

Notes

Gas Manifold for Olefin Polymerization and a Convenient Reactor Design for the Parallel Screening of Catalysts

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Introduction

An accelerated pace of research has been brought about recently by the introduction of high-throughput (HT) techniques to industrial and academic laboratories. In the realm of polymer science, new methodologies have been developed for rapid characterization involving HT GPC, FT-IR¹ and mass spectroscopy^{2–4} as well as combinatorial approaches to the evaluation of crystallization kinetics, phase segregation, and adhesion.^{5–7}

There have been tremendous advancements in the design of novel homogeneous organometallic catalyst systems for the polymerization of olefins.^{8,9} Studies involving gaseous monomers are usually performed at elevated pressures in commercially available stainless steel apparatus or in glass reaction vessels.^{10,11} The procedure typically involves loading the reactor with catalyst, cocatalyst (if required), and solvent generally under inert atmosphere conditions and then pressurizing with monomer. This becomes a time-consuming process especially if a series of catalysts, cocatalysts, and reaction conditions all need to be evaluated in a traditional sequential series of reactions followed by subsequent correlation of the results to polyolefin properties. The use of combinatorial methodology and high-throughput reaction screening has led to the rapid identification of new catalysts and materials.^{12–20} However, this typically involves the use of expensive equipment that is well beyond the budget of many laboratories. A requisite step in the discovery of new olefin polymerization catalysts or novel polyolefin compositions is the development of efficient screening protocols for the evaluation of catalyst activity and to produce samples for subsequent analysis.^{21,22} Herein, we report the facile construction of a gas manifold line in which olefin polymerizations can be performed using heavy-walled glass reaction vessels in a sequential manner and a design for an inexpensive multiwell reactor that can

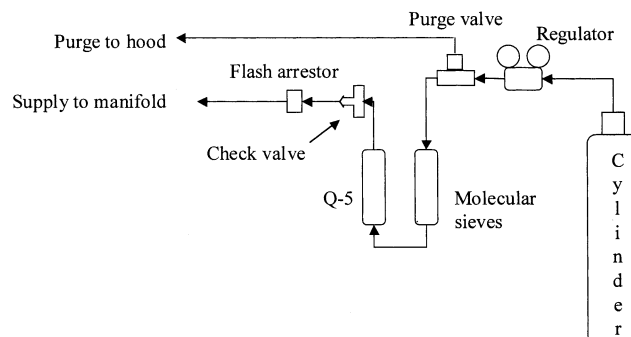


Figure 1. Tank farm schematic for a single monomer line of either ethylene or propylene. The nitrogen line schematic is the same except for removal of the flash arrestor.

be used to perform seven simultaneous polymerizations in a high-throughput fashion.

Manifold

Equipment Description. A representative diagram for the tank farm is shown in Figure 1. A detailed listing of the quantity, part number, and manufacturer for all materials needed to construct the manifold can be found in the Supporting Information. The pressure regulators are attached to the wall and connected to the gas cylinder, high-purity ethylene, propylene, or nitrogen via flexible stainless steel tubing. A purge valve is placed after the regulator in order to shut off the supply line to the manifold and purge the regulator after replacing a cylinder. Columns of molecular sieves and Q-5 oxygen scavenger are placed in line to remove any residual water and oxygen impurities. To maintain tank purity and laboratory safety, check valves and flash arrestors (for the ethylene and propylene lines) are placed after the columns. The location of the flash arrestor was chosen to protect the tank farm from a flash occurring at the reaction vessel. Additionally, a second flash arrestor can be placed between the regulator and purge valve to protect against a flash occurring within the tank farm system. Flexible stainless steel tubing is used to connect the flash arrestor to the manifold. All items have normal pipe thread (NPT) fittings and are connected with copper tubing.

A full diagram for the manifold is shown in Figure 2. The entire manifold is assembled on a 1.5 ft × 4 ft × 1/4 in. sheet of rolled aluminum in which the compound pressure gauges (160 psig–30 mmHg) and the ball valves are mounted with the plumbing on the backside. The pressure gauges and pressure relief valves (PRV) are placed in the line with branch tees. Copper tubing was bent, cut to length, and attached via Swagelok fittings. The manifold was fully constructed and tested for leaks by pressurizing with N₂ and monitoring for a pressure drop over a 24 h period. It was then mounted in a hood via lab feet bolted on the corners and the middle of the faceplate. Additionally, the manifold was

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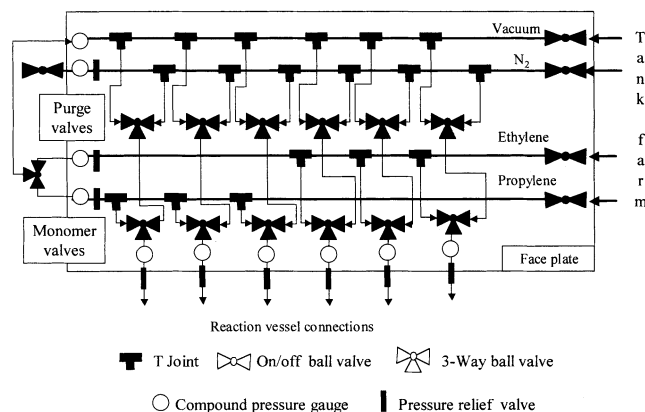


Figure 2. Manifold schematic, the ball valves, and compound pressure gauges are mounted in the faceplate with the plumbing being behind the plate.

stabilized with horizontal legs attached directly behind the plate, which also forms a lattice to support the reaction vessels.

The tank farm is connected to the manifold by flexible stainless steel tubing placed through the side panel in the hood, connecting to a master on/off ball valve on the manifold lines. Each of the gas mains has pressure gauges and pressure relief valves (PRV) set at 80 psig. Additionally, the two-monomer mains are connected via a three-way ball valve to the vacuum line to allow for purging the gas mains at initial setup and in the event of contamination. The N₂ line is equipped with an on/off ball valve to purge the line to the hood in the case of contamination. These valves are placed well behind the faceplate to avoid accidental opening and evacuation of the supply cylinder. The N₂ and vacuum lines are connected to the first set of three-way ball valves (purge valves). The purge valves are then connected to the right side of the lower set of three-way ball valves (monomer valves) with the monomer supply connected on the left side. Finally, copper tubing is used to connect an in-line pressure gauge and pressure relief valve to the reaction vessel. Flexible stainless steel tubing is used to attach the manifold assembly to the reaction vessel.

Heavy walled glass reaction vessel assemblies are suitable for reactions conducted in a sequential fashion and are rated to 100 psig (Figure 3). (Additional information about the vessels is available in the Supporting Information.) Additionally, mesh metal sleeves are used to shield the vessel in the case of explosion, and the use of a portable blast shield is recommended whenever working at elevated pressures. The small reaction vessel has a 70 mL working volume and can be agitated via a magnetic stir bar. An on/off ball valve or quick connect is attached to the factory coupling assembly via a 1/8 in. NPT male adaptor. The large reaction vessel has a working volume of approximately 300 mL. This reaction vessel can be used with the coupling for the small reaction vessel or a stainless steel coupling designed for manual agitation and having multiple ports for reagent addition.

Stainless steel double-ended cylinders, with an internal volume of 10, 25, or 50 mL, on which two-way ball valves with Swagelok fittings are attached, can be used for liquid reagent additions (Figure 3). The cylinder can be attached to the top of the small vessel or to the additional ports on the large vessel coupling. This allows for greater flexibility in reaction design and will be discussed in the next section.

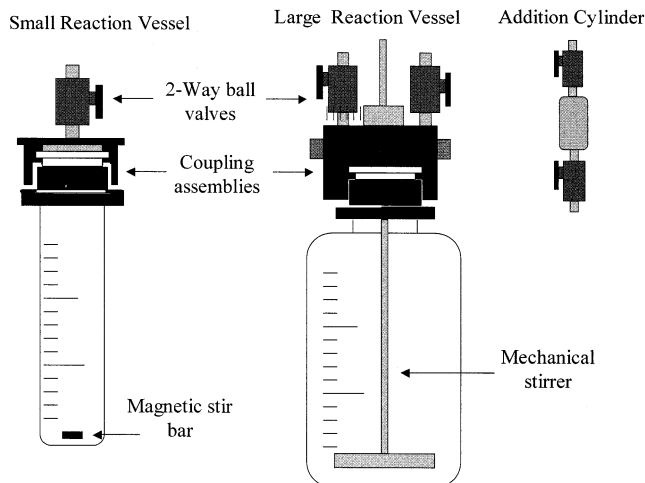


Figure 3. Diagram of the small and large heavy walled glass reaction vessels and an addition cylinder. The ball valve on the reactor fittings can be replaced with a self-sealing quick connect stem.

Experimental Procedures. The reaction vessels can be connected to the manifold line via self-sealing quick connects or on/off ball valves. The body of the quick connect is attached to the manifold line and the mating stem to the reaction vessel. The reaction vessel is charged with reagents and assembled in an inert atmosphere glovebox. Since the quick connects open on coupling, the line must be purged before attachment. To purge the manifold line, the monomer valve is turned to the purge position (i.e., the right-hand side of the ball valve), and then the purge valve is alternated between evacuation and N₂ refill. Once the line has been sufficiently purged and left under vacuum, the monomer valve can be switched to the monomer supply position and the reaction vessel attached. If on/off ball valves are used, the valve is attached to the reaction vessel in the glovebox and then attached to the manifold line via Swagelok fittings. The line must then be purged as previously mentioned before the reaction vessel is opened to the monomer supply.

The small reaction vessel is ideal for quickly assessing catalyst activity, in which the solvent, catalyst, and cocatalyst are added to the vessel in the glovebox. Additionally if desired, comonomer can be added by attaching a sample cylinder to the vessel coupling. The reaction vessel is charged with monomer, and comonomer in the case of copolymerizations, once connected to the manifold. Temperature and agitation control can be maintained using an oil bath and stirring hot plate.

The large reaction vessel allows for more sophisticated catalyst screenings, mainly by control over the order of reagent additions. Normally solvent and comonomer are added to the vessel in the glovebox. Solutions of diluted catalyst and cocatalyst are placed in a sample cylinder and attached to a port on the vessel coupling. The vessel is then removed from the glovebox and attached to the manifold with a ball valve or quick connect (following purging procedures). The vessel is pressurized with monomer, and the catalyst solution is injected by pressurizing the cylinder with nitrogen and opening it to the vessel. An equal or greater nitrogen pressure must be used to overcome the vapor locking that occurs in the ball valve. Additionally, attaching a mechanical stirrer to the coupling assembly can control the stirring rate.

Table 1. Experimental Data for Standardization of the Glass Reaction Vessels for Polyethylene Synthesized by *tert*-Butylamidodimethylsilyltetramethylcyclopentadienyltitanium Dichloride and Polypropylene by *rac*-Ethylenebis(indenyl)zirconium Dichloride

| reactor | monomer | toluene (mL) | Al/M ^e | time (min) | temp (°C) | activity (kg/(h mol psi)) | yield (g) | M _w × 10 ⁻⁵ | PDI |
|--------------------|------------------------|--------------|-------------------|------------|-----------|---------------------------|-----------|-----------------------------------|------|
| small ^a | ethylene ^c | 20.0 | 5414 | 5 | 80 | 343 | 1.42 | 1.63 | 2.48 |
| large ^a | ethylene ^c | 250 | 5414 | 7 | 80 | 1328 | 5.20 | 3.80 | 1.77 |
| small ^b | propylene ^d | 70 | 430 | 60 | RT | 1229 | 8.51 | 1.01 | 2.02 |
| large ^b | propylene ^d | 250 | 425 | 120 | RT | 2432 | 68.71 | 6.14 | 2.17 |

^a Using *tert*-butylamidodimethylsilyltetramethylcyclopentadienyltitanium dichloride. ^b Using *rac*-ethylenebis(indenyl)zirconium dichloride. ^c Ethylene pressure of 60 psig. ^d Propylene pressure of 44 psig. ^e MAO is 30% Al in toluene.

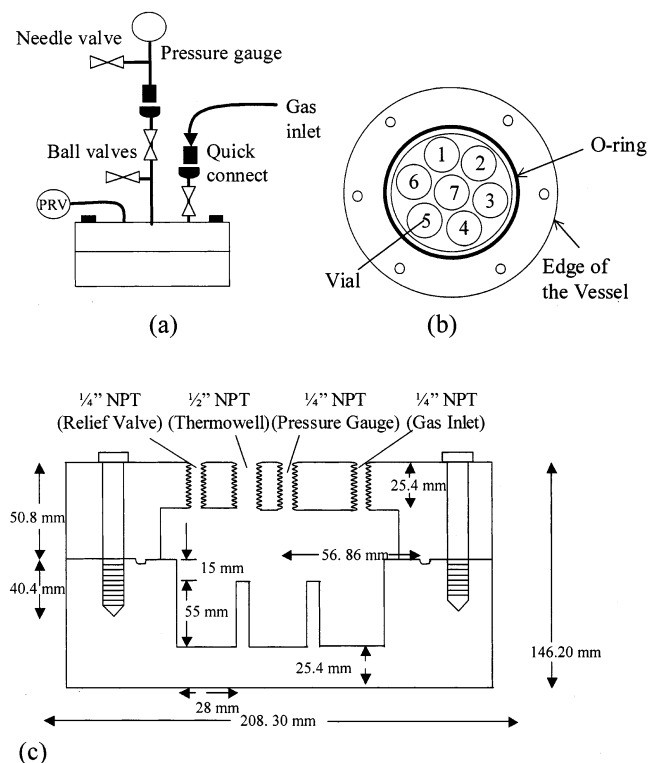


Figure 4. Schematic of the multiwell reaction vessel: (a) fully assembled, side view; (b) top-view of the bottom section, enlarged to show the internal dimensions; (c) side view, with dimensions.

Multiwell Reaction Vessel

Equipment Description. A multiwell reaction vessel (MRV), made of aluminum alloy 6061-T6, was designed in-house and built by a local vendor (Figure 4). This material was chosen for its good heat conductivity and tensile yield strength. These characteristics allow for heating the vessel and its contents as well as reaching pressures greater than those achievable using commercial glass vessels. Specific calculations to determine the maximum pressure were performed through a series of failure analysis calculations and are available in the Supporting Information. [CAUTION: These calculations were performed as approximations to model the current system from sources in the literature. They are in no way an absolute prediction by which this vessel could be considered for high-pressure service. Therefore, caution should be taken when deciding on a particular operational pressure, and an appropriate pressure relief valve and shielding must always be in place.] In short, it was decided to take the value of maximum allowable working pressure (MAWP) as 1560 psig. To enforce a safety factor greater than 4, the reactor has a PRV set at 375 psig.

For reactions involving the use of air-sensitive compounds, the MRV was designed to permit it to be introduced in an inert atmosphere glovebox for facile reagent additions to the seven internal chambers built into the reactor body. These internal chambers were machined to accept commercial 20 mL disposable glass vials. The headspace above the vials ensures a sufficient gas reserve for continuous feed of monomer. The total internal volume of the MRV, including the seven chambers and the headspace, is 556 mL. Since aluminum is a nonmagnetic material, agitation is possible by inserting magnetic stirring bars into the vials and placing the entire reactor on a stir plate. The seal is achieved, according to American Society of Mechanical Engineers (ASME) recommendations, by a Viton O-ring placed in the groove around the reactor. Both reactor halves are joined by six $\frac{3}{8}$ in. × 3 in. carbon steel, hexagonal head, full threaded bolts, with washers between the hexagonal heads and the reactor surface.

Gas is supplied through $\frac{1}{4}$ in. o.d. copper tubing on the top of the reactor. The pressure is monitored by a digital pressure gauge, with an operational range of 0–500 psig. Based on the temperature ratings of all materials used, the reactor can reach temperatures up to 100 °C, with an external heating source (e.g., hot plate, oil bath). The maximum allowable working temperature represents a safety factor of 1.2. Temperature can be monitored if a thermometer/thermocouple is inserted into a thermowell installed in the reactor top.

Experimental Procedures. For reactions involving air-sensitive compounds, the unassembled reactor is placed inside a glovebox and evacuated overnight to ensure water/air removal. Seven previously dried vials are placed inside the chambers of the reactor's bottom half. For solution/slurry reactions, each vial is charged with the desired amount of solvent, catalyst/cocatalyst, and a stirring bar. The reactor is assembled and removed from the box and attached to the desired monomer line of the manifold, if an operational pressure less than 80 psig is desired. Quick connects are used to attach the manifold line and the pressure gauge assembly. The MRV is pressurized to 45 psig with nitrogen, and the air that could have entered into the reactor as a result of the quick connect joint (0.1 cm³ of air) is purged via a needle valve in the pressure gauge assembly. After purging three times, the monomer valve is switched from purge to monomer supply. A rapid cycle of 15 purges from 45 to 30 psig (while injecting fresh monomer) is required to reduce the nitrogen concentration inside the vessel to less than 1% in volume and to ensure a monomer-rich atmosphere.²³ The reaction can be stopped by purging the vessel with N₂ for 5 min. Venting should be performed via the available ball valve and not the needle valve, especially if the reaction temperature is above 45 °C. Failure to do so would damage the quick connects, since they are not rated for

Table 2. Experimental Data for Standardization of the MRV Reactor for Polypropylene Synthesized by Bis(2-methyl-4-phenylindenyl)dimethylsilylzirconium Dichloride

| vial ^a | Al/Zr ^b | yield (mg) | | | |
|-------------------|--------------------|----------------------|----------------------|----------------------|----------------------|
| | | trial 1 ^c | trial 2 ^d | trial 3 ^e | trial 4 ^e |
| 1 | 5 000 | 39.7 | 33.2 | 367.4 | 224.0 |
| 2 | 10 000 | 174.1 | 337.6 | 701.9 | 688.1 |
| 3 | 15 000 | 248.7 | 1057.0 | 833.9 | 994.0 |
| 4 | 20 000 | 901.5 | 1111.0 | 912.4 | 1094.0 |
| 5 | 5 000 | 13.7 | 52.0 | 298.0 | 256.0 |
| 6 | 10 000 | 173.0 | 382.1 | 700.0 | 655.0 |
| 7 | 15 000 | 269.8 | 616.5 | 907.0 | 1004 |

^a Propylene pressure of 44 psig for 30 min, initial activation time of 25 min. ^b Bis(2-methyl-4-phenyl)dimethylsilylindenylzirconium dichloride. ^c Reaction vessel was purged 5 times, leaving 10% N₂. ^d Reaction vessel was purged 10 times, leaving 5% N₂. ^e Reaction vessel was purged 15 times, leaving 1% N₂.

high-temperature conditions. Should pressures greater than 80 psig be desired, the reactor can be connected to an independent delivery system of monomer and inert gas utilizing suitable regulators, flexible hose, and three-way ball valves. The purging procedure described above would also apply to this situation.

Discussion

Polymerization protocols demonstrating the utility of the manifold design with the small and large glass reaction vessels and the MRV are described. Ethylene was polymerized in the small vessel at 80 °C using catalyst A (*tert*-butylamidodimethylsilyltetramethylcyclopentadienyltitanium dichloride) with toluene as the solvent (Table 1). The reaction produced 1.42 g of polyethylene of M_w 1.63×10^5 in 5 min with an activity of 343 kg/(h mol psig). It was observed that, by increasing the amount of toluene from 20 to 250 mL and using the mechanical stirrer of the large reaction vessel, the activity dramatically increased about 4-fold and yielded 5.20 g of polyethylene of M_w 3.8×10^5 in 7 min with an activity of 1328 kg/(h mol psig). A similar trend of increased activity and molecular weight was observed in the case of propylene polymerization using catalyst B (*rac*-ethylenebis(indenyl)zirconium dichloride) conducted in the small and the large vessels.

To demonstrate the utility of the MRV for high-throughput reaction evaluation, the effect of catalyst-cocatalysts ratio on propylene polymerization was studied. The vials were charged with Al/Zr ratios of 5000, 10 000, 15 000, and 20 000, and the reactor was assembled and connected to the gas manifold. A precontact time of 25 min was selected to ensure optimal active catalyst concentration.²⁴ The system was purged by pressurizing with propylene at 44 psig and then venting to the atmosphere until the MRV pressure gauge read 30 psig. This protocol was performed rapidly 15 times, leaving the nitrogen concentration at 1% of the total volume. Solutions of catalyst were stirred using small spinvane stir bars to create a vortex to solubilize the monomer in the liquid phase. The activity of the catalyst increased with an increase in the Al/Zr ratio and leveled off at a ratio of 15 000:1 (Table 2). A trend of monotonically increasing yield was observed in all cases. Yield reproducibility between experimental runs (comparing

vials 1 and 5, 2 and 6, 3 and 7) is acceptable. This experiment demonstrates that this simple reactor design can be used as a semiquantitative system to quickly establish optimum polymerization conditions. The utility of the MRV can be further extended, for example, to select a catalyst from among a series of candidates in a more timely fashion as compared to sequential reaction evaluations.

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Supporting Information Available: Parts lists for the manifold and MRV, specific calculations and detailed diagrams of the MRV, and molecular weight data for the MRV standardization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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