Settling Characteristics of Microparticles Modified by Hydrophilic Semi-Interpenetrating Polymer Networks

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SYNOPSIS

Microparticles of 2-hydroxyethyl methacrylate cross-linked with ethylene glycol dimethacrylate were produced by suspension polymerization. Semi-interpenetrating polymer networks were prepared by diffusion of poly(ethylene oxide) (PEO) solution into the particles. The PEO was allowed to diffuse into the dried particles and the resulting swollen particles were treated with an excess of acetone to collapse them. The ensuing networks consisted of the collapsed particles and the trapped PEO. The modified particles were allowed to settle in water, and characteristic settling times were measured as a function of swelling time. The settling times were compared to those of the unmodified particles. It was found that the settling time changes with volume fraction, particle size, degree of functionality, and amount of swelling. An increased volume fraction in both unmodified and modified particles causes a slower settling rate. The smaller particle sizes fall more slowly, and size difference plays a more significant role in hindering the settling for lower amounts of trapped PEO. As the amount of PEO increases, the settling rate decreases dramatically. Swelling also slows the settling rate, until the particles reach equilibrium. Equilibrium swelling occurs near 10 min for both unmodified and modified particles. Optical photomicroscopy verified the amount of swelling and demonstrated the process of PEO penetration.

INTRODUCTION

Hydrogels, or three-dimensional polymer networks that swell in water, have found a number of applications in the biomedical field due to their nontoxic, nonirritant biocompatible nature. They have been widely used in dentistry,[1] immobilization of cells,[2] drug-delivery systems,[3] implants and blood cleansing,[4] artificial emboli,[5] contact lenses,[6] chromatography,[7] etc. The purpose of this project was to develop a system using these hydrogels that can be adapted for use in environmental purifications. The project entails producing polymer microparticles from 2-hydroxyethyl methacrylate (HEMA) cross-linked with ethylene glycol dimethacrylate (EGDMA). These microparticles, ranging from 200 to 600 μm in diameter, are modified through the creation of a semi-interpenetrating polymer network that increases the ability of the particles to suspend.

An interpenetrating polymer network (IPN) is created when a cross-linked polymer is randomly penetrated by another cross-linked polymer without any covalent bonding between the networks. The polymers exist together due to their physical rather than to their chemical entanglements. A semi-interpenetrating polymer network (SIPN) consists of a cross-linked polymer penetrated by a linear polymer. It can be prepared by cross-linking a functionalized polymer in a linear polymer blend or by polymerizing a multifunctional monomer dispersed in a linear polymer.

A number of methods for creating IPNs and SIPNs are mentioned in the literature. These include UV curing of acrylic monomers in a polymer matrix such as polyurethane;[8] cross-linking of poly(dimethyl siloxane) with 3-aminopropyltrieth-oxysilane, and penetration of polyurethane to create an SIPN;[9] using poly(2-hydroxyethyl methacrylate) or pHEMA penetrated by polycaprolactone[10,11] or

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polystyrene.[12] Similar techniques include production of nonuniform gradient IPNs of pHEMA hydrogels and polyols through simultaneous diffusion and polycondensation of the reactants[13] and synthesis of SIPNs from a copolymer of poly(ethylene glycol) (PEG) and acrylic acid entangled with linear PEG.[14]

The experimental focus of this project was to create microparticles that are capable of suspension. These suspendable particles will later have reactive sites attached to accomplish affinity separations of aqueous pollutants. The polymer microparticle is formed by suspension polymerization in an aqueous solution using a free-radical mechanism. The hydrophilic surface polymer is poly(ethylene oxide) (PEO).

Reaction conditions are controlled so that uniform spheres 200–600 μm in diameter are produced. The ratio of monomer to the aqueous phase is varied, as is the agitation rate, in order to generate a narrow particle-size distribution of cross-linked particles. An SIPN is created by allowing the particles to swell in a PEO solution until they reach equilibrium. The swollen particles are immediately immersed in a nonsolvent, causing them to collapse and trapping the PEO within the particle and on the surface. When the modified particles are then placed in water, the trapped PEO diffuses out and dissolves, raising the viscosity of the solution and enhancing the ability of the particles to suspend. The molecular weight and concentration of the PEO are varied to determine the effects of changing molecular weight and concentration on the settling characteristics.

The measurement phase of this research concentrates on the settling rates and swelling behavior of the microparticles. The settling rates of both modified and unmodified particles at various volume fractions are measured, and the effects of volume fraction, particle size, and functionality are studied. Settling rates for different regimes of swelling are examined, and functionalization conditions are varied.

This project applies polymer science to the area of affinity separation, resulting in the development of a simple and safe method that can be adapted to a number of applications. This work produces SIPNs in the form of modified hydrogels to which a number of different reactive sites for permanent or reversible binding can be attached. These microparticles are large enough to be easily collected and therefore must contain hydrophilic surface polymers to enable them to suspend. The resulting suspensions allow for efficient use and high concentration of the reactive sites, providing an effective system for the eradication of a variety of trace elements in polluted streams or purification of any domain that requires a safe, simple and nontoxic solution.

EXPERIMENTAL

Materials

The monomer chosen to produce the microparticles was 2-hydroxyethyl methacrylate (HEMA, Aldrich

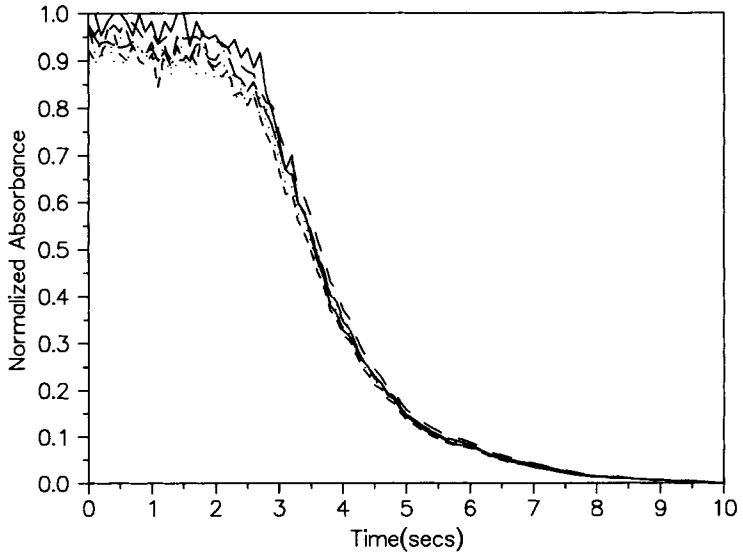

Figure 1 Normalized absorbance as a function of time for 10% volume fraction of 355–425 μm unmodified particles swollen for 10 min at six different wavelengths: (——) 300 nm; (– – –) 340 nm; (· · ·) 380 nm; (– · –) 420 nm; (· – ·) 460; (— —) 500 nm.

Chemical Co., Milwaukee WI). The cross-linking agent was ethylene glycol dimethacrylate (EGDMA, Aldrich Chemical Co.) and the surface polymer was poly(ethylene oxide) (PEO, Aldrich Chemical Co.). The suspension polymerization was initiated with 2,2 azobisisobutyronitrile (AIBN, Polysciences Inc., Warrington, PA). The inhibitor was removed from the HEMA using an inhibitor column packed with Dehibit macroreticular ion-exchange resin (Polysciences Inc.). Reagent-grade $MgCl_2 \cdot 6H_2O$, NaOH, HCl, and NaCl were used. All compounds were used without further purification.

Procedure

Microparticle Formation

The technique used to create the microparticles was an adaptation of the suspension polymerization of Scranton et al.[15] Typically, 180 g of a 20 wt % aqueous solution of NaCl, used as the salting-out agent, was placed along with 11.5 g of $MgCl_2 \cdot 6H_2O$ in a three-neck 500 mL flask. Using a Lightnin Labmaster DS1010 agitator (General Signal) with a swing-out paddle of 50 mm, the mixture was slowly heated under agitation (350–600 rpm) for about 15 min until a temperature of 70°C was reached. A 1*N* aqueous solution of NaOH, 61.5 mL, was added dropwise, forming a gel-like precipitate of $Mg(OH)_2$ that acts as the suspending agent. After precipitation of the $Mg(OH)_2$, the agitation speed was reduced to 250 rpm.

The polymerization solution, consisting of 100 g of the monomer, HEMA, 17.7 g of the cross-linking agent, EGDMA, and 0.1 g of the initiator, AIBN, was added to the flask and the mixture was maintained at a constant 70°C for 3 h. The temperature was raised to 90°C, and the particle-forming reaction continued until completion, usually requiring 45 min to 1 h.

The resulting product was cooled under agitation, and 10–25 mL of 37 wt % HCl was added, dissolving the residual $Mg(OH)_2$. The microparticles were acquired by vacuum-filtration and washed with water and ethanol. They were then dried at room temperature for 24 h and under vacuum at 40°C and 150 mmHg for 72 h.

The particles were sieved using Tyler sieves (Aldrich Chemical Co.) and separated into their respective size ranges. The dried particles were separated using a mortar and pestle, and the particles were sieved. This process was repeated a minimum of three times, and the particles were examined under a microscope to ensure that the particles were discrete.

Table I Change in Settling Time for 500–600 μm Particles Caused by Increase of Volume Fraction

Volume Fraction	PEO Mol. Wt.	PEO Concn (g/100 mL)	Half-life Time (s)	10% Absorbance Time (s)
0.05	0	0	0.4	0.9
0.07	0	0	0.6	1.0
0.10	0	0	1.0	1.6
0.05	100,000	5	0.5	2.0
0.07	100,000	5	0.6	2.8
0.10	100,000	5	1.2	3.7
0.05	600,000	1	2.9	6.7
0.07	600,000	1	2.6	5.4
0.10	600,000	1	2.0	4.3

Table II Change in Settling Times for 5% Volume Fractions Caused by Differences in Size

Particle Size (μm)	PEO Mol. Wt.	Concn of PEO (g/100 mL)	Half-life Time (s)	10% Absorbance Time (s)
500–600	0	0	0.4	0.9
425–500	0	0	0.5	0.9
355–425	0	0	1.2	2.2
500–600	100,000	10	1.2	2.9
425–500	100,000	10	1.7	4.2
355–425	100,000	10	1.9	4.4
500–600	600,000	1	2.6	5.4
425–500	600,000	1	2.9	5.5
355–425	600,000	1	3.0	7.3

Table III Change in Settling Times for 5% Volume Fraction of 425–500 μm Caused by Swelling

Swelling Time (min)	PEO Mol. Wt.	PEO Concn (g/100 mL)	Half-life Time (s)	10% Absorbance Time (s)
0	0	0	0.5	0.9
10	0	0	0.6	1.2
20	0	0	0.6	1.3
0	100,000	5	0.2	2.8
10	100,000	5	3.3	7.5
20	100,000	5	3.3	7.6
0	600,000	1	3.4	7.9
10	600,000	1	3.8	8.2
20	600,000	1	4.1	8.3

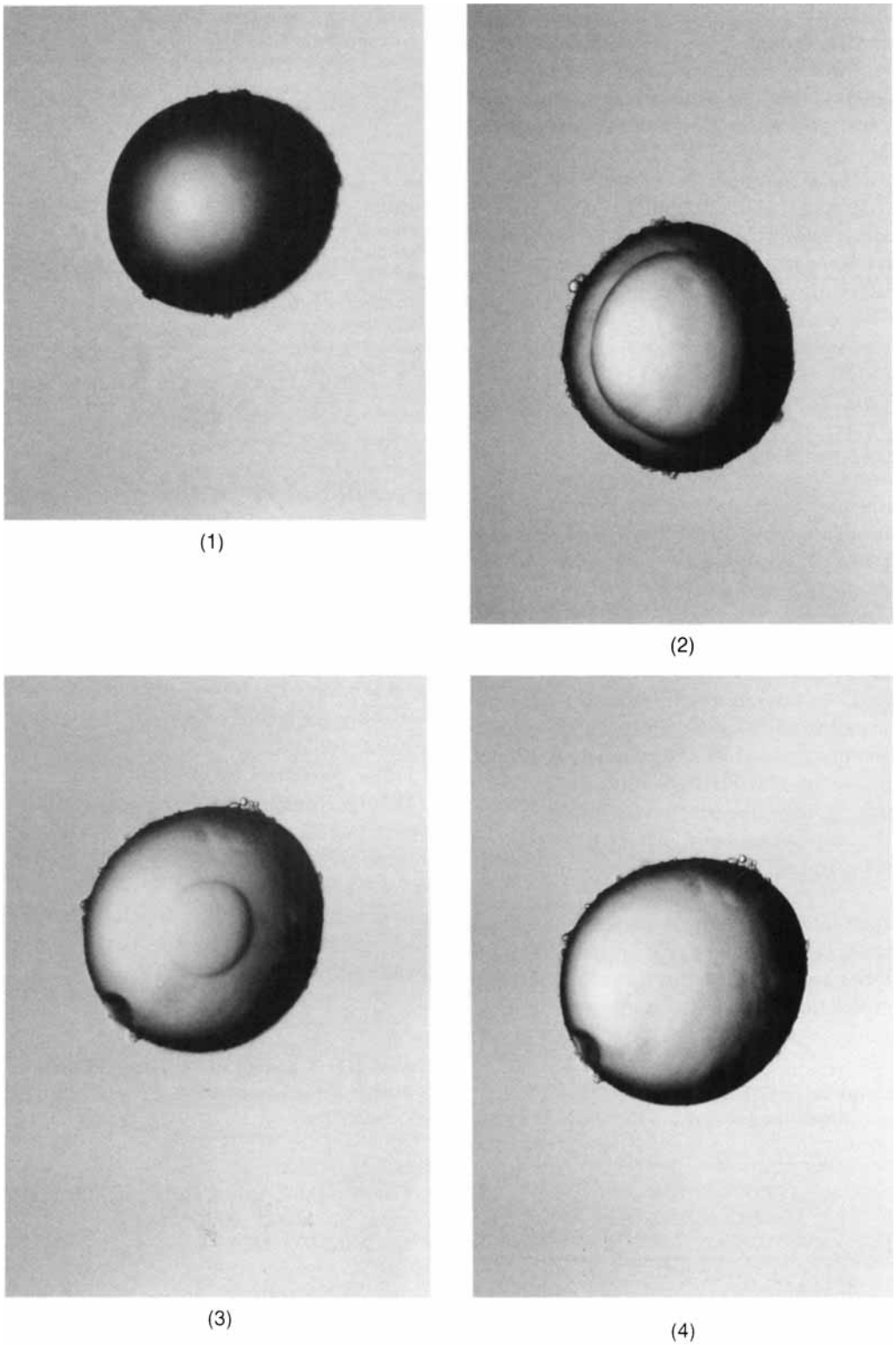

Figure 2 Optical microscope photographs of an unmodified 355 μm particle at different times of swelling: (1) dry; (2) swollen 2 min; (3) swollen 5 min; (4) swollen 10 min; (5) swollen 20 min.

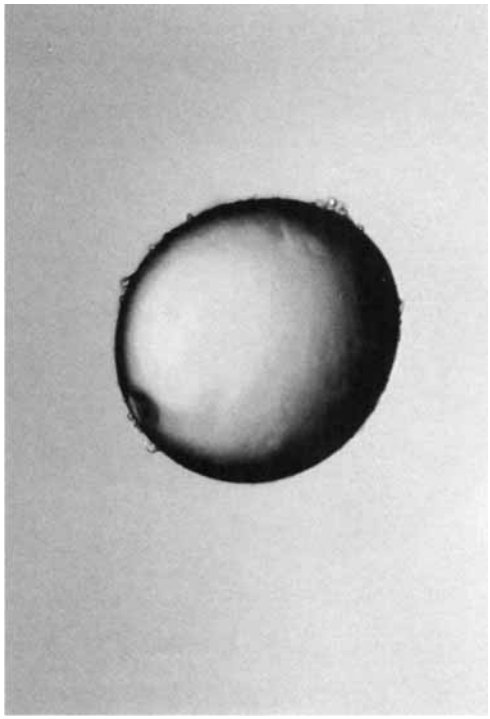

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Figure 2 *(Continued from the previous page)*

Semi-interpenetrating Polymer Network (SIPN) Formation

Varying concentrations of 1000, 100,000, and 600,000 molecular weight PEO in water were made up. One to three grams of dried and sieved microparticles were placed in a small vial and sufficient PEO in solution was added, resulting in a 20% volume fraction of particles. The vials were shaken vigorously, stoppered, and allowed to sit for 48 h. Five milliliters of acetone was added, the vials were shaken, and the particles were sieved immediately by vacuum-filtration. The filtered particles were washed several times with acetone and then placed in an open container to dry overnight. The resulting particles were then tested without further drying or sieving.

Comparative settling rates of the modified microparticles were determined by measuring the absorbance vs. time at a wavelength of 340 nm. Various amounts of microparticles were weighed out, corresponding to a range of volume fractions from 0.05 to 0.10. A blank 3.75 mL cuvette of distilled water was scanned, using an HP8452A diode array ultraviolet-visible light spectrometer (Hewlett-Packard [HP]). The sample was 3.5 cm high, and the beam of light entered the sample 1.75 cm from the top of the sample. The microparticles were then placed in a cuvette, gently stirred to separate the particles, and allowed to settle during a scan by the HP spectrometer. The particles were then allowed to swell for 10 min in the water. They were then shaken vigorously and allowed to settle and a minimum of three scans was taken. After another 10 min, the procedure was repeated and a final three scans were taken. Plots of absorbance vs. time were produced, and plots were created for the various volume fractions, molecular weights of the PEO, concentrations, and time periods for all the particle diameter ranges.

A Nikon optical microscope was used to compare swelling profiles of unmodified vs. modified particles and confirm settling time measurements. Particles were photographed dry, and then a drop of water was added. Pictures were taken at different time intervals for 20 min. Photomicroscopy was also utilized to follow the process of diffusion of PEO into an unmodified particle. Particles were photographed dry, and then a drop of PEO in solution was added. Pictures were taken at different time intervals for 1 h. Different concentrations and molecular weights of PEO were examined.

RESULTS AND DISCUSSION

The absorbance from the settling rate measurements was normalized by setting it equal to the recorded absorbance minus the minimum absorbance divided by the difference between the maximum and minimum absorbances. Two characteristic times were used as the measure of comparison for all effects. The half-life was the time when a normalized absorbance of 0.5 was reached and the 10% time occurred when the normalized absorbance decreased to a value of 0.1. Scans began immediately after the particles were placed in the water. The particles were allowed to swell in water for 10 min, the cuvette was shaken again, and the settling particles were scanned. This process was repeated after another 10 min.

Originally, scans of the settling particles were taken at six different wavelengths: 300, 340, 380, 420, 460, and 500 nm. Each scan was performed at the six different wavelengths at the same time and the resulting plots were compared. Figure 1 is a typical scan of settling particles at six different wavelengths. This particular plot shows a 10% volume fraction of 355–425 μm unmodified particles measured after swelling for 10 min and demonstrates the settling characteristics of the particles. The first,

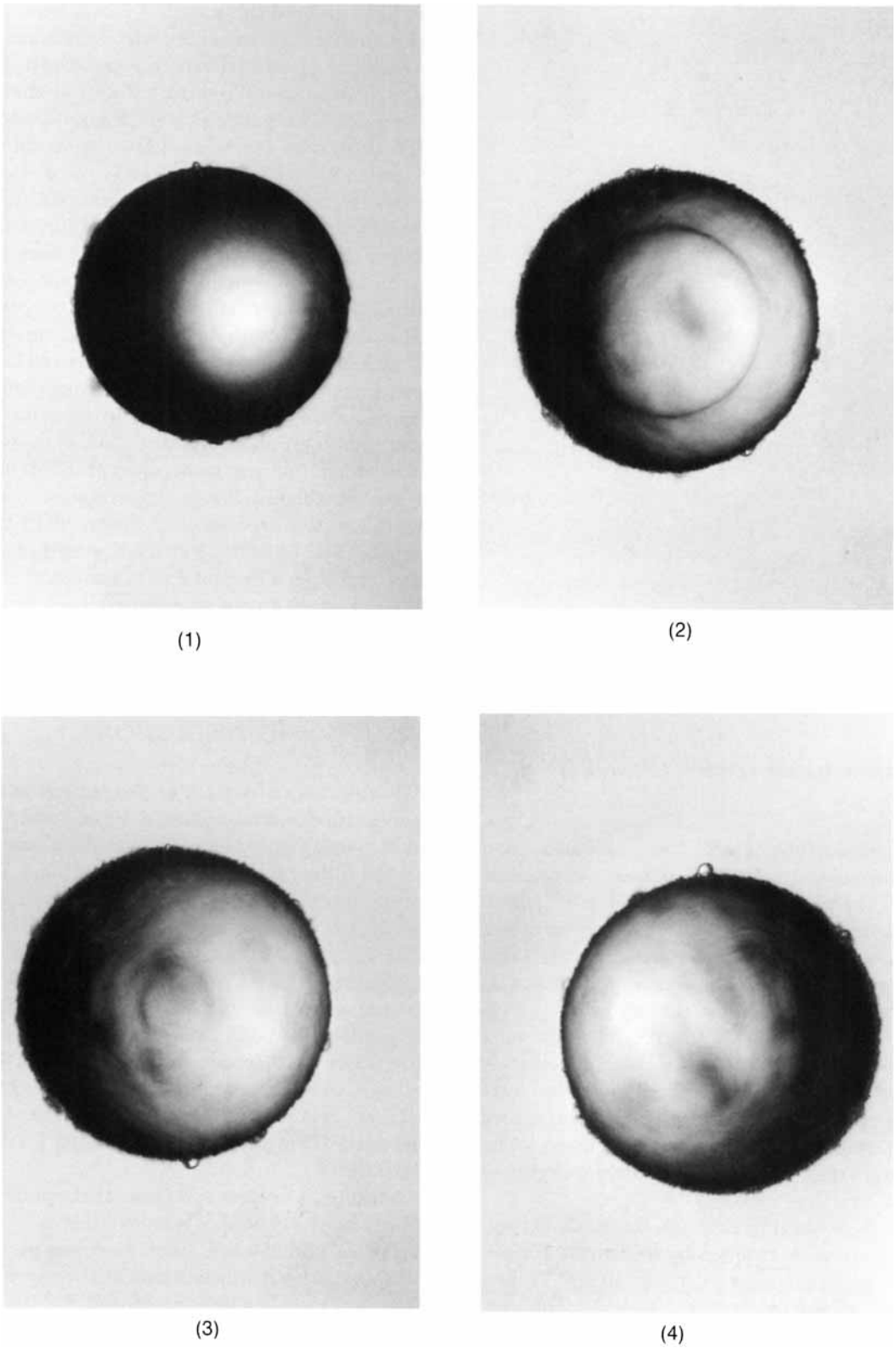

Figure 3 Optical microscope photographs of a 425 μm particle penetrated by 1000 PEO at a concentration of 40 g/100 mL at different times of swelling: (1) dry; (2) swollen 2 min; (3) swollen 5 min; (4) swollen 10 min; (5) swollen 20 min.

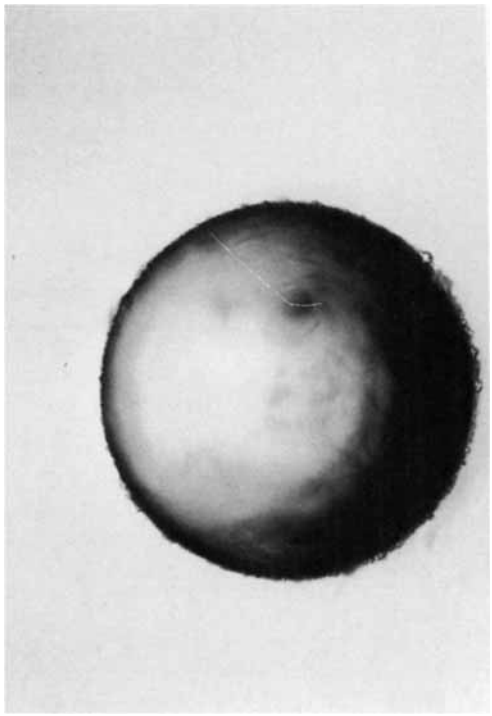

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Figure 3 *(Continued from the previous page)*

almost flat, portion indicates complete absorbance of the light. Although particles are settling, there is a lag before the number of particles in the beam decreases. The second phase shows the settling of the particles. This part is very steep for particles that settle out of suspension quickly and flattens out for particles that settle more slowly. The final stage involves the settling of the last few particles out of suspension. Scans at all six wavelengths were run for several different particle sizes, volume fractions, and amounts of PEO. Since the resulting plots showed only the slight differences indicated in Figure 1, it was decided that all the scans could be safely run at one wavelength: 340 nm was chosen because the operating procedures for this machine indicate that this wavelength produces the highest degree of accuracy.

Volume fractions of 0.05, 0.07, and 0.10 were chosen for comparison. Larger volume fractions generally resulted in slower settling rates for both unmodified and modified particles. Particles with diameters of 500–600 μm were compared and it was found that both the half-lives and 10% absorbance times increased with increasing volume fractions, but that the settling time for the particles penetrated by 600,000 PEO at a concentration of 1 g/100 mL actually decreased as the volume fraction increased (see Table I). This effect can be explained by the networks' propensity for agglomeration. The networks that contained higher molecular weights of PEO tended to clump together, and the higher volume fractions therefore settled in a cluster. Particles penetrated by 600,000 molecular weight PEO were examined under the microscope, and this tendency for agglomeration was verified.

Particles in size ranges of 500–600 μm, 425–500 μm, and 355–425 μm were examined. Comparisons were made for changes in particle size within the same volume fraction and concentration of PEO. An examination of Table II demonstrates the effects of particle size on the settling rate. The unmodified particles showed the effects of particle size very strongly, especially with the smallest particles. The IPNs showed many of the same tendencies, but to a a lesser degree. It is interesting to note that as the PEO increased in size and concentration the effect of particle size often decreased. In fact, the particles penetrated by 600,000 PEO had the smallest increase in settling rate as the particle size decreased.

Measurements were taken of all the particles immediately after they were placed in water, after the particles swelled in water for 10 min, and after the particles swelled another 10 min. Unmodified particles were investigated first and then networks with increasing amounts of PEO (see Table III). All the unmodified particles showed an increase in settling time after 10 min of swelling due to the increased volume fraction and drag of the particles. Allowing the samples to swell another 10 min did not have such a profound effect. In fact, an examination of all the data for unmodified particles indicated that most of the swelling was accomplished in the first 10 min, and allowing the particles to swell in the water another 10 min was not particularly beneficial. The IPNs also generally showed an increase in settling time after swelling for 10 min. In fact, the increase was often quite significant, with settling times of swollen particles over 200% greater than those of dry particles. This can be attributed to the dual effects of particle swelling as well as to the diffusion of the trapped PEO into the water that increases the viscosity. As with the unmodified particles, the bulk of the effects of swelling and PEO dissolution occurred in the first 10 min.

Optical microscopy was used to verify that the time dependence of the settling rate was because of the swelling. Figure 2 depicts an unmodified particle with a diameter of 355 μm. The first photograph shows the particle dry, the next after 2 min of swelling, then after 5 and 10 min of swelling, and, finally,

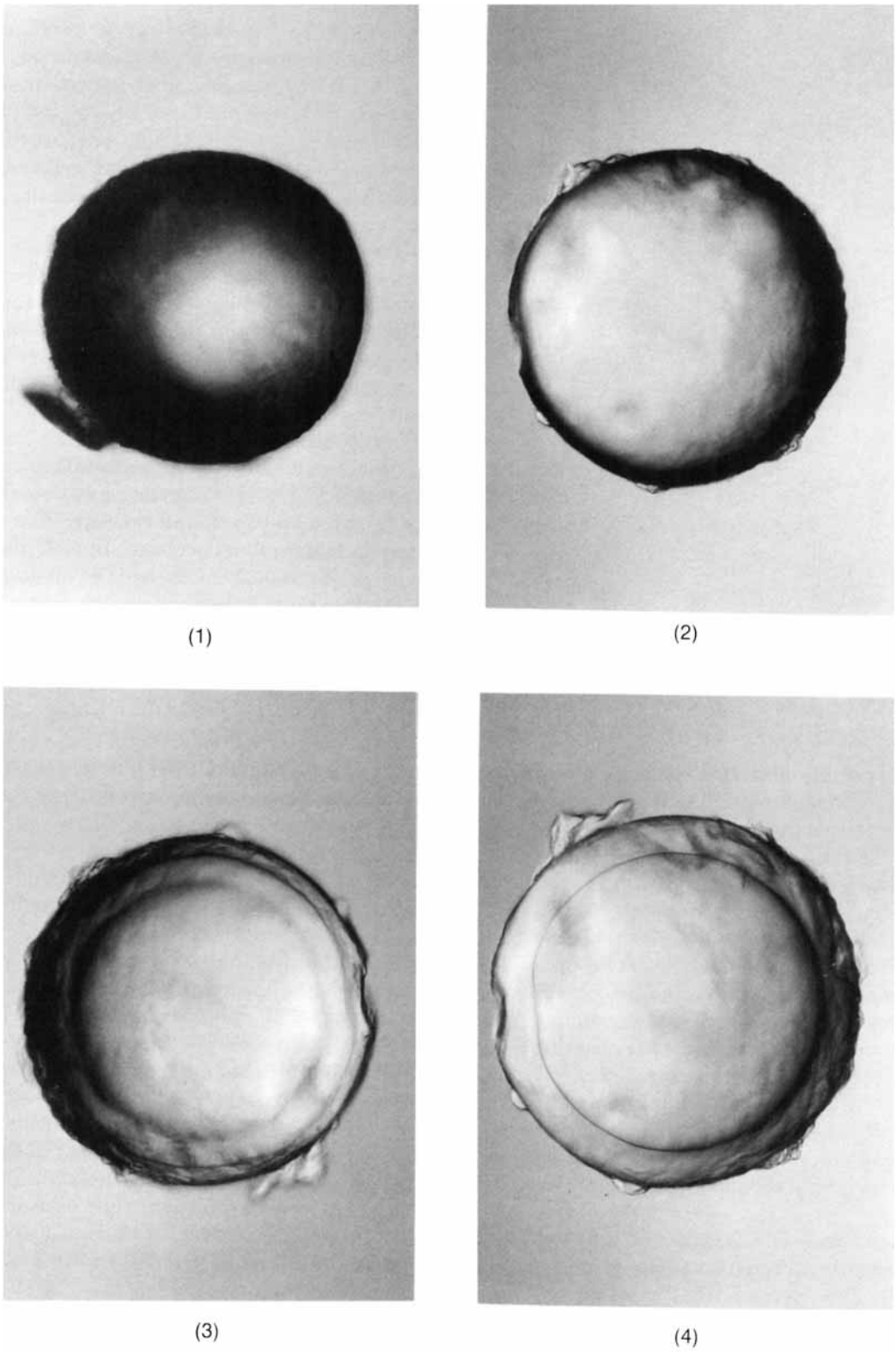

Figure 4 Optical microscope photographs of 1000 PEO at a concentration of 40 g/100 mL diffusing into a 425 μm particle: (1) dry; (2) after 10 min; (3) after 15 min; (4) after 30 min; (5) after 45 min; (6) after 1 h.

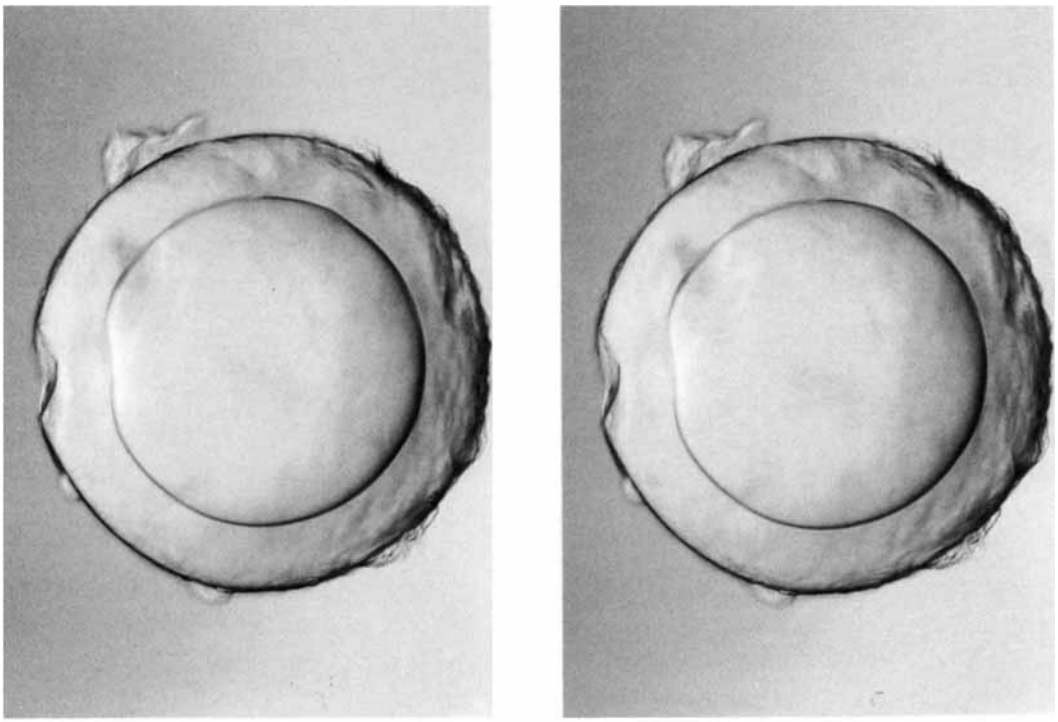

Figure 4 *(Continued from the previous page)*

after 20 minutes of swelling. It is clear that by 10 min the particle is almost completely swollen, and there is no appreciable difference between a particle swollen for 10 min and one swollen for 20 min. The results are similar for a 425 micron particle penetrated by 1000 PEO at a concentration of 40 g/100 mL (see Fig. 3), although the modified particles appear to reach equilibrium even more quickly.

It is interesting to note that as the molecular weight and concentration of PEO increased the differences caused by swelling decreased, although the overall settling times were still longer. This can be explained if the larger weights and amounts of PEO do not penetrate as far into the particle, and therefore a long swelling time will not cause any more PEO to diffuse out. This explanation is supported by the fact that the relatively high cross-linking density (0.124 mol EGDMA/mol HEMA) will prevent significant PEO penetration beyond the surface. Optical microscopy was also used to examine the process by which the PEO diffuses into the particle and to confirm these results. As expected, the 1000 PEO diffuses in very quickly, with the particle almost completely swollen in the first hour (Fig. 4). It appears that after 15 min there are actually two fronts in the particle. By 1 h, the bulk of the PEO has diffused into the particle. But the 100,000 PEO takes a great deal longer to diffuse into the particle. After the first hour, the particle is only partially swollen (Fig. 5).

The particles should settle more slowly as the molecular weight and concentration of PEO increases. The amount of PEO that is trapped in the network and later released into the water will determine how much the viscosity of the medium will increase and therefore how much more slowly the particles will settle. Also, the viscosity of a polymer solution increases exponentially with molecular weight, so particles with higher molecular weights of PEO should settle considerably slower. Particles were weighed before and after functionalization to determine the amount of PEO that was trapped, and the increase in mass ranged from 15 to 28%.

Table IV shows a comparison of particles penetrated by PEO of differing molecular weights and concentration. Particles of all three size ranges with a volume fraction of 10% were examined. It was anticipated that the unmodified particles would settle the fastest, followed by 1000 PEO at 10 g/100 mL, 1000 PEO at 40 g/100 mL, 100,000 PEO at 5 g/100 mL, 100,000 PEO at 10 g/100 mL, and 600,000 PEO at 1 g/100 mL. The 500–600 μm particles, in general,

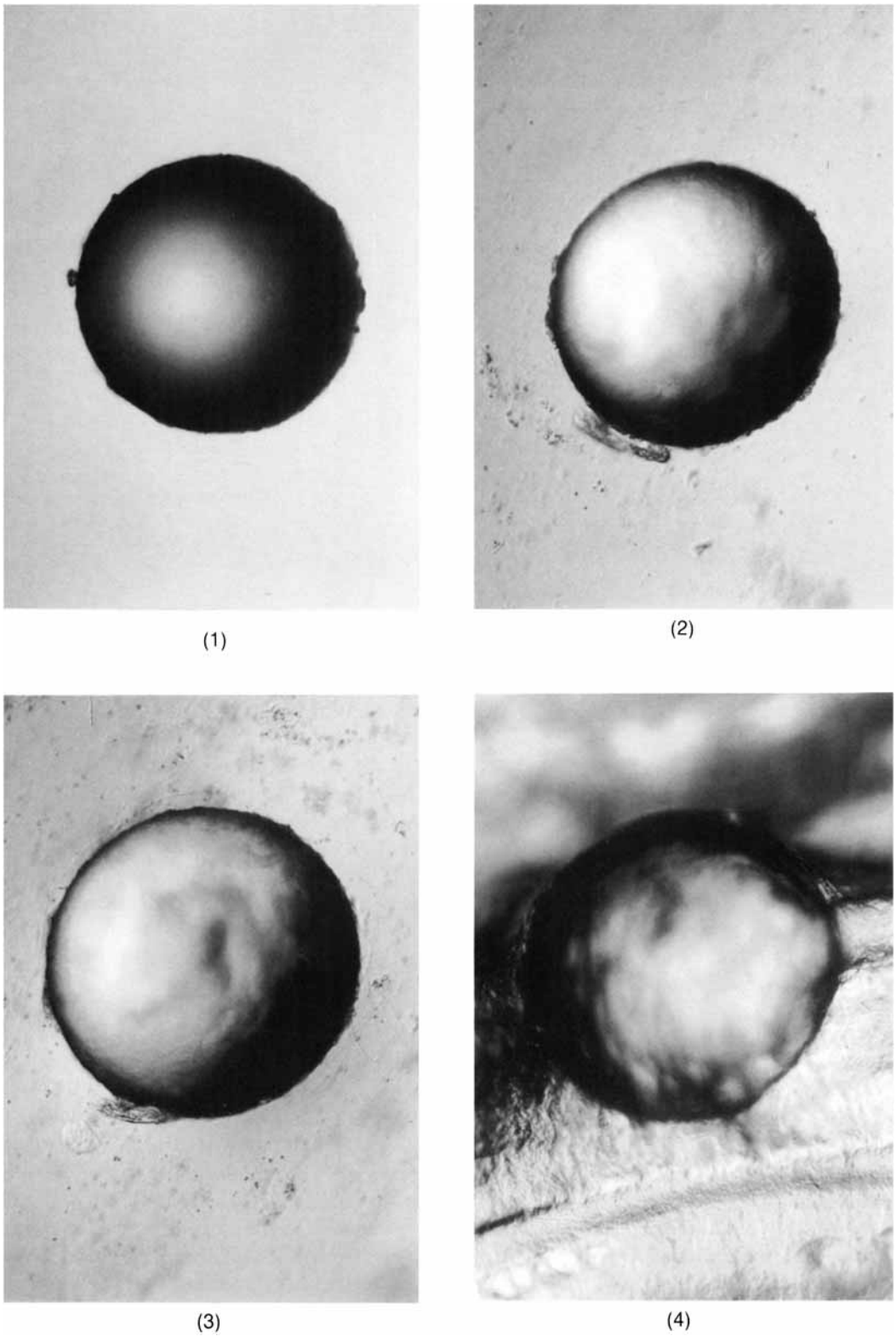

Figure 5 Optical microscope photographs of 100,000 PEO at a concentration of 5 g/100 mL diffusing into a 355 μm particle: (1) dry; (2) after 10 min; (3) after 30 min; (4) after 1 h.

Table IV Change in Settling Times for 5% Volume Fraction of 500–600 μm Particles Caused by PEO Molecular Weight and Concentration

PEO Mol. Wt.	Concn of PEO (g/100 mL)	Half-life Time (s)	10% Absorbance Time (s)
0	0	0.4	0.9
1000	10	0.5	1.9
1000	40	1.2	3.6
100,000	5	0.5	2.0
100,000	10	1.2	2.9
600,000	1	2.9	6.7

followed the expected pattern. The one anomaly occurred with the networks penetrated by the 100,000 PEO at a concentration of 5 g/100 mL, which actually settled faster than those of 1000 PEO at a concentration of 40 g/100 mL. Because the molecular weight of the PEO increased by two orders of magnitude, the diffusion into the particles was necessarily slowed down. So, although the molecular weight of the overall PEO was greater, the amount that was actually trapped was apparently much less. The same pattern can be seen in the 425–500 μm particles as well as in the 355–425 μm particles. In general, there was an increase in settling times as expected, except from the 1000 PEO at 40 g/100 mL to 100,000 PEO at 5 g/100 mL. There were also a few instances when the networks with 1000 PEO at 10 g/100 mL settled more quickly than did the unmodified particles, but this observation is attributable to the clumping of particles caused by the functionalization. The 10% absorbance times as well as the data for the swollen particles showed the expected increase in settling time for the networks.

The effect of the dissolution of PEO into the water was confirmed by allowing the modified particles to settle in a nonsolvent for PEO. Measurements were made of unmodified and modified particles in volume fractions of 0.05, 0.07, and 0.10 settling in hexane. Data were taken of dry particles and those swollen for 20 min. Figure 6 shows that the modified particles actually settle more quickly than do the unmodified particles because of aggregation and that settling times do not increase with time. This experiment verifies that the dissolution of PEO into

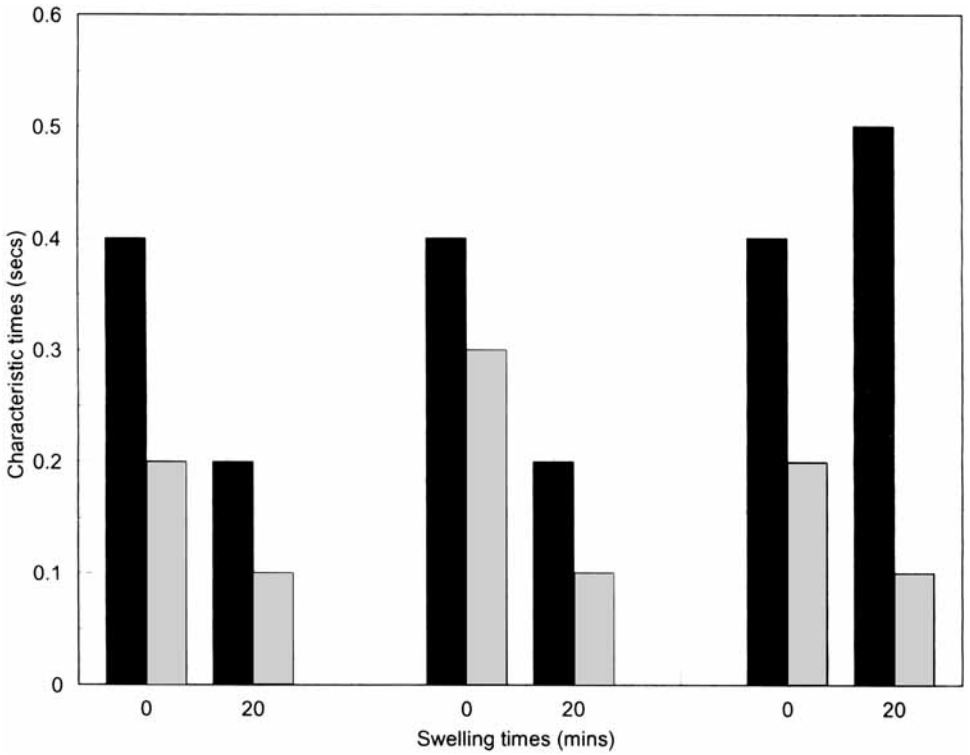

Figure 6 Comparison of unmodified and modified 425–500 μm particles in volume fractions of 0.05, 0.07, and 0.10 settling in hexane at different times of swelling: (■) unmodified particles; (▩) particles penetrated by 600,000 PEO at a concentration of 1 g/100 mL.

the water caused the settling rate of the modified particles to decrease.

It was hypothesized that changing the conditions for creating the networks might alter the amount of PEO that was trapped by the particles. Therefore, a number of experiments were run at higher temperatures, and drying times for the particles were increased. The results were compared with those run at standard conditions.

Figure 7 shows the results of the scans run at different temperatures. The immediate scan shows little appreciable difference between modified particles prepared at room temperature and those produced at 75°C. But after the particles were allowed to swell for 10 min, there were significant increases in settling rates for the networks produced at higher temperatures, suggesting that a great deal more PEO was trapped inside the particles at the higher temperatures.

Further experiments were performed to test the effects of allowing the modified particles to dry for 48 h instead of 24 h. Particles that dried for the extra day generally had settling rates that improved by a factor of two. For example, Figure 8 shows data for the 425–500 μm particles that were penetrated by 1000 PEO at a concentration of 10 g/100 mL. These particles showed increases of 100–300% upon drying for 48 h. Apparently, the extra 24 h creates drier and, therefore more discrete, particles. Drying the particles 72 h instead of 48 h did not show any appreciable differences.

CONCLUSIONS

This work has provided a novel method of slowing the settling of relatively large microparticles, involving synthesis of these modified particles as well as measurement of their settling times and examination of their structures through swelling studies.

As expected, it was found that increased volume fraction and decreased particle size hindered the settling for both unmodified and modified particles. Swelling played a dual role in slowing the settling rate. First, the swelling of the particle itself increased the volume fraction and diameter size, thereby slowing the settling. Swelling also allowed the PEO that was trapped inside the particle to diffuse out, raising the viscosity of the medium and increasing settling times. The addition of PEO was the major factor in hindering the settling. Higher concentrations and molecular weights caused a greater effect, but the experiment was limited by the relatively low concentrations of higher molecular weight PEO that could be used. Functionalization conditions were changed to optimize the diffusion of the PEO into the microparticles. It was found that raising the temperature to 75°C caused a threefold increase in

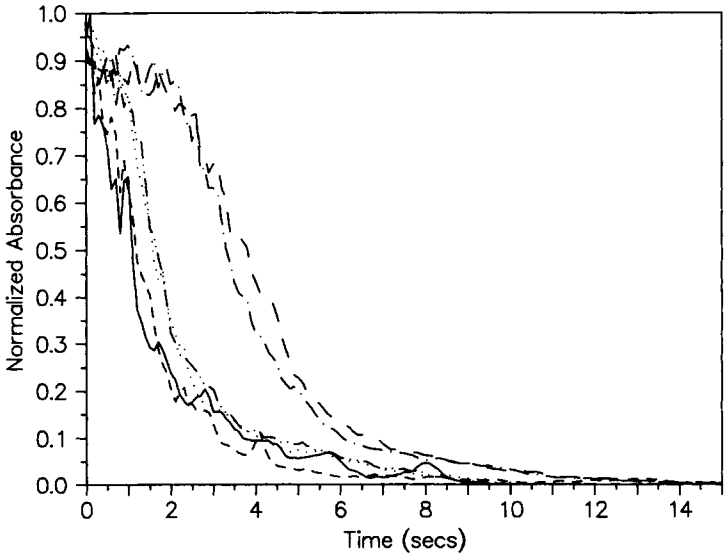

Figure 7 Normalized absorbance as a function of time for 10% volume fraction of 500–600 μm particles penetrated by 100,000 PEO at a concentration of 5 g/100 mL at 25 and 75°C with measurements taken of dry particles and particles swollen for 10 and 20 minutes: (——) 25°C functionalization—dry; (– – –) 75°C functionalization—dry; (· · ·) 25°C functionalization—10 min; (– · –) 75°C functionalization—10 min; (· – ·) 25°C functionalization—20 min; (— —) 75°C functionalization—20 min.

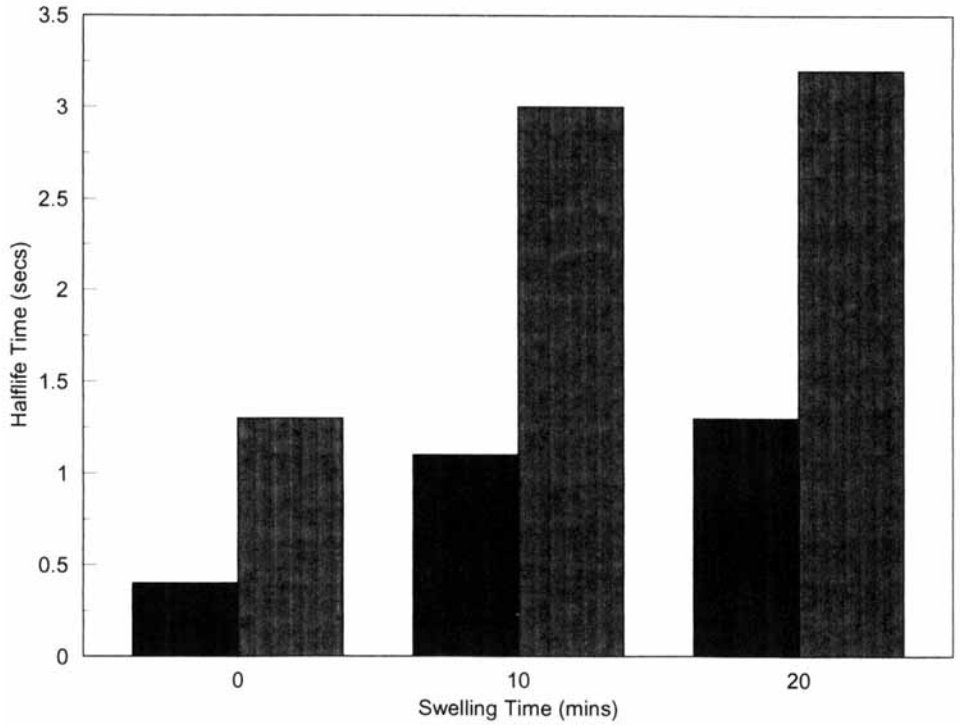

Figure 8 Effects of increased drying times on 425–500 μm particles penetrated by 1000 PEO at a concentration of 10 g/100 mL: (■) particles dried for 24 h; (▩) particles dried for 48 h.

settling times. Optical microscopy yielded pictures of swelling particles that supported the absorbance measurements. It was demonstrated that the bulk of the swelling occurs in the first 10 min for both unmodified and modified particles. The microscopy also showed that the lower molecular weight PEO diffused much more quickly into the particle. This work proved that the modification of microparticles by SIPNs creates particles that will settle considerably more slowly than will unmodified ones. Under the ideal optimization conditions, settling times could be improved by nearly a factor of 6.

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