

One Step Preparation of Spherical Silicon Resins from Immiscible Reaction Mixtures

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Abstract: Spheres of silicon resins with different compositions were prepared in one-step reaction from mixtures of water and water-insoluble precursors of polysiloxanes (PSO) and polysilsesquioxanes (PSQ) using different amines as catalysts. The presence of PSO and PSQ in the spheres was confirmed by their mechanical properties and FTIR spectroscopy. Spheres of pure PSO were obtained from only dimethoxymethylvinylsiloxane (DMMVS) and 3-mercaptopropylmethyldimethoxysilan (MPMDMS) when the reaction was induced with appropriate catalysts. DMMVS and MPMDMS always gave the most promising results regarding the formation of discrete solid spheres with the minimum tendency to form monolithic solids or fluid-like, premature products. The spheres were characterized by optical microscopy, scanning electron microscopy (SEM), and Fourier transform infrared (FTIR) spectroscopy. The mixtures containing larger amounts of PSO precursors commonly gave lower yields and softer spheres.

Keywords: polysiloxane, polysilsesquioxane, spheres, silicon resins, one-pot preparation.

Introduction

Silica, $(\text{SiO}_2)_n$, silsesquioxanes, $(\text{SiRO}_{1.5})_n$, and siloxanes, $(\text{SiR}_2\text{O})_n$, are the most representative silicon based materials. There are numerous reports on the application of these materials in a wide variety of fields including electronic industries, cosmetics, and medical industries.^{1,2} The polysiloxanes (PSO) and polysilsesquioxanes (PSQ) are especially attractive because materials with different properties can be prepared by incorporating different organic groups. Furthermore, the organic groups in silsesquioxanes molecules can be chemically modified to prepare more useful materials.³

There are several methods that have been used to produce PSO and PSQ in different forms such as films, particles, and oils. Among these methods, hydrolysis and condensation reactions of organoalkoxysilanes are the most attractive because the reaction conditions are mild and different organoalkoxysilanes are easily synthesized and commercially available. However, the hydrolysis and condensation reac-

tions of these precursors do not always lead to the formation of spherical particles.⁴⁻⁸ The natures of the products are dependent on the structures of the precursors, reaction conditions, and the catalysts.

Although PSO and PSQ have been so intensively used in different fields, there are only a few types of PSO and PSQ that are produced as bulk materials. It is difficult to find bulk materials made of PSO and PSQ other than polydimethylsiloxane (PMDMS) and polymethylsilsesquioxane (PMSQ). Instead, the most organoalkoxysilanes have been employed in modification of the surfaces of the pre-existing materials. The most probable reasons for this are that the properties of bulk PSO and PSQ are not useful, and the preparation of bulk PSO and PSQ are not easy to accomplish. The latter is true considering that the spheres made of only PMDMS and other PSO have never been reported although PSO spheres are expected to be useful as fillers to improve impact strengths of brittle polymers. There were previous reports where only colloids of PDMS oil were obtained from an attempted sol-gel reaction of dimethyldiethoxysilane (DMDES) using ammonium hydroxide as the catalyst. PDMS-PMSQ spherical particles were obtained from mixtures of DMDES

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and methyltriethoxysilane (MTES) only when the mixture contained more than 50 vol% of MTES.^{6,8,9} Also, all the earlier literatures reported on the preparation of polyphenylsilsesquioxane (PPSQ) spheres described the formation of soluble side products in significant amounts.^{4,5,7}

In our recent report, we have described one step preparation of functional PSQ spheres from reaction mixtures of water and water-insoluble precursors.¹⁰ The spheres were virtually monodisperse and showed unique behaviors regarding the production of metal nanoparticles. We have expanded our research to the preparation of spheres of PSO and PSO-PSQ composites by the similar method using two types of catalysts of amine compounds; aminoalkylalkoxysilanes¹¹ and organic amines. The aminoalkylalkoxysilanes not only catalyzed the reaction but also co-condensed to form the spheres. This report describes the production of solid materials from different mixtures of PSO, and mixtures of PSO and PSQ precursors. The most important objective in this study was to prepare functional PSO spheres in a very simple and convenient method. It should also be emphasized that there has been only a few reports where the production of bulk PSO materials from diorganodialkoxysilanes was described.^{6,12,13}

Experimental

Materials. Triethylamine (TEA), hexylamine (HA), dimethyldimethoxysilane (DMDMS), aniline, phenethylamine (PA), benzylamine (BA), dicyclohexylamine (DCA), ethylenediamine (EDA), dimethoxymethylvinylsilane (DMMVS), and 3-mercaptopropylmethyldimethoxysilane (MPMDMS) were purchased from Aldrich Chemicals. 3-Aminopropyltrimethoxysilane (APTMS) and *N*-[(3-trimethoxysilyl)propyl]ethylenediamine (TMSPEDA) were purchased from Acros Chemicals. All the chemical reagents used were used as received if not otherwise mentioned.

Preparation of Spheres and Characterization. The PSO precursors and methyltrimethoxysilane (MTMS) were mixed in different ratios. The mixtures were added to distilled water of twenty times of the total volumes of the precursors. The mixtures were shaken gently with hands and then appropriate amounts of catalysts were added to the mixtures. The mixtures were then shaken with hands and allowed to stand at room temperature until solid products are formed or for three weeks. The products were usually collected by filtration because centrifugation often caused the products to agglomerate to give monoliths. The recovered solids were dried at room temperature for 1 day and then dried under vacuum at 40 °C until the weight did not change after drying for another 24 h. The physical states of the products were visually examined, followed by confirmation by observing with an optical microscope. The solid spherical products were observed with a JEOL JSM-840 SEM. The yields of the products were determined only

when recoverable spheres were produced.

The ATR-FTIR spectra of spherical products were recorded using a BOMEN 102 FTIR spectrophotometer equipped with accessories for ATR.

The size distributions of the spheres were determined from their SEM images. The diameters of at least 30 spheres were measured and used to calculate diameters.

Calculation of Yields. The yields of products were calculated assuming that the reactions of diorganodialkoxysilanes and organotrialkoxysilanes proceeded to completion. The products from diorganodialkoxysilanes, $\text{Si}(\text{OR})_2\text{R}'\text{R}''$, were assumed to be $(\text{SiOR}'\text{R}'')_n$ and the products from organotrialkoxysilanes, $\text{Si}(\text{OR})_3\text{R}'$, were assumed to be $(\text{SiO}_{1.5}\text{R}')_n$. As a result, the yields calculated can be higher than 100% when the precursors did not react completely and contained SiOH groups.

Results and Discussion

The non-condensing catalysts used were TEA and HA, and the co-condensing catalysts were TMSPEDA and APTMS. The non-condensing catalysts, TEA and HA, simply induce hydrolysis and condensation reactions of the precursors while the co-condensing catalysts, TMSPEDA and APTMS, react with the precursors to be incorporated into the solid products. The precursors of PSO used were DMDMS, DMMVS, and MPMDMS. These precursors were chosen because they contained the substituents that were significantly different from one another in sizes and polarities; methyl, vinyl, and 3-mercaptopropyl groups. The methyl group in DMDMS is unreactive and small, vinyl group in DMMVS is reactive and mid-sized, and 3-mercaptopropyl group in MPMDMS is more reactive, polar, and large.

Table I shows the results obtained from different combinations of the PSO precursors and catalysts. The products were classified according to their physical states. Colloid (C) indicates the products were stable colloidal solutions where fine oil droplets were dispersed in water⁸ without formation of any solid products, elastomer (E) indicates the products were elastomeric, soft and fragile solids, rubber (R) indicates the products were very soft rubbery solids that were easily elongated without being ruptured, aggregates (A) indicates sponge-like products that probably formed by aggregation of soft spherical particles, oil (O) indicates the products were oily that formed separate oil layers that usually had higher densities than water, grease (G) indicates the products were viscous creamy products, and particles (P) indicates that the products were discrete solid spheres. Except the products indicated by P, all the solid products were amorphous monolithic solids or aggregates of premature spheres that stuck to the bottom and the wall of the reaction vessels.

Table I shows that only DMMVS gave discrete spherical solid products when catalyzed with more than 10 vol% of

Table I. Types of Products Obtained from Different Mixtures of Diorganodialkoxysilanes

Catalyst	DMDMS ^a					DMMVS ^b					MPMDMS ^c				
	I ^d	II ^e	III ^f	IV ^g	V ^h	I	II	III	IV	V	I	II	III	IV	V
TMSPDEA ⁱ	O ^j	O	G ^k	E ^l	E	E	E	E	A ^m	A	O	R ⁿ	G	E	E
TEA ^o	C ^p	C	G	C	C	C	C	O+C	C	O+C	O	O	O+E	O+E	E
APTMS ^q	O	C	G	R	R	E	E	P ^r	P	P	G	E	E	E	E
HA ^s	O	O	O	G	O	O	O	O	R	R	O+E	E	E	E	E
Aniline	C	C	C	C	C	C	C	C	C	C	C	C	C	C	C
PA ^t	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O
DCHA ^u	O	O	O	O	O	O	O+C	O	O	O	O	O	O	O	O
BA ^v	C	O+C	O+C	O	O	C	C	C	C	O+C	O	O	O	O	O
EA ^w	C	C	C	C	C	C	C	C	C	C	O	O	O	C	C

^aDimethoxydimethylsilane; ^bDimethoxymethylvinylsilane; ^c3-Mercaptopropylmethylmethoxydimethylsilane; ^dPrecursor(mL):catalyst(mL):water(mL) = 0.5: 0.005:10; ^e0.5:0.01:10; ^f0.5:0.025:10; ^g0.5:0.05:10; ^h0.5:0.1:10; ⁱN-[(3-trimethoxysilyl)propyl]ethylenediamine; ^jOil; ^kGrease; ^lElastomer; ^mAggregate; ⁿRubber-elastic solid; ^oTriethylamine; ^pColloid; ^q3-Aminopropyltrimethoxysilane; ^rParticles; ^sHexylamine; ^tPhenethylamine; ^uDicyclohexylamine; ^vBenzylamine; ^wEthylene diamine.

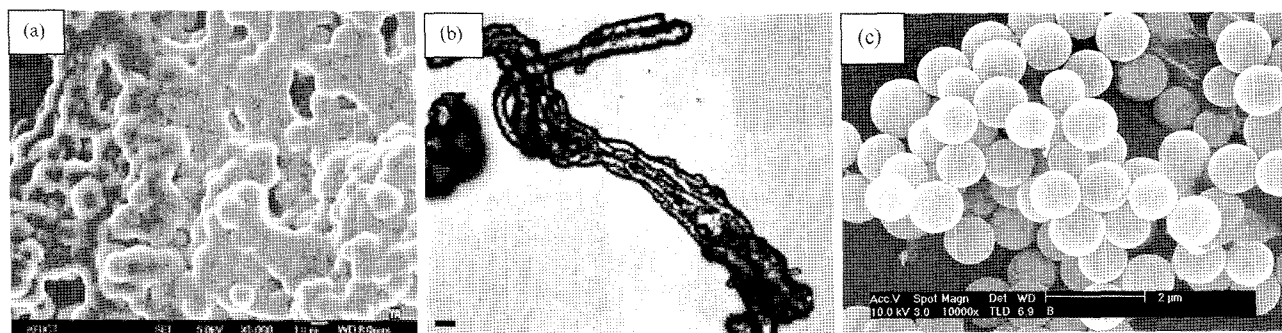


Figure 1. (a) SEM image of the product obtained from a 10:1 (vol:vol) mixture of DMDMS and TMSPDEA, (b) optical microscopic image the product shown in (a) that was sheared between glass slides (scale bar = 10 μ m), and (c) SEM image of the spheres obtained from a 2:3.5:1 mixture of DMDMS, MTMS, and TMSPDEA.

APTMS. The SEM images of the spheres obtained from a 10:1 (vol:vol) mixture of DMDMS and TMSPEDA, and from a 1:4:1 molar mixture of DMDMS, MTMS, and TMSPEDA are shown in Figure 1. The optical microscopic and SEM images of spheres obtained from different mixtures of DMVMS, MTMS and APTMS are shown in Figure 2. Figures 1 and 2 show that the spheres produced from the mixtures containing MTMS had narrow size distributions. Figure 1(a) shows that the elastomeric products indicated as E in Table I were most likely aggregates of premature spherical products. Sheared between two glass slides, the product shown in Figure 1(a) became as shown in Figure 1(b) indicating the products were very soft.

Our previous results with PSQ precursors showed that spheres with narrow size distributions were produced even when the amounts of the catalysts were as low as 1 vol% of the precursors. The sizes of the PSQ spheres decreased as the amounts of the catalysts increased and eventually transparent solutions formed when the amounts of the catalysts

were high. Table I shows that much larger amounts of catalysts are required to produce solid materials from PSO precursors compared to those required to produce solid spheres from PSQ precursors. These results might be explained in terms of the lower tendency of hydrolysis of PSO precursors caused by the electron-donating nature of alkyl substituents. The processes for the formation of products from these precursors are schematically illustrated in Scheme I. The best results regarding the formation of solid spheres and the narrowness of the size distribution are obtained when the reaction follows (a), (b) and (c) in Scheme I; the precursor droplets release precursors into water and the nuclei are formed ((b) in Scheme I), the precursor droplets become smaller as more nuclei are formed and the nuclei consume precursors to become larger ((c) in Scheme I). The worst results are obtained when the reaction proceeds following (a), (d) and (e); the precursor droplets become viscous as the result of random reactions, the viscous droplets merge one another ((d) in Scheme I) to yield different prod-

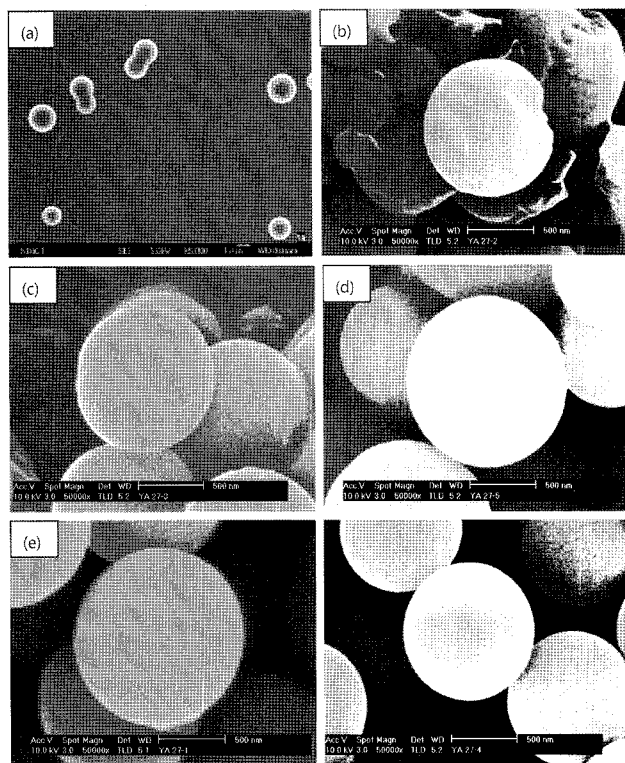
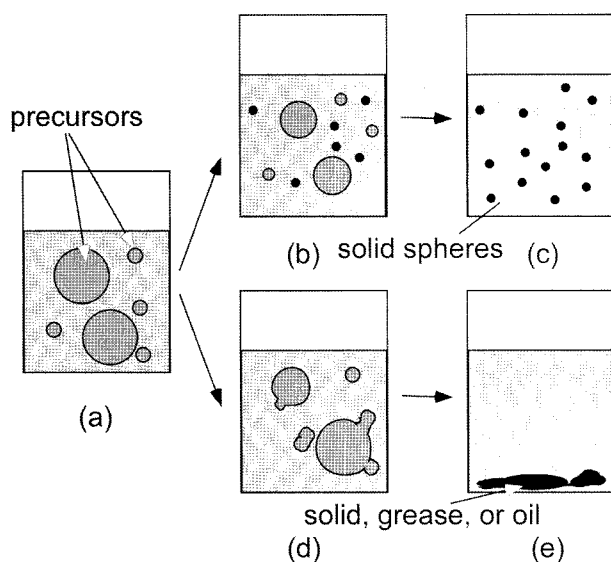


Figure 2. SEM images of spheres obtained from mixtures of DMVMS, MTMS, and APTMS in molar ratios of (a) 10:0:1, (b) 3:2:1, (c) 5:5:2, (d) 2:3:1, (e) 1:4:1.



Scheme I. The process of forming solid spheres and amorphous monolithic products from PSO and PSQ precursors.

ucts depending on their reactivities and efficiencies of the catalysts ((e) in Scheme I). The process following (a), (b) and (c) in Scheme I is virtually identical to that in emulsion polymerization and is often observed in the preparation of PSQ spheres from organotrialkoxysilanes. The process fol-

lowing (a), (d) and (e) in Scheme I is similar to that in suspension polymerization if only the precursor droplets do not merge one another. In practice, the two extreme processes shown in Scheme I frequently take place simultaneously to give mixtures of spheres and monolithic products. Table I also shows that many of the precursor mixtures reacted following (a), (d) and (e), often giving no solid products.

The yields of solid spheres obtained from different mixtures of PSO precursors and MTMS using different catalysts are listed in Table II. The yields were calculated assuming that all the precursors and co-condensing catalysts reacted to completion as explained in Experimental. The yields higher than 100 % indicates incomplete condensation reactions between silanols and TMSPEDA gave the yields higher than 100 % the most frequently. These results might be ascribed to the fact that TMSPEDA had two amine groups and produced the most hydrophilic products leading to incomplete condensations of silanol groups as the amine groups formed internal hydrogen bonding.¹¹ Table II shows that TEA gave the lowest yields for all the reaction mixtures investigated. However, the size distributions of spheres were the largest when HA was used as the catalyst. It is also to be noted that the yields of spheres from mixtures listed in Table II seemed to be slightly higher when amines containing larger substituents were used as the catalysts.

Tables I and II show that the mixtures of DMDMS and MTMS, and MPMDMS and MTMS gave solid spheres even when the fraction of MTMS was lower than 50 vol%. These results are quite different from those reported in the previous study where MTES and DMEDES were used.⁶

The SEM images of the spheres shown in Figures 1 and 2 proved that the mixtures containing MTMS in higher fractions gave more rigid spheres. The damages in the spheres shown in Figures 2(b) and 2(c) indicated that the spheres were connected to each other and torn apart during the sample preparation for the SEM analysis. There was no such torn trace in the spheres prepared from DMVMS and MTMS mixtures containing 50 mole% and higher amounts of MTMS. These results clearly showed that the spheres obtained from mixtures of DMDMS, DMMVS and MTMS contained both PSO and PSQ and had different properties in accordance to the compositions.

Figure 3 shows the effect of the amount of different catalysts on the yields of solid spheres from approximately 2:3 molar mixtures of different PSO precursors and MTMS. Figure 3 shows that the overall yields were not significantly affected by the types of catalyst and the maximum yield were generally obtained when the mole% of the catalysts was lower than 10 mole%. The decreases of the yields in the presence of higher amounts of catalysts were ascribed to the formation of more water soluble products and smaller products that were not recovered efficiently. All the catalysts gave transparent solutions when used in amounts of 200 mole% the precursors and higher.

Table II. The Yields of Solid Spheres Prepared from Different Combinations of Precursors and the Catalyst

DMDMS:MTMS:Catalyst ^a	Yield(%)							
	APTMS	TMSPEDA	TEA	HA	PA	DCHA	BA	EA
1:4:1	73	100	74	81	99	99	90	86
2:3:1	75	96	68	75	76	99	94	88
3:2:1	76	92	0 ^b	82	84	82	92	- ^c
4:1:1	68	70	0	48	-	-	-	0
DMMVS:MTMS:Catalyst	APTMS	TMSPEDA	TEA	HA	PA	DCHA	BA	EA
1:4:1	88	114	81	82	96	94	100	88
2:3:1	83	112	68	80	95	97	98	93
3:2:1	75	103	46	84	89	-	82	81
4:1:1	57	87	0	79	-	-	-	0
MPMDMS:MTMS:Catalyst	APTMS	TMSPEDA	TEA	HA	PA	DCHA	BA	EA
1:4:1	88	105	75	82	90	113	90	96
2:3:1	85	104	80	84	89	109	94	77
3:2:1	87	99	64	77	95	79	92	72
4:1:1	82	90	4	76	-	-	-	-
MTMS:Catalyst	APTMS	TMSPEDA	TEA	HA	PA	DCHA	BA	EA
5:1	88	115	75	70	94	117	95	102

^aVolume ratio. ^bGave no solid products. ^cGave non-spherical solids.

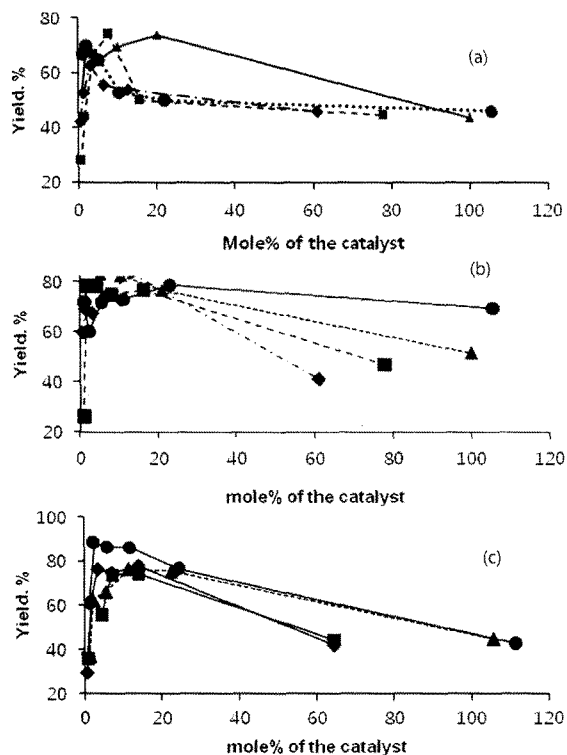


Figure 3. The yield of spheres against the mole% of the catalysts (◆, TMSPEDA; ■, APTMS; ▲, TEA; ●, HA). (a) 2:3 molar mixture of DMDMS and MTMS, (b) 2:3 molar mixture of DMMVS:MTMS, and (c) 2:3 molar mixture of DMMST:MTMS.

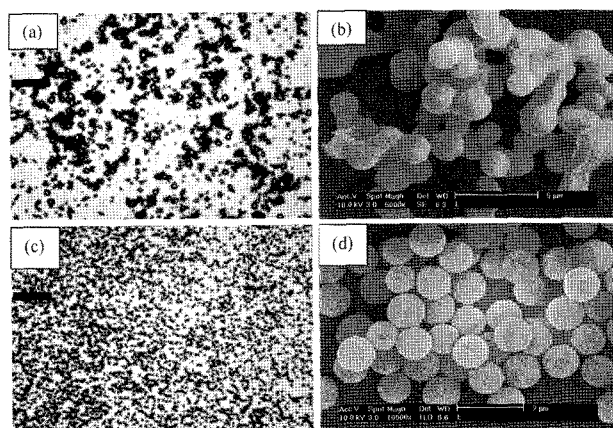


Figure 4. (a) Optical microscopic image, (b) SEM image of spheres obtained from 1.4:2.6:1 molar mixtures of MPMDMS, MTMS, and HA, (c) optical microscopic image, and (d) SEM image of spheres obtained from 1.4:2.1:0.5 molar mixtures of MPMDMS, MTMS, and TMSPEDA (scale bar = 10 μ m).

The effects of different catalysts on the production of spheres were examined using approximately 2:3 molar mixtures of PSO precursors and MTMS. The sizes and size distributions of spheres obtained using different catalysts were very similar regardless of the catalyst except hexylamine. Hexylamine gave spheres with wider distributions of diameters as shown in Figure 4(a) for the spheres

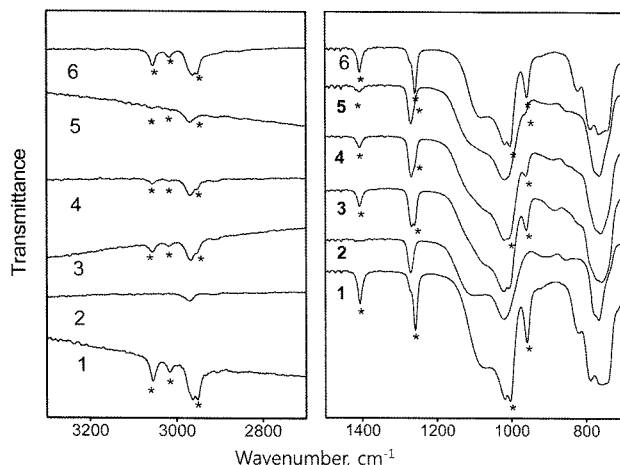


Figure 5. FT-IR spectra of spheres obtained from different mixtures of different precursors in different molar ratios; (1) DMMVS: APTMS=3:1, (2) MTMS:TEA=5:1, (3) DMMVS:MTMS:TEA=3:2:1, (4) DMMVS:MTMS:TEA=3:2:1, (5) DMMVS:MTMS:TES=1:4:1, and (6) DMMVS: DEMSPA=6:1.

prepared from a 1.1:2.1:0.8 molar mixture of MPMDMS, MTMS and HA.

The IR spectra of the spheres obtained from different mixtures of DMMVS and MTMS, and MPMDMS and MTMS are respectively compared in Figure 5 and Figure 6.¹⁴ The peaks related to the vinyl and 3-mercaptoproyl groups are indicated by stars. The IR spectra of the spheres obtained from a 5:1 molar mixture of MTMA and APTMS, and the monolithic solids obtained from a 6:1 molar mixture of DMMVS and diethoxymethylsilylpropylamine (DEMSPA) are respectively shown in Figures 5-(1) and 5-(6) for comparisons. The peaks for Si-O-Si stretching in PMPSQ appeared at 1107 and 1020 cm^{-1} while those in polymethylvinylsiloxane (PMVSO) appeared at 1080 and 1020 cm^{-1} . As the amounts of PSO increased in the spheres, the peaks around 1100 cm^{-1} appeared to be broadened due to overlapping of the peaks of 1107 and 1080 cm^{-1} . The peaks from Si-CH₃ in PSO and PSQ were also resolved from each other and respectively appeared at 1260 and 1271 cm^{-1} . The relative intensities of these two peaks varied in accordance to the relative amounts of PSO and PSQ precursors. Although the amine peaks did not appear above 3000 cm^{-1} , the broad peaks appeared at 750 cm^{-1} commonly in Figure 5-(1) and Figure 5-(6) were most likely from amines because only these products were prepared using amine containing co-condensing catalysts. Figures 5 and 6 show that the intensities of the peaks from functional groups increased as the fraction of functional PSO increased indicating that the spheres formed by co-condensation of both PSO and PSQ precursors.

Conclusions

Results in this study show that spheres of PSO and com-

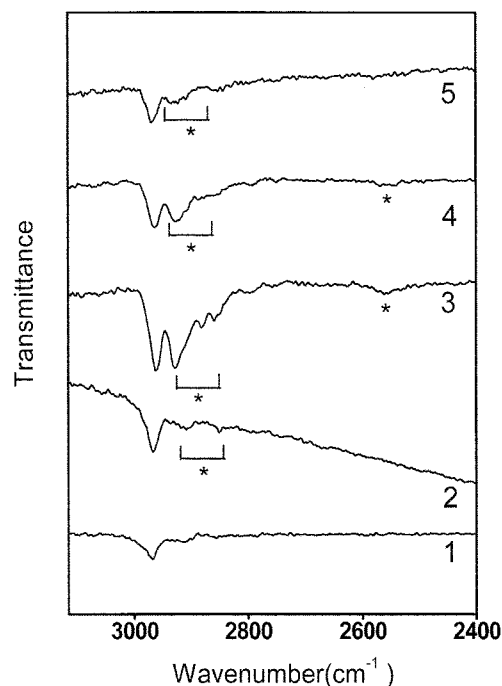


Figure 6. FT-IR spectra of spheres prepared from different mixtures of different precursors in different molar ratios. (1) MTMS: TEA=5:1, (2) DMMSPT:MTMS:TEA=3:1:1, (3) DMMSPT:MTMS: TEA=5:4:1, (4) DMMSPT:MTMS:TEA=3:4:1, and (5) DMMSPT: MTMS: TEA=1:4:1.

posites of PSO/PSQ can be prepared in heterogeneous one step reactions. DMMVS gave the most promising results regarding the production of the solid spheres although only APTMS induced production of solid spheres when DMMVS was the only precursor. Except TEA, all the catalysts used in this study produced solid spheres in good yields from PSO precursors in the presence of MTMS in 16 vol% and higher. The spheres had different mechanical properties depending on the compositions. These spheres will be useful as exfoliator, fillers to enhance impact strength, and carriers of different useful ingredients.

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