The other difference comes in the threshold temperature for aluminum deposition, which is below 100 °C for $(Me_3N)_2AlH_3$ and around 180 °C for TIBA. The high rates and low temperatures of deposition should make $(Me_3N)_2AlH_3$ especially attractive for growing aluminum on temperature-sensitive substrates.

Acknowledgment. This research was supported by a grant from the National Science Foundation (CHE-8711821) and the NSF Center for Interfacial Engineering at the University of Minnesota. We are also grateful to Dr. Donald McClure of 3M for providing a sample of polyimide film and assisting with the reflectivity measurements and to Richard Haasch and Roland Schulze for Auger electron spectroscopic measurements.

Registry No. Al, 7429-90-5; $(Me_3N)_2AlH_3$, 92818-52-5; Si, 7440-21-3.

Preparation of Polymer Composites. A Colloidal Pathway

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The preparation of a new type of polymer blend by a two-step procedure is described. The composite consists of hydrophilic (hydrophobic) polymer particles dispersed in a hydrophobic (hydrophilic) polymer. In the first step, polymer latex particles are obtained by the concentrated emulsion method by polymerizing the dispersed phase. The volume fraction of the dispersed phase in these emulsions can be as large as 0.995. In the second step, the polymerized concentrated emulsion is dispersed in another monomer (or a solution of the monomer in water when the latter monomer is hydrophilic) that has characteristics (in regard to hydrophilicity or hydrophobicity) of the same type as those of the continuous phase of the concentrated emulsion. This ensures the formation of a stable colloidal dispersion of latex particles in the monomer, without introducing any additional dispersant. The obtained dispersion yields upon polymerization a composite with a homogeneous microstructure. Composites of poly(styrenesulfonic acid) salt latexes dispersed in cross-linked polystyrene matrices as well as polymer composites of polystyrene latexes dispersed in cross-linked polyacrylamide matrices are thus obtained. The composites prepared by the two-step method are compared with those obtained in a single step from concentrated emulsions, emulsions, or microemulsions.

Introduction

Polymer composites are prepared to control the mechanical properties of the polymeric materials as well as for obtaining permselective membranes for separation processes. Many important polymer composites are, however, blends of incompatible polymers.[1] In spite of their high impact strength[2] or high liquid permselectivity,[3,4] the large-scale application of these conventional polymer composites is sometimes limited due to the difficulty of controlling their morphology. Indeed, because of the tendency for segregation caused by the incompatibility, the materials will have a nonuniform structure. It is, therefore, useful to develop blends whose structures can be more easily controlled and, hence, can be more uniform.

The composites developed here constitute a new type of polymer blend in which the incompatibility of the polymers is taken advantage of. They are prepared by a two step polymerization method. In the first step, hydrophilic (hydrophobic) polymer latex particles are prepared. They are then dispersed in a hydrophobic (hydrophilic (to increase the hydrophilicity of the hydrophilic phase, the hydrophilic monomer is in general replaced by its solution in water)) monomer containing a thermal initiator, and the mixture is subsequently polymerized. In this work, the concentrated emulsion polymerization method[5,6] is employed to produce relatively uniform polymer latex particles of submicron sizes. As in the case of the conventional emulsions, the dispersed phase in concentrated emulsions is either hydrophobic or hydrophilic, and the continuous phase is the opposite (hydrophilic or hydrophobic). However, in contrast to conventional emulsions, the volume fraction of the dispersed phase in the concentrated emulsions is very large[7] (>0.74, which represents the volume fraction of the most compact arrangement of spheres of equal radius, and as large as 0.995). In concentrated emulsions, the spheroidal globules of the conventional emulsions are replaced by polyhedral cells separated by thin films of the continuous phase. The thin films form a network, similar to that in a foam, whose stability is ensured by the adsorption of the dispersant from the continuous phase onto the cell-film interface. The concentrated emulsions have the appearance of gels and are prepared in the present experiments at room temperature. A suitable initiator is introduced in the dispersed

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phase, and an appropriate dispersant is dissolved in the continuous phase. One can obtain latex particles by heating the gel at about 40 °C. The size of these particles can be controlled by controlling the size of the cells of the gel. This control can be achieved by changing the nature of the surfactant as well as the ionic strength and pH in the aqueous phase. In the present experiments, the monomer–precursor of the continuous phase of the composite or water, when this monomer was hydrophilic, was selected as the continuous phase of the gel. In the second step, the gel whose dispersed phase was polymerized is dispersed in the continuous-phase monomer of the composite or its solution in water when the monomer is hydrophilic, after a suitable initiator is introduced in the continuous phase. The submicrometer size hydrophilic (hydrophobic) latexes are thus dispersed in the hydrophobic (hydrophilic) continuous phase without the addition of a dispersant. Our experimental observations indicate that the above colloidal dispersions are stable. The stability is probably ensured by (1) the dispersant introduced in the first step and (2) by the presence of the films of the continuous phase of the gel around the latex particles. These films consist of either the same monomer as the monomer–precursor of the continuous phase of the composite or water when the monomer–precursor is hydrophilic. This ensures the compatibility of the particles with the continuous phase. One may note that the use of the concentrated emulsion method to prepare latexes plays an important role in the stability of the colloidal dispersion that is prepared in the second step. Herein, preparation and some properties of composites of poly(styrenesulfonic acid) salt latexes dispersed in cross-linked polystyrene matrices as well as composites of polystyrene latexes dispersed in cross-linked polyacrylamide matrices are reported. Finally, the two-step method is compared to single-step processes based on concentrated emulsions or microemulsions pathways.

Experimental Section

Materials. Styrene (Aldrich), methyl methacrylate (Aldrich), and divinylbenzene (Polysciences) were distilled and stored in a refrigerator. Azobisisobutyronitrile (AIBN, Alfa) and acrylamide (Polysciences) were purified by recrystallization in methanol. Potassium peroxodisulfate (Aldrich) was recrystallized from water. Styrenesulfonic acid sodium salt hydrate (Aldrich), *N*,*N*-methylenebisacrylamide (Kodak), sodium dodecyl sulfate (SDS, Aldrich), aerosol OT (American Cyanamide), and sorbitane monooleate (Span 80, Fluka) were used as received. Spectrophotometric grades of toluene, cyclohexane, and ethyl alcohol were purchased from Aldrich Chemical Co. and used as received. Water was deionized and distilled.

Preparation of the Poly(styrenesulfonic acid) Salt Latex Particles. A small amount of styrene containing sorbitane monooleate as dispersant was placed in a 250-mL three-neck flask equipped with a mechanical stirrer, an addition funnel, and a nitrogen inlet. An aqueous styrenesulfonic acid sodium salt solution was placed in the addition funnel. To avoid the inhibiting action of oxygen on the polymerization of styrenesulfonic acid salt, the air in contact with the organic and aqueous phases was displaced by bubbling with nitrogen. An aqueous solution of $K_2S_2O_8$ (initiator) was prepared under nitrogen. This solution was injected with a syringe into the aqueous styrenesulfonic acid salt solution. The concentrated emulsion was prepared at room temperature by dropwise addition of the aqueous styrenesulfonic acid sodium salt solution to the stirred mixture of styrene and surfactant. Subsequently, polymerization under a nitrogen stream was carried out, by immersing the flask in a temperature-controlled water bath.

Preparation of the Polystyrene Latex Particles. The polystyrene latexes were prepared as described before.[5] A small quantity of an aqueous solution of SDS (dispersant) was placed in a 250-mL flask equipped with a mechanical stirrer. Styrene containing AIBN as initiator was added to the stirred aqueous solution. Polymerization of the dispersed phase of the concentrated emulsion was carried out in a water bath at 40 °C.

Preparation of the Polymer Composites. Once the polymerized gels containing the latexes of polystyrene or polystyrenesulfonic acid salt were prepared, they were placed in the three-neck flask. [The polymerization times were 6 h for the polystyrene latexes and 3 h for the poly(styrenesulfonic acid) salt latexes.] The monomer–precursor of the continuous phase of the composite containing a suitable initiator or a solution of that monomer in water for a hydrophilic monomer was placed in the addition funnel. Prior to polymerization, air was removed from the reactor by nitrogen bubbling. The monomer was added dropwise to the stirred polymer latexes. The polymerization was carried out in a water bath at 40 °C under nitrogen.

Preparation of Polymer Composite Films. Well-cleaned and dried glass plates (100 cm × 15 cm) were used for the preparation of films. A small amount of glycerol as a lubricant was placed on the surface of the glass plates. The mixture of polymer latexes and initiator containing monomer were placed between the glass plates and squeezed slowly to avoid trapping of air bubbles. The glass plates sandwiching the above dispersion were placed in an oven at 40 °C for 24 h for polymerization to occur.

Preparation of Emulsions or Microemulsions and of Polymer Composites Based on Them. A hydrophilic (hydrophobic) continuous phase monomer containing a surfactant and a suitable initiator was placed in a flask under a nitrogen atmosphere. (The hydrophilic monomer was in general replaced by its solution in water, and the hydrophobic one was sometimes replaced by its solution in octane. In order to obtain a microemulsion, a cosurfactant (alcohol) is also, in general, needed.[8] There are exceptions. The double-chain surfactants and the nonionic ones do not need a cosurfactant. Cosurfactants have not been employed in the present experiments; however, the hydrophilic monomer can play the role of the cosurfactant.) A hydrophobic (hydrophilic) dispersed phase containing an appropriate initiator was placed in the addition funnel. The emulsion or microemulsion was prepared, at room temperature, by dropwise addition of the dispersed phase to the mildly stirred continuous phase. Polymerization was carried out in a water bath at 40 °C under a nitrogen stream.

Molecular Weight Measurements. The molecular weight of poly(styrenesulfonic acid) salt was measured by gel permeation chromatography (GPC) with μ Bondagel columns (Waters) using a solution of 10% isopropyl alcohol in water as mobile phase. The GPC was calibrated by using poly(styrenesulfonic acid) salt standards (Polymer Laboratories) with molecular weight between 10^4 and 10^6.

Electron Microscopy. The polymer latexes and the microstructure of the polymer composites were examined by transmission electron microscopy (TEM, Hitachi HS-8) and scanning electron microscopy (SEM, Amray 100A). The specimens were prepared by placing a drop of very dilute latex solution on copper grids coated with carbon films for TEM and on clean cover glass for SEM. The grids were allowed to dry before observation. In the case of SEM, a thin layer of gold was deposited prior to observation. Microtomed thin sections (~900 Å) of polymer composites were also examined by TEM.

Swelling Test. The extent of swelling of the polymer composite was determined by measuring its change in weight. Dried polymer composite films of about 600-μm thickness were placed in flasks filled with various liquid mixtures. The films were allowed to equilibrate for a week, and the changes in weight were noted. The swelling of the composite is defined as

$$S = (W_s - W_0)/W_0$$

where W_0 and W_s stand for the weights of the dry and equilibrated polymer composite films, respectively.

Results

Preparation of Poly(Styrenesulfonic acid) Salt Latex Particles.

First let us note that the concentrated

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[8] Prince, L. M. In *Microemulsions, Theory and Practice*; Prince, L. M., Ed.; Academic Press: New York, 1977.

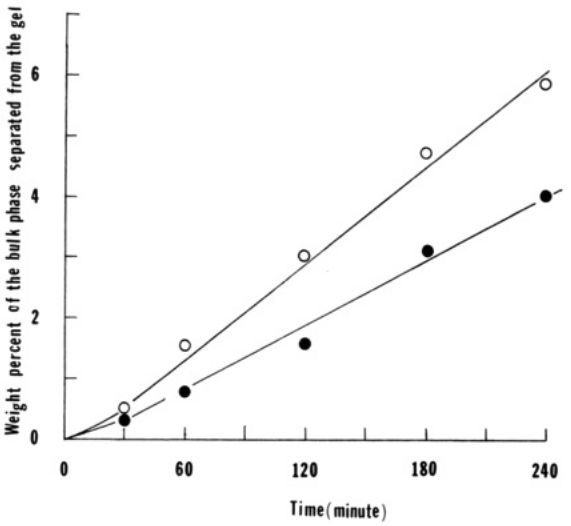

Figure 1. Weight fraction of bulk phases separated from the concentrated emulsion after heating at 40 °C (●) and at 50 °C (○) as a function of time. The dispersed phase is an aqueous solution of monomer (9 g of styrenesulfonic acid salt and 40 g of water). The continuous phase is an organic solution (3 mL of styrene and 1.5 mL of sorbitane monooleate).

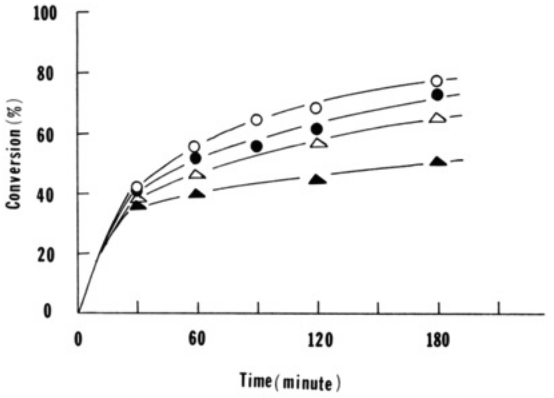

Figure 2. Polymer conversion as a function of time in the concentrated emulsion at 50 °C (●) and 40 °C (▲) and in the solution polymerization at 50 °C (○) and at 40 °C (△).

Table I. Representative Compositions in the Preparation of Poly(styrenesulfonic acid) Salt and Polystyrene Latexes

Compositions for the Preparation of Poly(styrenesulfonic acid) Salt Latexes	
dispersed phase	
styrenesulfonic acid sodium salt	9 g
water	40 g
initiator (sodium persulfate)	0.008 g/g of styrenesulfonic acid salt
continuous phase	
styrene	3 mL
initiator (AIBN)	2.0×10^{-2} mol/L of styrene
surfactant (sorbitane monooleate)	1.5 mL
Compositions for the Preparation of Polystyrene Latexes	
dispersed phase	
styrene	1.5 mL
initiator (AIBN)	1.26×10^{-2} mol/L of styrene
continuous phase	
water	2 mL
surfactant (SDS)	0.3 g

Table II. Molecular Weight of Poly(styrenesulfonic acid) Salt Prepared at 40 °C by the Concentrated Emulsion and Solution Methods

	mol wt	
polymerization time, h	concentrated emulsion	solution
3	0.89×10^6	0.40×10^6

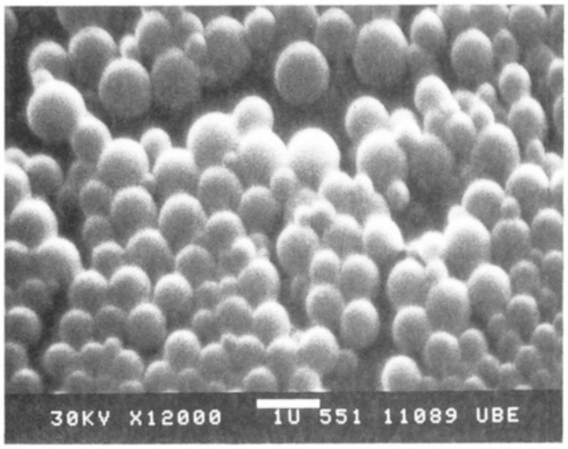

Figure 3. Scanning electron micrograph of poly(styrenesulfonic acid) salt latex particles.

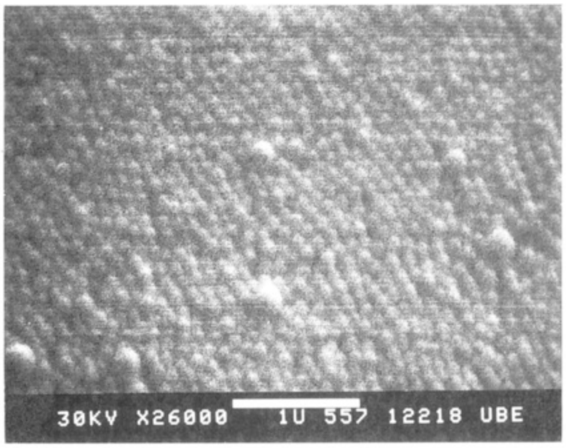

Figure 4. Scanning electron micrograph of polystyrene latex particles.

emulsions prepared at room temperature are relatively stable. Indeed, Figure 1 shows that their heating at 40 and 50 °C generates only small amounts of bulk phases. The amounts of various components employed in the first polymerization step are listed in Table I and the conversion as a function of time is plotted in Figure 2. Also included in this figure are results obtained, under the same conditions, when solution polymerization is employed. The conversion is higher for solution polymerization than for concentrated emulsion polymerization. The conversions in both solution and concentrated emulsion polymerization increase with temperature. Table II shows that the molecular weights of the polymers obtained by concentrated emulsion polymerization are slightly larger than those obtained by solution polymerization. Figure 3 is a scanning electron micrograph of the poly(styrenesulfonic acid) salt latex particles produced by concentrated emulsion polymerization. This micrograph shows that polymerization leads to spherical latex particles of submicrometer sizes in the 0.1–1.0-μm size range.

Preparation of Polystyrene Latex Particles. For the preparation of polystyrene latexes, the compositions listed in Table I were employed. The molecular weight and conversion after 24 h of polymerization were 3.1×10^6 and 65%, respectively. Figure 4 represents a scanning electron micrograph and shows that the sizes of the latex particles were of about 0.1 μm. Figure 5 is a transmission electron micrograph which indicates that the polystyrene latex

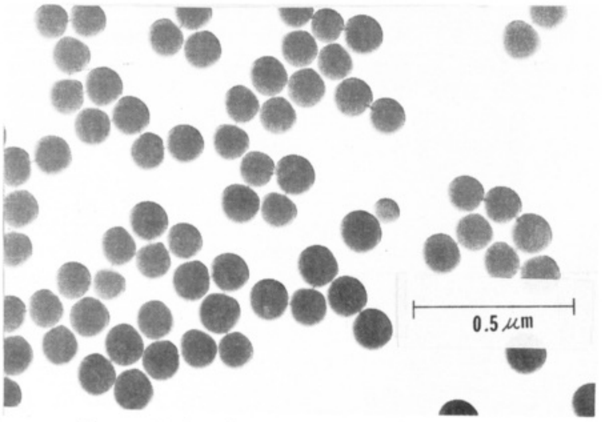

Figure 5. Transmission electron micrograph of polystyrene latex particles.

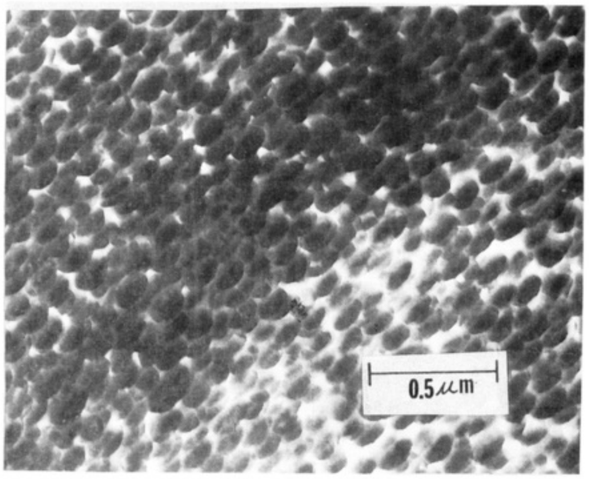

Figure 6. Transmission electron micrograph of a composite with the composition H_1 (Table III). The black regions represent the polystyrene and the white regions represent the cross-linked polyacrylamide.

Table III. Representative Compositions in the Preparation of Polymer Composites: Polystyrene Particles Dispersed in Cross-Linked Polyacrylamide

H_1	polystyrene latexes[a]	15 g
	acrylamide	1.5 g
	N,*N*-methylenebisacrylamide	0.1 g
	initiator (potassium persulfate)	0.01 g/g of acrylamide
	water	1.5 g
H_2	polystyrene latexes[a]	10 g
	acrylamide	1.5 g
	N,*N*-methylenebisacrylamide	0.1 g
	initiator (potassium persulfate)	0.01 g/g of acrylamide
	water	1.5 g

[a] The compositions of the polymer latexes are given in Table I.

particles are more uniformly distributed and smaller in size than the poly(styrenesulfonic acid) salt latex particles.

Polymer Composites. Figure 6 represents a transmission electron micrograph of a polymer composite, denoted H_1 in Table III, in which polystyrene latexes are dispersed in a polyacrylamide matrix. It clearly shows that polystyrene latexes of submicrometer size are uniformly dispersed in the polyacrylamide matrix without agglomeration. Figure 7 represents a polymer composite, denoted I_1 in Table IV, of poly(styrenesulfonic acid) salt latexes dispersed in a cross-linked polystyrene matrix. The poly(styrenesulfonic acid) salt latex particles are uniformly dispersed in the cross-linked polystyrene matrix.

Swelling Test. Figure 8 plots the swelling of the polymer composites composed of polystyrene latexes dispersed in cross-linked polyacrylamide as a function of the concentration of cyclohexane in a mixture of cyclohexane and toluene. The mixture toluene–cyclohexane was chosen for the swelling test because (i) polyacrylamide, being hydrophilic, is insoluble in both components; (ii) the benzenic ring makes polystyrene compatible with toluene. The swelling, which in this case is mainly due to the dissolution of toluene in polystyrene, is a measure of the strength of the polyacrylamide continuous phase. It is also a measure of the capability of the composite to separate toluene from cyclohexane (aromatics from paraffinics). The compositions of the polymer composite films are given in Table III. The swelling of the film of composition H_1 is of about 3.2 in toluene and 1.1 in cyclohexane. The swelling increases with the fraction of polystyrene latexes in the composite and decreases with the concentration of cyclohexane. This occurs because of the higher solubility of toluene in polystyrene. The composites of compositions I_1 and I_2 (Table IV), in which poly(styrenesulfonic acid) salt latexes are dispersed in cross-linked polystyrene, exhibit selective swelling for water from mixtures of water–ethanol, because of the presence of the hydrophilic poly(styrenesulfonic acid) salt in the polymer composite. The

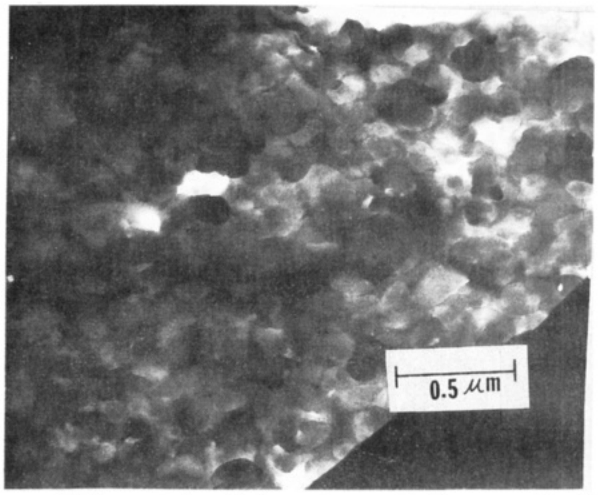

Figure 7. Transmission electron micrograph of a composite with the composition I_1 (Table IV). The white regions represent the cross-linked polyacrylamide and the grey regions represent the poly(styrenesulfonic acid) salt.

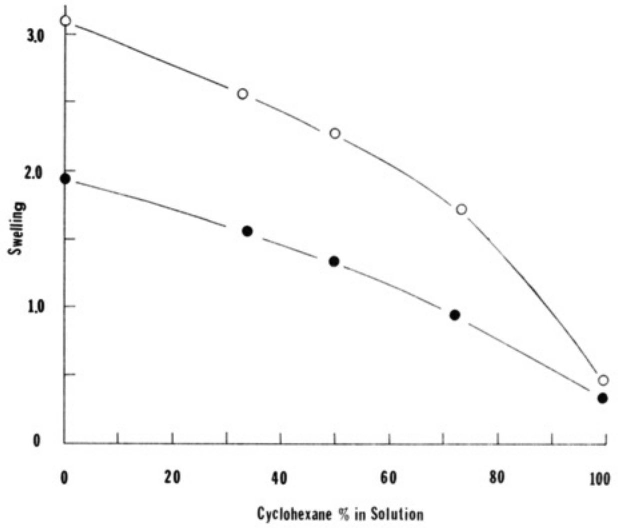

Figure 8. Swelling as a function of cyclohexane concentration for a cyclohexane–toluene mixture at 25 °C. ○ and ● denote the polymer composites H_1 and H_2 (Table III), respectively.

Table IV. Representative Compositions in the Preparation of Polymer Composites: Poly(styrenesulfonic acid) Salt Particles Dispersed in Cross-Linked Polystyrene

I_1	poly(styrenesulfonic acid) salt latexes[a]	15 g
	styrene	1.6 g
	divinylbenzene	0.4 g
	initiator (AIBN)	0.02 g/g of styrene
I_2	poly(styrenesulfonic acid) salt latexes[a]	8 g
	styrene	1.6 g
	divinylbenzene	0.4 g
	initiator (AIBN)	0.02 g/g of styrene

[a] The compositions of polymer latexes are given in Table I.

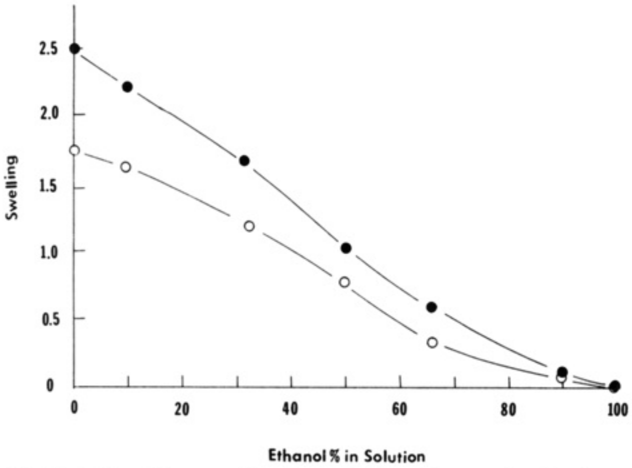

Figure 9. Swelling as a function of ethanol concentration in an ethanol–water mixture at 25 °C. ● and ○ denote the polymer composites I_1 and I_2 (Table IV), respectively.

swelling of the composites I_1 and I_2 in ethanol–water mixtures is plotted in Figure 9. The swelling increases with the fraction of poly(styrenesulfonic acid) salt latexes in the composite and decreases with the concentration of ethanol in the mixture.

Table V. Representative Compositions for Composites by One-Step Microemulsion Polymerization

J_1: Compositions of the Composites in Which Polyacrylamide Is Dispersed in a Poly(methyl methacrylate) Matrix	
continuous phase	
acrylamide	4 g
water	10 g
initiator (sodium persulfate)	0.01 g/g of acrylamide
surfactant (SDS)	2 g
dispersed phase	
methyl methacrylate	3 g
initiator (AIBN)	0.03 g/g of methyl methacrylate
J_2: Compositions of the Composites in Which Poly(methyl methacrylate) Is Dispersed in a Polyacrylamide Matrix	
continuous phase	
methyl methacrylate	10 g
initiator (AIBN)	0.03 g/g of methyl methacrylate
surfactant (Aerosol OT)	3 g
dispersed phase	
acrylamide	0.6 g
water	1.4 g
initiator (sodium persulfate)	0.01 g/g of acrylamide

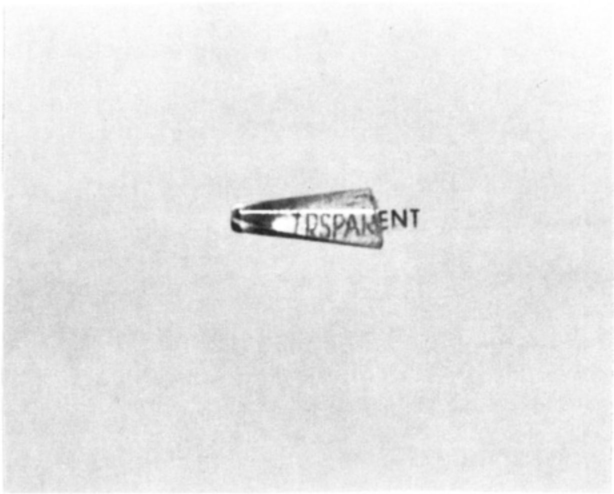

Figure 10. Polymer composite J_1 (Table V) prepared by the microemulsion method.

Single-Step Pathways to Composite Polymers. Single-step preparations of composite polymers have been also developed in this laboratory. In a previous paper,[9] concentrated emulsions have been used to prepare composites in a single step. The volume fraction of the continuous phase is, however, relatively small in such cases. In contrast, the present method allows us to prepare composites with larger volume fractions of the continuous phase. Composites with large volume fractions of the continuous phase can also be obtained in a single step by polymerizing an emulsion or microemulsion. An emulsion of a hydrophobic (hydrophilic) monomer in another hydrophilic (hydrophobic) monomer can be extremely stable (even thermodynamically stable, and then it is named a microemulsion) if a sufficiently large amount of surfactant is introduced in the system. The latter method was used to prepare composites by employing acrylamide (hydrophilic) and methyl methacrylate (hydrophobic) as monomers and SDS or aerosol OT as surfactants. The compositions are listed in Table V. No phase segregation was observed in the composites J_1 and J_2 thus obtained. The composite J_1 is completely transparent (Figure 10), like the initial dispersion. The two-step colloidal pathway suggested in the present paper uses much smaller amounts of low molecular weight surfactants compared to the microemulsion pathway. As a result, the two-step colloidal pathway is expected to lead to composites with better mechanical strength than those from the single emulsion (microemulsion) step.

Conclusions

Two types of polymer composites have been prepared by a two-step polymerization method. In one, hydrophilic latexes have been uniformly dispersed in a hydrophobic polymer matrix, while in the other hydrophobic latexes have been uniformly distributed in a hydrophilic polymer matrix. Poly(styrenesulfonic acid) salt latexes dispersed in cross-linked polystyrene matrices constitute an example of the first kind, and polystyrene latexes dispersed in cross-linked polyacrylamide constitute an example of the second kind. In the first step, latexes are prepared by the concentrated emulsion method, using as the continuous phase the monomer–precursor of the continuous phase of the composite or water when the continuous phase is hydrophilic. In the second step, the concentrated emulsion is dispersed, after its dispersed phase was polymerized, in the continuous-phase monomer of the composite or its solution in water when the monomer is hydrophilic. A stable colloidal dispersion without the addition of a dispersant is thus generated. Its stability is probably due to (1) the dispersant adsorbed on the surface of the cells of the gel in the first step and (2) the films of the continuous phase of the gel. These films are compatible with the continuous-phase monomer of the composite since both

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[9] Ruckenstein, E.; Park, J. S. *J. Polym. Sci., Polym. Lett. Ed.* **1988**, *26*, 529.

are either hydrophilic or hydrophobic. Finally, the colloidal dispersion is polymerized again.

Compared to the one-step method based on emulsions or microemulsions, the two-step method can employ a smaller amount of surfactant. As a result, composites with better mechanical properties are expected to be obtained.

Registry No. Poly(styrenesulfonic acid) sodium salt, 62744-35-8; polystyrene, 9003-53-6; (acrylamide)(*N*,*N*-methylenebisacrylamide) (copolymer), 25034-58-6; (divinylbenzene)(styrene) (copolymer), 9003-70-7.

Surface-Modified Electrodes Based on Nickel(II) and Copper(II) Bis(salicylaldimine) Complexes

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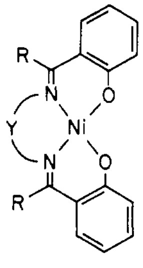
Received August 22, 1988

Surface-modified electrodes have been prepared by the oxidative polymerization of nickel(II) *N*,*N*′-ethylenebis(salicylaldimine) {[Ni(H-sal$_2$en)]}, copper(II) *N*,*N*′-ethylenebis(salicylaldimine) {[Cu(H-sal$_2$en)]}, and substituted nickel(II) and copper(II) bis(salicylaldimine) complexes. The modified electrodes were prepared in weak-donor solvents by repetitively cycling the potential in the oxidative region or by constant-potential electrolysis. For [Ni(H-sal$_2$en)], the surface coverage increased linearly for the first several voltammetric scans, and the initial rate of film growth increased linearly with the concentration of [Ni(H-sal$_2$en)]. For [Cu(H-sal$_2$en)], the rate of film growth decreased steadily from the initial scan. The resulting modified electrodes exhibited single reversible redox waves of modest stability in fresh electrolyte solution. Scan rate dependence of the current and peak potential separations are consistent with slow electron transfer for surface-immobilized redox couples. Electrodes prepared in various weak-donor solvents (acetonitrile, acetone, methylene chloride) showed essentially identical electrochemical behavior in fresh acetonitrile electrolyte, although scanning electron microscopy revealed a difference in surface morphology. The properties of this new family of surface-modified electrodes are discussed in terms of the proposed mechanism for polymer film formation and electron transfer.

Introduction

The study of polymer-modified electrodes continues to be an area of great interest and intense activity.[1-3] Much of the work in this area has been stimulated by the potential application of these new materials as electrocatalysts, chemical sensors, electrochromic displays, and microelectronic devices.[2b] An important theme in the design and development of chemically modified electrodes has involved extending the known redox reactivity of discrete homogeneous species to the electrode surface, and the rich redox chemistry of transition-metal complexes has played a prominent role in this area. The development of heterogeneous electrocatalysts based on known homogeneous transition-metal catalysts is one important example of this approach.[4]

We recently reported a solvent dependent mechanism for the oxidation of nickel(II) bis(salicylaldimine) complexes (I).[5,6] The nickel(II) complexes are reversibly oxidized in strong-donor solvents which stabilize the nickel(III) oxidation state. In weak-donor solvents, however, the complexes are oxidatively polymerized at the electrode surface. Electropolymerization is a particularly attractive method for preparing modified electrodes given the good stability and high density of redox sites often observed for the resulting polymer films.[1d,3] Therefore, the oxidative polymerization of bis(salicylaldimine) complexes may offer a potentially useful route to surface-modified electrodes based on these complexes.



I [Ni(R-sal$_2$Y)]

In this paper we report the preparation and properties of surface-modified electrodes obtained by the oxidative polymerization of nickel(II) *and copper(II)* bis(salicylaldimine) complexes. Bis(salicylaldimine) complexes of a number of transition metals (including nickel[7] and copper[8]) have shown catalytic activity for the oxidation of organic molecules[7-10] and the reduction of CO$_2$.[11] Given

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