A New Concentrated Emulsion Polymerization Pathway

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SYNOPSIS

To ensure the stability of the concentrated emulsions that are employed as precursors for polymerization, a two-step concentrated emulsion polymerization pathway is described. In the first step, the monomer is partially polymerized by heating at 50°C until a certain conversion is reached. Subsequently, the partially polymerized monomer is used as the dispersed phase to prepare a concentrated emulsion in which water constitutes the continuous phase. The concentrated emulsion has a large volume fraction of the dispersed phase (0.74–0.99) and the appearance of a gel. Several typical monomers are employed to correlate the stability of the concentrated emulsion and the extent of partial polymerization of the dispersed phase. It was found that monomers, which cannot lead to stable concentrated emulsions, can generate them after partial polymerization. Subsequent polymerization of the concentrated emulsion leads to latex particles. Copolymers and polymer composites were also prepared by the two-step procedure. In the latter case, water was replaced with a solution of a hydrophilic monomer in water as the continuous phase. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

The concentrated emulsion polymerization has been suggested recently[1] as a new method to prepare polymers, copolymers, and polymer composites. A concentrated emulsion has a large volume fraction of the dispersed phase, larger than 0.74 (which is the volume fraction of the most compact arrangement of monosized spheres) and as large as 0.99.[2,3] One of its advantages consists in its gellike appearance, which ensures easier handling. When the volume fraction of the continuous phase is sufficiently small, the dispersed phase is composed of polyhedral cells separated by thin films of the continuous phase.[4,5] The shape and size of the cells in the concentrated emulsions remain relatively unchanged during subsequent polymerization.[6] The polymerization of the monomer that constitutes the dispersed phase of a gellike emulsion is found to be more rapid and to lead to higher molecular weights than does polymerization in bulk.[1,6] In a concentrated emulsion that can serve as a precursor for

obtaining latexes, a hydrophobic (hydrophilic) monomer constitutes the dispersed phase, and water (decane), the continuous phase. Hydrophilic–hydrophobic polymer composites have been also prepared by employing concentrated emulsions of a solution of a hydrophobic (hydrophilic) monomer in another solution of a hydrophilic (hydrophobic) monomer as precursors.[7] Membranes prepared from composite gels were employed to separate water from ethanol[8] and cyclohexane from toluene.[9]

The main prerequisite for the use of concentrated emulsions as precursors for polymers, copolymers, and polymer composites is the stability of the gel at the polymerization temperature.[10,11] By stability, one understands the resistance of the system to the separation into the two phases. Large efforts have been made in this direction[11] by investigating the effects of (1) the chemical natures of the dispersed and continuous phases; (2) the nature and amount of surfactant; (3) the volume fraction of the dispersed phase; (4) the viscosity of the continuous phase; (5) the ionic strength; and (6) the temperature on the formation and stability of the concentrated emulsions. So far, only a few monomers such as styrene, divinylbenzene, and acrylamide could be employed to prepare gels that were stable at the preparation

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Table I Amounts Used in the Preparation of the Concentrated Emulsion

Dispersed phase: hydrophobic monomer (MMA, EMA, BMA, EHA, ST)	13.5 mL
Continuous phase: water	1.5 mL
Surfactant: SDS	0.152 g
Initiator[a]: AIBN	0.033 g
Inhibitor[b]: MEHQ	0.010 g

[a] AIBN was used in the partial polymerization of the monomer.
[b] MEHQ was used to terminate the polymerization in the partial polymerization.

temperature (20°C) and remained stable at the polymerization temperature (50°C). This drawback limits the applications of the concentrated emulsion polymerization.

In this paper, a two-step method is suggested to prepare concentrated emulsions that are stable at the polymerization temperature. In the first step, the monomer is partially polymerized in bulk by heating at 50°C until a certain conversion is reached. Further, the partially polymerized monomer is used as the dispersed phase to generate a gel. Several typical monomers were employed to study the correlation between the stability of the concentrated emulsion thus obtained and the viscosity of the partially polymerized monomer. Polymers, copolymers, and polymer composites were obtained by using the two-step concentrated emulsion polymerization. The effect of partial polymerization on the microstructure of the samples was investigated using scanning electron microscopy. It was found that monomers that could not lead to stable concentrated emulsion could generate such gels after partial polymerization.

EXPERIMENTAL

Materials

Styrene (ST, Aldrich), methyl methacrylate (MMA, Aldrich), ethyl methacrylate (EMA, Aldrich), buthyl methacrylate (BMA, Aldrich), and (±)2-

ethyl hexyl acrylate (EHA, Aldrich) were purified by distillation. Acrylamide (AAM, Polysciences), azobisisobutyronitrile (AIBN, Kodak), and potassium persulfate ($K_2S_2O_8$, Aldrich) were purified by recrystallization in methanol and water, respectively. Sodium dodecyl sulphate (SDS, Aldrich) and methylhydroquinone (MEHQ, Aldrich) were used as received. Water was deionized and distilled.

Preparation by the One-Step Concentrated Emulsion

A small amount of an aqueous solution of SDS was placed in a flask (100 mL capacity), equipped with a mechanical stirrer. The hydrophobic monomer (oil phase) was injected into the stirred system with a syringe. The preparation was carried out at room temperature.

Preparation by the Two-Step Concentrated Emulsion

In the first step, the hydrophobic monomer was partially polymerized in bulk, using AIBN as initiator, by heating at 50°C until a certain conversion was reached. Then, the inhibitor MEHQ was introduced to terminate polymerization. In the second step, the partially polymerized monomer was injected into the stirred aqueous solution of SDS that was placed in a flask (100 mL). The preparation of the concentrated emulsion was carried out at room temperature.

Preparation of Polymers by the Two-Step Concentrated Emulsion Polymerization

The starting procedure was the same as that used for the preparation of the two-step concentrated emulsion but without introducing MEHQ at the end of the partial polymerization step. Subsequently, the concentrated emulsion was again subjected to polymerization by heating at 50°C for 50 h. The procedure was applied to the preparation of polymers and polymer composites.

Table II Stability of the Concentrated Emulsion Prepared in a One-Step Method and the Interfacial Tension between Monomer and Water in the Absence of Surfactant

Monomer	MMA	EMA	BMA	EHA	ST
φ (%)	100[a]	80	40	14	8
γ (dyn/cm)	16.38	17.69	23.90	24.74	37.41

[a] The concentrated emulsion of MMA in water fully separated in 3 h by heating at 50°C.

The Stability of the Concentrated Emulsions

The concentrated emulsions prepared at room temperature and free of initiators were transferred into centrifuge tubes of 15 mL capacity with the help of a spatula. A mild centrifugation was employed to pack the concentrated emulsion gels. The measurement of the stability was conducted by placing the centrifuged gels in a 50°C temperature-controlled water bath for 24 h. The stability was characterized in terms of the weight fraction of bulk phases that separated from the concentrated emulsion.

Measurement of the Interfacial Tension

The interfacial tension of the samples was measured by the "drop weight" method[12] using a Rame Hart Model 100-00 115 NRL C. A. Goniometer.

Scanning Electron Microscopy

The polymer samples were washed in methanol before investigation. The fractured pieces were mounted on SEM stubs using colloidal graphite cement. The samples were sputter-coated with a thin layer of gold in a Hexaland CT 100 Cryotrans system attached to the SEM. Then, the samples were examined with a Hitachi S-450 microscope.

RESULTS AND DISCUSSION

A concentrated emulsion can be used as precursor for polymerization if, prepared at room temperature, it remains stable at the polymerization temperature of 50°C. The weight percent φ of bulk phases separated from the concentrated emulsions after 24 h of heating at 50°C is taken as a measure of its stability. The amounts of the components involved in the concentrated emulsions are listed in Table I.

The weight percent φ of bulk phases separated from the concentrated emulsions prepared in one step at room temperature, in the absence of initiator, and subsequently heated for 24 h at 50°C is presented in Table II. This table also contains the interfacial tension γ, measured at room temperature, between the hydrophobic monomer and water, in the absence of surfactant. (The stability of the concentration emulsion is almost unaffected by the presence of AIBN and MEHQ.)
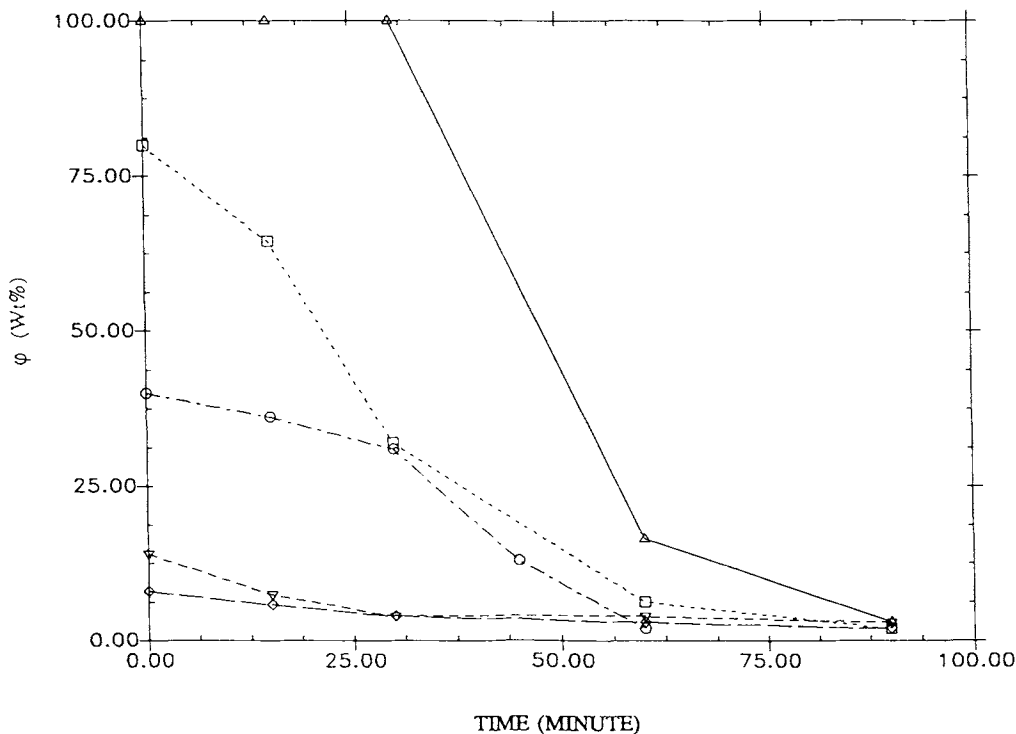

Figure 1 Weight percent φ of bulk phases separated from concentrated emulsion after heating for 24 h at 50°C against partial polymerization time of monomer: ($\Diamond$) ST; ($\triangle$) MMA; ($\square$) EMA; ($\bigcirc$) BMA; ($\triangledown$) EHA.

Table II shows that in the one-step preparation the stability is the highest for styrene and the lowest for MMA and that the stability increases with increasing interfacial tension between water and monomer in the absence of surfactant.

The values of φ for the concentrated emulsions prepared by the two-step procedure, the viscosity of the partially polymerized monomer, and the partial conversion of the monomer against polymerization time are presented in Figures 1–3, respectively.

Figures 1–3 show that the concentrated emulsions prepared by a two-step procedure are much more stable—the longer the polymerization time, the more stable the concentrated emulsion. The stability of the concentrated emulsion depends on the viscosity of the dispersed phase. When a certain viscosity is reached, even MMA can generate stable concentrated emulsions. Of course, the conversion and, hence, the viscosity should not be too large, since large values of the viscosity will impede the dispersion of one phase in the other.

Without introducing the inhibitor MEHQ at the end of partial polymerization, the concentrated emulsion can be further polymerized by heating the concentrated emulsion prepared at room temperature, at 50°C for 50 h. Several typical polymers, copolymers, and polymer composites were prepared by using the two-step concentrated emulsion polymerization. The amounts of components employed to prepare copolymers and polymer composites are listed in Table III, whereas the amounts of components employed to prepare polymers are the same as those in Table I but without MEHQ.

For comparison purposes, the preparation of the corresponding materials was also attempted using the one-step concentrated emulsion pathway. Large phase separation occurred, however, in all the systems, except those employed to prepare polystyrene (PS) and the PS/PAAM composite. Furthermore, PMMA, PEMA, and PBMA/PAAM composite could not be prepared by the one-step concentrated emulsion polymerization.
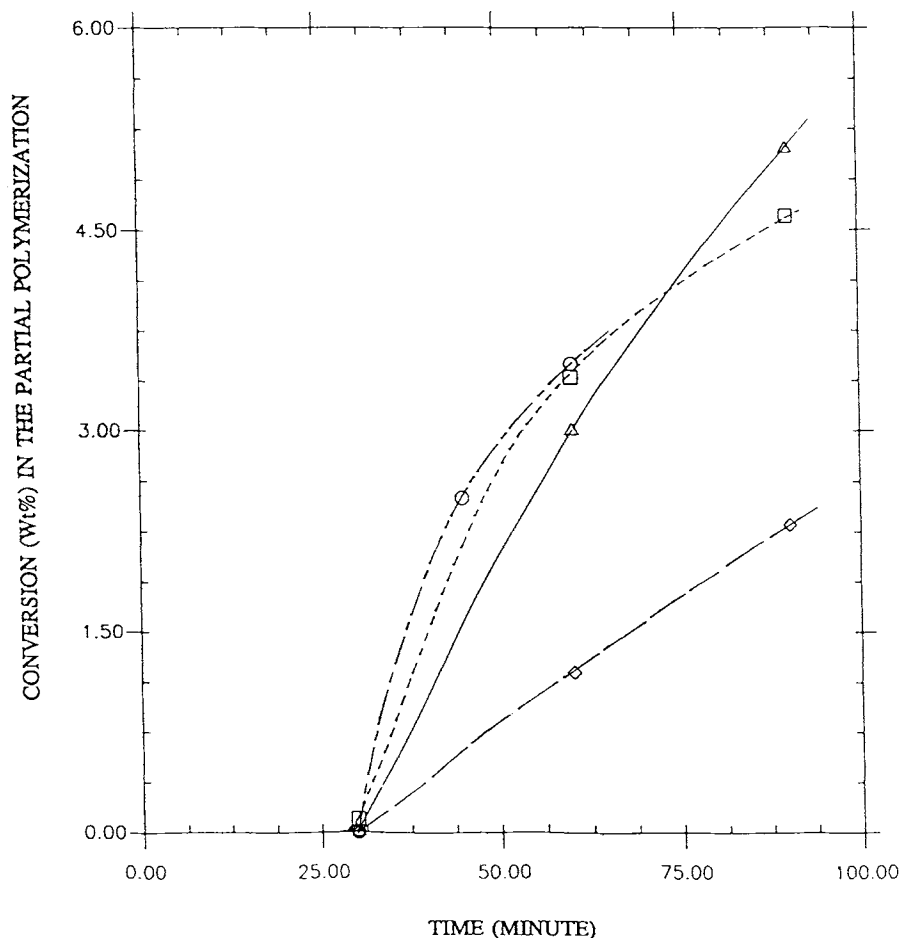

Figure 2   Polymer conversion (wt %) against partial polymerization time of monomer: (◇) ST; (△) MMA; (□) EMA; (○) BMA.
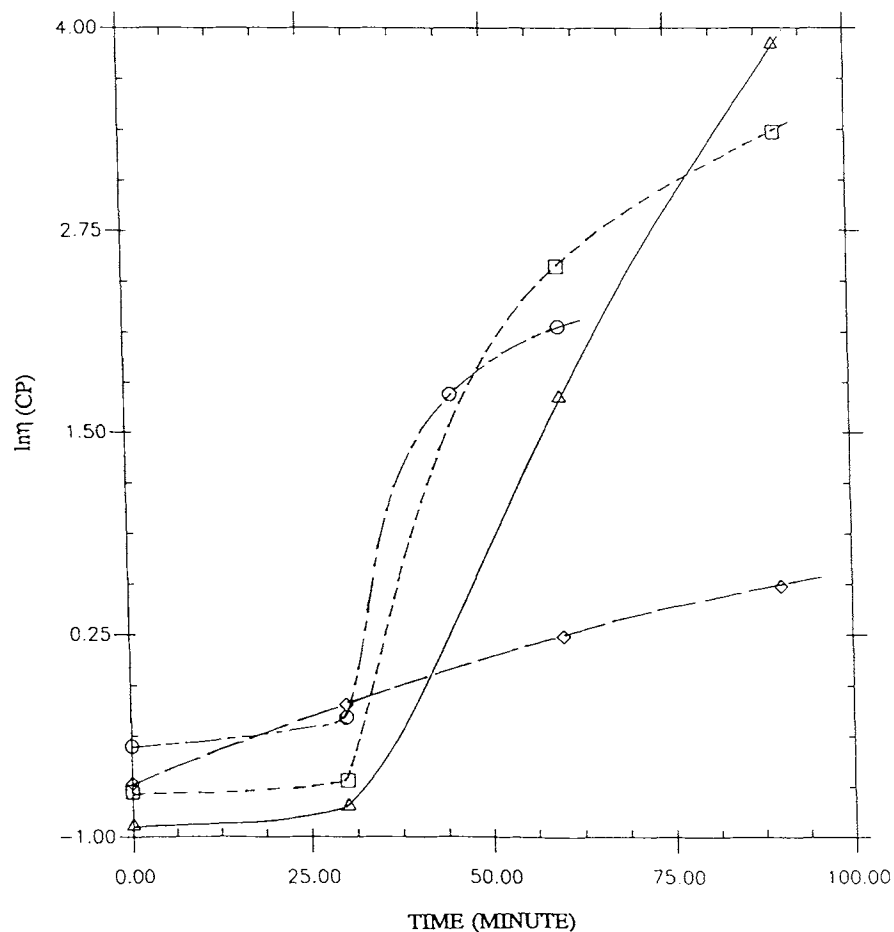
Figure 3 Logarithm of the viscosity of the partially polymerized monomer against partial polymerization time: ($\Diamond$) ST; ($\triangle$) MMA; ($\square$) EMA; ($\bigcirc$) BMA.
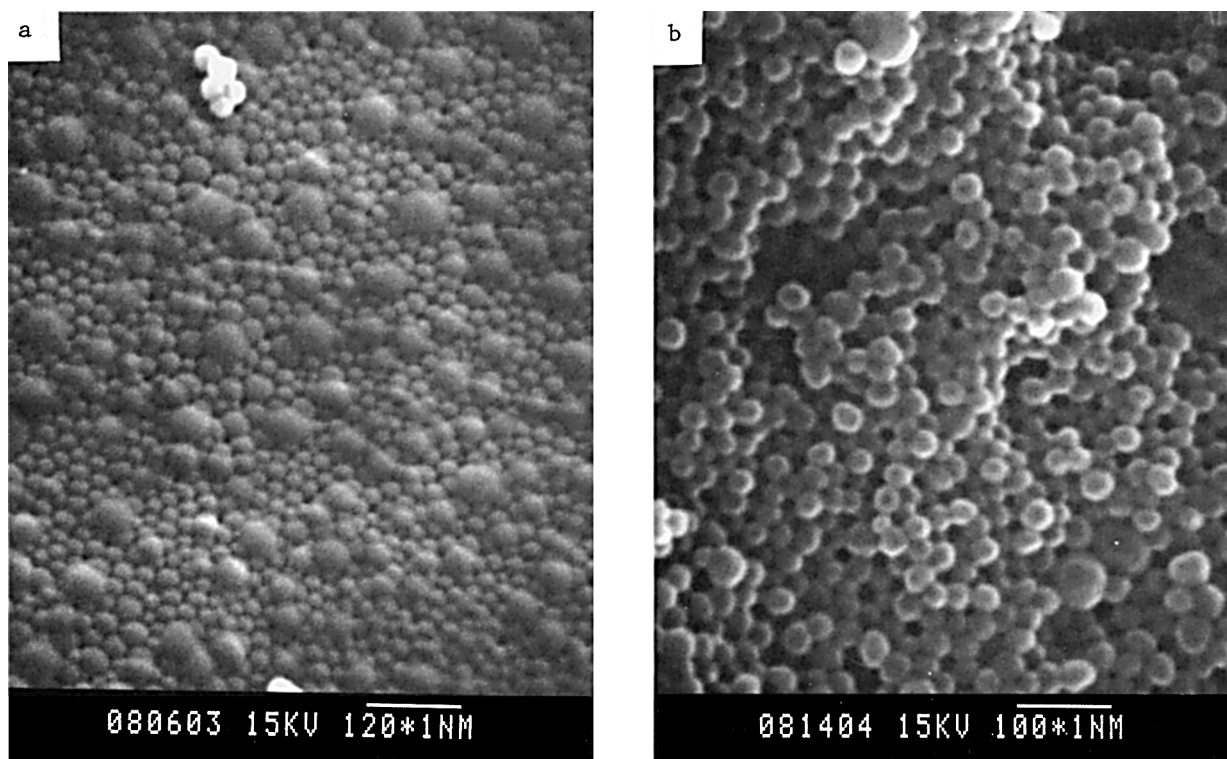

Figure 4 Scanning electron micrographs of PS, prepared by (a) one-step and (b) the two-step concentrated emulsion polymerization; styrene was prepolymerized for 1.5 h in bulk.
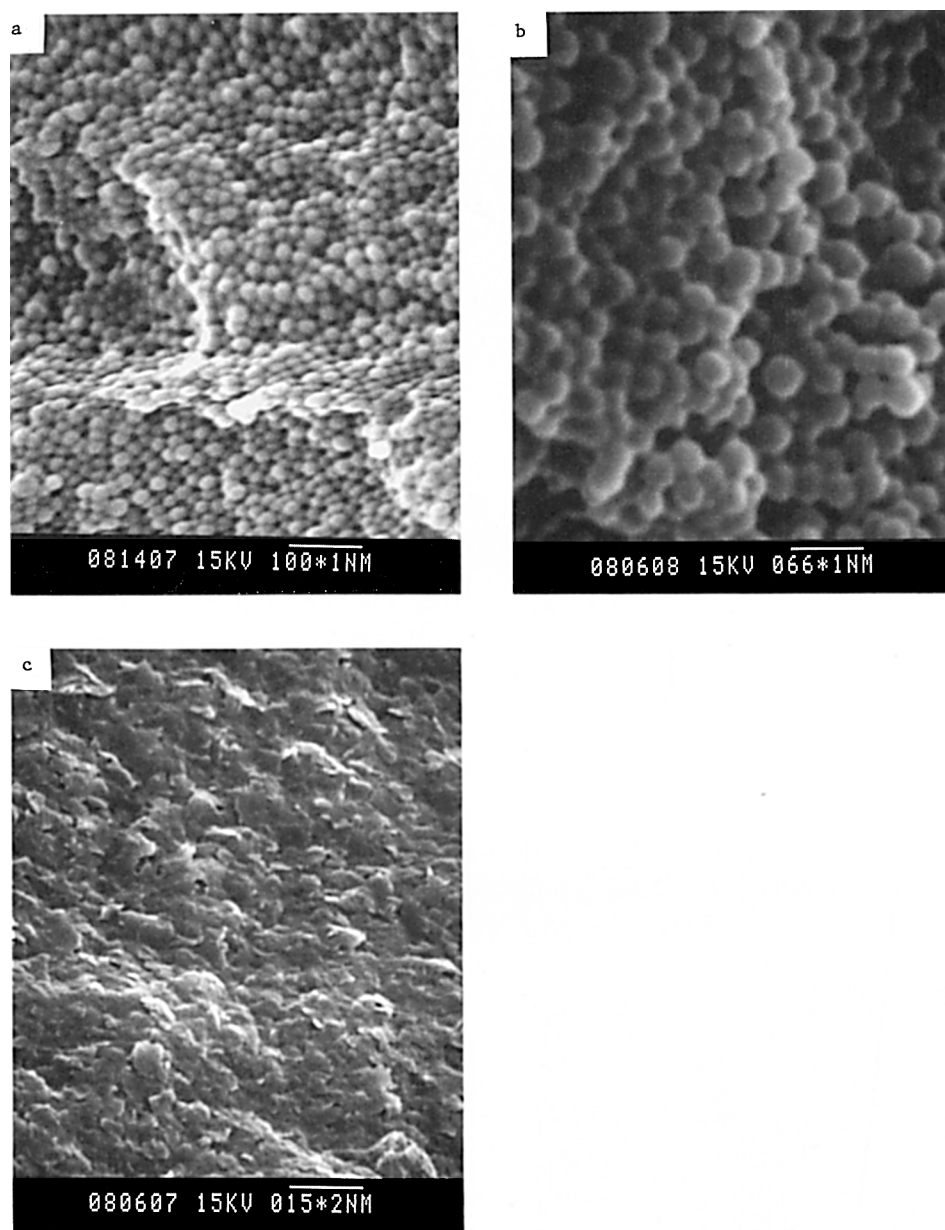
Figure 5 Scanning electron micrographs of some copolymers and a polymer composite: (a) PMMA/PS copolymer; (b) PMMB/PS copolymer; (c) PS/PAAM composite.

Figures 2 and 3 show that the conversion of the monomer and its viscosity do not change in a detectable way during the first 30 min, whereas Figure 1 indicates that the stability increases in a continuous fashion in this interval. This can be explained by noting that even though small amounts of polymer are produced in the first 30 min their adsorption upon the interface between the dispersed and continuous phases of the concentrated emulsion contributes, because of steric stabilization, to the increased stability of the system.

Figure 4 presents scanning electron micrographs

of the surfaces of PS prepared by the concentrated emulsion polymerization. As expected, spherical latexes with diameters in the submicron range are obtained for PS. Comparing Figure 4(a) and (b), it is found that the shape and size of the latexes are almost the same for PS prepared by the one- and two-step concentrated emulsion polymerizations. Spherical latexes with diameters in the submicron range have been obtained for PMMA, PEMA, and PBMA prepared by the two-step concentrated emulsion polymerization as well.

Figure 5 presents scanning electron micrographs

Table III Amounts of Components Used in the Preparation of Copolymers and Polymer Composites

Hydrophobic-Hydrophobic Copolymer[a]

Dispersed phase: ST	6.75 mL
other monomer (MMA, EMA, BMA)	6.75 mL
Continuous phase: water	1.5 mL
Initiator in the dispersed phase: AIBN	1.5×10^{-2} mol/L monomer
Surfactant: SDS	0.152 g

Hydrophobic–Hydrophilic Polymer Composite[b]

Dispersed phase: hydrophobic monomer (ST or BMA)	13.5 mL
Initiator in the dispersed phase: AIBN	1.5×10^{-2} mol/L monomer
Continuous phase: water and AAM	1.5 mL 0.24 mol/L water
Initiator in the continuous phase: $K_2S_2O_8$	4.02×10^{-4} g/mL water
Surfactant: SDS	0.152 g

[a] The copolymers were prepared by the two-step polymerization; MMA, EMA, and BMA were partially polymerized for 1.5 h.

[b] The polymer composites were prepared by the two-step polymerization. ST and BMA were partially polymerized for 1.0 h.

of some copolymers and a polymer composite prepared by the two-step concentrated emulsion polymerizations method. The stability of the concentrated emulsion is of kinetic origin. Two factors contribute to the stability of the gels prepared by the two-step concentrated emulsion. The repulsive forces between the charged surfactant molecules adsorbed on the surface of neighboring cells of the dispersed phase is one of the factors. The viscosity of the monomer, which constitutes the dispersed phase, constitutes the second factor. The increased viscosity of the dispersed phase prevents the motion of the molecules that induces the separation of the phases. The partial polymerization increases the

viscosity of the dispersed phase, thus increasing the stability of the concentrated emulsion.

CONCLUSION

The stability of the concentrated emulsion is of kinetic origin and is affected by the viscosity of the dispersed phase. Monomers that could not generate stable gels, or even could not form gels in the one-step concentrated emulsion method, are able to generate stable gels because of the increased viscosity when the two-step concentrated emulsion pathway is employed. Almost all monomers can be employed to prepare polymer materials by this pathway. The two-step concentrated emulsion polymerization pathway can, therefore, widen the application of this method.

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