Viscosity Transitions in Aqueous Suspensions of Hydrogel Microspheres

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ABSTRACT: Large transitions in viscosity are demonstrated for suspensions of environmentally sensitive gel microspheres upon application of external stimuli. Depending on the number concentration of microspheres, these suspensions may thicken to become semisolid, essentially undergoing a sol–gel transition. These reversible viscosity transitions are directly related to the volume transitions observed previously in the literature for individual environmentally sensitive gels. Temperature-sensitive poly-N-isopropylacrylamide microspheres were synthesized, and the effects of microsphere concentration on the temperature-induced viscosity transitions were measured. The viscosity of poly-N-isopropylacrylamide microsphere suspensions could also be increased by addition of sodium dodecyl sulfate. Non-temperature-sensitive, commercially available polyacrylamide microspheres were used to demonstrate viscosity transitions as a function of solvent composition in acetone/water mixtures. Potential applications for these systems were suggested. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63**: 1369–1372, 1997

Key words: viscosity transitions; aqueous suspensions; hydrogel microspheres; solvent composition

INTRODUCTION

The volume of an environmentally sensitive hydrogel changes dramatically and sometimes discontinuously in response to external stimuli such as a change in temperature, solvent concentration, electric field strength, pH, etc. Many authors reported changes in gel volume or mass for macroscopic articles (e.g., disks) placed in excess solvent[1] or for highly dilute gel microspheres.[2,3] In this study we measured the bulk viscosity of concentrated suspensions of environmentally sensitive microspheres. We observed large transitions in suspension viscosity that occur in conjunction with the volume transition of the microspheres. Depending on the particle number concentration, we observed viscosity transitions exceeding 3 orders of magnitude, whereas microsphere volume changed only by 1 order of magnitude.

A well-known example of a temperature-sensitive gel is poly-N-isopropylacrylamide (NIPA) hydrogel, whose volume expands several hundred percent as the temperature is lowered from 34 to 32°C.[4] Figure 1 illustrates the basis for a viscosity, or sol–gel, transition in a suspension of such microspheres and compares this phenomenon to the viscosity–volume fraction relationship for a suspension of solid particles. In a suspension of solid particles, particle volume fraction (and therefore viscosity) is increased by adding particles [Fig. 1(a)]. In a suspension of temperature-sensitive gel microspheres, viscosity can be increased at a fixed number count by expanding each microsphere [Fig. 1(b)].

We prepared aqueous suspensions of microspheres of poly-NIPA hydrogel and measured the suspension viscosity as a function of temperature and volume fraction of microspheres. At temperatures below the transition temperature of an individual hydrogel, each microsphere is swollen. If the volume fraction of expanded microspheres is

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Suspension of Solid Particles
(e.g., polymer latex)

Suspension of Enivronmentally Sensitive Hydrogel Microspheres
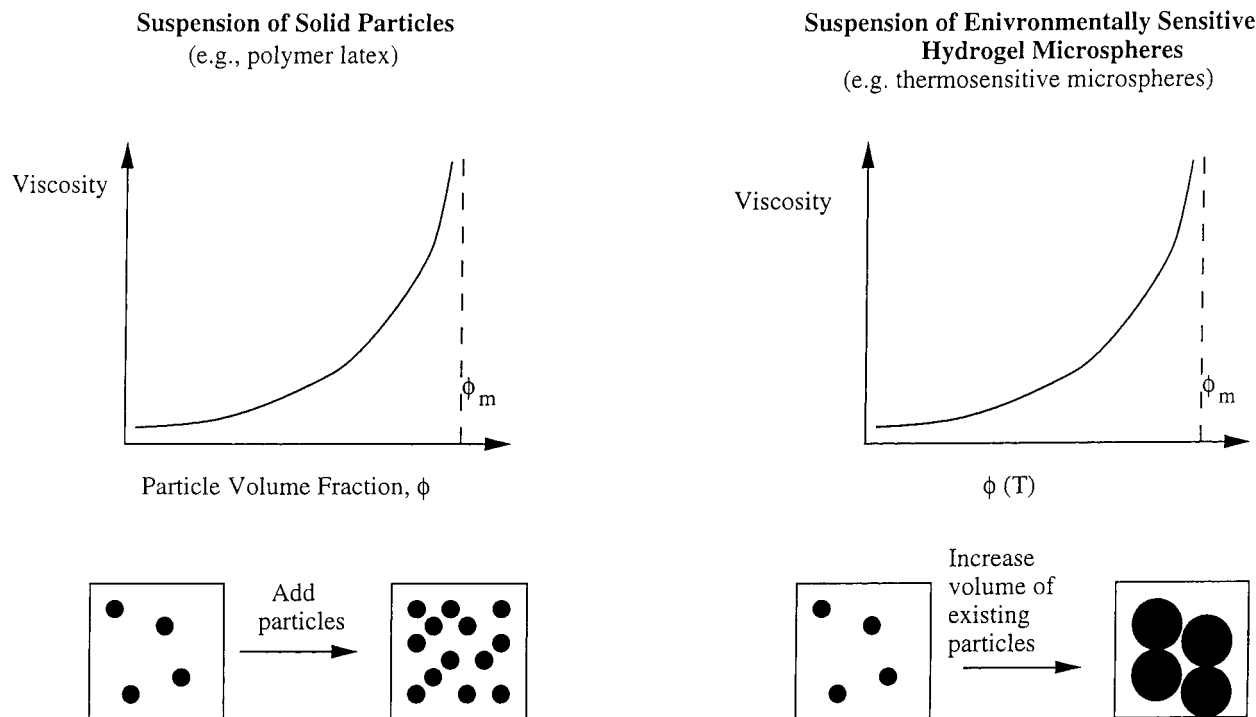(e.g. thermosensitive microspheres)

Figure 1   Basis for viscosity transitions in particle suspensions. (a) By adding particles to a suspension of rigid spheres, viscosity increases as the particle volume fraction, ϕ, increases. (b) By expanding the volume of individual temperature-sensitive microspheres, viscosity increases as the effective microsphere volume fraction, ϕ, increases. In both systems, viscosity approaches infinity at some maximum particle packing fraction, ϕ_m.

high, a suspension is extremely viscous and, in some cases, solidlike. At temperatures above the transition temperature, each microsphere is collapsed. If the volume fraction of collapsed microspheres is small, a suspension is highly fluid. Thus, under appropriate conditions (controlled swelling ratios in expanded and collapsed states, and a corresponding percentage of solids), expansion and collapse of individual gel microspheres causes a sol–gel transition.

PREPARATION OF GEL MICROSPHERES

We prepared poly-NIPA microspheres by precipitation polymerization in a 1-L reaction vessel with overhead stirring, by the recipe: 9.8 g N-isopropylacrylamide (Kodak), 0.2 g methylene bisacrylamide (crosslinking agent; Sigma), 0.48 g IGEPAL 887 surfactant, and 0.195 g IGEPAL 630 surfactant in 380 g of deionized, distilled water. IGEPAL surfactants were obtained from Rhône–Poulenc. We heated the solution to 70°C and added 20 g of water containing 0.4 g of an initiator, potassium persulfate. The reaction proceeded overnight. The microspheres were recovered by centrifugation and found to be less than 1 μm in diameter. We measured the polymer content of a suspension by drying to constant mass in an oven at 100°C, reported as $\%p$ (the percent solids of the suspension). Using a Brookfield DVII+ viscometer with a water-jacketed temperature cell, we measured the viscosity as a function of temperature.

RESULTS AND DISCUSSION

Figure 2 shows the effect of temperature on the viscosity of aqueous poly-NIPA microgel suspensions at different $\%p$. The viscosity was measured at a shear rate of 0.1 s^{-1}. For the 9%p suspension, the viscosity fell between 30 and 34°C from over 100,000 centipoise (cP) to less than 1000 cP. As we diluted the suspension (lowering $\%p$), the
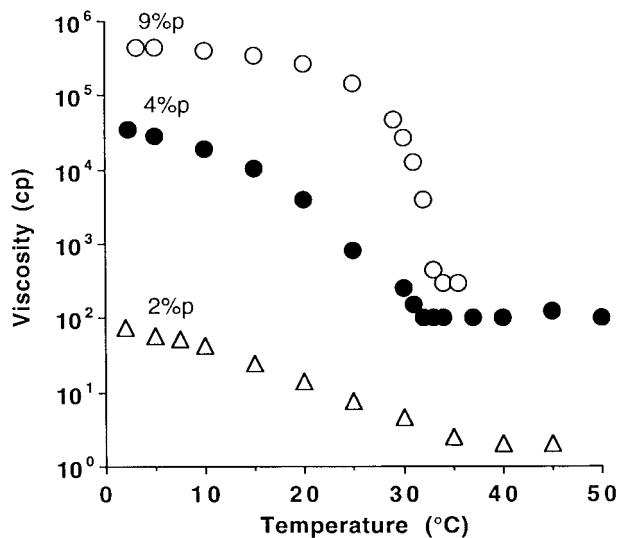
Figure 2 Effect of temperature and $\%p$ on viscosity of aqueous suspensions of temperature-sensitive, poly-N-isopropylacrylamide microspheres. Increasing temperature causes a sharp and dramatic decrease in the viscosity of a $9\%p$ suspension. As the suspension is diluted (lowering $\%p$), the viscosity transition occurs over a wider range of temperatures.
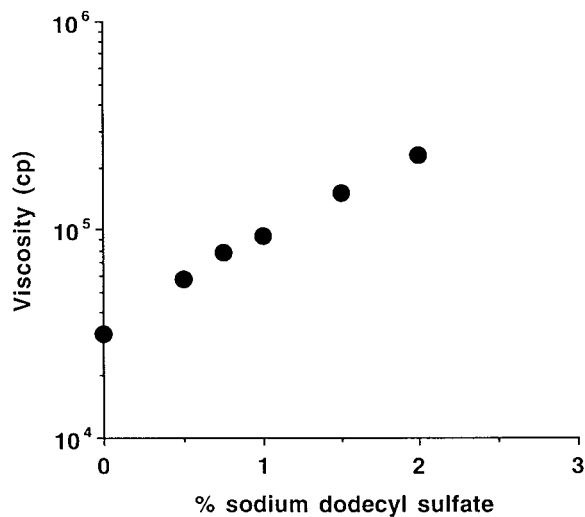

Figure 3 Effect of surfactant concentration on the viscosity of a suspension of expanded poly-N-isopropylacrylamide microspheres at 20.7°C. Addition of sodium dodecyl sulfate increases viscosity.

transition in viscosity became less sharp and occurred over a wider range of temperature.

Upon heating, the suspension viscosity decreased because each microsphere collapsed, expelling water. The extent of water expulsion determined the magnitude and broadness of the viscosity transition. Thus, we could control the viscosity transition through $\%p$ and/or microsphere chemistry and synthesis conditions.

We can also affect the viscosity transition of a suspension of microspheres if we add components that change the swelling transition of each microsphere. Figure 3 shows the viscosity as a function of concentration of a surfactant, sodium dodecyl sulfate (SDS), for a suspension of poly-NIPA microspheres ($8\%p$) at 20.7°C (i.e., in the expanded or swollen state). Viscosity was measured at a shear rate of 0.1 s^{-1}. The addition of 2% SDS increased viscosity by more than an order of magnitude. Inomata et al. previously reported the expansion of poly-NIPA gel rods in solutions containing SDS.[5]

Figure 4 presents the effect of acetone on the viscosity of an aqueous suspension of Bio-Rad P-100 polyacrylamide gel ($7\%p$). P-100 microspheres are 40–90 μm in diameter when fully swollen in pure water. As we increased the acetone concentration from 10 to 25 wt %, the suspen-

sion viscosity decreased approximately 5 orders of magnitude. In 1978 Tanaka reported that a polyacrylamide gel collapses in water/acetone solutions as acetone concentration increases.[6,7] With hydrolysis of polyacrylamide, the volume transition became larger and discontinuous; however, even after 60 days of hydrolysis, the volume transition was only 3 orders of magnitude.
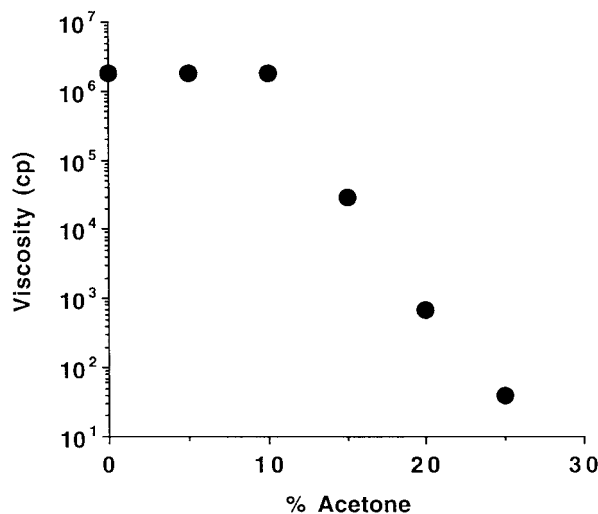
The examples above demonstrate the univer-

Figure 4 Effect of acetone concentration on the viscosity of a suspension of Bio-Rad P-100 polyacrylamide microspheres in acetone/water mixed solvents. Increasing the acetone concentration from 10 to 25% decreases the viscosity by 5 orders of magnitude.

sality of sol–gel transitions in microsphere suspensions above a certain loading level induced by changes in microsphere volume. Suspensions of environmentally responsive hydrogel microspheres represent a new class of "smart" materials. Using the same stimuli that induce gel volume transitions, we can convert these suspensions from high-viscosity, near-solid gels to low-viscosity fluids. Like gel volume transitions, viscosity transitions are reversible. Matsuo and Tanaka studied the kinetics of volume transition for gel microspheres.[3] These studies indicate that rapid viscosity transitions can be obtained, limited primarily by heat transfer to and from the suspension. Thermoreversible microsphere suspensions can be compared to thermoreversible polysaccharide or polypeptide gels such as agarose, gelatin, and β-1,3 glucans. However, the intrinsic network topology of a microsphere is never broken during cycling of temperature, and gel microsphere suspensions do not exhibit hysteresis.

We envision many possible novel and useful applications for these viscosity-responsive suspensions. For example, we can use the viscosity change as a mechanism to deliver (e.g., pump or pour) a prepolymerized gel medium at low viscosity into a cavity and subsequently convert the medium to its high-viscosity, nonflowing state. Precisely engineered pore structures can thus be created in a pseudocontinuum. In addition to viscosity, we noted that other bulk properties changed dramatically around the transition temperature. Electrophoretic sieving characteristics were one such property.[8] In a separate report[9] we will describe the use of thermoreversible microgel suspensions as novel electrophoretic matrices.

CONCLUSIONS

This work discusses how the volume transition of individual gel microspheres can be harnessed to create suspensions that display large transitions in viscosity as a result of environmental stimuli. These stimuli may be relatively small changes in temperature, solvent composition, or surfactant concentration, for example. As $\%p$ increases, the viscosity transition increases. At sufficiently high number concentrations of microspheres, a suspension of gel microspheres may even display a bulk sol–gel transition. Furthermore, the processes of gelation and formation of network topology are decoupled in these types of suspensions. Because the sol/gel or viscosity transitions are caused by transitions in microsphere volume, suspensions of microspheres prepared from responsive polymers have many potential applications as smart materials.

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