Study of the incorporation of alkoxysilane monomers into model latex systems.

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STUDY OF THE INCORPORATION OF ALKOXYSILANE MONOMERS INTO MODEL LATEX SYSTEMS

by

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“…and nothing of importance will come without effort.”

Daniel Baird Wesson, 1849

ABSTRACT

A miniemulsion copolymerization technique was applied to incorporate vinylalkoxysilanes into acrylate latex systems by an one-step batch polymerization. The use of the miniemulsion approach yields lower coagulum amounts at high silane feed contents compared to the conventional emulsion polymerization. The reactivity ratio of vinyltriethoxysilane (VTES) (1) was found to be significantly lower than that of n-butyl acrylate (BA) (2) ($r_1 = 0.044$, $r_2 = 8.56$); a direct incorporation of the silane by batch vinyl copolymerization is not effective.

Oil-soluble 2,2'-azobis(2-methyl-butyronitrile), is a suitable initiator for the study of silane incorporation into acrylate latexes, giving good silane incorporation with an acceptable rate of hydrolysis. Alkoxysilane hydrolysis in miniemulsions depends on the acrylate hydrophobicity; the best protection from hydrolysis is achieved using the least hydrophobic acrylate. The VTES/BA latex particle morphologies are pH-dependent; a lower pH induces a core/shell morphology. Phase separation and domain formation were found to occur in the VTES/acrylate latexes. Latex aging results in a lower solubles content and higher rigid polymer fraction in the latex (NMR spin diffusion). The rigid domains observed in films cast from aged latexes were found to be crystalline and were formed in the continuous phase.

The incorporation of vinylalkoxysilanes into acrylate latexes by miniemulsion polymerization involves: (a) vinyl copolymerization between the acrylate and the vinylalkoxysilane, (b) hydrolysis of the silane alkoxy groups, followed by the condensation of the resulting hydroxyl groups leading to the formation of a Si-O-Si network that is organized in rigid domains, and (c) chain transfer to the silane vinyl

group, with the formation of chemical bonds between the crosslinked network and the poly(n-butyl acrylate) (PBA) chains. The observed features of the poly(VTES-co-BA) latex particle morphology are: (1) rigid domains of Si-O-Si crosslinked VTES/BA copolymer moieties, (2) a soft matrix of non-extractable PBA chains, and (c) solvent-extractable silane moieties containing double bonds. At low silane contents (2–4 mole %), the tensile strength of silane/acrylate latex films can be dramatically modified by small changes in the process parameters, such as polymerization procedure (conventional emulsion vs. miniemulsion), initiator (oil-soluble vs. water-soluble), and use of pre-polymerized VTES vs. neat VTES.

CHAPTER 1

BACKGROUND

1.1 The Use of Alkoxysilane Monomers in Film-Forming Latexes

The main purposes of the present study are to investigate the incorporation of alkoxysilane monomers into film-forming latex systems and to elucidate the mechanism(s) of the incorporation of the alkoxyvinylsilanes into latex systems. The correlations of the latex synthesis parameters, latex particle morphology and latex film properties will allow for a better understanding of these systems, as well as improvements in the desired properties of the final product.

In recent years, in the field of paints and adhesives, formulators are developing water-soluble or water-dispersible resins for paints and adhesives, due to environmental concerns, the compositions comprising a resin and an organic solvent being gradually replaced by less polluting systems. Of particular concern is the amount of volatile organic compounds (VOC) released into the atmosphere from such coatings. In water-based coatings, volatile solvents are used to promote coalescence and film formation of the latex particles. This is usually done by preparing a dispersed (co)polymer having a glass transition temperature (T_g) above room temperature and then plasticizing it with a volatile solvent to effectively lower its T_g in order for the latex to be able to form a film at room temperature. Evaporation of the solvent after film formation leaves a polymer that was applied below its actual T_g; hence, no external heating is required to achieve film formation. This concept is also increasingly becoming obsolete as the levels of VOC's in coatings are to be reduced due to stricter environmental regulations [1].

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. Another disadvantage of this type of coating is that, because of the difference in the film formation mechanism, the gloss of these films is inferior compared to those films prepared using organic solvents [1,2].

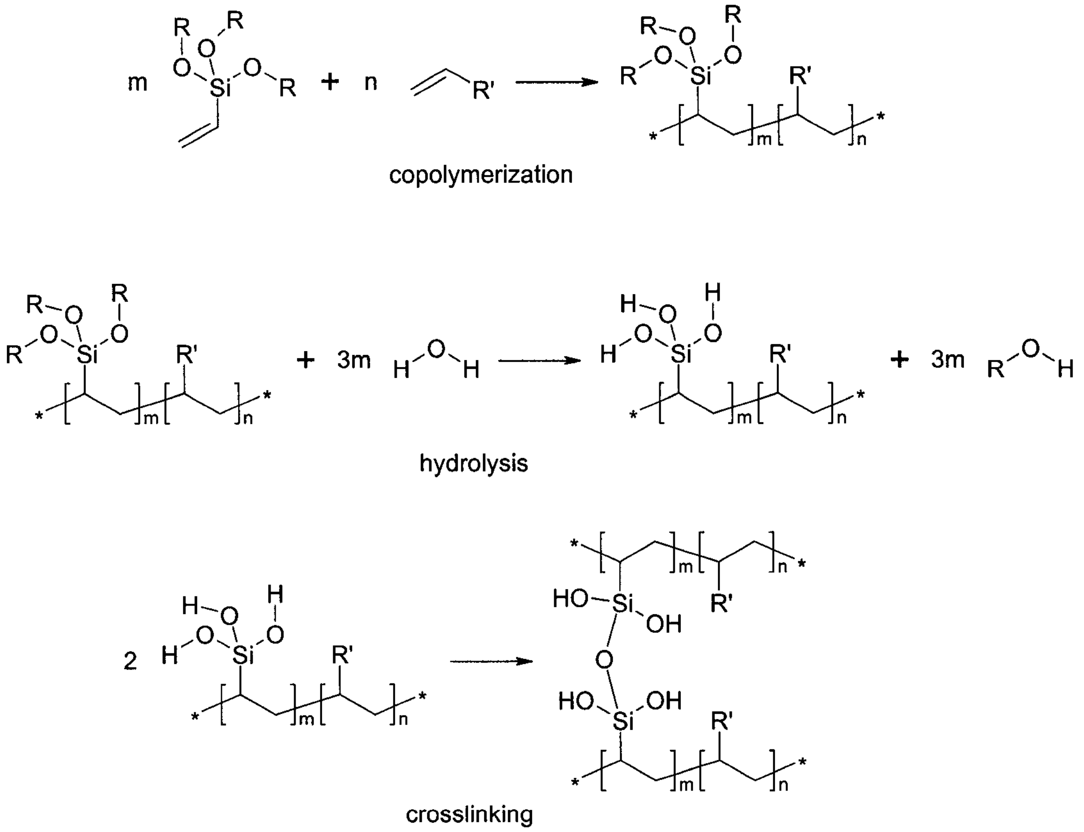
One way to help reduce the amount of VOC's is to crosslink emulsion polymers, preferably after removal of water. In the field of water-based paints, it is known that the presence of a post-application crosslinking mechanism in aqueous coating compositions offers major advantages with regards to the quality and the ultimate properties of the dried film paint, such as a greater wear and solvent resistance, impact resistance, flexural and tensile strength, and hardness. The incorporation of a post-application crosslinking mechanism into one-pack paint systems, such as acrylic paints, which cure at room temperature, can be achieved by using alkoxysilanes. In this case, the post-application crosslinking arises from the formation of grafting links from the alkoxysilane monomers.

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

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

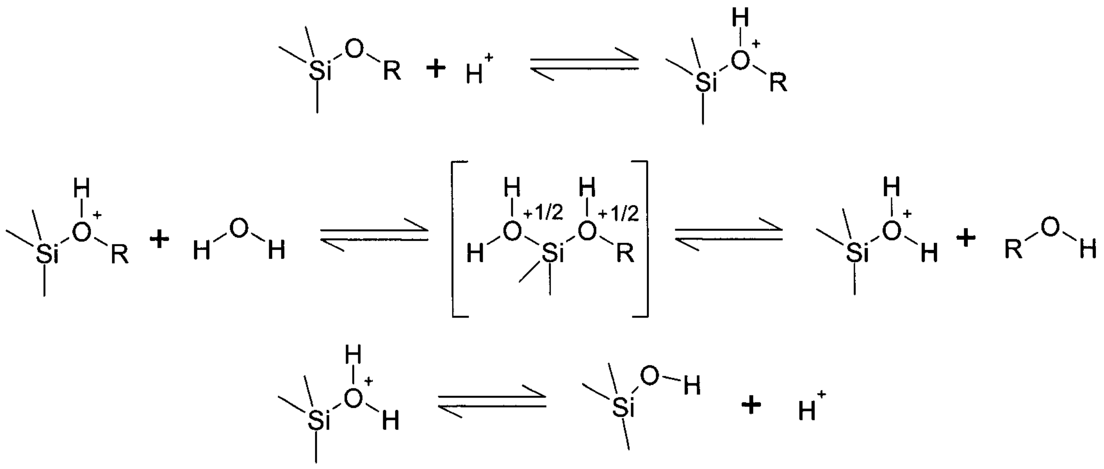
where Y is a non-hydrolyzable organic group that can be either an alkyl, aromatic, organofunctional group, or a combination of any of these. This group provides organic compatibility that allows the silane to react with monomers commonly used in coating formulations. The term X represents alkoxy moieties, most typically methoxy or ethoxy, which can react with various hydroxyl groups and liberate methanol or ethanol. These groups can provide the self-crosslinking ability of the resulting copolymer films. They are also involved in 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-crosslinking films prepared with alkoxysilanes can be summarized as follows:

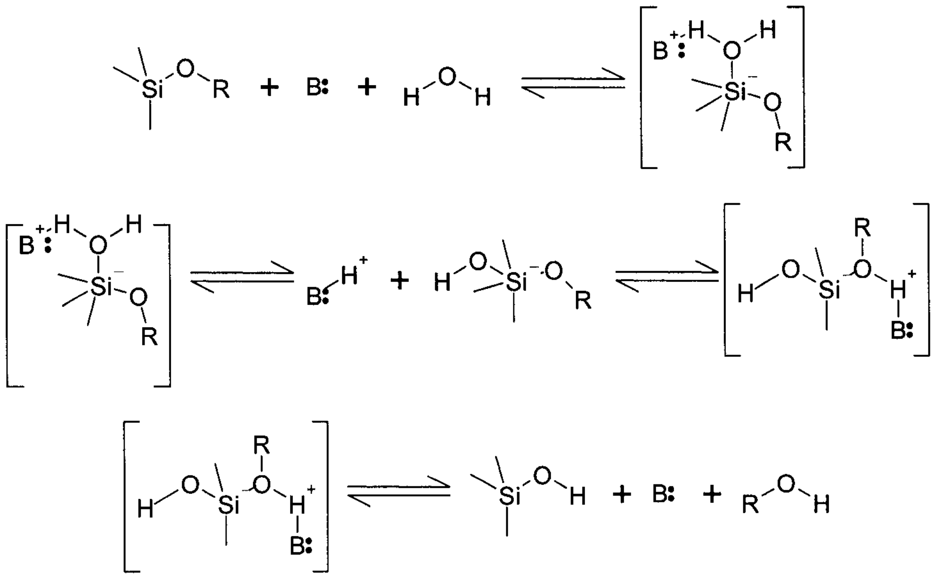


Premature hydrolysis and crosslinking reactions need to be avoided in order to obtain stable latexes with good shelf stability.

The hydrolysis of alkoxysilane was proven to be both acid and base catalyzed. The proposed mechanisms are [2]:



for acid-catalyzed (H^+) hydrolysis, and:



for base-catalyzed (B:) hydrolysis.

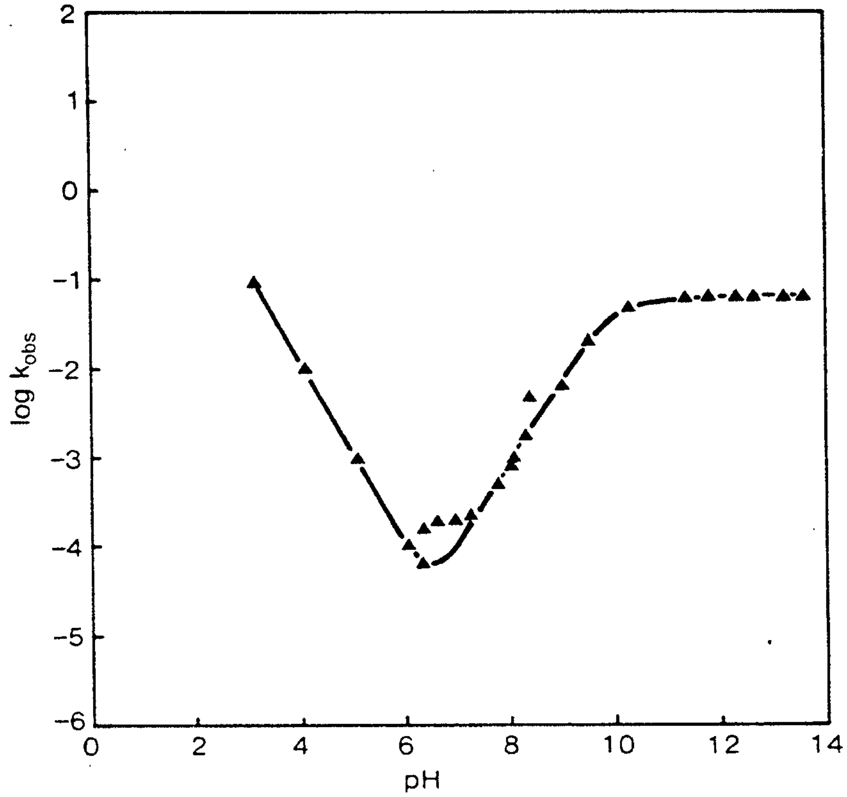


Figure 1.1: *pH profile for the hydrolysis of phenyl bis-(2-methoxyethoxy) silanol in aqueous solution at 25 °C (k_{obs} is the observed hydrolysis reaction rate coefficient) [2].*

In order to minimize premature crosslinking, good pH control is required for the polymerization system since the minimum hydrolysis rate occurs at a neutral pH for most systems (Figure 1.1) [2]. The polymerization temperature has a profound effect on the rate of polymerization, the molecular weight of the polymer, the critical micelle concentration of the surfactant, particle size and latex stability, and, more importantly, the tendency of the alkoxysilane functionality to undergo premature crosslinking. Studies were conducted whereby the polymerization temperature was varied in increments of 10 °C over a range from 50 °C to 90 °C. The suitability of a specific reaction was determined as a function of percent conversion and degree of premature crosslinking for a ethyl acrylate (EA)/γ-methacryloxypropyltrimethoxysilane (γ-MOPTMS) system [3].

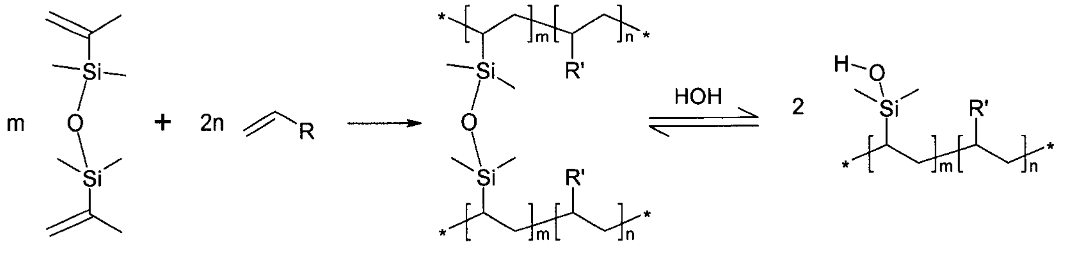
The percent conversion and degree of premature crosslinking (expressed as percent insolubles in acetone) were found to increase with increasing reaction temperature. Since high conversion is essential for achieving residual monomer-free model latexes, a problem arises in finding an optimum copolymerization temperature. Because the use of unnecesarily long polymerization times at high temperatures would lead to further loss of the alkoxysilane, an optimum reaction period at 80 °C was determined to achieve an acceptable balance between percent conversion to polymer and the degree of premature crosslinking. A four hour reaction period was selected as a reasonable compromise between adequate percent conversion and excessive premature crosslinking [3]. However, pH and temperature are not the only parameters that affect the hydrolysis and the crosslinking reactions of alkoxysilanes. When a water/methyl-trimethoxysilane mixture was subjected to simulated emulsion reflux conditions, approximately 7% of the alkoxysilane model compound was converted to crosslinked product after 4 hours at 80 °C. However, when a water/methyltrimethoxysilane/surfactant combination was subjected to the same conditions, approximately 50% of the model compound was converted to crosslinked product.

Even though the premature crosslinking of alkoxysilane-containing latexes strongly depends on the conditions employed (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 yields less premature crosslinking than methacryloxypropyltriisopropoxysilane, even though in the latter compound, the silicon atom carries sterically larger alkoxy substituents [3]. On the basis of these investigations, the following sequential order for the hydrolysis resistance of alkoxysilanes was found: trimethoxy, methyldimethoxy < triethoxy, triisopropoxy << methyldiethoxy, without giving any explanation for the fact that the methyldiethoxysilane compound gives less premature crosslinking than the sterically more hindered triethoxy- or triisopropoxysilanes. It was also reported that methyldiethoxysilane, even if it is the most suitable of the investigated compounds, still yields too high premature crosslinking for general use in advanced aqueous coating compositions, so that the use of these siloxanes is restricted to applications in which pre-crosslinked latexes are used [3].

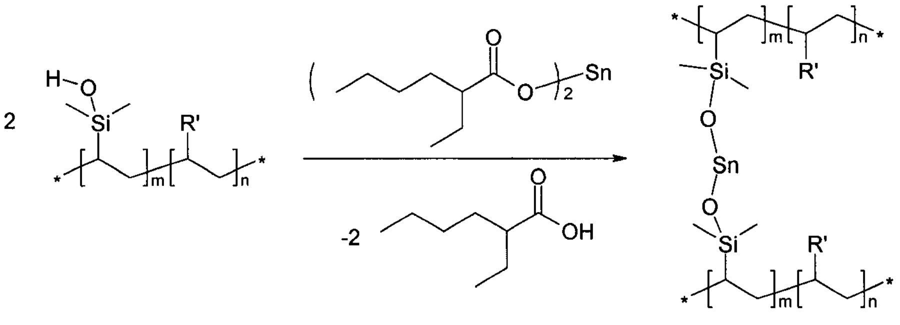
1.2 CURRENT STATUS OF INCORPORATION OF ALKOXYSILANES IN EMULSION POLYMER SYSTEMS

If alkoxysilane functional emulsions are to achieve the salient status sought by industry, then hydrolysis-resistant monomers or aqueous-barrier techniques must be developed to prevent premature crosslinking of the alkoxysilane moiety. It has been found that by emulsion copolymerizing a particular crosslinker, either a disiloxane or a disilazane (i.e., divinyltetramethyldisiloxane or divinyltetramethyldisilazane) with an organic monomer, a latex is formed having particles consisting of organic polymer chains that are either crosslinked or uncrosslinked, depending on the nature of the crosslinker and the reaction conditions. The uncrosslinked chains are then crosslinked at a later point by addition of a suitable catalyst [4].

It has been stated that under controlled conditions (pH below 5), the Si-O-Si bonds or Si-N-Si bonds of the crosslinker will cleave during emulsion polymerization to form Si-OH bonds (or Si-NH bonds). These latter functionalities between different polymer chains are then condensed, either on their own or by addition of an organotin catalyst and/or similar additive, according to the following scheme:



pH-controlled uncrosslinking reaction

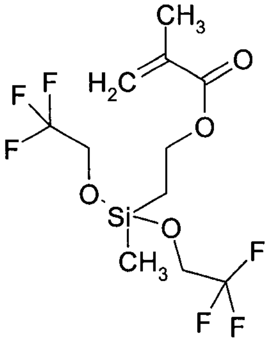


crosslinking in the presence of stannous octoate

Monoalkoxysilanes (vinyltrimethoxysilane, vinyltriethoxysilane, vinyldimethylethoxysilane, γ-methacryloxypropylmethyldiethoxysilane, vinylmethyldimethoxysilane, vinylmethyldiethoxysilane, vinyltris(2-methoxyethoxysilane, γ-methacryloxypropyltrimethoxysilane and vinyltriacetoxysilane) were used in copolymerization reactions with organic monomers (semicontinuous process), and the subsequent crosslinking reactions could also be pH-controlled [4,5]. Preparation of latexes that yielded crosslinked silicon-modified organic compositions upon the removal of water were carried out by various procedures, mostly through discontinuous (batchwise) or semicontinuous procedures (the alkoxysilanes were usually added late in the reaction to avoid their prolonged contact with water) [4-10].

Stable copolymers containing protected siloxane functional groups were prepared by the 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. One of these comonomers is a silane monomer containing both a free radical polymerizable functionality and a silicon functionality capable of self-condensation crosslinking (vinyltrimethoxysilane, vinyltriethoxysilane, acryloxypropyl-trimethoxysilane, methacryloxypropyltrimethoxysilane) and the other comonomer being a cationic initiatable polysiloxane precursor which is present at a concentration sufficient to inhibit the self-condensation crosslinking of the bifunctional silane comonomer at ambient conditions (octamethylcyclotetrasiloxane (D4), octaphenyl-cyclotetrasiloxane, hexamethylcyclotrisiloxane (D3), decamethylcyclopentasiloxane (D5), and derivatives). The polysiloxane precursor is believed to act as a cap on the reactive silane functional groups. According to this theory, in order to achieve a complete capping of the reactive silane groups at equilibrium, there must be a molar excess of the cyclic siloxane to the reactive siloxane of at least 3 to 1 [11].

Studies in obtaining stable emulsion compositions of copolymers between a silyl group-containing monomer and another ethylenically-unsaturated comonomer copolymerizable therewith were carried out by using longer chain organosilanes, such as decen-9-yl trimethoxy silane, 4-vinylphenyltrimethoxysilane, and hexen-5-yl methyldiethoxysilane as a means of achieving a better steric hindrance [9]. Novel alkoxysilanes having a lower hydrolysis rate, which result in a lower degree of premature crosslinking were synthesized. These objectives were achieved by designing a siloxane in which one silyloxy group has an electronegative character (methacryloxypropyl-methylbis-(2,2,2-trifluoroethoxy)silane [12]:



Owing to the presence of these electronegative silyloxy groups, these compounds have a much lower hydrolysis rate (Table 1.1)

Table 1.1: Hydrolysis Rate Constant for Several Siloxane Monomers

Alkoxysilane	**$K_{hydrolysis}$ (liter s^{-1} mol^{-1})**
Methacryloxypropyltrimethoxysilane (47 °C)	4.1×10^{-5}
Methacryloxypropyltrimethoxysilane (62 °C)	6.1×10^{-5}
Methacryloxypropylmethyldiethoxysilane (62 °C)	2.4×10^{-5}
Methacryloxypropylmethyldiethoxysilane (81 °C)	8.0×10^{-5}
Methacryloxypropylmethylbis-(2,2,2-trifluoroethoxy)silane (85 °C)	1.0×10^{-5}

1.3 CONVENTIONAL EMULSION POLYMERIZATION VS. MINIEMULSION POLYMERIZATION

1.3.1 Conventional Emulsion Polymerization

Conventional emulsion polymerization, involves the polymerization of monomers in the form of emulsions (i.e., colloidal dispersions), yielding disperse systems known as *polymer latexes*. A latex is synthesized by mixing monomer(s), surfactant, and an initiator into the water. Surfactants are amphiphilic molecules, which dissolve in water at a molecular level. As the surfactant concentration is increased, some surfactant molecules will eventually begin to aggregate into groups known as micelles. The concentration at which these micelles begin to form is the Critical Micelle Concentration (CMC). Above the CMC, the free surfactant concentration does not increase, but more micelles will be formed. Since the interior of the micelles is hydrophobic, monomer from the droplets diffuses to swell the micelles. The initiator, most commonly water-soluble, is usually activated by heat, generating free radicals. In conventional batch emulsion polymerization, the main loci of polymer particle nucleation are considered to be the monomer-swollen micelles (*micellar nucleation*) and the aqueous phase (*homogeneous nucleation*). Depending on the amount of surfactant used and on the water solubility of the monomer, one or the other of these nucleation loci may be favored (e.g. a monomer with a low water solubility and a high amount of surfactant (above CMC) would favor micellar nucleation) [13]. In the case of micellar nucleation [14], the oligoradicals formed by solution polymerization in the aqueous phase enter the micelles, where they continue to propagate till the termination takes place. As polymerization occurs, the micelles grow by the addition of the monomer from aqueous solution, whose concentration is balanced by the dissolution of monomer from the monomer droplets (Figure 1.2). In the case of homogeneous nucleation (favored by a low surfactant concentration, below CMC) the monomer dissolved in the aqueous phase reacts with the water-borne radicals to form oligomers, that grow until they become water-insoluble. These oligoradicals precipitate to form the growing precursor particles [15]. The precipitated species stabilize by adsorbing surfactant (from solution, micelles and monomer droplets).

A very low amount of polymer (< 0.1 %) is usually found in the monomer droplets. Monomer droplets are relatively large (1-10 mm) compared to the size of monomer-swollen micelles (10-20 nm). Monomer droplets do not compete effectively with micelles in capturing radicals produced in solution, because of the much smaller (several orders of magnitude) total surface area of the droplets [16, 17].

1.3.2 Miniemulsion Polymerization

Miniemulsions are submicron dispersions of monomer droplets. The droplets have an average diameter of 50-500 nm, and the miniemulsions can be stable for as long as several months. The miniemulsion droplets are usually stabilized by the synergic effect of an ionic surfactant (i.e. sodium lauryl sulfate) and a costabilizer, that can be either a long-chain alcohol (cetyl alcohol) or a long-chain alkane (hexadecane). Cetyl alcohol forms a barrier structure or "condensed phase" with the surfactant, thereby reducing coalescence. The costabilizing function of hexadecane is to limit the diffusion of the oil phase from small droplets to large ones (Ostwald ripening), by the means of its extremely

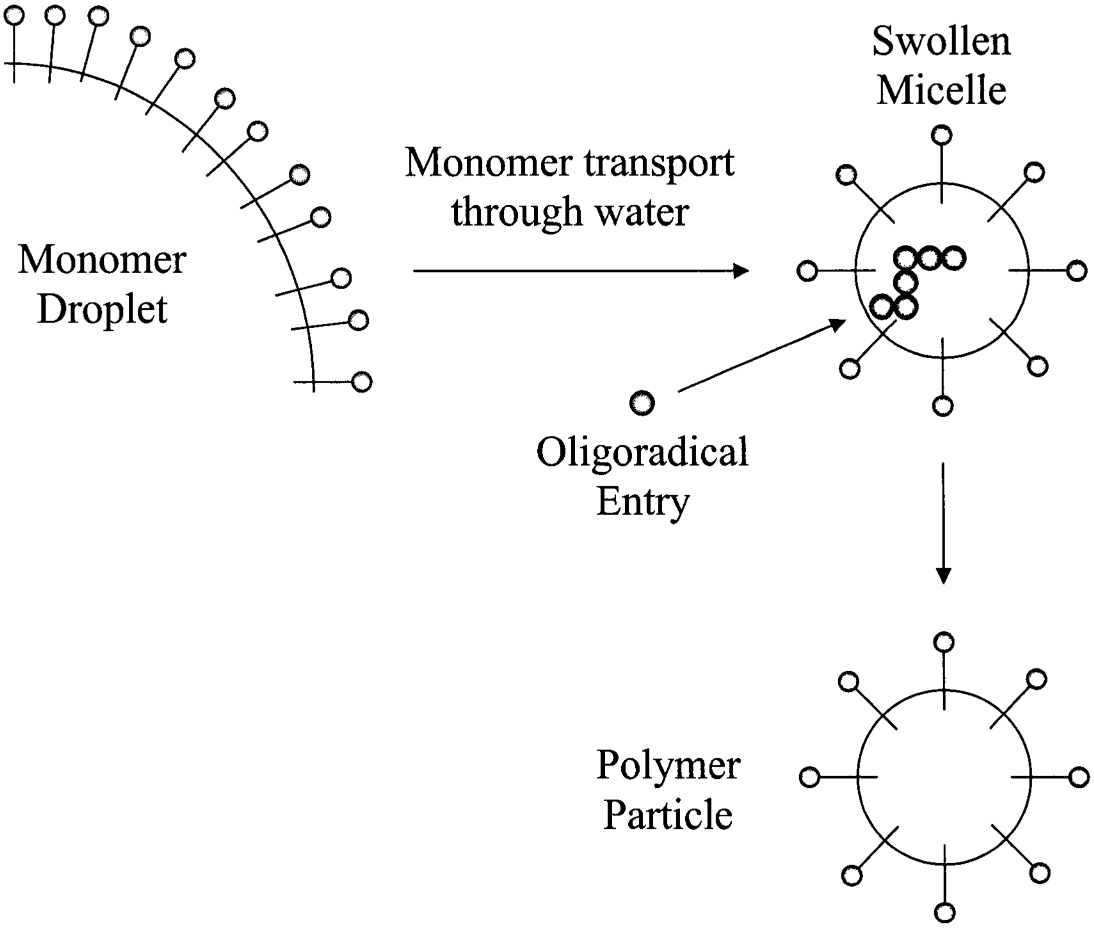


Figure 1.2: *Schematic representation of the conventional emulsion polymerization process.*

low water solubility, that allows for a thermodynamic pseudo-equilibrium to be established between monomer droplets [18]. Under conditions in which the droplet size is small enough to assure a large total droplet surface, nucleation of monomer droplets can account for the most important part of the particles formed [19]. In this case, the nucleation occurs by (oligo)radical entry into the monomer droplets (droplet nucleation). The droplets act as individual "reactors" in which monomer is converted to polymer. The miniemulsion polymerization (droplet nucleation) mechanism is presented in Figure 1.3a. In miniemulsions, the monomer droplets are small, and their interfacial area is large, so that most of the surfactant resides on the droplet surface, and relatively little is present in the aqueous phase. This significantly reduces the probability of homogeneous nucleation and does not favor micellar nucleation, since the free surfactant concentration is below the CMC.

An alternative to this mechanism is the use of a highly water-insoluble initiator, pre-dissolved in the oil phase. The vast majority of radicals will be generated in the oil droplets, depending on the partition coefficient of the initiator species between the aqueous and organic phases (Figure 1.3b). This does not guarantee an exclusive droplet nucleation, though, since radicals can also be present in the aqueous phase either as single radicals formed by desorption from the droplet of one of the two radicals formed by initiator decomposition, or generated in the aqueous phase from the fraction of the initiator dissolved in water. The initiation in the oil droplet occurs at the expense of the generated radicals that neither desorb, nor recombine [24-25].

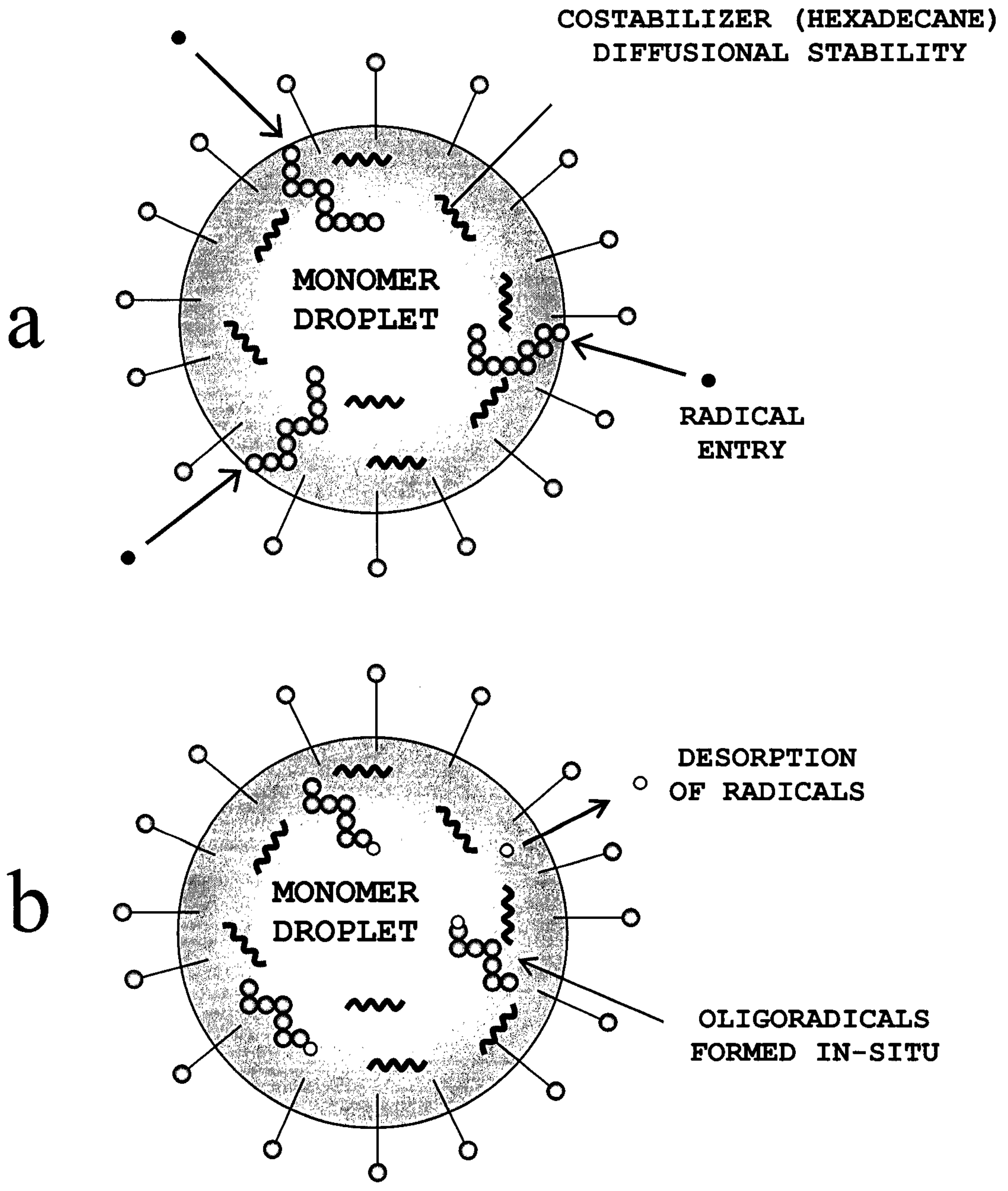


Figure 1.3: *Schematic representation of the miniemulsion polymerization process: (a) water-soluble initiator; (b) oil-soluble initiator.*

The field of miniemulsion polymerization receives numerous contributions in terms of publications every year. The reader will be referred to a few of the most comprehensive recent reviews [16, 18, 24, 25].

1.4 PROJECT OBJECTIVES

1. To investigate the miniemulsion approach for the incorporation of alkoxysilane monomers into film-forming latex systems, in order to reduce the premature crosslinking of the copolymer chains by minimizing their contact with water.
2. To develop suitable recipes for the incorporation of alkoxysilane moieties into model latex systems.
3. To conduct studies on the kinetics of copolymerization, hydrolysis and copolymer properties as functions of initiator, pH, nature of organic monomer, and alkoxysilane concentration.
4. To elucidate the mechanism(s) of the incorporation of the alkoxyvinylsilanes into latex systems.
5. To identify and to explain the latex particle morphologies.
6. To study film properties of the synthesized alkoxysilane-containing copolymers.

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CHAPTER 2

INCORPORATION OF ALKOXYSILANES INTO MODEL LATEX SYSTEMS BY MINIEMULSION POLYMERIZATION: VINYL COPOLYMERIZATION OF VINYLALKOXYSILANES AND *N*-BUTYL ACRYLATE

2.1 INTRODUCTION

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. The miniemulsion approach was deemed to be most appropriate for obtaining stable latexes, with silane groups incorporated into the copolymer structure, and allowing subsequent formation of crosslinked films. Although the hydrolysis and condensation reactions still occur, the particles remain colloidally stable due to the use of a surfactant/costabilizer stabilization system (Figure 2.1). The silane moiety is protected from the aqueous phase by the "waterproof" oil droplet. A subsequent study of the reaction kinetics (Chapter 3) and particle formation and morphology (Chapter 4) helps in the understanding of the phenomena occurring in such systems and allows for further developments in the end-uses of these materials. Vinyltriethoxysilane was chosen as a typical trialkoxysilane, with a low-toxicity hydrolysis co-product (ethanol), and *n*-butyl acrylate as the base monomer for the film-forming polymer.

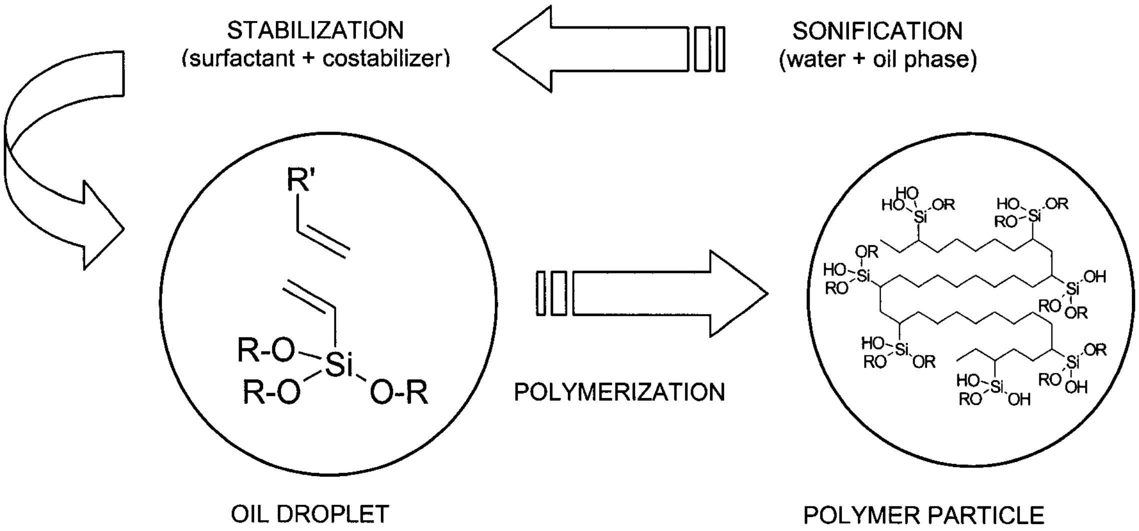

Figure 2.1: *Schematic representation of silane incorporation into latexes through a miniemulsion approach.*

2.2 EXPERIMENTAL

2.2.1 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 hours. Sodium lauryl sulfate (SLS; Fisher Scientific), sodium bicarbonate and hexadecane (both Aldrich), ammonium persulfate (APS; Merck) and 2,2'-azobis(2-methyl-butyronitrile) (AMBN; VAZO 67, DuPont) were used as received. Vinyltriethoxysilane (VTES) and vinylmethyldimethoxysilane (VMDMS) (OSi Specialties, C.K. Witco) were 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.

2.2.2 Methods

Miniemulsions (Table 2.1) 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 minutes with a magnetic stirrer. The mixture was then sonified (Branson Sonifier, Model 450) for 180 seconds 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 reflux condenser and agitator (half-moon teflon blade, 180 rpm), at 60 °C for 2 hours. Ammonium persulfate (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 buffer (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.

Table 2.1: VTES/BA Miniemulsion Copolymerization Recipe

Ingredient		**Amount**
Deionized water		80 wt.% (112 g)
Sodium lauryl sulfate (SLS)		10 mM on aqueous phase (0.323 g)
Ammonium persulfate (APS)		1 mole % on monomers (0.456 g)
Sodium bicarbonate		1 mole % on monomers (0.168 g)
VTES/BA (20 wt. %)	5/95*	1.9 g VTES/24.36 g BA
	7.5/92.5*	2.85 g VTES/23.72 g BA
	10/90*	3.8 g VTES/23.08 g BA
Hexadecane		3.7 wt. % on monomers (0.98 g)

VTES: vinyltriethoxysilane

BA: *n*-butyl acrylate

*molar ratios

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 filtering 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 role of vinyl copolymerization in the mechanism of silane incorporation.

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 seconds 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 ($\delta_{ethylbenzene}$ = 18.0 MPa$^{1/2}$; $\delta_{toluene}$ = 18.2 MPa$^{1/2}$; δ_{BA} = 18.0 MPa$^{1/2}$) [18]. AMBN was used as 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 °/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 hour at 60 °C. AMBN was used as initiator (1 mole % based on the comonomer mixture). Chloroform (δ = 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. The same procedures were employed for the evaluation of the reactivity ratios between VMDMS and BA.

2.3 RESULTS AND DISCUSSION

A parameter of major interest for both conventional and miniemulsion polymerizations 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 mole %), the coagulum amount is significantly lower compared to the conventional emulsion systems (Table 2.2). 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 2.2).

Table 2.2: Amount of Coagulum in Miniemulsion versus Conventional Emulsion Copolymerization of VTES and BA

Mole % 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

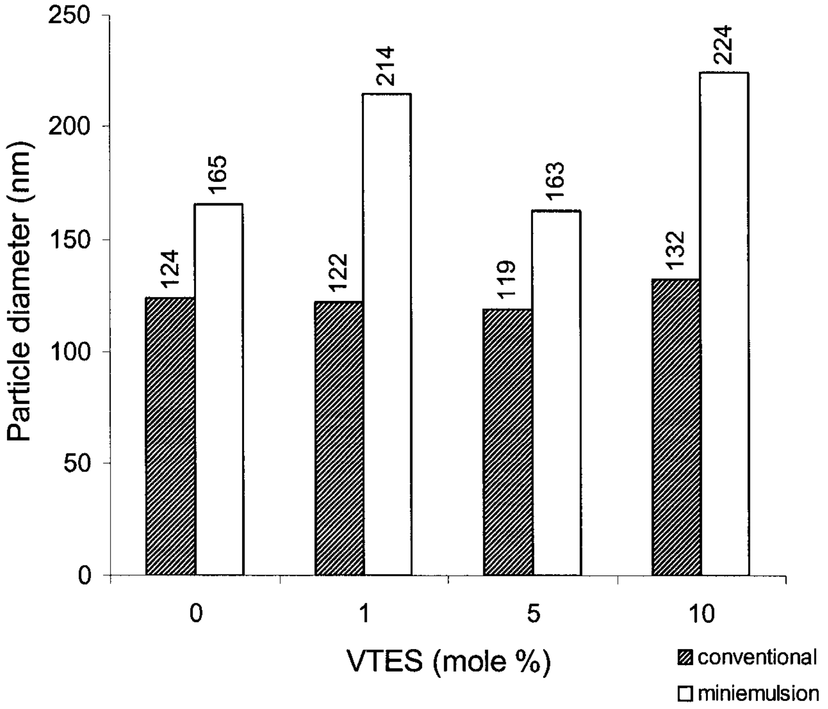

Figure 2.2: *Volume-average particle sizes (D_v) in miniemulsion versus conventional emulsion copolymerizations of VTES and BA as a function of the amount of silane in the feed.*

Measurements of the overall fractional conversions in the miniemulsion copolymerization systems indicate that the presence of the alkoxysilane induces a “limited conversion” effect for higher amounts of alkoxysilane (Figure 2.3). 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 of the monomers and formation of any volatile by-products 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 2.4.

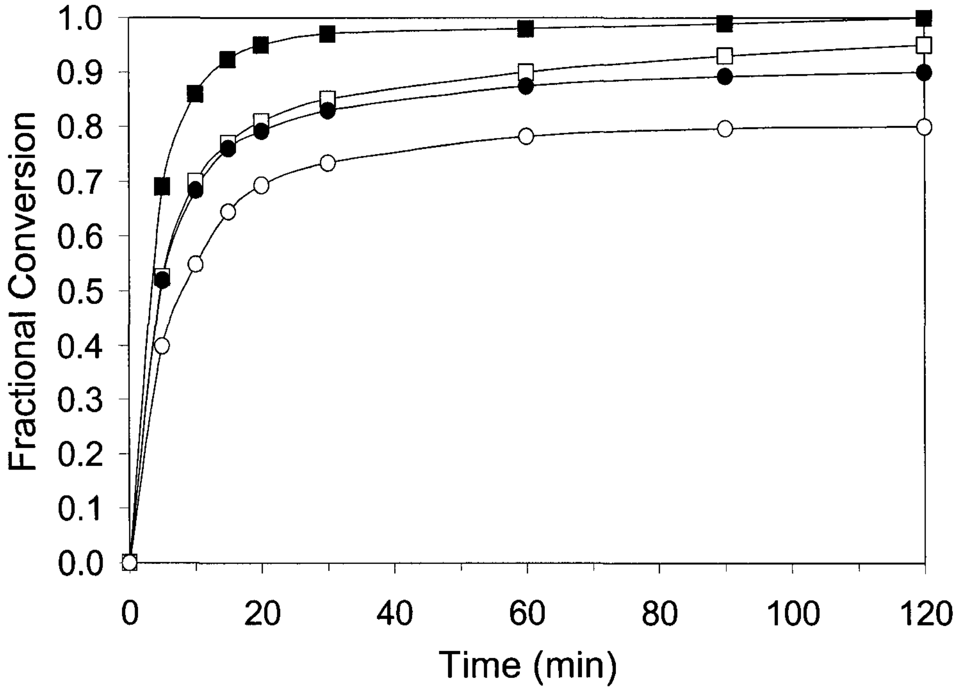

Figure 2.3: *Overall fractional conversion determined by gravimetry for the miniemulsion copolymerization of BA/VTES for a SLS concentration of 10 mM.* ■ *reference PBA;* □ *0.072 feed weight fraction VTES;* ● *0.107 feed weight fraction VTES;* ○ *0.142 feed weight fraction VTES.*

The alkoxyvinylsilanes exhibit a very slow consumption rate compared to *n*-butyl acrylate. The silane moiety is much less reactive than the acrylate component. The copolymerization rate decreases as the silane content in the system is increased. 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 two orders of magnitude smaller for the silane than for *n*-butyl acrylate. For VTES (monomer 1) and BA (monomer 2), $r_1 = 0.044$, $r_2 = 8.56$. Feed and copolymer compositions are shown in Table 2.3. 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 2.5 [23]. 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 2.4. In this case, calculations yield $r_1 = 0.086$ (VTES) and $r_2 = 8.51$ (BA).

Table 2.3: Feed and Copolymer Compositions for Bulk Copolymerization of VTES (Monomer 1) and BA (Monomer 2) via FT-IR Analysis

Fractional Conversion	Monomer Composition (mol fraction)		Copolymer Composition (mol fraction)			
			Experimental		Calculated	
	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

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 mole % alkoxysilane in the monomer feed mixture to incorporate 10 mole % silane moieties into the copolymer. Incorporation of the silane components carried out exclusively by batch vinyl copolymerization reactions would not be effective.

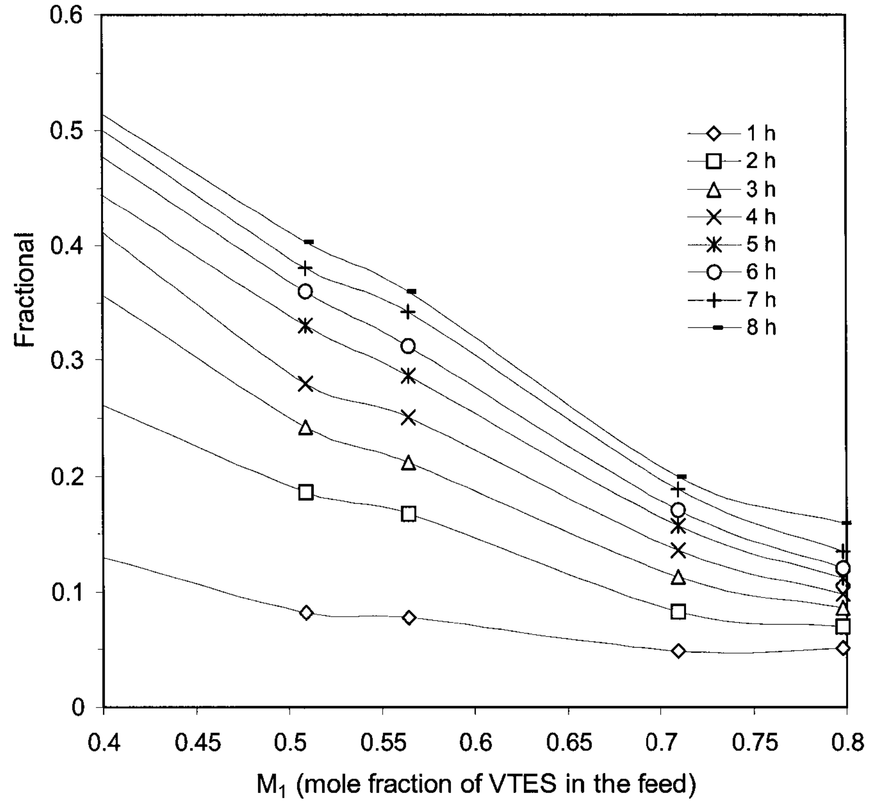

Figure 2.4: *Overall fractional conversion in the solution copolymerization of BA and VTES as a function of the alkoxyvinylsilane content in the monomer feed for different reaction times.*

Table 2.4: Feed and Copolymer Compositions for Solution Copolymerization of VTES (Monomer 1) and BA (Monomer 2) via GC Analysis

Conversion	Feed Composition		Copolymer Composition			
			Experimental		Calculated	
	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

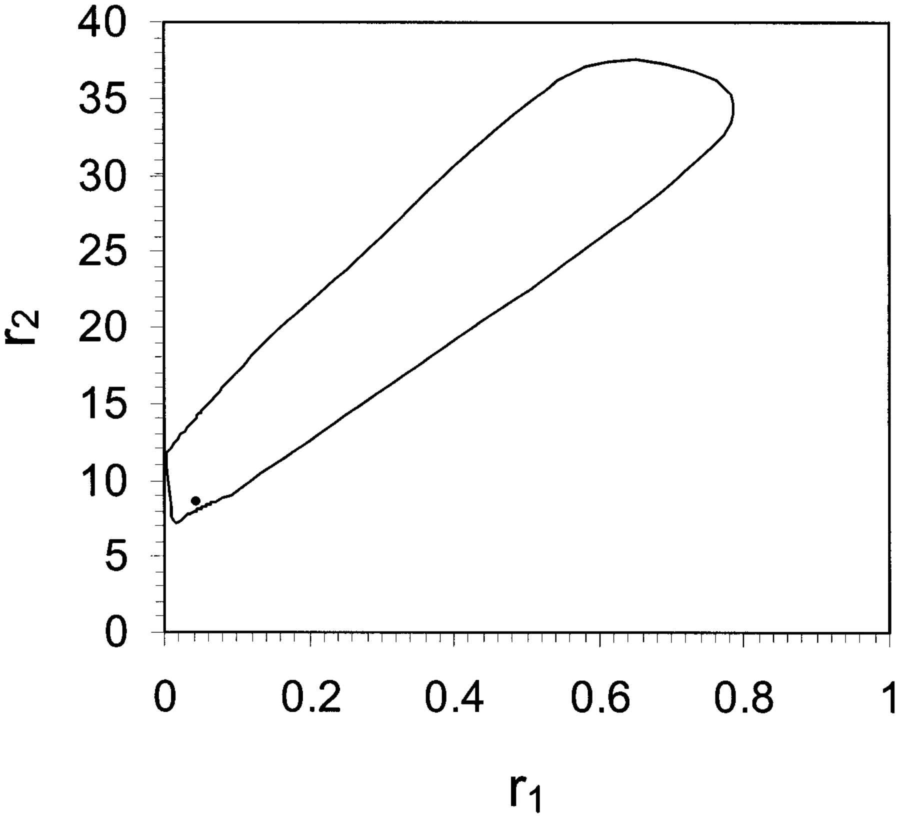

Figure 2.5: *95% confidence region calculated using PROCOP® software for reactivity ratios between VTES (r_1) and BA (r_2) determined by GC method. $r_1 = 0.044$; $r_2 = 8.56$.*

The limiting conversion effect in miniemulsion copolymerization of VTES and BA *in the investigated time frame* (Figure 2.3) arises from the difference in the reactivity ratios. *N*-butyl acrylate 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 2.5.

Table 2.5: Weight Fractions of VTES as Compared to Weight Fractions of Unreacted Material Inferred from Figure 2.3

VTES in the feed	VTES in the copolymer*	Unreacted material**	Unreacted VTES †	Unreacted material ‡
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

* calculated with PROCOP® according to the determined reactivity ratios ($r_1 = 0.044$; $r_2 = 8.56$)
** at the end of the investigated time frame (Figure 2.3)
† column 1 – column 2
‡ other than VTES (column 3 – column 4)

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 be incorporated according to the determined reactivity ratios. The third value, corresponding to the highest VTES feed fraction, can reasonably be assigned to unreacted acrylate monomer trapped within the crosslinked 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 2.6 [23]. 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 crosslinking. The presence of the vinyl, OH, and Si-O peaks represents evidence in favor of the second mechanism for the incorporation of the alkoxysilane (Chapter 5).

Reactivity ratios were also determined for the VMDMS/BA pair, both by the GC analysis of unreacted monomer, and by the determination of copolymer composition using FT-IR, as previously described. In the case of GC analysis, for VMDMS (monomer 1) and BA (monomer 2), $r_1 = 0.030$, $r_2 = 7.16$ (data in Table 2.6). These reactivity ratios were also confirmed by an FT-IR analysis of poly(VMDMS-co-BA) synthesized by bulk copolymerization. The plot of absorbance versus wavenumber (Figure 2.7) shows the appearance of two characteristic peaks (Si-CH_3 at 825 cm^{-1} and Si-O-C at 1110 cm^{-1}). Calculations yield a reactivity ratio two orders of magnitude smaller for VMDMS compared to that of BA ($r_1 = 0.035$, $r_2 = 3.11$).

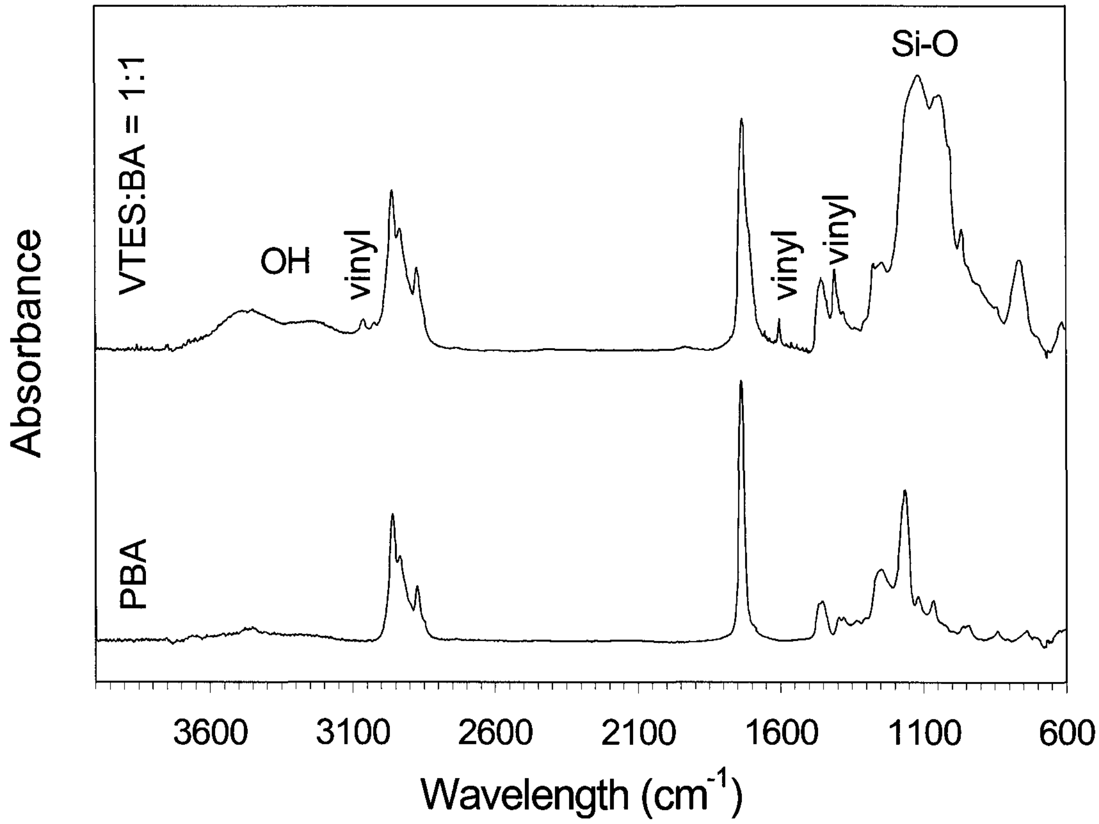

Figure 2.6: *FT-IR spectrum of a VTES/BA copolymer film for a 1:1 mole feed ratio as compared to the spectrum of PBA. The presence of Si-O and OH peaks is an evidence of silane incorporation. The presence of vinyl peaks indicates that the incorporation is not exclusively achieved by vinyl copolymerization, but also by silane hydrolysis and subsequent crosslinking. Both samples were synthesized by miniemulsion polymerization.*

Table 2.6: Feed and Copolymer Compositions for Solution Copolymerization of VMDMS (Monomer 1) and BA (Monomer 2) via GC Analysis

Conversion	Feed Composition		Copolymer Composition			
			Experimental		Calculated	
	M_1	M_2	m_1	m_2	m_1	m_2
0.302	0.3831	0.6169	0.095	0.905	0.092	0.908
0.359	0.3831	0.6169	0.084	0.916	0.097	0.903
0.413	0.3831	0.6169	0.084	0.916	0.102	0.898
0.458	0.3831	0.6169	0.092	0.908	0.107	0.893
0.492	0.3831	0.6169	0.098	0.902	0.111	0.889
0.518	0.3831	0.6169	0.103	0.897	0.115	0.885
0.611	0.3831	0.6169	0.1	0.9	0.131	0.868
0.196	0.4789	0.5211	0.085	0.915	0.12	0.880
0.261	0.4789	0.5211	0.079	0.921	0.126	0.874
0.307	0.4789	0.5211	0.101	0.899	0.132	0.868
0.337	0.4789	0.5211	0.099	0.901	0.135	0.864
0.373	0.4789	0.5211	0.113	0.887	0.141	0.859
0.396	0.4789	0.5211	0.121	0.879	0.144	0.855
0.418	0.4789	0.5211	0.132	0.868	0.148	0.852
0.191	0.6033	0.3967	0.169	0.831	0.18	0.820
0.199	0.6033	0.3967	0.165	0.835	0.181	0.819
0.228	0.6033	0.3967	0.173	0.827	0.186	0.814
0.239	0.6033	0.3967	0.169	0.831	0.188	0.812
0.093	0.7052	0.2948	0.229	0.771	0.228	0.772
0.117	0.7052	0.2948	0.232	0.768	0.233	0.767
0.136	0.7052	0.2948	0.244	0.756	0.237	0.763
0.160	0.7052	0.2948	0.241	0.759	0.242	0.757
0.186	0.7052	0.2948	0.278	0.722	0.249	0.751
0.194	0.7052	0.2948	0.279	0.721	0.251	0.749
0.026	0.7998	0.2002	0.322	0.678	0.293	0.707
0.041	0.7998	0.2002	0.295	0.705	0.297	0.703
0.091	0.7998	0.2002	0.363	0.637	0.311	0.689
0.104	0.7998	0.2002	0.365	0.634	0.315	0.685
0.108	0.7998	0.2002	0.361	0.639	0.316	0.684

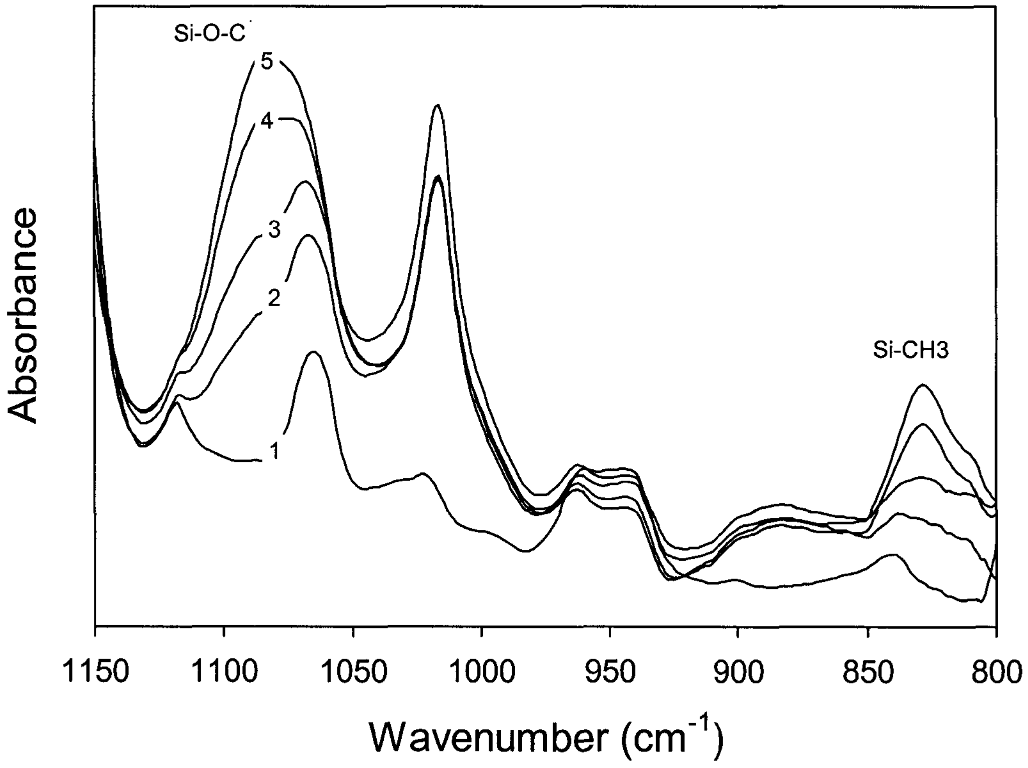

Figure 2.7: *FT-IR spectra of poly(VMDMS-co-BA). 1: poly(n-butyl acrylate), 2: 40 mole % VMDMS, 3: 50 mole % VMDMS, 4: 60 mole % VMDMS, and 5: 70 mole % VMDMS.*

2.4 CONCLUSIONS

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

The reactivity ratio of vinyltriethoxysilane is two 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.

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CHAPTER 3

REACTION KINETICS IN VINYLALKOXYSILANE/ACRYLATE MINIEMULSION SYSTEMS

3.1 INTRODUCTION

A study of the reaction kinetics is required in order to understand the mechanism(s) of vinylalkoxysilane incorporation using the miniemulsion approach. The alkoxysilane/acrylate miniemulsion systems represent the complexity of several reactions occurring in parallel [1]. Vinyl polymerization occurs mainly as an acrylate homopolymerization, the determined reactivity ratios being unfavorable to the actual vinylalkoxysilane/acrylate copolymerization (Chapter 2). The hydrolysis of the alkoxy group in the silane moieties is also taking place in the miniemulsion systems, and it has to be investigated in order to identify methods of minimizing it, since it leads to premature condensation (condensation of the hydroxyl groups in the latex phase, rather than in the film-forming stage). The techniques used to monitor the vinylalkoxysilane hydrolysis are gas chromatography (with the advantage that the evolution of the alcohol in the system can be easily followed) and reaction calorimetry. Calorimetry can be used to study the cumulative effect of the two reactions (vinyl polymerization and alkoxysilane hydrolysis) and to investigate only the caloric effect of hydrolysis by inhibiting the polymerization.

3.2 EXPERIMENTAL

3.2.1. Materials

n-Butyl acrylate (BA) (Aldrich) and 2-ethylhexyl acrylate (EHA) (Fluka), both inhibited with hydroquinone monomethyl ether (15 ppm), were purified by contacting them with an excess amount of a specific inhibitor remover for hydroquinone and hydroquinone monomethyl ether (Chromosorb 101, mesh size 100-120 from Aldrich) for at least 48 hours. Sodium lauryl sulfate (SLS), ammonim persulfate (APS), sodium bicarbonate (Fisher Scientific), hexadecane (HD) (Aldrich), and 2,2'-azobis(2-methylbutyronitrile) (AMBN) (VAZO 67, DuPont) were used as received. Vinyltriethoxysilane (VTES) (C. K. Witco, OSi Specialties). Deionized water was boiled and cooled under nitrogen.

3.2.2 Methods

For GC kinetic studies, miniemulsion copolymerizations were carried out in a 250 mL four-neck stirred flask (half-moon teflon blade, 180 rpm) at 20 % solids, 60 °C for 3 hours. The mixture was sonified for 2 minutes with a Branson 450 sonifier (power 7, 60 % duty cycle) in a 250 mL cylindrical beaker, prior to reaction [2] (Table 3.1).

Table 3.1: Miniemulsion Polymerization Recipes for Reaction Monitoring by GC

Ingredients		Amount
Deionized water		80 wt. % (120 g)
Sodium lauryl sulfate (SLS)		10 mM on aqueous phase (0.346 g)
VTES/BA (20 wt. %)	1/4*	7.61 g VTES/20.51 g BA
	1/1*	19.03 g VTES/12.82 g BA
Hexadecane		3.7 wt % on monomers (1.11 g)
Initiator (APS or AMBN)		1 mole % on monomers (0.456 g APS, 0.3884 g AMBN respectively)
Buffer ($NaHCO_3$)**		1 mole % on monomers

*molar ratios

**used for the standard APS-initiated miniemulsion polymerization

Particle diameters were estimated with a Nicomp C370 dynamic light scattering instrument. For gas chromatography, 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.

Calorimetric kinetic studies were carried out in a 1 L MP10 Mettler RC1 reaction calorimeter at 60 °C. The volume of the reaction mixture was 700 mL. The mixture was sonified for 5 minutes with a Branson 450 sonifier (power 10, 60 % duty cycle) in a 1000 mL cylindrical beaker, prior to reaction. Separate experiments were carried out to evaluate the heat of VTES hydrolysis and the influence of the oil phase on the rate of hydrolysis in miniemulsion systems. The conditions for the calorimetric studies are given in Tables 3.2, 3.3 and 3.4.

Table 3.2: Miniemulsion Polymerization Recipes for Reaction Monitoring by Calorimetry

Ingredient		**Amount**
Deionized water		80 wt. % (570 g)
Sodium lauryl sulfate (SLS)		10 mM on aqueous phase
VTES/Acrylate (20 wt. %)	1/9*	19.03 g VTES/115.38 g BA
		13.71 g VTES/119.43 g EHA
	2/8*	38.06 g VTES/102.56 g BA
		27.4 g VTES/106.16 g EHA
	3/7*	57.09 g VTES/89.74 g BA
		40.8 g VTES/92.15 g EHA
Hexadecane		3.7 wt % on monomers
Initiator (AMBN)		1 mole % on monomers

*molar ratios

Table 3.3: Reaction Conditions for the Evaluation of the Heat of VTES Hydrolysis in Water by Calorimetry

Reaction Conditions	
Volume	700 mL (Mettler RC-1)
Temperature	60 °C
pH	3.5 (HCl)
VTES	2 % by volume (14 mL)
Hydroquinone	10 ppm on monomer (1.27×10^{-4} g, predissolved in DI water)
Stirring speed	400 rpm (Rushton turbine)

Table 3.4: Reaction Conditions for Evaluation of VTES Hydrolysis in Miniemulsions in the Presence of Acrylic Monomers and Hexadecane by Calorimetry

Reaction Conditions		
Emulsification		Branson 450 sonifier (5 min., power 10, duty cycle 60 %) in a 1000 mL cylindrical beaker
Volume		700 mL (Mettler RC-1)
Temperature		60 °C
pH		5.5
Oil phase	Acrylate/HD	111 g acrylate/5 g HD
	HD	116 g
VTES concentration		20 wt. % on oil phase (29 g)
Hydroquinone concentration		10 ppm on oil phase
Stirring speed		150 rpm (anchor impeller)

3.3 RESULTS AND DISCUSSION

3.3.1 Reaction Monitoring by Gas Chromatography

The gas chromatography technique allows for monitoring of the volatile species in the reaction mixture (i.e., monomers and the alcohol resulting from the alkoxysilane hydrolysis in the aqueous environment). This technique makes possible the estimation of monomer consumption, and at the same time, the evaluation of the rate of the hydrolysis of VTES.

Three initiator systems were used for the investigation of the miniemulsion copolymerizations of VTES and BA: a water-soluble persulfate (APS) in a buffered medium (sodium bicarbonate, pH 6.5), APS in unbuffered medium (pH 1.5) and an oil-soluble azo initiator (AMBN) with a low water solubility (0.74 wt % at 70 °C) [3] in an unbuffered medium (pH 5.5).

First, APS was used as initiator for the miniemulsion copolymerization of a 1:1 mole ratio of VTES and BA. The results of GC monitoring of the volatile species during the reactions are presented in Figure 3.1. In a buffered environment (sodium bicarbonate, pH 6.5), most of the VTES was found to remain unreacted. The evolution of ethanol in the system is an indication that hydrolysis of the ethoxy groups occurs slowly and is responsible for the slight decrease in the concentration of VTES. Vinyl copolymerization is expected to play a minor role in reactions involving silanes due to their unfavorable reactivity ratios, i.e., $r_{VTES}= 0.044$, $r_{BA}= 8.56$ [4]. The use of APS initiator at pH 6.5 does not provide for satisfactory silane incorporation. When the same synthesis is carried out in an unbuffered system, at pH 1.5, the highly acidic environment triggers fast silane hydrolysis, evidence for this reaction being the high amount of ethanol present in the system and the absence of VTES at the beginning of the process. In unbuffered APS-initiated systems (pH 1.5) the VTES concentration at the end of the reaction was zero, the silane appearing to be completely incorporated into the latexes for both 50 mole % VTES and 20 mole % VTES in the monomer mixture (Figure 3.2). When oil-soluble AMBN was used as initiator in unbuffered systems for the same silane contents in the monomer mixtures (50 mole % and 20 mole % respectively), at pH 5.5 (Figure 3.3), the silane hydrolysis was found to occur at a moderate rate, with the corresponding formation of ethanol, the final concentration of the volatile VTES also being zero. The use of the oil-soluble initiator for the incorporation of VTES by the miniemulsion approach provides for a more controllable rate of hydrolysis, at the same time assuring good silane incorporation (i.e., no unreacted VTES at the end of the reaction).

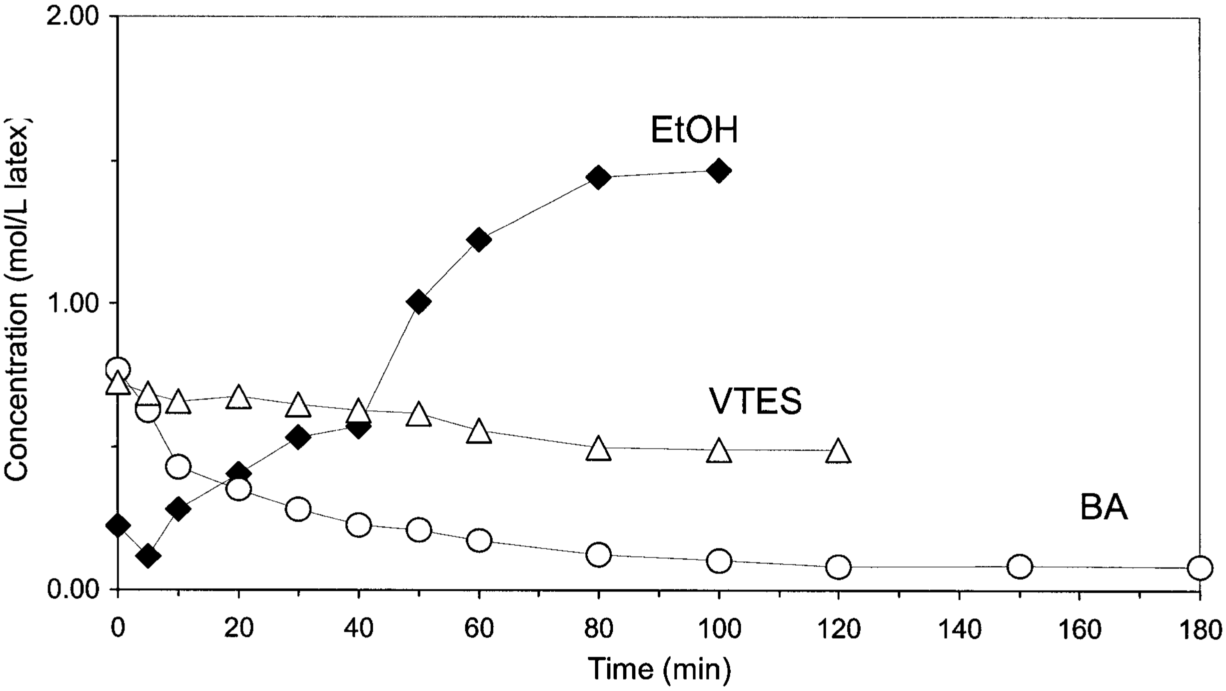

Figure 3.1: *Concentration of volatile species in the VTES/BA (1:1 mole:mole) latex during synthesis by miniemulsion polymerization using APS as initiator in a buffered system (pH 6.5).*

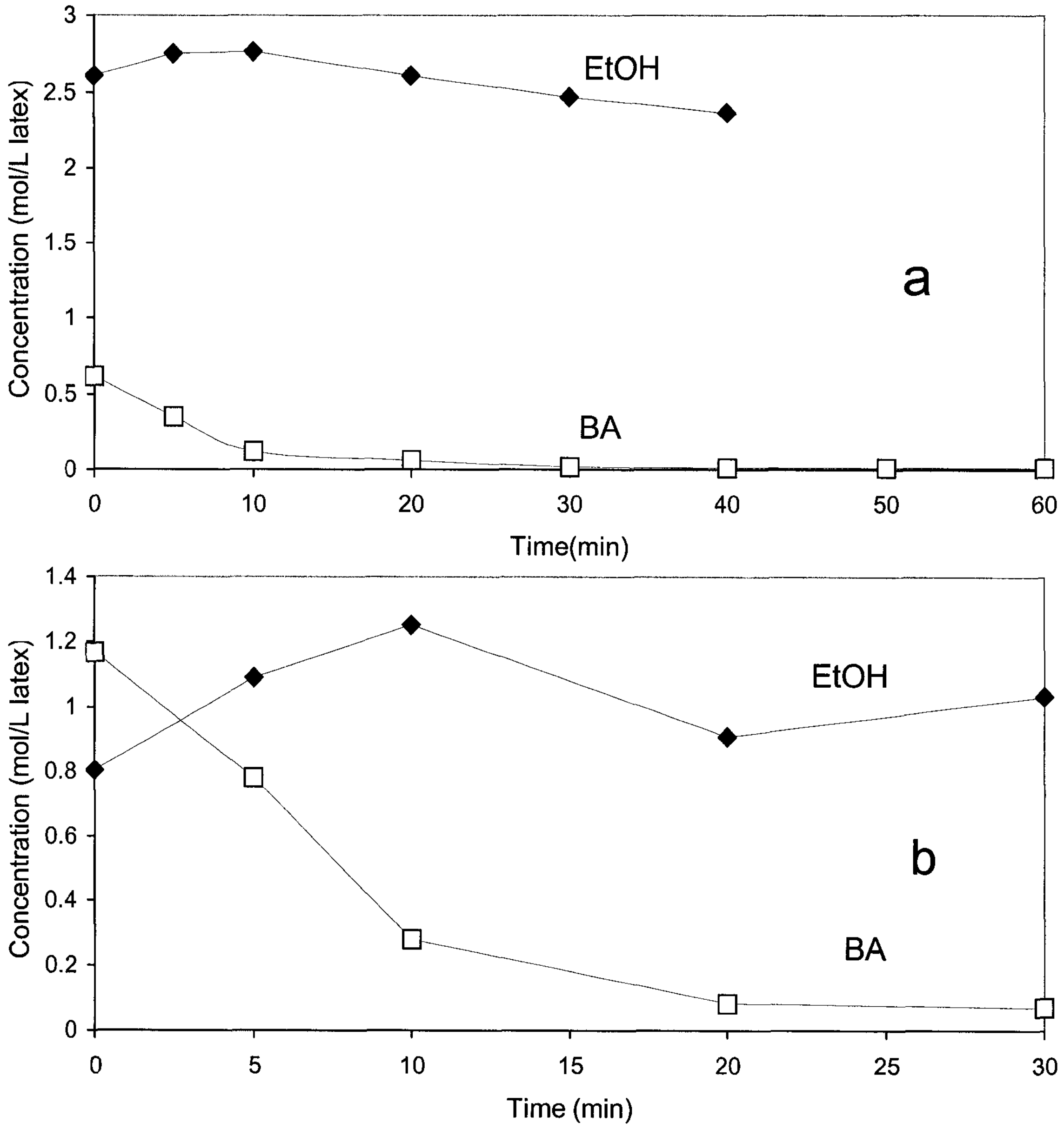

Figure 3.2: *Concentration of volatile species in the VTES/BA latex during synthesis by miniemulsion polymerization using APS as initiator in an unbuffered system (pH 1.5): (a) 50 mol % VTES; (b) 20 mol % VTES.*

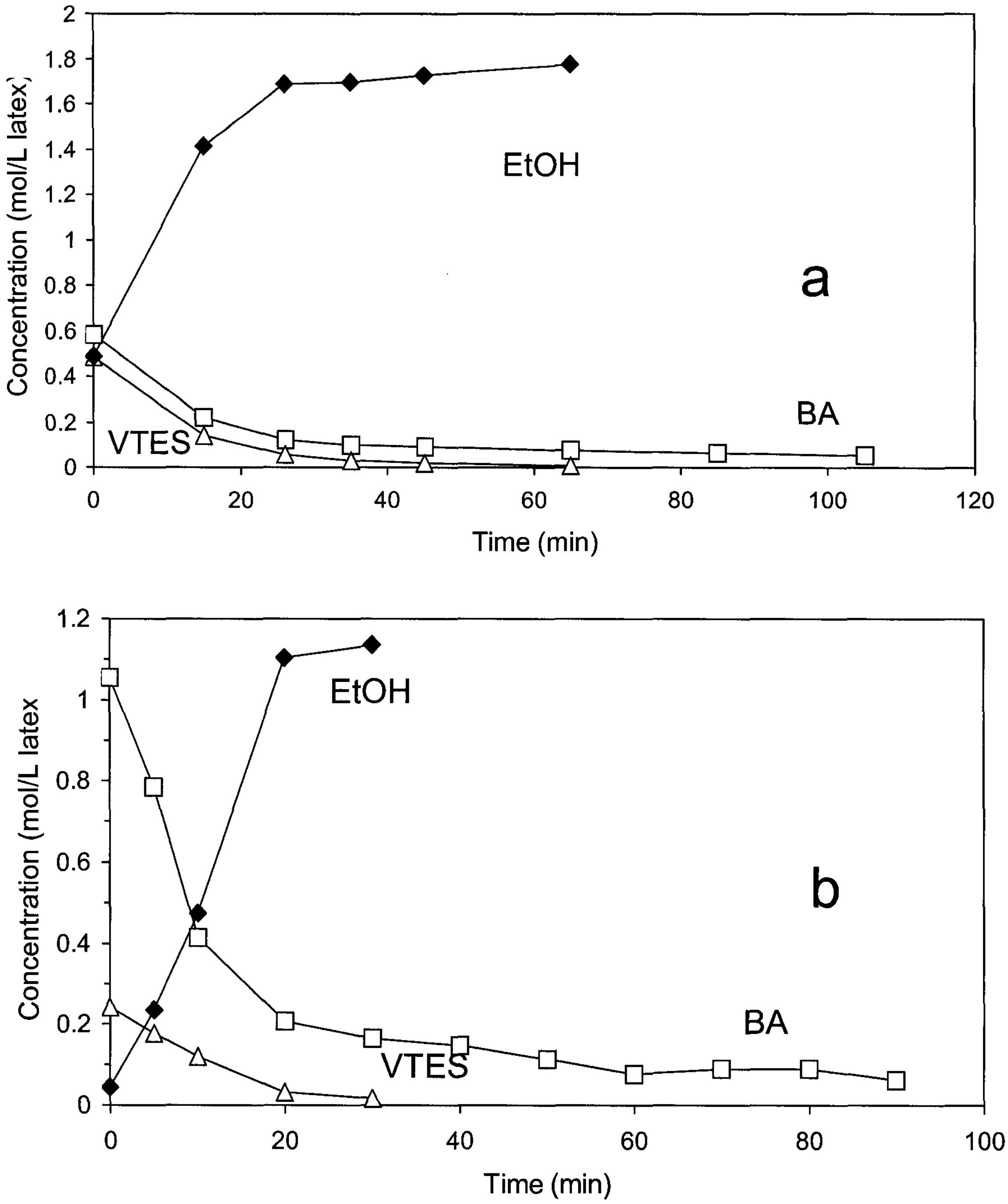

Figure 3.3: *Concentration of volatile species in the VTES/BA latex during synthesis by miniemulsion polymerization using AMBN as initiator in an unbuffered system (pH 5.5): (a) 50 mol % VTES; (b) 20 mol % VTES.*

3.3.2 Reaction Monitoring by Calorimetry

The VTES/acrylate miniemulsion is a complex reaction system in which at least two reactions occur simultaneously. On one side there is the polymerization of the vinyl group, with the formation of carbon chains, and on the other side there is the hydrolysis of the alkoxy groups from VTES. Calorimetry is not able to differentiate between the caloric effects of different concomitant reactions, but it offers the advantage of the on-line monitoring. Moreover, one can eliminate the influence of the vinyl polymerization by using an inhibitor and observe the caloric effect of the hydrolysis alone.

The heat of reaction for VTES hydrolysis in an aqueous environment was determined by reaction calorimetry. The experimental conditions were chosen to favor only the hydrolysis reaction and not the condensation reaction or vinyl polymerization (Table 3.3). The hydrolysis of VTES absorbs 88.106 kJ/mole of heat (Figure 3.4). In order to achieve a more complete insight into the hydrolysis of the alkoxysilane in the miniemulsion systems, one must study this reaction in this type of system. An experiment was designed in which the possibility of vinyl polymerization was eliminated by the addition of an inhibitor (Table 3.4). Besides *n*-butyl acrylate, more hydrophobic materials, 2-ethylhexyl acrylate and hexadecane respectively (Table 3.5) were employed to investigate the influence of the hydrophobicity of the oil phase on silane hydrolysis in miniemulsion systems. The heat profiles are shown in Figure 3.5.

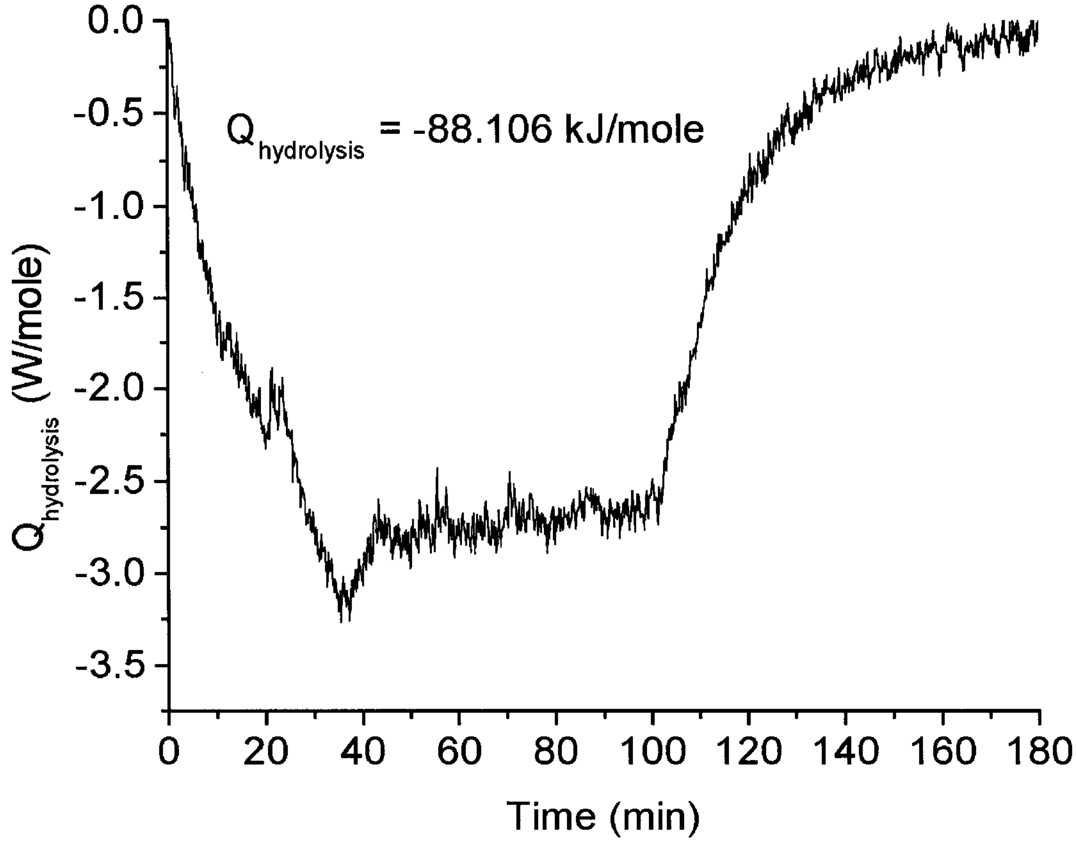

Figure 3.4: *Heat profile for the VTES hydrolysis reaction in an aqueous environment as determined by reaction calorimetry. The experimental conditions were chosen to favor only the hydrolysis reaction and not the condensation reaction or vinyl polymerization.*

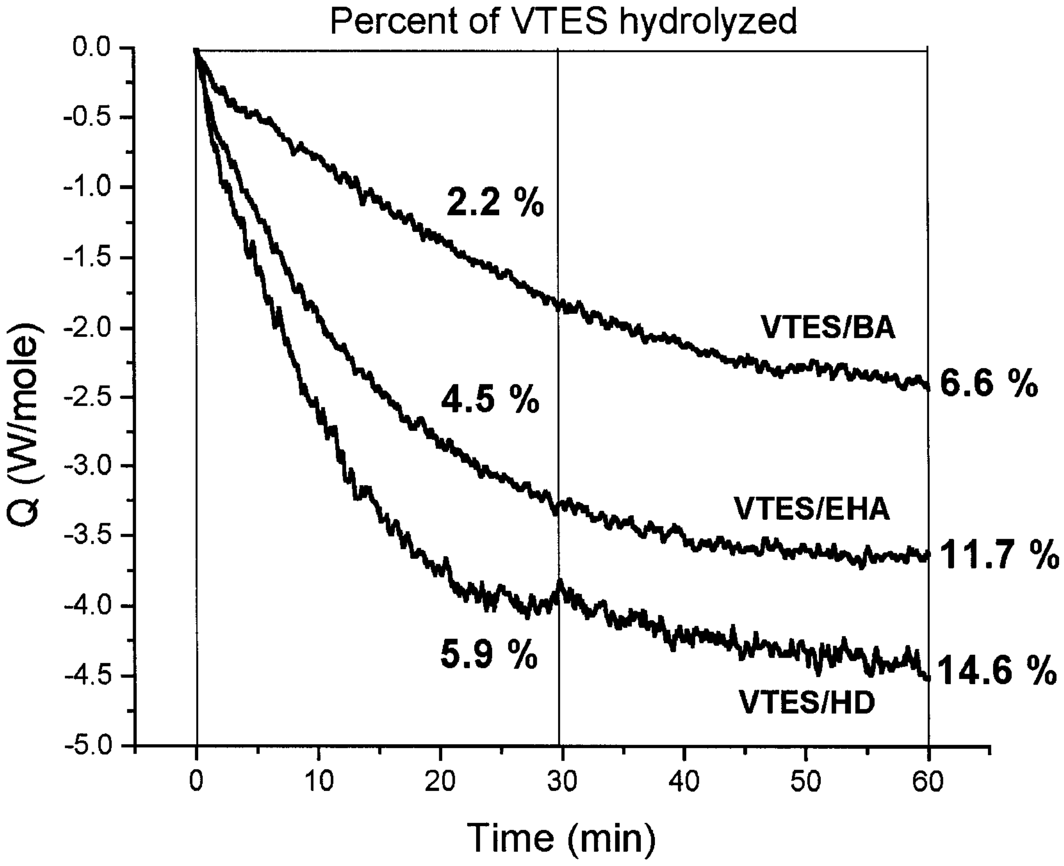

Figure 3.5: *Rate of alkoxysilane hydrolysis increases with the hydrophobicity of the oil phase. The best protection of the silane from the aqueous phase is achieved by using the least hydrophobic monomer (n-butyl acrylate).*

Table 3.5: Water Solubility (at 25 °C) of the Oil Phases used in the Study of VTES Hydrolysis in Miniemulsion Systems (BASF Technical Bulletin, 1982)

Oil phase	BA	EHA	HD
Solubility of water in oil phase (wt %)	0.7	0.15	-
Solubility of oil phase in water (wt %)	0.2	0.01	2.3×10^{-7}

As the hydrophobicity of the oil phase increased, the rate of hydrolysis was found to increase (Figure 3.5). This phenomenon can be explained by considering that phase separation occurs between the acrylate and the hydrolyzing alkoxysilane. The more hydrophobic oil phase "rejects" the silane to the droplet surface, allowing it to contact the surrounding water and undergo hydrolysis. The best protection of the silane from the aqueous phase was achieved by using BA. The effectiveness of the acrylate miniemulsion systems in preventing silane hydrolysis is expressed as the mole percentage of the total VTES hydrolyzed (Figure 3.5). Computations were performed taking into account the amount of heat absorbed by VTES hydrolysis (88.106 kJ/mole, as shown in Figure 3.4). These results represent evidence that *phase separation* occurs between the silane and the acrylate, and that silane hydrolysis occurs predominantly at the oil/water interface. To confirm that phase separation indeed did take place under the reaction conditions, a separate miscibility experiment was carried out, in which 7 g of BA, inhibited with 0.01 g hydroquinone, were mixed with 2 g of VTES and kept at 60 °C for an hour. No phase separation was observed (Figure 3.6 a). A second sample was identically treated, but 0.15 g water were added to the mixture (at 60 °C, under agitation) Phase separation occurred

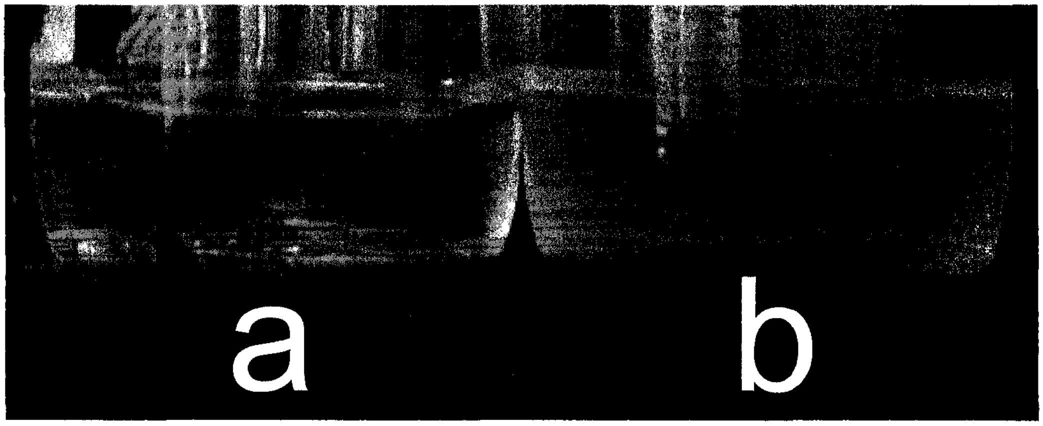

Figure 3.6: *VTES/BA miscibility experiment: (a) 7 g BA, 2 g VTES at 60 °C, (b) 7 g BA, 2 g VTES, 0.15 g water at 60 °C. VTES hydrolysis and subsequent crosslinking yields a solid precipitate immiscible with BA.*

immediately due to the rapid hydrolysis/condensation of the silane moiety and formation of a precipitate (Figure 3.6 b).

The evolution of the caloric effects for the miniemulsion copolymerizations of VTES/BA and VTES/EHA are shown in Figure 3.7 a, and 3.7 b, respectively. The decrease in the observed heat of reaction is expected as the VTES feed content increases, due to the decrease in the relative amount of acrylate, the major contributor to the vinyl polymerization [4] and to the endothermic effect of the alkoxysilane hydrolysis [2]. For the VTES/BA miniemulsion systems in the case of 30 mole % VTES (Figure 3.7 a, curve 4), the initial steep slope in the heat profile corresponds to an acrylate homopolymerization stage, unhindered by the silane moieties, which subsequently undergo hydrolysis. This behavior at higher alkoxysilane feed contents is most probably related to the phase separation occurring between the hydrolyzing silane moieties and the acrylate. The heats of reaction were calculated taking as reference the BA homopolymerization (Table 3.6).

Table 3.6: Heats of Reaction (Mettler RC-1) for VTES/BA Miniemulsion Systems

System	Q_r (kJ)	Moles BA	Moles VTES	Q from BA (kJ)	Q from silane (kJ/mol)	Particle size D_V (nm)
PBA	77.638	1	0	77.638	0	80
10 mole % VTES	69.644	0.9	0.1	69.874	-2.3	117
20 mole % VTES	60.558	0.8	0.2	62.11	-7.76	128
30 mole % VTES	48.078	0.7	0.3	54.347	-20.897	117

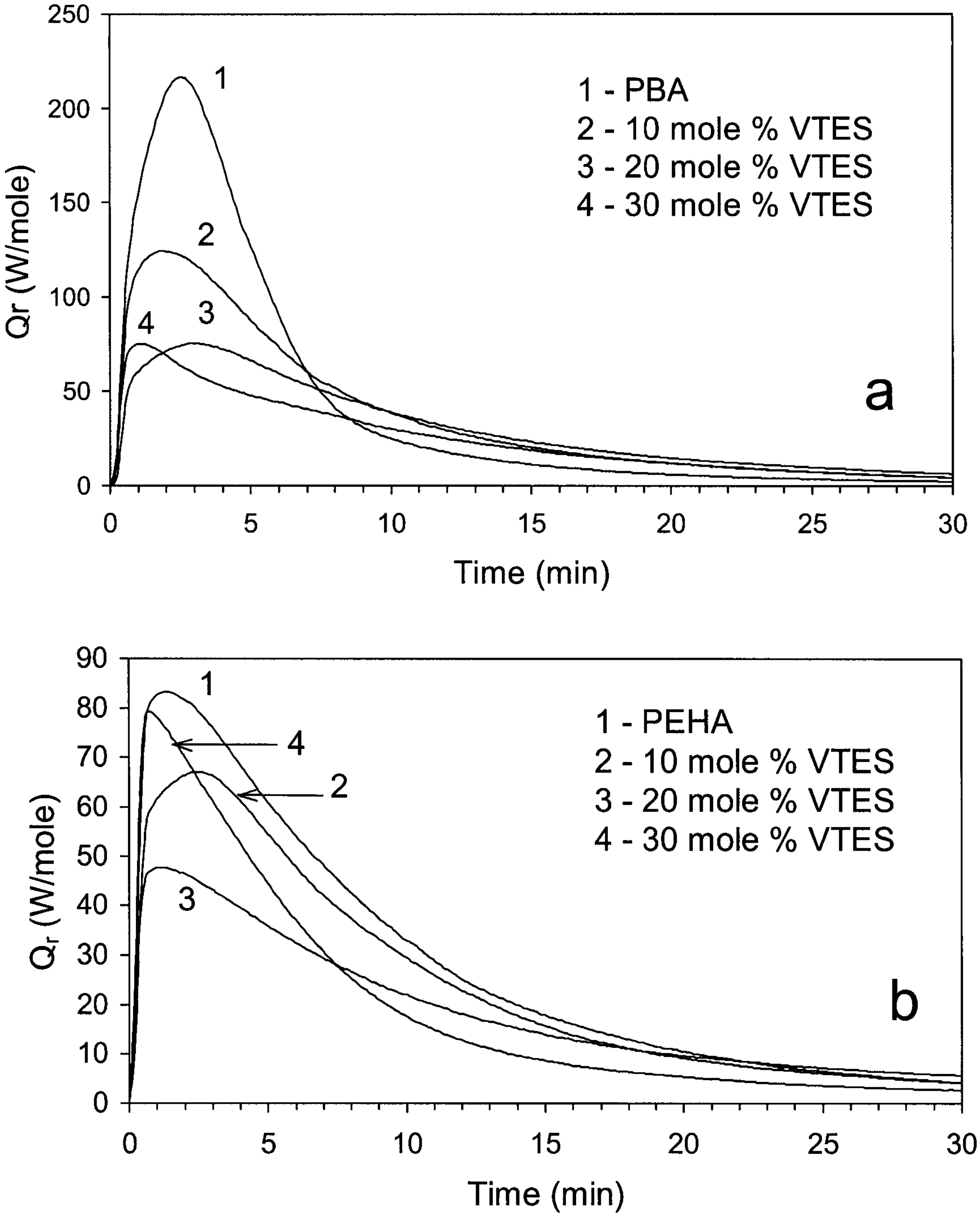

Figure 3.7: *Heat profile of the VTES/acrylate miniemulsion reaction: (a) VTES/BA, and (b) VTES/EHA.*

The *per mole* silane contribution to the heat of reaction shows a significant increase (endotherm) as the feed silane content is increased (Table 3.6). This translates to an increased rate of hydrolysis, which can occur due to greater water exposure of the silane moieties as a consequence of phase separation and migration of the silane towards the particle surface. The VTES/EHA systems behave in a similar manner (Figure 3.7 b), at 30 mole % alkoxysilane, the initial relative increase in the detected caloric effect being more obvious than for the VTES/BA system (Figure 3.7 b, curve 4). This behavior is due to the higher hydrophobicity of EHA and represents a confirmation of the phase separation trend identified for the VTES hydrolysis in miniemulsion systems (more significant for the more hydrophobic oil phase, as shown in Figure 3.5). The heats of reaction for the VTES/EHA miniemulsion copolymerization were calculated taking as reference the EHA homopolymerization (Table 3.7).

Table 3.7: Heats of Reaction (Mettler RC-1) for VTES/EHA Miniemulsion Systems

System	**Q_r (kJ)**	**Moles EHA**	**Moles VTES**	**Q from EHA (kJ)**	**Q from silane (kJ/mol)**	**Particle size D_V (nm)**
PEHA	52.663	0.72	0	52.663	0	168
10 mole % VTES	46.902	0.648	0.072	47.397	-6.875	174
20 mole % VTES	39.591	0.576	0.144	42.13	-17.632	211
30 mole % VTES	36.793	0.5	0.214	36.572	1.033	138

The *per mole* silane contribution to the heat of reaction shows a significant increase (endotherm) as the feed silane content is higher (Table 3.7). This translates to an increased rate of hydrolysis, which can occur due to a greater water exposure of the silane moieties as a consequence of phase separation and migration of the silane towards the oil/water interface. An exception to this trend is observed in the VTES/EHA miniemulsion systems for 30 mole % VTES, case in which the calculated alkoxysilane contribution to the total caloric effect is positive (Table 3.7). In this case, due to the more advanced degree of phase separation, the hydrolyzed silane moieties are likely to form better defined, relatively larger silane domains that allow for the occurrence of the OH-OH condensation reaction (exotherm), the condensation caloric effect having a decisive influence on the silane contribution to the total heat of reaction. This hypothesis is verified and confirmed by subsequent studies on the latex particle morphology (Chapter 4).

3.4 CONCLUSIONS

The incorporation of VTES into latex systems by the miniemulsion approach is feasible by a batch polymerization process yielding stable copolymer latexes with high levels of alkoxysilane incorporation. The oil-soluble AMBN with no added buffer (pH 5.5) was found to be the most suitable initiation system for the study of silane incorporation into acrylate latexes, giving good silane incorporation, and a moderate rate of alkoxysilane hydrolysis. Incorporation of silane groups into acrylate latexes is achieved by at least two mechanisms: vinyl copolymerization (to a low extent due to the unfavorable reactivity ratios), and Si-O-Si bond formation following alkoxy group hydrolysis, the mechanism that is primarily responsible for the silane incorporation in miniemulsion systems. The use of APS in buffered systems (pH 6.5) does not favor this mechanism, hence the poor VTES incorporation into the latex for these systems (most of the VTES remains unreacted).

Alkoxysilane hydrolysis in miniemulsion systems depends on the acrylate hydrophobicity; hydrolysis occurs mainly at the oil/water interface, due to the phase separation between the oil phase (acrylate monomer) and the hydrolyzing silane moieties, so that the best protection from hydrolysis (the lowest hydrolysis rate) was achieved in the VTES/BA miniemulsion reaction system, *n*-butyl acrylate being the least hydrophobic among the investigated oil phases. The more hydrophobic oil phase will "reject" the silane moieties towards the oil/water interface, determining an increase in the observed rate of hydrolysis.

3.5 REFERENCES

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3. Blythe, P. J., Klein, A., Phillips, J. A., Sudol, E. D., El-Aasser, M. S. (1999) *J. Polym. Sci., Part A: Polym. Chem.* 37 (23), 4449
4. Marcu, I., Daniels, E.S., Dimonie, V.L.; Hagiopol, C., Roberts, J.E., El-Aasser, M.S. (2003) *Macromolecules* 36(2), 328

CHAPTER 4

CHARACTERIZATION OF VINYLALKOXYSILANE/ACRYLATE POLYMER LATEXES

4.1 INTRODUCTION

The incorporation of VTES into latex systems by the miniemulsion approach was found to yield stable copolymer latexes. Both the water-soluble APS and the oil-soluble AMBN in unbuffered systems were found to be suitable initiation systems for incorporating silane moieties into acrylate latexes. The influence of the initiation system (water-soluble vs. oil-soluble) on the latex particle morphology and latex properties will be investigated.

Alkoxysilane hydrolysis in miniemulsion systems depends on the acrylate hydrophobicity; the hydrolysis occurs mainly at the oil/water interface, due to the phase separation between the oil phase (acrylate monomer) and the hydrolyzing silane moieties. The influence of the acrylate monomer on the latex particle formation will be analyzed by comparing the properties of latexes synthesized with acrylate monomers with different affinities for the water phase (*n*-butyl acrylate and 2-ethylhexyl acrylate). The evolution of phase separation upon latex aging and the possible changes in morphology induced by aging for 12 months at room temperature will also be investigated.

4.2 EXPERIMENTAL

4.2.1. Materials

Latexes prepared as described in Chapter 3 were used for the characterization work (Table 4.1). Toluene and deuterated chloroform (Aldrich) were used as received.

Table 4.1: Silane/acrylate Latexes Used for the Characterization Work

Latex Code	**Initiator**	**pH**	**VTES Mole %**	**Acrylate**	**Preparation Method**
P12	APS	1.5	20	BA	Recipes in Table 3.1
P15	APS	1.5	50	BA	
A12*	AMBN	1.5	20	BA	
A51	AMBN	5.5	10	BA	Recipes in Table 3.2
A52	AMBN	5.5	20	BA	
A53	AMBN	5.5	30	BA	
A55	AMBN	5.5	50	BA	Recipe in Table 3.1
A51E	AMBN	5.5	10	EHA	Recipes in Table 3.2
A52E	AMBN	5.5	20	EHA	
A53E	AMBN	5.5	30	EHA	

*HCl was added to drop the pH

4.2.2 Methods

Swelling

Swelling experiments for the evaluation of the swelling coefficient were carried out on polymer films dried at room temperature and atmospheric pressure for 24 hours, and then under vacuum for another 24 hours. The films were swollen in toluene for 7 days. Swelling of the copolymers for determination of the soluble contents was carried out on freeze-dried latexes. Dry samples were weighed, swollen in toluene for 1 week (half of solvent volume was replaced after 2 days, and half after 4 days), dried, and weighed again.

Differential Scanning Calorimetry and Dynamic Mechanical Analyses

Differential scanning calorimetry analyses were performed on a TA Instruments DSC 2920 scanning calorimeter (temperature range 20-350 °C, heating rate 10 °/min). Dynamic mechanical analyses (DMA) were performed on a Rheometrics RDA II instrument, under compression, between 8 mm diameter parallel plates. The temperature range was –100 to 50 °C, with a heating rate of 1 deg/min.

FT-IR

For FT-IR studies, latexes were diluted to 1% solids and thin films were cast on ZnSe plates. FT-IR spectra (64 scans per sample, 4000–600 cm^{-1} frequency sweep range) were obtained with a Mattson-Polaris Hi-Res Spectrometer at a resolution of 4 cm^{-1}.

NMR

Proton NMR spectra were obtained on samples dissolved in deuterated chloroform. The instrument used was a Bruker DX-500 operating at 500 MHz. For solid-state NMR studies, latexes were freeze-dried under vacuum, using liquid nitrogen as a cooling agent. Quantitative ^{13}C NMR spectra (spectra with relaxation delays of 16 s and 32 s were compared and found to be identical in terms of their relative peak areas) were taken on a 300 MHz General Electric GN-300 instrument operating at 75.4 MHz for ^{13}C, equipped with a magic angle spinning 7 mm probe (Doty Scientific). Samples were swollen to saturation in deuterated chloroform and spun at 1.667 kHz. 3000 scans were averaged for each spectrum. Proton-detected spin diffusion experiments were run on the same instrument. Dry samples were spun at 2.5 kHz at room temperature. The working frequency was 300.107 MHz and the 90° pulse lengths were 3.6 μs. The mobile component was selected by using a dipolar filter in which the delay time (t_d) was increased between 2 and 80 μs, and the mixing time (t_m) was varied between 2 μs and 1 s. The repetition time was 4 s; 8 scans were averaged for each measurement.

Microscopy

The SEM micrographs were taken on a JEOL 6300F field emission scanning electron microscope, at a field intensity of 1 kV. The transmission electron micrographs and electron diffraction micrographs were taken on a Philips model 400T electron microscope, at a field intensity of 140 kV.

4.3 RESULTS AND DISCUSSION

4.3.1 Influence of the Initiation System on the Vinyltriethoxysilane/*n*-Butyl Acrylate Latex Properties

Two initiator systems were used for the investigation of the miniemulsion copolymerizations of VTES and BA: a water-soluble persulfate (APS) and an oil-soluble azo initiator (AMBN) with a low water solubility (0.74 wt % at 70 °C) [1]. The results of GC monitoring of the evolution of volatile species during the reactions were presented in Chapter 3. First, APS was used as initiator for the miniemulsion copolymerization of a 1/1 mole ratio of VTES and BA. In a buffered environment (sodium bicarbonate, pH 6.5), most of the VTES was found to remain unreacted (Figure 3.1). The evolution of the ethanol in the system is an indication that hydrolysis of the ethoxy groups occurs slowly [2] and is responsible for the slight decrease in the concentration of VTES. Vinyl copolymerization is expected to play a minor role in reactions involving silanes due to their unfavorable reactivity ratios, i.e., r_{VTES}= 0.044, r_{BA}= 8.56 [3]. The use of APS initiator at pH 6.5 does not provide for satisfactory silane incorporation. As soon as the same synthesis is carried out in an unbuffered system, at pH 1.5, the highly acidic environment triggers fast silane hydrolysis, evidence for this reaction being the high amount of ethanol present in the system and the absence of the VTES peak at the beginning of the process. When oil-soluble AMBN was used as initiator in an unbuffered system, at pH 5.5 (latexes A52 and A55), the silane hydrolysis was found to occur at a moderate rate, with the corresponding formation of ethanol (Figure 3.3). In the unbuffered systems (P12, P15, A52 and A55) the VTES concentration at the end of the reaction was zero, the silane being completely incorporated into the latexes. The volume-average latex particle diameters measured by dynamic light scattering for both latex systems were found to be identical (110 nm).

Swelling coefficients (W_S) were determined [4] for films prepared from P12, P15, A52 and A55 latexes, using toluene as the swelling agent (Figure 4.1). $W_S = [(m_{swollen} - m_{dry}) / m_{dry}] / \rho_{solvent}$, where W_S is the swelling coefficient; $m_{swollen}$ is the weight of the swollen gel; m_{dry} is the weight of the dry gel; $\rho_{solvent}$ is the solvent density.

Latexes prepared with APS initiator at pH 1.5 (P12 and P15) were found to have significantly lower swelling coefficients than those initiated by AMBN at pH 5.5 (A52 and A55); in the former case the material being more rigid.

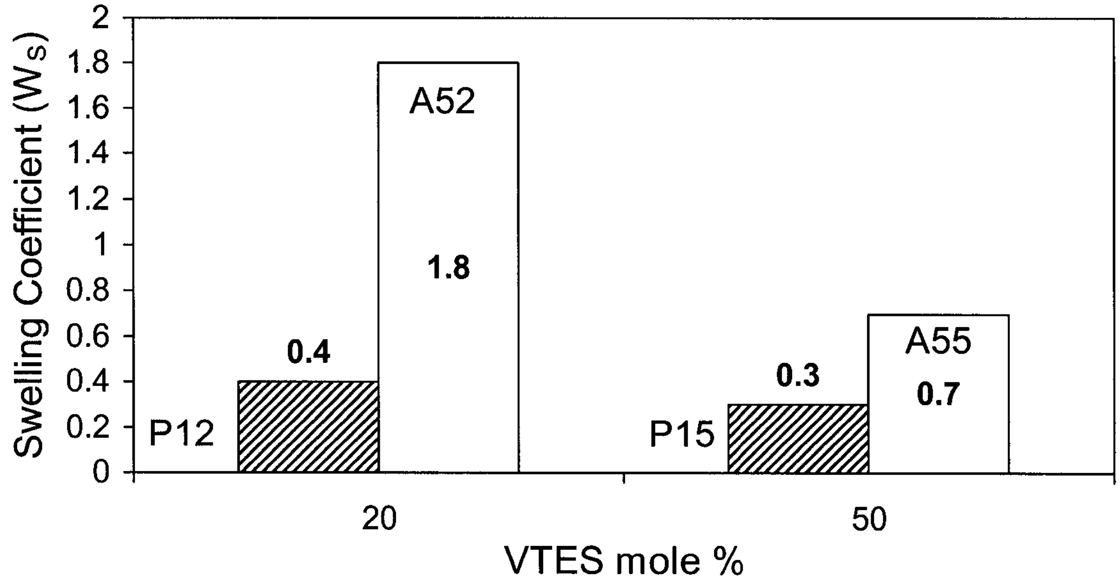

Figure 4.1: *Swelling coefficients (W_S) for films prepared from P12, P15, A52 and A55 latexes, using toluene as swelling agent.*

The relative amounts of residual OH groups in thin films cast from P12, P15, A52 and A55 latexes were determined by FT-IR spectroscopy (Table 4.2) and expressed as absorbance ratios between OH groups and C=O groups in dry latex films (Figure 4.2). The films cast from A52 and A55 latexes were found to contain more OH groups available for further crosslinking.

Table 4.2: Relative Amount of Hydroxyl Groups, Expressed as the Absorbance (A) Ratios Between Hydroxyl and Carbonyl FT-IR Peaks, for Dry Latex Films

Latex	**A(OH)/A(C=O)**
P12	0.26
P15	0.55
A52	0.31
A55	0.93

DSC analyses of the freeze-dried latexes (P12, P15, A52 and A55) were run (Figure 4.3), with the areas under the curves being assigned to the heat evolved upon OH-OH condensation. In the case of the soft (high swelling coefficient) latexes (A52 and A55), the amount of OH groups available for crosslinking in the freeze-dried materials was significantly higher compared to that found for rigid (low swelling coefficient) latexes (P12 and P15, respectively).

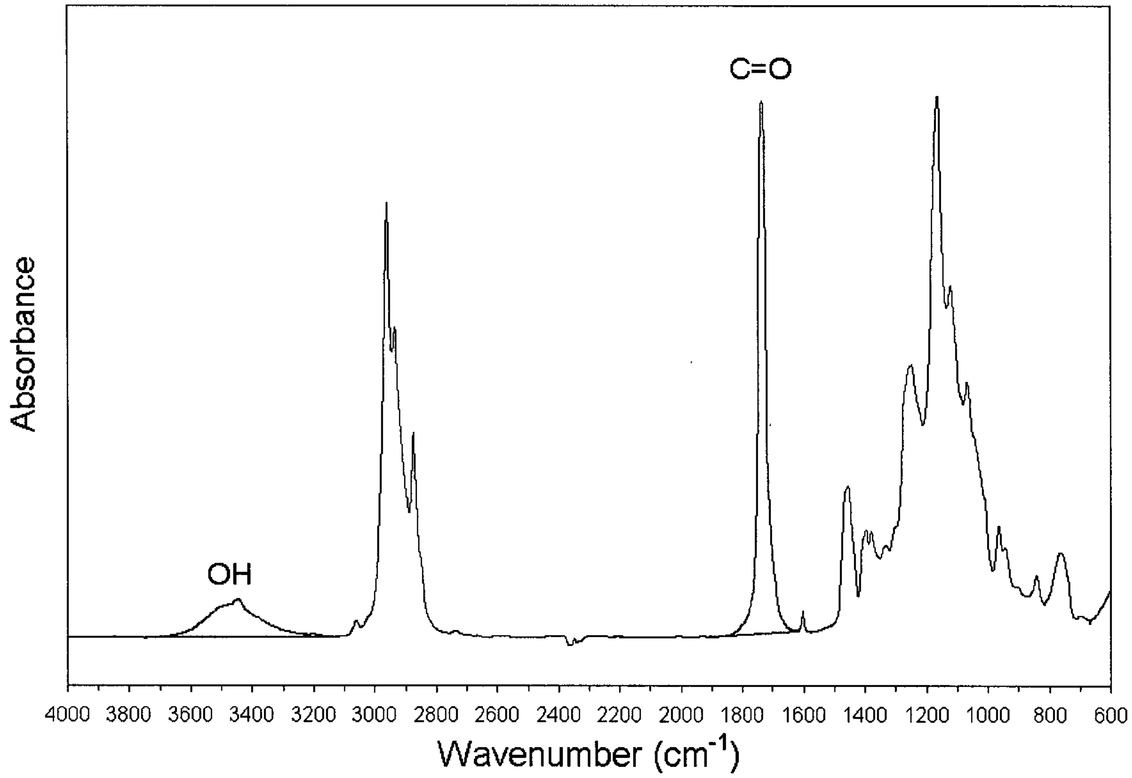

Figure 4.2: *FT-IR spectrum of VTES/BA dry latex film cast on a ZnSe plate. The relative amount of OH groups in the material is expressed as the ratio between the area of the OH peak (3470 cm^{-1}) and the area of the C=O peak (1735 cm^{-1}).*

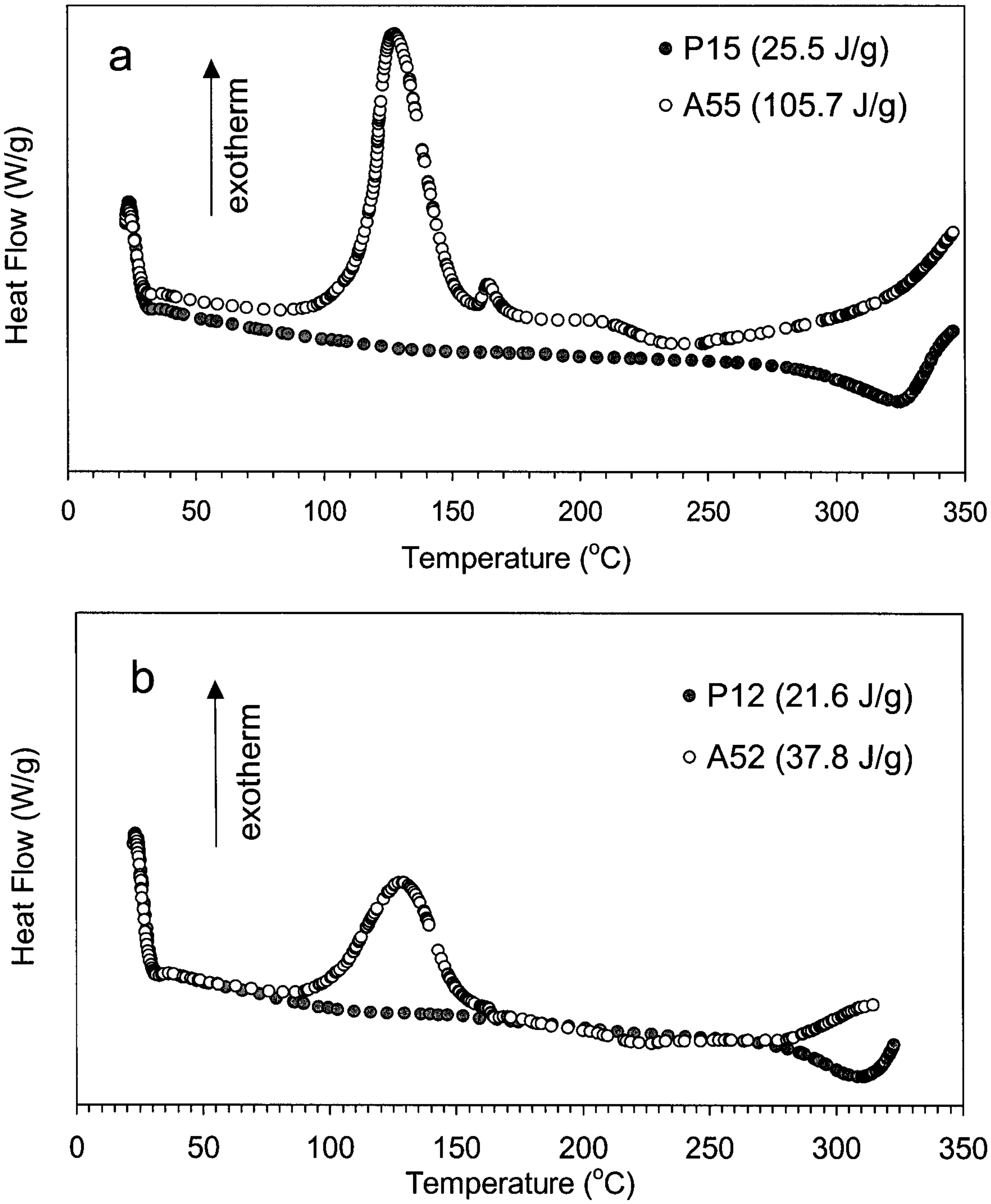

Figure 4.3: *Differential scanning calorimetry traces of VTES/BA freeze-dried latexes: (a) 50 mole % VTES, (b) 20 mole % VTES.*

The differences in the properties of the APS-initiated and AMBN-initiated polymer latexes are a result of the hydrolysis/condensation behavior of the silane moieties, since the amount of unreacted silane vinyl groups was found to be the same in both P15 and A55 latexes (85 % of the initial silane vinyl groups) as determined by quantitative ^{13}C NMR (Figure 4.4). By analyzing these spectra one also can observe the absence of the ethoxy carbon peaks (^{13}C NMR spectrum of neat VTES, Figure 4.5, peaks A' and B') from both P15 and A55 latexes. The explanation for this absence is given by the hydrolysis of the ethoxy groups, that occurred to a high extent in both copolymer latex systems.

The silane vinyl peaks are broad in the APS-initiated system (P15), and spinning side bands are displayed (Figure 4.4 a), while for the AMBN-initiated system (A55), the same peaks are narrower and no spinning side bands are observed (Figure 4.4 b). The copolymer prepared with the water-soluble initiator (APS) at pH 1.5 (P15) display less mobility of the unreacted silane vinyl groups, the sample being more rigid than the A55 latex (prepared with AMBN at pH 5.5). This observation confirms the evidence of different network mobilities (different swelling coefficients) found by swelling studies (Figure 4.1) for the two polymers and the different degree of OH-OH condensation expressed through the relative content of OH groups in the latex films identified by FT-IR (Table 4.2). The higher observed mobility of the AMBN-initiated system is in part due to the different initiation mechanism, allowing for a higher termination rate, hence the formation of shorter, more mobile polymer chains.

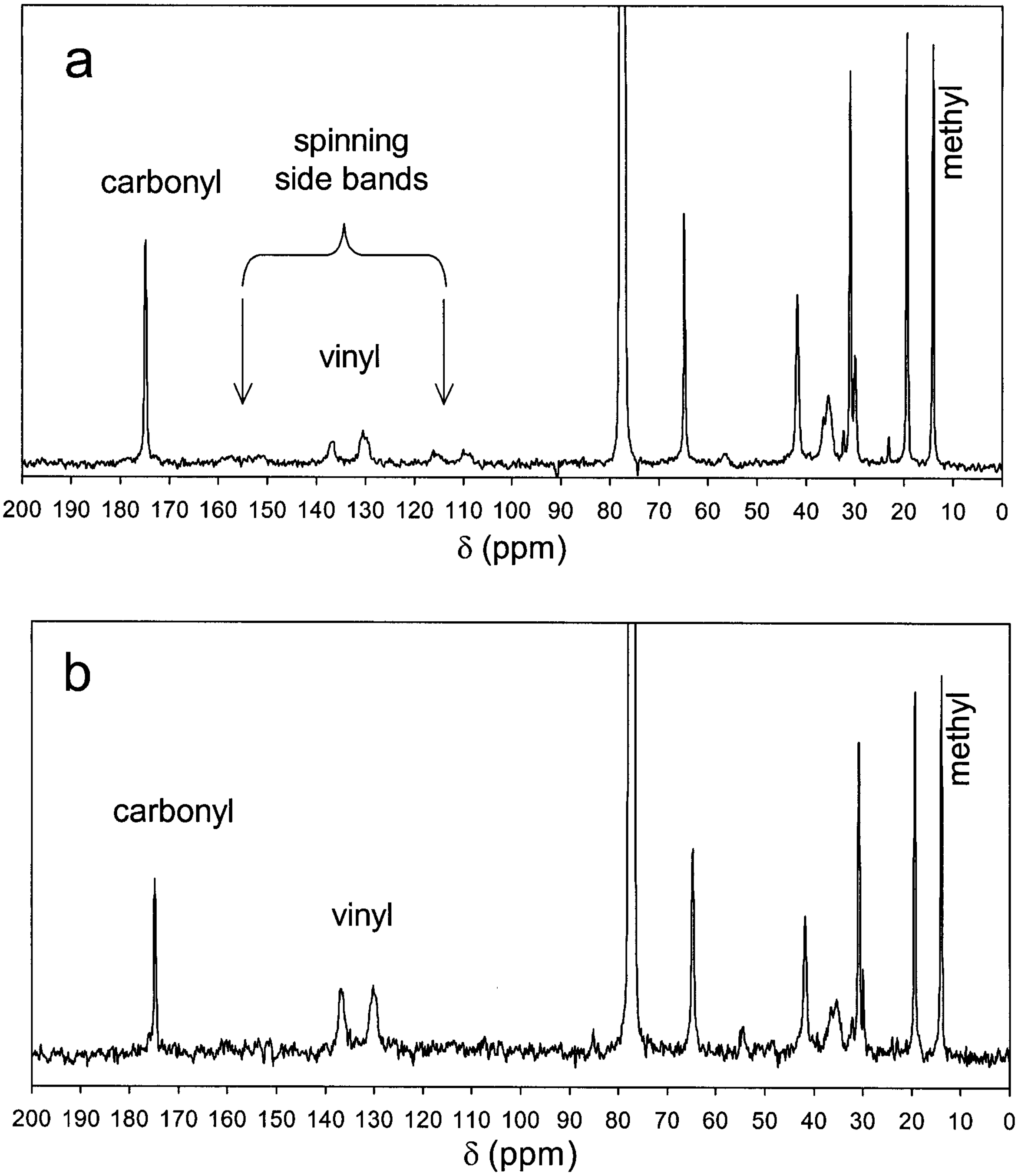

Figure 4.4: *^{13}C NMR spectra of VTES/BA freeze-dried latexes for 50 mole % VTES: (a) polymerization initiated by APS (pH 1.5), and (b) polymerization initiated by AMBN (pH 5.5).*

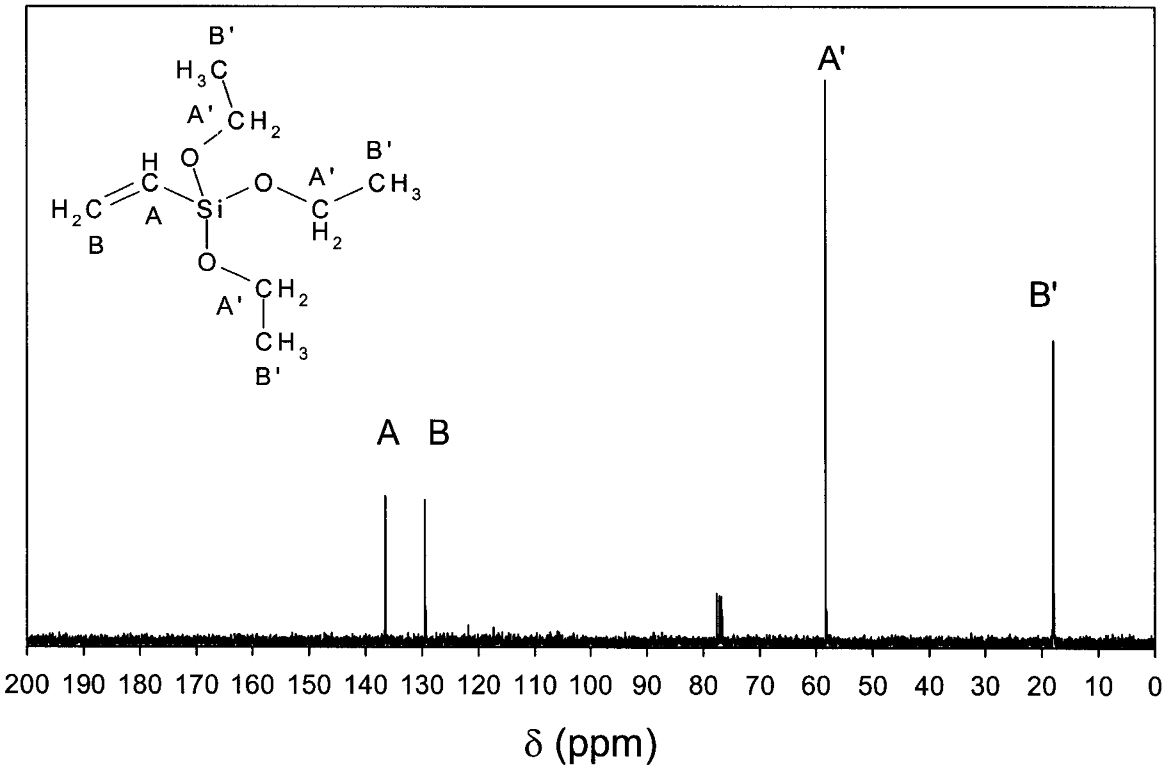

Figure 4.5: *^{13}C NMR spectrum of neat vinyltriethoxysilane.*

In order to better understand the properties and behavior of the alkoxysilane-acrylate systems, the resulting particle morphology needs to be identified. In this respect, one of the most modern and effective methods to investigate the morphology is the use of NMR spin diffusion experiments (Figure 4.6). The method requires significant differences in mobility between the components of the system and basically consists of a preparation stage by selection of the mobile component only, followed by a time-dependent equilibration with the rigid component [5]. The dipolar transfer of magnetization depends on the strength of the dipolar coupling compared to the other interactions of the magnetic nuclei, the number of spins involved and the distance between the nuclei transferring the magnetization. The measurement of spin diffusion requires a magnetization transfer experiment, starting with a selection period, followed by a mixing period of duration t_m during which the spin diffusion process takes place, and ending with a detection period (Figure 4.7). The morphological features of the analyzed latexes may be correlated to the evolution of normalized signal intensity from the mobile component as a function of the square root of mixing time (Figure 4.8) [6].

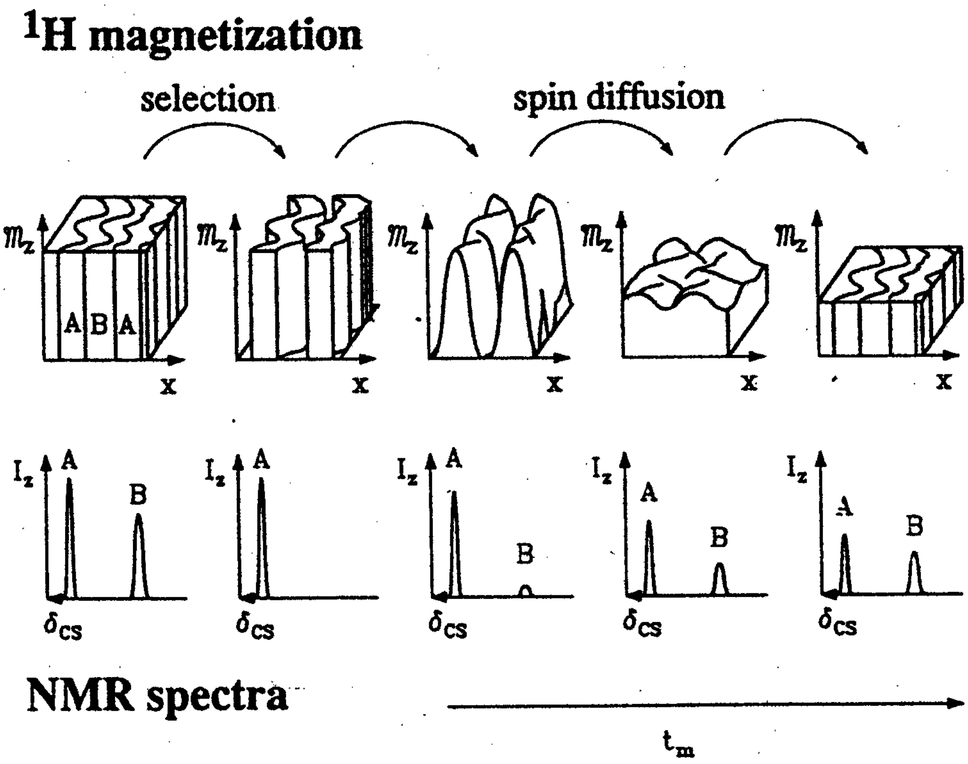

Figure 4.6: *Schematic representation of* ^1H *spin diffusion in a two-phase system with spatially constant proton density. After the selection period, only protons in the mobile phase remain polarized. The NMR spectrum shows the signals corresponding to the selected phase A only. The redistribution of magnetization by* ^1H *spin diffusion is monitored by NMR spectroscopy; with increasing mixing times, the intensity of signals corresponding to the selected region A decreases, whereas the signal intensity of the initially depleted region B increases [5].*

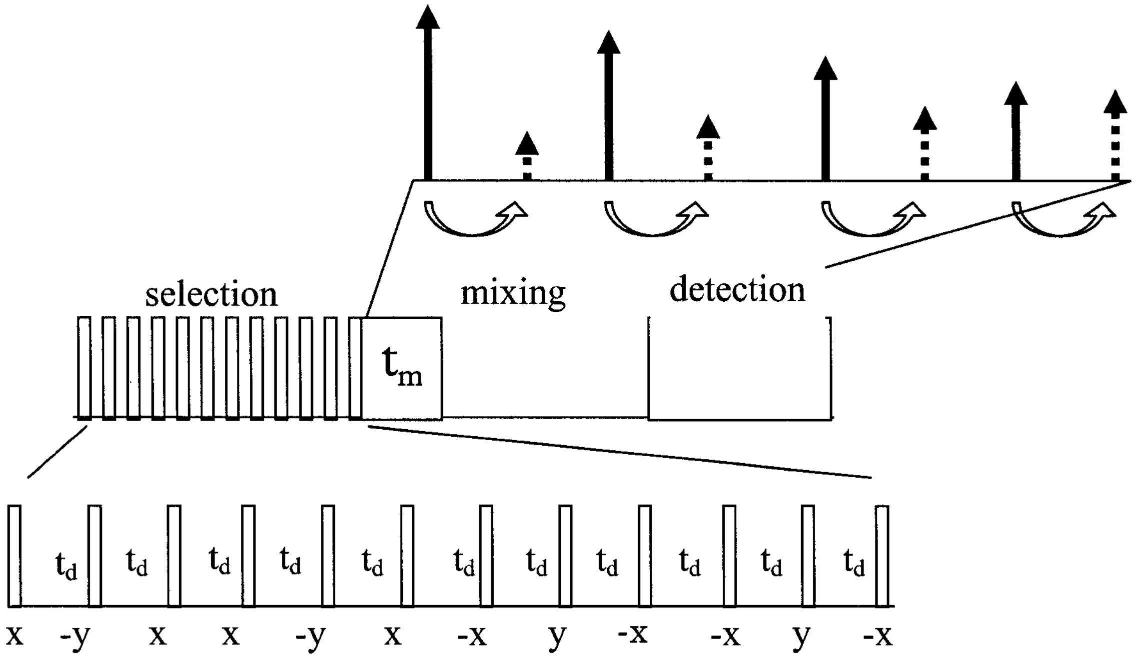

Figure 4.7: *Schematic representation of a NMR spin diffusion experiment. The intensity decay for the detected signal of the mobile component depends on the time of mixing (t_m) and on the interfacial area between the mobile and rigid components.*

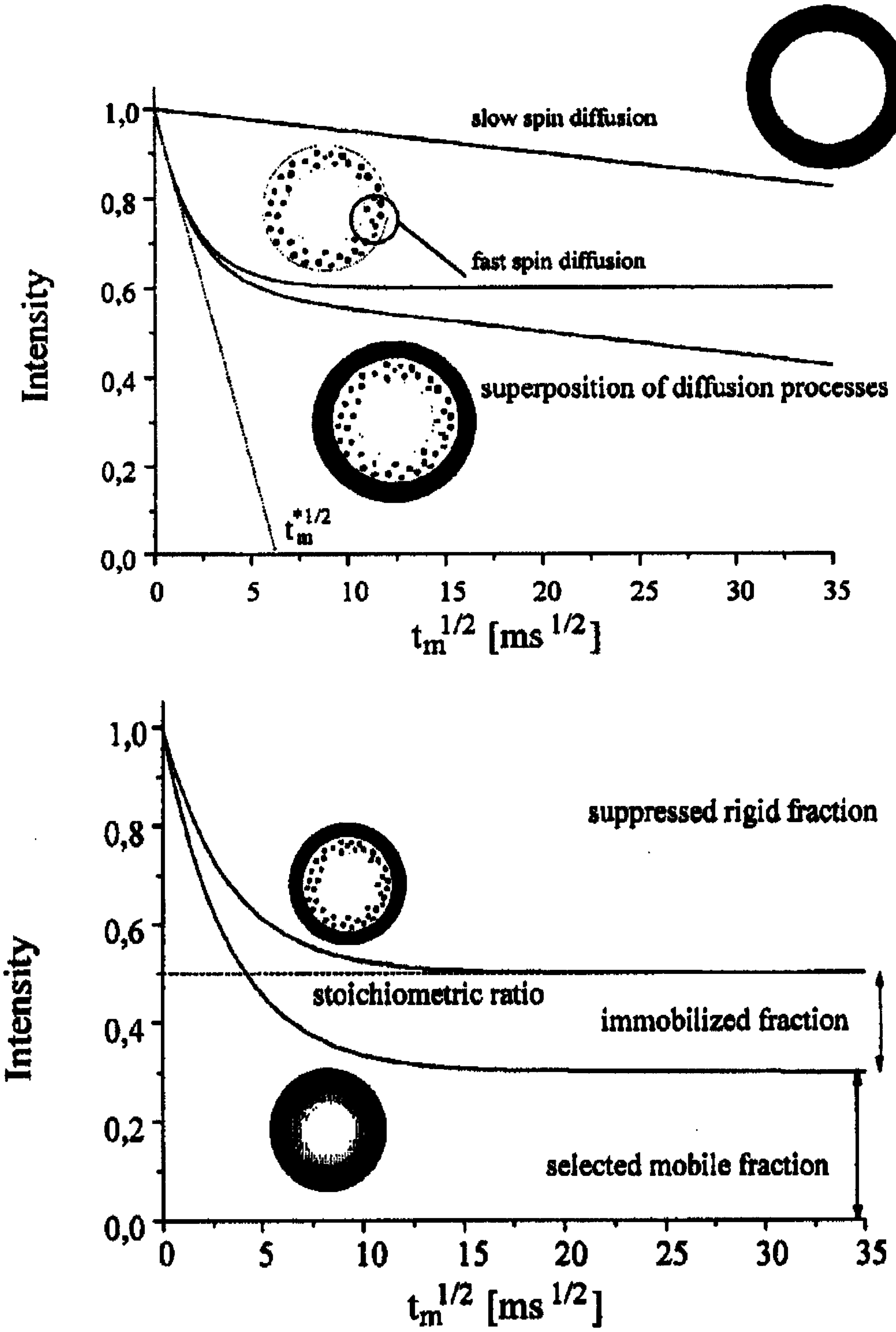

Figure 4.8: *Ideal spin diffusion behavior for different particle morphologies [6].*

The NMR spin diffusion data for the polymer latexes prepared with APS and AMBN initiators (P12, A52 and A12) are shown in Figure 4.9. The latex prepared using APS initiator at pH 1.5 (P12) displays a mixed core-shell/domain morphology (two signal intensity decays, Figure 4.8 a), while the latex prepared with AMBN initiator at pH 5.5 (A52) yields an exclusive domain morphology, characterized by the signal intensity plateau at large mixing times, i.e., the absence of the second (slow) decay [6] (Fig. 4.9 b). The mixed core-shell/domain morphology can also be inferred for the AMBN-initiated system at pH 1.5 (latex A12, Figure 4.9 c). The core-shell feature found in both oil-soluble and water-soluble initiating systems at pH 1.5 can be explained by the silane hydrolysis and subsequent crosslinking favored by the highly acidic environment [2]. In both cases, the crosslinked silane moieties form a rigid shell at the surface of the latex particle. As expected, the pH of the environment has a dominant influence on the chemical behavior of the alkoxysilane. The latex particle morphology is dependent on the reaction pH, a combination of domain and core/shell morphologies being identified at pH 1.5 and an exclusive domain morphology at pH 5.5 (Figure 4.9).

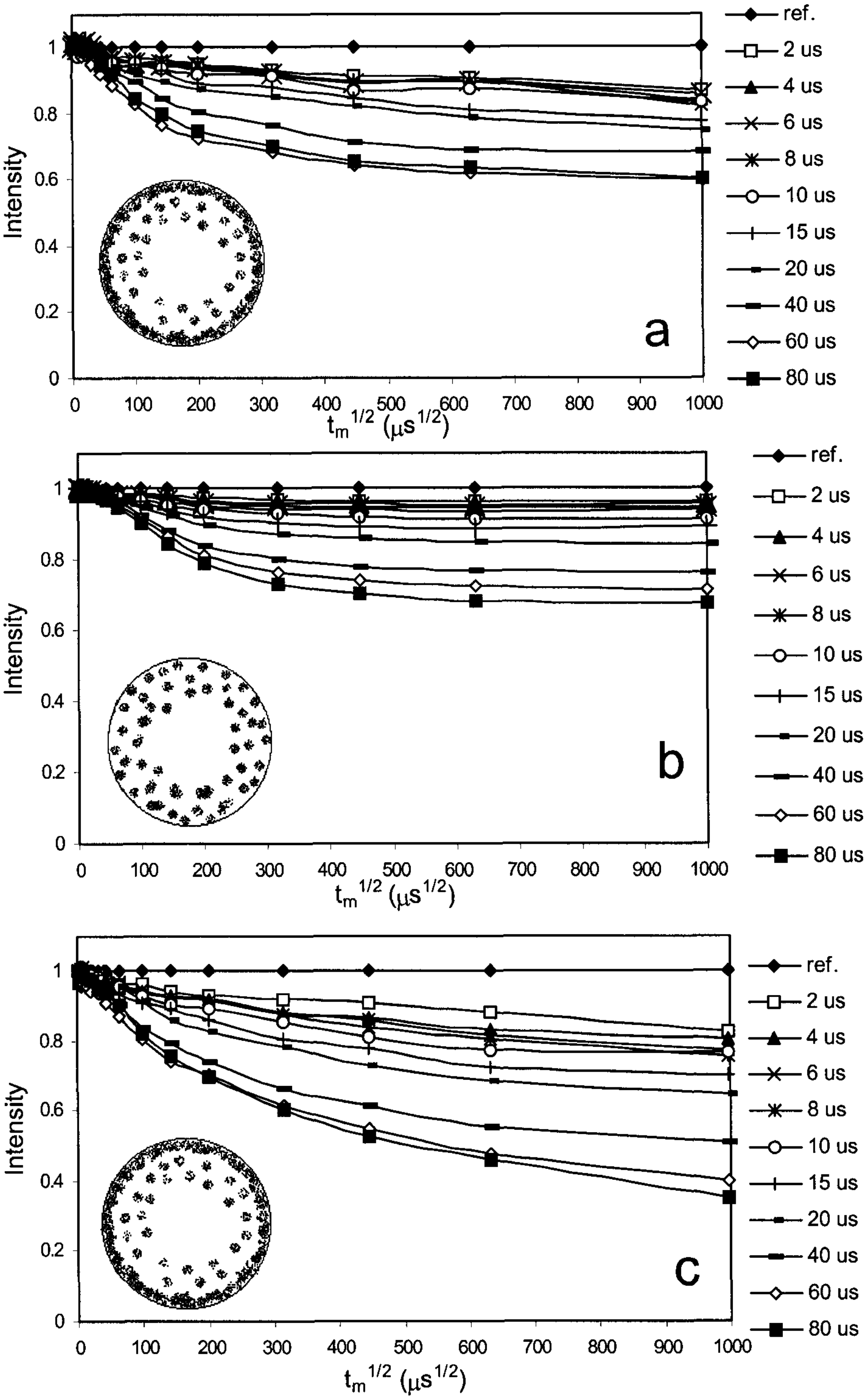

Figure 4.9: *^{1}H-detected spin-diffusion results for different initiator systems for VTES/BA freeze-dried latexes and their inferred morphologies: (a) P12: domains and core/shell; (b) A52: domains; and (c) A12: domains and core/shell.*

4.3.2 Influence of the Acrylate Monomer on the Vinyltriethoxysilane/Acrylate Latex Properties

The chemical nature of the acrylate monomer is an important factor in the study of the incorporation of vinylalkoxysilanes into acrylate latexes by miniemulsion polymerization. Different degrees of compatibility between the acrylate moieties and the alkoxysilane will induce different kinetic behaviors during the miniemulsion process (as described in Chapter 3), and as a consequence, the latex particle morphology is expected to be affected. For the investigation of the influence of the acrylate monomer on the properties of the vinyltriethoxysilane/acrylate latexes prepared by miniemulsion polymerization, the acrylates of choice were *n*-butyl acrylate (BA) and 2-ethylhexyl acrylate (EHA). The most significant difference between these two acrylates is represented by their affinities for the aqueous phase (Table 4.3)

Table 4.3: Solubility Properties of the Acrylate Monomers used in the Study [7]

***n*-Butyl acrylate (BA)**	
Solubility of water in BA	0.7 g / 100 g @ 25 °C
Solubility of BA in water	0.2 g / 100 g @ 25 °C
2-Ethylhexyl acrylate (EHA)	
Solubility of water in EHA	0.15 g / 100 g @ 25 °C
Solubility of EHA in water	0.01 g / 100 g @ 25 °C

The phase separation between the silane and acrylate moieties during the miniemulsion process, as hypothesized in Chapter 3, is confirmed by the analysis of solubles content in the synthesized latexes (Figure 4.10). An increase in the solubles content is observed as the amount of VTES in the sample is increased. Given the fact that silane moieties undergo crosslinking reactions, this could be explained as follows. At low silane contents the VTES is more uniformly distributed in the droplet, acting like a conventional crosslinker and the polyacrylate segments are caught in the network. As the silane content increases, phase separation occurs and there is more "free" soluble material in the particle, outside the tri-dimensional network. In the latter case, the loci of hydrolysis are not randomly distributed throughout the particle, but they form separate regions, giving rise to a morphological pattern. The unusually high initial heat in the copolymerization reactions for 30 mole % VTES in both BA and EHA systems (Figure 4.11) is also indicative of an initial fast acrylate polymerization, that most probably excludes the silane moieties, giving rise to separate domains in the particles.

The phenomenon can also be investigated by analyzing the dynamic mechanical spectra of the cast film samples throughout a temperature sweep starting below the glass transition of the polyacrylate (-54 °C for poly(*n*-butyl acrylate), -55 °C for poly(2-ethylhexyl acrylate)) [8]. The dynamic mechanical spectra are shown in Figure 4.12. For both VTES/BA and VTES/EHA latex films, the spectrum of the polyacrylate was taken as reference. For 10 mole % VTES there is only one tan δ peak (one glass transition temperature) for both latex systems. This can mean that either there is no phase separation in the films between hard, crosslinked silane moieties, and the soft, rubbery polyacrylate, or the

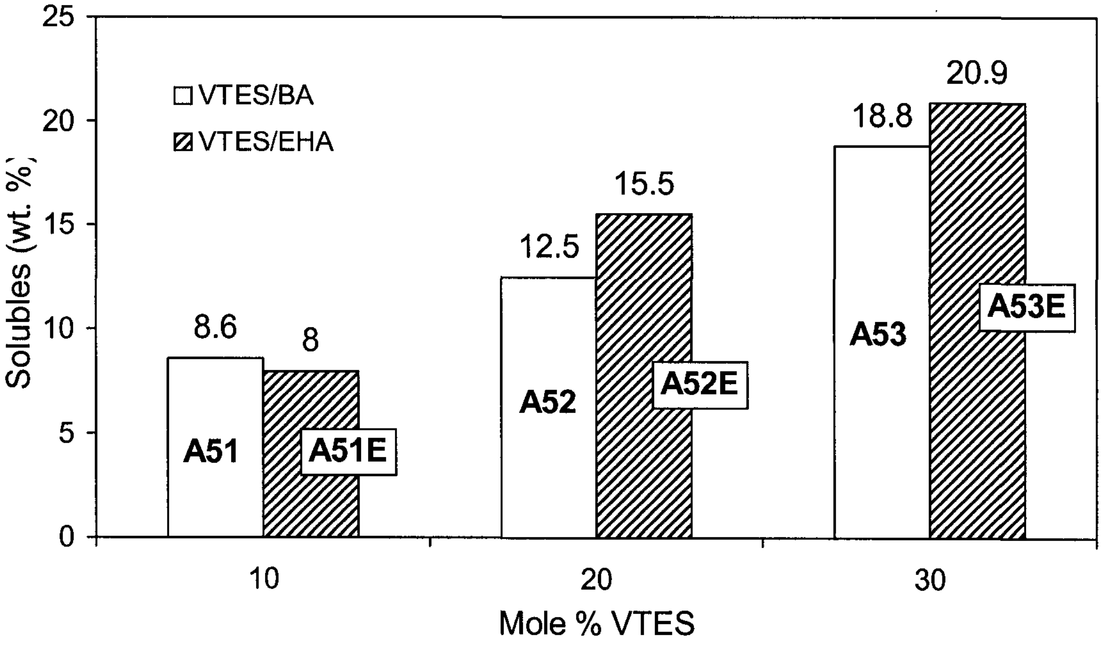

Figure 4.10: *Percent solubles for the freeze-dried VTES/BA and VTES/EHA latex samples.*

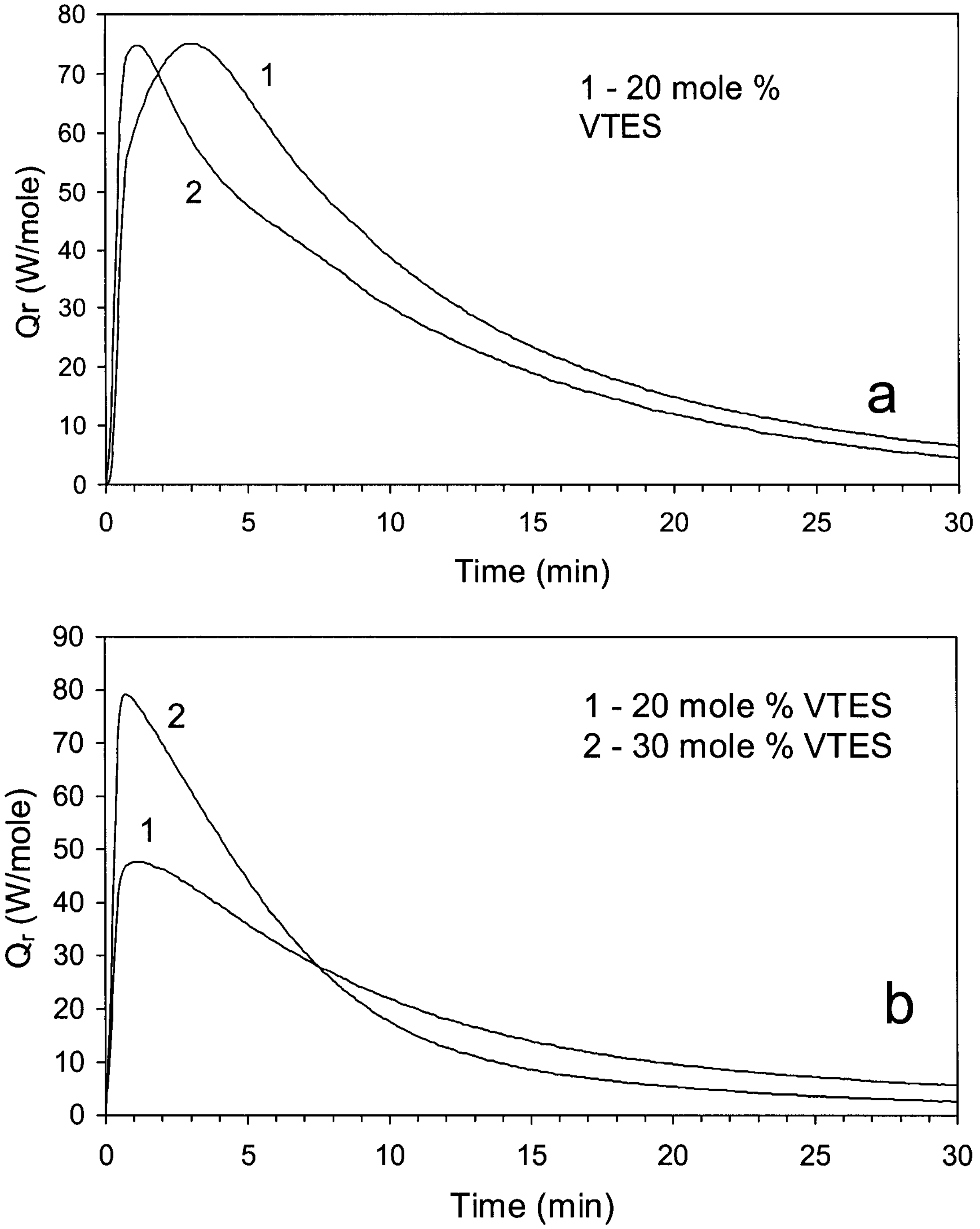

Figure 4.11: *Heat profile of the VTES/acrylate miniemulsion reaction: (a) VTES/BA, and (b) VTES/EHA.*

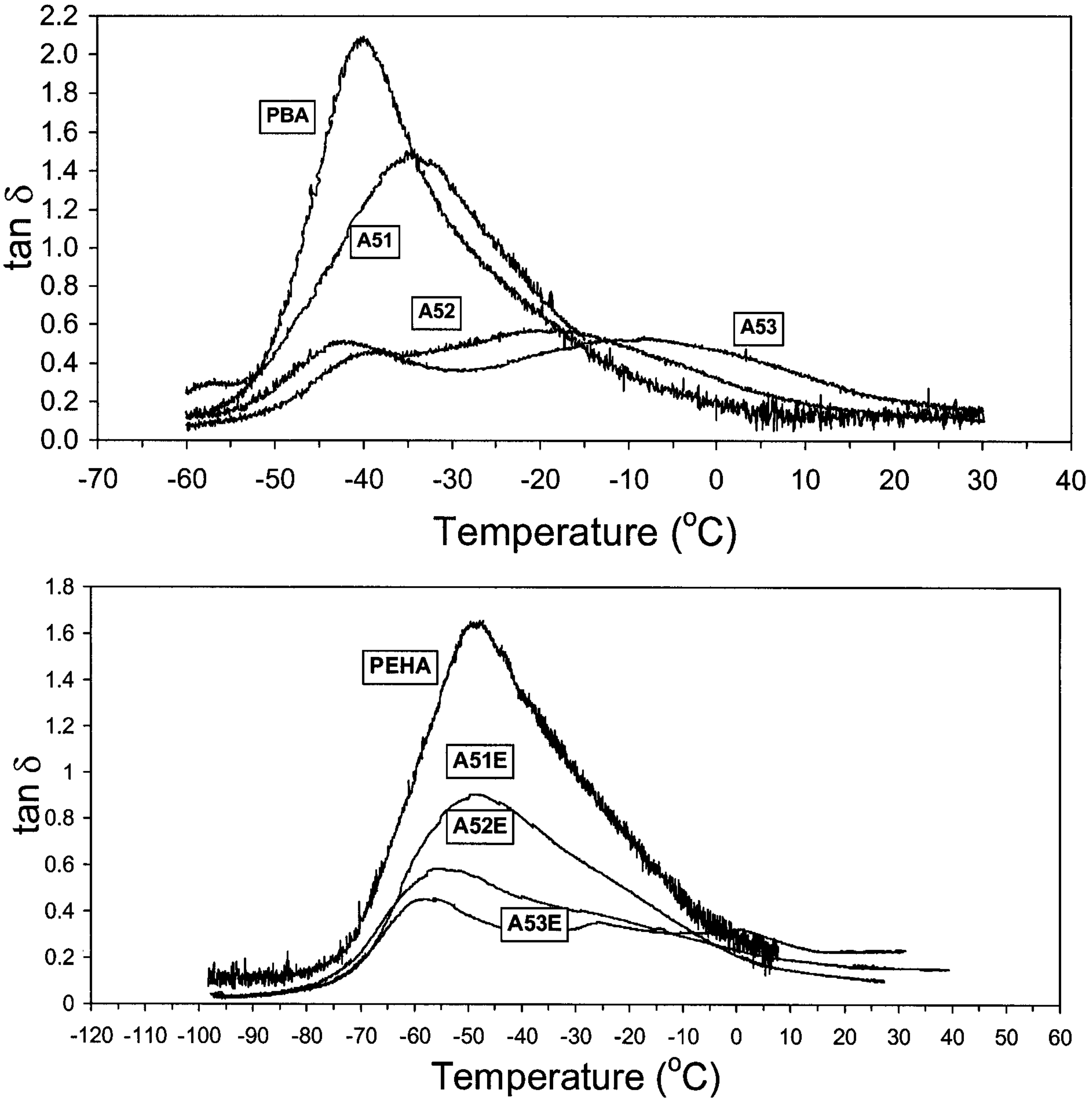

Figure 4.12: *Tan δ vs. temperature plots of: (a) VTES/BA and (b) VTES/EHA latexes.*

domains are very small and evenly distributed, so that the dynamic mechanical analysis is not able to distinguish between the soft and the rigid phase. The answer to this issue will be found by using the NMR spin diffusion technique. At high silane contents (20 and 30 mole %), two tan δ peaks are observed. Thus, phase separation is confirmed in these cases for both VTES/BA and VTES/EHA latex systems.

In order to clarify the phase separation issues and to identify the morphological features of the VTES/acrylate latex particles, a series of proton-detected NMR spin diffusion experiments was performed. The spin diffusion results for VTES/BA and VTES/EHA latexes are presented in Figures 4.13 and 4.14, respectively. In all cases, domain (occluded) morphologies are inferred from the shape of signal intensity decays (the leveling of signal at large mixing times). The $t_m{*}^{1/2}$ parameter (Figure 4.7) which is a measure of the relative interfacial area between the mobile (soft) component and the rigid component of the latex particles was evaluated using the slope of the signal intensity decay for the strongest filter (80 μs) and is shown in Figure 4.15. The volume fractions of the rigid phase, as determined from the spin diffusion plots, are represented in Figure 4.16. In order to interpret the $t_m{*}^{1/2}$ parameter, the correlation with the relative volume to area ratios has to be made (Equation 4.2) [6]

$$\frac{V_{tot}}{S_{tot}}\Phi_A = \frac{1}{\Phi_B}\cdot\frac{2}{\sqrt{\pi}}\cdot\frac{\sqrt{D_A D_B}}{\sqrt{D_A}+\sqrt{D_B}}\cdot\sqrt{t_m^*} \tag{4.2}$$

$$\Downarrow$$

$$\frac{V_{tot}}{S_{tot}}\Phi_B = \frac{V_B}{S_{tot}} \propto \frac{t_m^{*\,1/2}}{\Phi_A} \tag{4.3}$$

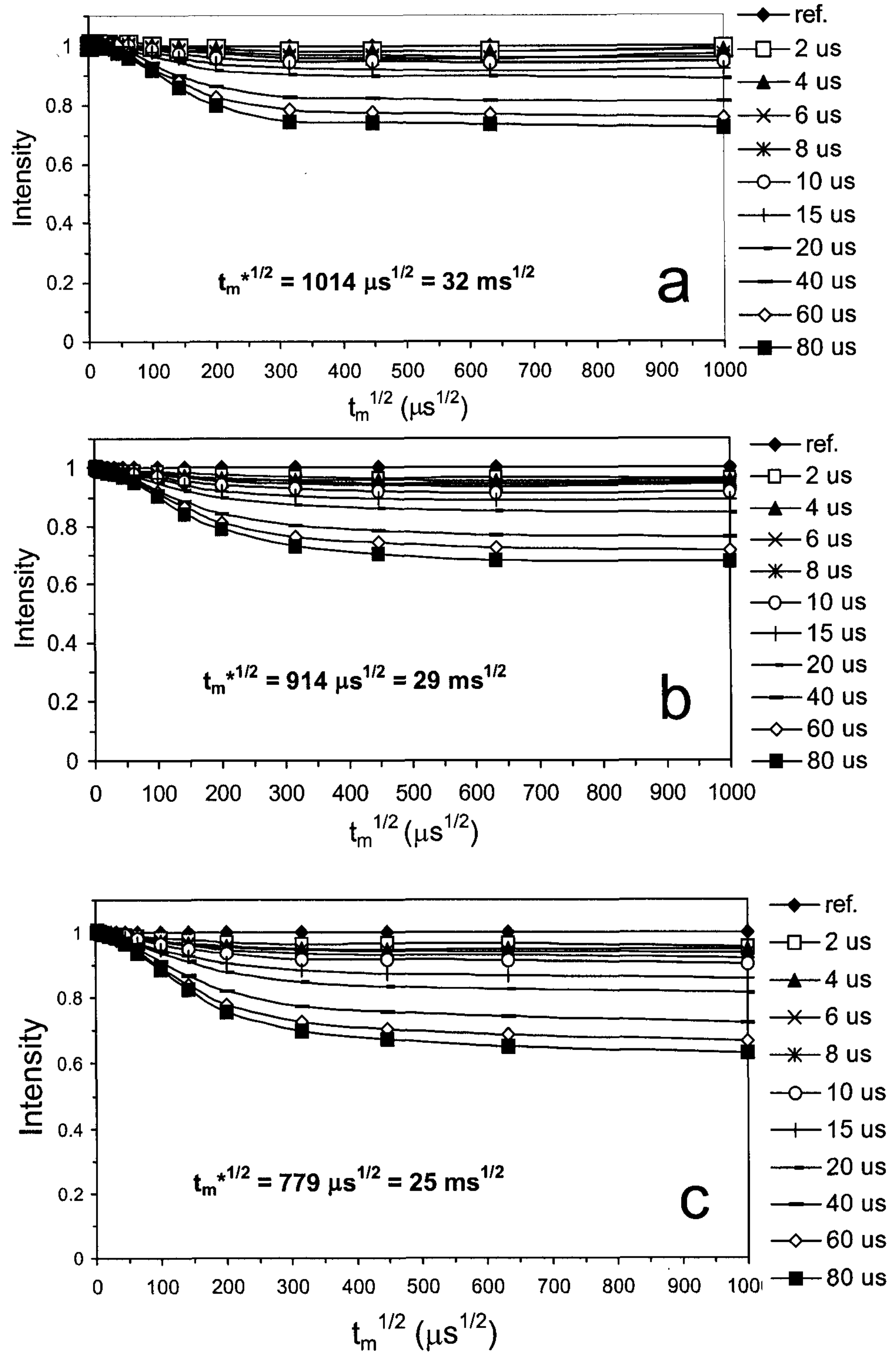

Figure 4.13: *Decay of normalized intensity of the mobile component as determined from spin diffusion experiments in VTES/BA freeze-dried latexes: (a) 10 mole % VTES, (b) 20 mole % VTES, and (c) 30 mole % VTES.*

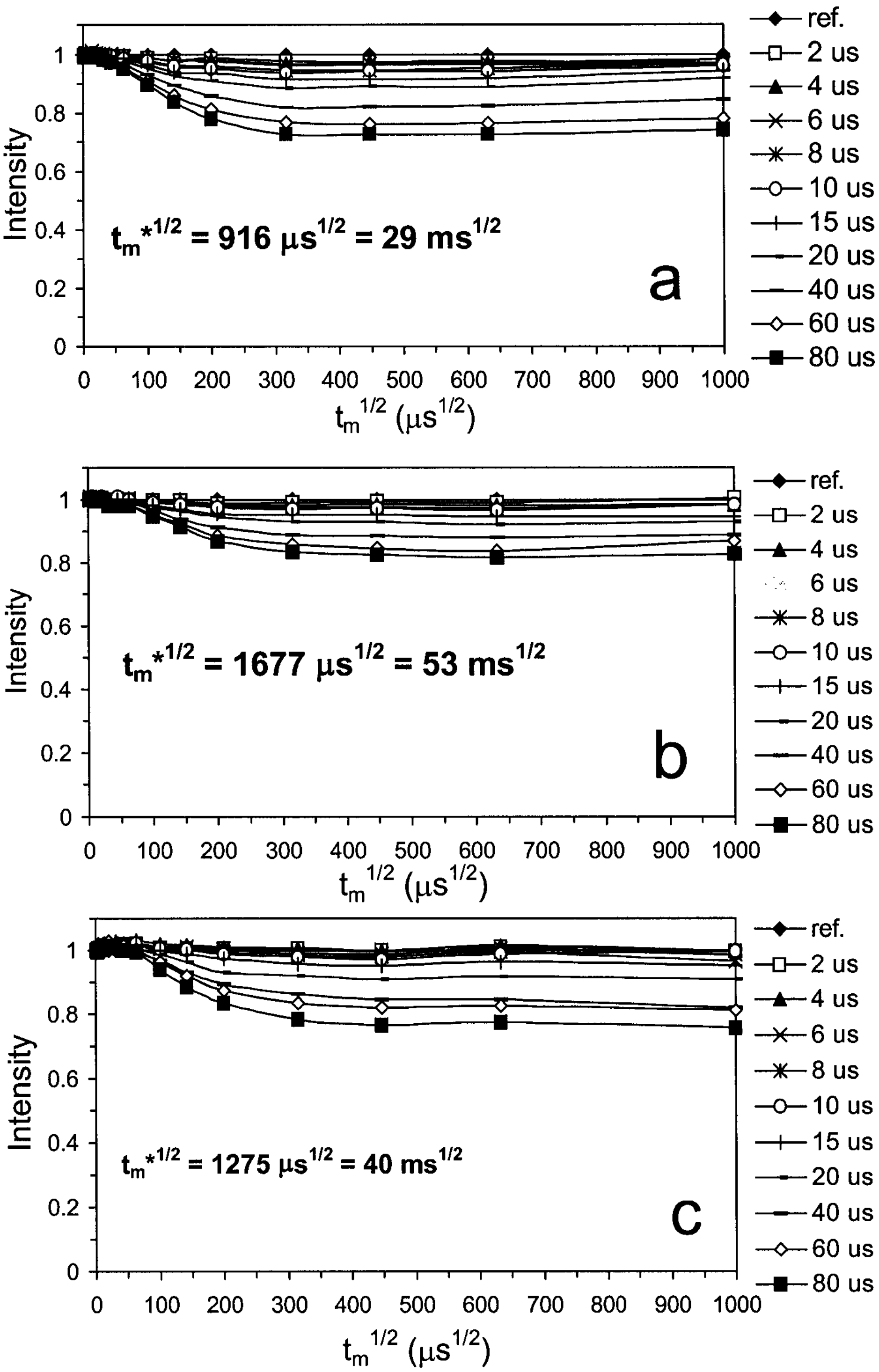

Figure 4.14: *Decay of normalized intensity of the mobile component as determined from spin diffusion experiments in VTES/EHA freeze-dried latexes: (a) 10 mole % VTES, (b) 20 mole % VTES, and (c) 30 mole % VTES.*

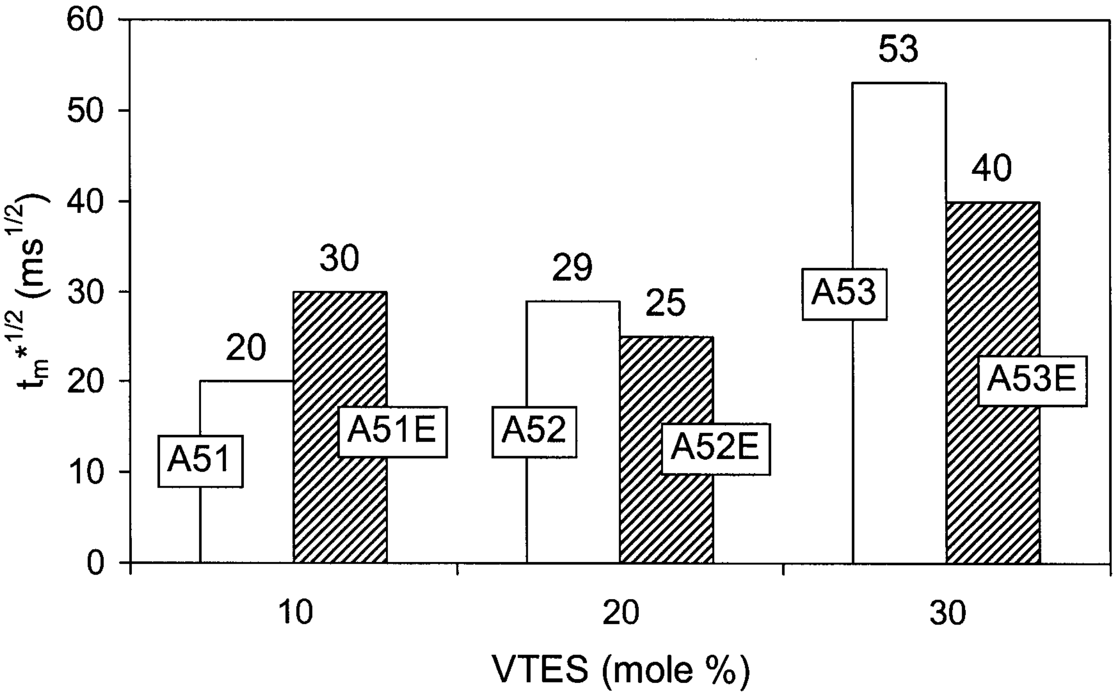

Figure 4.15: *The* t_m*$^{1/2}$ *parameter for VTES/BA and VTES/EHA latexes as a function of VTES content.*

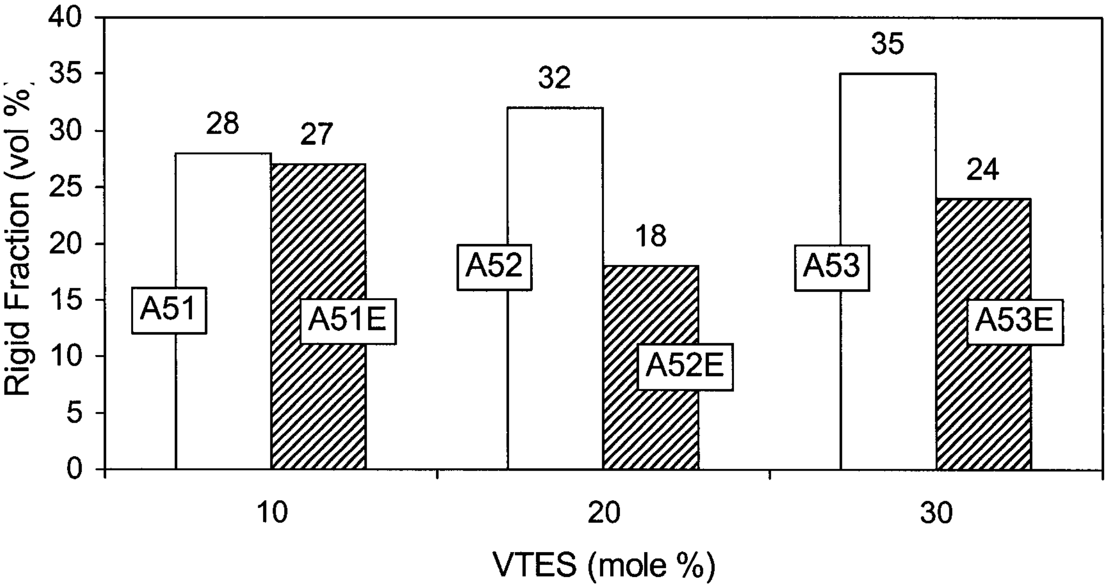

Figure 4.16: *Volume fraction of rigid component as estimated from spin diffusion studies for VTES/BA and VTES/EHA latexes.*

where Φ_A = volume fraction of retained component A (soft); Φ_B = volume fraction of suppressed component B (rigid); D_A and D_B = spin diffusion coefficients of the two components; V_{tot} = particle volume; S_{tot} = total A/B interfacial area

Since the spin diffusion coefficients are not known for these particular systems, they are eliminated by transforming the equality into a proportionality. The volume to area ratio for the rigid component, representing the relative rigid domain size is proportional to $t_m{*}^{1/2}$ divided by the volume fraction of the soft component (Equation 4.3). The plots of the normalized volume to area ratios for the rigid phase domains are shown in Figure 4.17. The observed trends in the evolution of the volume to area ratios (relative size) for the rigid domains are different in the two systems (VTES/BA and VTES/EHA, respectively). In the case of VTES/BA latexes, as the VTES content increases, the relative size of the rigid domains remains relatively constant and the higher VTES content has, as a consequence, an increase in the number of rigid domains (Figure 4.18 a). In the case of VTES/EHA latexes, the increase in the amount of VTES leads to a relative increase in the volume to area ratios for the rigid domains. This can be translated into an increase in the relative size of the rigid domains with the VTES content (Figure 4.18 b) [9]. The phase separation between the rigid and the soft phases becomes more significant in the VTES/EHA latex systems at high silane contents. This observation confirms the hypothesis of a more advanced degree of phase separation in the VTES/EHA latexes, a case in which the hydrolyzed silane moieties are likely to form better defined, relatively larger silane domains that allow for a more significant occurrence of the OH-OH condensation reaction (Chapter 3).

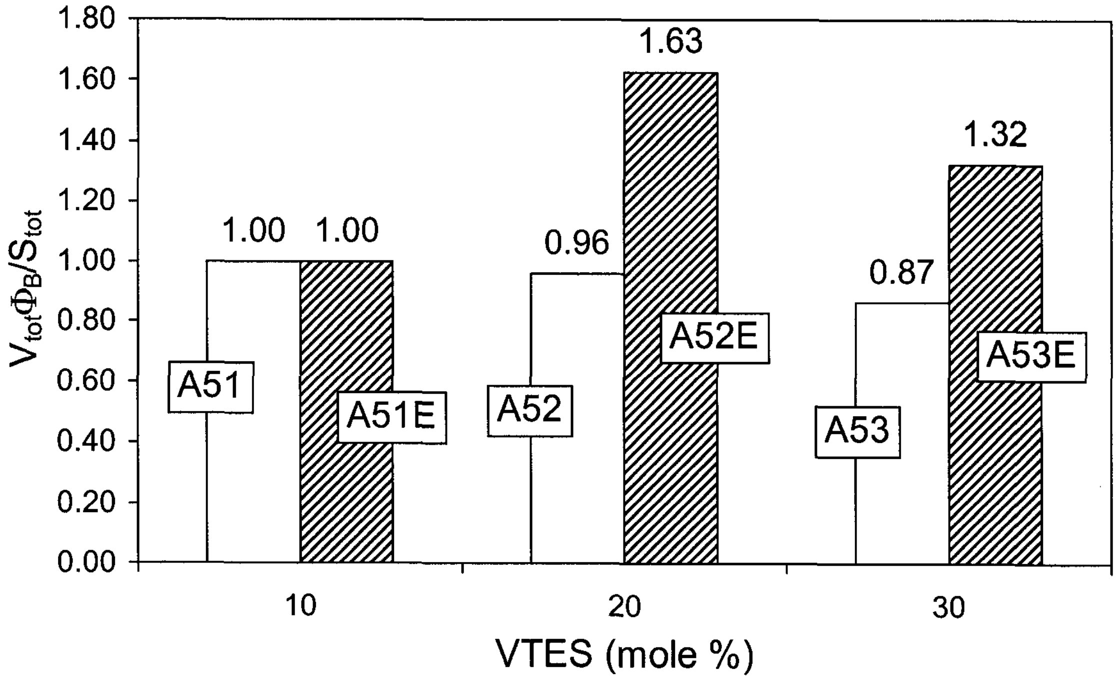

Figure 4.17: *Normalized volume-to-area ratios of the rigid component in VTES/BA and VTES/EHA latexes as a function of VTES content.*

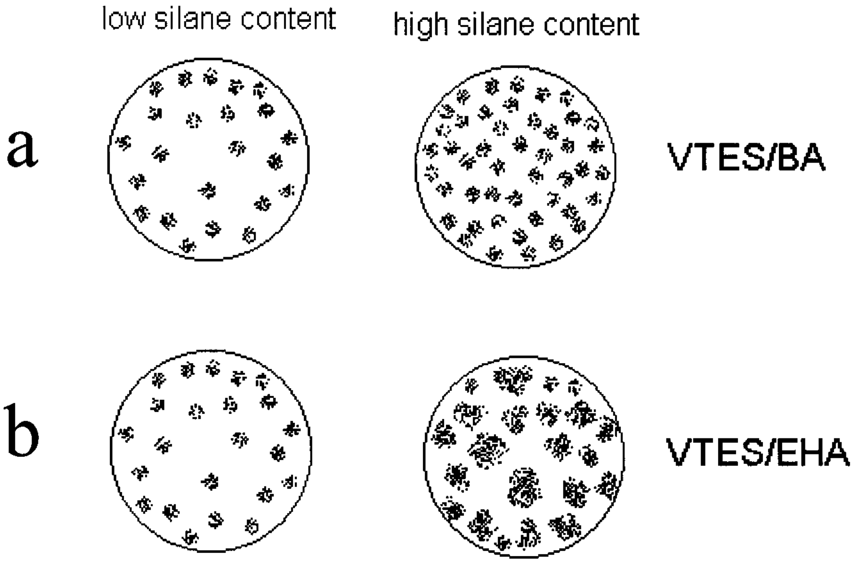

Figure 4.18: *Evolution of the relative domain size for: (a) VTES/BA, and (b) VTES/EHA latexes as inferred from the volume to area relative values.*

These data were also verified by the FT-IR analysis of the relative OH group content in dried films, expressed as absorbance ratio between OH and C=O groups (Figure 4.19). Latexes were diluted to 1 % solids and cast on ZnSe plates. The first series of films was dried overnight at room temperature and the second series was aged for 48 more hours at 75 °C in the oven. The aging process was meant to accelerate the condensation of the OH groups. It can be observed that aging has less influence on VTES/EHA films for high silane contents (Figure 4.19 b). This could mean that more OH groups have already been condensed in these systems compared to VTES/BA films. This result confirms the unusually high (positive) contribution of silane to the heat of reaction, found in the VTES/EHA system for 30 mole % VTES (Chapter 3) and the morphology patterns identified by the spin diffusion experiments.

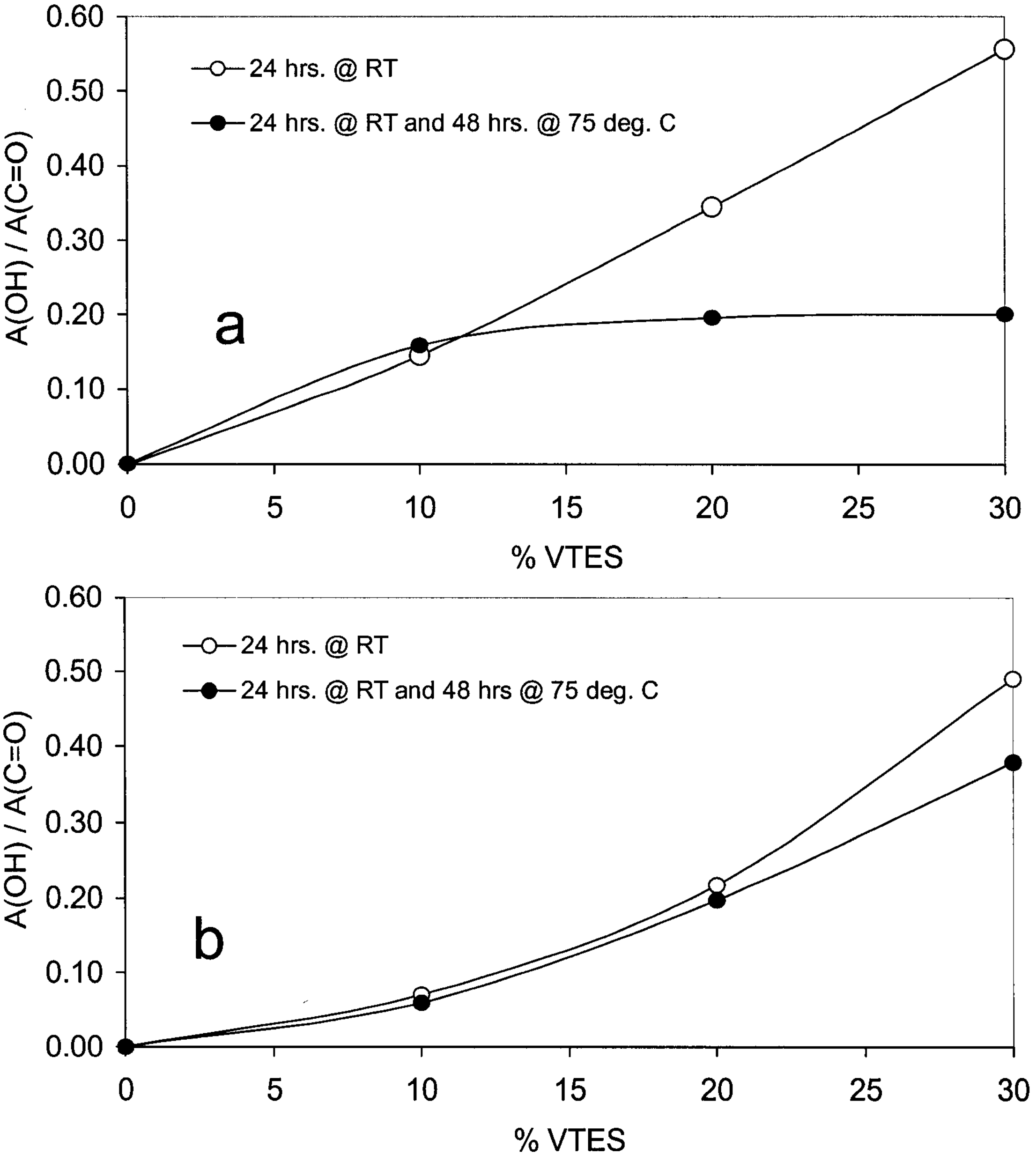

Figure 4.19: *Relative OH group content for aged and non-aged: (a) VTES/BA films, and (b) VTES/EHA films as a function of VTES content.*

4.3.3 Influence of Latex Aging on the Vinyltriethoxysilane/Acrylate Latex Particle Morphology

The occurrence of phase separation was demonstrated in the VTES/acrylate latex systems. This phenomenon starts as soon as the latex is being synthesized (Chapter 3) and becomes more significant as the VTES content in the material is higher. A question arises on how does this phase separation evolve over time and how does it affect the latex particle morphology. The evolution of the latex particle morphology can be determined by analyzing the changes in the solubles content in the material, as well as the modifications in the NMR spin diffusion patterns after one year of latex storage at room temperature.

The soluble fraction for the VTES/BA latexes was determined for the 12 month-old samples of the A51, A52 and A53 latexes and compared with the soluble fraction found in the same fresh latexes. The results are presented in Figure 4.20. It can be observed that the amount of solubles decreases significantly upon aging in all three samples. In order to explain this process, one has to identify the chemical structure of the soluble fraction of the fresh latexes. The method employed makes use of high resolution proton NMR [10]. The solubles from the A51 and A52 freeze-dried latexes were extracted in deuterated chloroform and solution ^{1}H NMR spectra were taken (Figure 4.21). Unexpectedly, PBA peaks are not found in the spectrum of the soluble fraction either, indicating that the polyacrylate chains were completely incorporated into the crosslinked network. The soluble fraction of the A52 latex displays significant peaks from the silane moieties (VTES).

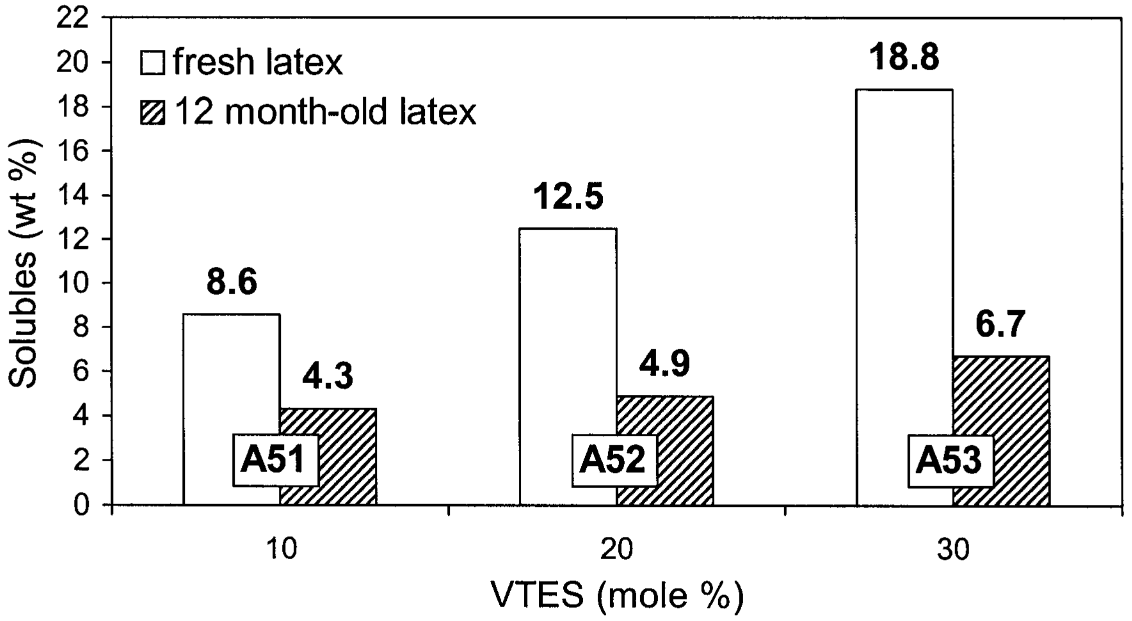

Figure 4.20: *Percent solubles in the fresh and 12 month-old freeze-dried VTES/BA latexes as a function of VTES content.*

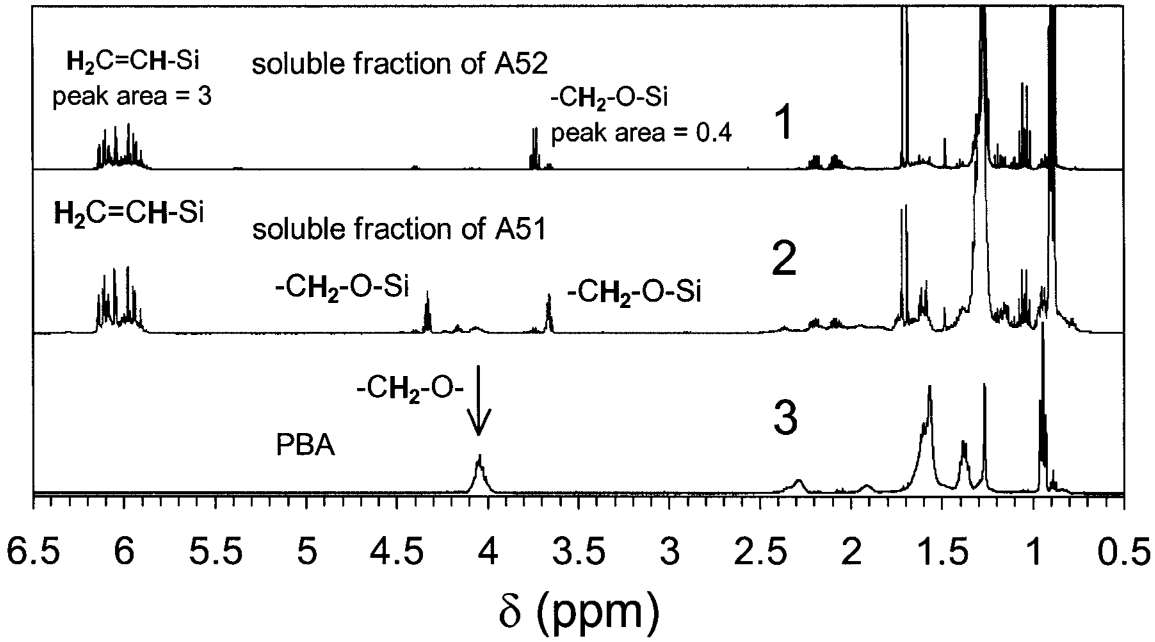

Figure 4.21: *Proton NMR spectra of the soluble fraction of: (1) VTES/BA latex synthesized by miniemulsion polymerization (20 mole % VTES), (2) VTES/BA latex synthesized by miniemulsion polymerization (10 mole % VTES), and (3) PBA.*

In the case of VTES, the ratio between the vinyl peaks (centered at about 6.1 ppm) and the methylene peaks on the oxygen (at 3.6 and 3.8 ppm), is 3/6 (Figure 4.22 a), but in the soluble fraction of the A52 latex, this ratio is found to be 3/0.4. This may occur if the ethoxy group hydrolysis is followed by a condensation yielding non-volatile compounds containing cyclic structures (for a matching vinyl/methylene proton ratio), as generally depicted in Figure 4.23. The signals in the case of the soluble fraction are an average of the signals of all the possible soluble siloxane cyclic structures.

Analyzing the spectra of the soluble fractions in Figure 4.21, one can observe multiple peaks assigned to the methylene belonging to the silane alkoxy group. The suplementary methylene peaks appear due to the hydrolysis and condensation reactions that induce changes in the atomic neighborhood of some of the methylene groups, so that not all of the methylene protons will be identical any more from the magnetic resonance point of view. To confirm this hypothesis, the soluble fraction of the reaction product of VTES and water was extracted in deuterated chloroform and analyzed by proton NMR. New methylene peaks were also observed in this case (Figure 4.22 b).

The soluble fraction of the VTES/BA latexes was found to consist of VTES-derived structures featuring unreacted vinyl groups and being most probably represented by soluble siloxane oligomers containing branches and/or cyclic structures, resulting from a certain degree of condensation between the hydrolyzed alkoxysilane moieties. These structures contain OH groups capable of undergoing condensation reactions with time. Upon latex aging, these condensation reaction take place with the participation of the soluble silane moieties and the total amount of solubles in the material decreases.

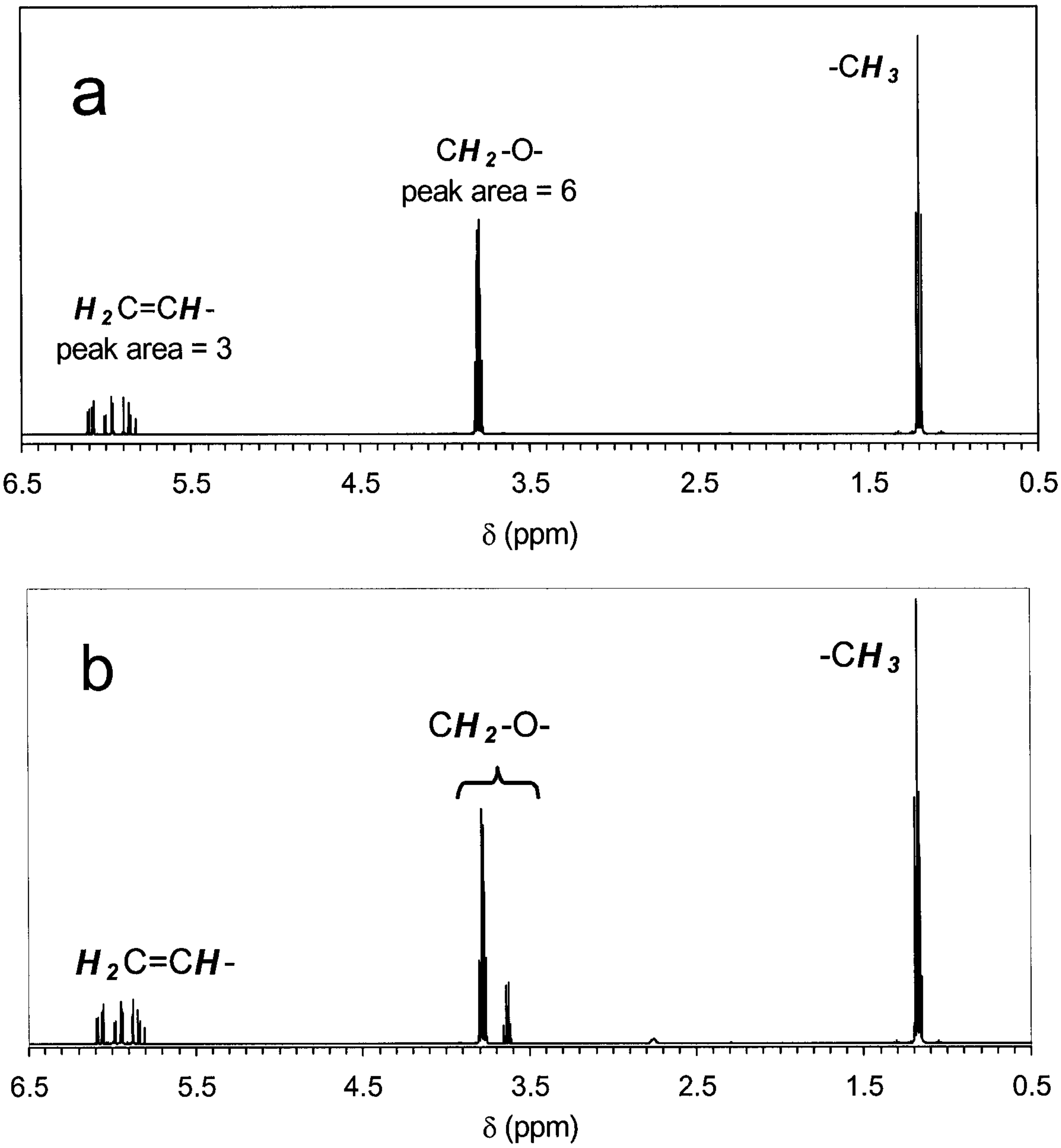

Figure 4.22: *Proton NMR spectra of: (a) neat VTES, and (b) soluble fraction of the reaction product between VTES and water.*

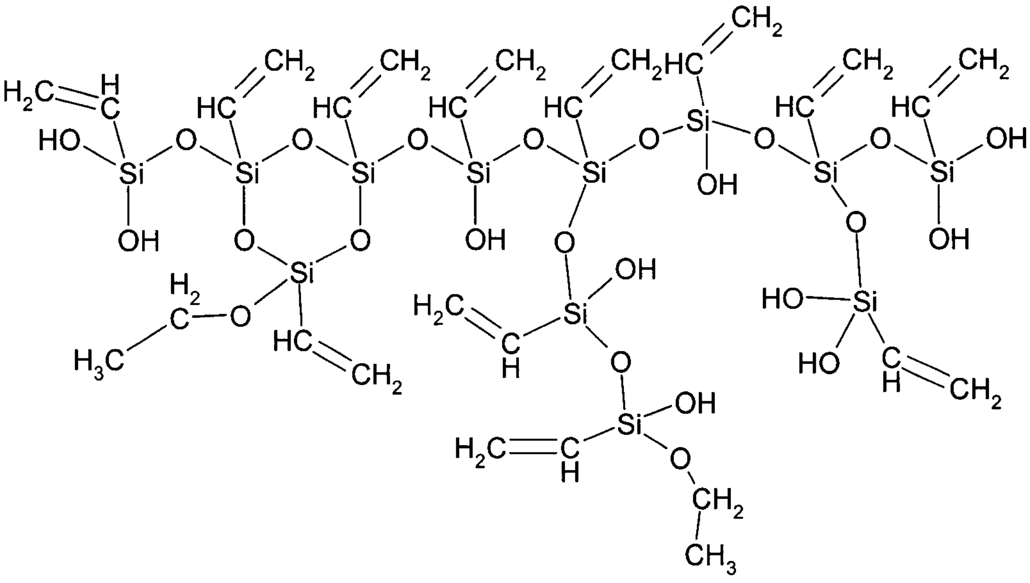

Figure 4.23: *Schematic representation of hypothesized cyclic structures present in the soluble fraction of the VTES/BA latexes (vinyl/methylene = 3/0.33).*

In order to verify this hypothesis, the fractions of rigid material in the latexes were evaluated in the aged samples by NMR spin diffusion experiments and compared to the fractions of rigid material found in the fresh samples. The 12 month-old latexes were freeze dried and spin diffusion experiments were performed using the same parameters as for the fresh latexes. The signal intensity plots are shown in Figure 4.24. The rigid fractions were determined from these plots [6] and were found to increase upon aging (Figure 4.25). The relative volume to area ratios for the rigid domains were determined using the calculated $t_m{}^{*1/2}$ parameters (Equation 4.3) and normalized (Figure 4.26). The observed increase of the rigid fraction confirms the hypothesis of the evolution of crosslinking in time. The relative decrease of the calculated volume-to-area ratios with aging can be explained by the formation of a new population of small domains in the system as a result of crosslinking of the soluble species. This process will determine a decrease in the average volume-to-area ratio for the rigid fraction.

The characterization of films cast from fresh latexes included the evaluation of the relative amount of OH groups in cast films by FT-IR (Figure 4.19). The relative amount of hydroxyl groups was expressed as the ratio between the absorbances of OH groups and C=O groups in the films. The same evaluation was carried out for films cast from 12 month-old latexes. The relative amount of OH groups in the dried films was found to decrease, as expected, due to the occurrence of condensation reactions upon aging (Figure 4.27).

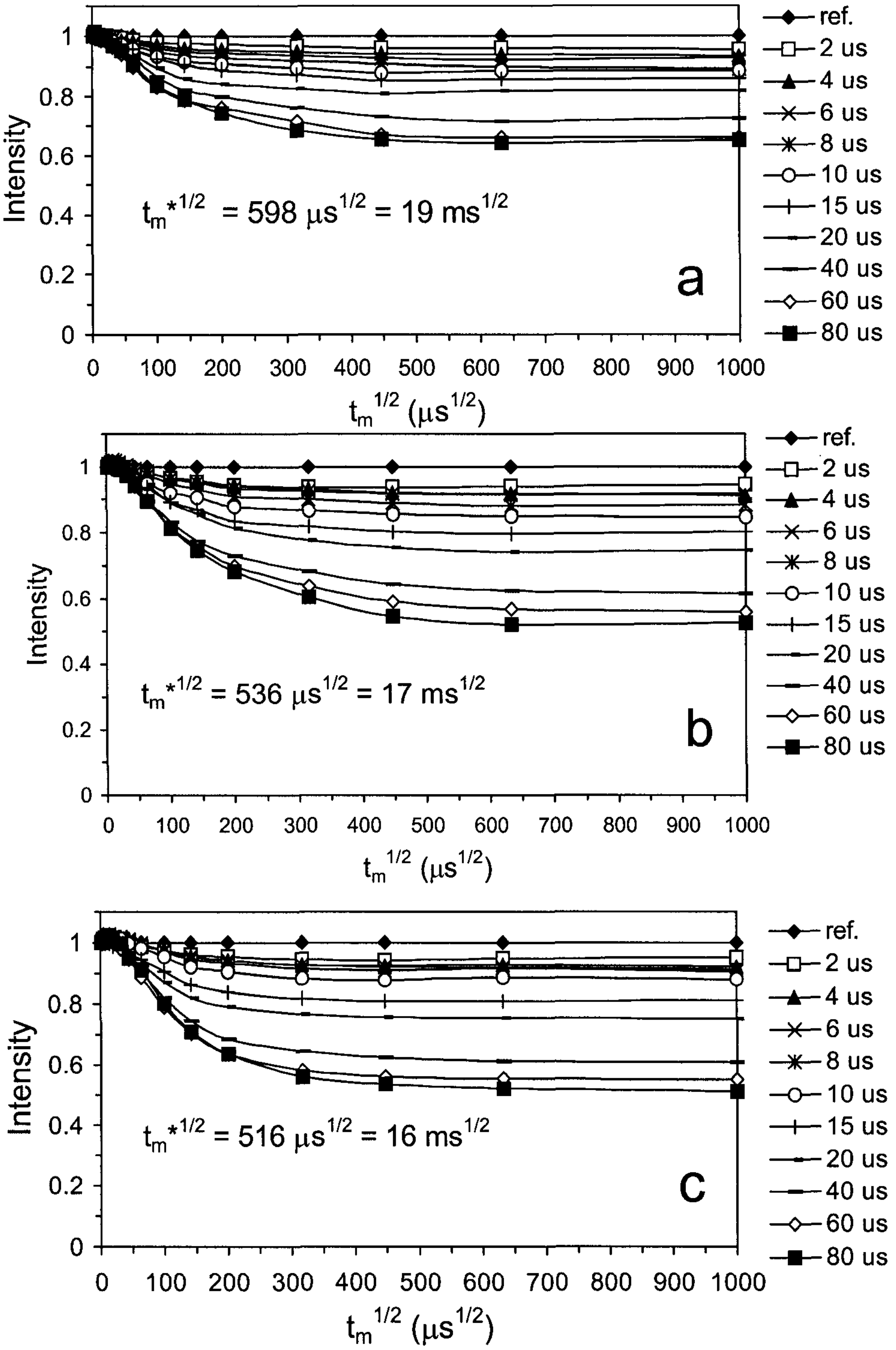

Figure 4.24: *Decay of normalized intensity of the mobile component as determined from spin diffusion experiments in VTES/BA freeze-dried 12 month-old latexes: (a) 10 mole % VTES, (b) 20 mole % VTES, and (c) 30 mole % VTES.*

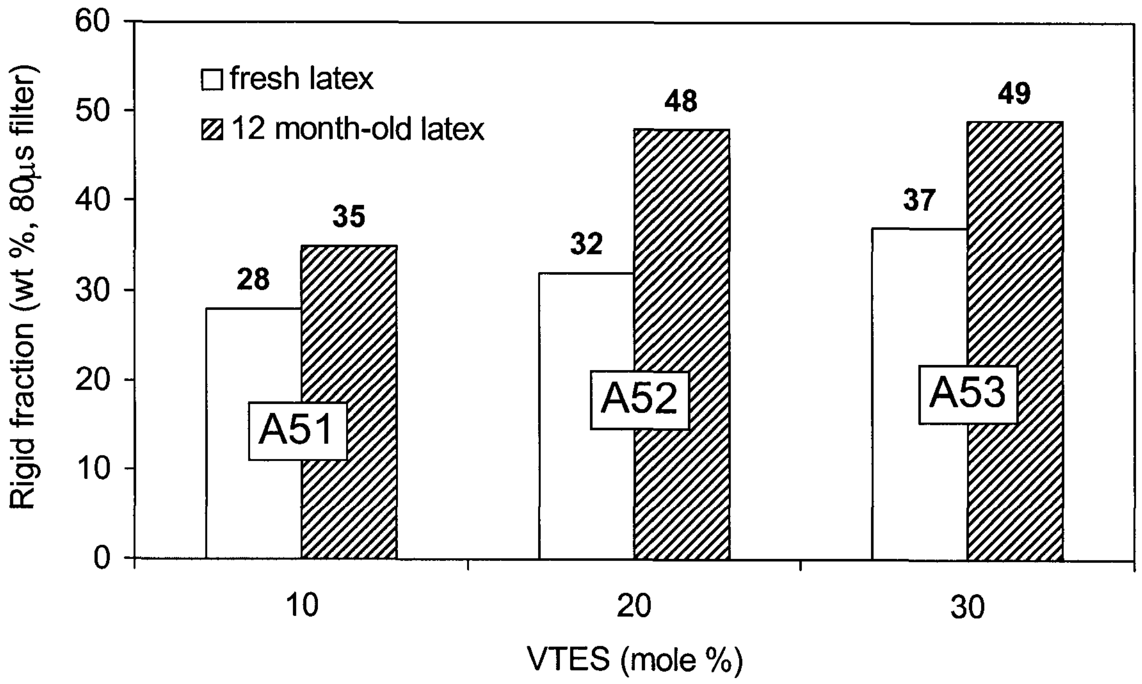

Figure 4.25: *Volume fraction of rigid component as estimated from spin diffusion studies for fresh and 12 month-old VTES/BA latexes.*

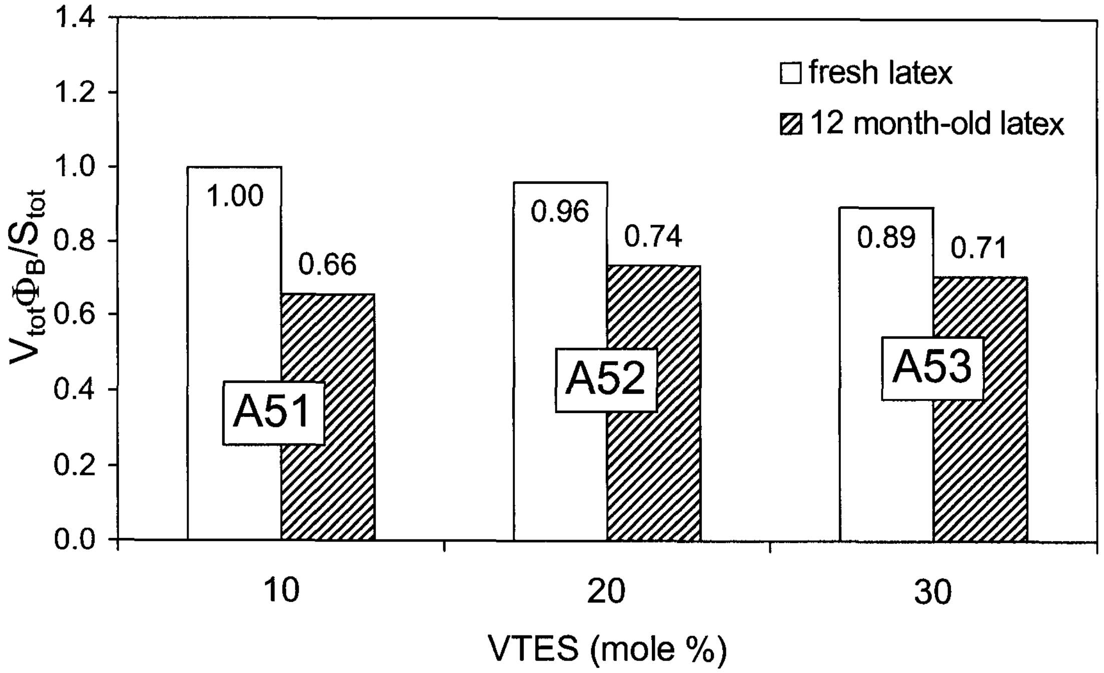

Figure 4.26: *Volume-to-area ratios for the rigid component as estimated from spin diffusion studies for fresh and 12 month-old VTES/BA latexes.*

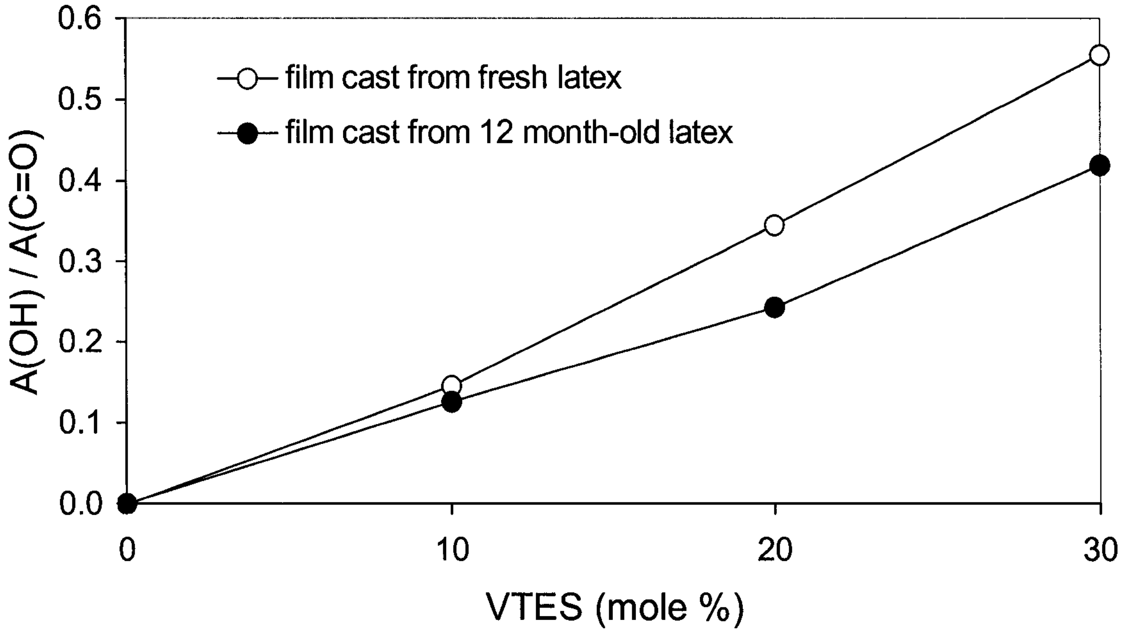

Figure 4.27: *Relative OH group content for fresh and 12 month-old VTES/BA films as a function of VTES content.*

Intraparticle crosslinking upon latex aging is possible at the expense of the silane-containing moieties found in the soluble fraction of the miniemulsion-synthesized latexes. This hypothesis is also supported by the observed decrease in the solubles content upon latex aging (Figure 4.20). Crosslinking is also possible outside the latex particles, in the continuous phase, especially for high VTES contents. Micrographs of cross-sections of high silane-content aged latex films obtained by scanning electron microscopy (SEM) show rectangular structures that appear to exist outside of the latex particles (Figure 4.28). The crystalline nature of these structures was demonstrated by electron diffraction experiments [11] for 30 mole % VTES latexes (Figure 4.29). In this case, small crystalline structures were identified in the diluted latex cast on a carbon-coated copper grid. At high alkoxysilane contents, crystalline structures in the continuous phase are most probably formed by supramolecular aggregation of tridimensional siloxane networks generated by the crosslinking of the soluble siloxane moieties that phase separate from the latex particles. A question arises as to when do these structures form in the latex systems. Based on the kinetic studies (Chapter 3) and on the evidence of phase separation in fresh latexes, the presence of such structures in fresh latexes at high silane contents is expected. The SEM micrograph of a sample of fresh VTES/BA latex containing 20 mole % VTES (A52) confirm the presence of these rectangular structures in fresh latexes (Figure 4.30).

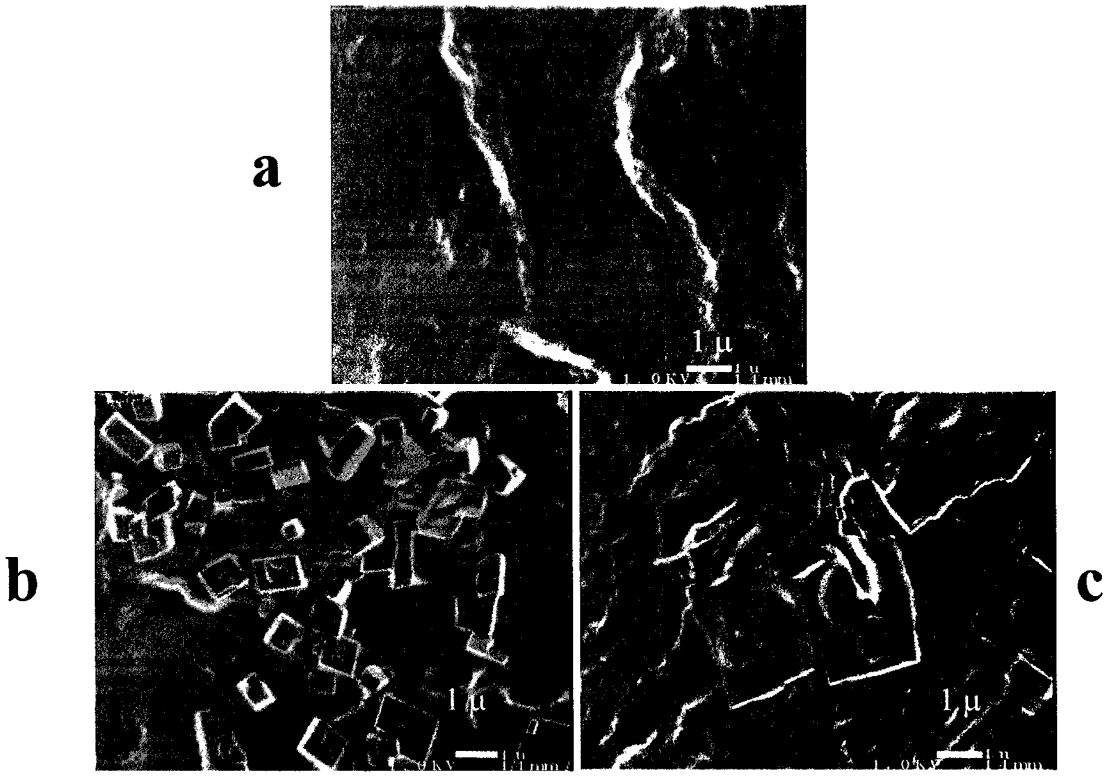

Figure 4.28: *SEM micrographs of cross-sections of 12-month-old VTES/BA latex films: (a) 10 mole % VTES, (b) 20 mole % VTES, and (c) 30 mole % VTES.*

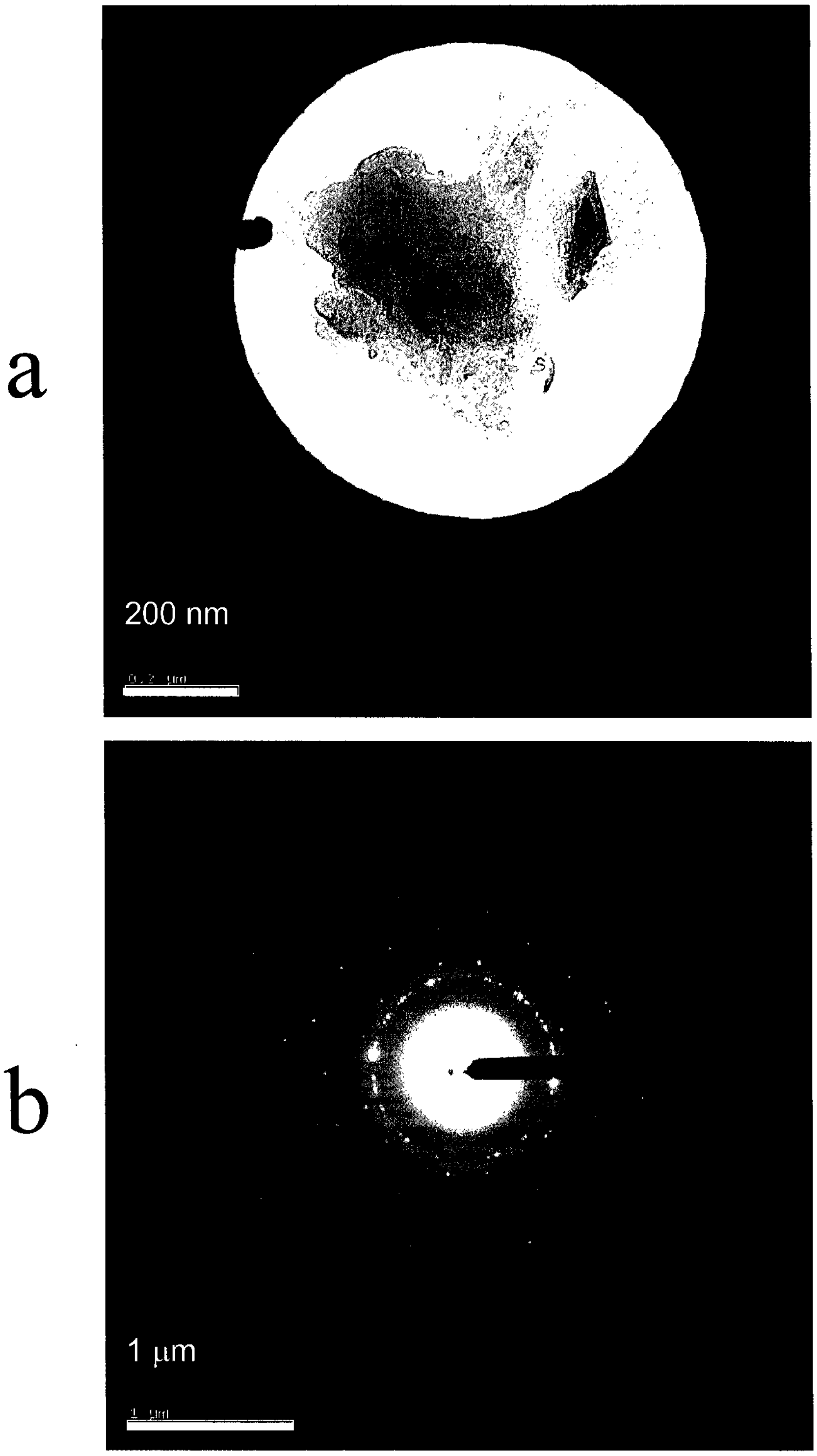

Figure 4.29: *(a) TEM micrograph, and (b) electron diffraction pattern for 12-month-old latexes (30 mole % VTES) cast on carbon-coated copper grids.*

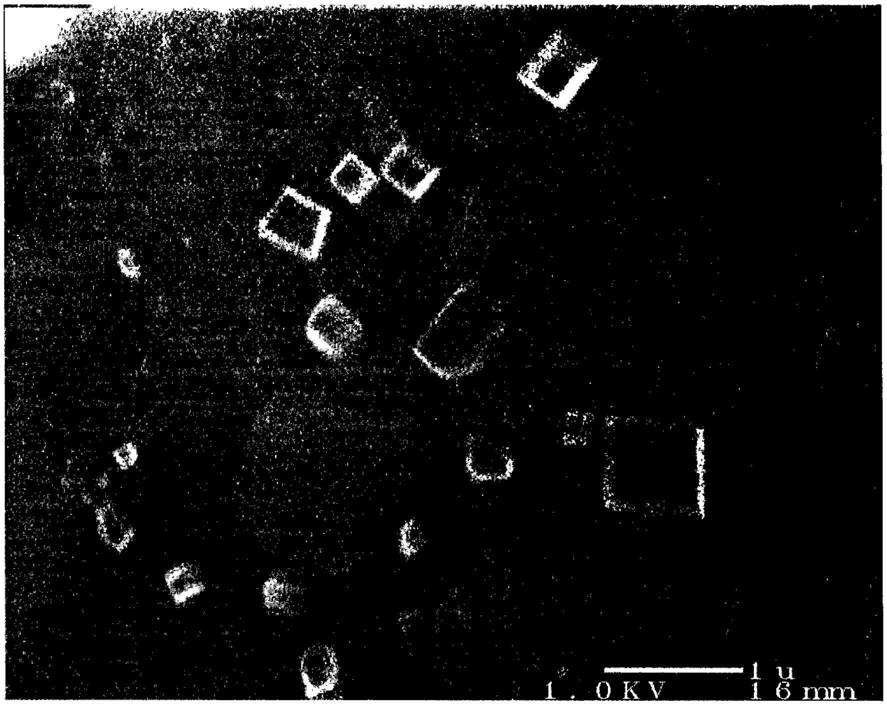

Figure 4.30: *SEM micrograph of a VTES/BA fresh latex film (20 mole % VTES).*

4.4 CONCLUSIONS

The initiation system (water-soluble ammonium persulfate at pH 1.5 vs. oil-soluble 2,2'-azobis(2-methyl-butyronitrile)) does influence the mechanism of silane incorporation and particle formation, not only by the different degree of acidity induced in the environment (pH), but also by the initiation mechanism in itself. The VTES/BA latex particle morphologies depend on the pH of the system, with a lower pH stimulating hydrolysis of alkoxysilane groups and subsequent crosslinking that occurs primarily at the particle/water interface and induces a core/shell morphology. The factors contributing to the different mobilities of the APS and AMBN-initiated latexes, expressed by the degrees of swelling, DSC traces, and ^{13}C NMR spectra are a result of both the influence of the pH of the system (a low pH in the case of APS stimulates the alkoxysilane hydrolysis and subsequent condensation yielding a more rigid network) and the initiation mechanisms (the AMBN-initiated systems are characterized by the formation of the radicals in the oil droplet, with a higher termination rate, hence shorter, more mobile polymer chains).

Phase separation and domain formation were found to occur in the VTES/acrylate latexes. These phenomena are dependent on the amount of alkoxysilane in the feed and on the hydrophobicity of the acrylate monomer. A higher degree of phase separation was observed for the most hydrophobic acrylate (2-ethylhexyl acrylate). The relative size of rigid, crosslinked domains in the latex was found to increase with the silane contents for the VTES/EHA systems. In the case of VTES/BA latexes, the relative size of domains does not increase with the VTES content in the feed, but rather the number of domains grows.

Latex aging was found to tresult in a decrease in the solubles content and an increase in the rigid fraction evaluated by NMR spin diffusion. The explanation for these phenomena was found by investigating the chemical composition of the soluble fraction in fresh latexes, that contains mostly silane moieties, probably siloxane oligomers with free hydroxyl groups that are capable of undergoing condensation reaction upon latex aging. The relative size of the rigid domains was found to decrease, most probably due to the formation of new populations of small domains resulting from the partial crosslinking of the soluble fraction. The rigid domains observed in the cross-sections of the films cast from aged latexes with high silane contents were found to have a crystalline nature and were formed in the continuous phase as a consequence of the supramolecular aggregation of tridimensional siloxane networks generated by the crosslinking of the soluble siloxane moieties that phase separate from the latex particles. The presence of such structures was also confirmed in fresh latexes at high silane contents.

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CHAPTER 5

MECHANISMS OF INCORPORATION OF VINYLALKOXYSILANE MONOMERS INTO ACRYLATE-BASED LATEXES BY MINIEMULSION POLYMERIZATION

5.1 INTRODUCTION

The incorporation of vinylalkoxysilanes into acrylate latex systems was found to be achieved by at least two mechanisms. The first mechanism was vinyl copolymerization, which is not quantitatively effective in batch polymerization systems due to the unfavorable reactivity of the vinylalkoxysilane [1]. The second, more effective mechanism of alkoxysilane incorporation in the latex systems is the hydrolysis of the silane alkoxy groups followed by the condensation reactions of the resulting hydroxyl groups [2]. The resulting tridimensional network was found to form rigid domains in the latex particles. A third possible mechanism, the chain transfer to the silane vinyl group will be investigated and its contribution to the silane incorporation into the latex particles wil be evaluated.

5.2 EXPERIMENTAL

5.2.1. Materials

Latexes prepared as described in Chapter 3 were used for the characterization work (Table 5.1) *n*-Butyl acrylate (BA) (Aldrich) inhibited with hydroquinone monomethyl ether (15 ppm), was purified by contacting it with an excess amount of a specific inhibitor remover for hydroquinone and hydroquinone monomethyl ether (Chromosorb 101, mesh size 100-120 from Aldrich) for at least 48 hours. 2,2'-azobis(2-methyl-butyronitrile) (AMBN) (VAZO 67, DuPont) and vinyltriethoxysilane (VTES) (OSi Specialties) were used as received. Toluene, tetrahydrofurane (THF) and deuterated chloroform (Aldrich) were used as received.

Table 5.1: Latexes Used for the Investigation of the Alkoxysilane Incorporation Mechanisms

Latex Code	**Initiator**	**pH**	**VTES Mole %**	**Acrylate**	**Preparation Method**
A51	AMBN	5.5	10	BA	Recipes in Table 3.2
A52			20	BA	
A53			30	BA	

5.2.2. Methods

For the evaluation of the copolymer chemical structure by one- and two-dimensional proton NMR, a bulk copolymerization reaction between *n*-butyl acrylate (80 mole %) and vinyltriethoxysilane (20 mole %) was carried out at 60 °C using 2,2'-azobis(2-methyl-butyronitrile) (AMBN) as initiator (1 mole % on monomers). Proton NMR spectra were obtained on samples dissolved in deuterated chloroform. The instrument used was a Bruker DX-500 operating at 500 MHz. For solid-state NMR studies, latexes were freeze-dried under vacuum, using liquid nitrogen as a cooling agent. Quantitative ^{13}C NMR spectra (spectra with relaxation delays of 16 s and 32 s were compared and found to be identical in terms of their relative peak areas) were taken on a 300 MHz General Electric GN-300 instrument operating at 75.4 MHz for ^{13}C, equipped with a magic angle spinning 7 mm probe (Doty Scientific). Samples were swollen to saturation in deuterated chloroform and spun at 1.667 kHz. 3000 scans were averaged for each spectrum. The amount of unreacted vinyl groups was calculated using Procop® software [3]. Molecular weights and molecular weight distributions were determined by gel permeation chromatography (Waters 515 HPLC pump / Waters 410 differential refractometer) using THF as mobile phase.

5.3 RESULTS AND DISCUSSION

The reactivity ratio of vinyltriethoxysilane was found to be two orders of magnitude lower than that of *n*-butyl acrylate [1]; therefore a direct incorporation of the silane exclusively through batch vinyl copolymerization cannot be effective. Copolymerization reactions between the two comonomers do occur to a certain extent, and the amount of unreacted VTES vinyl groups in the material (Figure 2.6) can be calculated by using the determined reactivity ratios [1,3]. The amount of unreacted vinyl groups can also be evaluated from the ^{13}C NMR spectra of the freeze dried latexes swollen in deuterated chloroform. The calculated amount of unreacted vinyl groups and the amount of vinyl groups found in the materials by NMR spectroscopy are presented in Table 5.2

Table 5.2: Calculated and Determined amount of Unreacted Silane Vinyl Groups in VTES/BA Latexes

Latex	**Unreacted VTES Double Bonds (mole % of the initial amount)**	
	Calculated	**Evaluated by ^{13}C NMR**
A51	87	-
A52	86	100
A53	70.5	94

The amount of double bonds found in the freeze-dried latexes does not match with the values calculated by using the reactivity ratios. The discrepancies can be explained if two factors are taken into account:

(a) The reactivity ratios were determined in bulk and solution copolymerization systems, with no water present, while the latexes were prepared in presence of an aqueous phase. VTES hydrolysis and subsequent condensation lead to formation of a crosslinked network. Some of the vinyl groups are thus “trapped” in the network, becoming unable to react with a propagating chain, so the amount of unreacted double bonds in the material is higher than expected according to reactivity ratios.

(b) The amounts of double bonds in the latexes were estimated by analyzing the peaks in solid-state ^{13}C NMR. This method is not capable of discerning between a vinyl group ($H_2C{=}CH\text{-}R$) and a substituted vinyl group ($H_2C{=}CR'\text{-}R$) that may result from chain transfer to silane; the carbon-carbon double bond peaks appear in the same spectral region. In this case, some of the double bonds found in the material may reflect the presence of chain-transferred moieties, rather than unreacted vinyl groups.

The analysis of the chemical structure of the reaction product of bulk copolymerization between VTES and BA can help in identifying the occurrence of a chain transfer reaction to silane. The two-dimensional NMR proton-proton correlation spectroscopy (COSY technique) [4] (Figure 5.1) was performed on the copolymer

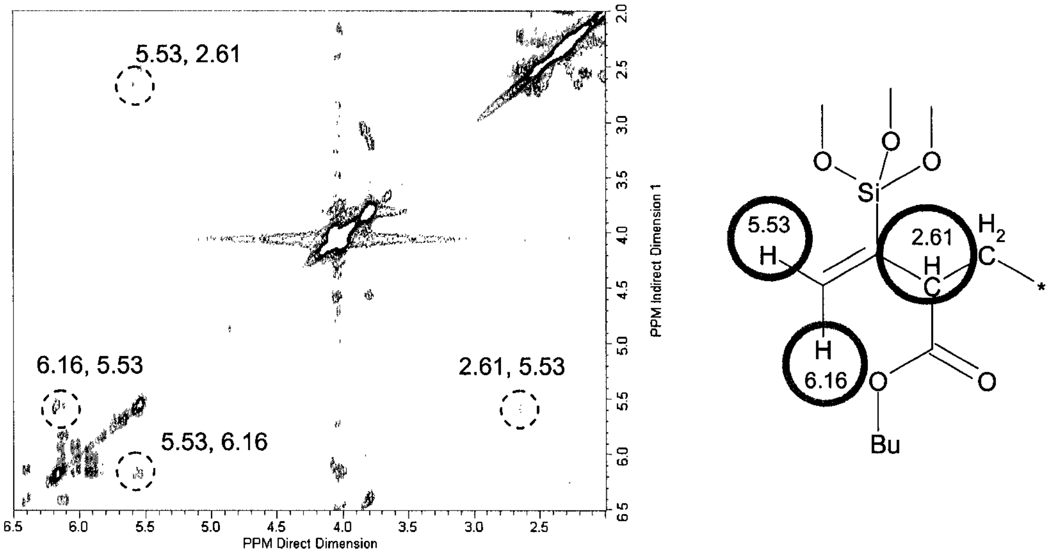

Figure 5.1: *Two-dimensional proton-proton correlation spectrum (COSY) of bulk copolymerized VTES and BA. The structure on the right was inferred from the spectrum.*

dissolved in deuterated chloroform. The 2-D spectrum features peaks at 6.16 ppm, 5.53 ppm, and 2.61 ppm, representing the fingerprint of chain-transferred moieties.

The extent of chain transfer to alkoxysilane can be evaluated by calculating the chain transfer constant [5]. The chain transfer constant to silane was determined by carrying out bulk copolymerizations of VTES with BA for different silane/acrylate ratios and by measuring the molecular weights of the resulting macromolecular species by GPC. The chain transfer constant is calculated using the equation:

$$\frac{1}{\overline{x}_n} = \frac{[S]}{[M]} \cdot C_S + \left(\frac{1}{\overline{x}_n}\right)_0 \qquad (5.1)$$

where: x_n = degree of polymerization, S = chain transfer agent (VTES), M = monomer (acrylate), and C_S = chain transfer constant. The results are shown in Figure 5.2. The value of the chain transfer constant to alkoxysilane was found to be $C_S = 1.2 \times 10^{-3}$. Compared to the chain transfer constant to monomer in the case of BA homopolymerization, $C_M = 7 \times 10^{-5}$ [6], this value represents a rather significant extent of chain transfer in the VTES/BA systems. In order to gain a better understanding of the latex particle formation and the mechanism of alkoxysilane incorporation, the role of the chain-transfer in particle formation has to be identified.

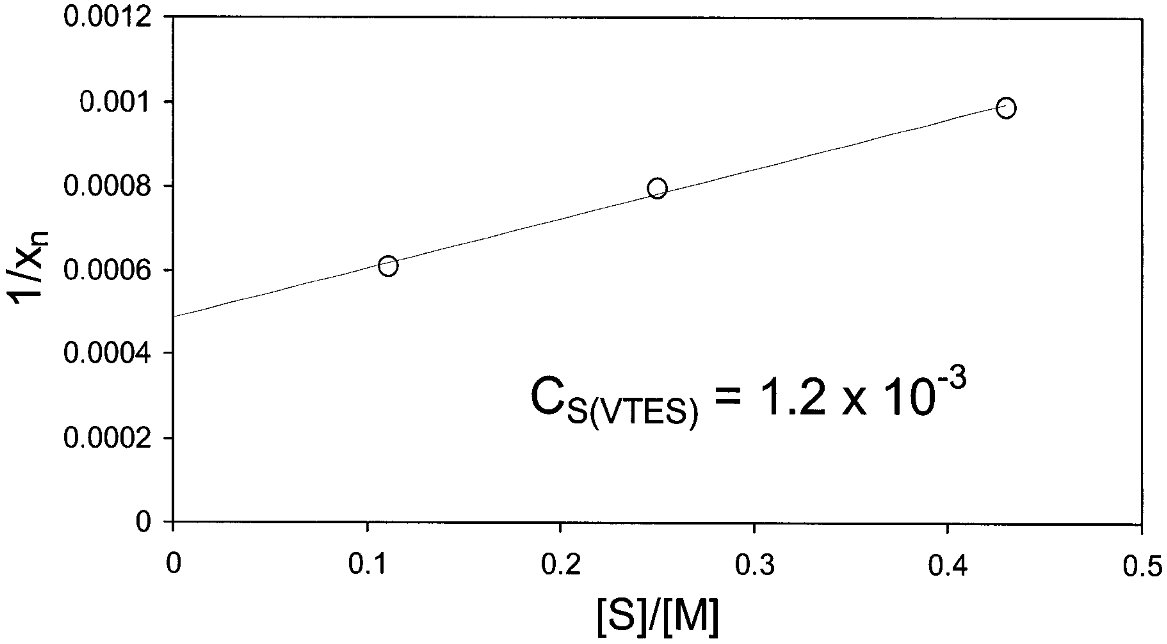

Figure 5.2: *Evaluation of the chain transfer constant to vinyltriethoxysilane from its bulk copolymerization with n-butyl acrylate. The constant is estimated from the plot of* $1/x_n$ *vs.[S]/[M].*

The one-dimensional spectra of bulk-copolymerized poly(VTES-co-BA) and the soluble fraction of miniemulsion-synthesized poly(VTES-co-BA) were compared in order to identify the implication of the chain transferred moieties in the latex particle formation. The proton peaks at 6.16 ppm and 5.53 ppm are both absent from the spectrum of the soluble fraction of the miniemulsion-synthesized poly(VTES-co-BA) (latex A52), as shown in Figure 5.3. The absence of the chain-transferred moieties from the soluble fraction of VTES/BA latexes, along with the observed absence of PBA from the same soluble fraction (Figure 4.19) will explain the retention of the polyacrylate chains in the Si-O-Si crosslinked network not only by physical entanglement, but also through chemical bonds formation as a result of the chain transfer to silane.

5.4 CONCLUSIONS

The incorporation of vinylalkoxysilane monomers into acrylate latexes by batch miniemulsion polymerization is a complex process, involving at least three different mechanisms:

(1) Vinyl copolymerization between the acrylate and the vinylalkoxysilane represents only a minor contribution to the incorporation of the alkoxysilane due to the reactivity ratios of the two monomers, that were found to be two orders of magnitude different. The very small reactivity of the vinylalkoxysilane does not favor the batch copolymerization reaction, most of the silane vinyl groups being found unreacted in the final latex.

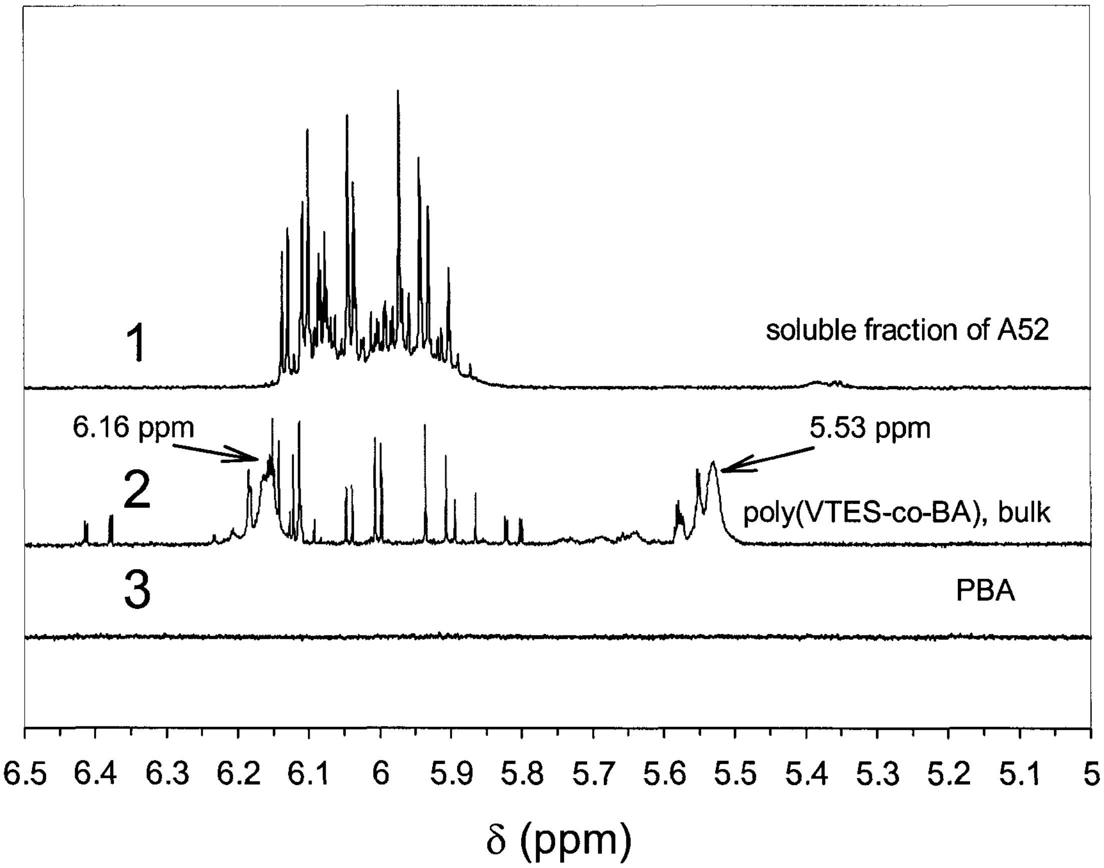

Figure 5.3: *Proton NMR spectra of: (1) soluble fraction of VTES/BA latex (20 mole % VTES), (2) bulk synthesized poly(VTES-co-BA), and (3) PBA.*

(2) Hydrolysis of the silane alkoxy groups, followed by the condensation of the resulting hydroxyl groups leads to the formation of a Si-O-Si crosslinked network that is organized in rigid domains inside the latex particle.

(3) Chain transfer to the silane vinyl group allows for the formation of chemical bonds between the crosslinked network and the PBA chains, having an important role in the incorporation of the silane moieties.

The data collected to this point allow us to describe the features of the poly(VTES-co-BA) latex particle morphology:

(1) Rigid domains of chain-transferred and Si-O-Si crosslinked VTES/BA copolymer moieties,

(2) Soft matrix of entangled, non-extractable PBA chains, and

(3) Solvent-extractable, unreacted silane moieties (siloxane oligomers) containing vinyl double bonds

5.5 REFERENCES

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CHAPTER 6

MECHANICAL PROPERTIES OF SILANE/ACRYLATE LATEX FILMS

6.1 INTRODUCTION

The studies on the incorporation of alkoxysilanes into acrylate latex systems were performed on high silane content latexes. This approach was necessary in order to be able to study the kinetics of the reactions that take place in the systems, to elucidate the incorporation mechanisms and the latex particle morphology. The accomplishment of these tasks could only be possible by using a wide range of instrumental techniques (GC, reaction calorimetry, DSC, NMR, FT-IR, microscopy, etc.) that have certain sensitivity limitations. The amount of incorporated silane moieties had to be high enough to overcome these limitations. For practical purposes (i.e., the applications of silane/acrylate latexes in coatings), one has to take advantage of the knowledge acquired by studying the high silane content latexes and to design low silane content materials with superior properties. The influence of different factors such as the initiation system, polymerization technique, and pre-polymerization of the silane monomer will be investigated with the purpose of optimizing the mechanical strength of the silane/acrylate latex films with a minimal amount of added silane.

6.2 EXPERIMENTAL

6.2.1 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 for hydroquinone and hydroquinone monomethyl ether (Chromosorb 101, mesh size 100-120 from Aldrich) for at least 48 hours. Sodium lauryl sulfate (SLS; Fisher Scientific), potassium persulfate (KPS), sodium bicarbonate, and hexadecane (Aldrich) and 2,2'-azobis(2-methyl-butyronitrile) (AMBN; VAZO 67, DuPont) were used as received. Vinyltriethoxysilane (VTES) (OSi Specialties) was used as received. Toluene, tetrahydrofurane and deuterated chloroform (Aldrich) were used as received. Deionized water was first boiled and cooled under nitrogen in order to eliminate any dissolved oxygen.

6.2.2 Methods

Miniemulsion and conventional emulsion copolymerizations were carried out in a 250 mL three-neck stirred flask (half-moon Teflon blade, 180 rpm) at 20 % solids, 60 °C for 2 hours. For miniemulsion polymerizations, the mixture was sonified for 2 minutes with a Branson 450 sonifier (power 7, 60 % duty cycle) in a 250 mL cylindrical beaker, prior to reaction [1] (Table 6.1). For the conventional emulsion polymerizations hexadecane was not added.

Table 6.1: Miniemulsion Polymerization Recipes

Ingredient		Amount
Deionized water		100 g
Surfactant (SLS)		10 mM (0.346 g)
VTES/ BA	2/98*	0.76 g VTES/25.13 g BA
	4/96*	1.52 g VTES/24.61 g BA
Hexadecane		3.7 wt % on monomers
Initiator (AMBN or KPS)		1 mole % on monomers (0.388 g AMBN or 0.541 g KPS)

*molar ratios

Particle diameters were estimated with a Nicomp C370 dynamic light scattering instrument. VTES homopolymerization was carried out in bulk, using 1 mole % AMBN as initiator. The reaction was performed in a sealed tube, under a pillow of nitrogen, at 70 °C, for 48 hours. The residual monomer was evaporated at high vacuum. Proton NMR spectra were obtained on samples dissolved in deuterated chloroform. The instrument used was a Bruker DX-500 operating at 500 MHz. Molecular weight of poly(VTES) was determined by gel permeation chromatography (Waters 515 HPLC pump / Waters 410 differential refractometer) using THF as mobile phase. Since the K and a values for the polymer are not known, the universal calibration method [2] was used. Polystyrene standards with molecular weights of 580, 3250, 28500, 156000 and 2880000 g/mol were used for the calibration curve. For polystyrene $K = 14\times10^{-3}$ ml/g, a=0.725 [3]. The intrinsic viscosity of the poly(VTES) was evaluated by viscometry (Canon 75 Übellohde viscometer). Measurements were taken at 20 °C. Latex films were cast on Tedlar® sheets and left to dry for a week at room temperature prior to being cut into specimens for tensile tests. The swelling studies were performed on the dry films using toluene as the swelling agent. The film samples were cut in rectangular shapes, weighed and measured prior to being immersed in toluene for a week. The swollen samples were then weighed again. The Flory-Rehner equation [4] was employed for the computation of the molecular weight between the crosslinks (M_C). The stress/strain behavior of the latex films was evaluated using an Instron small frame instrument (500 N load cell) in the tensile mode at an extension rate of 25 mm/min [5-7]. Specimens were cut with a standardized dye (24 mm long, 8 mm wide). Measurements from five specimens were averaged for each sample.

6.3 RESULTS AND DISCUSSION

6.3.1 Factors affecting the mechanical properties of VTES/BA latex films

Low concentrations of alkoxysilane groups are usually required to improve latex film properties, such as tensile strength and solvent resistance. Since instrument sensitivity is an issue at low alkoxysilane concentrations, high silane feed contents have been used in this study in order to gain a better understanding of the phenomena occurring in the colloidal alkoxysilane/acrylate polymeric systems. An insight of the synthesis-property relationships for the low alkoxysilane content latexes is also necessary.

VTES/BA copolymers were prepared with 2 mole % and 4 mole % VTES in the feed by conventional emulsion polymerization, using KPS as initiator and sodium bicarbonate as buffer (pH 7), by miniemulsion polymerization with KPS and sodium bicarbonate, or by miniemulsion polymerization using AMBN as initiator without adding a buffer (pH 6.2). The load/extension (stress/strain) plots for 2 mole % silane are shown in Figure 6.1 a. The same plots for 4 mole % silane are presented in Figure 6.1 b. The plots in Figure 6.1 show that the tensile strength of the latex films is strongly influenced by at least two factors: the type of polymerization (conventional emulsion vs. miniemulsion), and the initiator type (oil-soluble vs. water-soluble).

In the case of conventional versus miniemulsion polymerization using the same initiator (KPS), the lower tensile strength and the higher elongation of the miniemulsion-synthesized latex film might be a result of the plasticizing effect of hexadecane, and/or of the smaller particle size obtained for the conventional emulsion systems (81 nm and 75 nm for 2 and 4 mole % VTES, respectively in the case of conventional emulsion, vs. 100 nm and 105 nm for the miniemulsion). This can be translated into a higher particle surface area available for crosslinking upon casting a film for conventional latexes, and hence, a higher tensile strength for the conventional emulsion-synthesized latex films.

The systems containing oil-soluble initiator (AMBN) were found to have a pH value of 6.2, versus 7.0 for the buffered KPS systems. This slight advantage in the rate of acid-catalyzed hydrolysis/condensation might not be enough to explain the significant differences in the mechanical behavior in this case. The different initiation mechanisms have to be analyzed in order to understand the differences reflected in the mechanical properties.

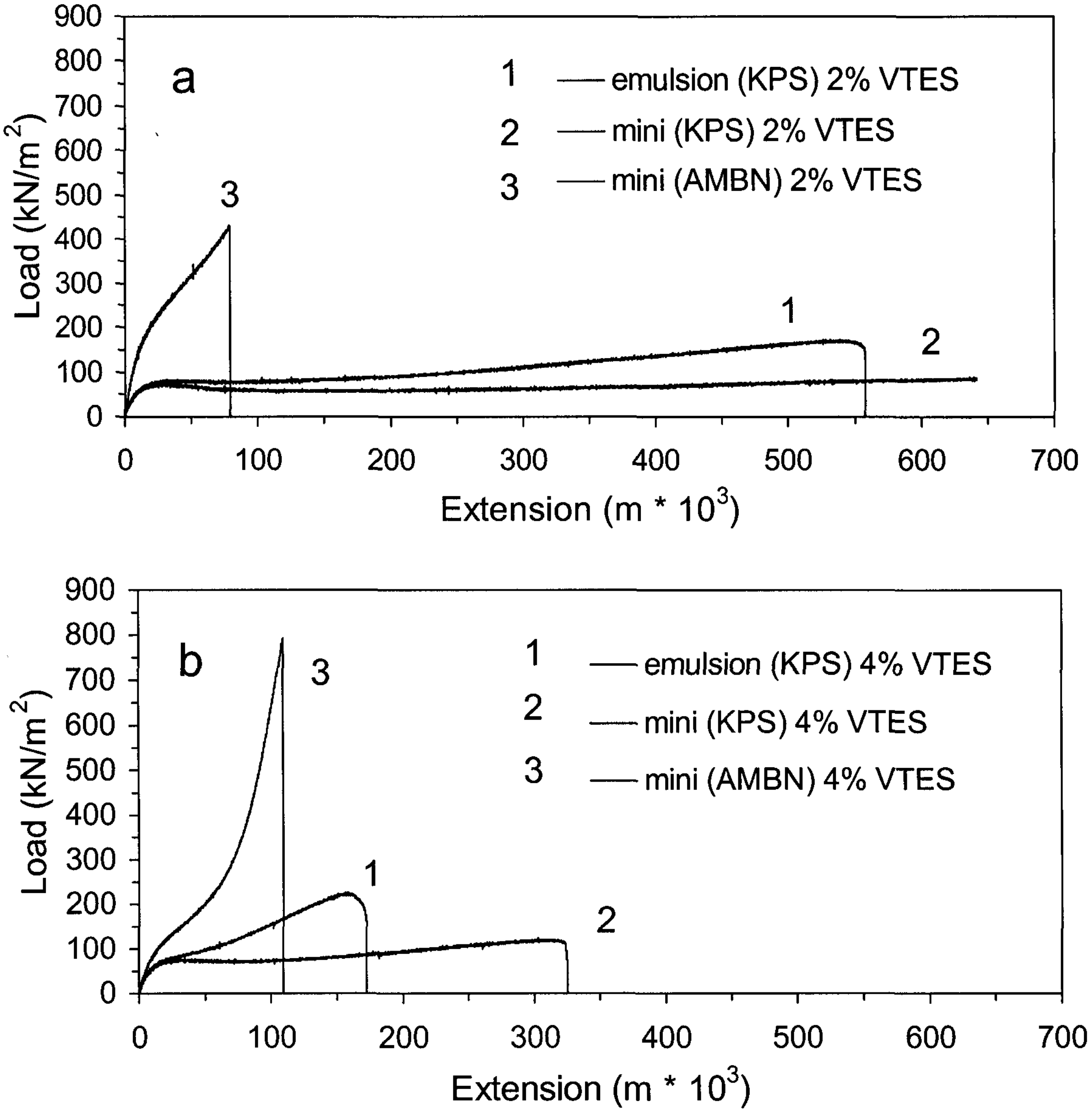

Figure 6.1: *Stress-strain curves for VTES/BA latex films. (a) 2 mole % VTES, (b) 4 mole % VTES; curve 1 – latex synthesized by conventional emulsion polymerization with KPS as initiator, curve 2 – latex synthesized by miniemulsion polymerization with KPS as initiator, curve 3 – latex synthesized by miniemulsion polymerization with AMBN as initiator.*

In the case of the water-soluble initiator (Figure 1.3 a), the radicals are being generated in the water, react with the monomer dissolved in the aqueous phase and enter the droplet upon reaching a critical chain length. Chain propagation starts from the droplet surface and hinders the VTES migration through the oil droplet, impeding the silane mobility. Therefore, the rate of VTES hydrolysis and subsequent condensation reactions will be affected. The presence of hydrolyzed silane moieties at the latex particle surface will not be favored, since it is competing with the acrylate chain propagation.

When using an oil-soluble initiator (Figure 1.3 b), the vast majority of the radicals are being formed in the oil droplet with the propagating chains uniformly distributed throughout the droplet volume. In this case, the rate of termination becomes important, the resulting short polyacrylate chains allowing the free migration of the silane moieties and their hydrolysis and subsequent condensation.

If the above hypothesis is true, then the degree of crosslinking for the films cast from latexes synthesized by using oil-soluble initiator should be higher than the same parameter in the case of the water-soluble initiator, since the longer polyacrylate chains do hinder the mobility of silane moieties and their ability to undergo hydrolysis and subsequent condensation (crosslinking). The degree of crosslinking is usually expressed as the molecular weight between crosslinks (M_C) and is calculated starting from the Flory –Rehner equation [4]

$$-\left[\ln(1-v_2)+v_2+\chi_1 v_2^2\right]=V_1 n\left[v_2^{1/3}-\frac{v_2}{2}\right] \tag{6.1}$$

$$M_C=\frac{\rho}{n} \tag{6.2}$$

where v_2 is the volume fraction of polymer in the swollen mass, V_1 is the molar volume of the solvent, χ_1 is the Flory-Huggins polymer-solvent dimensionless interaction term, n represents the number of active network chain segments per unit volume and ρ is the polymer density. The swelling experiments were carried out using toluene as swelling agent (solvent). The gel contents of the cast films were also determined. The results are synthesized in Table 6.2.

Table 6.2: Molecular Weight Between Crosslinks (M_C) and Gel Content for Films Cast from VTES/BA Latexes Prepared by Miniemulsion Polymerization with KPS and AMBN (2 mole % VTES)

Initiator	**M_C (g/mol)**	**Gel content (wt. %)**	**D_V (nm)**
KPS	297000	64	100
AMBN	10200	98	117

D_V is the volume-average latex particle diameter

It can be observed that the calculated M_C parameter is much larger in the case of water-soluble initiator and in the same time, the amount of gel in the latex film is significantly lower than in the case of oil-soluble initiator. These data are in accordance with the tensile tests results and confirm the proposed influence of the initiation mechanisms on the mechanical properties of the cast films.

6.3.2 Incorporation of poly(VTES) into acrylate latexes

The silane moieties were shown to form crosslinked domains in the silane/acrylate latex particles (Chapter 4). The occluded (domain) morphology of the particles containing rigid tri-dimensional networks does not favor further interparticle crosslinking upon film casting, since most of the silane moieties are "locked in place" by the rigid network formation.

One solution to reduce the rate of alkoxysilane hydrolysis and premature crosslinking during latex synthesis, while improving the ability of the hydrolyzed silane moieties to crosslink upon film casting, is represented by the incorporation of poly(VTES) in the poly(n-butyl acrylate) latexes, instead of the vinylalkoxysilane monomer (VTES). In this case, the mobility of the alkoxy groups and their rate of hydrolysis and subsequent condensation will be diminished. In the same time, one can obtain a continuous silane phase, instead of domains, the presence of the poly(VTES) macromolecules being able to assure a better uniformity of the silane moieties throughout the particles, their diffusion and phase separation being more difficult due to their size. Some limitations have to be taken into account though, since a very large molecular weight of the silane polymer can lead to immiscibility and phase separation from the acrylate monomer.

The radical homopolymerization of VTES was carried out in bulk using AMBN as initiator. The reaction was performed at 70 °C for 48 hours. The occurrence of vinyl polymerization was confirmed by solution ^{1}H NMR (Figure 6.2). The residual monomer was evaporated at high vacuum. The conversion was found to be 56 % by gravimetry.

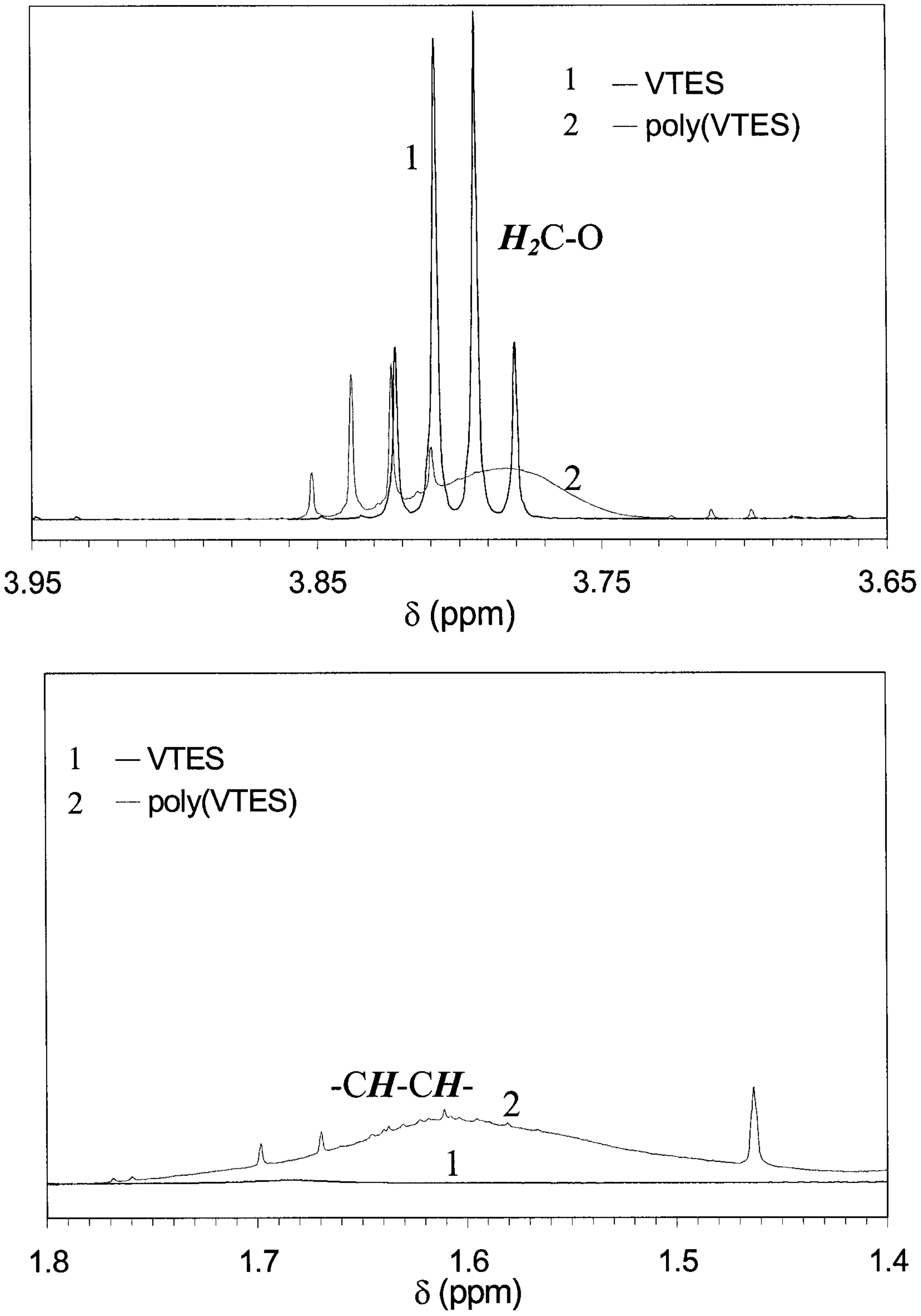

Figure 6.2: *Comparative proton NMR spectra of: (1) neat VTES, and (2) poly(VTES) synthesized by bulk free radical polymerization.*

The molecular weight of the synthesized poly(VTES) was determined by using the universal calibration method. The plots of the GPC calibration curve and viscometric evaluation of the intrinsic viscosity are presented in Figure 6.3. The resulting number-average molecular weight for the poly(VTES) is 2100 g/mol. Since the monomeric unit weighs 190.3 g/mol, the resulting degree of polymerization is 11. These oligomeric molecules are soluble in n-butyl acrylate. A mixture containing 1 part poly(VTES), 3 parts PBA and 6 parts BA inhibited with 10 ppm hydroquinone was found to be homogeneous (no phase separation was observed) after being kept 1 hour at 60 °C. Silane-containing acrylate latexes were prepared by the miniemulsion procedure using poly(VTES) instead of VTES, in the same amounts by weight. Films were cast from the latexes, and tensile tests were performed. The stress-strain curves are presented in Figure 6.4 in comparison with the curves obtained for latex films synthesized with the monomer (VTES). By using the poly(VTES) oligomer, an improvement in tensile strength and a significant increase in extension to breakage are achieved for both amounts of silane (2 mole % and 4 mole % of functional units respectively). The effect was expected and can be explained by the presence of silane oligomer molecules in the latex. These molecules provide a higher degree of *network* mobility and coherence throughout the film. There are no chemical bonds between the polyacrylate chains and the poly(VTES) oligomers, the incorporation being achieved by physical entanglements between the two macromolecular species. The values for M_C for the oligomer-containing latex films are accordingly higher and the gel content lower compared with the values found for the VTES/BA latexes (Table 6.3). The use of poly(VTES) instead of VTES in the

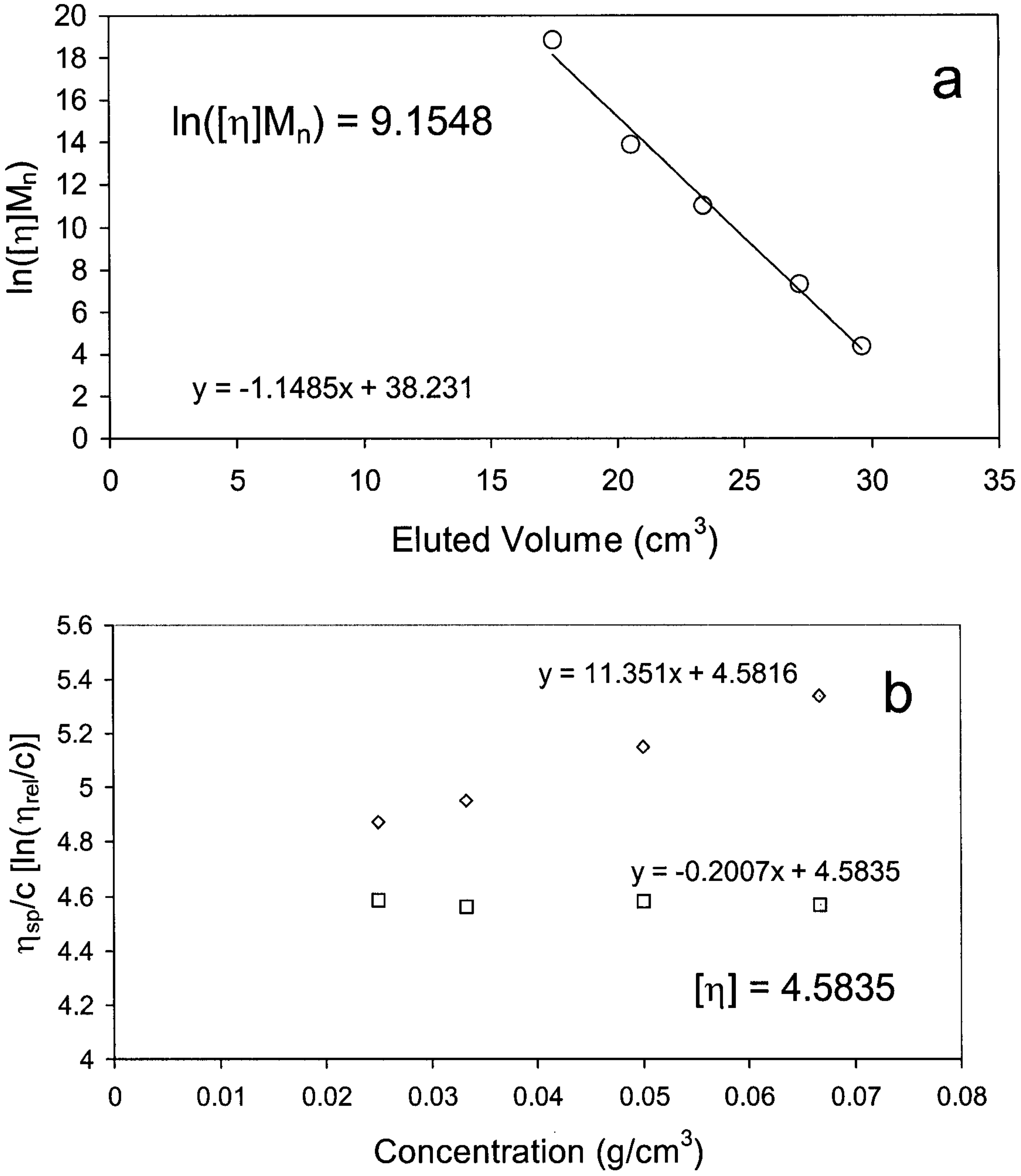

Figure 6.3: *Evaluation of the molecular weight of poly(VTES) by universal calibration method: (a) GPC calibration curve using polystyrene standards, and (b) estimation of the intrinsic viscosity.*

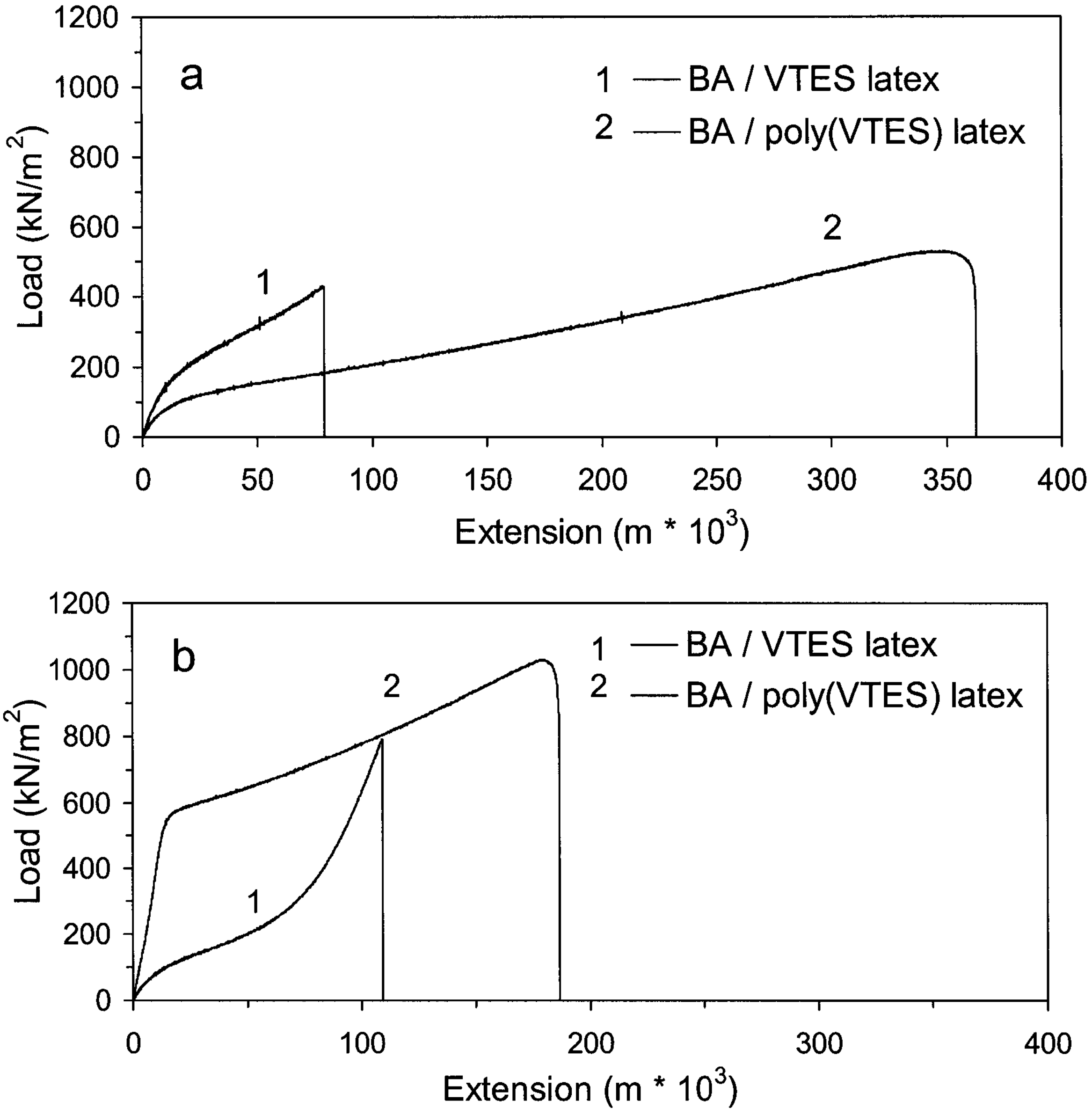

Figure 6.4: *Stress-strain curves for VTES/BA and poly(VTES)/BA latex films. (a) 2 mole % VTES, (b) 4 mole % VTES; curve 1: VTES/BA latex film, curve 2: poly(VTES)/BA latex film.*

miniemulsion incorporation of silane moieties into PBA latexes does not affect the final latex particle size (Table 6.3).

Table 6.3: Molecular Weight Between Crosslinks (M_C) and Gel Content for Films Cast from VTES/BA Latexes Prepared by Miniemulsion Polymerization with VTES and Poly(VTES) (2 mole %)

Incorporated Silane Moiety	M_C (g/mol)	Gel content (wt. %)	D_V (nm)
VTES	10200	98	117
Poly(VTES)	16200	83	118

D_V is the volume-average particle diameter

6.4. CONCLUSIONS

Mechanical properties (maximum load and maximum extension) of silane/acrylate latex films can be dramatically modified by changing the process parameters (miniemulsion vs. conventional emulsion, oil-soluble vs. water-soluble initiator, silane contents, incorporation of VTES vs. poly(VTES)).

In the case of conventional versus miniemulsion polymerization, a lower tensile strength and a higher elongation of the miniemulsion-synthesized latex films were found. The use of a water-soluble initiator in miniemulsion polymerization yields latexes with a poor tensile strength compared with that of materials synthesized with an oil-soluble initiator. The mechanical properties of latex films (tensile strength and extension) were significantly improved when a poly(VTES) oligomer was employed in latex syntheses instead of VTES.

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CHAPTER 7

GENERAL CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

7.1 General Conclusions

Miniemulsion copolymerization techniques have a real potential for incorporating high amounts of vinyltriethoxysilane into *n*-butyl acrylate latex systems by an one-step batch polymerization 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 was found to be two orders of magnitude lower than that of *n*-butyl acrylate; therefore a direct incorporation of the silane by batch vinyl copolymerization cannot be effective.

The oil-soluble AMBN with no added buffer (pH 5.5) was found to be the most suitable initiation system for the study of silane incorporation into acrylate latexes, giving good silane incorporation, and a moderate rate of alkoxysilane hydrolysis. Incorporation of silane groups into acrylate latexes is achieved by at least two mechanisms: vinyl copolymerization (to a low extent due to the unfavorable reactivity ratios), and Si-O-Si bond formation following alkoxy group hydrolysis, the mechanism that is basically responsible for the silane incorporation in miniemulsion systems. The use of APS in buffered systems (pH 6.5) does not favor this mechanism, hence the poor VTES incorporation into the latex for these systems (most of the VTES remains unreacted).

Alkoxysilane hydrolysis in miniemulsion systems depends on the acrylate hydrophobicity; the hydrolysis occurs mainly at the oil/water interface, due to the phase separation between the oil phase (acrylate monomer) and the hydrolyzing silane moieties, so that the best protection from hydrolysis (the lowest hydrolysis rate) was achieved in the VTES/BA miniemulsion reaction system, *n*-butyl acrylate being the least hydrophobic among the investigated oil phases. The more hydrophobic oil phase will "reject" the silane moieties towards the oil/water interface, determining an increase in the observed rate of hydrolysis.

The initiation system (water-soluble ammonium persulfate at pH 1.5 vs. oil-soluble 2,2'-azobis(2-methyl-butyronitrile)) does influence the mechanism of silane incorporation and particle formation, not only by the different degree of acidity induced in the environment (pH), but also by the initiation mechanism in itself. The VTES/BA latex particle morphologies depend on the pH of the system, a lower pH stimulating the silane hydrolysis and subsequent crosslinking mainly at the particle/water interface and inducing a core/shell morphology. The factors contributing to the different mobilities of the APS and AMBN-initiated latexes, expressed by the degrees of swelling, DSC traces and ^{13}C NMR spectra are a result of both the influence of the pH of the system (a low pH in the case of APS stimulates alkoxysilane hydrolysis and subsequent condensation yielding a more rigid network) and the initiation mechanisms (the AMBN-initiated systems are characterized by the formation of the radicals in the oil droplet, with a higher termination rate, hence shorter, more mobile polymer chains).

Phase separation and domain formation were found to occur in the VTES/acrylate latexes. These phenomena are dependent on the amount of alkoxysilane in the feed and on the hydrophobicity of the acrylate monomer. A higher degree of phase separation was observed for the most hydrophobic acrylate (2-ethylhexyl acrylate). The relative size of rigid, crosslinked domains in the latex was found to increase with the silane contents for the VTES/EHA systems. In the case of VTES/BA latexes, the relative size of domains does not increase with the VTES content in the feed, but rather the number of domains grows.

Latex aging was found to determine a decrease in the solubles content and an increase in the rigid fraction evaluated by NMR spin diffusion. The explanation of these phenomena was found by investigating the chemical composition of the soluble fraction in fresh latexes, that contains mostly silane moieties, probably siloxane oligomers with free hydroxyl groups that are capable of undergoing condensation reaction upon latex aging. The relative size of the rigid domains was found to decrease, most probably due to the formation of new populations of small domains resulted from the partial crosslinking of the soluble fraction. The rigid domains observed in the cross-sections of the films cast from aged latexes with high silane contents were found to have a crystalline nature and were formed in the continuous phase as a consequence of the supramolecular aggregation of tridimensional siloxane networks generated by the crosslinking of the soluble siloxane moieties that phase separate from the latex particles. The presence of such structures was also confirmed in fresh latexes at high silane contents.

The incorporation of vinylalkoxysilane monomers into acrylate latexes by batch miniemulsion polymerization is a complex process, involving at least three different mechanisms:

(1) Vinyl copolymerization between the acrylate and the vinylalkoxysilane represents a minor contribution to the alkoxysilane incorporation due to the reactivity ratios of the two monomers, that were found to differ by two orders of magnitude. The very small reactivity of the vinylalkoxysilane does not favor the batch copolymerization reaction, most of the silane vinyl groups being found unreacted in the final latex.

(2) The hydrolysis of the silane alkoxy groups, followed by the condensation of the resulting hydroxyl groups leads to the formation of a Si-O-Si crosslinked network that is organized in rigid domains inside the latex particle.

(3) The chain transfer to the silane vinyl group allows for the formation of chemical bonds between the crosslinked network and the PBA chains, having an important role in the incorporation of the silane moieties.

The features of the poly(VTES-co-BA) latex particle morphology are: (a) rigid domains of chain-transferred and Si-O-Si crosslinked VTES/BA copolymer moieties; (b) soft matrix of entangled, non-extractable PBA chains and (c) solvent-extractable, unreacted silane moieties (siloxane oligomers) containing vinyl double bonds.

Mechanical properties (maximum load and maximum extension) of silane/acrylate latex films can be dramatically modified by changing the process parameters (miniemulsion vs. conventional emulsion, oil-soluble vs. water-soluble initiator, silane contents, incorporation of VTES vs. poly(VTES)). In the case of conventional versus miniemulsion, a lower tensile strength and a higher elongation of the miniemulsion-synthesized latex films were found. The use of a water-soluble initiator in miniemulsion polymerization yields latexes with a poor tensile strength compared with that of materials synthesized with an oil-soluble initiator. The mechanical properties of latex films (tensile strength and extension) were significantly improved when a poly(VTES) oligomer was employed in latex syntheses instead of VTES.

7.2 RECOMMENDATIONS FOR FUTURE RESEARCH

The study of the incorporation of alkoxysilane monomers into model latex systems was performed on acrylate-based latexes, since the main known application for these systems (coatings) requires good film-forming materials. The next steps in this research can take advantage of the fundamental knowledge achieved and further investigate the intimate chemical structure of the silane/acrylate latexes.

The evaluation of the amount of premature crosslinking in the latex form can be done indirectly by running ^{29}Si NMR spectra on latexes. The Si-O-Si peaks can be compared with the Si-OH and Si-O-R peaks and information can be extracted that will allow an optimization of the latex synthesis process for the minimization of crosslinking. The kinteics of phase separation of crystalline aggregates in the continuous phase and latex particles can be quantified.

An improvement in the amount of silane chemically bound to the polyacrylate will be searched. Alkoxysilanes with better reactivity ratios can be tested. The synthesis of the latexes can also benefit from changes in reaction temperature, surfactant, and solids content. In the present study these factors were kept constant.

In terms of latex film properties, one may take advantage of the reactive vinyl groups and attempt to use those groups in further crosslinking reactions (by adding controlled amounts of UV or heat-initiated crosslinkers) in order to improve the mechanical resistance of the coating.

The influence of the hexadecane on the latex particle morphology mechanical properties of the latex films and the ability of poly(VTES) to act as a costabilizer in absence of hexadecane are also recommended to be investigated.

An acrylate/alkoxysilane copolymer (synthesized in bulk or solution) can be employed as an alternative to the VTES in the miniemulsion systems in order to gain a better control on the hydrolysis of the alkoxy groups.

The role of hexadecane in the particle morphology of latexes prepared with poly(alkoxysilane) or acrylate/alkoxysilane copolymers can be investigated. Can these oligomers act as costabilizers?

The changes in mechanical properties of the acrylate/alkoxysilane latexes are to be compared to the changes induced by a silica filler mixed into the latex. Morphological studies on the two types of materials will explain how the structure-properties relationships work in these materials.

APPENDIX

Influence of Hexadecane on Mechanical Behavior of Poly(VTES)/BA Latex Films

The use of poly(VTES) for improving mechanical properties of silane/acrylate latex films (Chapter 6) was taken a step further by observing that the characteristics of the polymerized alkoxysilane (low molecular weight, miscibility with the acrylate monomer) might allow its employment as a miniemulsion costabilizer, even without hexadecane present in the system. If this oligomer can play a costabilizing role and the latexes obtained are stable, at least one important objective, the minimization of the volatile organic compounds in the latex, can be achieved by eliminating hexadecane from the miniemulsion recipe. Poly(VTES)/BA latexes with 2 mole % (on monomeric units) of poly(VTES) were synthesized as described in Chapter 6, but without adding hexadecane. The obtained latex was stable, with no significant amount of coagulum. To examine the resulting stress/strain curve of the material, a film was cast from the latex on a Tedlar® sheet, specimens were cut and a mechanical test was run as shown in Chapter 6. The load/extension curve is plotted in Figure A1 in comparison with the load/extension curve for the latex prepared with the same amount of poly(VTES), but containing hexadecane. The tensile strenght of the latex films increases significantly by elimination of hexadecane, and in the same time the elongation to breakage decreases. This evolution can be explained by the plasticizing effect of hexadecane and by the compatibility between hexadecane and poly(VTES). If the two do not have affinity for each other, the

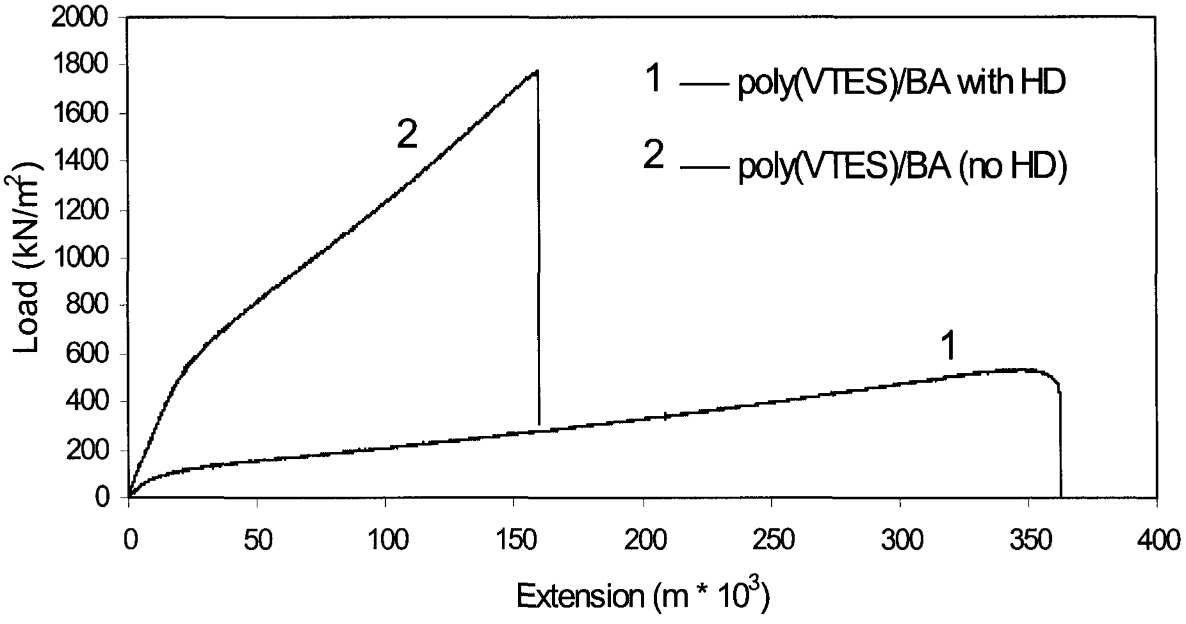

Figure A1: *Stress-strain curves for poly(VTES)/BA latex films: (1) using hexadecane as costabilizer, and (2) without hexadecane.*

polymer will adopt a "coiled" conformation, and its ability to contribute to the increase in the tensile strength of the film will be significantly affected. Other effects, such as differences in particle sizes and swelling capabilities in the presence of hexadecane may also play an important role in the final mechanical strength of the films. The M_C parameter and the soluble contents were evaluated for the poly(VTES)/BA latex prepared without hexadecane and are shown in Table A1.

Table A1: Molecular Weight Between Crosslinks (M_C) and Gel Content for Films Cast from poly(VTES/BA) (2 mole % of monomeric units) Latexes Prepared by Miniemulsion Polymerization with and without Hexadecane

HD as costabilizer	**M_C (g/mol)**	**Gel content (wt. %)**	**D_V (nm)**
Yes	16200	83	118
No	7500	77	78

D_V is the volume-average particle diameter

In order to verify if the plasticizing effect of hexadecane does have the expected influence on the latex film properties, a proportional amount of HD was added to a poly(VTES)/BA latex initially prepared without HD. The particles have swollen and the latex coagulated. A different approach has to be used by swelling the cast latex films with proportional amounts of hexadecane. The stress/strain curves of these films can be analyzed and compared with those from latexes prepared with hexadecane as costabilizer and without hexadecane (Figure A1). The plasticizing effect of hexadecane can then be confirmed (or not) to have the proposed effect on the mechanical behavior of the latex films. Even though the synthesis-properties relationships are not yet fully elucidated, an encouraging increase in the mechanical strength of the silane/acrylate latex films was achieved for small silane contents by small changes in the reaction conditions.

Alkoxysilane Behavior in the Presence of a Water-dispersed Non-polymerizable Oil Phase

The hydrolysis of an alkoxysilane in the presence of an oil phase in miniemulsion systems was found to be dependent on the hydrophobicity of the oil phase (Chapter 3). The more hydrophobic the oil phase, the more it "rejected" the alkoxysilane to the droplet surface, allowing it to come into contact with the surrounding aqueous phase and undergo hydrolysis. This concept was used in an attempt to incorporate a highly hydrophobic oil phase (hexadecane) into crosslinked, silane-based particles. The method consists of mixing the alkoxysilane with hexadecane, dispersing the oil phase in water, and dropping the pH to trigger the hydrolysis and the subsequent crosslinking. The expected result is a population of surface-crosslinked particles containing the hexadecane as the core material. The alkoxysilanes used for the screening experiments were ethyltriethoxysilane (ETES), octyltriethoxysilane (OTES) and vinyltriethoxysilane (VTES). The screening series contain silane dispersions with and without hexadecane present, preemulsified (by sonification), and synthesized without the use of the sonifier. Figure A2 presents an SEM image of the particles obtained by dispersing ETES in water by magnetic stirring at pH 1.5.

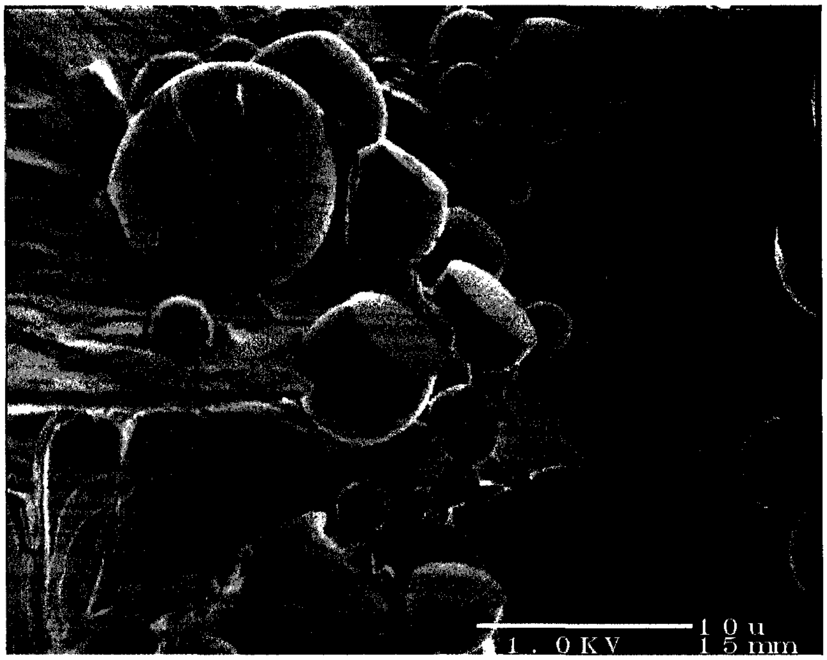

Figure A2: *Scanning electron micrograph of ETES dispersion synthesized by magnetic stirring at pH 1.5 (10 μm bar).*

The dispersion of OTES in water by magnetic stirring at pH 1.5 yields rectangular structures (lamellar organization) (Figure A3).

The sonification approach also yields lamellar structures both in the case of OTES/hexadecane (Figure A4) and ETES/hexadecane dispersions in water/SLS (10 mM SLS) (Figure A5) Spherical particles were obtained under the same conditions when using VTES as the silane moiety (Figure A6). For the alkoxysilane/hexadecane systems investigated to date, the oil phase supernatant obtained was found to contain exclusively hexadecane as measured by ^{1}H NMR after 24 hours. Further experiments can continue with the purpose of finding an optimum set of conditions for obtaining good hexadecane incorporation into spherical crosslinked silane-based particles.

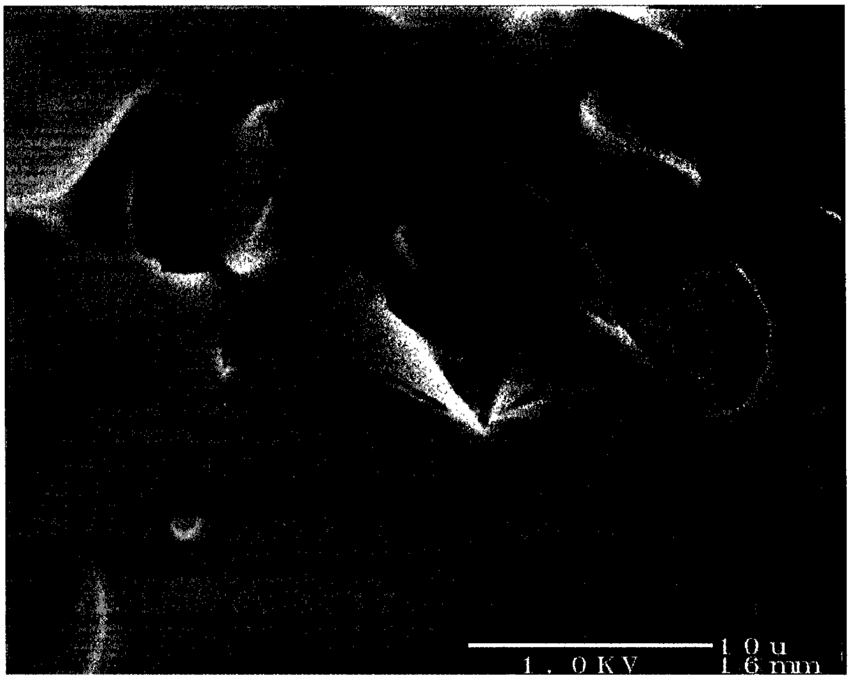

Figure A3: *Scanning electron micrograph of OTES dispersion synthesized by magnetic stirring at pH 1.5 (1 μm bar).*

Figure A4: *Scanning electron micrograph of OTES/hexadecane dispersion synthesized by sonification and magnetic stirring at pH 1.5 (1 μm bar).*

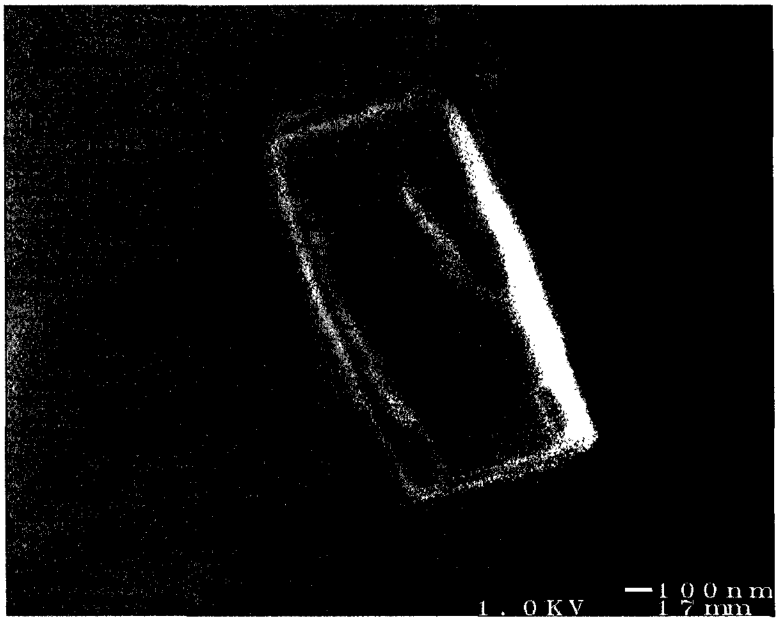

Figure A5: *Scanning electron micrograph of ETES/hexadecane dispersion synthesized by sonification and magnetic stirring at pH 1.5 (0.1 μm bar).*

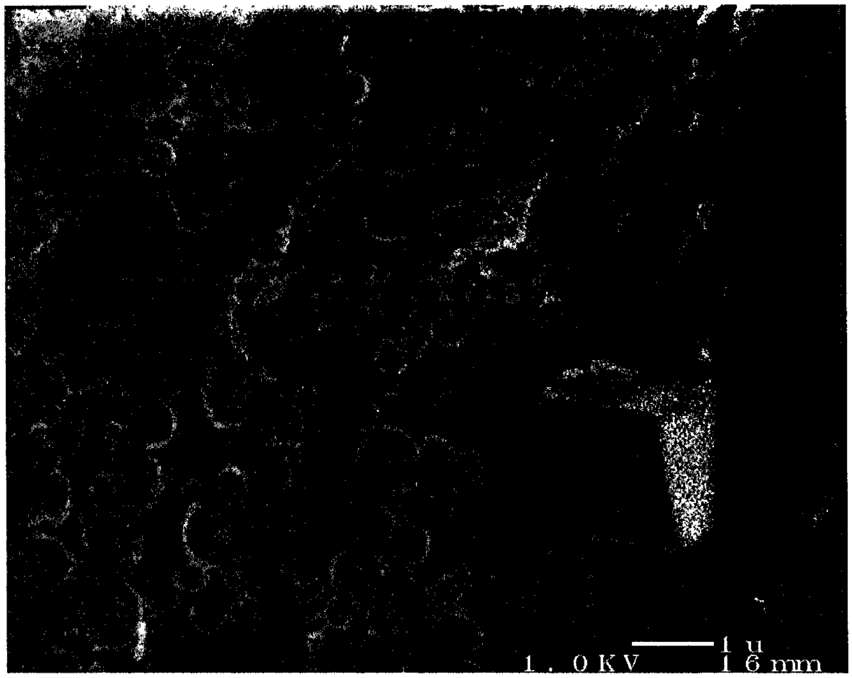

Figure A6: *Scanning electron micrograph of VTES/hexadecane dispersion synthesized by sonification and magnetic stirring at pH 1.5 (1 μm bar).*

VITA

Ioan Marcu was born in 1968 in Iasi, Romania to Mihai and Cynthia Marcu. He pursued his undergraduate studies at the "Gh.Asachi" Technical University of Iasi in the field of Engineering of Macromolecular Compounds. After earning his Diploma of Engineer, in 1993, he obtained a full time position as teaching assistant, then assistant professor of Analytical Chemistry at the University of Agricultural Sciences and Veterinary Medicine of Iasi. In 1994 he took a part time position as associate research scientist in the Department of Macromolecules of the Technical University of Iasi, working on stimuli-responsive polymers. In 1997 he married Irina and in 1999 their daughter Valeria was born. In 1999 he started his graduate studies at Lehigh University in the Department of Chemical Engineering, opting for the Ph.D. program in Polymer Science and Engineering within the Emulsion Polymers Institute. His research encompassed the study of incorporation of alkoxysilanes into acrylate latexes by miniemulsion polymerization, as well as instrumental analysis of polymeric materials. He has also been a teaching assistant in the Polymer Synthesis and Characterization Laboratory and the Unitary Operations Laboratory. He co-authored five papers published in U.S. and international journals, four papers in Romanian journals and two laboratory textbooks of chemical analysis published in Romanian. After graduation, Ioan will join Noveon Inc. in Cleveland, Ohio, as a research scientist.