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Mechanisms of Polymer-Supported Catalysis. 6. Quaternary Phosphonium Ions on Polystyrene Latexes as Catalysts for Nucleophilic Displacements

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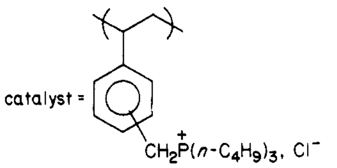
ABSTRACT: Cross-linked polystyrene latexes with benzyltri-*n*-butylphosphonium ions substituted on 16% of the aromatic rings have been synthesized and tested as catalysts for reactions of aqueous sodium cyanide with 1-bromooctane and with benzyl bromide. The 0.12–0.27-μm-diameter latex catalysts were more active than the analogous 10–37-μm polystyrene-supported catalyst previously found most active in the benzyl bromide reaction. Coagulation of the catalysts under reaction conditions was minimized by treatment of the latex with the benzyl bromide in toluene before exposure to concentrated aqueous sodium cyanide.

Insoluble polystyrene-bound benzyltri-*n*-butylphosphonium ions catalyze nucleophilic displacement reactions in triphase aqueous/organic mixtures.[1-4] Previous studies of the reactions of cyanide ion with alkyl bromides showed higher reaction rates with smaller catalyst particles, using catalysts 20–250 μm in diameter prepared by suspension polymerization.[5-7]

$$\mathrm{RBr} + \mathrm{NaCN(aq)} \longrightarrow \mathrm{RCN} + \mathrm{NaBr}$$



The rate dependences on particle sizes are due to partial rate limitation by diffusion of reactants from the catalyst particle surface to the active sites within the polymer gel. Depending on exact reaction conditions, diffusion of either the organic reactant or the anionic reactant (ion exchange) can be rate limiting.[8-11] The hydrophile/lipophile balances in the polymer matrix and at the polymer surface strongly influence organic reactant and anion transport into the polymer. This paper reports an extension of catalyst particle size studies to latex particles 2 orders of magnitude smaller than the catalysts studied previously. The goal is higher catalytic activity. Once intraparticle diffusional limitations are overcome with polymer-supported phase-transfer catalysts, reaction rates should depend only on intrinsic reactivity at the active site. This is the first report of latex particles as phase-transfer catalysts of which we are aware. Acid catalysis by sulfonic acids on polystyrene latexes[12] and basic catalysis of ester hydrolysis by primary amines on methacrylic microgels[13] have been reported.

Results

Emulsion polymerizations of styrene containing 25% (chloromethyl)styrenes and either 2% or 10% divinylbenzene were carried out with hexadecyltrimethylammonium bromide as surfactant and azobis(isobutyronitrile) as initiator to give latex particles 0.08–0.2 μm in diameter. The copolymers were converted directly to the phosphonium salts by refluxing the emulsions 24 h with tri-*n*-butylphosphine, or they were coagulated with saturated aqueous sodium chloride, washed, dried, resuspended in methanol, and then treated with tri-*n*-butylphosphine to provide the catalysts listed in Table I. Chloride contents of the phosphonium ion polymers were 0.89–1.04 mequiv of Cl^-/g of dried polymer, which corresponds with 75–90% phosphonation of the original chloromethyl polymers.

Table I
Benzyltri-*n*-butylphosphonium Ion Catalysts

cat.	mequiv of P/g	% cross-linked	physical form
1	1.01	2	spherical beads, 10–37-μm diameter[a]
2	0.98	2	10–37-μm dried coagulated powder[b]
3	1.04	2	emulsion, 10% solids
4	0.90	2	emulsion, 13% solids
5	0.89	10	emulsion, 20% solids
sol[c]	1.14	0	

[a] Suspension polymerization. [b] Emulsion polymerization. [c] Reference 10.

Table II
Rate Constants for Catalyzed Reactions of 1-Bromooctane with Cyanide Ion[a]

cat.	conditioned in	$10^5 k_{\mathrm{obsd}}$, s^{-1}
1	toluene/aqueous NaCN	38[b]
2	toluene	31
sol	toluene/aqueous NaCN	53.4[c]

[a] 90 °C, 600 rpm mechanical stirring, 10 mol of NaCN/mol of 1-bromooctane, 2 mol % catalyst based on 1-bromooctane. [b] Reference 7. [c] Reference 10.

Table III
Rates of Reaction of Benzyl Bromide with Cyanide Ion[a]

cat.	% DVB	diam,[b] μm	$10^5 k_{\mathrm{obsd}}$, s^{-1}
1	2	10–37	510
3	2	0.5–1.2	510
4	2	0.27	2200[c]
4	2	0.27	2200[c,d]
4	2	0.27	2100[c,e]
5	10	0.116	1120
5	10	0.116	990[f]
$n\text{-}Bu_3P$[g]			51
$n\text{-}C_{16}H_{33}N^+Me_3Br^-$ [h]			74

[a] At 80 °C with 5 mol of NaCN/mol of $PhCH_2Br$, 2 mol % catalyst, and 600 rpm mechanical stirring unless noted otherwise. Catalyst was conditioned in organic phase. [b] Emulsion particle sizes of catalyst, except for **3**, which was determined as the copolymer. [c] Only 0.5 mol % catalyst was used. The observed rate constant has been multiplied by 4 for comparison with data obtained with 2.0 mol % catalyst. [d] 520 rpm stirring. [e] 640 rpm stirring. [f] After dialysis of **5**. [g] 0.35 mol % based on benzyl bromide. [h] 0.25 mol % based on benzyl bromide.

Rate constants of reactions of aqueous sodium cyanide with 1-bromooctane and with benzyl bromide in toluene are in Tables II and III. Rate constants were independent

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of stirring speed in the range 510–670 rpm using the most active catalyst **4** with the faster reacting benzyl bromide. All other runs were stirred at 600 rpm, previously found[5-7] to overcome mass-transfer limitations on reaction rates with 200–300-μm spherical catalysts. In all experiments with coagulated latexes and with emulsions, a small fraction (<0.1) of the catalyst came out of the reaction mixture and stuck to the upper walls of the flask, causing minor reduction in observed rate constants. The stuck particles had irregular shapes by light microscopic examination, in contrast to the spherical 10–37-μm catalyst particles prepared by suspension polymerization, which did not stick to the upper walls of the flask and maintained their shape.

Approximate critical concentrations of aqueous sodium cyanide required to precipitate catalyst **3** were 0.2 M at 25 °C and 0.1 M at 80 °C. Thus in a kinetic experiment if the emulsion had been added to the aqueous sodium cyanide before addition of the organic phase, the catalyst would have precipitated.

In 1-bromooctane experiments the coagulated emulsion catalyst **2** remained in the aqueous phase and emulsion **3** partially coagulated in the aqueous phase when they were added to toluene/aqueous NaCN mixtures, whereas the spherical bead catalyst **1** migrated to the aqueous/organic interface of a quiet mixture. Attempted kinetic runs that were preceded by conditioning the catalysts **2** and **3** in toluene/aqueous NaCN gave very slow initial rates (k_{obsd} ca. 9×10^{-5} s^{-1}) and increasing rates as the reaction proceeded, probably because the catalysts were "wetted" slowly by the organic phase.

In contrast to the 1-bromooctane results, addition of catalyst emulsions to benzyl bromide alone resulted in transfer of the catalyst to the organic phase, where it remained without coagulation even after addition of toluene and aqueous sodium cyanide. Thus all kinetic experiments in Table III were performed by conditioning the catalyst in benzyl bromide before addition of toluene and aqueous sodium cyanide. Control experiments were run to determine if residual tri-*n*-butylphosphine, present in **3** from its preparation, or surfactant, hexadecyltrimethylammonium bromide, from the polymerization, acted as catalysts. The last two lines of Table III show they have very low activity. Such low activity of surfactant quaternary ammonium ions in phase-transfer catalysis is well-known.[14] Also dialysis of catalyst **5** to remove surfactant had little effect on its activity (lines 6 and 7 of Table III).

Discussion

The phase-transfer-catalyzed reaction of benzyl bromide with cyanide ion at 80 °C is a prime candidate for increased activity with smaller-sized polymeric catalysts because the reaction had a half-life of only 2 min with 37–48-μm catalyst particles under previous standard conditions.[7] On that time scale intraparticle diffusional limitation of the rate is expected. A 10% cross-linked latex catalyst **5** was examined in addition to the usual 2% cross-linked catalysts **3** and **4** to increase the likelihood of intraparticle diffusional rate limitation. Conditioning of the catalyst in the organic phase (first in benzyl bromide, the better swelling solvent, before addition of toluene) before addition of the aqueous phase was required for highest activity. The rate constants in Table III correlate qualitatively with particle size. The 2% cross-linked suspension polymer-supported catalyst **1** and partly coagulated latex **3** (size not determined at the catalyst stage) were both 0.25 times as active as 0.27-μm latex **4**. The still smaller latex **5** was less active than **4** because its 10% cross-linking slowed intraparticle diffusion of reactant to the active sites.

The latex particle sizes in Table III should not be interpreted as actual sizes during triphase reactions, because catalyst **4** recovered from a mixture of toluene and water had partly coagulated to particles 4.4 μm in diameter, as determined by light scattering. Presumably all of the latexes underwent similar coagulation on exposure to the phase-transfer catalysis mixture, but the relative sizes of the coagulum were similar to the relative sizes of the single particles in the original aqueous emulsions.

We were unable to carry out reactions of 1-bromooctane and aqueous sodium cyanide with a true latex catalyst because the emulsions coagulated during preparation of the reaction mixtures using every possible order of addition of reactants, solvent, and catalyst. The coagulated emulsion **2**, sieved to the same range of particle sizes as the previous most active suspension polymer catalyst **1**, was slightly less active than catalyst **1**. A comparable soluble catalyst (Table II) was 1.4 times as active as **1** and 1.7 times as active as **2**, indicating that even 10–37-μm insoluble catalyst particles suffer from rate limitation by intraparticle diffusion.[10]

The benzyl bromide results show that higher activity of a polymer-bound phase-transfer catalyst in a very fast reaction (half-lives of 1–4 min) is attained by use of much smaller latex particle catalysts. However, catalyst reuse is also essential for a practical large-scale application of phase-transfer catalysis. In principle, the latex catalysts could be coagulated, recovered by filtration, redispersed, and reused. In limited attempts we have not yet reduced that principle to practice.

Experimental Section

Materials. Benzyl bromide, 1-bromooctane, styrene, divinylbenzene (55% active, Polysciences, Inc.), and (chloromethyl)styrenes (70/30 *m*/*p*, Dow Chemical Co.) were distilled under vacuum. Other chemicals were reagent grade from Aldrich Chemical Co. or Eastman Kodak Co. and were used as received. Water was deionized by mixed-bed ion exchange and distilled in glass from $KMnO_4$. Catalyst **1** was available from an earlier investigation.[6]

Particle size analyses were carried out by dynamic light scattering.[15] Scanning electron micrographs were obtained with a JEOL JSM 35 instrument at 15-kV accelerating voltage. Samples were dried on Al stubs and coated with Au/Pd. NMR spectra were obtained with a Varian XL-300 pulsed Fourier transform instrument.

Polymerization. Copolymer 2. Solution A: A 250-mL round-bottomed flask equipped with an overhead stirrer with a Teflon blade, a condenser, an addition funnel, and a nitrogen inlet was charged with 50 mg of *n*-hexadecyltrimethylammonium bromide, 600 mg of *n*-hexadecane, and 82 mL of water. The mixture was purged with nitrogen for 15 min and heated to 70 °C. Solution B: A mixture of 150 mg of hexadecyltrimethylammonium bromide in 18 mL of water, 20.63 g of styrene, 7.57 g of (chloromethyl)styrenes, 1.28 g of divinylbenzene, and 200 mg of azobis(isobutyronitrile) was purged with nitrogen for 15 min. The milky white emulsion was transferred to the addition funnel. Solution B was added dropwise to solution A with stirring over 30 min. Stirring was continued 3 h at 70 °C. The emulsion was neutralized to pH 7 with 2–3 mL of 1 N NaOH and filtered through a coarse-porosity glass frit to remove a large amount of coagulum. ^{13}C NMR analysis of the emulsion at 75.4 MHz showed a strong peak at 46.4 ppm due to $-CH_2Cl$ and no peak at 65 ppm due to $-CH_2OH$. The particle size was 0.18 μm by light scattering and 0.12 μm by SEM. The solids content was determined as follows: 10 mL of the emulsion was added dropwise to 40 mL of acetone. The precipitate so formed was left overnight to settle, collected on a medium-porosity glass frit, washed with 4/1 acetone/water, and dried under vacuum at 50 °C overnight. Recovered solid corresponded with 12.5 g of solids (46% yield of 10% solids emulsion) in the whole sample.

Copolymer 3. The procedure for copolymer **2** was used except that the surfactant was 100 mg of hexadecyltrimethylammonium bromide and 4.4 g of the nonionic Triton X-100 (Sigma Chemical Co.). The product emulsion was obtained in 75% yield with 18% solids. The particle size was 0.5–1.2 μm by light scattering and 0.08–0.18 μm by SEM. The larger value by light scattering was likely due to loose aggregation of particles, also seen by SEM.

Copolymer 4. The procedure for copolymer **2** was used except amounts of reagents were 14.5 g of styrene, 0.915 g of divinylbenzene, 5.35 g of (chloromethyl)styrenes, 1.0 g of hexadecyltrimethylammonium bromide, and 1.5 g of hexadecane. The product emulsion was 17% solids with particle diameter 0.08 μm by light scattering.

Copolymer 5. The procedure for copolymer **2** was used except the quantities of reagents were 18.7 g of styrene, 4.8 g of divinylbenzene, 7.5 g of (chloromethyl)styrenes, 1.0 g of hexadecyltrimethylammonium bromide, and 1.5 g of hexadecane. The product emulsion was obtained in 70% yield with 18% solids. The particle size was 0.082 μm by light scattering.

Catalyst 2. A mixture of 7.0 g (11.2 mequiv of Cl) of dried copolymer **2**, 70 mL of methanol, and 4 mL (15.2 mmol) of tri-*n*-butylphosphine under nitrogen was stirred at 70 °C for 20 h, filtered, washed with acetone and methanol, and dried. Analysis by titration of liberated Cl^-[16] showed 0.98 mequiv of phosphonium sites/g of dry polymer (82% conversion, 16.5% ring substitution).

Catalyst 3. Diluted emulsion copolymer **3**, 100 mL (11.6 mequiv of Cl), was purged with nitrogen for 10 min, and 3.0 mL (11.4 mmol) of tri-*n*-butylphosphine was added. The mixture was refluxed for 24 h, and 10 mL of it was added dropwise to 50 mL of hot saturated aqueous NaCl. The coagulum was filtered, washed, and dried as before. Chloride analysis showed 1.04 mequiv/g (86% yield, 17% ring substitution).

Catalyst 4. Phosphonation of copolymer **4** by the procedure used for catalyst **3** gave an emulsion containing 0.90 mequiv of Cl^-/g (75% yield, 16% ring substitution).

Catalyst 5. Phosphonation of copolymer **5** by the procedure used for catalyst **3** gave a product containing 0.89 mequiv of Cl^-/g (80% yield, 16% ring substitution).

Kinetics. Reactions of 1-Bromooctane. Catalyst **2**, 0.464 g (0.438 mmol) was allowed to swell in 20 mL of toluene for 1 h before addition of 0.684 g of *o*-dichlorobenzene (internal standard for GLC), 30 mL of water, and 9.8 g of NaCN. The mixture was stirred at 600 rpm for 60 min at 90 °C, and 3.927 g (20.13 mmol) of 1-bromooctane was added. Sampling and data analysis were carried out as before.[6]

Reactions of Benzyl Bromide. The experiment of line 2, Table III, is given as an example. A mixture of 3.3 mL (0.33 mmol) of emulsion catalyst **3**, 0.71 g of *o*-dichlorobenzene, 6.7 mL of water, and 3.97 g (23.2 mmol) of benzyl bromide was stirred at 600 rpm at 80 °C for 15 min. When the latex particles appeared to be in the organic phase, 10 mL of toluene was added, and 20 min later a solution of 4.98 g of NaCN in 20 mL of water (heated to 80°C) was added. Sampling and data analysis were carried out as before.[6] In the fastest reactions the initial data point recorded 2.0 min after addition of the aqueous NaCN corresponded to 50% conversion of benzyl bromide to benzyl cyanide. Although five data points were taken, the rate constants reported are initial values except as noted in Table III. Succeeding data points to >90% conversion showed <20% changes in calculated rate constants with time except as noted in Table III.

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Registry No. Sodium cyanide, 143-33-9; 1-bromooctane, 111-83-1; benzyl bromide, 100-39-0.

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