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The morphology of alkyd/acrylate latexes produced via hybrid miniemulsion polymerization: grafting mechanisms

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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 paper 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 towards 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. Grafting occurs in this type of system through termination of living PMMA chains with that radical produced on the resin. 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 directly add through a resin double bond.

Keywords Emulsion · Alkyd · Hybrid · Acrylic · Graft

Introduction

Several papers have appeared describing systems in which acrylic monomers are polymerized in the presence of an unsaturated resin or oil with the object of grafting the acrylic polymer onto the resin [1–9]. 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 paper investigates these mechanisms and reveals some of the underlying reasons behind limitations seen in several of these systems.

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 (macroemulsion) or miniemulsion polymerization is most often the process of choice. Nucleation in macroemulsion polymerization predominantly occurs in micelles 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 prevent the resin from diffusing through the continuous phase at all. In the latter case, phase separation occurs negating the objective of the hybrid polymerization [3]. For this reason, a miniemulsion becomes likely the most suitable environment for this class of hybrid polymerization.

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 will may include homopolymer from the homopolymerization of A, homopolymer B which 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, or hydrogens allylic to those double bonds (abstraction). If one only considers the energy required to interact with a n-bond versus a σ-bond, addition to a double bond is energetically favored over abstraction of an allylic hydrogen [11]. However, the structure of groups that surround the reactive polymer site and steric features of the attacking monomer or chain, often influences this choice enough to make abstraction the more preferred route of attack [11, 12].

Experimental

McWhorter Chemicals (now part of Eastman Chemicals) supplied the alkyd resins. Monomers used were obtained from Aldrich and included methyl methacrylate (MMA), butyl acrylate (BA), and acrylic acid (AA). Monomers were first distilled to remove any inhibitors present. Other chemicals were used as purchased. Monomer conversion was determined through gravitimetric analysis. Selective extraction was performed in a Soxhlet extractor with either diethyl ether or methanol as solvent. 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 non-solvent for homoacrylic polymer [13]. Residual weight after extraction was assumed to be homoacrylic polymer. From a weight analysis, the degree of grafting could be obtained.

For polymerization, monomer was mixed with alkyd, hexadecane (and AIBN or BPO, if applicable) until completely homogeneous. The organic phase was added to a solution of sodium lauryl sulfate (SDS) in deionized water under vigorous stirring, and then stirred for 60 minutes after which the emulsion was sonicated (Fisher Sonic Dismembrator) at 70% output (maximum output of 300 W) for durations of 25 minutes. 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. The base recipe is given in Table 1.

Table 1 Generalized recipe for all experiments

Component	Concentration
Deionized water	200 parts
Monomer[a]	20 parts
Alkyd	20 parts
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

Results and discussion

Methyl methacrylate/alkyd

Results of grafting experiments are summarized in Table 2. The degree of grafting for MMA/alkyd initiated with KPS is given at two different monomer conversions to be 48%. In Bimodal MWD was observed suggesting that this hybrid system leads to both homopolymer of PMMA and poly(alkyd-*g*-MMA). The chain length of the PMMA polymer formed during the hybrid reaction is considerably smaller than what forms in a homoenvironment. Even though the chains are relatively small, some degree of free PMMA is formed distinct from neat alkyd and poly(alkyd-g-MMA). The most likely scenario as to why a significant portion of homopolymer was present even though hybrid poly(alkyd-g-MMA) was formed is as follows: The methyl group of the MMA vinyl bond renders it sterically more difficult for the radical center of MMA to be involved in grafting reactions [11]. The radical is on a tertiary carbon that aids radical stability since the alkyl groups are electron donating [13]. For this reason, MMA is more likely to abstract an α-hydrogen on the alkyd and to graft predominantly through termination by combination with that generated site.

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 homogenous nucleation. However, Table 2 indicates that the use of AIBN over KPS did not impart noticeable changes in grafting. This can be explained from two perspectives. AIBN has been reported not to participate in primary radical attack [14] Based on this, the similar results of the KPS and AIBN initiated systems would be expected. Table 2 indicates that the substitution of BPO for either KPS or AIBN did not significantly affect the degree of grafting. An alternate explanation for the lack of grafting difference between KPS and BPO in MMA/alkyd miniemulsion systems could be postulated due to primary 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

Table 2 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 byKPS
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, *3xnormal*)
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, *3xnormal*)
BA/Alkyd	medium (soya, linseed)	100%	100%	KPS initiated, Hexadecane omitted, ([SDS] = 0.03
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

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 encompasing the T_g of alkyd (low), of PMMA (high) and of any graft copolymer (intermediate). In the MMA/alkyd systems, irrespective of initiator choice, homopolymer of PMMA was observed.

Butyl acrylate/alkyd

In contrast to MMA, BA grafts almost completely to alkyd when initiated by KPS Extraction data in Table 2 show that the degree of grafting is nearly 100% 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. 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. Differential scanning calorimetry for the BA/alkyd system show 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.

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 2, 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. 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 MMA/alkyd system generates a hybrid polymer of intermediate flexibility due to the dramatically divergent T_g's of the individual components of −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 at −56 °C and −30 °C. The hybrid

coacrylic polymer of MMA/BA/alkyd (Table 5) results in an intermediate T_g, of approximately 35 °C.

Butyl methacrylate/alkyd

In light of the dramatically divergent grafting tendencies of MMA and the BA) discussed above, a new monomer was chosen which has similarities to both of the previous monomers. MMA has high water solubility, and so may be susceptible to homogenous nucleation. Butyl methacrylate (BMA) has essentially the same hydrophobicity as BA [15], due to the oily nature of the butyl substituent on the tail of the molecule. 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 homogenous 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 The magnitude of the difference in grafting between MMA and BMA should give an estimate of the relative importance of hydrophobicity versus 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 stearic hindrance of grafting). The data are shown in Table 3. It should be noted that a different extraction solvent (methanol) was used here than in Table 2 (diethyl ether). Methanol has been reported to be a much more suitable selective solvent [15] than diethyl ether for the BMA/alkyd system while also effective for MMA and BA The disparity between degree of grafting for MMA/alkyd in Table 3 versus Table 2 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.

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 both in process and product. Previously, the impact of monomer choice has not been documented. This paper shows that the choice of monomer(s) dramatically impacts the grafting mechanism between the two components. The following conclusions can be drawn:

1. Grafting is observed between methacrylates and typical resins, but steric hindrance at the methacrylate reactive center prevent it from facilitating direct addition to a resinous double bond. This is thought to be the mechanism for optimum grafting efficiency. Instead, methacrylates tend towards allylic 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.
2. 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.
3. 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.
4. 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 as 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.

Table 3 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)	**95**%	**44%**	Initiated by KPS

5. Several earlier studies reported conflicting views on the grafting efficiency of such hybrid miniemulsion polymerizations. Certain authors [4, 6] studied MMA/resin systems where others [1, 5] studied MMA/BA/resin systems. This paper 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.

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