

# Water-Based Crosslinkable Coatings via Miniemulsion Polymerization of Acrylic Monomers in the Presence of Unsaturated Polyester Resin

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**ABSTRACT:** Hybrid miniemulsion polymerization was performed with a three-component acrylic system of methyl methacrylate, butyl acrylate, and acrylic acid in the presence of a Bayer® Roskydal TPLS2190 unsaturated polyester resin. Latexes were obtained in which the polyester resin was grafted to the acrylic polymer, forming a water-based crosslinkable coating. Grafting between the resinous component and the acrylic polymer is a feature different from the work of others who have attempted to combine the properties of both systems in water-based blends. Both emulsions and latexes were shelf-stable for over 6 months, shear-stable, and resistant to at least one freeze/thaw cycle. Resin-to-monomer ratios were studied as high as 1 : 1 (wt : wt), and total emulsion solids, as high as 45%. Monomer droplet and latex particle sizes were similar, suggesting evidence of the preponderance of droplet nucleation. A high level of crosslinking (>70%) during polymerization was observed in this particular hybrid system in contrast to those involving alkyd or polyurethane resins (<5%). Films, both homogeneous and hard, were achieved with exceptional adhesion. Electron microscopy showed the hybrid particle morphology to have internal domains of polyester resin in an acrylic matrix. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 916–927, 2000

**Key words:** miniemulsion; polyester; acrylic; coatings; graft

## INTRODUCTION

Emulsion and miniemulsion polymerizations have many similarities, but their differences are apparent in particle nucleation and reagent-transport phenomena. Conventional emulsion polymerization (macroemulsion polymerization) is initially composed of a monomer emulsion of relatively large (circa 5–10 microns) monomer droplets and significant free or micellar surfactant.

Particle nucleation takes place early in the reaction via homogeneous (water-phase) polymerization followed by precipitation or via free-radical entry into monomer-swollen micelles. Radicals can enter the monomer droplets, but this phenomenon is generally ignored due to the relatively small droplet interfacial area. Nucleation stops or significantly slows after the surface area of the particles becomes sufficiently large to adsorb all of the surfactant from the micelles. The major locus of polymerization, thereafter, is in the nucleated particles. The monomer must move from the monomer droplets to the particle reaction sites by diffusion.

Miniemulsion polymerization, by contrast, begins with submicron monomer droplets (circa 150–300 nm). High-intensity fluid deformation

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**Table I Hybrid Miniemulsion Polymerization General Recipe**

Ingredients	Recipe Distribution <sup>a</sup>
Methyl methacrylate (MMA)	49% total monomer weight <sup>b</sup>
Butyl acrylate (BA)	50% total monomer weight
Acrylic acid (AA)	1% total monomer weight
Sodium lauryl sulfate (SLS)	0.02 mol/L H <sub>2</sub> O
Potassium persulfate (KPS)	0.02 mol/L H <sub>2</sub> O
Roskydal TPLS 2190 resin	1 : 3, 2 : 3, 1 : 1 (wt resin : wt monomer)

<sup>a</sup> Total emulsion weight 500 grams. DI water as continuous phase.

<sup>b</sup> Monomer + resin weight varied from 25 to 45%.

and a hydrophobe (or cosurfactant) is employed to generate and stabilize these small droplet sizes. No micelles are present in miniemulsions since excess surfactant has been adsorbed onto the large droplet–water interfacial area. Particle nucleation is primarily via droplet penetration<sup>1</sup> and the monomers or comonomers are located at the sites of polymerization. Mass transport, except for the radicals, is not involved.

If it is desired to graft any sort of resin (e.g., polyester) into an acrylic polymer, the resin must be at the site of the reaction. Since most resins of interest are quite water-insoluble, macroemulsion polymerization does not offer significant grafting efficiency as resin conveyance from the droplets to the polymer particles is limited by mass transport. Miniemulsion polymerization, conversely, does not require this transport and so should result in higher grafting efficiencies. Numerous possibilities for new characteristics in coatings products arise when the polymerization process allows for *in situ* grafting of condensation polymers (e.g., polyesters) into an acrylic or other free-radical polymer matrix. Such products could be some of the first hybrid acrylic–polyester coatings available in a water-borne form, free of solvent, that are not blends.

In a recent publication, Sharma<sup>2</sup> proposed a blend of an acrylic resin and a polyester polymer in order to gain the benefits of each system. These blends were prepared in ratios by weight of 10/90–35/65. With 30 wt % solid content, a viscosity was achieved between 40 and 200 cps and it was reported that the polymer blends exhibited superior properties when compared to either system alone. Sharma also suggested that this combination of an acrylic system and polyester system could not be prepared without this blend process. The hybrid miniemulsion work presented here is evidence of another such procedure. An advan-

tage over Sharma's blend system is the incorporation of polyester into each acrylic latex particle prepared via miniemulsion polymerization. This is a result of *in situ* grafting of the acrylic and polyester systems.

The objective of this article was to show that stable water-based latex coatings can be prepared that also have the ability to cure (by crosslinking) in film formation from the presence of an unsaturated resin component. Monomer droplet and latex particle size, emulsion stability, kinetics, particle morphology, film formation, and film properties were all investigated.

## EXPERIMENTAL

### Reagents

Bayer Chemicals (Pittsburgh, PA) supplied the unsaturated polyester resin, Roskydal<sup>®</sup> TPLS 2190. The monomers used were obtained from Aldrich (Milwaukee, WI) and included methyl methacrylate (MMA), butyl acrylate (BA), and acrylic acid (AA). Monomers were first distilled to remove any inhibitors present. The surfactant and initiator used were sodium dodecyl sulfate (SDS) and potassium persulfate (KPS), respectively, both supplied by Aldrich. Hydroxyethylcellulose (HEC), a thickener used in film formation, was also from Aldrich. Hydroquinone, for quenching, was supplied by Fisher (Atlanta, GA) and the water used throughout the work was deionized.

### Miniemulsion Preparation and Polymerization

The recipe for polymerization is shown in Table I. Emulsions were prepared by dispersing the monomer and resin mixture into an SDS–water solution by magnetic stirring. The monomer and

resin mixture was first prepared by stirring the monomers (MMA, BA, and AA) and then dissolving the resin into the solution. Prior to sonication, the emulsion was subjected to mechanical shear by fast magnetic stirring for the duration of 30 min. To prepare the miniemulsion droplet size, the emulsion was then sonicated with a Fisher 300W sonic dismembrator for 30 min at 70% output (210 W).

The miniemulsion was then transferred to a 1000-mL four-neck baffled glass reactor. The reactor was equipped with a condenser, thermometer, mechanical impeller stirrer, and a nitrogen inlet–outlet. Prior to charging the reactor, the system was subjected to a nitrogen purge for 10–15 min. Following the purge, the reactor was charged with the miniemulsion and another 10–15 min was allowed to heat to the reaction temperature. During this time, the droplet size was measured to ensure a miniemulsion size range and to check that Ostwald ripening was not occurring detrimentally. Polymerization was initiated by injecting an aqueous potassium persulfate solution. A half-moon paddle stirrer at around 250–300 rpm provided agitation. Reaction conversion kinetics were followed gravimetrically by sampling the reactor every 5–10 min and quenching the samples with a 1% (wt : wt) aqueous hydroquinone solution. Dry solids analysis was performed by drying a known sample weight in an oven at 70°C overnight. Conversion was based upon solid content after drying.

### Droplet and Particle Size

Dynamic light scattering with a Malvern IIc autosizer was used to measure both droplet and latex particle diameters. Samples for monomer droplet-size measurements were prepared by diluting a miniemulsion sample by adding 2 drops to a 25 g 0.003M SDS solution saturated with MMA. About 2 mL of this solution was placed in a quartz cuvette to be inserted into the Malvern instrument. Samples for latex particle size were prepared by diluting around 100 : 1 (vol : vol) in deionized water. After dilution, the latex samples were subjected to an oven environment for around 1 h to evaporate any unreacted monomer.

### Emulsion Stability

Shelf-life stability was measured by placing around 30 mL of the miniemulsion in a capped glass vial and measuring the time needed for a

cream line to appear. In some cases, a red dye was also added to help distinguish the cream line.

Shear-stability samples were prepared in much the same fashion. The vials were filled, three to five boiling chips were added, and the vials were capped and shaken vigorously for around 5–10 min. Observation was made in reference to any coagulation or separation.

Freeze/thaw stability was measured by subjecting samples to cycles of a frozen environment followed by an ambient one. Capped vials containing samples were put in a freezer at  $-5^{\circ}\text{C}$  for 12 h and then put on the shelf for the same time. This cycle was then repeated until coagulation or separation occurred.

### Latex Particle Morphology

Particle morphology was measured by transmission electron microscopy (TEM). Samples were prepared by first diluting the latex in water to 100 : 1 (vol : vol). Three drops of a 1% osmium tetroxide aqueous solution were then added to 100 mL of the dilution to stain the latex. Osmium tetroxide complexes with double bonds are only present in the polyester resin, thus providing contrast between the acrylic-rich and polyester-rich portions of a particle in a micrograph. The stain was allowed to react for 24 h in the diluted latex before application of one drop of the latex to a 200-mesh nickel TEM grid. The drop was allowed to dry overnight, evaporating the water and letting the polymer deposit onto the grid. The instrument used was a 150 kV Hitachi HF-2000 FE-TEM.

### $^{13}\text{C}$ -Nuclear Magnetic Resonance ( $^{13}\text{C}$ -NMR)

A Bruker AMX 400 spectrometer was used for the  $^{13}\text{C}$ -NMR results. Preparation of samples involved only dissolving the sample into deuterated chloroform ( $\text{CDCl}_3$ ). A delay time of 3 s, a pulse length of  $90^{\circ}$ , and 1000 scans were used. The data were acquired quantitatively using inverse gated decoupling with a long relaxation time while not irradiating during that relaxation. This, in effect, starves any nuclear Overhauser effects (NOE) and allows all nuclei to relax before the next irradiation pulse.

### Solid-state NMR

Solid-state NMR was run in a Bruker X 300, CP MAS  $^{13}\text{C}$  spectrum using spinning side-band suppression by TOSS. Solid samples were first dried

in a vacuum oven overnight and then ground into a powder in a mortar/pestle setup. Ground samples were then tightly packed (100 mg) into a ceramic pan with a cap designed for the high-spin pressure of solid-state NMR.

### Crosslinking from Polymerization

Crosslinking was based on the percentage of polymer mass that remained after exhaustive extraction with various good polymer solvents, that is, the polymer postpolymerization was dried in a vacuum so as not to allow further crosslinking from autooxidation. This polymer was then weighed and extracted into the various solvents for 12+ h per solvent. At the finish of the extraction series, the polymer mass was weighed again. Since crosslinked material by definition does not dissolve into a solvent, the percentage remaining mass was determined to have been crosslinked by polymerization.

### Latex Films

Films were prepared on cleaned flint glass sheets of dimension 4 × 8 in. The latex was first prepared for film drawing by mixing with 5 wt % HEC thickener, generally at 1 part thickener to 20 parts latex. The prepared latex solutions were cast as a film onto the glass with a Baker Coater draw-down.

Ambient formed films were prepared in two ways: The first involved the addition of the thickener, casting onto the glass substrate, and shelving for 24+ h. The second involved adding a small concentration of an organometallic drying agent (mixture of Ca<sup>2+</sup>, Co<sup>2+</sup>, Mg<sup>2+</sup>, and Cr<sup>2+</sup> metals at 6% of total drying agent weight and naphthenate or octoate as the organic). The incorporation of this drying catalyst not only improves the drying efficiency, but it also increases the degree of hardness achieved by films. A heated cure can be employed if room temperature is below the minimum film-forming temperature for a specific emulsion system. This process only deviates from the ambient cure in that the prepared films are placed in an oven until full curing is achieved.

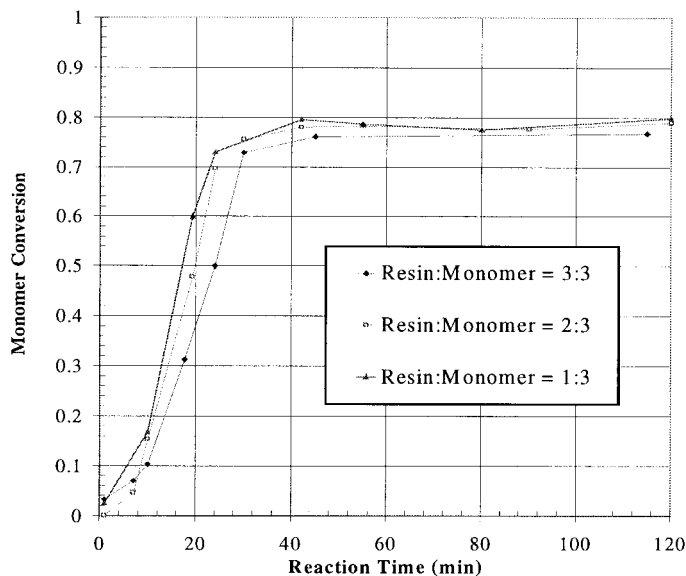
Film properties measured were hardness, adhesion, and homogeneity. Homogeneity is observed in the degree of transparency, pencil hardness by ASTM D 3363-74, and adhesion by ASTM D 3359-78.

## RESULTS AND DISCUSSION

### Kinetics

To study how compatible the hydrophobic resin component was with our miniemulsion system, a series of experiments were performed, varying the ratio of resin weight to total monomer weight. It was predicted that the amount of resin would not have an appreciable effect on the stability of the reaction due to droplet nucleation. Without transport of the reactant mass across the aqueous phase, the stability of the emulsion during polymerization should be more a function of the total emulsion solid content than of what component constituted that mass.

Figure 1 shows the total monomer conversion as a function of time for a standard miniemulsion recipe varying the ratio of the Roskydal TPLS 2190 resin to the monomer. The monomer mixture in these runs was a blend of MMA, BA, and AA in the ratio 49 : 50 : 1 by weight. Both the initiator and surfactant concentrations were 0.02 mol per L aqueous phase in each run and the reaction temperature was 75°C. In Figure 1, it is shown that as the resin-to-monomer ratio was increased the reaction rate decreased. The presence of resin at the polymerization site can be seen as a steric obstacle that each monomer unit must bypass to be able to polymerize onto a growing acrylic chain. Figure 1 illustrates that an increased concentration of resin creates a larger impeding effect on monomer unit transport to the growing polymer chain. This explains why at low-to-moderate monomer conversions a decrease in polymerization rate is observed, yet at higher conversions, a different phenomenon is occurring. Polymerization progressed to approximately 80% conversion (defined as acrylic conversion, on a polyester-free basis) in less than 1 h, then remained fairly constant. Higher levels of resin resulted in lower rates of polymerization and slightly lower limiting conversions. This is thought to be due to the grafting process. Grafting is thought to occur by chain transfer to a polymer at the site of the resin unsaturation. The resulting polyester macroradical is thought to be less reactive than is the acrylic macroradical. At high conversion, chain transfer dominates, slowing the polymerization rate to near zero. Although a slight decrease in limiting conversion is observed with increasing resin content, the excess of resin double bonds makes the polyester macroradical insensitive to polymerization. This is reflected in

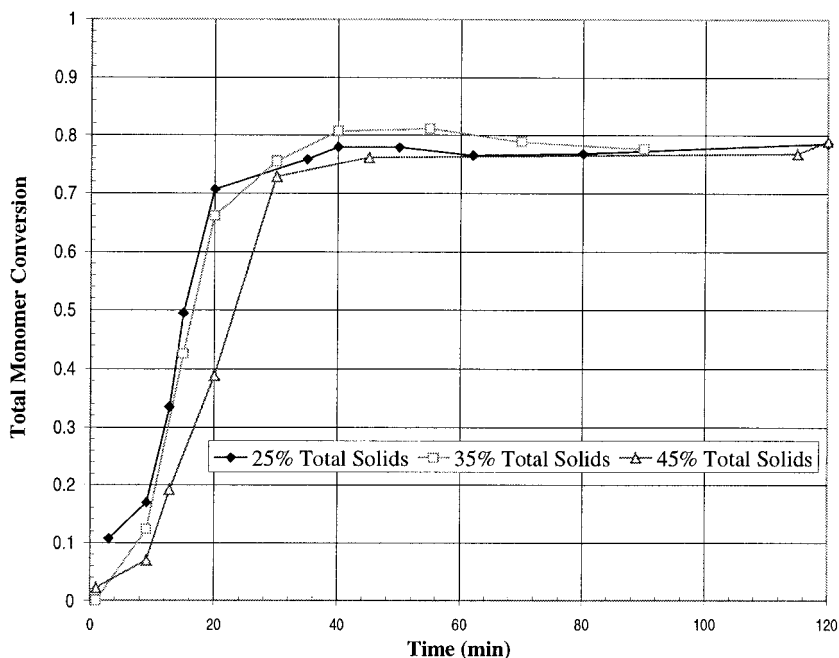


**Figure 1** Kinetics of varying resin-to-monomer solids ratio.

the limiting acrylic conversion value of roughly 80%.

Figure 2 shows conversion profiles for the Roskydal TPLS 2190 polyester resin and MMA/BA/AA acrylic polymerization system for several levels of total emulsion solids. The monomer ratio was held constant at weight fractions of 49 : 50 :

1 of MMA, BA, and AA, respectively. Again, both the initiator and surfactant concentration were at 0.02 mol per L aqueous phase. The ratio of monomer-to-resin was held constant at 1 : 1. Figure 2 shows that successful polymerizations were achieved even when percent total emulsion solids was increased to near 50%. The only purely ki-



**Figure 2** Kinetics of varying total solids content. (monomer : resin ratio held constant at 1 : 1).



netic observation that should be made from these data is that all monomer conversions, regardless of recipe, only reached around 80%. In systems that do not involve resin, full conversion is achieved. Thus, it seems that at over 75% conversion alternate kinetic mechanisms might be favored, limiting the attainable monomer conversion. This is not a function of total solids, yet is present in all reactions. Most likely, chain transfer to resin or chain transfer to polymer mechanisms are occurring at high conversion, *as previously discussed*.

### Droplet Size, Particle Size, and Nucleation

The size of particles in a colloidal system affects chemical, physical, and mechanical aspects of that system. Particle diameter helps determine bulk density and viscosity, both physical characteristics that play determining roles in rheology and latex stability. In emulsion systems, or suspensions and dispersions, these particle diameters become so important as to affect reaction rates and mechanisms, emulsion and latex stability, the formation of coagulum or other forms of agglomeration, polymer solubility, film-formation mechanisms, and film properties such as gloss or opacity.

The crux behind this research is the differing nucleation mechanism from macroemulsion polymerization. The preponderance of miniemulsion nucleation occurs in the monomer droplets themselves,<sup>1,3,4</sup> allowing for the incorporation of highly hydrophobic reactants or components that cannot otherwise be transported across the continuous aqueous phase. This nucleation mechanism, however, is dependent on a size restriction of those monomer droplets. Miniemulsions are constricted to submicron droplet diameters, 50–500 nm, as compared to macroemulsion micron-sized monomer droplets. Since nucleation is in the droplets themselves, the droplet and latex particle diameters should not differ, within statistical levels of uncertainty. Table II shows dynamic light scattering data of the monomer droplet and latex particle diameters. Comparing the droplet diameter to the particle diameter, only very small differences are observed. This lack of diameter change is evidence of droplet nucleation.

The nucleation mechanism can also be inferred from conductivity measurements. Large changes in interfacial area are observed in conventional emulsion polymerization and can be seen in the theory of Harkins<sup>6</sup> or experimentally by monitor-

**Table II Droplet and Particle Diameters as Measured by Dynamic Light Scattering**

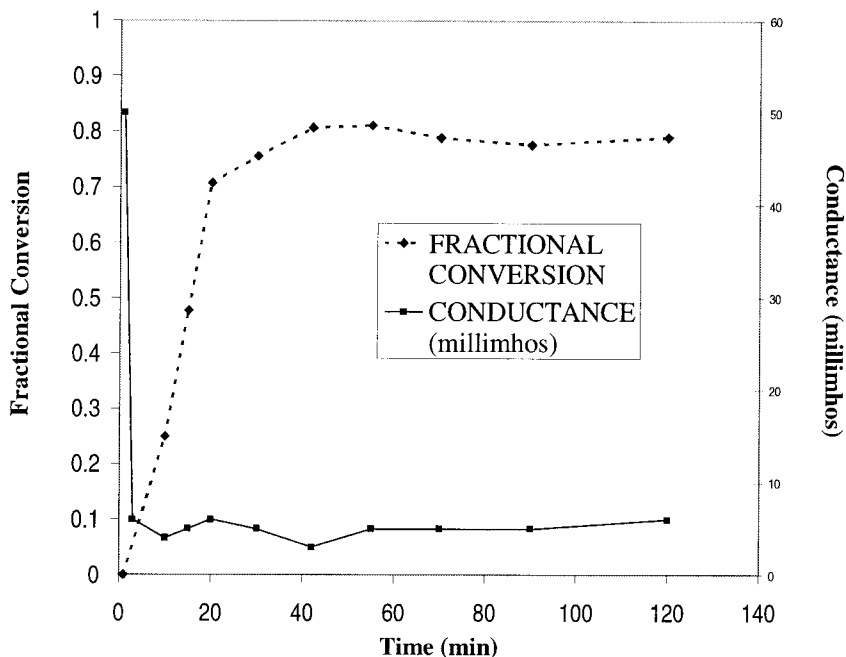
Run Label	Droplet, Particle Size (nm)
TPLS35/17.5-1	175, 162
TPLS35/17.5-2	159, 158
TPLS35/17.5-3	194, 183
TPLS35/17.5-4	142, 151
TPLS35/17.5-6	158, 142
TPLS25/12.5-1	181, 146
TPLS45/18-1	216, 185
Acrylic only	155, 166
Typical macroemulsion	Roughly 1 micron, roughly 200 nm (ref. 9)

Run labels are defined as (Resin)/(total solids)/(resin solids) – run #, where TPLS is the Roskydal TPLS 2190 resin.

ing the conductivity<sup>7</sup> of the continuous phase during polymerization. Reimers and Schork<sup>1</sup> demonstrated that the conductivity does not change during miniemulsion polymerization. The conductivity of this hybrid miniemulsion polymerization was measured to ensure that the hybrid system did not behave differently than did conventional miniemulsion polymerization. Figure 3 shows the conductivity and monomer conversion through the reaction progression. The initial surge in conductivity is due to the charge of initiator into the vortex of the reactor and, hence, a high electrolytic concentration near the conductivity probe. Rapid mixing and distribution of the initiator reduces the false sense of high ionic concentration near the probe. The lower, and more true, concentration of ions is then reflected in the conductivity reading, after which the reading does not noticeably change versus reaction time. This lack of change in conductivity, corresponding to a lack of change in interfacial area of droplets, is then indicative of droplet nucleation in these hybrid miniemulsion systems similar to conventional miniemulsions.

### Elimination of Conventional Hydrophobe

The hybrid miniemulsion system also allows for the elimination of the conventional hydrophobe, hexadecane, which is considered a volatile organic compound (VOC). Instability evolves when a monomer attempts to diffuse out of the small droplets (referred to as Ostwald ripening<sup>8</sup>), thus reducing the internal pressure and lowering the



**Figure 3** Conductivity of hybrid miniemulsion during reaction progression.

surface area-to-volume ratio of the droplet. Smaller droplets have a higher chemical potential than that of larger ones; therefore, the energy of the system is minimized when a monomer diffuses out to increase the droplet size. Ugelstad et al.<sup>4</sup> (1973) reported the use of hexadecane or cetyl alcohol and later Reimers and Schork<sup>1</sup> (1996) used a small amount of a PMMA polymer to stabilize the small droplets. Hexadecane and cetyl alcohol are considered VOCs because they do not react with the polymerization reactants and thus must leave the film either upon drying or gradually over time after application. This later case can be detrimental to film properties, causing wrinkles, cracks, or nonhomogeneity in film adhesion over the surface. All results reported in this article have omitted hexadecane from the reaction recipes. It is believed, with this hybrid

work, that the hydrophobic resin performs the same function as does a conventional hydrophobe.

Table III shows that the monomer droplet size, without hexadecane present, did not increase during the 10-min time that followed sonication to the initiation of polymerization. Thus, the resinous component must perform the same function as a hydrophobe, stabilizing the small monomer droplets against Ostwald ripening. This is significant because the resin is included in the final polymer product, providing some of the properties of the product, and is in no way considered a VOC.

### Stability

Varying resin solids was not found to noticeably influence the emulsion shelf stability in a detrimental manner. In fact, the resin itself is postu-

**Table III** Run TPLS 35/17.5-1. 35% Total Emulsion Solids, Half of Which is Composed of Resin Weight

Monomer Droplet Measurement	Malvern % Merit	Number Average (nm)	Z Average (nm)	Standard Deviation
Before initiation	6.4	187.9	182.2	46.7
After initiation	61.3	161.8	180.8	30.4

Conventional hydrophobe eliminated.

**Table IV Stability Results**

Run Label	Type of Experiment	Emulsion Shelf-stability Duration	Shear-stable	Max # Freeze/Thaw Cycles Without Coagulation
TPLS35/17.5-1	Original system	>5 months	Yes	2
TPLS35/17.5-2	Higher BA percentage	>5 months	Yes	2
TPLS35/17.5-3	Methacrylic acid substituted for AA	>5 months	Yes	2
TPLS35/17.5-4	AA increased to 4%	>5 months	Yes	2
TPLS35/17.5-6	Higher BA percentage	>5 months	Yes	2
TPLS25/12.5-1	Low solids	>5 months	Yes	2
TPLS45/18-1	High solids	>5 months	Yes	1
Acrylic only miniemulsion	No resin present	1–3 months	Yes	1
Typical macroemulsion	No sonication	12 h or less	No	Not measured

lated to act as a cosurfactant as described earlier. All polymerized latex samples prepared by hybrid miniemulsion polymerization in the presence of polyester Roskydal TPLS 2190 were shelf-stable for the duration of research. Polymerized latex stability is mainly a function of particle size and polymer density, so it seems these properties were suitable to arrest the latex from creaming in shelf tests as all samples were found to be shelf-stable. Table IV shows results of the shelf life along with shear and freeze/thaw stability test results.

All hybrid miniemulsions were shear-stable, yet no system lasted more than two freeze/thaw cycles. In most documented cases, without the addition of poststabilizers, miniemulsions only last one freeze/thaw cycle. During the freezing stage, ice crystals form in the aqueous phase effectively, increasing the ionic concentration of that phase. This tends to break down the electrostatic double layer with ionic emulsifiers and leads to coagulation or phase separation. The fact that the hybrid systems, in some cases, lasted an extra cycle suggests that the resinous component played a role in stabilization.

### Latex Particle Morphology

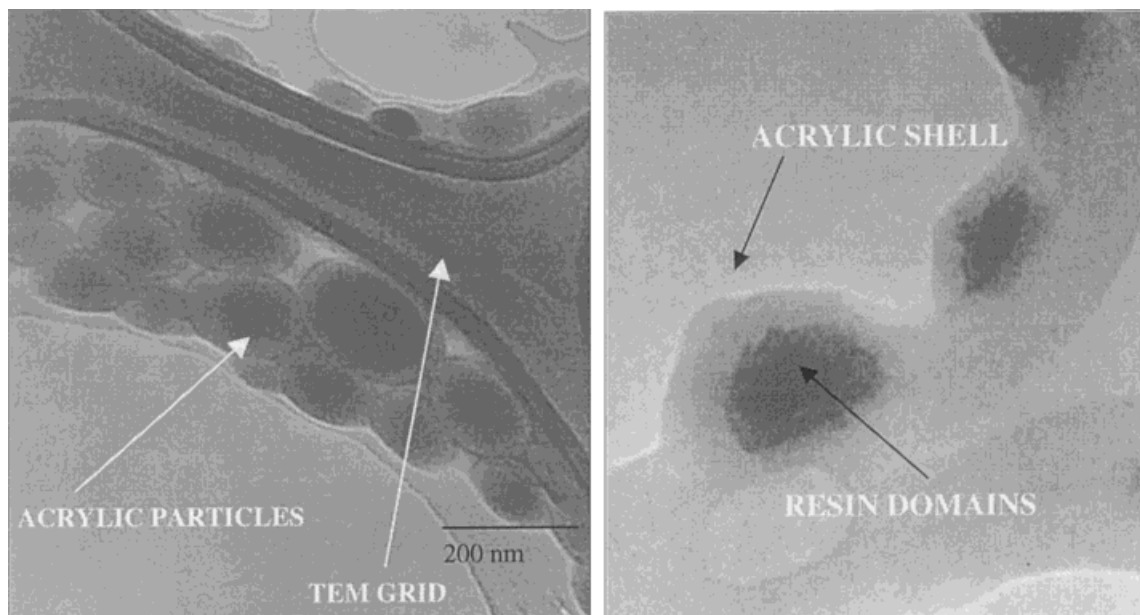
Further characterization of the polymer particle can be seen in the particle morphology. Morphology is determined by electron microscopy. This technique not only provides a means to measure particle size and size distribution, but also shows details of the surface and internal portions of individual particles. This makes it easy to distin-

guish between two polymer particles of different composition, but similar diameter. Distinguishing between and identifying different types of particles, or finding varying morphology in a single system, is important for understanding how the particles will behave in application. Film formation, for example, is optimized when the particle system is homogeneous. Since the resin is preferentially stained by osmium tetroxide, it is possible to observe resin-rich and acrylic-rich portions of a hybrid latex particle.

Figure 4 shows two TEM micrographs of latex particle systems. The micrograph on the left is of a purely acrylic system prepared by miniemulsion polymerization. No polyester resin is present, thus making a basis morphology to compare to the hybrid system. The micrograph on the right is of a hybrid latex prepared from a weight ratio of roughly 1 : 1 resin-to-acrylic monomer. The resin-rich phase is seen as the dark black shade in the particles, and the acrylic-rich phase, the same shade as in the left micrograph of the pure polyacrylic system.

These resin domains could indicate a variety of things: They could indicate a degree of immiscibility between the acrylic polymer and the polyester. In that case, the polymerization kinetics would have proceeded faster than would have the phase-separation kinetics, leading to resin entrapment in the polymer particle. Another scenario deals with the greater degree of double bonds in the resin versus the monomer during polymerization. If crosslinking during a reaction were to occur to a noticeable degree, the heavily





**Figure 4** TEM micrographs of latex particles. The left micrograph depicts a purely acrylic latex system. The right micrograph shows particles obtained from the TPLS35/17.5-6 hybrid polymerization.

crosslinked resin would have more limited mobility than that of the acrylic polymer. This limited mobility would restrict the resin to its minimum free energy faster than the energy restriction would apply to the acrylic. This could explain resin domains in a more mobile acrylic phase. Further, grafting of the acrylic to the polyester resin could result in a final location of the resin that resembles internal or surface domains in the spherical arrangement of the final polymer particle. Many factors affect particle morphology, and without extensive study, only postulations of reasons can be expected from morphological micrographs.

#### Crosslinking and Grafting During Polymerization

Particle morphology studies have shown that the resin is indeed incorporated into the final polymer particles. This indicates that a level of compatibility exists between the resin and the acrylic system. The goal of this work was to have the polyester resin graft to the acrylic and retain some unsaturation for later curing reactions. For residual double bonds to exist postreaction, the degree of crosslinking during the polymerization should also be minimized.

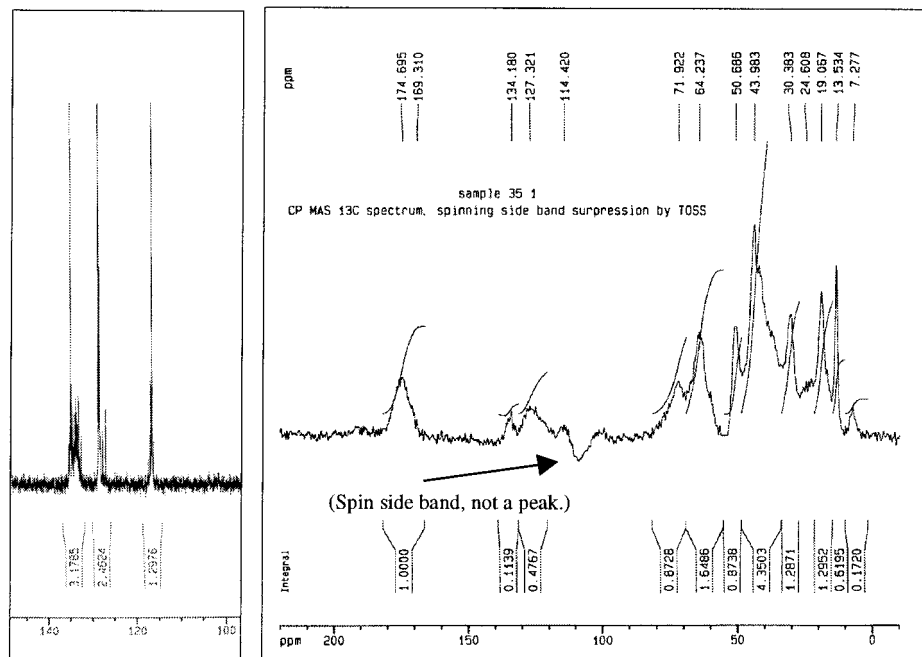
Percent crosslinking during the polymerization can be established by extraction procedures. In

this case, a series of good polymer solvents are selected and the polymer is sequentially extracted into each solvent. By definition, crosslinked material will not dissolve, so the experiment bases its results on the amount of polymer that remains after the series of exhaustive extractions. The mass remaining is assumed to be heavily crosslinked. For Wang's<sup>3</sup> hybrid alkyd/acrylic system, the crosslinking during polymerization was found to be less than 5%. The polyester/acrylic system in this work, however, exhibited crosslinking of over 72%, as seen in Table V. These differences are thought to be due to the location of the resin double bonds. In the alkyd resin, the double bonds are located on unsaturated fatty acid chains pendant from the resin backbone. In the polyester resin, the sites of unsaturation are

**Table V** Crosslinking Results

System	Total Extraction Duration	% Crosslinking
TPLS 35/17.5-1	96h	76.3
TPLS 35/17.5-6	96h	71.9
TPLS 40/18-1	96h	76.5

Percent crosslinking is based on total emulsion solids.



**Figure 5** (Left)  $^{13}\text{C}$ -NMR of olefinic groups in resin alone; (right) complete solid-state NMR spectra of TPLS35/17.5-1.

along the backbone. It is conjectured that the pendant sites are sterically hindered, while backbone sites are not. It is really not surprising that the level of crosslinking in polyesters is high, since polyester coatings are routinely crosslinked by graft copolymerization with acrylic or styrenic monomers.

Solid-state NMR was used to investigate the existence of residual double bonds in the polymerized latex. Here, residual double bonds are defined as those olefinic sites still unused after grafting and crosslinking during polymerization. These bonds are then available for crosslinking during film curing. In the right spectrum of Figure 5, evidence of residual double bonds in the hybrid polymer is clearly seen in the peak cluster of 120–140 ppm. The integrated areas of those olefinic peaks, 120–140 ppm, can be used to quantify the residual double bonds. The original per-

centage of double bonds is determined from the integrated olefinic areas indicated by the left  $^{13}\text{C}$ -NMR solution spectrum of the resin alone, shown in Figure 5. Table VI shows that nearly 10% of the original double bonds are left after polymerization and can be used to cure the polymer in film formation.

Both extraction experiments and micrographs of the particle morphology suggest that a significant degree of both crosslinking and grafting occurred during polymerization. Although the percentage of total mass crosslinked was able to be determined, a quantitative measure of the percentage of double bonds involved in grafting could not be extracted from the available data. It might even be argued that some polyester branches which were originally grafts later reacted with other acrylic chains to become crosslinks in the final polymer.

**Table VI Usage of Polyester Resin Double Bonds During Polymerization**

	TPLS35/17.5-1	TPLS35/17.5-6
% Double bonds converted	90.48	87.07
% Residual double bonds	9.52	12.93
% Total mass crosslinked from polymerization	76.30	71.90

### Film Formation and Properties

The formation of a film from the colloidal dispersion of a latex is the final application of such a system. The hybrid miniemulsion product offers many advantages over existing emulsion products in its versatility of achievable film properties. This is based on the ability to incorporate more components, mostly hydrophobic in nature, along with higher solids systems. Although film properties are easier to tailor with the hybrid system, the complexities of film formation still exist. The hydrophobic resin, polyester in this research, interacts with the acrylic polymerization in different ways depending on the nature of that resin. The degree of unsaturation and location of those unsaturation points in the resin structure influences the mechanisms by which the polymer grafts with the resin and plays a deterministic role in the final surface properties of the polymer particles. The structure and saturation characteristics of the resin can also effect the degree of crosslinking that occurs during the polymerization. All these factors play a role in influencing the adhesive properties of the particles and their ability to be mobile, both important factors in preparing a homogeneous film.

The adhesion of these films attained the highest classification of 5 and pencil hardness gave reasonable values of 2H without the aid of a drying catalyst. The hardness improved to 3H with addition of organometallic drying catalyst, 0.5 wt % of the resin recipe weight, added to the latex emulsion before drawing the film.

To obtain these successful films, several constrictions were found: The most important of these was that no heat should be added. In all cases, added heat during drying would crack and break up the film. The film thickness should also be constricted to 1–3 mil—anything over 3 mil would lead to cracks in the film. Cracking in thick films would even occur when no heat was added. Finally, a concentration of an HEC thickener of at least 5 wt % of the latex emulsion is needed for film homogeneity. Exceptional hardness, adhesion, and homogeneity were obtained when those listed criteria were met.

There are surely several factors that lead to these needed constrictions to form a good film from this hybrid latex system. The high level of crosslinking during polymerization is the most dramatic contribution to these film-formation limitations. Crosslinking limits the mobility of the latex particles during coalescence, making the

residence time of the solvent extremely important in this film-formation system. If the solvent evaporates out of the wet film too quickly, the particles will not have enough time to migrate to each other and crosslink or adhere. The rate at which the solvent leaves the wet latex also affects the volume changes of the system that could lead to the aforementioned cracks in heated films where solvent evaporation is accelerated.

The HEC thickener is needed in this drying system for two reasons: Overall film homogeneity is the first, as the thickener helps keep the latex surface tension from pulling areas of the film during the initial wet application to the substrate. This surface tension effect would distribute the film in a nonuniform manner on the substrate. The second aid of the thickener is in the particle-adhesion process. It has been found that in acrylic latex systems HEC not only increases the aqueous-phase viscosity, but also coats the surface of the polymer particles acting as an associative thickener.<sup>9</sup> HEC has much higher water solubility than that of latex particles and, after adsorbing onto the particle surface, helps bridge the gaps between adjacent particles improving coalescence. HEC may also act as a plasticizer for particles, increasing their mobility by lowering their  $T_g$  and can retard water evaporation, giving particles a longer time to coalesce in film formation.

Successful films made by restricting the film thickness to under 3 mil can also be explained by the low mobility of an already crosslinked polymer. In thicker films, each polymer particle sees many more other particles than substrate adsorption sites. For this reason, adsorption and adhesion upon solvent evaporation is more prominent between adjacent particles and not with the substrate. With this weak substrate interaction, even a homogeneous film would fail in a standard adhesion test. Conversely, with thin films of one or two mil, the relative number of substrate sites used is high compared to particle/particle interfacial interactions (i.e., most binding is with the substrate). The particle's limited mobility due to high crosslinking makes substrate adsorption a lower-energy path process than that involving full bonding coalescence with other particles. This is an explanation of why the crosslinked system with limited residual double bonds could form a successful film. Another improvement with thin films is oxygen diffusion through the film thickness for the curing reactions. Thinner films will have more consistent oxygen transport through-

out the film. Thicker films will encounter some diffusional problems unless crosslinking aids are employed to improve the efficiency of oxygen transport. Thick films also do not dry homogeneously. Although reasonable hardness and adhesive properties were observed in the thin air-dried films, chemical resistance and other potential environmental threats were not tested.

## CONCLUSIONS AND RECOMMENDATIONS

Hybrid miniemulsions were prepared with acrylic monomers and an unsaturated polyester resin. The hydrophobic nature of the resin makes it impossible to be accommodated by traditional emulsion polymerization due to mass-transfer limitations in crossing the aqueous phase to micellar nucleation sites. Miniemulsion polymerization allowed for these two systems (acrylic and polyester) to coexist in the same reaction environment, the acrylic monomers copolymerizing while also grafting to the unsaturated polyester resin. Droplet nucleation, as compared to micellar or homogeneous nucleation, enables highly hydrophobic components to be involved in the latex product since all reagents are originally at the site of polymerization and transport is eliminated.

Results herein showed that the hybrid polyester/acrylic system produced stable latexes with the acrylic and polyester components coexisting in each latex particle. Although a high degree of crosslinking (>70%) was observed during polymerization, residual double bonds were present in the hybrid latex for curing reactions during film formation. The terms "curing" and "latex" traditionally have not been associated with each other, while solvent-free latexes involving condensation polymers also have not previously existed. This work's *in situ* grafting between a polyester resin and acrylic polymer in a nearly zero-VOC environment offers a novel, water-based, crosslinkable latex coating incorporating properties from both water-based and traditionally solvent-based systems.

Kinetic studies showed that as the resin content increased in comparison to the monomer con-

tent the polymerization rate decreased. In a purely acrylic system, complete conversions are typically observed. However, kinetic studies involving the presence of unsaturated resin were found to favor chain-transfer reactions at higher conversions. These chain-transfer reactions, which seemingly inhibit the polymerization, are also what led to grafting.

This article has shown the possibilities of new latex properties that come from the ability to graft condensation polymers to free-radical polymerizing species via miniemulsion polymerization. In this work, the resin used was shown to function as the grafting species while also stabilizing the small droplets against Ostwald ripening. This allowed the recipe omission of a conventional hydrophobe, virtually eliminating VOCs in the process and product. Continuing work involves studying the effect of resin choice on the crosslinking obtained in polymerization and the effect that degree of crosslinking has on morphological and film properties.

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