationic surfactant (CTAB) was replaced by cetyl alcohol because this type of surfactant is more capable of decreasing surface tension between styrene phase and water phase.[26] Figure 12 shows the effect of CTAB on particle size and size distribution.

As can be seen, the particle size so obtained using CTAB is smaller than that of cetyl alcohol under the same conditions. Mean bead size decreases gradually from 500 to 150 $\mu$m when the amount of CTAB increases from 0 to 0.12 wt %. According to Liu et al.,[27] the quaternary ammonium group of a surfactant strongly affected the particle size by means of the electrostatic stabilizer. In this case, the quaternary ammonium group of PMAPTAC radicals was anticipated to further enhance the stabilization of droplet phase. This combination could effectively prevent the coalescence of styrene droplets, leading to a decrease in the final particle size with an increase in amount of surfactant. As the concentration of surfactant increased

further, the stable emulsion was formed. A very fine small particle with irregular shape described as powder was produced.

Morphology of the final particle revealed by SEM analysis (Fig. 13) exhibits different shapes and degree of surface irregularity depending on the amount of CTAB used. Spherical particle with increased degree of surface roughness was found when the content of CTAB increased from 0.05 wt %. It is believed that the coarse surface of the outer layer represents the poly-(MAPTAC-*co*-styrene) copolymer, rendering the positive charge to the bead surface. The coarser the bead surface, the higher the surface charge density. It could be concluded that cationic surfactant of a certain range of concentrations is crucial to achieve the desirable bead size with optimum surface charge density.

**Anionic dye adsorption isotherm**

To elucidate the cationic group (PMAPTAC) segment on the bead surface, a dye adsorption experiment was carried out by using three commercial reactive dyes, C.I. Reactive Blue 171, C.I. Reactive Red 195, and C.I. Reactive Yellow 84. Polymer beads with particle sizes of 150 and 500 $\mu$m obtained from the case of cationic surfactant addition was chosen. In the case of pristine polystyrene bead, no dye adsorption was observed because of its hydrophobic surface. For the beads containing cationic charge, a marked increase in dye adsorption was observed. Figure 14 shows the curves of contact time for the dye removal in relation to the particle size. As indicated by initial declined lines, the rate of dye adsorption is high with the first 5 min, and the dye removal reaches equilibrium at 20 min. Dye adsorption was related to ionic interaction between cationically charged surface and anionic dye molecule
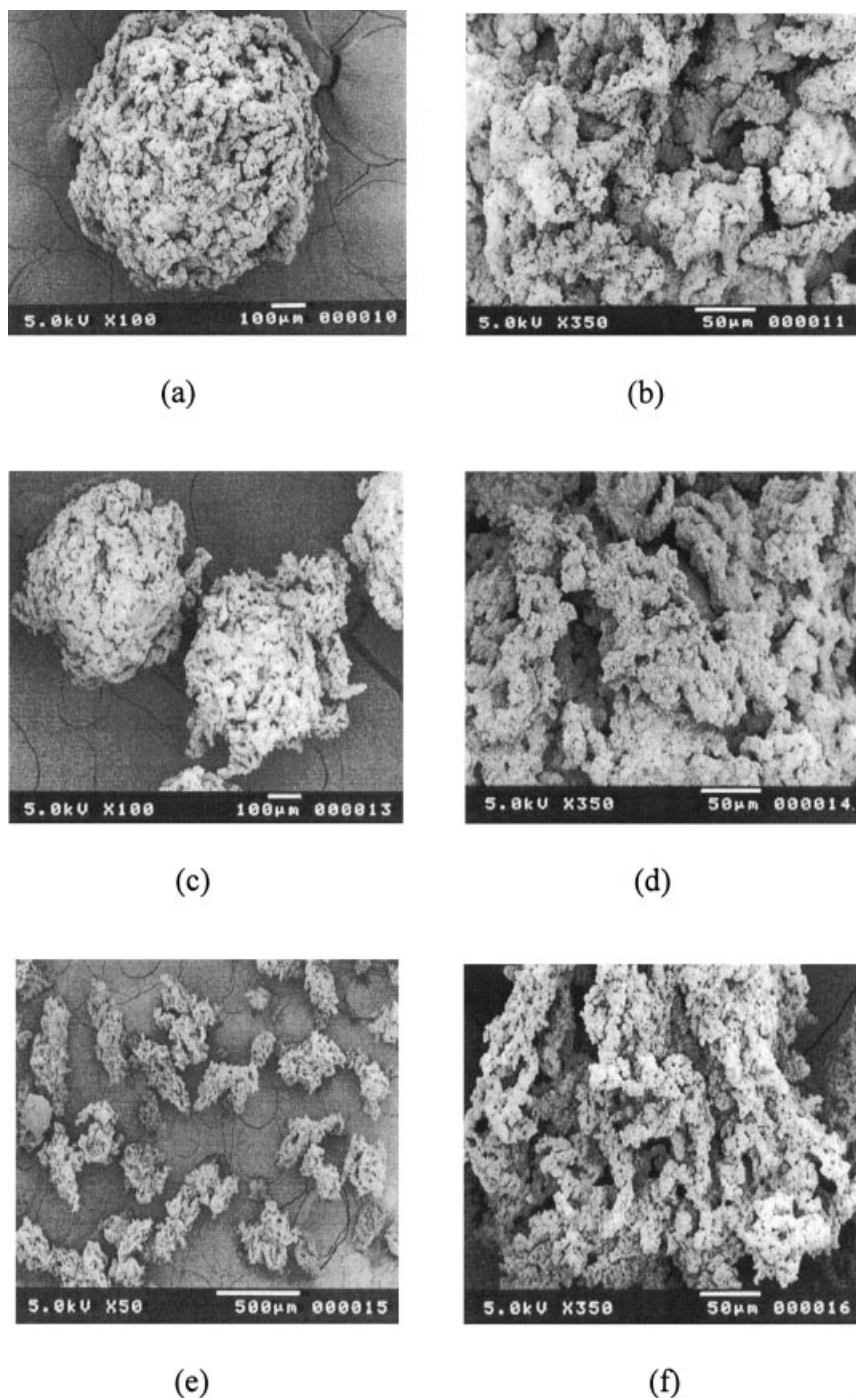
**Figure 13** SEM micrographs of polymer bead with different amounts of CTAB: (a, b) CTAB content 0.002 g; (c, d) CTAB content 0.004 g; (e, f) CTAB content 0.005 g.

(the dye sulfonate group, $SO_3^-$); the higher the amount of cationic charges, the higher the amount of adsorbed dyes. The degree of surface charge density was expected to be varied depending on the capacity of the attachment of PMAPTAC radicals and the final particle size. Indeed, as seen from Fig. 14, the small particle size adsorbs more amount of dyes because of its higher surface area. Further, anionic dye adsorption isotherm was investigated to evaluate the surface

charge density. Figure 15 shows the adsorption isotherm of C.I. Reactive Blue 171, C.I. Reactive Red 195, and C.I. Reactive Yellow 84 at the adsorption temperature of 30°C. The shapes of the all isotherms are Langmuir type, judged by the initial sharp increase of curves and adsorption equilibrium obtained. Langmuir isotherm typically is governed by ionic–ionic interactions as usually found when dyeing nylon with acid dyes (anionic dyes) or dyeing acrylic with cat-
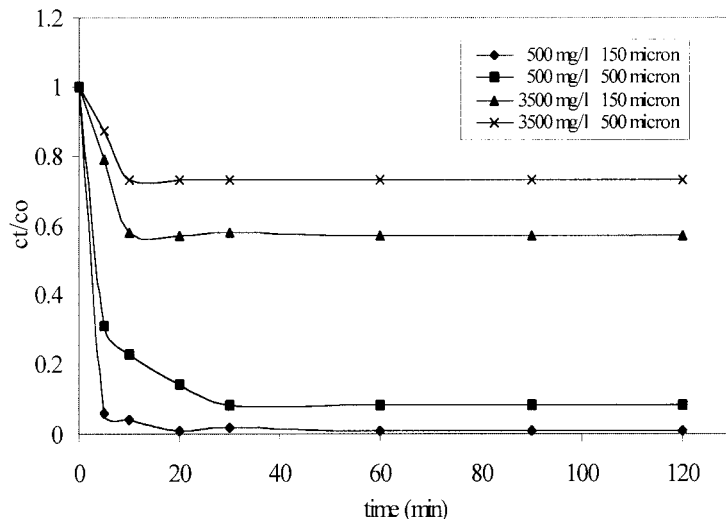
**Figure 14**  Adsorption of reactive yellow on polymer bead as a function of time at a temperature of 80°C.

ionic dyes.[28] The results from the adsorption clearly confirm that the prepared polymeric beads contained cationic functional groups. The amount of dyes adsorbed per unit weight of the bead particle ($qe$) were measured according to equation $qe = (C_0 - C_e)V/W$, where $C_0$ and $C_e$ are the initial and equilibrium concentration of dye in solution, respectively, in mg/L, $V$ is the volume of dye solution, and $W$ is the weight of polymer bead. The adsorptive capacity of reactive blue, red, and yellow are 11.52, 10.99, and 15.67 mg/g, respectively.

## CONCLUSION

Preparation of anion exchange adsorbent was carried out by using one-pot suspension polymerization of styrene and DVB in the presence of cationic oligomeric radicals. The cationic radicals were generated by polymerization of cationic functional monomer in aque-

ous solution initiated by water-soluble initiator. From the SEM result, the cross-section view revealed that the prepared bead comprised two layers: the inner core of the poly(styrene-*co*-DVB) and the outer layer (the copolymerization product of styrene, DVB, and functional chain segment) (PMAPTAC). Particle sizes and size distribution were influenced by polymerization temperature, stirring speed, and surfactants. Of all synthetic parameters, types of surfactants were found to play an important role in controlling the particle size having the surface charge.

An increase in amount of a nonionic surfactant (cetyl alcohol) tended to produce large particle size with a majority of the population falling in the range of 500-1800 $\mu$m. The replacement of cetyl alcohol by the cationic surfactant resulted in better control of particle size and size distribution due to its effective electrostatic stabilizer. In this case, an increase in amount of CTAB content led to a decrease in the
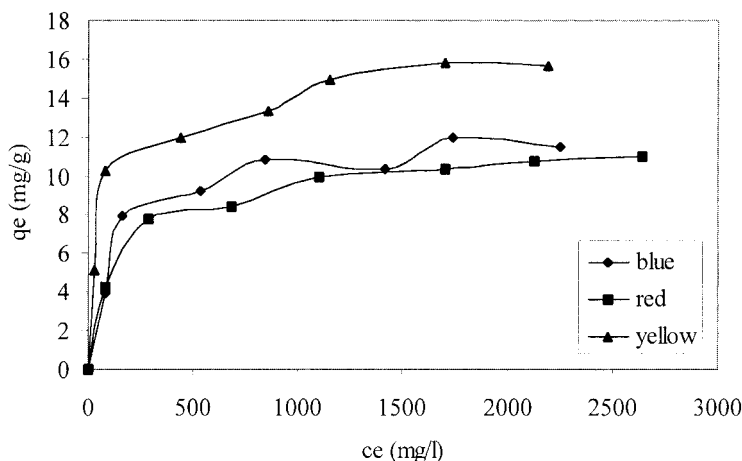


**Figure 15**  Equilibrium adsorption isotherm of reactive dyes at room temperature on polymer bead.

particle size. A small particle size of 150 $\mu$m could be obtained when CTAB content of 0.12 wt % was employed.

Cationic charge surface of the bead was derived from the copolymerization of styrene, DVB, and PMAPTAC radical on the bead surface. Cationic charge density was dependent on the reaction capability of PMAPTAC, surface tension (types of surfactants), and particularly, the amount of DVB, which greatly affected the availability of styrene monomer on the surface.

Finally, dye adsorption isotherm of the prepared bead was investigated to elucidate its ion exchange performance. The results showed that the polymer bead was capable of adsorbing anionic dyes, confirming that the cationic functional group was incorporated into the outer shell of the polymer bead. From the results, it can be concluded that one-pot synthesis of polymer bead bearing charge surface is experimentally practicable.

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