

Emulsion and Miniemulsion Copolymerization of Acrylic Monomers in the Presence of Alkyd Resin

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SYNOPSIS

Emulsion and miniemulsion copolymerizations were carried out with acrylic monomers (methyl methacrylate, butyl acrylate, and acrylic acid) in the presence of an alkyd resin. Poly(methyl methacrylate) was used as a hydrophobe or cosurfactant in the miniemulsion reactions. The results demonstrate that miniemulsion polymerization is the preferred process, probably because of mass transport limitations of the alkyd in the conventional emulsion polymerization reactions. The monomer emulsions prepared for the miniemulsion reactions were much more stable and the polymerizations were free of coagulum. Reaction rates, particle size characteristics, grafting efficiencies, and some film properties were measured. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Water-based coatings, and polymer latexes in particular, have become more widely used in the past several decades because they are environmentally friendly, offer easier clean up and, last but not least, their properties and application performance characteristics have improved. Solvent-based systems such as alkyd resins have remained important for some applications because of superior properties such as gloss and hardness.

The purpose of this work was to examine the feasibility of polymerizing acrylic monomers in the presence of alkyd resins to determine if this hybrid system could offer the advantages of some alkyd properties in a typical water-based acrylic coating. Experiments were carried out with emulsion and miniemulsion reaction techniques.

All reactions with alkyd were carried out with the resin dissolved in a mixture of three acrylate monomers. The emulsion polymerizations contained a standard emulsifier (sodium laurylsulfate, SLS) and a water-soluble initiator. The miniemulsion reaction also included poly(methyl methacrylate) (PMMA) as a costabilizer, and the emulsion was intensely sheared prior to reaction.

Emulsion and miniemulsion polymerizations have many similarities, but the particle nucleation and reagent transport phenomena are very different. Conventional emulsion polymerization is started with a monomer emulsion comprising relatively large (in the range of 5 μm) monomer droplets and significant free or micellar emulsifier. Particle nucleation takes place early in the reaction via homogeneous (water phase) reactions or via free radical entry into monomer-swollen micelles. Radicals can enter the monomer droplets, but this phenomenon is generally discounted because of the relatively small droplet surface area. Nucleation stops or slows significantly after the surface area of the particles becomes sufficient to adsorb all of the emulsifier. The major locus of polymerization thereafter is in the nucleated particles. The reagents (monomer, chain transfer agents, etc.) must move from the monomer droplets to the reaction sites in the particles. Miniemulsion polymerization, by contrast, begins with submicron droplets that are able to accommodate most of the added emulsifier. High intensity fluid deformation and a hydrophobe (or cosurfactant) are employed to generate and stabilize the small droplet size miniemulsion. Particle nucleation is primarily via droplet penetration; and, if most droplets are nucleated, the reagents are located at the polymerization sites, and mass transport, except for the radicals, is not involved. Either water-

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soluble or oil-soluble initiators can be employed in miniemulsion polymerization.

Transport of large hydrophobic molecules such as alkyd resin can be a problem in conventional emulsion polymerization. Hence, an important goal of this research was to compare the two processes.

EXPERIMENTAL

Materials

Alkyd resin was supplied by McWhorter Technologies as brand Durama 2768 which contains 80% durable medium soya-linseed alkyd and 20% solvents, that is, 6.3% *n*-butyl acetate, 4.4% xylene, 2.9% solvent naphtha (petroleum), 5.2% trimethylbenzene, and 0.9% ethylbenzene. The solvents were removed by vacuum distillation before use. Methyl methacrylate (MMA), butyl acrylate (BA), acrylic acid (AA), potassium persulfate (all from Aldrich), PMMA ($M_w = 100,000$, Polyscience), SLS (Fisher), and benzoyl peroxide (BPO) (Fisher) were used as supplied. The water was deionized.

Emulsion Preparation and Polymerization

Miniemulsion and macroemulsion polymers were produced from the recipes shown in Table I. The miniemulsions were prepared by dispersing the desired amount of monomer-PMMA-alkyd solution (some additional runs contained 0.5 wt % BPO) in the aqueous SLS solution by mixing with a rotating stirrer at room temperature. The resulting emulsion was sheared further by sonification with a Heat Systems 474 W Sonicator Ultrasonic Processor XL for 10 min at 21% output (100 W). The beaker containing the emulsion was immersed in cool water during sonification to maintain constant temperature.

The monomer miniemulsion was transferred to a 1000-mL, four-neck flask equipped with a nitrogen inlet-outlet tube, condenser, and mechanical stirrer. The system was purged with nitrogen for 20 min and heated to 60 or 80°C. Agitation was provided by a paddle stirrer at 500 rpm. The polymerization was started by injection of 20 mL sodium persulfate solution. When BPO was present in the monomer mixture the polymerization started during the heating period. The reaction was followed by gravimetric conversion analysis. Samples were removed by a syringe at different times and injected in a weighing dish containing a 0.5% hydroquinone solution. The samples were dried in an oven at 70°C for 24 h. The emulsion polymerizations were carried out in the

Table I Recipe for Emulsion and Miniemulsion Polymerizations

Sample Code	Ingredients (wt %)				
	MMA	PMMA	BA	AA	Alkyd ^a
EA00	49	0.0	50	1.0	0.0
EA05	49	0.0	50	1.0	5.0
EA100	49	0.0	50	1.0	100
MA00	45	4.0	50	1.0	0.0
MA30	45	4.0	50	1.0	30
MA60	45	4.0	50	1.0	60
MA100	45	4.0	50	1.0	100

EA, emulsion polymerizations and MA, miniemulsion polymerizations. The continuous phase consists of 250 parts water/100 parts total monomer, 0.02 mmol/L water sodium lauryl sulfate, and 0.02 mmol/L water potassium persulfate.

^a The alkyd resin percentage is based on the total monomer weight.

same manner except that no sonication preemulsification process was used and the PMMA hydrophobe was not employed.

Droplet and Particle Size

Monomer droplet and particle sizes were measured by quasielastic light scattering with a Malvern Autosizer IIc. The measurement process for monomer droplets involved dilution of the emulsion with a monomer saturated solution of 0.1% SLS to about 50 : 1. Then 2 mL of this diluted emulsion was put into a quartz cuvette and the droplet diameter, distribution, and standard deviations were recorded in 5 min. The latex particle size was measured in the same way but the dilution was with 0.1% SLS solution to 100 : 1.

Shelf-life Stability

Emulsion and latex shelf life were measured by placing approximately 30 mL of sample in a capped glass vial and observing the time necessary for a visible creaming line to appear. Two drops of a water-soluble red pigment solution were added to each sample to increase the contrast between phases.

Double Bond Content Analysis

The double bond content in alkyd-monomer mixtures and in the alkyd latex were measured by ¹³C-NMR. The copolymer spectra of ¹³C-NMR were obtained with a Varian XL-400 spectrometer operating at 100 MHz. The measurement conditions were 0.1

Table II Monomer Emulsion Shelf Lives and Droplet Size Characteristics

Sample Code	Shelf Life	Size (nm)	Polydispersity Index
MA00	7 h	307	1.054
MA30	> 10 days	91.3	1.016
MA60	> 10 days	175.6	1.017
MA100	> 50 days	260.5	1.004
EA00	2 min		Not tested
EA100	8 min		Not tested

g/mL sample concentration, 20,000-Hz spectral width, 0.4-s acquisition time, 45° flip angle, 1.6-s pulse delay, and 512 scans. Chloroform was used as an internal standard for all NMR spectra.

RESULTS AND DISCUSSION

Shelf Life and Size of Monomer Droplets

A stable miniemulsion must be obtained in order to carry out a successful miniemulsion polymerization. The monomer miniemulsions with PMMA as hydrophobe were prepared with different amounts of alkyd resin. The monomer droplet shelf lives, the droplet sizes, and polydispersities are shown in Table II. The PMMA hydrophobe is effective in the preparation of kinetically stable miniemulsions. Table II shows that the alkyd-acrylate miniemulsions are much more stable than normal emulsions prepared without PMMA. Their shelf life varies from 7 h to more than 50 days. The size of monomer droplets is below 300 nm. Based on the shelf-life and droplet size data, it seems likely that these emulsions are somewhere between kinetically stable systems (shelf life of a few hours) and truly stable miniemulsions (shelf life of a few months). PMMA alone^{1,2} has been shown to form kinetically stable emulsions. The presence of water-insoluble alkyd, in addition to the PMMA, evidently stabilizes the droplets against Ostwald ripening, forming emulsions that are nearly true miniemulsions. Table II also shows that the monomer droplet size increases as the alkyd resin content is increased. The droplet sizes are smaller, however, than the droplets in the miniemulsions that do not contain alkyd.

Figure 1 is a picture of five shelf-life samples after 10 days. The normal emulsion with alkyd separated into three phases: monomer on the top, clear water in the middle, and alkyd resin on the bottom. The miniemulsion without alkyd shows two phases, monomer and water. All miniemulsions with alkyd resin appear to remain uniform.



Figure 1 Monomer emulsions after 10 days. Samples (from left to right): EA100, MA00, MA30, MA60, and MA100.

Alkyd resin is highly hydrophobic and hence not very soluble in the aqueous phase. Monomer droplet instability in emulsion systems can be caused by diffusion of monomer from one droplet to another. The high hydrophobicity of the alkyd decreases the diffusion rate of monomer from the monomer droplets to water, which results in long shelf life for these emulsions. The droplets containing alkyd and/or PMMA are somewhat like the monomer-saturated polymer particles in conventional emulsion polymerization. Hence these droplets should be more stable. This is confirmed by the shelf life and size of the monomer droplets in systems without PMMA (Table III and Fig. 2). If no PMMA is present, the alkyd-acrylate droplets become small, and the shelf life also becomes longer as the alkyd content increases. Very stable miniemulsions can be obtained when the alkyd content is higher than 30%. Comparing Table II with Table III shows that PMMA

Table III Monomer Droplet Shelf Life, Size, and Distribution Without PMMA

Alkyd (%) ^a	Shelf Life	Size (nm)	Polydispersity
1.6	35 min	816.5	1.005
4.0	131 min	459.3	1.008
8.0	160 min	301.9	1.008
24	6 h	163.3	1.009
48	> 42 h	100.3	1.013
80	> 42 h	79.5	1.010

^a Based on the total monomer amount.

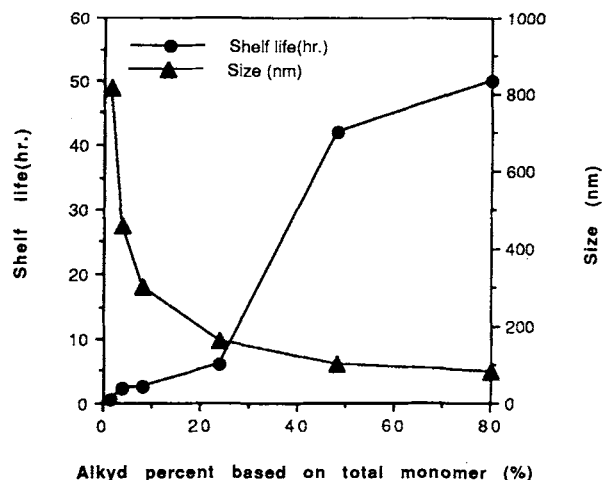


Figure 2 Monomer emulsion shelf life and droplet size without PMMA.

plays an important role in producing stable miniemulsions. The shelf life can be increased by PMMA additions even though a stable miniemulsion can be obtained at high alkyd content without PMMA. By contrast, the shelf life of normal emulsions is very short, only 2–8 min.

Polymerization

Miniemulsion conversion-time profiles with and without alkyd resin and with different emulsifier and initiator concentrations at 60 and 80°C are shown in Figure 3. The polymerization rate with alkyd is slower than that without alkyd. Doubling the initiator and emulsifier concentration can increase the reaction rate, but not to the level achieved with the miniemulsion polymerization without alkyd. Similar reaction rates for miniemulsions with alkyd are observed if the reaction temperature is raised from 60 to 80°C and organic initiator, BPO, is added in ad-

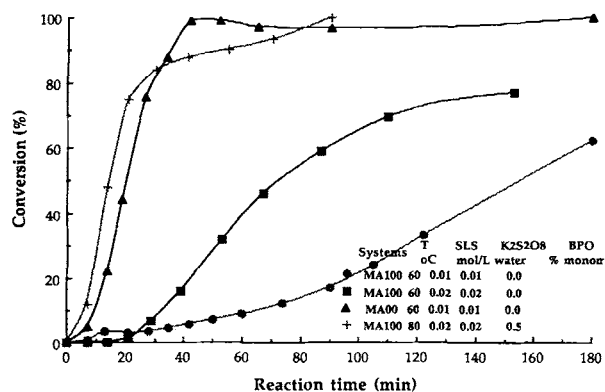


Figure 3 Conversion-time curves for miniemulsion polymerizations.

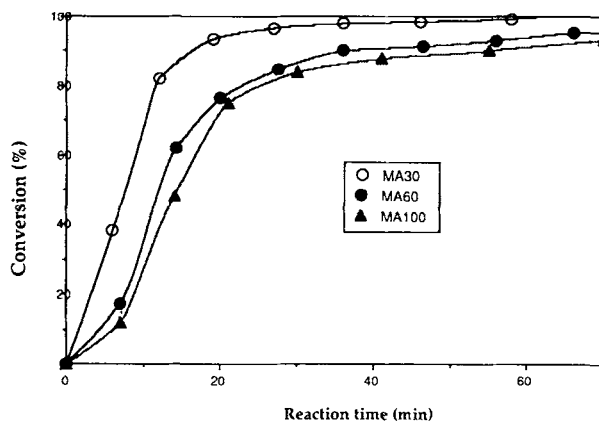


Figure 4 Conversion profiles for miniemulsion polymerizations with different amounts of alkyd at 80°C.

dition to doubling the amount of the water-soluble initiator, potassium persulfate, and the emulsifier (SLS). The retarding influence of alkyd is also evident with the miniemulsion polymerizations with different amounts of alkyd (Fig. 4).

The low reaction rates in the presence of alkyd may be caused by a retarding impurity in the alkyd or by resin chain transfer that produces an inactive radical. Low reactivity when emulsion polymerizing vinyl acetate and styrene in the presence of alkyd was noted by Cummings.³ To circumvent this problem, he used a mixed initiator (water- and oil-soluble components) in much the same way as was done here.

The latexes obtained from the miniemulsion polymerization of the alkyd-acrylate mixtures are uniform emulsions, and no coagulation occurs during polymerization with the recipes listed in Table I. Table IV and Figure 5 shows the polymer particle sizes and polydispersities. The polymer particle sizes increase and polydispersity decreases as the alkyd content is increased. The particle sizes of the alkyd-acrylate polymer are larger than particles formed by miniemulsion or normal emulsion polymerization

Table IV Particle Size and Distribution

Sample Code	Polymer Particle Size (nm)	Polydispersity
MA00	110.7	1.008
MA30	126.2	1.032
MA60	159.9	1.028
MA100	241.6	1.017
EA00	70.3	1.002
EA05	Separated	
EA100	Separated	

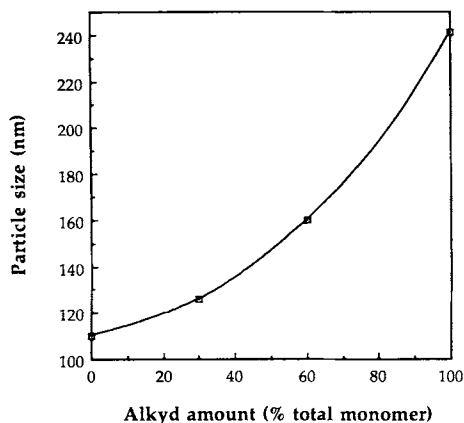


Figure 5 Particle size versus alkyd amount for miniemulsion polymerizations.

without alkyd, and the polydispersities are also larger.

Conversion profiles for emulsion polymerizations with and without alkyd are shown in Figure 6. The results are similar in one respect with miniemulsions: the addition of the alkyd decreases the reaction rate. We were not successful, however, in obtaining good latex products via normal emulsion polymerization with alkyd. The alkyd separated from the polymerization system when the polymerization entered interval II (Figs. 6, 7).

The initial number of monomer droplets and the final number of polymer particles is the same for the alkyd-acrylate miniemulsion polymerization (see Tables II and IV). Hence, it would appear that nearly all droplets become particles. Mass transfer from monomer droplets to micelles or monomer-saturated particles is not required. The alkyd can stay in the same place, that is, in the initial monomer droplets that become the final polymer particles. In contrast, particle nucleation in normal emulsion polymerizations takes place in micelles or in the aqueous phase. Monomer must then diffuse out of the monomer droplets, across the aqueous phase, and into the growing particles in interval II. In the alkyd-acrylate system, the acrylate monomer can move from the monomer droplets to the micelles or polymer particles, but alkyd is mass transfer limited. Therefore, as the monomer in alkyd-acrylate droplets migrates out of the droplets, the remaining alkyd-acrylate droplets become unstable and agglomeration occurs (Fig. 7). This problem is not encountered in the miniemulsion polymerization, because the site of polymerization is the monomer droplets containing the alkyd resin. Hence, the results of these alkyd-acrylate polymerizations fit with the widely accepted miniemulsion and emulsion polymerization mechanisms.

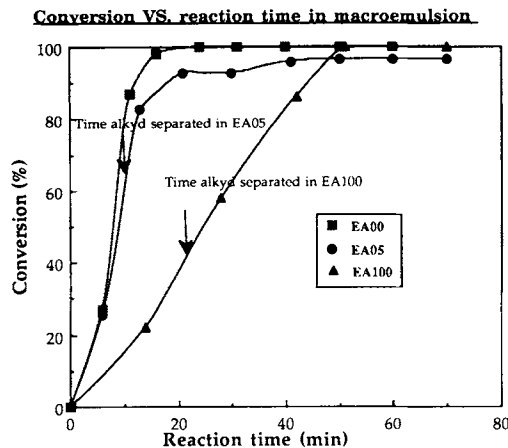


Figure 6 Conversion versus reaction time in macroemulsion polymerization with alkyd.

Reaction, Grafting and Crosslinking of Double Bonds in Alkyd

The alkyd used in this experiment is made from linseed and soya fatty acids and polyols. The main fatty acids in: linseed oil are 52% linolenic (*cis*-9-, *cis*-12-, *cis*-15-octadecatrienoic), 22% oleic (*cis*-9-octadecenoic), 16% linoleic (*cis*-9-, *cis*-12-octadecadienoic), and small amounts of other acids; soya oil

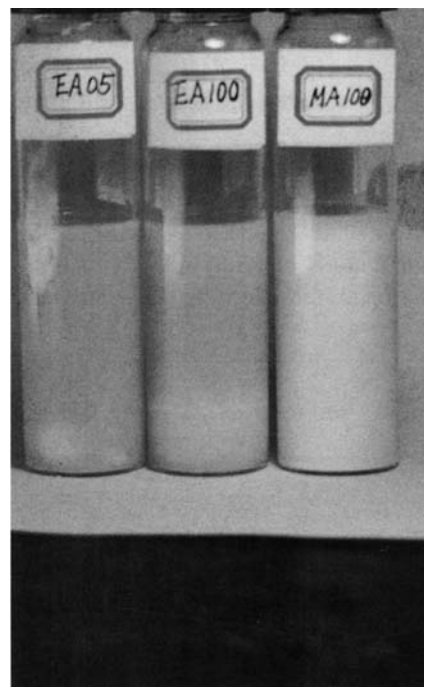


Figure 7 Photograph of latex obtained by macroemulsion (EA05, 5% alkyd) at left and (EA100, 100% alkyd) at middle and miniemulsion (MA100, 100% alkyd) at right. The top layer in EA05 and EA100 is latex; the bottom layer is alkyd.

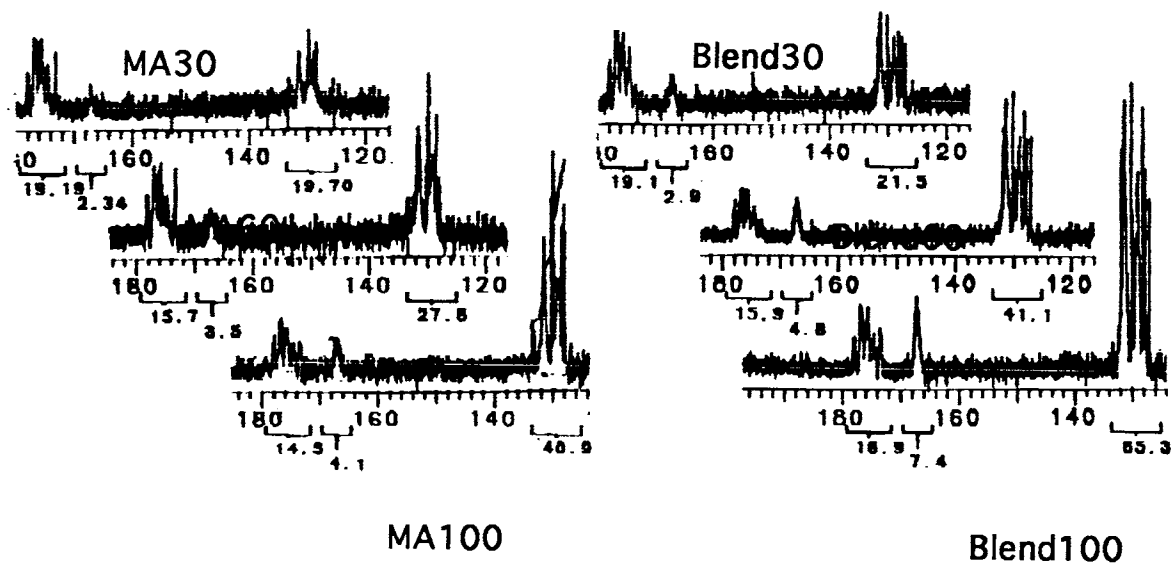


Figure 8 ^{13}C -NMR for alkyd-acrylate copolymer and alkyd-polyacrylate blends. From left to right and top to bottom: MA30, blend 30, MA60, blend 60, MA100, blend 100.

are 51% lanolin, 25% oleic, and other acids.⁴ These unsaturated acids comprise the alkyd, a special unsaturated polyester. The double bonds in the alkyd can react with free radicals, but the double bond structure leads to different reactivities from the vinyl bond in acrylate monomers. Hence, it becomes an interesting question as to how the alkyd double bonds react or what the alkyd-acrylate polymer is, a real copolymer or a blend. Furthermore, one would like to know how many alkyd double bonds react.

The alkyd-acrylate polymers and blends of pure alkyd and pure MMA-BA-AA copolymer were analyzed by ^{13}C -NMR. The results are shown in Figure 8 and Table V. The ^{13}C -NMR spectra of both the alkyd-acrylate copolymer and the alkyd-polyacrylate blend have some chemical shifts at lower than 100 ppm; but the interesting chemical

shifts are around 176 ppm, the multiplex resonance by carbon in ester groups of polyacrylate and alkyd, and around 130 ppm, the multiplex resonance by carbon in double bonds. Another peak at 165 ppm is caused by a special ester group in the alkyd. The useful peaks are shown in Figure 8.

Comparing the peak area at 130 ppm of alkyd-acrylate polymer with that of the corresponding alkyd-polyacrylate blend, it can be seen that the peak area of copolymer is smaller than that of the blend while the peak area at 176 ppm is relatively unchanged. This indicates that some alkyd double bonds react and some remain. This can be quantified by comparing the ratio of the peak area at 130 ppm to the peak area at 175 ppm (S_{130}/S_{175}) in Table V. The double bond conversion can be approximated with the following formula:

Table V ^{13}C -NMR Results for Alkyd-Latex and Alkyd-Polyacrylate Blends

Sample Code	Peak Area at (ppm)			Ratio of S_{130}/S_{175}	Conversion of Double Bonds
	175	167	130		
Alkyd	3.6	13.3	110	30.556	0.00
Blend 30 ^a	19.1	2.9	21.5	1.1257	0.00
Blend 60 ^a	15.9	4.8	41.1	2.5849	0.00
Blend 100 ^a	16.9	7.4	65.3	3.8639	0.00
MA30	19.2	2.3	19.7	1.0266	21.37
MA60	15.7	3.5	27.8	1.7707	31.50
MA100	14.5	4.1	40.9	2.8207	27.17

^a Alkyd percent based on polyacrylate.

Table VI Extraction with Chloroform–Toluene–THF–Methylene Chloride–Methyl Ethyl Ketone

Sample Code	Solid Weight		Degree of Crosslinking (%)
	Before Extraction	After Extraction	
MA00	4.7144	0.0000	0.00
MA30	5.0884	0.1846	≤ 3.63
MA60	5.0285	0.2636	≤ 5.24
MA100	3.1256	0.0719	≤ 2.30

% double bond conversion

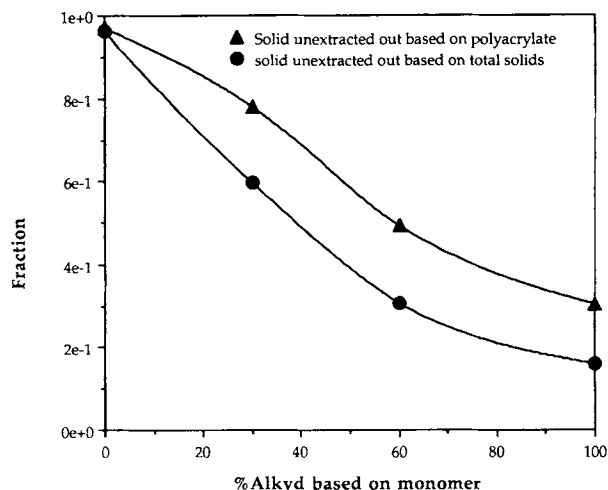
$$= 100 \left[\frac{1 - \left(\frac{S_{130}}{S_{175}} \right)_{\text{copolymer}}}{\left(\frac{S_{130}}{S_{175}} \right)_{\text{blend}}} \right] \quad (1)$$

where $(S_{130}/S_{175})_{\text{copolymer}}$ is the ratio of resonance of alkyd-acrylate polymer at 130 and 175 ppm, and $(S_{130}/S_{175})_{\text{blend}}$ is the corresponding ratio of resonance of alkyd-polyacrylate blend. The results in Table V show only 20–30% of the double bonds in the alkyd react. This confirms that the alkyd is copolymerized with the acrylates, and that the final polymer product is an alkyd-acrylate copolymer not an alkyd-polyacrylate blend. Approximately 70–80% of the double bonds in the alkyd remains in the alkyd-acrylate latex after reaction, which could enhance curing as the latex is dried during application.

The results cited above indicate that the polyacrylate can be grafted to the alkyd molecules. The grafting ratio was tested by extraction. Ethyl ether is a good solvent for alkyd and for some of the lightly grafted alkyd and a bad solvent for polyacrylate. The alkyd-acrylate products were extracted with ethyl ether, and the alkyd and most grafted alkyd were removed from the total polymer in a Soxhlet extractor. The polymer remaining consists of acrylic

Table VII Extraction with Ethyl Ether Solvent and Degree of Grafting

Sample Code	Solid Percent Left after Extraction Based on		Degree of Grafting (%)
	All Solids	Polyacrylate	
MA100	15.81	30.38	≥ 69.62
MA60	30.70	49.29	≥ 50.71
MA30	59.70	78.13	≥ 21.87
MA00	96.20	96.89	0.00


Figure 9 Extraction data of alkyd-polyacrylate polymers with ethyl ether.

polymer and very highly grafted alkyd. If the amount of highly grafted alkyd is neglected (results in Table VI indicate that this must comprise less than 5.24% of the total polymer), the grafting efficiency of alkyd can be calculated by the following formula:

% grafting efficiency

$$= 100 \left(\frac{\text{wt polyacrylate grafted to alkyd}}{\text{wt total acrylate monomer}} \right) \quad (2)$$

The extraction data and calculated grafting efficiencies are shown in Table VII. When more alkyd is added to the miniemulsion polymerization system, more polyacrylates are grafted onto the alkyd. Approximately 70% of the polyacrylate was grafted onto alkyd in run MA100 that contained equal amounts of monomers and alkyd (Fig. 9).

The alkyd is a multifunctional resin that contains at least two double bonds per molecule. Hence, there is a possibility that the alkyd-acrylate copolymer is crosslinked by the multifunctional molecule even though most of the double bonds are not reacted (Table V). This was investigated by extracting the alkyd-acrylate copolymer with different good solvents. The results are shown in Table VI. Five solvents were used in the extraction of the copolymer. The solvent was changed every 12 h. Table VI shows that there is less than 5.24% crosslinked or highly branched copolymer. The small amount of crosslinked or highly grafted polymer may play an important role in increasing material strength, but it should not affect the coating application.

Table VIII Preliminary Film Test Results

Sample	Hardness	Adhesion
MA00	B	Passed
MA100	B	Passed
MA60	B	Passed
MA30	B	Fair
EA00	B	Passed

Films were less than 1 mil thick. Best results are performed on films 1–3 mil in thickness. These films have good adhesion, acceptable hardness, and poor coverage and uniformity on panels that could be improved with thickeners and pigments.

Coating Properties of Alkyd–Acrylate Latex

To obtain preliminary information on potential application performance, films were formed from five products on wood and metal substrates. These films were made from latex product directly from the reactor with 1% (wt/wt latex) hydroxy ethyl cellulose as a thickener, using a Baker Coater draw-down, and dried at room temperature. No pigment or dyeing agents were added. The results are given in Table VIII. ASTM hardnesses were all “B,” which is acceptable for common coatings. These results, considering that there was no formula optimization or compounding, are encouraging.

SUMMARY AND CONCLUSIONS

The miniemulsion polymerization process has proved to be effective for incorporating an alkyd

resin into acrylic coating copolymers.[†] The reaction produces stable, small particle size latexes that contain graft copolymer of the acrylic and alkyd components. This technique may be useful for obtaining some of the desirable properties of solvent-based alkyds in a solvent-free aqueous latex form.

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[†] Cummings³ reports the emulsion polymerization of vinyl acetate and styrene in the presence of alkyd. His patent stresses the need for high shear and mixed initiators. It is probable that the alkyd was acting as a cosurfactant, and, when exposed to high shear, was forming a miniemulsion (unknown at the time of his work).