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# New Telechelic Polymers and Sequential Copolymers by Polyfunctional *Ini*tiator-Trans*fer* Agents (Inifers)

## 47. Dehydrochlorination Studies of $^t$Cl-PIB-Cl$^t$: Quantitative Dehydrochlorination to α, ω-Di (Isopropenyl)-PIB by NaOEt

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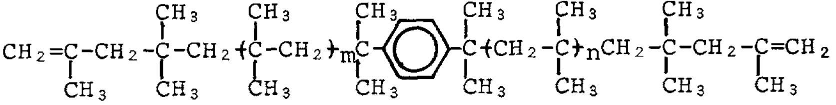
## Summary

The dehydrochlorination of $^t$Cl-PIB-Cl$^t$ of $\overline{M}_n < 6000$ to $CH_2{=}C(CH_3)CH_2$-PIB-$CH_2(CH_3)C{=}CH_2$ by various bases i.e., pyridine, tributylamine, sodium hydroxide, sodium methoxide, sodium ethoxide, in various refluxing solvent mixtures has been studied. While the extent of dehydrochlorination varied, all the bases yielded the 1-olefin. Quantitative dehydrochlorination was achieved with sodium ethoxide in homogeneous refluxing solutions of THF/EtOH mixtures. According to NMR spectroscopy the product is:



## Introduction

In the course of our continuing investigations concerning larger scale (∿1 kg) preparation of telechelic polyisobutylenes and its derivatives, in particular that of α,ω-di(tert.-chloro)polyisobutylene $^t$Cl-PIB-Cl$^t$, we have investigated relatively inexpensive dehydrochlorination methods for the synthesis of α,ω-di(isopropenyl)polyisobutylene $CH_2{=}C(CH_3)CH_2$-PIB-$CH_2(CH_3)C{=}CH_2$ of $\overline{M}_n < 6000$. The earlier method called for the use of the bulky and relatively expensive strong base *t*-BuOK (1).

According to Brown et al. (2-4) predominantly pure 1-olefin is obtained from 2-bromo-2,4,4-trimethylpentane by dehydrobromination with the bulky *t*-BuO$^{\ominus}$ group in *t*-BuOH. In line with this finding we have shown earlier that $^t$Cl-PIB-Cl$^t$ can be dehydrochlorinated quantitatively to $CH_2{=}C(CH_3)CH_2$-PIB-$CH_2(CH_3)C{=}CH_2$ by the use of the relatively expensive *t*-BuOK(1). The present experimental challenge was to find conditions under which exclusively 1-olefins will arise quantitatively even in the presence of low cost non-bulky bases, e.g., pyridine, tributyl amine, NaOH, NaOMe, NaOEt.

The solubility characteristics of the bases and PIB are quite different: The bases are insoluble in solvents for PIB and PIB is insoluble in solvents for the bases considered. Thus a solvent system had to be developed that would permit sufficient contact between the base and the tert.-chlorine end groups of PIB. After considerable experimentation we found that NaOEt in certain THF/EtOH mixtures leads to quantitative Hoffman elimination, i.e., 1-olefin, with $^{t}$Cl-PIB-Cl$^{t}$ of $\bar{M}_n <$ 6000.

## Experimental

### Materials

The syntheses and characterization of $^{t}$Cl-PIB-Cl$^{t}$ have been described (5). Pyridine (Aldrich Chem. Co.), tributylamine (Aldrich Chem. Co.), sodium hydroxide (Fisher Scientific Co.), sodium methoxide (Aldrich Chem. Co.), sodium ethoxide (Pfaltz and Bauer, Inc.), ethyl alcohol (Malinckrodt, Inc.) and hexanes (Fisher Scientific Co.) were used as received. Tetrahydrofuran (THF) (Fisher Scientific Co.) was refluxed overnight under nitrogen over calcium hydride and distilled before use.

### Dehydrohalogentation

Dehydrohalogenations were carried out in 250 ml one neck flasks equipped with magnetic stirrer and condenser under a dry nitrogen atmosphere. Experiments were carried out by adding under stirring bases dissolved in cosolvents (i.e., EtOH, MeOH, $H_2O$) to $^{t}$Cl-PIB-Cl$^{t}$ dissolved in THF, refluxing for 20 hrs, and then cooling to room temperature. Subsequently hexanes (10 ml hexanes for 1g PIB) was added, stirred for a few minutes, the organic layer was washed several times with water, separated and dried with anhydrous magnesium sulfate. Finally the product was filtered, the solvent removed by evaporation, and dried in vacuo at 60°C overnight.

For quantitative dehydrochlorination of $^{t}$Cl-PIB-Cl$^{t}$ by NaOEt we used 1.2 mole NaOEt per t-chlorine end group. To dissolve 1g NaOEt we employed a mixture of 240 ml EtOH plus 320 ml THF (cf. Expt. 15 in Table 1).

### Analyses

$^1$H NMR spectroscopy was performed by a Varian Associates T-60 NMR spectrometer using 10-15% polymer solutions in $CCl_4$ and TMS standards at room temperature. VPO was performed using a Knauer Vapor Pressure Osmometer Model No. 11.00 (Utopia Instrument Co.) and toluene solvent at 40°C.

## Results and Discussion

Table 1 summarizes representative data. Neither pyridine nor tributyl amine (2.5 mole per tert.-chlorine) led to dehydrochlorination of $^{t}$Cl-PIB-Cl$^{t}$ of $\bar{M}_n = 2700$ although the systems were homogeneous (Expts. 1 and 2). Dehydrochlorination of a $\bar{M}_n = 2700$ $^{t}$Cl-PIB-Cl$^{t}$ sample was incomplete (80-84%) in the presence of 3.37 to 5.06 mole NaOH per tert.-chlorine end group in homogeneous THF/$H_2O$ systems (Expts. 3,4), and the extent of dehydrochlorination did not improve (indeed it seemed to decrease) in the presence of phase transfer catalysts (Expt. 6 and 7). In these experiments we used the minimum amount of $H_2O$ (i.e. 7 ml) to dissolve the NaOH and to maintain system homogeneity. The NaOH concentration could not be increased beyond $\sim$5.06 mole per PIB end group because the larger amount of $H_2O$ needed to dissolve the base would have caused polymer precipitation. With $\bar{M}_n = 5150$ $^{t}$Cl-PIB-Cl$^{t}$ under similar conditions (Expt. 5) the solution became hazy indicating the onset of polymer precipitation. Thus it is not surprising that the extent of dehydrochlorination decreased to $\sim$59%.

TABLE 1

Dehydrochlorination of Telechelic α,ω-di(tert-chloro)polyisobutylene by Base[a]

| Expt. No. | $^{t}$Cl-PIB-Cl$^{t}$ | Base | | | THF | Cosolvent | Phase transf. cat. | Nature of solution | Extent dehydro chlorination | $\bar{F}_n$ [b] |
|---|---|---|---|---|---|---|---|---|---|---|
| | $M_n$ | name | g | Mole per PIB end group | ml | ml | g | | % | |
| 1 | 2700 | Pyridine | 0.31 | 2.5 | 25.0 | - | - | homog. | 0 | 0 |
| 2 | 2700 | Tributyl-amine | 0.69 | 2.5 | 25.0 | - | - | homog. | 0 | 0 |
| 3 | 2700 | NaOH | 0.20 | 3.37 | 20.0 | $H_2O$,7.0 | - | homog. | 84.0 | 1.68 |
| 4 | 2700 | NaOH | 0.30 | 5.06 | 20.0 | $H_2O$,7.0 | - | homog. | 80.0 | 1.6 |
| 5 | 5150 | NaOH | 0.20 | 6.43 | 20.0 | $H_2O$,7.0 | - | hazy | 59.0 | 1.18 |
| 6 | 2700 | NaOH | 0.20 | 3.37 | 20.0 | $H_2O$,7.0 | $Bu_4NHSO_4$, 0.025g | homog. | 74.0 | 1.48 |
| 7 | 2700 | NaOH | 0.20 | 3.37 | 20.0 | $H_2O$,7.0 | Adogen, 0.025g | homog. | 63.0 | 1.26 |
| 8 | 2700 | NaOMe | 0.20 | 2.5 | 20.0 | MeOH,15.0 | - | homog. | 70.0 | 1.4 |
| 9 | 5150 | NaOEt | 0.125 | 2.4[c] | 20.0 | - | - | heterog. NaOEt insoluble | 0 | 0 |
| 10 | 2700 | NaOEt | 0.25 | 2.48 | 20.0 | $H_2O$,10.0 | - | homog. | 61.5 | 1.23 |
| 11 | 2700 | NaOEt | 0.25 | 2.48 | 20.0 | $H_2O$,10.0 | $Bu_4NHSO_4$, 0.025g | homog. | 71.4 | 1.43 |
| 12 | 2700 | NaOEt | 0.25 | 2.48 | 20.0 | $H_2O$,10.0 | Adogen, 0.025g | homog. | 70.0 | 1.4 |
| 13 | 5150 | NaOEt | 0.062 | 1.2 | 20.0 | EtOH,5.0 | - | heterog. NaOEt partially soluble | 46.0 | 0.92 |
| 14 | 5150 | NaOEt | 0.062 | 1.2 | 20.0 | EtOH,10.0 | - | heterog. NaOEt partially soluble | 88.5 | 1.77 |
| 15 | 5150 | NaOEt | 0.062 | 1.2 | 20.0 | EtOH,15.0 | - | homog. | 98.0 | 1.95 |
| 16 | 3750 | NaOEt | 0.086 | 1.2 | 27.5 | EtOH,20.5 | - | homog. | 100.0 | 2.0 |
| 17 | 2700 | NaOEt | 0.119 | 1.2 | 38.0 | EtOH,28.5 | - | homog. | 100.0 | 2.0 |
| 18 | 6400 | NaOEt | 0.050 | 1.2 | 16.0 | EtOH,12.0 | - | heterog. | 76.5 | 1.53 |
| 19 | 6400 | NaOEt | 0.050 | 1.2 | 20.0 | EtOH,15.0 | - | heterog. | 76.5 | 1.53 |
| 20 | 6400 | NaOEt | 0.050 | 1.2 | 32.0 | EtOH,24.0 | - | heterog. | 72.0 | 1.44 |
| 21 | 6400 | NaOEt | 0.050 | 1.2 | 40.0 | EtOH,24.0 | - | heterog. | 66.2 | 1.32 |

a) 2.0g polymer, reflux, 20 hrs.

b) Number average terminal olefin functionality

c) NaOEt insoluble in THF, true NaOEt concentration unknown

Similarly disappointing results were obtained by the use of NaOMe (Expt. 8) in a homogeneous THF/MeOH system.

Dehydrochlorination was absent in bulk THF (Expt. 9) most likely because NaOEt is only sparingly soluble in THF even under extended reflux conditions. Evidently the concentration of NaOEt even in a saturated THF solution is insufficient to yield measurable dehydrochlorination.

Dehydrochlorinations of $\underline{^{t}}$Cl-PIB-Cl$\underline{^{t}}$ of $\overline{M}_n$ = 2700 in THF/$H_2O$ systems with or without phase transfer catalyst gave only partial HCl elimination (61.5-71.4%) using the maximum quantity of NaOEt attainable (Expt. 10-12).

Since possible hydrolysis of NaOEt in aqueous systems to NaOH and EtOH was thought to be disadvantageous, we turned to THF/EtOH solvent mixtures. Indeed the extent of dehydrochlorination increased with increasing amounts of EtOH (Expts. 13-15) and quantitative HCl elimination was achieved at THF/EtOH = 1.33 with $\overline{M}_n$ = 5150 (Expt. 15). Similarly quantitative dehydrochlorinations have been obtained with lower $\overline{M}_n$ polymers (Expts. 16,17). In contrast, only partial dehydrochlorinations were obtained using THF/EtOH - 1.33 and 1.66 with the higher $\overline{M}_n$ product ($\overline{M}_n$ = 6400) under essentially identical conditions (Expts. 18-21). Evidently the relative quantities of materials, i.e., $\underline{^{t}}$Cl-PIB-Cl$\underline{^{t}}$/NaOEt/THF/EtOH, significantly influence quantitative dehydrochlorination. The strong base must be in excess and the system must be homogeneous. It is difficult to dissolve sufficient amounts of NaOEt in the THF/EtOH mixture and to keep a high molecular weight polymer in solution. Either the polymer precipitates due to the presence of increasing amounts of EtOH, or NaOEt precipitates due to larger amounts of THF (NaOEt is insoluble in THF). Evidently system homogeneity is mandatory for quantitative dehydrochlorination.

The extent and regiospecificity of dehydrochlorination was analyzed by $^1$H NMR spectroscopy. The resonances associated with $-CH_2C(CH_3)=C\underline{H}_2$ at 4.58 and 4.78 ppm were quantitatively related to the sharp aromatic proton resonance at 7.15 ppm (internal standard) due to the inifer rest in the polymer (see formula in Summary). Details of quantitative analysis by $^1$H NMR spectroscopy have been described (1).

It is of interest that exclusively 1-olefin has formed in all these eliminations. According to Brown and Berneis (6) exo-olefin is the preferred but not the <u>exclusive</u> product of dehydrochlorination of 2-chloro-2,4,4-trimethylpentane under neutral conditions. Similarly, both 1- and 2-olefins have been obtained upon dehydrobromination of 2-bromo-2,4,4-trimethylpentane under basic conditions (KOEt, dry alcohols, 70°C) (2, 7,8).

Model experiments have been carried out to corroborate our findings obtained under basic conditions. Thus mimicking the conditions of $\underline{^{t}}$Cl-PIB-Cl$\underline{^{t}}$ hydrochlorination, 2-chloro-2,4,4-trimethylpentane has been treated with NaOEt in refluxing THF/EtOH 1.33 mixtures. According to $^1$H NMR spectra only the 1-olefin has formed (sharp symmetrical resonances at 4.58 and 4.78 ppm). It is remarkable that dehydrochlorination was quantitative and regioselective toward the 1-olefin in our experiments carried out with NaOEt in refluxing (∿70°C) THF/EtOH mixtures for 20 hrs, whereas it was neither quantitative nor regioselective (both 1- and 2-olefin has formed in Brown et al.'s experiments (2,3,6,7,8) carried out under neutral and basic conditions at various temperatures (from 25° to 80°C) in alcohols for various times (from 3 to 72 hrs). The reason(s) for this difference apparently caused by the use of THF in our experiments is unknown.

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