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Transesterification in poly(ethylene terephthalate) and poly(ethylene naphthalene 2, 6-dicarboxylate) blends; the influence of hydroxyl end groups

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Abstract

Two samples of a single composition blend of PET and PEN were prepared by solution blending using different solvents such that the hydroxyl end groups in one blend were modified. The rate of transesterification in each blend was studied using proton NMR, an established technique for this system. The results indicate that the rate of transesterification is influenced dramatically by end group modification, providing clear evidence that hydroxyl end groups participate in the reaction mechanism. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Transesterification; Hydroxyl end group; Composition blend

1. Introduction

The chemistry of polyesters has been reported widely in the literature [1–12]. Our particular interest here is in the interchange reactions that occur readily in molten polyesters as chains undergo the scission and recombination reactions, collectively referred to as transesterification [13,14]. As a result of transesterification, monomers from a single chain may become distributed over all the chains in the system, and thus the reaction can be exploited to ‘smooth’ out molecular weight differences or, for blends of different polyesters, to form copolymers [11,12]. Clearly such reactions, and their products, are of both academic and industrial interest. In particular, because polyesters are associated with large-scale melt processing and because virgin and recycled polymers are processed together, exploiting transesterification reactions to produce a product with a single molecular weight distribution may be of importance. The possibility of exploiting transesterification during processing for copolymer synthesis also has a number of advantages, not least the fact that the reaction is single step, requiring no modification to existing plants. However, in order to establish control and exploit the reaction fully, a fundamental understanding of the reaction mechanism and rate is required. Surprisingly, whilst the existence of transesterification has been known for some time [12], the understanding of the reaction at a molecular level, i.e. the reaction mechanism and influence of catalysts, has so far not been reported in detail [15,16].

We discuss here transesterification in a blend of poly (ethylene terephthalate) and poly(ethylene napthalene-2, 6-dicarboxylate). Poly(ethylene terephthalate), PET, is the most commonly encountered polyester and is used in many everyday applications, mainly due to its low production cost and good mechanical properties [17]. Poly(ethylene naphthalene-2, 6-dicarboxylate), PEN, has emerged recently as a polyester with better mechanical properties than PET but is currently prohibitively expensive for large volume use [18,19]. Transesterification in blends of these two polyesters offers the potential of property improvement of PET by the relatively facile incorporation of PEN sequences. This approach has been considered by a number of groups and the kinetics of the reaction in PET/PEN blends have been reported [6,7,20,21]. Direct comparison of all these studies is not easy because different methods of blend preparation have been used and the catalyst content of the blend is generally unspecified. However, it is clear that transesterification occurs between PET and PEN and the kinetics of the reaction can be studied using proton NMR.

Although the kinetics of transesterification between PET

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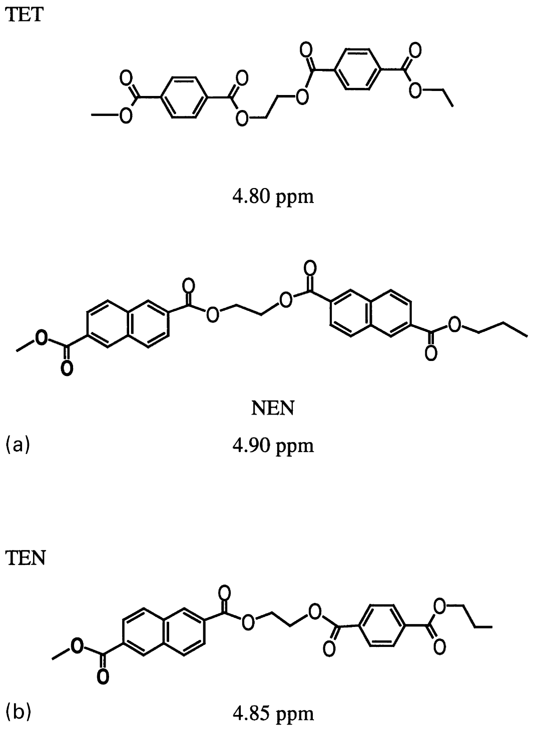

Fig. 1. Schematic of the different environments experienced by ethylene protons in blends of PET and PEN: (a) before transesterification; and (b) after transesterification.

and PEN have been reported, there have been no attempts to understand the reaction at a mechanistic level. This is true of the literature in general. Transesterification kinetics have been reported for a variety of complex systems but often these are somewhat lacking in explanation at a molecular level. Mechanisms proposed for transesterification are intermolecular acidolysis or alcoholysis, occurring via end groups, or 'direct ester exchange', an adventitious process occurring along the polyester chains [14]. Currently, opinion on the relative contributions of these processes to transesterification is divided [22,23] and there is little experimental evidence for or against any of these routes. In this work, we present the first direct evidence demonstrating the participation of end groups in transesterification and, specifically, the contribution of alcoholysis to transesterification.

1.1. NMR theory

Recently proton NMR has been exploited to follow transesterification reactions in PET/PEN blends by a number of groups [6,20,21,24]. The region of interest is 4.5 to 5.0 ppm, where the protons of the ethylene glycol moieties resonate (see Fig. 1). Where these protons are between two consecutive terephthalate units, TET, their chemical shift is 4.80 ppm. In contrast, where they are adjacent to naphthalate units, NEN, their shift is 4.90 ppm [see Fig 1(a)]. Sequences where terephthalate units are adjacent to naphthalate units, TEN, are formed by transesterification. The chemical shift for ethylene protons in such environments is 4.85 ppm, intermediate between the two homopolymers [see Fig. 1(b)].

From this, it follows that by monitoring the evolution of the new signal in the proton spectra as a function of heat treatment time, it is possible to determine the variation in x, the mole fraction of TEN dyads formed by transesterification at time t. In principle, knowledge of x, in combination with the initial mole fraction of both PET and PEN in the blend, a and b, respectively, should provide information about the reaction kinetics. However, before a kinetic expression is derived, information about the reaction order is required. There seems to be some confusion over this in the current literature, Devaux et al. have published extensive studies on bisphenol-polycarbonate (bPC)– polyester systems [25–28] and, following earlier work by Yamadera and Murano [29], assumed the reaction kinetics to be second order reversible. Later Goddard et al. [30] determined a kinetic expression, in which the order with respect to each reagent was explicit. The resulting integration was solved numerically and the results compared with experimental data; the best agreement was obtained for second order kinetics. Recently Stewart et al. [6] applied Devaux's method for determining the reaction rate from NMR for extruded blends of PET and PEN. Stewart et al. [6] state that the transesterification kinetics may be modelled as first order, although Devaux's method is only applicable to second order reactions. This inconsistency is somewhat alarming, and it is not clear whether the authors have evidence for the reaction being first order and have modified Devaux's approach, or have in fact applied it in the original form.

In an attempt to resolve these ambiguities, four different reaction orders have been considered here, starting from the simplest cases, and the expressions derived in terms of x and the initial mole fraction of NEN and TET dyads in the blend, a and b, respectively. For the case where the reaction is first order with respect to either PET of PEN, we find:

$$\ln\left(\frac{c}{c-x}\right) = kt \qquad (1)$$

where c may be either a or b depending upon which reagent is being considered, k is the reaction rate and t is time.

For the case when the reaction is second order overall, i.e. first order with respect to both PET and PEN, we find:

$$\frac{1}{b-a}\ln\left[\frac{a(b-x)}{b(a-x)}\right] = kt \qquad (2)$$

Finally, for a second order reversible reaction, as given by Devaux.

$$\ln\left(\frac{b}{b-r}\right) = kt \qquad (3)$$

where $r = x/a$ and is referred to as the 'transesterification ratio'.

These kinetic models have each been considered in turn

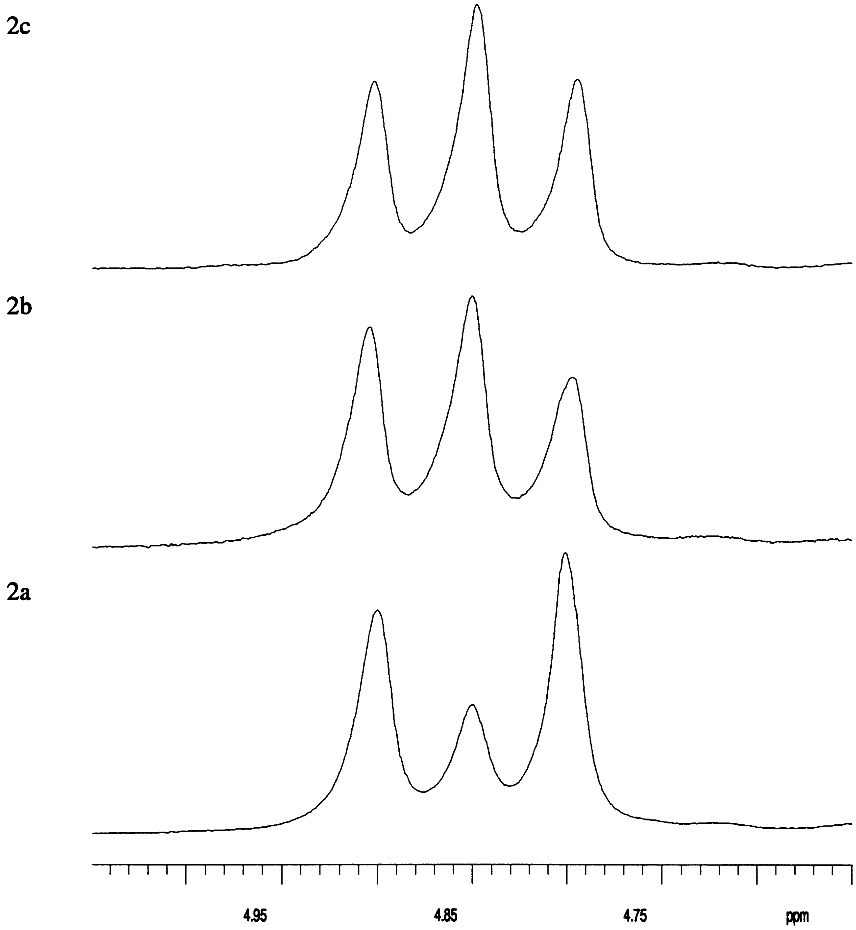

Fig. 2. Expansions of proton NMR spectra for blends of 50-OCP heat treated for: (a) 10 min; (b) 20 min; and (c) 30 min at 300°C.

and, by application to experimental data, the best model for behaviour of this system determined.

2. Experimental

2.1. Polyesters and blend preparation

Samples of PET (E47) and PEN supplied by ICI, were dried under vacuum at 160°C for 3 h prior to use. The intrinsic viscosity of the samples was determined in hexafluoroisopropanol at 25°C and was found to be 0.74 dl g^{-1} for PET and 0.63 dl g^{-1} for PEN. Using Mark–Houwink parameters in the literature for PET [31], molecular weights of 34 400 g mol^{-1} and 27 300 g mol^{-1}, respectively, were indicated. Note that the Mark–Houwink parameters for PEN are not available, using the values for PET may not be correct, so the value obtained can only be considered to represent an apparent molecular weight. Equal weights of PET and PEN were dissolved in the chosen solvents (see later), the blends were then precipitated out, recovered by filtration and dried. Two blends were prepared; one with no end group modification and one where the hydroxyl end groups were capped.

The blend with no end group modification was prepared by adding 10 g of each polyester to 200 ml of 2-chlorophenol. The mixture was warmed to around 80°C and left stirring for 12 h to ensure complete dissolution. The blend was recovered by precipitation into methanol and filtered; residual solvent was removed by Soxhlet extraction for 2 days using dry methanol. This blend is referred to as 50-OCP.

A second blend, in which the hydroxyl ends were capped, was prepared using a mixed solvent system of trifluoroacetic acid and dichloromethane, 1:4 by volume. As before, 10 g each of PET and PEN were placed in a flask with 200 ml of the mixed solvent and left stirring for 5 days. Previous studies have demonstrated that over this time, end capping of the hydroxyl groups in PET, by an esterification reaction with trifluoroacetic acid, is complete [32]. We have evidence, from ^{19}F NMR, that the hydroxyl end groups in PEN also react with TFA and have assumed that the kinetics of this esterification reaction are as for PET. This was confirmed by ^{1}H NMR which demonstrated that, within the sensitivity of the technique, the blend prepared did not contain any methylene protons adjacent to hydroxyl groups. This blend is referred to as 50-TFA.

X-ray fluorescence measurements on the blends

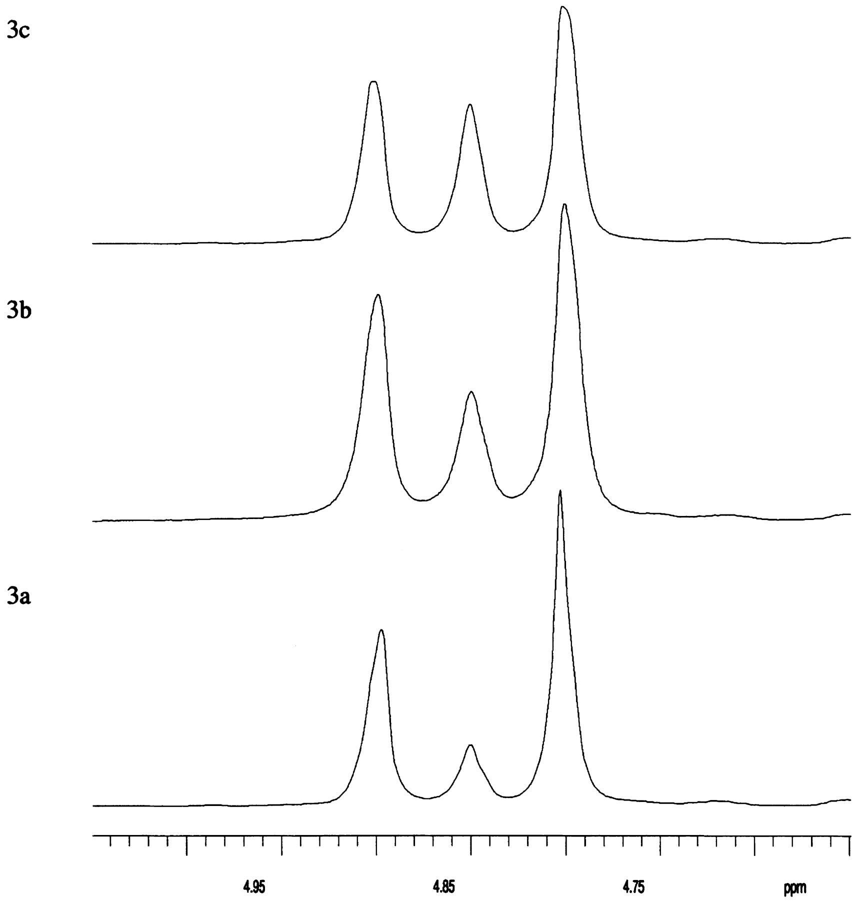

Fig. 3. Expansions of proton NMR spectra for blends of 50-TFA heat treated for: (a) 10 min; (b) 20 min; and (c) 30 min at 300°C.

demonstrated that the solution–precipitation procedure removes metal catalysts from the polymers and leaves only trace quantities of phosphorus, used as a stabiliser.

2.2. Transesterification

A Perkin Elmer DSC7 was used for heat treatment of the blends. Samples were weighed into aluminium pans, sealed and placed in the DSC under a dry nitrogen atmosphere. Using a heating rate of 200°C min^{-1} the samples were taken to a final temperature of 300°C, where both polyesters are molten and transesterification reactions take place. The blends were maintained at this temperature for a variety of time intervals, between 30 s and 30 min, before quenching to room temperature. The products of the heat treatment were recovered, dissolved in deuterated trifluoroacetic acid/dichloromethane, 1:4 by volume, and the ^{1}H NMR spectra obtained.

2.3. NMR analysis

Proton NMR spectra were recorded on a Varian VXR-S operating at 400 MHz for ^{1}H, using tetramethylsilane as the internal standard.

3. Results

Proton NMR spectra for 50-OCP after being held at 300°C for 10, 20 and 30 min are presented in Fig. 2. This series of data demonstrate the evolution of the peak at 4.85 ppm and the corresponding decrease in the intensity of the TET and NEN peaks, and with reference to the TEN peak, confirms that transesterification occurs between PET and PEN, as observed by other authors [6,20]. Notice that the peaks are well resolved and can be integrated separately without difficulty.

The corresponding data for 50-TFA are presented in Fig. 3. There is clear evidence of transesterification in this blend, however a direct comparison with the data for 50-OCP shows that the extent of the reaction is far less. Comparing the relative peak heights, for 50-OCP [Fig. 2(c)], the peak corresponding to TEN sequences is the most intense for reaction times greater than 10 min. In contrast, for 50-TFA [Fig. 3(c)], heat treated for the same length of time as 50-OCP, the TEN peak is the least intense of the three characteristic resonances.

NMR spectra were collected for 50-OCP heat treated for times between 2.5 and 30 min. From each of these, the parameter x was calculated and used to investigate the reaction order. The data, plotted according to Eqs. 1–3, are

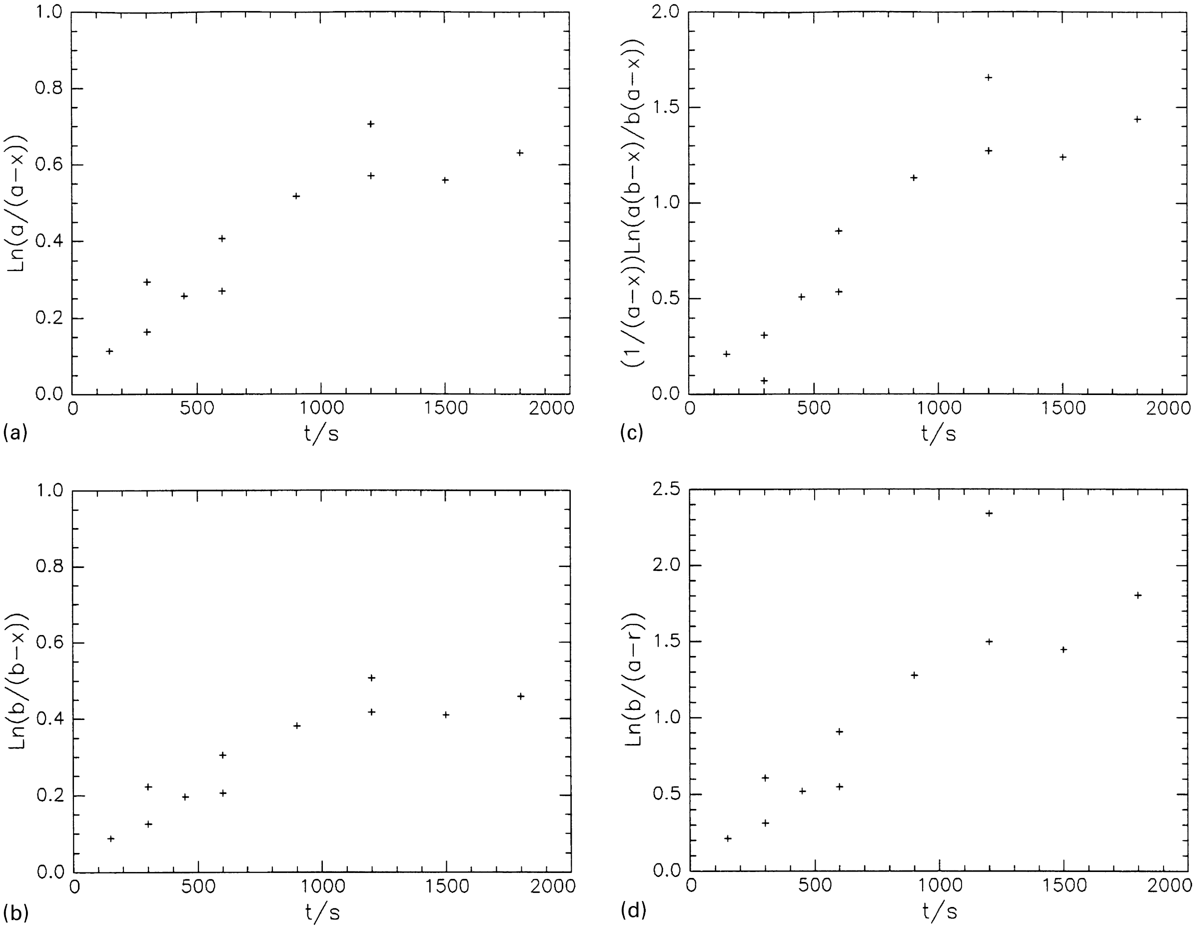

Fig. 4. Data for 50-OCP plotted assuming the reaction kinetics are: (a) first order with respect to PET; (b) first order with respect to PEN; (c) second order; and (d) second order and reversible.

presented in Fig. 4. On inspection, it is clear that neither of the first order kinetic expressions (Eq. 1) describe the behaviour adequately and a non linear dependence on *t* is evident [Fig. 4(a) and (b)]. Modelling behaviour as a simple second order reaction (Eq. 2) is no more successful [see Fig. 4(c)].

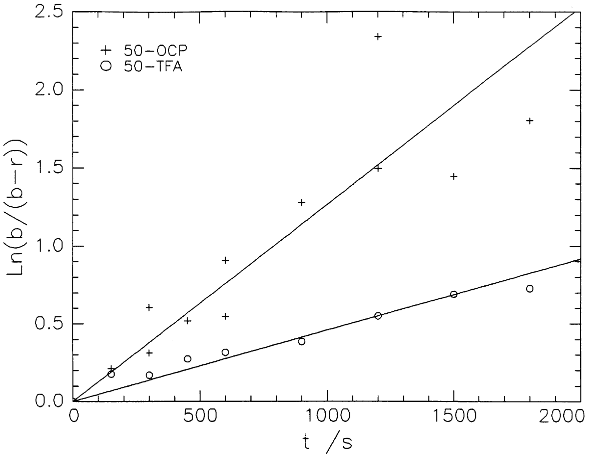

Fig. 5. Data for 50-OCP (crosses) and 50-TFA (open circles), plotted according to Eq. 3. Least squares-fits to the data are overlaid.

However, when we examine the application of second order reversible reaction kinetics (Eq. 3). hereafter referred to as Devaux's analysis, there is a clear linear dependence on *t*, as seen in Fig. 4(d). We conclude that transesterification reactions between PET and PEN follow second order reversible kinetics and all subsequent data were analysed in this way.

Data for both 50-TFA and 50-OCP are plotted according to Devaux's analysis (Eq. 3) in Fig. 5. Clearly, the reaction proceeds more slowly in the end capped blends. The least squares fits to the data are also overlaid in Fig. 5 and the values of *k*, determined from a least squares fit to the data, are given in Table 1.

4. Conclusions

From a qualitative inspection of peak heights for the TEN sequences alone, it is evident that transesterification occurs more slowly when the hydroxyl ends of both polyesters are capped with trifluoroacetate groups. Quantitative analysis of the data according to the reversible second order kinetics proposed by Devaux confirms this and also demonstrates that the reaction kinetics are consistent with a reversible

Table 1
Rate constants for transesterification in 50-OCP and 50-TFA at 300°C

Sample	k (10^{-3} s^{-1})
50-OCP	1.27 ± 0.09
50-TFA	0.46 ± 0.02

second order reaction, as assumed by other authors [6]. The rate constant for transesterification at 300°C was reduced by a factor of almost three when the participation of the hydroxyl end groups was removed by capping. As far as we are aware, this is the first direct evidence that hydroxyl end groups play a major role in transesterification between PET and PEN. This result almost certainly extends to other polyester blends and consequently has implications for all studies where strong organic acids have been used in the blend preparation, inadvertently leading to end group modification that, in turn, may influence reaction rates.

Finally we stress that the kinetic data for transesterification presented here for 50-TFA does not exclude the influence of carboxylic acid end groups which remain unmodified.

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