# Waterborne Oil-Modified Polyurethane Coatings via Hybrid Miniemulsion Polymerization

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**ABSTRACT:** As part of a wider effort to develop a new class of waterborne coatings, hybrid miniemulsion polymerization was carried out with acrylic monomers (methyl methacrylate, butyl acrylate, and acrylic acid) in the presence of oil-modified polyurethane resin. Latexes with different ratios of resin to acrylic monomers were synthesized. The monomer emulsions prepared for hybrid miniemulsion polymerization showed excellent shelf-life stability (>5 months) and the polymerization was run free of coagulation. Solvent extraction indicated that the grafting efficiency of polyacrylics was greater than 29% for all the samples produced. A $^{13}C$ solution NMR spectrum showed that a substantial fraction of the original carbon double bonds (>61%) in oil-modified polyurethane remained after polymerization for film curing. Films obtained from the latexes presented good adhesion properties and fair hardness properties. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 105–114, 2000

**Key words:** waterborne coatings; hybrid miniemulsion polymerization; oil-modified polyurethane resin; shelf life; solvent extraction; grafting

## INTRODUCTION

Oil-modified polyurethanes (OMPU) are, in terms of volume produced and sold, the most important polyurethane coatings, with superior properties such as gloss, chemical resistance, and film formation. Most urethane coatings are solvent based, and solvent-based coatings are less than desirable due to the environmental impact of their high volatile organic compounds (VOC). To meet the increasing concern for health, safety, and the environment, there has been a strong preference in recent years for waterborne coatings. Recently Hegedus and Kloiber[1] have published work on the development of aqueous acrylic–polyurethane hybrid dispersions. In their work, polyurethane was obtained by step growth polymerization and polyacrylics were synthesized through chain growth mechanism. The two polymers formed an interpenetrating network (IPN) at the molecular level. Historically, polyacrylics and polyurethane have long been combined together either through IPN or copolymerization via a solvent-based process because of their complementary properties.[2,3] Wang et al.[4] have demonstrated the production of acrylic/alkyd graft copolymers for coatings applications by hybrid miniemulsion polymerization. The object of this work was to obtain oil-modified polyurethane

grafted onto polyacrylics by free-radical polymerizing acrylic monomers in the presence of oil-modified polyurethane resin via hybrid miniemulsion polymerization. This process can offer stable waterborne coatings for resins that could not be obtained by conventional emulsion process because of the difficulty in transport of the polyurethane resin across the aqueous phase.

In miniemulsion polymerization, an effective surfactant/hydrophobe system is used to stabilize very small monomer droplets (50–500 nm). In order to break up monomer droplets to such size, high agitation is applied by sonication or homogenization.[5] The hydrophobe (also known as a cosurfactant) is a highly monomer-soluble, highly water-insoluble material added to increase diffusional stability of the emulsion. Usually long-chain alkanes such as hexadecane, or long-chain alcohols such as cetyl alcohol, are employed as hydrophobes.[6,7] Because these hydrophobes cannot diffuse readily through the aqueous phase (due to their high water insolubility), removing the monomer from a small monomer droplet will cause an increase in the concentration of the hydrophobe, which in turn will increase surface energy. Therefore, the employment of hydrophobe will significantly retard, or even prevent, Ostwald ripening (transfer of monomer from small droplets to large droplets to reduce the total surface energy of the system), and thus keep the small droplets stable during polymerization. Hence, for an ideal miniemulsion polymerization, there is no mass transport involved. The large droplet surface area in miniemulsion (because of small droplet size) results in most of the surfactant being adsorbed to the droplets with little free surfactant available to form micelles or stabilize aqueous phase polymerization. Therefore, the predominant nucleation mechanism in miniemulsion polymerization is droplet nucleation. Moreover, because monomer diffusion is retarded, there may be no true Interval II as described by Ewart–Smith kinetics. This is exactly what is desired for the current application, since if there is significant micellar or homogeneous nucleation, particles will be formed that contain little or no polyurethane, since the total water insolubility of the polyurethane makes it difficult for diffusion of the resin from the monomer droplets to the particles, which are the loci of polymerization. In contrast, in miniemulsion polymerization, polymerization takes place in the (very small) droplets, in the presence of the polyurethane resin, and without the need for diffusion of the resin across the aqueous phase. If a conventional emulsion polymerization were run in the presence of the OMPU, the result would be polyacrylic particles in a physical blend with dispersed polyurethane, with very little chance of grafting between the two species.

Polymer has also been used as hydrophobe with the advantage of higher purity of the final products.[4,8] In the current work, the resin (OMPU) was employed as both reactant and hydrophobe.

## EXPERIMENTAL

### Reagents

Oil-modified polyurethane 138-0634 supplied by McWhorter Technologies was used as the OMPU. This resin contained 60% solid linseed-modified polyurethane, 20% solvent naphtha (heavy alkylate), 20% naphtha (hydrotreated heavy), 0.07% dibutyl tin oxide, and 0.03% triphenyl phosphite. The polyurethane portion was made from TDI (toluene diisocyanate), and no free TDI was left unreacted. The solvents were removed by vacuum evaporation before use. Methyl methacrylate (MMA), butyl acrylate (BA), acrylic acid (AA), potassium persulfate (KPS) (all from Aldrich), sodium lauryl sulfate (SLS) (Fisher), and benzoyl peroxide (BPO) (Fisher) were employed as supplied. The water was deionized.

### Emulsion Preparation and Polymerization

Miniemulsion were prepared and polymerized according to the recipes shown in Table I. The desired amount of SLS was dissolved in about 220 g of DI water and the KPS was dissolved in about 30 g deionized water. The BPO was dissolved in the acrylic monomer mix (MMA, BA, and AA), and the OMPU was added. The mixture was stirred for several hours to complete dissolution of the OMPU. Then the oil phase was added to the SLS solution and sheared for 5 min at high speed with a magnetic stirrer. This pre-emulsion was then sonicated for 15 min at 70% output with the Fisher 300W Sonic Dismembrator while a magnetic stirrer provided bulk mixing.

Upon completion of sonication, the monomer miniemulsion was transferred to a 500-mL, 3-neck flask equipped with a nitrogen purge, condenser, and a paddle stirrer. The flask was placed into a water bath. The system was purged for 15 min with nitrogen and brought to the polymeriza-

**Table I   Recipe for Miniemulsion Polymerization[a]**

| Miniemulsion | Ingredients (wt) | | | | |
|---|---|---|---|---|---|
| | OMPU | MMA | BA | AA | |
| 1 | 100 | 49 | 50 | 1.0 | 0.3 |
| 2 | 60 | 49 | 50 | 1.0 | 0.3 |
| 3 | 30 | 49 | 50 | 1.0 | 0.3 |
| 4[b] | 0 | 49 | 50 | 1.0 | 0 |

[a] The continuous phase consists of 200 parts water/100 parts total solids, 0.02 mol KPS/L water and 0.02 mol SLS/L water; BPO 0.3 wt % (based on total oil phase).
[b] Run 4 was run to obtain pure polyacrylics where 3 g poly(methyl methacrylate) was employed as hydrophobe, and the reaction temperature was 60°C. KPS was 0.013 mol/L-water.

tion temperature by adjusting the temperature of the water bath. Once the polymerization temperature was reached, the stirring rate was adjusted to about 220 rpm and the water-soluble initiator was injected by syringe. Approximately 5 g of samples were taken by a syringe at intervals during polymerization and injected into vials containing 0.5% hydroquinone solution in an ice bath. Monomer conversion was determined gravimetrically from these samples.

### Droplet and Particle Size

Droplet and particle size distributions were measured by quasi-elastic light scattering with a Malvern Autosizer IIc. The monomer emulsion was diluted about 50:1 with a monomer-saturated DI water solution containing 0.1 wt % SLS. The polymerized latex was diluted about 100 : 1 with a DI water solution containing 0.1 wt % SLS. Droplet size was recorded immediately after sonication. Measurements were made at 5 min intervals. The Autosizer provides average diameters, standard deviations, and distributions.

### Shelf-Life Stability

Shelf life was measured by placing approximately 5 mL of an unpolymerized emulsion in a capped glass vial and observing the time necessary for a visible creaming line to appear at room temperature. In order to observe the line easily, two drops of water-soluble red pigment solution were added.

### ^{13}C Solution NMR and Solvent Extraction

The ^{13}C solution NMR spectra were recorded by a Bruker AMX 400, using deuterated chloroform as solvent. Pulse delay time was 2.0 s, and inverse gated decoupling were applied with a 90° pulse length. Solvent extraction experiments were per-

formed in a Soxhlet extractor with approximately 0.5 g dried latex. Ethyl ether was applied for 24 h. All resin and grafted copolymers were assumed to be dissolved completely. Grafting efficiency was calculated from the quantity of polymer extracted. Chloroform, toluene, tetrahydrofuran (THF), and 1,4-dioxane were used sequentially in an exhaustive extraction to determine the percentage of the polymer, which was crosslinked. Each solvent was applied for 12 h. Material that remained after extraction with the four solvents was considered to be crosslinked.

### Dynamic Mechanical Analysis

A SEIKO Instruments DMS 210 Tension Module was used to measure the dynamic viscoelasticity of films prepared from the synthesized latexes. The temperature ranged from −60 to 100°C, and the frequency was 1 Hz. Films were dried at room temperature with thickness of about 1 mm.

### Transmission Electron Microscopy

Transmission electron microscopy (TEM) analysis was performed with a Hitachi HF-2000 FE-TEM. The synthesized latexes were diluted with deionized water to about 100:1. These diluted latexes were stained for 24 h by using 2 drops of 1 wt % osmium tetroxide solution in water. One drop of the stained latexes was placed on the coated side of a 200-mesh nickel grid in a petri dish. After 24 h of drying, the samples were ready to be tested.

### Gel Permeation Chromatography

The latexes were dried in a vacuum oven and then dissolved in THF at a concentration of 1 mg/mL. Gel permeation chromatography (GPC) was used to determine molecular weight. Uninhibited THF was used as the eluent with a flow rate of 0.7

**Table II   Droplet Size and Shelf Life Versus Sonication**

| Sonication Time[a] (min) | | 0 | 5 | 10 | 15 | 20 |
|---|---|---|---|---|---|---|
| Sample[b] | Shelf life | <1 min | ~2 days | ~2 months | >5 months | >5 months |
| 1 | Droplet size[c] (nm) | 1567.8 | 351.9 | 278.0 | 225.4 | 212.6 |
| Sample[b] | Shelf life | <1 min | ~1 month | >5 months | >5 months | >5 months |
| 2 | Droplet size[c] (nm) | Not tested | 360.4 | 241.4 | 199.9 | 172.1 |
| Sample[b] | Shelf life | <1 min | >5 months | >5 months | >5 months | >5 months |
| 3 | Droplet size[c] (nm) | Not tested | 241.6 | 203.8 | 143.0 | 119.8 |

[a] Sonication was performed at 70% output.
[b] Sample recipe is the same as shown in Table I except that no initiators were added.
[c] Here droplet size is characterized as $Z$-average diameter.

mL/min pumped by a Waters 510 HPLC Pump. A Waters 410 Differential Refractometer was used for detection of concentration. The chromatography conditions were: three columns (300 7.8 mm, pore sizes: $10^3$, $10^4$, and $10^5$ Å); temperature, 30°C. TriSEC Conventional GPC Software (Viscotek) was used to calculate the molecular weight with respect to polystyrene.

## RESULTS AND DISCUSSION

### Shelf Life and Droplet Size

Emulsion stability is very important for both miniemulsion and emulsion polymerization. The particles in the emulsion should remain stable for long periods of time, often years, dispersed as single entities by Brownian motion. Particles that are too large will settle or rise under the influence of gravity and do not remain dispersed by Brownian motion. There is a certain value of critical particle size for a given system (determined by Stoke's Law) above which the dispersion will not be stable. In emulsion and miniemulsion polymerization, surfactant is added to prevent droplet (and particle) agglomeration. However, due to the Ostwald ripening, the monomer in smaller droplets will diffuse to the larger ones, leading eventually to an unstable dispersion. For a conventional emulsion system, the polymerized latex will remain stable for a long time, but monomer emulsion can only last for a few minutes before a cream line appears due to Ostwald ripening. In a miniemulsion, a hydrophobe is employed to prevent Ostwald ripening. Shelf life is a quick measure of the effectiveness of the surfactant/cosurfactant system. Miniemulsions were prepared using the recipes for Runs 1–3 in Table I. No initiator was added. The resulting emulsions were subjected to varying levels of sonication and the shelf lives and droplet sizes were determined. The results

are shown on Table II. It can be seen that, with increasing sonication, the emulsion becomes more stable, and the droplet size becomes smaller. For the same level of sonication, the higher the concentration of resin, the larger the size. This is because the viscous resin requires more energy to break up. When sonication time is greater than 10 min with an output of 70%, at all of the samples are very stable (shelf life of several months). This indicates that the OMPU resin can serve as a good hydrophobe for the acrylic monomers employed in this study.

### Particle Size Evolution During Polymerization

As described above, the dominant nucleation mechanism in miniemulsion polymerization is droplet nucleation. Consequently, the final latex particle size will be similar to the initial monomer droplet size. Figure 1 shows this feature in the current system. The particle size decreased slightly during polymerization. This can be attributed to the increase of particle density, because polymer density is higher than that of monomers. Both the long shelf-life stability (>5 months) and the similar particle size throughout polymerization suggest that the method of polymerization was hybrid miniemulsion polymerization. That means the predominant locus nucleation mechanism was droplet nucleation. Although there may have been micellar or homogeneous nucleation, the very large interfacial area of the very small monomer droplets adsorbs most of the surfactant, leaving little to initiate micellar of homogeneous nucleation.

### Process of Polymerization

Runs were first made according to the recipes in Table I, but with a polymerization temperature of 60°C. The rates of polymerization in the presence of OMPU were found to be much slower than in the
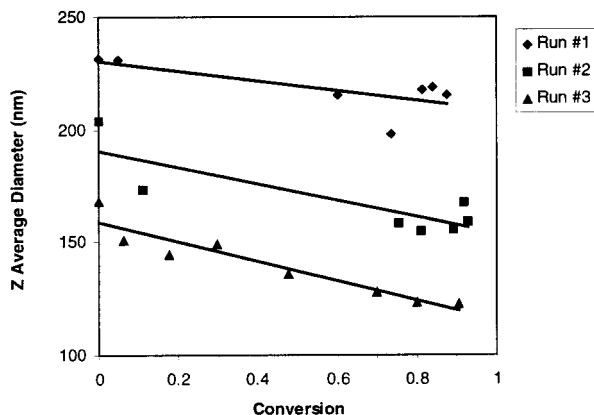
**Figure 1** Development of particle size as a function of conversion.
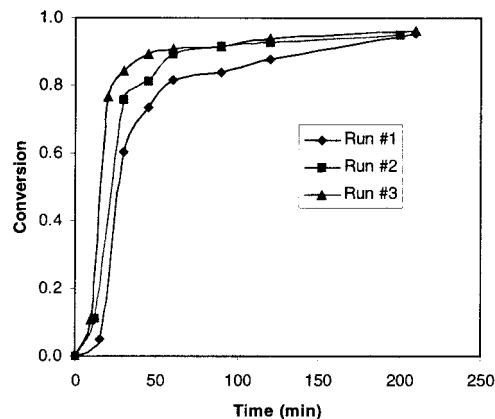


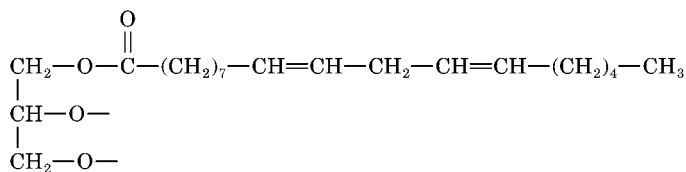**Figure 2** Conversion-time plots for the hybrid mini-emulsion polymerizations.

equivalent recipe without OMPU. The reason could be that some impurities in the resin act as retarding agent (these impurities can be introduced into the resin as additives during resin synthesis), or the resin itself reduces the polymerization rate by diluting monomer concentration and by resin chain transfer that produces less active radicals. To overcome this problem, the temperature was increased from 60 to 80°C, the amount of KPS added was doubled, and 0.5 wt % (based on total monomer) oil soluble initiator (BPO) was added. The results are shown in Figure 2. The polymerization rate was increase significantly, bringing the reaction time

back to the level of conventional emulsion polymerization. As can be seen from Figure 2, the rate of reaction decreases as the level of OMPU is increased. This suggests that the resin might be retarding the polymerization.
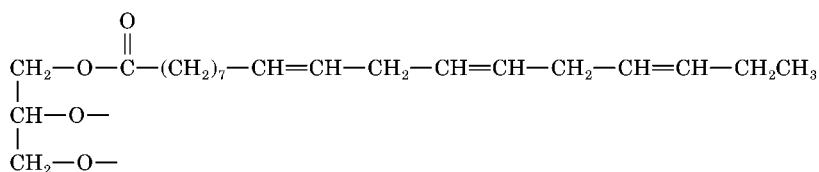
As mentioned before, a linseed oil- modified polyurethane was used as the resin. The main fatty acids in linseed oil are 35–60% linolenic, 17–24% linoleic, 12–34% oleic, and less than 10% saturated fatty acids. The structures of unsaturated fatty acids are shown below. All double bonds are in the *cis* form.

$$CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_7-CH=CH-(CH_2)_7-CH_3$$
$$|$$
$$CH-O-$$
$$|$$
$$CH_2-O-$$
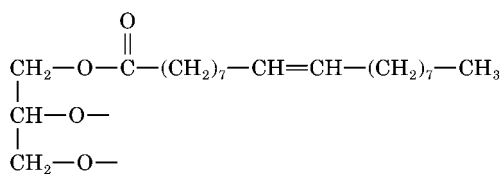
Oleic acid triglyceride (monounsaturated)

$$CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_7-CH=CH-CH_2-CH=CH-(CH_2)_4-CH_3$$
$$|$$
$$CH-O-$$
$$|$$
$$CH_2-O-$$

Linoleic acid triglyceride (diunsaturated)

$$CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_7-CH=CH-CH_2-CH=CH-CH_2-CH=CH-CH_2CH_3$$
$$|$$
$$CH-O-$$
$$|$$
$$CH_2-O-$$
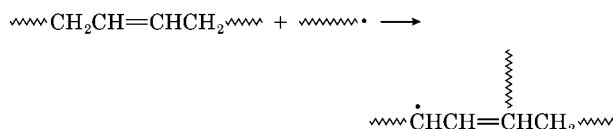
Linolenic acid triglyceride (triunsaturated)

During polymerization, grafting can occur by chain transfer from the propagating free radical to the resin:[9] The resulting fatty acid radical may be substantially less reactive than the acrylic radical, resulting in a reduction in polymerization rate.

$$\sim\!\!\!\!\sim\!CH_2CH\!=\!CHCH_2\sim\!\!\!\!\sim + \sim\!\!\!\!\sim\!\cdot \longrightarrow$$

$$\sim\!\!\!\!\sim\!\overset{\cdot}{C}HCH\!=\!CHCH_2\sim\!\!\!\!\sim + \sim\!\!\!\!\sim\!H$$

Monomers

$$\sim\!\!\!\!\sim\!CHCH\!=\!CHCH_2\sim\!\!\!\!\sim$$
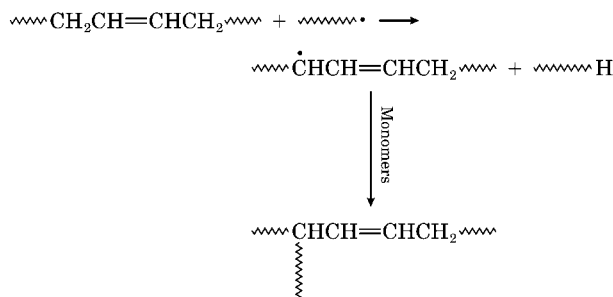
The second main mechanism for grafting involves copolymerization between the polymerizing radical and the double bonds of oil-modified polyurethane:

$$\sim\!\!\!\!\sim\!CH_2CH\!=\!CHCH_2\sim\!\!\!\!\sim + \sim\!\!\!\!\sim\!\cdot \longrightarrow$$

$$\sim\!\!\!\!\sim\!\overset{\cdot}{C}HCH\!=\!CHCH_2\sim\!\!\!\!\sim$$

Therefore, considering the possible grafting reactions, one would expect to get a mixture of pure polyacrylics, grafted copolymer of acrylics, and oil-modified polyurethane, and the remaining resin.

### Product Characterization

The determination of grafting efficiency will help to determine if grafting has occurred, or if the product is a blend of polyacrylic homopolymer and polyurethane. Curing ("drying") in oil-modified polyurethane occurs through reactions of the residual double bonds in the fatty acids with atmospheric oxygen in much the same way as in the alkyd resins in common oil-based paints. Because the drying reactions require residual double bonds, it is important to know what fraction of the original double bonds in the fatty acids have been reacted during the polymerization process. Since many of the fatty acids have more than one carbon–carbon double bond, it is possible to have crosslinked material. Polymer that is heavily crosslinked will not form good films, and so it is important to determine the percentage of crosslinked material. ^{13}C solution NMR was used

to determine the residual double bonds available after polymerization for film curing. Solvent extractions were performed to determine the grafting efficiency of acrylic monomers and percent crosslinking. GPC measurements were used to determine the molecular weight of the products.

### Residual Double Bond Analysis

A delay time of 2.0 s and inverse gated decoupling with a 90 pulse length was used to obtain quantitative ^{13}C NMR spectra. Figure 3 is a full spectrum of the starting resin, oil-modified polyurethane. The interesting peaks include the single peak at 153 ppm, which belongs to the carbon of urethane bond, and the multipeaks at 126–133 ppm, which mainly belong to the carbon–carbon double bonds of the fatty acids. This has been determined from the spectra of linseed alkyds.[4] The peaks around the multipeaks derive from the carbons on the benzene ring introduced by 2,4-TDI.[10,11] The sixth carbon on the benzene ring introduced by 2,4-TDI has a chemical shift of 133 ppm, is also in the region of carbon–carbon double bonds. Therefore, one must subtract its contribution from the peak area of 126–133 ppm to get the peak area for the double bonds in the fatty acids. The important features of the spectra are shown in Table III. The carbon in the urethane bond was used as internal standard because its concentration will not change during polymerization. The contribution of the sixth carbon of the benzene ring is equal to one half of the peak area of urethane bond, since each benzene ring is attached to two urethane bonds. The residual double bonds of fatty acids can then be calculated with the formula below:

$$\% \text{ double bonds remained} = \frac{(S_{\text{double bonds}}/S_{153})_{\text{run\#}}}{(S_{\text{double bonds}}/S_{153})_{\text{OMPU}}}$$
$$\times 100\%$$

where $S_{\text{double bonds}}$ is the peak area of fatty acids' double bonds and $S_{153}$ is the peak area of carbon in urethane bonds. From Table III it may be seen that most of the original double bonds ($>61\%$) remained for film curing.

### Crosslinked Percentage

The crosslinked percentage is defined as the weight percent of the total polymer that is crosslinked. To determine the crosslinked percentage, chloroform, toluene, THF, and 1,4-diox-
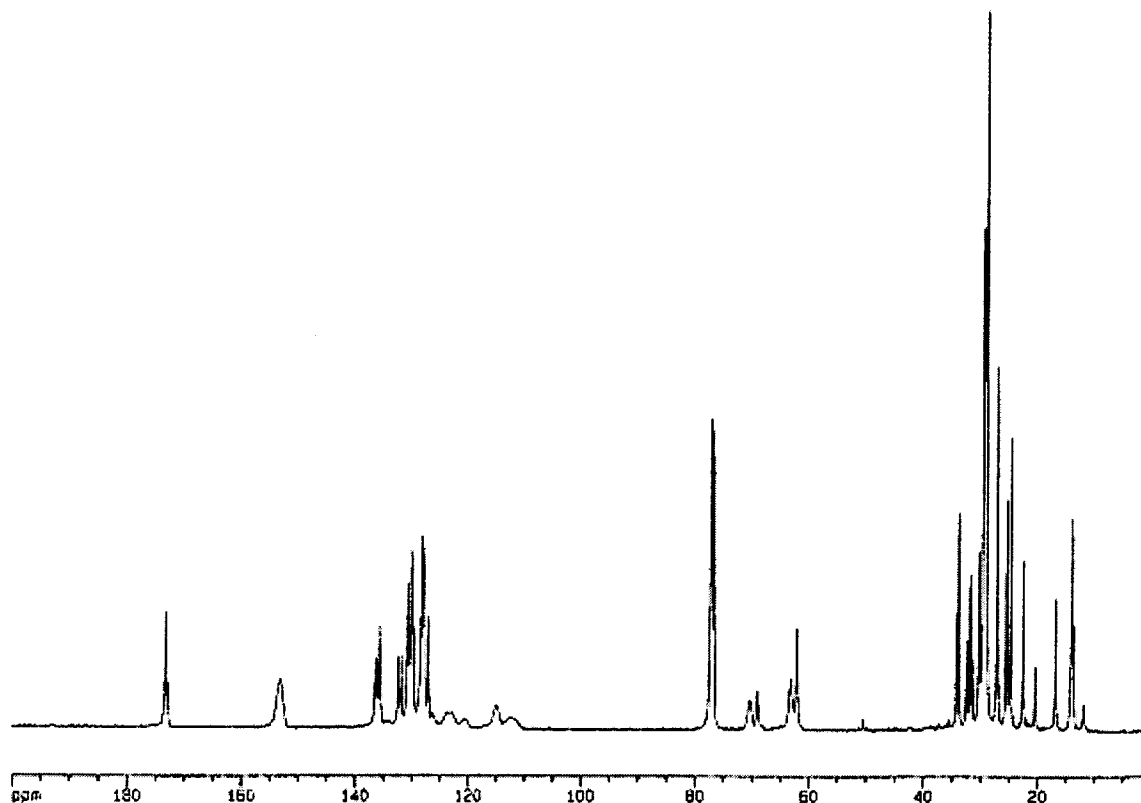
**Figure 3**    $^{13}$C-NMR spectrum of oil-modified polyurethane.

ane were used sequentially to extract soluble polymer. The remaining polymers after all extractions were assumed to be crosslinked:

$$\text{Crosslinked Percentage} = \frac{m_{\text{ae}}}{m_{\text{be}}} \times 100\%$$

where $m_{\text{be}}$ is the mass of polymer before extraction and $m_{\text{ae}}$ is the mass of polymer after extraction. Table IV shows that for all samples, crosslinked percentage is less than 4.8%. At this

level, it should not adversely affect the film forming properties of the latexes.

### Grafting Efficiency

The grafting efficiency is defined as the percent of the total acrylic monomer polymerized which is grafted to the OMPU. Ethyl ether is a good solvent for OMPU, but does not dissolve polyacrylics at all. Thus, it was used to determine the grafting efficiency of polyacrylics:

**Table III    Results of $^{13}$C-NMR**

| Sample Code | Peak Area at | | Double Bonds of Fatty Acids | Double Bonds Remained |
|---|---|---|---|---|
| | 153 ppm | 126–133 ppm | | |
| Run 1 | 1 | 4.29 | 3.79 | 70% |
| Run 2 | 1 | 3.79 | 3.29 | 61% |
| Run 3 | 1 | 4.15 | 3.65 | 68% |
| OMPU | 1 | 5.84 | 5.34 | N/A |

**Table IV   Grafting Efficiency and Crosslinked Percentage**

|                        | Run 1 (%) | Run 2 (%) | Run 3 (%) |
| ---------------------- | --------- | --------- | --------- |
| Grafting efficiency    | 53        | 56        | 29        |
| Crosslinked percentage | 4.8       | 1.3       | 2.8       |

Grafting Efficiency

$$= \frac{m_{be} * \left(\dfrac{m_{acrylic}}{m_{ompu} + m_{acrylic}}\right) - m_{ae}}{m_{be} * \left(\dfrac{m_{acrylic}}{m_{ompu} + m_{acrylic}}\right)} \times 100\%$$

where $m_{ompu}$ is the mass of oil-modified polyurethane used in the reaction and $m_{acrylic}$ is the mass of acrylic monomers used in the reaction. Grafting will enhance the miscibility between polyacrylics and the resin, which in turn will benefit the film properties formed by the latex. Table IV shows that all of the latexes have a grafting efficiency of at least 29%.

### Molecular Weight

Figure 4 shows the GPC chromatograms of all three samples. The chromatograms for each sample show four peaks. The number average molecular weight was calculated for separately for Peaks A–C with respect to polystyrene a polystyrene standard. The results are shown in Table V. The molecular weight of Peaks D is just a few hundred, which can be attributed to surfactant, THF contamination, and/or residual BPO and KPS.

The area of Peak A increases with the increasing ratio of acrylic to resin. The molecular weight
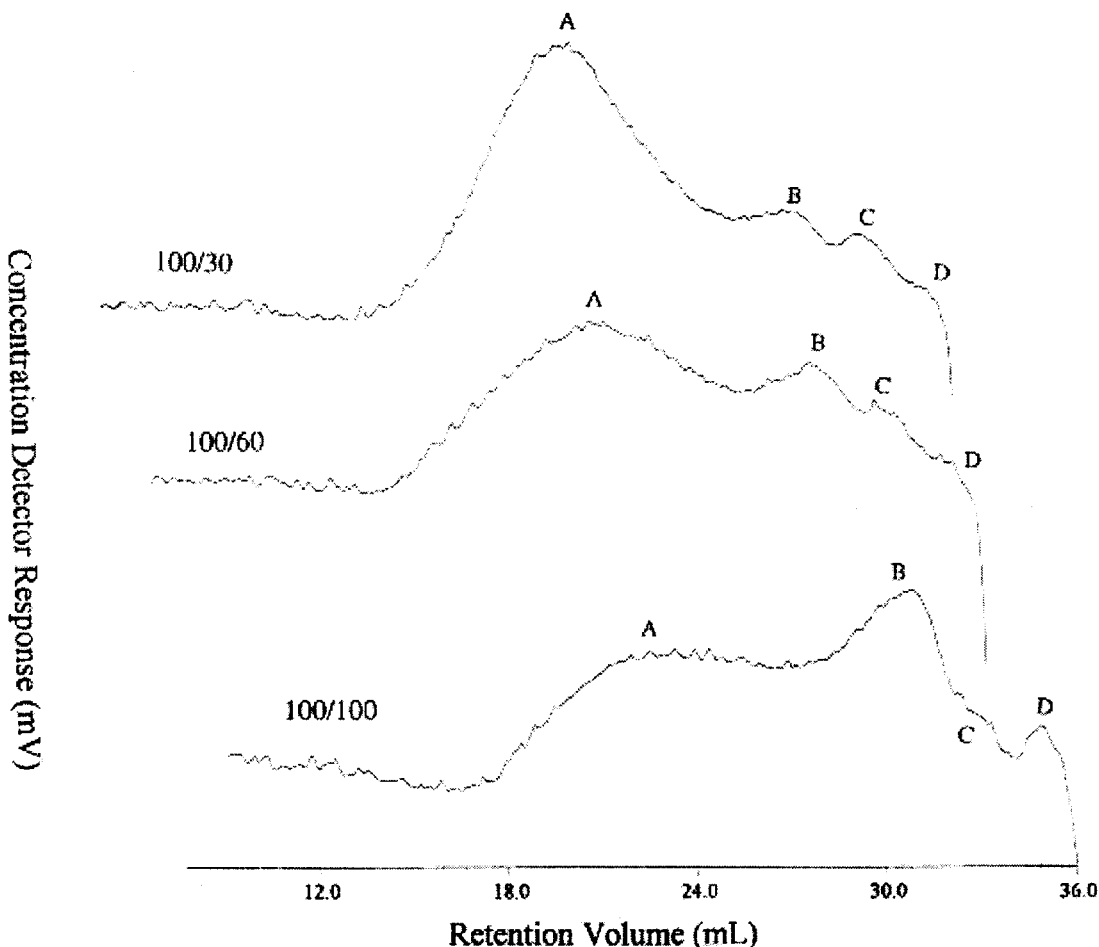


**Figure 4**   GPC chromatograms of latexes (where 100/xx indicates the ratio of acrylic monomers to resin with xx = 100, 60, and 30 for Runs 1, 2, and 3, respectively).
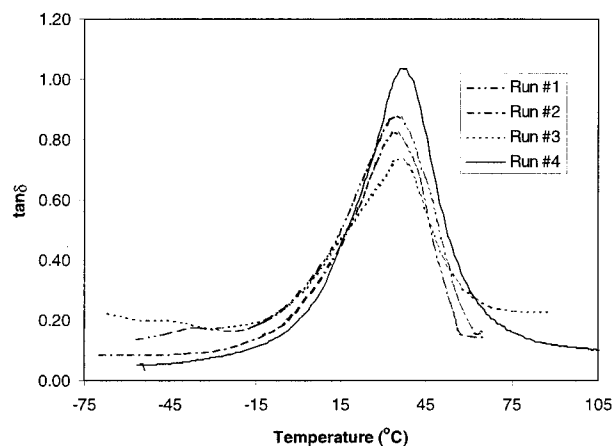
**Table V  Molecular Weight Averages**

| Run | Ratio of Acrylic Monomer to Resin | Number Average Molecular Weight (g/mol) | | |
|-----|------------------------------------|---------|---------|---------|
| | | Peak A | Peak B | Peak C |
| 1 | 100/100 | 67,400 | 4210 | 1490 |
| 2 | 100/60 | 85,000 | 5470 | 2010 |
| 3 | 100/30 | 51,300 | 4390 | 1580 |



**Figure 5**  Dynamic mechanical analysis results.

of this peak is in the range of several ten thousands and is probably pure polyacrylic or graft polymer. The interesting thing is that Run 2 (acrylic : resin = 100 : 60) has a much larger molecular weight than those of Runs 1 and 3. The addition of resin could reduce the polymer molecular weight by chain transfer. On the other hand, since the OMPU is multifunctional, grafting could raise the molecular weight of the grafted material. It would appear that at some ratio of acrylic to resin, these two opposing mechanisms cause a maximum in the molecular weight. The molecular weight of Peak B is approximately 4,500, which corresponds to that of the OMPU. As expected, the peak area increases when the acrylic-to-resin ratio decreases. Peak C has a molecular weight of approximately 1500–2000, which is substantially lower than that of resin, and its area increases with the increasing ratio of monomer to resin. These two factors indicate the possibility of low molecular weight acrylic oligomers generated by the chain transfer.

### Morphology and Coating Properties

It has been determined by solvent extraction that a significant amount of acrylic monomer reacted with resin to produce graft copolymer, while the remaining monomer formed pure polyacrylic. The

miscibility between those two kinds of polymer and other possible components will be important for the film properties. Figure 5 shows that each sample clearly has the same glass transition at 35°C, which corresponds to the $T_g$ of pure polyacrylics. Although the glass transition of other components does not appear on the DMA spectrum at the recording temperature range, this result indicates that polyacrylic was phase separated from other possible components in the films. TEM analysis was performed to confirm this. The results were not conclusive. No evidence of heterogeneity was evident in the latex particles. Only the osmium tetroxide-stained phase could be seen. This result suggests that there is a core/shell structure with a resin-rich shell. The graft copolymer found by solvent extraction should act to mitigate the immiscibility, thereby benefit the film property.

Film hardness testing was performed by the Pencil Test (ASTM D 3363–74), and film adhesion was measured by the Tape Test (ASTM D 3359–78). These films were cast from latex with 5% hydroxyethyl cellulose added as a thickener, using a Baker Coater draw-down. The films were

**Table VI  Film Hardness and Adhesion Properties**

| Sample[a] | 1 | 2 | 3 | 4 | 5 | 6 |
|-----------|---|---|---|---|---|---|
| Hardness | B | B | B | HB | HB | HB |
| Adhesion[b] | 5 | 5 | 4 | 5 | 5 | 4 |

[a] Film Samples 1, 2, and 3 were made from latex Runs 1, 2, and 3 respectively with air drying; Film Samples 4, 5, and 6 were made from latex Runs 1, 2, and 3 respectively with drying agent. Mixed metal catalyst ($Ca^{2+}$, $Co^{2+}$, $Mg^{2+}$, and $Cr^{2+}$) was added to accelerate drying.

[b] Adhesion is classified to 5 scales according to the standard, with "5" as the best.

dried at room temperature for two days. The results were given in Table VI. Adhesion is good for all samples. Hardness depends on the extent of curing ("drying"). As shown in Table VI, the addition of drying agent improved the curing rates of the films. Further results show that the pencil hardness of all the samples reach H1 after 3 months of curing. It is expected that with proper addition of drying agents, H1 hardness can be reached in only several days.

## CONCLUSION

Based on the study presented here and previous research,[4] the hybrid miniemulsion polymerization process has been shown to have a promising role in converting solvent-based coatings into environmentally friendly water-based coatings. A wide range of coatings resins might be used in this way, providing they are highly water insoluble and highly monomer soluble in order to act as good hydrophobes. There are a number of advantages associated with hybrid miniemulsion polymerization. First, It is a very stable process without coagulation and flocculation. Second, the robust droplet nucleation makes it easier to control the particle number and particle size during production process. It also enhances the likelihood that the composition of each particle is the same as formulated, and provides a means of incorporating resins that could not be incorporated by conventional emulsion polymerization due to the extremely low water solubility of the resin, and its resultant extremely retarded transport across the aqueous phase. Finally, by employing resin as both reactant and hydrophobe, higher purity of product can be achieved, since no additional hydrophobe is required.

Films obtained from the acrylic/OMPU latexes show good adhesion property and fair hardness property. Mixed metal drying agents can enhance the drying rate substantially.

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