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Continuous Heterogeneous Polymerization. I. A Laboratory-Scale Stirred Tank Reactor

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Synopsis

Design, calibration, and operation is described of a unique, 2-liter laboratory-scale continuous stirred tank reactor for the heterogeneous stereospecific polymerization of α-olefins under pressure.

Introduction

Although continuous processing is common practice in chemical manufacture, the preceding laboratory research is usually conducted as a batch reaction. Transfer from the static to the economically more attractive dynamic system is then carried out in the intermediate-sized pilot plant. Difficulties during this scale-up process are well known and expected. Not infrequently they are due to an incomplete understanding of important reaction parameters which are difficult to extract from batch kinetic data. This is particularly true for complex reaction systems in which simultaneous and consecutive steps combine to form an end-product. Moreover, the end-product obtained batchwise is not necessarily identical to that produced continuously. In the case of polymers, molecular weight distributions, copolymer compositions, and monomer distributions in the copolymer might be significantly different for both processes and cause considerable changes in physical properties.

The progress of a batch reaction approaching a certain degree of conversion is described by differential equations. In contrast, a continuous reaction in a stirred tank reactor (STR) assumes a steady state in which the concentrations become time-invariant. The progress of such a reaction at a certain degree of conversion is described by algebraic equations. Hence, a complex reaction system becomes more tractable to a mathematical analysis of its kinetics. The fundamental concepts of this technique were initially described by Denbigh.[1-7]

In contrast, references are scarce in the literature of laboratory-scale continuous STR's for heterogeneous polymerizations. An all-glass, atmospheric pressure reactor, apparently for demonstration purposes, was described[8] and operated for a considerable period of time.

General reluctance to make use of continuous flow systems on a research scale appears to be traceable to the view that its construction is timeconsuming, its operation expensive and wasteful. Our experience, however, indicates that this is only partly true, a conclusion expressed previously by other authors.[9] Moreover, it will be shown in a later publication that the information obtainable by experimentation with a continuous system compensates amply for minor disadvantages.

From a practical point of view, a continuous system allows collecting of a uniform reaction product at any point of a reaction path in quantities sufficient for evaluation. Thus, samples representative of an eventual commercial nature are available in adequate size in the early stages of research.

In the following, a laboratory-scale STR will be described which was developed for heterogeneous stereospecific polymerizations under pressure. Its use for the elucidation of polymer kinetics will be discussed in subsequent papers.[10]

Continuous Reactor Design

Determinants for the design of an STR as a research tool of high flexibility and versatility were: module construction for easy exchange and service of components, low capacity to minimize waste of reactants, adaptability to a wide range of reaction conditions, and use of inert construction materials with optimum visual observability. For conducting stereospecific heterogeneous polymerizations, a minimum pressure rating of 17 atm. (250 psig) at 100°C. was set. For the same reason, a drying and purification section was incorporated.

As inert construction materials, exposed to the reactants, 316 stainless steel, Pyrex glass and Teflon were specified. Lines were of $^1/_4$-in. O.D. stainless steel tubing (ASTM-A-213) and connected with Swagelok fittings. Where possible, quick-connect fittings (Swagelok) were employed to permit easy exchangeability.

A simplified flow sheet of the equipment is given in Figure 1; a detailed drawing in Figure 2. A photograph of the completed installation is shown in Figure 3. The overall dimensions are $7^1/_2$ ft. long, 6 ft. high and 2 ft. wide. In the following, details pertinent to Figures 1 and 2 are discussed.

Liquid and gaseous reactants are predried over Linde Molecular Sieves (Type 4A) and further passed through beds of the same material impregnated with $AlEt_3$. Here, polar impurities in the feed streams, which otherwise would react with $AlEt_3$ in the catalyst, are removed.

Gas pressures are preset manually and the flow controlled by calibrated flow meters (max. 830 ml./min. air at 25°C., 1 atm.) and solenoid valves. Liquids are metered by means of diaphragm pumps (Lapp Pulsafeeders, maximum capacity 1040 ml./hr.) continuously adjustable via vernier settings. To insure trouble-free operation, stainless steel cartridge filters (15 μ pore size) and check valves (5 psi) are positioned before the pumps.

Ten feed lines are available for the simultaneous addition of reactants. Of these, one line is reserved for blanketing with inert gas (N_2), three lines for gaseous monomers, two lines for liquid monomers, one line for solvent

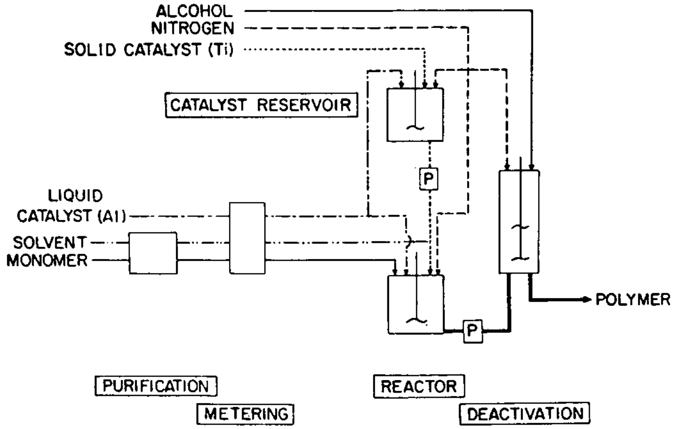

Fig. 1. Schematic of continuous reactor.

and the three remaining lines for liquid catalyst components, or optionally, for solvent. All gas lines, the nitrogen line excepted, are joined to a manifold and fed from there as a single line to the reactor. The liquid monomer lines are combined similarly. Catalyst and solvent lines are carried separately to the reactor, permitting switching to the solid catalyst reservoir for catalyst aging studies.

The essential details of the reactor design are shown in Figure 4. The catalyst vessel was designed identically.

Both vessels are constructed from a stainless steel pipe line flow indicator (4 in. I.D., 10 in. long), modified by jacketing to facilitate temperature control, and insulated to the outside by a 1-in. layer of rockwool. The vessel's interior can be observed through oppositely located ports of 4 in. diameter, $^3/_4$-in. thick sight glasses (tempered Pyrex) sealed with Teflon gaskets. Top and bottom of $^3/_4$-in. stainless steel plates are also sealed with Teflon gaskets and bolted to the body. All feed lines are

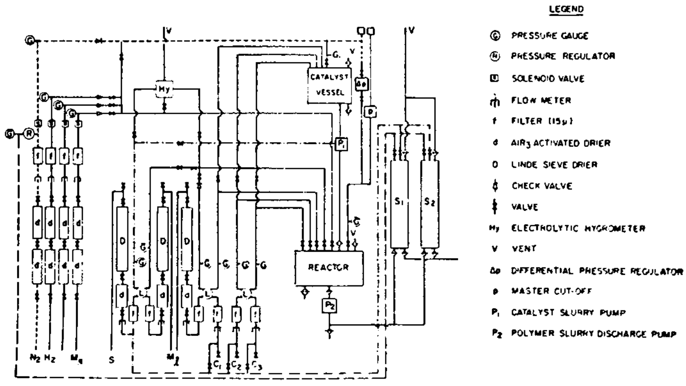

Fig. 2. Detailed flow plan of continuous reactor.

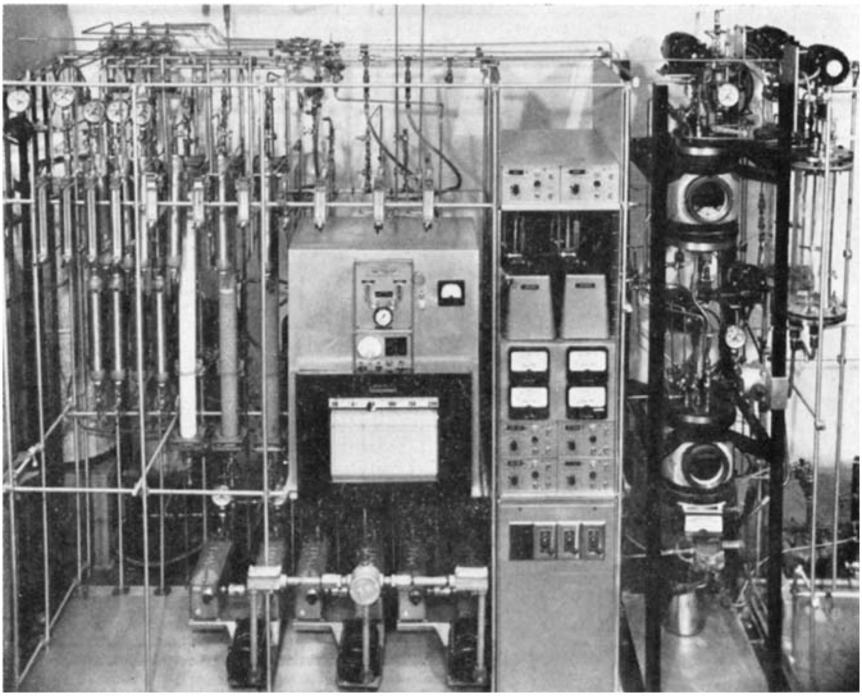

Fig. 3. Photograph of completed continuous reactor.

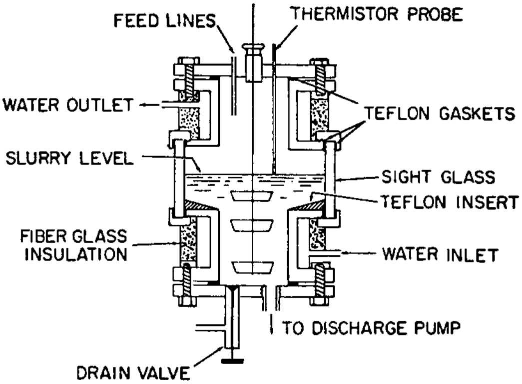

Fig. 4. Details of reactor design.

carried through the top and the contents withdrawn through the bottom of the vessels.

Solid-state controlled dc-shunt motors with servogenerator-driven rpm indicators permit the adjustment of the stirring speed to the viscosity of the reaction mixture. Thus, no problems were encountered due to settling of the heterogeneous polymerization or catalyst mixtures. Teflon-coated inlets prevented build-up of polymer formed from the monomer in the vapor phase.

The catalyst vessel is positioned above the reactor. The suspension of solid $TiCl_3$, or preformed catalyst, is withdrawn by a slurry pump mounted flush with the bottom of the vessel. Details of this pump are shown in Figure 5.

A constant pressure differential between the two vessels forces the slurry into the metering chamber of a rotating Teflon cylinder. This volume (0.35 ml.) is discharged by depressurizing on opening into the line leading to the reactor. In this position the chamber and line are rinsed by a thin spray of solvent which also carries the catalyst to the reactor. The operation of the pump can be checked through the sight glasses.

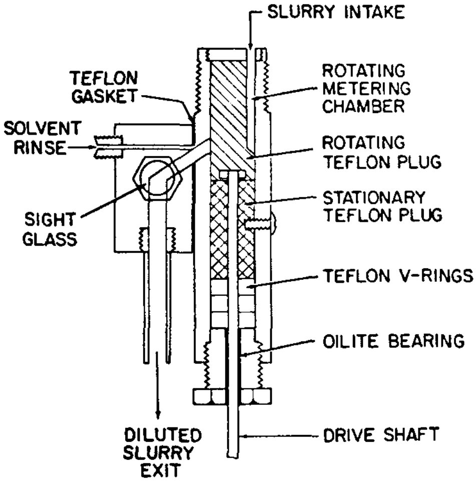

Fig. 5. Catalyst slurry pump.

A differential pressure regulator (±3 psi) supplied the necessary 50 psi differential against the reactor by actuating a solenoid valve in the high-pressure N_2 line. Delivery rate of the pump is read from the rpm indicator receiving the signal from the servogenerator on the driving motor, controlled as described above. Thus, small quantities of catalyst (10–80 ml./hr.) could be reproducibly fed to the reactor, eliminating settling and inhomogeneity problems otherwise caused by employing a diluted slurry. The use of heavy oil as suspension medium was rejected on the grounds of possible solvent effects influencing the kinetics.

The polymer slurry is brought from the reactor to atmospheric pressure by the revolving-reciprocating pump shown in Figure 6. The reciprocating action is obtained from a cam follower riding in an eliptical groove cut into the rotating shaft. The pump is controlled as described above.

The discharge operation is fully automated by using the signal of a thermistor probe, positioned at the desired slurry level, in conjunction with a solid-state proportional controller actuating the discharge pump. The probe is rinsed with incoming solvent and monomer providing a constant

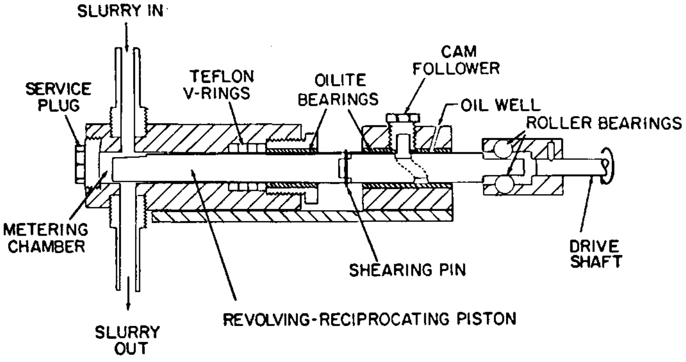

Fig. 6. Polymer slurry discharge pump.

zero potential. The stability of the steady-state volume was found to be ±3% or better.

The discharged polymer slurry is collected in a heavy-walled cylindrical glass reservoir, stirred, and flushed with N_2. Catalyst is deactivated here with alcohol through a feed line from the top of the vessel. To avoid gassing of the reaction mixture on depressurizing through the slurry pump, the intake to the pump and lines to the reservoir are all water cooled. Two reservoirs are provided for switching from one turnover to another.

The reaction temperature is controlled to ±0.5°C. by means of a Haake Ultrathermostat circulating water through the jackets of the reactor. Temperatures at various points of the system are recorded with a 12-point Honeywell recorder.

As a guard against runaway reactions, a variable master pressure control (±10 psi), monitoring the gas phase of the reactor, is connected to the main power input of the system. Instantaneous cut-off of all feed streams and venting of the reactor would take place in case of a fast pressure build-up. However, no such emergency arose at any time of the operation.

Also connected to the gas phase of the reactor is an adjustable bleed to an electrolytic hygrometer to monitor the overall moisture level. Through a manifold arrangement, individual streams can be checked similarly. During a polymerization, the average moisture level was kept at 3–5 ppm in the feed streams, and at ca. 1 ppm or below in the reactor.

Calibration

Catalyst slurry pump and polymer slurry discharge pump were calibrated against the rpm indicators (cf. above) under operating conditions. The metering pumps (Lapp Pulsafeeders) were calibrated separately at pressures from 15 to 500 psig.

Fine calibration was then achieved by pumping oil-soluble dye solutions of known concentrations through the system and colorimetrically analyzing the effluent. In a stepwise procedure, all pumps could be checked in this manner, providing also an easy way to recalibrate the system frequently.

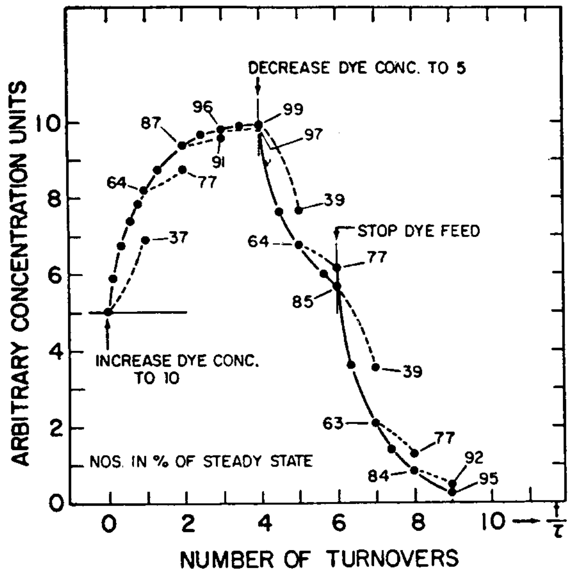

Fig. 7. Steady-state approach. Instantaneous and average composition in reactor.

However, the pumps were found to operate accurately over extended periods of use, showing no detectable deviations (less than 1%) after almost three years of operation. Pump reliability was established by continuous operation over 6-hr. periods. In prolonged polymerization runs, volume variations over periods up to 85 hr. were found to be ±3% based on the calculated steady-state volume. Temperature variations in the reactor were smaller than the expected ±0.5°C. at 70°C.

The dye method was also used to check the steady-state approach of the system on changing feed concentrations. A typical curve is shown in Figure 7. The theory for a single-stage STR predicts the steady-state approach to follow eq. (1):

$$C_t = C_0(1 + e^{-t/\tau}) \tag{1}$$

wherein C_t is instantaneous effluent concentration, C_0 is feed concentration, and τ is average residence time (≡ feed rate/steady-state volume). By definition, the steady state is reached for $C_t = C_0$, i.e., $dc/dt = 0$.

Under experimental conditions, the average composition of a volume element collected between t_1 and t_2 is of interest, and is obtained from eq. (1) as

$$\bar{C}_t = \int_{t_1}^{t_2} C_t dt/\Delta t \tag{2}$$

to give eq. (3)

$$\bar{C}_t = C_0(1 + e^{-t_2/\tau} - e^{-t_1/\tau}) \tag{3}$$

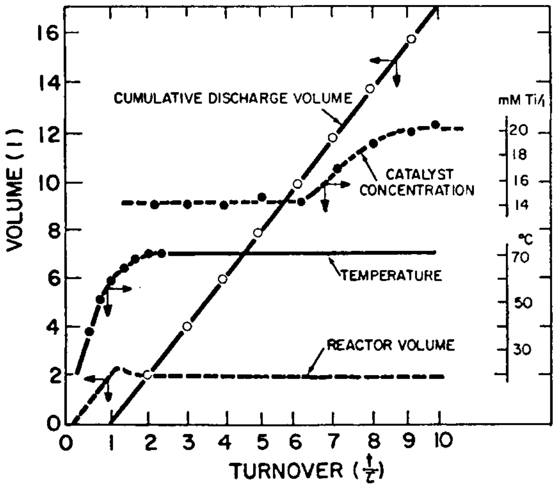

Fig. 8. Typical run record.

In Table I, calculated instantaneous and average compositions are compared with experimentally determined values (cf. also Fig. 7).

TABLE I

t	C_t/C_0 Calculated	C_t/C_0 Found	$\bar{C}_t/C_0$ Calculated	$\bar{C}_t/C_0$ Found
	0.632	0.64, 0.63	0.368	0.37, 0.39
2	0.865	0.87, 0.85	0.767	0.77, 0.77
3	0.950	0.96, 0.95	0.914	0.91, 0.92
4	0.990	0.99	0.968	0.97

The agreement is satisfactory, taking into account the average steady-state volume fluctuation of ±3%. At the same time, it can be concluded that no mixing problems exist, and the steady-state theory can be applied to experimental values without further corrections.

In Figure 8, a typical run record is reproduced showing the performance of the equipment in an actual polymerization. A $TiCl_3/AlEt_3$ catalyst was employed with 3 mole/l. of 3-methylbutene in cyclohexane. The average residence time τ was set at 45 min. at a steady-state volume of 2000 ml. After an initial overshoot, the system settled down after $\tau = 2$, and a constant temperature profile was established at almost the same time. Steady-state condition for the polymerization was reached at $\tau = 5$. At $\tau = 6$ the $TiCl_3$ feed was increased from 14 to 20 mmole./l. From the polymer yield it can be concluded that the polymerization reached the second steady state at $\tau = 9$, simultaneously with the $TiCl_3$ concentration.

Details of the reaction kinetics of heterogeneous stereospecific polymerizations under continuous flow conditions will be described in subsequent publications.

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Résumé

Le présent article a pour objet de décrire la réalisation, le calibrage et l'opération d'un nouveau réacteur d'une capacité de deux litres travaillant en continu et à l'échelle de laboratoire, utilisé pour la polymérisation hétérogène et stéreospécifique sous pression des α-oléfines.

Zusammenfassung

Aufbau, Eichung und Arbeitsweise eines neuentwickelten, kontinuierlich arbeitenden 2-Liter Laboratorium Reaktors für die heterogene, stereospezifische Druckpolymerisation von α-Olefinen wird beschrieben.

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