

# Determination of Terminal OH Groups in Butadiene Telechelics by Calorimetry and by Inverse Gas Chromatography

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## Synopsis

Direct injection enthalpimetry (DIE) with improved sensitivity constitutes a reproducible method for terminal OH group determination in telechelic oligomers. However, it requires calibration for each individual type of telechelic. Inverse gas chromatography (IGC) can also be applied to determine endgroups of butadiene oligomers using polar probe molecules which do not interact with the polymer backbone.

## INTRODUCTION

Accurate determination of endgroups is of paramount importance in the field of telechelics since it constitutes an essential entity to judge the efficiency of the synthesis and to calculate overall functionality for subsequent conversion.<sup>1</sup>

For the case of OH terminal groups, a variety of classical methods is well documented.<sup>1-3</sup> Variations, e.g., active hydrogen determinations<sup>4</sup> from reaction with  $\text{Al}(\text{ibut})_2\text{H}$ , have not proved to be completely satisfactory for butadiene telechelics.<sup>5</sup> The same holds for modified gas-chromatographic estimations<sup>5</sup> after conversion of the oligomers with phenyl isocyanate<sup>6</sup> or phenyllithium.

There are problems with NMR and IR (near-IR) spectroscopy,<sup>1,5</sup> although the latter has been proposed for quantitative determination of such telechelics.<sup>7</sup> During screening tests, the adaption and refinement of a calorimetric method described as direct injection enthalpimetry (DIE)<sup>8</sup> for OH number determination of alkyl phenols<sup>9</sup> and polyesters<sup>10</sup> yielded very accurate figures. Here, the enthalpy of the acetylation reaction with acetic anhydride is measured through a thermistor. Additionally, it was conceived that the technique of inverse gas chromatography (IGC)<sup>11</sup> might lend itself to the problem of OH group determination. A comparison of both methods will then help to decide on the respective merits; both methods are indirect and require calibration.

## BASIC PRINCIPLE OF IGC

The polymer to be investigated is coated on the solid support, and from its interaction with a volatile solute injected as a probe, conclusions on structural, transitional, and thermodynamic properties of the polymer can be obtained. Depending on the temperature of the experiment, the partition of the gaseous solute occurs between the liquid (GLC) or the solid (GSC) polymer phase; and with the different states of penetration it is obvious that polymer transitions are detectable from measurements over a wider range of temperatures.<sup>11</sup>

The assumption made in the present case is different and novel in that the interaction of a polar probe molecule with the hydrocarbon polymer should depend on its endgroup ( $-\text{OH}$ ) concentration, i.e., longer retention times should correspond to higher OH numbers.

## EXPERIMENTAL

### Direct Injection Enthalpimetry (DIE)

**Procedure.** For the reagent, 360 ml dry ethyl acetate, 60 ml acetic anhydride ( $\text{Ac}_2\text{O}$ ), and 10 ml sulfuric acid (96%) are thoroughly mixed and left 20 hr for conditioning. Twenty ml of the reagent is transferred to a 50-ml two-necked flask which contains a thermistor and is stirred magnetically. Of the liquid polybutadiene ( $\text{LPB}(\text{OH})_2$ ) sample, 2.5 g is weighed (to 1 mg accuracy) into a 10-ml measuring flask and filled up with anhydrous ethyl acetate. After complete temperature equilibration, 1 ml of the solution is rapidly injected into the reagent solution. The reaction is over within 10 sec. The insert of Figure 1 shows a recorder trace.

**Apparatus.** In order to maintain good temperature stability, all components of the system (flasks, syringes) are installed into bores of an Al block, which is further insulated by encasing it with polystyrene foam. Syringes have a Plexiglas coating in order to minimize temperature changes by handling. Room temperature is kept to  $23 \pm 0.5^\circ\text{C}$ . The NTC thermistor (ITT F 53D) is part of a Wheatstone bridge supplied with high-constancy voltage from a well-stabilized direct current unit. In order to minimize self-heating of the thermistor, a low bridge voltage (2.35 V) is applied. Sensitivity of the 10-mV recorder is such that

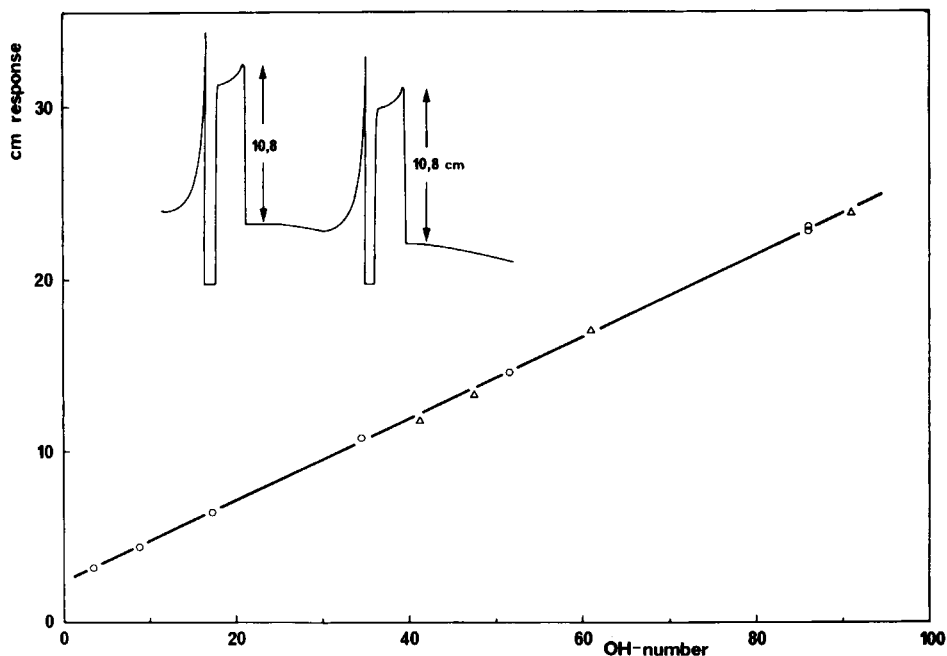


Fig. 1. Calibration for determination of OH endgroups by DIE: (O) synthetic blends (LPB + octanol); (Δ) linear polypropylene glycols. Insert: Reproducibility of calorimetric peak.

a 10-cm response corresponds to a temperature difference of  $0.1^{\circ}\text{C}$ , which is equivalent to an OH number of 32 for the solution concentrations given above.

### Inverse Gas Chromatography (IGC)

The experiments are conducted on a Perkin-Elmer F 22 GC instrument with FID and low-temperature program unit. Two-meter steel columns with 3 mm O.D. are used. To the instrument a Hewlett-Packard 3370 A integrator is hooked up. For the preparation of columns, diluted  $\text{LPB}(\text{OH})_2$  solutions in chloroform or cyclohexane (2 g/150 ml) are mixed with 18 g Chromosorb P (60/80 mesh) for 30 min and then vacuum stripped in a rotary evaporator.

Methanol was chosen to be the preferred reagent; methane is used as reference compound. It is passed into the MeOH solutions. Retention times measured ( $t_{dr}$ ) are always determined between MeOH and methane peaks. A typical GC trace is shown in the insert of Figure 2. Table I gives the GC conditions.

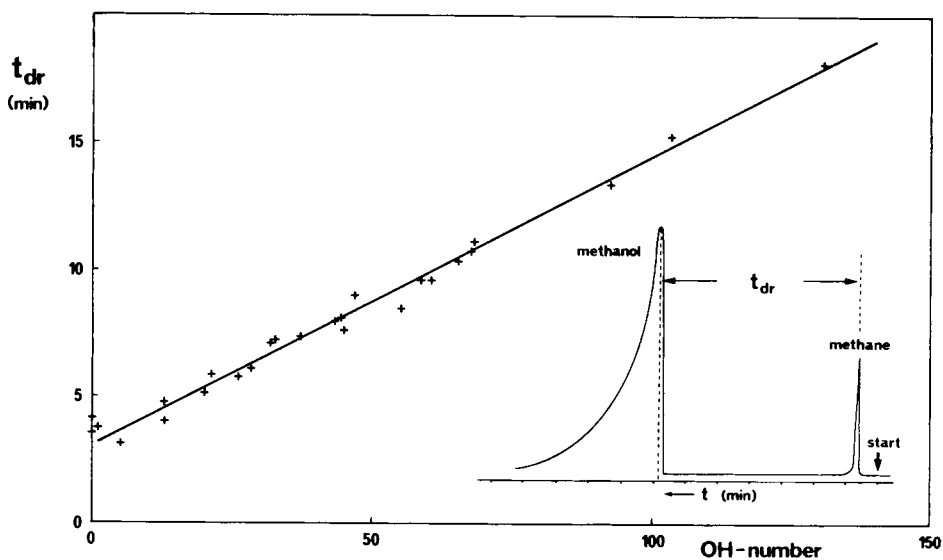


Fig. 2. Calibration of OH endgroup concentration by IGC. Insert: Typical GC diagram.

TABLE I  
GC Conditions

Instrument	Perkin-Elmer F 22
Mode of operation	isothermal
Temperature of column	$10.0^{\circ} \pm 0.1^{\circ}\text{C}$
Temperature of detector	$30.0^{\circ} \pm 0.5^{\circ}\text{C}$
Temperature of injector	$30.0^{\circ} \pm 0.5^{\circ}\text{C}$
Injection volume	0.3 $\mu\text{l}$
Preconditioning	20 min
Carrier gas	$\text{N}_2$
Carrier gas speed	17.5 ml/min
Coating on Chromosorb P	3.74 $\mu\text{g}/\text{cm}^2$ ~10 wt-% of polymer

## CALIBRATION

Using standard OH determinations to calibrate DIE (e.g.,  $\text{Ac}_2\text{O}$  titration, active H measurements), one obtains scattered points for  $\text{LPB}(\text{OH})_2$  as expected from the deviations experienced with such methods.<sup>5</sup> The correlation between conventional acetylation and DIE is better with polypropylene glycols; the most accurate calibration is obtained from blends of nonfunctional LPB with known fractions of higher aliphatic alcohols, e.g., octanol, as shown in Figure 1.

DIE was then in turn used to calibrate IGC. In Figure 2,  $t_{dr}$  figures are thus plotted as a function of OH number (mg KOH/g polymer).<sup>2,3</sup>

## RESULTS

Reproducibility in the DIE determinations of terminal OH groups from  $\text{LPB}(\text{OH})_2$  was found to be very good; standard deviations for repeat experiments are usually <1%. In IGC, the corresponding figure was definitely higher, ca. 5%.

The experimental conditions given above for IGC are optimal with regard to temperature, polymer film thickness, and carrier gas velocity. At higher temperatures (>20°C) and polymer loadings (>20 wt-%), deviations from linearity commence.

With respect to molecular weight and microstructure dependence, Table II gives a selection of the considerable range of samples used which all fit the curve shown in Figure 2. On the other hand, as with some other OH number determinations, both methods are sensitive to the variation in ethylene oxide (EO) concentration, a monomer widely used for end-capping.<sup>1</sup> This can be shown by blending  $\text{LPB}(\text{OH})_2$  with polyethylene glycol (PEO) of comparable OH number; the dependence of  $t_{dr}$  with increasing proportions of PEO is shown in Figure 3. Although the termination technique requires some excess EO in the polymerization vessel, there are indications<sup>5</sup> that no blocks of EO are present in our  $\text{LPB}(\text{OH})_2$ . In the range of the molecular weights of Figure 3 (ca. 2000), the presence of three EO-units instead of one at each end of the chain would increase the OH number by ca. 7 (+12.5%), indicating indeed how responsive the method is with respect to EO.

To a lesser extent this also holds for DIE. It must be noted that the calibration curve for PEO is not identical with the one shown in Figure 1 [for polypropylene glycol and  $\text{LPB}(\text{OH})_2$ ], indicating a different enthalpy contribution of the polymer chain.

DIE is highly sensitive toward water and necessitates rigorous drying of samples. With IGC, requirements are less stringent due to conditioning on the column. For broader application of DIE with telechelics, solubilities in the reaction mixture may sometimes be a problem as well as availability of suitable standards for calibration, i.e., nonfunctional materials of polyesters, for example.

## CONCLUSIONS

Both DIE and IGC can successfully be employed for determination of OH groups in  $\text{LPB}(\text{OH})_2$ . From the calibration procedure, DIE would appear more direct and reliable. It also is less time consuming than the preparation of a

TABLE II  
Dependence of Retention Time  $t_r$  and OH Number on Molecular Weight and Microstructure of Telechelic Polybutadienes LPB(OH)<sub>2</sub>

Sample no.	LPB(OH) <sub>2</sub> <sup>a</sup>	$M_n$	1,2-content <sup>b</sup>	$T_g$ , °C <sup>c</sup>	$T_{10} - T_g^d$	$t_r$	OH number
1	D 1245	897	80	-54	55	17.4	130.0
2	1285	2505	80	-42 <sup>d</sup>	52	7.1	37.0
3	1316	5500	80	-42 <sup>d</sup>	52	3.0	5.0
4	1311	1625	40	-81 <sup>e</sup>	91	10.3	67.4
5	1332	3465	40	-83	93	3.8	13.0
6	PB III	2585	20	-98	108	5.6	26.2
7	R-45 M <sup>f</sup>	2950	20	-86	96	7.3	45

<sup>a</sup> Lab samples; anionic synthesis.<sup>1,5</sup>

<sup>b</sup> From IR or NMR spectrum.<sup>1,5</sup>

<sup>c</sup> From DTA measurement.

<sup>d</sup> Distance at measuring temp. (+10°C) from  $T_g$ .

<sup>e</sup> Calculated from 1,2-content.<sup>1,5</sup>

<sup>f</sup> Commercial product, ARCO Chemical Co.

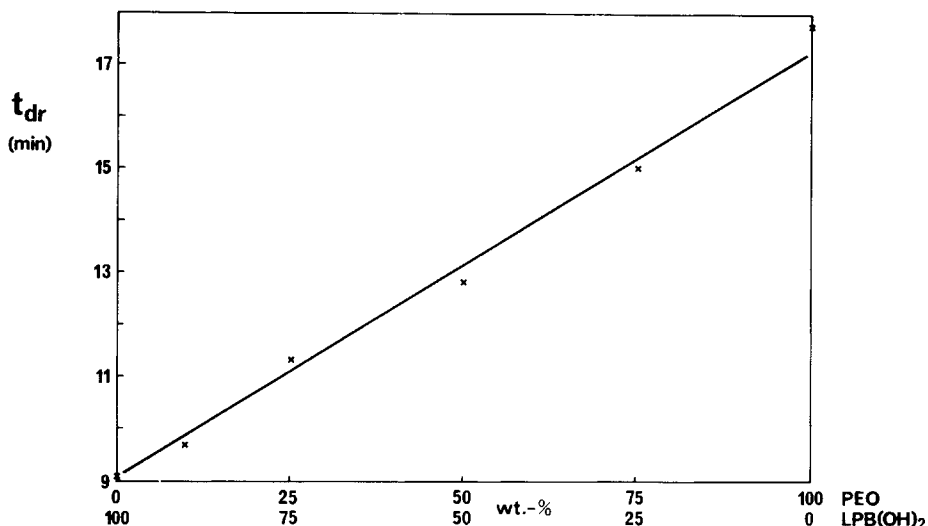


Fig. 3. Increase in retention time with replacement of LPB(OH)<sub>2</sub> by PEO of corresponding OH number.

column for each sample in IGC. In that sense, IGC should never be considered for routine measurements. On the other hand, the somewhat unusual extension of IGC to a special analytical problem of polymers deserves some further comments.

The investigation has shown that there is a significant interaction of telechelics OH with low molecular weight probe OH, probably adsorption (as evidenced from peak tailing, cf. Fig. 1), possibly H bonding. Obviously, the endgroups are accessible to the probe; it is unknown in how far they stick out from the hydrocarbon phase. In any case, they do not seem to be buried on the surface of the solid support. It might be stressed that OH group detection is not limited to terminal positions; higher than two functional polymers (e.g., R-45 M) which must have pendent OH groups in the chain are also determined.

Apparently, there is not much interaction of the polar alcohol probe molecule with the hydrocarbon backbone—otherwise there should be some dependence on the widespread temperature distance to  $T_G$  (cf. Table II, column 6) stemming from the change in microstructure. Thus, in a rigid sense, our method is no true IGC to the extent that it does not utilize any effects of the solute with the polymer backbone.<sup>11</sup>

One might argue that there should be some interaction of the reference compound, methane, with the polymer; but if so, it is undetectable due to its very short retention time. Moreover, the results are unchanged if one works without an internal reference compound and takes injection as starting point.<sup>5</sup> Internal standards are preferable because of higher accuracy and of elimination of column filling defects.

Polar constituents in the polymer do make a contribution to the results. As evidenced from Figure 3, MeOH retention is sensitive to the presence of PEO, at constant OH concentration. It is not known what the distribution of the two polymers in the coating is—there might be a compatibility problem which could be less severe in the case of block copolymers with, for example, terminal EO units. At any rate, this dependence indicates the limitations of the method.

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