NMR and Electron Microscopic Investigation of Polymerized Coatings Prepared from Methacrylate-Functionalized Silica in an Acrylic Monomer Matrix

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Coating formulations comprised of [(methacryloxy)propyl]trimethoxysilane-functionalized colloidal silica in hexanediol diacrylate can exhibit two problems that are detrimental to their application. Higher viscosity, which hinders ease of application, has been found by transmission electron microscopy (TEM) to arise primarily from the presence of agglomerated colloidal silica. Gel formation also results in higher viscosity of the formulation. TEM and solid-state ^{13}C and ^{29}Si NMR spectroscopy showed that gelation was due to polymerization of the acrylates, with reaction at the carbon–carbon double bond of the methacrylate more prevalent than reaction of the acrylate functionality.

Introduction

Paint and coatings represent a multibillion dollar industry.[1] Coatings provide resistance to damage due to weathering and abrasion for plastic substrates[2] ensuring years of outdoor life when appropriately coated. Likewise, substrates can be rendered scratch and wear resistant when abrasion resistant coatings are applied.

Many paints and coatings have relied on solvent-containing delivery systems. For environmental reasons 100% solids, UV-curable coatings are quite desirable. Ideally these coatings should be low viscosity and easy to apply and then cure rapidly with low-energy utilization. Finally, the cure of these types of coatings should not result in the release of any harmful volatile organic compounds (VOC's).[3-7]

Surface modification of silica is well-known and is a convenient method for combining silica with an organic matrix.[8-12] Very high loadings of silica in an organic carrier can be obtained using colloidal silica. Functionalized silica was first described in the 1950s by Iler and others.[13-17] Subsequent work on functionalized colloidal silica has employed silane coupling agents.[18-20]

In the 1980s several reports described the preparation of UV curable coating formulations containing organofunctionalized colloidal silica in an acrylic matrix.[21-23] The process gives a product with up to 40% by weight colloidal silica. If the silica has functionality which is chemically different from the matrix, phase separation can occur. If, however, the functionality is chemically similar to the matrix, compatibilization occurs and a clear coating is obtained. For example, colloidal silica functionalized with a methacrylate is compatible with the acrylic matrix. Failures of formulations of this type include high viscosity and/or gelation which render the coating impossible to apply. This report describes our efforts to understand the mechanisms of failure of a UV-curable coating of this type.

Experimental Section

Inputs. Nalco 1034A was obtained from the Nalco Corp. Lot CM011 had a viscosity of 10 cP and gave acceptable product. Lot BN010 had a viscosity >60 cP and gave unac-

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ceptable product. MAPTMS was obtained from several sources (Alfa, Huls, Gelest, and Aldrich) and was used without purification. MEHQ was recrystallized from water.

Preparation of 1. A 1 L, single-necked flask was charged with *i*-PrOH (200 mL), Nalco 1034A (86.9 g, 29.5 g SiO_2, 57.4 mL of H_2O), MAPTMS (13 g, delivers 8.9 g of hydrolysate), and MEHQ (0.07 g). The mixture was heated using an oil bath for 1 h at 60–80 °C. After heating, the remaining *i*-PrOH (375 mL) and HDDA (36.2 g) were added. Water/*i*-PrOH was removed using a rotary evaporator (rotovap) with bath temperature set at 60 °C and with a vacuum maintained above 100 mmHg. The vent of the rotovap was cracked open to permit an air bleed.

Lightly gelled acrylates were prepared by combining HDDA (36.2 g), MAPTMS (13 g), water (57 mL), and *i*-PrOH (570 mL) in a 1 L single-neck flask and then subjecting the mixture to vacuum stripping on the rotovap. In this case full house vacuum was applied with a slight N_2 bleed.

Bulk polymerized acrylates were prepared by heating with benzoylperoxide. A mixture of HDDA (36.2 g), MAPTMS (13 g) and benzoyl peroxide (0.5 g) were combined in a flask and heated. Rapid and exothermic formation of a hard solid occurred.

Analytical Measurements. Light scattering was carried out using a Nicomp submicron laser light scattering instrument. Viscosities were measured using a Brookfield Model DV II cone and plate viscometer employing a no. 40 spindle. Solution- and solid-state NMR spectra were obtained on Varian XL-300 and GE Omega 300 WB NMR spectrometers, respectively, operating at 75.4 MHz for ^{13}C and 59.7 MHz for ^{29}Si. Detailed NMR spectral parameters are noted in the figure captions.

TEM. TEM analysis of colloidal silica agglomeration in the lightly gelled and bulk polymerized acrylates were performed by first dissolving the acrylate in *i*-PrOH and placing a drop of this solution on a carbon membrane coated copper grid. The *i*-PrOH is evaporated off, leaving behind the colloidal silica. These samples were examined in a Hitachi H-600 STEM operated at 100 kV. A large number of TEM micrographs were taken at random locations to insure statistical accuracy.

TEM micrographs were digitized using a macrolens equipped camera interfaced to an Image Analyzer (Clemex 1024). There were two magnifications used for this study: 200 000× magnification for determining the primary particle diameter and 50 000× magnification for quantifying the agglomerate dimensions.

The primary particle diameters were quantified by first segmenting the characteristic gray level range of the colloidal silica to distinguish between the silica and the background. Some spurious background noise was eliminated by filtering small features and using an octagonal structuring element to erode/dilate the features of interest. An ultimate erosion algorithm was then used to separate agglomerated particles. In simple terms, this algorithm erodes features until separated and then reconstructs the feature with a contiguous line of pixels separating parts of a feature which had a significant amount of changing slopes (e.g., a line of touching spherical particles). This algorithm does not work well with agglomerates which fold in on themselves since an individual particle periphery may be almost completely indistinguishable. There were a sufficient number of single particles and agglomerates which worked well with the ultimate erosion algorithm to obtain an average primary particle diameter without any manual image editing.

The agglomerates were also segmented to distinguish between the colloidal silica and background. Since the agglomerates tended to be solid masses of particles when agglomerated, a hole filling algorithm was used to "fill in" areas which did not have sufficient contrast. The area of each agglomerate was then measured for several micrographs.

Results and Discussion

The coating of interest in this study, **1**, contained colloidal silica functionalized with [(methacryloxy)-propyl]trimethoxysilane (MAPTMS) in a matrix of hexanediol diacrylate (HDDA). The process for making **1** is shown in Scheme 1.[21] First, aqueous colloidal silica is combined with *i*-PrOH and MAPTMS and heated. HDDA is then added to the mixture, and water/*i*-PrOH is removed as an azeotrope. Sufficient *i*-PrOH is added to remove all of the water in the system. In the ideal case, upon successful removal of water and *i*-PrOH, a free flowing liquid is obtained with a viscosity <100 cP.

Scheme 1

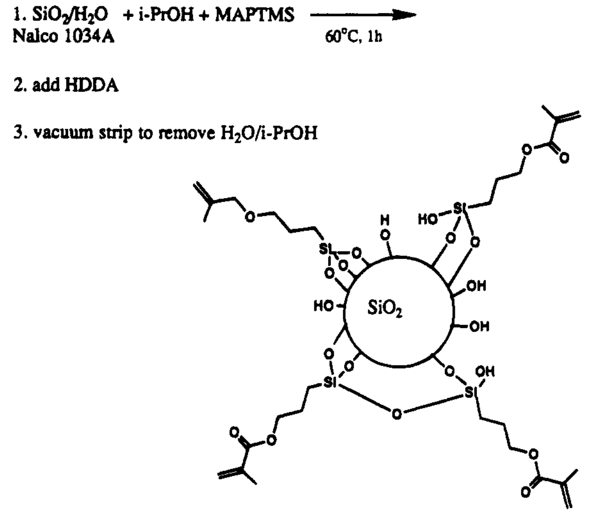
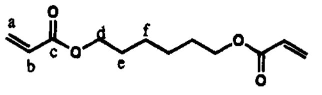
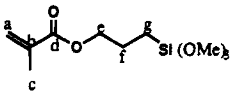


Table 1. Parameters for Light-Scattering and Light-Scattering Data

sample	viscosity (cP)	RI	% solids	light-scattering data (nm) % in parentheses
1A in i-PrOH	3.66	1.383		7(4), 16(26), 100 (70)
1B	3.14	1.383		2(1), 12(41), 47(58)
Nalco 1034A, lot BN010	68.6	1.358	34.7	7.7(10), 38 (36), 400 (54)
Nalco 1034A, lot CM011	10	1.357	34.5	1.1(4), 13.3(34), 54(62)



HDDA



MAPTMS

During the vacuum stripping step, however, prepolymerization of the formulation can occur if care is not taken to prevent it. The method shown in Scheme 1 employed methyl hydroquinone (MEHQ) as a gel inhibitor. MEHQ is well-known in the acrylate industry to require oxygen to be effective as an inhibitor.[24] The need for oxygen necessitated aeration during the manufacturing process for **1** and large scaleups often failed due to the difficulty of ensuring complete aeration in large-volume reactors. When oxygen deficiency occurred during heating, the acrylates gelled. Initial efforts to understand the formulation problems focused on the starting materials.

MEHQ

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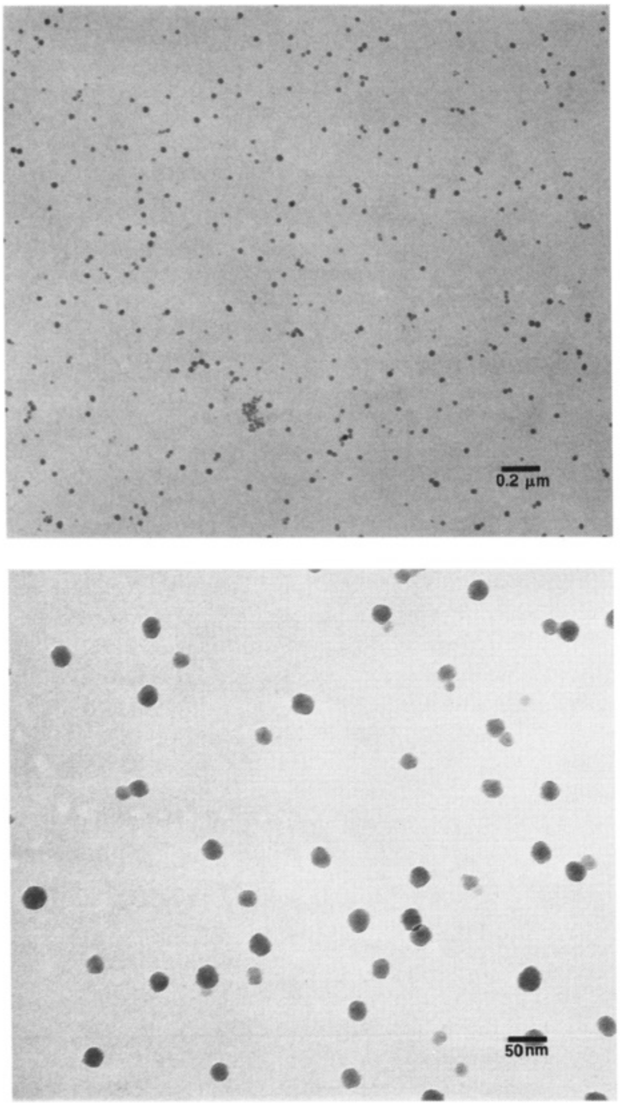

Figure 1. TEM of **1B** made with a "good" batch of colloidal silica. Top: low resolution. Bottom: higher resolution.

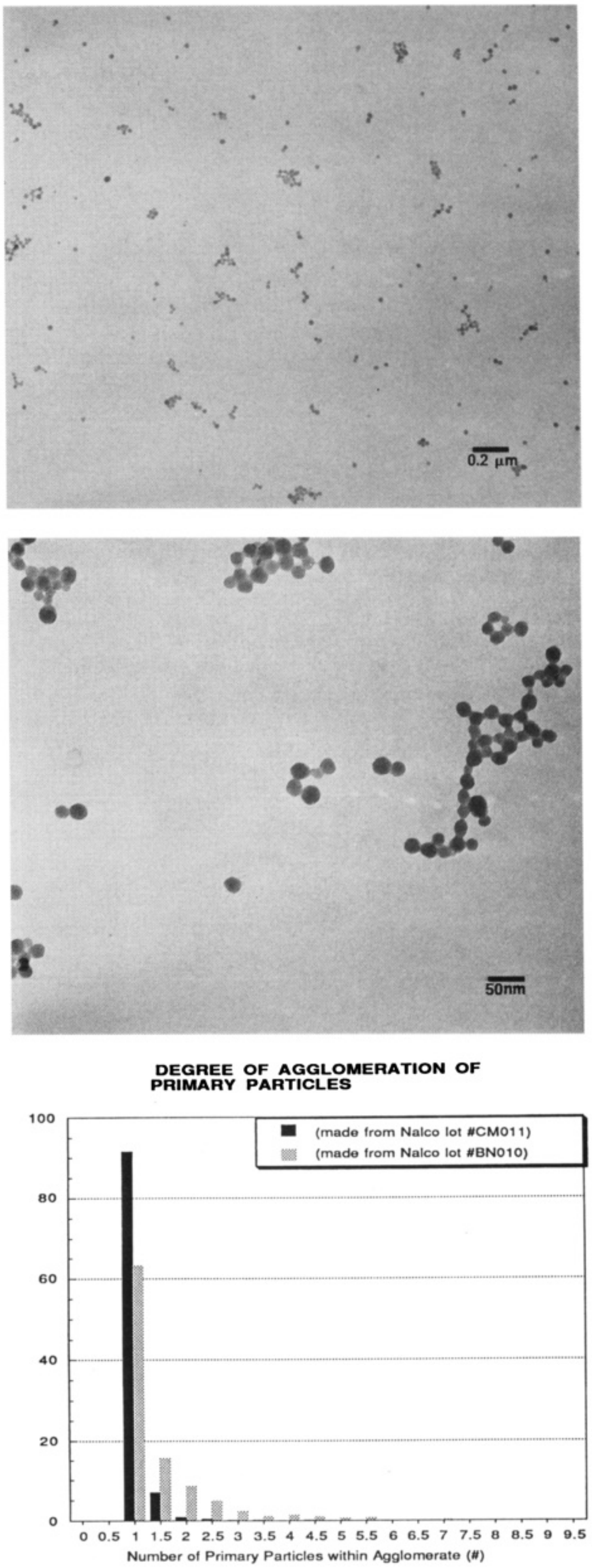

Figure 2. TEM of **1A** made with "old" batch of colloidal silica. Histogram (lower) comparing **1A** and **1B**. Top: low resolution. Middle: higher resolution.

Effect of the Colloidal Silica. The typical procedure for making **1** (Scheme 1) required the following inputs. Nalco 1034A is a 34 wt % aqueous dispersion of colloidal silica with a pH of 3–4 and a reported average particle size of 20 nm. The process for making **1** yields a colloidal silica grafted with MAPTMS in an HDDA matrix.[25-27] When an old lot (>6 months) of Nalco 1034A, BN010, was used to make **1**, a formulation with a viscosity of 920 cP was obtained (**1A**). Acceptable viscosity for **1** is <100 cP with 50–90 cP preferred due to its use as a flowable coating formulation. When a second, newer lot of Nalco 1034A, CM011, was employed in the coating preparation, the viscosity of the finished product was <100 cP (**1B**). The two lots of Nalco 1034A and formulations **1A** and **1B** which were prepared with them were analyzed by laser light scattering. The light-scattering measurements required measurement of viscosity (η) and refractive index (RI) for the liquid under examination. Their values revealed important differences between the two lots, as shown in Table 1. Since the instrument used for measuring light scattering was limited to fluids with a viscosity <100 cP, *i*-PrOH solutions of the **1A** and **1B** formulations were used in the light scattering analyses.

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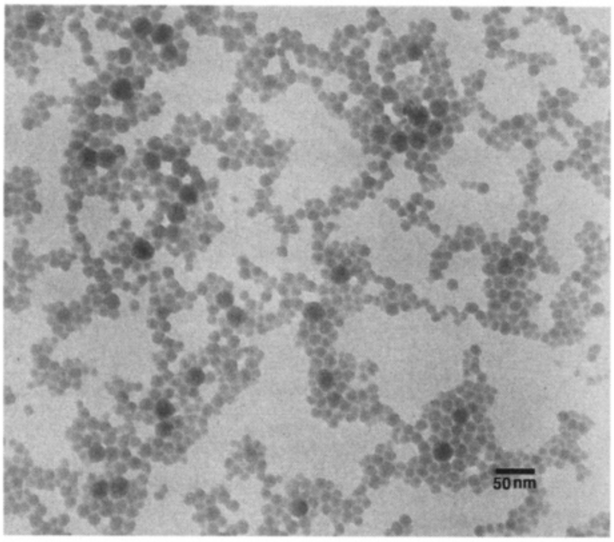
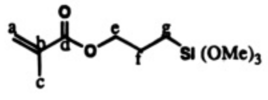
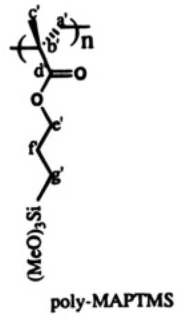


Figure 3. TEM of **1** that gelled upon vacuum stripping; note apparent polymer border on each particle.

Table 2. ^{13}C NMR Chemical Shifts for [(Methacryloxy)propyl]trimethoxysilane Monomer and Methacrylate Polymerization Product^a



MAPTMS

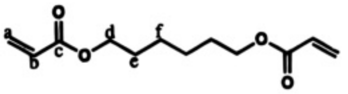


poly-MAPTMS

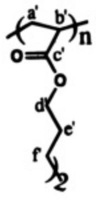
carbon	δ_C (ppm)^b	carbon	δ_C (ppm)^c
a	125.0	**a′**	**45.0**
b	136.3	**b′**	**22.7**
c	18.1	c′	19.2
d	**167.2**	**d′**	**176.3**
e	66.3	e′	67.0
f	21.9	f′	22.0
g	5.1	g′	5.8
MeO	50.3	MeO′	50.3

^{a} Poly-MAPTMS has strong resonances at 45, 22.7, and 176.3 (carbonyl). ^{b} Data from solution and MAS spectra. ^{c} Data from CPMAS spectrum.

Table 3. ^{13}C NMR Chemical Shifts for HDDA and Acrylate Polymerization Product



HDDA



poly-HDDA

carbon	δ_C (ppm)^a	carbon	δ_C (ppm)^b
a	130.0	**a′**	**40.0**
b	126.3	**b′**	**40.0**
c	**166.0**	**c′**	**173.0**
d	64.0	d′	65.0
e	28.3	e′	27.0
f	25.4	f′	27.0

^{a,b} As in Table 2.

The data in Table 1 show that the different lots of Nalco 1034A had significantly different viscosities as well as much larger particles as shown by light scattering. The formulations of **1** in *i*-PrOH also had significant differences in their particle sizes. ^{29}Si NMR analysis of formulations of **1** made with either lot of Nalco 1034A had equivalent spectra consistent with a similar degree of condensation of MAPTMS about the colloidal silica.[28,29] Thus it was concluded that the origin of the high viscosity for the formulation made from lot BN010 was due to the agglomeration of the colloidal silica. TEM analysis confirmed the high degree of silica agglomeration in **1A** vs **1B**. Figure 1 shows the **1B** sample made from CM011, whose viscosity was about 70 cP. Figure 2 shows a TEM of **1A** made using BN010. In this case a higher degree of agglomeration of the primary particles was noted. The histogram in Figure 2, which was generated by image analysis of several photographs from this sample and from **1**, shows the degree of agglomeration of the primary particles. Note also that the agglomerates were overlapping in **1A**, suggesting that agglomeration occurred in the original Nalco sample and not by polymerization of a surface methacrylate; vide infra.

Acrylate Polymerization. The procedure shown in Scheme 1 reproducibly gave gelled product even in the presence of MEHQ if the vacuum stripping process was carried out in the absence of air. Vacuum stripping with intentional aeration, however, gave a product with acceptable viscosity, <90 cP. Free radical polymerization was considered the likely origin for failure upon vacuum stripping in the absence of air.

TEM analysis was carried out for samples of **1** that gelled upon vacuum stripping under anaerobic conditions. Figure 3 shows that these agglomerated particles appeared to be polymer coated, suggesting that the agglomeration was due to polymerization of the surface methacrylate (MAPTMS, with or without the matrix acrylate HDDA) rather than gross agglomeration of the colloidal silica.

Solid-state and solution ^{29}Si and ^{13}C NMR were employed to determine the exact nature of the polymerization process that occurred during failure.[30,31] Cross-polarization magic-angle spinning (CPMAS) with a short contact time is a solid-state NMR technique that is preferentially sensitive to highly cross-linked regions while at the same time having a reduced sensitivity to highly mobile regions of a sample.[32-34] The complementary technique to CPMAS is a simple one-pulse sequence, analogous to that used to obtain solution NMR spectra, but with magic-angle spinning (FTMAS). Under these conditions and using appropriate pulse delays, semiquantitative data can be obtained. Solution

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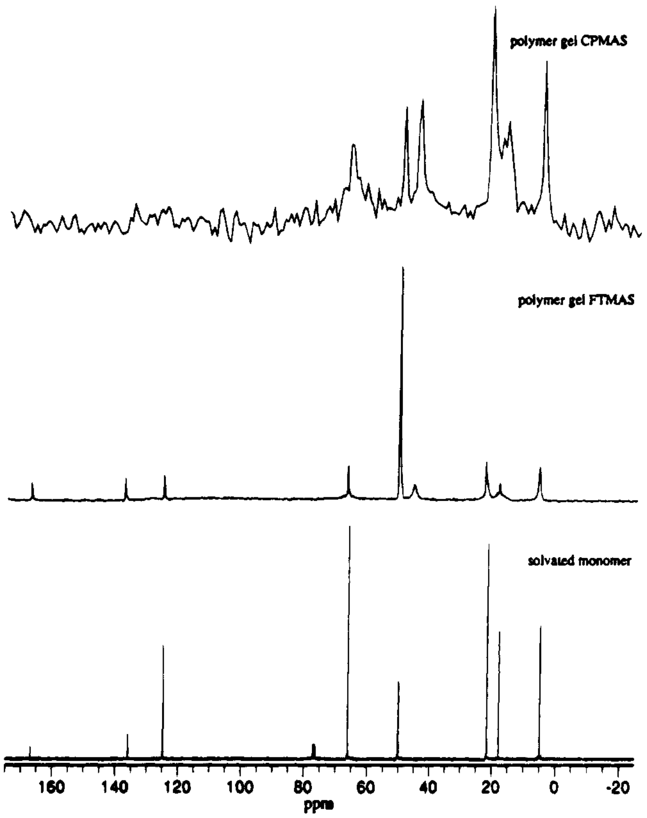

Figure 4. Comparison of ^{13}C NMR spectra of the MAPTMS monomer (in solution) with FTMAS and CPMAS spectra of the polymer gel. For the CPMAS spectrum, 10 000 scans were accumulated using a cross polarization contact time of 1.8 ms with carbon and proton rf fields of 54 kHz, collecting one scan per second. The FTMAS spectrum used the same decoupling field strength, collecting 1000 scans with 90° carbon pulses every 15 s. For both the FTMAS and CPMAS experiments, the sample was spun at ~8 kHz. The solution state monomer spectrum was obtained in $CDCl_3$ accumulating 1232, 2 s scans using ~50° observe pulses and Waltz-16 broadband proton decoupling.

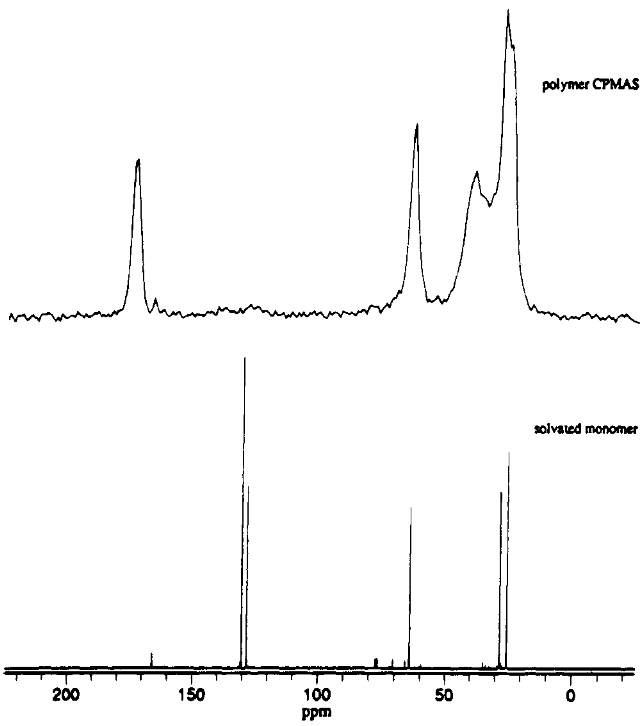

Figure 5. Comparison of ^{13}C NMR spectra of the HDDA monomer (in solution) along with the CPMAS spectrum of the polymer. For the CPMAS spectrum, 10 000 scans were accumulated using a cross polarization contact time of 2.5 ms with carbon and proton rf fields of 54 kHz, collecting one scan per second. The sample was spun at ~8 kHz. The solution state monomer spectrum was obtained in $CDCl_3$ accumulating 1032, 2 s scans using ~50° observe pulses and Waltz-16 broadband proton decoupling.

and MAS spectra were measured for HDDA, MAPTMS, and mixtures of the two. In a few cases, solutions were examined in the solid-state NMR probe employing a homemade polyethylene insert. Each formulation was then bulk polymerized by heating in the presence of 1 wt % benzoyl peroxide. As shown in Tables 2 and 3, the polymerized regions of MAPTMS and HDDA could be distinguished from the unpolymerized monomer. For MAPTMS the carbonyl resonance at 167.2 ppm shifted downfield to 176.3 ppm upon polymerization. The polymerized MAPTMS also had new resonances at 22.7 and 45 ppm. Figure 4 shows the solution, FTMAS, and CPMAS ^{13}C NMR spectra for monomeric and polymerized MAPTMS, respectively. For HDDA, Table 3, polymerization resulted in a shift in the carbonyl from 166 to 173 ppm. Furthermore poly-HDDA had a new resonance at 40 ppm; Figure 5 shows the solution and CPMAS ^{13}C NMR spectra for monomeric and polymerized HDDA.

MAPTMS and HDDA were combined in a molar proportion identical to that used to prepare **1**. This mixture was added to a water/*i*-PrOH mixture also identical to that used in **1** except without colloidal silica. This mixture was then subjected to vacuum stripping under a N_2 atmosphere. A lightly cross-linked gel, **2**, was obtained by this process. The solution NMR (swell in $CDCl_3$) and solid-state FTMAS spectra of **2** were equivalent and looked like a mixture of the two monomers, MAPTMS and HDDA (Figure 6). The ^{13}C CPMAS spectrum of **2** had a low-intensity, broad resonance at 30–40 ppm. These results suggested that the lightly cross-linked gel formed, as expected, with very few cross-links, producing the low-intensity signal under cross-polarization conditions. The top spectrum in Figure 6 shows the CPMAS spectrum of a more highly cross-linked mixture of MAPTMS and HDDA which had been bulk polymerized with 1 wt % benzoyl peroxide.

Next, a failed batch of the complete formulation, **1C**, was prepared as described in Scheme 1 with MEHQ inhibitor and vacuum stripping under a N_2 atmosphere. The FTMAS spectrum of **1C** (Figure 7) was identical to a solution spectrum of a mixture of MAPTMS and HDDA. The CPMAS spectrum (Figure 7) showed resonances equivalent to those seen for poly-MAPTMS with some resonances for poly-HDDA (Tables 2 and 3 above, Figure 8). The carbonyl region showed unreacted MAPTMS/HDDA at 167 ppm and a peak at 175.6 ppm which is closer to that observed for poly-MAPTMS than poly-HDDA. The CPMAS spectrum in Figure 7 also showed two resonances in a roughly 2:1 ratio at 45 and 39 ppm. The 45 ppm resonance matched that observed for poly-MAPTMS while the 39 ppm resonance closely matched that seen for poly-HDDA; the other identifying resonance for poly-MAPTMS at 22 ppm was obscured by the monomer peaks.

The "good" sample, **1B**, was analyzed by ^{13}C solid-state NMR using the polyethylene (PE) insert. The

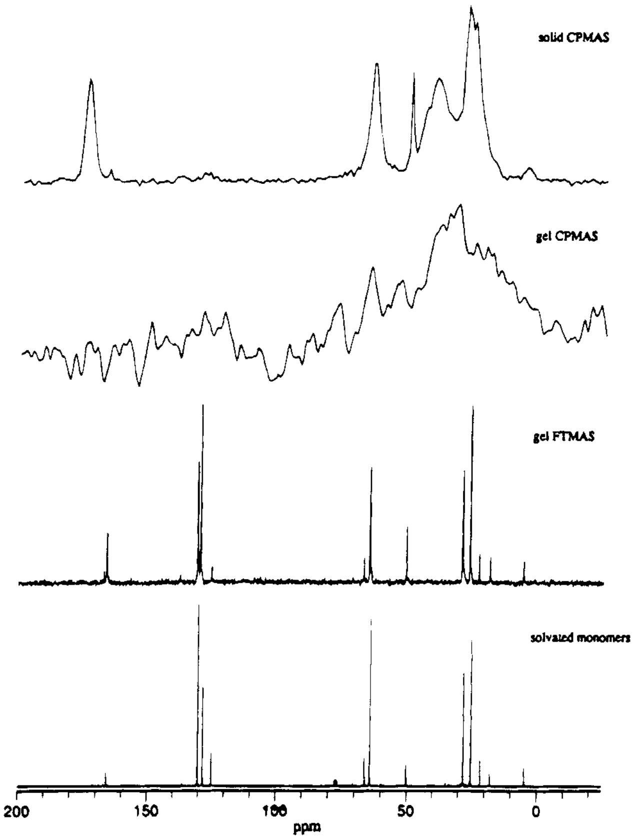

Figure 6. Carbon-13 NMR spectra of MAPTMS and HDDA. The $CDCl_3$ solution spectrum of the mixture of MAPTMS and HDDA monomers is 1248 scans with other conditions identical to the solution-state spectra of Figures 4 and 5. The FTMAS spectrum is of a lightly crosslinked gel of MAPTMS and HDDA. 1000 scans were acquired at 5 s intervals with ~54 kHz gated proton decoupling. The gel CPMAS spectrum is of the same lightly cross-linked gel. 17 000 scans were accumulated at 1.5 s intervals. A 3 ms cross-polarization contact time was used with observe and decoupling field strengths of ~54 kHz. The top CPMAS spectrum is of a MAPTMS and HDDA mixture bulk polymerized with 1 wt % benzoyl peroxide. 10 000 scans were acquired at 1 s intervals and a 2.5 ms cross-polarization contact period.

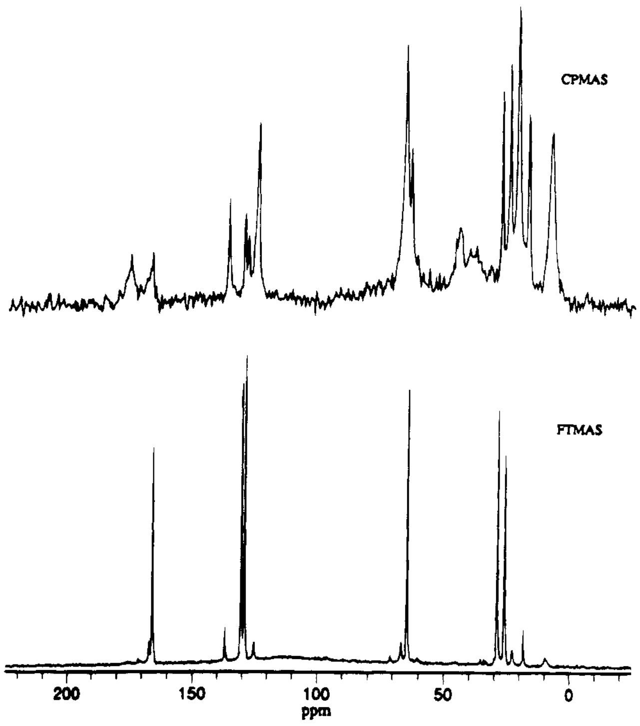

Figure 7. FTMAS/CPMAS comparison of a failed batch of MAPTMS/HDDA polymer. For the FTMAS spectrum, 2000 scans were accumulated at 15 s intervals with gated, ~54 kHz proton decoupling. The very broad resonance centered at ~115 ppm is background from the Kel-F material in the probe. For the CPMAS spectrum, 32 000 scans were acquired at 1.5 s intervals with a cross-polarization contact time of 1.0 ms.

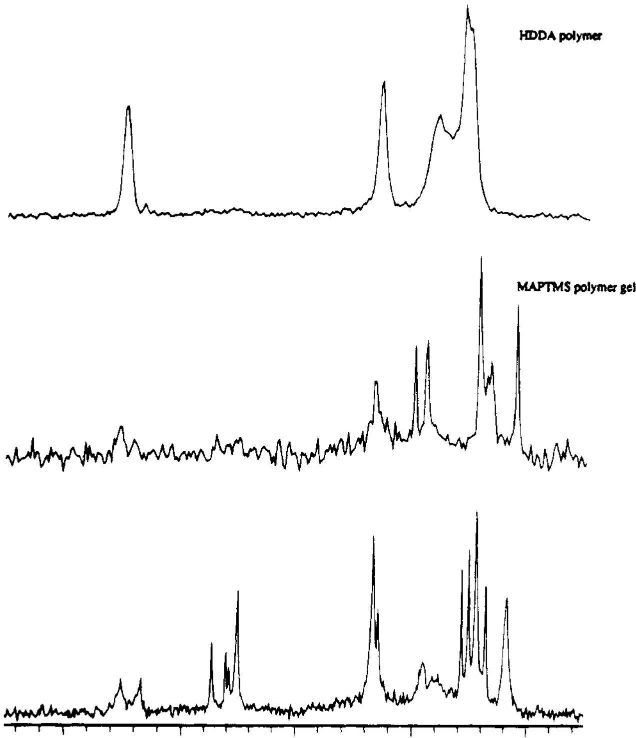

Figure 8. Comparison of the ^{13}C CPMAS spectra of a failed batch (bottom), polymerized MAPTMS (middle) and HDDA (top). For a description of the experimental conditions of these spectra see Figures 4, 5, and 7.

FTMAS spectrum for **1B** (Figure 9) was identical to the spectrum for the mixed acrylates shown in Figure 6. The CPMAS ^{13}C NMR spectrum (Figure 9) had a large PE resonance at 45 ppm which overlapped with the sample peaks, but there was no interference in the carbonyl region. The carbonyl resonances for MAPTMS and HDDA were observed, but no carbonyl resonance above 170 ppm was observed. This suggested little, if any, cross-linked material was present in this "good" sample.

^{29}Si NMR of **1B** (Figure 10) showed a typical pattern for condensation of the MAPTMS around the colloidal silica.[31] The liquid was also analyzed by MAS in the solid-state NMR spectrometer using the polyethylene insert. This FTMAS spectrum (not shown) was identical to the solution spectrum in Figure 10, indicating that the insert and the change in spectrometer had no influence on the spectrum. The **1B** formulation was bulk-polymerized with 1 wt % benzoylperoxide (**1D**). The ^{29}Si CPMAS spectra for **1B** and **1D** were compared (Figure 11). For **1B**, the "good" batch, essentially no trifunctional silicon (T) resonances were observed (bottom). The absence of T resonances in the CPMAS spectrum suggests that the silicon nuclei of the T groups are in a highly mobile environment and that little or no cross-linking has occurred in the acrylate functionalities. The spectrum for **1D** (top), which had been intentionally cross-linked through the acrylate func-

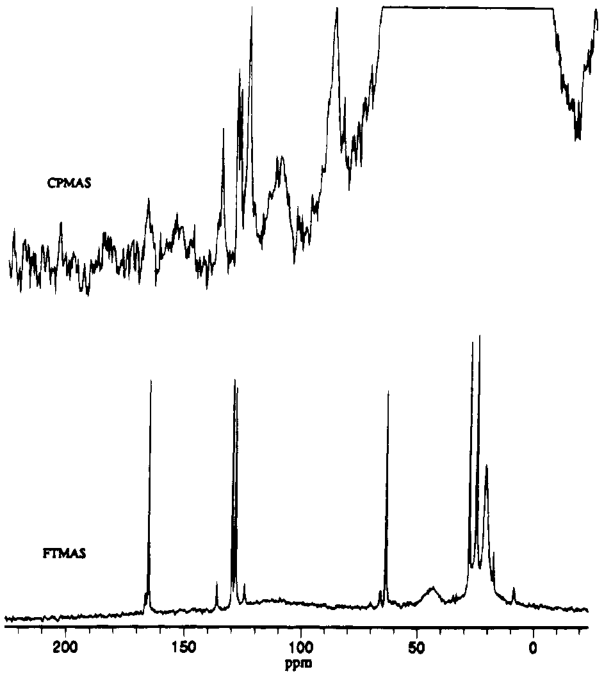

Figure 9. ^{13}C CPMAS and FTMAS spectra of a good batch of HDDA/MAPTMS. MAS spectra were obtained in a polyethylene sleeve to prevent the liquid sample from escaping the rotor. For this experiment, a larger, 7 mm diameter probe was used, and the sample was spun at ~3 kHz. For the FTMAS spectrum, 2000 scans were accumulated at 15 s intervals with ~36 kHz gated decoupling. For the CPMAS spectrum, 51 000 scans were accumulated at 1 s intervals. A 1 ms cross polarization contact time was used with ~36 kHz observe and decoupling field strengths.

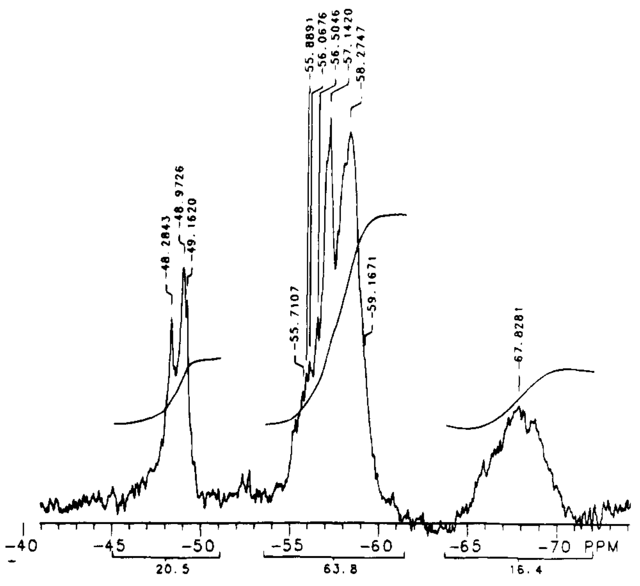

Figure 10. ^{29}Si NMR solution spectrum of **1B** in $CDCl_3$. Approximately 4000 scans were collected with approximately 45° silicon observe pulses at 5 s intervals with gated proton decoupling. A small amount of $Cr(acac)_3$ relaxation reagent was added to the solution to shorten the silicon T_1's.

tionality, showed a large T resonance due to more efficient cross polarization in the rigid network structure of **1D**.

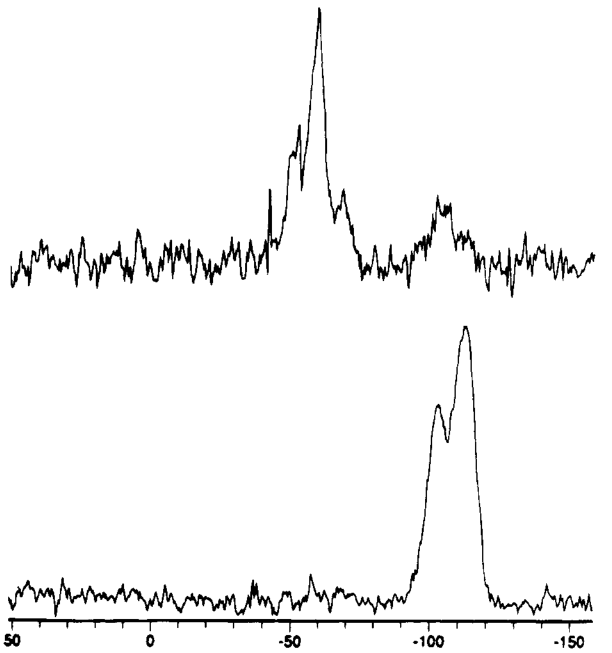

Figure 11. ^{29}Si CPMAS comparison of bulk polymerized batch **1D** (top) and "good" batch **1B** (bottom). For the bottom polymer spectrum, 24 000 scans were acquired at 3 s intervals. A 5 ms cross-polarization contact time was used with ~31 kHz observe and decoupling fields. The sample was spun at ~4.5 kHz. For the top spectrum, 120 000 scans were collected at 0.5 s intervals. A 1 ms cross-polarization contact time was used with ~31 kHz observe and decoupling fields. The sample was spun at ~3 kHz in a polyethylene sleeve at 0.5 s intervals.

Differential scanning calorimetry (DSC) was employed to compare the percent reaction between a "good" sample of **1** and one that had failed after vacuum removal of water/*i*-PrOH (**1C**). The good batch of **1B** had a total heat of 129.9 J/g, while **1C** had a total heat of 124.4 J/g. These data suggest that approximately 4% reaction had occurred in **1C** vs the "good" sample **1B**.

Conclusions

The most common failure mechanism identified during manufacture of **1** was polymerization of the acrylate which occurred during heating and anaerobic vacuum stripping. Polymerization occurred at both methacrylate and acrylate, but approximately 50% more cross-links at methacrylate were evident. Higher viscosity of the formulation can also arise from agglomeration of the colloidal silica particles.

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