

Cationic Polymerization

Living Carbocationic Polymerization

VI. Continuous Living Polymerization of Isobutylene by a Bifunctional Initiator

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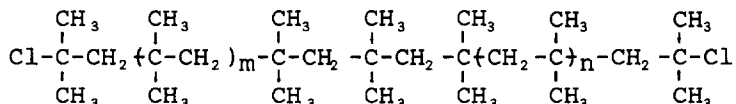
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Abstract

The living continuous polymerization of isobutylene initiated by a bifunctional initiator, i.e., 2,4,4,6-tetramethylheptane-2,6-diacetate·BCl₃ complex, in CH₂Cl₂ and C₂H₅Cl diluent in the -12 to -20°C range is described. Experimental conditions have been found under which rather narrow molecular weight distribution α,ω -tert.-chloro-ended polyisobutylenes of theoretical \bar{M}_n and $I_{eff} = 100\%$ can be continuously prepared in a tubular reactor in a homogeneous system (in C₂H₅Cl at -12°C). System heterogeneity tends to increase the molecular weights, decrease the I_{eff} , and increase the \bar{M}_w/\bar{M}_n .

Introduction

It has been demonstrated in the previous publication of this series (1) that telechelic α,ω -tert.-chloro-ended polyisobutylenes (PIBs):



can be rapidly and efficiently (conv. $\approx 100\%$, $I_{eff} \approx 100\%$) prepared by a living polymerization process using the 2,4,4,6-tetramethylheptane-2,6-diacetate (TMH₂DiOAc)/BCl₃ initiating system under remarkably mild conditions. In view of the ease of this synthesis it was of interest to prepare larger quantities of this valuable intermediate preferably by a continuous process for further physical-mechanical investigations.

This paper describes the preparation of liquid narrow molecular weight distribution (MWD) α,ω -tert.-chloro telechelic PIBs by a continuous living polymerization process using the TMH₂DiOAc/BCl₃ system in CH₂Cl₂ or C₂H₅Cl diluents and a simple tubular reactor in the -12 to -20°C range.

Experimental

Materials. The source and purification of the chemicals, i.e., isobutylene, BCl₃, 2,4,4,6-tetramethylheptane-2,6-diacetate (TMH₂DiOAc), and methylene chloride have been described (1). Ethyl chloride (Linde) was dried by passing the gas through a column packed with powdery BaO and condensing it under a dry nitrogen atmosphere in a stainless steel dry box.

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Equipment and Polymerizations. Experiments have been carried out under a dry nitrogen atmosphere in a stainless steel dry box at -20° and -12°C . Figure 1 shows the assembly used for the continuous experiments. Reservoir I (a 1000 ml round bottom flask) contained a solution of monomer (IB) and initiator (TMH₇DiOAc) while the similar Reservoir II was charged with the coinitiator (BCl₃) solution. The contents of the reservoirs were simultaneously displaced by nitrogen under constant pressure and were led via diptubes and twin syringe needles into a Teflon coil that served as the reactor III. The dimensions of the tubular reactor were: length 6.5 m, inside diameter 2.5 mm, giving a total volume of 32 ml. Mixing of the reagent streams occurred by turbulent flow at the exit of the needles. The flow rate was regulated by adjusting the nitrogen pressure; the input rate was from 10 to 20 ml/min. which corresponds to a linear flow velocity of about 3 to 6 cm/sec. The reservoirs and the tubular reactor were placed into a cooling bath in the dry box (2). Polymerizations were followed by continuously collecting the effluents in series of Erlenmeyer flasks (100 ml) containing ~ 10 ml MeOH to quench the reaction (IV). The homogeneity/heterogeneity of the system was judged by visual observation of the effluent stream at the end of the Teflon coil. The receivers were changed after \sim three residence times and an experiment consisted of at least 30 residence times.

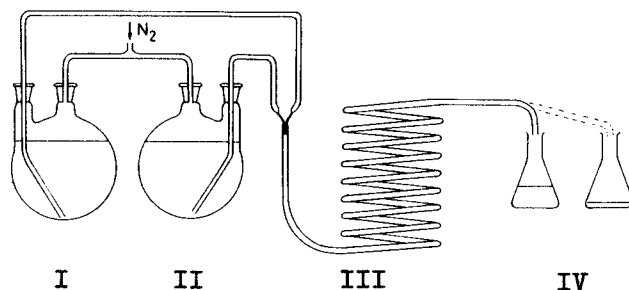


Figure 1. Tubular Reactor Used for Continuous Polymerization

After a continuous experiment the products in the series of receivers were harvested by evaporating the solvent, dissolving the polymer in *n*-hexane, washing with water, drying over CaCl₂, and recovering the product by evaporating the solvent (rotavap).

The molecular weights and molecular weight distributions ($\overline{M}_w/\overline{M}_n$) were determined by GPC. The equipment and the procedure have been described in a previous publication of this series (3).

The titration method for the quantitative analysis of tert-chlorine end groups has been described (4).

Results and Discussion

Among the objectives of these studies were to demonstrate the living polymerization of isobutylene in a continuous polymerization system, to prepare sufficient quantities of α,ω -di-tert-chloro ended PIB for characterization studies by a continuous process, and to prepare narrow molecular weight distribution telechelic materials in a continuous system. The latter goal was thought to be attainable by plug flow in a tubular reactor where every living chain must have the same lifetime.

After a series of orienting experiments carried out at various temperatures, feeding rates, concentrations, solvents, etc., conditions have been found under which systematic investigations could be carried out. Table 1 and Figure 2 show representative results.

The first experiment (Run XVII) carried out by the use of CH_2Cl_2 at -20°C yielded acceptable \bar{M}_n s but the MWDs were broader than desired ($\bar{M}_w/\bar{M}_n = 2.1-2.8$). The latter deficiency was most likely due to the heterogeneity of the system and because propagation was relatively fast relative to initiation. Polymer precipitation could be observed in the effluent immediately after the polymerization started. While the CH_2Cl_2 used is a good solvent for the $\text{TMH}_7\text{DiOAc}/\text{BCl}_3$ initiating complex, it is a poor solvent for PIB. Thus the broader than Poisson MWDs are partly due to the (partial) precipitation of living PIB diacetate/ BCl_3 complex whose reactivity in the precipitated state must be lower than in solution.

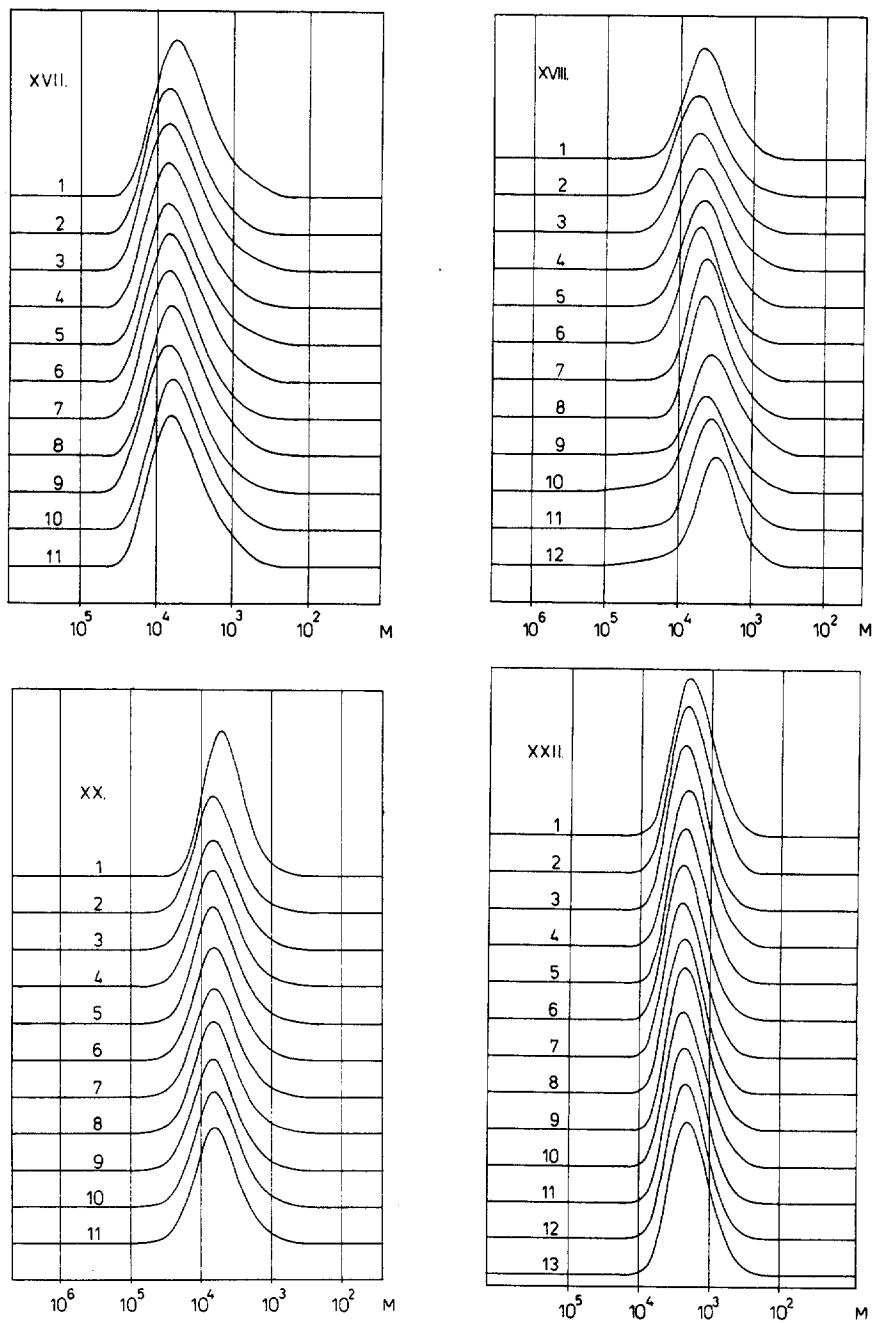
Since according to previous experience with similar systems PIBs with narrower MWDs can be obtained in less polar diluents (3), it was decided to use $\text{C}_2\text{H}_5\text{Cl}$ as the polymerization medium in subsequent experiments. This liquid was expected to be a better solvent for the polymer but a somewhat worse (but still acceptable) solvent for the initiating complex. While experiments XVIII and XX still gave unsatisfactory products, they suggested the use of lower monomer concentrations and possibly higher temperatures to achieve system homogeneity. The theoretical molecular weights (\bar{M}_n , theo.) and I_{eff} s were lower than expected most likely due to the heterogeneity of the system at -20°C . In contrast, lowering the monomer concentration to $[\text{IB}] = 0.16 \text{ M}$ and raising the temperature to -12°C yielded a homogeneous system and rather satisfactory products, i.e., close to theoretical \bar{M}_n and I_{eff} values, and acceptably narrow MWDs, (see Expt. XXII).

Based on the results of earlier investigation (3) efforts have been made to further lower \bar{M}_w/\bar{M}_n to ~ 1.0 by adding the monomer solutions to premixed $\text{TMH}_7\text{DiOAc}/\text{BCl}_3$ systems in $\text{C}_2\text{H}_5\text{Cl}$. Under these conditions complex formation and ion generation would occur in the absence of monomer and the rate of initiation (relative to propagation) would

TABLE I. Results of Continuous Polymerizations

	Exp. XVII	Exp. XVIII	Exp. XX	Exp. XXII
[M] ₀	= 0.6 mole/l	= 0.92 mole/l	= 0.32 mole/l	= 0.16 mole/l
[I] ₀	= $1.51 \cdot 10^{-2}$ mole/l	= $2.51 \cdot 10^{-2}$ mole/l	= $7.5 \cdot 10^{-3}$ mole/l	= $7.7 \cdot 10^{-3}$ mole/l
[BCl ₃]	= 0.25 mole/l	= 0.15 mole/l	= 0.10 mole/l	= 0.12 mole/l
solvent	= CH ₂ Cl ₂	= CH ₃ -CH ₂ -Cl	= CH ₃ -CH ₂ -Cl	= CH ₃ -CH ₂ -Cl
Input rate	= 25 ml/min	= 10 ml/min	= 20 ml/min	= 20 ml/min
T	= -20°C	= -20°C	= -20°C	= -12°C
	\bar{M}_n	\bar{M}_n	\bar{M}_n	\bar{M}_n
1	2600	3060	3540	1380
2	2910	3460	3980	1380
3	3100	3280	3760	1650
4	2900	2860	3930	1400
5	2940	3180	3840	1520
6	2800	3390	3840	1660
7	3100	2840	3840	1680
8	2820	2800	3920	1670
9	3200	2050	3980	1520
10	2910	2680	3920	1520
11	2800	2430	3980	1550
12		2380		1520
13				1310
\bar{M}_w/\bar{M}_n				
1	2.34	1.83	1.59	1.59
2	2.24	2.07	1.85	1.58
3	2.88	2.00	2.00	1.50
4	2.37	2.01	1.93	1.58
5	2.54	1.84	1.96	1.53
6	2.25	1.78	1.94	1.57
7	2.18	1.65	1.98	1.54
8	2.37	1.59	1.93	1.51
9	2.61	2.18	1.99	1.53
10	2.14	3.15	1.93	1.59
11	2.27	1.90	1.93	1.49
12				1520
13				1520
\bar{M}_n, theo	= 2450	= 2280	= 2610	= 1390
I _{eff}	= 83%	= 78%	= 66%	= 90%

Figure 2. GPC Traces of Products Prepared by Continuous Living Polymerization (For details refer to Table I)



increase. Experimentally we mixed initiator/coinitiator systems and after aging the mixture for up to 2 hours at -20°C we added monomer solutions. Polymerization was instantaneous in every experiment. In contrast to earlier results observed with CH_3Cl and CH_2Cl_2 solvents where initiator/coinitiator premixing tended to narrow the MWD (3), in $\text{C}_2\text{H}_5\text{Cl}$ the MWD broadened. Interestingly the \bar{M}_n values obtained were the same as those obtained in experiments in which BCl_3 was added to $\text{TMH}_7\text{DiOAc/IB}$ mixtures (conventional procedure). According to these experiments the living nature of premixed initiator/coinitiator systems persists for extended times, i.e., up to at least two hours. A further narrowing of the MWD may be achieved by the use of premixed initiator/coinitiator systems under controlled homogeneous continuous polymerization conditions.

Importantly, the end groups of representative products have been analyzed quantitatively (titration of tert-chloro groups, see the previous publication of this series (1)) and, according to titration results, all the PIBs carried one chlorine per end group, i.e., $\bar{F}_n = 2.0 \pm 0.1$. Evidently the products were telechelic as shown by the formula in the Introduction.

Acknowledgement

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