

Synthesis and Characterization of Styrene-Based Microbeads Possessing Amine Functionality

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SYNOPSIS

Microbeads possessing amine functionality at the surface have been prepared by two methods: In the first method, poly(4-vinylpyridine/styrene) P(4VP/S) copolymer microbeads containing 13–69 mol % 4-vinylpyridine (4VP) were synthesized from the monomers. In the second method, animated polystyrene (PS) particles were prepared by postpolymerization reactions on cross-linked PS and polychloromethylstyrene particles to obtain poly(aminomethylstyrene/styrene) and polydiethylaminomethylstyrene particles, respectively. Scanning electronic microscopy of P(4VP/S) microbeads showed regular and spherical particles having a diameter between 80 and 200 nm depending on 4VP content. The chemical structure of the various particles made was studied using Fourier transform infrared spectroscopy, electron spectroscopy for chemical analysis (ESCA), and elemental analysis, whereas thermal properties were determined by differential scanning calorimetry and thermogravimetric analysis. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Over the last two or three decades, micron-size and submicronic polymer particles have become more and more attractive in several fields: In biomedical applications, they are used in diagnostic test kits, as carriers for drug release or chromatographic separation, for bioactive agent production, and many other applications.^{1,2} Polymeric microspheres are also used in colloid chemistry, as fillers for plastics, in the pulp and paper and cosmetic industries, and to calibrate instruments.^{3,4} Monodisperse spherical polymer particles also provide useful model substances for academic studies concerning the structure, stabilization, and dispersion of emulsions and their rheological properties.⁵ The most widely used microspheres are made of polystyrene (PS). These microbeads are easily synthesized, hydrophobic, hard, and highly spherical. However, they are relatively inert even if grafting is sometimes feasible.^{6–8}

On the other hand, microbeads formed from vi-

nylpyridine monomers present interesting properties for biological uses because of their relative hydrophilicity and their reactivity with acids or alkyl halides to form ammonium salts.² These properties may render them also useful in colloid chemistry and solid-state ionomer studies. In contrast to PS, poly(4-vinylpyridine) (P4VP) microspheres are not easily synthesized because of the instability of the droplets formed during emulsion polymerization. One way of obtaining microspheres with polyvinylpyridine (PVP) units is to graft or adsorb vinylpyridine onto an inorganic or polymeric support.⁹ For example, chloromethylated PS beads can react with sodium hydride and hydroxypropylpyridine to form a pyridine-grafted resin.¹⁰ However, ether links, which may be undesirable for some applications, are created between the aromatic and pyridine groups.

Another technique involves emulsion polymerization in the presence of surfactants. Using such a method, Sugii and co-workers prepared PVP beads having particle sizes around 200 microns (11), whereas Rembaum et al. synthesized microspheres of 4.5 microns.¹² Porous macrospheres formed by agglomeration of microspheres having an ultimate particle size of 300 nm have also been obtained.¹³ It

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must be noted that these studies do not report on the formation of free submicronic particles.

Recently, diblock copolymer microspheres containing 2-vinylpyridine (2VP) units have been synthesized.¹⁴ These monodisperse and ultrafine (50 nm) particles have “hairy ball” structures and their surface properties were found to be similar to those of pure PS. Ma and Futukomi reported on the synthesis of P4VP microspheres having a narrow-size distribution with diameters between 70 and 700 nm.¹⁵ In this method, partially quaternized P4VP is used as an emulsifier. Because of their hydrophilic properties, pure P4VP microspheres are soft and easily swell in presence of an aqueous or a polar nonaqueous solvent, forming a film upon drying. Drying such microspheres would therefore damage their structure and dispersability.

In the context of another study that we are presently conducting on the reinforcement of polymers through the addition of dry and hard microspheres possessing amine functionality at the surface, the “spongelike” nature of P4VP beads is a great disadvantage. However, if the microspheres contained mostly styrene or functionalized styrene, a more satisfactory product could conceivably be obtained. In this article, we report on the preparation and characterization of several poly(4-vinylpyridine/styrene) [P(4VP/S)] particles obtained by modifying an emulsion polymerization method previously used for pure PS microspheres. We also briefly report on the preparation and characterization of two kinds of aminated PS particles.

EXPERIMENTAL

Materials

Styrene monomer (Matheson Coleman Co.), chloromethylstyrene (CMS) (Aldrich), and divinylbenzene (DVB) (Aldrich) were filtered through an inhibitor remover column (Aldrich), whereas 4-vinylpyridine (4VP) (Aldrich) was distilled under 10 mm vacuum. Other chemicals were purchased from Aldrich Chemical Co and used without further purification.

Synthesis of Cross-linked 4VP-containing Microspheres

Emulsion polymerizations were conducted in a 1 L three-neck flask thermostated to $\pm 1^\circ\text{C}$ using the method previously described by Zou and coauthors

to obtain PS beads.¹⁶ Nine different attempts were carried out at various 4VP/S ratios, monomer and emulsifier concentrations, and temperature (Table I). The procedure was as follows: Deionized water (650 mL) was poured into the flask. Nitrogen was bubbled and agitation begun by rotation of a glass paddle stirrer. After 15 min, monomer was added and the mixture was agitated during 20 min. A 1% by weight aqueous solution of potassium persulfate, the initiator, was then added. After polymerization, the latex was cooled down. The microbeads were separated by centrifugation at a low speed (< 9000 rpm) and washed several times with deionized water before drying under vacuum at 70°C for several days.

Synthesis of polydiethylaminomethylstyrene (PDAMS) Particles [Fig. 1(a)]

It has been suggested that aminated PS particles may be prepared by reaction of polychloromethylstyrene (PCMS) particles with amines.¹⁷ Therefore, PCMS particles were synthesized according to a method previously described by Margel et al.¹⁸ Using the same setup as described before, isobutanol (540 mL) and polyvinylpyrrolidone (6 g), a surfactant, were mixed in the flask kept at 95°C . After nitrogen was bubbled for 20 min, CMS (60 mL) and DVB (6 mL) were added. Fifteen minutes later, a solution of azobisisobutyronitrile (AIBN) (600 mg), the initiator, in isobutanol (150 mL) was added to the reaction mixture. It was stirred at this temperature for 5.5 h. The latex was then centrifuged and the particles obtained were washed twice with ethanol and methanol. They were then suspended in methanol and sonicated for 15 h to break the agglomerates before being centrifuged again. The PCMS particles were suspended in freshly distilled diethylamine and the mixture was refluxed overnight. Following centrifugation and washing, the PDAMS particles thus obtained were washed with methanol several times, centrifuged again, and kept at 80°C under vacuum for several days.

Synthesis of poly(aminomethylstyrene/styrene) [P(AMS/S)] Microspheres [Fig. 1(b)]

Cross-linked PS microspheres were synthesized according to a previously reported procedure.¹⁶ Direct aminomethylation was performed through the synthetic route developed by Mitchell et al.⁷ Briefly, PS beads (10 g) were suspended in a trifluoroacetic/dichloromethane (1:1 volume) mixture (100 mL) containing hydroxymethylphthalimide (8.86 g). Trifluo-

Table I. Conditions (a) for the Synthesis of P(4VP/S) Microbeads

Batch No.	4VP Volume (mL)	Styrene Volume (mL)	Water Volume (mL)	Mass of Emulsifier (g)	Temp (°C)	Reaction Time (h)	Mol % 4VP (± 1) by Titration	Approximate Bead Diameter (nm)
1	10	—	700	—	90	~ 2.0	—	—
2	10	—	700	SDS : 1.0	90	~ 2.0	—	—
3	10	—	700	SDS : 0.1	90	~ 4.5	—	—
4	15	5	700	SDS : 0.1	90	~ 4.5	69	80
5	10	10	700	SDS : 0.1	90	~ 1.5	47	100
6	7	14	200	SDS : 0.1 cetyl alcohol : 0.3	70	~ 4.5	31	110
7	4.5	13.5	700	SDS : 0.1	90	~ 4.5	23	120
8	2.5	18	700	SDS : 0.1	90	~ 4.5	13	150
9	—	25	700	—	95	~ 2.0	—	150–200

^a Cross-linking agent DVB: 10% of monomer volume. Initiator: 200 mg potassium persulfate.

romethanesulfonic acid catalyst (1.5 g) was added to the mixture, which was then stirred for 23 h at room temperature. After filtration, the microbeads were washed successively with a 1:1 trifluoroacetic/dichloromethane mixture, dichloromethane, ethanol, and methanol. They were then added to ethanol (80 mL) containing hydrazine (4 mL) and the mixture was refluxed for 20 h. The beads were then washed, filtered, and dried under vacuum.

Characterization of Particles

Determination of 4VP Content

Titration of the vinylpyridine in P(4VP/S) microbeads was carried out according to a procedure previously developed by Burleigh and co-workers.¹⁹ Dried microspheres were suspended in a chlorobenzene/glacial acetic acid mixture containing a drop

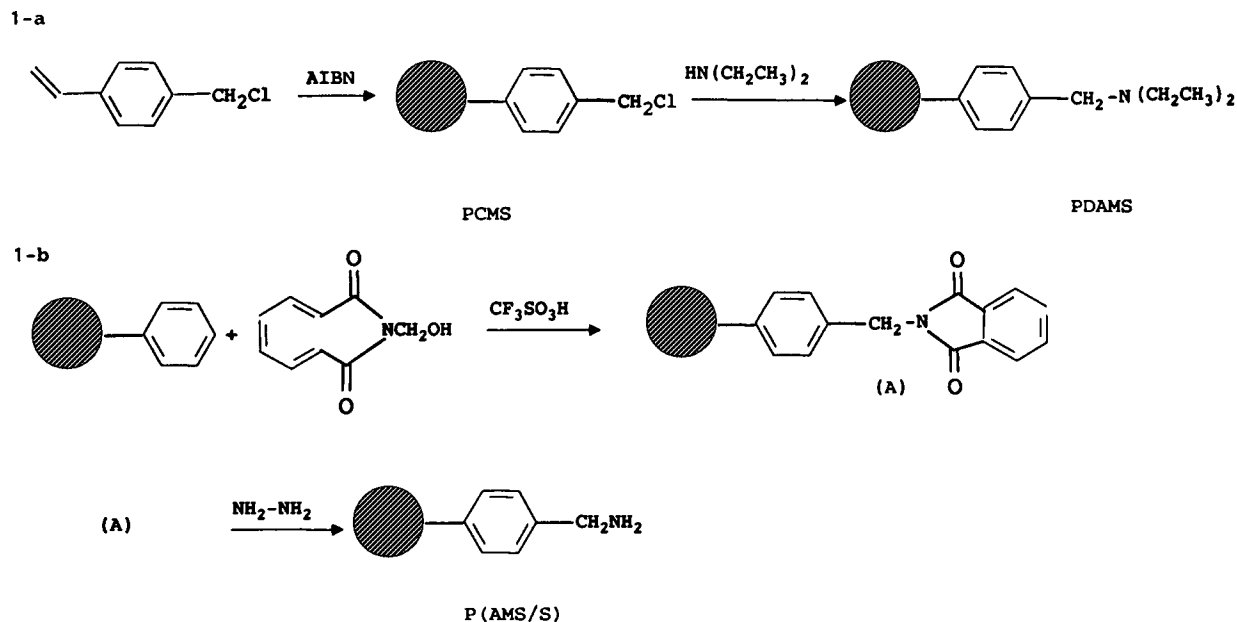


Figure 1 (a) Synthesis of PDAMS particles from PCMS. (b) Synthesis of P(AMS/S) microspheres by direct aminomethylation of PS microbeads.

of a 0.05% aqueous solution of methyl violet indicator and titrated with a 0.1*N* solution of perchloric acid in acetic acid to a green end point.

Scanning Electronic Microscopy (SEM) Experiments

SEM was carried out on a Jeol JSM-840A scanning microscope at 50000 magnification. The samples were previously sputter-coated with gold/palladium.

Elemental Analysis

Elemental analysis (Galbraith Labs, Tennessee) was conducted on P(AMS/S) and PDAMS particles. P(AMS/S) particles were found to contain 83.2 wt % C and 4.3 wt % N, for a C/N mol ratio of 22.6. It can be shown that this corresponds to amination of 37% of styrene units. PDAMS microspheres were found to contain 82.0 wt % C, 6.4 wt % N, and 0.84 wt % Cl. The N/Cl mol ratio of 20 indicates that 95% of the chlorinated groups in PCMS have reacted to give aminated units. Hence, PDAMS can be considered as a homopolymer.

Surface Composition

The chemical composition of the surface of P(4VP/S), P(AMS/S), and PDAMS particles was determined by ESCA measurements using a VG Escalab MkII apparatus equipped with a Mg source at 12 kV and 20 mA. In this technique, H atoms are not counted and atomic content is reported on the basis of C, N, and O atoms only. For the P(4VP/S) microspheres, the particle surface content was as follows—batch 5: 90.4 mol % C and 8.1 mol % N; batch 6: 93.9 mol % C and 4.4 mol % N; and batch 7: 93.8 mol % C and 4.7 mol % N. From these results, the percentage of 4VP at the surface of the particles coming from batches 5, 6, and 7 was estimated at 66, 36, and 38 mol %, whereas the overall composition was 47, 31, and 23 mol %, respectively (Table I). The surface of pyridine-containing microspheres is then necessarily richer in pyridine units than is the core. The distribution of functional units throughout the particles is determined by the monomer reactivity ratios and also by the affinity between the two monomers and water. It has been reported that the 4VP free-radical copolymerization reactivity ratio is larger than that of styrene, at least between 50 and 80°C.²⁰ Therefore, the chains produced should contain progressively smaller amounts of 4VP, yielding microspheres having a 4VP-rich core. However, the strong affinity between 4VP and water likely reverses the phenomenon as the polar

4VP comonomer preferably remains at the periphery of the microbeads.¹⁷

For the P(AMS/S) microspheres, it was determined that the particle surface contained 85.9 mol % C and 8.9 mol % N. Therefore, 92% of the styrenic units located at the surface bear an aminomethyl group, compared to 37% for the entire particle. This clearly shows that direct aminomethylation occurs mainly at the surface of the microbeads, leading to a surface layer almost completely aminated.

Fourier Transform Infrared Spectroscopy (FTIR) Spectroscopy

FTIR spectra were collected on a Bomem MB-122 spectrometer under nitrogen. Samples were mixed with KBr powder and pressed. Twenty-four scans were averaged with a resolution of 4 cm⁻¹. Band absorbance was measured as peak height, with values not exceeding 0.9.

Differential Scanning Calorimetry (DSC)

DSC measurements were carried out on a Setaram DSC 92 apparatus equipped with a CS 92 controller at a heating rate of 10°C/min to a maximum temperature of 200°C. Glass transition temperatures (*T_g*'s) were measured during the second passage.

Thermogravimetric Analysis (TGA)

TGA was performed on a Setaram TGA 92 apparatus under an argon atmosphere at a heating rate of 2°C/min, to a maximum temperature of 275°C.

RESULTS AND DISCUSSION

Synthesis of P(4VP/S) Microbeads

Emulsion polymerization of pure P4VP (batch 1 in Table I) does not lead to the formation of microspheres. Attractive forces between monomer or polymeric droplets lead to aggregation and precipitation of particles. To avoid this coalescing phenomenon, sodium dodecylsulfate surfactant was added at different concentrations to the two following syntheses (batches 2 and 3). Agglomeration of particles decreased greatly and a stable latex was formed for which loose agglomerates of microbeads were easily broken by stirring. Although very fine particles may be obtained by the addition of emulsifiers, their separation from the aqueous medium remains very difficult to carry out. Subsequent washings removed the surfactant from the particle

surface, leading to gel formation upon centrifugation, the solvated microbeads being too soft to resist the centrifugal forces. After drying, this gel could no longer be dispersed in several common solvents.

The subsequent five batches were obtained by addition of various amounts of styrene monomer in

order to generate a copolymer that would be more resistant to mechanical forces. Copolymers having 4VP contents from 69 to 13 mol % were prepared with a yield greater than 90%. The 4VP/S mol ratio of the product measured by titration was similar to that of the reaction mixture.

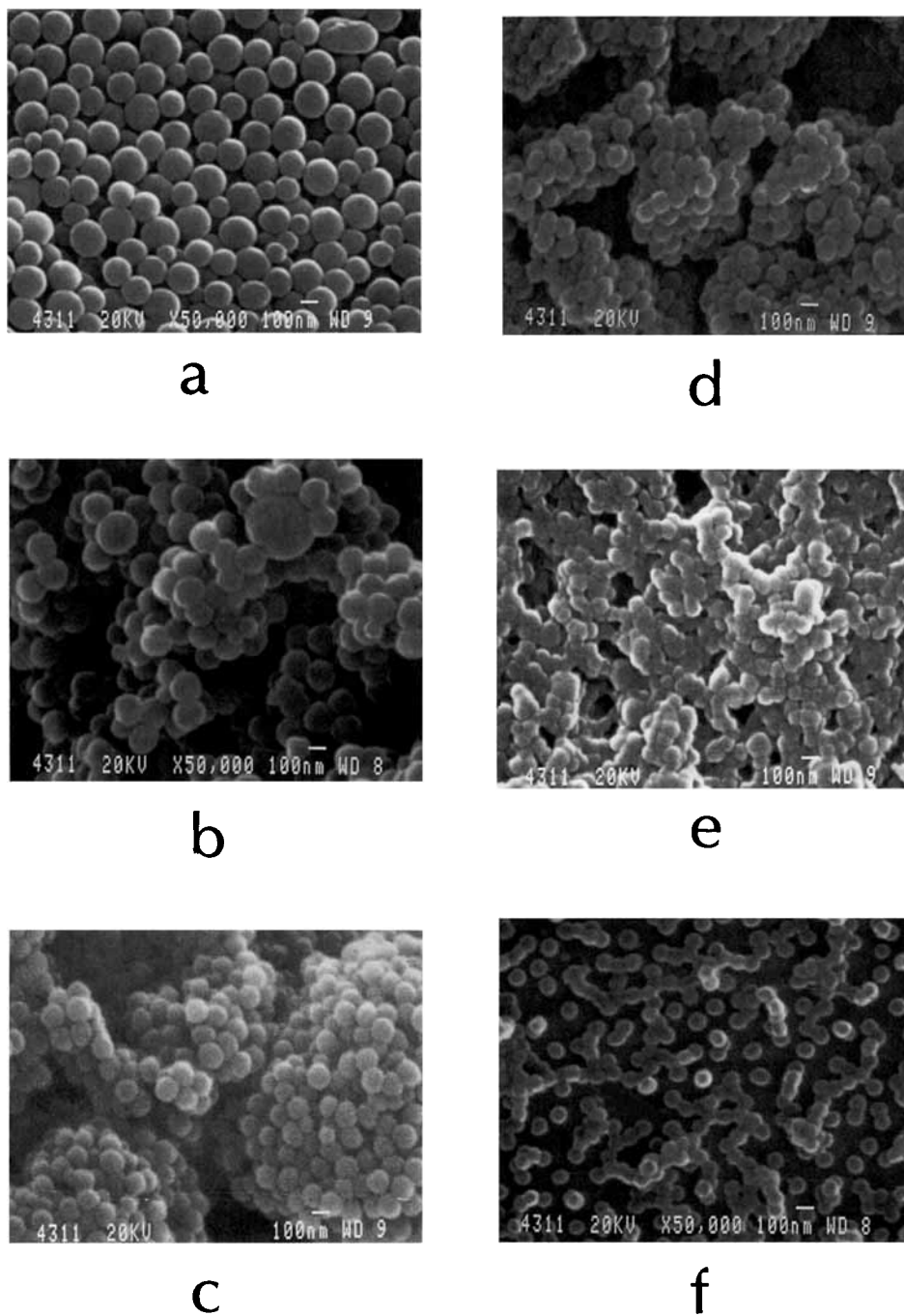


Figure 2 Micrographs of (a) pure PS microspheres and 4VP-containing microspheres. The 4VP content for micrographs (b), (c), (d), (e), (f) are 13, 23, 31, 47 and 69 mol %, respectively.

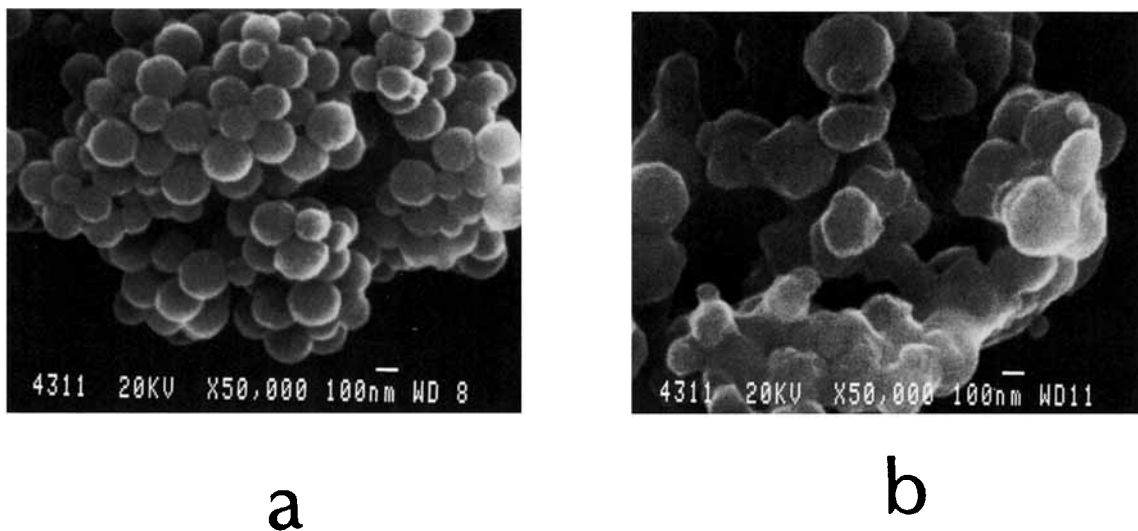


Figure 3 Micrographs of (a) P(AMS/S) and (b) PDAMS particles.

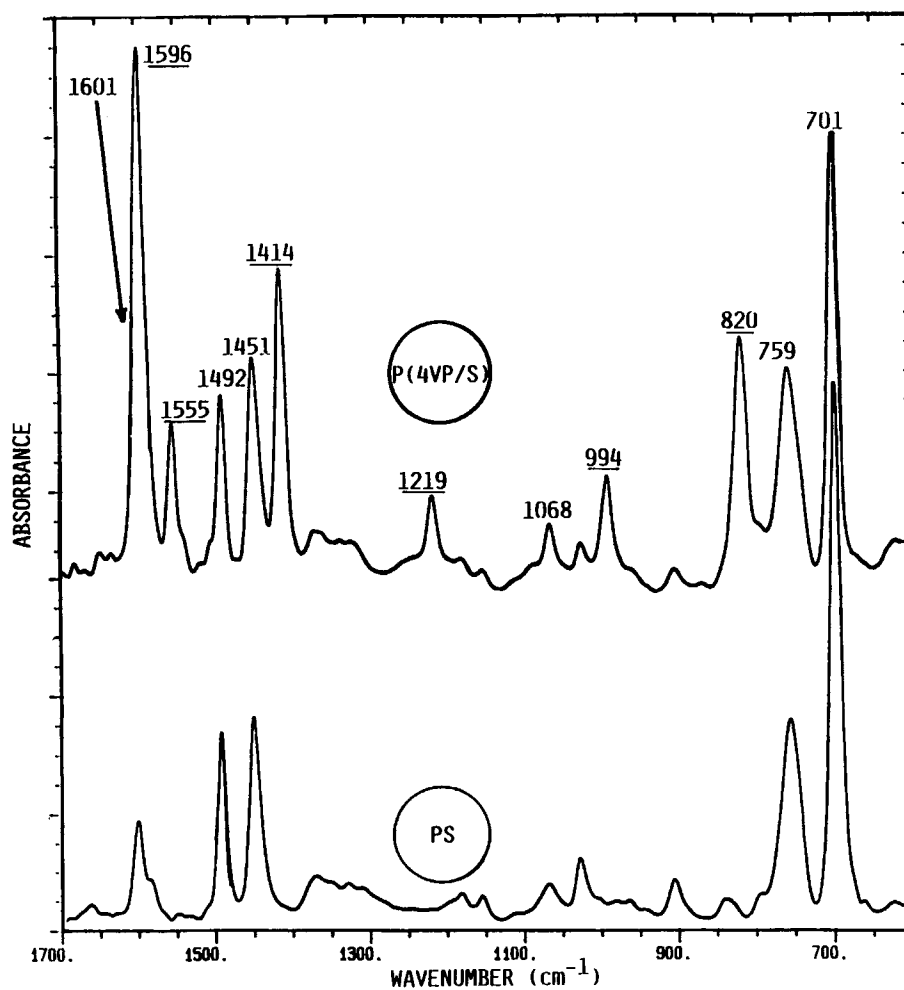


Figure 4 FTIR spectra of pure PS and P(4VP/S) microspheres. The copolymer contains 47 mol % 4VP. Bands characteristic of 4VP are underlined.

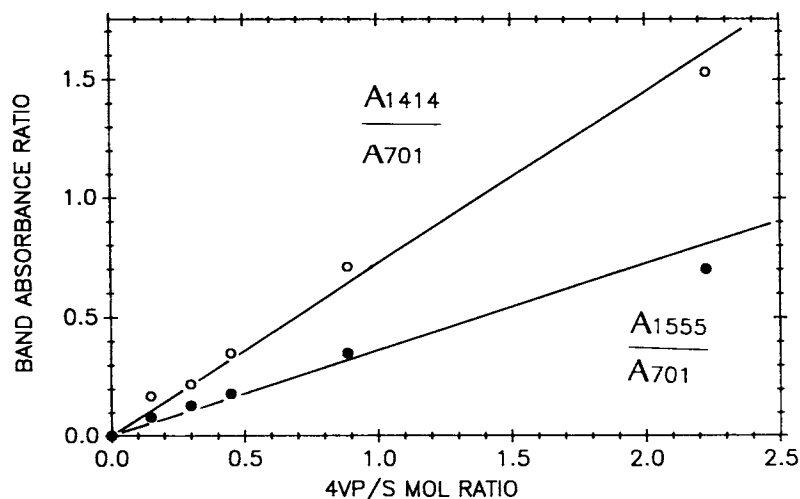


Figure 5 Ratio of the intensity of the 1414 and 1555 cm^{-1} peaks to that of the PS 701 cm^{-1} peak as a function of microsphere composition for the P(4VP/S) system.

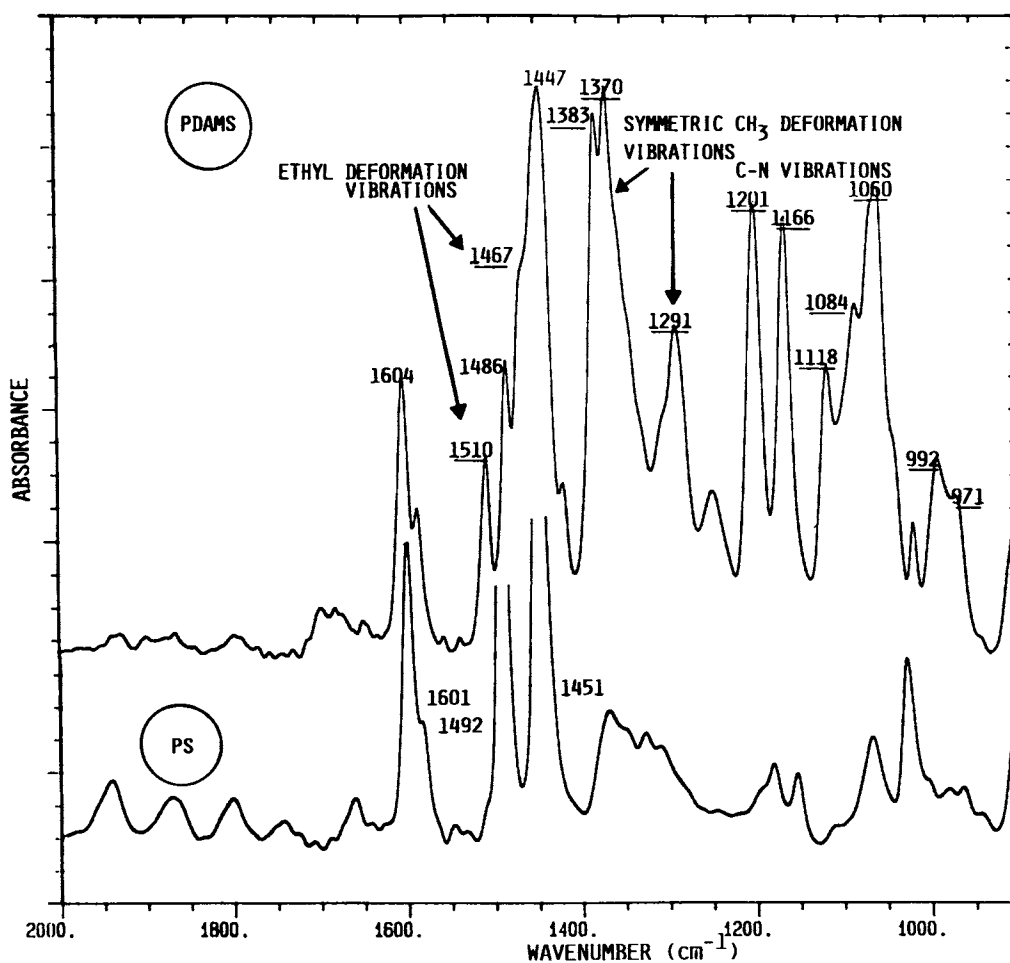


Figure 6 FTIR spectra of PDAMS and PS particles. Bands characteristic of diethylamino units are underlined.

SEM Observations

Figure 2 shows micrographs of pure PS microbeads [Fig. 2(a)] and several P(4VP/S) microbeads. Although agglomeration occurred for some copolymers, the shape of all the particles remained spherical. Particle size decreased regularly as the 4VP content increased; whereas the average diameter of pure PS microspheres was between 150 and 200 nm, the size of P(4VP/S) beads varied from 200 to 80 nm as the 4VP content increased from 13 to 69 mol % (Table

I). Particle-size polydispersity seemed to decrease with the presence of 4VP and sodium dodecylsulfate surfactant. The latter homogenizes the suspension during polymerization.

Figure 3 presents micrographs of particles of P(AMS/S) copolymer [Fig. 3(a)] and PDAMS [Fig. 3(b)]. As might be expected, P(AMS/S) microspheres have the same physical structure as that of cross-linked PS microbeads [Fig. 2(a)], implying that the grafting reaction does not affect the physical structure of the particles. PDAMS particles, which

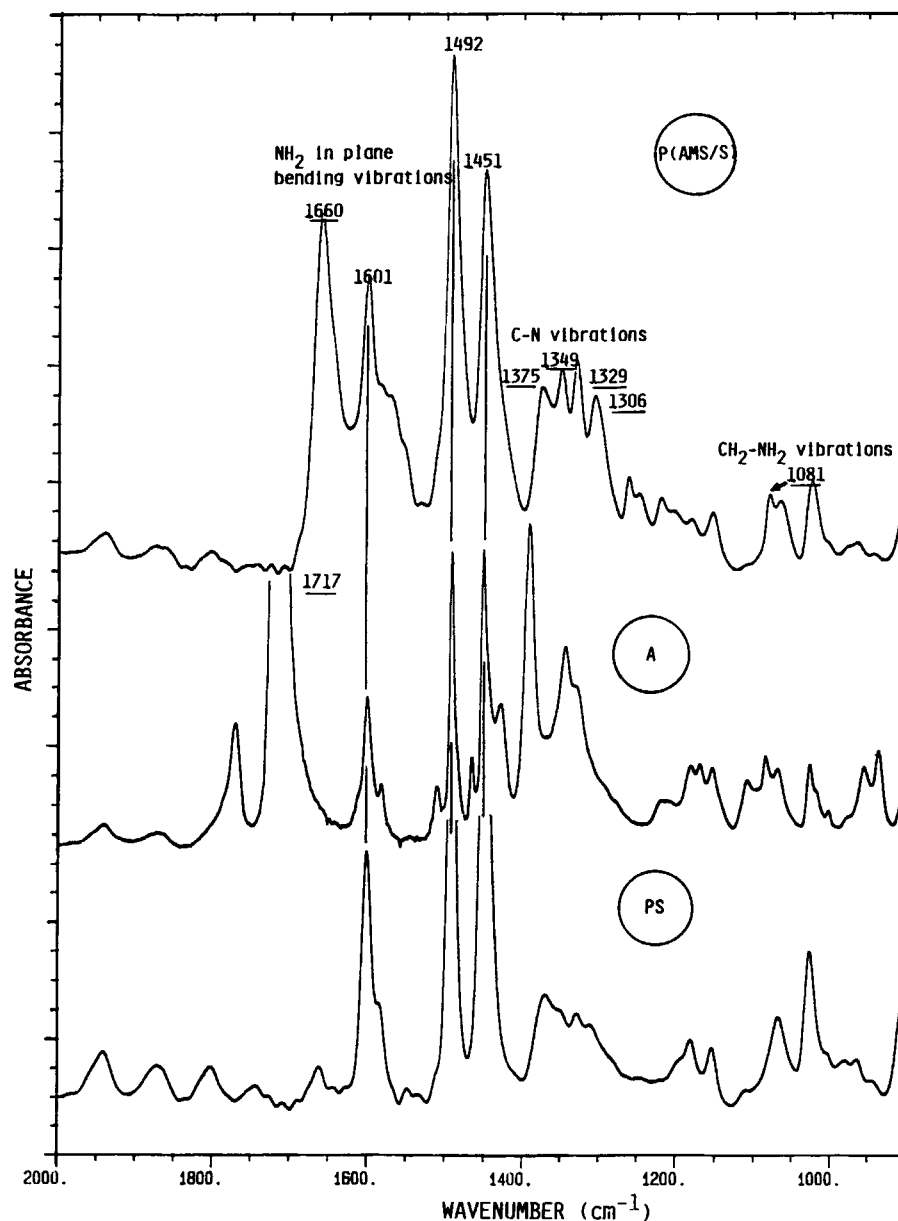


Figure 7 FTIR spectra of P(AMS/S), phtalimidomethylated PS (A), and PS microspheres. Bands appearing following modification of PS are underlined.

were prepared from irregularly shaped PCMS particles, showed particle sizes larger than for other particles previously described (between 200 and 400 nm) and agglomeration.

FTIR Spectroscopy

FTIR spectra of the various P(4VP/S) microspheres were collected. A representative example is presented in Figure 4, where the spectrum of the P(4VP/S) microspheres of 47% 4VP content is presented together with that of pure PS microspheres. The introduction of 4VP leads to the appearance of six new peaks at 820, 994, 1219, 1414, 1555, and 1596 cm^{-1} , this latter peak overlapping the peak of pure PS located at 1601 cm^{-1} . The ratios of the intensity of the 4VP 1414 and 1555 cm^{-1} peaks to that of the PS 701 cm^{-1} peak are presented in Figure 5 as a function of copolymer composition. Here, the maximum peak absorbance of a band located at x cm^{-1} will be denoted A_x . It may be noted that the A_{1555}/A_{701} and the A_{1414}/A_{701} ratios are linear functions of the 4VP/S ratio.

Figure 6 shows the spectrum of PDAMS microspheres. Relative to the spectrum of PS, it may be observed that many new peaks corresponding to the diethylaminomethyl unit appear in the 1000–1500 cm^{-1} region. The two peaks located at 1510 and 1467 cm^{-1} are related to the ethyl deformation vibrations. The two peaks located at 1383 and 1370 cm^{-1} correspond to the symmetric CH_3 deformation vibrations. The multiple vibrations occurring between

1000 and 1300 cm^{-1} are difficult to characterize but likely correspond to C—N vibrations.²¹

Figure 7 presents the spectra of the products obtained after each of the two steps of the direct aminomethylation of PS beads. The intermediate compound shows a very strong absorption band related to the carbonyl groups at 1717 cm^{-1} . The final product, P(AMS/S), shows a strong absorption at 1660 cm^{-1} and four bands of medium intensity between 1300 and 1380 cm^{-1} , characteristic of the NH_2 in-plane vibration and of the C—N vibrations, respectively. A small peak characteristic of $\text{CH}_2\text{—NH}_2$ bonds also appears at 1081 cm^{-1} .^{21,22}

DSC Measurements

Figure 8 presents the T_g 's of P(4VP/S) microspheres as a function of 4VP content. PS beads have a relatively high T_g (123°C) compared to pure PS (108°C) because of the presence of approximately 10 mol % DVB cross-linking agent. We observed a large increase in T_g with increasing 4VP content up to approximately 60 mol %. Above this concentration, no significant increase was visible, indicating that chain mobility had reached a minimum. The width of the transition as observed in the DSC does not show any significant variation over the 4VP content range. This suggests that the copolymers are homogeneous and that the copolymerization is random. Glass transition temperatures of PDAMS and P(AMS/S) particles were found to be 130 and 134°C, respectively.

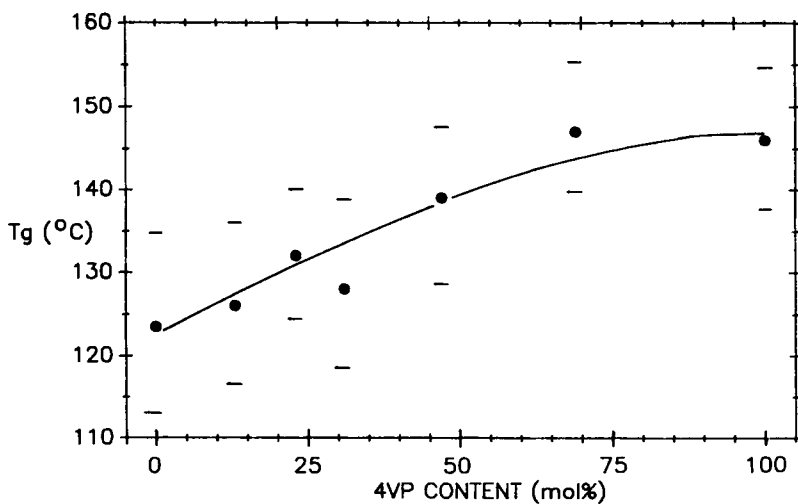


Figure 8 Glass transition temperatures of P(4VP/S) microspheres as a function of composition. The onset and end-point temperatures are shown.

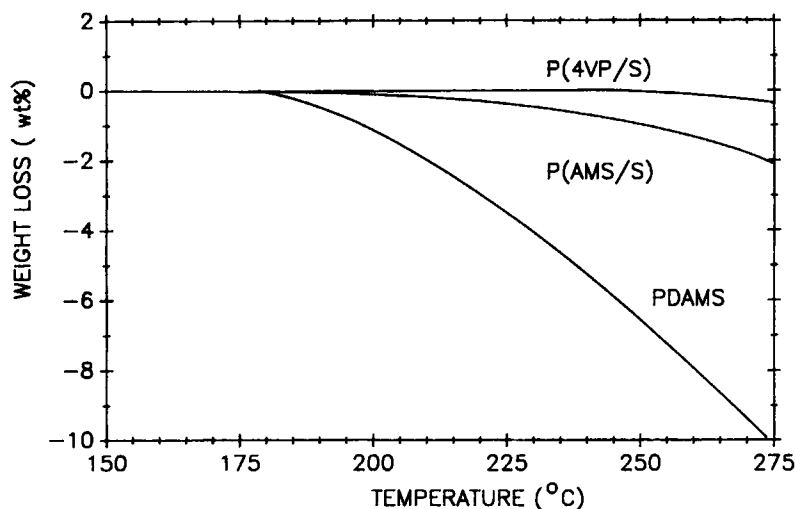


Figure 9 Mass loss of a P(4VP/S) copolymer of 47% 4VP content, P(AMS/S), and PDAMS particles during a TGA run.

Thermogravimetric Analysis (TGA)

TGA was performed on P(4VP/S) of 37 mol % 4VP content, P(AMS/S), and PDAMS particles (Fig. 9). PDAMS particles were especially unstable, with weight loss beginning at ca. 175°C, reaching a value of 10% at 275°C. P(AMS/S) beads were also unstable, losing 2% of mass by the time 275°C is reached. These thermal degradations may be ascribed to a breaking of the methylene group–nitrogen bond. When the nitrogen atom bears two ethyl groups, it is obvious that weight loss is much more important than in the case of a primary amine. Comparatively, P(4VP/S) copolymers do not present any weight loss below 250°C, reflecting their thermal stability.

CONCLUSION

The emulsion synthesis of cross-linked P(4VP/S) copolymer particles containing from 13 to 69 mol % 4VP leads to the formation of microspheres having submicronic free particle sizes, the particle size decreasing from 200 to 80 nm with increasing 4VP content. However, these microspheres become soft and difficult to isolate at high 4VP contents. The T_g 's of these beads vary from 123 to 147°C as 4VP content increases. They are stable until at least 250°C.

P(AMS/S) microbeads have been prepared from PS particles. They present a core/shell structure as the bead surface is almost completely aminated,

whereas only 37% of all styrenic unit are. PDAMS particles have been synthesized by amination of PCMS particles, with a yield of 95%. Comparatively to other particles, PDAMS particles present an irregular structure. P(AMS/S) and PDAMS particles are only stable to 175°C.

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