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Living carbocationic polymerization

XIII. Telechelic polyisobutylenes by the linear bifunctional aliphatic initiator system: $CH_3OC(CH_3)_2CH_2C(CH_3)_2CH_2C(CH_3)_2OCH_3/BCl_3$

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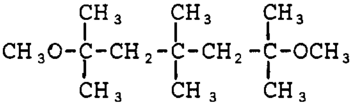
Summary

2,6-Dimethoxy-2,4,4,6-tetramethylheptane (TMHDiOMe) in conjunction with BCl_3 has been found to be an efficient linear bifunctional aliphatic initiator for the living carbocationic polymerization of isobutylene in CH_2Cl_2 or CH_3Cl solvents at -30°C (using both the IMA and AMI techniques) and in CH_2Cl_2 at -10°C (using AMI). The living nature of the polymerization was demonstrated by linear $\overline{M}_n$ versus amount of PIB formed (W_{PIB}) plots starting at the origin, i.e., $\overline{DP}_n$ obeyed [IB]/[TMHDiOMe·BCl_3]. The molecular weight distributions of polyisobutylenes (PIB) synthesized at -30°C in CH_2Cl_2 were narrower (1.3-2.0) than those synthesized at -10°C in CH_2Cl_2 (1.7-1.9). Forced termination by quenching with methanol produces α,ω- tert.-chlorine capped telechelic PIBs.

Introduction

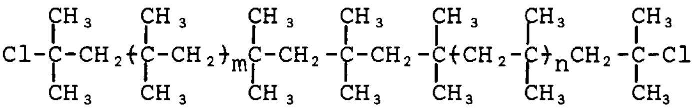
Initiation of living IB polymerization by aromatic tert.-ether/BCl_3 complexes has been amply demonstrated (1-4). This research has now been extended to initiation by aliphatic ethers. Thus we have synthesized the linear bifunctional aliphatic ether 2,6-dimethoxy-2,4,4,6-tetramethylheptane(TMHDiOMe)



$$CH_3O-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OCH_3$$

and used it in conjunction with BCl_3 for the living polymerization of isobutylene.

This paper describes the synthesis of liquid narrow mol. wt.dispersity α,ω-tert.-chloro-telechelic PIBs by the TMHDiOMe/BCl_3 initiating system in CH_2Cl_2 or CH_3Cl diluents in the range from 0° to -30°C and quenching with CH_3OH. Based on previous experience we anticipated the following structure of the tert.-chlorine-telechelic PIB:



$$Cl-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2\!\left(\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2\right)_m\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}\!\left(CH_2-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}\right)_nCH_2-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-Cl$$

Experimental

A. Materials

1,5-Dimethyl-3,3-dimethylpropyl dicarboxylate ($CH_3OOC·CH_2-C(CH_3)_2-CH_2COOCH_3$) was prepared by refluxing a

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mixture of 20 g (0.125 mole) 3,3-dimethyl glutaric acid, 500ml (12.5 mole) anhydrous methanol and 25 ml concentrated sulfuric acid under stirring for 48 hrs. The mixture was cooled to room temperature and the product was extracted with benzene, washed with water several times until the waste water was acid free. The benzene solution was dried with anhydrous magnesium sulfate, filtered, and the solvent was evaporated (rotavap). The product was a colorless liquid, yield 20,8 g (88%). ^1H NMR spectroscopy using CCl_4 showed resonances at 1.1, 2.35 and 3.65 ppm characteristic of the $C\underline{H}_3$-, -$C\underline{H}_2$- and $C\underline{H}_3O$- protons, respectively.

2,6-Dihydroxy-2,4,4,6-tetramethylheptane was synthesized as follows: To a solution of 20.7 g (0.11 mole) 1,5-dimethyl-3,3-dimethylpropyl dicarboxylate in 200 ml THF under a blanket of N_2 were added dropwise 200 ml (2.8M, 0.56 mole) methylmagnesium bromide (Aldrich) in ethyl ether and stirred for 15 hrs at $< 5°C$. Then the charge was slowly added to a 35 g NH_4Cl-400 g ice mixture under stirring. The system was extracted with ethyl ether and the extract was washed with water, dried over anhydrous magnesium sulfate overnight, and the solvent was evaporated. The crude product was purified by recrystallization from ethyl acetate. White needles, yield 10.2 g (49%), m.p. 91.0-92.5°C, ^1H NMR (CCl_4), δ(ppm) 1.0 (methyl, s,6H), 1.25 (methyl, s,12H) 1.6 (methylene, s,4H), 3.8 (hydroxy, s,2H).

2,6-Dimethoxy-2,4,4,6-tetramethylheptane (TMHDiOMe) was prepared by etherification of the corresponding alcohol by sodium hydride and methyl iodide. To 2.3 g (0.096 mole) sodium hydride in a 50 ml flask were added 2.7 g (0.014 mole) melted (heating gun) 2,6-dihydroxy-2,4,4,6-tetramethylheptane under nitrogen and the system was stirred at 90-95°C for 12-15 hrs. After cooling to room temperature 12 ml (0.19 mole) methyl iodide was added and stirred for 12 hrs. The product was extracted with n-hexane, filtered, dried over sodium sulfate overnight, and the solvent was removed (rotavap). A colorless liquid was obtained, yield 2.1 g (68%). ^1H NMR δ(ppm), 1.05 ($C\underline{H}_3$-, s,6H), 1.15 ($C\underline{H}_3$-, s,12H), 1.55 (-$C\underline{H}_2$-, s,4H), 3.15 (-$OC\underline{H}_3$, s,6H). According to this evidence, the ether was essentially pure. Figure 1 shows the ^1H NMR spectrum.

B. Polymerization and Characterization

Experiments have been carried out under dry nitrogen in a stainless steel dry box using test tubes at -30°, -10° and 0°C. Both the "incremental monomer addition" (IMA) and "all monomer in" (AMI) techniques have been used (5). Charges were quenched by prechilled MeOH. Molecular weights were determined using a Waters high-pressure GPC instrument equipped with a Model 6000 A pump, Differential Refractometer R-401, UV Absorbance Detector Model 440, and five microstyragel columns (500, 10^3, 10^4, 10^5, 10^6). Flow rate: 1 ml/min. The calibration curve was made by well-fractionated PIB standards. ^1H NMR spectra were obtained by a Varian T-60 NMR spectrometer.

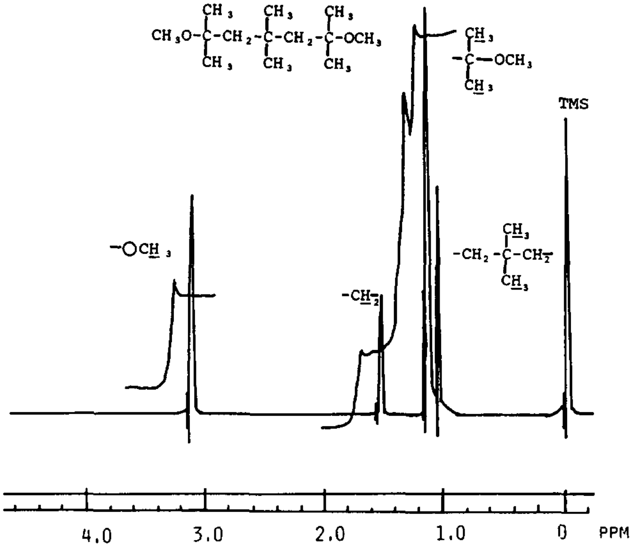

Figure 1. ^{1}H NMR Spectrum of 2,6-Dimethoxy-2,4,4,6-tetramethylheptane (TMHDiOMe)

Results and Discussion

1. Kinetic Studies

Table I shows the results of experiments designed to test the activity of the TMHDiOMe/BCl_3 system for the polymerization of IB. Polymerizations were induced by adding BCl_3 to TMHDiOMe/IB/CH_2Cl_2 charges. After about 40 mins the appearance of haziness indicated polymerization. By this measure the polymerizations appeared to be slower than those induced by the aromatic ethers. In view of these relatively slow polymerizations the reaction time was arbitrarily set at 60 mins.

Table I. Demonstration of Initiating Activity of TMHDiOMe/BCl_3 System*

TMHDiOMe mole/ℓ	Conv. %	$\overline{M}_n$ g/mole	$\overline{M}_w/\overline{M}_n$	I_{eff} %
-	70	55,300	1.8	-
1.88×10^{-2}	93	3,050	1.4	85
9.07×10^{-3}	80	4,300	1.5	107
6.11×10^{-3}	81	7,075	1.4	99

*[BCl_3] = 2.4×10^{-1}mole/ℓ. [IB] = 0.94 mole/ℓ, -30°C, 60 min., CH_2Cl_2, total volume = 25 ml

Promisingly, the $\overline{M}_n$s were much lower than that obtained in the absence of TMHDiOMe. Conversions were consistently very high (80-93%), I_{eff}s ($W_{PIB}/\overline{M}_n\cdot$[TMHDiOMe]) were $\sim$100% and $\overline{M}_w/\overline{M}_n$s were less than 2.0.

Figure 2 shows a representative $\overline{M}_n$ versus W_{PIB} (g polymer formed) plot obtained in a series of polymerizations carried out in CH_3Cl and CH_2Cl_2 diluents at -30°C using the IMA technique. The insert shows the number of PIB chains N (i.e., $W_{PIB}/\overline{M}_n$) as a function of W_{PIB}. Linear $\overline{M}_n$ versus W_{PIB} plots starting at the origin and the horizontal N versus W_{PIB} plots demonstrate living polymerizations i.e., $\overline{DP}_n \approx$ [IB]/[TMHDiOMe]. The solid lines in the figures are "theoretical" i.e., reflect the relationship $\overline{DP}_n \approx$ [monomer]/[initiator].

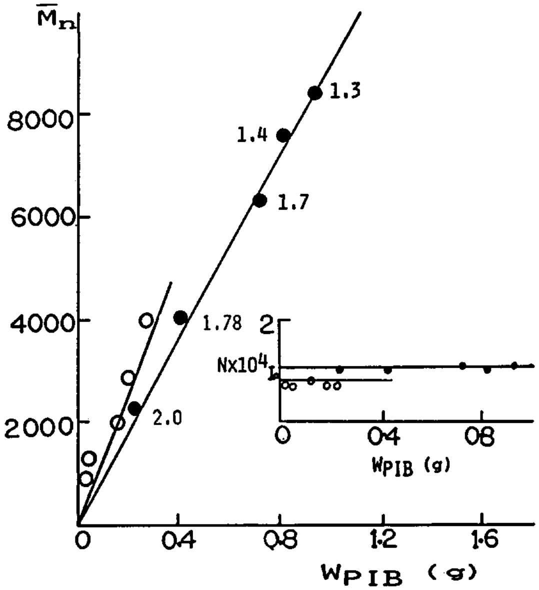

Figure 2. $\overline{M}_n$ and N versus W_{PIB} plots for TMHDiOMe/BCl_3/IB/-30°C using the IMA technique. [TMHDiOMe] = 3.47×10^{-3} mole/ℓ in CH_3Cl (o), [TMHDiOMe] = 4.72×10^{-3} mole/ℓ in CH_2Cl_2 (●), [BCl_3] = 2.4×10^{-1} mole/ℓ. The solid lines are theoretical. Numbers indicate $\overline{M}_w/\overline{M}_n$ values

Figure 3 shows the GPC traces of polymers prepared at -30°C in CH_2Cl_2 diluent by using the IMA technique. The width of distributions decreases from 2.0 to1.3 with increasing $\overline{M}_n$. This observation also indicates living polymerizations (5,6).

Figure 4 shows the results obtained by using both the AMI and IMA techniques and CH_2Cl_2 at -10°C. Evidently living polymerization has been obtained by the AMI method as indicated by the proximity of the data to the theoretical line and decreasing $\overline{M}_w/\overline{M}_n$ values. In contrast, by the use of the IMA technique chain transfer to monomer occurs as shown by the lower than theoretical $\overline{M}_n$s obtained (cf. dotted line).

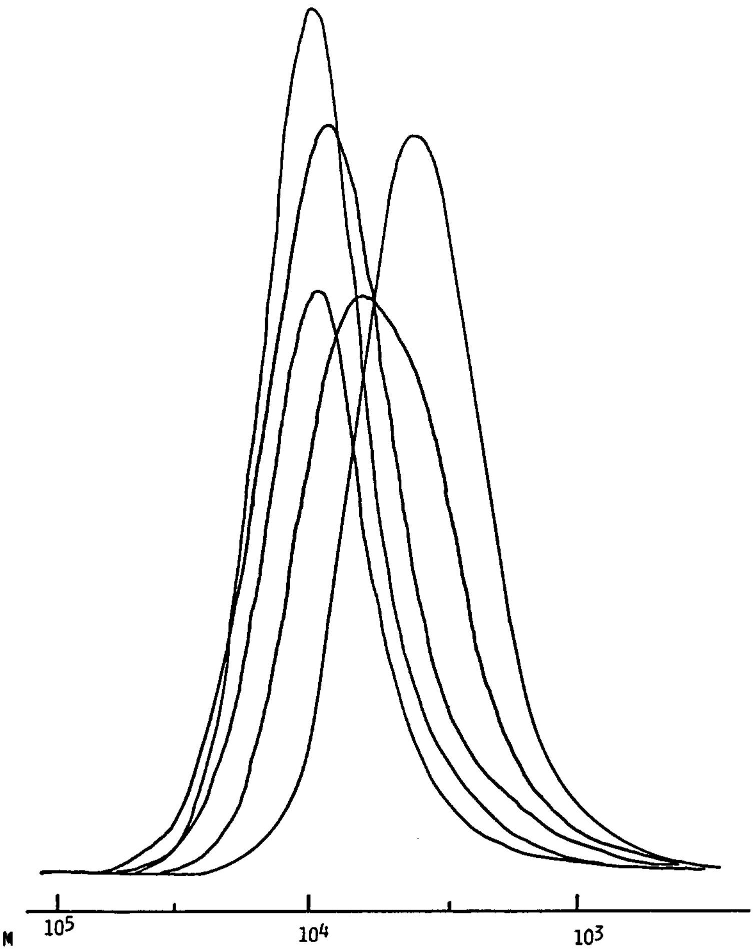

Figure 3. GPC traces of PIBs obtained by using the TMHDiOMe/BCl_3/IB/-30°C/CH_2Cl_2 system and the IMA technique. [TMHDiOMe] = 4.72 x 10^{-3} mole/ℓ. [BCl_3] = 2.4 x 10^{-1} mole/ℓ. Total volume = 25 ml.

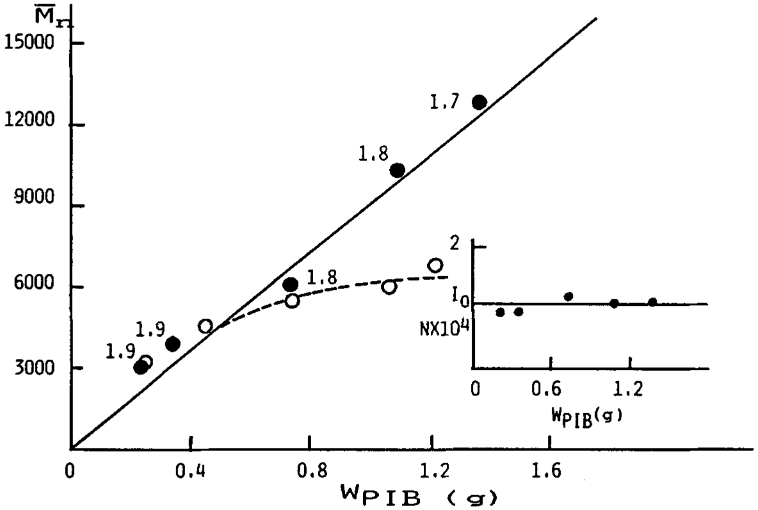

Figure 4. $\overline{M}_n$ and N versus W_{PIB} plots for TMHDiOMe/ BCl_3/IB/CH_2Cl_2/-10°C experiments using the AMI (●) and IMA (o) techniques. [TMHDiOMe]= 4.72×10^{-3} mole/ℓ, [BCl_3] = 2.4×10^{-1} mole/ℓ. Total volume = 25 ml. Numbers indicate M_w/M_n values. The solid line is theoretical.

A similar set of experiments has been carried out with CH_2Cl_2 diluent at 0°C under conventional (i.e., AMI) conditions. In these experiments the same amount of BCl_3 was injected into a series of five sealed tubes containing increasing amounts of monomer under moderate pressure. The results are shown in Figure 5. Obviously, chain transfer to monomer is operational, i.e., the $\overline{M}_n$s (dotted line) are below the theoretical (solid line).

2. Termination Studies

The end groups of PIBs obtained by the TMHDiOMe/BCl_3 living initiating system and quenched by CH_3OH have been determined and quantitated. Since from past experience we suspected that the end groups will be $-CH_2C(CH_3)_2Cl$ (3-5,7-11) the analysis involved our routine method, i.e., quantitative dehydrochlorination by t-BuOK followed by quantitative ^1H NMR analysis (12). According to these investigations, the end groups indeed were found to be tert.-chlorides. Evidently the end groups of PIBs prepared by living ester or ether/BCl_3 complexes or by various inifer systems, when quenched with nucleophiles (e.g., CH_3OH) are invariably $-CH_2C(CH_3)_2Cl$.

In sum, we propose that the formula shown in the Introduction represents the structure of telechelic PIBs produced by the TMHDiOMe/BCl_3 initiating system by a living polymerization process. It is of interest that this structure has previously also been obtained by the use of the linear aliphatic diacetate (2,4,4,6-tetramethylheptane-2,6-diacetate)/BCl_3 initiating system (8,9).

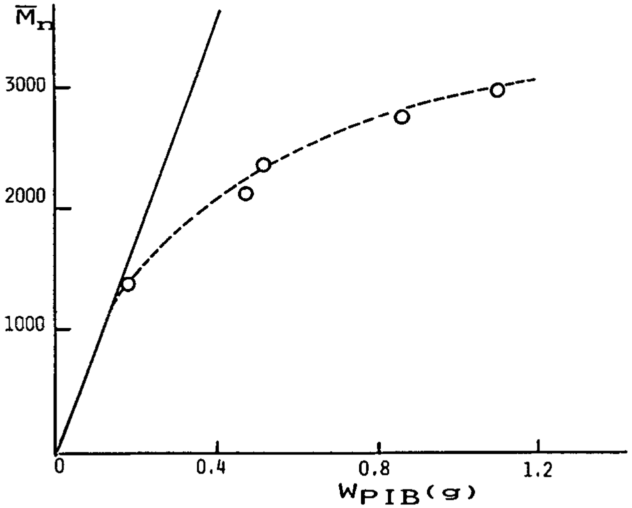

Figure 5. $\overline{M}_n$ versus W_{PIB} plot for TMHDiOMe/BCl_3/IB/CH_2Cl_2/0°C experiments using the conventional AMI technique. The solid line is theoretical. [TMHDiOMe] = 4.72×10^{-3} mole/ℓ, [BCl_3] = 2.4×10^{-1} mole/ℓ, Total volume = 25 ml.

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