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Living carbocationic polymerization

LX. Continuous process for the synthesis of *tert*-chlorine ended polyisobutylene (PIB-Cl^t)*

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ABSTRACT

Laboratory scale glass equipment was designed, assembled, and used for the continuous preparation by living cationic polymerization of tert-Cl monotelechelic polyisobutylene (PIB-Cl^t). The process involves the continuous feeding of controlled amounts of isobutylene (IB), a stream of premixed initiator (2-chloro-2,4,4-trimethylpentane, TMPCl) and electron donor (triethylamine, TEA) in methylene chloride/hexane, and a stream of coinitiator ($TiCl_4$) in hexane into a series of three stirred reactors maintained at about -42°C under a blanket of dry N_2. By controlling the residence times of the living charges in the reactors and continuously quenching the feeds in a quenching reactor, the continuous synthesis of well-defined (in terms of molecular weights, $\overline{M}_n$, and narrow molecular weight distribution, MWD) PIB-Cl^t prepolymer was demonstrated.

I. INTRODUCTION

The synthesis of well-defined (in terms of $\overline{M}_n$ and MWD) PIB-Cl^t by batch living cationic polymerization is well documented in the patent and scientific literature [1-4]. The continuous synthesis of tert-chlorine ditelechelic polyisobutylenes by batch and tubular reactors installed in a dry box has also been demonstrated [5-7]. The purpose of this communication is to describe small (laboratory) scale equipment assembled of commercially available components for the continuous synthesis of PIB-Cl^t , and to demonstrate that by the use of this equipment predetermined $\overline{M}_n$ (in the range $\overline{M}_n$= 40-60K g/mole) and narrow MWD ($\overline{M}_w/\overline{M}_n < 1.4$) products can conveniently be prepared.

II. EXPERIMENTAL

Chemicals

The source and purification of chemicals, i.e.,IB, CH_2Cl_2 and hexane (Hex) have been described [1, 3-7]. The synthesis of TMPCl has been described [8]. TEA was distilled over KOH. $TiCl_4$ and MeOH were used as received. The necessary quantities

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of TMPCl/TEA (in CH_2Cl_2/Hex = 60/40 v/v%, 10.5L) and $TiCl_4$ (in hexane, 1.2L) solutions were freshly prepared in a N_2 filled dry box and placed in 1 gallon brown bottles. The IB was condensed directly into the reactor (see Figure 1).

Equipment and Operational Details

Figure 1 shows the scheme of the assembly used and the legend identifies the components. All the components are commercially readily available.

The entire assembly is under a blanket of dry N_2 gas. The N_2 enters the system through drying column 1, is led through rotameter 2 and thence through reactors 11-15, and leaves via bubbler 7. N_2 is also fed into reservoirs 28, 29 and 30. The

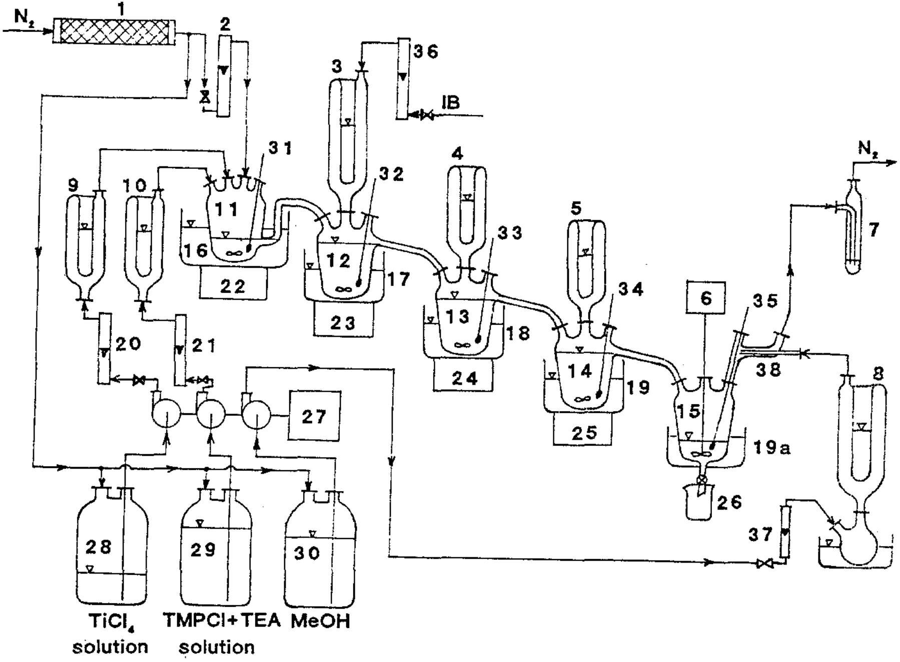

Figure 1. Assembly for the continuous synthesis of PIB-Cl^t
1 drying column (d=2cm, L=45cm) filled with molecular sieves (3Å) and Drierite; 3 IB condenser; 4 and 5 reflux condensers; 8, 9 and 10 cooling units filled with Dry Ice-isopropanol mixtures; 6 stirrer; 7 bubbler; 11 four-neck "aging" reactor; 12, 13 and 14 continuous cascade reactors (250mL); 15 quenching reactor (500mL); 16, 17, 18, 19 and 19a cooling receptacles filled with Dry Ice-isopropanol; 2, 20, 21, 36 and 37 flow meters (rotameters); 22, 23, 24 and 25 magnetic stirring plates; 26 product receiver cup; 27 peristaltic pump (Cole-Palmer Instrument Company; Model No. 7568-00); 28, 29 and 30 containers for coinitiator (in Hex), initiator plus electron donor (in CH_2Cl_2/Hex 60/40 v/v%) and terminating agent (MeOH); 31, 32, 33, 34 and 35 thermometers, ⋈ valves, ∞ magnetic stirring bars.

use of a stream of N_2 is essential for the satisfactory continuous operation because of the following reasons: 1.) The stream of N_2 prevents the back-diffusion of even trace amounts of methanol vapors from quenching reactor 15 into polymerization reactors 14, etc; 2.) It compensates for the pressure drop in condenser 3 which occurs because of the condensation of IB, and thus helps to maintain pressure equilibrium in the entire assembly; 3.) It prevents the decrease of the pressure in reservoirs 28, 29 and 30 during continuous operations (i.e., when the solutions are pumped out from these reservoirs) and thus assures controlled outflow of the solutions.

The premixed TMPCl plus TEA solution in reservoir 29 is pumped by peristaltic pump 27 through rotameter 21 and Dry Ice filled cooler 10 into the "aging" reactor 11 equipped with magnetic stirrer 22, external cooling receptacle filled with Dry Ice 16, and thermometer 31. At the same time the $TiCl_4$ solution is also pumped into the same reactor 11 through rotameter 20 and Dry Ice filled cooler 9. Ion generation and complexation between the electron donor and the initiating entity to produce the living initiator [2,3] take place in the "aging" reactor.

The active initiator enters the first polymerization reactor 12. Reactors 12, 13 and 14, the "heart" of the continuous assembly, are equipped with condensers, 3, 4, 5, magnetic stirrers, 23, 24, 25, thermometers, 32, 33, 34, and external cooling receptacles filled with Dry Ice - isopropanol, 17, 18, 19. Condensers 4, 5 serve to prevent the evaporation of gaseous ingredients from reactors 13 and 14.

The IB, whose flow rate is monitored by rotameter 36, is liquefied by condenser 3 and enters dropwise reactor 12. Living polymerization starts immediately upon contact of IB and the initiator system in reactor 12, and propagation is allowed to progress until the desired molecular weight is reached. The living product cascades into reactors 13 and 14, and propagation may occur in all three reactors. By the use of correctly chosen residence times, i.e., with properly controlled volumes and flow velocities, the $\overline{M}_n$ increases to predetermined values while the MWDs tend to become narrow ($\overline{M}_w/\overline{M}_n$ < 2.0) with increasing residence times. At long residence times all the IB may be converted to polymer in the first reactor 12 and additional reactors are not needed.

The living charge from reactor 14 is led by gravity flow into quenching reactor 15 where the polymerization is stopped by methanol. The last unit in the series of reactors is the "quenching" reactor 15 (equipped with thermometer 35, mechanical stirrer 6, and Dry Ice filled cooling receptacle 19a). The gaseous N_2 leaves the reactor through adapter 38 and bubbler 7 which contains some paraffin oil to judge the rate of N_2 exit. The terminating agent is stored in reservoir 30 and is pumped into reactor 15 by peristaltic pump 27, through rotameter 37, holding flask and Dry Ice filled cooler 8.

Samples or final products (i.e., the sought PIB-Cl^t) are collected in a series of beakers 26 (only one shown) by periodical opening the valve on the bottom of quenching reactor 15. The rate of sampling is mainly determined by the flow rates of the ingredients and by the aim of investigation.

Calibrations

Reagent concentrations in the reactors were controlled by manually controlling the flow rates of the $TiCl_4$ and TMPCl/TEA solutions, and the IB and MeOH inputs. The flow rates were monitored by calibrated flow meters (rotameters). Figures 2A-D show the calibration curves of the individual flow meters. Thus, the flow rate of the TMPCl/TEA solution was 15.8 mL/min (Figure 2A, [TMPCl] = $5.14 \cdot 10^{-5}$ mole/min and [TEA] = $5.18 \cdot 10^{-5}$ mole/min) at the arbitrary mark of 5 on the flow meter. Similarly, the flow rate of the $TiCl_4$ solution was 1.8 mL/min ($[TiCl_4] = 1.45 \cdot 10^{-3}$ mole/min) at the arbitrary mark of 5 on the flow meter (Figure 2B). As shown in Figure 2C, the input rate of the IB was 0.92, 1.11 and 1.18 L/min at marks 8, 10 and 11 on the flow meter. The flow velocity of gaseous IB was determined at room temperature and the gas was liquefied by the Dry Ice - isopropanol filled condenser 3.

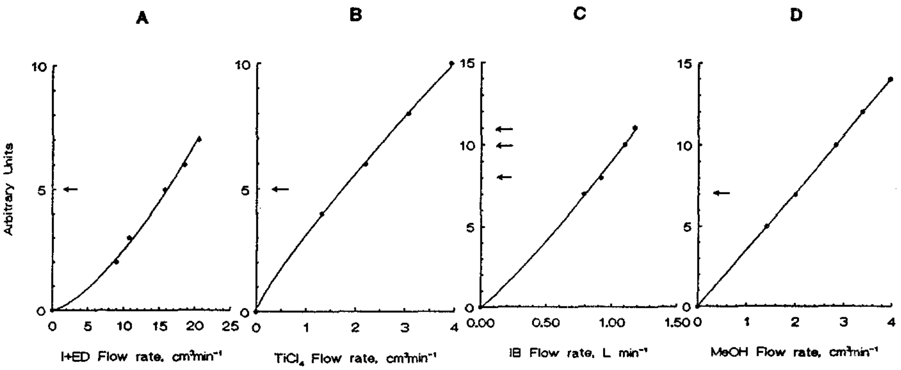

Figure 2. Calibration curves of rotameters ;
A: Arbitrary units vs. flow rate of TMPCl+TEA in CH_2Cl_2/Hex 60/40 v/v% (mL/min);
B: Arbitrary units vs. flow rate of $TiCl_4$ in Hex (mL/min);
C: Arbitrary units vs. flow rate of gaseous IB (L/min);
D: Arbitrary units vs. flow rate of MeOH (mL/min).

Figure 3D shows the calibration curve of the methanol flow meter 37; for example, the arbitrary mark 7 on the flow meter indicates a methanol input rate of 1.98 mL/min.

It should be remarked that the calibrations were carried out with CH_2Cl_2/n-C_6H_{14} mixtures and n-C_6H_{14} only, i.e., in the absence of TMPCl, TEA or $TiCl_4$; the error caused by this simplification is viewed to be negligible.

III. RESULTS AND DISCUSSION

The TMPCl/TEA and $TiCl_4$ solutions were prepared and bottled in a glove box under N_2, and were introduced into the system as described above. As soon as the $TiCl_4$ stream was started opalescence became visible in the glass lines and in the reactors, and after contact with TEA the combined stream

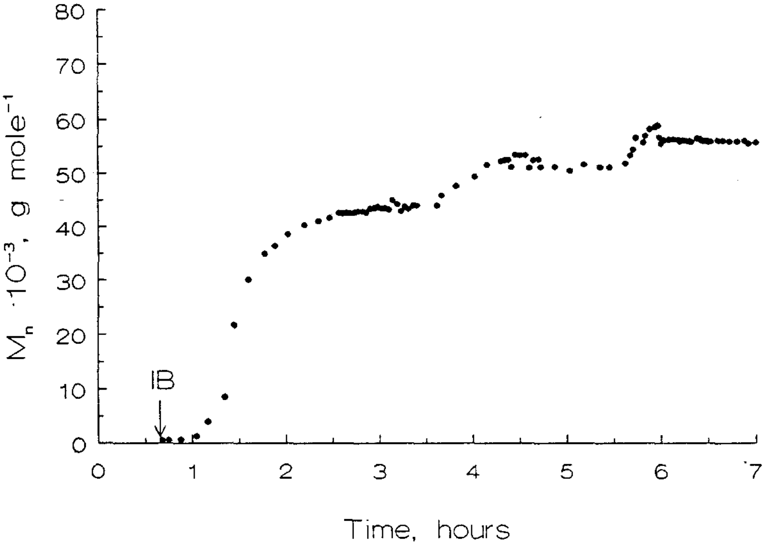

Figure 3. Overall kinetics of the continuous polymerization of IB initiated by the TMPCl/TEA/$TiCl_4$ system ([TMPCl]=$5.14 \cdot 10^{-5}$ mole/min; [TEA]=$5.18 \cdot 10^{-5}$ mole/min; [$TiCl_4$]=$1.45 \cdot 10^{-3}$ mole/min; CH_2Cl_2/Hex=60/40 v/v% ; at -42±2°C).

became yellowish-green. After about ten minutes of flow the opalescence faded and finally disappeared. Opalescence is likely due to a reaction between the $TiCl_4$ and surface-adsorbed impurities (mostly moisture). Throughout the entire experiment the contents of the entire system remained transparent and homogeneous with a distinct yellowish-green tint.

The introduction of MeOH was started when the combined TMPCl/TEA plus $TiCl_4$ stream reached the quenching reactor 15 and thermal equilibrium (~42±2°C) was attained (~37 min). The thermoequilibrated stream was allowed to flow for ~3 additional minutes after which we started the introduction of IB (0.922 L/min) into reactor 12 with intermittent sampling as a function of time.

Figure 3 helps to visualize the entire experimental profile: It shows the times the samples were collected and their $\bar{M}_n$s. Specifically, the first pre-stationary phase runs from 0 to ~2.5 hours and the first stationary phase from 2.5 to 3.5 hours. Figure 4A shows the amount (g) of PIB samples harvested per minute and the corresponding $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values (numbers beside experimental points) obtained during the first 3.5 hours. The solid lines are theoretical, calculated for 100% initiation efficiency ($\bar{M}_n$ of PIB-Cl^t/[TMPCl]). The N vs. w_p (number of moles of chains/min vs. g PIB-Cl^t formed/min) plot, inset in Figure 4A, shows that the moles of PIB-Cl^t obtained are initially higher than theoretical. This is most likely due to putative protic impurities which after a short self-cleaning period are con-sumed so that the experimental points reach the theoretical horizontal line.

The $\overline{M}_n$ of the 21 samples taken during the first stationary phase (i.e., during the 2.5-3.5 hours interval) increase until a plateau at $\overline{M}_n$=45,000 g/mole. The $\overline{M}_w/\overline{M}_n$s show a rapidly narrowing tendency. They start out rather broad ($\overline{M}_w/\overline{M}_n$ =3.34) but after a short self-cleaning period become rather narrow ($\overline{M}_w/\overline{M}_n$=1.2-1.3) and remain narrow throughout the first stationary period ($\overline{M}_w/\overline{M}_n$=1.35, see Figure 4A). At lower IB input rates the $\overline{M}_w/\overline{M}_n$s would be expected to be narrower.

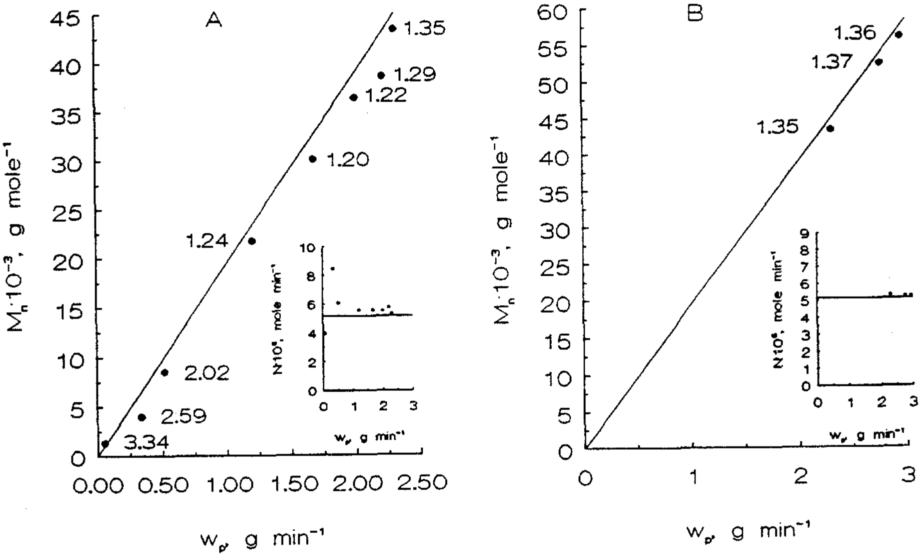

Figure 4. Diagnosis of living continuous polymerization of IB
A: $\overline{M}_n$ vs. w_p and N vs. w_p during the first pre-stationary phase (see Figure 3).
B: $\overline{M}_n$ vs. w_p and N vs. w_p during the three stationary phases (see Figure 3).

After 3.5 hours the IB input rate was enhanced from 0.922 to 1.11 L/min, where it was then maintained for 120 minutes. As indicated in Figure 3, a short second pre-stationary phase developed (5 samples) during which the $\overline{M}_n$s increased to a second stationary plateau at $\overline{M}_n$=52,000 g/mole (average of 16 samples), however, the $\overline{M}_w/\overline{M}_n$s remained unchanged ($\overline{M}_w/\overline{M}_n$=1.37). Finally, 5.5 hours after the start of IB addition, the rate of IB input was again increased from 1.11 to 1.18 L/min where it was maintained for 90 additional minutes (see Figure 3). The third pre-stationary phase was quite short (<20 minutes, 5 samples) and the $\overline{M}_n$s rapidly reached a new, third stationary plateau at $\overline{M}_n$=56,000 g/mole (average of 21 samples) with $\overline{M}_w/\overline{M}_n$s unchanged ($\overline{M}_w/\overline{M}_n$=1.36).

Figure 4 shows the $\overline{M}_n$ vs. w_p plot in which the 3 data points represent the average $\overline{M}_n$s and the average weights of samples per minute collected during the three stationary phases (see above), and the corresponding N vs. w_p plot (inset), i.e., the rate of TMPCl mole input vs. average sample weights per minute. The solid lines were calculated assuming 100% TMPCl efficiency (theoretical lines).

If the poly-merization is living, then by increasing the input rate of the monomer at constant flow rate of the premixed initiator, electron donor and coinitiator, the $\overline{M}_n$ of the product will increase linearly with the amount of the product formed (w_p), and the rate of growth of $\overline{M}_n$ will be determined by 1/[TMPCl].

The fact that the experimental points are within experimental error of the theoretical lines is strong indication that the continuous process under investigation was indeed living.

Structure

The structure of the product PIB-Cl^t, i.e., $(CH_3)_3C$~~~ $[(CH_2C(CH_3)_2]_n$~~~$CH_2C(CH_3)_2Cl$ was determined routinely by the use of several representative samples by 1^H NMR spectroscopy. Analytical methodology has been described [1,2].

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