

Inifers

New Telechelic Polymers and Sequential Copolymers by Polyfunctional Initiator Transfer Agents (Inifers)

48. Continuous Synthesis of Linear Telechelic Polyisobutylenes

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Summary

The continuous polymerization technique developed earlier for the synthesis of three-arm star telechelic polyisobutylenes (PIBs) has been extended and used for the preparation of linear telechelic PIBs. It is demonstrated that for a period of 6-10 residence times liquid α, ω -ditert.-chloropolyisobutylenes with close to theoretical terminal functionalities, molecular weights and molecular weight distributions can readily be produced at -80°C . During the latter stages of the continuous process the polymerization tends to become heterogeneous and the molecular weights increase. The expected telechelic structure has been corroborated by conventional ^1H NMR spectroscopy and by the recently developed modified Kennedy-Smith plot.

Introduction

Earlier publications in this series concerned a semi-continuous (1) and a continuous (2) polymerization technique mainly for the preparation of three-arm star telechelic polyisobutylenes PIBs carrying tert.-chlorine end groups. These papers also contain kinetic expressions that describe the continuous systems, in particular the effect of reagent concentrations on molecular weights.

It has been demonstrated that virtually perfectly telechelic PIBs can be produced by these techniques with predetermined molecular weights and close to theoretical molecular weight distributions. The present publication concerns an extension and minor modification of our earlier technique, and demonstrates that α, ω -ditert.-chloro PIBs (i.e., linear telechelics) with essentially theoretical number average end group concentrations ($\bar{F}_n = 2.0 \pm 0.1$) and molecular weights ($\bar{M}_n = [M]_0/[I]_0$) can also be readily and conveniently synthesized. Results obtained by ^1H NMR spectroscopy and by the use of the modified Kennedy-Smith plot demonstrate the compositional homogeneity of the telechelic products obtained.

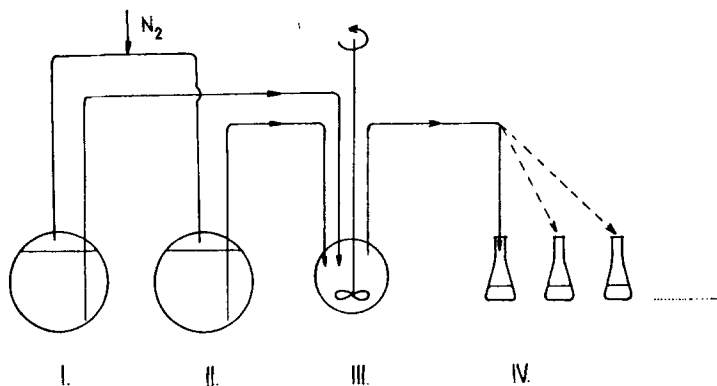
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Experimental

The purification of isobutylene, BCl_3 , and methyl chloride together with the preparation and purification of the binifer, *p*-bis(α, α -dimethyl chloromethyl)benzene, have been described (3). Purification of hexane has also been described (1). Continuous experiments have been carried out in a stainless steel dry-box under a dry nitrogen atmosphere at -80°C .

Figure 1 shows the scheme of the glass assembly used. This equipment is similar to that used for the preparation of three-arm star telechelic PIBs (2) except the volume of the stirred reactor (III) has been reduced from 250 ml to 100 ml to decrease the residence time. Thus we were able to run continuous experiments for 17-20 residence times. Reservoir I (1000 ml) contained the monomer, binifer, in a CH_3Cl :hexane (75:25 vol %) solvent mixture. Reservoir II (1000 ml) was charged with BCl_3 in a CH_3Cl :hexane (75:25) mixture. Erlenmeyer flasks (100 ml) containing ~ 10 ml MeOH were used as receivers (IV). The glass reservoirs and flasks were immersed in a thermostatted cooling bath at -80°C . By the use of this assembly we were able to follow every phase of the continuous process.

Figure 1. Scheme of Glass Assembly Used for Continuous Polymerization



Molecular weights were determined by a Waters high-pressure GPC instrument (Model 6000A pump). Details of our GPC methodology have been described (1). The RI and UV traces produced by the Differential Refractometer (Model 2401) and UV Absorbance Detector (Model 440), respectively, have been used to construct and calculate the modified Kennedy-Smith plot. Details of this recently developed technique have been described (4).

Results and Discussion

A) Reaction Profiles

It has been repeatedly demonstrated that mono-, di- and tri-functional telechelic polyisobutylenes with close to

theoretical number average end group concentrations (i.e., $\bar{F}_n = 1.0 \pm 0.05$, 2.0 ± 0.1 and 3.0 ± 0.1 , respectively), predetermined molecular weights and molecular weight distributions can be obtained by a semicontinuous or continuous polymerization technique (1,2). Importantly, the molecular weights can be readily controlled by the input ratio of monomer and inifer, under stationary polymerization conditions. If the monomer and inifer are combined in a common solvent and this mixed feed is added to excess dilute BCl_3 in a solvent (semicontinuous technique), or if the mixed monomer/inifer solution and a separate BCl_3 solution are fed simultaneously to a common overflow reactor (continuous technique):

$$\overline{\text{DP}}_n = \frac{[\text{M}]_0}{[\text{I}]_0} \quad (1)$$

where $\overline{\text{DP}}_n$, $[\text{M}]_0$ and $[\text{I}]_0$ are the number average degree of polymerization, and monomer and inifer concentrations in the feed, respectively.

A series of continuous polymerizations have been carried out using the assembly shown in Figure 1 and different $[\text{M}]_0$ and $[\text{I}]_0$. Table I shows the data and Figure 2 a set of representative RI traces obtained by GPC in Expt XII. The eluograms are normalized to the same "trash peak" and area. Initially the polymerizations were homogeneous (optically clear) and conversions were complete, however, after 7-10 residence times polymer started to precipitate (slight haze in the reactor, cf. Table I). At this stage the molecular weights of the products started to increase from the theoretical value. Beyond this point Eq. 1 does not describe the system, conceivably because nonstationary conditions prevail. The onset of heterogeneous conditions can be readily perceived by examining the data in Figure 2: The eluogram obtained after the 10th residence time is shifted to higher molecular weights and is broader than the previous ones.

Figure 3 shows a plot of $\Sigma g/g_0$ (%) i.e., the weight percent of polymer exiting the reactor relative to the initial amount of monomer, versus $\Sigma V/V_0$ (%), i.e., the volume percent of polymer solution exiting the reactor relative to the initial volume. The dotted line shows the ideal case i.e., when conversion is 100% throughout the run (about 20 residence times). Until about 7 residence times the systems exhibit virtually theoretical behavior. After 7-10 residence times (i.e., after the systems tend to become heterogeneous) the experimental points start to fall below the theoretical line i.e., the conversions drop below 100%, the amount of unreacted binifer accumulates and consequently the molecular weights start to increase above the theoretical value ($\bar{M}_{n\text{theo}}$).

To overcome the uncertainty caused by polymer precipitation (which is particularly apt to occur at -80°C) the monomer concentrations were decreased from 1.16 mole/l (Expt. XII) to 0.61 and 0.32 mole/l (Expts. XIII and XV), respectively; however precipitation was still noticeable after 7-9 residence times in both experiments. Efforts are in progress to combat

TABLE I. Results of Continuous Polymerizations

Expt. XII		Expt. XIII		Expt. XV			
Res. time	\bar{M}_n	\bar{M}_w	\bar{M}_n	\bar{M}_w	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n
	$[M]_0 = 1.16 \text{ mole/l}$	$[M]_0 = 0.61 \text{ mole/l}$	$[M]_0 = 0.32 \text{ mole/l}$				
	$[I]_0 = 2.4 \cdot 10^{-2} \text{ mole/l}$	$[I]_0 = 2 \cdot 10^{-2} \text{ mole/l}$	$[I]_0 = 1.16 \cdot 10^{-2} \text{ mole/l}$				
	$[BCl_3] = 0.14 \text{ mole/l}$	$[BCl_3] = 0.11 \text{ mole/l}$	$[BCl_3] = 5.5 \cdot 10^{-2} \text{ mole/l}$				
	$\bar{M}_{n,theo} = 2900$	$= 1900$	$= 1800$				
	Input rate = 60 ml/min	= 16 ml/min	= 30 ml/min				
1	3350	8180	2200	4600	1670	3470	2.08
2	3150	7450	2200	4600	1700	3460	2.03
3	3620	8260	1950	4100	1680	3440	2.05
4	3040	6860	2000	4150	1650	3500	2.12
5	2630	6140	1950	4050	1870	3890	2.08
6	3140	6700	1850	3950	2050	4340	2.13
7	2640	5580	2000	4300	2200*	4810	2.18
8	2680	5680	2150	4900	2300	5050	2.19
9	3040*	6420	2400*	5300	2400	5400	2.26
10	3850*	8840	2600	6100	2600	5760	2.18
11	6230	12800	3100	6800	3200	7330	2.30
12	8170	16300	3800	7700	3900	9060	2.30
13	8890	17600	3800	8300	5070	11300	2.23
14	12900	24100	4200	9400	6900	14000	2.02
15	8900	22900	2900	7900	6970	14500	2.08
16	14800	27500	3000	7000	8610	18400	1.90
17	16500	29700			8910	16800	1.89
18	18400	31600			7850	16300	2.08
19	20700	35000			7450	15500	2.08

* approximate onset of precipitation (heterogeneous system)

this problem and to extend the homogeneous phase of the continuous polymerization by the use of a tubular reactor.

Figure 2. GPC RI Traces of Experiment XII

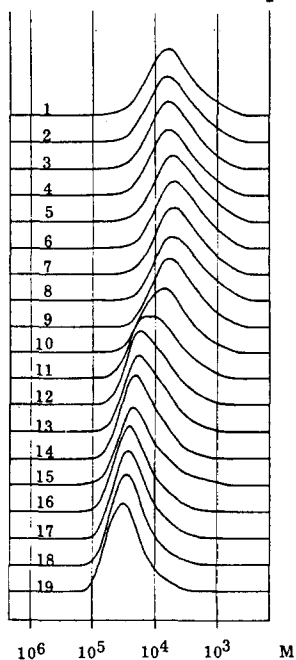
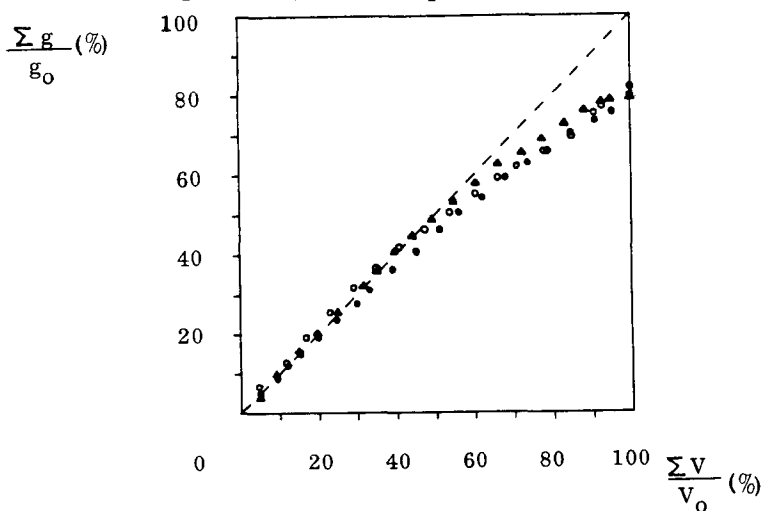
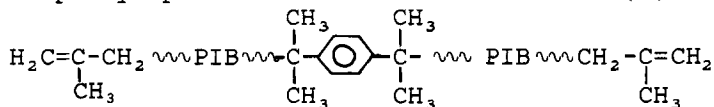


Figure 3. Weight percent polymer exiting the reactor relative to the initial amount of monomer [$\Sigma g/g_0$ (%)] vs. the volume percent of polymer solution exiting the reactor relative to the initial volume [$\Sigma V/V_0$ (%)]. Dotted line shows 100% conversion. ● = Exp. XII; ○ = Exp. XIII; ▲ = Exp. XV.



B) Structural Analysis

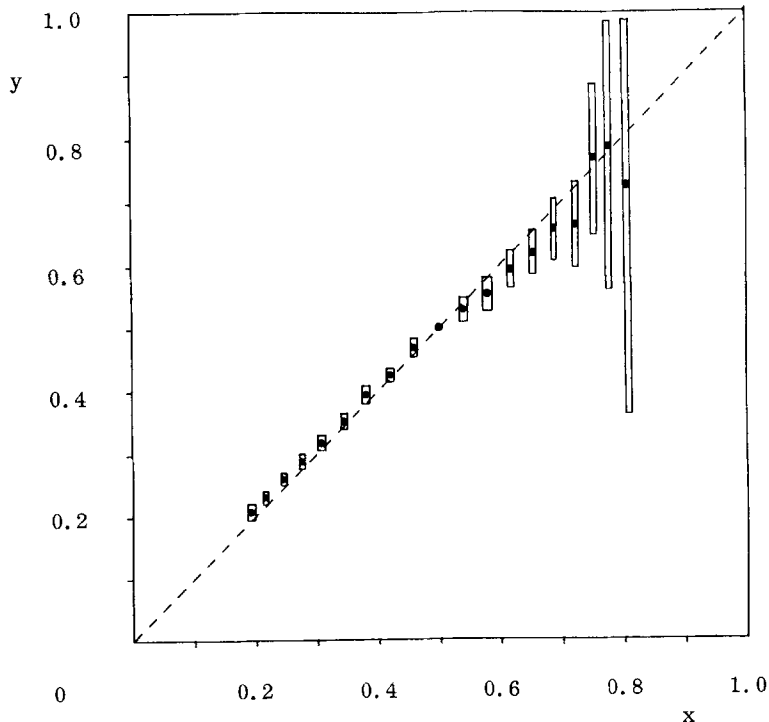
The structure of the products has been quantitatively characterized by ^1H NMR spectroscopy and by a recently developed sensitive plotting method (4). For ^1H NMR analysis the α, ω -ditert.-chloroPIBs were quantitatively dehydrochlorinated to α, ω -diisopropenylPIBs and the concentrations of the terminal vinylidene protons quantitated by integrating against the four phenyl protons as internal standards (5):



Integrations yielded the expected equivalency of vinylidene/aromatic protons, i.e., $\bar{F}_n = 2.0 \pm 0.1$.

The modified Kennedy-Smith plot (3,4) has been used to further corroborate quantitatively the expected structure. Figure 4 shows a representative plot of the data obtained with the polymer harvested during the 10th residence time in Expt. XII. The fact that the experimental points fall within experimental error on the theoretical line of unity slope indicates that each polymer molecule in the sample contained the same number of chromophores (i.e., one phenyl group) in the chain.

Figure 4. Modified Kennedy-Smith Plot of Expt. XII/10



Conclusions

According to the evidence presented herein, as long as the continuous polymerization system remains homogeneous, essentially perfectly telechelic PIB is produced ($\bar{F}_n = 2.0 \pm 0.1$), its molecular weight is governed by eq. 1, the conversion is 100%, and the molecular weight distribution is close to the theoretical value for linear telechelics ($\bar{M}_w/\bar{M}_n \sim 1.5$) (6).

Acknowledgement

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