Polymer Bulletin 17, 7–13 (1987)

Polymer Bulletin

Living carbocationic polymerization

VIII. Telechelic polyisobutylenes by the $MeO(CH_3)_2C$-p-C_6H_4-$C(CH_3)_2OMe/BCl_3$ initiating system

Munmaya K. Mishra and Joseph P. Kennedy

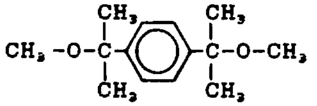
Institute of Polymer Science, University of Akron, Akron, OH 44325, USA

Summary

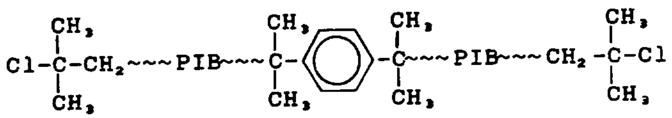
The efficient synthesis of symmetrical telechelic polyisobutylenes carrying $\sim^{t}CH_2C(CH_3)_2Cl$ groups at either end of the molecule, ^{t}Cl-PIB-Cl^{t}, has been accomplished by rapid living polymerization using aromatic di-tert.-ether/BCl_3 initiator system in CH_3Cl at -70°. The living nature of the polymerization was demonstrated by linear $\bar{M}_n$ versus amount of PIB formed (W_{PIB}) plots starting at the origin. The effect of temperature and solvent composition (polar/nonpolar) on the polymer structure has been investigated. Undesirable indanyl end groups which form during polymerizations carried out at -30° and -50°C can be eliminated by decreasing the temperature to -70°C. The apparent activation energy differences have been determined in the -30 to -70°C range at different polar/nonpolar solvent compositions: ΔE_a of ^{t}Cl-PIB-Cl^{t} decreases from 2.6 to 1.0 kcal/mole by decreasing the polarity of the medium from 100% CH_3Cl to a 60/40 v/v CH_3Cl/hexanes mixture.

Introduction

As a continuation of our discovery that MeOR^{t}/BCl_3 systems induce the living polymerization of isobutylene IB (1), we have carried out experiments with the di-tert.-ether (DiCuOMe):



in conjunction with excess BCl_3. Justification for this research was our desire to synthesize by a living process α,ω-difunctional (telechelic) polyisobutylenes PIBs. On the basis of earlier experiences (1,2) we anticipated that the DiCuOMe/BCl_3/IB system will yield the following tert.-chloro telechelic PIB:



Experimental

Materials and procedures have been described (2,3,4). Experiments have been carried out by the use of large (60 ml) culture tubes (2) and in 500 ml round bottom flasks with mechanical stirrer. 1,4-Bis(2-methoxypropane)benzene (dicumyl methoxy, DiCuOMe) was synthesized by etherifying 1,4-bis(hydroxylisopropyl)benzene. In a 500 ml one neck round bottom flask equipped with a condenser and a magnetic stirring bar a solution of 1,4-bis(hydroxylisopropyl)benzene (Goodyear Tire & Rubber Co., 48.5 g, 0.25 mole) in 200 ml methanol was placed to which was added concentrated sulfuric acid (Fisher, reagent grade, 0.025 ml). After refluxing for 16 hrs. the solution was cooled to room temperature, 200 ml hexanes was added and stirred for a few minutes. The organic layer was washed several times with water, separated, and dried with anhydrous sodium sulfate. The product was filtered and the solvent removed (rotavap). Finally the solid product was recrystallized from n-pentane, yield: 80%, m.p.: 49°C. The extent of etherification was determined by ^{1}H NMR spectroscopy, by quantitatively relating the resonance associated with $-OC\underline{H}_3$ at 3.0 ppm to the sharp aromatic proton and $-C\underline{H}_3$ resonances at 7.3 and 1.45 ppm, respectively. According to ^{1}H NMR and GC analysis pure material was obtained.

Results and Discussion

A. Kinetic Studies

According to orienting experiments the polymerization of IB with the DiCuOMe/BCl_3 initiating system in CH_3Cl at -30° and -50°C gave rise to undesirable indanyl end groups, however, at -70° indanyl termini did not form. Products synthesized in CH_2Cl_2 contained indanyl end groups even at -70°C. These observations are similar to those made with the IB/p-dicumyl chloride/BCl_3 systems where indanyl end group formation could not be avoided even at -80°C in pure CH_2Cl_2 (5). It appears that indanyl end group formation is easier to "freeze out" in CH_3Cl than in CH_2Cl_2 diluent.

Table I shows the results of experiments designed to test the activity of the DiCuOMe/BCl_3 systems for the living polymerization of isobutylene IB using CH_3Cl diluent at -70°C. Inspection of the $\overline{M}_n$ values indicate that the molecular weights are determined by the DiCuOMe concentration ($\overline{M}_n \sim [IB]/[DiCuOMe]$).

Figure 1 shows the $\overline{M}_n$ versus g PIB formed plots, and in the insert the number of polymer moles formed, $N = g\ PIB/\overline{M}_n$, versus g PIB formed plot generated by experiments using the incremental monomer addition (IMA) technique (1,2). The solid lines are "theoretical" i.e., expected to arise at $\overline{M}_n = [IB]/[initiator]$ at 100% conversion and initiator efficiency. The living nature of the system is indicated by the linear $\overline{M}_n$ versus g PIB formed plot starting at the origin and the horizontal N versus g PIB formed plot. The molecular weight dispersities ($\overline{M}_w/\overline{M}_n$ values) show a decreasing tendency with increasing $\overline{M}_n$, also indicating a living polymerization system.

B. The Nature of the End Groups and Product Homogeneity

According to our previous experience (5) intramolecular cycloalkylation is quite favorable with aromatic inifers, and indeed the dicumyl chloride/BCl_3/IB system yields two condensed indanyl ring systems:

TABLE I

Demonstration of Initiating Activity of DiCuOMe/BCl_3 Systems in CH_3Cl at -70°C *

Conditions				Results			
DiCuOMe mole/ℓ	Total volume,ml	[BCl_3] mole/ℓ	[IB] mole/ℓ	Conv. %	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	I_{eff} %
0	25	$2.5x10^{-1}$	$9.35x10^{-1}$	∿10	85,000	2.0	-
$5.35x10^{-2}$	25	$2.5x10^{-1}$	$9.35x10^{-1}$	>98	1300	2.0	97
$1.38x10^{-2}$	25	$2.5x10^{-1}$	$9.35x10^{-1}$	>98	4,050	3.1	100
$3.8x10^{-3}$	25	$2.5x10^{-1}$	$9.35x10^{-1}$	92	13,650	2.0	92
$1.66x10^{-2}$**	300	1.10^{-1}	$1.12x10^{-1}$	>98	4,800	1.8	85

* 30 min., in large culture tubes

**30 min., in a 500 ml stirred round bottom flask

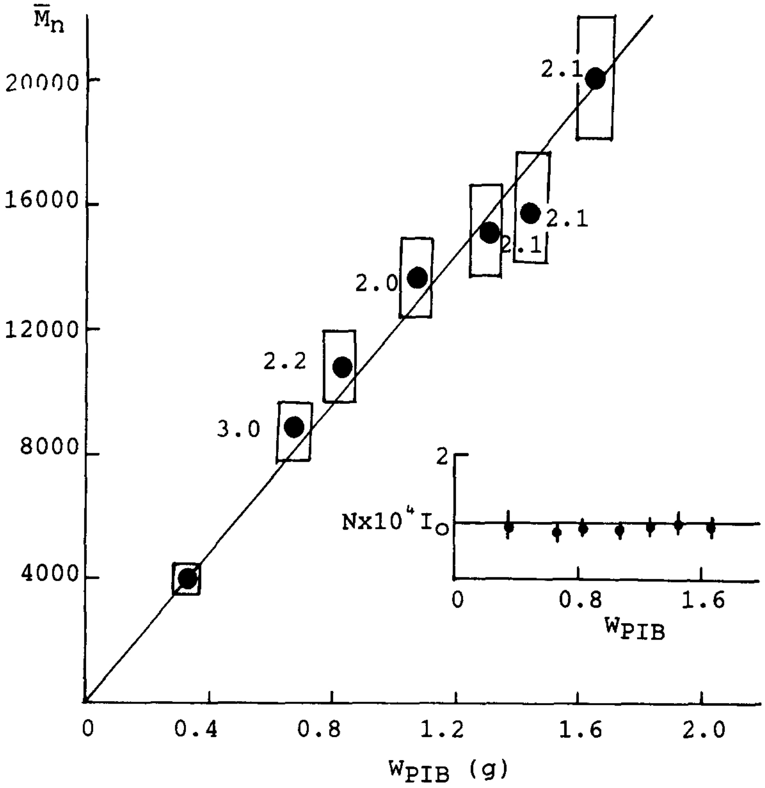
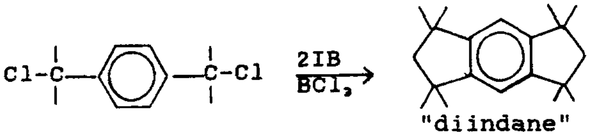
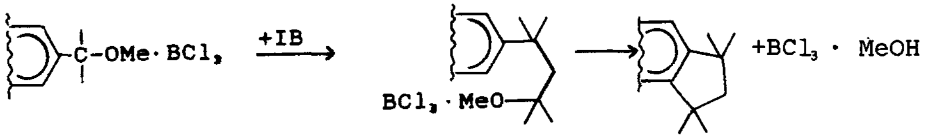


Figure 1. $\overline{M}_n$ and N, the number of polymer moles(insert),versus W_{PIB} weight of PIB formed in the DiCuOMe/BCl_3 /IB/CH_3Cl/-70°C system using the IMA technique: [DiCuOMe] = $3.74x10^{-3}$mole/ℓ [BCl_3] = $2.12x10^{-1}$ mole/ℓ, total volume = 25 ml. The numbers in the figure indicate $\overline{M}_w/\overline{M}_n$ values. Solid lines are theoretical. Error bars constructed by assuming ± 10% for $\overline{M}_n$ and 0.05 g for W_{PIB}.



The formation of indanyl rings is undesirable in inifer systems and this side-reaction has been studied in detail to find ways to avoid it (5). Indanyl ring formation in the DiCuOMe/BCl_3 system may be visualized to proceed similarly to that proposed for the dicumyl chloride/BCl_3 binifer system(5):



Ample direct evidence for indanyl ring formation has been found in the present investigation using the DiCuOMe/BCl_3 system at relatively high temperatures (e.g., at -30°C). Thus ^1H NMR analysis of PIBs showed the presence of indanyl termini in the product, i.e., aromatic proton resonances at $\delta = 6.95$ ppm and $\delta = 6.6$ ppm which are characteristic of mono- and diindanyl rings, respectively (5).

Indanyl ring-free products can be obtained with the dicumyl chloride/BCl_3/IB system by reducing both the polarity and the temperature of the polymerization (5). Thus efforts have been made to eliminate the undesirable intramolecular cycloalkylation in the DiCuOMe/BCl_3 system also by reducing the polarity of the medium, and by lowering the temperature. Table II and Figure 2 show the experimental conditions and results.

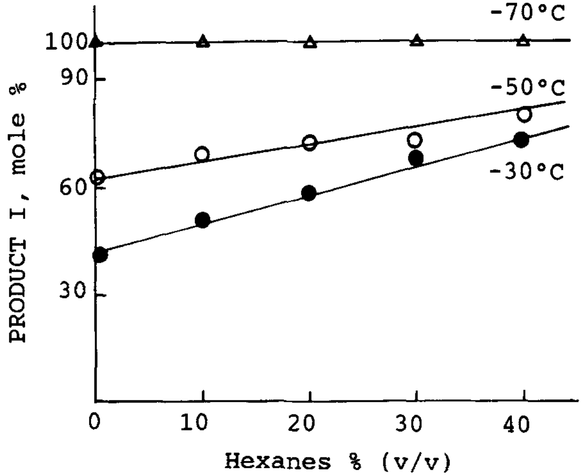


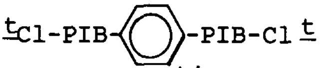
Figure 2. The Effect of Medium Polarity and Temperature on the Formation of Relative Amount of Indanyl-Free PIB

TABLE II

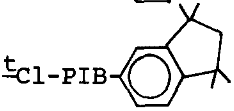
The Effect of Medium Polarity and Temperature on the Formation of Indanyl Structures*

Temp. °C	CH_3Cl/hexanes v/v	E_a of formation of Product I kcal/mole	Product[a], mole %			Conv. %
			I	II	III	
-30	100	2.6	42	34	24	>98
-50	100		63	21	16	>98
-70	100		∿100	0	0	>98
-30	90/10	2.0	52	28	20	98
-50	90/10		70	16	14	90
-70	90/10		∿100	0	0	98
-30	80/20	1.6	58	26	16	95
-50	80/20		72	19	9	95
-70	80/20		∿100	0	0	95
-30	70/30	1.2	68	20	12	97
-50	70/30		72	18	10	90
-70	70/30		∿100	0	0	95
-30	60/40	1.0	72	16	12	90
-50	60/40		80	12	8	90
-70	60/40		∿100	0	0	>98

[a]I:

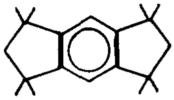


II:



(undesirable)

III:



(undesirable)

---

* [DiCuOMe] = $2.36\times10^{-2}\underline{M}$, [$BCl_3$] = $3.7\times10^{-1}\underline{M}$, [IB] = $1.172\underline{M}$, 30 min. Total volume = 20 ml.

The composition of the products in terms of components I, II, and III (see bottom of Table II) was quantitated by ^1H NMR spectroscopy. By increasing the content of the nonpolar component (hexanes) of the solvent the proportion of desirable product I increases at -30° and -50°C, and at -70°C essentially pure I is obtained at all polarity levels. The effect of temperature is most pronounced in pure CH_3Cl and seems to diminish with decreasing polarities.

Figure 3 shows log of product I vs. 1/T (Arrhenius) plots at different CH_3Cl/hexanes composition, and the relative activation energies of product I formation calculated from the slopes of the lines are given in Table II. It is of interest that the largest ΔE_a is obtained in the most polar medium.

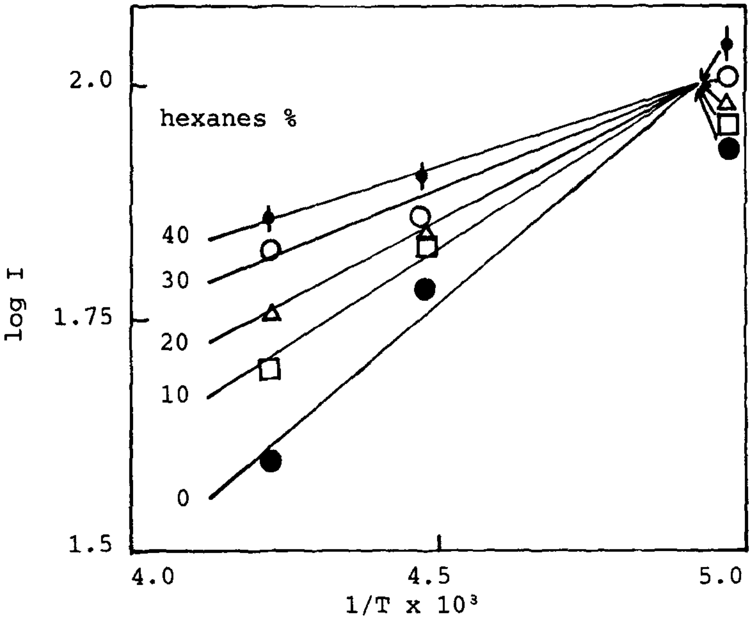


Figure 3. log Product I versus 1/T plot

According to end group studies by ^1H NMR spectroscopy, the termini of telechelic PIBs obtained by the DiCuOMe/BCl_3 system and quenched with methanol are tert.-chloro groups. To facilitate quantitative analysis of polymers synthesized at -70°C, the tert-chloro end groups were converted to isopropenyl termini $-CH_2C(CH_3)=CH_2$ by our well established method (6,7). The spectrum of the final product, the overall formula of which is shown in the introduction, was essentially identical to that published earlier (8).

The homogeneity of a representative product synthesized at -70°C has been examined by the Kennedy-Smith-Nagy plot(9) shown in Figure 4. According to this powerful diagnostic tool the distribution of the aromatic ring incorporated into the telechelic polymer is virtually homogeneous.

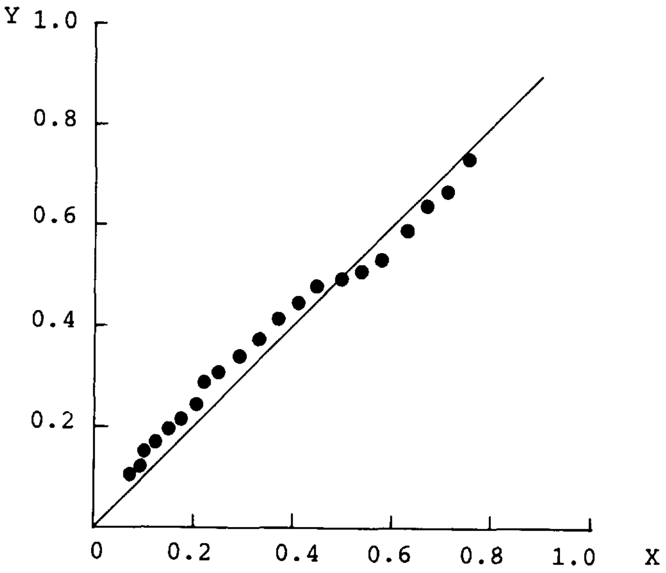


Figure 4. Kennedy-Smith-Nagy Plot of a Representative Sample (Table I, row 4)

Acknowledgements

This work has been supported by the Akron Cationic Polymer Development Corporation.

References

1. M. K. Mishra and J. P. Kennedy, J. Macromol. Sci. Chem., in press
2. R. Faust and J. P. Kennedy, Polym. Bull. 15, 317 (1986), J. Polym. Sci., in press
3. J. P. Kennedy and R. A. Smith, J. Polym. Sci., Polym. Chem. Ed. 18, 1523 (1980)
4. M. K. Mishra, B. Sar-Mishra, and J. P. Kennedy, Macromol. Syn., 10, in press (1986)
5. V.S.C. Chang, J. P. Kennedy, and B. Iván, Polym. Bull. 3, 339 (1980)
6. M. K. Mishra, B. Sar-Mishra, and J. P. Kennedy, Polym. Bull. 13, 435 (1985)
7. J. P. Kennedy, V.S.C. Chang, R. A. Smith and B. Iván, Polym. Bull. 1, 575 (1979)
8. A. Fehérvári, J. P. Kennedy, and F. Tüdös, J. Macromol. Sci.-Chem., A15(2), 215 (1981)
9. A. Nagy, Polym. Bull., 14, 259 (1985)

Accepted October 28, 1986 K