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A novel method for determination of polyester end-groups by NMR spectroscopy

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Abstract

An efficient, convenient and quantitative method for characterising polyester end-groups is described. We have found that trichloroacetyl isocyanate (TAI) reacts rapidly and quantitatively with both carboxyl [C(O)OH] and hydroxyl (OH) chain ends to form derivatives that can be readily determined by ^{1}H NMR spectroscopy. The TAI capped end-groups give rise to characteristic imidic NH resonances in a normally clear region of the ^{1}H NMR spectrum [$\delta \sim 10$–11.5 for C(O)–O–C(O)–N*H*–C(O)CCl_3 from C(O)OH, $\delta \sim 8$–9 for O–C(O)–N*H*–C(O)CCl_3 from OH]. The method has been successfully applied to quantitative determination of the end-groups of a wide variety of oligomeric polyesters. It has also been applied to higher molecular weight polyesters including commercial, bottle grade, poly(ethylene terephthalate) (PET) and PET based copolyesters (e.g. PETG).

Keywords: Trichloroacetyl isocyanate; Polyester end-group determination; ^{1}H NMR spectroscopy

1. Introduction

A major thrust of our recent work has been the design and preparation of polyethylene terephthalate (PET) based block copolymers with enhanced gas barrier (O_2, CO_2) performance via reactive extrusion [1,2]. The method used has involved reaction between a low molecular weight functional polyester and poly(ethylene terephthalate). The efficiency of incorporation was found to be highly dependent on the end-groups of the polyester and potentially of the PET. The work necessitated the synthesis of a wide variety of oligoesters that differ in monomer composition, block lengths and chain ends. Consequently, a simple, quick and efficient method for quantitative determination of polyester end-groups was required. In this communication, we report that both carboxyl and hydroxyl end-groups of polyesters react rapidly and quantitatively with trichloroacetyl isocyanate (TAI) to form derivatives that can be readily determined by ^{1}H NMR spectroscopy.

Many analytical methods have been employed for the analysis of polyester end-groups. These methods include Fourier transform infra-red spectroscopy (FTIR) [3–7], matrix assisted laser desorption ionization mass spectrometry (MALDI) [7–10] and high performance liquid chromatography (HPLC) [11]. Classical titration methods [12,13] can also be applied either directly, in the case of carboxyl end-groups, or through prior derivatisation, in the case of hydroxyl end-groups.

NMR spectroscopy offers information on both the number and the type of end-groups present in a sample and can be applied directly when resonances attributable to the end-groups are sufficiently resolved from backbone signals [14–17]. Thus, ^{13}C NMR has been used to directly determine the end-groups of PET [14,18]. However, the technique requires long acquisition times and does not have general applicability.

Fox et al. [14] observed that the hydroxyl end-groups of PET underwent slow trifluoroacetylation in trifluoroacetic acid/chloroform mixtures complicating end-group determination by direct ^{1}H or ^{13}C NMR in that solvent mixture ($CF_3COOD/CDCl_3$ is a common NMR solvent for PET and similar polyesters). Kenwright et al. [19] used this knowledge to develop a method for formal derivatisation of PET

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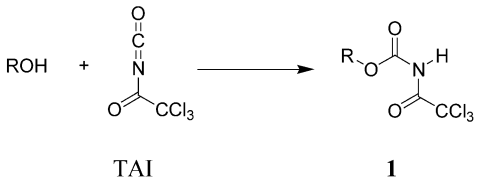


Scheme 1.

and subsequent end-group determination by ^{19}F NMR analysis. A disadvantage of this method is that the derivatisation process requires relatively long reaction times and isolation of the product prior to analysis is necessary. Ma et al. [20] have reported a ^{19}F NMR-based method for determining both hydroxyl and carboxyl end-groups in PET that involved esterification of carboxyl end-groups with hexafluoroisopropanol and trifluoroacetylation of the hydroxyl end-groups with trifluoroacetic anhydride. Two dimensional NMR methods can also be useful for resolving and providing more positive identification of signals [21].

Recently, derivatisation with a phosphitylation reagent (2-chloro-4,4,5,5-tetramethyldioxaphospholane) and ^{31}P NMR has been successfully employed to determine hydroxyl end-groups [22] and both hydroxyl and acid end-groups [23,24]. Although the experiment can be carried out in the NMR tube and no product isolation is required, the experimental protocol remains relatively complex and long acquisition times and an internal standard are required for quantitative results.

1.1. Hydroxyl end-groups

TAI has been previously used to determine hydroxyl groups in small molecules [25]. The reaction between alcohols and TAI proceeds as expected to yield a urethane derivative (**1**) as shown in Scheme 1.

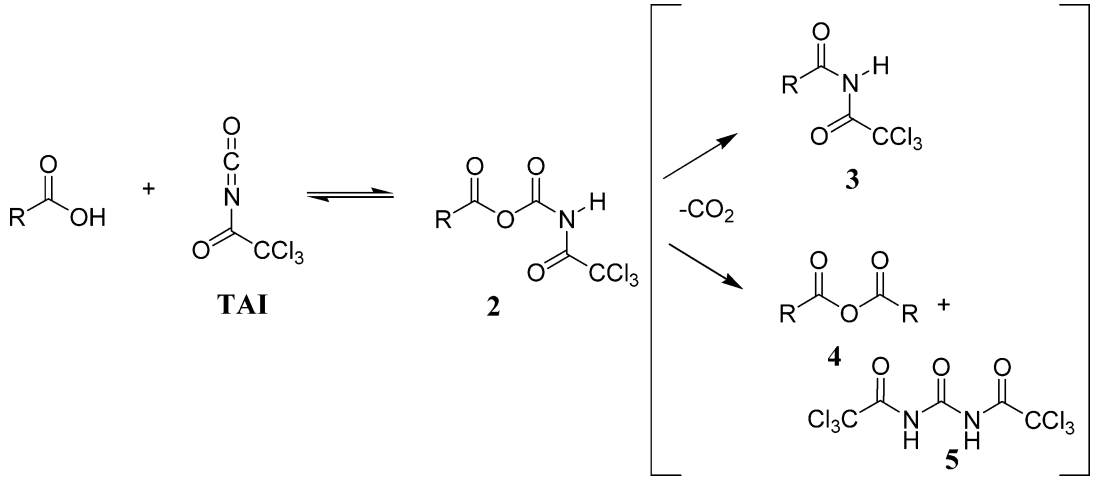
Roos et al. [26] employed TAI as a probe to determine the diastereomeric excesses of reaction products in aldol and related reactions. The in situ TAI-derivatisation of crude reaction mixtures in the NMR tube afforded the diastereomeric trichloroacetylcarbamates with distinct imidic NH signals in the generally vacant δ 8–9 region of the ^{1}H NMR spectrum. Integration of these signals provided the diastereomeric excess directly.

Whilst use of TAI is not uncommon in the derivatisation of small molecules it has received little attention with regard to polymers. However, TAI has been used for the determination of both primary and secondary hydroxy end-groups in poly(phenyl glycidyl ether) [27] and hydroxy terminated poly(vinyl ethers) [28] and poly(ethylene glycol) and related polymers [29–31].

1.2. Carboxyl end-groups

To our knowledge, TAI-derivatisation has not previously been applied to successfully derivatise carboxylic acids. The few reports for low molecular weight acids indicate that the reaction product is unstable and is in equilibrium with the starting materials and that decarboxylation occurs to provide the trichloroacetyl amide (**3**) or an anhydride (**4**) and 1,3-bis(trichloroacetyl)urea (**5**) as shown in Scheme 2 [32]. In accord with these literature reports, we also found reaction with small carboxylic acids (e.g. benzoic acid, acetic acid) was slow and the reaction products unstable.

However, the reaction products from acid end-groups of oligo- and poly-esters were sufficiently stable to allow NMR determination. Moreover, no changes in the NMR spectra were observed over 24 h. The spectra also did not depend on the excess of TAI indicating that no equilibrium with starting materials is involved or that the equilibrium lies entirely on the side of products (**2**). The proposed reaction is thus analogous to that observed with alcohols. The imidic NH signal of **2** appears in the ^{1}H NMR spectrum in the region δ 10–11.5.



Scheme 2.

Table 1
Correlation of $\bar{M}_n$ and acid numbers for a sample of Eastman 9663 using various techniques

	Titration[a]	NMR[a,b]	IV
$\bar{M}_n$ (g/mol)	–	31,000	29,500[c]
C_{COOH} (μequiv./g)	10.57±2	13.5±2	–
C_{OH} (μequiv./g)	–	50.2±5	–

[a] Titration performed by Leading Synthetics Pty. Ltd., Melbourne. Errors estimated from variance in replicate experiments.
[b] From integration of NMR spectrum (Fig. 2).
[c] Calculated for an IV 0.82 using the relationship $IV = 7.5\times10^{-4}(\bar{M}_n)^{0.68}$ [6].

2. Experimental section

The 400 MHz ^{1}H and 100.6 MHz ^{13}C NMR spectra were obtained with a Bruker Avance AV400 spectrometer. Unless indicated otherwise spectra were recorded at room temperature with $CDCl_3$ solvent and chemical shifts are reported in ppm from tetramethylsilane. The differential scanning calorimeter (DSC) used was a Mettler Toledo DSC821 equipped with a TSO801RO sample robot. Gel permeation chromatography (GPC) on oligomeric polyesters was carried out with a Waters Associates Chromatograph equipped with 3×Mixed C and 1 mixed E PLgel column (each 30 mm×7.5 mm, Polymer Laboratories). Tetrahydrofuran was used as eluent at 1 mL/min at 22 °C. The columns were calibrated with narrow polydispersity polystyrene standards (Polymer Laboratories) and number average molecular weights ($\bar{M}_n$) are reported as polystyrene equivalents. Resorcinol-O,O′-diacetic acid. (RDOA) and O,O′-bis(2-hydroxyethyl) resorcinol (HER) were obtained from Indspec Chemical Corporation, neopentyl glycol (NPG) from Perstorff, and butylhydroxyoxostannanne from Kynar. Trichloroacetyl isocyanate, isophthalic acid (IPA), ethylene glycol (EG), cylclohexanediol (CHD), cyclohexanedimethanol (CHDM) and tetramethylcyclobutanediol (TMCB) were obtained from Aldrich. The quality of each reagent was established by ^{1}H NMR and they were used without purification. The PET used was Eastman 9663;

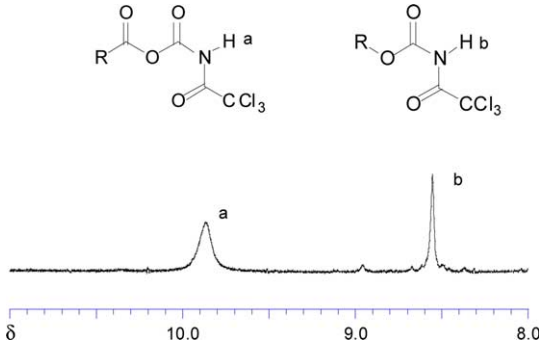


Fig. 1. Portion of ^{1}H NMR spectrum (256 scans) of TAI derivatised P(RDOA-*co*-NPG) oligomeric polyester containing both acid and hydroxyl end-groups. NMR: M_n 7213, acid number 198 μequiv./g, hydroxyl number 79 μequiv./g.

Table 2
Imidic proton ^{1}H NMR chemical shifts of various TAI derivatised polyesters

Polymer[a]	Solvent	COOH[b] δ	OH[b] δ
PET	TCE-d_2	10.26	8.53
PETG[c,d]	$CDCl_3$	10.36	8.65, 8.50
P(IPA-*co*-HER)	$CDCl_3$	11.40	8.81
P(IPA-*co*-NPG)	$CDCl_3$	11.23	8.51
P(RDOA-*co*-NPG)	$CDCl_3$	9.91	8.55
P(RDOA-*co*-EG)	$CDCl_3$	10.68	8.52
P(RDOA-*co*-CHDM)[c]	$CDCl_3$	10.30	8.08
P(RDOA-*co*-CHD)[c]	$CDCl_3$	10.58	8.60, 8.42
P(RDOA-*co*-HER)	$CDCl_3$	10.78	8.63
P(RDOA-*co*-TMCB)[c]	$CDCl_3$	10.87	8.44, 8.42

[a] Monomer abbreviations are given in the Experimental Section.
[b] Precise chemical shifts show a small dependence on the concentration of TAI.
[c] CHDM is present as a mixture of *cis* and *trans* isomers.
[d] PETG is a terephthalate copolyester containing two glycols (CHDM ~40% and EG ~60%).

a PET homopolymer with an intrinsic viscosity of 0.82. PETG used was Eastar 6763; a PET/CHDM copolyester with an intrinsic viscosity of 0.70. Two samples of P(IPA-*co*-NPG) were obtained from UCB: Crylcoat 2988 (Current designation Crylcoat 4488-0) had $\bar{M}_n$ (polystyrene equivalents) 6352, $\bar{M}_w$ 14,020, $\bar{M}_w/M_n$ 2.21 (acid value from data sheet of 30 mg KOH/g), Crylcoat 690 (Current designation Crylcoat 4890-0) had M_n (polystyrene equivalents) 7057, $\bar{M}_w$ 21,302, $\bar{M}_w/\bar{M}_n$ 3.02 (hydroxyl value from data sheet of 30 mg KOH/g).

2.1. Oligoester synthesis

The low molecular weight polyesters listed in Table 2 were prepared using the following procedure exemplified for P(RDOA-*co*-NPG). The synthesis and characterization of other polyesters will be reported in a forthcoming paper.

A 1 L flange flask equipped with a mechanical stirrer and a Dean-Stark water trap was charged with RDOA (495 g, 2.2 mol), NPG (229 g, 2.2 mol) and catalyst (butylhydroxyoxostannane) (45 mg, 0.01 mol%). The contents were heated (ca. 180 °C) for 4 h and water (78 mL) was collected. The Dean-Stark apparatus was then removed, a vacuum line attached and heating was continued for 2 h under vacuum (40 mm Hg). An electric diaphragm pump was then attached and heating was continued for a further 17 h under vacuum (2 mm Hg). The reaction mixture was then poured onto a polished metal sheet and allowed to cool. ^{1}H NMR: δ_H ($CDCl_3$), 7.16 (1H, m, *arom*), 6.49 (3H, m, *arom*), 4.60 (4H, s, OCH_2CO_2), 3.91 (4H, s, $CO_2CH_2C(CH_3)_2$), 0.89 (6H, s, CH_3). $\bar{M}_n$ (polystyrene equivalents) 9208, $\bar{M}_w$

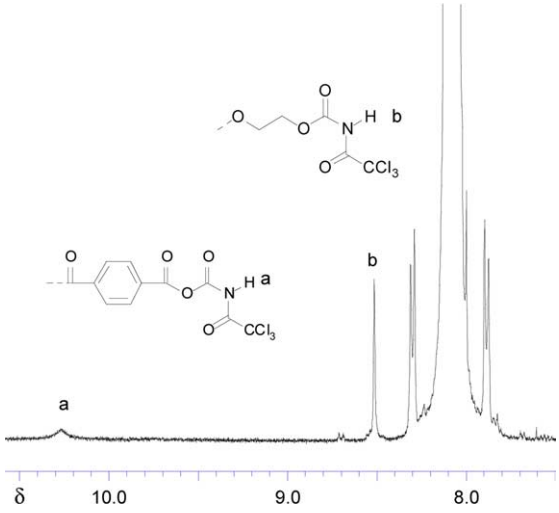


Fig. 2. Portion of ^{1}H NMR spectrum (1024 scans) of TAI derivatised PET (Eastman 9663) containing both acid and hydroxyl end-groups.

27,576, $\bar{M}_w/\bar{M}_n$ 2.99. NMR: $\bar{M}_n$ 7213, acid number 198 μequiv./g, hydroxyl number 79 μequiv./g.

2.2. TAI derivitization procedure and ^{1}H NMR analysis for oligoesters

The following procedure is typical for the oligoesters ($\bar{M}_n$ 2000–10,000).

A sample of P(RDOA-*co*-NPG) (15 mg) was dissolved in $CDCl_3$ (0.5 mL), after dissolution the mixture was transferred to an NMR tube and an excess of trichloroacetyl isocyanate (4 μL, 6.3 mg, 3.36×10^{-2} mmol) was added and the ^{1}H NMR spectrum recorded for 32 scans. ^{1}H NMR: δ_H ($CDCl_3$) 10.50 (1H, s, end-group N*H*COOCOR), 8.62 (1H, s, end-group N*H*COOR), 7.16 (1H, m, backbone *arom*), 6.49 (3H, m, backbone *arom*), 4.60 (4H, s, backbone *arom*-OCH_2CO$_2$), 3.91 (4H, s, backbone CO$_2$CH_2C(CH$_3$)$_2$), 0.89 (6H, s, backbone CH_3). A portion of the spectrum is shown in Fig. 1.

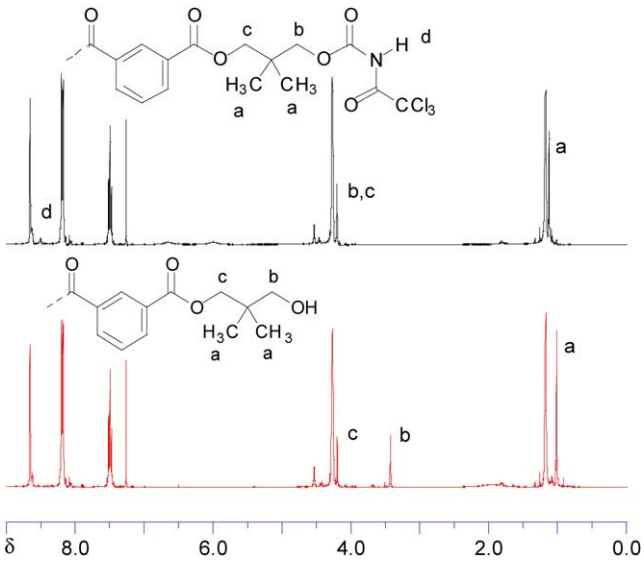


Fig. 3. Comparison of the ^{1}H NMR spectrum (32 scans) of OH end capped IPA-NPG oligomer, Crylcoat 690 (lower spectrum) with that of its TAI derivative (upper spectrum).

Additional scans were used to provide better signal to noise for the higher molecular weight samples or when higher precision was required. A summary of chemical shifts for the TAI derivatised end groups is provided in Table 2.

2.3. TAI derivatisation procedure and ^{1}H NMR analysis for poly(ethylene terephthalate)

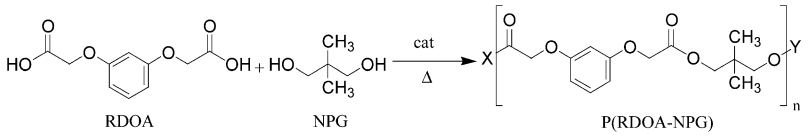
A sample of PET (15 mg) was first rendered amorphous by rapid thermal quenching. The sample was placed in an open aluminium sample pan and heated to 270 °C at 10 °/min in a DSC furnace then removed from the furnace by the sample robot and allowed to cool to ambient temperature. The entire operation was carried out under nitrogen. The amorphous material was then powdered and dissolved in tetrachloroethane-1,2-d_2 ($CDCl_2$)$_2$ (0.5 mL) at 140 °C. After dissolution the mixture was transferred to an NMR tube, an excess of trichloroacetyl isocyanate (4 μL, 6.3 mg, 3.36×10^{-2} mmol) was added and the ^{1}H NMR spectrum recorded for 1024 scans. ^{1}H NMR: δ_H (($CDCl_2$)$_2$, 400 MHz)), 10.26 (1H, s, end-group N*H*COOCOR), 8.53 (1H, s, end-group N*H*COOR), 8.11 (4H, s, backbone *arom H*), 4.68 (4H, s, backbone OCH_2). A typical NMR spectrum is shown in Fig. 2.

3. Results

The analytical procedure involves dissolving a sample of oligoester (typically 5–10 mg) in a suitable aprotic solvent such as $CDCl_3$ in an NMR tube, adding a drop of TAI and recording the ^{1}H NMR spectrum. Reaction appears to be essentially instantaneous and is complete within the time taken to place the sample in the spectrometer. Any excess TAI, being aprotic, causes no additional signals in the spectrum. While it is desirable that samples and solvent are dry, reaction with extraneous water yields carbon dioxide and trichloroacetamide, neither of which give signals that interfere in the region of interest, ie. δ 8–11.5. Trichloroacetamide exhibits two broad singlets that appear at δ 6.0 and 6.7 (see, for example, Fig. 3). It is important to store TAI under anhydrous conditions. It has been observed that use of aged TAI, stored under less appropriate conditions, can give rise to unidentified by-products that provide extraneous peaks in the spectrum.

The method has been applied to a number of in-house synthesised oligoesters (Table 2, Scheme 3).

The spectra of oligoesters designed stoichiometrically to be wholly acid end capped (i.e., where an excess of diacid monomer was used in the synthesis) exhibit a single imidic hydrogen resonance at approximately δ 10.5. Similarly, the



Scheme 3. For acid end capped X=OH, Y=RDOA, hydroxyl end capped X=NPG, Y=H.

spectra of oligoesters synthesised with the design of being alcohol end capped (i.e., excess diol used in the synthesis) show a single imidic hydrogen resonance at approximately δ 8.5. Where more nearly equimolar quantities of diacid and diol monomers were used in the synthesis both peaks were observed in the spectrum. An example is provided in Fig. 1. The methodology thus allows for both the quantitative and qualitative analysis of both hydroxyl and carboxyl polyester end-groups by ^{1}H NMR spectroscopy.

The method has also been applied to commercial polyesters such as PET (Fig. 2), PETG (a PET based copolyester also containing 1,4-cyclohexanedimethanol units) and Crylcoat [low molecular weight P(IPA-*co*-NPG)]. PETG and Crylcoat are amorphous and freely soluble in $CDCl_3$ at room temperature. PET is insoluble in $CDCl_3$. To enable dissolution, the PET sample was first rendered amorphous, by rapid thermal quenching, and then dissolved in tetrachloroethane-d_2 at 140 °C. The sample was cooled to ambient temperature before addition of TAI (no precipitation of PET occurred). Application of the method to Eastman 9663, a PET homopolymer, and analysis of the ^{1}H NMR spectra indicated the carboxyl and hydroxyl end-groups were in a 21:79 ratio. The peaks attributed to the derivatiszed carboxyl (a) and hydroxyl (b) end-groups are discrete from the terephthalate aromatic signal at δ 8.1. Due to the low concentration of end-groups in PET samples 1024 scans were required for adequate signal to noise. Integration of the end group signals vs. the signals attributable to the backbone aromatic hydrogens enabled calculation of the concentration of the hydroxyl (C_{OH}) and carboxyl end-groups (C_{COOH}). The value of C_{COOH} was in accord with a value determined by titration. The number average molecular weight calculated from the end-group concentration (assuming polymer only has hydroxyl and carboxyl end-groups and neglecting the presence of cyclic oligomers) was 31,350 which is consistent with a value calculated from the intrinsic viscosity of 0.82 (Table 1).

Even though TAI has been used previously for the quantitative determination of hydroxyl moieties in small molecules and hydroxyl terminated polymers, it remained necessary to determine that the reagent reacted quantitatively with both acid and hydroxyl end-groups in polymer samples.

It can be seen from Fig. 3 that there are a number of changes in the spectra which clearly show that the reagent has reacted quantitatively with all of the OH end-groups. The signal (a) at δ 1.0 is attributable to the geminal methyls of the -IPA-NPG-H end-group. Upon reaction with TAI this signal disappears completely and a new signal appears at δ 1.1 close to that of the geminal methyls of the -IPA-NPG-IPA- repeat unit. The signal (b) at δ 3.4, due to the terminal methylene, of the -IPA-NPG-H end-group shifts to δ 4.2. The new signal (d) at δ 8.5 is attributable to the imidic hydrogen of the derivatised end-group and the integral of 0.117H is consistent with a quantitative reaction when compared to for example signal (b) where the methylene CH_2 has an integral of 0.223H. These values are within experimental error of $\pm$5%.

Derivatisation of acid end capped IPA-NPG (Crylcoat 2988) with TAI yields a singlet in the NMR spectrum at $\sim\delta$ 11.65 (b). No other diagnostic changes are observed in the spectrum upon addition of the reagent (Fig. 4).

A portion of the ^{1}H NMR spectrum of an acid end capped IPA-NPG oligomer (Crylcoat 2988) recorded in $CF_3COOD/CDCl_3$ is shown in Fig. 5. In this solvent system the end-groups attributable to the H(a) of the NPG-IPA-H

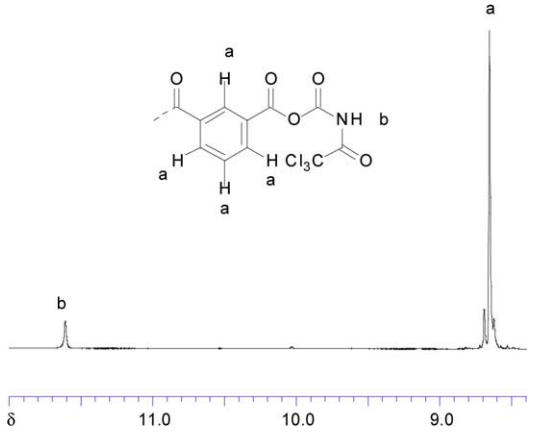


Fig. 4. Portion of ^{1}H NMR spectrum (32 scans) of TAI derivatised acid end capped IPA-NPG (Crylcoat 2988).

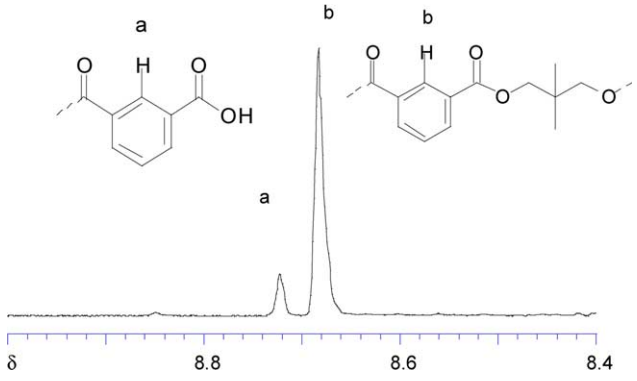


Fig. 5. Portion of ^{1}H NMR spectrum (32 scans) of acid end capped IPA-NPG (Crylcoat 2988) recorded in $CF_3COOD/CDCl_3$.

Table 3
Comparison between various NMR techniques for end-group quantification

NMR technique	Peak ratio	End-group ratio	Acid No μequiv./g
^{1}H NMR TAI[a]	1:8.4±0.3	1:7.4	577
^{13}C NMR Cr(acac)$_3$[b]	1:16.4±1.6	1:7.7	555
^{1}H NMR direct[c]	1:7.6±0.3	1:7.6	562

[a] See Fig. 4.
[b] ^{13}C NMR with Cr(acac)$_3$ relaxtion agent (3%). Carboxy end-group carbonyl appears at δ 169.3 while isophthalate repeat unit carbonyl appears at δ 165.1 in ^{13}C NMR ($CDCl_3$).
[c] ^{1}H NMR ($CF_3COOD/CDCl_3$ 1:1), see Fig. 5.

end-group appear distinct from the H(b) of NPG-IPA-NPG repeat unit and can be integrated directly [2]. The result correlates well with data obtained using the present method for the same sample derivatised with TAI (Fig. 4 and Table 3).

Quantitative ^{13}C NMR determination of the isophthalate carbonyl resonances for a sample containing added Cr(acac)$_3$ (to reduce relaxation times [33]) also provides a consistent value for the end-group ratio within experimental error (Fig. 6 and Table 3). It can be seen from this spectrum (Fig. 6) that even recording for 10,240 scans the signal to noise is quite poor rendering this technique less practical than ^{1}H NMR based methods.

4. Conclusions

Trichloroacetyl isocyanate reacts rapidly and quantitatively with both acid and hydroxyl chain ends to form derivatives that can be readily determined by ^{1}H NMR spectroscopy thus providing a convenient means of characterising polyester end-groups. We anticipate the method will have more general application in polymer end-group determination. Recently, we have applied the method for determination of end-groups (amino, hydroxyl) of polymers formed by living radical polymerization [34–36] and polyethylene–poly(ethylene glycol) block copolymers [37].

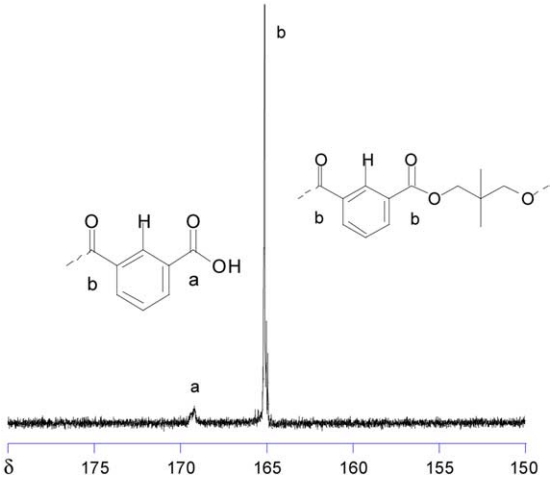


Fig. 6. Portion of ^{13}C NMR spectrum (10240 scans) of acid end capped IPA-NPG (Crylcoat 2988) recorded in $CDCl_3$ with 3% Cr(acac)$_3$.

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