Incorporation of Alkoxysilanes into Model Latex Systems: Vinyl Copolymerization of Vinyltriethoxysilane and *n*-Butyl Acrylate

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ABSTRACT: The increase in industrial interest in the incorporation of alkoxysilanes in organic polymer coatings arises from their ability to form self-cross-linkable films at room temperature. In the past few years, many patents were published, offering solutions for avoiding premature cross-linking of alkoxysilane-containing latexes and for obtaining good film-forming properties without using organic solvents. The present paper proposes a miniemulsion approach for the incorporation of alkoxysilanes into acrylate latex systems in order to protect the silane moieties from hydrolysis and premature cross-linking by reducing their contact with water. Vinyltriethoxysilane (VTES)/*n*-butyl acrylate (BA) copolymer latexes were synthesized by both conventional emulsion and miniemulsion procedures. The amount of coagulum and conversion were determined by gravimetry. Differences in coagulum levels were observed with respect to the copolymerization procedure (1.1−32.7 wt % based on monomers in conventional systems vs 1.2−5.5 wt % on monomers in miniemulsion systems for a VTES feed of 1−50 mol %) and acrylate/alkoxysilane molar ratio. Gas chromatography was used to determine the reactivity ratios of VTES/BA pairs by analyzing the evolution of unreacted comonomers during copolymerization. The reactivity ratios between the alkoxysilane and acrylate differed by 2 orders of magnitude for VTES (monomer 1) and BA (monomer 2), where $r_1 = 0.044$ and $r_2 = 8.56$. These results were confirmed by FT-IR analysis of the copolymer composition ($r_1 = 0.086$, $r_2 = 8.51$).

Introduction

In recent years, paint and adhesive formulations based on a water-soluble or water-dispersible resin have been displacing organic solvent-based systems to address pollution concerns. On the other hand, conventional water-borne resins are produced exclusively by emulsion polymerization using surfactants, and as a result, cured products (i.e., paint films) tend to deteriorate in terms of their weather resistance and water and stain resistance due to the presence of the surfactants. The gloss of these films is inferior compared to those films prepared using organic solvents due to the differences in the film formation mechanisms.

One way to reduce the amount of volatile organic compounds (VOC) is to cross-link emulsion polymers, preferably after removal of water. The presence of a postapplication cross-linking mechanism in aqueous coating compositions offers major advantages with regard to the quality and the ultimate properties of the dried film. The incorporation of a postapplication cross-linking mechanism into one-pack paint systems, such as room temperature curing acrylic paints, can be achieved by using alkoxysilanes. In this case, the postapplication cross-linking arises from the formation of cross-links between the alkoxysilane monomers.

The general formula of an alkoxysilane reflects two types of moieties attached to the silicon atom:

$$Y_nSiX_{(4-n)}$$

where Y is a nonhydrolyzable organic group that can be an alkyl, aromatic, organofunctional group, or a combination of any of these. This group provides organic compatibility which allows the silane to react with monomers commonly used in coating formulations. X represents alkoxy moieties, typically methoxy or ethoxy, which can react with various hydroxyl groups and liberate methanol or ethanol. These groups provide the self-cross-linking ability of the resulting copolymer films. They are also responsible for the linkage with inorganic substrates, pigments, or fillers to improve coating integrity and adhesion. Typical values for *n* are 1−3.[1]

The reactions involved in the formation of self-cross-linking films utilizing alkoxysilane systems can be summarized as shown in Figure 1. Premature hydrolysis and cross-linking reactions must be avoided to obtain stable latexes with good shelf stability. The hydrolysis of alkoxysilane was proven to be both acid and base catalyzed. Good pH control is required to minimize premature cross-linking for the polymerization system since the minimum hydrolysis rate occurs at a neutral pH for most systems.[2]

Even though the premature cross-linking of alkoxysilane-containing latexes strongly depends on the conditions employed (e.g., pH, temperature, surfactant), this undesirable reaction can be minimized by using sterically hindered alkoxysilanes, for example, alkyltriisopropoxysilane instead of alkyltrimethoxysilane. Studies have also shown, however, that methacryloxypropylmethyldiethoxysilane gives less premature cross-

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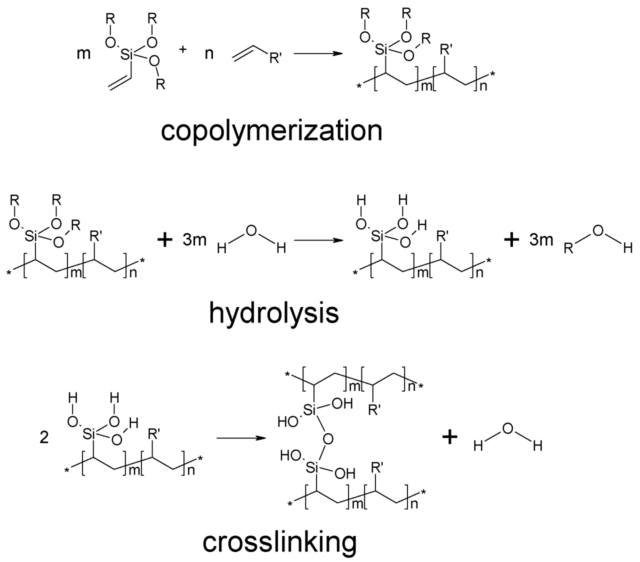

Figure 1. Schematic representation of alkoxysilane-based cross-linking mechanism.

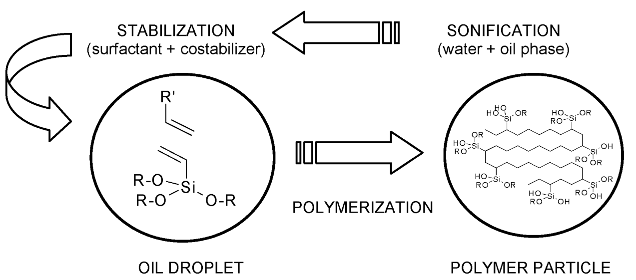

Figure 2. Silane incorporation through a miniemulsion approach.

linking than methacryloxypropyltriisopropoxysilane, even though in the latter compound, the silicon atom carries sterically larger alkoxy substituents. It was also reported that methyldiethoxysilane, even if it is the most suitable of the investigated compounds, still gives too much premature cross-linking for general use in advanced aqueous coating compositions, so that the use of these siloxanes is restricted to applications in which pre-cross-linked latexes are utilized.[3]

Latexes have been prepared by emulsion copolymerization of a particular cross-linker, either a disiloxane or a disilazane with an organic monomer, the resulting polymer chains being either cross-linked or not, depending on the nature of the cross-linker and the reaction conditions. The un-cross-linked chains can then be cross-linked at a later point by addition of a suitable catalyst.[4]

Alkoxysilanes were used in copolymerization reactions with organic monomers (in a semicontinuous process), and the subsequent cross-linking reactions could be pH-controlled.[5] Preparation of silicon-modified self-cross-linkable latexes was carried out primarily through semicontinuous procedures (the alkoxysilanes were usually added late in the reaction to avoid their prolonged contact with water).[6−12] Stable copolymers containing protected siloxane functional groups were prepared by concurrent free radical and cationic-initiated aqueous emulsion copolymerization of a predominant amount of a free radical polymerizable organic monomer and minor amounts of two other comonomers.[13]

Studies in obtaining stable emulsion copolymers with a silyl group-containing monomer and another ethylenically unsaturated comonomer were carried out by using longer chain organosilanes, as a means of achieving better steric hindrance.[9] Novel alkoxysilanes having a lower hydrolysis rate, which results in a lower degree of premature cross-linking, were synthesized. These alkoxysilanes were prepared by designing a siloxane in which one silyloxy group had an electronegative character.[14]

The objective of the present work is to apply a batch miniemulsion polymerization technique to incorporate high amounts of alkoxysilane moieties into film-forming acrylate latex systems. Miniemulsions are dispersions of stabilized oil droplets with sizes between 50 and 500 nm that are prepared by shearing a system containing oil, water, a surfactant, and a costabilizer (a hydrophobic moiety with low molecular weight and very low water solubility, such as hexadecane). Polymerization of the miniemulsions results in the formation of latex particles that are approximately the same size as the initial miniemulsion droplets, indicating that the proper formulation of a miniemulsion suppresses the coalescence of the emulsion droplets. The polymerization of miniemulsions provides advantages with respect to the incorporation of hydrophobic materials and stability of the formed latexes. The formation of a miniemulsion also requires a high amount of mechanical shear to obtain stable miniemulsion droplets dispersed in the aqueous phase.[15−17]

The miniemulsion approach was deemed to be most appropriate in obtaining stable latexes, with silane groups incorporated into the copolymer structure, and allowing subsequent formation of cross-linked films. Although the hydrolysis and condensation reactions will still occur, the particles will remain colloidally stable due to the use of a surfactant/costabilizer stabilization system (Figure 2). The silane moiety will be protected from the aqueous phase by the “waterproof” oil droplet. A subsequent study of the reaction kinetics and particle formation and morphology will help in the understanding of the phenomena occurring in such systems and will contribute to further developments in the end uses of these materials. Vinyltriethoxysilane was chosen as a typical trialkoxysilane, with a low-toxicity hydrolysis coproduct (ethanol), and *n*-butyl acrylate as the base monomer for the film-forming polymer.

Experimental Section

Materials. *n*-Butyl acrylate (BA) (Aldrich) inhibited with hydroquinone monomethyl ether (15 ppm) was cleaned by contacting it with an excess amount of specific inhibitor remover (Aldrich) for at least 48 h. Sodium lauryl sulfate (SLS; Fisher Scientific), sodium bicarbonate and hexadecane (both Aldrich), ammonium persulfate (APS; Merck), and 2,2′-azobis-(2-methylbutyronitrile) (AMBN; VAZO 67, DuPont) were used as received. Vinyltriethoxysilane (VTES) (Silquest A-151, C.K. Witco) was used as received. Toluene, ethylbenzene, and chloroform (Aldrich) were used as received. Deionized water was first boiled and cooled under nitrogen in order to eliminate any dissolved oxygen.

Methods. Miniemulsions (Table 1) were prepared by dissolving the costabilizer (hexadecane) in the monomer mixture. The oil phase was then added to a 10 mM aqueous SLS solution and mixed for 2 min with a magnetic stirrer. The mixture was then sonified (Branson Sonifier, model 450) for 180 s at a duty cycle of 80% and an output power of 7 in an ice bath. Copolymerizations were performed under nitrogen in a 250 mL four-necked flask equipped with a reflux condenser and agitator (half-moon Teflon blade, 180 rpm) at 60 °C for 2 h. APS (dissolved in 2 mL of deionized and degassed water) was added immediately after the temperature in the flask reached 60 °C. Sodium bicarbonate was used as a buf-

Table 1. VTES/BA Miniemulsion Copolymerization Recipe

ingredients	amount
deionized water	80 wt %
sodium lauryl sulfate (SLS)	10 mM on aqueous phase
ammonium persulfate (APS)	1 mol % on monomers
sodium bicarbonate	1 mol % on monomers
VTES/BA, 5/95, 7.5/92.5 and 10/90 molar ratios[a]	20 wt %
hexadecane	3.7 wt % on monomers

[a] VTES = vinyltriethoxysilane and BA = *n*-butyl acrylate.

Table 2. Amount of Coagulum in Miniemulsion vs Conventional Emulsion Copolymerization of VTES and BA

mol % VTES in the feed	coagulum (wt % of monomers)	
	emulsion	miniemulsion
0	0	0
1	1.1	1.2
5	2.3	2.5
10	3.4	2.9
20	15.1	4.8
50	32.7	5.5

fer (pH = 6.5) in order to minimize the alkoxysilane hydrolysis reaction. Reference conventional emulsion polymerizations were carried out using the same basic recipes, but with no hexadecane present and without using the sonification step.

Particle sizes were determined by dynamic light scattering measurements using a Particle Sizing Systems, Inc., NICOMP 370 instrument. The amounts of coagulum obtained in the reaction systems were evaluated by gravimetry, after filtration through a no. 200 mesh (0.074 mm) stainless steel wire cloth (Small Parts Inc.). Reactivity ratios between VTES and BA were evaluated to determine the degree of silane incorporation through the vinyl copolymerization.

Solution copolymerizations used for the determination of the reactivity ratios were carried out with five different molar ratios of vinyltriethoxysilane/*n*-butyl acrylate (2:3, 1:1, 3:2, 7:3, and 4:1) in 2 mL vials that were flushed with nitrogen for 30 s before being capped. Copolymerizations were performed in a constant temperature shaking water bath that was maintained at 60 °C. Ethylbenzene was used as a solvent for the comonomers, and toluene was used as an internal standard for gas chromatography (GC) measurements due to their solubility parameter (δ) compatibility with that of BA ($\delta_{\text{ethylbenzene}} = 18.0$ MPa$^{1/2}$, $\delta_{\text{toluene}} = 18.2$ MPa$^{1/2}$, $\delta_{\text{BA}} = 18.0$ MPa$^{1/2}$).[18] AMBN was used as an oil-soluble initiator (1 mol % based on the comonomer mixture). The monomer concentration in solution was 50 wt %, so that the reaction mixture could be injected into the GC instrument even in the latter stages of the copolymerization. A Hewlett-Packard 5890 instrument equipped with an Alltech EC-1 column (length 15 m, i.d. 0.53 μm) and a flame ionization detector was used (initial temperature 40 °C, final temperature 100 °C, ramp 10 °C/min). The same instrument was employed for monitoring the evolution of the volatile species in the miniemulsion copolymerization.

Bulk copolymerizations were also carried out at five different molar ratios of alkoxyvinylsilane/*n*-butyl acrylate (4/6, 5/5, 6/4, 7/3, and 8/2) for subsequent FT-IR analysis. These reactions were performed in 4 mL vials for 1 h at 60 °C. AMBN was used as initiator (1 mol % based on the comonomer mixture). Chloroform ($\delta = 19.0$ MPa$^{1/2}$)[18] was employed for preparing 1 g/dL copolymer solutions for FT-IR analysis (Mattson-Polaris HiRes spectrometer, NaCl cell, 64 scans per sample, 2 cm^{-1} resolution, 4000−600 cm^{-1} frequency sweep range). The same instrument was used for the analysis of dry (co)polymer films cast on ZnSe plates. PROCOP software[19] was employed for the reactivity ratio computations.

Results and Discussion

A parameter of major interest in both conventional and miniemulsion polymerizations that were carried out is the amount of coagulum formed in the system. The amount of coagulum increases with the silane content in the monomer mixture for both conventional and miniemulsion copolymerization systems. In the case of miniemulsion reactions, at high silane contents (>10 mol %), the coagulum amount is significantly lower compared to the conventional emulsion systems (Table 2). The particle sizes in the synthesized latexes do not seem to be significantly influenced by the VTES feed amount and are smaller for the conventional systems (Figure 3).

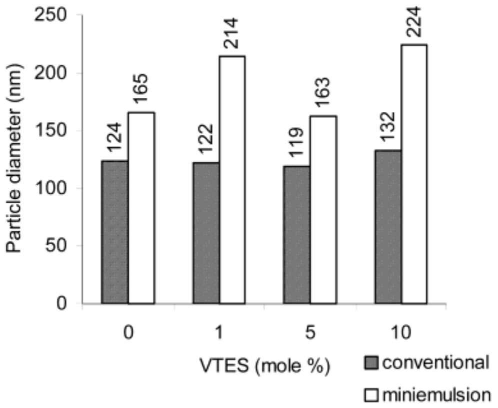

Figure 3. Volume-average particle sizes (D_v) in miniemulsion vs conventional emulsion copolymerizations of VTES and BA as a function of the amount of silane in the feed.

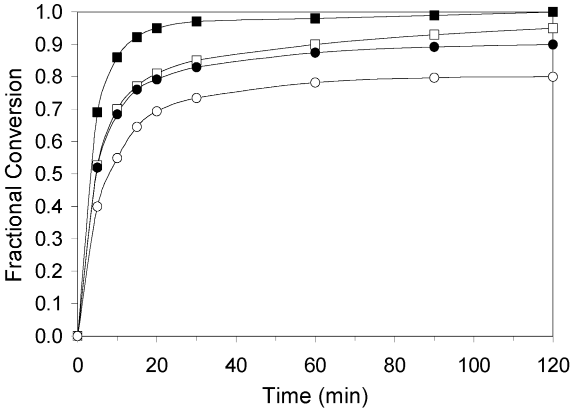

Figure 4. Overall fractional conversion determined by gravimetry for the miniemulsion copolymerization of BA/VTES for a SLS concentration of 10 mM: ■, reference PBA; □, 0.072 feed weight fraction VTES; ●, 0.107 feed weight fraction VTES; ○, 0.142 feed weight fraction VTES.

Measurements of the overall fractional conversions in the miniemulsion copolymerization systems show that the presence of the alkoxysilane induces a “limited conversion” effect for higher amounts of VTES (Figure 4). The method could not be applied to the conventional systems due to the high levels of coagulum. Reactivity ratios between VTES and BA were determined in order to clarify the role of the silane in the observed limited conversion.

Reactivity ratios between comonomers in a copolymerization reaction are usually determined by analyzing the copolymer composition at low conversions. An alternative method is to determine the quantity of unreacted monomers by gas chromatography (GC).[20−22] The GC method allows for a detailed study of the course of a copolymerization reaction and, unlike the calorimetric method, is able to follow the consumption of each

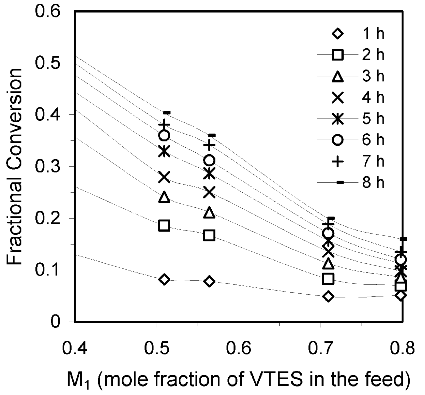

Figure 5. Overall fractional conversion in the solution copolymerization of BA and VTES as a function of the alkoxyvinylsilane content in the monomer feed for different reaction times.

Table 3. Feed and Copolymer Compositions for Solution Copolymerization of VTES (Monomer 1) and BA (Monomer 2) via GC Analysis

	feed composition		copolymer composition			
			exptl		calcd	
conv	M_1	M_2	m_1	m_2	m_1	m_2
0.358	0.3994	0.6006	0.086	0.914	0.091	0.909
0.412	0.3994	0.6006	0.078	0.922	0.097	0.903
0.445	0.3994	0.6006	0.090	0.910	0.101	0.899
0.478	0.3994	0.6006	0.095	0.905	0.105	0.895
0.501	0.3994	0.6006	0.1	0.9	0.108	0.892
0.515	0.3994	0.6006	0.097	0.902	0.11	0.889
0.186	0.5091	0.4909	0.125	0.875	0.117	0.883
0.242	0.5091	0.4909	0.117	0.883	0.123	0.877
0.28	0.5091	0.4909	0.113	0.887	0.128	0.872
0.33	0.5091	0.4909	0.132	0.868	0.135	0.865
0.361	0.5091	0.4909	0.137	0.863	0.14	0.86
0.381	0.5091	0.4909	0.135	0.865	0.144	0.856
0.404	0.5091	0.4909	0.15	0.85	0.148	0.852
0.167	0.5643	0.4357	0.148	0.852	0.139	0.86
0.212	0.5643	0.4357	0.143	0.856	0.146	0.854
0.251	0.5643	0.4357	0.144	0.856	0.152	0.848
0.287	0.5643	0.4357	0.146	0.854	0.158	0.842
0.312	0.5643	0.4357	0.152	0.848	0.163	0.837
0.342	0.5643	0.4357	0.17	0.83	0.169	0.831
0.113	0.7096	0.2904	0.197	0.803	0.219	0.781
0.136	0.7096	0.2904	0.183	0.817	0.225	0.775
0.157	0.7096	0.2904	0.171	0.829	0.23	0.77
0.171	0.7096	0.2904	0.189	0.811	0.234	0.766
0.189	0.7096	0.2904	0.198	0.802	0.239	0.761
0.2	0.7096	0.2904	0.191	0.809	0.242	0.758
0.07	0.798	0.202	0.383	0.616	0.291	0.709
0.086	0.798	0.202	0.383	0.617	0.296	0.704
0.098	0.798	0.202	0.367	0.633	0.3	0.7
0.112	0.798	0.202	0.346	0.654	0.305	0.695

of the monomers and any volatile byproducts that could develop in the system. Reactivity ratios can then be computed using an algorithm that takes into account instantaneous conversions; stopping the reaction at low conversions is not necessary.[19]

Solution copolymerizations of VTES/BA were carried out as described above, and unreacted monomer concentrations were measured by GC at various times during the reaction. Copolymer compositions were determined by difference from the monomer feed. Conversion as a function of the silane content for different reaction times is shown in Figure 5.

The alkoxyvinylsilanes exhibit a very slow consumption rate compared to *n*-butyl acrylate. These results indicate that the silane moiety is less reactive than the acrylate component. The copolymerization rate decreases as the silane content in the system is increased.

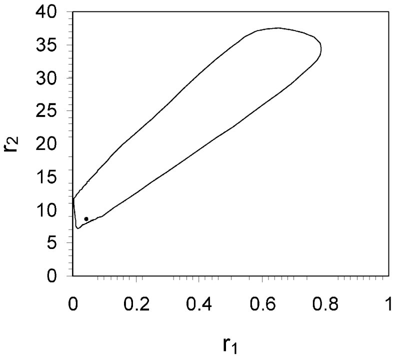

Figure 6. The 95% confidence region calculated using PROCOP software for reactivity ratios between VTES (r_1) and BA (r_2) determined by GC method. $r_1 = 0.044$; $r_2 = 8.56$.

Table 4. Feed and Copolymer Compositions for Bulk Copolymerization of VTES (Monomer 1) and BA (Monomer 2) via FT-IR Analysis

	monomer composition		copolymer composition			
			exptl		calcd	
conv	M_1	M_2	m_1	m_2	m_1	m_2
0.36	0.4	0.6	0.09	0.91	0.095	0.905
0.19	0.49	0.51	0.12	0.88	0.115	0.885
0.17	0.56	0.44	0.15	0.85	0.145	0.855
0.11	0.71	0.29	0.19	0.81	0.237	0.763
0.07	0.8	0.2	0.36	0.64	0.324	0.676

The reactivity ratios for the VTES/BA system were calculated from GC conversion data, using PROCOP software. The computational algorithm takes into account the conversions of the two comonomers during the reaction. Reactivity ratios were found to be 2 orders of magnitude smaller for the silane than for *n*-butyl acrylate. For VTES (monomer 1) and BA (monomer 2), $r_1 = 0.044$ and $r_2 = 8.56$. Feed and copolymer compositions are shown in Table 3. The *calculated* values of the copolymer compositions were back-calculated using the estimated reactivity ratios.[19] The 95% confidence region was also calculated using PROCOP and is plotted in Figure 6. These reactivity ratios were confirmed by an FT-IR analysis of poly(VTES-*co*-BA) synthesized by bulk copolymerization. Feed and copolymer compositions are given in Table 4. In this case, calculations yield $r_1 = 0.086$ (VTES) and $r_2 = 8.51$ (BA).

Good agreement has been obtained for the reactivity ratios determined from GC (solution copolymerization) and FT-IR (bulk copolymerization). According to these results, it will take approximately 50 mol % alkoxysilane in the monomer feed mixture to incorporate 10 mol % silane moieties into the copolymer. Incorporation of the silane components carried out exclusively by batch vinyl copolymerization reactions would not be effective.

The limiting conversion effect in miniemulsion copolymerization of VTES and BA *in the investigated time frame* (Figure 4) arises from the difference in the reactivity ratios. BA reacts quickly, and the amount of unreacted material is approximately equal to the amount of VTES fed in the reaction. The details are given in Table 5. The weight fractions of the unreacted material other than VTES for the VTES feed weight fractions of 0.072, 0.107, and 0.142 are −0.013, 0.007, and 0.077, respectively. The first two values are small and may be considered negligible, meaning that the conversion limitation reflects the difference between the feed amount of VTES and the amount that was supposed to

Table 5. Weight Fractions of VTES As Compared to Weight Fractions of Unreacted Material Inferred from Figure 4

VTES in the feed	VTES in the copolymer[a]	unreacted material[b]	unreacted VTES[c]	unreacted material[d]
0.072	0.009	0.05	0.063	−0.013
0.107	0.014	0.1	0.093	0.007
0.142	0.019	0.2	0.123	0.077

[a] Calculated with PROCOP according to the determined reactivity ratios ($r_1 = 0.044$; $r_2 = 8.56$). [b] At the end of the investigated time frame (Figure 4). [c] Column 1 − column 2. [d] Other than VTES (column 3 − column 4).

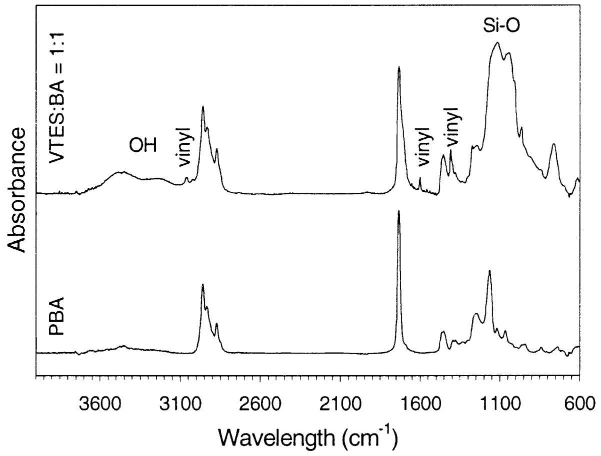

Figure 7. FT-IR spectrum of VTES/BA copolymer film for a 1:1 mole feed ratio as compared to the spectrum of PBA. The presence of Si−O and OH peaks is evidence of silane incorporation. The presence of vinyl peaks indicates that the incorporation is not exclusively achieved by vinyl copolymerization, but also by silane hydrolysis and subsequent cross-linking. Both samples were synthesized by miniemulsion polymerization.

be incorporated according to the determined reactivity ratios. The third value, corresponding to the highest VTES feed fraction, can be reasonably assigned to unreacted acrylate monomer trapped within the cross-linked network of the alkoxysilane that underwent hydrolysis/condensation reactions in the presence of the aqueous phase.

Transmission FT-IR spectra of the latexes synthesized by miniemulsion polymerization (molar feed ratio VTES:BA = 1:1) were obtained for films cast and dried on ZnSe plates and are shown in Figure 7. A significant amount of VTES was found to be incorporated into the copolymer, although not entirely via a vinyl copolymerization route, but rather by alkoxysilane hydrolysis and subsequent cross-linking. The presence of the vinyl, OH, and Si−O peaks offering evidence in favor of the second mechanism for the incorporation of the alkoxysilane.

The evolution of the volatile species in the miniemulsion system was monitored by GC for a molar feed ratio of 1:1 VTES/BA (Figure 8). The development of ethanol was an indication that alkoxysilane hydrolysis occurs during the reaction. No other GC peak was observed besides those for VTES, BA, and ethanol. The hydrolysis of the alkoxysilane was quickly followed by the condensation of hydroxyl groups, yielding nonvolatile species. Alkoxysilane hydrolysis seems to play a significant role in the VTES incorporation into latex systems synthesized by miniemulsion copolymerization. This aspect will be investigated in a subsequent publication.

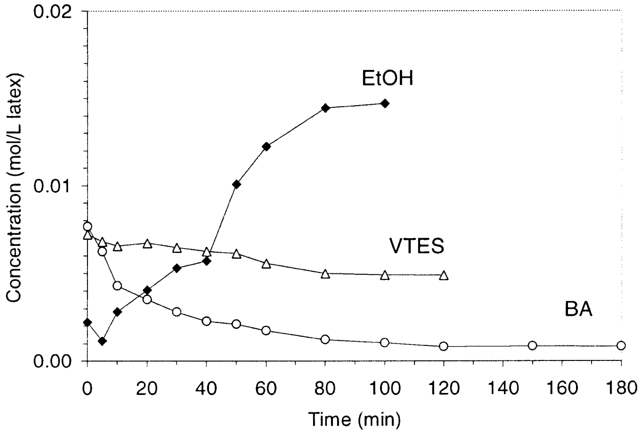

Figure 8. Evolution of volatile species in the miniemulsion copolymerization of VTES and BA for a feed ratio (molar) of 1:1. The development of the ethanol in the system indicates the occurrence of alkoxysilane hydrolysis.

Conclusions

Miniemulsion copolymerization techniques have real potential for incorporating high amounts of vinyltriethoxysilane into *n*-butyl acrylate latex systems by a one-step batch procedure. The use of the miniemulsion copolymerization approach yielded significantly lower coagulum amounts at high silane feed compositions compared to the conventional method.

The reactivity ratio of vinyltriethoxysilane is 2 orders of magnitude lower than that of *n*-butyl acrylate; therefore, a direct incorporation of the silane by batch vinyl copolymerization cannot be effective. Other reaction conditions (pH, initiator) are to be investigated in order to maximize the amount of silane incorporated into the copolymer and to lower the coagulum content.

References and Notes

(1) Witucki, G. L. *J. Coat. Technol.* **1993**, *65*, 57.
(2) Osterholtz, F. D.; Pohl, E. R. *J. Adhes. Sci. Technol.* **1992**, *6*, 127.
(3) Bourne, T. R.; Bufkin, B. G.; Wildman, G. C.; Grawe, J. R. *J. Coat. Technol.* **1982**, *54*, 69.
(4) Liles, D. T.; Murray, D. L. EP 0 771 826 A2, 1997.
(5) Liles, D. T.; Murray, D. L. US Pat. 5 932 651, 1999.
(6) Ando, N.; Masuda, T.; Hatano, T.; Nakayama, K. EP 0 621 325 A1, 1994.
(7) Liles, D. T.; Murray, D. L. EP 0 818 497, 1997.
(8) Liles, D. T.; Murray, D. L.; Revis, A.; Tselepis, A. J.; Weyenberg, D. R. EP 0 684 266 A1, 1995.
(9) Masaaki, Y. US Pat. 5 240 992, 1993.
(10) Masuda, T.; Hatano, T.; Ando, N. EP 0 578 229 A2, 1993.
(11) Phan, L.; Farwaha, R.; Tinamisan, J. M. EP 1 018 522, 2000.
(12) Ladika, M.; Rose, G. D. WO 0 043 427, 2000.
(13) Lavoie, A. US Pat. 5 214 095, 1993.
(14) Moelnaar, H. A.; Vercauteren, F. F.; Tinnemans, A. H. WO 95/14700, 1995.
(15) Ugelstad, J.; El-Aasser, M. S.; Vanderhoff, J. W. *Polym. Lett.* **1973**, *11*, 503.
(16) Kitzmiller, E. L.; Miller, C. M.; Sudol, E. D.; El-Aasser, M. S. *Macromol. Symp.* **1995**, *92*, 157.
(17) Blythe, P. J.; Sudol, E. D.; El-Aasser, M. S. *Macromol. Symp.* **2000**, *150*, 179.
(18) Grulke, E. A. In *Polymer Handbook*, 4th ed.; Brandrup, J., Immergut, E. H.,Grulke, E., Eds.; Wiley-Interscience: New York, 1998; Vol. II, p 675.
(19) Hagiopol, C. In *Copolymerization. Toward a Systematic Approach*; Kluwer Academic/Plenum Publishers: New York, 1999.
(20) Guyot, A.; Guillot, J. *J. Chim. Phys.* **1964**, *61*, 1434.
(21) Mano, E. B.; Riva de Almeida, R. *J. Polym. Sci., Part A-1* **1970**, *8*, 2713.
(22) German, A. L.; Heikens, D. *Anal. Chem.* **1971**, *43*, 1940.

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