Surface Reactive Acetal Functional Waterborne Microparticles

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SYNOPSIS

Small particles have been prepared by means of emulsion polymerization from styrene and ethyl acrylate, using different concentrations of emulsifier. The particle size can be controlled in the range of 45–85 nm. The particle surface was modified by introducing an acetal functionality, suitable for acid catalyzed processes. Surface functionalization was performed in two principally different ways. First, by using an acrylic monomer with acetal functionalities in the polymerization step and, second, by means of a surface grafting technique, using nonacrylic monomers. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Microgels are referred to as spherical polymer particles with submicroscopic sizes forming colloidal solutions.[1] Their sizes compare with the coil diameter of linear macromolecules. The particles are given a stable, three-dimensional structure, by means of controlled crosslinking in the polymerization process and, due to this fact, the mobility of chain segments is more restricted than for conventional macromolecules in solution. Consequently, microgels can be considered as intermediates between large macromolecules and small particles, having properties characteristic of each.

The viscosity of solutions of linear macromolecules is increased severely by the expanded conformation, due to swelling in good solvents. Solution viscosity of microgels, however, is considerably lower, since they behave as rigid balls that obey the Einstein law of viscosity. Consequently, microgels can be used for reduction of viscosity in polymer solutions, and hence improve fluidity and solid content of, for instance, solvent-based paint systems. An important characteristic of microgels is their small size. Since they are small, microgels have large surface areas and small steric hindrance and thus can interact strongly with a polymeric binder.[2]

A new generation of microgels are the reactive microgels, which have surface bound functional groups available for subsequent crosslinking reactions.[3,4] Incorporation of reactive microgels in curable paint systems seems promising, however, literature on this topic is scarce.

This article deals with reactive microgels dissolved in water. Since water does not swell the particles in question, the internal crosslinking is not critical. The microgels, described in this article, consist of particles made up of more or less linear polymer chains and, hence, will be referred to in the following as microparticles. Emulsion polymerization is a suitable method for preparing spherical polymer particles in water solution. The combination of emulsifier, initiator, monomer types, and process parameters controls the particle size and distribution. This article describes the method that was developed in order to control the preparation of well-defined microparticles with a particle size of 55 nm. As a surfactant, sodium dodecyl sulfate (SDS) was used, since it has a low critical micelle concentration (cmc) and is a well adsorbing surfactant. Surfactants with a low cmc are much more effective in producing small particles at the lowest possible concentration.[5]

Further, this article describes two principally different ways of introducing surface reactive acetal groups on the microparticle surface: first, in the emulsion polymerization step, by using an acrylic monomer with the desired functionality and second, by means of surface grafting methods, using non-

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acrylic molecules with the desired functionality. The functionality in question is a diacetal, which recently has proved to undergo acid catalyzed crosslinking at ambient temperatures.[6,7,8] This article presents, for the first time, microparticles with this type of reactive functionality.

EXPERIMENTAL

Reagents

The following reagents were used: styrene (ST, Merck), ethyl acrylate (EA, Merck), acrylamido butyraldehyde dimethyl acetal (ABDA, Air Products and Chemicals, Inc.), 4-aminobutyraldehyde dimethyl acetal (ABAA, Air Products and Chemicals, Inc.), lactic acid titanate chelat catalyst (Tyzor LA, DuPont), sodium dodecyl sulfate (SDS, Janssen), potassium peroxidisulphate (KPS, Merck), sodium hydroxide (NaOH, Eka Nobel), glycidyl acrylate (GA, Aldrich), and glycidyl methacrylate (GMA, Aldrich). When needed, the monomers were purified by letting them pass through a column filled with aluminum oxide (Merck). The monomers were kept at 8°C before use. The water used was deionized and distilled. Other chemicals were of analytical grade and were used as supplied.

Preparation of Microparticles

The polymerizations were carried out batchwise in a calorimetric reactor, which allowed close monitoring of the reactions.[9] A batch process was used to produce particles consisting 70 wt % ST and 30 wt % EA in aqueous media. To 100 mL of water, 21 g ST, 9 g EA, and one pellet of NaOH were added. SDS was used as surfactant. The reactor was repeatedly degassed and was purged with nitrogen. One g of KPS was dissolved in 25 mL water. When the temperature equilibrium at 60°C was reached, 2.5 mL of initiator solution was added.

The particle diameter was controlled in the range of 45 to 85 nm by changing the concentration of the surfactant, while the initiator concentration (KPS) was kept constant. This can be seen in Figure 1, where the effect of the surfactant concentration, based on the water phase, is plotted against the particle diameter, which was measured by quasielastic light scattering. From this study, the conditions for producing model latexes, with a particle size of 55 nm, $\sigma <$ 10 nm, were obtained when using a surfactant concentration of 0.069 M.
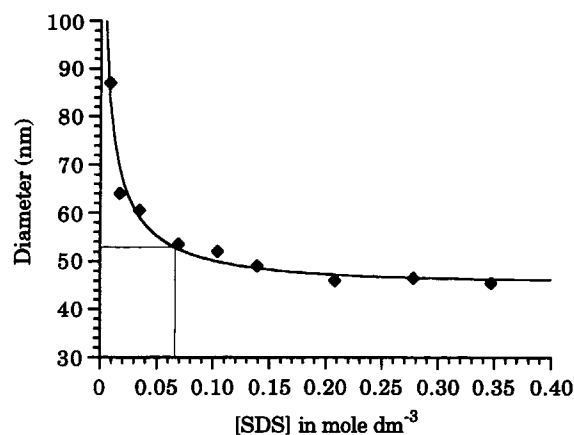

Figure 1 SDS-concentration, based on the water-phase, plotted against the particlediameter, $\sigma \pm$ 10 nm.

Surface Modification

Surface Modification Using an Acrylic Acetal Functional Monomer

The polymerizations were carried out in the calorimetric reactor as previously described. Microparticles were prepared as described above and, when the polymerization entered the termination stage, 1 g of ABDA was added. The reaction scheme is shown in Figure 2(a).

Surface Grafting by Transesterification

Microparticles were prepared as described previously. When needed, the pH was adjusted to a neutral condition. For surface grafting, 300 mL polymer dispersion, 100 mL water, 10 g ABAA, and 10 g catalyst were used. The temperature was kept at 80°C for 8 h. Nitrogen was continuously added. Experiments were also performed at 95°C for 16 h. The reaction scheme is shown in Figure 2(b).

Surface Grafting by Epoxy Group Reactions

Microparticles were prepared as described previously. When needed, the pH was adjusted to a neutral condition. When the polymerization entered the termination stage, 3 g GA and 3 g GMA, respectively, were added. A delayed addition of GA and GMA was used in order to obtain more epoxy groups at the surface of the particles available for grafting.[10]

The grafting operation was carried out in the calorimetric reactor by adding 3.3 g ABAA after the polymerization at a temperature of 60°C. The reaction scheme is shown in Figure 2(c).
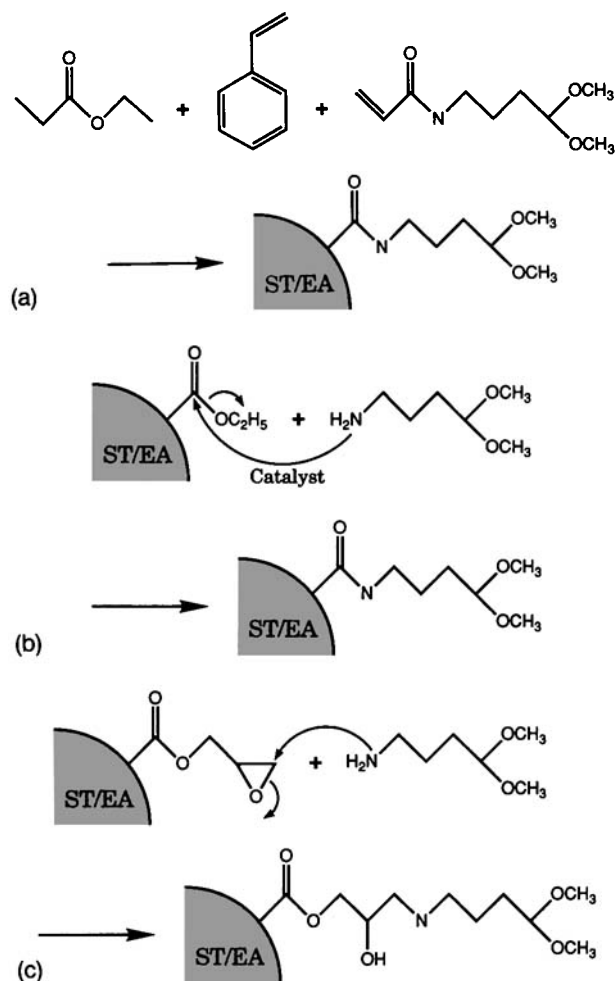
Figure 2 (a) Surface modification, using an acrylic acetal functional monomer, (b) surface grafting by transesterification, and (c) surface grafting by epoxy group reactions.

Ultrafiltration and Dialysis

All samples of reactive microparticles were thoroughly cleaned by dialysis for 14 days. The latexes were purified through dialysis in order to eliminate the grafting chemicals. When using the dialysis tubing (molecular cut 6000–8000), deionized water, with the same SDS concentration as the latexes, was changed daily.

Quasielastic Light Scattering

All systems were measured by quasielastic light scattering (QLS), by using a Coulter N4 submicron particle size analyzer. In order to check dispersion stability, the measurements were carried out after 3 days and 6 months. The results are presented in Table I.

Electron Microscopy

Selected samples were measured by transmission electron microscopy (TEM) after 6 months, by using a JEOL 100U transmission electron microscope on the samples, which can survive the electron beam. The measurements were carried out in order to elucidate the particle association and particle distribution. The pictures are shown in Figures 3(a–c), and the histograms of the particle size distribution are shown in Figure 4(a–c).

Detection of Acetal Functional Groups

Microanalytical elemental analysis (Perkin–Elmer 240 Elemental Analyzer) gives the weight ratio of nitrogen in the polymer particles. The nitrogen content originates from the acetal functionalized materials.

The content of active methyl acetal groups was measured by means of basic hydrolysis. The mixture is hydrolyzed in a closed teflon reactor at 150°C for 6–8 h, and the deliberated methanol was quantified using gas chromatography.

Crosslinking

The crosslinking ability of the surface grafted particles, for an acid-curing aqueous emulsion binder system, was examined. One reference sample was used, containing a traditional polyvinyl alcohol, hexamethoxy methyl melamine and methylated urea formaldehyde resin. Another formulation was prepared, using the nongrafted microparticles with no crosslinking ability. This was compared with the different types of grafted reactive microparticles with acetal functional groups on the surface able of crosslinking with the polyvinyl alcohol. The formulations used are shown in Table II. As curing agent, a combination of ethanol, paratoluene sulfonic acid, and phosphoric acid was used. The films were applied at a glass plate with a thickness of 120 μm. The plates were placed for 15 min at 23°C for flash off, were dried for 15 min at 60°C, and were cooled at 23°C and 50% relative humidity. The samples were also cured at 23°C and 50% relative humidity. The results, from pendulum hardness measurements, are presented in Table III.

RESULTS AND DISCUSSION

Detection of Acetal Functional Groups
Elemental Analysis

In Table I is presented an estimation of the number of acetal functional groups on the particles and of

Table I   Estimation of Diacetal Functional Groups

Sample	N (μmole/g Polymer)	MeOH (μmole/g Polymer)	D_{LSI}[a] (nm) 3 Days (sdev ± 10 nm)	6 Months (sdev ± 10 nm)	Diacetal (Func. Gr./Particle)	Diacetal (Func. Gr./nm 2)
0[b]	0		56	55	0	0
0[b]		0	56	55	0	0
1.1[c]	186		58[h]	56[h]	11,900	1.1
1.1[c]		324	58[h]	56[h]	10,400	0.98
1.2[c]	150		60[h]	58[h]	10,700	0.94
1.2[c]		262	60[h]	58[h]	9300	0.82
1.3[c]	121		56[h]	58[h]	7000	0.71
2.1[d]	64		56	59	3700	0.38
2.2[d]	114		58	62	7300	0.69
2.3[e]	450		58	64	28,800	2.7
2.3[e]		806	58	64	22,000	2.3
2.4[e]	457		55	58	24,900	2.6
2.4[e]		825	55	58	26,400	2.5
3.1 A[f]	493		62[i]	Sediment	38,500	3.2
3.2 A[f]	507		65[i]	Sediment	45,600	3.4
3.3 B[g]	457		64	65	39,300	3.1
3.3 B[g]		717	64	65	30,800	2.4
3.4 B[g]	443		67	64	43,700	3.1
3.4 B[g]		803	67	64	39,600	2.8

[a] LSI = Light scattering intensity.
[b] Seed containing microparticles of 70 wt % ST/30 wt % EA.
[c] Surface grafting, using an acrylic acetal functional monomer and the same reaction parameters.
[d] Surface grafting, using transesterification 80°C/8 h.
[e] Surface grafting, using transesterification 95°C/16 h.
[f] Surface grafting, using epoxy group reaction, as monomer GA is used.
[g] Surface grafting, using epoxy group reaction, as monomer GMA is used.
[h] Standard deviation ± 20 nm.
[i] Standard deviation ± 30 nm.

acetal functional groups/nm^2. The assumptions are: monodisperse samples with the mean diameter, measured after 3 days, and density of polystyrene for the particles.

Samples 1.1–1.3 were functionalized using an acrylic acetal functional monomer and the same reaction conditions. It can be noted that a broad particle size distribution is obtained in Figure 4(c). The standard deviation from the QLS, in Table I, is also large. This might be explained by the formation of homopolymer particles, but this will be further discussed.

Samples 2.1–2.2 were functionalized by surface grafting using transesterification. Grafting was performed at 80°C for 8 h. The results, from the elemental analysis, show poor yield. Samples 2.3–2.4 were grafted at 95°C for 16 h and produced a much better yield.

Samples 3.1–3.2A were grafted, using epoxy group reactions, where the epoxy groups originate from glycidyl acrylate (GA). Samples 3.3–3.4 B were grafted using epoxy group reactions, where the epoxy groups originate from glycidyl methacrylate (GMA). The high reactivity of epoxy groups is probably the explanation of the good yields obtained. The standard deviation from the QLS, shown in Table I, is much larger when using GA than when using GMA.

Hydrolysis

Detection of the methyl acetal groups on the surface of the particle, using basic hydrolysis and GC analysis, was performed for selected samples. The results are shown in Table I. To check the reproducibility of the analysis, the seed was hydrolyzed with an added amount of ABAA. There is a good resemblance using this method. An estimation of the number of surface acetal functional groups on the particles, and of acetal functional groups/nm^2, were obtained, based on the previously mentioned assumptions. One diacetal functional group contains one nitrogen atom (elemantal analysis) and yields
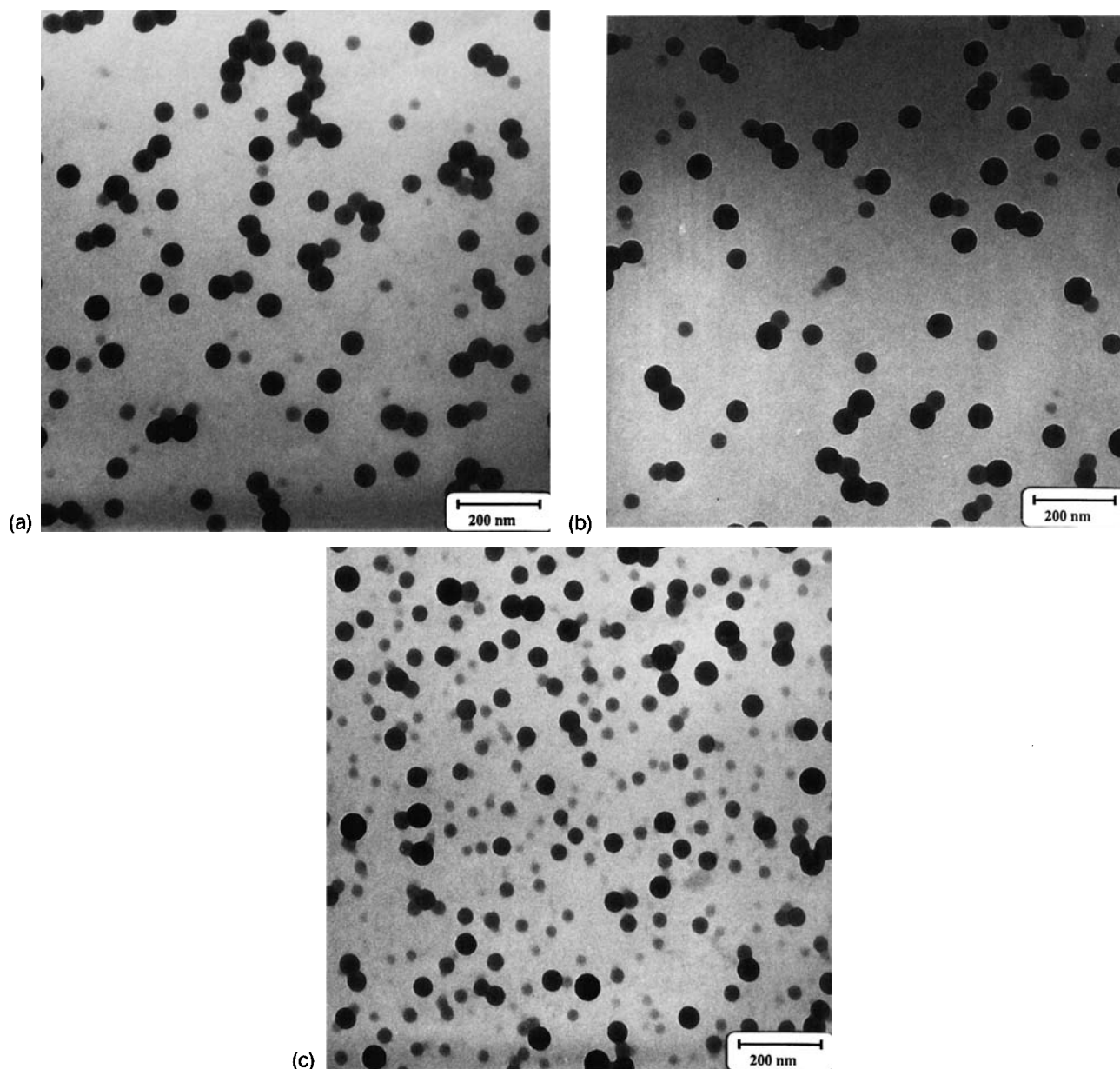
Figure 3 (a) Seed consisting of ST/EA-copolymer, (b) surface grafting by transesterfication, and (c) surface modification, using an acrylic acetal functional monomer.

two methanol molecules when hydrolyzed. This can be seen in Table I. The advantage of using hydrolysis is that the functional groups, present at the surface of the microparticle, thus available for hydrolysis, and hence for subsequent crosslinking, are measured. It could be expected that the functional groups/nm^2 would be less, based on hydrolysis than based on elemental analysis, since the latter analysis yields the total amount of acetal functional groups.

Pendulum Hardness

The acid curing crosslinking ability of the surface grafted particles, as compared with the seed, was measured. As a reference sample, a conventional acid curing melamin and a urea binder was used. The seed had a pendulum hardness of about 100–130 seconds (s), depending on the curing temperature after 24 h. The cured ABDA-sample showed no increased hardness. This can be understood in terms of homopolymer particle formation, which can be seen from the TEM-photograph in Figure 4(c). The samples, grafted by transesterification and epoxy group reactions, showed an increased hardness of about 30–60% as compared with the seed. The result indicates that there are reactive acetal functional groups present at the surface available for subse-
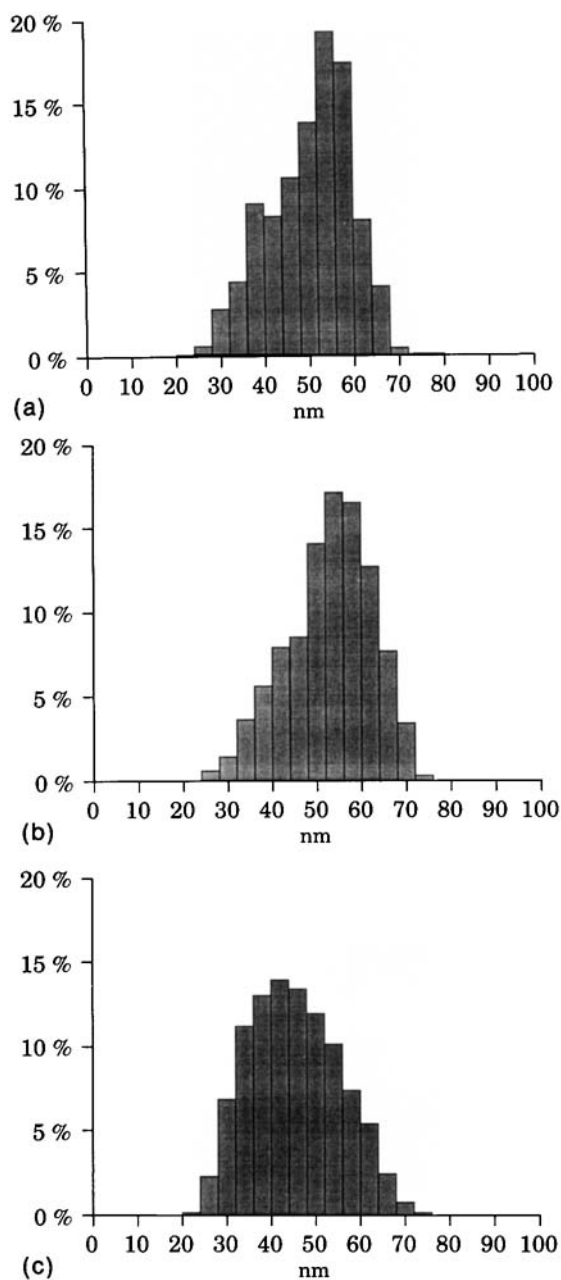
Figure 4 (a) Particle size distribution for seed consisting of ST/EA-copolymer. D_n = 50.3 nm; D_w = 53.5 nm; σ = 9.3 nm; PDI = 1.09, (b) particle size distribution after surface grafting by transesterification. D_n = 52.8 nm; D_w = 56.0 nm; σ = 9.5 nm; PDI = 1.09, and (c) particle size distribution for surface modification using an acrylic acetal functional monomer. D_n = 45.3 nm; D_w = 49.7 nm; σ = 19.1 nm; PDI = 1.14.

quent crosslinking. These two systems are comparable in hardness after curing with the reference sample. Two measurements were made for each sample.

Characterization

Quasielastic Light Scattering

The reactive microparticles were measured by light scattering 3 days after preparation. The samples were measured after 6 months, as well to check the dispersion stability. These results can be seen in Table I.

For samples 1.1–1.3, a broad particle size distribution is obtained by comparing the grafted particles with the seed. This might be explained by the formation of ABDA homopolymer particles.

For samples 2.1–2.4, a narrow particle size distribution was obtained, as was obtained for the seed, indicating that the grafting process does not affect the particle size distribution. The dispersions also showed good stability after 6 months.

The samples 3.1–3.2A, containing GA, showed an increased particle diameter and a very broad particle size distribution. After 6 months, the dispersions had sedimented. This was not the case with GMA (3.3–3.4B). From the results obtained in this work, delayed addition of GMA seems to work well in contrast to the case with GA. This might be explained by the higher water solubility of GA as compared with GMA. Work has been done by Magnet et al.[10] with delayed addition of GMA to a system of butyl acrylate and styrene in order to obtain particles with epoxy groups at the surface.

Transmission Electron Microscopy

For selected samples, TEM-photographs were taken. In Figure 3 (a) the ST/EA copolymer seed can be studied. The seed was used for surface grafting by transesterification, which can be seen in Figure 3(b). Functionalization, using an acrylic acetal functional monomer, can be seen in Figure 3(c). This TEM-photograph shows that it is likely that new particles are formed when the monomer is added at the termination stage.

The particle diameters were measured from the TEM-photograph and histograms of the particle size distributions were made from these data, which can be seen in Figure 4(a–c). From these results, the number average (D_n) and weight average (D_w) are calculated. The polydispersity index (PDI) was calculated as the weight average to number average ratio. It can be seen that there is almost no change in particle size and distribution, comparing the seed Figure 4(a) and the particles grafted by transesterification in Figure 4(b). Particles, grafted using an acrylic acetal functional monomer, are shown in

Table II   Recipes Used for Formulating an Acid Curing Aqueous Emulsion Binder System

	Reference Sample (g)	Microparticle (g)	Reactive Microparticle (g)
Ethanol 96%	40	40	40
Water	110	110	110
Polyvinyl alcohol in water	50	50	50
Methylated urea-formaldehyde resin	40	20	20
Microparticle		25	
Reactive microparticle			25
Hexamethoxymethylmelamine	10	5	5

Figure 4(c). It can be noted that the particle size distribution is broad. The same result is obtained from the light scattering results. The PDI is broad and the average particle diameter is small as compared with the seed. This indicates that homopolymer particles are formed when ABDA-monomer is added at the termination stage.

CONCLUSIONS

The process parameters for the emulsion polymerization of styrene (70 wt %) and ethyl acrylate (30 wt %) microparticles, with the size of 55 nm, have been defined.

The surface activity, consisting of a diacetal functionality, has been introduced by two principally different methods. The first method is based on emulsion polymerization, using acrylamido butyraldehyde dimethyl acetal. The second method is based on surface grafting, using 4-aminobutyraldehyde dimethyl acetal, where the amino group performs the coupling functionality to the particle surface. The amino group has been reacted with the surface by two different means: First, by reacting with an epoxy group incorporated during the microparticle preparation and second, by transesterification involving the amino group and the ethyl ester group. In particular, the latter process is difficult to perform in a water environment. However, the use of lactic acid titanate chelate catalyst yields good results. The acetal functionality remains unaffected by the surface activating process.

The resulting reactive microparticles, made from the two, in principle, different methods, differ as far as particle size and distribution are concerned. There is a strong tendency that the emulsion polymerization method affects the desired particle size giving, for instance, homopolymers of the functionalized acrylic monomer. The grafting process, however, does not affect the particle size distribution after the distribution has been obtained.

The reactive microparticle acts as curing agent with a polyvinyl alcohol binder in an aqueous formulation.

Table III   Pendulum-Hardness, Measured after 24 h

Curing Temperature	Reference (s)	Microparticle (s)	Reactive Microparticle		
			ABDA[a] (s)	Transesterification[b] (s)	GMA[c] (s)
23°C	155	98	107	157	163
23°C	154	105	110	153	165
60°C	161	128	119	169	166
60°C	163	132	121	171	164

[a] Surface grafting, using an acrylic acetal functional monomer, ABDA.
[b] Surface grafting, using transesterification.
[c] Surface grafting, using epoxy group reaction, as monomer GMA is used.

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