

## Polymer-Bound Catalysts for Acrylonitrile Dimerization

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Alkyl diarylphosphinites bonded to various polymers via the P-O and P-C bonds have been prepared and their catalytic efficiency in acrylonitrile dimerization was investigated. Phosphinites bound to polystyrene-divinylbenzene (1%) copolymer beads via P-C bonds were found to be very effective, selective, and stable catalysts with relatively high turnovers as tested in a flow system. Two synthetic routes have been developed. The first is based on brominated polystyrene which in two steps, reaction with butyl lithium followed by treatment with ethyl arylphosphonochloridite, gives the catalyst in high yield. The second, based on a novel Friedel-Crafts route, gives purer catalysts, requires only  $\text{PCl}_3$  as the source of phosphorus, and is amenable to commercial scale-up. Phosphinites bound to polymer supports via P-O bonds were found unstable or completely inactive. The reasons for the lack of activity in these systems are discussed. © 1987 Academic Press, Inc.

The dimerization of acrylonitrile to a mixture of linear and branched dimers has been studied for many years as a route to adiponitrile for subsequent hydrogenation to the nylon-6,6 monomer, 1,6-diaminohexane. Only the electrochemical hydrodimerization discovered in Monsanto has been practiced commercially (1). However, due to economic factors a facile catalytic process would be more desirable. The first system which partially achieved this goal is hydrodimerization catalyzed by ruthenium-based complexes (2). The main advantage of this catalyst is a high selectivity (~98%) to the linear dimers (*cis*- and *trans*-1,4-dicyanobutene and adiponitrile). However, the reaction must be run in the presence of hydrogen which leads to the formation of propionitrile as the main (minimum 30%) by-product. The stability of this catalyst is low.

The second system for catalytic dimerization of acrylonitrile is based on phosphorus compounds. This work started in the early 1960s in National Distillers, Rhone-Poulenc, and BASF employing ter-

tiary phosphines as the catalysts (3). Despite various modifications of this catalyst, the branched chain dimer, 2,4-dicyanobutene, remained the main product. This drawback has been overcome by the very promising phosphinite-catalyzed dimerization developed recently at ICI (4).

Although catalysts of this structure were synthesized and tested by others as early as 1966, the reaction conditions used did not give high yields of *cis*- and *trans*-1,4-dicyanobutene (linear dimers) (5). In the ICI process, the desired linear dimers are formed in high selectivity along with lesser amounts of 2,4-dicyanobutene (branched dimer) and oligomers. The major drawback of this process is the complicated work-up procedure necessitated by the fact that the catalyst and the products are not easily separated. This requires introduction of costly separation and purification steps. Polymer-bound catalysts could obviate the disadvantages of the homogeneous system.

In this paper we report the synthesis and purification of highly active polystyrene-bound phosphinite catalysts and their utilization in a flow reactor for the dimerization of acrylonitrile. These catalysts retained

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their activity for hundreds of hours when maintained under scrupulously anhydrous and anaerobic conditions and produced linear dimers in high selectivity at moderate conversions. Work-up of the resulting reaction mixtures is exceedingly simple—flash evaporation of the low-boiling reagents leaves only dimeric and oligomeric products, from which the desired dimers can be obtained by vacuum distillation.

## EXPERIMENTAL

### Materials

All solvents were reagent grade. Phosphorus trichloride and high-purity anhydrous aluminum trichloride were used without further purification. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride into a solvent reservoir containing sodium–potassium alloy and a magnetic stirring bar sealed in glass. Reagent-grade toluene, cyclohexane, *o*-xylene, and 1,2,3- and 1,2,4-trimethylbenzenes were distilled and dried over sodium–potassium alloy. Pyridine and 2-propanol were distilled from calcium hydride and stirred over oven-dried 3A molecular sieves. Neopentyl alcohol was sublimed, *t*-butyl alcohol was refluxed for at least 3 h with calcium hydride, and 2,4-pentanediol was stirred at room temperature with bis(2-propyl)-phenyl-phosphonite. These alcohols were then stored over flame-dried 4A molecular sieves.

The styrene–divinylbenzene (1%) copolymer beads (Bio-Beads SX-1, 200–400 mesh) were obtained from Bio-Rad Laboratories. Toyopearl 55 was received as a water slurry in superfine (20–30  $\mu\text{m}$ ) and coarse (50–100  $\mu\text{m}$ ) grades from MCB. Before use it was repeatedly washed with water and acetone and then dried under vacuum at 110°C for at least 24 h.

### Synthetic Methods

All synthetic steps were carried out in H-shaped reactors (Fig. 1), which consist of two chambers separated by a coarse- or

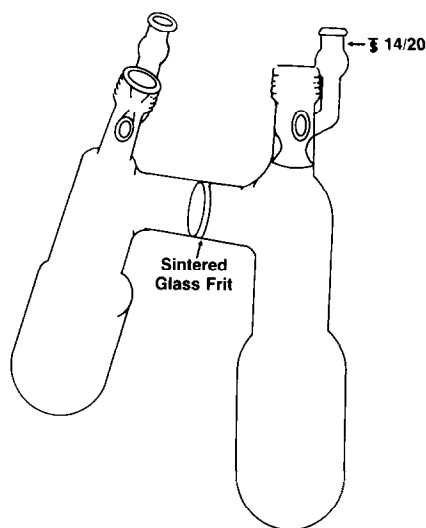


FIG. 1. H-Reactor

medium-porosity sintered glass filter; each chamber was equipped with a high-vacuum stopcock and a standard taper 14/20 glass joint for attachment to a vacuum line. Transfer of liquid to and from the H-reactors was effected either by vacuum transfer or by syringing the liquid through the empty barrel of the vacuum stopcock while a stream of prepurified argon was flowing into the reactor via the 14/20 joint. All transfers of aluminum trichloride, the catalyst intermediates, and final products were carried out in a Vacuum Atmospheres dry box in the complete absence of moisture and oxygen.

Infrared spectra were recorded as KBr pellets on a Nicolet 7199 FT-IR. Phosphorus NMR spectra were collected on either a Varian FT-80A or Varian XL-200 spectrometer; spectra of the polymer beads were taken on suspensions of the beads swollen in dry, degassed dichloromethane and were referenced to external 85% phosphoric acid. Gas chromatographic analyses were performed on a Hewlett–Packard 5880A gas chromatograph using a 1 m  $\times$  3.3-mm Porapak P column.

Elemental maps of the distribution of phosphorus across the catalyst beads pre-

pared by the Friedel–Crafts method were measured by energy dispersive spectrometry (EDS) using a JEOL 840 scanning electron microscope and a Tracor EDS system.

*Trimethylsilyl dibutylphosphinite (6).* A solution of dibutylphosphine oxide (7) (3.3 g, 20.4 mmol) and triethylamine (28 mmol) in dry toluene (20 ml) was treated with a solution of trimethylsilyl chloride (2.22 g, 20.4 mmol) in toluene (5 mmol). The solution became warm and a precipitate began to form. The mixture was then heated at 80°C for 2 h, and filtered and the toluene evaporated. Kugelrohr distillation at 80°C (1.5 mm) afforded the product as a colorless oil, 4.1 g (81%); Ref. (6), bp 99–101°C (12 mm).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 1.8–2.2 (m, 6 H), 1.1–0.7 (m, 3 H), 0.17 (s, 9 H).

Trimethylsilyl diphenylphosphinite was prepared using the same procedure. It was redistilled through a short Vigreux column, bp 111–112°C (0.3 mm); Ref. (6), bp 103–106°C (0.5 mm).

*Preparation of di(p-tolyl)phosphinites.* Ethyl and 2-propyl di(p-tolyl)phosphinites were prepared according to a literature procedure (4f) by the reaction of ethyl or 2-propyl phosphonodichloridite with p-tolyl magnesium bromide in THF. After treatment with pyridine to precipitate the magnesium halide complex, the product was purified by Kugelrohr distillation at 120–125°C (0.1 mm). Ethyl di(p-tolyl)phosphinite was also synthesized from the phosphinous chloride (next entry) by reaction with ethanol and pyridine in ether.

*Di(p-tolyl)phosphinous chloride.* The phosphinous chloride was prepared in small batches, according to the procedure of Montgomery and Quin (8), by stirring di(p-tolyl)phosphine oxide (10 g) with a tenfold excess of phosphorus trichloride for 2 h at room temperature. The solution was filtered under argon, the phosphorus trichloride evaporated on the rotary evaporator, and the residue distilled in a Kugelrohr at 100°C (0.1 mm) affording an 86% yield of the product; Ref. (8), bp 125–128°C (0.21 mm).

*(2-Cyanoethyl)di(p-tolyl)phosphine oxide.* Di(p-tolyl)phosphine oxide (2.3 g, 10 mmol) and acrylonitrile (0.53 g, 10 mmol) were dissolved in ethanol (6 ml) and treated at 2-h intervals with 0.35 ml of 0.9 M LiOEt in ethanol. After stirring overnight, the ethanol was evaporated, the residue dissolved in hexane (50 ml), and filtered, and the hexane evaporated. The oily residue was distilled (Kugelrohr) at 210–215°C (0.1 mm) giving 1.8 g of the product:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 7.8–7.2 (m, 8 H), 2.8–2.5 (m, 4 H), 2.4 (s, 6 H);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 26 ppm.

*Fully phosphinited toyopearl.* A 1.0-g sample of dried coarse Toyopearl (7 meq of OH) was treated with excess di(p-tolyl)phosphinous chloride (2.5 g, 10 mmol) in pyridine (20 ml) in an H-reactor. After 2 days the reaction was stopped. The mixture could not be filtered, so the pyridine was pumped off and dichloromethane distilled in. The polymer was stirred briefly and then filtered. After several more washings with dichloromethane the product was dried on the vacuum line, giving 1.45 g. The phosphorus NMR showed a strong peak at  $\delta$  = 115 ppm.

*Partially phosphinited toyopearl (OH/P) = 15.7.* A 4.0-g sample of coarse Toyopearl (28 meq of OH) was treated with di(p-tolyl)phosphinous chloride (0.44 g, 1.77 mmol) in pyridine (30 ml). The mixture was stirred overnight, filtered under argon, washed with dichloromethane, and dried on the vacuum line, affording 4.35 g of the product. The phosphorus NMR showed a single resonance at  $\delta$  = 115 ppm.

The same procedure was used to make partially phosphinited Toyopearl with OH/P = 3.

*4-(2-Hydroxypropyl)polystyrene.* A 3.0-g sample of brominated polystyrene containing 29% bromine (10.9 mmol of Br) was placed on one side of an H-reactor. Butyl lithium (20 ml, 2.4 M) was syringed into the other side; the hexane solvent was mostly evaporated and replaced by dry toluene (30 ml). The toluene solution was filtered onto

the polymer and the mixture was heated at 60°C for 3 h. The polymer was filtered, the toluene poured off, and fresh toluene distilled in. After several washings the toluene was poured off and the polymer dried. Fresh toluene (30 ml) was distilled onto the polymer followed by propylene oxide (1.1 ml, 15.7 mmol). The mixture was stirred at room temperature for 20 h and then filtered. The solvent was poured off and 2-propanol (20 ml) distilled in. After stirring the polymer was filtered again and then washed in the air with 2-propanol (2 × 100 ml), with 2-propanol containing several drops of concentrated hydrochloric acid (2 × 100 ml), and again with 2-propanol (2 × 100 ml). Drying overnight in a vacuum oven gave 2.5 g of product. Analysis for hydroxyl content gave a value of 3.7 meq of OH per gram of polymer.

*Partially phosphinited hydroxypropylpolystyrene.* A 1.0-g sample of the hydroxypropylpolystyrene (3.7 meq of OH) was treated in an H-reactor with di(*p*-tolyl)phosphinous chloride (0.37 g, 1.49 mmol) in pyridine (15 ml). After 3 days the mixture was filtered and washed with pyridine once and with dichloromethane several times. The dried polymer weighed 0.95 g. Phosphorus NMR showed a single peak at  $\delta = 107$  ppm. Fully or partially phosphinited hydroxypropylpolystyrene was prepared similarly.

*Reaction of ethyl di(p-tolyl)phosphinite with acrylonitrile and 2,4-pentandiol.* Dry 2,4-pentandiol (2 ml) was syringed into a pressure tube and degassed on the vacuum line and then ethyl di(*p*-tolyl)phosphinite (0.5 g) was syringed into the tube under a flow of argon. Toluene (10 ml) and acrylonitrile (3 ml) were distilled in on the vacuum line, the mixture was thawed and stirred, and then a sample was taken under argon and sealed in an NMR tube. The pressure tube and the NMR tube were heated in an oil bath at 60°C. After 3, 20, and 48 h the NMR tube was removed from the bath and the phosphorus NMR spectrum recorded. The initial spectrum

showed three peaks: two at  $\delta = -52$  and  $-53$  (80% of the total) are due to the two cyclic phosphorane diastereoisomers and the other peak at  $\delta = +30$  ppm is due to the tertiary phosphine oxide. No peak was found for the starting phosphinite ( $\delta = 110$  ppm). After 20 h the peaks at high field decreased to about 23% of the area, while the one at  $\delta = 30$  ppm had increased to 77%. After 48 h the conversion was nearly complete. GC analysis of the contents of the pressure tube after 48 h showed only a small amount of acrylonitrile dimers and only a 10% decrease in the acrylonitrile concentration. Distillation of the residue after concentration gave a high-boiling fraction [bp = 210–220°C (0.2 mm), 0.56 g] which was identified by proton, carbon, and phosphorus NMR as (2-cyanoethyl)di(*p*-tolyl)phosphine oxide.

#### *Phenyl Lithium Route*

Brominated polystyrene beads containing 17.1% of bromine (27% of the phenyl rings brominated) were prepared according to a literature procedure (9). The brominated polymer (3.0 g, 6.4 meq of Br) was placed in an H-reactor and degassed. Into the other arm of the reactor was syringed, under a stream of argon, a threefold excess of *n*-butyl lithium in hexane. This was concentrated on the vacuum line to a volume of ~3 ml; then ~20 ml of dry toluene was distilled onto the butyl lithium and 10 ml of toluene onto the polymer. The butyl lithium solution was filtered onto the polymer at  $-78^\circ\text{C}$ , and the mixture was warmed to room temperature and heated in an oil bath at 60°C for 3 h. The suspension was then filtered through the glass frit and part of the toluene redistilled back onto the side of the polymer. After brief stirring and filtering again, the toluene was poured off under a stream of argon. Fresh toluene (~25 ml) was distilled onto the polymer, the mixture stirred for a few minutes and filtered, and the toluene poured out under a stream of argon. Fresh toluene (25 ml) was again distilled onto the polymer, and the mixture

was cooled to 0°C and treated via syringe with 2 to 3 eq of ethyl *p*-anisylphosphonochloridite or ethyl *p*-tolylphosphonochloridite, prepared by the method of Steinger (10). The reaction mixture was warmed to room temperature and stirred for 1 h. It was then filtered through the frit and some of the toluene distilled back onto the polymer. This was stirred briefly and filtered again, and then the toluene was poured off under argon. The polymer was washed repeatedly with THF and with THF : isopropanol (1 : 1) in order to remove all traces of base, lithium chloride, and unreacted phosphorus reagent.

Elemental analysis of a product from ethyl *p*-tolylphosphonochloridite gave C, 83.2; H, 7.90; P, 4.32; Br, 0.11. It was calculated for complete replacement of Br with *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>P(OEt): C, 81.0; H, 8.09; P, 5.3. The <sup>31</sup>P NMR spectrum showed a peak (~80% of the total area) centered at about  $\delta = 110$  ppm, a minor peak at  $\delta = -18$  ppm (tertiary phosphine), and two minor peaks between  $\delta = 20$  and 40 ppm (phosphorus (V) species). Similar results were obtained with the *p*-anisyl analog.

#### *Friedel-Crafts Route*

*Preparation of polymer-bound phosphonous dichloride.* In a typical reaction, 6 g (57.6 mmol of phenyl rings) of Bio-Beads and 1.92 g (14.4 mmol) of aluminum trichloride were placed in one side of a large H-reactor. Phosphorus trichloride (90 ml) was syringed into the other side of the reactor, degassed, and filtered through the glass frit onto the polymer. A condenser equipped with an argon bubbler was attached to a side-arm of the reactor and after the polymer was allowed to swell for about 15 min, the vessel was heated in an oil bath at 60°C for 3 h. After cooling, the mixture was filtered through the frit and the PCl<sub>3</sub> was poured out under a stream of argon. The reactor was attached to a vacuum line and approximately 70 ml of dry THF was distilled onto the polymer. The mixture was stirred for a few minutes and then filtered

through the frit. The THF was distilled back onto the polymer and the stirring and filtration repeated. This procedure was repeated once more, and then the THF was poured out of the reactor under a stream of argon. A fresh batch of THF (50–70 ml) was distilled onto the polymer and the washing procedure was repeated three times. The washing was repeated with a third fresh batch of THF, after which the polymer was dried thoroughly on the vacuum line. The washing and drying procedure effectively removes all but traces of the aluminum and phosphorus trichloride.

The <sup>31</sup>P NMR showed a single peak at  $\delta = 162$ . This procedure afforded a polymer with about 25% of the rings substituted with phosphorus. The level of substitution was determined by stirring a 100-mg sample of the polymer with dilute nitric acid for 1 h. Then the liberated chloride was titrated with silver nitrate using a chloride-specific electrode. Equivalents of phosphorus were assumed to be one-half that of chloride.

*Preparation of polymer-bound phosphinous chloride.* The polymer-bound phosphonous chloride (6 g, 11.6 mmol phosphorus) and AlCl<sub>3</sub> (2.63 g, 19.7 mmol) were loaded into an H-reactor in the dry box. The reactor was attached to the vacuum line and about 90 ml of *o*-xylene was syringed into the empty side of the H-reactor under a stream of argon. The xylene was degassed and filtered onto the polymer, and then the reactor was heated in an oil bath at 100°C for 1 h. After cooling, the mixture was filtered through the glass frit and the xylene poured out under a stream of argon. THF (ca. 50 ml) was distilled onto the polymer and the washing procedure described in the preceding example was repeated. After removing the final batch of THF, the polymer was thoroughly dried on the vacuum line. Phosphorus NMR showed a single resonance at  $\delta = 84$  ppm.

*Hydrolysis of polymer-bound phosphinous chloride.* A sample of the polymer-bound phosphinous chloride (1.5 g, 2.55 mmol phosphorus) was placed in a large

H-reactor and THF (35 ml) was distilled in on the vacuum line. Under a stream of argon, 35 ml of degassed, deionized water was syringed onto the polymer suspension while it was still cold. The mixture was allowed to warm to room temperature, stirred for 2 h, and filtered, and the filtrate poured off under argon. Fresh THF (35 ml) was distilled onto the polymer and degassed; deionized water (35 ml) was syringed into the mixture. The resulting suspension was stirred for 15 min and filtered, and the liquid poured off under argon. The polymer was washed with three batches of fresh THF (only once with each) and then dried on the vacuum line overnight. The decoupled phosphorus NMR showed a singlet for the phosphine oxide at  $\delta = 20$  ppm; the proton-coupled spectrum showed a 1:1 doublet with  $J_{P-H} = 501$  Hz.

*Regeneration of polymer-bound phosphinous chloride.* The polymer-bound phosphine oxide (1.5 g, 2.6 mmol) was placed in an H-reactor and  $\text{PCl}_3$  was added to the other side under a stream of argon, degassed, and filtered onto the polymer. The mixture was stirred for 1 h at room temperature and filtered, and the  $\text{PCl}_3$  redistilled back onto the polymer. The mixture was stirred an additional 15 min and filtered, and the  $\text{PCl}_3$  poured off under argon. The polymer was washed with three batches of THF (20 ml, once with each), and then dried on the vacuum line. Phosphorus NMR showed a single peak at  $\delta = 84$  ppm relative to external  $\text{H}_3\text{PO}_4$ .

*Preparation of polymer-bound phosphinite.* The regenerated polymer-bound phosphinous chloride (1.5 g, 2.55 mmol) was placed in an H-reactor, and then THF (30 ml) and pyridine (4 ml) were distilled in on the vacuum line. This suspension was stirred at room temperature for  $\frac{1}{2}$  h. 2-Propanol (4 ml) was distilled into the other side of the reactor and then warmed gently so that it slowly distilled through the frit into the polymer suspension, which was maintained at  $0^\circ\text{C}$ . After distillation was complete, the mixture was allowed to warm

to room temperature and stirred an additional hour. The mixture was filtered and the liquid poured off under argon. The polymer was then washed with three batches of a THF:2-propanol mixture (1:1, ca. 25 ml), three times with each, and then dried on the vacuum line. Phosphorus NMR showed a single resonance at  $\delta = 106$  ppm.

*Preparation of polymer-bound phosphonite.* Polymer-bound phosphonous dichloride bearing about 50% of the rings substituted was prepared in the manner described above, except that the amount of aluminum chloride employed was twice as much per gram of polymer. This material (3 g, 9.7 mmol of P) was placed in an H-reactor, and then THF (50 ml) and pyridine (5 ml) were transferred onto the polymer on a vacuum line. The suspension was stirred at room temperature for about 1 h to allow the polymer to swell fully, and then 2-propanol (5 ml) was distilled into the other arm of the reactor. The polymer suspension was cooled to  $-30^\circ\text{C}$  and the 2-propanol warmed gently so that it distilled into the side containing the polymer. After distillation was complete, the mixture was allowed to slowly warm to room temperature and stirred for an additional 1.5 h. The mixture was filtered and the liquid poured off under argon. Then the polymer was washed three times each with three separate batches of a THF:2-propanol mixture (1:1, ca. 50 ml), and dried on the vacuum line. Although the  $^{31}\text{P}$  NMR showed this material to be mainly the desired phosphonite, it proved to have residual aluminum impurities that rendered it useless as a drying agent. Consequently, it was treated as described below.

The polymer-bound phosphonite (3.65 g, 10.2 mmol) was placed in an H-reactor and THF (35 ml) was distilled in. To this cold suspension 35 ml of a mixture of 1 N aqueous HCl/2-propanol (10/25) was added via syringe under argon. This mixture was then degassed and allowed to stir at room temperature for 2 h and filtered, and the

liquid poured off under argon. An additional 35 ml of THF was distilled in, and then 35 ml of distilled water (degassed) was added via syringe. After stirring at room temperature for 1 h, the mixture was filtered, the filtrate poured off under argon, and the polymer washed with three batches of THF (40 ml, once with each). After drying on the vacuum line, phosphorus trichloride (90 ml) was added to the other side of the reactor, degassed, and poured onto the polymer. The mixture was stirred at room temperature for 1 h and filtered, and the  $\text{PCl}_3$  distilled back onto the polymer. After stirring for an additional 15 min, the mixture was filtered, the  $\text{PCl}_3$  poured off, and the polymer washed with three batches of THF (40 ml, once with each). The polymer was then dried on the vacuum line and the phosphonite prepared again using the same procedure as in the preceding paragraph. The phosphorus NMR showed two resonances in about a 3:1 ratio. The major peak at  $\delta = 156$  ppm is due to the desired phosphonite, while the minor peak at  $\delta = 21$  ppm is due to a P(V) species, perhaps the phosphinate.

#### Acrylonitrile Dimerization

**Batch reactor.** Batch dimerization runs were carried out in heavy-walled glass reactors equipped with a vacuum stopcock and 14/20 joint for connection to a vacuum line. In a typical experiment, 500 mg of catalyst beads (0.8 mmol of phosphorus for Structure 1, ArH = di- or trimethylbenzenes, 0.55 mmol for Structure 1, Ar = *p*-anisyl) was placed in the reactor, and then the following dry reagents were distilled in on a vacuum line: toluene (9 ml), acrylonitrile (3 ml), 2-propanol (1 ml), and cyclohexane (internal standard, 0.80 g, accurately weighed). The mixture was sampled via syringe for GC analysis, and then the stopcock was sealed and the reactor heated in an oil bath at 60°C. At appropriate intervals, the reactor was removed from the bath, cooled to room temperature, and

sampled under a stream of argon. Conversion and selectivity were determined from the peak areas relative to cyclohexane using response factors determined separately.

**Dimerization using fully phosphinited toyoppearl and neopentyl alcohol.** A dimerization reaction was carried out in the usual way using the fully phosphinited Toyoppearl as the catalyst and neopentyl alcohol as a replacement for 2-propanol. After 20 h the reaction mixture was analyzed. Conversion was 90% with 90% selectivity to *cis*- and *trans*-1,4-dicyanobutenes. The catalyst beads were filtered off, the filtrate was concentrated, and  $^{31}\text{P}$  NMR was obtained. The spectrum showed several peaks, the major ones being at  $\delta = 112$  ppm, due to neopentyl di(*p*-tolyl)phosphinite, and at  $\delta = 29$  ppm, due to 2-cyanoethyl-di(*p*-tolyl)phosphine oxide. The NMR spectrum of the recovered polymer beads showed no presence of polymer-bound phosphorus.

**Dimerization in the presence of toyoppearl catalyzed by soluble phosphinite.** A dimerization reaction was carried out in the usual way except that the 2-propanol was replaced with 1.0 g of dried Toyoppearl and the catalyst was ethyl di(*p*-tolyl)phosphinite (0.10 ml). After 21 h at 60°C the reaction mixture was analyzed. Conversion was only 39% and selectivity to dicyanobutenes was 19%; with 2-propanol replacing the Toyoppearl, these conditions would give greater than 90% conversion and greater than 80% selectivity.

**Flow reactor.** The apparatus for the flow acrylonitrile dimerization runs is schematically depicted in Fig. 2. Flasks A and B were fabricated to our specification by a glassblower. Flask A was used for collecting all components of the reaction mixture on a vacuum line and for its transfer into flask B which served as a reservoir for the flow system. In this reservoir the reaction mixture was kept under argon atmosphere. An in-line 5- $\mu\text{m}$  stainless-steel filter removed all small dust particles and allowed a flawless performance of the Milton

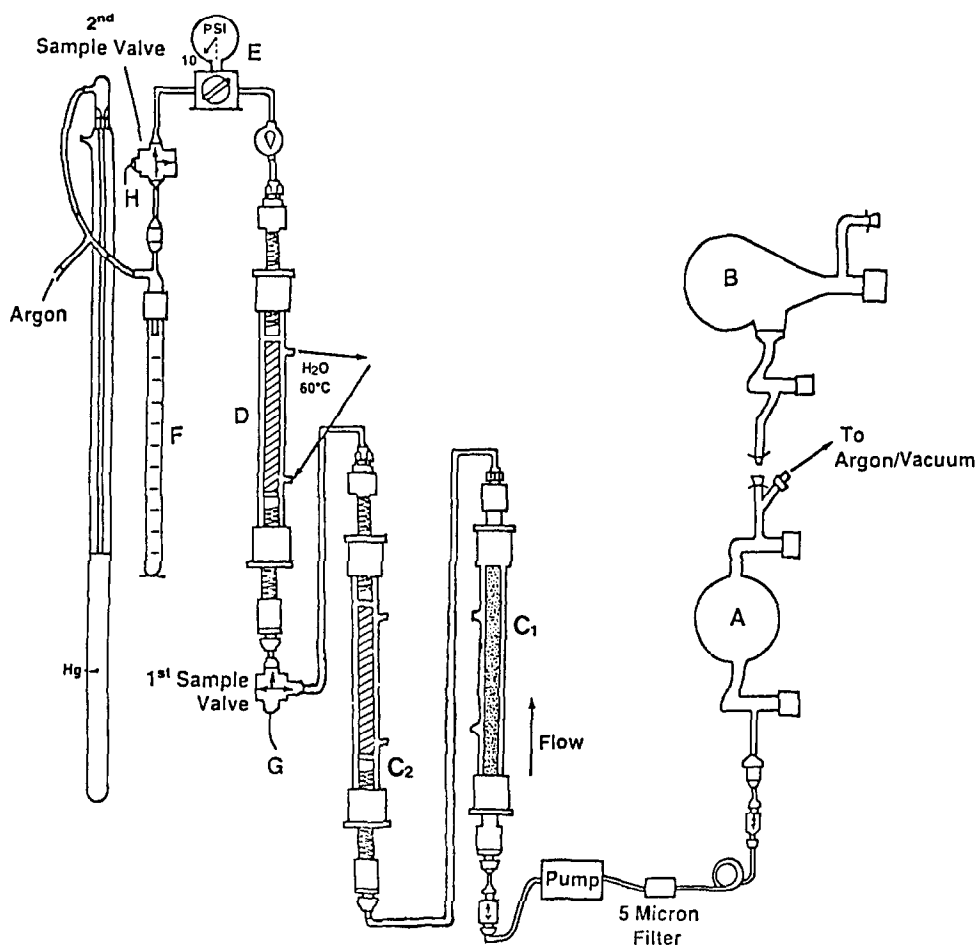


FIG. 2. Flow reactor scheme. (A) Reagent reservoir, (B) reagent flask for collection of the reaction mixture components on a vacuum line and for transfer of the reaction mixture into the reagent reservoir, (C<sub>1</sub>) molecular sieves column, (C<sub>2</sub>) polymer-bound phosphonite column, (D) reactor containing the polymer-bound catalyst, (E) pressure gauge, (G and H) valves for removal of analytical samples.

Roy Model NC1-1105 minipump. Next in line were placed three water-jacketed chromatographic columns (30 × 0.9 cm) with an adjustable length of Teflon plungers. These columns contained 3A molecular sieves (10 g), polystyrene-bound phosphonite (2 g, drying agent), and the polymer-bound phosphonite catalyst (2 g). The columns were connected with Teflon-lined aluminum tubing to prevent oxygen permeation. Valves at either end of the columns provided a means of isolating the contents from the atmosphere after charging the columns in a dry box. They also allowed

sampling of the reaction mixture before and after every column. Downstream from the reactor (the last column) were a pressure gauge and a receiver connected to a mercury bubbler which allowed pressurization of the system to ~7 psi (48.3 kPa). This slight pressure prevented formation of bubbles of acrylonitrile vapors in the reactor. The first two columns containing the molecular sieves and the polymer-bound phosphonite were kept at room temperature. The reactor was heated to 60°C by circulating water from a constant temperature bath.



*Analytical methods in the flow system.* Approximately 100-ml samples were collected in the receiver and analyzed. Conversion of acrylonitrile was determined by GC analysis using cyclohexane as the internal standard which was added to the reaction mixture. The collected portions of the reaction mixture were concentrated on the rotary evaporator at 35°C and 1 mm Hg. The residue (R) contained no acrylonitrile and was entirely composed of products derived from acrylonitrile, i.e., dimers, trimers, and higher oligomers. This residue was then subjected to Kugelrohr distillation at 75–85°C and 0.1 mm Hg. This distillate consisted of only acrylonitrile dimers, *cis*- and *trans*-1,4-dicyanobutenes (DCB), and 2-methyleneglutaronitrile (MGN). The selectivity to total dimers  $S_d$  can be expressed as

$$S_d = \frac{[(\text{weight of distillate})]}{(\text{weight of the residue R})}.$$

The mixture of dimers was then analyzed by GC for determination of the selectivity to linear DCB and branched MGN dimers. The overall selectivity to linear dimers (*cis* and *trans*)  $S_{ld}$  based on consumed acrylonitrile is then equal to

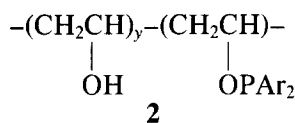
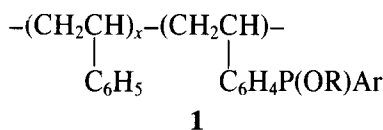
$$S_{ld} = \frac{(S_d \times \text{DCB})}{(\text{weight of the distillate})}.$$

Gas chromatographic analyses were performed with a Porapak P column and a temperature program starting at 60°C, increasing 8°C/min for 4 min, then increasing 30°C/min to 240°C and holding this final temperature for 8 min.

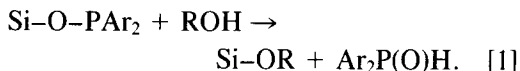
## RESULTS AND DISCUSSION

### *Choice of Catalyst Support*

The phosphorus atom in the polymer-bound phosphinites can be bonded to the support (as random copolymers) via either P–C (e.g., Structure 1) or POC (e.g., Structure 2) bonds. We have examined both options.



*Oxygen-bound phosphinites.* Inorganic supports such as high-surface alumina, silica, titania, etc. do contain appreciable amounts of surface hydroxyl groups. These have been used very successfully for bonding of various functional groups to these inorganic supports. However, media suitable for acrylonitrile dimerization require the presence of aliphatic alcohols. In these media silica- and alumina-bound phosphinites have been found inactive (4a). This agrees with our observation that silyl phosphinites  $\text{Ph}_2\text{POSiMe}_3$  and  $\text{Bu}_2\text{POSiMe}_3$ , model compounds for silica-bound phosphinites, did not catalyze acrylonitrile dimerization. Instead they underwent easy conversion to P(V) species:

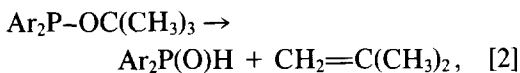


Esterification of organic polymers containing pendant hydroxyl groups by treatment with readily available diarylphosphinous chlorides appeared to offer an easy, one-step synthesis of polymer-bound phosphinites. On hydrolysis these catalysts should regenerate the starting support. Therefore, their recycle should be facile. However, alcohols needed in the reaction mixture may also cause transesterification of the polymer-bound catalysts which leads to the formation of the virgin polymer support with pendant hydroxy groups and of soluble alkyl phosphinites. Therefore, use of sterically hindered alcohols would be necessary. One could also speculate that, if only a portion of the hydroxyl groups on the polymer is converted to phosphinite, the remaining hydroxyl groups might function as the required alcohol component.

This would not only solve the problem of possible transesterification, it would also substantially simplify the system. Because of the potential attractiveness of hydroxyl-containing polymer supports, we undertook careful investigation of both options.

Two polymeric supports were chosen. One is Toyopearl 55, a commercially available polymer for gel permeation chromatography. Although the manufacturer will not reveal the nature of the polymer, it appears to be crosslinked and partially hydrolyzed polyvinyl acetate. It contains 7 meq of hydroxy groups per gram of dry polymer. The second polymer is a styrene-divinylbenzene(1%) copolymer in which some of the pendant phenyl groups are substituted in the *para* position by 2-hydroxypropyl groups. It contains 3.7 meq of hydroxyl groups per gram of dry polymer. All the hydroxyl groups present in the above polymers were reacted with di(*p*-tolyl)phosphinous chloride. The  $^{31}\text{P}$  NMR demonstrates that at least 95% of the phosphorus is present as phosphinite. These catalysts have been tested in a standard batch reactor using *t*-butyl and neopentyl alcohols instead of 2-propanol.

When *t*-butyl alcohol is used with either catalyst no acrylonitrile dimers are produced; the phosphorous is removed from the polymer support and is converted into soluble P(V) species. A model reaction using ethyl di(*p*-tolyl)phosphinite in combination with *t*-butyl alcohol revealed gradual degradation of the homogeneous catalyst due to the formation of an inactive phosphine oxide (Eq. [2]). In the presence of neopentyl alcohol,



some very selective dimerization takes place, but this was shown to be entirely due to transesterification, which produces soluble neopentyl di(*p*-tolyl)phosphinite. These results demonstrated that the transesterification cannot be avoided. Conse-

quently, we turned to partially phosphinited polymer supports.

Acrylonitrile dimerizations in the presence of homogeneous catalysts are carried out with a molar ratio of alcohol to phosphinite to about 35:1. This ratio, if preserved in the case of polymer-bound catalysts, would result in a very low phosphinite content. We, therefore, carried out a set of homogeneous dimerizations using various ratios of 2-propanol to ethyl di(*p*-tolyl)phosphinite. The results in Table 1 show that a molar ratio of at least 15 is required for good conversion and selectivity to the linear dimers. Accordingly, we have prepared Toyopearl and styrene-divinylbenzene (1%) copolymer, modified by 2-hydroxypropyl groups, in which only 5–6% of the present hydroxy groups is converted to the corresponding phosphinites. Dimerization runs carried out with these polymers in the absence of alcohol gave no reaction after 24 h in the case of polystyrene and only 11% conversion and 37% selectivity in the case of Toyopearl. This should be compared with 30% conversion and 90% selectivity in 3 h using equimolar amounts of soluble phosphinite. No acrylonitrile dimer formation was observed when phosphinited polymers with a free OH to P ratio of 2.5 were used.

TABLE I

Dimerization Run with Varying Ratio of OH/P <sup>a</sup>				
2-Propanol (ml)	OH/P	Time (h)	Percentage conversion	Percentage selectivity
0.10	3.5	24	45	45
0.25	8.8	3	<5	—
		24	33	50
0.40	14	3	18	(62) <sup>b</sup>
		24	72	78
0.50	18	3	18	(66) <sup>b</sup>
		24	72	89
1.00	35	3	30	90
		24	87	87

<sup>a</sup> 60°C. Typical composition of the reaction mixture: 9 ml of toluene, 3 ml of ACN, 1 ml of cyclohexane, ~1 g of hexamethylbenzene, 0.37 mmol of ethyl di(*p*-tolyl)phosphinite. Cyclohexane and hexamethylbenzene are employed as internal standards for GC.

<sup>b</sup> Selectivities at low conversion less accurate.



from the Arbuzov-type rearrangement to phosphinates during the reaction. Phosphonous dichlorides proved to be too reactive and produced crosslinked resins containing large amounts of tertiary phosphines due to reaction with two different lithiated phenyl rings of the polystyrene support. With phosphonochloridous esters, ~80% of the phosphorus incorporated into the polymer is in the desired form. Elemental analyses suggest that ~90% of the amount of phosphorus expected for the case of complete replacement of the bromine is present in the polymer. The most effective catalysts contain about 25% of the phenyl groups of the support substituted with phosphinites. This route gives consistent results and is suitable for laboratory conditions. The disadvantage of this synthesis is the need for preparation of phosphonochloridous esters, an excess of butyl lithium, and an inability to produce catalysts completely free of tertiary phosphine and P(V) species. The presence of the tertiary phosphine suggests crosslinking via C–P–C bonds and could decrease the selectivity to the desired linear acrylonitrile dimer. The P(V) species do not affect the selectivity of the dimerization but decrease the specific activity of the catalyst. Therefore, a more practical route leading to purer catalyst has been examined.

*Friedel–Crafts route.* Only the reaction of polystyrene with phosphorous trichloride in the presence of aluminum trichloride has been described in the literature. However, the product, phosphonous dichloride, has been isolated only in one case (11). In all other cases the product was oxidatively hydrolyzed to phosphonic acid. Our procedure appears to be superior.

Polystyrene beads are treated with a large excess of phosphorus trichloride in the presence of various amounts of aluminum trichloride. The extent of ring substitution is very well regulated by the molar ratio of aluminum trichloride to phenyl rings. For ratios of less than ~0.7 the fraction of the ring substituted corresponds approximately to that ratio. Thus using 0.25

eq of aluminum trichloride gives polymers with 22 to 28% of the rings substituted by  $-\text{PCl}_2$  groups. Polymers with up to 80% of the rings substituted can be prepared with higher ratios of aluminum trichloride.

Synthesis of diarylphosphinous chlorides by a Friedel–Crafts method is not straightforward. Two types of approaches are reported in the literature. Diarylation of phosphorus trichloride in the presence of aluminum chloride does not go to completion and the product is not readily separated from its aluminum chloride complex; disproportion of an arylphosphonous dichloride in the presence of catalytic quantities of either aluminum chloride or zinc chloride requires high temperatures (~200°C) and gives poor to moderate yields (12). Neither of these approaches appears applicable to the synthesis of polystyrene-bound phosphinites. We decided to attempt the arylation of the polystyrene-bound phosphonous dichloride in the hope that the insolubility of the polymer would enable us to remove the aluminum or zinc salts.

Anisole cannot be employed as the arene in the Friedel–Crafts reaction since conditions stringent enough to effect the reaction invariably cleaved the  $\text{CH}_3\text{--O}$  bond. Accordingly, this approach was abandoned in favor of alkyl-substituted arenes.

After 1 h at 100°C in an excess of 1,2,3-trimethylbenzene and in the presence of 1.7 eq of  $\text{AlCl}_3$  per equivalent of P, the polymer-bound phosphonous dichloride is quantitatively converted into the corresponding polymer-bound diarylphosphinous chloride as shown by the presence of a single  $^{31}\text{P}$  NMR peak at  $\delta = 86$  ppm. Lower temperatures or smaller quantities of aluminum chloride lead only to a partial conversion even after prolonged reaction times. These conditions work equally well for 1,2,4-trimethylbenzene and *o*-xylene.

Extensive washing of the polymer-bound phosphinous chloride with anhydrous THF removed most of the aluminum chloride. The remaining aluminum content was in the range of 200–1000 ppm. Treatment of the

washed polymer with an excess of 2-propanol and pyridine in THF, followed by thorough washing with a THF/2-propanol mixture to remove pyridine hydrochloride, gave the desired polymer-bound phosphinite. The  $^{31}\text{P}$  NMR spectrum of the product showed a peak at  $\delta = 105$  ppm, as expected for alkyl diarylphosphinite. A second peak at  $\delta = 32$  ppm was invariably present in the range of a few percent of the phosphinite peak. This peak corresponds to a tertiary phosphine oxide, which is formed by an Arbuzov rearrangement of the phosphinite, probably catalyzed by the residual aluminum species.

Despite the fact that, as judged by  $^{31}\text{P}$  NMR, the best polymer-bound phosphinites, prepared by the Friedel–Crafts method, were of better purity than those prepared by the phenyl lithium route, they proved to be very poor acrylonitrile dimerization catalysts. The phosphorus (III) species in these catalysts were, after a few hours in the dimerization mixture, completely rearranged into inactive phosphorus (V) compounds. We suspected that this is caused by the small amounts of residual aluminum species (200–1000 ppm) left in the polymer-bound catalysts. In these first catalysts, prepared by the Friedel–Crafts route, ~75% of the polystyrene phenyl groups carried the phosphinite functions and they swelled much less than the catalysts prepared via phenyl lithium route with ~25% of phosphorus loading. This lack of swelling could contribute to the difficulty in removing the last traces of aluminum compounds. Nevertheless despite their increased swellability, removal of the aluminum residues from the catalysts with 25% loading did not improve and they underwent deactivation during attempted acrylonitrile dimerization reactions. The aluminum content and the activity of the catalysts did not improve even after numerous washings of the intermediate polymer-bound phosphinous chloride with various coordinating solvents or their mixtures with dry HCl. This led us to a conclusion that

the remaining aluminum species are of an oligomeric nature with chains containing Al–O–Al bonds and that they may be removed only by reaction with aqueous HCl. Indeed, treatment of the polymer-bound phosphinous chloride with a mixture of THF and 1 *N* aqueous HCl or a mixture of THF and water (which liberates HCl) yielded diarylphosphine oxide,  $^{31}\text{P}$  NMR of which showed a doublet centered at  $\delta = 20$  ppm ( $J_{\text{P-H}} = 501$  Hz). Reaction of the polymer-bound phosphine oxide with phosphorus trichloride regenerates the phosphinous chloride. In sharp contrast to soluble compounds, these reactions on the polymer-bound systems proceed cleanly and quantitatively. Esterification with a 2-propanol/pyridine mixture afforded the desired polymer-bound phosphinite in high purity. These pure phosphinites proved to be excellent catalysts for the dimerization of acrylonitrile.

*Acrylonitrile dimerization.* Catalytic activity of the prepared catalysts was first tested in a batch reactor. Two best catalysts, one prepared via the phenyl lithium route and the second prepared by the Friedel–Crafts route, were then tested in a flow system with the aim to evaluate long-term stabilities and selectivities.

*Batch reactor system.* Representative results summarized in Table 2 demonstrate that the polystyrene-bound phosphinites are effective catalysts for the acrylonitrile dimerization, giving high conversions and acceptable yields. Comparison of the data in the Table 2 leads to several conclusions.

The homogeneous catalysts carrying similar substituents on their aryl groups (Table 2, entries 1 and 7) are more active than their polymer-bound analogs. This may suggest dependence of the acrylonitrile dimerization rates on the rate of acrylonitrile diffusion into the polymer beads. Indeed, this is an important factor in the case of catalysts, prepared by the Friedel–Crafts route, in which more than 30% of the pendant phenyl rings are substituted by the phosphinite groups. In these catalysts

TABLE 2  
Activity of Various Catalysts in Batch Reactor

Entry	Catalyst (mmol)	Conversion	
		3 h	24 h
1	Homogeneous ( <i>p</i> -tolyl) <sub>2</sub> POEt (0.4)	30	88
	Polymer-bound ArH = <i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> (0.22)		
2	(0.55)	20	76
3	ArH = 1,2,3-trimethylbenzene (0.80) <sup>b</sup>	46	82 <sup>a</sup>
4	(0.80) <sup>c</sup>	36	91
5	ArH = 1,2,4-trimethylbenzene (0.80) <sup>b</sup>	20	55
6	ArH = <i>o</i> -xylene (0.80) <sup>b</sup>	15	—
7	(0.80) <sup>b</sup>	39	90

<sup>a</sup> After 12 h.

<sup>b</sup> The ratio of possible isomers is not known since <sup>31</sup>P and <sup>13</sup>C NMR give relatively broad peaks. Correspondingly, only the arene reacted with polymer-bound phosphonous chloride is shown.

<sup>c</sup> Phosphorus is bound to 46% of the polystyrene phenyl groups.

swellability as well as activity per mole of phosphorus decreases proportionately to the phosphorus content in the beads. The observed dependence of the catalyst beads' swellability on the phosphorus loading may be caused by crosslinking in the aluminum trichloride moderated reaction of the polymer-bound phosphonous dichloride with the added arene. At a higher local phosphorus concentration the less reactive pendant phenyl groups of polystyrene can compete with the more reactive xylene or 1,2,3-trimethylbenzene because the concentration of these arenes in the polymer beads is limited by their rate of diffusion. The extent of crosslinking is substantially reduced by preswelling of the beads with the arene. However, at higher phosphorus loading it cannot be completely eliminated.

Activity of the polymer-bound phosphinites per mole of phosphorus reaches its maximum at ~25% substitution of the pendant phenyl rings by the phosphinite groups. This corresponds to Structure 1 in which the average value of *x* is 3, although we know nothing about the actual distribution of phosphorus along the polystyrene chain. The catalysts with this relatively low

phosphorus loading are highly swellable, increasing their volume by a factor of about 6 when immersed in the reaction medium at room temperature. The catalysts prepared by the phenyl lithium route, where no or very low crosslinking is expected, exhibit the same swellability. Dimerization reactions catalyzed by both types of catalyst (Ar = xylyl or *p*-anisyl) appear to follow first-order kinetics in respect to the phosphorus concentration as is the case with their homogeneous analogs (4). These observations demonstrate that the catalysts with 25% and lower substitution are not affected by the rate of acrylonitrile diffusion into the catalyst beads. The distribution of phosphorus throughout the polystyrene beads is very uniform. Figure 3 shows an energy dispersive spectrometry map of a cross section of one of the beads; although the amount of phosphorus incorporation varied slightly from bead to bead, the loading across a single bead is remarkably constant. We have previously shown that the distribution of bromine in the polystyrene beads used for the aryl lithium route is also uniform across the bead (9).

Activity of the soluble phosphinites is strongly dependent on the ratio of alcohol to hydrocarbon cosolvent (Table 1). The slightly lower activity of the highly swellable catalysts may then be explained by a less polar, hydrocarbon-like environment in the polymer beads. The activity of the polymer-bound catalysts increases with increasing electron-donating power of the

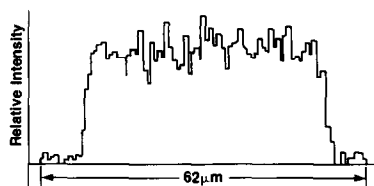


Fig. 3. Energy dispersive spectrometry map of the phosphorus distribution in a cross section of a polystyrene bead prepared by the Friedel-Crafts method. The phosphine oxide, P(V), stage of the synthesis was examined.

aryl substituents (anisyl vs xylyl, entries 3 and 7 in Table 2). The same dependence in a much more extended series has been also observed in the case of soluble phosphinite catalysts (4c,e).

The presence of an *ortho* substituent next to the phosphorus decreases the activity of the resulting catalysts. Thus, the catalyst containing 1,2,3-trimethylbenzene is about twice as active as the polymer-bound phosphinite based on 1,2,4-trimethylbenzene (Table 2, entries 4 and 6). This is apparently caused by the inevitable presence of an *ortho* methyl group in the latter catalyst, a situation which can be avoided in the catalyst based on 1,2,3-trimethylbenzene.

The selectivity to the formation of the linear *cis*- and *trans*-1,4-dicyanobutenes is slightly lower (85–90%) for the polymer-bound catalysts than for the soluble phosphinites (90% and higher). This can be attributed to a slightly higher formation of oligomers rather than to an increase in the formation of the branched 2,4-dicyanobutene dimer. This result is not surprising since the same phosphinite which catalyzes dimerization of acrylonitrile also catalyzes conversion of dimers into higher oligomers. Thus, the increased tendency of the oligomer formation can possibly be attributed to a high local concentration of the phosphinite and the acrylonitrile dimers in the catalyst beads.

#### Flow Reactor System

Representative results obtained with the catalysts prepared by both synthetic routes are summarized in Fig. 4. The catalysts in the swollen form are very sensitive to water and oxygen. Therefore, drying and degassing of all components of the reaction mixture are prerequisites to a successful run. For these reasons the components of the reaction mixture were dried, degassed, and collected in one flask on a vacuum line. In the first run (Ar = *p*-anisyl) the phosphonite column was not used. Instead, small amounts of di(2-propyl)-phenylphosphonite (0.04%) were added to the reaction mixture

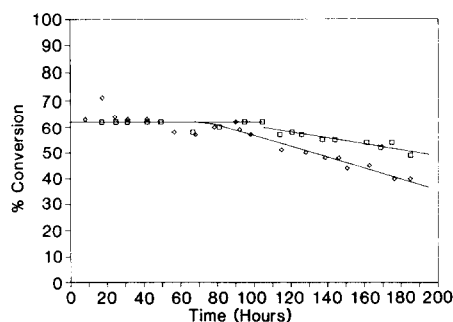


Fig. 4. Conversion of acrylonitrile as a function of time. The reactor was heated to 60°C, pressure was kept at 7 psi (48.3 kPa), and the reaction mixture was pumped at a rate of 7.7 ml/h; (□) 2 g of Structure 1 (Ar = xylyl), 3.2 mmol of P; (◇) 2 g of Structure 1 (Ar = *p*-anisyl), 2.2 mmol of P in the form of phosphinite.

as a drying and deoxygenating agent. Unfortunately, this caused the formation of very small amounts of an acrylonitrile hexamer which tends to precipitate in the critical points of the flow system such as pump check valves. This resulted in numerous exposures of the system to the open atmosphere. Despite these difficulties the conversion of acrylonitrile decreased from 63% at the start to only 45% after 185 h of operation at which time we elected to terminate the run. During this time 1400 ml of the reaction mixture was pumped through the catalyst bed containing 2.2 mmol of phosphinite in 2 g of the catalyst; 110 g of acrylonitrile was converted into the linear dimers at a selectivity of 84%, which remained constant during the run.

In the second run, the catalyst of Structure 1 (ArH = xylene) prepared by the Friedel–Crafts route was tested. In this case polymer-bound phosphonite (Fig. 2, column C<sub>2</sub>) kept at room temperature was used as an oxygen scavenger and a drying agent. The test lasted 216 h. During this time 1700 ml of the reaction mixture was passed through the reactor containing 3.2 mmol of phosphinite in 2 g of the catalyst and 151 g of acrylonitrile was converted to dimers at a selectivity of 86% to the linear dimers. Again, the selectivity remained

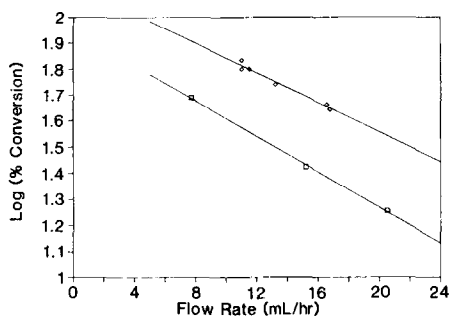


Fig. 5. Dependence of conversion on the flow rate. The acrylonitrile dimerization was carried out at 60°C, 10 psi (69 kPa) with 3.2 mmol of P; (□) Structure 1 (Ar = xylyl), (◇) Structure 1 (Ar = *p*-anisyl).

constant throughout the run. The conversion was constant at 62% for the first 100 h at which time the phosphonite column became exhausted. After switching to a second phosphonite column the conversion started to decrease gradually till it reached 50% after 185 h. During the remaining time of the test the effect of the flow rate on the conversion was examined.

Results summarized in Fig. 5 show that in the flow system the rate of acrylonitrile dimerization follows a first-order dependence on the polymer-bound phosphinite. Furthermore, the activity of Structure 1 (Ar = *p*-anisyl) is 1.9 times higher than that of Structure 1 (Ar = xylyl), which is in agreement with the relative reactivities found for the same catalysts in the batch reactor and with the effect of substituents observed in the case of homogeneous catalysts (4). This again strongly suggests that, at least in the range of the tested flow rates, the reaction rate is not limited by the rate of the reagent diffusion into the polymer beads.

#### Mechanism of Acrylonitrile Dimerization

With the limited information available at this time the mechanism of acrylonitrile dimerization can be represented by Scheme 1. Phosphorane (Structure 4, Scheme 1) is the main and relatively stable product when acrylonitrile is reacted at room temperature with stoichiometric amounts of various

phosphinites in the presence of alcohols (13). The same reaction is observed when the alcohol is replaced by polymers containing many pendant OH groups on their backbone. In agreement with the proposed mechanism, our data demonstrate (Table 1) that the presence of alcohols is essential for the acrylonitrile dimerization to proceed. The observed first-order kinetics on the phosphinite concentration would suggest that the addition of the phosphinite on acrylonitrile is the rate-determining step.

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