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Living carbocationic polymerization

IX. Three-arm star telechelic polyisobutylenes by $C_6H_3(C(CH_3)_2OCH_3)_3/BCl_3$ complexes

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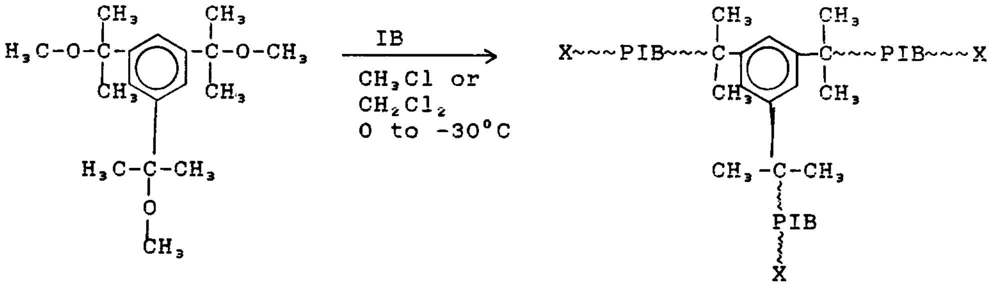
Summary

Three-arm star telechelic liquid polyisobutylenes PIB carrying exactly three $-CH_2C(CH_3)_2Cl$ end groups have been synthesized by living carbocationic polymerization using $C_6H_3(C(CH_3)_2OCH_3)_3/BCl_3$ complexes in CH_3Cl and CH_2Cl_2 diluents in the 0° to -30°C range. The living nature of the polymerizations was demonstrated by linear $\bar{M}_n$ versus W_{PIB} (g PIB) formed plots starting at the origin and horizontal N (moles of PIB) versus W_{PIB} plots. Initiating efficiency (I_{eff}) was close to $\sim$100% and $\bar{M}_n$ was determined by the [monomer]/[initiator] ratio. Polymerizations quenched by methanol yield tert.-chlorine end groups which have been quantitatively converted to isopropylidene ($-CH_2C(CH_3)=CH_2$) termini.

I. Introduction

Since the introduction of the living carbocationic polymerization technique (1) a variety of linear telechelic polyisobutylenes PIB carrying one (1,2) and two(3,4) $-CH_2C(CH_3)_2Cl$ end groups have been synthesized and characterized. We have now extended the living technique used for the syntheses of linear telechelics (3) to the preparation of 3-arm star telechelic polymers. This paper concerns the synthesis (and characterization) of the first 3-arm star PIB carrying $-CH_2C(CH_3)_2Cl$ termini by the trifunctional 1,3,5-tris(2-methoxypropane)benzene/BCl_3 initiating system. The tert.-chlorine end groups have been quantitatively converted to isopropylidene functions. Schematically:



Where X = $-CH_2-C(CH_3)_2Cl$,

$-CH_2-C(CH_3)=CH_2$

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II. Experimental

A. Materials

1,3,5-Tri(2-methoxyisopropyl)benzene(tricumyl methoxy, TriCuOMe) has been synthesized by etherifying 1,3,5-tris(2-hydroxylisopropyl)benzene. The latter was obtained from trimethyl-1,3,5-benzenetricarboxylate synthesized from 1,3,5-benzenetricarboxylic acid (trimesic acid). Thus: In a 1000 ml. two neck round bottom flask equipped with a magnetic stirring bar, condenser and pressure equalized separatory funnel, a solution of trimesic acid (Amoco Chem. Co., 18g, 0.086 mole) in 500 ml anhydrous methanol was placed to which was added dropwise conc. sulfuric acid (Fisher, reagent grade, 20 ml) under reflux. After refluxing for 48 hrs the charge was cooled to room temperature and stored at ∼-5°C for about 16 hr. The solid product was filtered and washed with distilled water several times until the filtrate was acid free. The trimethyl-1,3,5-benzenetricarboxylate is a colorless solid; Yield 21.6g (>98%) m.p. 145-147°C (lit. 145-147°C). ^{1}H NMR spectroscopy (CCl_4) shows resonances at 9.0 and 4.0 ppm characteristic of aromatic and methyl protons, respectively. The trimethyl-1,3,5-benzene-tricarboxylate was converted to the corresponding alcohol by Grignard reaction: In a 500 ml two neck round bottom flask equipped with a magnetic stirring bar, pressure equalized separatory funnel under dry N_2 atmosphere a solution of trimethyl-1,3,5-benzene-tricarboxylate (16g, 0.063 mole) in anhydrous THF (280 ml) was cooled to 0°C. Then a solution of MeMgBr in Et_2O (Aldrich Chem. Co., 0.448 mole) was added dropwise and the system was stirred at 0°C for 12-18 hrs. The mixture was poured under stirring into a mixture of 280g crushed ice and 18g ammonium chloride, extracted with ethyl ether, and dried with anhydrous $Mg(SO_4)_2$. Then the solution was filtered, and the solvent removed (rotavap). The crude 1,3,5-tris(2-hydroxylisopropyl)benzene was recrystallized from ethyl acetate. Yield: 15.9g (>98%), m.p. 143-145°C (literature m.p. could not be found). ^{1}H NMR spectroscopy (60 MHz Varian instrument, $CCl_4 + CD_3OD$) shows resonances at 7.4 and 1.6 ppm characteristic of aromatic and methyl protons, respectively. The alcohol was etherified to TriCuOMe as follows: In a 250 ml one neck round bottom flask equipped with a condenser and magnetic stirring bar a solution of 1,3,5-tris(2-hydroxylisopropyl)benzene (14g, 0.056 mole) in methanol (72.5 ml) was placed and concentrated sulfuric acid (Fisher, reagent grade, 0.0084 ml) was added. After refluxing (∼65°C) for 16 hrs, the charge was cooled to room temperature, hexanes (100 ml) was added and stirred for a few minutes. The organic layer was washed several times with water, separated, and dried with anhydrous sodium sulfate. Finally the product was filtered, the solvent removed (rotavap) and recrystallized several times from hexanes (rotavap). Yield: 15g (>90%), m.p. 43-45.5°C (literature m.p. could not be found). The extent of etherification was analyzed by ^{1}H NMR spectroscopy (60 MHz, Varian instrument). The resonance at 3.26 ppm associated with $-OC\underline{H}_3$ was quantitatively related to the resonance at 7.4 ppm characteristic of aromatic protons and to the resonance at 1.73 ppm associated with $-C\underline{H}_3$. According to this evidence the ether was essentially pure.

B. Polymerization and Characterization Methods

Polymerization and characterization methods have been described (1,2,5,6). Polymerization experiments at 0°C were carried out in large (60 ml) test tubes sealed with rubber septums, tied with wires and fastened with teflon tape. The tubes were filled by injecting with a syringe CH_2Cl_2, TriCuOMe solution in CH_2Cl_2, and isobutylene IB (cooled to -30°C to aid syringing) in this order at 0°C ± 2°C. Polymerizations were initiated by injecting BCl_3 cooled to -30°C. The systems were thoroughly mixed (turbomix) and replaced in the constant temperature bath at 0 ± 2°C. After an arbitrary 30 mins. the reactions were quenched with prechilled MeOH and the products worked up as described (2,5,6).

C. Error Analysis

Figures 1-3 (see Kinetic Investigations) contain error bars constructed by assuming an error of ±10% for $\overline{M}_n$ by GPC, and that of ±0.05g for W_{PIB}. The error limits in the N versus W_{PIB} inserts of Figures 1-3 were calculated as follows:

$$N = W_{PIB}/\overline{M}_n$$

thus considering the errors

$$N = (W_{PIB} \pm \delta W_{PIB})/(\overline{M}_n \pm \delta \overline{M}_n)$$

Since $N = f(W_{PIB}, \overline{M}_n)$ the Gaussian error, including the error limit of the variables, may be expressed as

$$\Delta N = \pm \sqrt{\left(\frac{\partial N}{\partial W_{PIB}} \cdot \delta W_{PIB}\right)^2 + \left(\frac{\partial N}{\partial \overline{M}_n} \cdot \delta \overline{M}_n\right)^2}$$

$$\frac{\partial N}{\partial W_{PIB}} = \frac{1}{\overline{M}_n} \quad \text{and} \quad \frac{\partial N}{\partial \overline{M}_n} = -W_{PIB} \cdot \frac{1}{\overline{M}_n^{\,2}}$$

so that the minimum error ($0.05 < W_{PIB} < 0.1$):

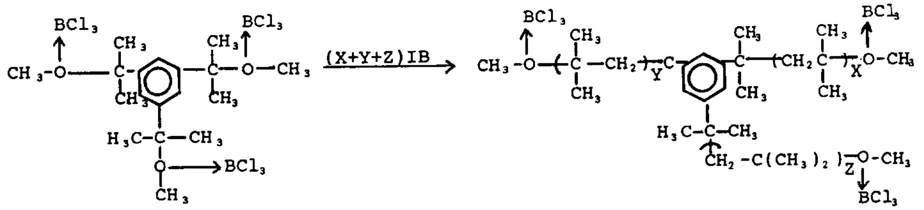
$$\Delta N = \pm \sqrt{\left(\frac{1}{\overline{M}_n} \cdot \delta W_{PIB}\right)^2 + \left(\frac{W_{PIB}}{\overline{M}_n^{\,2}}\right)^2 (\delta \overline{M}_n)^2}$$

The error bars in the inserts in Figures 1-3 show the minimum errors calculated for each point by this equation.

III. Results and Discussion

A. Kinetic Investigations

In our earlier publications (2,3) we have described that complexes of BCl_3 with certain tert.-ethers are efficient initiators for the living polymerization of IB. In line with these investigations we postulated that the TriCuOMe/BCl_3 system will give rise to three-arm living stars, i.e., three living PIB chains propagating at the three tert.-ether sites:



The results of orienting experiments shown in Table I showed that TriCuOMe in the presence of BCl_3 is indeed an efficient initiator for IB polymerizations in both CH_3Cl and CH_2Cl_2 diluents at -10 and -30°C.

TABLE I

Representative Results of Orienting Experiments using the TriCuOMe/BCl_3 Initiating System*

[TriCuOMe] mole/ℓ	Diluent	Temp. °C	Conv. %	$\bar{M}$ g/mole	$\bar{M}_w/\bar{M}_n$	I_{eff} %
-	CH_3Cl	-30	14	96,800	1.4	-
5.25×10^{-2}	CH_3Cl	-30	>98	1,200	1.7	100
1.75×10^{-2}	CH_2Cl	-30	>98	3,500	2.0	89
5.84×10^{-3}	CH_3Cl	-30	>98	13,000	1.4	70
-	CH_2Cl_2	-30	70	55,300	1.8	-
5.25×10^{-2}	CH_2Cl_2	-30	>98	1,300	2.4	98
1.75×10^{-2}	CH_2Cl_2	-30	>98	4,100	2.3	76
5.84×10^{-3}	CH_2Cl_2	-30	>98	13,350	1.6	68
-	CH_2Cl_2	-10	75	64,000	1.7	-
5.25×10^{-2}	CH_2Cl_2	-10	>98	1,500	2.2	86
1.75×10^{-2}	CH_2Cl_2	-10	>98	4,800	2.9	75
5.84×10^{-3}	CH_2Cl_2	-10	>98	13,700	2.0	55

*$[BCl_3] = 5.1 \times 10^{-1}$ mole/ℓ [IB] = 0.94 mole/ℓ, 40 min, total volume = 25 ml

Figure 1 shows a representative $\bar{M}_n$ versus W_{PIB} plot, and the insert the number of polymer moles formed, N = gPIB/$\bar{M}_n$, versus W_{PIB}. The polymers have been obtained by the incremental monomer addition (IMA) technique with CH_2Cl_2 (plot 1a) and CH_3Cl (plot 1b) diluents at -30°C. The linear $\bar{M}_n$ versus W_{PIB} plots starting at the origin demonstrate living polymerizations. The solid lines are "theoretical", i.e., expected to arise at $\bar{M}_n$ = [IB]/[initiators]. Theoretical results have been obtained by the use of CH_2Cl_2, and the [IB]/[TriCuOMe] ratio controlled $\bar{M}_n$s. The I_{eff}s in these experiments were ∿100%. Higher than expected $\bar{M}_n$s have been obtained by the use of CH_3Cl, but the data are quite close to the theoretical (solid) line even in this instance. In both series the number of polymer moles remained constant during the experiment (note the horizontal N versus W_{PIB} plots within experimental error). Importantly, also, the $\bar{M}_w/\bar{M}_n$ values decreased, i.e., the molecular weight distributions show a narrowing tendency, with incremental monomer addition.

Figure 2 shows the results of experiments carried out at -10°C using both the IMA technique and conventional AMI (all monomer in) conditions. Evidently these results are essentially the same as those obtained with other tert.-ether/BCl_3 systems (2). Similar results have also been obtained with tert.-ester/BCl_3 systems (1). In experiments in which the same amounts of BCl_3 were added to a series of five reactors containing an increasing amount of monomer at -10°C (i.e., AMI conditions), essentially theoretical $\bar{M}_n$s have been obtained with conversions close to 100%. Table II shows conditions and results. Evidently living polymerization can be obtained even at -10°C, provided the charge contains all the monomer at the instant of initiation. These results are further corrorborated by the horizontal N versus W_{PIB} plot shown in the insert of Figure 2.

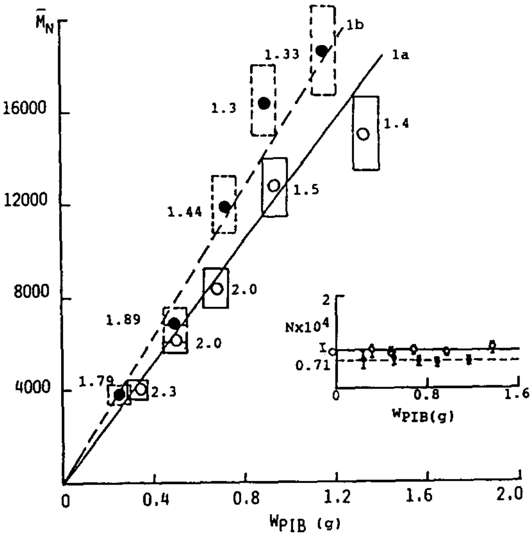


Figure 1. $\bar{M}_n$ and N, the number of PIB moles(insert) versus W_{PIB} weight of PIB formed in TriCuOMe/BCl_3 /IB/ -30°C experiments using the IMA technique: CH_3Cl (●), and CH_2Cl_2 (O), [TriCuOMe]= 3.53×10^{-3} mole/ℓ, [BCl_3]= 1.9×10^{-1} mole/ℓ. Total volume = 25 ml. The numbers are $\bar{M}_w/\bar{M}_n$ values. The solid lines are theoretical. Error bars constructed by assuming ± 10% for $\bar{M}_n$ and 0.05 g for W_{PIB}.

Figure 2. $\bar{M}_n$ and N, the number of PIB moles(insert), versus W_{PIB} the weight of PIB formed in TriCuOMe/ BCl_3/IB/CH_2Cl_2/-10°C experiments: IMA technique (O), AMI technique (●), [TriCuOMe] = 4.35×10^{-3} mole/ℓ [BCl_3] = 1.9×10^{-1} mole/ℓ. Total volume = 25 ml. The numbers are $\bar{M}_w/\bar{M}_n$ values. The solid lines are theoretical. Error bars constructed by assuming ± ± 10% for $\bar{M}_n$ and 0.05 g for W_{PIB}

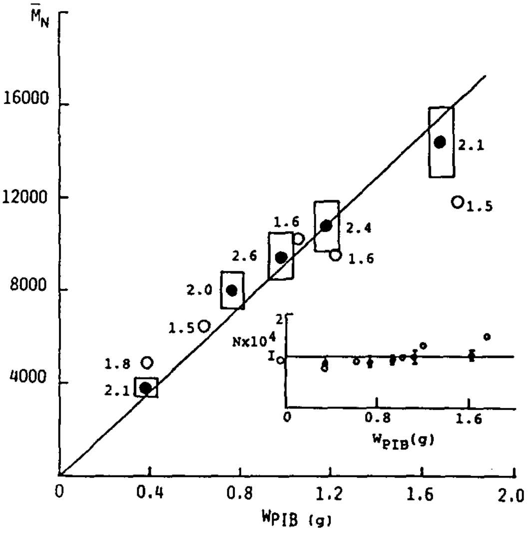


TABLE II

Polymerization of Isobutylene at Various Monomer Concentrations*

[M] mole/ℓ	Conv. %	$\bar{M}_n$ g/mole	$\bar{M}_w/\bar{M}_n$	I_{eff} %
0.266	>98	3,950	2.1	87
0.543	>98	8,200	2.0	85
0.694	>98	9,650	2.6	93
0.840	>98	10,900	2.4	99
1.20	>98	15,250	2.1	102

* [TriCuOMe] = 4.35×10^{-3} mole/ℓ, [BCl_3] = 1.9×10^{-1} mole/ℓ, CH_2Cl_2 -10°C, 30 min, total volume = 25 ml, conventional (AMI) conditions.

Having demonstrated living polymerization of IB at -10°C under conventional (i.e., AMI), conditions, we have carried out polymerizations under moderate pressure at 0°C in CH_2Cl_2. In these experiments the same amount of BCl_3 was injected into a series of five sealed tubes containing an increasing amount of monomer. Figure 3 and Table III show conditions and results. Evidently, virtually theoretical PIB $\bar{M}_n$s have been obtained even at 0°C.

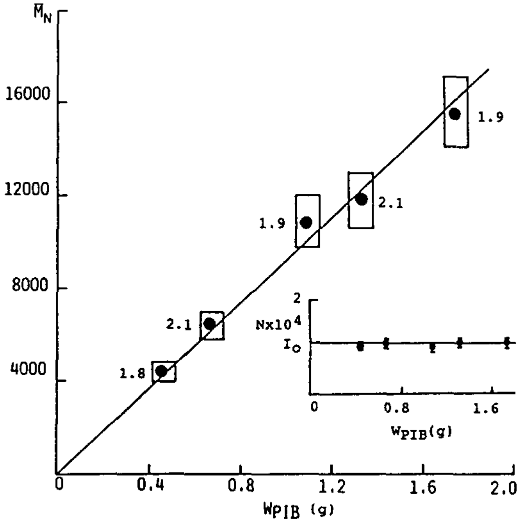


Figure 3. $\bar{M}_n$ and N, the number of PIB moles (insert), versus W_{PIB} the weight of PIB formed in TriCuOMe/BCl_3/IB/CH_2Cl_2/0°C experiments using the AMI method. [TriCuOMe] = 4.35×10^{-3} mole/ℓ, [BCl_3] = 1.9×10^{-1} mole/ℓ. Total volume = 25 ml. The numbers are $\bar{M}_w/\bar{M}_n$ values. The solid lines are theoretical. Error bars constructed by assuming ± 10% for $\bar{M}_n$ and 0.05 g for W_{PIB}

TABLE III

Polymerization of Isobutylene at Various Monomer Concentrations*

[M] mole/ℓ	Conv. %	$\bar{M}_n$ g/mole	$\bar{M}_w/\bar{M}_n$	I_{eff} %
0.320	>98	4,400	1.8	95
0.478	>98	6,350	2.1	97
0.783	>98	10,950	1.9	92
0.950	>98	11,850	2.1	103
1.25	>98	15,600	1.9	103

*[TriCuOMe] = 4.35×10^{-3} mole/ℓ, [BCl_3] = 1.9×10^{-1} mole/ℓ, CH_2Cl_2, 0°C,30 min, total volume = 25 ml, AMI conditions.

In polymerizations at 0°C a fraction of the IB is in the gas phase (bp. of IB = -6.9°C) due to the relatively high temperature employed. The products remain in solution up to $\overline{M}_n$ $\sim$6500, and the systems are homogeneous. In the $\overline{M}_n$ = 10,000-12,000 range the charges are cloudy and above $\overline{M}_n$ = 15,000 polymer precipitates (milky charges).

According to these data living polymerization of IB proceeds at a remarkably high temperature for cationic polymerizations by the use of this new initiating system.

B. Structure, End Group Determination, and Quantitation

The structures of the products have been characterized mainly by ^{1}H NMR spectroscopy and dual detection GPC (1-4). According to spectroscopic studies the PIBs obtained upon quenching with MeOH carry the $-CH_3C(CH_3)_2Cl$ end group. The ^{1}H and ^{13}C spectra were essentially identical to those obtained by and described in conjunction with the tricumyl chloride/BCl_3 trinifer system (7,8).

Quantitative end group analysis was performed by the use of dehydrochlorinated samples. Dehydrochlorination of $-CH_2C(CH_3)_2Cl$ capped PIBs by sterically hindered bases is quantitative and the sole product is the isopropylidine ($-CH_2C(CH_3)=CH_2$) capped product (9,10). The latter end group can be readily quantitated by ^{1}H NMR spectroscopy by relating the $=C\underline{H}_2$ protons from 4.5 to 5 ppm against the aromatic protons from 7 to 7.5 ppm (10). By this routine method the number average end group functionality was $\overline{F}_n$ = 3.0 ± 0.1.

In addition we have analyzed the structural homogeneity of a representative three-arm star PIB ($\overline{M}_n$ = 4000, $\overline{M}_w/\overline{M}_n$ = 2.3) by the use of the Kennedy-Smith-Nagy method (11). This method provides quantitative insight into the distribution of chromophores (in this case the central phenyl moiety) incorporated into the polymer. Figure 4 shows the corresponding plot. The unity slope indicates uniform chromophore distribution in each fraction of the sample.

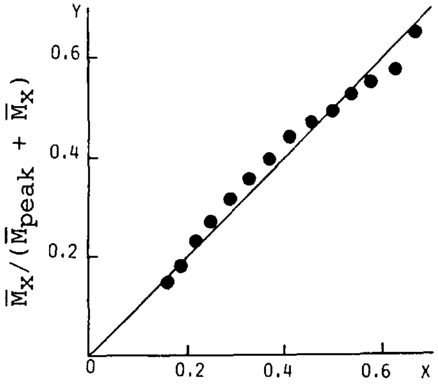


Figure 4. $(UV/RI)_{peak}/[(UV/RI)_{peak} + (UV/RI)_x]$

On the basis of the above data we are confident that the overall structure of our product is that shown by the formula in the introduction.

Acknowledgement

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