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# Molecular Weight and Functionality Determination of Polyisobutylenes Containing Tertiary Chlorine Chain Ends by Thermal Dehydrochlorination

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## ABSTRACT

A sensitive thermal dehydrochlorination method has been used to determine quantitatively the HCl arising from $-CH_2C(CH_3)_2Cl$ endgroups in polyisobutylenes synthesized by $BCl_3$ as the coinitiator. Quantitative endgroup analyses provided number-average molecular weights, $\overline{M}_n$, and functionality, $\overline{F}_n$. Select $\overline{M}_n$ data obtained by this endgroup analysis is in agreement with those obtained by osmometry, GPC, and NMR techniques; indeed, $\overline{M}_n$'s obtained by this dehydrochlorination technique appears to

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be more accurate (2-3% error) than conventional methods (~5-10% error). The rate of HCl loss from $-CH_2C(CH_3)_2Cl$ termini is first order in HCl with an $\Delta E_a$ of 19.1 kcal/mol in the 170-200°C range. This relatively low activation energy is most likely due to internal strain in the $-CH_2C(CH_3)_2CH_2C(CH_3)_2Cl$ endgroup. These studies quantitatively substantiate earlier conclusions in regard to the mechanism of endgroup formation in $BCl_3$ coinitiated isobutylene polymerization.

## INTRODUCTION

By understanding the mechanism of initiation, termination, and chain transfer in carbocationic polymerization, macromolecules with well-defined head and endgroups have recently been synthesized [1-5]. Thus isobutylene polymerizations coinitiated by $BCl_3$ yielded polyisobutylenes (PIB) carrying one or two $-CH_2C(CH_3)_2Cl$ termini [1-3, 5].

Tertiary chlorine containing structures are known to be heat sensitive even at relatively low temperatures and tend to eliminate HCl [6-10].

In the course of our continuing mechanism studies concerning the polymerization of isobutylene, we have prepared PIB's with one and two $-CH_2C(CH_3)_2Cl$ endgroups and employed a sensitive thermal dehydrochlorination method to determine quantitatively the HCl arising from these endgroups. Subsequently we used this endgroup determination method to calculate number-average molecular weights, $\overline{M}_n$, and to obtain independent confirmation as to the number of functional groups, $\overline{F}_n$, in the polymer.

## EXPERIMENTAL

### Polyisobutylenes

PIB's containing one $-CH_2C(CH_3)_2Cl$ terminus, Samples 1 and 2 in Table 1, were synthesized by using the "$H_2O$"/$BCl_3$ initiating system, 0.5 mol isobutylene per liter in $CH_2Cl_2$ at -70 and -50°C, respectively [1, 2]. PIB's containing two $-CH_2(CH_3)_2Cl$ termini, Samples 3, 4, and 5 in Table 1, were prepared by using p-dicumyl chloride (p-DCC) inifer with $BCl_3$ coinitiator, 1 M monomer/L and $CH_3Cl$ at -70°C. p-DCC concentrations were $2.1 \times 10^{-3}$, $1.9 \times 10^{-2}$, and $4.2 \times 10^{-3}$ M/L, respectively [5].

TABLE 1. Molecular Weights of PIB's Determined by GPC, Osmometry, NMR, and Thermal Dehydrochlorination

| | | $\overline{M}_n \times 10^{-3}$ | | | |
|---|---|---|---|---|---|
| No. | Sample | GPC | Osmometry | NMR | Thermal dehydrochlorination |
| 1 | PIB-Cl | 11.96 | 12.3 | | 11.52 |
| 2 | PIB-Cl | 6.63 | 6.9 | | 6.71 |
| 3 | Cl-PIB-Cl | 7.54 | 7.6 | | 7.53 |
| 4 | Cl-PIB-Cl | 4.93 | 5.1 | 4.74 | 4.88 |
| 5 | Cl-PIB-Cl | 2.31 | 2.4 | 2.09 | 2.17 |

### Thermal Dehydrochlorination

The essentials of the dehydrochlorination technique and apparatus have been described elsewhere [11, 12]. Samples were prepared in the form of films deposited in U-shaped glass tubes (6 mm i.d.) by filling the tubes with a THF solution of the sample, evaporating the solvent, and drying to constant weight under vacuum for 10-50 days. Drying to constant weight is mandatory since HCl loss is normalized to the original weight of the sample. Prior to degradation, 100 mL/min $N_2$ was passed over the film for at least 30 min at room temperature. The amount of HCl evolved was determined by conventional conductivity measurements.

### Molecular Weight Determinations

GPC measurements were carried out by a Waters Associates 6000A High Pressure GPC, equipped with $10^6$, $10^5$, $10^4$, $10^3$, and 500 Å μ-Styragel columns. Approximately 0.2 mL of 0.2% solutions of PIB in THF were used. The column set was calibrated with polystyrene (Waters), PVC (National Physical Laboratory) standards, and fractionated polyisobutylene samples (The University of Akron) of known molecular weight. The universal calibration concept [13] was used to calculate molecular weight averages.

A Hewlett-Packard Mechrolab High Speed Osmometer, Model 503, and a Mechrolab Vapor Pressure Osmometer, Model 302, were used at 37°C with toluene.

$^1$H NMR spectra were taken using a Varian T-60 NME instrument and carbon tetrachloride solutions (~20%) of low molecular weight PIB's. Integrated $^1$H NMR spectra of relatively low molecular weight

$(\overline{M}_n < 4000)$ PIB's containing an internal

standard can be used for molecular weight determination [14].

## RESULTS AND DISCUSSION

It has been demonstrated that PIB's synthesized by "$H_2O$"/$BCl_3$ or certain $RCl/BCl_3$ initiating systems contain one $-CH_2C(CH_3)_2Cl$ endgroup [1, 2] and those prepared by the $Cl(CH_3)_2CC_6H_4C(CH_3)_2Cl/BCl_3$ inifer system contain two such termini [5]. It occurred to us that our sensitive thermal dehydrochlorination method, used to investigate the detailed structure of polychloroprene, cationically modified polychloroprenes [11, 19], and other chlorinated polymers [15], could also be employed to define the structure/concentration of $-CH_2C(CH_3)_2Cl$ termini in PIB.

### Kinetics of Dehydrochlorination

In the first phase of this research we determined the rate of dehydrochlorination of a well-defined telechelic polyisobutylene containing two terminal tertiary chlorine groups [4, 5, 14]:

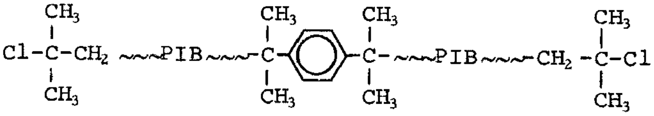

Figure 1 shows the extent of HCl loss, $\xi$ (mol HCl/mol PIB), as a function of time in the 170 to 220°C range. At 220°C dehydrochlorination is complete after ~30 min and the extent of HCl loss was found to correspond to 2.0 mol HCl/mol PIB. This result conclusively proves that the sample contained two tertiary chlorine termini.

In the absence of side reactions the rate of dehydrochlorination $V_{HCl}$ should be first order in respect to HCl:

$$V_{HCl} \equiv \frac{d\xi}{dt} = k\,(\xi_\infty - \xi) \tag{1}$$

where k is the rate constant and $\xi_\infty$ is the initial tertiary chlorine content (see Appendix). From Eq. (1),

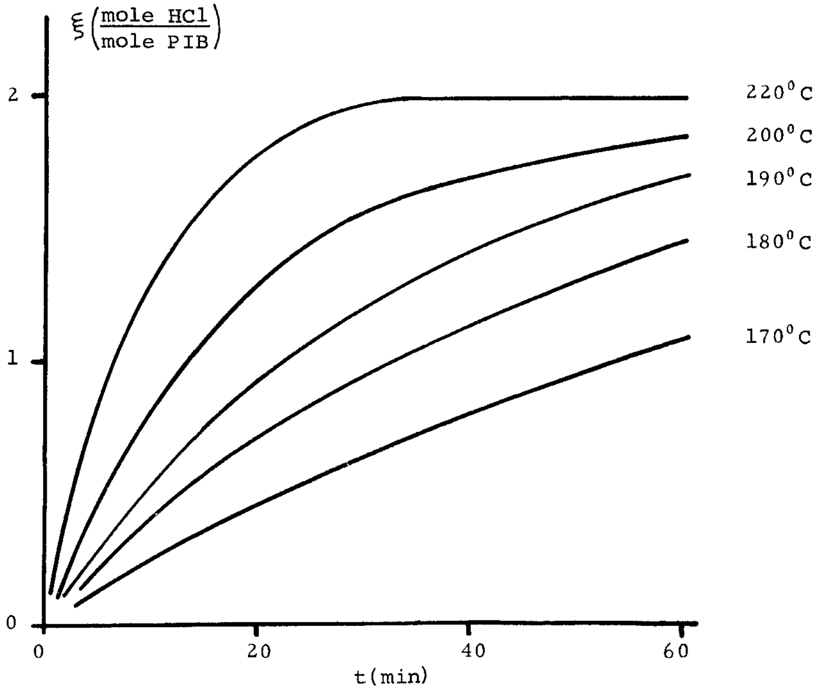

FIG. 1. Extent of HCl loss ($\xi$) as a function of time for Cl-PIB-Cl (Sample 3) at different temperatures under $N_2$ atmosphere.

$$\xi = \xi_\infty (1 - e^{-kt}) \tag{2}$$

and

$$\log \left(1 - \frac{\xi}{\xi_\infty}\right) = -kt \tag{3}$$

$\xi_\infty$ is readily obtainable by determining HCl at complete dehydrochlorination, e.g., at 220°C after ~30 min, while $\xi$ is available from the $\xi$ versus time curves. $\xi_\infty$ values were independently determined in every experiment by increasing the temperature after 60-70 min to 220-230°C and maintaining it at this level for an additional ~2 h. The linear plots corresponding to Eq. (3), together with the rate constants, are shown in Fig. 2. The Arrhenius plot exhibited in Fig. 3 gives $\Delta E_a$ = 19.1 kcal/mol and $\log_{10} A$ = 8.5.

The relatively low $\Delta E_a$ of $-CH_2C(CH_3)_2CH_2C(CH_3)_2Cl$ terminated PIB is regarded as an indication for the presence of considerable

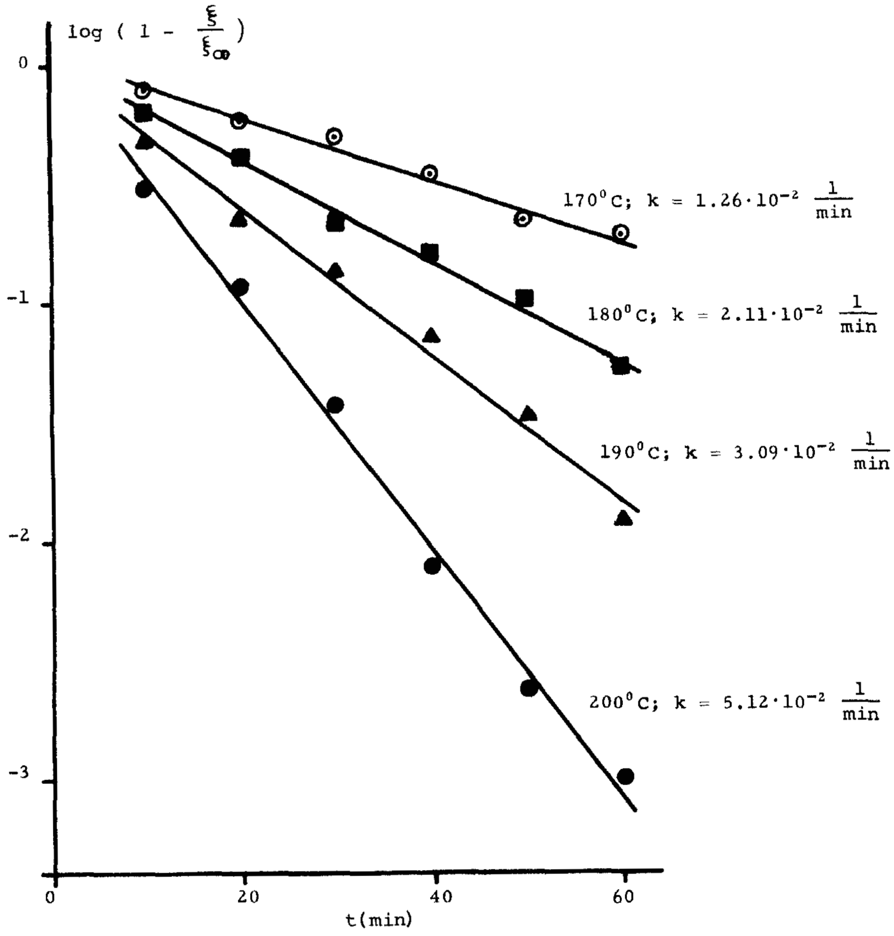

FIG. 2. Logarithm of 1 - ($\xi/\xi_\infty$) as a function of time for Cl-PIB-Cl (Sample 3).

steric strain at the terminus that facilitates dehydrochlorination. According to Brown et al. [16, 18], the steric size of substituents around the tertiary chlorine determines the rate of solvolysis and elimination of these halides.

## Molecular Weight Determination

The numer-average molecular weight of a polymer possessing a known number of tertiary chlorines can be calculated by

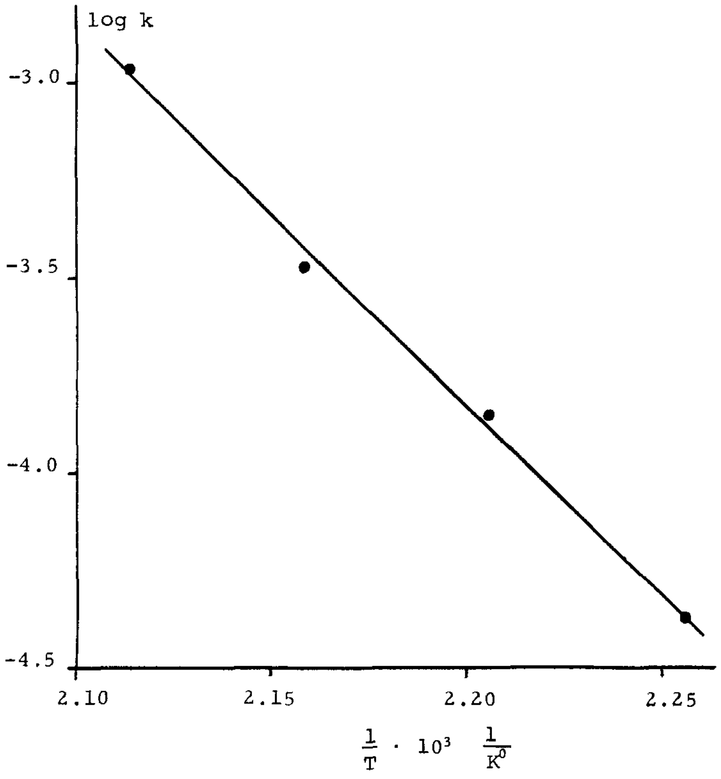

FIG. 3. Arrhenius plot of rate constants of thermal dehydrochlorination of Cl-PIB-Cl (Sample 3).

$$\overline{M}_n = \overline{F}_n \frac{G}{N} \tag{4}$$

where $\overline{F}_n$ is the number-average functionality and N is the moles of HCl that evolve after complete dehydrochlorination of a polymer of G weight (gram).

Table 1 summarizes the results obtained with PIB samples containing one or two tertiary chlorines per chain. Molecular weights determined by conventional techniques, i.e., GPC, osmometry, and NMR, are in very good agreement with those determined by thermal dehydrochlorination at 220-230°C. The error of molecular weight determination by thermal dehydrochlorination has been found to be lower, ~2-3%, than that obtained by GPC or osmometry, ~5-10%. NMR is applicable only with low molecular weight ($\overline{M}_n < 4{,}000$) well-defined polymers containing internal standard. Another advantage of thermal dehydrochlorination experiments is the relatively low sample requirement (~20-80 mg).

The fact that $\overline{M}_n$'s determined by thermal dehydrochlorination agree with those obtained by reliable conventional methods (cf. Table 1) is independent proof for the mechanisms of termination and transfer proposed for $H_2O/BCl_3$, $RCl/BCl_3$, and $Cl(CH_3)_2CC_6H_4C(CH_3)_2Cl/BCl_3$ induced isobutylene polymerizations [1, 2, 5]. According to these propositions, tertiary chlorine endgroups arise by chlorination of the propagating center by the $BCl_4^{\ominus}$ or $BCl_3OH^{\ominus}$ counteranion and chain transfer to the monomer is absent.

## Functionality Determination

Equation (4) can also be used to determine $\overline{F}_n$ if $\overline{M}_n$ is known. Indeed, we have used the thermal dehydrochlorination method to great advantage for the determination of functionality numbers of new PIB's containing less than one and more than two $-CH_2C(CH_3)_2Cl$ groups [20, 21].

In conclusion, complete thermal dehydrochlorination of polymers carrying tertiary chlorine chain ends combined with molecular weight determination by other methods, e.g., osmometry and GPC, gives valuable quantitative information as to the structure of polymers and mechanism of polymerization.

## APPENDIX

Let [t-Cl] be the concentration of $-CH_2C(CH_3)_2Cl$ termini. Then

$$-\frac{d[t-Cl]}{dt} = k[t-Cl] \tag{5}$$

The concentration of evolved HCl, $\xi$, is

$$\xi = [t-Cl]_0 - [t-Cl] \tag{6}$$

where $[t-Cl]_0$ is the initial concentration of $-CH_2C(CH_3)_2Cl$ termini. Thus

$$-\frac{d[t-Cl]}{dt} = \frac{d\xi}{dt} = k([t-Cl]_0 - \xi) \tag{7}$$

At t = 0, $\xi = 0$, and $t = \infty$, $\xi_\infty = [t - Cl]_0$, therefore

$$V_{HCl} \equiv \frac{d\xi}{dt} = k(\xi_\infty - \xi) \tag{8}$$

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