

Advances in preparation and application of monodisperse colloidal silica particles*

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Abstract The applications of monodisperse colloidal silica particles are constantly extended because of their uniformity in morphology and size as well as their easily-modified surface properties. This review summarizes the research progress made by the author and co-workers on the formation conditions and mechanism of monodisperse system and the applications in various fields such as particle analysis, chromatography, catalysis, optical physics, and intelligent materials.

Keywords: monodisperse silica particle, particle analysis, non-porous chromatographic packing, model catalyst, colloidal crystal, model electrorheological fluid.

Monodisperse colloidal silica has become one of the most widely studied monodisperse systems since Stöber et al. reported the preparation through hydrolysis and condensation of alkoxysilanes in a mixture of alcohol, water, and ammonia^[1]. The particles prepared in this way have high monodispersity, well defined morphology, controlled size, and surface with silanol groups by which they are functionalized. The constantly developing techniques of surface modification offer new opportunities for expanding their applications.

Our group has studied the preparation and application of monodisperse colloidal silica with other cooperators for several years. Firstly, based on Stöber's method, we developed a method for preparation of the particles, aiming at extending the size range of the synthesized particles and improving the monodispersity of the systems. Through the studies on formation conditions, mechanism, and kinetics of monodisperse systems, a seeding technique was developed and improved^[2-6]. The particles with diameters ranging from dozens of nanometers to 2.5 μm can be prepared by the seeding technique. Fig. 1 shows the transmission electron micrographs (TEM) of monodisperse silica particles with different sizes. The relative standard deviation of size distribution was less than 5% for ≥ 150 nm particles; final concentration of the disperse phase in the reaction systems reaches 10%. Secondly, the surface modifications of particles with $\text{Al}(\text{OH})_3$, Al_2O_3 , NiO , MoO_3 , TiO_2 , C_8 and C_{18} aliphatic groups, aminopropyl, phthalocyanine (tppS₄ or CuTsPc) were investigated respectively. Moreover, we found that the pore of the particle can be closed through hydro-thermal treatment^[7]. The functional-

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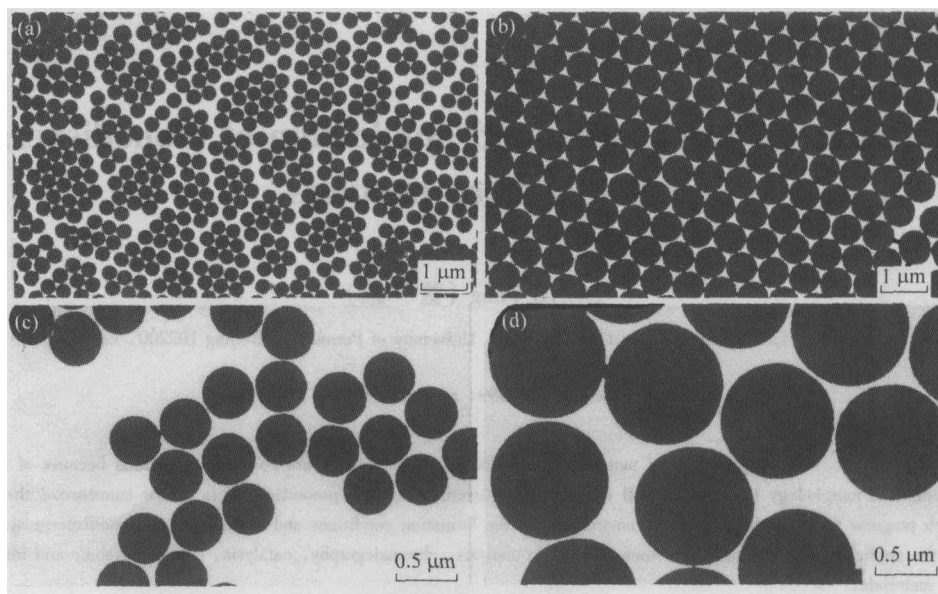


Fig. 1. TEM of monodisperse silica particles with different sizes.

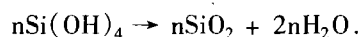
ized particles and particle systems have been utilized in various fields such as non-porous rapid high performance liquid chromatographic (HPLC) packings, model catalysts for hydrogenation of heavy oil, monodisperse model electrorheological fluids, colloidal crystals and their optical properties, etc. [8–14]. The possibility of using such particles as standard or reference particles to calibrate particle analyzers was also investigated.

1 Fundamental research on the preparation of monodisperse particles

The formation of the monodisperse systems is a multi-dimensional and dynamic process which is very sensitive to the preparation conditions and is restricted by many complicated factors. As a result, some reaction mechanisms, even with the Stöber's mechanism, have not yet been understood and the preparations of monodisperse particles are still confined in the laboratories. In order to improve this status, several fundamental subjects concerned in the preparation have been investigated, including the reaction kinetics of the hydrolysis and condensation of tetraethylorthosilicate (TEOS), the growth mechanism of monodisperse particles, and the critical conditions of new particle formation^[3–6].

1.1 Kinetics of hydrolysis and condensation of TEOS under the conditions of forming monodisperse sol

The reactions of the formation of the monodisperse silica system are the hydrolysis of alkoxy-silanes and the condensation of silicic acid. The overall reactions can be written as follows:



Although these reactions are well known in the progress of sol-gel processing in advanced ceramic pro-

duction, and the kinetics of the reactions has been studied, there are essential differences in reaction conditions and direction between sol-gel processing and monodisperse sol producing. The kinetics data of the former cannot be extrapolated to the latter. Early studies indicated that TEOS hydrolysis is the rate-limiting step of the reaction. Once the supply of TEOS exceeds the rate of TEOS hydrolysis under the reaction condition, the monodispersity of the system will be destroyed. Keeping appropriate rate of the hydrolysis and condensation is the prerequisite for the effective control of the formation process of monodisperse systems. We determined the rate constants of TEOS hydrolysis and condensation by means of the extraction/gas chromatography and a conductometer respectively^[3,4]. The relationships of the hydrolysis rate constant (K_H) and condensation rate constant (K_C) with the reaction condition variables in a wide range were empirically found to be

$$K_H = 74.36 \exp\left(-\frac{25211}{RT}\right) [H_2O]^{1.267} [NH_3]^{0.971} \quad (1)$$

$$K_C = 19408 \exp\left(-\frac{33202}{RT}\right) [H_2O]^{1.196} [NH_3]^{0.785} \quad (2)$$

Equations (1) and (2) enable us to calculate the disappearance rate of TEOS and silicic acid during the formation of monodisperse systems under the common preparing conditions, and provide favorable means for investigating the relationship of reaction rate and growth rate of particles.

1.2 Mechanism of new particle formation and particle growth

The condensation of silicic acid can be divided into two stages, particle nucleation and nuclear growth. Monodisperse particles are the result of nuclear growth. However, the mechanism of particle growth is still not fully understood and is open to debate. Some researchers suggested that the growth should be limited by diffusion and others thought it should be limited by surface reaction^[15,16]. In order to solve this problem, we have studied the relationship between the growth rate of monodisperse particles and the particle diameter. In the case of diffusion-controlled growth, the equation of growth rate of each particle can be derived from Fick's law:

$$\frac{dL}{dt} = 4DV \frac{C_\infty - C_s}{L}, \quad (3)$$

where L the particle diameter, V the mole volume of growth fraction deposited onto the particle, D the diffusion coefficient of the diffusing material, C_∞ the bulk concentration, and C_s the saturation concentration on the particle surface. In the case of surface reaction-limited growth, the particle growth rate in volume is proportional to the external surface area of the particle. One can derive the growth rate equation:

$$\frac{dL}{dt} = 2K_s V (C_m - C_s), \quad (4)$$

where C_m is the concentration of growth intermediate, and K_s the surface reaction rate constant. From eqs. (3) and (4), one can conclude that the growth rate is independent of particle size in surface re-

action-limited process and is inversely proportional to particle size in diffusion-limited process. Therefore, we analyzed the growth rates of the particles in a suspension of silica particles with a bimodal size distribution^[5]. It was found that when there was no formation of new particles, the diameter difference of the particles with two sizes was constant during the growth process. This means that particles with different sizes grow at the same rate, which demonstrates the properties of surface reaction-limited process. When there was the formation of new particles, however, we obtained the curves of fig. 2, which show that smaller particles grow faster than larger ones during the nucleation period, i.e. the growth proceeds through diffusion-limited process. But both smaller and larger particles grow at same rate before and after the formation of new particles. In the meanwhile the growth mechanism changes to surface reaction-limited process. This kind of transition of growth mechanism has never been reported before.

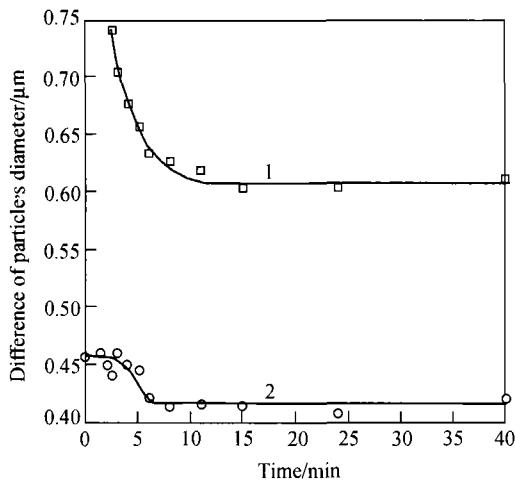


Fig. 2. Diameter differences vs. time during growth of particles. Curve 1, diameter difference between seeds and new particles; curve 2, diameter difference between larger and smaller particles.

before.

The key factor resulting in the formation of new particles is the insufficient surface area of seed particles, which increases the concentration of silicic acid-condensed species, and the latter tends to condense to form larger sub-particles. Some of the sub-particles partly aggregate to form new particles independent of seed particles, while others are partly condensed onto the surface of seed particles through diffusion-controlled process because of their low diffusion coefficient. In order to prepare the particle systems with high monodispersity, the formation of new particles must be avoided during the growth process. By experiments, we have determined the critical conditions for seeds with different sizes, i.e. critical specific surface area, S_{pc} , at which new particles are formed^[6]. The curve in fig. 3 indicates that S_{pc} is proportional to the size of seed particles. This result completely agrees with the foregoing conclusion about diffusion-controlled growth during the formation of new particles.

On the basis of the above studies, we have developed a seeding technique to grow monodisperse particles continuously, in which either commercial silica sol or the silica sol prepared by ourselves is selected to be seeds, then under the typical Stöber's

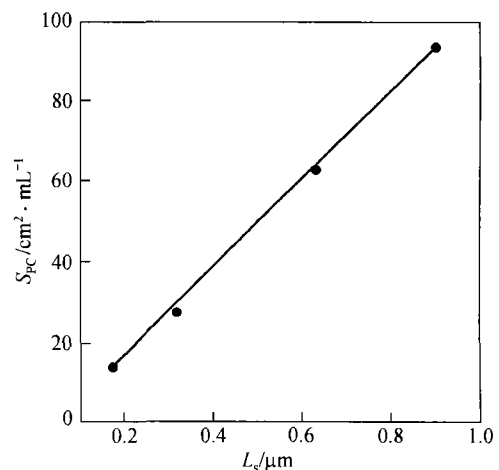


Fig. 3. Critical specific surface area S_{pc} vs. seeds diameters L_s .

conditions, the seed particles grow by feeding stock continuously until monodisperse system is formed. This method can precisely control and predict the particle size and size distribution. The deviation of the particle sizes between practical and predictive values is usually less than 10%, and the amount of one batch of particles can reach the scale of a hundred grams.

2 Applications of the particles with monosize

2.1 As the standard particles for calibration

Monodisperse latex (e.g. polystyrene) spheres have been regarded as the standard particles to calibrate particle analyzers for a long time. But the latex spheres have some shortcomings: their size undesirably changes in organic solvents; it is difficult to calibrate the particle analyzers of sedimentation type with water, because their specific gravity is close to unity; and sub-micron latex standard particles are rarely available. In contrast, silica particles have no such shortcomings as mentioned above. We synthesized 1 μm and 2 μm monodisperse silica particles to prepare a series of suspensions as the model water samples. The suspensions with known particle concentration and size were used to study the possible harm of the suspending solid particles to model oil reservoirs. The results were satisfactory and provided a base for setting up the standard of water quality in the water flooding of oil field recovery. In addition, the study proved that the influence of silica solubility in water on size of particles could be eliminated at extremely diluted condition of 10^{-4} wt% order concentration. And the number average diameter of monodisperse silica particles obtained by a calibrated transmission electron-microscopy (TEM) is consistent with the most probable diameter measured on a Coulter counter which was calibrated by polystyrene standard particles. The sub-micron monodisperse silica particles we developed were used successfully as the standard model dust particles to calibrate the first 0.1 μm dust particle counter made in China. The effectiveness of the particles we synthesized is the same as that of the standard provided by Particle Measuring Systems and Duke Scientific Corp.

When using monodisperse silica particles as the standard particles, it has to be noted that partial aggregation between the particles will cause serious error to the particle analyzers which can not give most probable diameter expressed in particle count (e.g. sedimentation type particle analyzers). Therefore we synthesized 1 μm particles, S10-1, which are hardly aggregated, for calibration usage and analyzed them by a TEM (H-800), a disc centrifuge particle analyzer (BI-XDC), and a dynamic laser scattering (DLS) particle analyzer (ZetaPlus) respectively. The results are presented in table 1.

Table 1 Diameter of S10-1 measured by different ways

Method	Diameter/nm	
TEM	number average diameter	1037
	most probable diameter	1033
Disc centrifuge	mass median diameter	1031
	volume average diameter	1080
	geometric average diameter	1040
DLS	effective diameter	1053

Table 1 indicates that the data obtained from different apparatuses are very similar although they

work on different principles and are expressed in different ways. Recently the S10-1 standard particles have been used for calibration of LKY-3 disc centrifuge particle analyzers made in China.

2.2 As HPLC packings for separation of bio-polymers

Traditional packings of HPLC with internal pores have great mass transfer resistance and lower column efficiency for the separation of bio-polymers, e.g. proteins. Non-porous monodisperse silica fine particles after surface modification used as HPLC packings present close packing and form uniform caves among the particles in the column. The size of caves is a function of the particle diameter. The separation of solutes occurs on the external surface of particles. This kind of novel packings effectively overcomes the shortcomings of traditional packings and becomes an important method for high-speed separation of bio-polymers. We and Wang's group in Chemical Physics Institute of Chinese Academy of Sciences synthesized $2.1\ \mu\text{m}$ monodisperse silica particles and prepared non-polar stationary phases bonded by C_8 and C_{18} aliphatic radicals, which were treated by hydro-thermal method to close the pores and dealt with octodecyltrichlorosilicate and octyldimethylchlorosilicate respectively^[8]. The chromatograms of five varieties of proteins under gradient elution on two kinds of non-porous packings (NPS- C_{18} , NPS- C_8) and a macro-porous packing (Chromgabond- C_4) are shown in fig. 4. It demonstrates that the peaks of two proteins with higher molecular weight (BSA and Ova) in the macro-porous packing expand obviously and, however, the peaks in the non-porous packings are narrowed. Moreover, the column length with non-porous packings is reduced to 1/3 of that with macro-porous packing, so the time for analysis is shortened.

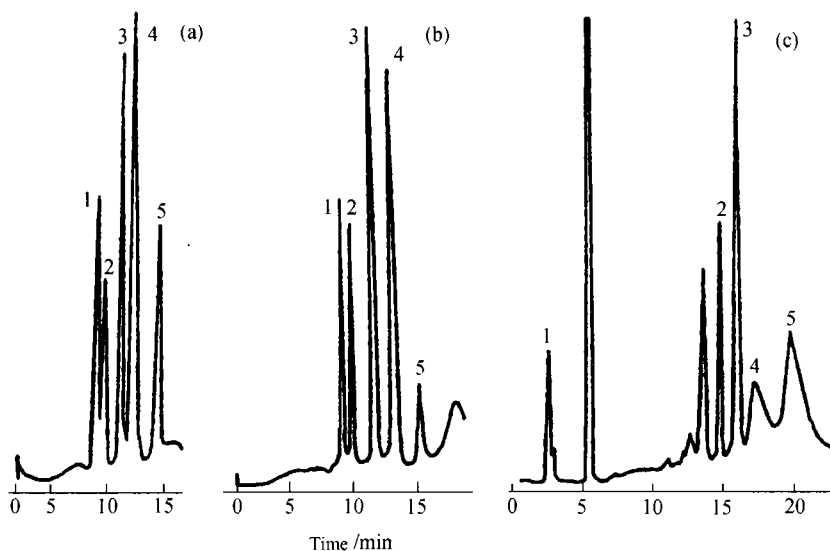


Fig. 4. Protein separation on non-porous packings and a macro-porous packing. Chromatographic columns: (a) NPS- C_{18} , $2.1\ \mu\text{m}$, $50 \times 5\ \text{mm}$ i. d.; (b) NPS- C_8 , $2.1\ \mu\text{m}$, $50 \times 5\ \text{mm}$ i. d.; (c) Chromgabond- C_4 , $150\ \text{mm} \times 4.6\ \text{mm}$ i. d.. Peaks: 1, ribonuclease-A; 2, insulin; 3, lysozyme; 4, bovine serum albumin (BSA); 5, ovalbumin (Ova).

2.3 Model catalysts with uniform and controlled pore size for heavy oil conversion

At present, the design and development of the catalysts with suitable macro-pore are the urgent assignments for heavy oil conversion. We developed a series of model catalysts with uniform and adjustable pore size ranging from 6 nm to 1 000 nm for improving and developing novel catalysts of heavy oil cracking and hydrogenation^[9,10]. Combined with the techniques of surface modification, the active surface of catalyst can be changed according to the requirements. Using these model catalysts in the experiments one can acquire the following important information: (i) the course and mechanism of catalytic reaction of heavy oil; (ii) the effect of pore structure of the catalyst on reactant molecular diffusion and the relationship between the pore structure and selectivity as well as reactivity; (iii) the match of the pore structure of catalytic supporter with the stock molecule; (iv) the single catalytic behavior of active surface without diffusion disturbances from wide pore distribution and micro-pore. This kind of model catalyst was prepared by aggregating non-porous monodisperse silica particles to form uniformly interstitial pores (see fig. 5)^[9]. They have the following characteristics, i. e. the most probable pore diameter is the function of built particle diameter; the range of pore size distribution is 0.14—0.50 times of the built particle diameter; the range of porosity is 26%—35%, roughly independent of the built particle diameter. The active components can deposit on the silica surface before or after the accumulation of the particles. The loading and distribution states of active components on the surface can be controlled. Six active components including Al_2O_3 , TiO_2 , NiO , MoO_3 , etc. were used respectively to modify the surface of monodisperse silica particles or model supporters^[17] 1), 2). We investigated the absorption and diffusion properties of Daqing vacuum residue oil (the calculated equivalent spherical diameter is 1.79 nm) at 110 °C on five model supporters with pore diameters ranging from 6.6 nm to 85.8 nm, respectively, It was found that on the supporters with the pore diameter of 20 nm, the restrictive diffusion of the residue oil molecules still existed. This result was consistent with that calculated from the Pawar's restrictive diffusion factor equation^[18]. The rates of hydrodesulfurization and denitrification of the straight gas oil for the model catalysts supported NiO and MoO_3 can reach 85.9% and 71.8% respectively in a continuous micro-reactor system.

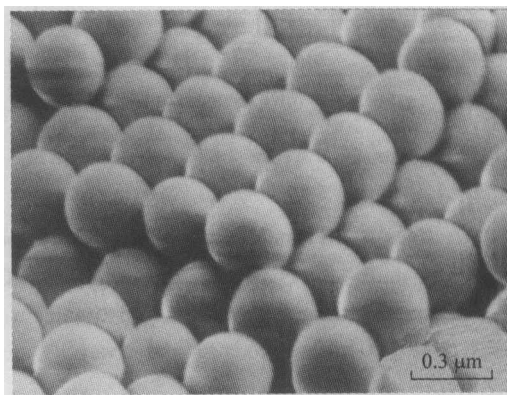


Fig. 5. SEM micro-graph of model supporter aggregated with monodisperse silica particles.

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2.4 Colloidal crystal and its optical effects

It has been known for a long time that monodisperse colloidal silica and polystyrene spheres with diameters comparable with the wavelength of visible light can be automatically arranged to form

1) Zhu, Y., Preparation and characterization of the model supporters with uniform pore size, Master degree thesis, University of Petroleum, China, 1997.

2) Lu, X. J., Preparation and characterization of the model catalysis with uniform pore size, Master degree thesis, University of Petroleum, China, 1999.

colloidal crystals. Recently, the studies on the optical effects of colloidal crystal have become a fresh focus of studies in the fields of optical physics and solid physics with the research progress of photonics and photonic crystals. A photonic crystal is a new type of material with a photonic band gap^[19]. Its typical structure is a three-dimensional substance with periodic refractive index. The period is the magnitude of light wavelength. The behavior of a photon in a photonic crystal is similar to that of electron in an atomic crystal. New photonic devices may be developed with this kind of photonic crystal. We, together with our cooperation partner Prof. Zhang Daozhong and his group, prepared a series of visible and near-infrared

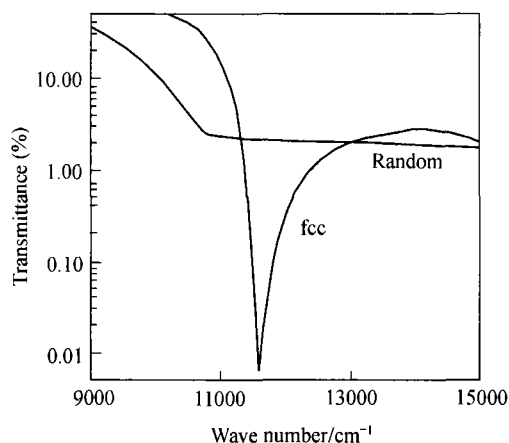


Fig. 6. Transmission spectra of a fcc silica colloidal crystal and a random silica suspension.

colloidal crystals made of sub-micron monodisperse silica spheres^[11,12]. The structure of silica colloidal face-centered-cubic (fcc) crystals was determined by the Kossel rings analysis. The real distance between crystal lanes and the positions of the high-symmetry points of the first Brillouin zone were measured. In addition, the transmission spectrum in the $[111]$ direction, i. e. L point of the first Brillouin zone, was also measured in the visible and near-infrared regions and is shown in fig. 6. The spectrum demonstrates a sharp dip around 11600 cm^{-1} . This result coincides quite well with the lowest gap calculated at the L and X points for our real fcc structure. Because of a lower SiO_2 refractive index ($n = 1.45$) the complete band-gap could not be found. We tried to increase the refractive index of the complex particles made of coating monodisperse silica sphere with titania (TiO_2 , $n = 2.50$). A multi-step coating procedure gives a 40 nm of coating thickness of titania on the silica core^[17]. This means that the volume fraction of titania in a $\text{SiO}_2/\text{TiO}_2$ complex sphere with 200 nm diameter may reach 50%. A further study is under way.

2.5 Monodisperse model electrorheological fluids

An electrorheological fluid (ERF) consists of an insulating oil and the solid fine particles suspended in the oil. Under an electric field, easily polarized particles become electric doublets. The electric doublets affect each other and form the chains between two electrodes to change the apparent viscosity and shear stress of liquid. The attributes of the fluids can quickly, continuously and reversibly vary between liquid and solid through programmed control of the field strength, so they are potentially intelligent materials. However, the performance of ERF cannot meet the requirements in engineering application right now. The reasons are that the ER response mechanism has not been thoroughly understood and many factors which affect ERF performance are to be further understood. One of the poorly understood areas, for example, is the effect of particle size on ER response. It is concerned with the stability of engineering application. In the previous work polydisperse systems were usually utilized, so definite conclusions could hardly be obtained. Monodisperse silica particles are not only uniform in size but also spherical in morphology. The apparent viscosity of suspensions with spherical particles is the lowest, and the ER response is the fastest under the conditions of the same particle size and concentration. So the monodisperse silica as a model system has been used in investigating the effect of particle size to get rid of the different influences on the response time and viscosity from a polydisperse system with various particle sizes and particle

shapes. We prepared a series of model ERFs with various sizes and surface properties to observe the rheological behavior under dc or ac field (fig. 7 is a photomicrograph of model ERF chaining)^[13,14]. It is found that the influence of particle size on ER behavior may be completely contrary to each other for the model systems with different types of particle surface. For the system with the particle surface modified by aliphatic groups, the ER response increases with the increase of particle size in a dc field due to the strong wetting ability. For the unmodified silanol surface, however, the ER response decreases with the increase of particle size under the same conditions due to the weak wetting ability. In an ac field, the results obtained at low-frequency were similar to that in dc field, but in a high-frequency field both particle systems with different surface properties showed the same characteristics, i. e. the ER response of the system with smaller particles is higher than that with larger ones. The discovery of these phenomena obviously deepens the understanding of the particle size effect. It is of significance for optimizing the performance of ERF and provides new criteria for revealing the ER response mechanism.



Fig. 7. Photomicrograph of the chain structures formed by aminopropyl group-modified silica particles in silicone oil in a dc electric field.

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