mance. Its high T_g also results in poor dye uptake from an aqueous bath at the boil (low K/S). The two copolymers have T_g's in the range described previously and exhibit a desirable combination of performance and dyeability. The benefits derived from cocrystallization are clearly evident in comparing the crystallinity-related properties (tenacity and wet modulus) of the two copolymer fibers.

Experimental Section

Monomers. The diamines were vacuum distilled prior to use with the exception of *p,p'*-methylenedianiline, which was decolorized and recrystallized from benzene, and 1,6-hexanediamine (Eastman) and 1,3-bis(4-piperidyl)propane (Reilly), which were used as obtained. Dodecanedioic acid (Chemische Werkes Huls AG) and suberic acid (Aldrich) were used as obtained.

Polymers. The polyamides were prepared by conventional melt polymerizations involving equimolar diamine–diacid mixtures. Typical conditions involved a 2.5-hr heat up to a final temperature of 320°, 1 hr at 320° under 15–20 psig N_2, 1 hr at 320° under a slow N_2 flush, and 1 hr at 320°C at 30 mm Hg. Glass reactors prepared from ball/socket joint glass tubing were used, connected by rubber tubing to a manifold supplying N_2 and a vacuum.

Measurements. Inherent viscosities were measured in *m*-cresol on 0.5% solutions at 30°. Polymer melt temperatures,[7] reported for amorphous polymers, were determined on a heated brass rod with a temperature gradient (modified "Dennis bar").

The differential thermal analysis measurements were performed using a Du Pont Model 900 utilizing a DSC cell (constantan disk). The quantitative data were recorded on a time base Hewlett-Packard Model 7128A with a disk integrator. The samples (20 mg) were premelted at 300° for 3 min and quenched. The heat up was carried out at 10°/min under a helium atmosphere using an empty pan reference.

The X-ray diffraction data were obtained using a Norelco X-ray diffractometer with pulse height analyzer and a diffracted beam graphite monochrometer. Specimens were compression molded at 265° and cooled to 100° at a rate of 2°/min.

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Notes

Microprobe Analysis of Polystyrene-Attached Catalysts

R. H. GRUBBS* and E. M. SWEET

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824.
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In the past few years, research directed toward the preparations and uses of polymer-attached catalysts has developed rapidly.[1-5] These catalysts combine many of the best features of "homogeneous" with the ease of use of "heterogeneous" catalysts. It is becoming apparent that these catalysts retain their "homogeneous" character when examined on a molecular basis but are heterogeneous when considered on a functional basis. The major portion of the research to date has been directed toward the preparation and properties of d^8 complexes attached to polystyrene copolymer beads. One of the keys to understanding the properties of these catalysts, such as their size selectivity[2] and catalyst activation or deactivation,[4,5] is the determination of the distribution of the catalyst in the copolymer beads.

The electron probe microanalyzer provides a rapid nondestructive technique for such determinations.[6] The resolution (several microns) of this instrument is more than sufficient for the analysis of the polymer beads in question which are generally from 300 to 700 μ in diameter. Each element can be detected independently on the same sample.

Experimental Section

Samples of the functionalized copolymer were prepared as reported earlier.[2] Conditions and reaction times for the equilibration studies are summarized in Table I.

Sample Preparation. Sections (2 to 4 in.) of 4 mm inside diameter glass tube were sealed at one end. The tubes were cleaned (KOH–EtOH; HNO_3; distilled water) and dried. Each tube was wet with epoxy release agent and suspended with the open end up.

Table I
Summary Preparation of Beads

Complex used	Equiv Rh/equiv P (on beads)	Equilibration time	% Rh (analysis)
RhL_3Cl	1.00	2 weeks	3.43[a]
$[RhCOE_2Cl]_2$	0.310	12 hours	2.08
$[RhCOE_2Cl]_2$	4.30	4 days	2.62

[a] This batch had a greater per cent substitution of P than the latter which were from the same batch of phosphinated beads.

A small portion of mixed epoxy was placed in the bottom of the tube with a micropipet. A few beads were then added followed by enough epoxy to half-fill the tube. The epoxy and beads were gently mixed with a nichrome wire, and the epoxy was allowed to set.

The glass tube was carefully broken from around the epoxy rod. The rod was cut into sections 0.5 in. or less in length. A short rod containing beads was attached to a larger diameter epoxy rod (α-cyano acrylate glue) which was mounted in a microtome.

Sections were made at room temperature using a stainless steel knife and a very slow cutting stroke. Once the knife penetrated the rod to a depth of 1 to 2 mm it was necessary to hold the section against the knife with a flat edged dissecting instrument to prevent curling. Sections were cut at 7 to 10 μ. Thinner sections tended to shatter the beads.

Matrix sections were mounted on graphite disks or quartz plates. Any adhesive will work. α-Cyano acrylate cement, electronic tube coating (graphite base), and the sticky residue from pressing and then removing freezer tape on the plate were used. Disks or plates were covered with a thin film of graphite (from carbon arc under high vacuum). The sections with the maximum diameter were chosen to represent the cross section of the beads.

Spectroscopic Determinations. Spectra were run on an American Research Laboratories EMX-SM Microprobe. Beams of 20 and 15 kV at 0.05 μA were used. X-Ray intensities were measured from Rh L-α, P Kα, and Cl Kα line emission. X-Ray intensities were taken as a measure of the relative density of a given element

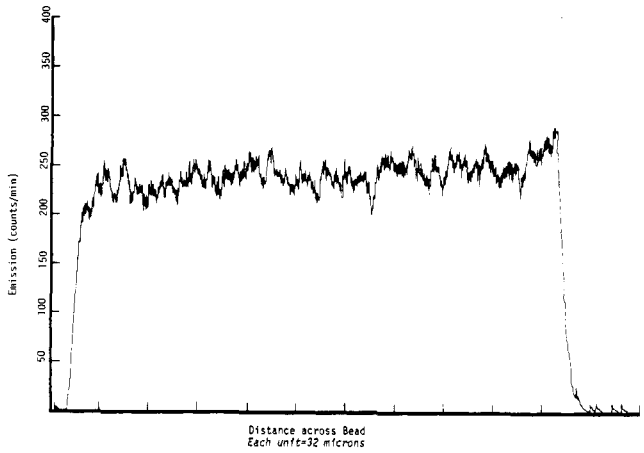

Figure 1. Phosphorous spectrum of phosphinated copolymer.

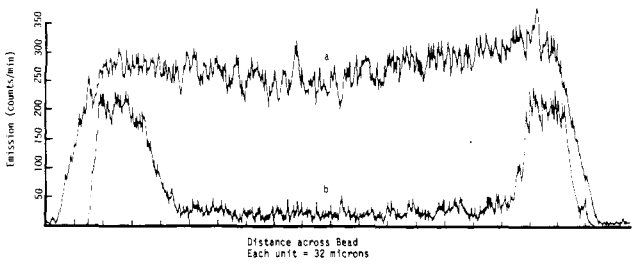

Figure 2. (a) Rhodium microprobe spectrum of Rh(I)-attached complex from $(Ph_3P)_3ClRh$. (b) Rhodium spectrum of Rh(I)-attached complex from deficiency of $[Rh(COE)_2Cl]_2$.

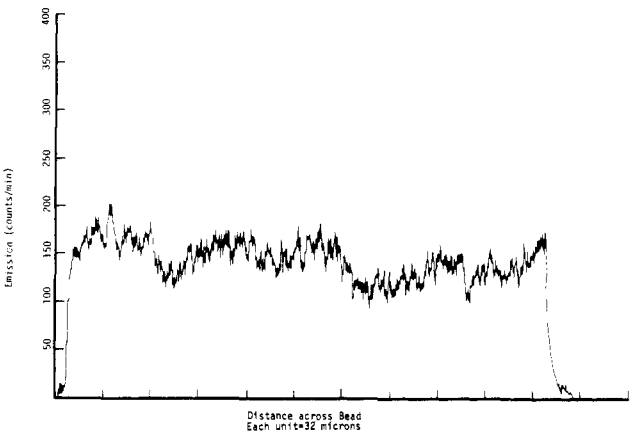

Figure 3. Rhodium spectrum from Rh(I)-attached complex from excess $[Rh(COE)_2Cl]_2$.

(to itself) as a function of position within the bead. Relative density comparison between elements, *i.e.*, Rh, P, and Cl, was not attempted. Direct comparison of X-ray intensities between elements is not a valid indication of their relative densities.

Beads were scanned by moving the stage at constant speed on a path corresponding to a diameter across the bead.[7] X-Ray intensities were recorded on the Y axis of an X–Y recorder driven at constant speed. Thus distance on the chart is directly related to the distance across the bead, and the relative elemental density can be determined as a function of distance from the edge of the bead.

Results and Discussion

A sample of 2% divinylbenzenepolystyrene beads (30–80 mesh μ) was chloromethylated by the procedure of Pepper and Paisley.[8] A portion of these beads, containing 0.67 mequiv Cl/g was phosphinated with lithiodiphenylphosphine.[2] These phosphinated beads were then equilibrated with chlorobis(cyclooctene)rhodium(I) dimer or chlorotris(triphenylphosphine)rhodium(I) under the conditions presented in Table I. After removal of the nonattached complex the samples were dried and then shown to be active hydrogenation catalysts. Random beads were selected from the phosphinated and the three samples of Rh(I)-attached copolymer. Individual beads were imbeded in epoxy and sectioned with a microtome. The cross sections of the beads were examined under a microscope for major surface flaws and to check the centering of the cut. Each of the four samples was subjected to electron microprobe analysis. Plots of X-ray emission *vs.* distance across the cross section are presented in Figures 1–3. Since good standards for each of the elements in a representative matrix were difficult to obtain, and the only interest at this stage of analysis was the relative distribution within each bead, the spectra were not corrected or normalized.

Figure 1 shows that the reaction of the bulky, ionic lithiodiphenylphosphine with the chloromethyl groups proceeds throughout the polymer bead and gave a smooth distribution of phosphine groups across the cross section.

The metal distribution could be controlled by the choice of conditions used in the attachment reaction. When the attached catalysts were prepared by ligand substitution, using a deficiency of the complex, the metal was distributed in the first 180 μ of the polymer bead with no metal in the center of the bead. Using an excess of either Rh(I) complex gave an attached catalyst which showed a distribution of rhodium which was similar to the distribution of the phosphine.

These results confirm the earlier assumptions concerning the metal distribution in the polymer and demonstrate that the reactions of the catalyst must be occurring within the polymer matrix.[2]

Experiments to determine the change in catalytic properties with metal distribution are now in progress.

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The Limiting Critical Behavior in Polymer Solutions at Infinite Chain Length

EDWARD F. CASASSA

Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213. *Received October 3, 1974*

Kennedy[1] has studied the chain-length dependence of the critical point in strictly binary polymer solutions obeying a generalized Flory–Huggins relation[2] for the free energy of mixing