Therefore, since one may think of proceeding to normal polymers by increasing the chain flexibility, the point of crossover between nematodynamics and conventional polymer rheology in these rigid polymer systems could give important clues to a fundamental understanding of polymer rheology.

Registry No. PBA (homopolymer), 25136-77-0; PBA (SRU), 24991-08-0.

References and Notes

(1) Ciferri, A. In *Polymer Liquid Crystals*; Ciferri, A., Krigbaum, R., Myer, R. B., Eds.; Academic: New York, 1982.
(2) Prevorsek, D. C. In *Polymer Liquid Crystals*; Ciferri, A., Krigbaum, R., Meyer, R. B., Eds; Academic: New York, 1982.
(3) de Gennes, P. G. *The Physics of Liquid Crystals*; Oxford, London, 1975.
(4) Taratuta, V. G.; Hurd, A. J.; Meyer, R. B. *Phys. Rev. Lett.* **1985**, *55*, 246.
(5) Guyon, E.; Meyer, R. B.; Salam, J. *Mol. Cryst. Liq. Cryst.* **1979**, *54*, 261.
(6) Lonberg, F.; Fraden, S.; Hurd, A. J.; Meyer, R. B. *Phys. Rev. Lett.* **1984**, *52*, 1903.
(7) Panar, M.; Beste, L. F. *Macromolecules* **1977**, *10*, 1401.
(8) Flory, P. J., *Proc. R. Soc. London, Ser. A* **1956**, *A234*, 73.
(9) Hui, Y.; Kuzman, M. R.; San Miguel, M.; Labes, M. M. *J. Chem. Phys.* **1985**, *83*, 288.
(10) Tsevtkov, V. N. *Liquid Crystalline Order in Polymers*; Blumstein, A., Ed.; Academic: New York, 1978.
(11) Bird, R. B.; Armstrong, R. C.; Hassager, O. *Dynamics of Polymeric Liquids*; Wiley: New York, 1977; Vol. 1.
(12) Lodge, A. S. *Elastic Liquids*; Academic: New York, 1964.

Mechanism of Polymer-Supported Phase-Transfer Catalysis. Effect of Phase Ratios on Low Percent Ring Substitution Microporous Polystyrene Resin

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Received January 2, 1986

ABSTRACT: The liquid-phase ratio was shown to have significant effect on the kinetics of the displacement reaction between 1-bromooctane and potassium cyanide by polystyrene-bound tri-*n*-butylphosphonium ion. It was illustrated that the organic phase must be the dispersed phase to carry out the reaction effectively with microporous, low cross-linked density and low percent ring substitution polystyrene chloromethylated resins. Drastic kinetic rate improvement was achieved with proper adjustment of phase ratios and the amount of catalyst for a given organic phase volume. The mechanism was explained with an alternating-shell model.

Introduction

The catalytic activities of polymer-supported phase-transfer catalysts often are much lower than those of their homogeneous analogues, and it is generally agreed that diffusional resistance within the polymer particle is an important factor.[1] Many of these discussions on mass-transfer limitations are based on seven basic steps of modeling heterogeneous catalysis: (1) transport of limiting reactant to particle surface, (2) diffusion of reactant into particle, (3) adsorption of reactant on active site, (4) chemical reaction, (5) desorption of product, (6) counter-diffusion of product out of particle, and (7) transport of product away from particle. These physicochemical processes in this model all refer to a single limiting reactant in one fluid phase. In earlier developments, a model assuming the existence of inverted micelles within the polymer matrix was proposed to explain the microenvironment of the catalysts.[2] Kinetic data also have been analyzed with a model assuming that the diffusion of the organic reactant is the rate-limiting step.[3] More recent attempts have illustrated that the mechanism is very different with low or high percent ring substitution polymer supports.[2,4] With low percent ring substitution, the ion transport in the ion-exchange process is the rate-limiting step.[4] External mass transport of the reactant to the particle surface is regarded as not important if the reactor is vigorously agitated, usually above 600–700 rpm with a stir bar or an impeller.

Our present effort attempts to elucidate the reaction mechanism with low percent ring substitution polystyrene resin. The objective is to show that the seven basic steps in heterogeneous catalysis are not adequate in explaining the mechanism of polymer-supported phase-transfer catalytic reactions. The major reason is that the two liquid solvents commonly used in phase-transfer reaction experiments are practically insoluble in each other. The solubility of toluene in water is 0.05 wt % and that of water in toluene is 0.03 wt % at 25 °C. Thus one must consider the consequence of having two immiscible liquid phases on the overall kinetics in more detail than the current view on the subject.[5] It will be shown here that the contacting times of the polymer particles with the respective aqueous and organic phases have a significant influence on the global kinetics, and these contacting times can be varied by adjusting the volume fractions of the two liquid phases.

The results are verified with the reaction of aqueous potassium cyanide with 1-bromooctane in toluene

$$n\text{-}C_8H_{17}Br + KCN_{aq} \rightarrow n\text{-}C_8H_{17}CN + KBr_{aq} \quad (1)$$

The reaction is catalyzed by polystyrene-bound benzyltri-*n*-butylphosphonium ions.[6] The polystyrene resins are microporous, cross-linked with 1% divinylbenzene, and have an effective 8.5% ring substitution.[7] To better illustrate our ideal, eq 1 is written as follows. The overall kinetic cycle[8] must be broken up into two steps by virtue of the presence of two practically insoluble liquid phases: an ion-exchange step in which the attached catalyst sites P^+ are in contact with the aqueous phase

$$P^+Br^-_s + K^+CN^-_{aq} \rightarrow P^+CN^-_s + K^+Br^-_{aq} \quad (2a)$$

and the chemical conversion step in which the active catalyst sites with cyanide ions react with the bromooctane in the organic solvent

$$P^+CN^-_s + n\text{-}C_8H_{17}Br_{org} \rightarrow P^+Br^-_s + n\text{-}C_8H_{17}CN_{org} \quad (2b)$$

The catalyst sites $P^+Br^-_s$ must be reactivated by ion-exchange step (2a) to provide the active form $P^+CN^-_s$. Hence we have to assess the immiscible liquid-phase effects *both*

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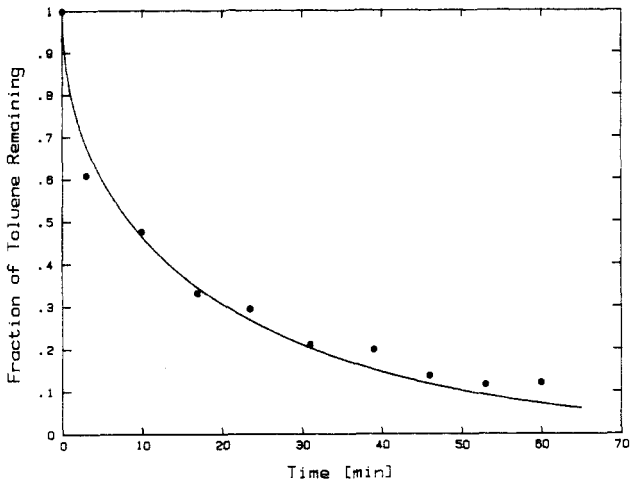

Figure 1. Time variation of the fraction of toluene remaining in catalyst beads as the beads are submerged in aqueous KCN. The solid curve is the solution of transient diffusion in a spherical particle with an effective diffusivity of 0.8×10^{-7} cm^2/s.

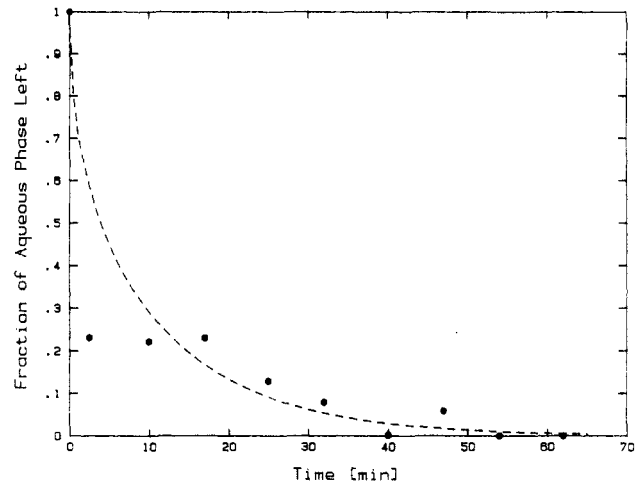

Figure 2. Time variation of the fraction of aqueous KCN remaining in catalyst beads as the beads are submerged in toluene. The dashed curve indicates how a purely diffusive process would behave with an effectively diffusivity of 1.7×10^{-7} cm^2/s.

external to the catalyst particle and within the particle. External to the polystyrene particles, the volume fractions of the two liquid phases affect the contacting times of the liquids with the particle surface. The intensity of agitation alone is not adequate to account for all external mass transport influences in a two-liquid-phase system. Phase contacting times affect how the liquids penetrate into the polymer particle. So far, it has only been established that the diffusion of the aqueous phase in the ion-exchange step (2a) is rate limiting.[4]

Results and Discussion

Relative Rates of Solvent Elution in Particle. The solvent elution experiments are used to establish the relative rates of displacement in the polymer resin by different fluid phases. The data of the solvent elution experiments are given in Figures 1 and 2 and presented as the fraction of solvent remaining in the swollen gel beads vs. time of elution. The elution of aqueous KCN measures the rate of toluene to penetrate and replace the aqueous phase. Similar interpretation can be made with the elution of toluene by aqueous KCN. The solid curve and the dashed curve in the two figures represent the solution of a transient diffusional process in a sphere with a constant surface concentration.[9] The effective diffusion coefficients of water and toluene were estimated to be 0.8×10^{-7} and 1.7×10^{-7} cm^2/s, respectively, in the two figures.[10] The displacement of the organic phase by the aqueous phase (Figure 1) can be approximated quite well by a simple diffusional process. However in Figure 2, there is a substantial deviation from the transient diffusion solution, especially the first three data points under 20 min. The data points are highly reproducible and it is apparent that the initial displacement of the aqueous phase by toluene in the polymer matrix is not a simple diffusional process. Hence the dashed curve in Figure 2. This observation can be missed easily if short time scale data are not taken, since the data above 20 min in Figure 2 do follow a trend indicative of diffusive transport. It is highly probable that the displacement of the aqueous phase by the organic solvent is extremely rapid due to an affinity of the polystyrene for the organic solvent (lipophilic behavior). In fact, toluene and polystyrene have nearly the same solubility parameter, about 9 $(\text{cal/cm}^3)^{0.5}$, while the solubility parameter of water is 23 $(\text{cal/cm}^3)^{0.5}$.

Visual observations of particle swelling under a microscope confirmed the above results. Polystyrene beads, originally soaked in aqueous KCN solution, swelled rapidly to the eventual size when contacted with toluene within several seconds. On the other hand, there was no noticeable size alteration when the polystyrene beads saturated with toluene were contacted with aqueous KCN for the initial several minutes. A toluene-swollen polystyrene matrix appeared to reject aqueous KCN.

The swelling of native resin beads and quaternized resins also was observed in water and toluene. The swelling ratios (swollen volume/dry volume) for the quaternized gel beds (15% ring substitution) indicate that the resins have a preference for the organic solvent. Swelling ratios for the beads in water, toluene, and water with toluene (triphase conditions) at 25 °C were 1.1, 2.8, and 2.4, respectively.[11] The swelling ratio of the unquaternized resin in toluene is 5.3, much higher than the 2.8 observed with quaternized beads. Hence, the additional attachment of onium salts has significant effects on the lipophilic nature of the polymer beads.

The results so far clearly support that the ion (aqueous phase) transport is the rate-limiting step. We can further state comfortably that because the time scales of the penetration of the two liquid phases into the particle are so different, *the relative phase ratios in the reactor must be important*. The relative volume of the two phases will influence the contact time of the polystyrene resins with each phase. On the average, the contact time is much longer with the continuous phase than with the dispersed phase. The results of the above experiments indicate that the aqueous phase is the preferred continuous phase. It should be noted that virtually all data reported are obtained in the range of 0.4–0.5 organic phase volume fractions.[12]

Effect of Phase Ratio on Pseudo-First-Order Rates

The effect of varying the organic phase volume fraction in the reactor is illustrated in Figure 3, with data points joined together with the solid curve. All kinetic runs on this curve have the same initial mole ratios among bromooctane to cyanide ions, and bromooctane to the total catalyst sites.[13] The amount of catalyst is also constant with respect to the total liquid volume. Thus the initial organic composition needs to be varied to satisfy the above constraints. The pseudo-first-order rate constant is on a per mole tri-*n*-butylphosphonium ion basis.[14] With organic volume fractions above 0.5, the observed first-order rate

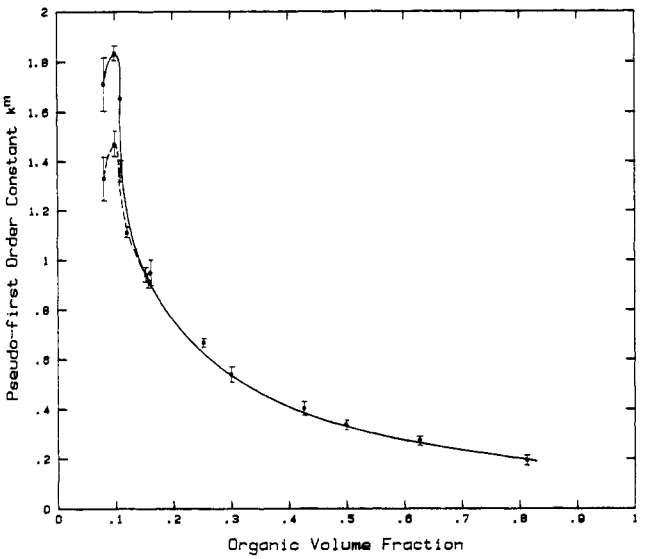

Figure 3. Pseudo-first-order constant k^m [(g mol of phosphonium ion)$^{-1}$ s^{-1}] as a function of the organic volume fraction. All data are obtained at 70 °C. The initial mole ratio of bromooctane to phosphonium ion groups is 75 and that of KCN to bromooctane is 5. The standard deviation of each point is indicated by the error bars. See text for explanation on the solid and dashed curves.

constant is rather low. The pseudo-first-order rate constant gradually increases as the amount of the organic fraction decreases. The incremental increase in rate becomes more pronounced as the organic fraction drops below 0.3 and becomes effectively the dispersed phase. The rate reaches a maximum at an organic volume fraction of 0.1 and afterward, the rate decreases again drastically as the organic volume fraction further decreases.[15] The maximum rate constant at an organic volume fraction of 0.1 is 3.68 times higher than that at an organic volume fraction of 0.426.[16] The value of 0.426 falls in the range of 0.4–0.5 of all reported data.[12] The higher reaction rates, with the organic as the dispersed phase, confirm the conjecture made with the solvent elution experiments. The maximum in rate is a consequence of the fact that at very low organic phase ratios, the amount of organic droplets becomes diminished and limits the collision frequency of a polystyrene resin with the organic phase. Without frequent phase contacting with the organic phase, the overall reaction cannot proceed effectively. (The current rate constant at an organic volume fraction of 0.4 compared very favorably with the results of Regen and co-workers and Tomoi and Ford.[12])

Since the contacting of individual catalyst particles with the two liquid phases is important, we should expect that the relative amount of catalyst to the dispersed phase will also be a factor. The points on the dashed line in Figure 3 indicate this effect. The data here are obtained with 4.5 times less catalyst by weight with respect to the total liquid volume while maintaining the same initial mole ratios of all reactants as the data points on the solid curve. In addition, the initial mole fraction of bromooctane is maintained at about 0.1. Above organic volume fractions of 0.16, the effect is negligible. The data with less catalyst have a slightly higher rate when the organic volume fraction drops below 0.12, and as the amount of organic phase is further decreased, the rate constant, on a per mole catalyst basis, becomes much higher. The maximum rate of the dashed curve is 1.25 times higher than that of the solid curve.

This feature is further illustrated in Figure 4, in which the amount of catalyst is varied while the organic volume fraction is fixed at 0.1 and the total liquid volume is kept

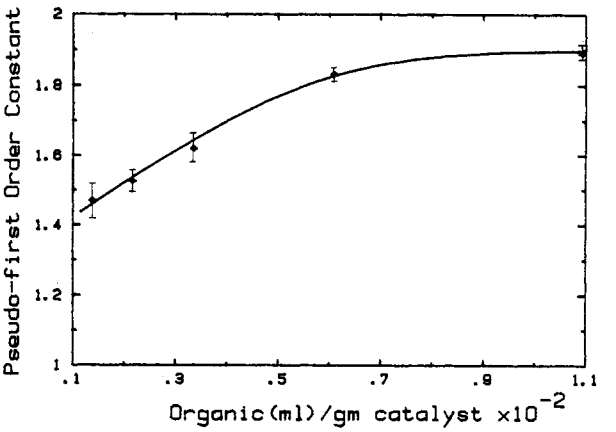

Figure 4. Pseudo-first-order constant k^m [(g mol of phosphonium ion)$^{-1}$ s^{-1}] as a function of the specific organic volume (the ratio of the total organic phase volume to the amount of catalyst used) [mL of organic phase/g of catalyst]. The organic volume fraction is fixed at 0.1. All data are obtained at 70 °C. The standard deviation of each point is indicated by the error bars.

constant. The pseudo-first-order rate constant clearly decreases as the specific volume of the organic phase available is decreased. The organic-phase droplets have a finite surface area and volume. Thus as the number of catalyst particles increases, they have to compete for the organic droplets and the efficiency of utilizing the catalyst will decrease if the amount of organic droplets becomes limited. For a given volume of organic phase, this effect should not be obvious as long as the relative amount of catalyst particles is not excessive. The data points with the least amount of catalyst (or high specific organic volume) in Figure 4 apparently approach an upper asymptote in which the actual amount of catalyst is not critical. With an increase in the relative amount of catalyst (the specific organic volume decreases), the pseudo-first-order rate constant decreases almost linearly with a decrease in the specific organic volume.

Effect of the Initial Organic Phase Composition

Low percent ring substitution resins are insensitive to salt concentrations, but we still have to address any possible consequence due to different initial bromooctane concentrations. Relative to toluene, bromooctane is a poor swelling solvent of polystyrene, with a swelling ratio of 1.5, and one would expect a decrease in overall rate as the amount of bromooctane increases. At organic volume fraction equal to 0.16 in Figure 3, there are three data points, each with very different initial bromooctane mole fractions in the organic phase: 0.092 (on dashed curve), 0.3 (on solid curve), and pure bromooctane; the respective pseudo-first-order constants, k^m, are 0.945, 0.956, and 0.899 (g mol of phosphonium ion)$^{-1}$ s^{-1}. The overall rate constant with pure bromooctane, 0.899, is only 5% less than the other two values, which are the same within experimental errors.

This result is surprising. However, with similar microscopic observations as mentioned in earlier sections, the bromooctane appears to penetrate the polystyrene resin extremely fast, despite not a good swelling solvent. Hence the relative rate of bromooctane transport within the polymer particle remains much higher than that of the aqueous phase of which transport remains rate limiting. The less swollen resin in pure bromooctane apparently affects the subsequent penetration of the aqueous phase, and thus the slight decrease in rate. In general, the overall rate is very insensitive to the bromooctane concentration. Thus, even though the initial bromooctane mole fractions

of the solid curve in Figure 3 ranges from 0.05 to 0.4, this variation does not affect our earlier discussions.

Alternating-Shell Model

The observations can best be described by the following alternating-shell model. The gist is that we need to account for both immiscible liquid phases. There are several assumptions: (1) That the two liquid phases are practically insoluble in each other, and the solubility of the aqueous anion in the organic is negligible and likewise with the organic reactant in the aqueous phase. Otherwise there is no need for a phase-transfer catalyst. (2) That the diffusion of the aqueous phase into a particle occupied by the organic phase is extremely slow. On the other hand, the penetration of organic into a particle occupied by the aqueous phase is instantaneous by comparison. (3) That the particles reside in either the bulk organic or the bulk aqueous phase; i.e., the amount adsorbed at the fluid interface is negligible. (4) That the penetration of fluid into the particles are symmetrical. Assumptions 1 and 2 are rigorous assumptions and are likely to hold in many circumstances. Assumptions 3 and 4 may not be true if the polystyrene resins only reside at the organic–aqueous interface. This situation can become important when the dispersed droplets become so small that they behave as a rigid body and inhibit internal droplet convective flow and capture of catalyst particles. In this case, transport or penetration of a solvent will predominate in one particular direction. Nevertheless, this limiting case will only complicate the model quantitatively and will not change the following qualitative description of the mechanism.

A schematic of the alternating-shell model is illustrated in Figure 5, using the displacement of bromooctane by cynadie ion as an example. The catalyst particle can be swollen initially with either the aqueous or organic phase. During the preconditioning period, in which the particles are agitiated in a mixture of the two liquid phases, the periphery of the particle will be occupied by the organic phase with at the most a small residual aqueous core in the center after at least one contacting with the organic phase.

At the beginning of a kinetic experiment, bromooctane is added and we can construct the following scenario after the catalyst particles have contacted with both liquid phases several times. If the particle is now in contact with the aqueous phase, the aqueous KCN will diffuse into the particle slowly, displace the organic fluid and regenerate the particle active sites to contain the aqueous displacing anion. With virtually all phase-transfer catalysis experiments reported today, the cyanide ion is in large excess of the bromide ion and thus the ionic equilibrium will be forced toward saturation of catalyst sites with the cyanide ion.

Next, when the catalyst particle is in contact with the organic phase, the organic solvent will quickly displace all the aqueous phase from the particle and allow the organic reactant to react with the cyanide anion on the catalyst sites. With the organic as the dispersed phase, the contact time with the organic droplet is relatively short, probably just sufficient for the organic-phase penetration. The organic chemical conversion will have to continue with the particle in the aqueous phase while the aqueous phase will again diffuse slowly into the particle and in the process strip away any available cyanide anion from any unconverted bromooctane. The cycle continues as the particle will eventually come into contact with another organic droplet. The end result is that only the catalyst sites on the outer zone of the polymer particles are utilized effectively.

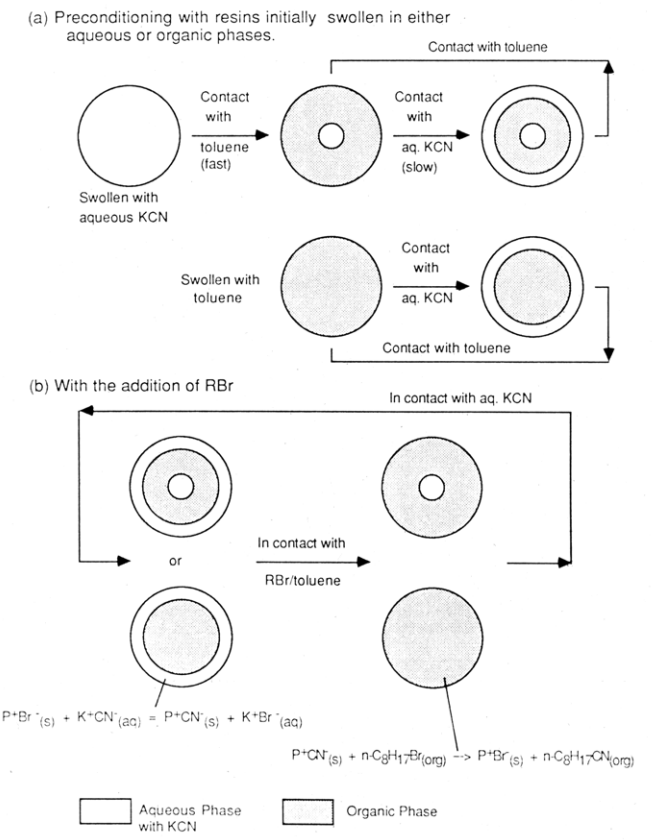

Figure 5. Schematic of the alternating-shell model. The figures are not drawn to scale, and thus the swelling ratio effect of different solvents is not included.

With the alternating-shell model, we can explain most of the experimental observations. The model accounts for the low utilization of the ion-exchange sites, the slow aqueous ion-exchange rate, and generally the low efficiency of the polymer-supported catalyst, as opposed to homogeneous analogues.

Conclusion

The results of varying phase ratio and the amount of catalyst support the importance of phase contacting and the necessary choice of the continuous and dispersed phases. In the present case, the organic phase must be the dispersed phase to force the particles to have a significantly longer contact time with the aqueous phase. Even though we consider that the contact time with the organic phase can be small, the catalyst particles must come in contact with the organic droplets with sufficient frequency to complete the kinetic cycle. With proper optimization of the phase ratio and amount of catalyst, the kinetic rate on a per mole catalyst can be at least 3–4 times higher than current conditions.

Experimental Section

Unless otherwise stated, all chemicals and solvents were analytical reagent grade and were used without further purification. Deionized water was used in the preparation of aqueous solutions.

Polymer-Bound Tri-*n*-butylphosphonium Chloride. The following procedure was adapted from that given by Tomoi and Ford.[1d] The catalyst was synthesized by binding tri-*n*-butylphosphine onto chloromethylated polystyrene beads (Bio Rad Laboratories), 200–400 mesh (0.074–0.037 mm). The beads were cross-linked with 1% divinylbenzene and contained 1.37 mmol of chloromethyl groups per gram of dry resin. The percent ring substitution is 15%.

Lower temperatures were used to minimize thermal degradation. A 20-g quantity of chloromethylated polystyrene beads was mixed with 240 mL of 1,2 dichloropropane. The reflux condenser,

thermometer, and gas sparger were placed in their respective ports and the system was sparged with nitrogen for 15 min. With a nitrogen-rinsed syringe, 30 mL of 95% tri-*n*-butylphosphine (Aldrich) was added. Agitation, with a 1.5-in. oval magnetic stir bar, was initiated and the oil bath was heated to 85 °C. Agitation and temperature were maintained for 70 h. The resin was then pipeted into filter cones. The contents of each cone were washed with 200 mL of acetone, followed by 100 mL of methanol, 100 mL of acetone, and finally 100 mL of methanol. The resins were vacuum-dried at 50 °C for 23 h. The procedure yielded 27 g of catalyst.

The amount of catalyst attached to the support was determined by a quantitative analysis of chloride ions. Three 0.2-g samples of the catalyst beads were placed in 125-mL conical flasks. *N,N*-Dimethylformamide (4 mL) was added to each flask and allowed to soak the beads for 30 min. Concentrated HNO_3 (4 mL) was added and the contents allowed to sit for 2 h before being diluted with 100 mL of water. Each sample was subjected to a Volhard titration. A 5-mL volume of 0.1 N $AgNO_3$ was added to each flask, followed by 2 min of stirring. Then 5-mL volumes of both nitrobenzene and Volhard indicator were added. Prior to the titration with KSCN, the mixture was again mixed thoroughly. The catalyst was assayed to have 0.7 mmol of chloride per gram of resin. Thus the effective ring substitution with phosphonium ions is 8.5%.

Catalyst Support Swelling. Both quaternized and unquaternized 200–400 mesh polystyrene beads were tested for their swelling in water and toluene. A 1-mL bulk settled volume of dry beads was placed in a 10-mL graduated cylinder. The cylinder was lightly tapped to ensure that the beads were well packed. Water or toluene was added dropwise until a total volume of 8 mL was attained. A thin wire was used to dislodge air trapped in the stack of resin. The cylinder was covered and allowed to sit overnight before a measurement of the total volume was taken.

Solvent Displacement. The liquid phases used were 3.2 M KCN and toluene. To determine the displacement rate of KCN solution by toluene in the resin, a 1.25-g sample of catalyst particles was placed in a 100-mL beaker containing aqueous KCN, soaked for approximately 16 h, and finally agitated for 2.5 h at room temperature. A 150-mL Berzilius beaker containing 125 mL of toluene was placed in an oil bath maintained at 70 °C. Agitation of the contents of the beaker was provided by a magnetic stir bar spinning at 1000 rpm. At time zero, approximately 0.6 g of the KCN solution soaked resin was dropped into the beaker containing the toluene. At regular intervals, agitation was stopped (for no more than 20 s), and a sample was taken and placed in a polyethylene culture tube. The following procedures were used to remove the liquid exterior to the particles. A 400-mesh screen was secured over the culture tube. This tube was then inverted and placed in a 40-mL glass centrifuge tube which was loaded into a centrifuge. The sample was centrifuged for 5 minutes at 1000 rpm. Preliminary tests showed no weight change in the samples beyond this time. The screen, which then had the resin stuck onto it, was quickly and carefully removed, folded, and placed in a 4-mL sample vial. The vial had its remaining volume filled with acetone (spectroscopic grade) and was sealed and shaken. The sample was allowed to sit for 24 h, after which 4-μL samples of the acetone solution were injected into a Varian gas chromatograph (Model 3700) with a Chromosorb 101 column and a thermal conductivity detector. Chromatography output was monitored by a Varian CDS 111 data system. A temperature program was used. The oven had an initial temperature of 120 °C for 11 min and then an 8 °C/min temperature ramp raised the temperature to 220 °C. The same procedure was repeated for KCN displacement of resins initially soaked in toluene. Experiments were repeated for reproducibility.

Kinetics. The entire reactor was constructed with Pyrex glass, 316 stainless steel, Teflon, and Viton. The reactor was a Pyrex tube 7.5 in. long, 2 in. internal diameter and capped at both ends with Teflon plugs. The working volume was 75 mL. Tube fittings in the top plug provided for feed and sampling ports. A septum covered the sampling port. Agitation was provided by a blunt bladed impeller, 1.5 in. long, located midway between the bottom and the liquid level and spinning at 1150 rpm. This high mixing speed was chosen to ensure that the reactor content was well mixed. Reactor temperature was maintained at 70 °C by a heating tape wrapped around the reactor and monitored by a submerged chromel–alumel thermocouple and an Omega temperature controller (Model 4001), operating through a variable autotransformer (Staco, Type 3PN1010). As a safety precaution, an Allihn condenser was added. The cooling water recirculating to the condensers was maintained at 10 °C by a refrigerated circulating bath. In a typical kinetic run, the weighed amount of catalyst was first placed in the ractor. Measured volumes of KCN solution and toluene were added. Agitation was initiated and the temperature was raised to 70 °C. Such conditions were maintained for an hour. After this catalyst preconditioning period, bromooctane was added to initiate the experiment. Organic-phase samples (100–150 μL) were taken with a syringe needle at 5–10-min intervals and were analyzed for toluene and bromooctane concentrations. The agitator was turned off during sample retrieval, but not longer than 20 s. Samples were analyzed by injecting 1 μL into the same gas chromatograph mentioned above.

Acknowledgment. This research was supported by NSF Grant No. CPE82-04211 and the University of California, San Diego.

Registry No. $Br(CH_2)_7CH_3$, 111-83-1; KCN, 151-50-8; $(H_3C(CH_2)_3)_3P$, 998-40-3.

References and Notes

(1) (a) Regen, S. L.; Besse, J. J. *J. Am. Chem. Soc.* **1979**, *101*, 4509–4063. (b) Regen, S. L.; Heh, J. C.; McLick, J. *J. Org. Chem.* **1979**, *44*, 1961–1964. (c) Tomoi, M.; Ford, W. T. *J. Am. Chem. Soc.* **1980**, *102*, 7140–7141. (d) Tomoi, M.; Ford, W. T. *J. Am. Chem. Soc.* **1981**, *103*, 3821–3828. (e) Tomoi, M.; Ford, W. T. *J. Am. Chem. Soc.* **1981**, *103*, 3828–3832.

(2) Ohtani, N.; Wilkie, C. A.; Nigam, A.; Regen, S. L. *Macromolecules* **1981**, *14*, 516–520.

(3) Marconi, P. F.; Ford, W. T. *J. Catal.* **1983**, *83*, 160–167.

(4) (a) Ford, W. T.; Lee, J.; Tomoi, M. *Macromolecules* **1982**, *15*, 1246–1251. (b) Tomoi, M.; Hosokawa, Y.; Kakiuchi, H. *Makromol. Chem., Rapid Commun.* **1983**, *4*, 227–230. (c) Tomoi, M.; Hosokawa, Y.; Kakiuchi, H. *J. Polym. Sci.* **1984**, *22*, 1243–1250.

(5) Ford, W. T.; Tomoi, M. *Adv. Polym. Sci.* **1984**, *55*, 49–104.

(6) The same reaction and catalyst had been used by: (a) Cinquini, M.; Colonna, C.; Molinari, H.; Montanari, F.; Tundo, P. *J. Chem. Soc., Chem. Commun.* **1976**, 394–396. See also: ref 1b–d and 4a.

(7) From ref 1d, 2, and 5, the most favorable polystyrene resin is microporous, has a low cross-link density, and low percent ring substitution. Resins with a low percent ring substitution are also insensitive to salt concentrations.

(8) Tomoi, M.; Ogawa, E.; Hosokama, Y.; Kakiuchi, H. *J. Polym. Sci.* **1982**, *20*, 3421–3429.

(9) Crank, J. *The Mathematics of Diffusion*; Clarendon: Oxford, 1979; p 90.

(10) The mass transport is not necessarily pure molecular diffusion—thus the use of effective diffusivity. The effective diffusivity of toluene in polystyrene beads with 2% divinylbenzene is estimated to be 1.3×10^{-7} cm^2/s in ref 3. Even though aqueous KCN was used, the GC only analyzed for the water content, and thus the effective diffusivity of the aqueous phase is that of water.

(11) The swelling ratios are 2.2 in toluene and 1.8 in water with 2% divinylbenzene polystyrene.[1d]

(12) All the following rate constants are measured at 90 °C. From ref 1b the organic volume fraction is 0.5 and k^m in (g mol of phosphonium ion)$^{-1}$ s^{-1} is 0.636; from ref 1c the organic volume fraction is 0.4 and k^m is 0.0155; from ref 1d the organic volume fraction is 0.4 and k^m is 0.0105; from ref 6 the organic volume fraction is 0.618 and k^m is 0.0208; and in ref 4a, the rate is from macroporous beads, the organic volume fraction is 0.4, and k^m is 6.85×10^{-3}.

(13) Total catalyst sites by measurement; not equivalent to effective catalyst sites not affected by mass transport effects.

(14) The conventional pseudo-first-order rate constant, k^* (s^{-1}), is proportional to the amount of catalyst used. A more appropriate unit for heterogeneous catalysts is to divide k^* by the molar amount of the quaternary phosphonium ion present, k^m (g mol of phosphonium ion)$^{-1}$ s^{-1}). Regen, S. L. *J. Am. Chem. Soc.* **1976**, *98*, 6270–6274.

(15) The actual location of the maximum rate depends on the particular mixing system, which governs the size distribution of the dispersed phase.

(16) From Figure 3, the rate constant at organic volume fraction 0.1 is 1.47 and at 0.426 is 0.4.