

Surface Reactive Acetal Functional Waterborne Core–Shell Particles

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SYNOPSIS

Core–shell particles were prepared using a two-stage emulsion polymerization of styrene and ethyl acrylate. The particle surfaces were modified by introducing an acetal functionality, suitable for acid-catalyzed crosslinking processes. Surface functionalization was performed in two principally different ways: In the first method, 4-aminobutyraldehyde dimethylacetal was used for grafting through transesterification of ethyl acrylate residues at the surface or through reactions with epoxy groups introduced in the second-stage polymerization. In the second method, 4-acrylamidobutyraldehyde dimethylacetal was used as a comonomer to ethyl acrylate in the second-stage polymerization. The reactive particles were used as crosslinking agents in an acid-curing coating system. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Microgels are spherical polymer particles with sizes comparable to the hydrodynamic diameters of linear macromolecules.¹ The particles form colloidal solutions, and because of a controlled crosslinking performed in the polymerization process, they may have a stable, three-dimensional structure. Reactive microgels have surface-bound functional groups which can be utilized in crosslinking reactions.² The surface reactivity can be introduced by postpolymerization surface reactions or by using functional monomers in the polymerization step. The reactive microgel particles can be used as crosslinkers in curable surface coatings, and because of their compact structures, high solids contents are attainable with a relatively low viscosity increase. Literature on this topic is scarce, however.

In aqueous systems, microparticles can be prepared from linear polymers by, e.g., polymerization of hydrophobic vinyl monomers. Such particles are not susceptible to swelling in the aqueous environment, and internal crosslinking is, consequently, not critical. Reactive microparticles of these types can

be used as curing agents for water-based coating resins.

In a previous article, we reported on the preparation, characterization, and properties of small reactive particles.³ By batch emulsion copolymerization of styrene and ethyl acrylate, particles with diameters of 45–55 nm were prepared. These particles were surface-modified by means of a postpolymerization grafting reaction with a dual functionality reagent, which introduced an acid-reactive acetal functionality into the particle surface. The diacetal functionality has recently been reported to undergo acid curing at ambient temperatures without emission of formaldehyde.^{4–6} Ester groups from the ethyl acrylate residues in the copolymer particles were used as reactive sites for the surface grafting. A comparatively low grafting density was obtained, presumably due to a low number of reactive ethyl ester groups present at the surface of the styrene/ethyl acrylate copolymer. The reactivity of the surface-bound acetal groups was demonstrated by curing of a model resin system.

The number of active surface groups may be increased by increasing the relative amount of ethyl acrylate in the copolymer, but this would also decrease the glass transition temperature of the particles. In the present study, a different technique was used. Core–shell particles consisting of a poly-

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Table I Preparation of Reactive Core–Shell Particles

	Core–Shell Particle							
	TR 1	TR 2	TR 3	TR 4	AB 1	AB 2	GMA 1	GMA 2
Seed latex used	ST 1	ST 1	ST 1	ST 1	ST 2	ST 2	ST 1	ST 1
Diameter (nm) ^a	110	100	110	110	101	101	110	110
Grafting conditions	80°C 8 h	80°C 8 h	95°C 16 h	95°C 16 h	Pol. ^b 60°C	Pol. ^b 60°C	60°C 1 h	60°C 1 h
Diameter of core–shell particles (nm) ^a	119	121	125	123	113	110	121	118

^a Determined by quasi-elastic light scattering.

^b Second-stage polymerization conditions.

styrene core and a reactive poly(ethyl acrylate) shell were prepared by a seeded batch process. The objectives were to obtain particles having a high surface density of reactive diacetal groups, and by using particles having a soft shell consisting of poly(ethyl acrylate), the grafting density was expected to increase as compared to the conventional copolymer particles. Core–shell particles are prepared by a two-step emulsion polymerization, and the combination of monomer types, emulsifier, initiator, and other process parameters controls the particle size, the size distribution, and the morphology.

EXPERIMENTAL

Reagents

Analytical grades of the following reagents were used: styrene (ST, Merck), ethyl acrylate (EA, Merck) 4-acrylamidobutyraldehyde dimethyl acetal (ABDA, Air Products and Chemicals, Inc.), 4-aminobutyraldehyde dimethyl acetal (ABAA, Air Products and Chemicals, Inc.), lactic acid titanate chelate catalyst (Tyzor LA, DuPont), sodium dodecyl sulfate (SDS, Janssen), octyl phenoxy polyethoxy-ethanol (Triton X 45, Merck), potassium peroxydisulfate (KPS, Sigma Chemical), sodium hydroxide (NaOH, Eka Nobel), and glycidyl methacrylate (GMA, Aldrich). Monomers were purified by passing through a column filled with aluminum oxide (Active basic, Merck). The monomers were kept at 8°C before use. Water used was distilled and deionized.

Preparation of Core–Shell Particles

Process conditions were investigated by carrying out polymerizations batchwise in a calorimetric reactor,

which allowed close monitoring of the reactions.⁷ Polystyrene seed particles were prepared by the following procedure: The reactor was charged with an emulsion containing 300 g ST, 1000 mL of water, and 2 g of SDS. Ten pellets of NaOH (about 1 g) were added, and the reactor was repeatedly degassed and purged with N₂. The reactor was heated to 60°C, and 25 mL of an initiator solution containing 10 g of KPS in 250 mL of water was added. The reaction was allowed to proceed at 60°C until completion. Two batches of polystyrene particles having average particle diameters of 110 nm (ST 1 in Table I) and 101 nm (ST 2), respectively, were prepared.

In the second step, EA was added to the polystyrene seed latex in order to produce core–shell particles. The polymerization was carried out at 60°C as a batch process, in which 130 g of EA and 20 mL of the initiator solution was charged to 1000 mL of a polystyrene seed latex (ST 2 in Table I). The mixture was allowed to polymerize until completion. Heterogeneous latex particles composed of 70 wt % of polystyrene and 30 wt % of poly(EA) having an average particle diameter of 124 nm (CS 1 in Table II) were obtained.

Surface Modification

Surface Grafting by Transesterification

ST/EA core–shell particles with an average particle size of 124 nm (CS 1 in Table II), prepared as described previously, were further stabilized before the grafting process by adding a nonionic surfactant. Triton X 45 (2 g) was added at 60°C to 300 mL of the latex under continuous stirring. The latex was then treated at 80°C for 8 h with 10 g ABAA in the presence of 10 g titanium chelate catalyst under a nitrogen blanket (TR 1 and TR 2 in Table I). Some

Table II Estimation of Diacetal Functional Groups

Sample	Nitrogen Content ($\mu\text{mol/g}$)	Methoxy Groups ($\mu\text{mol/g}$)	D_{QLS}^a (nm) 3 Days	D_{QLS}^a (nm) 6 Months	Diacetal Groups/Particle	Diacetal Groups/ nm^2
ST 1 ^b	0		110	108	0	0
ST 2 ^b		0	101	103	0	0
CS 1 ^c	0		124	125	0	0
TR 1 ^d	29		119	120	15,800	0.36
TR 2 ^d	71		121	114	45,700	0.87
TR 3 ^e	293		125	123	187,500	3.9
TR 3 ^e		617	125	123	197,300	4.0
TR 4 ^e	307		123	123	187,300	3.8
TR 4 ^e		639	123	123	194,800	4.1
AB 1 ^f	178		113	112	84,400	2.1
AB 1 ^f		387	113	112	84,200	2.1
AB 2 ^f	171		110	114	74,800	2.0
AB 2 ^f		353	110	114	69,700	1.8
GMA 1 ^g	278		121	121	161,700	3.5
GMA 1 ^g		644	121	121	150,600	3.3
GMA 2 ^g	243		118	120	130,800	3.0
GMA 2 ^g		531	118	120	142,800	3.3

^a QLS = quasi-elastic light scattering. Standard deviation ± 15 nm.

^b Styrene seed particles.

^c Core-shell particles.

^d Surface grafting by transesterification at 80°C for 8 h.

^e Surface grafting by transesterification at 95°C for 16 h.

^f Seeded batch polymerization using an acrylic acetal functional monomer. See Experimental part.

^g Surface grafting of epoxy-functional core-shell particles.

experiments were also performed at 95°C for 16 h (TR 3 and TR 4 in Table I).

Surface Modification Using an Acrylic Acetal Functional Monomer

In a batch process, 10.8 g EA and 2.2 g ABDA were added to 100 mL of a polystyrene seed latex having an average particle size of 110 nm (ST 1 in Table I). The calorimetric reactor was repeatedly degassed and purged with N_2 and heated to 60°C, and 2.5 mL of an initiator solution containing 1 g of KPS in 25 mL of water was then added. The polymerization was allowed to proceed until completion. Heterogeneous latex particles were obtained with a polystyrene core (70 wt %) and a shell (30 wt %) consisting of a copolymer of EA and ABDA in weight ratio 5 : 1 (AB 1 and AB 2 in Table I).

Surface Grafting by Epoxy-group Reactions

Polystyrene particles with an average particle size of 101 nm (ST 2 in Table I) were used as seed par-

ticles in a batch polymerization of GMA in order to produce core-shell particles. The calorimetric reactor, containing 100 mL of the polystyrene seed, was repeatedly degassed and purged with N_2 . GMA, 3.3 g, and 2 mL of the initiator solution were added and allowed to polymerize at 60°C until completion. Heterogeneous latex particles consisting of a polystyrene core (90 wt %) and a GMA shell (10 wt %) were obtained. The epoxy groups were subsequently used as grafting sites for 3.6 g ABAA (GMA 1 and GMA 2 in Table I). The reagent was added all at once and the reaction was allowed to proceed for 1 h at 60°C.

Dialysis

All samples of reactive core-shell microparticles were thoroughly cleaned by dialysis for 14 days at room temperature using dialysis tubing (Spectrapore™, Spectrum, USA, diameter 50 mm) with a molecular cutoff value of 6000–8000. Dialysis was

performed in order to eliminate grafting chemicals, i.e., the water-soluble ABDA monomer and ABAA, respectively, and other impurities. Dialysis was done against an aqueous solution of SDS with the same concentration as in the latex (2 g/L). The SDS solution was changed daily.

Quasi-elastic Light Scattering

Particle-size distributions for all latexes were measured by quasi-elastic light scattering (QLS) by using a Coulter N4 submicron particle size analyzer. To check the dispersion stability, the measurements were carried out after 3 days and 6 months. The results from the measurements are presented in Table II. The measurements were performed after dilution of the latexes with Milli-Q water to appropriate concentrations. All measurements were performed at room temperature and the results given in Table II are mean values of three measurements.

Electron Microscopy

Particle sizes and particle morphologies were determined for selected samples by transmission electron microscopy (TEM) after 6 months storage, by using a JEOL 100U transmission electron microscope. The latex samples were prepared for TEM measurements by negative staining using uranyl acetate at room temperature. The micrographs are shown in Figure 1(a)–(d). The particle diameters were measured from the micrographs. More than 1200 particles were measured for each sample. From these results, the number average (D_n) and weight average (D_w) diameters were calculated and histograms of the particle size distributions were prepared. The polydispersity index (PDI) was calculated as $(D_w)/(D_n)$. The particle-size distributions are shown in Figure 2(a)–(d).

Detection of Acetal Functional Groups

Determination of the nitrogen contents of the functional particles was performed by microanalytical elemental analysis (Perkin-Elmer 240 elemental analyzer) at the laboratory of H.C. Ørsted Institute, Denmark. The contents of active methyl acetal groups were measured using base hydrolysis. To a Teflon reactor, 3–4 g latex, 10 mL NaOH, and 10 mg *t*-BuOH were weighed and charged. The mixture was hydrolyzed at 150°C for 6–8 h and then neutralized with concentrated HCl and the pH measured. Liberated methanol was quantified using gas chromatography (Hewlett Packard 5890 Series 2,

50 m and 0.32 mm i.d., stationary phase crosslinked FFAP Carbowax).

Crosslinking

The resin formulations used for testing crosslinking reactions are shown in Table III. A mixture of 69 wt % ethanol, 23 wt % paratoluene sulfonic acid, and 8 wt % phosphoric acid was used as a catalyst. Glass plates were coated with the resin formulations using an applicator to give a film thickness of 120 μm . The plates were placed at 23°C for 15 min for flash-off and cured at 60°C for 15 min and were subsequently cooled at 23°C and 50% relative humidity. Some samples were also cured at 23°C and 50% relative humidity. Pendulum hardness was measured using an Erichsen 299/300 pendulum. Measurements were performed after 24 h. The results presented in Table IV are averages of three measurements on each sample.

RESULTS AND DISCUSSION

Preparation of Core-Shell Particles

We previously described the preparation and properties of reactive latex particles based on a copolymer of ST and EA. In the present work, we used the same monomer composition for the preparation of core-shell model particles consisting of 70 wt % polystyrene core and 30 wt % poly(EA) shell.

Core-shell particles can be produced by a two-stage, seeded emulsion polymerization, performed either as a batch or as a semibatch process. To avoid formation of new particles during the second-stage polymerization, the amounts of surfactant have to be kept below cmc for the system, which may give a colloidal instability of the final core-shell latex. In the present case, we chose to use a seeded batch process for the preparation of the core-shell particles. Sodium dodecyl sulfate (SDS) was used as a surfactant in both stages of the polymerization, together with potassium persulfate as an initiator.

As reported previously, the use of SDS as a surfactant allows the preparation of small particles, but the concentration of the surfactant has to be quite high. As noted above, a low surfactant concentration should be used in the second stage of a seeded polymerization. An excess of surfactant can be removed through dialysis before the second-stage polymerization, but we, rather, chose to use a low SDS concentration (2 g/L) for the preparation of the polystyrene seed latex, which gave particles of about

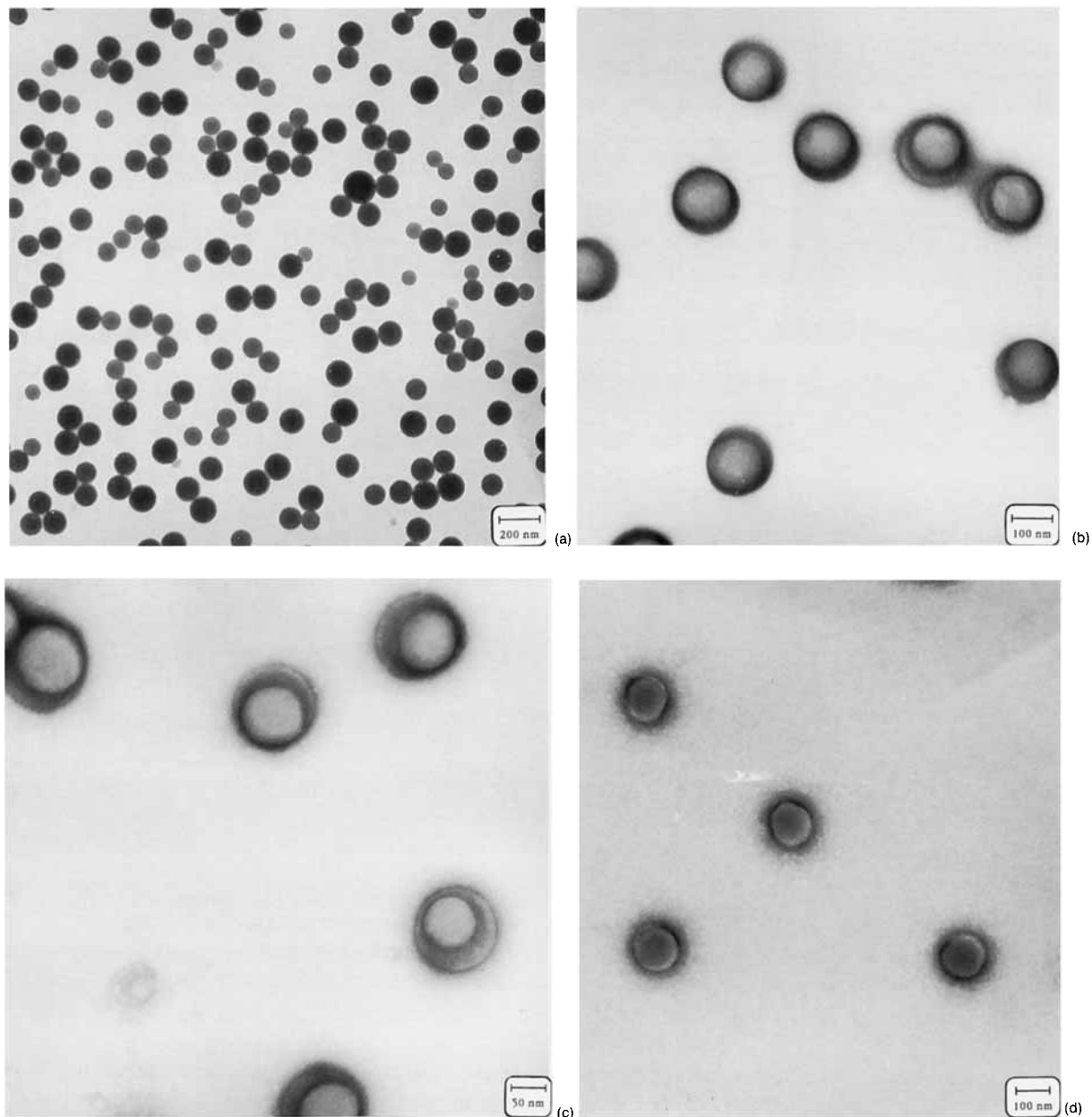


Figure 1 (a) Transmission electron micrograph of polystyrene seed particles ST 1. (b) Transmission electron micrograph of ST/EA core-shell particles CS 1. (c) Transmission electron micrograph of reactive core-shell particles TR 3 prepared by transesterification. (d) Transmission electron micrograph of reactive core-shell particles AB 1 prepared using an acrylic acetal-functionalized monomer.

100–110 nm, as seen in Table I. After stage two, i.e., the polymerization of EA, the amount of SDS was far below full-surface coverage of the particles, and the latex was, consequently, easily flocculated. To avoid problems with flocculation during the subsequent grafting process, the particles were further stabilized through the addition of a nonionic surfactant.

The morphology of the latex particles was studied by TEM after staining with uranyl acetate. From the micrographs, it can be seen that the particles exhibit a core-shell type morphology, with a polystyrene core and a poly(EA) shell. The morphology of the heterogeneous particles is governed by the interfacial free energies^{8–10} as well as by the internal viscosity during the phase separation.¹¹ In a batch

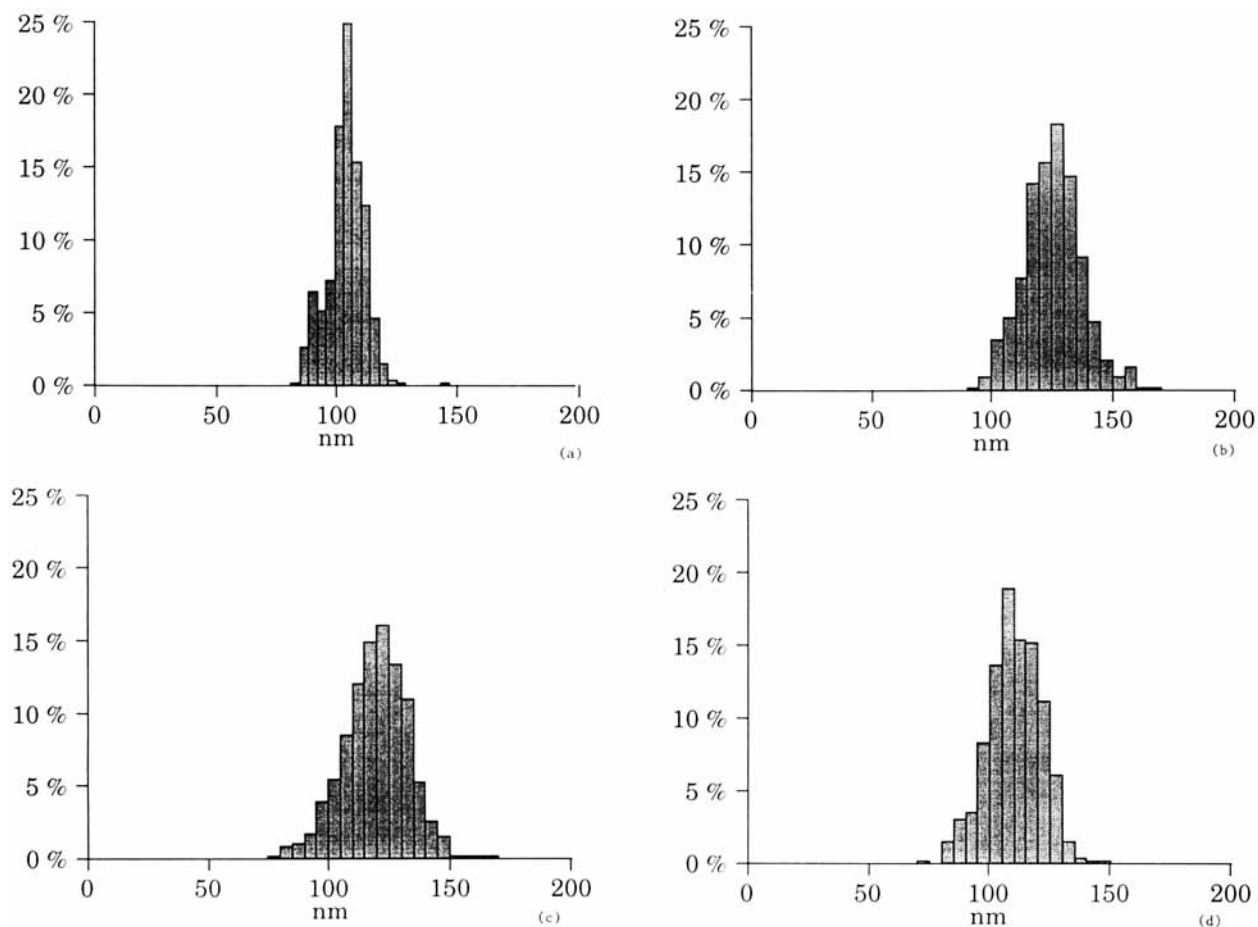


Figure 2 (a) Particle-size distribution for polystyrene seed particles ST 1. $D_n = 105$ nm; $D_w = 106$ nm; $\sigma = 8$ nm; PDI = 1.01. (b) Particle-size distribution for ST/EA core-shell particles CS 1. $D_n = 125$ nm; $D_w = 129$ nm; $\sigma = 12$ nm; PDI = 1.03. (c) Particle-size distribution for reactive core-shell particles TR 3 prepared by transesterification. $D_n = 120$ nm; $D_w = 123$ nm; $\sigma = 13$ nm; PDI = 1.03. (d) Particle-size distribution for reactive core-shell particles AB 1 prepared using an acrylic acetal-functionalized monomer. $D_n = 110$ nm; $D_w = 114$ nm; $\sigma = 11$ nm; PDI = 1.04.

operation, the internal viscosity of the particles can be regarded as low, and the interfacial free energies should be the dominant factor for the morphology development. The hydrophilicity of poly(EA) is much greater than that of polystyrene, as can be concluded from the solubilities in water for the corresponding monomers. The solubility of EA in water at 25°C is 1.5%, as compared to 0.027% for ST.¹² Because of this fact, EA and poly(EA) should be preferentially located in the interfacial region between the polystyrene phase and the aqueous phase, thereby minimizing the interfacial energy.

From the micrographs in Figure 1(b), it is clear that the polystyrene core is not centered in the particle. However, the poly(EA) phase seems to completely surround the polystyrene seed particles and should give possibilities for full-surface coverage by

reactive functional groups after modification. Some deformation of the poly(EA) shell during sample preparation for microscopy can be anticipated. The deformation tends to increase the average particle diameters observed by TEM, but has no relevance for the main conclusions drawn from the micrographs.

Reactive Core-Shell Particles

In our previous communication, we described the preparation of small latex particles carrying reactive surface-bound acetal groups and compared the grafting efficiency of different grafting processes. In our present work, we have introduced the reactive acetal groups onto the particle surfaces by similar processes, i.e., by the three following methods:

Table III Recipes Used for Formulating Acid-curing Aqueous Emulsion Binder Systems

	Reference System (g)	Core-Shell System (g)	Reactive Core-Shell System (g)
Ethanol, 96% by volume	40	40	40
Water	110	110	110
Poly(vinyl alcohol)	50	50	50
Methylated urea-formaldehyde resin (96% dry weight)	40	20	20
Core-shell latex (30% dry weight) ^a		25	
Reactive core-shell latex (30% dry weight) ^b			25
Hexa(methoxymethyl)melamine (98% dry weight)	10	5	5

^a Core-shell latex CS 1.

^b Reactive core-shell latex samples TR 3, AB 1, and GMA 1 (See Tables I and II and Experimental section) were used in three different formulations.

1. Surface grafting using ester groups.
2. Copolymerization with acetal functional monomer.
3. Surface grafting using epoxy groups.

In the first method, the core-shell particles prepared from ST and EA, as described above, were treated with ABAA in the presence of a titanium chelate catalyst. By a transesterification reaction, ABAA was substituted for ethoxy groups present at the particle surface. This reaction is difficult to perform in an aqueous environment, but the use of the lactic acid titanate chelate catalyst and carefully controlled process conditions facilitated the reaction. A reaction scheme is given in Figure 3(a).

In the second method, EA and an acrylic monomer containing an acetal group (ABDA) were copolymerized onto polystyrene seed particles in a batch process using process parameters similar to those used for preparation of the ST/EA core-shell particles. The weight ratio between the first and the

second phases was 70/30, and the shell contained EA and ABDA monomers in a weight ratio of 5 : 1. A reaction scheme is shown in Figure 3(b).

In the third method, glycidyl methacrylate (GMA) was substituted for EA in the preparation of the core-shell particles to give particles having a polystyrene core and a poly(GMA) shell in a weight ratio of 90/10. The seeded polymerization was carried out similarly to that described above, i.e., in a batch process using a polystyrene seed. Recently, Magnet et al.¹³ reported the use of delayed addition of GMA to a system of butyl acrylate and ST in order to obtain particles with epoxy groups at the surface. In our present work, we used the surface-bound epoxy groups as grafting sites for ABAA. The reaction scheme is shown in Figure 3(c).

Characterization

The preparation of reactive core-shell particles involves a number of consecutive reaction steps,

Table IV Pendulum Hardness of Cured Films Measured after 24 h^a

Curing Temperature (°C)	Reference System (s)	Core-Shell System CS 1 ^b (s)	Reactive Core-Shell System		
			AB 1 ^b (s)	TR 3 ^b (s)	GMA 1 ^b (s)
23	155	94	106	153	142
60	162	109	113	151	148

^a Values reported are averages of three measurements for each sample.

^b See Tables I and II and Experimental section.

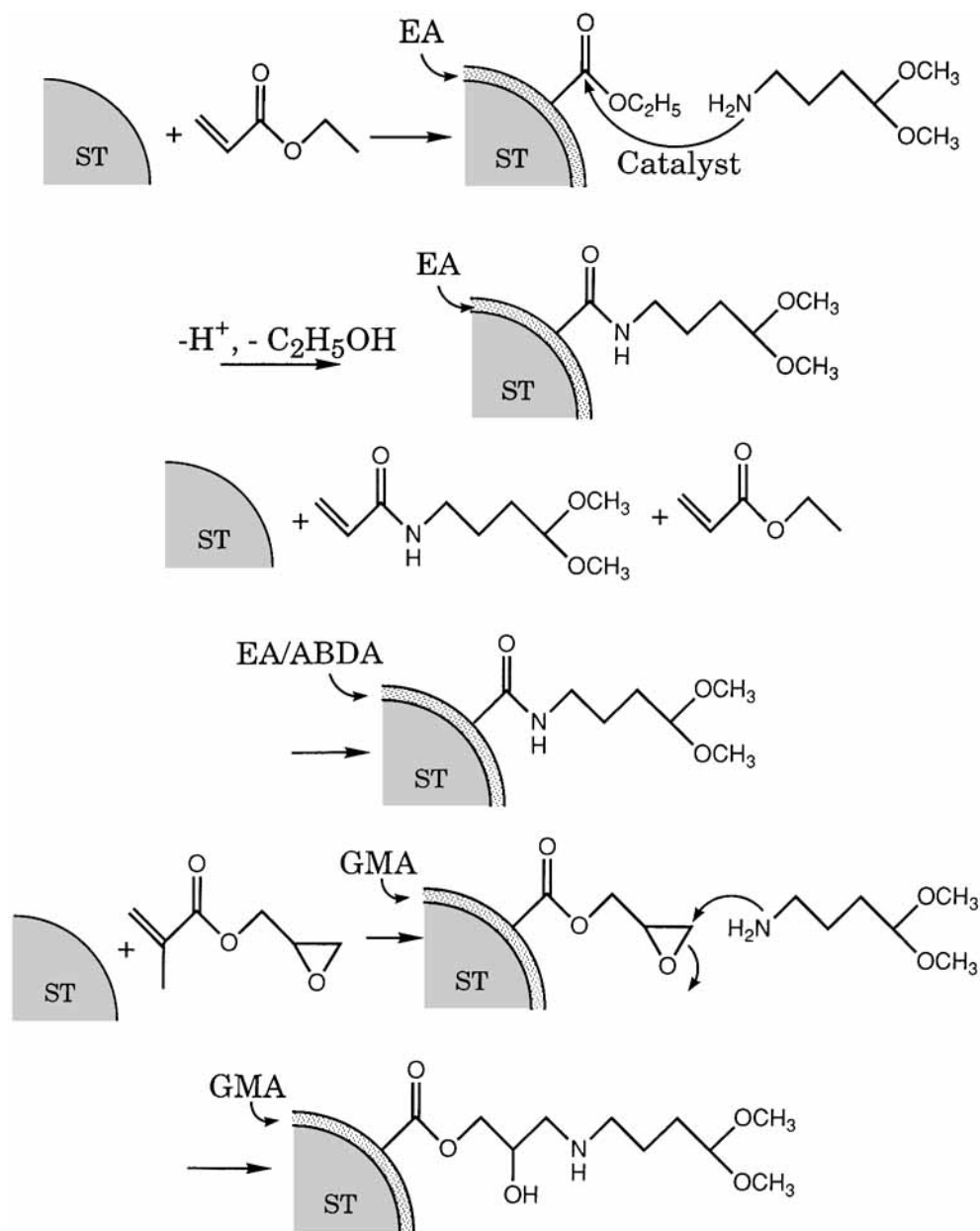


Figure 3 (a) Surface modification of ST/EA core-shell particles by transesterification. (b) Preparation of core-shell particles using an acrylic acetal-functionalized monomer. (c) Surface grafting of ST/GMA core-shell particles using epoxy-group reactions.

and it is necessary that all steps can be performed without any agglomeration of the latex. In Figure 1, TEM micrographs of the polystyrene seed particles [1 (a), ST 1 in Table I] and the ST/EA core-shell particles [1 (b), CS 1 in Table II] are shown. From the micrographs, it is clear that the poly(EA) shell is not perfectly centered in the heterogeneous particle, but, apparently, the polystyrene seed is completely covered by poly(EA). Furthermore, no signs of new particle formation in the second stage

are seen. This fact is also evident from the particle distributions calculated from the TEM micrographs, as shown in Figure 2(a) and (b). The distributions are quite symmetrical. The increase in the average particle size (13%) is somewhat larger than is the increase anticipated (9%) from the amount EA polymerized. The average diameters were also determined by quasi-elastic light scattering, and the results obtained for the seed and the core-shell particles (ST 1 in Table I and CS

1 in Table II) were in fair agreement with the sizes determined by TEM.

The ST/EA core-shell particles were further stabilized by a nonionic surfactant before grafting by transesterification. In Figure 1(c) (TR 3 in Table I), a TEM micrograph of the modified latex is shown, and it is clear that the grafting process did not impart any appreciable agglomeration. The particle-size distribution calculated from the TEM micrographs given in Figure 2(c), as well as the distribution obtained by dynamic light scattering (Table II), indicate that the grafting process neither affected the original particle size distribution nor the average particle diameters.

In Figure 1(d), a TEM micrograph of the reactive latex particles prepared through copolymerization of EA and the ABDA monomer in the second stage is shown (AB 1 in Table I). Also, in this case, the particles display a core-shell morphology. As previously reported, late addition of the ABDA monomer in the preparation of conventional copolymer particles resulted in a broad particle-size distribution, most probably due to new particle formation.³ From the particle-size distribution calculated from the TEM micrographs in Figure 2(d), it can be concluded that no new particles were formed during the second-stage polymerization, and this fact was also evident from the narrow distribution determined by quasi-elastic light scattering (Table II).

Acetal-reactive particles were also prepared by allowing latex particles having a thin shell of GMA to react with ABAA. Also, in this grafting reaction, a relatively narrow particle-size distribution was obtained, as shown in Table II. It can be noted that the particle-size distributions for all latex samples were measured after 6 months in order to check the dispersion stability. No changes were observed, as also can be seen in Table II.

Detection of Acetal Functional Groups

The reactivity of the latex particles depends on the number of reactive acetal groups at the surface. Because of the method of preparation, the acetal groups may be distributed throughout the second-stage polymer, but since this phase comprises only 30% of the total weight of the particles, most of the acetal functional groups should be close to the surface and be accessible for later curing reactions.

In Table II is presented an estimation of the total number of acetal functional groups present in the particles, on a weight basis. The surface reactivity is expressed as the number of acetal functional groups per surface area of the particles, calculated

from the average particle diameters under the assumption of monodisperse samples and a density corresponding to polystyrene for the particles. The functional groups were determined by elemental analysis for nitrogen and through hydrolysis of acetal groups.

Elemental Analysis

Samples TR 1 and TR 2 were functionalized by transesterification performed at 80°C for 8 h. The nitrogen analyses given in Table II show that poor grafting yields were obtained. By increasing the temperature and the reaction time (95°C for 16 h), the grafting yields increased significantly (samples TR 3 and TR 4). It can be noted that the grafting densities obtained for the core-shell particles were higher than those previously reported for the copolymer particles. This can be explained by the increased number of ester groups available for transesterification reactions present at the surface of the core-shell particles as compared to the copolymer particles.

Samples AB 1 and AB 2 in Table II were prepared by using an acrylic acetal functional monomer (ABDA) as a comonomer to EA in the second-stage polymerization. Compared to the corresponding copolymer particles, the number of reactive groups is relatively high in the core-shell particles, but low in comparison to the transesterified particles.

Epoxy groups originating from GMA present at the particle surfaces were used as reactive sites in the preparation of samples GMA 1 and GMA 2. Grafting densities more or less at the same level as for the previously reported copolymer particles were obtained.

Acetal Hydrolysis

Determination of methyl acetal groups present at the particle surfaces using base hydrolysis and GC analysis was performed for selected samples, as shown in Table II. To check the reproducibility of the analysis, the seed latex was hydrolyzed with a known amount of ABDA monomer added. An estimation of the number of surface acetal functional groups on the particles was obtained under the assumptions previously mentioned. One diacetal functional group corresponds to one nitrogen atom (elemental analysis) and yields two molecules of methanol when hydrolyzed. The results from the acetal determinations given in Table II were found to agree well with the nitrogen analyses.

Crosslinking of Surface Coatings

The crosslinking ability of the acetal-reactive core-shell particles was estimated using an acid-curing aqueous emulsion binder system containing poly(vinyl alcohol). Binder formulations in which different types of reactive core-shell latexes were substituted for the melamine/urea resin were prepared as shown in Table III. As a comparison, a sample containing nongrafted core-shell particles with no crosslinking ability was tested, and a conventional acid curing melamine/urea binder was used as a reference.

The crosslinking of the binders was measured as pendulum hardness vs. time. The nongrafted ST/EA core-shell particles developed a pendulum hardness of 94–109 s after 24 h, depending on the curing temperature. Results from the pendulum hardness measurements are presented in Table IV. The reactive latex particles prepared by transesterification as well as by epoxy group reactions showed an increase in the pendulum hardness of 30–60%, as compared to the nonreactive core-shell latex. These results clearly indicate that reactive acetal-functional groups are present at the surface and available for crosslinking. It is also evident from the results that these two latex systems (TR 3 and GMA 1) after curing give coatings comparable in hardness to the conventional acid-curing melamine/urea reference sample.

The sample prepared from the core-shell particles having ABDA as a comonomer in the shell showed only an increase in hardness of about 10% relative to the nonreactive particles. The reason for this may be the low functional group density on these particles.

CONCLUSIONS

Process parameters have been defined for the preparation core-shell particles consisting of a polystyrene core (70 wt %) and an EA shell (30 wt %) by a seeded batch-emulsion polymerization. Reactive diacetal groups can be introduced in the particle surface by reacting the poly(EA) shell with ABAA in a transesterification reaction. Acetal functional particles can also be prepared by allowing the amino-acetal reagent to react with latex particles containing surface-bound epoxy groups.

Another method to prepare acetal-functional core-shell particles is based on emulsion polymerization, using ABAA as a comonomer in the second step in a seeded emulsion polymerization. The use

of ABAA in transesterification or reaction with surface-bound epoxy groups are the preferred grafting methods, giving high numbers of reactive groups per particle. As compared to similar homogeneous copolymer particles, the reactive core-shell particles gave higher grafting densities, and their crosslinking abilities were greater than those of the reactive copolymer particles when used as curing agents in an acid-curing aqueous surface-coating model system containing poly(vinyl alcohol).

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