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ORIGINAL CONTRIBUTION

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Preparation of monodisperse PMMA microspheres in nonpolar solvents by dispersion polymerization with a macromonomeric stabilizer

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Abstract We discuss a dispersion polymerization procedure for preparing monodisperse and micron-sized poly(methyl methacrylate) (PMMA) particles in hexanes with methacryloxypropyl-terminated polydimethylsiloxane stabilizers. We investigate the effects of the stabilizer molecular weight, stabilizer concentration, and monomer concentration on the particle size and polydispersity. We find that a minimum molecular weight of 10 000 g/mol is necessary to synthesize colloidally stable PMMA dispersions. The particle polydispersity is minimal ($\leq 5\%$) for stabilizer to monomer weight ratios of 0.02 to 0.1, while PMMA particles prepared under conditions outside this range are polydisperse. The particle diameter can be varied from 0.4 to 1.5 μm by appropriate choices of stabilizer and monomer concentrations. Stable PMMA suspensions can be prepared at up to 26.3% solids. The dispersions are stable in most liquid aliphatics, and are monodisperse enough to form ordered domains at high concentration. This single-stage synthesis, requiring only commercially available materials, may be of interest to those seeking a simple way to prepare highly monodisperse non-aqueous dispersions in the micron size range.

Keywords Dispersion polymerization · Poly(methyl methacrylate) · Non-aqueous dispersions · Colloidal crystals

Introduction

Recently, monodisperse polymer colloids have found a new application as templates for photonic crystals [1]. At a sufficiently high volume fraction and low polydispersity, spherical particles will self assemble into a face-centered cubic lattice, even in the absence of attractive interparticle forces [2]. Such structures can diffract light if the wavelength is comparable to the spacing between the particles, though for optimum optical effect one would fill the interstices of this colloidal crystal and dissolve the colloid, thereby forming a macroporous material. Usually an aqueous polystyrene latex is used to make the crystalline template [3, 4]. However, a non-aqueous dispersion may be used instead, with the advantage that a water-reactive phase, such as a metal alkoxide, could be added to the dispersion and incorporated in situ in the interstices of the lattice during particle consolidation and crystallization. Thus, the appropriate colloidal particles for this application would be approximately micron sized (to match the wavelength of visible light), highly monodisperse (to form large crystals), stable in non-aqueous media (to allow compatibility with water-reactive additives), and relatively simple to synthesize. Here we describe the preparation of such particles.

The technique of dispersion polymerization has been used to synthesize stable and monodisperse colloids in different media [5, 6]. For our purposes we prefer nonpolar rather than polar solvents, which may contain significant amounts of water. Anionic dispersion polymerization of styrene in hexanes has been studied [7, 8, 9, 10], but although this technique leads to monodisperse particles, anionic polymerizations in general are considerably less simple than free-radical techniques. Most of the research on free-radical dispersion polymerization in nonpolar solvents involves methyl methacrylate as monomer [11] and various types of polymeric stabilizers, including comb [12, 13], diblock [14, 15, 16, 17], and triblock [18, 19] copolymers. For much of this prior work, the size distribution is either unquantified or too broad to make colloidal crystals. One exception is the poly(methyl methacrylate) (PMMA) system with grafted poly(12-hydroxy-stearic acid) as stabilizer, the crystallization behavior of which has been well-characterized and studied intensely [2] due to the nearly ideal hard-sphere particle pair potential. Unfortunately, the stabilizer for this system is not yet available commercially, and so must be synthesized prior to the polymerization [13].

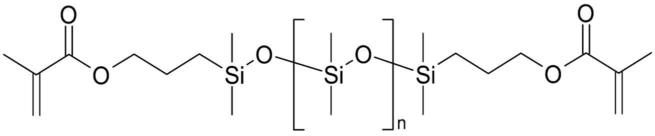
Polydimethylsiloxane (PDMS) macromonomers, on the other hand, are available commercially in a variety of molecular weights. These consist of a polymer chain with reactive end-groups that can covalently bond with the polymers that form the particles, thus providing steric stabilization against flocculation during particle growth. To the best of our knowledge the first successful dispersion polymerization with such stabilizers was reported by Pelton et al. [20, 21], who prepared stable PMMA particles with broad size distributions in n-heptane, using custom-synthesized vinyl terminated siloxanes as steric stabilizers. Most of the recent work in this area concerns particle synthesis in supercritical carbon dioxide [22, 23, 24, 25, 26] rather than liquid hydrocarbons. However, Srinivasan et al. [27] have reported the synthesis of micron-sized PMMA particles in hexanes using a commercially available mono(methacryloxypropyl)-terminated PDMS macromonomer. As the focus of their work was on preparing thermally labile particles rather than on the synthesis of monodisperse particles, they did not report the polydispersity of the particles.

Here we present a simple, single-stage synthesis procedure for micron-sized, monodisperse PMMA particles in hexanes using commercially available methacryloxypropyl-terminated PDMS stabilizers. We investigate the effect of changing synthesis conditions, such as the concentration and molecular weight of stabilizer, on the particle diameter and polydispersity. The results may be of interest not only to those in the photonic crystals field, but also to researchers seeking an easily-synthesized model colloidal dispersion.

Experimental

Materials

Methyl methacrylate (MMA, 99%, Aldrich, Milwaukee, WI, USA), was distilled under reduced pressure before use to remove polymerization inhibitors. The purified monomer was stored at 4 °C in a nitrogen-flushed bottle for no more than one month. The initiator, 2,2'-azobisisobutyronitrile (AIBN, 98%, Aldrich, Milwaukee, WI, USA), was recrystallized from ethanol. Methacryloxypropyl-terminated polydimethylsiloxane stabilizers with molecular weights of 5000, 10 000, and 25 000 g/mol were purchased from Gelest (Tullytown, PA, USA). A stabilizer with a molecular weight of 55 000 g/mol was purchased from United Chemical Technologies (Bristol, PA, USA). As shown in Structure 1, all PDMS stabilizers used here are terminated at both ends with methacryloxypropyl groups. The stabilizers and solvent, hexanes (98.5%, Fisher Scientific, Pittsburgh, PA, USA), were used as received.



Structure 1 Methacryloxypropyl-terminated polydimethylsiloxane stabilizer

Dispersion preparation

The synthesis was performed in a 250 mL three-neck flask placed in a heating mantle. The flask was equipped with a nitrogen inlet tube, a water cooled reflux condenser, and a rubber septum for adding chemicals via a syringe. The top of the condenser was connected to a water bubbler to prevent diffusion of oxygen into the system.

A typical synthesis proceeded as follows: Initially 0.5 g of macromonomeric stabilizer at 55 000 g/mol molecular weight were dissolved into 100 mL of hexanes, which was then purged with N_2 for 1 h. During this time the reaction mixture was heated to 74 °C. At this temperature the solution started to boil and provided the necessary mixing. Reflux conditions were maintained throughout the reaction.

After purging the hexanes, 0.15 g of AIBN were dissolved in 12 g of methyl methacrylate. The reaction was initiated by adding this monomer solution to the hexanes. After approximately 60 s, the initially transparent solution became cloudy, then turned milky white within a few minutes. The reaction was stopped after 2 h by placing the flask in an ice water bath. To remove unreacted stabilizer, the suspension was washed in fresh hexanes (or other dispersants) by centrifugation and redispersion. An ultrasonic bath (Fisher Scientific) was used to speed the redispersion.

Characterization

The average diameter and polydispersity of the dispersions were measured from scanning electron microscope (SEM, JEOL model 6300F) images. A drop of dispersion was placed on an aluminum sample stub, dried, then sputter-coated with gold. The actual size of the particles was determined by comparison with a colloid standard of surfactant-free polystyrene latex (aliphatic amine surface) of 1.0 μm diameter (Interfacial Dynamics, Portland, OR, USA). Here we use "particle size" to mean the arithmetic mean diameter and "polydispersity" the sample standard deviation divided by average diameter. For each data point at least 25 particles were measured.

PMMA is electron beam sensitive, resulting in a change of shape (and size) when subjected to the electron beam within the SEM. To limit the measurement error caused by deformation, images were quickly taken after exposing a region of the sample to the beam.

Because SEM is not widely used for analyzing size distributions—transmission electron microscopy (TEM) is more precise, but PMMA is still subject to e-beam damage under TEM conditions—we have taken precautions in interpreting our results. To minimize sampling bias, a random selection of particles from many different images in various portions of the dried samples was analyzed. Also, because the number of particles counted was relatively small, the confidence intervals for our measured polydispersities were calculated and are reported with the data.

Dispersion stability was determined by analyzing the samples in an optical microscope (Nikon Eclipse TE300, Japan) equipped with Nomarski differential interference contrast optics and an oil-immersion objective. This technique allows us to examine samples in the dispersed (liquid) state, and to observe the Brownian motion of individual particles. Aggregation can therefore be detected dynamically in situ. Also, with the high numerical aperture (1.4) of the objective, micron and even sub-micron sized features of dispersed materials could be resolved to determine whether these were individual particles or aggregates. Micrographs were taken with a high resolution digital CCD camera (Nikon HC-300Zi).

Results and discussion

The typical synthesis procedure reported above employs a stabilizer to monomer weight ratio of 0.04 and a monomer concentration of 15.15% w/w. The optical micrograph in Fig. 1a shows that the particles produced by this method are unaggregated and monodisperse. The scanning electron micrograph in Fig. 1b shows that the particles can pack to form well-ordered arrangements (colloidal crystals). This image is typical of the entire dried sample, and the order does not appear to be a result of size segregation upon drying. In bulk (undried) suspensions at high volume fraction, we observe Bragg reflections with the naked eye, indicating that the sample as a whole is monodisperse enough to crystallize.

Below, we report the effect of changing any one variable in the general formulation with all other variables kept constant.

Reaction period

The synthesis duration was varied between 15 min and 8 h to determine the time needed to complete the reaction. We find that the conversion of PMMA does not increase after a reaction period of 2 h, consistent with other reports on polymerization of PMMA in hexanes [13, 28]. Reaction times much greater than 2 h appear to yield slightly higher concentrations of PMMA in hexanes, as measured by drying the final dispersions, but we attribute these to evaporation of hexanes during the reaction and handling of the precursors. The evaporation of hexanes prevents a precise calculation of the fractional conversion, but we estimate that the conversion of methyl methacrylate after 1.5 h is about 95%. This value is calculated from the measured weight fraction of polymer in the suspension, taking into account the average evaporation rate of hexanes during the reaction.

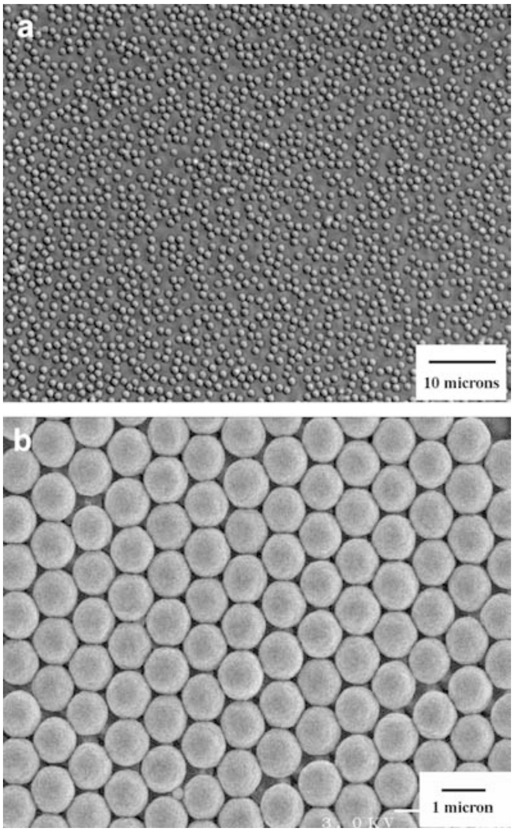


Fig. 1 **a** Optical micrograph of monodisperse and stable PMMA microspheres in hexanes, produced under the conditions listed in the experimental section. This is a snapshot of the suspension in its dispersed state. The Brownian motion of the particles occasionally brings them close to one another, so that the small clusters of particles seen in the picture are transient structures, not aggregates (compare to Fig. 3). **b** Scanning electron micrograph of dried particles from the same sample. Spheres are monodisperse enough to form ordered domains

The change in particle diameter as a function of reaction time is reported in Fig. 2. Because the polydispersity is low during the entire reaction, an effective way to make small particles—albeit at low yield—is to quench the reaction after a short time.

Molecular weight of stabilizer

The type and properties of the stabilizer used in a dispersion polymerization determine the colloidal stability and size distribution. Because hexanes and other hydrocarbons have a low dielectric constant, particles must be stabilized sterically rather than electrostatically. A good polymeric stabilizer should be soluble in the dispersant, cover most of the particle surface, and

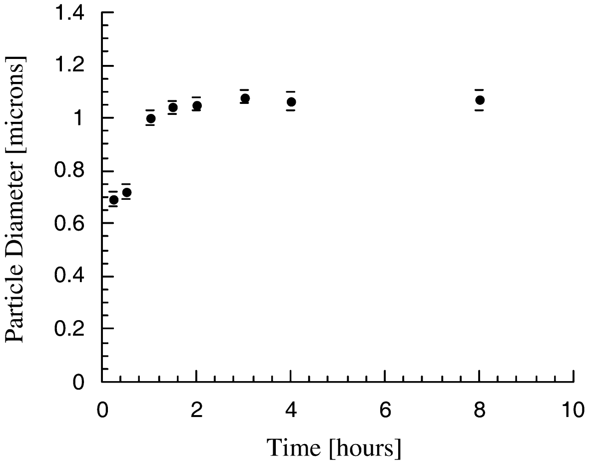


Fig. 2 Particle diameter as a function of synthesis time for PMMA dispersions at a stabilizer:monomer weight ratio of 0.04 and monomer concentration 15.15% w/w. The stabilizer has a molecular weight of 55 000 g/mol. The distance between *bars* is two sample standard deviations or, equivalently, the measured polydispersity of the particles

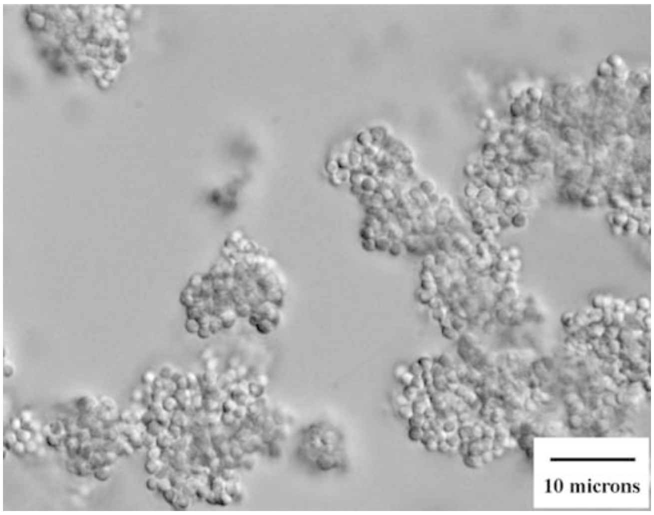


Fig. 3 Optical micrograph of unstable, aggregated PMMA dispersion produced using 5000 g/mol stabilizer

provide a repulsive interaction between particles that is longer-ranged than the attractive van der Waals forces. Since hexane is a good solvent for PDMS, the two most important variables affecting the stabilization of the particles are the molecular weight of the stabilizer, which determines the repulsive length scale, and the concentration, which determines surface coverage.

In Table 1 we show the influence of the stabilizer molecular weight on particle size, polydispersity, and colloidal stability. The data indicate that a minimum of about 10 000 g/mol is required to produce stable polymer suspensions. Above this weight, the particle size does not vary significantly with stabilizer length. Srinivasan et al. found that the minimum molecular weight of PDMS required to stabilize PMMA in hexanes was between 1250 and 25 000 g/mol [27], while Yates et al. found that 10 000 g/mol was sufficient in hexanes, though they did not report a lower bound. Our results are consistent with these, as well as with those of Pelton et al., who determined (by cleaving stabilizers already attached to particles) a PDMS critical chain length of approximately 14 000 g/mol, below which the particles flocculated.

An example of an unstable dispersion is shown in Fig. 3. Although individual particles within the aggregates can be seen, one cannot break apart the clusters using ultrasound. In the case of aggregation, the diameters and polydispersities we list in Table 1, as well as throughout the text, pertain to the component particles within the aggregates, not to the aggregates themselves.

We note that our stabilizer is terminated at both ends with methacryloxypropyl groups, whereas in most of the previous studies the stabilizer contains only a single functional group. Thus, it is possible for our stabilizer to form loops on the surface, which may lead to a shorter repulsive barrier than for singly-anchored chains.

Stabilizer concentration

Figure 4 shows how the particle diameter and polydispersity vary with the stabilizer concentration, which is expressed as the weight ratio of 55 000 g/mol stabilizer to monomer. Ratios below 0.02 lead to unstable (aggregated) PMMA suspensions; increasing the stabilizer content above this value leads to stable dispersions with particle sizes decreasing to 440 nm. Dispersions with small polydispersities are obtained for stabilizer to monomer weight ratios between 0.02 and 0.1. Very small weight ratios (< 0.01) as well as very large ratios (> 0.1) lead to highly polydisperse particle size distributions, though in the latter case the particles are not aggregated.

Table 1 Effect of stabilizer molecular weight on dispersion properties

Stabilizer molecular weight (g/mol)	Particle diameter (μm)	Polydispersity (%)	Colloidal stability
5000	0.79 ± 0.06	40.79	unstable
10 000	1.01 ± 0.01	3.84	stable
25 000	1.00 ± 0.01	5.02	stable
55 000	1.05 ± 0.01	4.73	stable

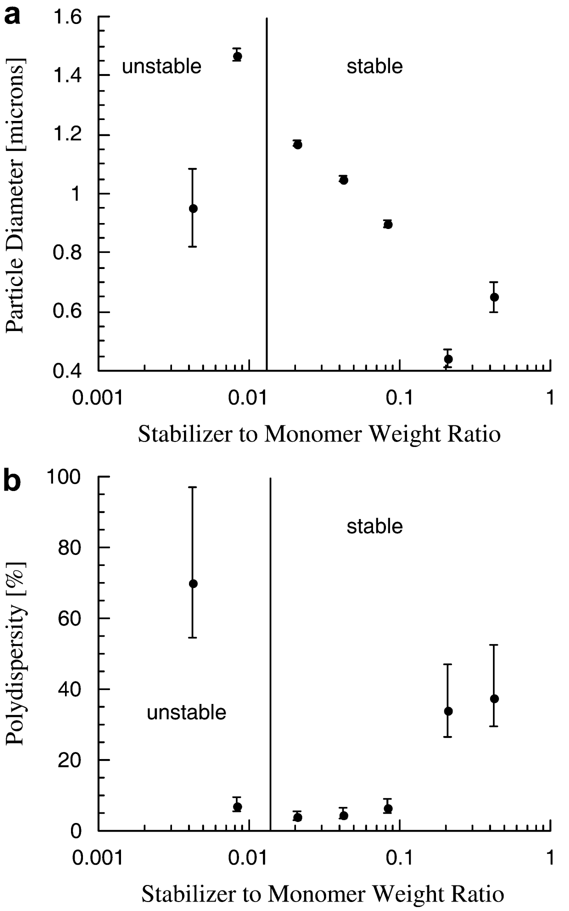


Fig. 4 a Particle diameter and **b** polydispersity as a function of concentration of 55 000 g/mol stabilizer, expressed as weight ratio of stabilizer to monomer, at a monomer concentration of 15.15% w/w. *Error bars* in **a** represent the statistical uncertainty in the mean diameter. Error bars in **b** represent a confidence interval for the polydispersity: given the number of spheres counted, there is a 95% chance that the actual polydispersity lies between the bars, if systematic errors are negligible and the true size distribution is approximately normal

We interpret the data in Fig. 4 in terms of how much surface is covered by the stabilizer. Low stabilizer concentrations (weight ratios of 0.01 and less) appear to be insufficient to saturate the surface during synthesis and are thus unable to prevent flocculation. Also, increasing the stabilizer content leads to an increase in the amount of surface area that can be stabilized, and therefore to a decrease in the particle size. The increase in polydispersity at high stabilizer concentrations (weight ratios greater than 0.2) is more difficult to explain with this model; however, it is believed that in the presence of large amounts of stabilizer, particles nucleate over a longer period of time [11]. If the nuclei all grow at approximately the same rate, a longer nucleation period will lead to a more polydisperse suspension.

Monomer concentration

For large scale synthesis it is desirable to maximize the total yield of polymer per batch. To investigate the highest possible concentration of PMMA in hexanes that could be produced while maintaining colloidal stability, we varied the amount of hexanes in the reaction mixture while keeping the amount of monomer constant. Table 2 shows that stable PMMA suspensions can be produced at up to 26.3% w/w monomer. At 47.2% w/w monomer we observe aggregates in the reaction mixture, though we can remove these by sedimentation, leaving a dispersion with large, monodisperse, and stable particles (see Table 2). Two issues complicate syntheses at high monomer concentration: the amount of hexanes is small, and the reflux (boiling) temperature of the reaction mixture is high. We believe that the aggregation is caused by rapid evaporation of hexanes at the elevated temperatures and "caking" of the polymer spheres near the walls of the reactor. It may therefore be possible to prepare dispersions at monomer concentrations higher than 26.3% by using a temperature-controlled reactor.

The electron micrographs in Fig. 5 illustrate the increase in particle size (at low polydispersity) with monomer content. Antl et al. [13] reported a similar trend in the PMMA/hexane/poly(12-hydroxy-stearic acid) system, though surprisingly they found a region of colloidal instability at intermediate monomer concentration (10–30%), which we did not observe in our limited trials. They attributed the increase in particle size to an increase in solvent quality for the polymer at high monomer concentration, which allows the polymer chains to grow larger before precipitating and forming nuclei. Winnik et al. [11] noted that another factor contributing to increasing particle size may be decreased effectiveness of the stabilizer in the presence of large amounts of monomer.

Table 2 Effect of monomer concentration on dispersion properties

Monomer (% w/w)	Particle diameter (μm)	Polydispersity (%)	Colloidal stability
15.15	1.05 ± 0.01	4.73	stable
26.3	1.16 ± 0.01	3.93	stable
47.2	1.80 ± 0.01	3.41	unstable

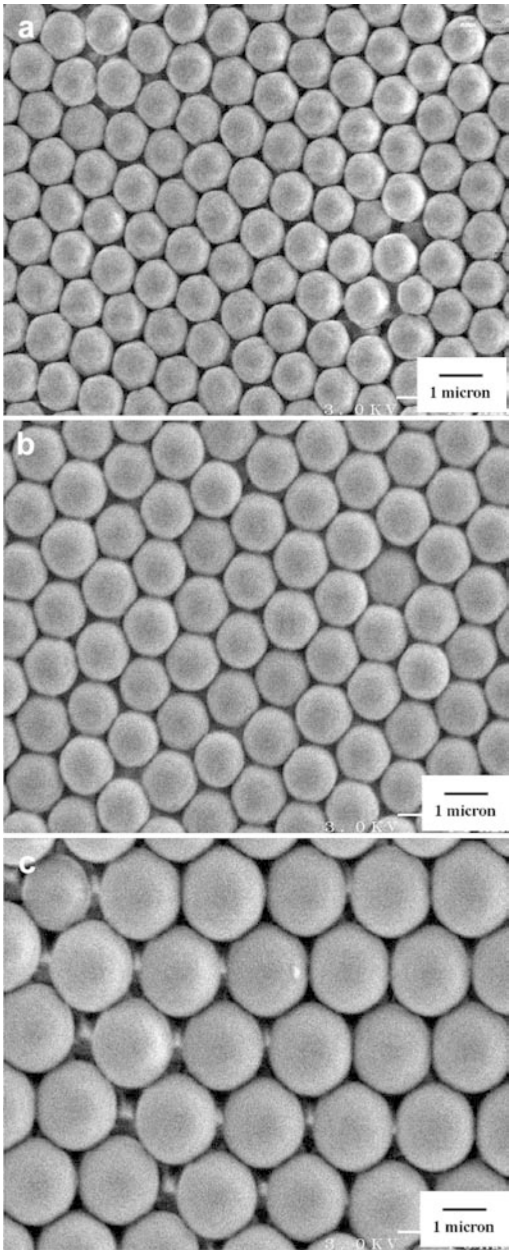


Fig. 5a–c Scanning electron micrographs of monodisperse PMMA particles prepared at monomer concentrations of 15.15% w/w (**a**), 26.3% w/w (**b**), and 47.2% w/w (**c**). All samples are well ordered after drying, but the sample at 47.2% contained aggregates, possibly from evaporation of hexanes, that were separated out and not pictured here

We note in passing that some form of mixing is required to keep the growing particles from sedimenting during the reaction. In our experiments the mixing is accomplished by operating under reflux. A temperature-controlled reactor, on the other hand, would have to be mechanically agitated. With our system we find that high stirring rates lead to the formation of linear aggregates of monodisperse particles (Fig. 6). A similar phenomenon was observed in computer simulations by Doi and Chen [29], who found that "sticky spheres" having a weakly repulsive pair potential with short-range attraction could form chains in a shear flow. In our system, the short-range attraction may be due to either van der Waals forces or to the stabilizer, which has functional groups at both ends, forming bridges between particles. Indeed, linear aggregates are observed only at high ratios (0.04 and greater) of stabilizer to monomer. In general, though, stirring leads to no discernable change in particle size or polydispersity, in accordance with other studies of dispersion polymerization [6].

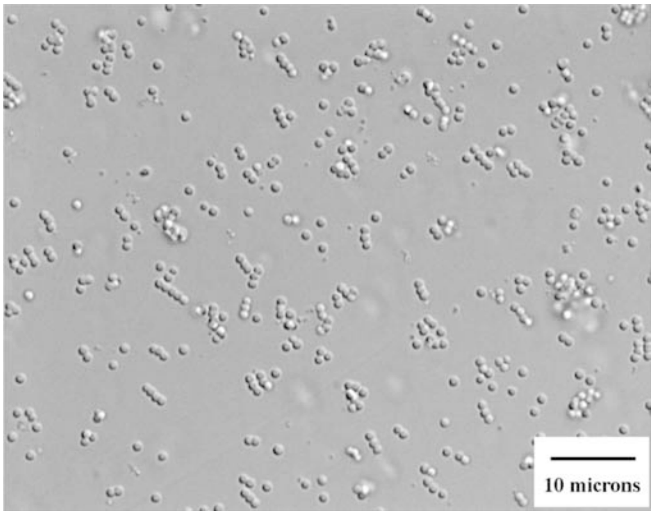


Fig. 6 Optical micrograph of linear or chain-like aggregates created at high stabilizer concentration and vigorous magnetic stirring

Stability in other solvents

By repeated centrifugation and redispersion we can successfully transfer the particles to alkanes ranging from hexane to dodecane with no loss of colloidal stability. The dispersions are not stable in either hexadecane or any alcohol up to and including decanol. Aromatic solvents such as toluene dissolve the particles, but the spheres remain intact and unaggregated in cyclic aliphatics such as cyclohexane and decahydronaphthalene.

Conclusions

We have shown that monodisperse and stable PMMA spheres can be synthesized in hexanes by a single stage dispersion polymerization with commercially available macromonomeric PDMS stabilizers. The particle diameter can be varied from 0.4 to 1.5 μm, with little change in polydispersity, by changing either the stabilizer concentration or monomer loading. Alternatively, the reaction may be quenched after the particles have reached the desired size, although this method necessarily results in smaller yields. Highly monodisperse particles (less than 5% polydispersity) are produced at stabilizer:monomer weight ratios from 0.02 to 0.08. Unaggregated particles are produced in most cases, except at very low stabilizer concentration, very high monomer concentration, or under vigorous stirring.

Because the dispersions are stable in most liquid aliphatics, and can form well-ordered domains at high concentration, they may be suitable for photonic crystal templating procedures using water-sensitive precursors. They may also prove useful, in part because of the relatively simple synthesis, in studies of colloidal crystals and order-disorder transitions. Further work in this area would require investigation of the properties of the attached stabilizer layer and, accordingly, the inter-particle pair potential.

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