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Preparation and characterization of novel organo-siloxane hybrid particles

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SUMMARY: Molecular organo-siloxane hybrid particles were prepared by a one-step procedure from methyltriethyloxysilane. The hydrolysis during the sol-gel process was incomplete leaving some of the ethoxy groups still associated with the silicon which gave rise to particles that tended to form loose aggregates rather than discrete particles. The degree of hydrolysis under different reaction conditions was evaluated during the sol-gel process by ^{1}H NMR, IR and thermogravimetric analysis. By controlling the ammonia and the water concentrations it was possible to obtain reproducible particles that were fairly uniform in size. The presence of the methyl groups on the surface of these particles imparted hydrophobic character to the surface. After calcination the particles became more porous and the surface was hydrophilic. The surface of these particles was further modified by radical chlorination and then aminated with sodium amide. Further modifications were carried out by reacting substrates with the amine.

Introduction

A number of organosiloxane polymer systems have been reported [1-3], however, the synthesis of controlled 'organic-inorganic' hybrid particles is still a challenging problem. Most of the studies have focused on tetraethoxysilane (TEOS) or tetramethoxysilane systems. Iler[4] reported that condensation of these silane monomers takes place so as to maximize the number of Si-O-Si bonds and minimize the number of terminal hydroxyl groups through internal condensation. Thus siloxy-rings are usually quickly formed to which other monomers add to create small three-dimensional microparticles. These particles then aggregate to form the most compact state with unreacted OH groups on the surface. According to Iler these microparticles serve as nuclei for aggregation. Further growth occurs

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by Ostwald ripening whereby particles grow in size and decrease in number. Growth stops when the difference in solubility between the smallest and largest particles is only a few ppm.

By the introduction of organic groups into the inorganic network, many novel physical and chemical properties can be developed, such as, improved compatibility with organic matrix, specific surface properties, and changeable particle density. In general, organicinorganic hybrid materials would include both physical mixtures and molecular level composites. However, the physical mixtures are not stable to solvent and aging. The hybrids would contain covalent bonding between organic structure and inorganic network.

In our laboratory, molecular hybrid particles were prepared by a one-step procedure2). The small organic domain in the hybrid particle was achieved by using alkyl trialkoxysilanes. In this paper, we report the structure, morphology and formation of polymethylsiloxane particles from methyltriethoxysilane (MTEOS) (Fig. 1).

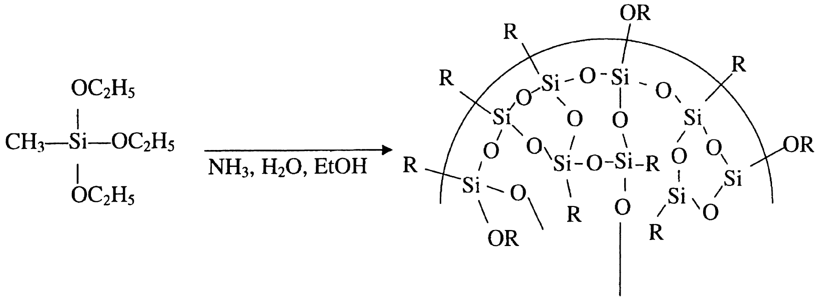

Fig.1: Synthesis of polymethylsiloxane particle

Under basic conditions, the TEOS hydrolysis mechanism is considered to be S_N2^{--} or S_N2^{-}[4]. The silicon acquires a formal negative charge in the transition state, therefore, electron-withdrawing substitutes should help stabilize the negative charge, causing the hydrolysis rate to increase, whereas, electron-donating substitutes should cause thehydrolysis rate to decrease. The methyl group in methyltriethoxysilane is an electron donor, therefore, the hydrolysis rate should occur slower than for tetraethoxysilane.

Experimental

Materials

The solvents, reagents and tetraethoxysilane and methyltriethoxysilane were obtained from Aldrich, St. Louis, and purified by standard procedures. All other chemical and solvents were also obtained from Aldrich, St. Louis, and used as received.

Preparation of particles

Methyl triethoxysilane (4 cm^3) in 90 cm^3 of 5M alcoholic ammonia solution and 6 cm^3 of water were added to a one-neck flask, which was then sealed. The reaction flask was mounted on a shaker and agitated at room temperature for 24 h. The product was washed (six times) with 200 cm^3 of ethanol to remove the remaining water and ammonia. Fine particles were obtained after the ethanol was removed by evaporation.

Thermogravimetric analysis

The weight loss of the particles at increased temperatures was investigated with a Perkin-Elmer Model 4 thermal analysis system and a 3600 data station. During TGA experiments, the temperature was scanned from 50-750°C at a rate of 10°C/min.

Surface modification of polymethylsiloxane particles

The surface methyl groups were chlorinated as follows: 100 g of polymethylsiloxane particles were dispersed in 400 cm^3 of carbon tetrachloride in a 1 dm^3 flask equipped with a drying tube, and 60 cm^3 of sulfuryl chloride were added under N_2 to the system with rapid stirring. A 275 W UV light was employed to initiate the reaction which was allowed to proceed for 4 h. This procedure was also repeated with 0.01 w/w % AIBN.

Amination of chlorinated particles

Ammonia gas was introduced slowly into a 250 cm^3: three-neck flask equipped with a dry-tube and condenser while being cooled in a dry ice-acetone bath. After 100 cm^3 of liquid ammonia was condensed, 3 g of sodium amide was added into the flask followed by 10 g of chlorinated particles with vigorous stirring. The reaction proceeded for 10 h, and the ammonia was evaporated with a slow temperature increase. The product was dispersed in ethanol, washed with 95% ethanol and then acetone (two times each) and dried in a vacuum oven at room temperature for 24 h.

Results and discussion

Synthesis of polymethyltrioxysilane particles by the sol-gel process

Tetraethoxysilane and methyltriethoxysilane were employed in the sol-gel process to evaluate the effect of reaction conditions on the particle size. By experimenting with different ratios of water and ammonia, we found that particles larger than 10 μm could be made by using concentrated aqueous NH_4OH (29 % ammonia and 71 % water) as the catalyst system. We found that the hydrolysis reaction during the sol-gel process for MTEOS was incomplete under the same reaction conditions used for TEOS.

^{1}H NMR monitoring the hydrolysis of methyl triethyloxysilane and TGA analysis

Since the hydrolysis of methyltriethoxysilane was incomplete we decided to monitor the reaction by ^{1}H NMR and TGA analysis. The residual alkoxide was estimated by the first weight loss of the particles during the reaction by TGA (Fig. 2).

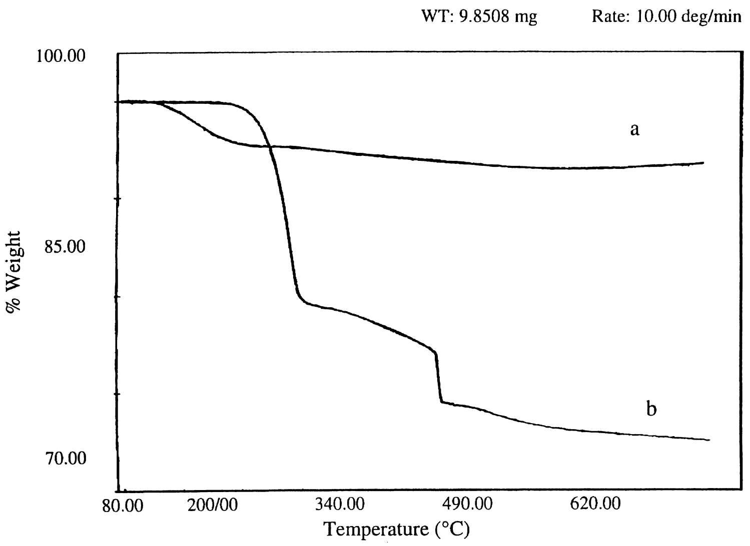

Fig. 2: TGA traces of particles prepared from (a) tetraethoxysilane; and (b) methyltriethoxysilane

In general, it was found that increasing the ammonia and water concentrations decreased the amount of unhydrolyzed alkoxide. If the concentrations of ammonia and water were too low then a number of the unhydrolyzed ethoxide groups remained. Although some researchers claimed that there is an apparent zero-order dependence on the water concentration under base-catalyzed conditions, our results show that the hydrolysis rate is in fact highly dependent upon the water content in the reaction system. ^1H NMR monitoring (Fig. 3) indicates that the MTEOS hydrolysis rate is much slower than the condensation rate and that some unhydrolyzed alkoxide groups were being trapped by the faster gelation process.

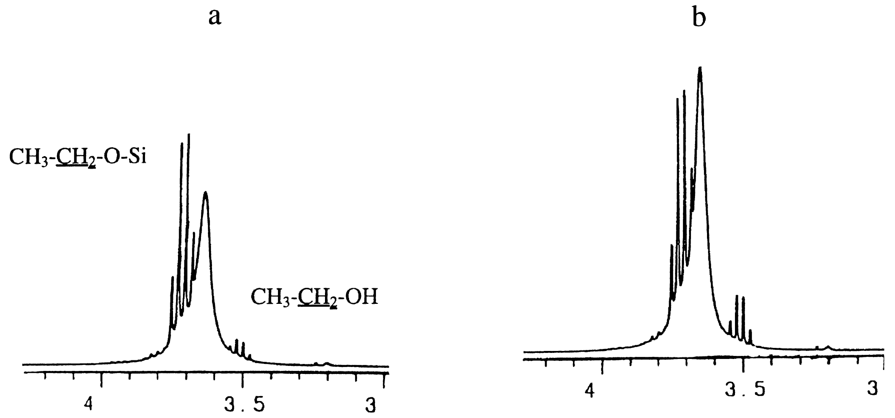

Fig. 3: The hydrolysis of methyltriethoxysilane monitored by ^1H MNR (a) 15 minutes and (b) 30 minutes after reaction

Effect of NH_3 and H_2O on particle size

A particle size analyzer and SEM were employed to evaluate the particle size, size distribution, and topography. More that 100 reactions were carried out to determine the effect of changing the ammonia and water concentrations. To increase the hydrolysis rate, methanol was replaced with ethanol as the solvent to enhance the polarity (solubility parameters: methanol = 32.6 $MPa^{1/2}$; ethanol = 24.3 $MPa^{1/2}$). Methanol purged with ammonia was substituted for ammonium hydroxide as the catalyst to achieve higher catalyst concentrations (saturated ammonia concentrations were 8M in methanol and 4M in ethanol, respectively). When the H_2O/Si mass ratio was changed from 5.5 to 55.6, and the NH_3/Si ratio was changed from 3 to 33, it was found that the particle size and morphology of the particles were affected by the water concentration. Increasing the water and ammonia concentrations increased the particle size when the H_2O/Si was >10. The higher water content favored the formation of uniform microspheres and lower water concentrations produced very low density, highly porous aggregates. Based on SEM analysis, most of the particles were 2-5 μm in size, which consisted of aggregates of many smaller particles from 0.1 to 0.3 μm. For optimum reaction conditions, H_2O/Si mass ratio of 30 are recommended to obtain uniform shaped particles with uniform particle size distribution.

Morphology of polymethylsiloxane particles

Based on the SEM, particles made from an NH_3/Si ratio of 28.9 were spherical in shape for H_2O/Si (Fig. 4a) and exhibit a highly porous surface for a H_2O/Si ratio of 5.5 (Fig.4b).

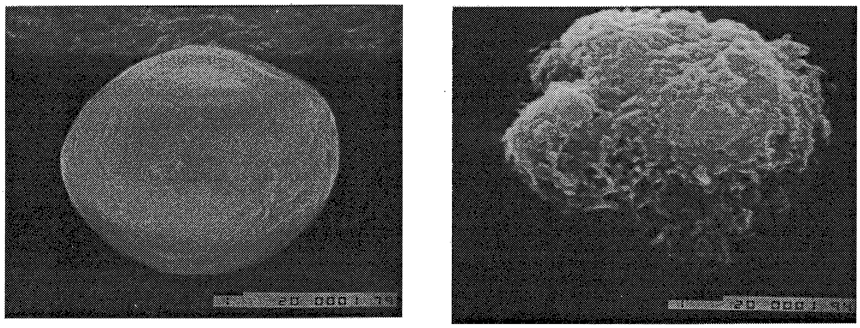

Fig. 4: SEM pictures of polymethylsiloxane particles; NH_3/Si: 28.9; a) H_2O/Si: 55.6; b) H_2O/Si: 5.5

Density analysis showed that the MTEOS particles were only 1.31 g/cm^3.The final particles were aggregates consisting of many smaller particles which are about 10 nm. The lower hydrolysis and condensation rates for MTEOS allowed us to observe particle growth, which is consistent with Iler's particle growth mechanism $^{4)}$. According to Iler, after nucleation, the particles basically grow from the nuclei by internal condensation of the hydroxyl groups within the particles.

TGA analysis and IR spectrum at different temperatures

The IR spectrum showed no hydrogen bond absorption for H_2O at 3400-3600 cm^{-1} (Fig.5).

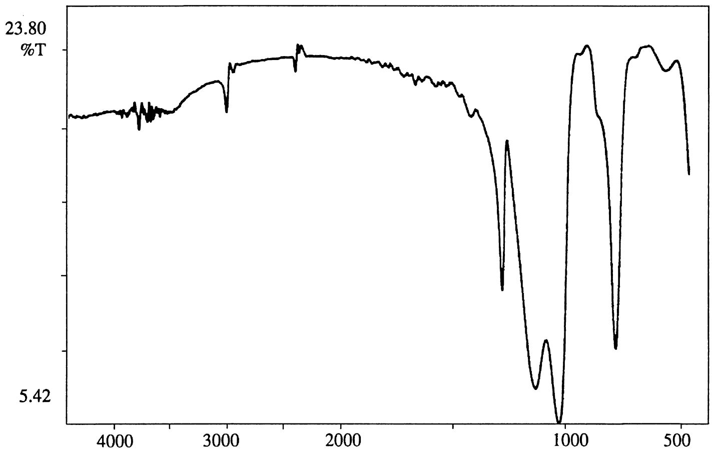

Fig.5: FTIR of polymethyltriethoxysilane particles

The TGA demonstrated that no weight loss occurred below 180°C. Neither the TGA nor IR analysis detected any surface water on the particles prepared from MTEOS by the sol-gel process indicating a hydrophobic surface. After calcination at 700°C for 10 mm, allowing the methyl group to pyrolyze, the surface of the particles changed from hydrophobic to hydrophilic. The enhanced hydrophilic character was evident by an observed increase in the particle dispersability in water and the appearance of adsorbed H_2O on the particle surface by IR. It was found that the IR peak area at 1119 cm^{-1} (O-C bond) greatly decreased as the temperature changed from 180 to 250°C, simultaneously, vibration bond at 1034 cm^{-1} (Si-O) increased (Fig. 6). This means that there were some alkoxide groups that were lost as the temperature increased. It is consistence with previous TGA analysis$^{5)}$. Above 400°C, the methyl groups gradually pyrolyzed as seen by the weaker adsorption at 1274 cm^{-1}.

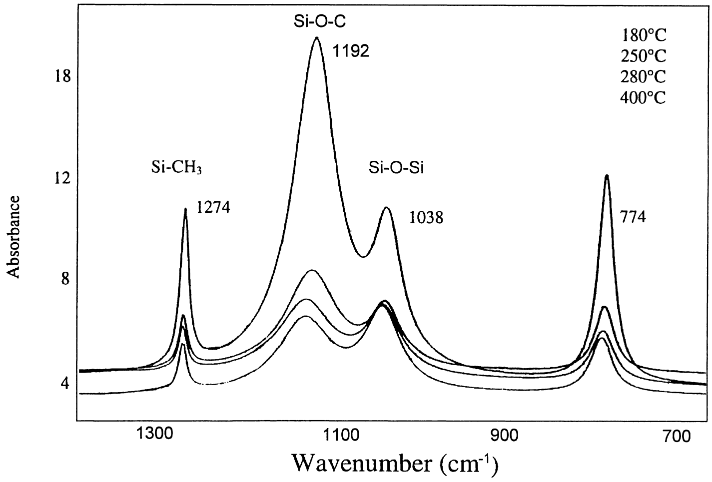

Fig. 6: IR Spectra of MTEOS particles at different temperatures

Aggregation behavior during the MTEOS sol-gel process

Particle formation during the sol-gel process was monitored by particle size analyzer for eight hours (Fig. 7).

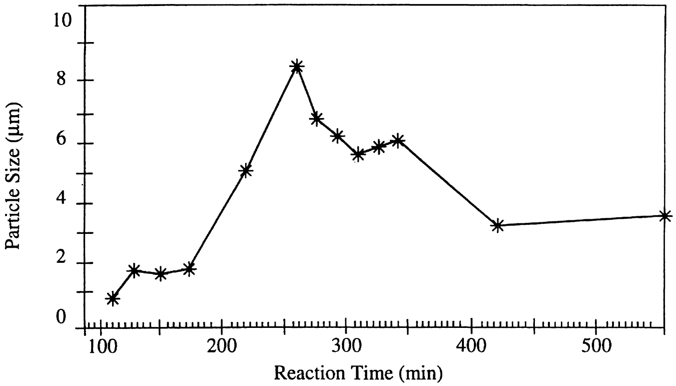

Fig. 7: Particle size and size distribution (D>50%) at different reaction times (NH_3/Si: 28.9; H_2O/Si: 34.6)

It was found that during the first three hours, the detectable particle sizes were < 1μm, and the average particle size did not change during this time period. Only a gradual increase in the number of particles, based on adsorption intensity, was observed. After three hours, an abrupt increase in particle size from <1 to >8 μm occurred in a short time span, followed by a slow decrease in particle size until finally particles approximately 2-5 μm were achieved. This temporary agglomeration was attributed to incomplete hydrolysis and condensation. Based on TGA and ^{1}H NMR observations (Fig. 2 and 3), there are unhydrolyzed silicone alkoxide groups as well as hydroxyl groups present in the early stages of particle formation. Apparently if the number of particles is high enough, and the particles are close enough (i.e. in high concentration), large agglomerates can form by hydrogen bonding and water molecules trapped among the particles. Further hydroxide attack on the unhydrolyzed Si-OEt increases the negative charges on the surface and breaks up the agglomeration to form smaller, more stable particles. Another reason for the temporary agglomeration may be due to the change of the surface from hydrophilic to hydrophobic during particle formation. This process may be characteristic for the MTEOS sol-gel process.

Although the conductivity and pH of the system changed very little during the reaction, the changes in the ammonia and water concentrations affected the particle size. An increase in the ammonia concentration or the H_2O/Si produced larger MTEOS derived particles and earlier aggregation. However, these two factors played different roles in the sol-gel process with TEOS. A high concentration of ammonia ($NH_3/Si=30$) produced a broad particle size distribution and an increase in this ratio favored the formation of uniform particles.

Surface modification of polymethylsiloxane particles

For the surface modification of polymethylsiloxane particles, the first step involved the free radical chlorination. A stable solvent for chloride radicals, carbon tetrachloride, was employed to eliminate chain transfer by the solvent. Small amounts of AIBN added to the reaction resulted in higher conversion. After chlorination, the second step was to substitute the chloro group with an amine group. Although sodium amide is a very active reagent, substitution of Cl by NH_2 needed a long reaction time (12 hours) at 50°C when benzene was used as the solvent. This may be due to the poor solubility of $NaNH_2$ in benzene. A two step method for the chloride substitution using sodium azide followed by reduction of the azide with $LiAlH_4$ gave better yields. Compared to the above two approaches, the best method for Cl substitution with amine was to replace benzene with liquid ammonium. Higher conversions were obtained due to better solubility of $NaNH_2$ in liquid ammonium. The presence of the amine was observed by IR at 1640.2 cm^{-1} due to N-H vibration.

Further modifications included reactions with succinic anhydride in THF to produce carboxylic group, with isophorone ddisocyanate in pyridine to provide the isocyanate group, a monomer reagent for polyurethane, with dimethyl-2,6-naphthalene dicarboxylate in xylene.

TEOS/MTEOS Particles

Our aim was to also prepare uniform microsphere sol-gel particles with the comonomers TEOS and MTEOS. Based on the previous experiments6), it is possible to prepare small spherical particles from tetraethoxysilane under basic conditions. Therefore, a new comonomer and synthesis method was designed using comonomers of TEOS and MTEOS to develop new hybrid particles. First TEOS was hydrolyzed, and then MTEOS was added to the reaction system just as gelation occurred. By controlling the molar ration of TEOS and MTEOS and using different adding times for MTEOS, uniform microspheres (0.2-0.5 μm) were obtained. By increasing the MTEOS content, the particle size and particle size distribution increased. By studying the particle size distribution in detail, two peaks were observed. The peak area of the larger sized particles increased with increased MTEOS. This suggested that the comonomer could produce two kinds of nuclei; those formed by TEOS and by MTEOS, respectively. Further research is being carried out to explore the mechanism and the copolymerization parameters of the TEOS and MTEOS process.

Acknowledgements

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