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Quantifying hydroxyl functionality of telechelic poly(ethylene ether carbonate) diols

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SUMMARY

A Fourier transform infrared-based method for quantification of hydroxyl functionality was developed and applied to several commercial poly(ethylene oxide) samples of known difunctionality and several experimental poly(ethylene ether carbonate) (PEEC) samples. The PEEC prepolymers were synthesized by ring-opening bulk polymerization of ethylene carbonate using dibutyltin diacetate, dibutyltin dilaurate or dibutyltin dimethoxide as catalysts. Absorption measurements were made of a sterically favored five-membered hydrogen-bonded ring, containing the terminal hydroxyl group, which forms under dilute solution conditions in methylene chloride. Calibration of the method was obtained by measuring the absorption of known concentrations of a model compound. The purified polymers were shown to be hydroxy-terminated using the infrared method in conjunction with measurements of number average molecular weight.

INTRODUCTION

Hydroxy-terminated prepolymers are valuable intermediates for the production of polyurethane thermoplastic and network polymers. To ensure proper reaction stoichiometry and development of a fully connected rubbery network of adequate strength and toughness, the value of the prepolymer hydroxyl functionality must be accurately known. A variety of techniques for quantitative determination of hydroxyl groups has been reported in the literature. These methods usually involve chemical derivatizations, i.e., transformations of the hydroxyl end group into a readily identifiable entity. Examples include an acylation step using acid anhydride followed by the selective hydrolysis and titration of the excess acid,[1] formation of the corresponding trimethylsilyl ether derivative followed by quantitative determination by NMR spectroscopy[2] and reaction with benzoyl chloride and analysis by ultraviolet spectroscopy.[3] All of the above techniques share the common disadvantages that they are degradative, require relatively large sample sizes and have reaction times as long as 24 h.

The quantitative determination of hydroxyl groups using solution Fourier transform infrared spectroscopy (FTIR) is well documented in the literature, and the requisite feature of most techniques is the restriction of the population of hydroxyl groups to a single hydrogen-bonded state. Thus, for example, the methods include measurement of the absorption of free (non-hydrogen-bonded) hydroxyl groups at 3640 cm^{-1} in dilute carbon tetrachloride (CCl_4) solution using long path cells[4] and the absorption of tetrahydrofuran (THF)-associated hydroxyl groups.[5]

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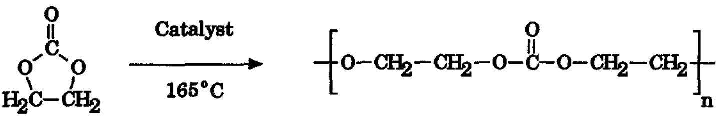
We have recently been involved in the synthesis of a variety of oxygenated, hydroxy-terminated prepolymers produced *via* ring-opening polymerization[6,7,8] and have experienced a need for routine hydroxyl functionality determination. We were reluctant to employ techniques involving post-polymerization chemistry because of the potential for destruction, under the required reaction conditions, of labile linkages along the polymer backbone. Thus, we investigated the use of solution FTIR methods. The insolubility of certain of our polymers in Ccl_4 and the possibility for intramolecular hydrogen bonding eliminated the possibility of examining the absorption of free hydroxyl groups. Initially, a THF-associated hydroxyl complex was examined, but this method was hindered by the presence of two overlapping absorptions which has been reported to result from the presence of moisture,[5] which could not be completely removed. Of the several types of prepolymers under investigation, those obtained from the ring-opening polymerization of ethylene carbonate (EC) in the presence of a tin catalyst, i.e., alternating poly(ethylene ether carbonate) (PEEC), have been among the most intensely studied,[6,7] and the method finally chosen is most specifically applied to them and other polymers which possess a hydrogen bond accepting group near the chain end such that the terminal hydroxyl group is involved in a sterically favored hydrogen-bonded ring.



EC

PEEC

EXPERIMENTAL

Materials

Ethylene carbonate (EC) (99.5%, Texaco Chemical Co.) and 2-hydroxyethyl butyl ether (HEBE) (Eastman Chemical Co.) were distilled from calcium hydride under vacuum prior to use. Methylene chloride (J.T. Baker) was distilled from calcium hydride prior to use. Dibutyltin diacetate (DBTDA) and dibutyltin dilaurate (DBTDL) from Aldrich Chem. Co. and dibutyltin dimethoxide (DBTDM) (Pfaltz & Bauer) were dried *in vacuo* at 80°C for 24 h before use. Poly(ethylene oxide) (PEO) of 300, 600, 1,500, 2,000, 8,000 and 14,000 molecular weight from Aldrich Chem. Co. and a PEO of 4,000 molecular weight from Polysciences Inc. were used as received.

Procedures

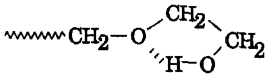
Synthesis of Poly(Ethylene Ether Carbonate) using Organotin Catalysts. All polymerizations were conducted in the bulk under a flow of nitrogen at 165°C. A typical reaction set-up was as follows: a 250 Ml three-neck flask was flame-dried under nitrogen, charged with 50.0 g (0.567 mole) ethylene carbonate and 7.20 g (0.0114 mole) DBTDL, and placed in a constant temperature bath. Reaction was allowed to proceed for 72 h (about 80% conversion), after which the PEEC oligomer was purified by filtration through a medium fritted-glass funnel to remove insoluble catalyst residues. The filtrate was dissolved in a minimal amount of chloroform, followed by precipitation into a tenfold excess of methanol. The oily residue was rinsed thrice more with methanol, freed of methanol, and finally eluted through a silica gel column using methylene chloride as the solvent. Solvent evaporation yielded a clear, light-yellow product which was dried *in vacuo* at 80° C at least 7 days prior to hydroxyl functionality determination.

Hydroxyl Functionality Determination. Hydroxyl functionalities of PEEC and PEO oligomers were obtained from FTIR spectra, measured on a Nicolet 5-DX FTIR spectrometer employing NaCl cells with a path length of 0.157 cm. All samples were dried *in vacuo* at 80° C for at least one week after which time methylene chloride solutions were prepared in oven-dried volumetric flasks. Absorption was measured by the peak height method; the height and position of the peak maximum were measured, a baseline was drawn from 3640 cm^{-1} to 3570 cm^{-1}, and this absorption was subtracted from the maximum value.

Characterization. Gel permeation chromatography (GPC) was performed on a Waters Associates system employing 100, 500, 10^4, and 10^5 Å ultra-styragel columns and a Model 410 differential refractometer; PEO molecular weight standards were used to obtain a calibration curve. FTIR spectra of bulk PEEC samples were measured on a Perkin-Elmer 1600 Series FTIR spectrometer using NaCl cells.

RESULTS AND DISCUSSION

Figure 1 shows an FTIR spectrum of a bulk PEEC oligomer with $\bar{M}_n$ = 1320. The broad peak located about 3500 cm^{-1} qualitatively shows the presence of terminal hydroxyl groups in the prepolymer, but quantification is difficult in the bulk due to the many different hydrogen-bonded states and the difficulty in measuring and attaining uniform film thickness. However, the hydroxyl groups of polymers such as PEEC and PEO can form, at suitable dilution in a non-hydrogen-bonding solvent, a sterically favored hydrogen-bonded (H-bonded) ring (1) which exhibits a sharp peak in the FTIR spectrum.



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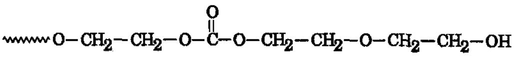
Hydroxyl functionalities of ethylene oxide-capped polypropylene glycol[9] and PEO in dilute Ccl_4 solution[10] have been determined by analysis of this structure. This technique, however, is obviously limited to alcohols with a specific structure, and evidence available in the literature clearly indicates that PEEC possesses such end group structures. For example, Vogdanis et al.[11,12] have shown that PEEC synthesized by organotin catalysts is hydroxy-terminated, and they have suggested that of the various possible end group structures, only 2-hydroxyethyl ether (2) end groups remain after polymer work-up. Furthermore, Harris and McDonald polymerized EC using sodium stannate trihydrate as catalyst and found that although both 2-hydroxyethyl carbonate (3) and 2-hydroxyethyl ether (2) end groups are present initially in the polymerization mixture, only (2) is present during the latter stages of the polymerization.[13]



$$\sim\sim\sim O-CH_2-CH_2-O-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-O-CH_2-CH_2-OH$$

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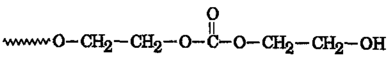

$$\sim\sim\sim O-CH_2-CH_2-O-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-OH$$

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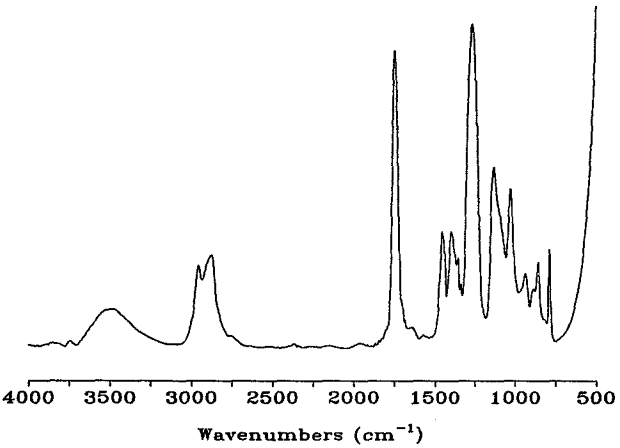


Figure 1. FTIR absorption spectrum of a bulk PEEC oligomer with $\bar{M}_n$ = 1320.

Due to solubility and other considerations, FTIR analysis was applied to CH_2Cl_2 solutions of PEEC to examine the formation of the sterically-favored five-membered ring containing the terminal hydroxyl group. In Figure 2 are shown the FTIR absorption spectra from 3850 to 3150 cm^{-1} of A) a CH_2Cl_2 solution of PEEC oligomer with M_n = 1870 at 1.852 g/dL, and B) neat CH_2Cl_2. The absorption spectrum of the PEEC oligomer shows only one peak in the hydroxyl stretching region (3650 to 3450 cm^{-1}), implying that only one type of hydroxyl structure is present. Although CH_2Cl_2 does absorb in the range from 3850 to 3150 cm-^{1}, it does not absorb in the hydroxyl-stretch region.

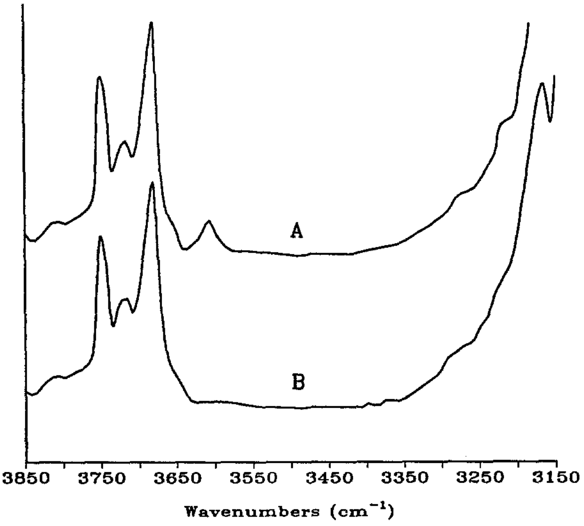
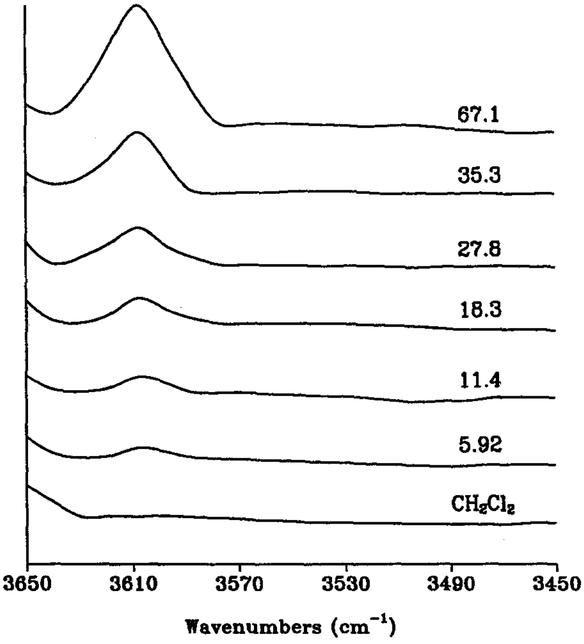


Figure 2. FTIR absorption spectra from 3850 and 3150 cm^{-1} of (A) PEEC oligomer with $\bar{M}_n$ = 1870 (1.982 g/Dl in CH_2Cl_2) and (B) CH_2Cl_2.

Formation of the Calibration Curve

To routinely determine the hydroxyl concentration of PEEC solutions it was necessary to construct a calibration curve which related absorption to hydroxyl concentration. 2-Hydroxyethyl butyl ether (HEBE) (4, Figure 3) served as a good model since its hydroxyl end group resembles that of both PEO and PEEC. The FTIR spectra from 3650 to 3450 cm^{-1} of selected concentrations of HEBE in CH_2Cl_2 along with the CH_2Cl_2 baseline are shown in Figure 3. The HEBE spectra show only one peak centered about 3610 cm^{-1}, and the absorption of the solvent was observed to be minimal. The presence of only one peak in CH_2Cl_2, implying that only one type of hydroxyl structure is present, was an unexpected simplification since the FTIR absorption spectrum of HEBE in CCl_4 shows a bimodal peak comprised of two distinct peaks located at 3610 and 3475 cm^{-1}.[14] These have been assigned to the stretching vibrations of the terminal H-bonded hydroxyl group when involved in the intramolecular five-membered ring, and an intermolecular ten-membered ring, respectively. The non-polar nature of CCl_4 may cause the highly polar hydroxyl group to be less selective among possible H-bonding acceptors, and thus two or more peaks corresponding to multiple H-bonding interactions result; however, in methylene chloride, due to the increased polarity of the solvent, the driving force for H- bond formation should not be as great, and this may allow for the formation of the most energetically favored H bond which results in only one distinct peak in the FTIR spectrum.



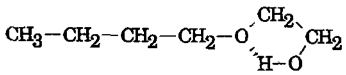


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Figure 3. FTIR absorption spectra from 3650 to 3450 cm^{-1} of 2-hydroxyethyl butyl ether (4) in CH_2Cl_2 at selected concentrations (meq) and the CH_2Cl_2 baseline.

A series of solutions with varying HEBE concentrations was prepared, and the FTIR spectra were measured to form a calibration. Absorption vs. hydroxyl concentration within the range 6.2 to 67 meq/L was found to follow the linear relationship: *Absorption = 0.00719 meq/L - 0.0152 abs units.* Since polymer molecular weight does not affect FTIR absorptivity,[15] the hydroxyl functionality of polymer samples was calculated from the absorption of a solution of the polymer in CH_2Cl_2, of known molar concentration (calculated from a knowledge of the polymer number average molecular weight).

Analysis of Poly(Ethylene Oxide)

To test the applicability of our method to hydroxy-terminated polymers, we used known molecular weight samples of PEO, since they have been shown to produce the necessary five-membered H-bonded ring[11] and their hydroxyl functionality is known. Dilute solutions of PEO display only one hydroxyl peak centered about 3610 cm^{-1}, and the single absorption may again be attributed to the polar nature of CH_2Cl_2 since in the FTIR absorption spectrum of PEO in CCl_4 a broad multimodal peak comprised of three distinct maxima located at about 3600, 3500 and 3450 cm^{-1} results. These absorptions have been assigned to the stretching vibrations of the terminal H-bonded hydroxyl group when involved in the intramolecular five-membered ring, an intermolecular ten-membered ring, and an intramolecularly H-bonded eight-membered ring, respectively.[15]

Table I shows the results for PEO samples of M_n = 1,500 and 2,000 at different concentrations, and as expected, the method confirmed that these materials are difunctional for concentrations ≤ 2 g/dL. Above this concentration the apparent hydroxyl functionality was less than 2 suggesting that this concentration is the upper limit of the dilute solution region, i.e., the region intramolecular H bonding is predominant.

TABLE I

Hydroxyl Functionality of Poly(Ethylene Oxide) Standards

Sample	Polymer Concentration (g/dL)	$\bar{M}_{n(GPC)}$	Absorbance	Hydroxyl Functionality
PEO 1500	2.182	1500	0.1896	1.96
PEO 2000	1.747	2000	0.1068	1.95
PEO 2000	1.929	2000	0.1197	1.95
PEO 4000	1.962	4000	0.0561	2.03
PEO 2000	3.358	2000	0.1680	1.52
PEO 4000	2.950	4000	0.0754	1.71

Analysis of Poly(Ethylene Ether Carbonate)

A representative solution FTIR spectrum of a purified PEEC oligomer with $\bar{M}_n$ = 650 synthesized using DBTDL as the catalyst is shown in Figure 4. Here again only one peak was observed in the hydroxyl-stretching region. The results of the solution FTIR characterization procedure for some selected PEEC samples are shown in Table II. Number average molecular weights were determined by GPC, and the primary PEO standards provided a quite good calibration for the structurally similar PEEC, as Vogdanis et al. have also reported.[11] The number average hydroxyl functionality was obtained as the ratio of $\bar{M}_n$, determined by GPC, and the equivalent weight determined by FTIR, and appears to be two (2) for PEEC catalyzed by DBTDA, DBTDL and DBTDM.

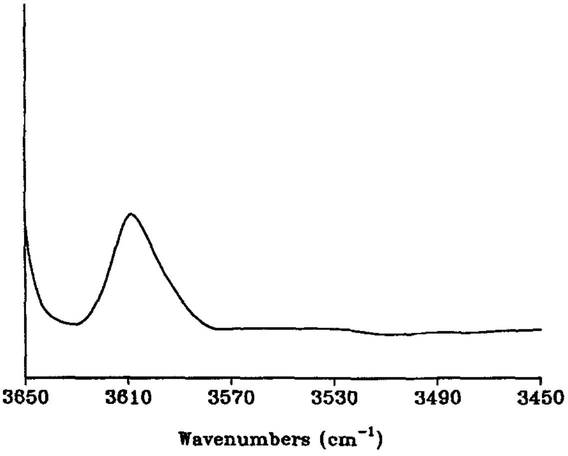

Figure 4. Expanded solution FTIR absorption spectrum from 3650 to 3450 cm^{-1} of a purified PEEC prepolymer with $\bar{M}_n$ = 650 at a concentration of 0.599 g/dL in CH_2Cl_2 synthesized using DBTDL as catalyst.

CONCLUSIONS

Purified PEEC prepolymers produced using organotin catalysts were shown to be hydroxy-terminated by quantifying, using FTIR, an intramolecular H-bonded ring involving the terminal hydroxyl group. The nearly perfect hydroxyl functionality of the oligomers suggests their utility as prepolymers for polyurethane synthesis; however their synthesis using organotin catalysts leaves much to be desired.[6] Both DBTDA and DBTDL produce an insoluble by-product in the polymerization reaction which is tedious to remove, and DBTDM, although it produces no by-product, yields lower than desired CO_2 retention. A better system results from the use of the heterogeneous catalyst, sodium stannate trihydrate, which is a less expensive catalyst and affords a much faster rate of polymerization and a simpler polymer purification procedure. We have shown that this catalyst also produces PEEC prepolymers of nearly perfect difunctionality.[6]

TABLE II

Hydroxyl Functionality of Poly(Ethylene Ether Carbonate) Samples

Sample[a]	Polymer Concentration (g/dL)	$\bar{M}_{n(GPC)}$	Absorbance	Hydroxyl Functionality
DBTDA (1%)	1.577	2220	0.0862	1.98
DBTDA (2%)	1.728	1420	0.1591	1.97
DBTDL (1%)	1.982	1870	0.1330	1.94
DBTDL (2%)	0.599	650	0.1120	1.92
DBTDL (2%)	2.072	650	0.4377	1.98
DBTDM (2%)	2.018	3600	0.0674	2.05
DBTDM (2%)	2.008	3600	0.0656	2.01

[a] catalyst used in mole %

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