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End group modification in poly(ethylene terephthalate)

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Abstract

The esterification reaction between the hydroxyl end groups in PET and trifluoroacetic acid on stirring at room temperature has been observed and studied. The reaction, which we refer to as end-capping, was found to be complete after 5 days. We demonstrate that whilst the reaction leads to modification of the end groups there is no significant degradation of the polymer chains. Proton nuclear magnetic resonance has been used to probe the kinetics of the reaction, and a pseudo first-order reaction rate constant of $(7.8 \pm 1.8) \times 10^{-6}\ s^{-1}$ has been obtained. The results of this study may have implications for other polyester systems where strong acids are used as solvents. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Polyesters, and in particular poly(ethylene terephthalate) (PET), are an important class of polymers that have widespread applications. PET was first prepared in 1946 [1] and has since been produced commercially as a film, fibre and as bottles. Commensurate with the widespread applications of polyesters there have been many studies of their properties and reactions, notably transesterification in their blends [2–9].

One of the major problems encountered when studying polyesters, particularly their blends which are often prepared by solution blending, is finding a suitable solvent system. Generally, polyesters are insoluble in common organic solvents, even more so when in their crystalline form. The most successful solvent systems include chlorinated phenols and strong organic acids such as trifluoroacetic acid (TFA) and dichloroacetic acid [10]. In many applications a mixed solvent system, typically dichloromethane (DCM) and an organic acid, is used as it is often found that only a small amount of the acid is required for solubility. Indeed for many systems once there is sufficient acid to dissolve the polymer, often only 10% by volume, further addition has little effect on solubility [11].

In this paper we present evidence of a chemical reaction between TFA and PET. This work forms part of a larger study on polyester blends in which we initially chose TFA and DCM as a solvent system. An inherent complication in this system is the possible esterification reaction between the acid solvent and hydroxyl end groups, as mentioned briefly by Moad et al. [12]. Here we describe two experiments in which this reaction is characterized. Firstly, ^{19}F nuclear magnetic resonance (n.m.r.) is used to provide evidence of the reaction between the acid and end groups, referred to as end-capping. Having established the presence of the reaction, the kinetics are studied in more detail using proton n.m.r. Finally the wider implications of our observations are discussed and summarized.

2. Experimental

All PET used was supplied by ICI and was dried under vacuum at 160°C for 3 h prior to use. The intrinsic viscosity of the PET was determined in hexafluorisopropanol at 25°C and found to be 0.74 dl g^{-1}, and using the Mark–Houwink parameters in the literature [13] this indicates a molecular weight of 34 400 g mol^{-1}. Solvents, except those for n.m.r., were purchased from Aldrich chemical company and used as received. N.m.r. solvents were purchased from Goss Scientific.

A sample of PET (10 g) was dissolved in 100 ml of a

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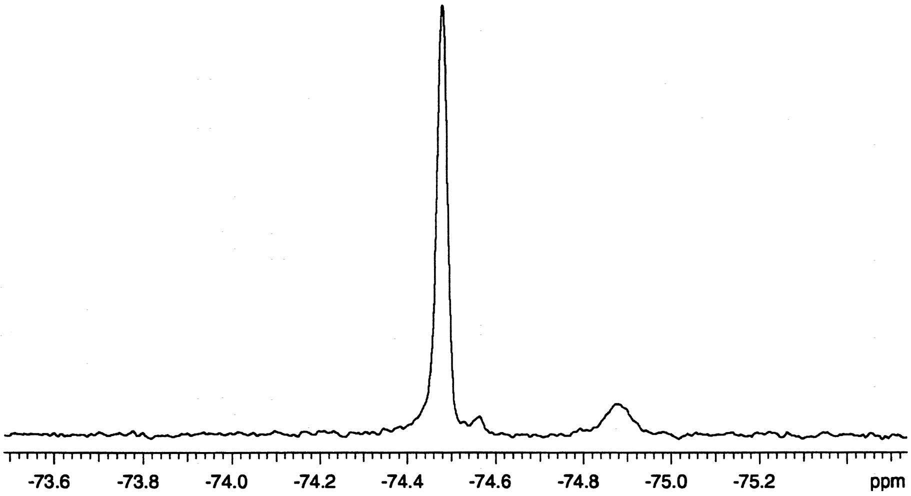

Fig. 1. ^{19}F spectrum for PET-TFA.

mixture of TFA and DCM, 1:4 by volume, and left stirring at room temperature for 12 h. This system appears to be a good solvent for PET and dissolution was complete within 4 h. The PET was recovered by precipitation into methanol and dried under vacuum for 48 h at 40°C and for a further 3 h at 160°C. This sample is referred to as PET–TFA.

As a comparison, a sample of PET (10 g) was dissolved in 100 ml of 2-chlorophenol. To dissolve highly crystalline PET within 12 h it was necessary to warm the solvent. Once dissolved the sample was precipitated into methanol, recovered by filtration and Soxhlet extracted for 48 h with dry methanol to remove 2-chlorophenol. The same drying procedure described previously was used; this sample is referred to as PET–OCP.

2.1. Fluorine n.m.r.

Amorphous samples of PET–TFA and PET–OCP, prepared by melting and rapid quenching, were dissolved in deuterated tetrachloroethane at 110°C. Fluorine spectra were recorded at 80°C on a VARIAN VXR 400-S operating at 376.3 MHz for ^{19}F, using trifluorotoluene as an internal secondary standard (– 62.2 ppm). A ‘blank’ sample of solvent and TFA was used to identify the chemical shift for free acid.

2.2. Proton n.m.r.

The kinetics of the end-capping reaction were monitored using proton n.m.r. Samples of PET chip, as received, and PET–OCP were sealed in dry n.m.r. tubes with 1 ml of deuterated TFA and deuterated DCM, 1:4, with tetramethylsilane as internal standard. A proton spectrum was collected once dissolution was complete, and thereafter at intervals of 12–24 h over 5 days. All spectra were recorded at room temperature on a VARIAN VXR 400-S, operating at 400 MHz for ^{1}H.

3. Results

As expected there were no signals in the ^{19}F spectrum of PET–OCP; this was confirmation that before dissolution in TFA the PET does not contain any fluorine. In contrast, as Fig. 1 demonstrates, three signals can be identified in the spectrum of PET–TFA. By comparison to the blank solvent spectrum we assign the signal at −74.88 ppm to residual TFA in the sample. It follows that the remaining signals in the spectrum at around −74.5 ppm can only arise from fluorine that has become incorporated in the polymer. This can occur via an esterification reaction between the hydroxyl end groups and TFA, illustrated schematically in Fig. 2. Clearly, the resonance of the F atoms in the TFA end

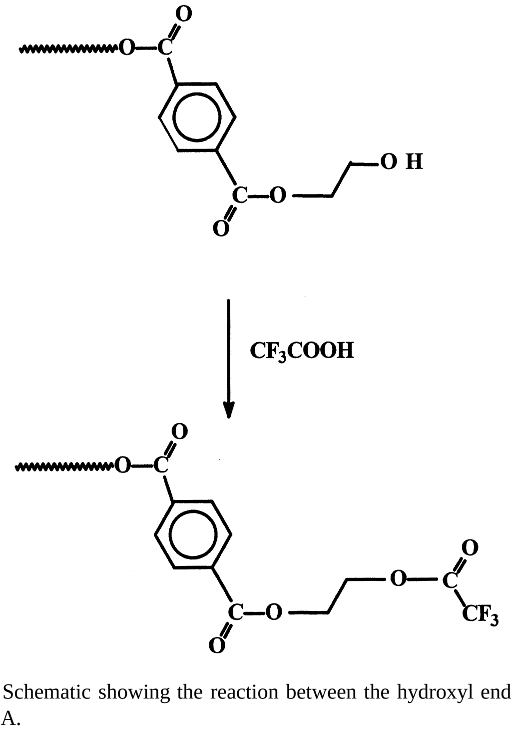

Fig. 2. Schematic showing the reaction between the hydroxyl end groups and TFA.

group would differ from that in TFA giving rise to a separate signal, although at around 0.4 ppm the difference in chemical shift is modest.

The reaction scheme in Fig. 2 fails to account for the two signals observed in the ^{19}F spectrum of PET–TFA, and to address this we must consider the chemistry of the PET chains in more detail. It is well known that side reactions during the polymerization of PET can lead to changes in the chemical structure, notably the formation of diethylene glycol (DEG) moieties [14]. One would expect these DEG units to be distributed randomly over the chains, and consequently some of the hydroxyl end groups will be adjacent to DEG units. Where a hydroxyl group is adjacent to a DEG segment the environment experienced by the TFA end following reaction will be modified, and hence the F atoms will exhibit a different chemical shift to those adjacent to a single ethylene glycol unit. Thus a single phenomenon, esterification between the hydroxyl end groups and TFA, leads to F atoms in slightly different chemical environments and hence two signals in the ^{19}F spectrum. Given these considerations we assign the most intense signal at −74.49 ppm to the reaction in Fig. 2; the signal at −74.57 ppm is where a DEG unit is adjacent to the end group.

The percentage of hydroxyl groups adjacent to DEG units can be calculated by integration of the ^{19}F spectrum, and a value of 4.3% is found. This compares well with the DEG content of the polymer determined by proton n.m.r. An expansion of a proton spectrum recorded in deuterated TFA(dTFA)/DCM(dDCM), is shown in Fig. 3. The ethylene glycol protons resonate at around 4.8 ppm, however in DEG the CH_2 protons in each glycol residue are not equivalent and two signals, at approximately 4.13 and 4.64 ppm, are observed. By integration of these three signals the percentage of CH_2 protons in DEG sequences can be determined, and for PET–TFA a value of 4.7% was found. Thus, within experimental error, the DEG content from end group concentrations is identical to the total DEG content of the polymer, indicating that the esterification reaction is not selective but occurs equally over all the hydroxyl groups.

The assignment of the DEG signal in the ^{19}F spectrum has been confirmed by performing the same experiment on a low molecular weight sample of PET, for which the DEG ends could be observed using proton n.m.r. Proton n.m.r. gave a DEG content of 3.2% for this sample, after capping with TFA and integration of the ^{19}F spectrum a DEG content of 2.8% was found. The agreement in the two measurements confirms the assignment given in the ^{19}F spectrum, an important result since DEG ends have not previously been observed directly in PET of the molecular weights commonly used.

3.1. Reaction kinetics

Proton n.m.r. provides a quantitative tool for studying the esterification reaction between TFA and hydroxyl end groups in PET. This is demonstrated by focusing on the resonance of the alkyl protons adjacent to the hydroxyl end group and noting the shift on esterification with TFA; see Fig. 4. The spectrum expanded in Fig. 4a was collected immediately following dissolution of PET chip in the dTFA/dDCM mixture. The signals around 4.8 ppm are from the

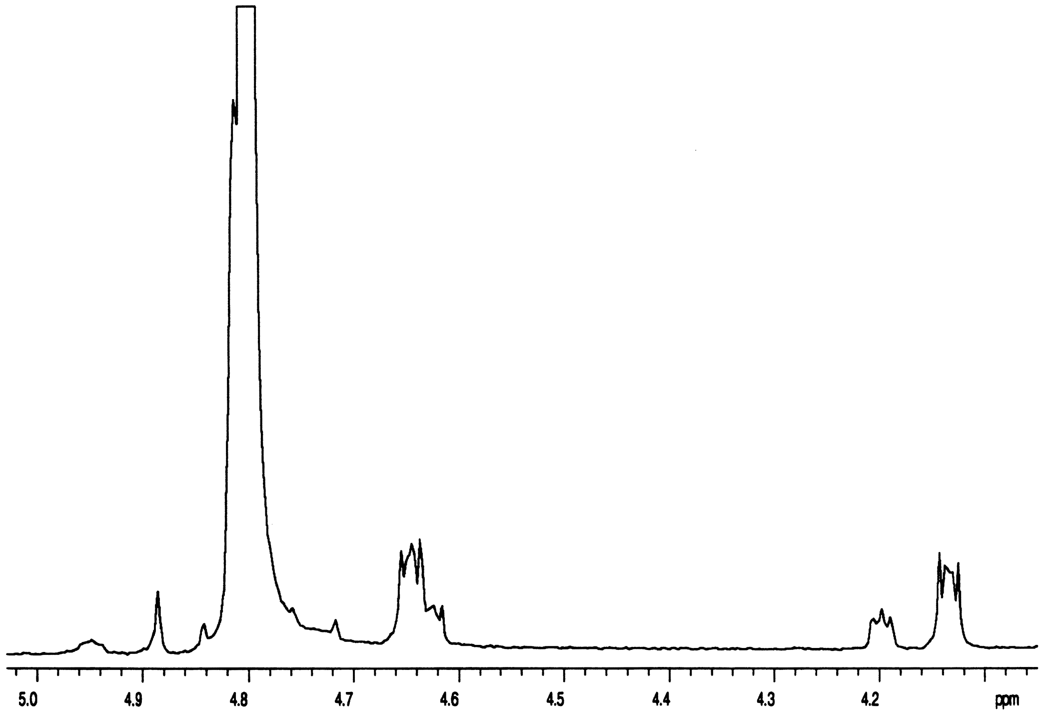

Fig. 3. Proton spectrum for PET-TFA.

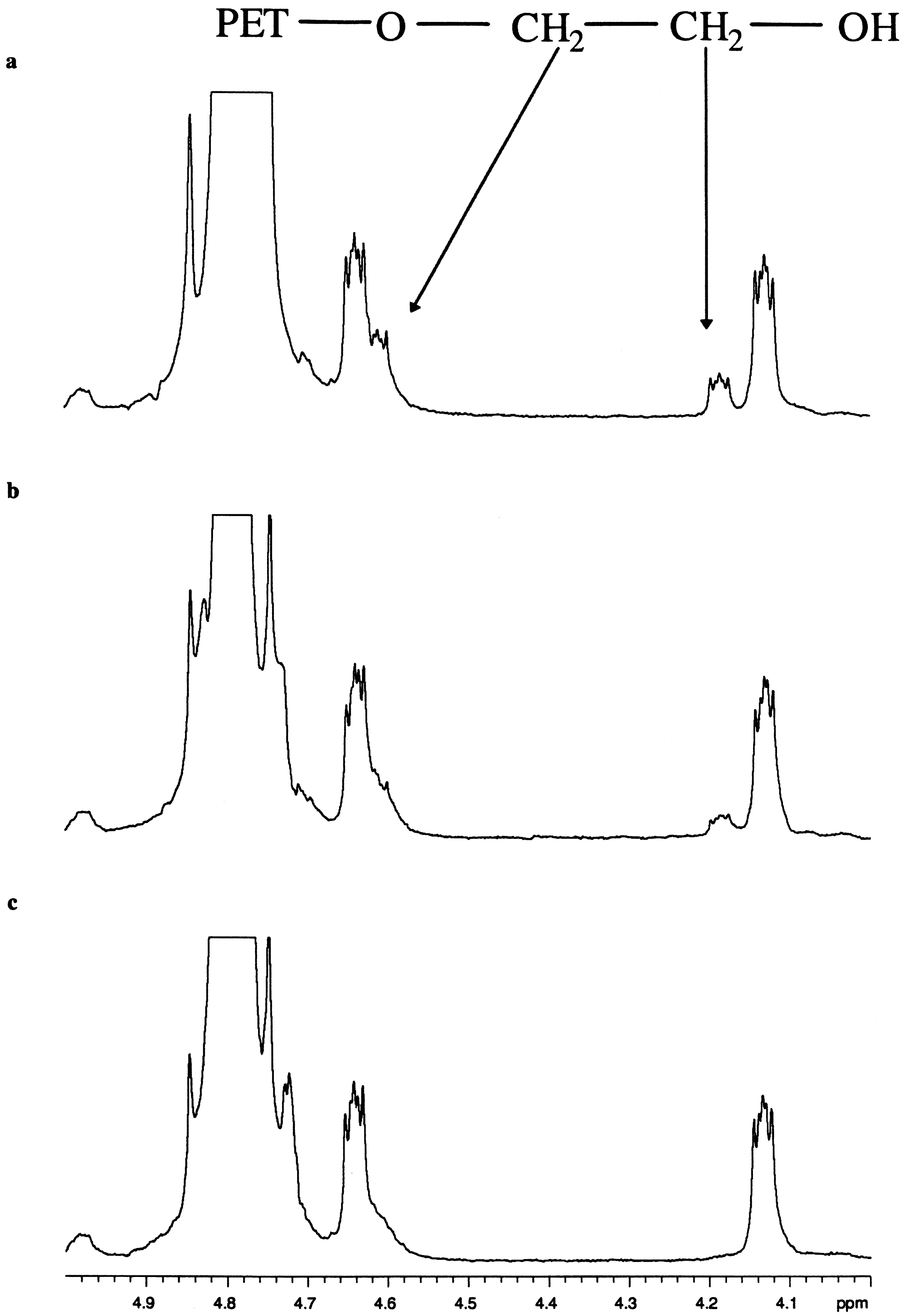

Fig. 4. Expansions of proton n.m.r. spectra of PET after: (a) 50 min; (b) 24 h; and (c) 5 days in TFA/DCM at room temperature.

ethylene glycol residues in the main chain, however for the present purposes interest is confined to the signals at 4.19 and 4.61 ppm corresponding, respectively, to the protons α and β to the hydroxyl end group. On esterification with TFA the environment experienced by these protons changes, the resonance of α protons shifts to a higher frequency and overlaps with the 4.6–4.8 ppm region. In contrast the resonance of the β protons shifts to a lesser extent, appearing as a shoulder on the peak at 4.65 ppm. A decrease in the intensity of the signals from the protons in the alkyl end

Table 1
Number of moles of hydroxyl end groups per mole of monomer after various times in TFA/DCM solution

Time (min)	Number of moles of OH per mole of monomer ($\times 10^{-3}$)
50	8.95
205	7.36
430	7.39
1465	2.82
2905	2.48
7275	0.00

groups, relative to the DEG protons at 4.13 and 4.64 ppm, consistent with the capping reaction, is clearly evident in the proton spectra. This is demonstrated by comparing Fig. 4a with Fig. 4b, collected after almost 24 h in the dTFA/dDCM mixture. After 5 days in the solvent mixture the signals at 4.19 and 4.61 ppm have disappeared (Fig. 4c), indicating completion of the esterification reaction.

A series of n.m.r. spectra was collected over the duration of the esterification reaction. From integration of each spectrum the mole ratio of hydroxyl end groups to monomer units was determined as a function of reaction time (Table 1). The decrease in the hydroxyl end group concentration reflects the kinetics of the reaction, and we analyse the data to exploit this. The reaction between end groups and TFA may be written as:

$$\text{–OH} + CF_3COOH \leftrightharpoons \text{–OCOCF}_3 + H_2O$$

The concentration of TFA is in large excess and essentially constant, forcing the equilibrium to the right, and the reaction appears to be first-order with respect to the hydroxyl end groups.

Thus, for a first-order reaction dependent only upon the concentration of hydroxyl end groups, [OH]:

$$-\frac{d[OH]}{dt} = k[OH]$$

where t is the time and k is the rate constant. On integration this gives:

$$\ln[OH]_t = -(kt + \ln[OH]_0)$$

where $[OH]_0$ is the mole ratio of hydroxyl end groups at $t = 0$.

The data are plotted in this form in Fig. 5 and are described well by a straight line with slope k, the rate constant, for which a value of $(7.8 \pm 1.8) \times 10^{-6}\,s^{-1}$ was obtained by a linear least squares fit to the data. Other information available from the least squares fit to the data is $[OH]_0$, the initial concentration of hydroxyl end groups, and is given by the intercept. The intercept was found to be -4.81 ± 0.16, which gives $[OH]_0 = (8.3 \pm 1.4) \times 10^{-3}$ mol of hydroxyl ends per mol monomer. This value is in reasonable agreement with the measured hydroxyl group concentration for PET of this grade, $(9.0 \pm 0.4) \times 10^{-3}$ mol of hydroxyl ends per mol monomer, determined routinely by infra-red (i.r.) measurements [15].

4. Discussion

The ^{19}F spectra provide clear evidence that TFA reacts with hydroxyl groups in PET. Under these conditions the only fluorine in the samples is in the end groups and ^{19}F n.m.r. provides a sensitive probe for studying end groups quantitatively. This sensitivity is demonstrated by noting that a resolvable signal can be obtained from the residual TFA in PET–TFA, even though it comprises less than 0.1% of the sample by mass.

The question of chain degradation in strong acids, particularly TFA, may be a source of concern since polyesters are easily hydrolysed. However, examination of the series of proton n.m.r. spectra collected during esterification proves that this is not an issue at the temperature used here. Over the timescale of the reaction (~5 days) the relative intensity

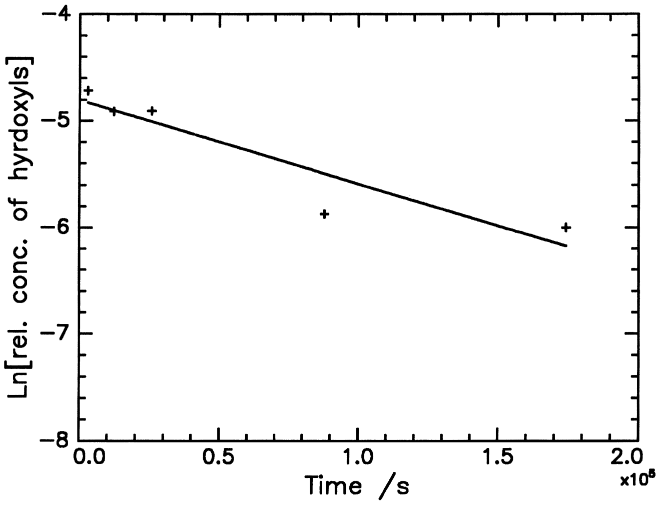

Fig. 5. Logarithm of the number of moles of hydroxyl end groups per mole of monomer plotted against time in TFA/DCM solution. The least squares fit to the data is overlaid.

of the signals from the DEG within the polymer chains to the shoulder from the β protons adjacent to the capped hydroxyl end groups remains constant, demonstrating that degradation was negligible within the sensitivity of n.m.r. This conclusion is also supported by the excellent agreement between the value of $[OH]_0$ determined by extrapolation of our data and the values determined by i.r. measurements at ICI, calibrated by independent proton n.m.r. experiments.

The esterification reaction observed is not unique to this system. Strong acids in general have the ability to react with hydroxyl groups in polyesters, thereby modifying the end groups in the system. The use of strong acids as solvents, or in mixed solvent systems, is relatively common for polyesters particularly in blend preparation, for example dichloroacetic acid has been a common choice. The tendency to esterify polyester end groups is no doubt accentuated by the fact that the acid solvents are generally in large excess compared to the end groups. Since esterification is an equilibrium reaction, these conditions will act to drive the esterification reaction. The observation that these commonly used solvents may modify polyester end groups has not been appreciated until now, indeed the role and nature of end groups in polyesters has received scant attention in the literature [16]. Further to this we have data which demonstrates that end group modification influences the kinetics of transesterification dramatically [17]. This has important implications on our understanding of reaction mechanisms, since the capping of the end groups is a means of ‘removing’, or at least modifying, their influence on the reaction.

5. Conclusion

An esterification reaction between TFA and the hydroxyl groups in PET has been identified. Similar behaviour is anticipated between other strong carboxylic acids and polyesters, and there is evidence that modifying end groups may have a marked influence on reaction behaviour. The kinetics of the capping reaction have been followed by proton n.m.r. and the rate constant for the pseudo first-order reaction was determined to be $(7.8 \pm 1.8) \times 10^{-6}\ s^{-1}$ at ambient temperatures. Following capping with TFA it was possible to observe the DEG end groups in the ^{19}F n.m.r. spectrum. This is an important result, as it is the first direct observation of DEG end groups and has the potential to be developed as a means of measuring DEG content.

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