

Preparation of Unsaturated Polyester–Styrene Beads Using Gamma Irradiation and Chemical Polymerization Routes for Use in the Recovery of Some Alkali Metal Ions

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ABSTRACT: Suspension polymerization of unsaturated polyester–styrene was carried out in different media using different routes of polymerization. The effects of matrix type and concentration hold up, viscosity, irradiation dose, and the agitation speed on the resultant polymer characteristics were examined. The formed beads were physically identified using scanning electron microscopy, hardness, and particle size analysis techniques. They were smooth having typical spherical surfaces; the beads diameters were in the range of about 5–200 μm . The size of the resin beads was found to decrease with increase in the concentration and viscosity of the dispersant and impeller speed. The resultant beads were applied in the recovery of Li^+ , Na^+ , K^+ , and Cs^+

ions from acidic media. The distribution coefficients of the alkali metal ions were calculated; the order of selectivity was $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+$ in case of the chemically processed resin beads, while the selectivity lies in the order of $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$ in case irradiation processed ones. Finally, the economics of production of the unsaturated polyester–styrene resins using different methodologies was studied. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1149–1160, 2007

Key words: unsaturated polyester–styrene; suspension polymerization; optimization; mechanism; characterization; recovery; alkali metal ions

INTRODUCTION

With the rapid progress of materials science, the use of polymeric materials has been widely developed, and therefore the molecular level design of polymeric materials has become very important.¹ The morphological aspects of the prepared materials are of quite importance; they must be integrated with resulting physical and mechanical properties of the end polymers.^{2,3} They could distinctively affect final characteristics, and in turn the selection of the applications of the prepared polymer. The diameter of the resultant beads is the most controlling factor in polymer technology.⁴

Micrometer-sized nonporous and porous particles of narrow size distribution have attracted much attention in many applications such as adsorbents for high-pressure liquid chromatography, calibration standards, spacers for liquid crystals, inks, catalysis, and so forth.^{5–12} Dispersion polymerization is the common method for preparing uniform nonporous micrometer-sized particles in a single step.^{13–16} However, the particles formed by this method possess a relatively small surface area and their properties, for example,

porosity, surface morphology, and functionality, can hardly be manipulated.^{13,16} Furthermore, uniform particles of a diameter larger than 5 μm usually cannot be prepared by dispersion polymerization. These limitations have been overcome by several swelling methods of template polystyrene (PS) micrometer-sized particles with appropriate monomers and initiators, e.g., multistep swelling,^{17–23} dynamic swelling,^{24,25} and a single-step swelling²⁶ of PS template particles, followed by polymerization of the monomers within the swollen template particles.

The crosslinked polystyrene microspheres can be modified to introduce functional groups on their surfaces; micron-size crosslinked polystyrene (MCPS) microspheres offer more advantages than the microspheres of commercial ion-exchange resins: (1) Higher specific surface areas can increase the capacity of incorporation of functional groups onto the polymer supports, especially of the highly rigid molecules; (2) solid structure, called “unfold framework,” has no steric hindrance and can increase the level of incorporation of functional groups on the support microspheres.^{27–29} Two main kinds of dispersion media were commonly used as hydrocarbons (i.e., hexane and heptane)^{30–32} and the most used polar solvents were alcohol and alcohol/water.^{33–35} The crosslinker was usually divinylbenzene (DVB). There are two problems in preparation of the higher crosslinked PS

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TABLE I
Chemical Composition of Batch I, Used for Preparation of Unsaturated Polyester–Styrene Beads through GISP Methodology

Type of material	Material concentration (%)	Composition (wt %)	Material function
UP–St copolymer	60% UP–40% St	40	Resin bead precursors
PVA (partially hydrolyzed type)	6% solution in bidistilled water	10	Dispersant matrix
HPMC	1.5% solution in bidistilled water	50	

Irradiation dose: 70 kGy; Agitation rate: 100 rpm/min; Beads' separation: gentle grinding of HPMC, washing with bidistilled and drying at 45°C for 20 min.

microspheres. First, until recently, only a very small amount of the crosslinker, DVB, could be incorporated to form stable latex in the dispersion copolymerization without the coagulum.³⁶

Concerning the use of organic materials in waste treatment, different organic materials were used in the treatment of radioactive wastes. Many thermoplastics such as bitumen, polystyrene, polyethylene, and polymethylmethacrylate were used in the solidification of low- and medium radioactive wastes. Also, other thermosetting organic materials were utilized for the same task, that are resistant to heat, radiation, mechanical shocks, and chemical attack. In the field of ion exchange, many organic ion exchangers are well known for this purpose because of their uniformity, chemical stability, and control of their ion exchange properties through the synthetic methods, and characterized with higher capacities rather than the corresponding inorganic materials.^{37–39} A chelating resin containing bis(2-benzimidazolylmethyl)amine, was synthesized for alkali metal-ion uptake; its behavior towards alkali and alkaline earth metal ions was studied in column applications.⁴⁰ On the other hand, the separation of alkali metal ions from other ions was achieved using new ion exchange resins that were prepared by incorporating the bis(2-benzimidazolylmethyl)amine into Merrifield polymer.⁴¹

In this concern, this study introduces a well defined thermosetting ion exchangers based on unsaturated polyester–styrene spheres that are not only of economic feasibility but also with high chemical and radiation resistances as well as enhanced physical characteristics

to study the sorption behavior of Li^+ , Na^+ , K^+ , and Cs^+ on them from nitrate media. The article describes two different types of suspension polymerization of unsaturated polyester–styrene (UP–St), namely, gamma irradiation suspension polymerization (GISP) and chemical suspension polymerization (CSP) in either hydroxypropyl methylcellulose (HPMC) or urea formaldehyde (UF) matrix. Furthermore, the influence of important parameters affecting the resin beads sizes and the rate of production on a pilot scale through GISP and CSP methodologies were also investigated.

EXPERIMENTAL

Materials

Unsaturated polyester–styrene monomer was supplied by the Saudi Industrial Resins Ltd., Jeddah, Saudi Arabia. Urea formaldehyde was donated by Grandy Co., Egypt. Partially hydrolyzed polyvinyl alcohol having about 8300–12,000 was purchased from Kuraray Co., Japan. Hydroxypropyl methylcellulose was purchased from Shin-Etsu Chemical Co. Ltd., Japan. Vegetable oil (trifatty acid) was supplied from El-Nile Co., Egypt. ²²Na and ¹³⁴Cs radiotracers were supplied by Amer-shan Life Science, England. Other chemicals were of analytical grade and used without additional purification.

Preparation of polymeric resin beads

GISP and CSP routes were extensively used to prepare unsaturated polyester–styrene resin beads by sus-

TABLE II
Chemical Composition of Batch II, Used for Preparation of Unsaturated Polyester–Styrene Beads through GISP Methodology

Type of material	Material concentration (%)	Composition (wt %)	Material function
UP–St copolymer	60% UP–40% St	50	Resin bead precursors
UF solution	60% in bidistilled water	40	Dispersant matrix
PEG solution	50% in bidistilled water	10	

Irradiation dose: 20 kGy; Agitation rate: 100 rpm/min; Beads' separation: grinding for the hard UF matrix, washing with bidistilled water, and drying at 45°C for 20 min.

TABLE III
Chemical Composition of Batch III Used for Preparation of Unsaturated Polyester-Styrene Beads through CSP Methodology

Type of material	Material concentration %	Ratio by weight %	Material function
UP-St copolymer	UP-40 % St	40	Resin bead precursors
PVA (partially hydrolyzed type)	6% in bidistilled water	10	
Cobalt naphthanate	50% in acetone	2	
MEKP	50% in acetone	6	
HPMC	1.5% in bidistilled water	50	Dispersant matrix

Agitation rate: 100 rpm/20–22 min; Beads' separation: gentle grinding, washing with bidistilled water, and drying at 45°C for 20 min.

pending the monomers in different media. The detailed procedures were accordingly discussed in terms of the batch composition, separation of the resultant beads, physical and mechanical properties of the prepared particles. Four batches with different compositions were prepared (I–IV); two describe the GISP methodology and a pair for the CSP one. For each batch composition, three series of suspension polymerization experiments were run to investigate the factors that affect the drop and particle sizes and the dispersion mechanism when stabilizers were used.

For the suspension polymerization experiments, a glass reactor with capacity of 0.5 L and diameter of 10 cm was used. The reactor had a flanged top and a dish base. A double flat 4-bladed impeller with diameter of 4 cm was used to ensure the complete dispersion of the monomer in the highly continuous phase. The suspension polymerization was run in nitrogen gas atmosphere in the reactor.

Gamma irradiation methodology

In this methodology, two batches (I, II) with different compositions were examined, which are typically

described in Tables I and II. Irradiation of the batches was carried out to the required dose using an irradiator of the Indian gamma chamber, 4000A type with a dose rate of about 7.6 kGy h⁻¹. The irradiation doses ranged between 10 kGy and 100 kGy, according to the specified test; the absorbed dose was 4 kGy h⁻¹ measured by Fricke dosimetry ($G(\text{Fe}^{3+}) = 1.62 \mu\text{mol J}^{-1}$); the error in dose estimation is $\pm 3\%$. Irradiation was carried out under atmospheric conditions at a temperature of about 40°C.

In batch I, the unsaturated polyester-styrene was suspended in 6% aqueous solution of partially hydrolyzed polyvinyl alcohol (PVA), stirred vigorously to give a milky oligomer, which then dispersed in 1.5% hydroxypropyl methylcellulose (HPMC) aqueous solution; the exact weights of the different components are illustrated in Table I. The heterogeneous system was then stirred with a velocity of 100 rpm/min and transferred to the gamma cell; 70 kGy irradiation dose was sufficient to obtain the resin beads.

Table II shows the exact concentrations of the different components and their ratios required for production of UP-St batch II. Urea formaldehyde (60% aqueous solution) and polyethylene glycol (50% aqueous

TABLE IV
Chemical Composition of Batch IV Used for Preparation of Unsaturated Polyester-Styrene Beads through CSP Methodology

Type of material	Material concentration %	Ratio by weight %	Material function
UP-St copolymer	UP-40%St	30	Resin bead precursors
UF	60% in bidistilled water	30	
Sodium silicate	50% in bidistilled water	5	
Phosphoric acid	2% in bidistilled water	5	
Vegetable oil (tri-fatty acid)	Pure oil	30	Dispersant matrix

Agitation rate: 100 rpm/5–10 min; Beads separation: washing with 2% sulfuric acid, mechanical separation, washing with bidistilled water, and drying at 30°C for 24 h.

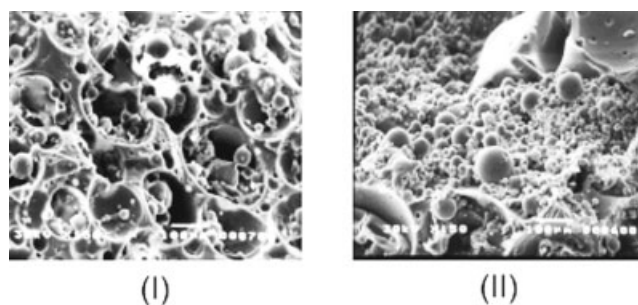


Figure 1 SEM micrographs of unsaturated polyester-styrene beads prepared via GISP.

solutions) were mixed together in the reactor to form the suspension and dispersant matrix for the unsaturated polyester-styrene monomers. The system was subjected to 20 kGy gamma rays irradiation dose, and then the resultant beads were mechanically separated from the urea formaldehyde matrix.

Chemical methodology

Tables III and IV describe the compositions of batches III and IV, used for production of UP-St beads in CSP methodology.

In the third batch, Table III, the initiator, cobalt naphthanate, was soluble in the reacting medium (UP-St emulsified with partially hydrolyzed PVA solution), while methyl ethyl ketone peroxide (MEKP) was used as a hardener. For heterogeneity, HPMC was used as a dispersant matrix. Agitation was applied continuously as 100 rpm/22 min till the solid spherical beads were clearly viewed and detected through the solution of HPMC matrix; the resultant beads were finally separated.

The last batch used for the preparation of the unsaturated polyester-styrene beads through chemical polymerization route was designed to use 2% phosphoric acid as acid catalyst for the polymerization process. On the other hand, 50% aqueous solution of sodium silicate was used as moderator for the reaction, while trifatty acid was used as a dispersant matrix. The exact composition of the batch and mixing conditions are shown in Table IV. The optimum agitation speed hold up was 100 rpm/5–10 min. The resin beads were then separated mechanically, sieved for consequent measurements.

Instrumentation

Viscometric measurements were performed by using a Brookfield LVDV-11 viscometer, Brookfield Engineering Laboratories Inc., Stoughton, MA.

Scanning electron microscopy (SEM) observations were achieved using a JSM-5400 instrument manufactured by JEOL, Japan. Particle sizes less than 100 μm

can be clearly identified. The samples were prepared by placing a drop of diluted particles in methanol onto a cover glass glued on an SEM aluminum stub, evaporating the solvent to dryness and coating the stub with a thin layer of gold.

On the other hand, Olympus BH-2 microscope, Tokyo, Japan, was used as an auxiliary and confirmatory instrument for graphing the particles of more than 50 μm in diameter.

In a general way for measuring the particle size distribution (PSD), A Shimadzu laser diffraction particle size analyzer, type SALD-2001, was used.

The Shore-A test used for surface hardness was controlled by ASTM, D2240 specification, model 306 L type A, D durometer for soft and hard plastics.

Mechanical stirrer with a semicircular anchor-type blade was used at various speeds ranging from 50 to 1000 rpm, model V50-1000, Briva Co., Egypt.

Swelling characteristics

Prior to distribution studies, swelling and sorption capacity measurements were conducted. The swelling behavior was carried out by immersing known weights of the resin beads in bidistilled water at room temperature for 24 h. Then, the beads were removed and weighted; the swelling was expressed in terms of water uptake in volume percent as

$$\text{Water uptake} = \frac{W_s - W_d}{W_d} \times 100 \text{ (Vol \%)} \quad (1)$$

where, W_d and W_s represent the weights of dry and wet resins, respectively.

To determine the ion exchange capacity (IEC) of the resin beads, a total of 500 mg portions of the exchanger were placed in each of several 250 mL conical flasks, followed by equimolar solutions of alkali metal nitrates and their hydroxides in different volume ratio; the final volume being 50 mL to maintain the ionic strength constant. The pH of the solution was recorded every 24 h until equilibrium was attained, which, under ≈ 8 days and pH at equilibrium, was

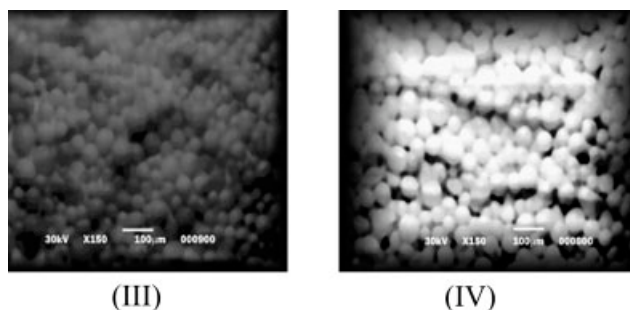


Figure 2 SEM micrographs of unsaturated polyester-styrene beads prepared via CSP.

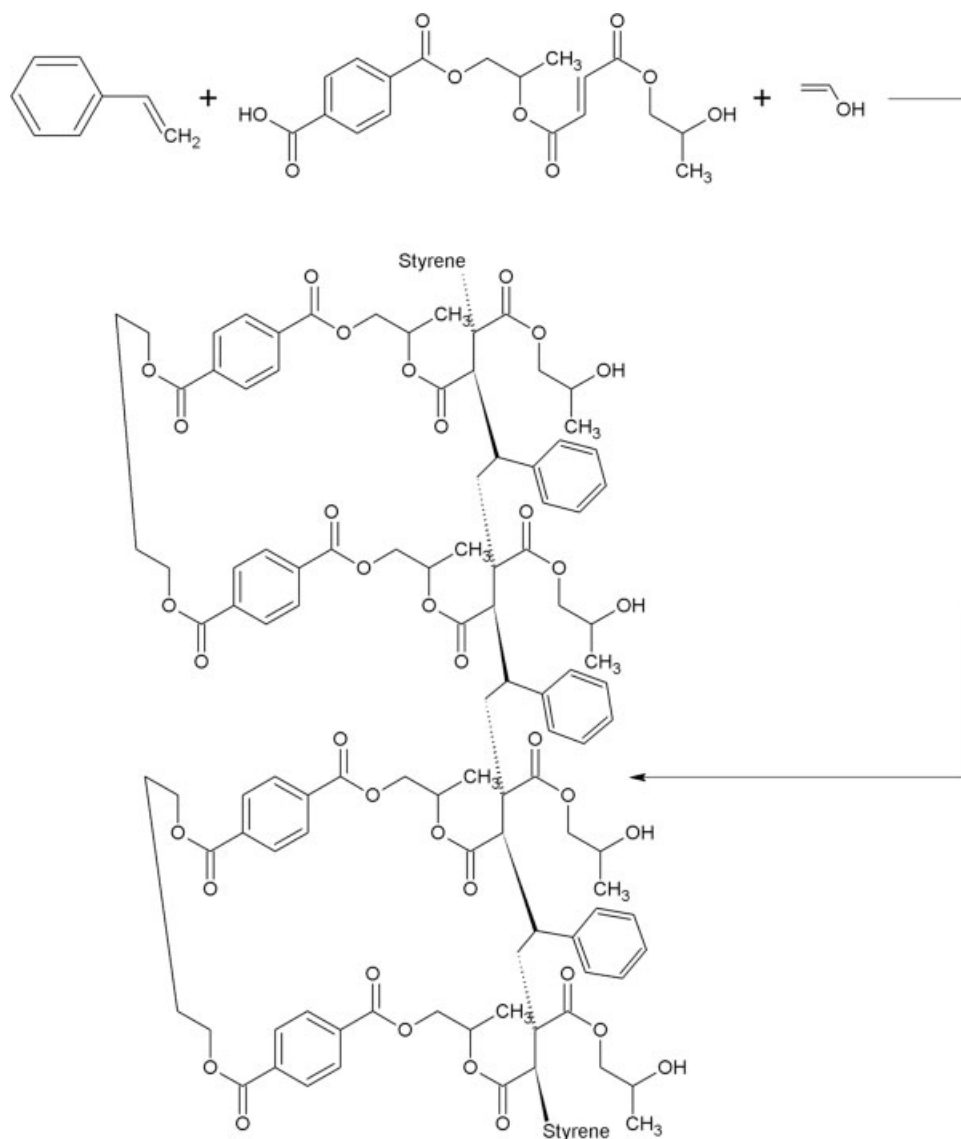


Figure 3 structural formula of batches I and III.

plotted against the milliequivalents of pH ions added. Also; the capacity of the prepared exchanger was tested as a function of pH at constant ionic strength.

Distribution studies

Various 200 mg portions of the exchanger in the H^+ -form were shaken with 20 mL of different metal solutions in the required medium and kept for 24 h with intermittent shaking to attain equilibrium. The initial metal ion concentration was so adjusted that it did not exceed 3% of its total ion exchange capacity; 10^{-4} M of the corresponding alkali metal nitrate solutions were used. The alkali metal ion concentrations for Li^+ and K^+ were determined by flame photometry, whereas the concentrations of ^{134}Cs and ^{22}Na ions were determined using direct radiometric measurements by means of NaI(Tl) scintillation detector connected to an

ORTEC assembly (Nuclear Enterprises), USA. Distribution coefficients were calculated by the formula

$$K_d = \frac{I - F}{F} \times \frac{V}{m} \quad (\text{mL/g}) \quad (2)$$

where I is the initial amount of the metal ion in the solution phase, F is the final amount of metal ion in the solution phase. V is the volume of the solution (mL) and m is the amount of the exchanger (g).

RESULTS AND DISCUSSION

Morphology of the resins

The morphological structures of the prepared resin beads through irradiation and chemical routes were studied via scanning electron microscopy.

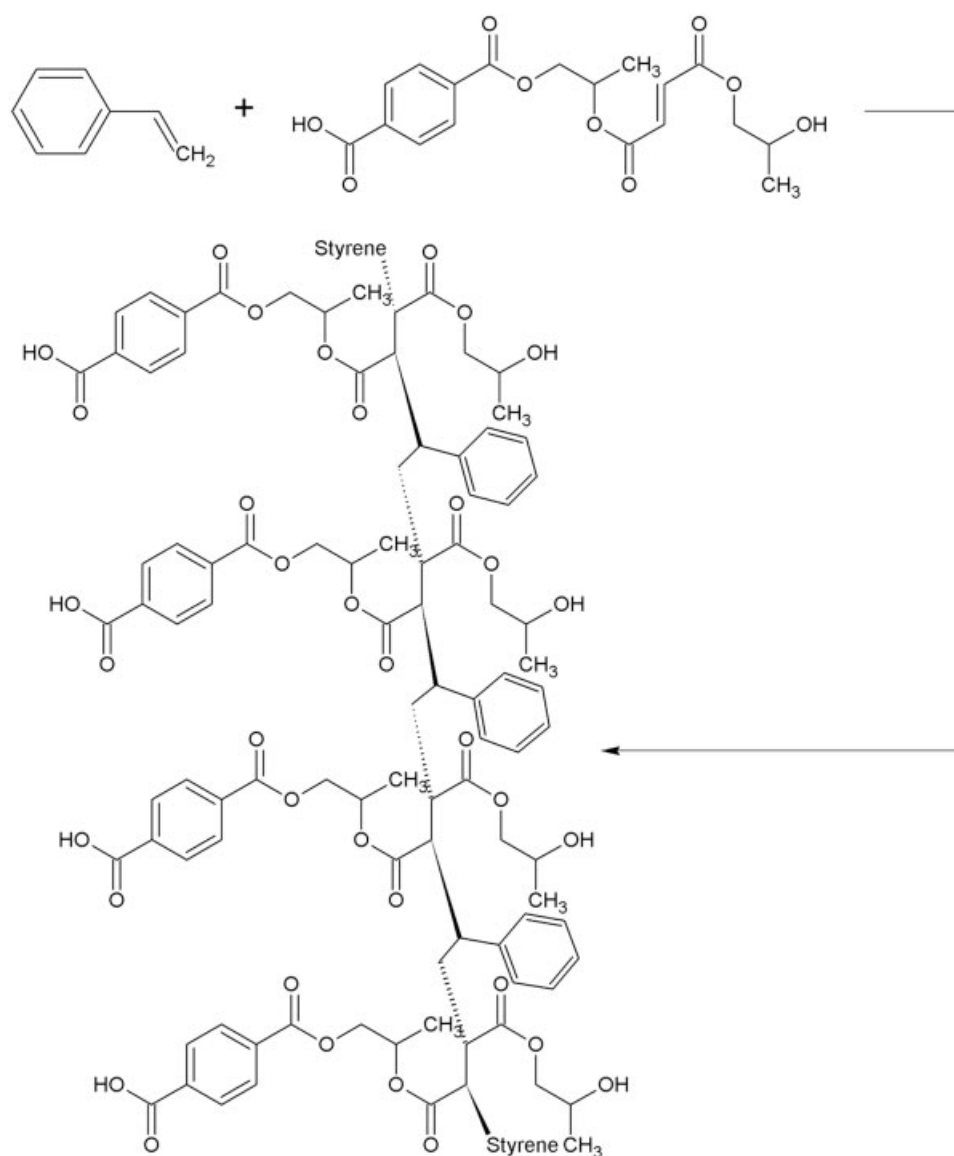


Figure 4 Structural formula of batches II and IV.

Figure 1 reveals the surface texture of the unsaturated polyester–styrene batches I and II, prepared via GISP. In the first batch, embedded white and solid beads within rings of HPMC matrix were observed. The HPMC rings are the main semisolid matrix that may differ in width and diameter; different shaped cavities of different diameters were also observed in the texture. The resin beads appear as attached groups together through a thin layer of HPMC matrix. Different sizes of precipitated beads were noted because of the lack of agitation during irradiation.

On the other hand, the composition of the second batch gives rise to transparent solid beads within a hard UF matrix. Hammering and grinding processes may be needed to release and separate the beads. After separation resin beads appear as a glassy and slightly yellow sphere, confirming its composition. The beads' diameter may vary from a site to another

because of the precipitation of beads during irradiation.

The morphologies of the produced resin batches III and IV were depicted in Figure 2. Full separated beads can easily be produced through the chemical preparation process. Nearly equal sizes of beads were also obtained because of the continuous agitation through the entire suspension process, which actually prevents the beads to settle down and stabilizes the liquid spheres during prior to curing without significant changes in their dimensions.

The dispersion of the copolymer in UF as shown in the optical micrograph (IV) gave solid and transparent yellow resin beads with homogenous and spherical shapes that are nearly equal in size, due to the continuous agitation during the chemical curing process. Also, the oil matrix enables fast separation of the beads from the matrix. The degree of transparency

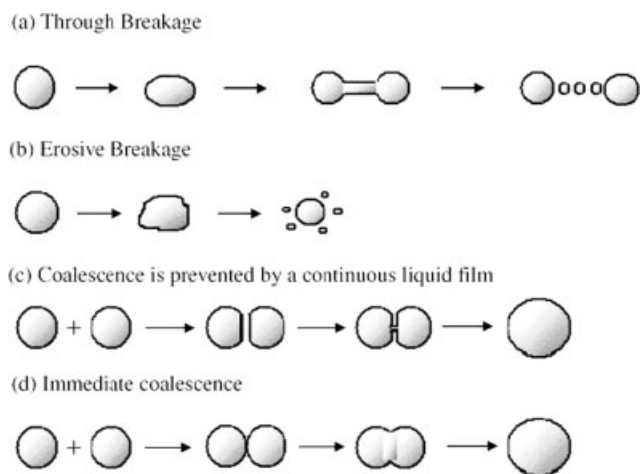


Figure 5 Illustrative scheme of breakage and coalescence mechanisms involved in suspension polymerization.³⁷

depends on the chemical composition of the reacting components; batches I and III have nearly the same degree of transparency. This can be explained by the similar compositions of the batches as indicated in Tables I and II and explored in Figures 3 and 4. The main chain of the polymer is composed of unsaturated polyester units (propylene glycol, maleic acid, and orthophthalic acid) as 60%, which is connected to the styrene monomer as shown in Figure 4. In presence of polyvinyl alcohol, an extra ester link could be formed by condensation with the orthophthalic terminals as shown in Figure 3.

Particle size distribution

The diameter of the prepared unsaturated polyester-styrene particles is expected to be above 20 μm ; the average particle size was conducted using laser diffraction particle size analysis technique in connection with scanning electron microscopy, by measuring more than 100 particles on the SEM photograph. The particle size distribution (PSD) can be controlled in suspension polymerization according to the following mechanism.

Generally, PSD depends on the type and concentration of the surface-active agents, the quality of agitation, and the physical properties (e.g., density, viscosity, and interfacial tension) of the continuous and dispersed phases. The transient droplet/particle size distribution is controlled by two dynamic processes, namely, the drop/particle breakage and coalescence rates, which are shown in Figure 5.⁴² The former mainly occurs in regions of high-shear stress (i.e., near the agitator blades) or as a result of turbulent velocity and pressure fluctuations along the surface of a drop. The latter is either increased or decreased by the turbulent flow field and can be assumed to be negligible

for very dilute dispersions at sufficiently high concentrations of surface-active agents.^{42,43}

When drop breakage occurs by viscous shear forces, the monomer droplet is first elongated into two fluid lumps separated by a liquid thread (see Fig. 5a). Subsequently, the deformed monomer droplet breaks into two almost equal-size drops, corresponding to the fluid lumps, and a series of smaller droplets corresponding to the liquid thread. This is known as thorough breakage. On the other hand, a droplet suspended in a turbulent flow field is exposed to local pressure and relative velocity fluctuations. For nearly equal densities and viscosities of the two liquid phases, the droplet surface can start oscillating. When the relative velocity is close to that required to make a drop marginally unstable, a number of small droplets are stripped out from the initial one (see Fig. 5b). This situation of breakage is referred to as erosive one. Erosive breakage is considered to be the dominant mechanism for low-coalescence systems that exhibit a characteristic bimodality in the PSD.^{43,44}

Two different mechanisms have been proposed in the literature to describe the coalescence of two drops in a turbulent flow field. The first one^{42,45} assumes that after the initial collision of two drops, a liquid film of the continuous phase is being trapped between the drops that prevents drop coalescence (see Fig. 5c). However, because of the presence of attractive forces, draining of the liquid film can occur, leading to drop coalescence. On the other hand, if the kinetic energy of the induced drop oscillations is larger than the energy of adhesion between the drops, the drop contact is broken before the complete drainage of the liquid film. The second drop coalescence mechanism⁴⁶ assumes that immediate coalescence occurs when the approach velocity of the colliding drops at the collision instant exceeds a critical value. In other words, if

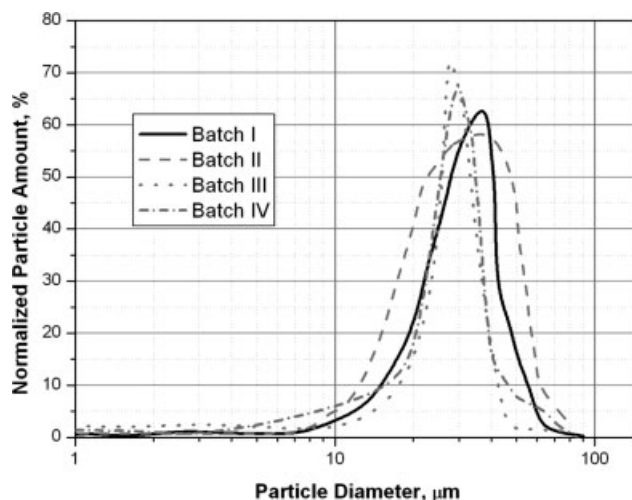


Figure 6 Particle size distribution of different polyester-styrene batches prepared by suspension polymerization.

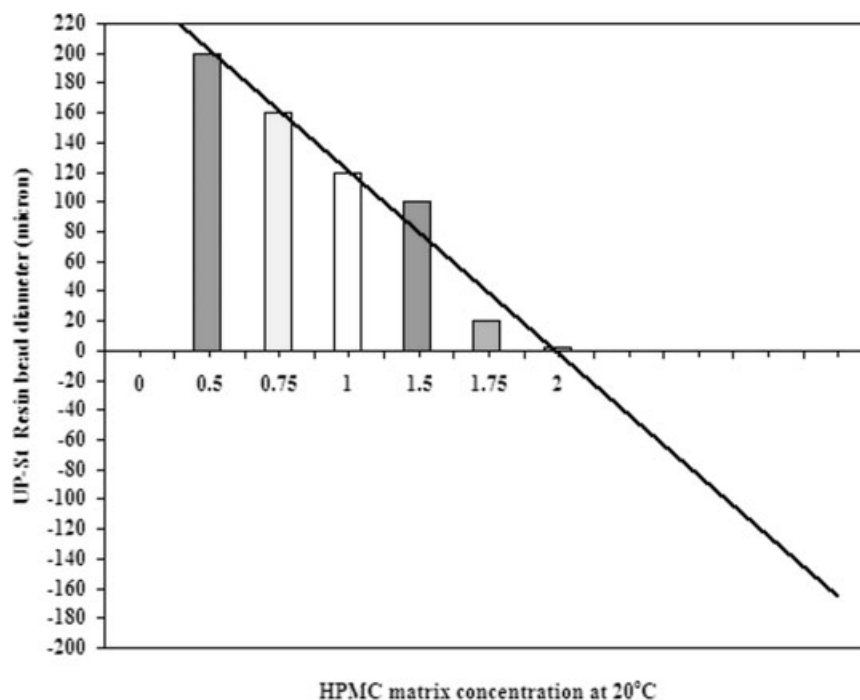


Figure 7 Effect of matrix viscosity (HPMC) on resin beads size (diameter).

the turbulent energy of collision is greater than the total drop surface energy, the drops will coalesce (Fig. 5d).

The particle size distribution of different batches used in preparation of UP–St is shown in Figure 6. Generally, the PSD obtained in case of CSP is more controlled than that obtained via GISP. This may be attributed to the controlled droplet size formation. In all cases, the use of partially hydrolyzed PVA leads to narrow PSD because of the suspension-stabilization of the monomer droplets in the dispersed matrix. The PSD of batches (I–IV) was found to be in the range of 9–60, 8–80, 10–40, and 10–50, having an average particle size of 40, 30, 28, and 30, for composition I, II, III, and IV, respectively.

Factors affecting the resin beads' formation

Surface-active agents play a very important role in the stabilization of liquid-liquid dispersions. In this connection, partially hydrolyzed PVA was used as a suspending agent; changing the degree of hydrolysis, one can alter the hydrophobicity of the PVA and, thus, the conformation and surface activity of the polymer chains at the monomer/water interface.⁴⁷ The solubility of the PVA in water depends on the overall degree of polymerization (i.e., molecular weight), the degree of hydrolysis, and temperature. Depending on the agitation rate, the concentration, and type of surface-active agent, the average droplet size can exhibit a U-shape variation with respect to the impeller speed or the degree of hydrolysis of PVA. This U-type behavior

has been confirmed both experimentally and theoretically and has been attributed to the balance of breakage and coalescence rates of monomer drops.⁴²

Immiscible dispersant matrix and its viscosity

The effect of the dispersant matrix and its stabilizing concentration are the most important parameters in suspension and dispersion polymerizations.⁴⁸ The HPMC, UF, PEG, and the trifatty acid were chosen to be immiscible and nonreacted with the resin beads

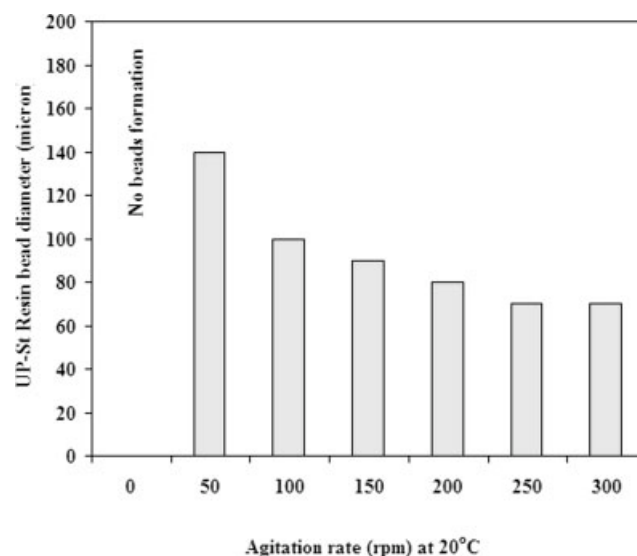


Figure 8 Effect of agitation rate on resin bead size.

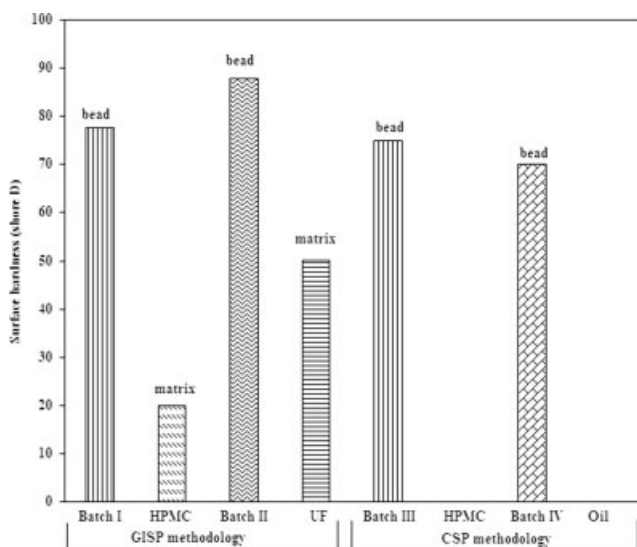


Figure 9 Surface hardness of different resin beads and matrices, obtained on preparation of UP-St by suspension polymerization.

precursors and also in a viscous or a colloidal state that constitute a protective colloidal layer surrounding the polymeric liquid sphere before curing.

In regard to the droplet/particle breakage and coalescence phenomena, the suspension polymerization process can be divided into three stages.^{49,50} During the initial low-conversion (i.e., low-viscosity) stage, drop breakage is the dominant mechanism. As a result the initial DSD shifts to smaller sizes. During the second sticky-stage of polymerization, the drop breakage rate decreases while the drop/particle coalescence becomes the dominant mechanism. Thus, the average particle size starts increasing. In the third stage, the PSD reaches its identification point while the polymer particle size slightly decreases because of shrinkage (i.e., the polymer density is greater than the monomer one).

In case of UP-St, the end of the first stage occurs at approximately 30% monomer conversion, corresponding to a critical viscosity of about 0.1 Pa s, while the second stage extends up to 70% monomer conversion.⁵¹ In this case, the PSD is essentially established up to monomer conversions of about 35–40% (i.e., end of the second stage).⁵²

As shown in Figure 7 the concentration, i.e., the viscosity of matrix, plays the main role in controlling the beads' diameter and consequently the intensity of beads produced. A semi-linear behavior as shown by the trend line in the Figure of the particle size with concentration of the matrix was observed; tailored particle sizes from 5 to 200 μm can be obtained. Low viscosity of HPMC leads to the formation of large beads. This can be explained by the formation of a protective and colloid HPMC layer around the monomer droplets. In low concentrations of HPMC, it can-

not sufficiently cover the surface of the droplets, leading to some particle coalescence. In this case, the number of particles would decrease, the particle size would increase, and a wide distribution would be obtained.^{48,53}

Agitation rate

As shown in Figure 8, good agitation was generally required to ensure a complete mixing of the reaction mixture and to prevent sedimentation of the reacting components to the bottom of the vessel.⁴⁸ It is seen that the size of the resulting particles could be effectively controlled by adjusting the agitation rate. In general, increasing the rate of agitation will lead to increasing the shear force, which in turn leads to decrease in the particle size. Additionally, the agitator in this system acts like a spacer or matrix between particles that inhibits coalescence. These dispersants would adsorb on the surface of particles, thus preventing the particle contact. As agitation rate increases, the space becomes smaller because of the system being more dynamic. As a result, smaller particles will be generated.⁴⁸

Resin beads' separation

As shown in Figure 9 the resin beads' separation were controlled according to the difference in physical characteristics between the resin beads formed and the dispersant matrix. The hardness was selected to be the main surface parameter used for bead separation.

In emulsified resin, hard polymeric matrix during the GISP process was obtained because of the partial release of styrene monomer from UP-St to the solu-

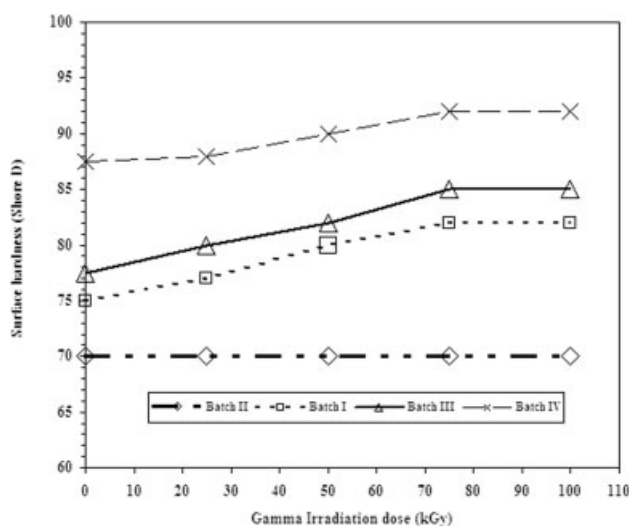


Figure 10 Effect of postirradiation dose on the surface hardness of solid resin, obtained on preparation of UP-St by suspension polymerization.

TABLE 5
Ion Exchange Capacity of Different Unsaturated Polyester–Styrene Resins

Composition	IEC (mmol/g)			
	Cs ⁺	Li ⁺	Na ⁺	K ⁺
Batch I	0.34 ± 0.01	0.37 ± 0.03	0.36 ± 0.04	0.38 ± 0.02
Batch II	0.41 ± 0.04	0.47 ± 0.01	0.45 ± 0.01	0.49 ± 0.06
Batch III	0.34 ± 0.02	0.33 ± 0.02	0.32 ± 0.01	0.36 ± 0.02
Batch IV	0.41 ± 0.07	0.43 ± 0.05	0.44 ± 0.03	0.41 ± 0.03

tion of HPMC, leading to the brittleness of the matrix. Therefore, gentle grinding was required to separate the formed beads. However, the reaction between UF matrix and styrene monomer leads to form UF–styrene adduct, which appears as a hard matrix and may need a hammering process for beads' separation.

On the other hand, no release of styrene monomer through the matrix of HPMC was detected in CSP, as chemical initiators and curing accelerators were added to the emulsified UP–St before mixing with the matrix solution. This action results in initial curing of beads that prevents the styrene monomer release from the continuous medium to the matrix. After beads' formation, the matrix was noted as a viscous liquid and easy to separate the beads by the washing process. In case of UF resin beads' formation, the ideal beads' separation can be obtained by washing of the resultant adduct with bidistilled water, after grinding the cured UF.

Gamma irradiation dose

After preparation of the polymer, the separated beads are subjected to gamma rays with different doses. As shown in Figure 10, the surface hardness of the prepared resin beads slightly increases with increasing the irradiation dose. After 70 kGy, the hardness remains almost constant. In case of batch II, no effect of irradiation on hardness was detected. This can be attributed to the complete curing of the polymer beads.

Swelling character of the resins

The swelling characters as well as the IEC of the prepared unsaturated resins depend merely on the batch composition, as indicated in Table V. The degree of swelling of batches I, II, III, and IV was found to be 32, 81, 29, and 75 vol %, respectively. This behavior may be explained by the difference of the structural formulae of resins as shown in Figures 3 and 4. The extra acidic groups present in batches II and IV could affect the wettability distinctively, and in turn the contact angles between the resin and water molecules are affected, so that higher water uptakes were observed.⁵⁴

In this direction, the IEC was also affected; the maximum sorption capacities ranged between 0.32 and 0.49 mmol/g for the earlier-mentioned resins. These values are comparable to the values obtained when the unsaturated polyester–styrene resins were used in studying their sorption behavior towards the ionic species of uranium from nitrate medium.⁵⁵ Also, these results are in good agreement of the IEC of the produced polystyrene nanofibers after sulfonation with sulfuric acid, so that 0.37 mmol/g was exchanged and 0.77 g H₂O/g dry fiber was swelled.⁵⁶

Recovery of alkali metal ions

To test the ability of the prepared resins in the recovery of the selected alkali metal ions, equilibrium preliminary studies must be conducted. Equilibrium was attained within 22 h, when the temperature was adjusted at (25 ± 1)°C, for the exchange reaction. To inspect the selectivity of different resin beads for Li⁺, Na⁺, K⁺, and Cs⁺, the distribution coefficients (K_d) were determined at different pH values using 50 μm particle size and indicated in Figures 11 and 12. A linear relationship with a slope value equal to the valency of the ion sorbed (0.9–1.1) were obtained for both the chemically processed and irradiation pro-

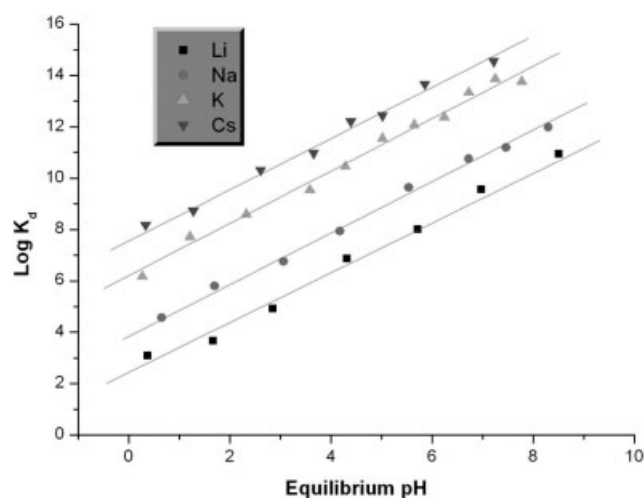


Figure 11 Distribution coefficients of Li⁺, Na⁺, K⁺, and Cs⁺ ions on irradiation processed resin beads (batch II).

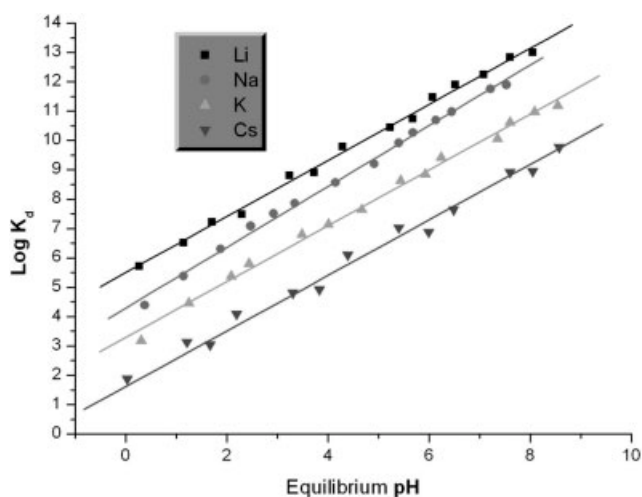
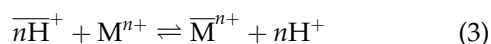


Figure 12 Distribution coefficients of Li^+ , Na^+ , K^+ , and Cs^+ ions on chemically processed resin beads (batch IV).

cessed resin beads. The explanation of this behavior^{57,58} is that the cation exchange process between H^+ ion-exchanger and M^{n+} ion in solution is represented by



According to Debye–Hückel theory, in the used diluted alkali metal ion solutions, the activity coefficient may be neglected, and the selectivity coefficient can be defined by the following equation⁵⁹:

$$K_H^M = \frac{[\overline{\text{M}^{n+}}][\text{H}^+]^n}{[\overline{\text{H}^+}]^n[\text{M}^{n+}]} \quad (4)$$

where, $[\overline{\text{M}^{n+}}]$ and $[\text{H}^+]^n$ express the concentrations of M^{n+} and H^+ ions in the exchanger phase, respectively, and $[\text{M}^{n+}]$ and $[\text{H}^+]$ ions are their concentrations in the solution. Then k_d is given by:

$$k_d = \frac{[\overline{\text{M}^{n+}}]}{[\text{M}^{n+}]} \quad (5)$$

$$k_d = K_H^M \cdot \frac{[\overline{\text{H}^+}]^n}{[\text{H}^+]^n}$$

$$\log k_d = \log K_H^M [\overline{\text{H}^+}]^n - n \log [\text{H}^+] \quad (6)$$

So

$$\log k_d = C - n \log [\text{H}^+] \quad (7)$$

Then, when $\log k_d$ values of $n+$ valent metal ions are plotted against pH, a straight line having a slope n should be obtained.

From Figures 11 and 12, it was found that the distribution coefficients for Li^+ , Na^+ , K^+ , and Cs^+ ions

were increased with increasing pH and the selectivity sequence is in the order of $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+$ in case of the chemically processed resin beads. This may be due to the increase of electrostatic interaction as a result of decreasing the ionic radius in this order⁶⁰ and to the fact that UP–St is a cation exchanger, its cationic behavior becomes more pronounced by the increase in the pH. On the other side of the irradiation processed UP–St resin, the selectivity lies in the order of $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$. This can be attributed to the sorption of these ions in their hydration forms on this exchanger. The high selectivity Li^+ , Na^+ , K^+ , and Cs^+ in neutral and alkaline solutions was observed in the adsorption of some radionuclides, using sodium titanosilicates cation exchanger.^{61–63} Also, this trend was obtained when ion-chromatographic behavior of alkali metal cations and ammonium ion were exchanged on zirconium-adsorbing silica gel.⁶⁴ In a comparison with the same organic category, Ion-exchange properties of hypercrosslinked polystyrene impregnated with methyl orange was studied.⁶⁵ The alkali metal behavior on this exchanger was almost the same except for some deviations in the order between Na^+ and Li^+ ions.

From the scientific point of view, the two types of processed resins prepared can be used as efficient sorbents for the different alkali metal ions, especially; they can be regenerated by impregnation in 0.2M HCl for about 50 min. The efficiency of sorption of Li^+ and Na^+ ions are more pronounced on chemically suspended polymerized resins, while batch II prepared via GISP is more efficient towards K^+ and Cs^+ ions. Since the prepared resin beads can be controlled in their particle size produced, the selection of the type of the resin depends on both technical feasibility of the production process. The chemically produced resins can be fabricated in a pilot scale, while those irradiation controlled can be fabricated in a semipilot scale. The two methodologies were economically feasible; a cost of about 83\$ was required to prepared 100 kg from either resins. However, the irradiation controlled resin beads are highly recommended as ion exchangers, as they possess higher mechanical properties and expected to be more thermally stable. Also, they are free-cation products that permit their use in studying the mechanism of sorption is of interest without interference.⁵⁵

CONCLUSIONS

Suspension polymerization was used for producing unsaturated polyester–styrene with different routes. The monomer is initially dispersed in the continuous aqueous phase by the combined action of surface-active agents (i.e., inorganic or/and water soluble polymers) and agitation. All the reactants (i.e., mono-

mer, initiator(s), etc.) reside in the organic or “oil” phase. The polymerization occurs in the monomer droplets that are progressively transformed into sticky, viscous monomer-polymer particles and finally into rigid, spherical polymer particles of size 2–200 μm . The polymer solid content in the fully converted suspension is typically 40–60% (w/w). The bead diameter generally decreased with increasing concentration and viscosity of the dispersant matrix and agitation rate. Beyond the suitable level of agitation, an odd shape and coalescence of the beads was observed. The resins prepared by GISP can be produced in a semipilot scale, while those fabricated by CSP can be produced in a larger scale. On the other hand, chemical processing can produce resin beads in a pilot scale. The application of these materials in the recovery of Li^+ , Na^+ , K^+ , and Cs^+ from acidic medium was achieved. The results support the use of these materials as efficient sorbents, especially in alkaline solutions.

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