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Mechanism of Preparing White Electrophoretic Composite Spherical Particles by Precipitation Polymerization

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Abstract: Under specific property of titanium dioxide and 4-vinylpyridine, titanium dioxide multi-core and poly(divinyl-benzene-styrene-4-vinyl pyridine) shell hybrid composite spherical and smooth particles were prepared in methanol by precipitation polymerization. DSC and TG had detected polymerizing effect, structure unit of polymer was confirmed by FT-IR, and SEM took photographs of composite microsphere. As a result, the stable spherical and smooth particles were obtained. The corresponding mechanism was confirmed by SEM photographs and changing some parameters of core/shell microspheres prepared in a series of methods. The dispersing order and amount of 4-vinylpyridine dominated the mechanism of forming composite spherical particle. Then, the electrophoretic property of the composite particle was verified with a quaternary ammonium salt combined with hydrocarbon bromide and pyridyl covered on the surface of microsphere prepared in methanol by precipitation polymerization.

Key words: synthesis; core-shell polymers; crosslinking; pigments; interfaces

沉淀聚合法制备电泳显示白色球形复合粒子的机理

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摘 要: 基于二氧化钛的特性和 4-乙烯基吡啶的功能, 利用沉淀聚合法在甲醇中合成出二乙烯基苯-苯乙烯-4-乙烯基吡啶共聚物包覆的二氧化钛多核的表面光滑的球形粒子。利用 DSC 和 TG 检测了聚合效果, 通过傅里叶红外光谱证实了聚合物的结构单元, 利用 SEM 观察了复合粒子的表面, 获得了具有稳定性、表面光滑的球形微粒。相应的聚合机理通过分析一系列制备核壳微球方法所得产物的 SEM 照片和改变一些参数所得的结果得以证实。分散的顺序和 4-乙烯基吡啶的用量决定了生成复合球形微粒的机理。进而, 通过溴代烷烃和在甲醇中沉淀聚合产物表面的 4-乙烯基吡啶化合而成的季铵盐证实了复合微粒的电泳特性。

关 键 词: 合成; 核-壳聚合物; 交联; 颜料; 界面

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1 Introduction

As the best white pigment, titanium dioxide was used in many fields of scientific research such as electrophoresis displays, coating technology, and biotechnology^[1-2]. However, the specific gravity of titanium dioxide is so high that a great deal of work was carried out to disperse or embed titanium dioxide particles^[3-7]. In radical polymerizing methods, mainly, there were two means: dispersion polymerization and precipitation polymerization.

Dispersion polymerization involved the utilization of a particle stabilizer or stabilizing groups, such as PVP [poly (N-vinyl pyrrolidone)] or poly (vinyl alcohol)^[8-11]. Nevertheless, precipitation polymerization was a method in the absence of any added stabilizer, and the relevant particle could be washed easily. It had been proposed that precipitation polymerization could be carried out through two means: the efficacious precipitation of nucleated oligomers or particle's effective heap up onto the surface of primary particles^[12-14].

Based on existing theory about titanium dioxide multi-core and polymer shell hybrid composite particle, it was intensive to synthesize titanium dioxide multi-core and functional polymer shell hybrid composite particle. Ulrike Diebold discovered and studied the surface of titanium dioxide^[15], and satisfied elucidation was announced. Pyridine was a Lewis base (the nitrogen atom in the aromatic ring acted as an electron donor). The molecule was absorbed on electron acceptors. Hence, the molecule was expected to bind with the nitrogen-end down to the titanium atoms on the titanium dioxide surface. However, a combined XPS/TPD/STM study showed that pyridine is generally only physisorbed on titanium dioxide (110).

4-vinylpyridine was a dual functional monomer containing both vinyl and pyridyl, and used to prepare polymers or copolymers^[16-22]. Simi-

larly, pyridyl physically absorbed on the surface of titanium dioxide particle. Then 4-vinylpyridine was regarded as a medium connecting titanium dioxide particle with covering polymer.

Meanwhile, divinylbenzene and styrene were used with 4-vinylbenzene to prepare cross-linked particle^[23-29]. Then all solicitude was shown by controlling parameters of precipitation polymerization due to chemical activity of divinylbenzene. Then the mechanism of preparing titanium dioxide multi-core and poly (divinylbenzene-styrene-4-vinyl ben-zene) shell hybrid composite particle designed in this paper would be released. In a part, the released mechanism of precipitation polymerization was different from existing theories.

After precipitation polymerization, the surface of obtained primary core/shell particle was ionized to generate the final product. The characterization of the final product even confirmed the mechanism of precipitation polymerization extensively.

2 Experiments

2.1 Materials

Titanium dioxide (Particle size: 25 nm) was purchased from Degussa Corporation, Germany. All monomers of divinylbenzene (20% mass fraction mixture of isomers), styrene and 4-vinylpyridine were purchased from Alfa Aesar Chemical Co., USA, and purified using cuprous chloride (Beijing Chemical Co., China) as a polymerization inhibitor and stored at $-5\text{ }^{\circ}\text{C}$ prior to use. Analytical grade of 2,2-azobisisobutyronitrile (AIBN, Beijing Chemical Co., China) was used as an initiator without purification. Methanol (Alfa Aesar Chemical Co., USA) in analytical grade was used as the polymerization medium. Ethyl bromide, n-propyl bromide and n-butyl bromide (Beijing Chemical Co., China) were separately used as a shell-ionizing reagent.

2.2 Synthesis

2.2.1 Copolymerization

The polymerization ingredients consisted of

methanol, various compositions of divinylbenzene, styrene and 4-vinylpyridine co-monomer mixture, titanium dioxide and AIBN. Above all, titanium dioxide powder was dispersed into the mixture of all monomers by ball grind for 3 h, and AIBN was dissolved into methanol in a four-neck flask with stirrer, condenser, and thermometer and gas pipe. Then the obtained turbid liquid was charged into the flask with agitation at 300 r/min and dry argon purged. After 0.5 h, polymerization was carried out in a water bath at 65 °C. It lasted 12 h.

The particles were filtered or centrifuged and washed repeatedly with ethanol, which washed residual monomers except cross-linking polymer. The products (powder type) were dried in vacuum at 40 °C for 3 d.

2.2.2 Ionization on the surface of core/shell particle

5 g of dried white powder synthesized by the basis of recipe was dispersed into 50 g of methanol by ball grind for 3 h, and another turbid liquid was obtained. After the turbid liquid was transferred into a flask with stirring, 8 g of hydrocarbon bromide was added into the flask and mixed completely. Then the ionizing reaction was carried out at 65 °C for 6 h. The final particles were filtered and washed with ethanol, repeatedly; and dried in vacuum at 40 °C for 3 d.

3 Characterizations

Scanning electron microscopy (SEM, S-4800, HITACHI, Japan), which was equipped with an energy dispersive spectrometry (EDS) (Horiba EMAX Energy, EX-350), was used to study the morphology of poly (DVB-St-4-VP) microsphere and test the content of titanium in the polymer. Number-average diameter was achieved using Image J, image analyzer software from Wayne Rasband, National Institutes of Health, USA; and diameters of more than 150 particles from SEM microphotographs were counted individual.

The mean square deviation of particle size

was calculated using a formula as follows:

$$\sigma = \frac{1}{n} \sum_{i=1}^n (X_i - \bar{X})^2$$

here, σ is mean square deviation; n is the number of microspheres; $\bar{X}$ is value of number-average diameter of microspheres; X_i is value of diameter of the i -th particle.

Differential scanning calorimeter (DSC, NETZSCH, 200PC, Germany) was used to observe glass transition temperature (T_g) of poly (DVB-St-4-VP). The samples were heated up to 80 °C at a rate of 10 °C/min under a nitrogen atmosphere, and were kept warm at 80 °C for 10 min. Then, the samples were quench-cooled at a maximum rate with liquid nitrogen before reheated in a second time. The data of T_g was collected in the second heating.

Thermal degradation temperature of the crosslinked and shell-ionized microsphere was studied using a thermo gravimetric analyzer (TG, NETZSCH, 209C, Germany). The samples were heated up from 40 °C to 600 °C at a rate of 10 °C/min under a nitrogen atmosphere; the residual mass percent and stability of samples were recorded.

FT-IR (Nicolet 50XC spectrometer, Nicolet, USA) was performed on a spectrometer. The sample was mixed with spectroscopic grade potassium bromide before they were placed in the sample cell.

4 Results

4.1 Confirmation of Polymerization and Structure Unit

DSC and TG confirmed polymerizing effect separately as shown in Fig. 1 and Fig. 2.

In Fig. 1, as amounts of divinylbenzene increasing, no glass transition temperature appeared. As known, polydivinylbenzene, as a homopolymer, had no glass transition temperature due to double C=C bonds in divinylbenzene molecule. The glass transition temperature of polystyrene was in the range of 95~100 °C^[30],

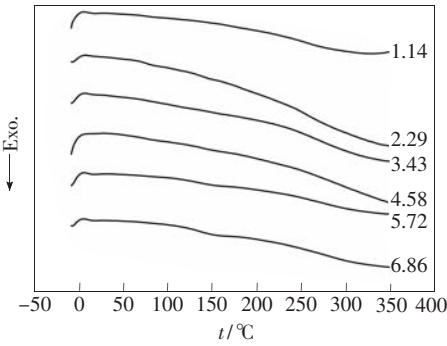


Fig. 1 DSC thermogram of poly (DVB-St-4VP) shell prepared with various mass fraction of DVB from 1.14% to 6.86%

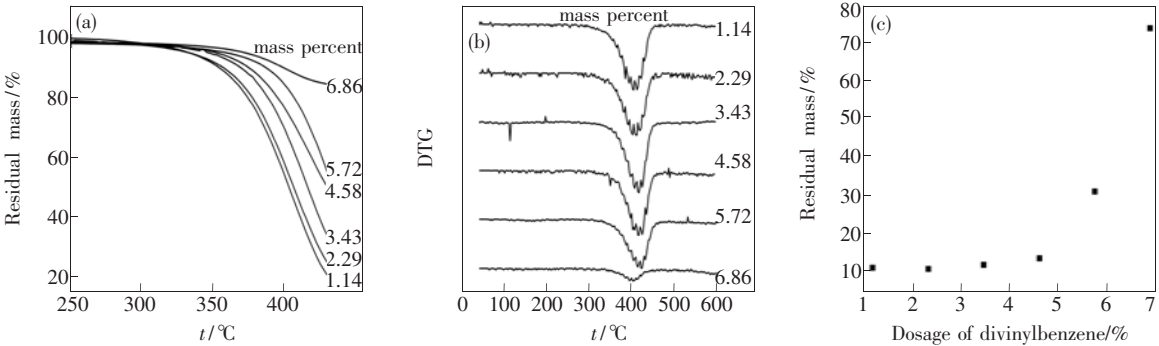


Fig. 2 TG thermogram of poly (DVB-St-4VP) prepared with various mass fraction of DVB from 1.14% to 6.86%

by TG thermogram as shown in Fig. 2.

Fig. 2 (b) showed the first-order differential curves of TG thermogram of poly (DVB - St-4-VP). In Fig. 2, with increasing amounts of DVB from 1.14% to 6.86% mass fraction, the initial weight-losing temperature was changed highly, the range of weight-losing temperature got narrowly, and the height of peaks became lowly.

It appeared that the residual mass ratio got increasingly due to more crosslinked structure. Then, the content of divinylbenzene structure unit in the polymer shell was raised with increasing amounts of divinylbenzene monomer. Fig. 2 (c) exhibited the relationship between dosage of divinylbenzene and residual mass percent. It appeared that the residual mass percentage went down with decreasing amounts of divinylbenzene, and dosage of divinylbenzene influenced the residual mass percentage greatly.

and the glass transition temperature of poly (4-vinyl pyridine) was about at $148\text{ }^\circ\text{C}$ [31]. Then, the inspected glass transition temperature of poly (DVB-St-4-VP) would have been in the range of $95\sim148\text{ }^\circ\text{C}$ if the transition temperature had existed. Practically, no absorption peak existed from $95\text{ }^\circ\text{C}$ to $148\text{ }^\circ\text{C}$ in the curve group even though the content of divinylbenzene was very low. Therefore, it showed that highly cross-linked polymer shell had been obtained.

And the proportion of ingredients with varying amounts of divinylbenzene was characterized roughly

Meanwhile, structure unit of polymer was detected by FT-IR, and the FT-IR spectra were shown in Fig. 3~Fig. 6. Fig. 3~Fig. 5 showed a series of changes of aromatic structures and their substitute groups in FT-IR spectrum.

In Fig. 3, the absorption peak at $2\text{ }230\text{ cm}^{-1}$ assigned to $\text{C}=\text{C}$ unsaturated bond became a little stronger with increasing amounts of divinylbenzene from 1.14% to 6.86%.

In Fig. 4, both absorption peaks of $1\text{ }630\text{ cm}^{-1}$

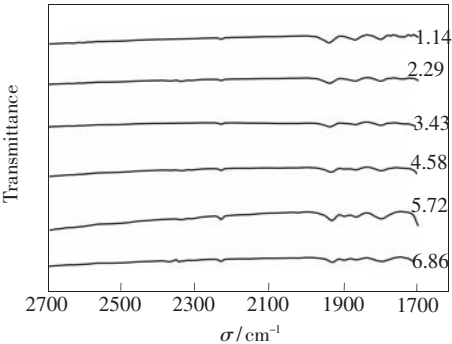


Fig. 3 Different FT-IR spectra in unsaturated bond zone

and $1\,510\text{ cm}^{-1}$ assigned to C—C stretching vibration in 1, 4-divinylbenzene were found obviously, and their intensity were changed strongly with increasing mass fraction of divinylbenzene from 1.14% to 6.86%. Meanwhile, the peaks at $1\,450\text{ cm}^{-1}$ and $1\,600\text{ cm}^{-1}$ assigned to C—C stretching vibration were changed widely, and it confirmed the content of structure unit of bisubstituted benzene, including 1, 2-, 1, 3- and 1, 4-divinylbenzene, had increased.

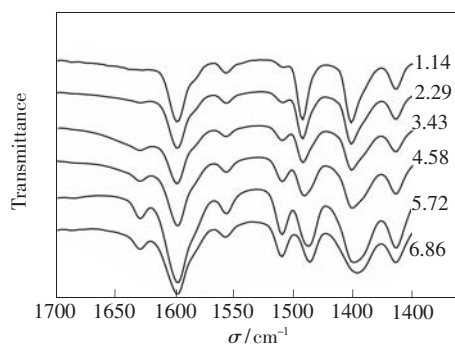


Fig. 4 Different FT-IR spectra in aromatic structure zone

In Fig. 5, the absorption peak at 800 cm^{-1} belonged to C—H wagging vibration in 1,3- or 1,4-divinylbenzene, another peak at 900 cm^{-1} belonged to C—H (isolated hydrogen) wagging vibration in 1,3-divinylbenzene, and the peak at 715 cm^{-1} belonged to ring deformation vibration. They were changed strongly or widely with increasing mass fraction of divinylbenzene from peak of C—H (4 adjacent hydrogens) wagging vibration in 1,2-divinylbenzene were in the 1.14% to 6.86%; like this, if the absorption range of

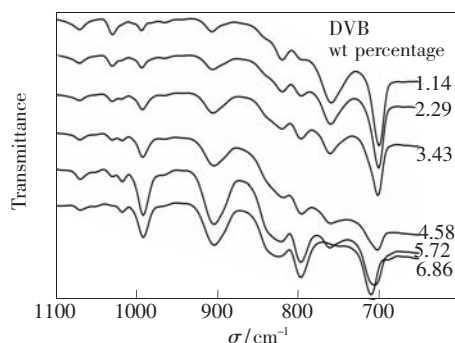


Fig. 5 Different FTIR spectra in aromatic substitute group zone

$770\sim 730\text{ cm}^{-1}$, it would become strongly. In practice, that peak got weaker. Then, the main ingredient of divinylbenzene used in this paper mainly contained 1,3- and 1,4-divinylbenzene.

In Fig. 6, characteristic absorption peaks of structure units of 4-vinylpyridine in shell polymer appeared clearly at $1\,500\text{ cm}^{-1}$ and 800 cm^{-1} ; the former was assigned to C=N stretching vibration in 4-vinylpyridine due to a doublet in FT-IR spectrum, the last one belonged to C—H deformation vibration of adjacent ring of 4-monosubstituted pyridine.

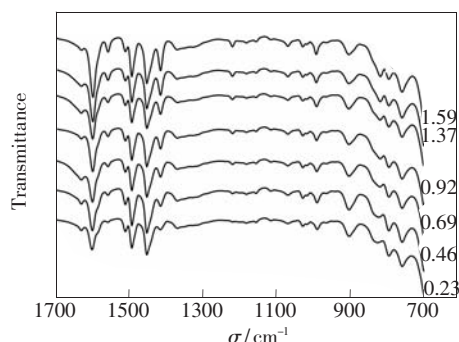


Fig. 6 Different FT-IR spectra among pyridyl groups

Additively, the content of titanium dioxide was tested by EDS, and the relationship between titanium dioxide's dosage and percentage content in core/shell particle was shown in Fig. 7.

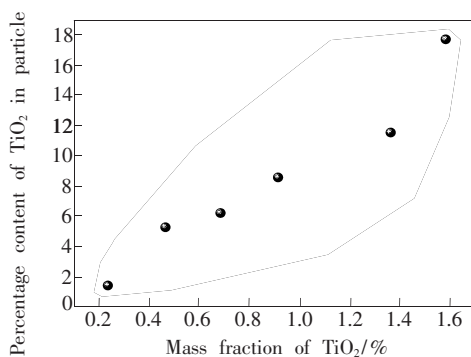


Fig. 7 Relationship between titanium dioxide's dosage and percentage content in particle

It showed that the percentage content of titanium dioxide in core/shell particle was not only changed increasingly with various mass fraction of titanium dioxide from 0.23% to 1.58%,

but a linear relationship between percentage content of titanium dioxide in core/shell particle and dosage of titanium dioxide in the original ingredient was also displayed on the whole.

On the basis of above physical characterizations, the photograph of composite microsphere was obtained by means of SEM, and it was shown in Fig. 8.

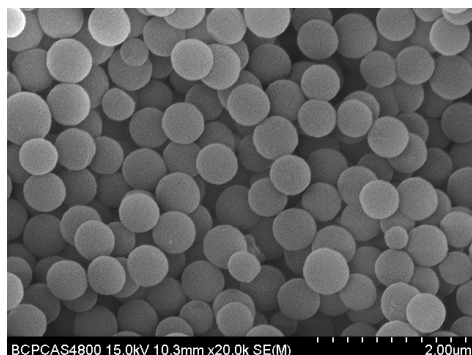


Fig. 8 SEM photography of titanium dioxide core and poly (DVB-St-4-VP) shell hybrid composite spherical particle

4.2 Discovery of mechanism of forming composite spherical particle

The relevant mechanism of forming spherical was analyzed by virtue of changing parameters. Therefore, discussion about the mechanism was carried out under control of constant stirring velocity.

4.2.1 Titanium dioxide core-embeded mechanism

Titanium dioxide was dispersed separately by means of four kinds of method. The SEM photographs of corresponding composite microspheres were displayed in Fig. 9.

In Fig. 9(a), titanium dioxide powder was dispersed into methanol by a ball-grind; the obtained turbid liquid was poured into the mixture of all monomers. Fig. 9(b), titanium dioxide powder was dispersed into the mixture of divinylbenzene and styrene by a ball-grind, the obtained turbid liquid was poured into 4-vinylpyridine/methanol solution. Fig. 9(c), titanium dioxide powder was dispersed into 4-vinylpyridine by a ball-grind, the obtained turbid

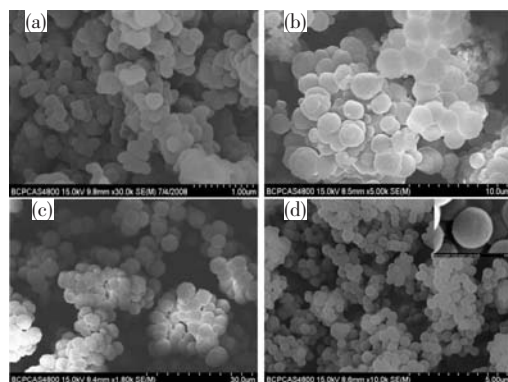


Fig. 9 Different appearances upon four TiO_2 core-dispersed methods

liquid was poured into divinylbenzene-styrene/methanol solution. Fig. 9(d), titanium dioxide powder was dispersed into the mixture of all monomers by a ball-grind. The obtained turbid liquid was poured into the mixture of AIBN and methanol. At last, precipitation polymerization occurred on the surface of titanium dioxide particle dispersed separately by above four methods. As a result, it was obvious that the shape of microsphere prepared with titanium dioxide powder dispersed by method(d) was spherical and smooth.

By method (a), experiments agree with the theory, and molecular and dissociative absorption between methanol and titanium dioxide occurred^[16]. Dissociation happened via breaking of the O—H bond of methanol, and absorbing methoxy species on Ti atom. Several absorption configurations were separated by a small or negligible barrier at room temperature. Interestingly, only molecular absorption was observed on TiO_2 (110), even when point defects were present. In contrast, a variety of products formed on TiO_2 (100). Then, TiO_2 particle absorbing CH_3OH was transferred into a novel particle whose surface was covered with $-\text{CH}_3$. Therefore, the appearance of corresponding shell polymer prepared on the surface of TiO_2 was not spherical and smooth as shown in Fig. 9(a).

In Fig. 9(b), core/shell microspheres were

heaped up due to Van de Waals force between TiO_2 particle and mixture of DVB and St. Just because of the weak interaction, TiO_2 particles were not dispersed sufficiently.

Besides the above mentioned, judging by Fig. 9(c), pyridyl group binded more strongly to steps with certain orientations to Ti atoms, and strong pyridyl group absorption was activated at room temperature^[32]. It was proposed that stable species had been formed via dehydrogenation, which would act as nucleation sites for the growth of larger pyridyl group condensates. Then the surface of TiO_2 core modified with 4-vinylpyridine was scattered with only ethenyl groups after dispersing. These ethenyl groups probably homopolymerized, and the interaction among modified core and both of divinylbenzene and styrene was abated. Therefore, the final microspheres were heaped up as shown in Fig. 9(c).

Fig. 9 (d) exhibited TiO_2 core and poly (DVB-St-4-VP) shell hybrid composite spherical and smooth particles. By method(d), on the basis of absorption of pyridyl group upon the surface of titanium dioxide particles, ethenyl group of 4-vinylpyridine was stretched into an unsaturated phase composed of divinylbenzene and styrene, and it was ensured that titanium dioxide particles was dispersed and mounted into shell polymer when all monomers were initiated into copolymerization. Consequently, titanium dioxide core-contained mechanism was shown in Fig. 10.

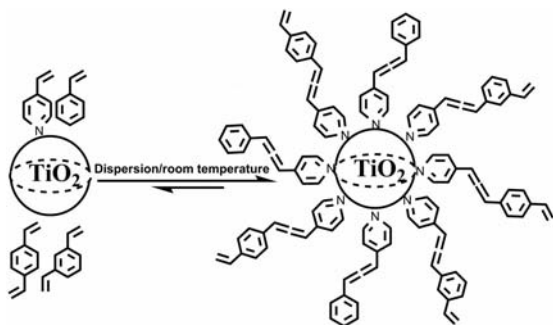


Fig. 10 Process of TiO_2 particles dispersed into all monomers

4.2.2 Active monomer and spheration

As known, divinylbenzene was the most active monomer among all monomers used in this paper. It was seen forever that a clear divinylbenzene/methanol solution was changed into turbid liquid before heated methanol refluxed. By virtue of the polymerizing phenomena and TiO_2 dispersing methods, it was proposed that, in the initial stage, the ethenyl groups on the compounded core with 4-vinylpyridine and TiO_2 particle was copolymerized with divinylbenzene and styrene. Then, the primary core/shell composite particle was formed and its stability was improved in methanol. Shortly, free 4-vinylpyridine in methanol was anticipated into copolymerization to form an interface between pyridyl group on the surface of core/shell particle and methanol. Consequently, spheration occurred inside. If strongly active monomer had not existed, a keen competition between methanol and 4-vinylpyridine would have occurred due to powerful absorption of them on the surface of titanium dioxide; the same reaction had ever been done only with 4-vinylpyridine and styrene, finally, latex-similar liquid was obtained.

In brief, titanium dioxide core and poly (DVB-St-4-VP) shell hybrid composite spherical and smooth particle were prepared in methanol by precipitation polymerization. The relevant processes of reaction mechanism and spheration

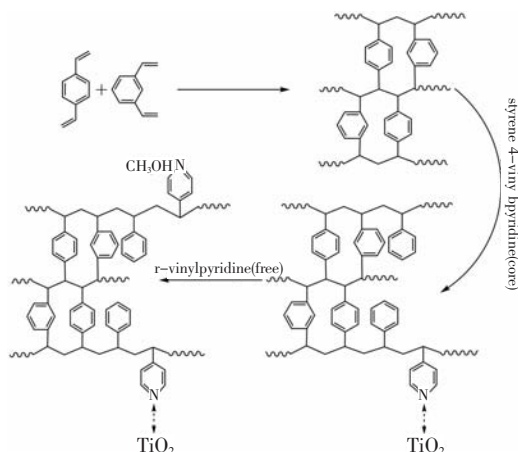


Fig. 11 Reaction process of core/shell microsphere prepared in methanol

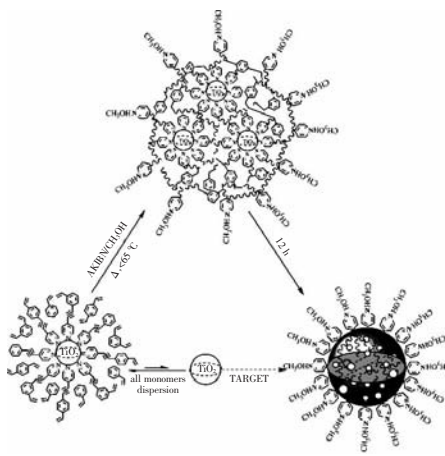


Fig. 12 Spheration process of core/shell microsphere prepared in methanol

mechanism were proposed separately in Fig. 11 and Fig. 12.

4.3 Controlling particle size under the above mechanism

This section was imperative to reveal the application of the mechanism of forming composite spherical particle. In this paper, diameter of composite spherical particle was influenced by some controlled parameters such as amounts of every material, stirring velocity, reaction temperature, and volume of reacting vessel, etc.

4.3.1 Particle size and varying amounts of 4-vinyl -pyridine

Fig. 13 exhibited the changes of particle size and its mean square deviation of microspheres prepared with increasing mass fraction of 4-vinylpyridine from 0.23% to 1.59% (to total). Overall, both of particle size and its mean square deviation of target microsphere went down with increasing mass fraction of 4-vinylpyridine from 0.23% to 1.59% (to total). It was implied that TiO_2 particles had been dispersed more sufficiently with increasing mass fraction of 4-vinylpyridine, and 4-vinylpyridine dissolved in methanol prevented primary seeds from growth while it was being involved in copolymerization. In addition, the spherical appearance of microsphere was shaped by hydrogen bond formed with nitrogen atom of pyridyl group and hydroxyl of

methanol. Then, one kind of interface stretching force between methanol and copolymerized 4-vinylpyridine was generated, and only spherical shape of target microsphere released the interface stretching force until stable microsphere was obtained.

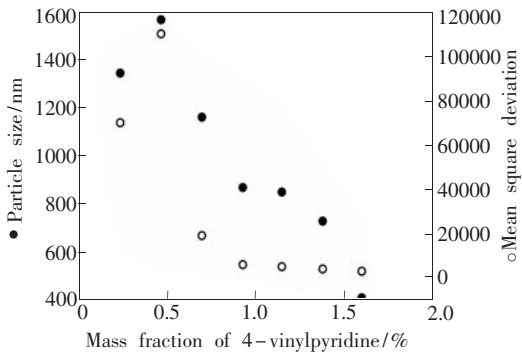


Fig. 13 Relationship between various mass fraction of 4-vinylpyridine and both particle size and its mean square deviation of corresponding microsphere

4.3.2 Particle size and various mass fraction of titanium dioxide

Fig. 14 showed the relationship between various mass fraction of titanium dioxide and particle size and its mean square deviation of corresponding microspheres. It appeared that particle size and its mean square deviation descended with increasing mass fraction of titanium dioxide. It was obvious that shell polymer was divided into more segments with increasing number of dispersed titanium dioxide core.

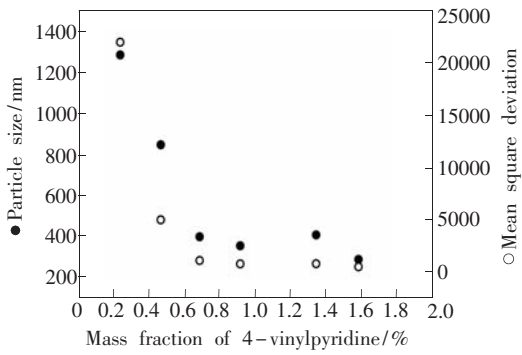


Fig. 14 Relationship between various mass fraction of titanium dioxide and both particle size and its mean square deviation of corresponding microsphere

4.3.3 Particle size and various mass fraction of methanol

Fig. 15 demonstrated that titanium dioxide core and all monomers had been dispersed more completely with increasing mass fraction of methanol as reaction medium, then the corresponding particle size of microsphere became smaller.

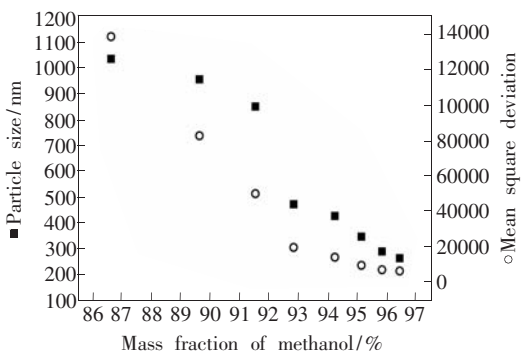


Fig. 15 Relationship between varying amounts of methanol and both particle size and its mean square deviation of corresponding microsphere

4.3.4 Particle size and various mass fraction of divinylbenzene

Fig. 16 showed that both particle size and its mean square deviation of microspheres changed increasingly with increasing mass fraction of divinylbenzene from 1.14% to 5.72% (to total), and the particle size and its mean square deviation of microspheres prepared only with divinylbenzene (6.86%) fell down rapidly. It was proposed that particle size and its mean square deviation was dominated with change of space structure of microsphere. As known, polystyrene was a linear homopolymer, and the relevant structure units marshaled well; polydivinylbenzene was a three-dimension homopolymer, and the structure units compacted very well. Then the difference between particle sizes and their mean square deviations of microspheres at both ends of X-axis was very small. Only when the dosage of divinylbenzene increased and the dosage of styrene decreased, the structure units of poly (DVB-St-4-VP) misarrange and particle size of corresponding microsphere swell until the maximum value existed. Then particle size

changed smaller due to the enhancement of degree of space order with increasing amounts of divinylbenzene.

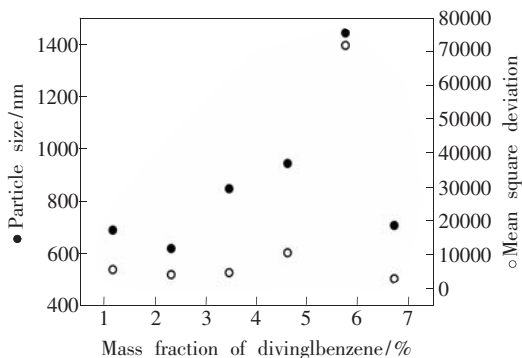


Fig. 16 Relationship between various mass fraction of divinylbenzene and both particle size and its mean square deviation of corresponding microsphere

4.4 Additional remarks

Pyridyl group on the surface of TiO_2 core and poly (DVB-St-4-VP) shell hybrid composite spherical particles were characterized by TG and zeta potential after combination reaction between pyridyl and hydrocarbon bromide.

Fig. 17 enumerated three curves of the first-order differential of TG thermogram of three kind of quaternary ammonium salts independently on the surface of core/shell particles; they were ethyl pyridinium bromide, n-propyl pyridinium bromide and n-butyl pyridinium bromide. As seen in Fig. 17, in the range from 40 ~ 300 °C, all slope-temperature curves had undulation, and thermogravimetry took place with different intensity. It was manifested that thermogravimetry broke out more strongly in order of n-butyl pyridinium bromide, n-propyl pyridinium bromide and ethyl pyridinium bromide. And equally, in the same order, losing mass were 8.87%, 7.13%, 5.44%. It conformed to the destabilizing ruler of quaternary ammonium salts.

In addition, three kinds of surface modified core/shell particles were dispersed separately into tetrachloroethylene, and three kinds of turbid liquid were obtained. After measuring, zeta potential of these turbid liquid were 31.0, 39.4,

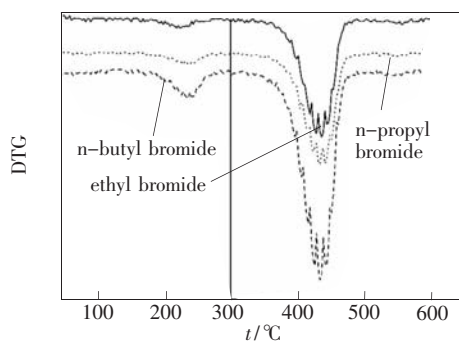


Fig. 17 The first-order differential curves of TG thermogram of pyridiniums

9.4 mV in the above order. It was proved that zeta potential was so high in that pyridinium salt had been generated with hydrocarbon bromide and pyridyl group on the surface of core/shell particle.

Then, pyridyl group on the surface of particles was characterized and final TiO_2 core and ionic poly (DVB-St-4-VP) shell hybrid composite spherical and smooth particle were obtained.

5 Conclusion

Under the absorption of pyridyl upon the surface of titanium dioxide particle, titanium dioxide core was contained and shell copolymerization was carried out on the surface of the core. Another, activity of divinylbenzene and interaction between pyridyl and methanol became a prerequisite for synthesizing spherical and smooth core/shell particle. And the mechanism of forming TiO_2 multi-core and poly (DVB-St-4-VP) shell hybrid composite spherical and smooth particle was proposed. Under this mechanism, spherical and smooth particles with varying diameters were prepared by controlling relevant parameters influencing upon the above mechanism. Moreover, utilizing the specific property of tertiary amine of pyridyl, the surface of core/shell particles was ionized for electrophoresis.

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