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Rapid microanalytical chlorine determination in polymers by ion selective electrode

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ABSTRACT

A rapid microanalytical method has been developed for the determination of very small amounts of chlorine in polymers. The gist of the method comprises quantitative dechlorination by sodium biphenyl or dehydrochlorination by tert-BuOK, aqueous extraction of the $Cl^{\ominus}$ formed, followed by $[Cl^{\ominus}]$ quantitation by chloride ion selective electrode (CSE). The method has been tested and is now used routinely for chlorine end group quantitation of telechelic polyisobutylene (PIB), poly(2,4,6-trimethylstyrene) (PTMSt), and poly(p-chlorostyrene) (PpClSt).

INTRODUCTION

During our research on terminally functional polymers, we have developed several syntheses for chlorine-ended macromolecules (1,2,3). For example, we have prepared by the inifer (1) or living (2,3) techniques PIBs and ring-substituted polystyrenes capped by tert-chlorines or sec-benzylic chlorines, respectively. The exact knowledge of number average end group concentration $\bar{F}_n$ is of paramount importance for the reliable synthesis of telechelic prepolymers. The quantitation of very small amounts of terminal chlorines, however, even in moderately high molecular weight ($\bar{M}_n \sim 10^4$) prepolymers is a difficult task.

Spectroscopic techniques require expensive instrumentation and are of limited sensitivity. The routine ^1H NMR method that we have developed and are extensively using (4) for the determination of terminal tert-chlorines ($-CH_2C(CH_3)_2Cl$) of PIB is an indirect method; it involves dehydrochlorination to isopropylidene end groups $\sim CH_2C(CH_3)=CH_2$ followed by ^1H NMR integration of the methylene protons against internal standard. With polystyrene or its derivatives the same method gives internal unsaturations $\sim CH(\emptyset)-CH=CH(\emptyset)$ the routine NMR, IR, or UV spectroscopic quantitation of which is not practical (ill-defined overlapped peaks and resonances). Elementary chlorine analyses in the <1 wt% range submitted to commercial organizations (who burn the polymer samples and determine the evolved HCl by GC or $AgNO_3$ titration) consistently yielded unreliable data.

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With the recent commercial availability of relatively inexpensive ion selective electrodes (ISE) the quantitative direct analysis of minute amounts of chlorine in polymers has become feasible. This paper describes two modifications of a simple technique for the quantitation of chlorine end groups in polymers. The methods comprise the quantitative conversion of the very small amounts of chlorine (i.e., chlorine end groups) in polymers by sodium biphenyl or *tert*-BuOK to $Cl^{\ominus}$, followed by multiple extractions of the organic phase with water, and $[Cl^{\ominus}]$ determination by CSE.

EXPERIMENTAL

1) Materials

Sodium biphenyl reagent and *tert*-BuOK (Aldrich Chemical Co.) were used as received. The source and purity of isobutylene, BCl_3, THF, p-chlorostyrene, 2,4,6-trimethylstyrene have been published (2,5,6).

2) Instrumentation

The chloride ion concentration $[Cl^{\ominus}]$ was measured by an ORION 9617-U type CSE in combination with an ORION SA-720 type PH/ISE meter.

3) Sources of the Polymers in Table I

The various polymers used in this work have been obtained from individuals actively engaged in telechelic research and therefore were prepared by a variety of syntheses. PIB-Cl^{t} was prepared by the $CH_3COOH/BCl_3/IB/CH_3Cl$/-35°C system. Synthesis, purification and characterization details have been described (2). ^{t}Cl-PIB-Cl^{t}-1 was synthesized by the dicumylmethyl ether/$BCl_3/IB/CH_3Cl$/-80°C system in the presence of an additive. Synthesis and characterization details will soon be published (7). ^{t}Cl-PIB-Cl^{t}-2 was obtained by the *trans*-2,5-diacetoxy-2,5-dimethyl-3-hexene/$BCl_3/IB/ClCH_2CH_2Cl$/-15°C system according to (8). ^{t}Cl-PIB-Cl^{t}-3 was prepared by the dicumylmethyl ether/$TiCl_4/IB/CH_3Cl$/-85°C system in the presence of N,N-dimethyl acetamide by the IMA (incremental monomer addition) method (7). ^{s}Cl-PTMSt-Cl^{s} was prepared by the dicumyl chloride/BCl_3/2,4,6-trimethylstyrene/CH_3Cl/-60°C system by the inifer technique (1). The details of synthesis were the same as those used in connection with PpClSt samples. ^{s}Cl-PpClSt-Cl^{s}-1 and 2 were prepared by the dicumyl chloride/BCl_3/pClSt/CH_3Cl/-60°C and 1,3-di(2-chloro-2-propyl)-5-*tert*-butylbenzene/BCl_3/pClSt/CH_3Cl/-35°C systems respectively. Details of polymerizations and characterization have been described (6).

4) Polymer Purification

In view of the chlorine-containing Friedel-Crafts coinitiators (BCl_3, $TiCl_4$) and chlorinated solvents used in the syntheses the greatest care had to be exercised in removing completely the residues of these chemicals without losing any of the fragile *tert*- or *sec*-benzylic chlorine end groups. Accumulated in-house experience with chlorine telechelics greatly helped in devising suitable separation methodologies.

Relatively low molecular weight PIBs ($\bar{M}_n$ <6000) are dissolved in _n_-hexane (∿ 2g/50 mL) and methanol is added such that precipitation should not occur. The two-layer clear solution is vigorously shaken, settled, and the lower methanol layer separated. This operation is repeated at least three times with fresh aliquots of methanol. The product is dried until constant weight (∿ 1 week) in vacuum at room temperature.

With higher molecular weight PIBs ($\bar{M}_n$ >10,000) and/or with samples that contain substantial amounts of coinitiator residues formed upon quenching with CH_3OH, the above procedure does not remove quantitatively chlorine-containing residues. In these instances the polymer is dissolved in _n_-hexane (∿5 g/50 mL) and is precipitated into a 10:1 v/v CH_3OH/conc. HCl mixture. The precipitated polymer is redissolved in _n_-hexane and reprecipitated into a 1:1 v/v methanol/acetone mixture. Then the product is reprecipitated from _n_-hexane into methanol. Then the product is redissolved in _n_-hexane and washed at least three times with water. The _n_-hexane solution is dried over anhydrous $MgSO_4$ over night, filtered, the _n_-hexane removed by rotavap, and the product dried _in vacuo_ at room temperature until constant weight (∿ 10 days).

These procedures can also be used with polystyrene and its derivatives, however, in these cases toluene and 50 v/v % $MeOH/H_2O$ are used instead of _n_-hexane and MeOH for the extraction.

5) Conversion of Chloride End Groups Into Chloride Ion

Both methods involve the quantitative transformation of chloride termini into aqueous $Cl^{\ominus}$ solutions.

a) Dehydrochlorination by tert-BuOK

By this method ∿0.1 g sample (PIB or PpClSt) dissolved in ∿5 mL THF is quantitatively added to a solution of 0.5 g _tert_-BuOK in 25 mL THF in a 100 mL three-neck round bottom flask equipped with a magnetic stirring bar and reflux condenser. After ∿20 hrs of refluxing the THF is evaporated, the excess _tert_-BuOK is decomposed by ∿10 mL H_2O and acidified with 2.5 mL 70.1% HNO_3. Then 25 mL toluene are added, the aqueous phase separated, and the toluene phase is extracted five more times with 15 mL aliquots of water. The aqueous extracts are collected in a 100 mL volumetric flask, and filled to 100 mL with distilled water for $Cl^{\ominus}$ analysis by CSE.

b) Dechlorination by Sodium Biphenyl

The polymers are dechlorinated by sodium biphenyl according to Liggett (9) and Carter (10). Thus ∿0.1 g sample dissolved in 25 mL toluene is quantitatively transferred to a dry 125 mL separatory funnel and the contents of a commercially available vial of sodium biphenyl (15 mL solution in 2-ethoxyethyl ether, Aldrich) are added. After ∿10 mins the excess sodium biphenyl is decomposed by the dropwise addition of 10 mL water, the solution is acidified by 2.5 mL 70.1% HNO_3 and extracted five times with 15 mL aliquots of water. The water extracts are collected in a 100 mL volumetric flask and filled to 100 mL for $Cl^{\ominus}$ analysis by CSE.

Chloride Ion Quantitation by Chlorine Selective Electrode

The CSE is calibrated just before analysis by NaCl solutions. The ionic strength of the solutions is adjusted to μ = 0.392 mole/L by $NaNO_3$.

The background (blank experiment) is measured under the same conditions as those described in Sections 5a and b in the absence of polymer.

RESULTS AND DISCUSSION

The objective of this work was to develop a simple rapid method suitable for the routine microanalytical determination of tert-chlorine end groups in PIB $\sim CH_2C(CH_3)_2Cl$, and sec-benzylic chlorines in polystyrene derivatives $\sim CH_2CH(C_6H_4R)Cl$ where R = H, CH_3, $C(CH_3)_3$ and Cl. An examination of the literature and drawing on in-house experience has led us to develop two techniques for this purpose: 1) quantitative dehydrochlorination by tert-BuOK (4) and 2) quantitative dechlorination by sodium biphenyl (9); either method yields $Cl^{\ominus}$ which is extracted by water from the organic phase and determined by CSE. The first method coupled with quantitation by ^1H NMR spectroscopy is routinely used in our laboratories for terminal chlorine determination (4). The second method is based on Liggett's work (9). This author has shown that small amounts of chlorine (and bromine) can be readily quantitated in a great variety of small molecule organic compounds by treating these with sodium biphenyl, followed by aqueous extraction of NaCl formed, and Volhard titration (i.e. by adding an excess of $AgNO_3$ and back titration with NaSCN). Recently Carter has shown that this methodology gives satisfactory results with tert-chlorine ended PIBs (10). Table I shows the polymers examined together with characterization and analytical data.

In regard to the tert-chlorine terminated PIB samples, the agreement between the $\bar{F}_n$s obtained by routine NMR method (4) and those by the sodium biphenyl/CSE method is within experimental variation and well within 10% of the theoretical values. For other comments see the remarks in the Table.

Repeated efforts to obtain independent [Cl] data by commercial elemental chlorine analyses gave unreliable information (irreproducible duplicates, a blank devoid of Cl was reported to contain Cl).

In regard to the PTMSt and PpClSt analyses, the ^1H NMR method that yields reliable routine information with tert-chlorine capped PIB, cannot be employed on account of the complexity of the spectrum (unresolved highly split resonance patterns due to the complex end groups arising before and after dehydrochlorination).

With PpClSt the analytical task was to quantitate a few terminal sec-benzylic chlorines $-CH_2CH(pC_6H_4Cl)Cl$ in the presence of large quantities of aromatic chlorines. Sodium biphenyl removed indiscriminately both aromatic and sec-benzylic chlorines, i.e., gave total chlorine, so that this method is unsuitable for $\bar{F}_n$ determination of PpClSt. In contrast, tert-BuOK selectively dehydrochlorinated the sec-benzylic end groups and gave close to theoretical $\bar{F}_n$ data.

TABLE I

Chlorine End Group Quantitation of Various Polymers

Polymer	$\overline{M}_n \cdot 10^{-3}$ g/mole	$\overline{M}_w/\overline{M}_n$	$\overline{F}_n$			
			Theor.	^{1}H NMR ±0.1	CSE[a] by NaBp[b]	CSE[a] by t-BuOK
PIB-Cl$^{\underline{t}}$	4.9	1.55	1	c	1.08	-
$^{\underline{t}}$Cl-PIB-Cl$^{\underline{t}}$-1	1.0	1.16	2	2.0	2.04	-
$^{\underline{t}}$Cl-PIB-Cl$^{\underline{t}}$-2	3.3	1.15	2	2.0[d]	2.13	-
$^{\underline{t}}$Cl-PIB-Cl$^{\underline{t}}$-3	14.1	1.24	2	e	2.10	-
$^{\underline{s}}$Cl-PpClSt-Cl$^{\underline{s}}$-1	3.1	2.05	2	f	g	1.87
$^{\underline{s}}$Cl-PpClSt-Cl$^{\underline{s}}$-2	6.1	2.18	2	f	-	2.12
$^{\underline{s}}$Cl-PTMSt-Cl$^{\underline{s}}$	3.2	1.15	2	f	2.0	-

a) Averages of five determinations

b) NaBp = sodium biphenyl

c) Initiator fragment not analyzable (CH_3)

d) $-CH_2OH$ content after hydroboration/peroxidation $\overline{F}_n = 1.96$

e) Unreliable data due to high $\overline{M}_n$

f) NMR unsuitable for quantitation due to spectrum complexity

g) Total chlorine content by NaBP 26.9%; theoretical value: 26.0%

The main source of error of this methodology is $\overline{M}_n$ determination by GPC ($\sim$10%); the error of chlorine determination is negligible relative to that of $\overline{M}_n$ analysis. Thus the average error of this method is equal to that of the $\overline{M}_n$ analysis.

The great advantage of the CSE method over spectroscopic chlorine determination methods is superior sensitivity: The CSE method can be reliably used for end group analysis with polymers up to $\overline{M}_n \sim 500{,}000$ g/mole! For example, a 2.8 g PIB sample of $\overline{M}_n = 560{,}000$ g/mole carrying one tert-chlorine end contains 5.10^{-6} mole chlorine. Reaction with sodium biphenyl or tert-BuOK followed by extraction to 100 mL yields 5.10^{-5} mole/L $[Cl^{\ominus}]$, i.e., a quantity that is still within the sensitivity limit of the CSE (11). The sensitivity of the method can be augmented by a factor of 10 by the use of a polymer membrane type electrode, also available commercially (Omega, ISE-9317-U).

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