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New telechelic polymers and sequential copolymers by functional *ini*tiator-trans*fer* agents (Inifer)

LVI. Quantitative synthesis of terminally-lithiated polyisobutylenes

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Summary

Conditions have been worked out for the quantitative synthesis of terminally lithiated polyisobutylenes. The process involves isobutylene polymerization by the inifer technique followed by a one-pot dehydrochlorination-lithiation step in the presence of n- and s-butyllithium combinations under specific conditions. Model experiments with 2-chloro-2,4,4-trimethylpentane greatly helped to quantitate the technique.

Introduction

In the course of our continuing studies concerning telechelic polyisobutylenes PIB by the inifer technique [1-3] or by living polymerization [4, 5], we have recently prepared olefin-terminated linear and three-arm star PIBs and lithiated them at the terminal allylic positions [6]. The syntheses involved a total of five steps: 1) Polymerization of isobutylene by the inifer technique; 2) Work-up (i.e., solvent evaporation, dissolution in THF, etc.) of telechelic t-chlorine capped PIBs; 3) Dehydrochlorination by t-BuOK to the isopropylidene-capped products PIB-$[CH_2C(CH_3)=CH_2]_2$ or $]_3$; 4) Isolation and work-up; and 5) Lithiation of the isopropylidene-capped PIBs. That lithiation was quantitative has been demonstrated by reaction with Me_3SiCl [6]. These end-lithiated PIBs are of great interest as intermediates toward the preparation of -OH or -COOH terminated product, or as initiators for the living block copolymerization of butadiene, styrene, etc.

Recently, these studies have been continued and a shorter more convenient route has been developed for the synthesis of end-lithiated PIB intermediates. This paper concerns the discovery which led to a "one-pot" synthesis and lithiation of PIB-$[CH_2C(CH_3)=CH_2]_2$ or $]_3$ by the use of a combination of butyllithiums (BuLi) in the presence of complexing agents.

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Experimental

a) Materials

Acetyl chloride, ferric chloride and methylmagnesium bromide in ether were used as received (Aldrich). The drying and purification of hexanes, tetrahydrofuran THF, and N,N,N',N'-tetramethylethylene diamine TMEDA have been described [6]. t-Butylbenzene (Aldrich) was washed several times with sulfuric acid at 0°C followed by washing with water and distillation. Methylene chloride was distilled over CaH_2 before use.

b) Characterization methods

Gel permeation chromatography (GPC), proton nuclear magnetic resonance (^1H-NMR) and gas chromatography (GC) analyses have been described [6].

c) Synthesis procedures

1) Synthesis of p-t-butyl acetyl benzene ($t\text{-}BuC_6H_4COCH_3$)

t-Butylbenzene (6.7 g) was added dropwise to a mixture of 7.1 mL acetyl chloride, 17.2 g $FeCl_3$, 15 mL CH_2Cl_2 and 5 mL olefin-free hexanes in a three-neck flask at 0°C under a blanket of dry nitrogen. A mechanical stirrer was used for mixing. After 1 hr, the reaction was stopped with ca. 10 mL precooled methanol. Then 200 mL hexanes were added and the system was washed with dilute aqueous HCl. The solution was washed with water, dried over anhydrous $MgSO_4$, and most of the solvent was removed under reduced pressure. A colorless liquid, p-t-butyl acetyl benzene, was obtained by vacuum distillation, bp. 82°C, yield 76%, ^1H-NMR (ppm) 1.8 (t-Bu, 9H, s), 2.5 (CH_3CO, 3H, s), 7.2-8.0 (aromatic, 4H, m).

2) Synthesis of p-t-butyl(2-hydroxylisopropyl)benzene ($t\text{-}BuC_6H_4C(CH_3)_2OH$)

p-t-Butyl acetyl benzene (1.04 g) was added dropwise to 14.3 mL (2.8M) CH_3MgBr at 0°C with vigorous stirring. After 1 hr of stirring, the charge was added to 10% H_2SO_4/ice-water, extracted with two portions of ether, and washed with aqueous $NaHCO_3$. The combined ether layers were dried over anhydrous $MgSO_4$. The pale yellow crystals were recrystallized from toluene and white feathery crystals were obtained; mp. 77°C, ^1H-NMR (ppm) 1.3 (t-Bu, 9H, s), 1.5 (isopropyl, 6H, s), 7.3 (aromatic, 4H, s). A broad IR absorption peak between 3100-3700 cm^{-1} indicates the existence of hydroxyl group.

3) Synthesis of $t\text{-}BuC_6H_4C(CH_3)_2Cl$

$t\text{-}BuC_6H_4C(CH_3)_2Cl$ was prepared similarly to p-di-(2-chloroisopropyl)benzene [7]. Thus, p-t-butyl-(2-hydroxylisopropyl)benzene (8.0 g) dissolved in 12 mL CH_2Cl_2 was treated with 140 mL concentrated HCl with vigorous stirring at 0°C. After 30 hr, another 83 mL CH_2Cl_2 was added and stirred for another 2 hr. The acid layer was extracted with five 100 mL portions of CH_2Cl_2 and the combined CH_2Cl_2 layers were dried over anhydrous K_2CO_3 at 0°C. After removing the solvent, the crystals obtained were recrystallized twice from olefin-free hexanes. White rod-like crystals were harvested; mp. 57°C, ^{1}H-NMR (ppm) 1.2 (*t*-Bu, 9H, s), 2.0 (CH_3, 6H, s) and 7.0-7.5 (aromatic, 4H, m).

4) Synthesis of *t*-BuC_6H_4-PIB-$C(CH_3)_2Cl$

This prepolymer was prepared in a similar way as α,ω-di-(2-chloroisopropyl)polyisobutylene ^{t}Cl-PIB-Cl^t [1] except that p-*t*-butyl-(2-chloroisopropyl)benzene was the inifer.

5) Dehydrochlorination of $(CH_3)_3CH_2C(CH_3)_2Cl$, (TMP-Cl)

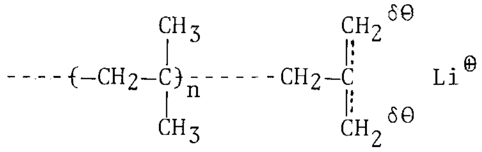
TMP-Cl (0.030 mL, 0.18 mmol), hexanes (2.0 mL), n-undecane (0.025 mL, internal standard for GC analysis), and if needed the complexing agent, i.e., TMEDA (0.044 mL, 0.29 mmol) or THF (0.133 mL, 1.64 mmol), were placed under nitrogen in a 5 mL reactor equipped with a Rotaflo® stopcock. Then 0.28 mmol BuLi (0.20 mL 1.4 mol/L *n*-BuLi in hexanes, or 0.28 mL 1.0 mol/L *s*-BuLi in cyclohexane, or 0.19 mL 1.5 mol/L *t*-BuLi in pentane) was introduced with a syringe under nitrogen at room temperature. Samples (ca. 0.5 mL) were removed after 2, 5, and 15 hr under nitrogen, deactivated with 0.5 mL H_2O, dried over $MgSO_4$ and subjected to GC and ^{1}H-NMR analyses.

6) Dehydrochlorination-lithiation-silylation of *t*-chlorine-capped polyisobutylene by *n*-BuLi/*s*-BuLi/TMEDA

A typical experimental procedure was as follows: *n*-BuLi (1.9 mL, 1.57M in hexanes) for dehydrochlorination was introduced into a flask containing premixed α,ω-di-(2-chloroisopropyl)polyisobutylene (1.9 g, $\bar{M}_n$ 2,500) and TMEDA (2.06 mL). The extent of dehydrochlorination was determined by obtaining small samples from the reaction mixture and analyzing by ^{1}H-NMR spectroscopy, i.e., comparing the peak areas under the resonances corresponding to the vinyl and phenyl protons. After 2-3 hr at room temperature, *s*-BuLi (10.9 mL, 1.37 M in cyclohexane) was added. The color of the mixture changed from light yellow to brown. Lithiation time was usually 5-6 hr. The silylation of the lithiated polyisobutylenes together with the analytical methodology has been described [6].

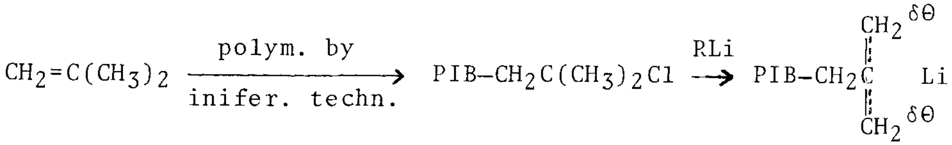
Results and Discussion

The aim of this research was to develop a simple route to terminally lithiated linear or three-arm star PIB intermediates:



$$\text{----}\!\left(-CH_2-\overset{CH_3}{\underset{CH_3}{C}}\right)_n\text{------}CH_2-\overset{CH_2^{\delta\ominus}}{\underset{CH_2^{\delta\ominus}}{C}}\quad Li^{\oplus}$$

Earlier research in these laboratories has shown access to these intermediates by a polymerization-dehydrochlorination-lithiation sequence [6]. Since quantitative dehydrochlorination of PIB-Cl^{t} is readily effected by base [7] and lithiation also proceeds by strongly basic alkyllithiums, the possibility of achieving the two steps in one operation arose. Thus it was decided to examine the feasibility of the following one-pot sequence:



$$CH_2{=}C(CH_3)_2 \xrightarrow[\text{inifer. techn.}]{\text{polym. by}} PIB{-}CH_2C(CH_3)_2Cl \xrightarrow{RLi} PIB{-}CH_2\overset{CH_2^{\delta\ominus}}{\underset{CH_2^{\delta\ominus}}{C}}\quad Li^{\oplus}$$

The first phase of this research concerned model studies with TMP-Cl, a small molecule whose structure mimicks the terminus of t-chlorine capped PIB. Table I shows the results of dehydrochlorination of TMP-Cl with different butyllithiums in the presence or absence of complexing agents. Evidently essentially quantitative dehydrochlorinations were obtained by the use of n-BuLi in the absence or presence of TMEDA. According to GC analyses n-BuLi/TMEDA combinations gave cleaner product (i.e., comparison of the dehydrochlorinated products by GC obtained in the presence and absence of TMEDA showed a large number of unidentified peaks in the experiment carried out in the absence of this amine). In contrast, both t-BuLi and s-BuLi gave much poorer yields ($\sim$50 and $\sim$60%) irrespective of the presence of THF or TMEDA.

These results may be explained as follows: The reaction between TMP-Cl and BuLi's may include dehydrochlorination and Li/Cl exchange. In the case of n-BuLi, TMP-Li is reluctant to form because this tertiary alkyllithium is much less stable than the primary alkyllithium. In contrast, the stabilities of t-BuLi or even s-BuLi are similar to that of TMP-Li, so that Li/Cl exchange may start to compete with dehydrochlorination. In line with this thought, the yields obtained with t-BuLi are worse than those with s-BuLi.

Based on these model experiments, dehydrochlorination of t-chlorine capped PIBs has been carried out with n-BuLi/TMEDA combinations. According to the data shown in Table II, quantitative dehydrochlorination of t-chlorine capped PIB was obtained with n-BuLi/TMEDA at $\sim$25°C.

Table I. Dehydrochlorination of TMP-Cl to $(CH_3)_3CH_2\!-\!C(CH_3)=CH_2$* (TMIP)

TMP-Cl	BuLi		Complexing Agent		TMIP (yield %)	
[M]	Type**	[M]	Type	[M]	^{1}H-NMR	GC
0.18	t	0.38	--	--	60	48
0.16	t	0.33	THF	1.54	--	56
0.17	t	0.36	TMEDA	0.27	--	41
0.16	s	0.31	--	--	55	63
0.14	s	0.27	THF	1.41	--	57
0.16	s	0.30	TMEDA	0.25	--	59
0.19	n	0.29	--	--	93	96
0.17	n	0.25	THF	1.64	80	77
0.18	n	0.28	TMEDA	0.29	93	96

* room temperature, 2 hr, hexanes.

** t = tertiary, s = secondary, n = normal

Table II. Dehydrochlorination of α,ω-di-(2-chloroisopropyl)-polyisobutylenes by n-BuLi/TMEDA*

^{t}Cl–PIB–Cl^t**		n-BuLi	TMEDA	Dehydrochlorination***
[M]	(w/v) %	[M]	[M]	%
0.10	26	1.02	0.61	100
0.17	42	0.67	1.01	100

* room temperature, 2 hr, hexanes

** M_n=2,500 (by GPC)

*** by ^{1}H-NMR spectroscopy

The dehydrochlorinated polymers have been characterized by ^{1}H-NMR spectroscopy. Figure 1 shows a representative spectrum. The resonances at 4.45 and 4.85 ppm characteristic of the terminal $=CH_2$ protons, relative to the four phenyl protons (internal standard), indicate quantitative dehydrochlorination.

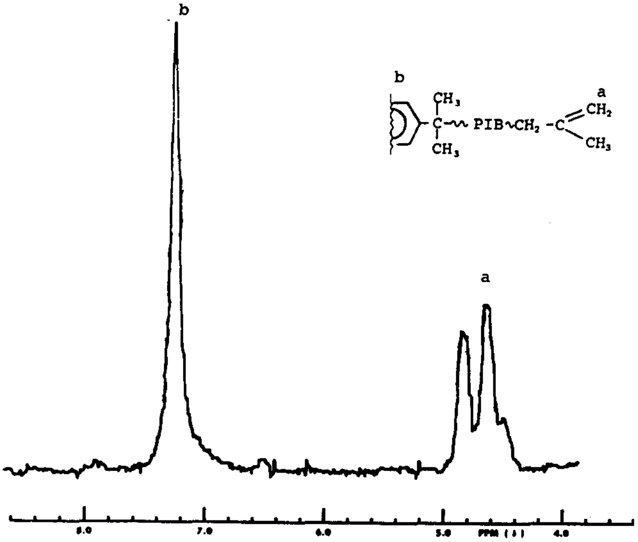
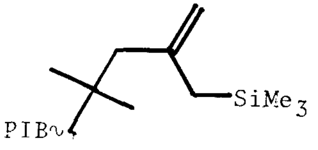
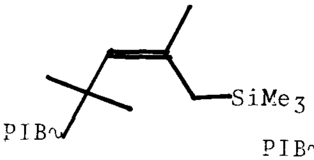


Figure 1. Proton NMR spectrum of a α,ω-di(isopropenyl)PIB.

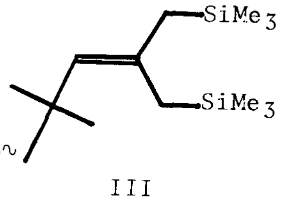
Guided by these results, conditions have been worked out for a one-pot dehydrochlorination-lithiation process of t-chlorine-capped PIB. Table III shows the results of representative experiments that led to achieve this objective. In agreement with model studies, dehydrochlorination of ^{t}Cl-PIB-Cl^{t} by s-BuLi was far from complete (first row, Table III). Adequate stirring was found to be mandatory; at too high polymer concentrations (viscosities), quantitative result might not be obtained. In addition to the desirable chain end (I), trace amounts of isomerized chain ends (II and III) may also be present:



I



II



III

Table III. "One-Pot" Dehydrochlorination-Lithiation-Silylation of t-Chlorine-Capped Polyisobutylenes

Polymer			n-BuLi	s-BuLi	TMEDA	Dehydrochlorination 25°, 2 hr	Silylation 0°, >5 hr
[M]	(w/v) %	[$\bar{M}_n$]	[M]	[M]	[M]	%*	%*
tCl-PIB-Clt							
0.05	13	2,500	---	1.04	0.83	45	---
0.08	20	2,500	0.33	0.49	0.49	100	44
0.04	22	6,010	0.14	0.70	0.56	100	100**
0.05	11	2,500	0.18	0.91	0.82	100	100
$^tBuC_6H_4$-PIB-Clt							
0.06	32	5,000	0.13	0.64	0.58	100	100

* by ^{1}H-NMR spectroscopy

** nonnegligible isomerization of chain ends

Figures 2 and 3 show the ^{1}H-NMR spectra of the products obtained with [TMEDA]/[s-BuLi]=0.56/0.70 and 0.82/0.91 (third and fourth rows in Table III). In agreement with the results obtained in the previous publication [6], more isomerized chain ends are obtained with the lower [TMEDA]/[s-BuLi] ratio. The small complex peak at 4.9-5.0 ppm in Figure 2 indicates the existence of isomerized chain ends besides the desirable product [6]. Figure 3 shows the product obtained in an essentially quantitative dehydrochlorination-lithiation-silylation (absence of isomerization) using the relative concentrations: [tCl-PIB-Clt]/[n-BuLi]/[s-BuLi]/[TMEDA]=1/4/20/18.

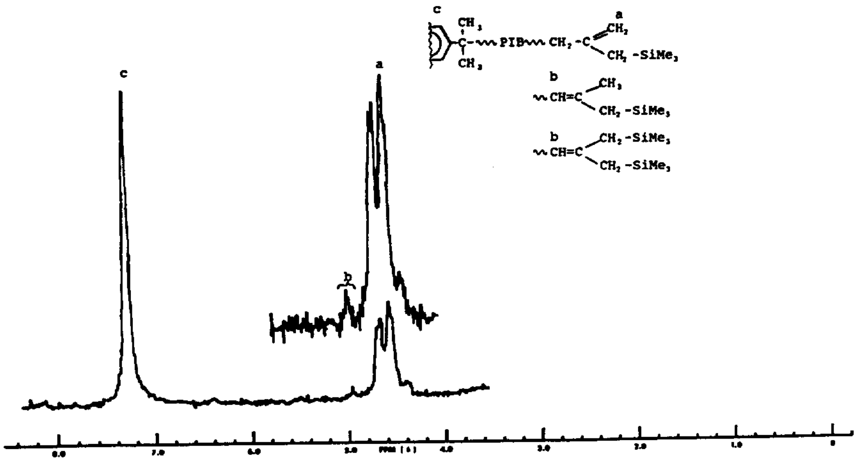


Figure 2. Proton NMR spectrum of PIB after dehydrochlorination-lithiation-silylation (isomerized products present).

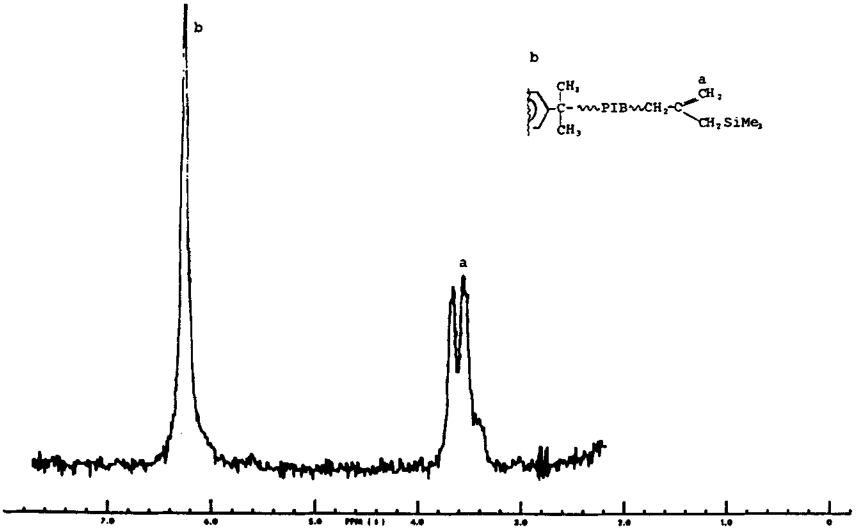


Figure 3. Proton NMR spectrum of a PIB after dehydrochlorination-lithiation-silylation (isomerization absent).

Quantitative dehydrochlorination-lithiation (as demonstrated by silylation) can be readily achieved by using about twice the stoichiometric amount of *n*-BuLi relative to the *t*-chlorine polymer end groups in the presence of a large excess of *s*-BuLi and TMEDA. These terminally quantitatively lithiated PIBs open new avenues toward the synthesis of a great variety of functionalized products, block copolymers.

Acknowledgement

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