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Polymer 47 (2006) 1899–1911
polymer
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A simple method for determining protic end-groups of synthetic polymers by ^{1}H NMR spectroscopy

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Received 9 August 2005; received in revised form 6 January 2006; accepted 13 January 2006
Available online 7 February 2006

Abstract

A simple method for the determination of protic end-groups (–XH) in synthetic polymers involves in situ derivatization with trichloroacetyl isocyanate (TAI) in an NMR tube and observation of the imidic hydrogens of the derivatized products [–X–C(O)–N*H*–COCCl$_3$] by ^{1}H NMR spectroscopy. In this paper, we report that the method is effective for the quantitative determination of hydroxy, primary amino and carboxy end-groups of polymers with $\bar{M}_n < 50,000$ g mol^{-1}. It may also be applied to detect chain ends in higher molecular weight polymers. The signals for the imidic (and, in the case of amines, amidic) hydrogens appear in a region (δ 7.5–11) that is clear of other signals in the case of most aliphatic polymers and many aromatic polymers such as polystyrene and poly(ethylene terephthalate). The method has been applied in the characterization of polymers formed by conventional and living radical polymerization (RAFT, ATRP, NMP), to end functional poly(ethylene oxide) and to polyethylene-*block*-poly(ethylene oxide). The method appears less effective in the case of sulfanyl end-groups. The chemical shift of the imidic hydrogen shows remarkable sensitivity to the microenvironment of chain end. Thus, the imidic hydrogens of TAI derivatized polyethylene-*block*-poly(ethylene oxide) [PE-(EO)$_m$OC(O)N*H*C(O)CCl$_3$] are at least partially resolved for $m = 0$, 1, 2, 3 and $\geqq 4$ in the 400 MHz ^{1}H NMR spectrum. It is also sensitive to the chain end tacticity of, for example, amino-end-functional polystyrenes and thus to the relative configuration of groups removed from the chain-end by two or more monomer units. TAI derivatization also facilitates analysis of amine functional polymers by gel permeation chromatography (GPC) which is often rendered difficult by specific interactions between the amine group and the GPC column packing.

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

1. Introduction

In order to fully characterize polymers and their reactions, it is important to have a precise knowledge of the polymer end-groups. The various methods described in the literature include techniques based on the use of classical titration [1,2], mass spectrometry (MALDI-TOF [3–5], ESI [6]), various chromatographic techniques [7,8], FTIR [9,10], NMR [11–16] and UV [17]. All of the methods described to date suffer from some limitations with respect to sensitivity and/or versatility.

NMR is one of the most used methods for polymer end-group determination. In ^{1}H NMR spectra, the exchangeable protons of functional groups such as hydroxy, amino and carboxy often produce signals that are broad and which integrate poorly. Even in polymers of modest molecular weight, there is an additional problem of the end-group signals being easily overwhelmed. Consequently, they can be difficult to resolve when they appear in close proximity of the much larger signals for protons associated with the polymer repeat units. Where the groups (X) are attached to primary or secondary carbon (i.e. –CH$_2$–X, $\rangle$CH–X), the presence of the protons adjacent to the functionality may permit identification and quantification. However, the same limitations with respect to the need for sufficient resolution from signals due to the polymer repeat unit apply, and when the functional groups are aryl or tertiary (i.e. ≡C–X, Ar–X) this option is not available.

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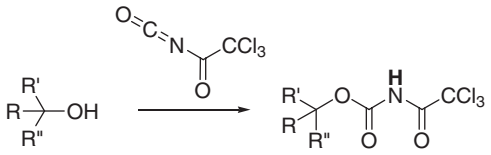
0032-3861/$ - see front matter © 2006 Published by Elsevier Ltd.
doi:10.1016/j.polymer.2006.01.050



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Scheme 1.

The use of selective labelling [15,16], special pulse sequences [14] or multidimensional NMR may alleviate the requirement that signals appear in a clear region of the NMR spectrum in some cases, though precise quantitation remains problematical.

In small molecule chemistry, derivatization strategies are often employed to simplify the characterization of functional groups and to overcome problems with direct NMR analysis. A simple technique for determining alcohols and glycols was devised by Goodlett et al. [18] who utilized trichloroacetyl isocyanate (TAI) as an in situ derivatization reagent. The derivatization was found to be both rapid and quantitative (Scheme 1). Their work [18] focused on observing the change in chemical shift of α-carbamate hydrogens for compounds **1**, where R′ and/or R″ = H. Subsequent work by other groups observed and/or quantified TAI-derivatized alcohols [19–21], phenols [19], amines [19,20] and hydroxy-acids [22] by ^{13}C and ^{1}H NMR. In these studies, while the presence of imidic hydrogen signals was sometimes noted [19,20,23], few used those signals for quantitation [21].

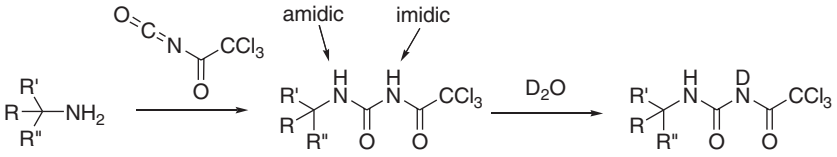
Buděšínský et al. [20] examined the reaction of primary, secondary and tertiary amines and amino alcohols with TAI (Scheme 2) and noted that while the chemical shift and appearance of the imidic hydrogen resonance (–NH–C(O)–N*H*–$COCCl_3$) of the derivative **2** was concentration dependent, the amidic hydrogen resonance (–N*H*–C(O)–NH–$COCCl_3$) showed no such dependence. The more acidic imidic hydrogen of **2** was also found to undergo H–D exchange upon the addition of deuterium oxide (this can be an aid in distinguishing the fickle imidic hydrogen from the constant amidic hydrogen, amongst complex polymer end-group signals—see later discussion).

There are some previous reports of the use of derivatization strategies in analyzing polymer end-groups by NMR [1,13,24–27]. Most recently, derivatization with reagents containing fluorine or phosphorus has been recommended. These methods have the advantage that most polymers do not themselves contain fluorine or phosphorus so the issue of resolving end-group signals from polymer backbone signals does not arise. Efficient derivatization/^{19}F NMR strategies applicable to hydroxy (esterification with trifluoroacetic acid/anhydride) [12,25,28], carboxy (esterification with trifluoroethanol or hexafluoroisopropanol/dicyclohexylcarbodimide) [12,29] and amine chain ends (3,5-bis(trifluoromethyl)benzaldehyde, see Scheme 3) [13] have been described. However, the methods may require relatively long reaction times. Moreover, different reagents are required for different end-groups. The ^{19}F NMR analysis also requires precise addition of a suitable internal standard for quantitative analysis.

A strategy for determination of hydroxy and carboxy end-groups involving derivatization with a phosphorus based reagent (2-chloro-4,4,5,5-tetramethyldioxaphospholane, see Scheme 4) with subsequent ^{31}P NMR analysis has been devised [30–32]. The method does not require product isolation and more recent reports indicate that the reaction is complete within 0.5 h at room temperature [30].

TAI derivatization and ^{1}H NMR has also previously been applied to polymer end-group analysis [1,24,26,27,33]. Ronda et al. [27] characterized the TAI derivatives of hydroxy end-functional polymers based on phenyl glycidyl esters. Analysis of the signals for the α-carbamate hydrogens allowed the proportion of primary and secondary hydroxy end-groups to be estimated. The signals for the imidic hydrogens (–O–C(O)–N*H*–$COCCl_3$) of the derivatized primary and secondary hydroxy end-groups were not sufficiently resolved to allow precise quantitation. Vinyl ethers prepared by living cationic polymerization initiated by 1-trimethylsiloxy-4-iodo-3-oxabutane in the presence of tetrabutylammonium triflate, yields a polymer with a trimethylsilyloxy end-group [26]. The hydroxy-terminated poly(vinyl ether)s formed following end-group hydrolysis were characterized by ^{1}H NMR of the TAI derivative. Commercial poly(ethylene oxide)s (PEO) [34], their monomethyl ethers [24] and poly(ethylene oxide-*co*-propylene oxide)s [34] have been investigated using TAI end-group analysis. Fallais et al. [1] studied the preparation of end functional polystyrenes by anionic polymerization. Primary amino and hydroxy end-groups were determined with the aid of TAI derivatization. In each of these studies, quantitation relied on determination of signals for protons adjacent to the end-group. In our laboratories, we [33] have recently demonstrated that the TAI derivatization method can be applied to quantitatively determine both the carboxy and hydroxy end-groups of various polyesters including, high molecular weight ($\bar{M}_n \sim 30,000$ g mol^{-1}), commercial polyethylene terephthalate (PET).

In this paper we show that the TAI derivatization method is a reliable method for the determination of a wide range of protic (hydroxy, carboxy, amino) end-groups in synthetic



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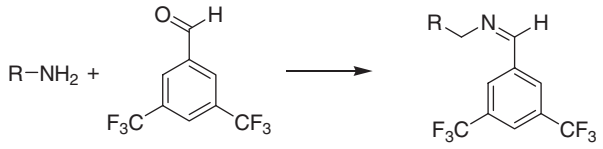
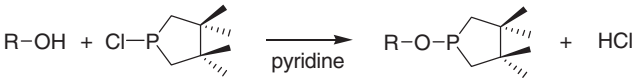
Scheme 2.



Scheme 3.



Scheme 4.

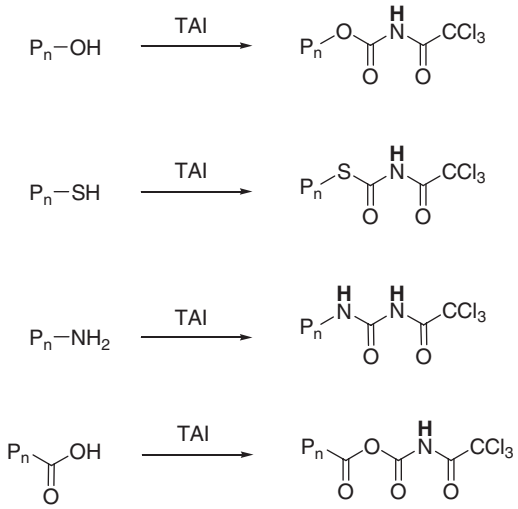
polymers. The proposed products from the reaction of various polymer end-groups with TAI are shown in Scheme 5.

The method has been applied in our ongoing work on synthesis of end-functional polymers by various living or controlled radical polymerization processes [35–37] including reversible addition-fragmentation chain transfer (RAFT) [38,39], atom transfer radical polymerization (ATRP) [40–42] and nitroxide-mediated polymerization (NMP) [43]. We also use the method to characterize polymers and block copolymers based on poly(ethylene oxide) PEO which have potential application as dispersants/intercalants/dispersants in polymer nanocomposites [44,45].

2. Experimental

2.1. NMR

The 400 MHz proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained with a Bruker Av400 spectrometer at 298 K. Thirty-two thousand data points were collected for the FID, over a sweep width of 6000 Hz (0.18 Hz/pt) and summed over 32 or 128 scans depending on signal-to-noise requirements. A relaxation delay of 1 s and an acquisition time of 2.73 s were used resulting in a total interpulse time of 3.73 s. The Pulse angle was 30°. Exponential



Scheme 5.

multiplication with a line broadening of 0.1 Hz was applied to the data before Fourier transformation over 64K data points. Spectra were recorded for samples dissolved in deuterochloroform ($CDCl_3$) and chemical shifts are reported as parts per million from external tetramethylsilane unless stated otherwise.

2.2. Two dimensional NMR

The 500.13 MHz ^{1}H NMR spectra were recorded in $CDCl_3$ (referenced to δ_H 7.26) at 25 °C/298 K using a Bruker DRX500 spectrometer. The COSY experiment used the standard Bruker library sequence (cosygpqf45) with the following parameters: 4096 FID data points, 5000 Hz sweep width, 0.41 s acquisition time, 1.0 s relaxation delay, 512 experiments. In processing the FID was multiplied by an unshifted sine function in both dimensions and Fourier transformed over 2048×1024 points. A portion of the COSY spectra of TAI derivatized α-(aminomethyl)polystyrene (**7**) is shown in Fig. 3.

The HMBC experiment used the standard Bruker library sequence (hmbcgplpndqf) with the following parameters: 4098 FID data points, 5000 Hz sweep width, 0.58 s acquisition time, 0.7 s relaxation delay, 512 experiments, 3.44 ms low-pass *J*-filter ($^1J_{CH} = 145$ Hz), 62.5 ms delay (for evolution of long-range coupling ($^nJ_{CH} = 8$ Hz)). In processing the FID was multiplied by a π/2-shifted sine function in both dimensions and Fourier transformed over 2098×1024 points.

2.3. Gel permeation chromatography

Gel permeation chromatography (GPC) was performed on a Waters Associates liquid chromatograph equipped with differential refractometer and 3×mixed C and 1 mixed E PLgel column (each 7.5 mm×30 mm) from Polymer Laboratories. Tetrahydrofuran (flow rate of 1.0 mL/min) was used as eluent at 22±2 °C. The columns were calibrated with narrow polydispersity polystyrene standards (Polymer Laboratories). A third-order polynomial was used to fit the $\log_{10}M$ vs time calibration curve, which appeared to be linear across the molecular weight range 2×10^2–2×10^6.

2.4. Materials

Trichloroacetyl isocyanate (96%) and model compounds were obtained from Aldrich and were used without further purification. Polyethylene glycol (PEO), α-methoxy-poly(-ethylene oxide-*co*-propylene oxide)-propan-2-amine (PEO-*co*-PPO, tradename JEFFAMINE® M-2070) were obtained from Aldrich and Huntsman, respectively. The synthesis of end-functional polymers (**6**) [36,37,46], (**9**) [36,46], (**13**) [35], and (**20**) [36] is described elsewhere.

2.4.1. Polystyrene (*22*)

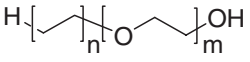
4-Hydroxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl (0.64 g), azobis(4-cyanovaleric acid) (1.02 g) and styrene (40 mL) were transferred to a flask and the solution purged with argon for 30 min then heated at 135 °C under argon for 45 min.

A sample (2 mL) was withdrawn, cooled, and purified by precipitation into methanol. The gravimetric monomer conversion was 40%, GPC analysis showed $\bar{M}_n = 2824$ g mol^{-1}, $\bar{M}_w/\bar{M}_n = 1.40$.

2.4.2. Polystyrene (*24*)

Water (1040 g) was purged with nitrogen for 20 min and styrene (40 mL) were transferred to a flask and azobis(4-cyanovaleric acid) (2.16 g in 64 g water), sodium dodecyl sulphate (12 g in 120 g water) and sodium bicarbonate (2 g in 40 g water) were added and the mixture purged for a further 30 min. The reaction mixture was then heated to 80 °C with stirring (270 rpm) when styrene (320 g) and a solution of 2-mercaptoethanol (10.8 mL of 10% (v/v) in water) was added. A further 16.2 mL of degassed mercaptoethanol solution was added at a rate of 0.09 mL/min (~180 min) by syringe pump. The reaction mixture was maintained at 80 °C for a further 30 min then allowed to cool. The gravimetric monomer conversion was 94.8%, GPC analysis showed a bimodal molecular weight distribution $\bar{M}_n = 10,300$ g mol^{-1}, $\bar{M}_w/\bar{M}_n = 6.85$.

2.4.3. Polyethylene-block-poly(ethylene oxide) (*3*)



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The polyethylene-*block*-poly(ethylene oxide) (PE-*block*-PEO) **3a–d** were obtained from Aldrich Chemical Co. The low molecular weight PE-*block*-PEO (**3e**), was supplied by Ciba Specialty Chemicals. The compositions and molecular weights of the PE-*block*-PEO **3a–d** are summarized in Table 1.

2.5. Derivatization and ^{1}H NMR analysis for model compounds

The following procedure is typical.

A sample of 1-phenylethylamine (10 mg, 82.5 μmol) was dissolved in $CDCl_3$ (0.5 mL), after dissolution the mixture was transferred to an NMR tube and an excess of trichloroacetyl isocyanate (30 μL, 18.9 mg, 0.10 mmol) was added and the ^{1}H NMR spectrum recorded. ^{1}H NMR ($CDCl_3$): δ 1.57 (d, J = 6.94 Hz, 3H, PhCHCH_3), 5.06 (p, J = 6.94 Hz, 1H, PhCH), 7.35 (m, 5H, Ar), 8.26 (d, J = 6.94 Hz, 1H), 8.96 (s, 1H, CONHCO).

An excess of D_2O (10 μL, 11.1 mg, 0.55 mmol) was added to the TAI derivatized 1-phenylethylamine prepared above in the NMR tube and the ^{1}H NMR spectrum was recorded. ^{1}H NMR ($CDCl_3$): δ 1.57 (d, J = 6.94 Hz, 3H, PhCHCH_3), 4.82 (br s, 1H, HDO), 5.05 (p, J = 6.94 Hz, 1H, PhCH), 7.35 (m, 5H, Ar), 8.23 (d, J = 6.94 Hz, 1H, CONHCO).

Table 1
Average composition of PE-*block*-PEO non-ionic surfactants (**3**)

Additive	$\bar{M}_n$	Av. n[a,b]	Av. m[a,b]	Av. n[b,c] (NMR^{TAI})	Av. m[b,c] (NMR^{TAI})
3a PE-*block*-PEO	1400	25	16	24.9	18.6
3b PE-*block*-PEO	920	15	10	22.8	15.9
3c PE-*block*-PEO	875	25	4	24.3	5.2
3d PE-*block*-PEO	575	16.4	2.6	20.9	3.4
3e PE-*block*-PEO	406	9	2	10.6	2.1

[a] Nominal number average molecular weight ($\bar{M}_n$) and composition based on information provided by supplier.
[b] Average degree of polymerization of PE (n) or PEO block (m).
[c] Determined by integration of NMR spectrum of TAI derivative (see text).

2.6. Derivatization and ^{1}H NMR analysis for end-functional polymers

The following procedures is typical.

A sample of ω-aminopolystyrene (**13**) (40 mg, $\bar{M}_n = 1230$ g mol^{-1}, $\bar{M}_w/\bar{M}_n = 1.10 = 1.10$) was dissolved in $CDCl_3$ (0.5 mL), after dissolution the mixture was transferred to an NMR tube and an excess of trichloroacetyl isocyanate (10 μL, 6.3 mg, 33.4 μmol) was added and the ^{1}H NMR spectrum of (**14**) was recorded. ^{1}H NMR ($CDCl_3$): δ 1.25–2.50 (br m, backbone CH, CH_2), 4.52 (m, 1H, –CHNHCO–), 6.25–7.40 (br m, ArH), 7.73 + 7.91 (br d, 1H, –CHNHC(O)–), 8.26 (tr, 1H, –C(O)NHC(O)–).

An excess of D_2O (10 μL, 11.1 mg, 0.55 mmol) was added to the TAI derivatized ω-aminopolystyrene (**14**) prepared above in the NMR tube and the ^{1}H NMR spectrum of (**15**) was recorded. ^{1}H NMR ($CDCl_3$): δ 1.25–2.50 (br m, backbone CH, CH_2), 4.52 (m, 1H, CH), 4.75 (br s, 1H, HDO), 6.25–7.40 (br m, ArH), 7.73 + 7.91 (br d, 1H, CHNHCO).

3. Results and discussion

3.1. Derivatization procedure

The analytical procedure is the same as that we reported previously [33] and involves dissolving a sample of the polymer (typically 5–10 mg) in a suitable aprotic solvent such as $CDCl_3$ or C_6D_6 directly in an NMR tube, adding a drop (10 μL) of TAI and recording the ^{1}H NMR spectrum. The reaction is essentially instantaneous being complete within the ca. 10 min taken to place the sample in the spectrometer. Excess TAI, being aprotic, causes no additional signals in the spectrum. While it is desirable that the 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, i.e. δ 8–11.5. The main by-product, trichloroacetamide, exhibits two broad singlets that appear at ca. δ 6.0 and 6.7. 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 spectra.

3.2. TAI derivatization of model compounds

In order to establish the ^{1}H NMR chemical shifts of the TAI end-group, the NMR spectra of a series of model compounds containing amino, carboxy, hydroxy and sulfanyl groups were examined. The chemical shifts of the imidic, and amidic in the

Table 2
Chemical shifts for imidic, amidic (δ N*H*) and adjacent hydrogens (δ CH_α) for trichloroacetyl isocyanate-derivatized model compounds with amino, sulfanyl or hydroxy end-groups

Model compound	Functionality	δ CH_α[a]	δ N*H*[a]	
			Amidic	Imidic[b]
1-Phenylethylamine	–CH(Ph)NH_2	5.06 (p)	8.26 (d)	8.96 (s)
2-Phenylethylamine	–CH_2NH_2	3.60 (q)	7.91 (br tr)	8.96 (s)
n-Butylamine	–CH_2NH_2	3.33 (q)	7.90 (tr)	9.41 (s)
Benzylmercaptan	CH_2(Ph)SH	4.22 (s)	–	9.14 (s)
n-Butylmercaptan	–CH_2SH	2.98 (t)	–	8.92 (s)
n-Butylmercaptan	–CH_2SH	2.63 (t)	–	8.78 (s)[c]
2-Mercaptoethanol[d]	–CH_2SH	4.49 (t)	–	8.99 (s)
2-Mercaptoethanol[e]	–CH_2OH	4.39 (t)	–	8.46 (s)
2-Mercaptoethanol[d]	–CH_2OH	3.32 (t)	–	8.42 (s)
Ethanol	–CH_2OH	4.32 (q)	–	8.40 (s)
2-Methoxyethanol	–CH_2OH	4.36 (t)	–	8.89 (s)

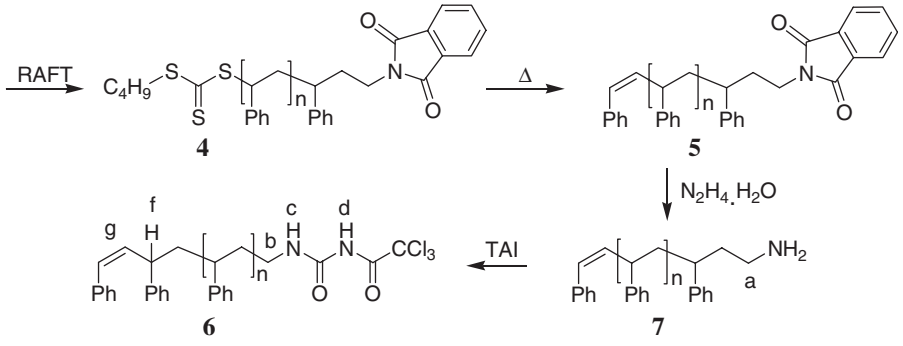
[a] Solvent $CDCl_3$.
[b] Precise chemical shifts show some concentration dependence ($\pm$0.05 ppm).
[c] Solvent C_6D_6.
[d] Both –SH and –OH groups derivatized.
[e] –OH only derivatized.

case of amines, (δ NH) and α-hydrogens (δ H_α) are reported in Table 2. In accordance with the literature report [20], the imidic hydrogens were found to be exchangeable such that the corresponding signals vanish in addition of D_2O. For the case of amines, signals attributable to the amidic hydrogens did not exchange and remained in addition of D_2O. Discussion of specific features of the spectra of the model compounds appears in the appropriate section below.

3.3. TAI derivatization of amino end-functional polymers

We have recently described the synthesis of amine end-functional polystyrenes by hydrazinolysis of phthalimido end-functional polystyrenes synthesized by ATRP [35] and RAFT [36]. RAFT-synthesized α-(phthalimidomethyl)polystyrenes (**4**) were converted to the α-(aminomethyl)polystyrenes (**7** or **9**) as shown in Scheme 6 [36,37] or Scheme 7 [36,46], respectively. Full details of the syntheses are reported elsewhere [36,37,46]. The NMR spectra for a series of polystyrenes prepared according to Scheme 6 with molecular weights in the range 1320–121,000 g mol^{-1}, as determined by the initial concentration of RAFT agent employed in the RAFT polymerization step, are shown in Fig. 1.

An expansion of the ^{1}H NMR spectrum showing signals attributed to the end-group of a low molecular weight α-(aminomethyl)polystyrene (**9**) ($\bar{M}_n^{GPC} = 1280$ g mol^{-1}), its TAI derivative (**10**), and the same material following addition of D_2O (**11**) are shown in Fig. 2. The signals for the amidic hydrogen (c) and imidic hydrogen (d) for the derivative **10** appear as 'doublets' reflecting the fact that the chain end is a mixture of diastereomers. The signal (e) is extraneous and is only observed when a large excess of TAI is used. This signal (e) disappears in addition of D_2O, while the signal for imidic hydrogen (d) for derivative (**10**) at δ 8.21 remains indicating that the exchange to form (**11**) is slow for this example. The signal for the methylene α- to the end group shifted from δ 2.3



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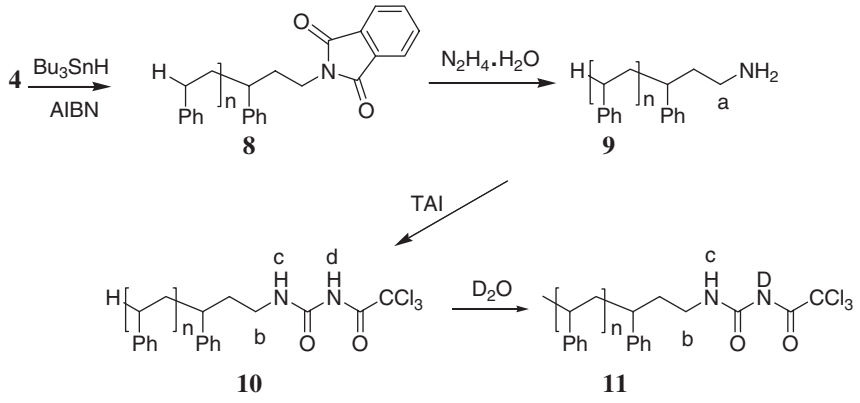


Scheme 7.

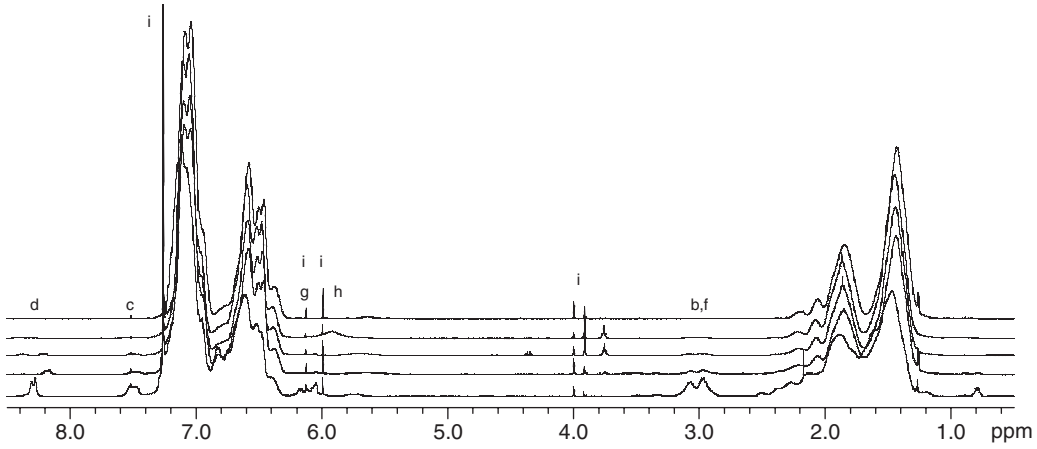


Fig. 1. ^{1}H NMR spectra of TAI derivatives of α-(aminomethyl)polystyrene (**10**). The samples correspond to those whose properties are given in Table 3 and in entries 3–7 of Table 4. Upper spectrum is for sample of highest molecular weight. Signal assignments are: (b) –C*H*$_2$–NH–C(O)– (**10**), (c) amidic –NH signal –CH$_2$–N*H*–C(O)– (**10**), (d) imidic –NH signal –CH$_2$–NH–C(O)–N*H*–COCCl$_3$ (**10**), (f) PhCH=CH–C*H*(Ph), (g) PhC*H*=C*H*–CH(Ph) (refer Scheme 5). Broad signals (h) are from trichloroacetamide (N*H*$_2$COCCl$_3$). The signals (i) are instrumental artifacts or solvent peaks.

in (**9**) to a clear region of the spectrum at δ 2.9–3.1 of the TAI derivative (**10**). The signals labeled (d), (c) and (b) for structure (**10**) integrate in the expected 1:1:2 ratio.

For the TAI derivative of the model compound, 2-phenylethylamine, the imidic and amidic hydrogens give rise to a singlet at δ 8.96 a broad triplet at 7.91, respectively, at significantly lower field than the analogous end-group signals. The signal for the imidic hydrogen for the model compound are removed by D_2O exchange. The slower rate of D_2O exchange and the different chemical; shifts for the polymer end-group when compared to the model compound may reflect the more hydrophobic environment of the end-group.

Two-dimensional spectra NMR (HMBC, HSQC and COSY) for the TAI derivative (**6**) of the polystyrene (**7**) were obtained to confirm the amidic and imidic signal assignments. A correlation was observed in the HMBC between the carbamate carbonyl at δ_C 150.6 and the α-methylene δ_H 3.1. A further correlation was found between the trichloroacetyl carbonyl δ_C 161.5 and the imidic hydrogen at δ_H 8.2. The COSY spectrum (Fig. 3) shows a correlation between the signal for the amidic hydrogen at δ 7.5 and that for the α-methylene at δ 2.9–3.1. In this polystyrene, the α-methylene signal at δ 2.9–3.1 overlaps with that for the aliphatic methine of the ω-(1,3-diphenylpropenyl) chain end at δ 3.1. The imidic signal at δ_H 8.2 shows no crosspeaks. A correlation (not shown) was also seen between the olefinic hydrogens at δ 6.1–6.3 and the methine of the ω-(1,3-diphenylpropenyl) δ 3.1 [37]. The overlap of the signals for the α-methylene and the methine of

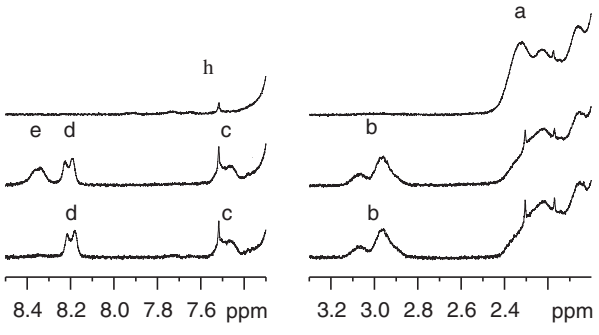


Fig. 2. Portions of the ^{1}H NMR spectra of (from top to bottom) α-(aminomethyl)polystyrene (**9**) and derivative (**10**) before and after D_2O exchange. The sample corresponds to entry 2 in Table 4 ($\bar{M}_n^{GPC}$ = 1280 g mol^{-1}). Signal assignments are: (a) –C*H*$_2$–NH$_2$ (**9**), (b) –C*H*$_2$–NH–C(O)– (**10**), (c) amidic –NH signal –CH$_2$–N*H*–C(O)– (**10**), (d) imidic –NH signal –CH$_2$–NH–C(O)–N*H*–COCCl$_3$ (**10**), (e) extraneous peak. The sharp signal (h) and the sharp signals appearing on top of (c) are instrumental artifacts.

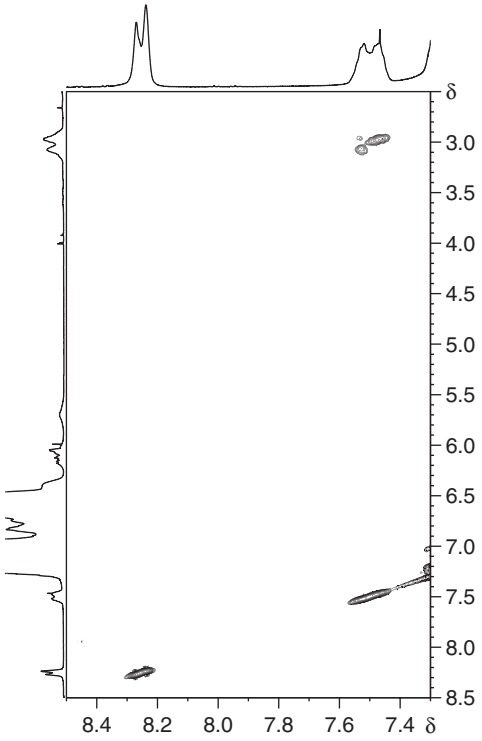
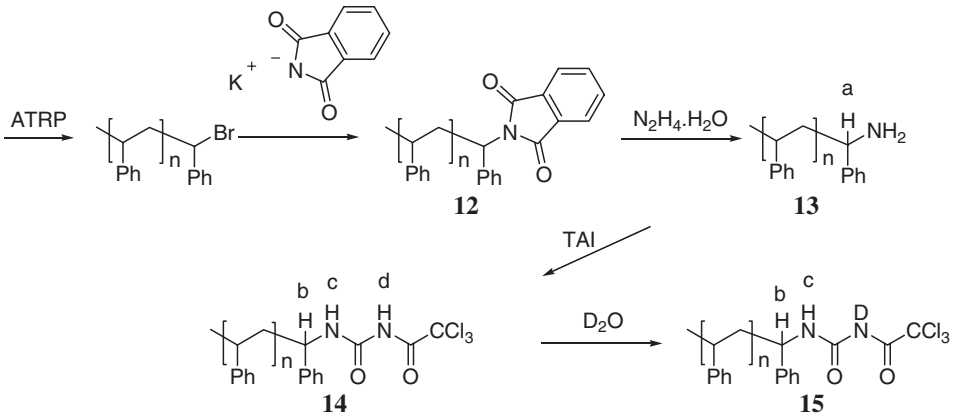


Fig. 3. Portion of the COSY spectrum of TAI derivative of polystyrene (**7**) ($\bar{M}_n^{GPC}$ = 1320 g mol^{-1}) showing connectivities between the amidic and α-methylene hydrogens. Spectrum recorded in $CDCl_3$ at 298 K using a Bruker DRX500 spectrometer at (signal assignments are shown in Fig. 1). See Experimental for NMR operating conditions.



Scheme 8.

the ω-(1,3-diphenylpropenyl) means that integration of the amidic or imidic hydrogens provides for more reliable end-group quantification.

The ^{1}H NMR spectrum of a low molecular weight ATRP-synthesized ω-aminopolystyrene (**13**, Scheme 8) [35] and its TAI derivative (**14**) before and after D_2O exchange are shown in Fig. 4. The signals attributed to the –C*H*(Ph)NH_2 methine proton show complexity which is attributed to the influence of the tacticity of the polystyrene chain. This influence is also evident in the appearance of signals for the amidic (at δ 7.7–8.0) and imidic hydrogens (δ 8.2–8.4) (Fig. 4). These signals appear at significantly higher field than those for the model compound 1-phenylethylamine where the amidic hydrogen is a singlet at δ 8.26 while the imidic hydrogen appears as a doublet at δ 8.96.

The signal for the more acidic imidic hydrogen disappears from the spectrum with D_2O exchange (Scheme 8). This is also observed for amine terminated PEO/PPO and for the model compounds. The result provides confirmation for the signal assignments.

In order to test the quantitative power of the technique, it was applied to determine the end-groups of RAFT-synthesized polymers, where it was important to determine how the fraction of amine chain ends depended on the reaction conditions used in synthesis. Molecular weights of the polymers were determined by GPC in THF and these are given in Table 3 for the amino-functional polystyrene (**7**), its precursor, the phthalimido-functional polystyrene (**5**) and its TAI derivative (**6**). It was found that polar amine end-group interfered with the GPC molecular weight determination by causing the peak to appear at longer retention times. Substantial band broadening was also observed. The effect was most significant for lower molecular weight polystyrenes. The GPC molecular weights for the TAI derivatives are very similar to those of the corresponding α-(phthalimidomethyl)polystyrene. It appears TAI derivatization can be an aid in achieving more reliable GPC molecular weight data for amine functional polystyrenes, and possibly other polymers subject to similar effects.

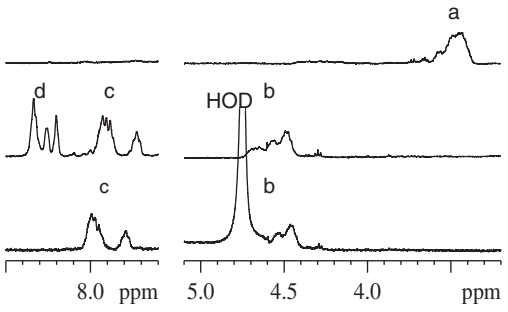


Fig. 4. Portions of the ^{1}H NMR spectra of (from top to bottom) ω-aminopolystyrene (**13**) ($\bar{M}_n^{GPC} = 1230$ g mol^{-1}), TAI derivative (**14**) and product of D_2O exchange (**15**). Sample corresponds to first entry of Table 4 (refer Scheme 7). The regions showing the polymer backbone signals have been removed for clarity. Signal assignments are as follows: (a) –C*H*(Ph)NH_2 (for **13**), (b) –C*H*(Ph)NH–C(O)– (for **14** or **15**), (c) –CH(Ph)N*H*–C(O)–NH–$COCCl_3$ (**14** or **15**), (d) –CH(Ph)NH–C(O)–N*H*–$COCCl_3$ (**14**), $f_n = 0.95$, $[NH_2] = 2.70$ μequiv./g.

It should be noted that for higher molecular weight polymer longer acquisition times are required to obtain adequate signal to noise. Spectrometer tuning and appropriate selection of gain settings is of greater significance in these circumstances. Instrument dynamic range is not usually an issue but can be a problem with data systems associated with older spectrometers. For the highest molecular weight polymer ($\bar{M}_n^{GPC} = 121,000$ g mol^{-1}) the errors in absolute peak size are likely to be large (estimated as $\pm 50\%$).

For polystyrene shown in Table 3 with molecular weight $<$ 40,000 g mol^{-1}, the end-group purity appears high ($>90\%$). However, the highest molecular weight sample has a significantly lower number of the desired end-groups. The low functionality is expected and can be attributed to the greater importance thermal initiation as a source of chain ends when low concentrations of RAFT agent are used to control polymerization. These and similar results will be discussed in detail in a forthcoming paper. The NMR spectra show that the efficiency of conversion of the phthalimido group to the amino group and the subsequent conversion of the amino group to the TAI derivative is quantitative within the detection and integration limits of NMR.

Table 3
GPC and NMR analysis of α-phthalimidomethyl, α-aminomethyl and TAI derivatized α-(aminomethyl)polystyrene

Entry	$\bar{M}_n^{calc}$ [a] (g mol^{-1})	$\bar{M}_n^{GPC}$ [b] (g mol^{-1})			$[NH_2]$ [c,d] (μequiv./g)	f_n [d,e] found	f_n [f] exp.
		Phthalimido (**5**)	Amino (**7**)	TAI (**6**)			
1	1220	1320	– [g]	1660	5.58	1.06	1.0
2	4810	4870	900	4990	1.29	0.97	0.98
3	13,300	14,400	6020	13,800	0.57	0.99	0.95
4	36,100	37,000	26,800	35,000	0.2	0.9	0.87
5	122,000	121,000	108,000	114,000	0.04	0.5	0.56

[a] Expected molecular weight based on the polymerization conditions and the concentrations of RAFT agent used. Phthalimido end-functional polystyrenes (**5**) were prepared by thermal polymerization of styrene at 110 °C for 24 h under nitrogen in the presence of the RAFT agent *S*-butyl *S*′-phthalimidomethyl trithiocarbonate and subsequently transformed to amino end-functional polystyrene (**7**) and derivatized with TAI as indicated in Scheme 6. Entries 1–5 correspond to polymerizations with $[styrene]_0/[RAFT\ agent]_0 = 0.208$, 0.689, 3.02, 6.00 and 30.3, respectively.

[b] GPC determined molecular weight for polystyrenes (**5**, **7**, **6**—refer Scheme) with end-group indicated. Error in GPC molecular weight should be $< \pm 5\%$ except for the lowest molecular weight sample where there is interference from solvent peaks.

[c] $[NH_2]$ is the concentration of amine functionality in microequivalents per gram (μequiv./g) calculated using Eq. (1), where *m* is the molar mass of the monomer unit and $\bar{M}_n^{NMR}$ is the apparent molecular weight determined by comparing the integral of the end-group resonances with those for the backbone Ar*H*

$$[NH_2] = \frac{\frac{1}{\bar{M}_n^{NMR}}}{m} 10^6 \quad (1)$$

[d] Error in $[NH_2]$ and f_n is estimated as $< \pm 5\%$ for entries 1–3, $< \pm 20\%$ for entry 4 and $< \pm 50\%$ for entry 5 (reproducibility of integration is $\pm 20\%$ for entry 5).

[e] f_n (number of functional groups per chain) was calculated using Eq. (2), where $\bar{M}_n^{GPC}$ is the molecular weight of the polymer determined by GPC (phthalimido or TAI)

$$f_n = \frac{\bar{M}_n^{GPC}}{\bar{M}_n^{NMR}} \quad (2)$$

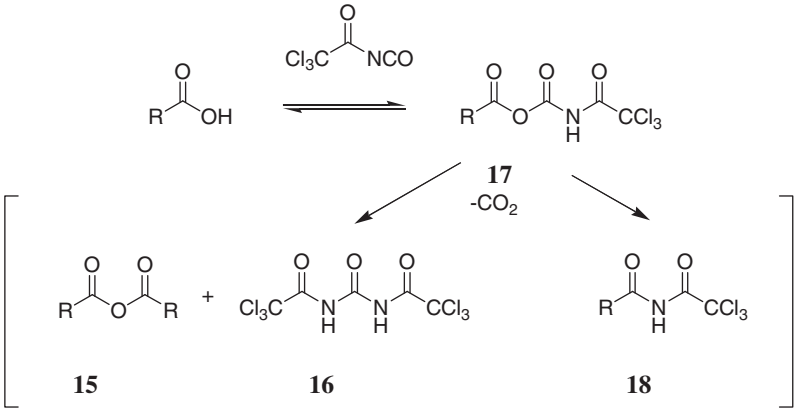
[f] Expected f_n based on comparison of $\bar{M}_n^{GPC}$ (TAI) and calculated molecular weight.

[g] Low molecular weight broad bimodal distribution.

3.4. TAI derivatization of carboxy functional polymers

It has been reported that the products (**17**) of the reaction between isocyanates and low molecular weight carboxylic acids are unstable and decarboxylate to form the corresponding anhydride (**15**) and the 1,3-bis(trichloroacetyl)urea (**16**), or the trichloroacetyl amide (**18**) (Scheme 9) [47–49]. Our observations for benzoic acid and acetic acid support these findings. Derivatization of carboxylic acid functional groups on the model compounds gave rise to complex sets of peaks in the ^1H NMR spectrum spanning the region upfield from 10 ppm.

However, our previous work with polyesters has shown that the acid end-groups are converted to TAI derivatives (**17**) that are stable for an extended period and do not change for over 16 h. In that work we successfully applied TAI derivatization in the quantitative determination of carboxylic acid and hydroxy end-groups of commercial 'bottle grade' PET ($\bar{M}_n \sim 30,000$) and to a wide range of oligo- and polyesters



Scheme 9.

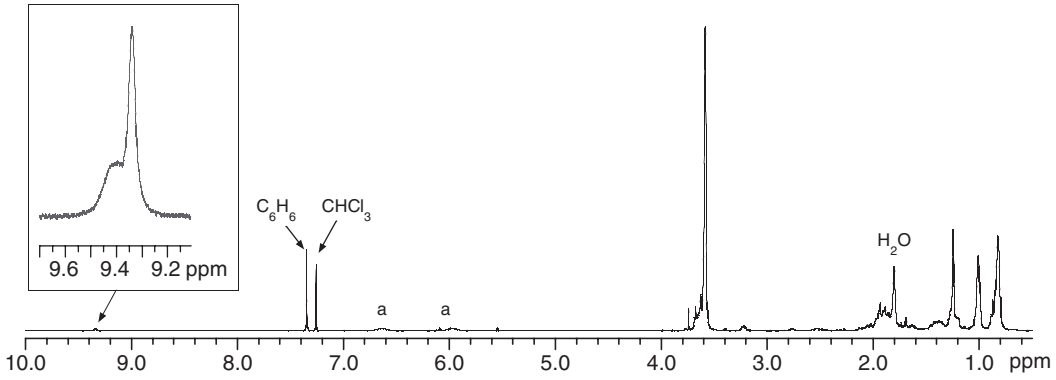
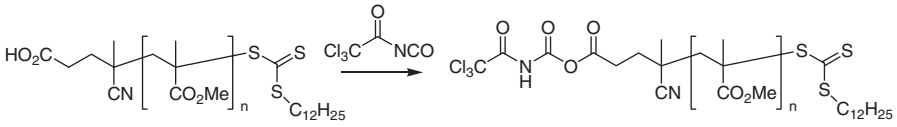


Fig. 5. ^{1}H NMR spectrum of TAI derivative (**21**) of low molecular weight carboxy functional poly(methyl methacrylate) (**20**) ($\bar{M}_n^{GPC} = 2620$ g mol^{-1}). Inset shows signals attributed to imidic hydrogen of the end-group –C(O)–O–C(O)–N*H*–COCCl$_3$. Broad signals (a) are from trichloroacetamide (N*H*$_2$COCCl$_3$). $f_n = 0.90$, [C(O)OH] = 2.41 μequiv./g.



20 **21**

Scheme 10.

[33]. We now report that TAI derivatization and ^{1}H NMR can also be applied to determine acid end groups in acrylic and styrenic polymers.

Poly(methyl methacrylate) with carboxy end-groups (**20**) ($\bar{M}_n^{GPC} = 2620$ g mol^{-1}) was prepared by RAFT polymerization as described elsewhere [36]. The ^{1}H NMR spectrum (Fig. 5) of the TAI derivative of poly(methyl methacrylate) with carboxy end-groups (**21**) showed two signals at δ 9.3 (narrow) and 9.4 (broad) that are attributed to the diastereotopic imidic hydrogens (Scheme 10). No signals attributable to decomposition products (**15**, **16**, **18**) were apparent and the signal intensity was consistent with the GPC-determined molecular weight.

The α-carboxy, ω-hydroxypolystyrene (**22**) was obtained by nitroxide mediate polymerization. TAI derivatization enabled quantitative determination of both the hydroxy- and carboxy-functionalities. The NMR spectra for the polymer (**22**) and its TAI derivative (**23**) are shown in Fig. 6. The signals for α-methylenes for both the carboxy and the derivatized carboxy group were partially obscured by polymer backbone signals. The quantitation of the carboxy end-group thus had to solely rely on the signals (d). The signals for the imidic hydrogens of the diastereomeric carboxy (d) the hydroxy (c) and other end-group signals (a) and (b) appeared in a $(0.675 + 0.336)^d$:1.03^c:1.08^b:0.98^a ratio consistent with structure (**23**) (Scheme 11).

3.5. TAI derivatization of hydroxy-functional polymers

Hydroxy groups in model compounds (Table 2) and polymers (Table 4) were readily derivatized and the end-groups quantified by ^{1}H NMR. The imidic hydrogens have chemical shifts in the range δ 8.2–8.8 depending on the specific structure.

A α-hydroxyethylpolystyrene (**24**), synthesized by emulsion polymerization of styrene with mercaptoethanol as a chain transfer agent, underwent quantitative derivatization to show a clear end-group signal in the NMR (Fig. 7). The intensity of the signals attributed to –S–CH$_2$–C*H*$_2$–OH (**24**), –S–CH$_2$–C*H*$_2$–O–C(O)– (**25**) or –CH$_2$–O–C(O)–N*H*–COCCl$_3$ (**25**) were consistent with 0.92 hydroxy end-groups per molecule (Scheme 12).

For a review on the determination of hydroxy groups in polymers, see Boiko et al. [50]. Methods for characterization of polymers containing PEO segments (ethoxylates) have been reviewed by Zalipsky [51]. The purity and average composition of the PEO surfactants can be determined directly by ^{1}H NMR analysis. However, peak resolution is such that ^{1}H NMR

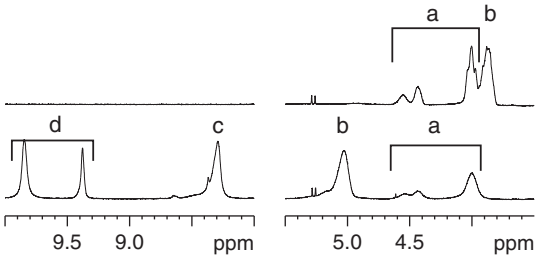
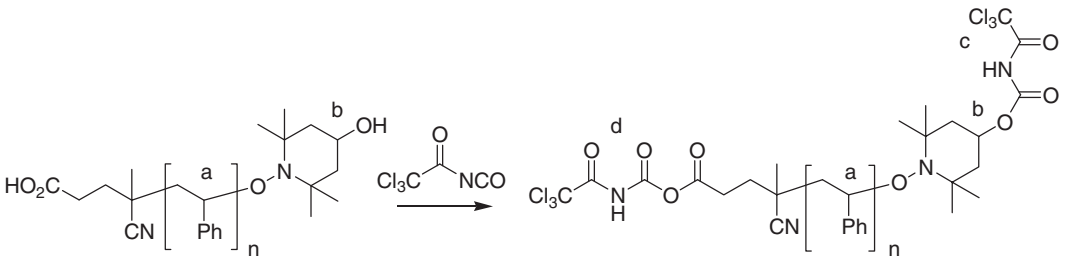


Fig. 6. Regions of the ^{1}H NMR spectra of polystyrene (**22**, upper spectrum, $\bar{M}_n^{GPC} = 2820$ g mol^{-1}) and TAI derivative (**23**, lower spectrum) showing signals attributable to the end-groups. Signal assignments as follows (refer Scheme 11): (a) –CH$_2$C*H*(Ph)O–, (b) (–CH$_2$)$_2$C*H*O–, (c) –CH$_2$–O–C(O)–N*H*–COCCl$_3$ (**23**), $f_n = 0.64$, [OH] = 2.12 μequiv./g, (d) –CH$_2$–C(O)O–C(O)–N*H*–COCCl$_3$ (**23**), $f_n = 0.64$, [C(O)OH] = 2.07 μequiv./g.



Scheme 11.

Table 4
^{1}H NMR chemical shifts for imidic and amidic (δ N*H*) and α protons (δ CH_α), signals for TAI derivatives of polymers with protic end groups

	Polymer	Chain-end functionality	δ CH_α	δ N*H*		$\bar{M}_n^{GPC}$
				Amidic	Imidic	
1	PS[a] (**13**)	–CH(Ph)NH_2	4.57	7.83	8.27	1230
2	PS[b] (**9**)	–CH_2NH_2	3.00	7.50	8.29	1280
3	PS[b] (**7**)	–CH_2NH_2	3.00	7.50	8.29	1320
4	PS[b] (**7**)	–CH_2NH_2	3.00	7.49	8.18	4870
5	PS[b] (**7**)	–CH_2NH_2	3.00	7.50	8.20	9150
6	PS[b] (**7**)	–CH_2NH_2	3.00	7.49	8.21	14,400
7	PS[b] (**7**)	–CH_2NH_2	3.00	7.50	8.20	32,100
8	PS[b] (**7**)	–CH_2NH_2	3.00	7.49	8.20	37,000
9	PS[b] (**7**)	–CH_2NH_2	3.00	7.48	8.16	121,000
10	PS[c] (**24**)	–S$(CH_2)_2$OH	4.17	–	8.31	10,300[d]
11	PS[e] (**22**)	(–$CH_2)_2$CHOH	5.03	–	8.29	2820
12	PS[e] (**22**)	–CH_2C(O)OH	–[f]	–	9.38, 9.85	2820
13	PMMA[g] (**20**)	–CH_2C(O)OH	2.77	–	9.34	2620
14	PEO/PPO[h]	–CH_2CH(CH_3)NH_2	3.99	7.95	8.70	2000
15	PEO	–O$(CH_2)_2$OH	4.38	–	8.80	300
16	PEO	–O$(CH_2)_2$OH	4.40	–	8.64	1000
17	ME[i] [47]	–O$(CH_2)_2$OH	–	–	8.76	–
18	PET [33]	–O$(CH_2)_2$OH	–	–	8.22–8.65	–
19	PET[33]	–ArC(O)OH	–	–	10.1–10.4	–
	Polyester [33]	–OH	–	–	8.08–8.81	–
	Polyester [33]	–C(O)OH	–		10.3–11.4	–
	PPGE[j] [27]	–OH	–		8.5	–

[a] Polystyrene synthesized by ATRP [35].
[b] Polystyrene synthesized by RAFT polymerization [36].
[c] Polystyrene synthesized by emulsion polymerization with mercaptoethanol as a chain transfer agent (see Experimental).
[d] Bimodal distribution.
[e] Polystyrene prepared by NMP with 4-hydroxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl and 4,4′-azobis(4-cyanovaleric acid) (see Experimental).
[f] Peak obscured by polymer backbone signal.
[g] PMMA synthesized by RAFT polymerization [36].
[h] Jeffamine® M-2070, molecular weight from Huntsman product information sheet.
[i] ME, ethoxylated linoleic acid [47].
[j] PPGE, poly(phenyl glycidyl ether) [27].

does not directly provide information on the homogeneity of ethoxylates. The analysis of **3a–d** was aided by derivatization of the hydroxy end-group with TAI. The use of ^{1}H NMR and TAI derivatization has been previously used in end-group characterization of PEO [34] and PEO monomethyl ethers [24]. However, those studies [24,34] focused on polymers with higher molecular weight PEO segments and the sensitivity of the chemical shift of the imidic hydrogen to the PEO block length was not recognized. It has also been reported that ^{13}C NMR can resolve signals for individual ethoxylates with $n \leq 5$ [52].

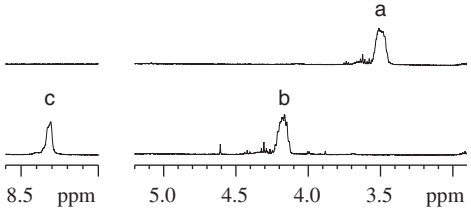
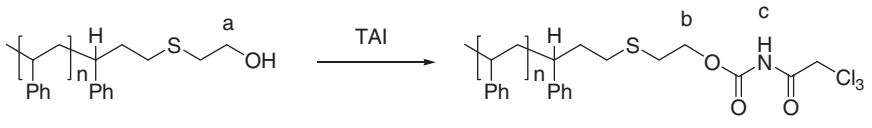


Fig. 7. Regions of the ^{1}H NMR spectra of polystyrene (**24**, upper spectrum, $\bar{M}_n^{GPC}$ 10,300) and TAI derivative (**25**, lower spectrum) showing signals attributable to the end-groups. Polymer backbone signals have been removed for clarity. (a) –S–CH_2–CH_2–OH (**24**), (b) –S–CH_2–CH_2–O–C(O)– (**25**), (c) imidic signal –CH_2–O–C(O)–N*H*–$COCCl_3$ (**25**), f_n = 0.92, [OH] = 0.86 μequiv./g.



Scheme 12.

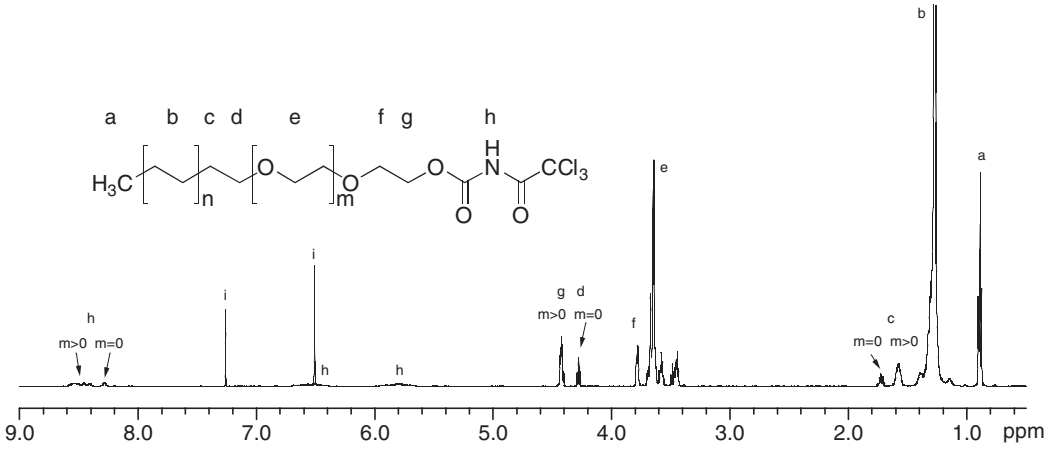
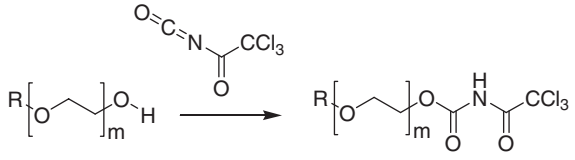


Fig. 8. ^{1}H NMR spectrum ($CDCl_3$, 50 °C) of trichloroacetyl isocyanate derivatized PE-*block*-PEO **3d**. Broad signals (h) are from trichloroacetamide (NH_2COCCl_3). The signals (i) are instrumental artifacts or solvent peaks.

The TAI derivatization procedure involves addition of a slight excess of TAI to the sample in $CDCl_3$ in an NMR tube. The PE-*block*-PEO are only partially soluble in $CDCl_3$ at room temperature but completely dissolve at 50 °C. The ^{1}H NMR spectrum of TAI derivatized PE-*block*-PEO **3d** is shown in Fig. 8. The ethoxylate ($m>0$) is readily distinguished from the precursor alcohol ($m=0$) in the signals for the α- and β-methylene hydrogens. However, the ^{1}H NMR chemical shift of the imidic hydrogen of TAI derivatized PE-*block*-PEO shows remarkably sensitivity to the number of PEO units (m, see Scheme 13). Thus, the imidic hydrogens of $R(PEO)_mOC(O)NHC(O)CCl_3$ with $m=$ 0,1,2,3 and ≧4 are at least partially resolved in the 400 MHz NMR (Fig. 9).

There is also some sensitivity to the chemical shift of the imidic hydrogens to the length and type of alkyl chain. The method was also tested in the analysis of a series of oligo(ethylene glycol) monomethyl ethers. For these examples, there is less chemical shift dispersion, nonetheless, the imidic hydrogens $CH_3(EO)_mOC(O)NHCO)CCl_3$ are resolved for $m=$ 1, 2, and ≧3 (Table 5).

The average chain lengths estimated from NMR for the PEO blocks of the various ethoxylates differ only slightly from the specifications provided by the suppliers (Table 1) and the molecular weight distributions (Fig. 9) are consistent with that expected from application of a conventional ethoxylation processes [52].



Scheme 13.

3.6. TAI derivatization of sulfanyl-functional polymers

The only literature report on TAI derivatization of a thiol relates to the compound **26**. This compound contains both a

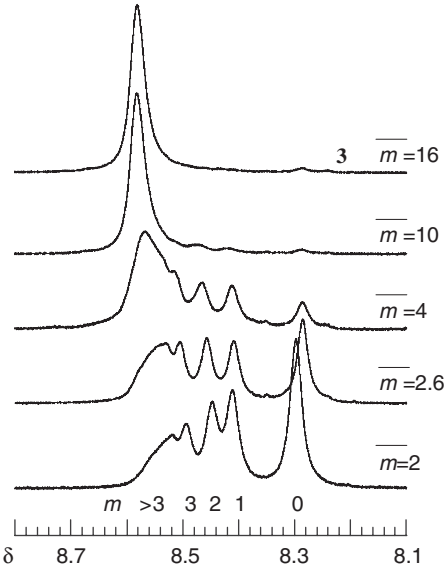


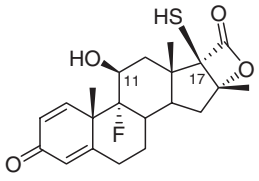
Fig. 9. Region δ 8.1–8.8 of 400 MHz ^{1}H NMR spectra ($CDCl_3$, 50 °C) of trichloroacetyl isocyanate derivatized PE-*block*-PEO **3a**–**e** showing peaks attributed to the imidic hydrogens [$R(EO)_mOC(O)NHC(O)CCl_3$]. Values of average chain length ($\bar{m}$) shown are the nominal values indicated by the supplier.

Table 5
^{1}H NMR chemical shifts ($CDCl_3$, 50 °C) of imidic hydrogens in TAI derivatized $R(EO)_mH$ block copolymers

Compound	$R(EO)_mOC(O)NHC(O)CCl_3$ Chemical shift (δ) 50 °C ($CDCl_3$) for $m=$					
	0	1	2	3	4	>4
CH_3	–[a]	8.48	8.51	8.58	8.58	–[a]
Dodecanol	8.30	–[a]	–[a]	–[a]	–[a]	–[a]
PE (**3e**)	8.30	8.41	8.45	8.49	–[b]	–[b]
PE (**3d**)	8.28	8.41	8.45	8.50	–[b]	–[b]
PE (**3c**)	8.28	8.41	8.46	8.51	–[b]	8.58
PE (**3b**)	8.28	8.41	8.47	–[b]	–[b]	8.58
PE (**3a**)	8.28	–[a]	–[a]	–[a]	–[b]	8.58

[a] Not determined or not applicable.
[b] Not sufficiently resolved (see Fig. 9).

thiol and a hydroxy group. The 11β hydroxy of **26** was observed to react rapidly, however, the 17β thiol reacted only slowly taking up to 3 days for complete conversion [53]. Singlets for imidic hydrogens were observed at δ 9.02 and 9.66, but were not specifically assigned.



26

We examined the TAI derivatization of several thiol model compounds. These gave clear signals in the region δ 8.7–9.2 (Table 2) that can be attributed to the imidic hydrogen (–S–C(O)–*NH*–CO–CCl_3). The reactions with simple thiols were rapid (complete within 30 min) and appeared quantitative. In the case of 2-mercaptoethanol, a spectrum after ca. 10 min showed that while the hydroxy was completely converted, the thiol had only partly reacted. Conversion of the thiol was completed after 2 h.

Application of the method to polymer samples proved more problematic. A sample of ω-sulfanylpolystyrene synthesized by aminolysis of a RAFT-synthesized polymer with *N*-butylamine [36], showed a weak signal (<10% of expected intensity) at δ 8.8 that might be attributed to an imidic hydrogen. The signal intensity did not increase after 25 h. The precursor polymer gave a positive test to Ellman's reagent (5,5′-dithio-bis-[2-nitrobenzoic acid]) indicating the presence to sulfanyl groups. After treatment with TAI the polymer gave a negative test with Ellman's reagent. Difficulties in the synthesis and isolation of polymers with thiol end-groups made by RAFT [54–56] or ATRP [57] have been reported. Several commercial samples of thiol-terminated PEO (precise end-group structure unknown) were also examined. Again, signal intensities were substantially lower than expected on the basis of the known molecular weights.

4. Conclusion

Trichloroacetyl isocyanate reacts rapidly with amine, hydroxy and carboxyl chain ends to derivatives which can be readily determined and characterized by ^{1}H NMR spectroscopy. The method is useful both in qualitative analysis to identify signals and prove assignments and in quantitative analysis. The experimental procedure does not require product isolation or sample purification step and is conveniently carried out in situ in an NMR tube. The signals for the imidic (and, in the case of amines, amidic) hydrogens appear in a region (δ 7.5–11) that is clear of other signals in the case of aliphatic polymers and many aromatic polymers such as polystyrene and poly(ethylene terephthalate). The signals are characteristic of the particular end-group and show remarkable sensitivity to its environment. Though they may be useful in special circumstances, no additional internal standards are required for quantitation.

The method has been shown effective in the determination of hydroxy, primary amino and carboxy end-groups and has been applied in the characterization of polymers formed by conventional and living radical polymerization (RAFT, ATRP, NMP), to end functional poly(ethylene oxide) and to polyethylene-*block*-poly(ethylene oxide).

Acknowledgements

AP would like to acknowledge CRC for Polymers for a PhD Scholarship in association with CAMD, School of Chem. Eng. and Ind. Chem., University of New South Wales. TPD thanks the ARC for the receipt of a Federation Fellowship. We are grateful to Dr Bronwyn Fox for the synthesis of polystyrene (**24**) and to Dr Jo Cosgriff for assistance with NMR.

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