Polymer Bulletin 17, 205-211 (1987)

Polymer Bulletin

Living carbocationic polymerization
XII. Telechelic polyisobutylenes by a sterically hindered bifunctional initiator

Biao Wang*, Munmaya K. Mishra, and Joseph P. Kennedy

Institute of Polymer Science, University of Akron, Akron, OH 44325, USA

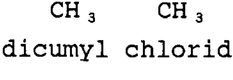
Summary

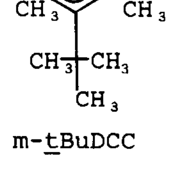
The "living" synthesis of α,ω-di-tert.-chloropolyisobutylene ($^{\underline{t}}$Cl-telechelic PIB) has been accomplished by the use of the sterically hindered bifunctional initiator 1,3-di-(2-methoxy-2-propyl)-5-tert.-butylbenzene (tBu-m-DiCuOMe) in conjunction with BCl_3 coinitiator in CH_3Cl or CH_2Cl_2 diluents at -30°C and -10°C. The living nature of the polymerizations was demonstrated by linear $\overline{M}_n$ versus W_{PIB} (g of PIB formed) plots starting at the origin and horizontal N (number of PIB moles) versus W_{PIB} plots. The molecular weight distributions are narrow ($\overline{M}_w/\overline{M}_n < 2.0$) and tend to decrease with increasing molecular weights. Number average end functionalities have been quantitated and found to be $\overline{F}_n = 2.0 \pm 0.1$.

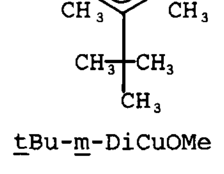
Introduction

Recently we have shown that $^{\underline{t}}$Cl-telechelic PIB can be synthesized by a living polymerization process using the p-dicumyl ether/BCl_3 bifunctional initiator system at -70°C(1). Under essentially identical conditions but higher than -70°C polymerizations gave rise to undesirable indanyl end groups. To overcome the necessity of operating at cryogenic temperatures a search for a sterically hindered living bifunctional initiating system has been instituted.

About three years ago we found (2) that the "unhindered" dicumyl chloride·BCl_3 binifer system yielded $^{\underline{t}}$Cl-telechelic-PIB at or below -70°C(the low temperatures were needed to "freeze out" undesirable terminal indanyl group formation) and that the synthesis temperature could be raised to -20°C without compromising the telechelic purity of the product by the use of the "sterically hindered" binifer 1,3-di(2-chloro-2-propyl)-5-tert.-butylbenzene (m-tBuDCC):


dicumyl chloride


m-tBuDCC


tBu-m-DiCuOMe

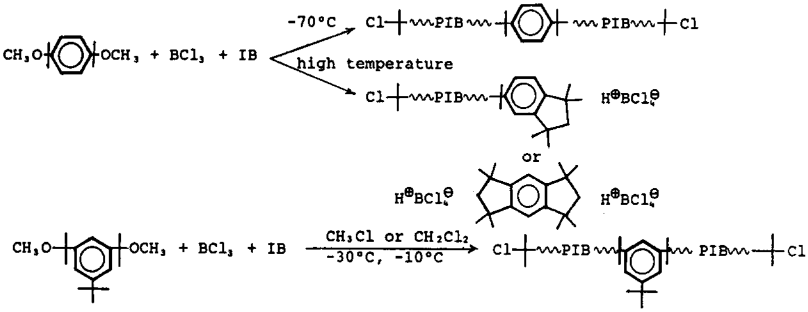
---

* Permanent address: Scientific Research Institute of Petroleum Exploration and Development, Beijing, People's Republic of China

The synthesis of m-tBuDCC is difficult and results in unsatisfactory low yields (3).

Keeping in mind the teachings of the earlier investigation (3), we theorized that pure ^{t}Cl-telechelic-PIBs could be synthesized by a living process at relatively high temperatures e.g., from -30° to -10°C, by the use of the sterically hindered living initiating system tBu-m-DiCuOMe.

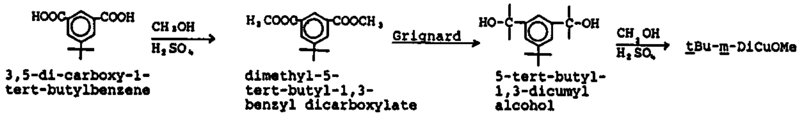
This paper concerns the synthesis of tBu-m-DiCuOMe by an efficient route and the use of this new compound (in conjunction with BCl_3) for the living synthesis of ^{t}Cl-telechelic-PIB in the range from -30° to -10°C. The following equations help to visualize the systems referred to:



Experimental

A. Syntheses

1,3-Di(2-methoxy-2-propyl) tert.-butylbenzene (tBu-m-DiCuOMe) was prepared from 3,5-dicarboxy-1-tert.-butylbenzene by the following set of transformations:



1. Synthesis of dimethyl-5-tert.-butyl-1,3-benzyl dicarboxylate

3,5-Dicarboxyl-1-tert.-butylbenzene (Amoco Chemicals Co.) (20 g, 0.09 mole), was esterified by refluxing for 48 hrs. in CH_3OH (600 ml, 15 mole) in the presence of concentrated H_2SO_4 (38 ml). The mixture was cooled to room temperature, stored at 0°C overnight, the solid was filtered, and washed with water until the filtrate was acid free. The wet solid was dried at ∿50°C and recrystallized from methanol. Yield 20 g (89%). ^{1}H NMR spectroscopy using CCl_4 showed resonances at 1.28, 3.9 and 8.20-8.50 ppm characteristic of methyl protons of the t-butyl group, methyl protons of the ester groups and aromatic protons, respectively.

2. Synthesis of 5-tert.-butyl-1,3-dicumyl alcohol

The alcohol was prepared from the corresponding ester. Thus methyl magnesium bromide (Aldrich, 70 ml. 2.8M, 0.2 mole) in ethyl ether was added dropwise to a solution of the ester (10 g, 0.04 mole) in 100 ml anhydrous THF between 0-5°C under N_2. After stirring for 15-18 hrs. the charge was slowly added to a stirred NH_4Cl (11 g) - ice (160 g) mixture. Then the product was extracted with ethyl ether and the organic layer was dried over magnesium sulfate. The solvent was evaporated and the product was purified by recrystallization from ethyl acetate. Yield: 9.5 g (95%). M.P. 119.5-122°C. ^1H NMR spectroscopy using a CCl_4/CD_3OD mixture showed resonances at 1.25, 1.45 and 7.1-7.25 ppm characteristic of methyl protons of the t-butyl group, methyl protons of isopropyl groups and aromatic protons, respectively.

3. Synthesis of 1,3-di(2-methoxy-2-propyl)-5-tert.-butylbenzene (tBu-m-DiCuOMe)

Etherification was carried out by refluxing a solution of 5-tert.-butyl-1,3-dicumyl alcohol (9.5 g, 0.038 mole) in methanol (30.4 ml) with concentrated H_2SO_4 (0.0038 ml) for 16 hrs. The charge was cooled to ambient temperature, n-hexane (50 ml) was added, and stirred for a few minutes. The organic layer was washed a few times with water, separated, and dried with anhydrous sodium sulfate. The solvent was evaporated and a liquid was obtained. Yield: 8.3 g (80%). ^1H NMR spectroscopy showed resonances at 3.0 ppm ($-OC\underline{H}_3$), 7.2-7.3 ppm (aromatic protons), 1.35 ppm ($-C(C\underline{H}_3)_3$) and 1.5 ppm ($-CH(C\underline{H}_3)_2$). Integration gave 6:3 for the methoxy/aromatic proton ratio. Figure 1 shows the ^1H NMR spectrum. According to this evidence the ether was essentially pure.

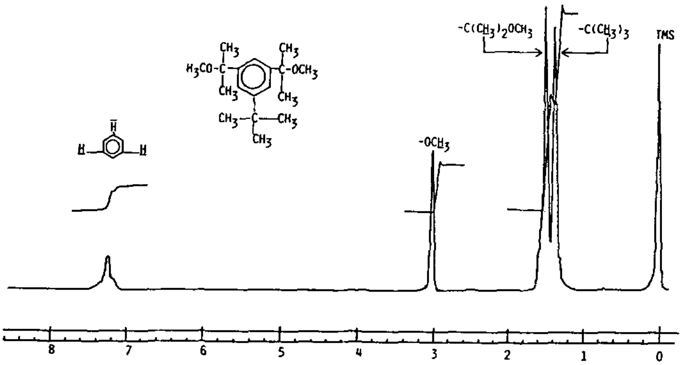


Figure 1. ^1H NMR Spectrum of 1,3-di(2 methoxy-2-propyl)-5-tert.-butylbenzene (tBu-m-DiCuOMe)

B. Polymerization, Characterization and Error Analysis

Polymerizations were carried out in a stainless steel enclosure under N_2. The details of polymerization, characterization methods and error analysis have been described (4,5).

The solid lines in the figures are "theoretical", i.e., reflect the relationship $\overline{DP}_n \approx$ [monomer]/[initiator].

Results and Discussion

1. Demonstration of Living Polymerization by Kinetic Studies

Table I shows the results of representative experiments carried out under various conditions. Polymerizations were very fast and some heat evolution may have occurred upon the addition of BCl_3 to the *t*Bu-*m*-DiCuOMe/IB/solvent charges. The test tubes were rapidly mixed by a turbomixer and then placed into a bath at -30°C. Although final conversions (>98%) probably have been reached much earlier, we have waited for 30 mins before quenching with prechilled MeOH. Conversions were incomplete in the absence of *t*Bu-*m*-DiCuOMe and the $\bar{M}_n$s were high. Similar phenomena have been consistently observed and discussed earlier (5,6). In the presence of the living initiator the $\bar{M}_n$s are lower, I_{eff}s (gPIB/$\bar{M}_n \cdot$[*t*Bu-*m*-DiCuOMe]) are close to 100%, and $\bar{M}_w/\bar{M}_n$s are lower than 2.0. Importantly, $\bar{DP}_n \approx$[IB]/[*t*Bu-*m*-DiCuOMe]. Again these observations are in line with previous experience with similar initiators(1,4,5,6).

TABLE I

Demonstration of Initiating Activity of *t*Bu-*m*-DiCuOMe/BCl_3 Systems*

*t*Bu-*m*-DiCuOMe mole/ℓ	Diluent	Conv. %	$\bar{M}_n$ g/mole	$\bar{M}_w/\bar{M}_n$	I_{eff} %
-	CH_3Cl	10	86,000	2.0	-
1.41×10^{-2}	CH_3Cl	>98	4,360	1.8	85
6.7×10^{-3}	CH_3Cl	>98	8,119	2.0	95
4.4×10^{-3}	CH_3Cl	>98	12,229	1.6	95
-	CH_2Cl_2	70	55,300	1.8	-
1.41×10^{-2}	CH_2Cl_2	>98	4,751	1.9	90
6.7×10^{-3}	CH_2Cl_2	>98	10,234	1.6	78
4.4×10^{-3}	CH_2Cl_2	>98	12,815	1.6	96

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

Figures 2 and 3 show representative $\bar{M}_n$ versus W_{PIB} (g PIB formed) plots obtained in a series of polymerizations carried out using CH_3Cl and CH_2Cl_2 diluents with incremental monomer addition (IMA) and all monomer in (AMI) conditions at -30°C. The inserts show the number of PIB moles formed (N = $W_{PIB}/\bar{M}_n$ versus W_{PIB}. The linear $\bar{M}_n$ versus W_{PIB} plots starting at the origin and the horizontal N versus W_{PIB} plots demonstrate living polymerizations.

The fact that the $\bar{M}_w/\bar{M}_n$s decrease with increasing $\bar{M}_n$s also indicate living systems (cf. numbers in the Figures).

A similar set of experiments has also been carried out with CH_2Cl_2 diluent at -10°C. As shown by the data in Figure 4, living polymerizations have been obtained by the AMI method as shown by the close to theoretical $\bar{M}_n$s obtained; however chain transfer to monomer was present by the IMA technique as indicated by the dotted line (i.e., lower than theoretical $\bar{M}_n$s). Similar observations have been made with ester/BCl_3 and other ether/BCl_3 systems, and the phenomenon has been discussed (4,5,6). Briefly, by the use of the IMA technique

(30 mins incremental monomer addition) proton elimination may slowly occur by a 1st order process, however, under AMI conditions monomer is always present during growth and proton elimination cannot occur (5,6).

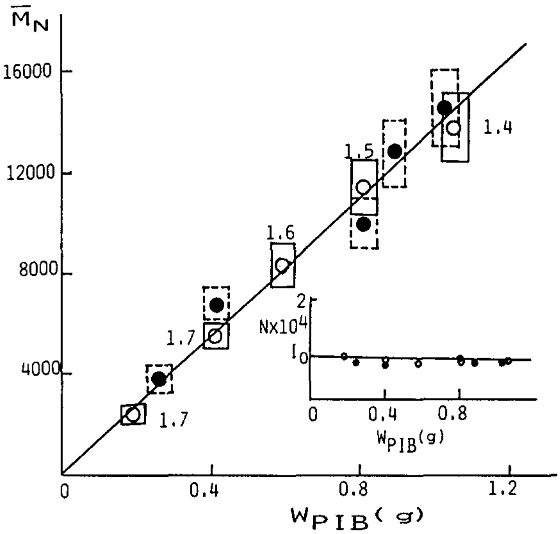


Figure 2. $\overline{M}_n$ and N versus W_{PIB}, plots for *t*Bu-*m*-DiCuOMe/BCl_3/IB/-30°C/CH_3Cl experiments using AMI (●) and IMA (o) techniques. [*t*Bu-*m*-DiCuOMe]= 3.53×10^{-3}mole/ℓ, [BCl_3] = 2.4×10^{-1}mole/ℓ. Total volume = 25 ml. Numbers indicate $\overline{M}_w/\overline{M}_n$ values. The solid lines are theoretical. Error bars constructed by assuming ±10% for $\overline{M}_n$ and 0.05 g for W_{PIB}.

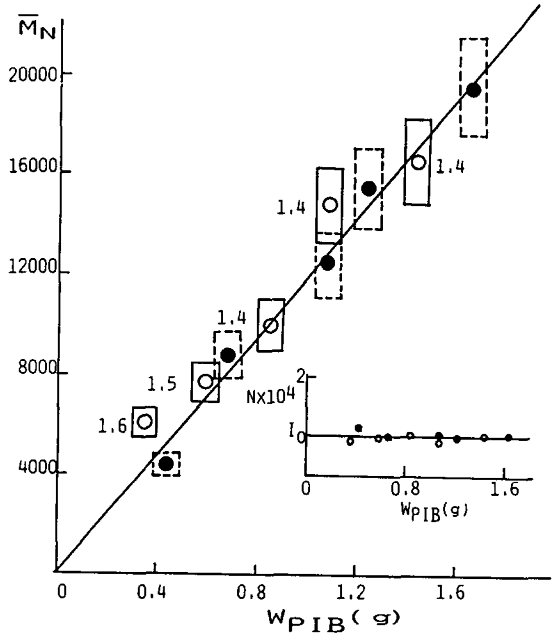


Figure 3. $\overline{M}_n$ and N versus W_{PIB} plots for *t*Bu-*m*-DiCuOMe/BCl_3/IB/-30°C/CH_2Cl_2 experiments using AMI (●) and IMA (o) techniques. [*t*Bu-*m*-DiCuOMe] = 3.53×10^{-3} mole/ℓ, [BCl_3] = 2.4×10^{-1} mole/ℓ. Total volume = 25 ml. Numbers indicate $\overline{M}_w/\overline{M}_n$ values. The solid lines are theoretical. Error bars constructed by assuming ±10% for $\overline{M}_n$ and 0.05 g for W_{PIB}.

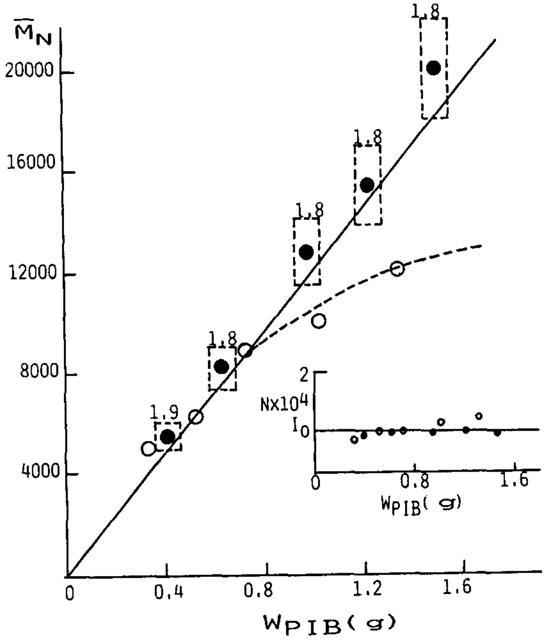
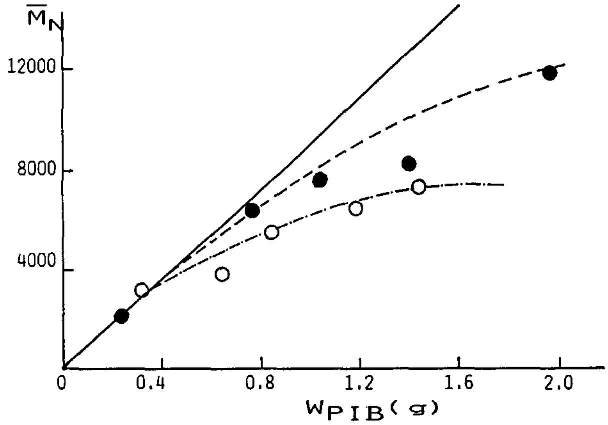


Figure 4. $\overline{M}_n$ and N versus W_{PIB} plots for *t*Bu-*m*-DiCuOMe/BCl$_3$/IB/-10°C/CH$_2$Cl$_2$ experiments using AMI (●) and IMA (o) techniques. [*t*Bu-*m*-DiCuOMe] = 3.53 x 10^{-3} mole/ℓ, [BCl$_3$] = 2.4 x 10^{-1} mole/ℓ. Total volume = 25 ml. Numbers indicate $\overline{M}_w/\overline{M}_n$ values. The solid lines are theoretical. Error bars constructed by assuming ±10% for $\overline{M}_n$ and 0.05 g for W_{PIB}.

Having demonstrated living polymerizations of IB at -10°C under conventional (i.e. AMI) conditions, we have carried out a series of experiments under moderate pressure at 0°C in CH$_2$Cl$_2$. The polymerization details have been described (4). The results are shown in Figure 5. Evidently the $\overline{M}_n$s are less than theoretical (i.e., chain transfer to monomer is operational) and the systems are not living even in the presence of unreacted monomer (AMI). In light of the fact that

Figure 5. $\overline{M}_n$ and N versus W_{PIB} plots for *t*Bu-*m*-DiCuOMe/BCl$_3$/IB/0°C/CH$_2$Cl$_2$ experiments using AMI (●) and IMA (o) techniques. The solid line is theoretical. [*t*Bu-*m*-DiCuOMe] = 4.3 x 10^{-3} mole/ℓ. [BCl$_3$]= 2.4 x 10^{-1} mole/ℓ. Total volume = 25 ml.



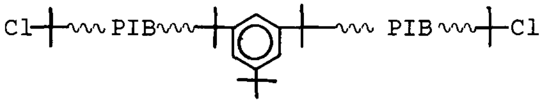
living polymerization has been obtained at 0°C with the symmetrical triester 1,3,5-tris(2-methoxypropane)benzene·BCl_3 initiating system (4), it is surprising that chain transfer has occurred with the structurally very similar hindered diester *t*Bu-*m*-DiCuOMe·BCl_3 combination at the same temperature.

2. End Group Characterization

Interestingly the end groups of PIBs prepared by ester or ether/BCl_3 complexes are tert.-chlorides (1,4,5,6) just as those obtained with inifer systems (3,7,8). Thus we were not surprised to find that the PIBs prepared by the *t*Bu-*m*-DiCuOMe/BCl_3 system were also capped by $-CH_2C(CH_3)_2Cl$ groups. Since the ^1H NMR quantitation of tert.-chloride end group is difficult (60 MHz ^1H NMR shows only qualitative evidence), the analyses were carried out with dehydrochlorinated products (9).

This routine method yields the isopropylidene $-CH_2C(CH_3)=CH_2$ ended PIB which can be readily quantitated. These studies consistently yielded $\bar{F}_n = 2.0 \pm 0.1$.

On the basis of these investigations we propose that the living polymerization of IB by the *t*Bu-*m*-DiCuOMe/BCl_3 initiating system in the range from -30 to -10° gives rise to



Acknowledgement

This material is based upon work supported by the NSF under Grant DMR-84-18617

References

1. M. K. Mishra and J. P. Kennedy, Polym. Bull. (in press) (1986)
2. R. Santos, A. Fehervari and J. P. Kennedy, J. Polym. Sci. Polym. Chem. Ed. Vol. 22, 2685-2697 (1984)
3. R. Santos, J. P. Kennedy and M. Walters, Polym. Bull. 11, 261-267 (1984)
4. M. K. Mishra, B. Wang and J. P. Kennedy, J. Polym. Sci. Polym. Chem. Ed. (in press)
5. R. Faust and J. P. Kennedy, J. Polym. Sci., Polym. Chem. Ed. (in press) and Polym. Bull. 15, 317 (1986)
6. M. K. Mishra and J. P. Kennedy, J. Macromol. Sci. Chem. (in press) (1986)
7. J. P. Kennedy and R. A. Smith, J. Polym. Sci., Polym. Chem. Ed. 18, 1539 (1980)
8. J. P. Kennedy and M. Hiza, Polym. Bull., **8**, 557 (1982)
9. J. P. Kennedy, V.S.C. Chang, R. A. Smith and B. Ivan, Polym. Bull., **1**, 575 (1979)

Accepted January 8, 1987 K