Macromolecular Reaction Engineering

Hybrid Miniemulsion Polymerization of Acrylate/Oil and Acrylate/Fatty Acid Systems

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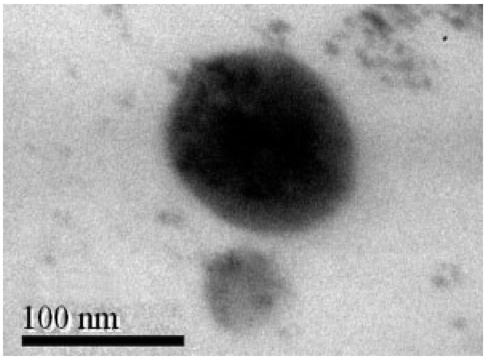
Acrylate–alkyd hybrid latex via miniemulsion polymerizations show promise as water-borne coating systems. However, poor homogeneity of the particles caused by the immiscibility of the alkyd in polyacrylate limits monomer conversion and film formation. To resolve this problem, the hybrid miniemulsion polymerization of acrylate in the presence of linoleic acid and sunflower seed oil was carried out. Products were characterized by solvent extraction, dynamic light scattering, gel permeation chromatography (GPC), differential scanning calorimeter (DSC), and transmission electron microscopy (TEM). The results provide clear evidence that substituting a fatty acid or natural oil with smaller molecular size (weight) for a conventional alkyd improves the grafting efficiency, and enhances the homogeneity of the hybrid polymer particles in water-borne latex systems.



Introduction

Previous Work on Acrylate–Alkyd Hybrid Coating Systems

Natural oils are triglycerides made up of glycerol condensed with three long chain fatty acids. These triglycerides, when treated with phthalic anhydride, chain-extend through phthalic anhydride linkages to form polyester oligomers known as alkyds. Alkyds have been widely used in the architectural and industrial coating applications for many years because of their properties such as gloss, hardness, chemical resistance, and low cost. However, solvent-based coatings contain volatile organic compounds (VOC) which are harmful to the environment and human health. In the last four decades, water-based polyacrylate latex coatings have been more and more widely used because of environmental and heath considerations, and ease of water cleanup. However, latex coatings still lack some properties of alkyds such as durability, hardness, and water and chemical resistance. The difference between solvent-based and water-based coatings is their different curing mechanisms. In the former system, the double bonds in the alkyd react with atmospheric oxygen during drying, forming a crosslinked film. Latex coatings lack any crosslinking mechanism, and film formation is exclusively due to the rise in the glass transition temperature of the film as water and small amount of organic solvent (coalescing aids) evaporates. There have been a number of investigations focusing on the development of water-based acrylate–alkyd hybrid coating systems via emulsion or miniemulsion polymerization since late 1990s, aiming at water-borne, environmental-friendly coating products with alkyd-like curing properties.

In 1996, Nabuurs et al.[1] studied emulsion polymerization of acrylate monomers in the presence of alkyd. They observed low monomer conversion caused by the unsaturated fatty acid chains in the alkyd stabilizing radicals through delocalization. They also found that as the polymerization proceeded, the polyacrylates and alkyd

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became immiscible and separated into different particles. Wang et al.[2] also studied the same alkyd–acrylate system via miniemulsion polymerization. They found that the alkyd was copolymerized with the acrylate. Moreover, it was concluded that most of the double bonds in the alkyd remained so that the curing capability was intact. In 1999, Wu et al.[3] investigated the performance of alkyd resin as costabilizer in miniemulsion polymerization. This study confirmed the previous results[2] and extended it by gel permeation chromatography (GPC), NMR, and differential scanning calorimeter (DSC) experiments that indicated poly(acrylate-*graft*-alkyd) is the predominant polymeric structure formed. Van Hamersveld et al.[4] studied the miniemulsion polymerization of methyl methacrylate (MMA) in the presence of partly hydroperoxidized sunflower oil (SFO-HP) as the oil soluble initiator. It was concluded that the use of fatty acid hydroperoxides as oil soluble initiator resulted in the formation of triglyceride modified polyacrylate molecules, which acted as compatibilizers between the oil and PMMA phase resulting in more homogeneous particles. However, another study[5] by the same group showed the contradicting observation against their previous study. In 2003, Schork and coworkers[6,7] investigated the grafting mechanisms in acrylate–alkyd hybrid miniemulsion polymerization. In another study,[8] Schork and coworkers studied the limited conversion in the hybrid miniemulsion polymerization of the acrylate–alkyd system. They proposed two mechanisms for the limited conversion of acrylate monomers. One is retardive chain transfer between acrylate monomers and the alkyd double bonds, and the other is microdomain phase separation blocking acrylate monomers from polymerization sites. Shoaf and Stockl[9] followed the hybrid miniemulsion polymerization study conducted by Wang et al. in 1996 and a patent by Schork et al. in 2002.[10] In Shoaf and Stockl's study, the formation for clear films from acrylate–alkyd hybrid, MEK resistance, and hardness of the films were tested. In 2004, Colombini et al.[11] used the interlayer model in both direct and reverse modes to investigate the viscoelastic properties of an acrylate–alkyd hybrid system in connection with its morphology. Also, Jowkar-Deriss and Karlsson[12] studied high solids content acrylate–alkyd hybrids prepared by dropping alkyd resin into acrylate dispersion. Tsavalas et al.[13] studied the morphology of hybrid acrylate–alkyd particles by transmission electron microscopy (TEM), SEM, AFM, and NMR. Results from this study confirmed the raspberry-like and core–shell morphology of acrylate–alkyd hybrid particles. NMR analysis confirmed significant phase separation in PMMA/alkyd polymer. Hudda et al.[14] developed a mathematical model to study the mechanisms of limited conversion in acrylate–alkyd hybrid miniemulsion polymerization. Their simulation results suggested chain transfer would reduce the rate of polymerization, but would not result in limiting conversion. Particle heterogeneity (polyacrylate shell and alkyd core) could adequately explain the limited conversion in acrylate–alkyd hybrid miniemulsion polymerization.

Emulsion and Miniemulsion Polymerization

The mechanisms of conventional emulsion and miniemulsion polymerization appear to be similar, but in some ways are significantly different. A conventional batch emulsion polymerization reaction can be divided into three intervals. Particle nucleation occurs during Interval I and is usually completed at low monomer conversion (2–10%) when most of the monomer is located in relatively large (1–10 μm) droplets. Particle nucleation is believed to take place when radicals formed in the aqueous phase grow via propagation and then enter into micelles or become large enough in the continuous phase to precipitate and form primary particles which may undergo limited flocculation until a stable particle population is obtained. Significant nucleation of particles from monomer droplets is discounted because of the small total surface area of the large droplets. Interval II involves polymerization within the monomer-swollen polymer particles with monomer supplied by diffusion from the droplets. Interval III begins when the droplets disappear, or at least reach a polymer fraction similar to that of the particles, and continues to the end of the reaction. Mass transport from the droplets (Interval II) can be a problem, however, for strongly hydrophobic species with very low water solubility.

Research[15,16] indicates that miniemulsion polymerization can provide benefits over the conventional emulsion polymerization. Miniemulsion polymerization involves the use of an effective surfactant/costabilizer system to produce very small (0.01–0.5 μm) monomer droplets. The droplet surface area in these systems is very large, and most of the surfactant is adsorbed at the droplet surfaces. Particle nucleation is primarily via radical (primary or oligomeric) entry into monomer droplets. The reaction then proceeds by polymerization of the monomer in these small droplets, hence there may be no true Interval II. Mass transport through the aqueous phase is not required with miniemulsion polymerization, and very water-insoluble reaction ingredients (i.e., natural oils and alkyds) can be effectively incorporated.

When an oil-in-water emulsion is created, the droplets must be stabilized against coalescence and diffusional instability (Ostwald ripening).[17] In creating a miniemulsion, besides adding appropriate surfactants, diffusional stabilization is achieved by adding a small quantity (1–2 wt.-% based on monomer) of a highly monomer-soluble, water-insoluble agent. Both long chain alkanes such as hexadecane and long chain alcohols such as cetyl alcohol have been used as stabilizing agents in miniemulsions.

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Polymer, chain transfer agent, and comonomers have been used successfully as well.[18–20] These stabilizing agents will be referred as costabilizers here.

Grafting Mechanism

There are two possible grafting mechanisms in the graft reaction between polyacrylate and alkyds.[8,14] Methacrylate monomers such as MMA with the methyl group adjacent to the vinyl bond are sterically hindered to directly react with the alkyd double bonds. Hence, MMA (or macroradical with MMA end) is more likely to graft via abstraction of the alpha-hydrogen on the fatty acid chain, forming a radical site capable of propagating or terminating (by combination) with another macroradical to form a graft. The radical site on the fatty acid chain is relatively stable, and so has a lower propensity to propagate. This is the origin of retardive chain transfer in these systems, and causes the commonly reported reduced polymerization rate of the acrylate monomers in the presence of alkyd resins. On the other hand, acrylate monomers such as BA, without methyl group hindrance, have higher radical reactivity. Macroradicals with BA end group can attack the double bonds by direct addition to form a grafted polymer chain. They may also participate in retardive chain transfer through hydrogen abstraction. Thus, acrylates will graft more extensively than methacrylates. The schemes of grafting mechanisms are shown in Figure 1.

Objective

Although there has been a great deal of work on acrylate–alkyd hybrids, there is still one fundamental problem remaining: most of the previous studies have shown that the hybrid acrylate–alkyd particles had core–shell structures. The shell was rich in polyacrylate,

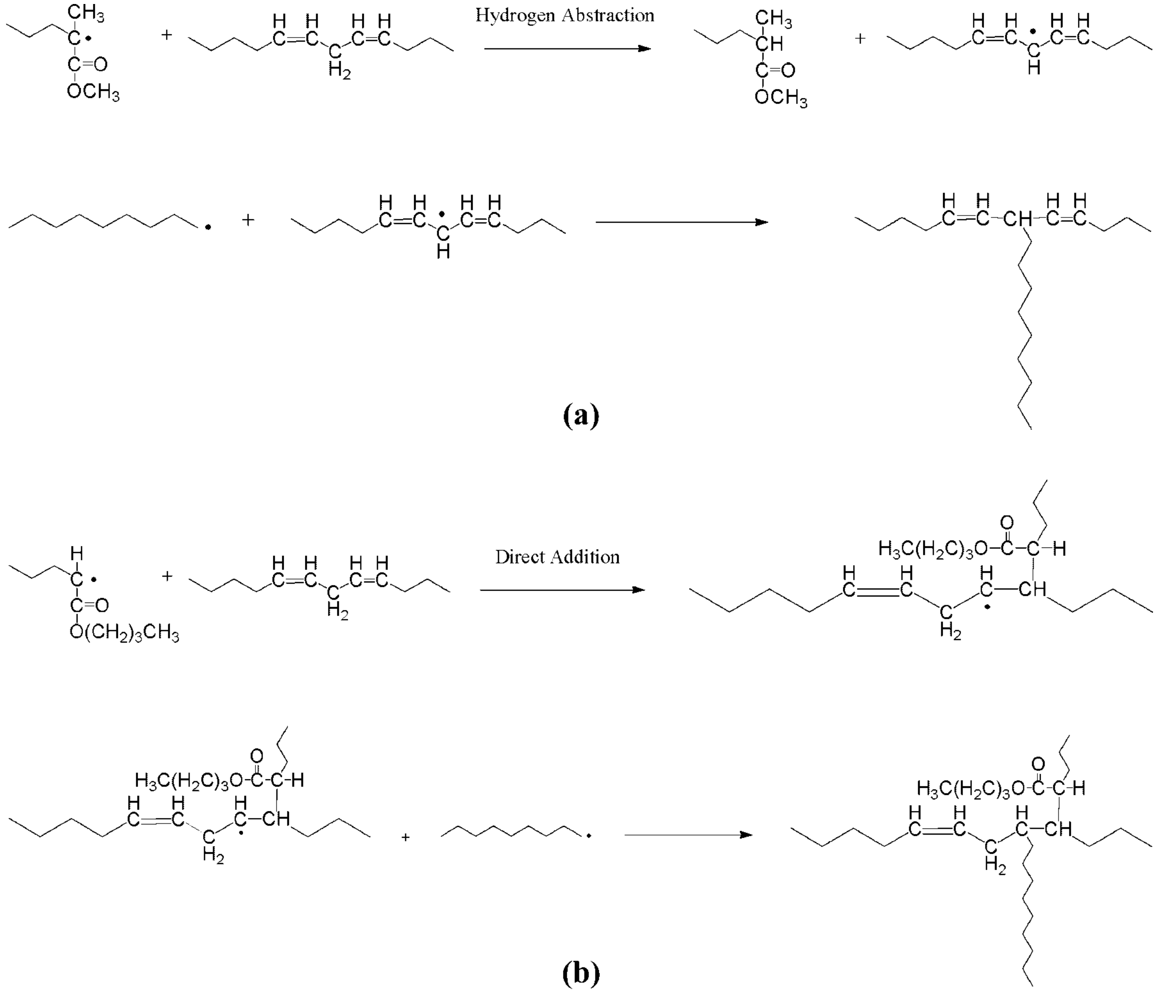

Figure 1. Schemes of grafting mechanisms: (a) hydrogen abstraction and (b) direct addition.

and the core was rich in alkyd. The reason for this is believed to be that as polymerization proceeds, the growing polymer chains become more and more immiscible with the alkyds. As a result, the more hydrophobic alkyds concentrate to the core. This is exactly what is not desired. The alkyd in the core is not only unavailable to graft to the growing polyacrylate chains in the shell, but also unable to provide crosslinking for film formation as polymer particles coalesce. The core–shell structure negates the desirable properties imparted by the alkyd (film hardness, durability, etc.).

To solve this problem, sunflower seed oil (SFO) and unsaturated fatty acid (linoleic acid) were proposed to replace alkyd in this study. Natural oils and fatty acids have similar curing capabilities as alkyds because of similar double bond contents, but they have significantly lower molecular weights (approximately 1 000 for natural oils, and 300 for common fatty acids). Hence, it is postulated that the hybrid particles with oil or fatty acid instead of alkyd should have better homogeneity than those from alkyd, due to better miscibility. Since fatty acids have lower molecular weights than oils, it is postulated that fatty acids should give even better homogeneity than oils.

In summary, the objective of this research is to study the acrylate/fatty acid and acrylate/oil hybrid system in terms of hybrid homogeneity, to explore the potential of replacing the alkyd with fatty acid or oil in hybrid coating systems. To the best of our knowledge, it is the first time for acrylate/fatty acid and acrylate/natural oil hybrid system to be investigated.

Experimental Part

In this study, acrylate/linoleic acid hybrid via miniemulsion polymerizations were conducted using two types of linoleic acids with different purities, 66 and 97%, respectively. The acrylate/SFO hybrid miniemulsion polymerizations were also conducted. Compositions of the two types of linoleic acid and the SFO are listed in Table 1. It should be noted that the linoleic acid with 66% purity has almost exactly the same composition as the SFO whose molecule is a triglyceride containing three fatty acid chains, of which 62.4% are linoleic acid chains. Based on the molecular weight and percentage of all components in the linoleic acid with 66% purity and the SFO, as shown in Table 1, it can be calculated that the double bond concentration in 66% linoleic acid is $3.44 \times 10^{21} \cdot g^{-1}$, and the double bond concentration in the SFO is $3.46 \times 10^{21} \cdot g^{-1}$. Hence, the difference between the double bond concentrations in these two materials can be neglected when the same amount is used, and the only difference between these two is their molecular sizes. A comparison of these two grafting agents will allow us to look at the effects of molecular size on the resultant hybrid material at constant double bond reactivity. Meanwhile a comparison of hybrid systems from two different linolenic acids will allow us to study the effect of double bond concentration at a constant molecular size.

Table 1. Composition of sunflower seed oil and linoleic acids.

Content (wt.-%)	Sunflower seed oil	Linoleic acid (66%)	Linoleic acid (97%)
	%	%	%
Linoleic acid	62.4	66.0	97.0
Oleic acid	26.5	23.3	–
Linolenic acid	0.2	≤1	–
Palmitic acid	5.8	6–10	–
Stearic acid	3.3	1–5	–

Methyl methacrylate and butyl acrylate (BA) are chosen to be the acrylate comonomers. As described in the grafting mechanism, fatty acid chains can be grafted onto BA by direct addition. But the grafting mechanism between MMA radicals and fatty acid chains are dominated by hydrogen abstraction because of the steric hindrance from the methyl group. Consequently the polymerization could be retarded by chain transfer reactions. However, bringing MMA in the polymerization is important and necessary for film formation. Because poly(butyl acrylate) (PBA) has a very low glass transition temperature (T_g) and will form a soft sticky film inapplicable for coatings. Poly(methyl methacrylate) (PMMA) with a high T_g around 105 °C can bring the glass transition temperature of the copolymer into the range of ambient temperature.

Materials

SFO and linoleic acids (66 and 97% purity) were all purchased from Aldrich. They were used as received, and their compositions are listed in Table 1.

MMA and BA were also purchased from Aldrich. They were passed through the inhibitor-remover column (from Aldrich) to remove the inhibitors before use. Sodium dodecyl sulfate (SDS), potassium persulfate (KPS), hydroquinone, hexadecane, diethyl ether, and chloroform (all from Aldrich) were used as received. The water used in this study was deionized.

Miniemulsion Preparation and Polymerization

Miniemulsion polymerizations were conducted from the recipes shown in Table 2.

The miniemulsion was prepared by dispersing the acrylate monomer–SFO–hexadecane (costabilizer) or acrylate monomer–linoleic acid–hexadecane solution into the aqueous SDS solution by mixing with a stirrer to form a course emulsion, which was further sheared to make a miniemulsion by sonication with an OmniRuptor 250 Ultrasonic Homogenizer for 6 min at 20% power output (30 W). The beaker containing the emulsion was immersed in ice water during the sonication to maintain low temperature.

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Table 2. Recipe for miniemulsion polymerization.

Sample code	Ingredients (wt.-%)				
	MMA	BA	Linoleic acid (66%)	Sunflower seed oil	Linoleic acid (97%)
MB	50	50	0	0	0
MBF1	37.5	37.5	25	0	0
MBF2	41.7	41.7	16.6	0	0
MBF3	45	45	10	0	0
MBS1	37.5	37.5	0	25	0
MBS2	41.7	41.7	0	16.6	0
MBS3	45	45	0	10	0
MBL1	37.5	37.5	0	0	25
MBL2	41.7	41.7	0	0	16.6
MBL3	45	45	0	0	10

The total weight consists of 150 parts water and 30 parts total monomer; 0.01 mol $\cdot$ L^{-1} SDS and 0.01 mol $\cdot$ L^{-1} KPS in water; 0.4 wt.-% hexadecane in oil phase.

The miniemulsion was transferred to a 250 mL three-neck flask equipped with a condenser and nitrogen gas inlet and outlet. The system was purged using nitrogen for 20 min to remove the oxygen in the miniemulsion and headspace, and then the flask was immersed into an oil bath at 70 °C. Moderate agitation was provided by a magnetic stir bar. The polymerization was started by injection of 10 mL KPS water solution (0.01 mol $\cdot$ L^{-1} based on the total water mass) into the system, and the polymerization was carried out under continuous nitrogen purging. Samples were drawn from the reactor with a syringe for gravimetric conversion analysis. At intervals, samples of the reactor contents were removed by syringe and put in pre-weighted pans containing a small amount of 0.5 wt.-% hydroquinone–water solution. The pans containing samples were dried in the oven at 50 °C for 24 h to evaporate all water and remaining monomer, and then weighted again. For extraction experiments to determine the degree of grafting, the samples were dried in a vacuum chamber at room temperature for 48 h to prevent post-polymerization crosslinking induced by the atmospheric oxygen and heat.

Degree of Grafting and Crosslinking

The degrees of grafting of acrylate/linoleic acid and acrylate/SFO hybrid systems were determined by solvent extraction. The extraction was performed in a Soxhlet extractor, using ethyl ether as a solvent for the determination of the degree of grafting. Then chloroform was used as a solvent for the determination of possible crosslinking during the polymerization. Ethyl ether is a good solvent for fatty acids, natural oils, and grafted fatty acids and oils, but a bad solvent for polyacrylates.[3] Chloroform is a good solvent for all components in these hybrid systems except crosslinked ones. About 1 g vacuum dried latex sample was placed into a cellulose extraction thimble (22 mm × 80 mm, Whatman) in the extractor. After 24 h extraction with ethyl ether at 45 °C, the remaining was dried in vacuum for 36 h at room temperature, and then weighted. To determine the degree of crosslinking during the polymerization, the residual from the ethyl ether extraction was extracted using chloroform at 70 °C for another 24 h. The remaining material was dried for 36 h and weighted.

Polymer Particle Size

Dynamic light scattering (DLS) was used to characterize the polymer particle size. A Photocor-FC light scattering instrument with a 5 mW laser source at 633 nm was used, with the scattering angle being 90°. To measure the polymer particle size, the latex was diluted with a water solution of 0.1 wt.-% SDS.

Molecular Weight Distribution

Following the polymerization experiments, the molecular weight and molecular weight distribution of the polymers were measured by GPC with a Waters 410 differential refractometer operated at 30 °C. HPLC grade chloroform was used as the solvent carrier (0.6 mL $\cdot$ min^{-1}).

Differential Scanning Calorimetry

T_g of the samples were measured by thermal analysis with a DSC, TA Instruments Q100. A heat–cool–heat cycle was run from −60 to 80 °C. The heating rate was 10 °C $\cdot$ min^{-1} and the cooling rate was 5 °C $\cdot$ min^{-1}. About 10 mg of polymer sample was used for each measurement.

Transmission Electron Microscopy

TEM was used to investigate the morphology of hybrid particles. Observations were conducted using JEOL TEM 2100 LaB_6 (100 kV). The latex sample was diluted in deionized water as 1:100 (volume ratio), and the diluted latex was stained by dripping about 20 μL of 2 wt.-% osmium tetroxide aqueous solution into 15 mL latex. The latex was placed in the fume hood for 24 h to be fully stained before depositing 5 μL stained latex on a cooper grid (200 mesh, coated with carbon/formvar). The drop on the grid was dried for 12 h before observation using TEM. Osmium tetroxide stains double bonds which only exist on the fatty acid chains in linoleic acid and SFO. If core–shell structure was formed in the hybrid particle, the TEM image should show a darker core which is rich in linoleic acid or SFO, and a lighter shell which is rich in polyacrylates.

Results and Discussion

Polymer Particle Size

The average polymer particle sizes are listed in Table 3. From the data, it can be confirmed that all particle sizes are in the typical miniemulsion range.

Table 3. Polymer particles size measurements.

Sample code	Particle diameter nm
MB	115.6 ± 0.4
MBF1	113.6 ± 0.5
MBF2	104.0 ± 0.4
MBF3	113.0 ± 0.7
MBS1	145.0 ± 0.8
MBS2	119.1 ± 1.1
MBS3	108.6 ± 0.5
MBL1	116.6 ± 1.1
MBL2	102.8 ± 0.6
MBL3	109.0 ± 0.6

Monomer Conversion

Comparing to MMA/BA copolymerization, the mechanism of MMA/BA polymerization in the presence of linoleic acid or SFO is more complicated because of the chain transfer reactions. All the influential reactions in the acrylate/linoleic or acrylate/SFO miniemulsion polymerization are listed below:[6]

$$I \xrightarrow{fk_{\mathrm{d}}} 2R \tag{1}$$

$$R^{\cdot} + M \xrightarrow{k_{\mathrm{i}}} M_1 \tag{2}$$

$$M_1^{\cdot} + M \xrightarrow{\sum_1^{n-1} k_{\mathrm{p}}} M_n \tag{3}$$

$$M_N^{\cdot} + M_m^{\cdot} \xrightarrow{k_{\mathrm{t},C}} M_{n+m} \tag{4}$$

$$M_n^{\cdot} + M_m^{\cdot} \xrightarrow{k_{\mathrm{t},D}} M_nH + M_m \tag{5}$$

$$M_n^{\cdot} + B_{\alpha-H} \xrightarrow{k_{\mathrm{abs}}} B^{\cdot} + M_nH \tag{6}$$

$$B^{\cdot} + M \xrightarrow{k_{\mathrm{a1}}} BM \tag{7}$$

$$BM^{\cdot} + M \xrightarrow{\sum_1^{n-1} k_{\mathrm{p}}} BM_n \tag{8}$$

$$B^{\cdot} + M_n^{\cdot} \xrightarrow{k_{\mathrm{t}}} BM_n \tag{9}$$

$$M_n^{\cdot} + B_{\mathrm{C=C}} \xrightarrow{k_{\mathrm{add}}} M_n\text{-}g\text{-}B \tag{10}$$

$$M_n\text{-}g\text{-}B^{\cdot} + M \xrightarrow{k_{\mathrm{a2}}} M_n\text{-}g\text{-}BM \tag{11}$$

$$M_n\text{-}g\text{-}BM^{\cdot} + M \xrightarrow{\sum_1^{m-1} k_{\mathrm{p}}} M_n\text{-}g\text{-}BM_m \tag{12}$$

$$M_n\text{-}g\text{-}B^{\cdot} + M_m^{\cdot} \xrightarrow{k_{\mathrm{t}}} M_n\text{-}g\text{-}BM_m \tag{13}$$

In the above equations, I is the initiator, R is the initiator-derived radical, M is the monomer, B is the branch point on fatty acid chain, and "-*g*-" means the grafted polymer.

In the above mechanism, Equation (1) and (2) are the initiation reactions and Equation (3)–(5) are the propagation and termination of MMA and BA monomers to form MMA–BA copolymer or homopolymers. Equation (6) describes the chain transfer reaction via hydrogen abstraction which is primarily relevant for MMA. Equation (7)–(9) are the propagation and termination reactions involving $B^{\cdot}$ radicals derived from hydrogen abstraction. Since $B^{\cdot}$ radicals are quite stable because of the conjugation with the adjacent double bonds, polymerization rate is reduced. Equation (10) is the chain transfer reaction via direct addition which is heavily favored for BA. Equation (11)–(13) describe the propagation and termination reactions involving M_n-g-$B^{\cdot}$ radicals derived from direct addition. The M_n-g-$B^{\cdot}$ is not conjugated with any double bonds, thus is more reactive than $B^{\cdot}$ radical. MMA monomers grafting relies mainly on hydrogen abstraction reactions (6)–(9), and BA monomers can graft via both hydrogen abstraction and direct addition reactions (6)–(13). Hence, grafting occurs mostly between BA and linoleic acid or SFO.

Monomer conversion (MMA and BA combined) versus time is plotted in Figure 2 for all runs listed in Table 2. Comparing the three monomer/linoleic acid and monomer/SFO systems in Figure 2, it can be generally concluded that the polymerization in the presence of linoleic acids (66 and 97%) is slower than that in the presence of SFO, while the polymerization of MMA and BA (MB) without either

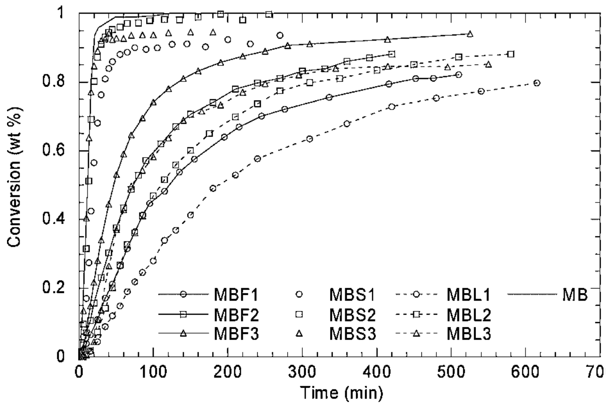

Figure 2. Monomer conversion of copolymerization of MMA and BA in present of linoleic acids and sunflower seed oil.

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linoleic acid or SFO is the fastest of all. This observation suggests that the existence of linoleic acids or SFO retards the polymerization, and it is consistent with the retardive chain transfer mechanism discussed previously. According to the proposed mechanism, grafting between MMA radicals and double bonds on the fatty acid chain is dominated by retardive chain transfer, which slows the rate of polymerization, but should also result in more grafted polymer chains. Hence, it can be seen in each monomer/linoleic acid (monomer/SFO) system, the polymerization rate is decreased by increasing the linoleic acid/monomer or SFO/monomer ratio.

In order to further look at the effects of double bond concentration and molecular size of the linoleic acid and the SFO on the polymerization rate of three hybrid systems, the conversion curves with same monomer/fatty acid and monomer/SFO ratio are plotted in Figure 3–5.

From Figure 3 to 5, it can be seen that the polymerization rate of MMA and BA in the presence of linoleic acid (97% purity) is lower than that in the presence of linoleic acid (66% purity), in all three monomer/linoleic acid ratios. The lower polymerization rate is caused by the retardive chain transfer reactions. Therefore, it is suggested that the linoleic acid with higher double bond concentration allows more grafting. Also, Figure 3–5 show that the polymerization rate of MMA and BA in the presence of SFO is even higher than that in the presence of linoleic acid (66% purity). As mentioned previously, the difference of the double bond concentrations between the SFO and the linoleic acid (66% purity) can be neglected, the only difference between these two is that molecular weight (size) of the SFO is much larger than that of the linoleic acid, 900 and 280 $g \cdot mol^{-1}$, respectively. Hence, the conversion curves in Figure 3–5 suggest that the larger molecules may result in higher polymerization rate, as well as lower degree of grafting. A possible interpretation for this observation is that as polymerization of MMA and BA proceeds, the polymer chains grow longer and become more immiscible with the large SFO molecules, which could result in phase separation to form core–shell structure, in which the shell is rich in polyacrylate and the core is rich in SFO molecules. Another possible phase separation scenario could be that small SFO molecule domains are isolated and distributed in the polyacrylates bulk phase to form raspberry-like particles. In both cases, SFO molecules are prevented from contact with growing MMA–BA chains, thus the polymerization of the acrylate monomers proceeds more rapidly without retardive chain transfer reactions.

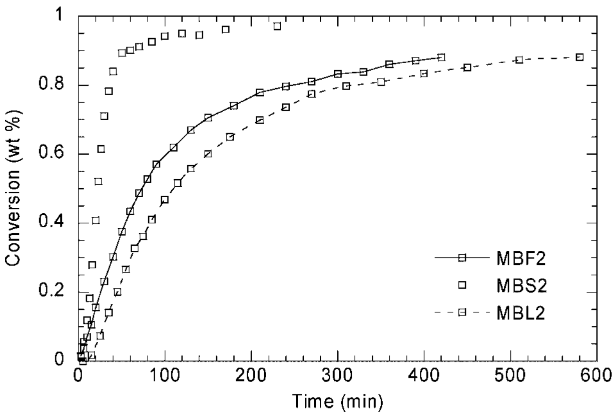

Figure 4. Monomer conversions with monomer/SFO and monomer/linoleic acid ratio of 5:1.

Molecular Weight Distribution

The molecular weight distributions of the polymers in each hybrid system were plotted in Figure 6–8, alongside the molecular weight distribution of the pure MMA–BA

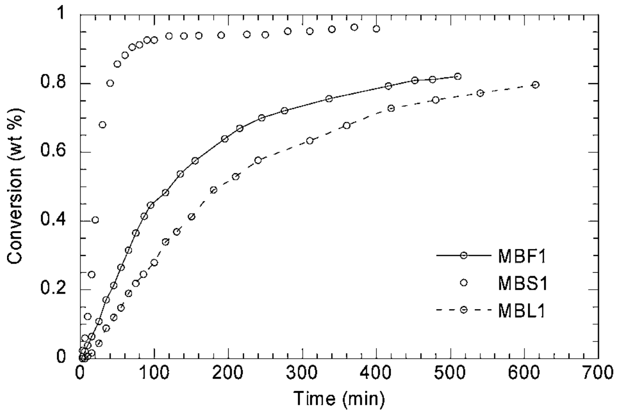

Figure 3. Monomer conversions with monomer/SFO and monomer/linoleic acid ratio of 3:1.

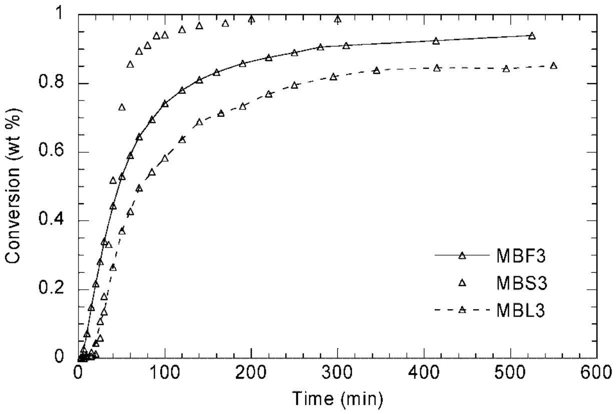

Figure 5. Monomer conversions with monomer/SFO and monomer/linoleic acid ratio of 9:1.

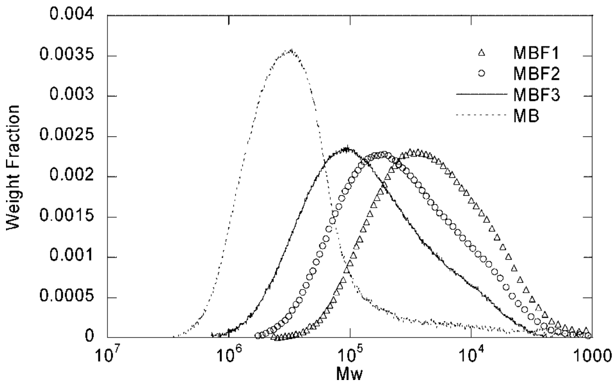

Figure 6. Molecular weight distribution of the MMA–BA–linoleic acid (66%) polymer.

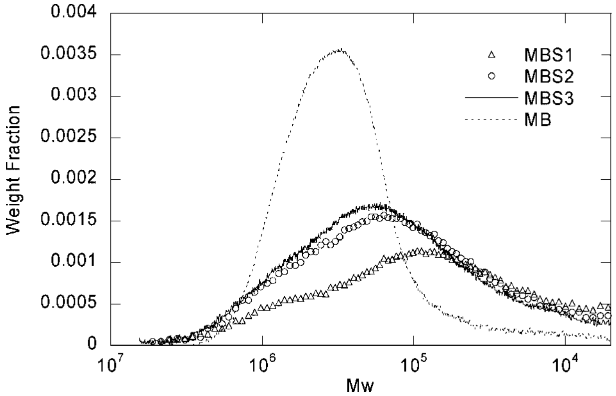

Figure 7. Molecular weight distribution of the MMA–BA–SFO polymer.

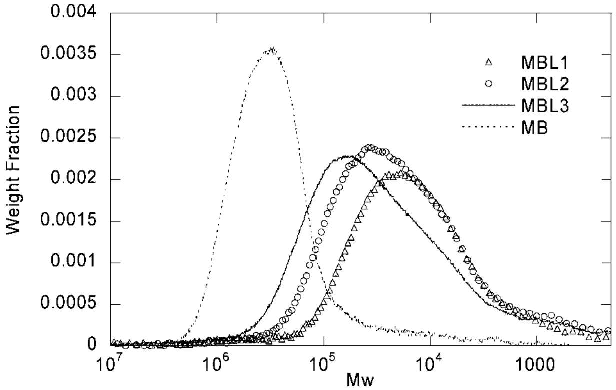

Figure 8. Molecular weight distribution of the MMA–BA–linoleic acid (97%) polymer.

copolymer which was polymerized in the absence of linoleic acid and SFO.

Figure 6–8 show that the molecular weights of polymers with grafted linoleic acid are smaller than those of the pure MMA–BA copolymer. Also, the acrylate/linoleic acid and acrylate/SFO polymers show very broad molecular weight distributions. These are due to the chain transfer reactions between acrylate monomers and linoleic acids. As described in the polymerization mechanism, chain transfer reactions enhance the variability of propagation and the possibility of termination. Figure 6–8 also show a trend that the molecular weight decreases with decreasing monomer/linoleic acid or monomer/SFO ratio, indicating that higher linoleic acid or SFO content brings higher degree of grafting in the hybrid system.

In Figure 7, the molecular weight distribution of sample MBS1 with the smallest monomer/SFO ratio (3:1) shows an obvious shoulder around molecular weight of 6×10^5, which is similar to the molecular weight of the pure MMA–BA copolymer. This could be the evidence of the existence of polyacrylates in the acrylate/SFO hybrid system. One interpretation for this observation could be that as the polymerization proceeds, the SFO molecules are phase separated from the growing polyacrylate chains because of the increasing immiscibility of the large SFO molecules and polyacrylates. In the acrylate-rich phase, the radicals polymerize acrylate monomers almost exclusively, with little grafting in the absence of SFO. This hypothesis will be further examined by determining the degree of grafting and the glass transition temperature(s) of this system.

In order to look at the effects of double bond concentration and molecular size, the molecular weight distributions of the hybrid system with same monomer/linoleic acid or monomer/SFO ratio are compared in Figure 9–11.

It can be seen from Figure 9 to 11 that the molecular weight of the acrylate/SFO hybrid polymer is higher than that of the corresponding acrylate/linoleic acid (66% purity) polymer. The only difference between the SFO and the linoleic acid (66% purity) is the larger molecular size of the SFO. As described above, larger SFO molecules could lead to phase separation inhibiting the grafting

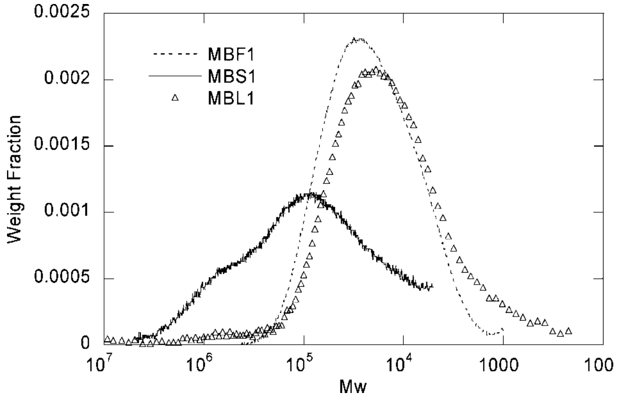

Figure 9. Molecular weight distributions of hybrid polymers with 3:1 monomer/linoleic acid (SFO) ratio.

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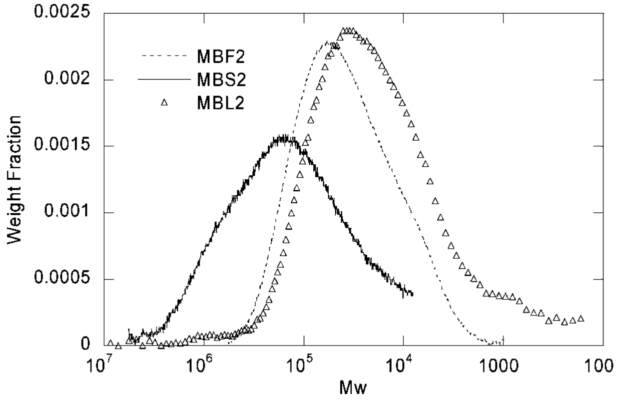

Figure 10. Molecular weight distributions of the hybrid polymers with 5:1 monomer/linoleic acid (SFO) ratio.

reactions, consequently, result in possible existence of polyacrylates in acrylate/SFO hybrid system. Molecular weight of polyacrylates is higher than that of grafted polymers, which could explain the higher molecular weight of acrylate/SFO systems. It is also shown that the molecular weight of the 66% linoleic acid hybrid polymer is higher than the corresponding one of the 97% linoleic acid hybrid polymer. The only difference between these two linoleic acids is the double bonds concentration. It is evident that the high double bond concentration could lead to more retardive chain transfer reactions resulting in lower molecular weight and higher degree of grafting.

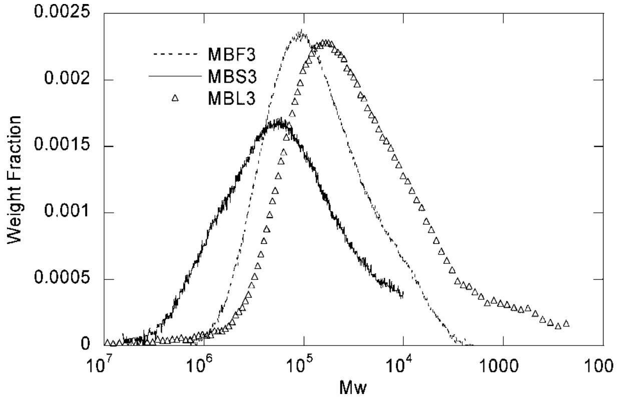

Figure 11. Molecular weight distributions of hybrid polymers with 9:1 monomer/linoleic acid (SFO) ratio.

Degree of Grafting and Crosslinking

As described before, the degree of grafting is determined by solvent extraction. Ethyl ether is a bad solvent for polyacrylates, thus after the extraction and drying, the residual should only contain ungrafted polyacrylates, surfactants and initiator, and the crosslinked polymer, if there is any. All the dried residuals from the ethyl ether extraction were extracted using chloroform resulting in no residuals. Hence, it can be concluded that there was no crosslinking during polymerization. Most of the ungrafted double bonds on the fatty acid chains were preserved, which is of great importance for the film formation in coating applications.

The degree of grafting can be calculated by the following formula:

$$\begin{aligned}\text{Degree of grafting} &= \left(\frac{\text{weight of acrylate grafted}}{\text{weight of converted acrylate monomer}}\right)100\% \\ &= \left(\frac{\text{total weight} \times (1\text{-oil}\%) - \text{residual weight}}{\text{total weight} \times \text{acrylate}\%}\right)100\% \end{aligned} \tag{14}$$

$$\text{where oil}\% = \frac{\text{oil weight}}{\text{monomer weight} \times \chi + \text{oil weight} + \text{surfactant weight} + \text{initiator weight}}$$

$$\text{acrylate}\% = \frac{\text{monomer weight} \times \chi}{\text{monomer weight} \times \chi + \text{oil weight} + \text{surfactant weight} + \text{initiator weight}}$$

where χ is the final monomer conversion.

The grafting degrees for all samples from three hybrid systems are listed in Table 4. From the results it can be seen that the degree of grafting decreases with increasing acrylate/linoleic acid or acrylate/SFO ratio. This is consistent with the observation from the molecular weight distribution data. The degree of grafting in the acrylate/SFO hybrid system is much lower than the corresponding ones in the acrylate/linoleic acid hybrid systems, which again suggests that higher molecular weight (larger molecular size) of the SFO is unfavorable for the grafting reactions due to the possible phase separation. Additionally, the degree of grafting in the 66% linoleic acid hybrid system is slightly lower than the corresponding ones in the 97% linoleic acid hybrid system. This also confirms the hypothesis proposed before that higher double bond concentration is favorable for grafting reactions. The relatively low grafting degrees of MBS2 and MBS3 indicate that a fraction of pure MMA–BA copolymer exists in the hybrid systems with MMA–BA–SFO copolymer; this will be investigated further using DSC.

Table 4. Degree of grafting and crosslinking.

Sample	Degree of grafting %	Degree of crosslinking %
MBF1	100	0
MBF2	94.1	0
MBF3	89.2	0
MBS1	84.8	0
MBS2	64.3	0
MBS3	58.4	0
MBL1	100	0
MBL2	98.0	0
MBL3	97.0	0

Glass Transition Temperature

For the hybrid miniemulsion polymerization system, grafted copolymers of acrylates and linoleic acid or SFO are expected. However, it is possible there is pure polyacrylates existing in the hybrid system as the results of grafting degree indicate. To confirm this, the polymer samples were analyzed by DSC. Figure 12 shows the DSC result of sample MB, which is the copolymer from miniemulsion polymerization of MMA and BA in the absence of linoleic acid and SFO. DSC result shows that the T_g of the MMA–BA copolymer from this miniemulsion polymerization system is about 23 °C. Figure 12 also shows a possible glass transition around −48.4 °C which could indicate the existence of pure PBA. According to Fox-Flory Equation, the T_g of a copolymer can be estimated as follows:

$$\frac{1}{(T_g)_{\text{copolymer}}} = \sum \left[\frac{f_i}{(T_{gi})_{\text{homopolymer}}} \right] \qquad (15)$$

where f_i is the weight fraction and T_{gi} is the glass transition temperature of the i-th homopolymer. If it is assumed that T_g of PMMA and PBA are 105 and −49 °C, respectively, and 23 °C is assumed to be the T_g of the MMA–BA copolymer, it can be calculated that the weight ratio of MMA and BA in the copolymer is about 3:2. Since the ratio of MMA and BA in the recipe was 1:1, pure PBA may exist with the MMA–BA copolymer.

Figure 13 shows the DSC of sample MBF1, which is the hybrid polymer with 66% linoleic acid and the monomer/linoleic acid ratio is 3:1. This figure shows a glass transition around −26.0 °C. Since it was determined that sample MBF1 was 100% grafted, this temperature can be assumed as the T_g of the MMA–BA–linoleic acid copolymer. Figure 14 shows the DSC of sample MBS3, which has a 58.4% degree of grafting. This figure shows two glass transitions, one is around −24.5 °C and the other is around 23.1 °C. The former one is believed to be the T_g of MMA–BA–SFO copolymer, and the later is believed to be the T_g of pure MMA–BA copolymer which is consistent with the observation in Figure 12. Figure 15 shows the DSC of sample MBL2 from the 97% linoleic acid hybrid system,

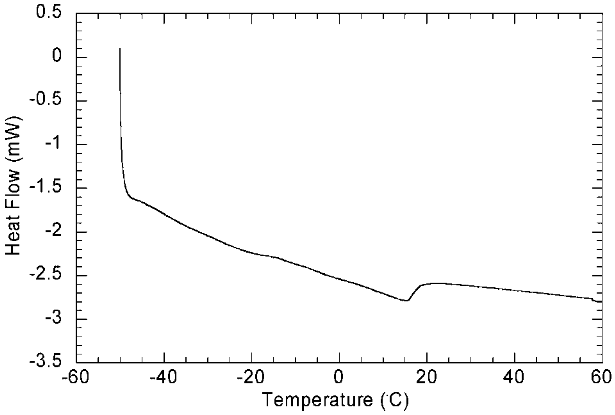

Figure 13. DSC of MBF1.

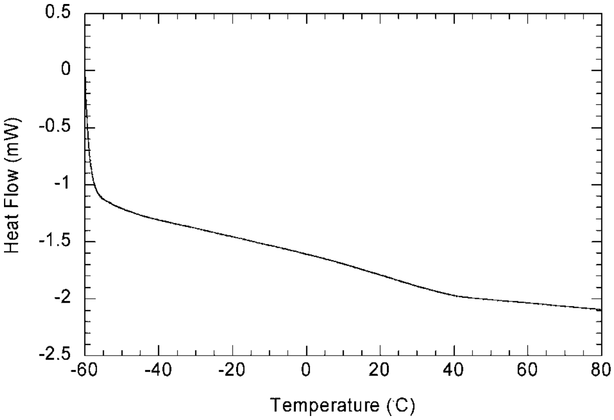

Figure 12. DSC of MMA–BA copolymer.

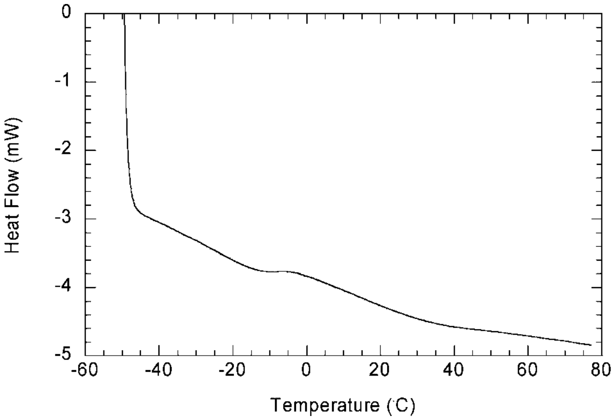

Figure 14. DSC of MBS3.

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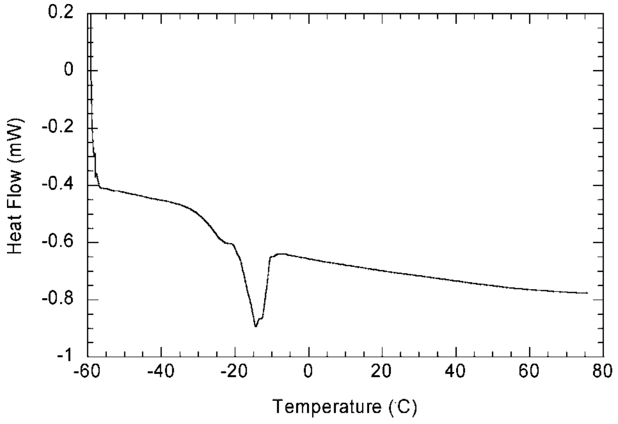

Figure 15. DSC of MBL2.

with 98% degree of grafting. This figure shows a single glass transition at around −26.6 °C, which is consistent with the observation in Figure 13 and believed to be the T_g of MMA–BA–linoleic acid copolymer. The negative peak (heat absorbance) in Figure 15 is believed due to the melting of the frozen unreacted linoleic acid which crystallizes at −20 °C.

Particle Morphology Study by TEM

As mentioned in the introduction, one of the most important concerns of the acrylate/alkyd hybrid miniemulsion polymerization system is the phase separation caused by the immiscibility of alkyd and polyacrylates. The core–shell structure of the acrylate/alkyd hybrid particles were observed in a few previous studies.[4,5,13] The polyacrylate-rich shell prevents alkyd-rich core from crosslinking during the film formation, and this is the reason why fatty acid and oil replace alkyd in this study. From the extraction and DSC results, it may be inferred that hybrid particles from acrylate/linoleic acid system may have more homogenous morphology, because their degrees of grafting are close to 100% and their DSC results show single glass transitions. The hybrid particles from acrylate/SFO system may have core–shell structures, because their degrees of grafting are low and their DSC results show two glass transitions indicating the existence of pure MMA–BA copolymer. In order to obtain the direct observation, the hybrid particles were observed with TEM.

Figure 16 shows a TEM image of a hybrid particle from the acrylate/linoleic acid system. There is no obvious core–shell structure observed, which indicates a homogenous particle. This observation is consistent with the high degree of grafting from the extraction experiment, and could lead to the conclusion that acrylate/linoleic acid hybrid system could eliminate the phase separation problem occurring in acrylate/alkyd hybrid system. Figure 17 shows a hybrid particle from the acrylate/SFO hybrid system. From this image, a lighter and rough shell structure can be observed as well as a darker irregular-shaped core. This observation is also consistent with the low degree of grafting of the acrylate/SFO system. Figure 16 and 17 show the evidence that large molecular size of the grafting agents (alkyd or SFO) contributes to phase separation in the hybrid coating systems.

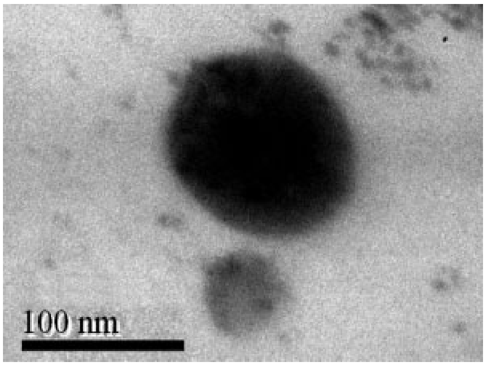

Figure 16. TEM image of MBF1 particle from acrylate–linoleic acid hybrid system.

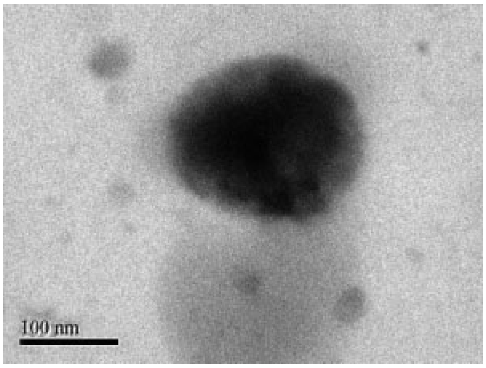

Figure 17. TEM image of MBS3 particle from acrylate–SFO hybrid system.

Conclusion

Three hybrid latex systems, acrylate/linoleic acid (66 and 97% purity), and acrylate/SFO were produced via miniemulsion polymerization. Results of monomer conversion, molecular weight distribution, degree of grafting, and particle morphology were presented and compared. There is strong evidence that using fatty acid with smaller molecular size and higher double bond concentration (particularly linoleic acid of 97% purity in this study) can increase the degree of grafting in the hybrid polymers and enhance the homogeneity of the hybrid particles. As expected, increased grafting causes a decrease in the molecular weight and broadens the molecular weight distribution. However, this should not affect the properties of the final coating, since the ungrafted double bonds in the fatty acid will form a highly crosslinked structure during the film formation. Latex film formation from the systems in this study will be investigated as the future work.

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