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NMR based determination of minute acid functionality: end-groups in PET

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Abstract

Conditions are determined for the carbodiimide-mediated room temperature esterification of the carboxylic acid end-groups of poly(ethylene terephthalate) with hexafluoroisopropanol. The hexafluoroisopropyl ester is quantified with ^{19}F NMR, using α,α,α-trifluorotoluene as a secondary standard. This provides a technique for accurate determination of minute amounts of carboxylic acid functionality in small samples of polymers, and potentially in animal and plant based foods.

Keywords: PET; End-groups; Determination

1. Introduction

Poly(ethylene terephthalate) (PET) is one of the most important commodity and engineering polymers with worldwide consumption next only to polyolefins. One of its critical properties is its thermal and hydrolytic degradation resistance, which is significantly controlled by the acid and hydroxyl end-groups [1–2]. Hence, their regular determination at production facilities is the key both for quality control and for monitoring the progress of polymerization aiming to minimize the acid end-groups [2,3].

Quantitative analysis of the end-groups in polymers is most often based on titration [4–8]. Some of the associated problems are: large sample size requirement, considerable amounts of toxic solvents, and difficulties with exact determination of the end-point when minute concentrations of acid functionality are involved. An infra-red based technique involving deuteration has been described for determination of hydroxyl end-groups [9–13]. Need for development of new techniques has recently been emphasized [2]. NMR based techniques can offer the advantage of small sample requirement and quick and reliable determination of the end-groups. A ^{1}H NMR based technique has been described in recent years for the determination of hydroxyl end-groups [14–16]. In this paper, we describe a ^{19}F NMR based technique for acid end-group determination in PET. In addition, the hydroxyl end-group concentration may also be determined from NMR of the same sample, thus enabling estimation of the number average molecular weight (M_n).

The following issues are crucial in NMR based end-group determination of PET. First, the ester groups of PET are liable to undergo degradation, generating additional acid/hydroxyl groups in acidic/basic environment at elevated temperature. Hence, it is desirable that the high molecular weight PET has sufficient room temperature solubility in the solvent used. Second, since the resolution of the chemical shifts of the aromatic hydrogen (minute acid linked vs. dominantly ester linked) in PET is poor, an indirect method such as reaction with an alcohol to form an NMR identifiable ester is desired. Third, since the end-group concentration is very low for up to 5 wt% solution (needed for NMR) of high molecular weight PET, an intrinsically rapid esterification reaction is desirable. Finally, since the $\delta \sim 4.7$ ppm region in ^{1}H NMR dominated by the large CH_2 peak of PET, it is essential that a new ester signal appears in an isolated δ region. Hexafluoroisopropanol (HFIP), applied both as solvent and as reactive alcohol, appears to satisfy these requirements as esterification is known to result in large shift of the CH peak [17,18].

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Since a rapid room temperature esterification of the acid end-groups of PET is required to avoid generation of additional acid end-groups, we explore carbodiimide-mediated esterification [17,19,20] at room temperature.

2. Experimental part

2.1. Materials

PET chips were obtained from Wilton Research Center (ICI, UK), and the following characteristics were determined at Twaron Research (Arnhem): intrinsic viscosity = 0.501 dl/g (in *m*-cresol at 30 °C), $M_n = 20,500$, diethyleneglycol (DEG) = 0.69 wt%, Sb = 212 ppm, Ti = 14 ppm, P = 78 ppm. Average weight = 0.045 g.

Deuterated chloroform ($CDCl_3$, 99.9 atom D%), hexafluoroisopropanol (HFIP, 99%), α,α,α-trifluorotoluene (TFT, 99%), 4-pyrrrolidino pyridine (98%), trifluoroacetic acid (TFA, 99%), benzoic acid (BA, 99%) and trifluoroacetic anhydride (TFAA, 99%) were obtained from Aldrich. Dicyclohexyl carbodiimide (DCC, 99%) was obtained from Merck. All chemicals were used as received.

2.2. NMR Analysis

400 MHz Varian Mercury Vx 400 was used to carry out the ^{1}H NMR and ^{19}F NMR measurements, using $CDCl_3$ mixture with HFIP or TFA as the solvent.

2.3. Esterification of benzoic acid with HFIP in $CDCl_3$

Benzoic acid (0.0244 g, 0.2 mmol) was dissolved in $CDCl_3$ (1.03 g), and the catalyst 4-pyrrolidinopyridine (0.011 g, 0.074 mmol) and DCC (0.0422 g, 0.205 mmol) were added. Finally HFIP (0.065 g, 0.386 mmol) was added. Characterization of hexafluoroisopropyl benzoate (**1**): ^{1}H NMR: δ 8.11 [d, 2H], 7.68 [t, 1H], 7.52 [t, 2H], 6.04 [septet, 1H]. ^{19}F NMR: δ −73.45 [d,6F]. Conversion (from ^{1}H NMR) of benzoic acid to **1** was complete. Caution: HFIP is extremely destructive to tissues of the mucous membranes and upper respiratory tract.

2.4. Esterification of highly diluted benzoic acid with large excess of HFIP in $CDCl_3$

Benzoic acid (0.0052 g, 0.042 mmol) was dissolved in a mixture of HFIP (0.102 g) and $CDCl_3$ (0.903 g). Part (0.106 g) of this solution was diluted with HFIP (0.101 g) and $CDCl_3$ (1.007 g). To the latter solution was added part (0.102 g) of a solution of a mixture of DCC (0.0096 g, 0.046 mmol) and 4-pyrrolidinopyridine (0.0012 g, 0.008 mmol) in $CDCl_3$ (1.03 g) to give the sample for NMR analysis. Characterization of **1**: as in Section 2.3. Benzoic acid (from ^{1}H NMR) conversion to **1** was complete.

2.5. Esterification of acid end-groups of PET with HFIP

Two pellets of PET (0.095 g, ~0.0047 mmol) were dissolved in a mixture of HFIP (0.203 g) and $CDCl_3$ (1.007 g) at room temperature. Firstly, part (0.105 g) of a solution of 4-pyrrolidinopyridine (0.0011 g) in $CDCl_3$ (1.012 g) was added and subsequently, part (0.303 g) of a solution of DCC (0.0075 g) in $CDCl_3$ (1.504 g) was added. After waiting for 10 min, part (0.102 g) of a solution of TFT (0.0103) in $CDCl_3$ (2.078 g) was added to the above reaction mixture to give the sample for NMR analysis. Characterization of the hexafluroisopropylester of PET (**3**): ^{1}H NMR δ 6.04 [septet, 1H], ^{19}F NMR: δ −73.41 [d, 6F].

2.6. Fluoroderivatization of the hydroxyl end-groups of PET with TFA

Two pellets of PET (0.092 g) were dissolved in a mixture of TFA (0.206 g) and $CDCl_3$ (1.03 g). Part (0.107 g) of a solution of TFT (0.011 g) in $CDCl_3$ (2.03 g) was added to the above reaction mixture. ^{19}F NMR analysis was carried out repeatedly at various times. Integration of the δ −75.21 [s, 3F] peak for the trifluoroacetate of PET (**4**) relative to the δ −62.9 [s, 3F] peak of TFT allowed quantification of the acid end-groups. Caution: TFA may cause burns to skin or eyes, inhalation or ingestion may cause burns to mucous membranes.

2.7. Fluoroderivatization of hydroxyl and acid end-groups of PET with TFAA and HFIP

Two pellets of PET (0.0976 g, ~0.0047 mmol) were dissolved in a mixture of TFA (0.531 g) and TFAA (0.203 g, 1 mmol) over 1 h. The solvent removal was carried out by threefold washing with $CHCl_3$ (1.023 g), evaporation by blowing nitrogen, drying under vacuum (5×10^{-3} mbar). The dried PET was dissolved in a mixture of HFIP (0.183 g) and $CDCl_3$ (1.012 g) at room temperature. Part (0.106 g) of a solution of 4-pyrrolidinopyridine (0.001 g) in $CDCl_3$ (1.002 g) was added and subsequently, part (0.310 g) of a solution of DCC (0.078 g) in $CDCl_3$ (1.503 g) was added. After waiting for 10 min, part (0.0735 g) of a solution of TFT (0.0181) in $CDCl_3$ (2.080 g) was added to the above reaction mixture to give the sample for NMR analysis. ^{19}F NMR **4**: δ −75.21 [s, 3F], **3**: δ −73.41 [d, 6F]. Caution: TFAA may cause burns to skin or eyes, inhalation or ingestion may be fatal.

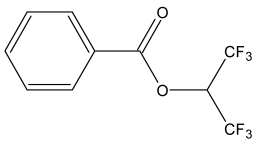
3. Results and discussion

3.1. Carbodiimide-mediated esterification of benzoic acid with HFIP

We started by examining the DCC mediated esterification of benzoic acid with HFIP to form hexafluoroisopropyl

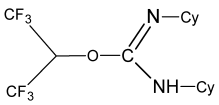
benzoate (**1**):

1



The ester **1** has been synthesized previously [18], albeit by reaction of benzaldehyde with hexafluoroacetone. The DCC mediated esterification is non-trivial due to the possibility of many side reactions [19,20]. For example, we found that DCC undergoes reaction with HFIP, leading to formation of adduct **2**.

2

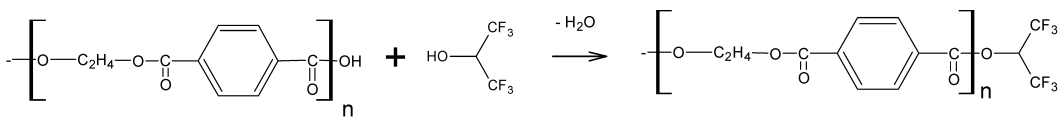


Thus, the sequence of addition of reactants can be critical, and seems to need optimization for individual reactions [20]. We found that it was essential to first add catalyst and DCC to benzoic acid before the addition of HFIP (Section 2.3), for complete conversion of the acid to **1** (septet, $\delta = 6.04$ ppm).

For similar esterification of the acid end-groups of PET, we wished to utilize HFIP also as a reaction medium since it enables PET dissolution at room temperature. However, the corresponding high concentration of HFIP resulted in complete conversion of the added DCC to adduct **2**. This problem was circumvented by utilizing $CDCl_3$-HFIP (10:1 by wt) as a mixed solvent for PET. We first established (Section 2.4) that for this solvent system, a low concentration of benzoic acid (3.4 meq per kg reaction mixture) could be completely converted to **1**.

3.2. Determination of the acid end-groups of PET by fluoroesterification

Having achieved quantitative 'fluoroesterification' of benzoic acid at very low concentration in $CDCl_3$–HFIP mixture, we applied (Section 2.5) this method to esterify the acid end-groups of PET with HFIP to afford the hexafluoroisopropyl ester **3** (Eq. (1)):



(1)

3

A ^{1}H NMR signal (septet, $\delta = 6.04$ ppm, $-C\ H(CF_3)_2$) was observed, corresponding to the formation of **3**. The ^{19}F NMR (Fig. 1) features sharp peaks for the ester **3** (d, $\delta = -73.41$ ppm, $J = 5.6$ Hz) and the adduct **2** (d, $\delta = -73.55$ ppm, $J = 5.6$ Hz), in addition to the HFIP doublet ($\delta = -75.98$ ppm).

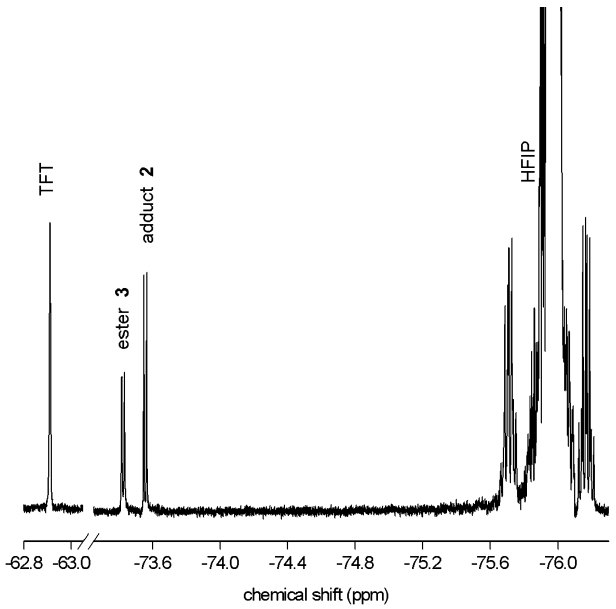


Fig. 1. ^{19}F NMR spectrum of the reaction product (Section 2.5) of PET with HFIP and DCC.

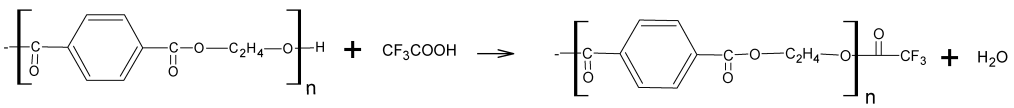
Quantification with respect to the PET was facilitated by addition (Section 2.5) of a ^{19}F NMR detectable secondary standard TFT (s, $\delta = -62.90$ ppm), allowing calculation (Fig. 1) of the acid end-group concentration as 20.1 meq/kg-PET. In this experiment, DCC was 6 times in excess of the measured acid end-groups. When the amount of DCC was only 1.5 times the stoichiometric requirement, the acid value was measured to be only 14 meq/kg, due to the competing conversion of DCC to the adduct **2**. Repeating this experiment four times with PET of same grade and quantity, but with varying amount of DCC (4–8 times the stoichiometric requirement) resulted in measured acid end-group concentrations of 20.5, 19.4, 19.1 and 21.2 meq/kg. This shows good reproducibility of this method, and the $\pm 5\%$ variations between measurements can be attributed to the limited accuracy of NMR peak integration, and some chip-to-chip variation arising during the polymerization process itself. This value also compares well with the acid end-group concentration of 23 meq/kg determined by titration method (at Twaron Research, Arnhem), since the expected accuracy of a single titration method measurement is ± 3 meq/kg. We also carried out the esterification experiments with reduced concentration of acid end-groups, by using the same grade but smaller quantities of the PET,

and maintaining HFIP:PET = 2:1 (w/w). Results in Fig. 2 show the expected linear variation of the measured hexafluoroisopropyl ester concentration with PET concentration. This suggests that acid concentrations as low as 6 meq/kg-PET can be reliably measured by using a 5 wt% polymer concentration in reaction mixture (i.e. 0.3 meq acid/kg reaction mixture).

It is straightforward to extend this method to simultaneous determination of the hydroxyl end-groups, using the known [16] peak assignments of the $CH_2C\underline{H}_2OH$ ends ($\delta = 4.01$ ppm). The masking of this peak by the large HFIP peaks ($\delta_{-CH=} = 4.40$ ppm, δ_{-OH} : ranging from 4 to 7 ppm, depending on DCC concentration) in that spectral region is eliminated by use of deuterated HFIP in place of HFIP. In addition, the ester peak in the ^{19}F NMR now appears as a singlet, thereby improving the peak integration for the acid determination. Furthermore, adding tetrachloroethane (s, $\delta = 6.0$ ppm) as internal standard for ^{1}H NMR has permitted easy quantification by integration, and the hydroxyl end-group concentration is determined as 82 meq/kg-PET. The concentration of acid and hydroxyl end-groups leads us to estimate $M_n = 2([COOH] + [OH])^{-1} = 1.96 \times 10^4$, consistent with the value determined from the measured intrinsic viscosity (Section 2.1).

3.3. Determination of the hydroxyl end-groups of PET by fluoroderivatization

The hydroxyl end-groups could also be determined by the slow fluoroderivatization (Section 2.6) with TFA (Eq. (2)).



(2)

4

At ($\delta = -75.2$ *ppm*), a singlet appeared in the ^{19}F NMR corresponding to the trifluoroacetate of PET (**4**). Comparison of the peak area with respect to the added (Section 2.6) secondary standard (TFT) (s, $\delta = -62.90$ ppm) allowed quantification of y, the concentration of **4** (Fig. 3). The concentration y was found to increase with time t lapsed between the dissolution and the NMR analysis, and leveled out in about 48 h. This is similar to the observation of Kenwright et al.. [15], but they had used ^{1}H NMR to monitor the concentration of unreacted hydroxyl end-groups. A first order kinetic fit

$$y = y_0(1 - e^{-kt}) \tag{3}$$

shown in Fig. 3 resulted in a rate constant as $k = 0.103$/h and the final concentration of **4** $y_0 = 82.9$ meq/kg-PET. This corresponds to the concentration of hydroxyl end-groups in the starting PET sample, and compares well with the value determined by the ^{1}H NMR of the starting sample (Section 3.2).

3.4. Simultaneous determination of the hydroxyl and acid end-groups of PET

We found that the fluoroderivatization of the hydroxyl

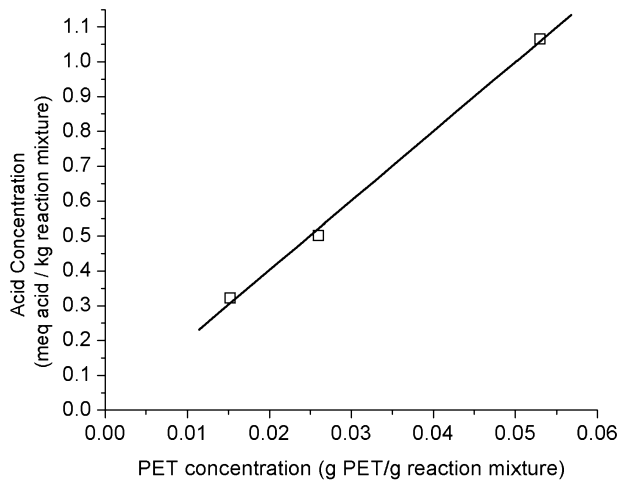


Fig. 2. Effect of the PET concentration (during reaction) on the measured acid concentration.

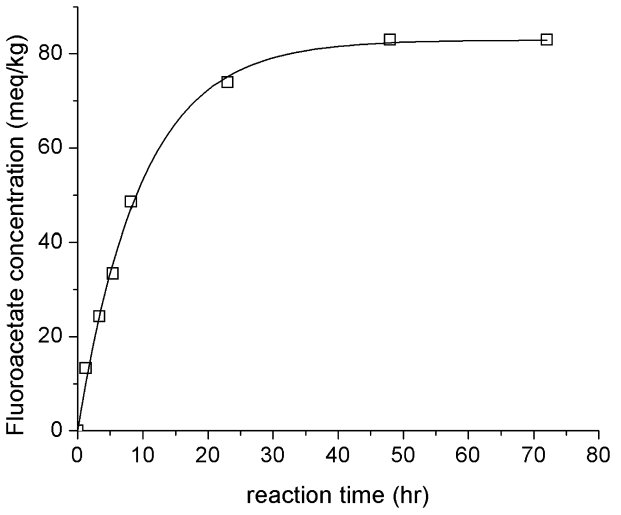
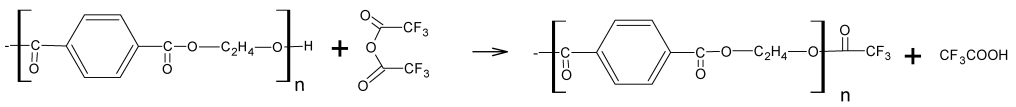


Fig. 3. Conversion of the hydroxyl end-groups of PET to the trifluoroacetate (**4**) (Eq. (2)). Symbols are the experimental measurements (Section 2.6) by ^{1}F NMR, and the continuous line represents the first order kinetics (Eq. 3).

end-groups can be carried out rapidly (Section 2.7) with TFAA in TFA.



(4)

5

Removal of the TFAA and TFA, and subsequent carbodiimide-mediated fluoroesterification (Section 2.7) of the acid end-groups allows NMR detection of both the carboxylic acid and the hydroxyl end-groups in a single ^{19}F NMR measurement (Fig. 4). Comparing with Fig. 1, the doublet at ($\delta = -73.41$ppm) corresponds to **3**, while the singlet at ($\delta = -75.21$ ppm) corresponds to **4**. In addition, the small singlet ($\delta = -74.53$ppm) and doublet ($\delta = -73.36$ ppm) correspond to hexafluoroisopropyl trifluoroacetate (HFIP-TFA ester) [21] and the large singlets ($\delta = -69.8$, -70.1 ppm) correspond to TFA-DCC adducts. This suggests that the removal of TFA was incomplete even after threefold washing with $CHCl_3$ and drying. Consumption of DCC in these reactions with the leftover TFA was responsible for the much higher amount of DCC needed (Section 2.7) as compared to the reaction in absence of TFA (Section 2.5). Using the integrations of the peaks corresponding to **4** and **3** relative to the TFT peak, the concentrations of the hydroxyl and the carboxylic acid end-groups are simultaneously determined as 76 meq/kg and 19 meq/kg, respectively. The marginally lower values of the acid and hydroxyl end-group concentrations measured here are within the accuracy of the NMR integrations, but could also be related to some loss of the smallest end-group carrying molecules during the repeated washings.

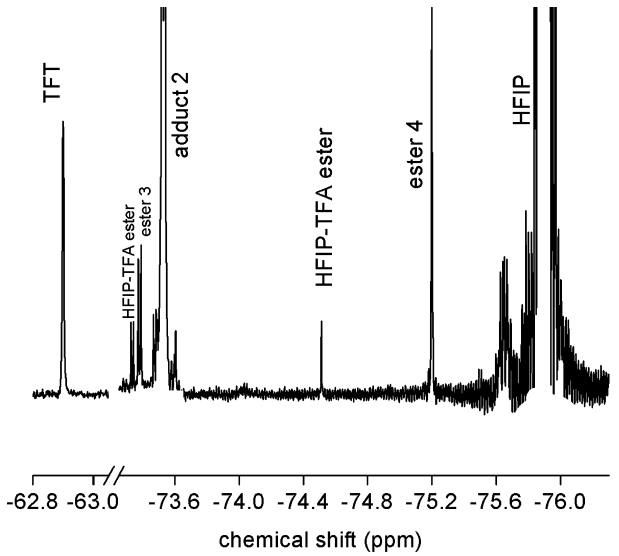


Fig. 4. ^{19}F NMR spectrum after consecutive reactions (Section 2.7) of PET with TFAA and with HFIP.

4. Conclusions

We have presented methods for determination of the acid and hydroxyl end-groups (and thus an estimation of M_n) of PET from small specimen analyzed by a combination of ^1H NMR and ^{19}F NMR, or by ^{19}F NMR alone. In an accompanying publication [22], we report application of this technique for samples of a wide range of end-group concentrations obtained during solid-state polymerization of PET. The fluoroderivatization enables identification of some new post-polymerization characteristics of PET: the influence of reaction environment (vacuum, inert gas) on the kinetics, and identification of the sublimate [22]. We will also extend this technique to carboxylic acid and hydroxyl content determinations in other polymers such as minutely functionalized polystyrenes. Potential applications exist in determination of minute quantities of acids in animal (meat/milk) and plant based foods, food supplements and pharmaceutical formulations, where chromatographic techniques are presently used.

Acknowledgements

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