

Grafting Mechanisms in Hybrid Miniemulsion Polymerization

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ABSTRACT: The ultimate objective of hybrid miniemulsion polymerization is to produce a water-based crosslinkable coating through *in situ* grafting of a free radical growing acrylic polymer with an unsaturated resin. Certain authors have reported low grafting while others have reported higher. This article explores the factors that influence the grafting tendencies of these systems. Methacrylates such as methyl methacrylate (MMA) have a sterically hindered radical center that lowers its reactivity toward unsaturated resin. This steric hindrance from the methyl group forces grafting of this type of monomer to occur by abstraction of a hydrogen allylic to a resinous double bond. This chain transfer produces a relatively inactive radical on the resin that reduces the grafting efficiency. The transfer process also inherently produces some degree of terminated PMMA polymer within the particle. Grafting occurs in this type of system through termination of living PMMA chains with that radical produced on the resin. For relatively water-soluble monomers such as MMA, grafting efficiency is fur-

ther lessened by homogeneous nucleation resulting from the monomer hydrophilicity. These newly created particles cannot contain alkyd due to its hydrophobicity and thus inability to transport across the aqueous phase, and hence cannot produce grafted polymer. Nonetheless, degree of grafting of nearly 50% was observed in these systems. For hybrid systems involving an acrylate monomer such as butyl acrylate (BA), virtually complete grafting with alkyd was observed. This is due to the uninhibited BA radical center allowing the molecule to add directly through a resin double bond. This process offers the possibility for complete grafting. Homogeneous nucleation is not involved in this system due to the insolubility of BA in the aqueous phase. Resin double bond content and degree of conjugation also play an integral role in the grafting process. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1825–1836, 2003

Key words: miniemulsion; alkyd; hybrid; acrylic; graft

INTRODUCTION

Hybrid miniemulsion polymerization is a field that has matured over the past half-decade in concept and application to various component systems. Several studies have appeared describing systems of such combination as coacrylic/unsaturated polyester resin,^{1,2} coacrylic/oil modified polyurethane resin,³ acrylic/alkyd resin,^{4–10} coacrylic/alkyd resin,^{4,7} acrylic/sunflower oil resin,¹⁰ coacrylic/epoxy resin,¹¹ and styrene/Kraton rubber.¹² However, a fundamental understanding of the *in situ* grafting mechanism and reaction limitations for this class of hybrid polymerizations has yet to be well documented. This article investigates these mechanisms and reveals some of the underlying reasons behind limitations seen in several of these systems. The experimental program herein deals with acrylic/alkyd resin and coacrylic/alkyd resin systems, yet the fundamental principles in-

involved in evaluation should apply to this class of hybrid polymers as a whole.

Hybrid miniemulsion polymerization deals with free radical (co)polymerization in the presence of an unsaturated resin such as alkyd or other polyesters. Since the end use for such materials is often paints and coatings, emulsion (referred to here as “macroemulsion”) or miniemulsion polymerization is most often the process of choice. Emulsion polymerization introduces several complications and limitations for this type of system. Nucleation in macroemulsion polymerization predominantly occurs in micelles¹³ dissolved in the continuous aqueous phase, whereas the dispersed oil-phase droplets serve mainly as reservoirs feeding reaction components to the micelles (which once nucleated become growing polymer particles). Transfer through the aqueous phase may introduce diffusion limitations. In the case of a macroemulsion, these limitations can either impede the rate at which components transfer to the sites of nucleation or in some cases the hydrophobicity of a reaction component can prevent it from diffusing through the continuous phase at all. In the latter case, phase separation occurs negating the objective of the hybrid polymerization.⁴ All attempts to use macroemulsion polymerization to graft resins such as polyesters, poly-

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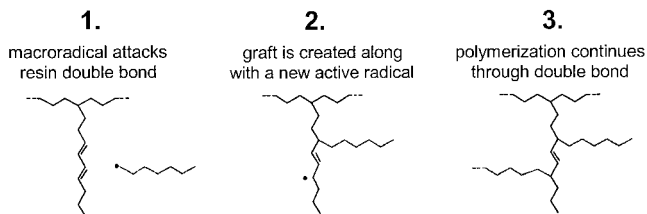


Figure 1 Grafting mechanism for addition through double bond.

urethanes, and alkyds into acrylics have resulted in complete phase separation of that component from the emulsion. For this reason, miniemulsion becomes likely the most suitable environment for this class of hybrid polymerization.

In a miniemulsion, the monomer droplets have a diameter approximately one order of magnitude smaller than the equivalent macroemulsion.¹⁴ With all other recipe details identical, this smaller droplet size ensures that the bulk of the surfactant present in the system will now be adsorbed onto the miniemulsion droplet surface aiding in the stability of the larger interfacial area. No micelles exist, and so no micellar nucleation takes place. Smaller droplets and larger interfacial area ensure that initiator radicals will nucleate the oil droplets directly.¹⁴ This modification of the locus of nucleation imparts dramatically different opportunities for reaction systems. Transfer across the continuous phase is eliminated, and the hydrophobicity of reaction components becomes a nonissue. Specifically, droplet nucleation is what allows *in situ* grafting to occur between growing polymer and a resinous component, as both components are in the same environment from the inception of polymerization through to the end of polymerization.

There has been much speculation over the mechanism by which growing polymer grafts with the resinous component. For the purposes of this article, growing polymer will either be homoacrylic or a copolymer of acrylic components, both in the presence of alkyd. As will be described, there is a distinct difference between homoacrylic hybrid polymerizations and coacrylic ones from both mechanistic and product property standpoints. This is a distinction that has not been reported in the hybrid miniemulsion literature to date and is a concept that alleviates some contradiction and confusion among previous work.

In a simplified description of grafting as it occurs in hybrid miniemulsion polymerization, monomer A (in the present work an acrylic monomer or a mix of acrylic monomers) is polymerized in the presence of polymer B (in the present work, an alkyd resin). The final distribution of polymer from such a graft copolymerization may include homopolymer from the homopolymerization of A, homopolymer B that has not undergone grafting, and graft copolymer with grafts

of poly-A on poly-B. The distribution of these three cases within the final hybrid polymer is heavily influenced by choice of monomer A and the reactivity of sites on polymer B.

For the present work, the predominant reactive sites for grafting on the alkyd are carbon-carbon double bonds (addition) in the natural oils making up the alkyd as shown in Figure 1, or hydrogens allylic to those double bonds (abstraction) as shown in Figure 2. If one only considers the energy required to interact with a π -bond versus a σ -bond, addition to a double bond is energetically favored over abstraction of an allylic hydrogen.¹⁵ However, the structure of groups that surround the reactive polymer site and steric features of the attacking monomer or chain often influence this choice enough to make abstraction the more preferred route of attack.^{16,17} The initiator also plays a role in determining the mechanism of grafting. In some cases, the primary initiator radical will attack polymer B, creating a radical site where growth of polymer A can occur. Graft site initiation can occur by means of a primary radical attack event and/or by macroradical attack (chain transfer to polymer). Given the mechanisms above, it may be seen that monomer choice will play a major role in determining which of these routes is favored in a particular hybrid graft copolymerization.

EXPERIMENTAL

Chemicals

McWhorter Chemicals (now part of Eastman Chemicals) supplied the alkyd resins. Monomers used were obtained from Aldrich and included methyl methac-

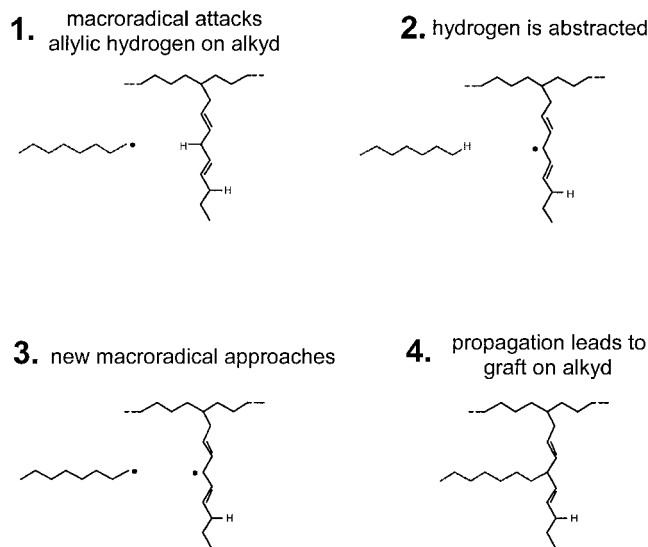


Figure 2 General mechanism for grafting through chain transfer. The allylic radical shown in (2) is conjugated with double bonds and is quite stable and of low reactivity.^{12,22}

TABLE I
Generalized Recipe for All Experiments

Component	Concentration
Deionized water	200 parts
Monomer ^a	20 parts
Alkyd	20 parts ^b
Sodium dodecyl sulfate (SDS)	0.01 mol/L water
Potassium persulfate (KPS)	0.01 mol/L water
2,2'-azobisisobutyronitrile (AIBN) ^c	0.5 wt % based on monomer
Hexadecane	4 wt % based on monomer

^a Methyl methacrylate (MMA), butyl acrylate (BA), and butyl methacrylate (BMA) where appropriate.

^b Accounting for solvent present in alkyd.

^c Where appropriate.

rylate (MMA), butyl acrylate (BA), and butyl methacrylate (BMA). Monomers were first distilled to remove any inhibitors present. The surfactant was sodium dodecyl sulfate (SDS) and initiators used included potassium persulfate (KPS), 2,2'-azobisisobutyronitrile (AIBN), and benzoyl peroxide (BPO), all supplied by Aldrich and used as received. Hydroquinone, for quenching, was supplied by Fisher and the water used throughout the work was deionized. Diethyl ether and methanol, used as solvents for extraction, and tetrahydrofuran (THF), eluent for gel permeation chromatography (GPC) analysis, were all obtained from Aldrich and used as received.

Analyses

Monomer conversion was determined through gravimetric analysis. The accuracy was $\pm 1\%$ on monomer conversion. Preparation of samples for GPC involved drying the sample in a vacuum oven and dissolving it into THF at a concentration of 8 mg/ml. Waters 410 Differential Refractometer was used as the detector with an eluent flow rate of 1 ml/min. Waters 510 HPLC pump was used with a three-column bed of pore sizes 10^3 , 10^4 , and 10^5 angstroms. Columns were 300×7.8 mm in dimension and were run at 30°C . Viscotek TriSEC software was used for data acquisition and analysis. A Setaram TG-DSC 111 thermoanalyzer instrument was used in DSC-only mode at a heating rate of $5^\circ\text{C}/\text{min}$ with a temperature cycle

encompassing all relevant transitions between -50°C and 110°C . The carrier gas was nitrogen at a flow rate of 0.06 mL/min. Liquid nitrogen was used to cool samples below room temperature.

Selective extraction was performed in a Soxhlet extractor with either diethyl ether or methanol as solvent. Vacuum-dried samples were weighed in filter paper of known weight and inserted into the extractor. Samples were extracted for durations of at least 24 h at the solvent boiling point (40°C for diethyl ether extractions and 72°C for methanol). Wet samples were then removed, dried, and residual weight was measured. The degree of grafting was measured by selective extraction. Ethyl ether was found to be a good solvent for both neat alkyd and hybrid graft copolymer, but a nonsolvent for homoacrylic polymer.¹⁸ Residual weight after extraction was assumed to be homoacrylic polymer. From a weight analysis, the degree of grafting could be obtained as

$$\text{degree of grafting} = \frac{\text{acrylic polymer in hybrid}}{\text{total polyacrylic}}$$

degree of grafting

$$= \frac{(\text{total polymer weight})(\text{acrylic \%})}{(\text{total polymer weight}) + (\text{extracted weight})}$$

where extracted weight is pure homoacrylic polymer and acrylic % is defined as

$$\text{alkyd \%} = \frac{\text{alkyd}_{\text{recipe}}}{(\text{monomer}_{\text{recipe}})(\chi) + \text{alkyd} + \text{KPS} + \text{SDS}}$$

where χ is monomer conversion.

Miniemulsion preparation

Monomer was mixed with alkyd and hexadecane (and AIBN or BPO, if applicable) until completely homogeneous. The organic phase was added to a solution of SDS in deionized water under vigorous stirring, and then stirred for 60 min, after which the emulsion was sonicated (Fisher Sonic Dismembrator) at 70% output

TABLE II
Composition of Oils Used in Alkyd Preparation

Fatty Acid	Number of Double Bonds	MW (g/mol)	Soya Oil	Linseed Oil	Tung Oil	Coconut Oil	Tall Oil
Oleic	1	282.5	25%	22%	8%		46%
Linoleic	2	280.5	51%	16%	4%	7%	41%
Linolenic	3	278.4	9%	52%	3%	2%	3%
Eleostearic	3	278.4			80%		
Stearic			4%	4%	1%	6%	3%
Palmitic			11%	6%	4%	11%	5%
"Other"						74%	2%

TABLE III
Compositions of Alkyds

Alkyd Name	Oils Used	Alkyd Solids	Oil in Alkyd	Moles of Double Bonds per g Alkyd
Long (soya)	SOYA	70%	70%	2.691 E-03
Medium (soya)	SOYA	50%	50%	1.373 E-03
Medium (soya, linseed)	SOYA, LINSEED	80%	50%	2.603 E-03
Short (linseed, tung)	LINSEED, TUNG	50%	30%	1.278 E-03
Short (coconut)	COCONUT	70%	30%	1.501 E-04
Medium (tall)	TALL OIL	100%	50%	2.437 E-03

(maximum output of 300 W) for durations of 25 min. During sonication, the miniemulsion was cooled by a water bath to keep its temperature below 20°C. The miniemulsion was then transferred into a round-bottom glass reactor equipped with reflux cooler and impeller, and the whole system was immersed in a water bath held at the reaction temperature (70°C). Once the reactor contents were at the reaction temperature, a solution of water-soluble initiator was injected into the reactor. Polymerization was carried out under nitrogen atmosphere. At regular time intervals, samples were taken for conversion measurement, GPC, extraction, and other analyses. The base recipe is given in Table I. Alkyds are composed of natural oils extended with phthalic anhydride to molecular weights of approximately 3,000. Compositions of the oils that make up the alkyds, and of the alkyds themselves, are given in Tables II and III, respectively.

RESULTS AND DISCUSSION

Hybrid miniemulsions of MMA/alkyd, BA/alkyd, BMA/alkyd, and coacrylic/resin systems of MMA/BA/alkyd were carried out. KPS, a water-soluble initiator, was chosen due to its common use in emulsion

systems; AIBN and BPO were both chosen as suitable oil-soluble initiators, as their effect on grafting has been well documented. Results of grafting experiments are summarized in Table IV.

Methyl methacrylate/alkyd

In Table IV, the degree of grafting for MMA/alkyd initiated with KPS is given at two different monomer conversions to be 48%. In Figure 3, raw GPC chromatogram overlays are shown of hybrid MMA/KPS/alkyd polymer versus polymer from a homoacrylic MMA polymerization (left) and the same hybrid MMA/KPS/alkyd system versus neat alkyd resin (right). The bimodal distribution observed suggests that this hybrid system leads to both homopolymer of PMMA and poly(alkyd-g-MMA). From the left comparison, it is evident that the chain length of the PMMA polymer formed during the hybrid reaction is considerably smaller than what forms in a homoenvironment. The comparison on the right clearly shows that even though the chains are relatively small, some degree of free PMMA is formed distinct from neat alkyd and poly(alkyd-g-MMA). Two possible scenarios might apply to the question of why a significant

TABLE IV
Degree of Grafting by Extraction with Diethyl Ether

System	Alkyd	Monomer Conversion	Degree of Grafting	Relevant Conditions
MMA/alkyd	Medium (soya, linseed)	93%	48%	Initiated by KPS
MMA/alkyd	Medium (soya, linseed)	75%	48%	Initiated by AIBN
MMA/alkyd	Medium (soya, linseed)	60%	55%	Initiated by BPO
MMA/alkyd	Medium (soya, linseed)	95%	51%	Initiated by [KPS]/2
MMA/alkyd	Medium (soya, linseed)	83%	59%	Initiated by KPS ([SDS] = 0.03 mol/L; 3 × normal)
MMA/alkyd	Medium (soya, linseed)	75%	59%	Hexadecane omitted
MMA/BA/alkyd	Medium (soya, linseed)	88%	90%	Initiated by KPS
BA/alkyd	Medium (soya, linseed)	100%	96%	Initiated by KPS
BA/alkyd	Medium (soya, linseed)	83%	97%	Initiated by KPS ([SDS] = 0.03 mol/L; 3 × normal)
BA/alkyd	Medium (soya, linseed)	100%	100%	KPS initiated, hexadecane omitted, ([SDS] = 0.03 mol/L)
MMA/alkyd	Short (coconut)	85%	44%	Initiated by KPS
MMA/alkyd	Short (linseed, tung)	65%	42%	Initiated by KPS
MMA/alkyd	Medium (soya)	70%	44%	Initiated by KPS
MMA/alkyd	Long (soya)	85%	45%	Initiated by KPS

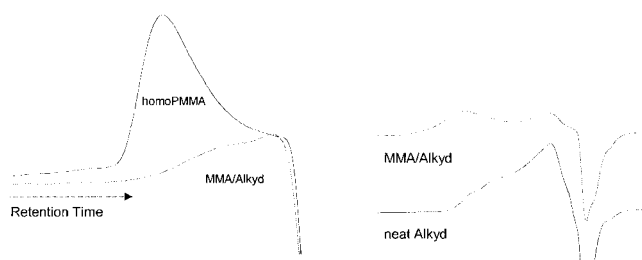


Figure 3 Molecular weight comparisons, from GPC analysis, of homopolymerized MMA versus hybrid MMA/alkyd (left). Neat Alkyd versus hybrid MMA/alkyd (right).

portion of homopolymer was present even though hybrid poly(alkyd-*g*-MMA) was formed.

First, MMA has some tendency to partition into the aqueous phase.¹⁹ Although the solubility of MMA in water is only around 1.5 wt %, ²⁰ it is enough to promote some homogeneous nucleation, especially since the initiator radicals (KPS) are derived in the continuous phase. Once some degree of polymer is formed outside the droplets/particles, the tendency for more monomer to transport to those sites is also increased, whether it be from hybrid particles or from un-nucleated droplets that will essentially act as reservoirs.

Second, the methyl group off the MMA vinyl bond renders it sterically more difficult for the radical center of MMA to be involved in grafting reactions.¹⁶ The radical is on a tertiary carbon that aids radical stability since the alkyl groups are electron-donating.¹⁸ The carbonyl group will draw electrons, but when compared to similar monomers, such as butyl acrylate, the effect cancels out. Butyl acrylate has a higher radical reactivity,²¹ primarily from its lack of steric hindrances surrounding the radical center. Styrene, on the other hand, is well known to have a low grafting efficiency.²² In that case, the stability of the radical comes from electron delocalization from conjugation with its benzyl ring and the large physical hindrance of that ring. Both features translate to relatively low monomer reactivity, seen in the k_p value for styrene.²⁰ For these reasons, MMA (or PMMA) is more likely to abstract an α -hydrogen on the alkyd, forming short-chain homopolymer that may or may not graft through termination by combination with that generated site.

Low levels of grafting have been documented in several MMA/resin systems and have often been explained by the propensity for a methacrylate radical to favor allylic hydrogen abstraction over addition to a double bond. Huang and Sundberg²¹ report that in systems where grafting can occur through either abstraction or addition, the latter mechanism is responsible for the majority of grafting. This is explained by the relative inactivity of radicals created by α -hydrogen abstraction. This inactivity is then conjectured to be a major influence on the retardation of the overall

polymerization rate. These authors²¹ chose several vinyl monomers to react with polybutadiene. In one particular study, the system of benzyl methacrylate and polybutadiene initiated by 2,2'-azobisisobutyronitrile in solution polymerization (benzene as solvent) was explored. Although there are certain differences between their and the current study, similarities are surely apparent. Mayo et al.¹⁸ have documented rate coefficients for several monomers dictating their reactivity. Benzyl methacrylate and methyl methacrylate were found similar in reactivity. AIBN was chosen for its relative inability to attack the polybutadiene backbone as a primary radical. Bevington²² reported that the inability of AIBN to abstract an α -methylene hydrogen is likely to do with the resonance stability of the $(\text{CH}_3)_2\dot{\text{C}}(\text{C}\equiv\text{N})$ radical formed upon AIBN decomposition. The reason Huang and Sundberg²¹ wanted an initiator that would not promote primary radical attack was to isolate and study a system dominated by macroradical attack (chain transfer to polymer). Although these authors were studying grafting by macroradical attack in a solution polymerization environment, the study of a miniemulsion initiated by KPS actually is quite similar. In the case of KPS, the initiator first dissociates in the continuous phase only to enter a droplet/particle after it has gained a certain number of monomeric units (the *z*-mer value specific to monomer).²³ For this reason, primary radical attack is a moot point, making it necessary for grafting to occur from some form of macroradical whether it be oligomeric or polymeric. A final resemblance of these two seemingly different grafting systems is the structure of the alkyd versus that of polybutadiene. A comparison of the complete structure will reveal very little in common, but in fact the only portion of the alkyd of interest is the fatty acid groups where grafting can take place. As can be seen in Figure 4, groups adjacent to double bonds in either a fatty acid or polybutadiene are quite similar, even though the distribution of those bonds is quite different. This is not regarded as a problem since the reactivity of those allylic hydrogen substituents should be fairly similar, at least qualitatively, when interacting with different monomers. For the reasons described above, principles derived in the benzyl methacrylate/AIBN/polybutadiene system²¹ can be utilized as a basis to explore principles relevant to the MMA/KPS/alkyd system.

Huang and Sundberg²¹ reported that when using AIBN as an initiator, styrene did not appreciably graft to polybutadiene, benzyl methacrylate formed slightly more grafts, and benzyl acrylate underwent a considerable amount of grafting with polybutadiene. The almost negligible grafting of styrene was attributed to the inability for AIBN and the polystyryl radical to abstract allylic hydrogens due to their respective resonance stabilities. Although AIBN cannot be involved in primary radical attack, the polymethacrylate radical

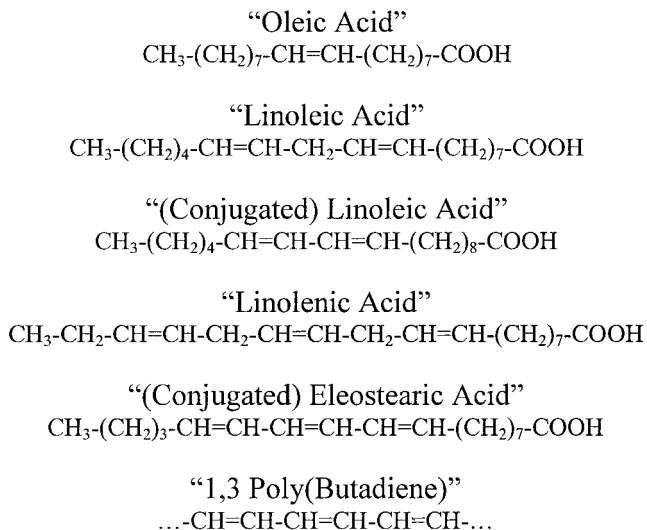


Figure 4 Structures of typical fatty acids compared to polybutadiene.

of benzyl methacrylate is capable of abstracting an allylic hydrogen and, to a much lesser extent, is also able to add directly to a double bond. This is what led to its somewhat higher degree of grafting. Benzyl acrylate, however, was noted to be easily capable of both abstraction and addition and even in light of the lack of primary AIBN radical attack; the levels of grafting were considerably higher. With the MMA/KPS/alkyd system, a result similar to the benzyl methacrylate/AIBN/polybutadiene system²³ was found. Since the KPS radical inherently could not perform primary radical attack, grafting reactions were limited to transfer of an oligomethyl methacrylic chain (radical) to the alkyd either through abstraction or double-bond addition. Grafting was observed in this methacrylate/alkyd system but was overshadowed by the degree of grafting in similar acrylate/alkyd systems. This was in complete agreement with fundamental results reported by Huang and Sundberg²¹ as well as others.¹⁶

It was postulated that the use of an oil-phase initiator such as AIBN in place of KPS would increase levels of grafting due to its oil solubility and thus the possibility for primary radical attack, as well as the suppression of homogeneous nucleation. However, Table II indicates that the use of AIBN over KPS did not impart noticeable changes in grafting. This can be explained from two perspectives. First, as discussed earlier, AIBN has been reported not to participate in primary radical attack.²⁴ On this basis alone, the similar results of the KPS- and AIBN-initiated systems would then be expected. Second, there is some evidence that the AIBN radicals involved in initiation of macro- or miniemulsion systems are actually those generated in the aqueous phase. AIBN partitioned in the droplets dissociates and can immediately recom-

bine, effectively creating very few live radicals from within the oil phase. Radicals derived from the AIBN partitioned in the aqueous phase can add several monomer units and enter a droplet, effectively becoming the more dominant form of nucleation. If this scenario is true, then there is no reason to suspect that the grafting results of the KPS or AIBN systems should be any different. In a miniemulsion, neither would have a chance at primary radical attack, even if they were prone to such an event.

A series of hybrid MMA/alkyd polymerizations were performed to test this hypothesis. Figure 5 shows the conversion-time curves for these experiments. In all three cases, the recipes were identical except for the choice of initiator. The decrease in MMA polymerization rate from the KPS- to the AIBN-initiated system can be explained by the reduction in AIBN initiator concentration due to a large percentage of oil-phase initiator being consumed in radical-radical termination reactions within the droplets. The effective initiator concentration used in propagation would then be closer to the percentage of AIBN partitioned in the aqueous phase. This is also compounded by the longer half-life of AIBN when compared to KPS, which translates to a slower decomposition rate. The third kinetic profile is of an AIBN-initiated MMA/alkyd miniemulsion polymerization with sodium nitrite (NaNO_2) present in the continuous phase. Sodium nitrite is known to scavenge aqueous-phase radicals.²⁵ If the conversions time curves were identical with and without aqueous-phase inhibitor, the theory of AIBN radicals entering from the aqueous phase would be unsupported. Figure 5, however, shows a dramatic reduction in rate, indicating in the least that a significant percentage of initiating radicals in fact do come from the aqueous phase. The fact that some polymerization still occurs indicates that some initiation does take place in the particles/droplets. It should be noted that there will also be some partition of NaNO_2 in the oil

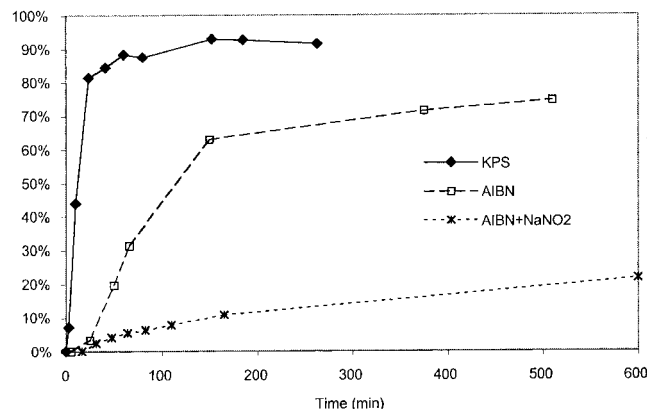


Figure 5 Comparison of initiation from KPS (filled diamond), AIBN (open square), and AIBN + NaNO_2 (X) for MMA/alkyd.

TABLE V
DSC Measured Glass Transitions (°C)

System	DSC-Measured Glass Transitions		
	Low	Intermediate	High
MMA/BA/alkyd	-22 to -19	30 to 38	70 to 78
MMA/Alkyd (KPS)	Roughly (-30)	Roughly 48	Roughly 105
MMA/Alkyd (AIBN)	Roughly (-30)	Roughly 38	Roughly 105
BA/alkyd	-22 to -3		
(Neat) alkyd	Roughly (-30)		

phase, but this contribution to termination is assumed to be negligible. So, for the MMA/alkyd system, initiation by KPS or AIBN does not introduce markedly different results in degree of grafting. Grafting occurs, but the final polymer is still a distributed mixture of hybrid graft copolymer, homo-PMMA, and unused alkyd (Table II).

Initiators with oxygen-centered radicals are documented to be efficient hydrogen abstractors.²⁰ Benzoyl peroxide (BPO), one such initiator, is known to attack polybutadiene as a primary radical and to abstract hydrogens in the allylic position to double bonds.²³ This feature is what usually leads to higher levels of grafting in systems that employ BPO as the initiator, as compared to those initiated by AIBN or other non-oxyl radicals. To test this in the current system, MMA/alkyd hybrid miniemulsion polymerization was carried out with BPO as the initiator. It was postulated that the oxyl radicals of BPO would aid in generating radicals on the alkyd (fatty acids) that could be utilized in grafting of the methacrylate component. In styrene/polybutadiene systems, this method proved successful in promoting greater degrees of grafting.²²

Surprisingly, BPO did not lead to higher grafting efficiencies for MMA/alkyd. In fact, Table II indicates that the substitution of BPO for either KPS or AIBN did not significantly affect the degree of grafting. Styrene/polybutadiene systems likely benefit from BPO solely through the aid of generation of grafting sites. The styrene radical's stability, derived from conjugation with the benzyl substituent, diminishes its ability to abstract hydrogens from polybutadiene. The coefficient of chain transfer to polymer for styrene is quite low.²⁰ Thus, the primary radical attack by BPO acts to pave the way for styrene to graft to polybutadiene. Conversely, the MMA radical is itself capable of chain transfer, at least when compared to styrene. This suggests that the lower efficiency of grafting in MMA/alkyd systems is not due to the lack of ability to produce grafting sites (hydrogen abstraction) but instead to do with the reactivity of methacrylate radicals toward those generated sites.

An alternate explanation for the lack of grafting difference between KPS and BPO in MMA/alkyd miniemulsion systems could be postulated due to pri-

mary radical termination in droplets. It is conceivable that if a large percentage of primary radicals undergo rapid termination in the droplets, the more dominant source of radicals involved in nucleation would again come from the small partition of BPO residing in the aqueous phase. If this were the case, one would truly expect the three chosen initiators to function in identical manner.

Further evidence of the formation of hybrid graft copolymer can be found by measurement of the glass transition temperature(s) of the final hybrid polymer. Differential scanning calorimetry (DSC) was used over a temperature window the T_g of alkyd (low), of PMMA (high), and of any graft copolymer (intermediate). Table V presents evidence corroborating that found by extraction. In the MMA/alkyd systems, irrespective of initiator choice, homopolymer of PMMA was observed. The oil-soluble radical-initiated polymer films were slightly softer to touch. This is seen in their slightly lower hybrid transition.

Butyl acrylate/alkyd

In contrast to MMA, BA grafts almost completely to alkyd when initiated by KPS. Extraction data in Table II show that the degree of grafting is nearly 100%. This is again directly in accord with what has been found in acrylate/polybutadiene systems. Irrespective of initiator choice, AIBN or BPO, grafting was found to be virtually complete in systems involving acrylate.²³ Those two initiators were chosen due to their different tendencies in relation to primary radical attack. AIBN is not able to abstract an allylic hydrogen, whereas BPO has a high tendency to do so. Even with this distinction, the levels of grafting were not found to be markedly different. This suggests that with monomers of acrylate structure, high levels of grafting seem to be due to their ability to undergo addition through double bonds. When the structure of butyl acrylate is compared to that of methyl methacrylate, it can be seen that the acrylate involves far fewer steric hindrances. Other than offering the ability to add to a double bond, it also increases reactivity toward α -hydrogen abstraction. This is seen in its larger chain transfer coefficient compared to that of MMA. (At 70°C, $k_{tr,BA} = 4.04 \text{ L mol}^{-1} \text{ s}^{-1}$ and $k_{tr,MMA} = 0.11 \text{ L}$

mol⁻¹ s⁻¹.) At first glance, one might try to correlate this higher transfer coefficient to the higher degrees of grafting seen in BA versus MMA. Such a correlation is not correct, however, when propagation is considered. The propagation rate coefficient for BA is at least an order of magnitude higher than that of MMA, and a more relevant comparison is made when one considers k_{tr}/k_p , the ratio of transfer rate to propagation rate constants, for each monomer/alkyd system (where transfer is to an α -hydrogen). On this basis, that value is quite similar for both systems. (At 70°C, $k_{tr}/k_{p,MMA} = 6.95 \text{ E-5}$ and $k_{tr}/k_{p,BA} = 9.37 \text{ E-5}$.) In light of the virtually complete grafting in the BA/alkyd hybrid system, and a fairly low k_{tr}/k_p value, this strongly suggests the mode of attack for BA/alkyd is through direct addition to a double bond on an alkyd fatty acid because hydrogen abstraction grafting is always accompanied by the formation of homopolymer.

Differential scanning calorimetry for the BA/alkyd system (Table V) shows a single broad transition; however, significant conclusions should not be drawn from this. The individual glass transition temperatures for BA and alkyd are so close to each other (-56°C, -30°C) that isolating a transition specific to the hybrid graft copolymer is quite difficult.

One should also consider that butyl acrylate has very little solubility in water (0.0062 mol/L).²⁰ This translates to a relative lack of homogeneous nucleation and thus less chance of homopolymer resulting from homogeneous nucleation. Although polymerization of BA often leads to some degree of self-grafting and crosslinking through backbiting reactions, the hybrid poly(alkyd-g-BA) polymer was fully soluble in THF. This suggests that a negligible amount of PBA crosslinking occurs in this type of system.

Methyl methacrylate/butyl acrylate/alkyd

The MMA/alkyd and BA/alkyd systems discussed behaved quite differently in terms of grafting. It is only natural then to study the behavior of an acrylic copolymer of the two in the presence of alkyd. For simplicity, the ratio of MMA to BA in the monomeric portion of the recipe was kept at 50:50 (wt:wt). Total monomer concentration (by weight) was also kept 50:50 (wt:wt) with the concentration of alkyd in the recipe.

As one might expect, grafting results from this copolymer/alkyd system were found to be more similar to those of the BA/alkyd systems than to the MMA/alkyd ones. Referring again to Table II, the difference between the degree of grafting of BA/alkyd and MMA/BA/alkyd systems is much less pronounced than that of MMA/alkyd and MMA/BA/alkyd. This is not unexpected. Considering only the free radical copolymerization of MMA and BA, one would expect to find an alternating copolymer since the reactivity

ratios of MMA and BA have been reported to be 1.74 and 0.20, respectively.²⁰ Another study²⁰ reported 1.8 ± 0.1 and 0.37 ± 0.1 ; in either case, the multiplication of r_1 by r_2 results in a value much less than unity (0.35 or 0.67), indicating alternating copolymer. Thus, after every other monomer unit adds to the growing polymer chain, the radical center will be on a BA unit. With an acrylate radical at the head of the chain, attack of the alkyd can easily occur at either the allylic hydrogen or directly on the alkyd double bond as discussed earlier. Thus, the MMA/BA/alkyd copolymer system exhibits a degree of grafting more similar to the BA/alkyd system than to the MMA/alkyd system. The incomplete grafting can be attributed to the tendency for MMA to be involved in homogeneous nucleation of new particles, as described earlier. The effective concentration of MMA in the droplet is less in this comonomer system, reducing the propensity of MMA to partition into the aqueous phase. Nonetheless, the possibility still exists for some portion of homogeneous nucleation to occur, leading to PMMA homopolymer.

The MMA/alkyd system generates a hybrid polymer of intermediate flexibility due to the dramatically divergent T_g s of the individual components (-56°C and 100°C). The BA/alkyd hybrid T_g does not differ much from those of the individual comprising compounds since both pure component transitions are similar and very low (-56°C and -30°C). The hybrid coacrylic polymer of MMA/BA/alkyd (Table V) results in an intermediate T_g of approximately 35°C.

Butyl methacrylate/alkyd

In light of the dramatically divergent grafting tendencies of the methacrylic monomer (MMA) and the acrylic monomer (BA) discussed above, a new monomer was chosen that has similarities to both of the previous monomers. Butyl methacrylate (BMA) has essentially the same hydrophobicity as BA,²¹ due to the oily nature of the butyl substituent on the tail of the molecule (Fig. 6). The hydrophobic character should effectively eliminate the tendency for homogeneous nucleation found in the MMA system. The molecular structure surrounding the radical reactive center is identical to MMA, so BMA should graft in the same manner as MMA. Due to its higher hydrophobicity and the resultant lessened likelihood of homogeneous nucleation, it was thought that BMA would give a higher degree of grafting than MMA, while the chemistry of grafting should be substantially the same as that of MMA. This experiment should isolate the effect of homogeneous nucleation from the grafting chemistry. The magnitude of the difference in grafting between MMA and BMA should give an estimate of the relative importance of hydrophobicity versus

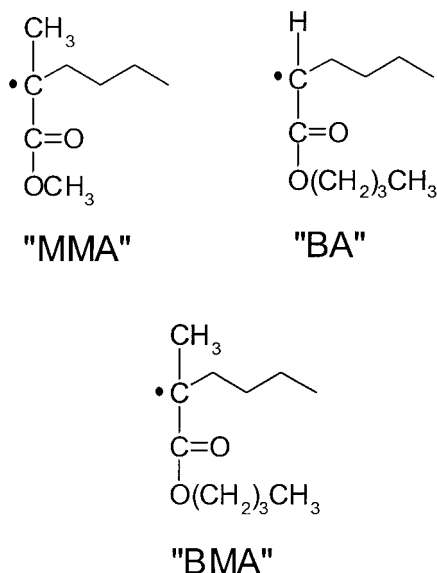


Figure 6 Comparison of MMA, BA, and BMA structures.

stearic hindrance at the radical site in reducing grafting efficiency.

As expected, the degree of grafting for BMA/alkyd was observed to be higher than for MMA/alkyd (due to increased hydrophobicity), but still much less than the virtual complete grafting seen in the BA/alkyd system (due to steric hindrance of grafting). The data are shown in Table VI. It should be noted that a different extraction solvent (methanol) was used here than in Table II (diethyl ether). Methanol has been reported to be a much more suitable selective solvent²¹ than diethyl ether for the BMA/alkyd system, while also effective for MMA and BA. The disparity between the degree of grafting for MMA/alkyd in Table VI versus Table II is likely due to methanol not being as selective a solvent as diethyl ether. Nevertheless, the comparison of MMA/alkyd and BMA/alkyd in the same solvent (methanol) is valid. The data suggest that homogeneous nucleation present in the MMA/alkyd system did in fact play a role in the lesser degree of grafting of that system, but that steric considerations (present in both MMA and BMA) are the critical factor in grafting.

Molecular weight analysis

Figures 7 and 8 show raw GPC chromatograms for several homo- and hybrid polymerizations. (Since mo-

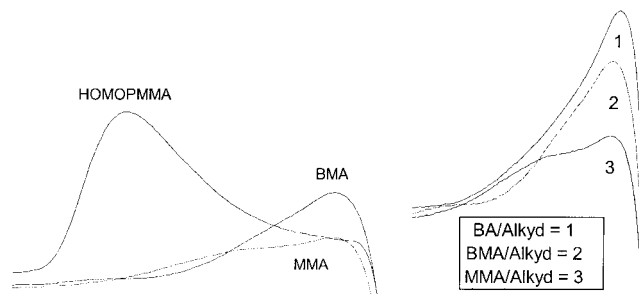


Figure 7 Molecular weight profiles for homopolymerized PMMA, BMA/alkyd, and MMA/alkyd (left). Molecular weight profiles comparing BA/alkyd, BMA/alkyd, and MMA/alkyd (right).

lecular weight standards are not available for these graft copolymers, the actual chromatograms are shown.) On the left of Figure 7, it may be seen that the MMA/alkyd system produces considerably more homo-PMMA polymer than the BMA/alkyd system. This is expected due to the hydrophobicity of BMA. The comparison to the homopolymerized PMMA polymer shows that the degree of polymerization of homo-PMMA chains in the MMA/alkyd system is considerably less than that of freely grown PMMA due to the chain transfer activity of the alkyd. An interesting observation may be made by comparing the profiles for each monomer/alkyd system in the right side of Figure 7. Homopolymer grown free of alkyd will have a higher degree of polymerization than grafted acrylic chains and thus will appear further to the left of the GPC trace. Shorter grafted chains then produce a peak that likely overlaps that of neat unused alkyd, which is the furthest right peak in these chromatograms. Thus, the similar shapes of the BMA and BA traces describe distributions of polymer formed solely within the original hybrid particles. A small peak of BMA homopolymer is observed and results from those BMA chains that were terminated by the hydrogen abstracted during chain transfer. This, of course, is not observed in the BA/alkyd system as grafting occurs almost exclusively through direct addition to alkyd double bonds, a process that does not create homopolymer.

The effect of initiator choice on MWD is shown in Figure 8. On the left, similarities between AIBN- and BPO-initiated systems are readily apparent, but a noticeable difference is observed between those and the KPS-initiated system. This is explained by the en-

TABLE VI
Degree of Grafting by Extraction in Methanol

System	Alkyd	Monomer Conversion	Degree of Grafting	Relevant Conditions
MMA/alkyd	Medium (soya, linseed)	85%	38%	Initiated by KPS
BMA/alkyd	Medium (soya, linseed)	90%	44%	Initiated by KPS

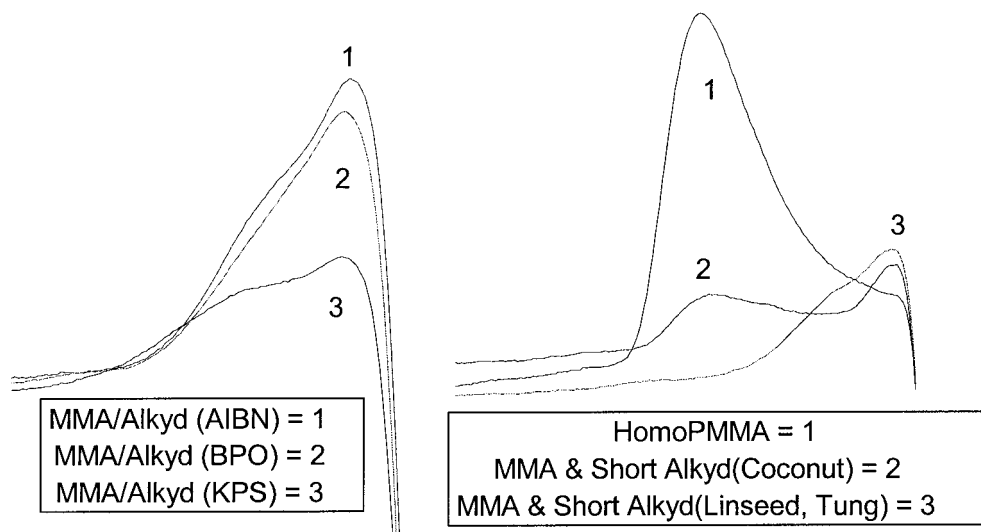


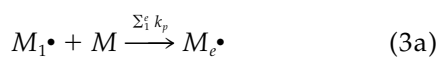
Figure 8 Molecular weight profiles of MMA/alkyd comparing initiation from AIBN, BPO, and KPS (left). Molecular weight profiles of MMA and short alkyd (coconut), MMA and short alkyd (linseed, tung), and homopolymerized PMMA (right).

hancement of homogeneous nucleation caused by the water solubility of KPS. Within a hybrid particle, however, the degree of grafting should be quite similar for each system, as the most influential factor is monomer structure. When the effect of different fatty acid structure is compared on the right of Figure 8, the effect of an extremely low concentration of double bonds (coconut oil) versus a high concentration compounded by conjugation (linseed, tung oils) is easily observed. High degrees of chain transfer lead to many short grafted chains, whereas low propensity for transfer leads to extremely long grafted chains, similar to those formed in the absence of alkyd.

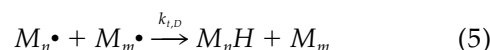
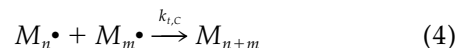
Proposed generalized grafting mechanism

In light of the findings in this article, the following mechanism is proposed for hybrid miniemulsion polymerization. None of these reactions is new to the literature; however, we list them all here for the sake of completeness, and in order to make some comments on their relative importance based on our investigations.

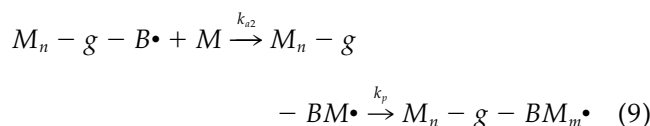
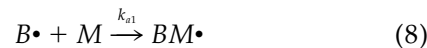
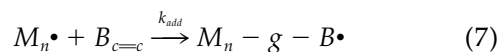
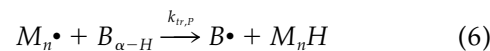
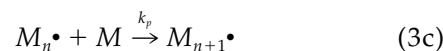
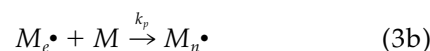
Aqueous-phase reactions

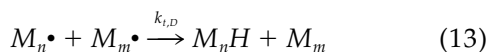
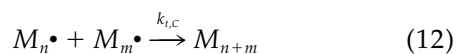
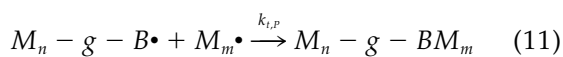


where e is the z -mer value for the particular monomer (e.g., $z_{BA} \approx 2-3$, $z_{BMA} \approx 3$, $z_{MMA} \approx 5+$).¹⁷



Oil-phase reactions





In the above equations, I = initiator, $R \cdot$ = initiator-derived radical (primary radical), M = monomer (MMA, BA, BMA), and B = branch point on alkyd fatty acid. The above mechanism does not account for oil-phase-derived initiator radicals, nor does it address primary radical attack. These two possible pathways were omitted from the mechanism in light of their negligible influence on systems of this study.

In the mechanism, eqs. (1) through (3a) illustrate that before any radicals enter droplets or particles, they have already acquired a certain oligomeric chain length from the z-mer constraint on entry. For more hydrophilic monomers such as MMA, this required chain length is longer than for highly water-insoluble monomers such as BA or BMA.¹⁹ Although BA and BMA require only 2–3 mer units for entry, their high propagation rate coefficients ensure that upon entry those chains will grow. This rules out both primary radical attack and monomeric radical attack on the fatty acid chains of the alkyd.

Equations (4) and (5) describe termination in the aqueous phase. These are important because they can lead to homopolymer in homogeneously nucleated particles. As described earlier, homoparticles derived in the aqueous phase are observed in the MMA/alkyd system. M_{n+m} from eq. (4), and $M_n H$, from eq. (5), become dead homopolymer, where M_m in eq. (5) can still propagate through its terminal double bond. This, of course, is relevant to eqs. (12) and (13) as well.

Equations (6) and (7) refer to oligoradical or macro-radical attack on the alkyd fatty acid by allylic hydrogen abstraction and direct addition to a double bond, respectively. As described earlier, eq. (6) is primarily relevant for MMA or BMA and eq. (7) is heavily favored over eq. (6) for BA. The resultant $B \cdot$ radical on the alkyd fatty acid after chain transfer is quite stable from conjugation with the adjacent double bond and thus the rate coefficient for eq. (8), k_{a1} , is projected to be quite low. This inactivity causes the reduced rate of polymerization reported widely in hybrid miniemulsion polymerization. In eq. (7), the resultant $M_n - g - B \cdot$ radical is not conjugated with a double bond and is thus less stable and more reactive ($k_{a2} \gg k_{a1}$). Since this equation is really only relevant to acrylate monomers, such as BA, eq. (9) explains why grafting in the BA/alkyd system is high. MMA and BMA rely mainly on the combination of eqs. (6) and (10) to graft with alkyd, whereas BA can create grafts through the same

mechanism or through any combination of eqs. (7), (9), and (11).

Considering the high percentage of homopolymer created in the MMA/alkyd system, eqs. (12) and (13) should be considered. Earlier, the production of homo-PMMA was attributed to homogeneous nucleation in the aqueous phase, derived from the high water solubility of MMA. Equations (4) and (5) describe homopolymer derived from the aqueous phase. Homotermination, by eqs. (12) or (13), is also a prospect for production of homopolymer from within the particles. Homopolymer derived from the transferred hydrogen in eq. (6) is likely the dominant mechanism for creation of that species. For the MMA/alkyd system, grafting has been shown to be highly probable from the combination of abstraction and termination events. Both transfer and termination are then somewhat unusual in that they involve two relatively large species. There is a possibility that these events could occur as an oligomer/polymer (short-polyacrylic/alkyd) interaction, but from the rates of propagation versus transfer, the interaction is more likely one of polymer-polymer (polyacrylic/alkyd). The relative immobility of these large molecules should shift contributions to the total termination rate coefficient in favor of reaction diffusion over center-of-mass diffusion. Certain monomers, such as MMA, have been documented to have termination events dominated by reaction diffusion after roughly 50% conversion.²⁵ If, after moderate conversion in this hybrid MMA/alkyd system, the radical-containing end groups of the alkyd and PMMA are in close proximity, propagation will eventually lead to termination creating a graft. This scenario seems more probable than termination dominated by center-of-mass diffusion for a system consisting of such immobile molecules.

CONCLUSIONS

Hybrid miniemulsion polymerization is a versatile tool for preparation of polymer architectures that synergistically combine properties from both traditionally water-based and solvent-based polymer components. Its inherent advantage is that the process can be performed in a completely solvent-free manner, environmentally benign in both process and product. Previously, the impact of monomer choice has not been documented. This article shows that the choice of monomer(s) dramatically impacts the grafting mechanism between the two components. The following conclusions can be drawn.

One, grafting is observed between methacrylates and typical resins, but steric hindrance at the methacrylate reactive center prevents it from facilitating direct addition to a resinous double bond. This method is proven to be the route of attack for optimum grafting efficiency. Instead, methacrylates tend toward al-

lylic hydrogen abstraction, a process that creates a relatively stable and unreactive radical on the resin along with terminating the abstracting methacrylate chain. These effects degrade both the grafting efficiency and the rate of polymerization.

Two, acrylate monomers produce high levels of grafting. Direct addition to resin double bonds is facilitated and virtually complete grafting of the component is observed. This is likely due to the lack of steric hindrances of the acrylate reactive center.

Three, hydrophilicity of monomer is a factor that cannot be ignored. When water-soluble initiators are used, this combination facilitates homogeneous nucleation. This can only lower the obtainable degree of grafting through the production of homopolymer. Due to the hydrophobic nature of most resins, transport to those newly created particles cannot occur without complete phase separation, and thus particles derived in the homogeneous phase remain isolated from the resin through to the completion of reaction.

Four, double-bond content of the resin is important to grafting. Even in systems where abstraction is the dominant route of attack, double bonds are needed because hydrogens allylic to them are good leaving groups. Density of double bonds directly correlates to concentration of possible grafting sites and thus higher double-bond content should offer higher levels of grafting.

Five, several earlier studies reported conflicting views on the grafting efficiency of such hybrid mini-emulsion polymerizations. Certain authors^{5,8} studied MMA/resin systems while others^{1,2,7} studied MMA/BA/resin systems. This article has shown that the choice of monomer(s) was the underlying reason behind those reported differences. Chain transfer dominates the interaction of methacrylate with resin, and thus there is lower opportunity for grafting. Conversely, the interaction of acrylate with resin is dominated by direct addition to a resin double bond, a highly efficient mode of grafting. MMA/BA/resin systems have been shown to benefit from the grafting mode of the acrylate component, and hence the higher

reported grafting efficiency from authors of those studies.

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