Communications to the Editor

Continuous Polymerizations in Supercritical Carbon Dioxide: Chain-Growth Precipitation Polymerizations

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Received March 12, 1999

Introduction. A wide variety of polymers have been synthesized in batch reactors utilizing supercritical carbon dioxide (scCO$_2$) as the reaction medium. Chain-growth polymers prepared by free-radical emulsion, suspension, solution, and precipitation polymerization and cationic and step-growth polymerizations have been carried out in scCO$_2$ using batch reactors. This work has been summarized by several recent reviews.[1,2] As industrial interest in using scCO$_2$ as a polymerization medium has grown, several disadvantages of batch reactions have been recognized, including (1) large reactors which are costly at the high pressures of scCO$_2$, (2) difficulty in separating polymer from the supercritical solvent, and (3) difficulty in recycling the CO$_2$ and the unreacted monomer.

To circumvent these potential disadvantages, we have developed a continuous process for the precipitation polymerization of various monomers in scCO$_2$. A continuous process requires smaller and hence cheaper equipment for large volume, commodity-based polymers. Moreover, continuous removal of polymer from the system and recycling of monomer and supercritical fluid should be facilitated in a continuous system. A continuous system in scCO$_2$ can also be exploited to incorporate in-situ steps to purify the resultant polymer by supercritical fluid extraction (SFE).[3]

The experimental system consists of an intensely mixed, continuous stirred tank reactor (CSTR), followed by two high-pressure filters in parallel, where the polymer is collected. This method is widely applicable to various monomers in heterogeneous polymerizations, both with and without surfactants. To date, experiments have been performed mainly with the surfactant-free precipitation polymerization of vinylidene fluoride (VF2) and acrylic acid (AA) utilizing diethyl peroxydicarbonate (DEPDC) as the free-radical initiator for VF2 and 2,2′-azobis(isobutyronitrile) (AIBN) as the free-radical initiator for AA. Herein we report on our experiments with VF2 performed at a temperature of 75 °C, a pressure of 275 bar, and at residence times from 15 to 40 min. The polymer was collected as a dry “free-flowing” powder and has been characterized by gel permeation chromatography (GPC).

Experimental Section. ***Materials.*** VF2 monomer was donated by Solvay Reseach, Belgium, and SFE/SFC grade CO$_2$ was donated by Air Products & Chemicals, Inc. All other chemicals were obtained from Aldrich Chemical Co.

Initiator Synthesis. The EPDC initiator was synthesized as previously reported, using water as a reaction medium and extracting the initiator into Freon 113.[4−6] All manipulations of the initiator were performed in an ice bath, and the final product was stored in a cold chest at −20 °C. The iodine titration technique, ASTM method E 298-91, was utilized to determine the concentration of active peroxide in the solution.

Polymerization Apparatus. A schematic of the equipment used for the polymerization of VF2 and AA is shown in Figure 1. Carbon dioxide and monomer are pumped continuously by Isco syringe pumps in constant flow mode and mixed by an eight-element static mixer, before entering the reactor. The initiator solution is also pumped continuously by an Isco syringe pump in constant flow mode and enters the reactor as a separate stream. All feed lines have check valves to prevent back-flow, thermocouples and rupture disks for safety in case of overpressurization. The CSTR is an 800 mL Autoclave Engineers (AE) autoclave with a magnedrive to provide mixing of ingredients with an AE dispersimax impeller. The reactor is heated by a furnace and has an installed pressure transducer (Druck) and a thermowell containing a thermocouple (Omega Engineering).

The effluent stream leaves the CSTR through the bottom and is directed by a three-way ball valve (HIP) to one of two 280 mL filter housings (Headline) containing 1 μm filters where the solid polymer is collected. Unreacted monomer, initiator, and CO$_2$ pass through the filters and flow through a heated control valve (Badger). This control valve functions as a back-pressure regulator, which controls the reactor pressure at the desired set point. The effluent stream passes through a water bath to remove unreacted peroxide, while the gaseous CO$_2$ and monomer are safely vented into a fume hood. Very low levels of polymer were found in the water bath, so essentially all precipitated polymer was collected on the 1 μm filters.

The entire polymerization apparatus was computer-controlled and monitored. The supervisory control and data acquisition (SCADA) system consists of National Instruments BridgeVIEW software and Fieldpoint input/output modules. Input modules were utilized for reading pressure transducers and thermocouples. Output modules were utilized to control the reactor furnace, control valve furnace, and the control valve. All control functions were performed utilizing PID algorithms.

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10.1021/ma990377t CCC: $18.00

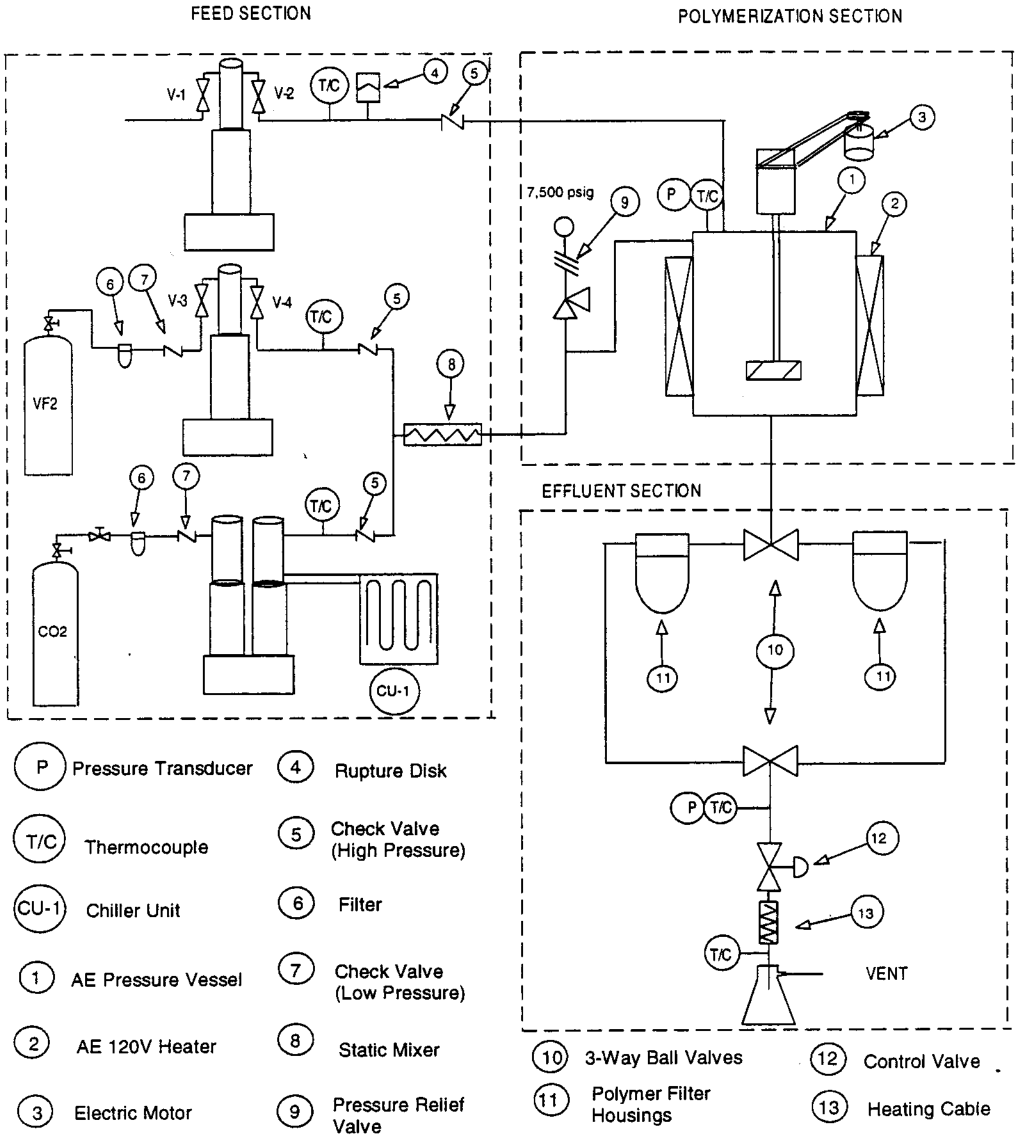

Figure 1. Schematic of continuous polymerization apparatus.

Polymerization Procedure. The reactor was first heated to the desired temperature, and the agitator was set to 1800 revolutions per minute (rpm). The system was then purged with N_2. After about 2 h, the control valve was closed, and the system was pressurized with CO_2 to the desired reactor pressure. The desired CO_2 flow rate was set, and the temperature and pressure of the system were allowed to stabilize. Temperature control was ± 0.2 °C, while pressure control was ± 1 bar. When the system had stabilized, the initiator flow rate was set, and initiator was allowed to flow through the system for at least three residence times in order to remove impurities. Monomer flow was then started. At least five residence times after the introduction of monomer, with the CSTR at steady state, the three-way ball valve was switched, and the stream exiting the CSTR was fed to the empty filter/collector, where steady-state polymer was collected for between 30 and 60 min. After this time, the ball valve was switched so that effluent flowed to the original collector, and the monomer and initiator feed streams were stopped so that only pure CO_2 was fed through the system for cleaning. The system was finally vented and the polymer collected and weighed.

Results and Discussion. We have developed and demonstrated a continuous, once-through system for precipitation polymerizations in $scCO_2$, as shown in Figure 1. Table 1 shows the reactor conditions for several experiments with VF2 polymerization initiated by DEPDC. Table 2 provides the polymerization results and GPC data for the poly(vinylidene fluoride) (PVDF) polymer produced in these experiments. The conversion of VF2 in these polymerizations (conversion = moles of monomer reacted/moles of monomer fed) ranged from 7 to 24%. Unlike a batch polymerization, high conversions are not required for a continuous system, as the monomer is recycled. The rate of polymerization (R_p) for the CSTR system reached a maximum of 19×10^{-5} mol/(L s), at a feed monomer concentration of 1.7 mol/L. This rate will increase as the concentration of monomer is increased. In the batch polymerization of VF2 in $scCO_2$, the average R_p at 3.0 M monomer concentration, using an acyl peroxide initiator at 65 °C, was 0.2×10^{-5} mol/(L s).[7] The CSTR system gave a R_p more than an order of magnitude higher.

The GPC results indicated that the molecular weight distributions (MWDs) were unimodal, although several of the samples had high-molecular-weight tails that led

Table 1. Reactor Conditions for Polymerization of Vinylidene Fluoride

run no.	press. (bar)	temp (°C)	τ[a] (min)	ν_{CO_2} (g/min)[a]	$\nu_{Initiator}$[b] (mg/min)	ν_{VF2} (g/min)	$[VF2]_{INLET}$ (mol/L)
1	275	75	22	26.5	4.9	1.9	0.83
2	275	75	30	20	14.7	1.4	0.82
3	275	75	22	26.5	19.5	1.9	0.82
4	275	75	22	26.5	32	1.9	0.82
5	275	75	15	40	29	2.8	0.82
6	275	75	22	26.5	20	3.8	1.7
7	275	75	22	26.5	19.7	0.95	0.41

[a] Reactor residence time = reactor volume/total volumetric flow rate. [b] ν = mass flow rate.

Table 2. Polymerization Results and Polymer Characterization Data for PVDF

run no.	X[a] (%)	R_p[b] (mol/(L s)) ($\times 10^5$)	M_n ($\times 10^{-3}$)	M_w ($\times 10^{-3}$)	M_w/M_n
1	6.9	4.2	16	28	1.75
2	18.4	8.5	11	114	10.4
3	18	11	10	29	2.9
4	24	14.6	8.6	16	1.86
5	11	10	12	44	3.7
6	16	19	17	36	2.1
7	20	6.1	7.4	28	3.8

[a] Conversion (X) was determined gravimetrically from steady-state polymer collection. [b] Rate of polymerization (R_p) was calculated by $R_p = ([VF2]_{INLET} - [VF2]_{OUTLET})/\tau$.

to large polydispersity indexes. We are presently trying to determine whether this high-molecular-weight broadening is a result of continuing polymerization in the effluent lines and the filters or are due to "secondary polymerization" as a result of partitioning of monomer and initiator into the polymer-rich phase in the reactor.

Conclusions. We have successfully developed a system for the continuous polymerization of various monomers in $scCO_2$. The feasibility of the continuous precipitation polymerization of VF2 and AA has been demonstrated using an intensely agitated, continuous stirred tank reactor (CSTR). Rates of polymerization of VF2 in the CSTR are significantly higher than the average rates of batch polymerization, under similar conditions.

This represents the completion of the first stage of a three-stage project. The second stage, which is in progress, involves continuous removal of the polymer powder from the high-pressure filters. An objective of this stage is to minimize the pressure drop of the supercritical fluid/monomer mixture in order to minimize the energy required to recompress the mixture for recycle. The third stage of this project will involve recycle of both monomer and $scCO_2$.

Acknowledgment. This work was supported by Solvay through the Kenan Center for the Utilization of Carbon Dioxide in Manufacturing. We thank Solvay Research, Belgium, for performing GPC analysis of the PVDF samples.

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MA990377T