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End Group Determination in Hydroxyl-Telechelic Polyisobutylenes by Infrared Spectroscopy

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SUMMARY

A convenient method for the quantitative determination of terminal hydroxy functionality of linear α,ω-di(hydroxy)-polyisobutylene and tri-arm star α,ω,δ-tri(hydroxy)polyisobutylene has been developed and evaluated. The method involves infrared quantitation of the free OH absorption at 3640 cm^{-1} by the use of long path liquid cells in very dilute CCl_4 solution (i.e., in a range where H bridges are absent) in conjunction with M_n determination (vapor phase osmometry or gel permeation chromatography). The results obtained by this method confirm earlier end-group analysis data obtained by more cumbersome methods and indicate that the number of OH end-groups in α,ω-di(hydroxy)polyisobutylene and α,ω,δ-tri(hydroxy)polyisobutylene produced by the inifer technique is 2.0 ± 0.1 and 3.0 ± 0.15, respectively.

INTRODUCTION

Polyurethanes embrace the greatest variety of elastomers, plastics, foams, coating materials, etc. and are the fastest growing segment of the polymer market. Polyurethanes are produced by rapidly mixing low molecular weight ($\bar{M}_n$ = 1000 - 4000) terminally functional (telechelic) primary alcohol prepolymers with multifunctional isocyanates. Synthesis and processing are most efficient because they involve the rapid mixing of liquid streams by low shear equipment. The ultimate properties of polyurethanes are strongly influenced by the exact alcohol/isocyanate stoichiometry employed so that the precise knowledge of OH content of the hydroxy-telechelic prepolymer is of paramount importance[1].

Recently we have synthesized a series of new liquid linear and tri-arm star hydroxy-telechelic polyisobutylenes (i.e., polyisobutylenes carrying terminal OH functions)[2,3] and used these prepolymers for the preparation of new polyurethanes (formulae on next page).

Thus the need arose for a convenient rapid quantitative method for the determination of terminal OH groups in rather low molecular weight ($\bar{M}_n$ = 1000 - 10,000) polyisobutylenes (PIB).

After a thorough examination of OH determination methods described in the literature[1-30] and some experimentation with

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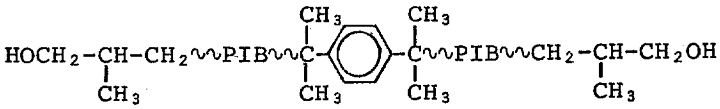
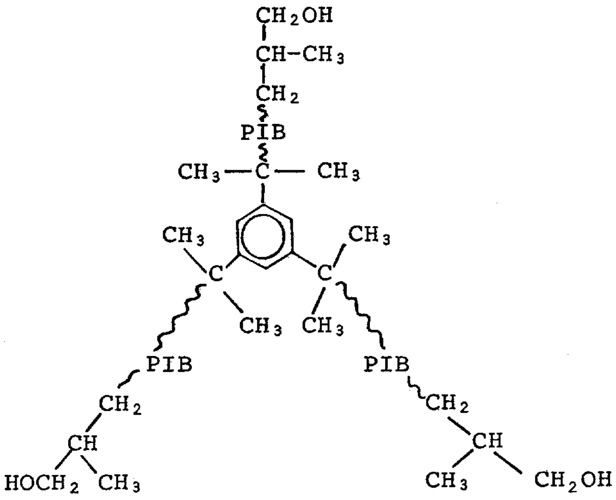


α,ω-Di(hydroxy)polyisobutylene
(PIBDO)



α,ω,δ-Tri(hydroxy)polyisobutylene
(PIBTO)

more cumbersome techniques[1,2,3,23] we developed a rapid and simple direct infrared method for the quantitation of primary OH groups in PIB liquids. This method may be of use for the quantitative determination of primary OH functions in low molecular weight polyhydrocarbons in general.

EXPERIMENTAL

A. Materials. The synthesis and purification of telechelic hydroxy polyisobutylenes have been described[2,3]. 2,4,4-Trimethyl-1-pentanol, TMPO (Aldrich Chemical) was distilled over Molecular Sieves (4Å). Carbon tetrachloride (Fisher Scientif- was dried and stored over Molecular Sieves (4Å without further purification. Toluene and tetrahydrofuran (Fisher Scientific) were distilled over calcium hydride under dry nitrogen before use. Zone-purified biphenyl (Aldrich) was used as received.

B. Molecular Weight Characterization. The $\bar{M}_n$ of low molecular weight polyisobutylenes ($M_n \geq 4,000$) was determined by a Knauer Vapor Pressure Osmometer (VPO) No. 11.00 at 40°C in toluene, calibrated by standard biphenyl solutions. The $\bar{M}_n$ of higher molecular weight polyisobutylenes ($\bar{M}_n > 4,000$) was obtained by gel permeation chromatography (GPC) (Waters M-6000A pump, five μ-Styragel columns of pore sizes of 10^6, 10^5, 10^4, 10^3, and 500 Å, Model R401 differential refractometer, flow rate 2.0 ml/min). Calibration plots were prepared by using fractionated polyisobutylenes with narrow molecular weight dispersities ($\bar{M}_w/\bar{M}_n$ = 1.1 - 1.3).

C. Infrared Method. The infrared spectra were recorded on a Perkin-Elmer Model 521 spectrophotometer. A pair of Perkin-Elmer matched 1.0 mm liquid cells and a pair of Barnes 50 mm long path cells with sodium chloride windows were used.

RESULTS AND DISCUSSION

Attempts were made to determine the OH content of TMPO, a model compound that mimicks the end group in α,ω-di(hydroxy)-polyisobutylene or α,ω,δ-tri(hydroxy)polyisobutylene in a solvent mixture containing a H bonding component i.e., methyl-ethyl ketone/carbon tetrachloride, 25/75 v/v. Figure 1 shows infrared spectra of TMPO at various concentrations. Evidently the broad band characteristic of the H bridges between OH functions becomes more pronounced with increasing concentrations and grows to a major peak at 3520 cm^{-1} at higher concentrations (∿0.1M). The shape of this band, however, changes with OH concentration, i.e., with the amount of "free" OH, so that a linear calibration curve cannot be constructed.

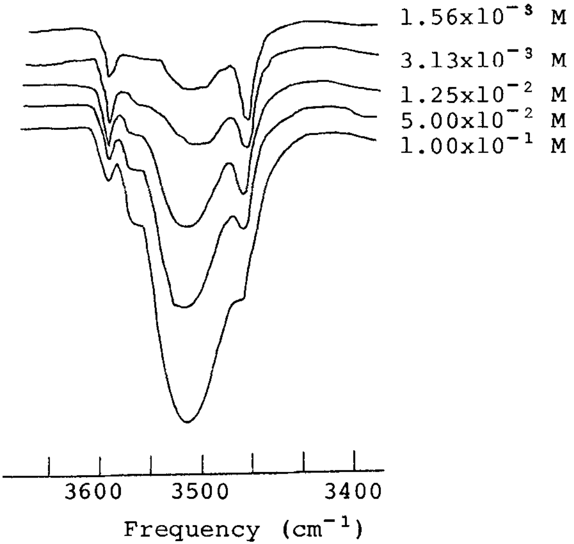


Figure 1. IR spectra of TMPO in MEK/CCl_4 (25/75, v/v) with 1.0 mm path length cell

Then, following Tompa's method[28], direct IR quantitation of the free OH absorbance at 3640 cm^{-1} was examined by the use of 1.0 mm path length cells and CCl_4 solutions. According to the spectra shown in Figure 2 at concentrations lower than 3.125 x 10^{-3} M the broad IR absorption due to associated hydroxy groups disappears indicating the exclusive presence of dissociated free OH groups. The free hydroxy peak could be amplified for quantitative analysis by the use of a long path (50 mm) cell. Figure 3 shows the IR spectrum of TMPO. Evidently at 2.75 x 10^{-3} mole TMPO/ℓ CCl_4 the IR spectrum reveals a single sharp absorption of 3640 cm^{-1} (OH stretching)

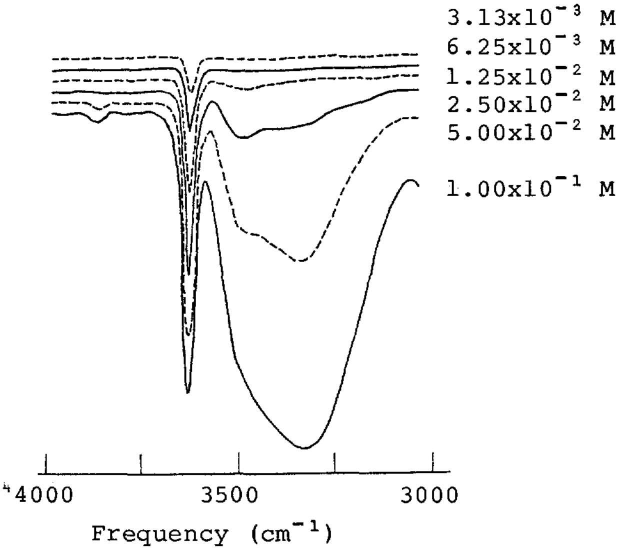


Figure 2. IR Spectra of 2,2,4-Trimethyl-1-pentanol (TMPO) in CCl_4 with 1.0 mm path length cells.

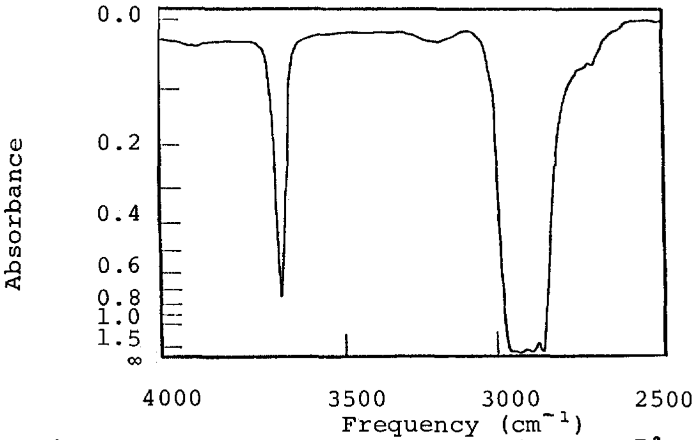


Figure 3. IR Spectrum of TMPO (2.75×10^{-3} M) in CCl_4 with 50 mm Long Path Cell.

indicating the presence of free hydroxy groups. With this information on hand the calibration curve shown in Figure 4 was constructed. According to Mirabella[31] polymer molecular weight does not affect IR absorptivity so that a calibration curve such as shown in Figure 4 is suitable for end-group quantification.

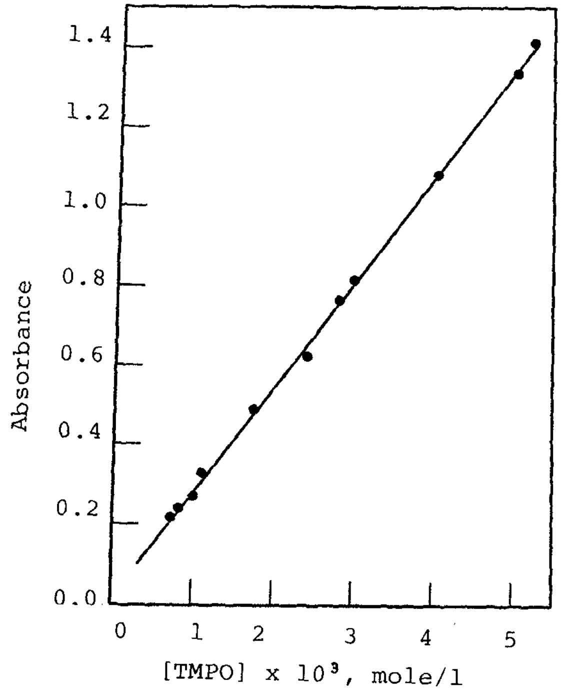


Figure 4. IR Calibration Curve of TMPO in CCl_4 with 50 mm Long Path Cells (Absorbance at 3640 cm^{-1}).

Figure 5 shows the IR spectrum of a representative PIBDO ($\bar{M}_n$ = 3,400) at a concentration of 2.05 x 10^{-3} mole/ℓ CCl_4. The hydroxy content was determined by the peak height method using the 3640 cm^{-1} free hydroxy band with the baseline drawn between 3700 and 3600 cm^{-1}. Table I is a compilation of results of a series of OH analyses of various linear and three-arm star OH-telechelic PIB's. The second column indicates $\bar{M}_n$ and the method used for $\bar{M}_n$ determination (VPO or GPC), the third column is the $\bar{M}_{OH}$ hydroxy equivalent weight obtained by the IR analysis, the last column gives $\bar{F}_n$ the number average OH functions in the polymers. Considering that the standard error of $\bar{M}_n$ determination is ± 3% and that of IR spectroscopy is ± 2%, the accuracy of $\bar{F}_n$ data is ± 5%. These results corroborate our previously obtained functionalities of PIBDO and PIBTO, i.e., 2.0 ± 0.1 and 3.0 ± 0.15, respectively[2,3].

In contrast to unavoidable intramolecular H bridging in polyethers, H bonding can be avoided by diluting hydroxy-telechelic PIB solutions and sharp free OH peaks suitable for quantitative analysis can be obtained.

ACKNOWLEDGEMENT

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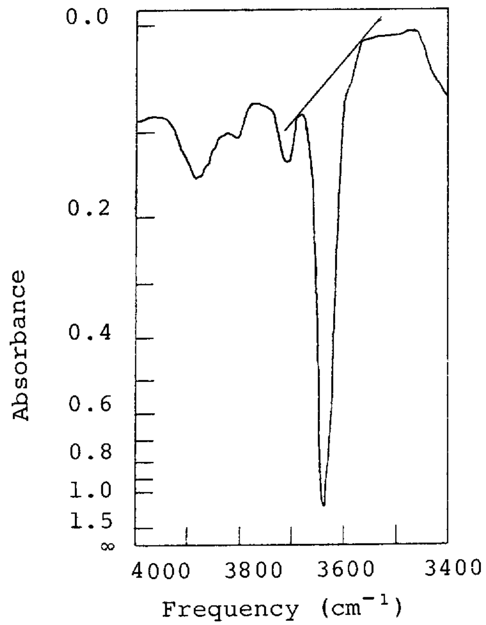

Figure 5. IR Spectrum of PIBDO (2.05×10^{-3} M) in CCl_4 with 50 mm Long Path Cell.

TABLE I

Terminal Hydroxyl Functionality of PIBDO and PIBTO by Direct Infrared Analysis

Sample	$\overline{M}_n$(±3%)[a]	$\overline{M}_{OH}$(±2%)[b]	$\overline{F}_n$(±5%)[c]
PIBDO	3,400 (VPO)	1,692	2.01
PIBDO	4,000 (VPO)	2,047	1.95
PIBDO	9,500 (GPC)	4,814	1.97
PIBDO	11,000 (GPC)	5,627	1.95
PIBTO	7,500 (VPO)	2,513	2.98

a) $\overline{M}_n$ = number average molecular weight determined by VPO or GPC

b) $\overline{M}_{OH}$ = hydroxyl equivalent weight = g/mole OH

c) $\overline{F}_n = \overline{M}_n/\overline{M}_{OH}$

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