# Fumed Silica as Stabilizer of Precursor Emulsions Used to Prepare Polymer Latexes

L. HONG and E. RUCKENSTEIN*

Department of Chemical Engineering, State University of New York at Buffalo, Buffalo, New York 14260

## SYNOPSIS

Introducing small amounts of fumed silica into mixtures of organic liquids, which contain ethylene glycol dimethylacrylate (EGDMA), a hydrocarbon (such as decane), and one of the following monomers: allylchloride (AC), 3,4-dichloro-1-butene (DCB), or methyl methacrylate (MMA), enabled their dispersion into an aqueous solution of surfactant with the generation of stable emulsions. Such emulsions cannot be generated in the absence of fumed silica. Functionalized polymer latexes of poly(AC–EGDMA), poly(DCB–EGDMA), and poly(MMA–EGDMA) could, thus, be prepared through the polymerization of the emulsions. The chloride units in the poly(AC–EGDMA) or in the poly(DCB–EGDMA) were subsequently converted to quaternary ammonium salts. The resulted polymer-supported quaternary ammonium salt together with $RuCl_3$, 4-$N$-methylmorpholine $N$-oxide (NMO) and ammonium persulfate were employed in the catalytic oxidation of toluene to benzoic acid. Furthermore, the presence of fumed silica in the emulsions enabled the preparation of latexes containing rather uniformly distributed inorganic particle clusters of submicrometer size. Polymer–inorganic blends of NaY zeolite-$(SiO_x)_n$/P(MMA–EGDMA), zeolite (4A)-$(SiO_x)_n$/P(MMA–EGDMA), $TiO_2$-$(SiO_x)_n$/P(MMA–EGDMA), CuO-$(SiO_x)_n$/P(MMA–EGDMA), and Cu-$(SiO_x)_n$/P(MMA–EGDMA) were thus obtained. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

In previous papers,[1] concentrated emulsions of hydrophobic monomers in water or hydrophilic monomers in a hydrocarbon have been employed as precursors for the preparation of polymer latexes. One can, however, obtain stable emulsions at room temperature that remain stable at the polymerization temperature only if the monomers are hydrophobic or hydrophilic enough with respect to water or decane, respectively.[2] In this paper, we suggest a simple and effective method to enhance the stability of the (o/w) concentrated emulsions by introducing small amounts of fumed silica into the dispersed phase. The monomers allylchloride (AC), 3,4-dichloro-1-butene (DCB), or methyl mathacrylate (MMA) together with ethylene glycol dimethacrylate (EGDMA) as the cross-linking agent cannot by

themselves generate (o/w) concentrated emulsions. However, the addition of fumed silica allows the preparation of such emulsions. The hydrophobicity of the submicron fumed silica particles is a result of the absence of hydroxyl groups on their surface.[3] Some of these particles accumulate in the interfacial region, thus retarding the coalescence among the dispersed droplets. After polymerization, most of the added fumed silica was found out of the polymer particles.

The prepared poly(AC-EGDMA) and poly(DC-EGDMA) particles are suitable as substrates for binding high-valence transition-metal anions, such as perruthenate $RuO_4^-$, which can be used for catalytic purposes.[4] First, some of the chloride units of the polymer particles are converted to quaternary ammonium salts that possess binding abilities for catalytic anions like $RuO_4^-$. Using such particles, the oxidation of toluene to benzoic acid was carried out under the solid (quaternary ammonium-supported polymer, persulfate salt, and an inorganic base)–liquid (4-$N$-methylmorpholine $N$-

oxide [NMO], RuCl$_3$, and toluene dissolved in dichloroethane) phase-transfer conditions. RuCl$_3$ is oxidized by the persulfate salt, and the resulted RuO$_4^-$ is captured by the quaternized polymer substrate, forming ion-pairs.[5] Fumed silica also stabilizes concentrated emulsions containing inorganic particles. This allows blending of inorganic materials with polymers in particles of colloidal size. Five inorganic powders (NaY zeolite, 4A zeolite, TiO$_2$, CuO, and Cu) were mixed with PMMA by using this emulsion pathway.

## EXPERIMENTAL

### Reagents, Solvents, and Materials Used

Methyl methacrylate (MMA) (Aldrich, 99%) and ethylene glycol dimethacrylate (EGDMA) (Aldrich, 98%) were purified by passing them through a packed column that removes the inhibitor. Allyl-chloride (AC) (Aldrich, 98%), 3,4-dichloro-1-butene (DCB) (Aldrich, 98%), toluene (Aldrich, 99+%), tributyl amine (Aldrich, 99%), dichloroethane (Aldrich, 99%), and other organic solvents purchased from Aldrich were used without further purification. Ruthenium(III) chloride (Aldrich), 4-$N$-methylmorpholine $N$-oxide (NMO) (Aldrich, 97%), ammonium persulfate (Aldrich, 98%), potassium carbonate (Aldrich, 99%), tetrabutyl ammonium bromide (Aldrich, 99%), fumed silica (Cabot Corp., grade HS-5), titanium oxide (purchased from Tam Ceramic and baked at 500°C for 10 h), NaY zeolite sieves (W. R. Grace & Co.), copper oxide (Aldrich 99.9+%), copper powder (Aldrich, submicron, 99+%), and poly(methyl methacrylate) (PMMA) (Scientific Polymer Products, MW = 33,000) were used as received.

### Instruments Employed

Energy-dispersive spectroscopy (EDS) analysis was performed on a PGT/IMIX field emission electron microscopy equipment. Scanning electron micrographs (SEM) were obtained on a Hitachi S-800 equipment.

### General Procedure for Preparation of Poly(AC-EGDMA), Poly(DCB-EGDMA), and Poly(MMA-EGDMA)

To a 150 mL round-bottom flask containing a mixture of DCB (14 mL), EGDMA (2 mL), decane (8 mL) and AIBN (0.15 g), fumed silica (0.4 g) was added with vigorous mechanical stirring (about 700

rpm) carried out with a Teflon blade. Subsequently, an aqueous solution of sodium dodecyl sulfate (0.5 g) in 4 mL H$_2$O was added dropwise to the stirred system. Generally, 5–10 min were needed to obtain a uniform concentrated emulsion. The resulted gel-like emulsions were packed in tubes under gently tapping to remove gas bubbles and subjected to polymerization at 40°C for 3 days. After washing the polymerized system with methanol, 2.8 g of fine poly(DCB–EGDMA) powders were obtained. Further purification of the powders with CH$_3$OH overnight in a Soxhlet funnel was used to remove the excess of surfactant and the nonpolymerized monomers. Poly(AC–EGDMA) and poly(MMA–EGDMA) were prepared in the same manner.

### Attaching Quaternary Ammonium Groups to the Poly(AC–EGDMA) and Poly(DCB–EGDMA) Substrates

Poly(DCB–EGDMA) (2.0 g, containing 5.4 mmol of chlorine) or poly(AC–EGDMA) (2.0 g, containing 4.14 mmol of chlorine) were reacted with a solution of tributylamine (2.5 g, 10 mmol) in DMF (15 mL) at 80°C for 96 h. A fraction of the pendant chloride groups (16–18 mol %) were thus converted to quaternary ammonium groups. The quaternized polymer powder was washed several times with a mixture of THF and petroleum ether.

### Oxidation of Toluene to Benzoic Acid Catalyzed by Quaternary Ammonium Perruthenate under Solid–Liquid Phase-transfer Catalytic Conditions

Ammonium persulfate and potassium carbonate were first ground to fine powders. A 50 mL round-bottom flask was charged with (NH$_4$)$_2$S$_2$O$_8$ (2.28 g, 10 mmol), K$_2$CO$_3$ (0.214 g, 1.5 mmol), NMO (0.1 g, 0.85 mmol), RuCl$_3$ (0.024 g, 0.115 mmol), and quaternized poly(DCB–EGDMA) (1.0 g, containing 0.46 mmol of ammonium salt). Dichloroethane (10 mL) and 0.5 mL of water were subsequently added. The mixture was stirred at room temperature until a deep green color appeared (after about 1 h), then toluene (0.92 g, 10 mmol) was added. The reaction was carried out by stirring this heterogeneous system at 60°C in an oil bath. Aliquots (0.1 mL each) of the organic phase were taken out every 2 h, followed by their centrifugation to precipitate the suspended particles. The analyses have been carried out with an HPLC [ISCO-2350 pump/ISCO-V$_4$ (UV-248 nm) detector] using the acetonitrile–water mixture (v/v = 7/3) as eluant. The column (4.6 mm × 25 cm) contained Adsorbosphere C$_8$ of 5 $\mu$.

**Table I    The Compositions of Gel-like Precursor Emulsions and the Resulting Functional Polymer Substrates[a]**

| Polymers | Dispersed Phsae | Elementary Analysis of Chlorine (mmol/g Polymer) | Mol % of Polymerized Chloride Monomer |
|---|---|---|---|
| Poly(AC–EGDMA) | AC (13 mL) + EGDMA (2 mL) + decane (6 mL) + fumed silica (0.4 g) (11.3 mmol Cl/g of monomers) + AIBN (0.15 g) | 2.07 | 18 |
| Poly(DCB–EGDMA) | DCB (13 mL) + EGDMA (2 mL) + decane (6 mL) + fumed silica (0.4 g) (13.8 mmol Cl/g of monomers) + AIBN (0.15 g) | 2.69 | 19 |
| Poly(MMA–EGDMA) | MMA (16 mL) + EGDMA (2 mL) + fumed silica (0.2 g)[b] + AIBN (30 mg) | | |

[a] The continuous phase is $H_2O$ (4 mL) + SDS (0.5 g) in all three cases.

[b] The lowest amount of fumed silica needed to stabilize the emulsion at the polymerization temperature.

## Preparation of Inorganic/Polymeric Blends

The preparation of $Cu-(SiO_x)_n/P(MMA-EGDMA)$ is given as an example: In a 150 mL round-bottom flask, a solution containing 1.0 g of PMMA ($M_w$ = 33,000) and 30 mg of AIBN in MMA (16 mL)–EGDMA (2 mL) was prepared. To this solution, 0.4 g of fumed silica and 0.6 g of submicron copper powder were introduced. Then, an aqueous solution of SDS (0.5 g) in 4 mL of water was added dropwise with mechanical stirring (about 700 rpm). A brown uniform solidlike concentrated emulsion was formed 5–10 min after the addition (both the PMMA and the fumed silica are necessary to generate the emulsion). The emulsion was packed tightly into glass tubes and polymerized at 40–45°C for 2 days. The obtained blend powders, $Cu-(SiO_x)_n/P(MMA-EGDMA)$, were washed by stirring several times in methanol. No Cu powder precipitated.

## RESULTS AND DISCUSSION

The fumed silica particles are of submicron size and have a large surface area. They can be extremely hydrophobic when the siloxanes are little hydroxylated and become less hydrophobic when they become hydroxylated.[6] Because of these unique characteristics, fumed silica can be employed as a dispersant. We found that concentrated emulsions of AC, DCB, or MMA monomer (containing EGDMA as a cross-linking agent) in water could be generated only by employing both fumed silica and a surfactant (SDS) as combined emulsifying agents. In the absence of fumed silica, the concentrated emulsions of these monomers are not stable even at room temperature. First, a small amount of fumed silica was
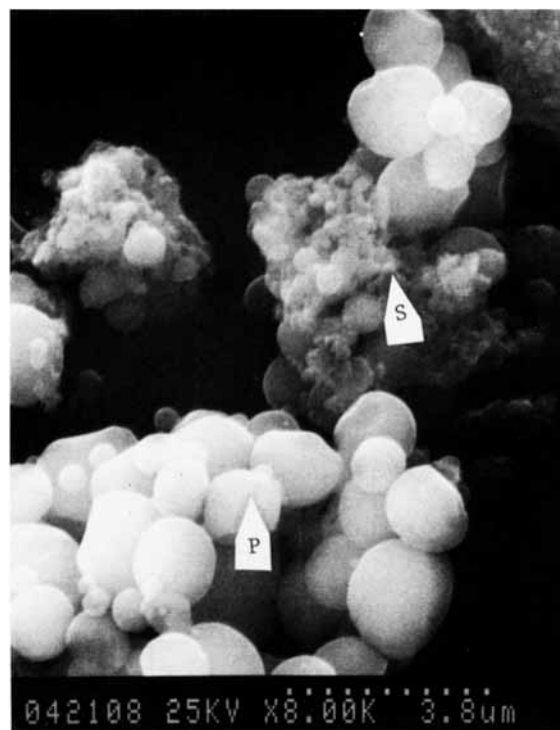


**Figure 1**    Scanning electron micrograph of poly(AC–EGDMA).

dispersed into the monomer-containing organic medium. Then, an aqueous solution of SDS was added dropwise into the organic medium under a very high shear rate (about 700–800 rpm). A gel-like emulsion was obtained (the various compositions are listed in Table I). To understand the stabilizing role of fumed silica, SEM micrographs of poly(AC–EGDMA) and the EDS analysis are presented in Figures 1 and 2, respectively. The micro-area elemental analysis by EDS reveals that the gray small particles (which are mixed with small white polymer particles) marked S in Figure 1 represent fumed silica. The polymer particles marked as P in Figure 1 have a larger diameter and contain only a small

amount of silica. Consequently, Figure 1 shows that most of the fumed silica appears as small particles mixed mainly with a few small polymer particles. The amount of fumed silica is relatively large in the concentrated emulsions corresponding to Figure 1. Perhaps for this reason, a fraction of silica particles migrates to the water phase where they aggregate. This may contribute to an increased viscosity of the continuous phase and thus to the increased stability of the concentrated emulsion. Other scenarios are, however, also possible. Fumed silica particles may be adsorbed upon the interface, where in contact with water they become hydroxylated. The dissociation of these groups generates a charge, which,
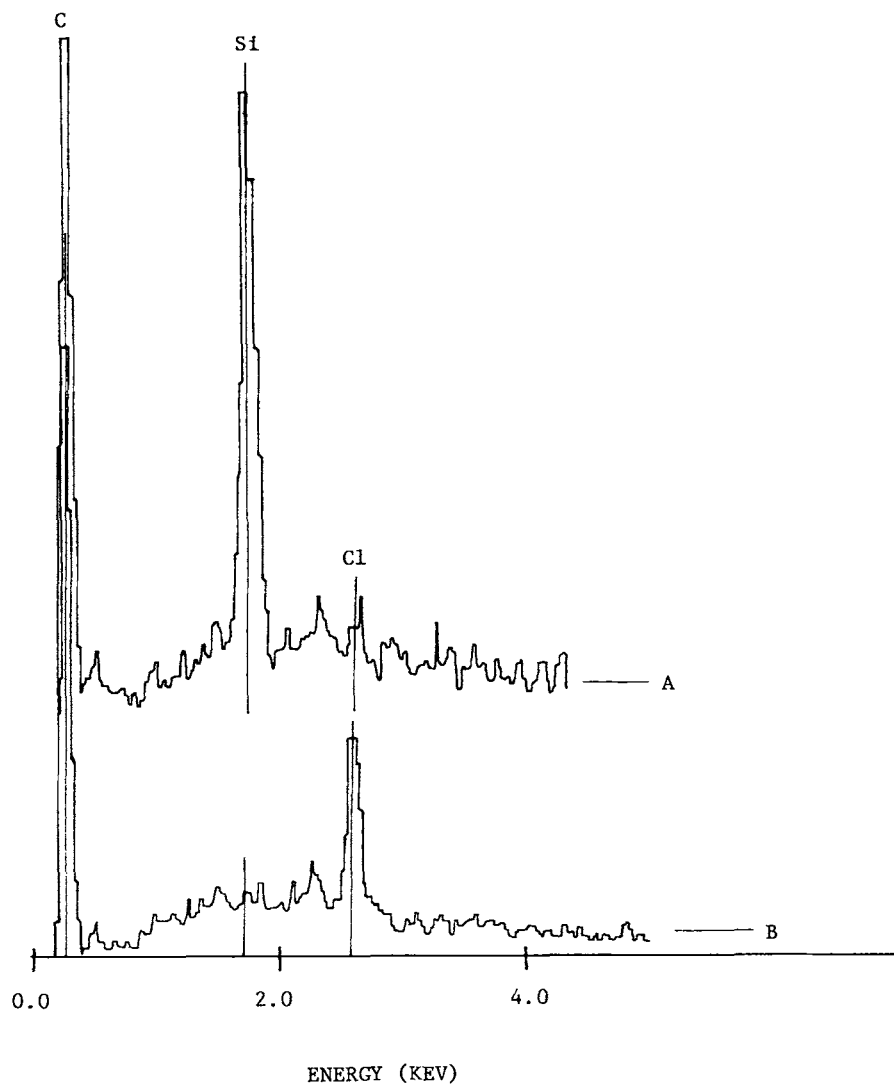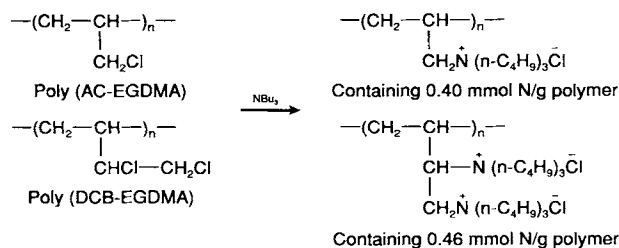


**Figure 2** EDS spot elemental analysis of the regions marked in the SEM micrograph of Figure 1: curve A gives the surface composition of area S (dominated by silica); curve B provides the surface composition of area P (dominated by the polymer).

$$-(CH_2-CH-)_n-$$
$$\quad | $$
$$\quad CH_2Cl$$

Poly (AC-EGDMA)

$$-(CH_2-CH-)_n-$$
$$\quad | $$
$$\quad CHCl-CH_2Cl$$

Poly (DCB-EGDMA)

$\xrightarrow{NBu_3}$

$$-(CH_2-CH-)_n-$$
$$\quad | $$
$$\quad CH_2\overset{+}{N} \ (n\text{-}C_4H_9)_3\bar{Cl}$$

Containing 0.40 mmol N/g polymer

$$-(CH_2-CH-)_n-$$
$$\quad | $$
$$\quad CH-\overset{+}{N} \ (n\text{-}C_4H_9)_3\bar{Cl}$$
$$\quad | $$
$$\quad CH_2\overset{+}{N} \ (n\text{-}C_4H_9)_3\bar{Cl}$$

Containing 0.46 mmol N/g polymer

**Scheme 1.**

$$RuO_4 \underset{S_2O_7^-/NMO}{\overset{S_2O_7^-/NMO}{\rightleftharpoons}} RuO_4^- \xleftarrow{S_2O_7^-/NMO} Ru \ (III)$$

(with $CH_3$ (toluene) and $COOH$ (benzoic acid) structures shown)

**Scheme 2.**

by electrostatic repulsion, contributes to the stability of the concentrated emulsion. The excess of silica present in the hydrophobic phase was probably pushed out from the polymer during the polymerization process. Another possibility is that the surfactant is more easily adsorbed on the silica particles present at the interface than on the liquid–liquid interface. Of course, these mechanisms can act simultaneously.

As application, poly(AC-EGDMA) and poly(DCB-EGDMA) particles have been employed as supports for catalytic oxidation under phase-transfer conditions. Since the styrenic-type substrates are chemically unstable to the oxidation reaction, AC or DCB was selected, instead of benzyl chloride, as the functional monomer for attaching organic cations to polymer matrixes (Scheme 1). Since AC and DCB monomers are weakly active in the free-radical polymerization,[7] EGDMA was used as a cross-linking agent as well as inducer of copolymerization with AC or DCB monomeric units.
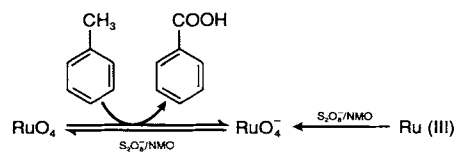
The catalytic oxidation of an aliphatic side chain of an aromatic compound to a carbonyl group constitutes an important fine organic process. To achieve this, a quaternary ammonium perruthenate ($R_4N^+ \ RuO_4^-$) was used recently as a mild homogeneous oxidation catalyst.[4] In the present work, the oxidative solid–liquid phase-transfer catalytic (PTC) system $(P) - Q^+ \ Cl^-)/(NH_4)_2S_2O_8 - NMO - K_2CO_3 / RuCl_3 / CH_2ClCH_2Cl - H_2O$ was employed for the oxidation of toluene to benzoic acid. Quaternary ammonium groups bound to a polymer substrate [denoted as $(P) - Q^+Cl^-$] were used as cationic anchors for binding perruthenate anions. The latter were generated in situ through the oxidation of $RuCl_3$ by the primary oxidant $S_2O_8^{2-}/NMO$ in the aqueous phase (Scheme 2). Compared to the liquid–liquid PTC system,[8] which consists of $RuCl_3 / NaOCl$ (aq)/$Bu_4NBr/ CH_2ClCH_2Cl$, and in which the pH has to be maintained within $9.0 \pm 0.1$, accurate control of the pH is no longer necessary and, in addition, the recovering of the ruthenium catalyst is possible. The conversion rate of toluene to benzoic acid was used to assess the catalytic activity of different systems (Fig. 3). The system in which the $(P) - Q^+Cl^-$ com-
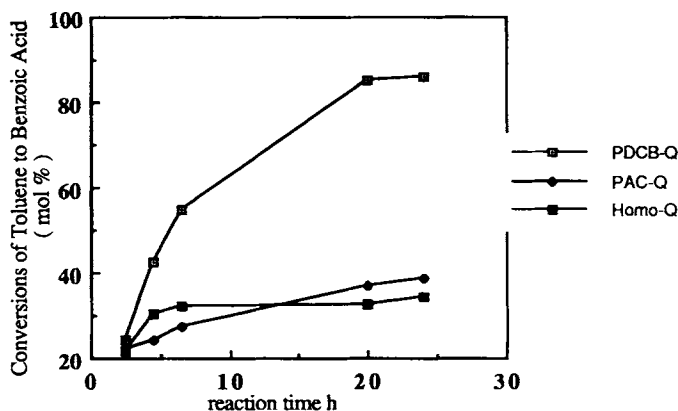


**Figure 3** Comparison of the oxidation activities of the three catalytic systems: PDCB–Q containing the quaternized poly(DCB–EGDMA), PAC–Q containing the quaternized poly(AC–EGDMA); and, Homo (homogeneous system) containing tetrabutylammonium bromide. The conditions are the same in the three cases and are indicated in the experimental section. Note that the amount of quaternary onium groups is the same in the three cases, namely, 0.46 mmol.
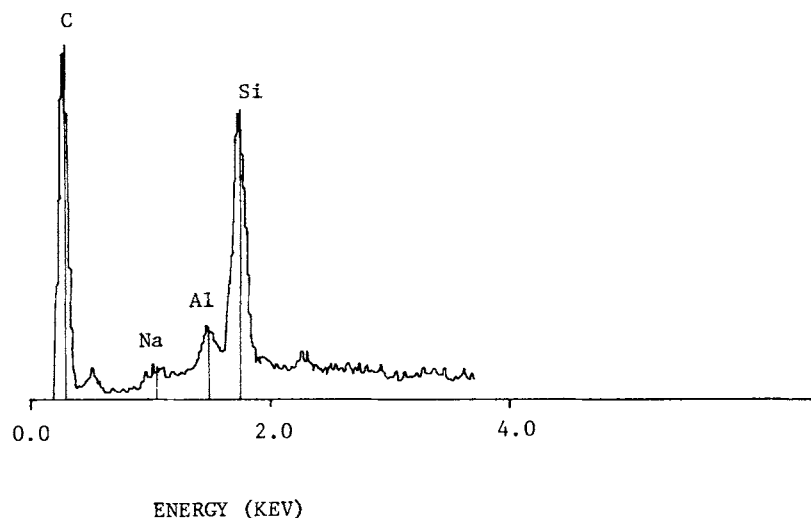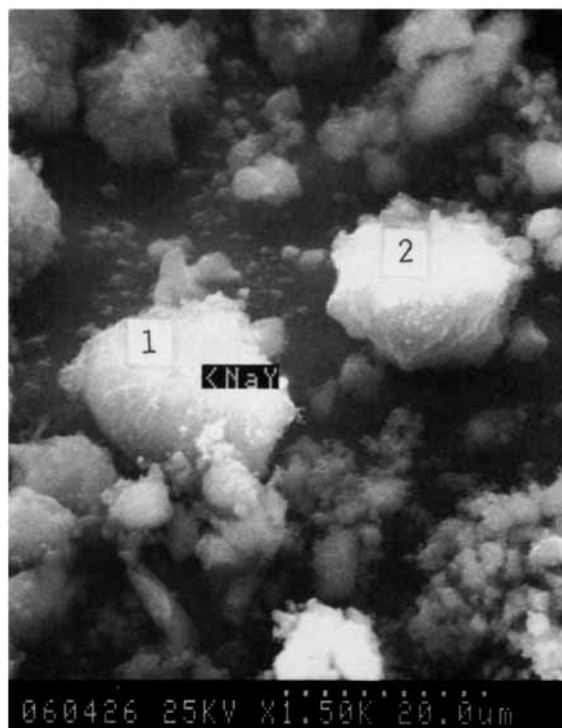
**Figure 4**   (a) Scanning electron micrograph of $NaY-(SiO_x)_n/P(MMA-EGDMA)$. (b) The average surface elemental analysis of particles 1 and 2 and of the spot marked in the micrograph.

ponent is prepared via the quaternization of poly(DCB-EGDMA) has the highest oxidation rate; the other two catalytic systems, in which the $(P) — Q^+Cl^-$ component is based either on the quaternization of poly(AC-EGDMA) or on the homogeneous low molecular weight catalyst $Bu_4N^+Br^-$, exhibit lower and comparable oxidation

rates. A possible reason for the different conversion rates of the two heterogeneous systems is that the quaternary ammonium groups are farther from the backbone of the polymer and therefore more accessible to the reactants for poly(DCB-EGDMA). The homogeneous system is less active than that based on the DCB-EGDMA network, probably because

**Table II    The Compositions of Precursor Gel-like Emulsions Used for the Preparation of Inorganic/Polymeric Blends[a]**

| Blends | MMA/ EGDMA (mL) | (In g) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | $(SiO_x)_n$ | PMMA | Cu | CuO | $TiO_2$ | NaY | Zelite 4A |
| Cu — $(SiO_x)_n$/poly(MMA–EGDMA) | 16/2 | 0.4 | 1.0 | 0.6 | | | | |
| CuO — $(SiO_x)_n$/poly(MMA–EGDMA) | 16/2 | 0.4 | 1.0 | | 0.6 | | | |
| $TiO_2$ — $(SiO_x)_n$/poly(MMA–EGDMA) | 16/2 | 0.4 | 1.0 | | | 0.6 | | |
| NaY zeolite–$(SiO_x)_n$/poly(MMA–EGDMA) | 16/2 | 0.4 | 1.0 | | | | 0.8 | |
| Zeolite 4A–$(SiO_x)_n$/poly(MMA–EGDMA) | 16/2 | 0.4 | 1.0 | | | | | 1.2 |

[a] The continuous phase is $H_2O$ (4 mL) + SDS (0.5 g) in all five cases; the dispersed phase contains AIBN (30 mg).

the probability of encounter among toluene, oxidant, and catalyst is relatively small. In the heterogeneous case, the oxidant and toluene are adsorbed upon the surface of the particles and this favors the encounter among the three species.

The gel-like emulsion structure obtained by employing fumed silica suggested to us the introducing of other inorganic colloidal particles into the dispersed phase. When a hydrophobic organic mono-



**Figure 5**    A secondary electron image of the cross section of a Cu—$(SiO_x)_n$/P(MMA–EGDMA) film (with a thickness of about 1 mm); the bright spots represent the copper particles.

mer liquid containing in suspension both an insoluble inorganic powder and fumed silica was dispersed into an aqueous phase, there was no precipitation of the inorganic powder from the gel-like emulsion thus generated. The particles of fumed silica are easily suspended in hydrophobic liquids because of the favorable interactions between the two. Since the colloidal silica particles have strong adhesion to inorganic materials,[6] the inorganic particles are also kept in suspension. Ozin[9] noted that optical data storage films of silver zeolites embedded in a poly(MMA) matrix can be prepared by mixing the former with a toluene–poly(MMA) mixture followed by the evaporation of the solvent. The present method allows for a more uniform suspension of inorganic particles of colloidal size in emulsion droplets and is expected to yield a more homogeneous material than that of the previous one. Table II lists the five blends of inorganic materials in poly(MMA) prepared by this method. Figure 4(a) is a scanning electron micrograph of the NaY zeolite–$(SiO_x)$/P(MMA–EGDMA) blend of Table II. The micro-area EDS analysis of this specimen shows that the average surface elemental analysis for the two particles 1 and 2 of Figure 4(a) as well as of the spot marked on particle 1 are almost the same. They are given by Figure 4(b). One can therefore conclude that the NaY zeolite is uniformly embedded inside the poly(MMA–EGDMA) particles. When powders of the five inorganic/poly(MMA–EGDMA) blends were pressed at a temperature near the melting point of PMMA, thin films with different homogeneous colors were obtained. To examine the distribution of inorganic particles inside the polymer, a secondary electron image of the cross section of a Cu— $(SiO_x)_n$/poly(MMA–EGDMA) film was taken (Fig. 5). The bake-scattered electron image in the atomic contrast mode shows clearly the copper
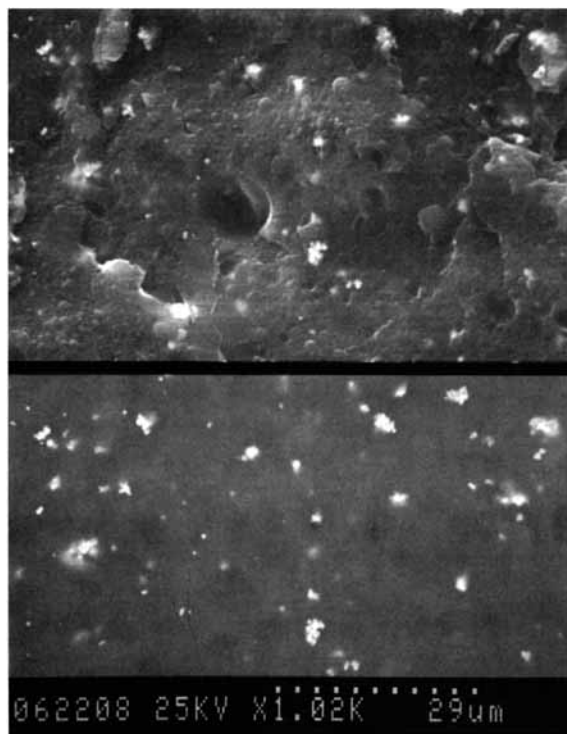
particles (bright regions), which are rather uniformly distributed as small clusters inside the polymer matrices.

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