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Transesterification in Poly(ethylene terephthalate). Molecular Weight and End Group Effects

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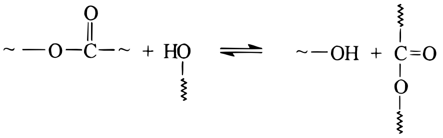
ABSTRACT: Small-angle neutron scattering has been used to determine the rate constants for transesterification reactions between hydrogenous and deuterated poly(ethylene terephthalate)s. Intimate mixtures of the two polymers at a weight fraction composition of 0.5 were pressed into plaques and heated for a range of times at temperatures of 543, 553, and 563 K. The small-angle-scattering cross sections were collected for the plaques on quenching to ambient temperature. These data were analyzed using a procedure based on second-order kinetics developed earlier and which has been applied to a range of polyesters. From the rate constants obtained the activation energy and preexponential factor for the transesterification reaction have been obtained. Aspects of the reaction that have been investigated were the molecular weight of the hydrogenous polymer and the ratio of hydroxyl to carboxyl end groups in a hydrogenous polymer, the molecular weight of which was close to that of the deuterio polymer. Although there is an increase in the rate constant as the average molecular weight decreases, there is no effect of molecular weight on the activation energy that has an average value of 168 kJ mol^{-1}. The increase in rate constant with a decrease in molecular weight indicates the importance of the role of end groups in the transesterification reaction. The relative contribution of hydroxyl or carboxyl groups to the reaction mechanism could not be discerned from these data. It is speculated that this is due to the dominant role of the hydroxyl end group in the reaction since the concentration of this varied but little in the mixtures.

Introduction

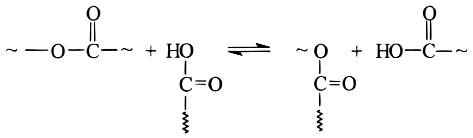
Interchange reactions between polymers can be of significant importance since they can lead to a more uniform molecular weight distribution and, where at least two chemically distinct polymers are involved, random copolymers are the final product.[1] These reactions are commonly associated with polyesters and polyamides, but interchange reactions of polycarbonates[2−7] have been reported. Interchange reactions between polyesters have been much discussed and a variety of methods applied to determining the mechanisms and kinetics of the reaction and the composition of the reaction products. These include NMR,[8−12] mass spectrometry,[13−16] and small-angle scattering methods,[17−25] NMR being particularly informative for reactions between chemically different polymers.

Such interchange reactions between polyesters are collectively termed transesterification and this encompasses three main reactions:

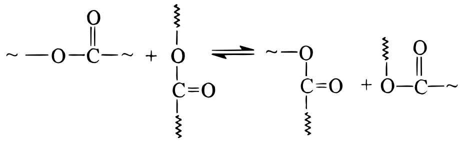
Alcoholysis:



Acidolysis:



Ester interchange:



Alcoholysis and acidolysis of polyesters by low molecular alcohols or carboxylic acids were first investigated some 60 years ago, and the rate of acidolysis was noted to be much less than that of alcoholysis.[26] Kinetic parameters for ester interchange are sparse, and in some cases, the role of end groups has not been appreciated and consequently the data could be used erroneously.

Investigations of transesterification reactions between chemically identical polyesters are even more infrequent than those between different polyesters because quantitative evaluation of the reaction progress is confined to one technique, small-angle neutron scattering. This requires that one of the polymers be deuterated, and there are few routes developed to provide a wide range of deuteriopolyesters. Transesterification studied by small-angle neutron scattering (SANS) was first applied

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to poly(ethylene terephthalate) (PET) by Zachmann et al.;[20] however, the kinetic analysis of the data was not fully developed and the absolute values of the rate constants need some correction. This notwithstanding, the activation energy obtained was on the order of the magnitude expected. Subsequently, the changes in the SANS cross section on transesterification were reevaluated from a theoretical viewpoint and related to the scission–recombination kinetics of transesterification reactions by Benoit, Fischer, and Zachmann[19] subsequently referred to here as BFZ. This procedure has been used since on a small range of polyesters, the majority being main chain liquid crystal polyesters and in one case a mixture of PET and polybutylene terephthalate.[18,21–23] There has been no reanalysis of transesterification in PET, as far as we are aware, and moreover, there are unresolved questions regarding the relative contributions of alcoholysis, acidolysis, and ester interchange to the transesterification reaction. In an earlier paper on a main chain liquid crystal polyester, based on experiments on polyesters using a limited range of molecular weights, MacDonald et al.[22] suggested that end groups had a significant influence on the reaction kinetics. Consequently this aspect still requires clarification and moreover the relative contribution of –OH and –COOH groups also needs evaluation.

We report here the results of a SANS study on transesterification between deuterio- and hydrogenous PET. We have explored the influence of temperature, molecular weight of the hydrogenous PET at one fixed temperature and the end group balance, i.e., the –COOH/–OH ratio, in hydrogenous PET over a range of temperatures. These data are preceded by an outline of the BFZ theory and the method of extraction of rate constants from the data together with some comments regarding the applicability of the SANS technique.

Theoretical Background

In a mixture of hydrogenous and deuterated polyesters transesterification leads to the distribution of H and D repeat units over all the polymer molecules in the system. In the absence of any degradation or continued polymerization (both of which are assumed to be absent), the number of polymer molecules does not change. As the transesterification reaction proceeds the sequence length of H and D units decreases, the reaction being symbolized by

$$\mathrm{H{-}H} + \mathrm{D{-}D} \rightleftharpoons 2\mathrm{H{-}D}$$

This equation illustrates the *effective* scission and recombination reactions because the same reaction between H–H molecules (or D–D molecules) only, produces no net effective change. The reverse reactions of relevance between H–D molecules are those leading to H–H and D–D molecules because only these are effective in influencing the H–D species concentration. Denoting the number of H–H, D–D, and D–H bonds in the system at any time t as $S_{\mathrm{H}}(t)$, $S_{\mathrm{D}}(t)$ and $S_{\mathrm{HD}}(t)$ then the rate of formation of H–D bonds is

$$\frac{\mathrm{d}S^{\mathrm{f}}_{\mathrm{HD}}(t)}{\mathrm{d}t} = k_{\mathrm{f}} S_{\mathrm{H}}(t) S_{\mathrm{D}}(t)$$

The reverse reaction is only half as effective because interreaction between H–D molecules may also result in no change in the distribution for half of the reactions

$$-\frac{\mathrm{d}S^{\mathrm{r}}_{\mathrm{HD}}(t)}{\mathrm{d}t} = k_{\mathrm{r}}\left[\frac{S_{\mathrm{HD}}(t)}{2}\right]^2$$

The two rate constants for a mixture of polyesters which differ only in their isotopic compositions will be equal, i.e.

$$k_{\mathrm{f}} = k_{\mathrm{r}} = k$$

Thus, the net rate of formation of H–D bonds is

$$\frac{\mathrm{d}S_{\mathrm{HD}}(t)}{\mathrm{d}t} = k\left[S_{\mathrm{H}}(t)S_{\mathrm{D}}(t) - \frac{S_{\mathrm{HD}}{}^2(t)}{4}\right] \qquad (1)$$

At equilibrium

$$S_{\mathrm{HD}}{}^2(t) = 4S_{\mathrm{H}}(t)S_{\mathrm{D}}(t)$$

In the polyester mixture the total number of repeat units (of all types) is N_{T} and the mole fraction of D repeat units is x, then before any transesterification has taken place, S_{D} and $N_{\mathrm{T}}x$ and $\mathrm{SH} = N_{\mathrm{T}}(1 - x)$. When reaction is in progress and there have been $S(t)$ efficient scissions, i.e., leading to a change in average D or H sequence length, then

$$S_{\mathrm{D}}(t) = N_{\mathrm{T}}x - S(t)$$

$$S_{\mathrm{H}}(t) = N_{\mathrm{T}}(1 - x) - S(t)$$

$$S_{\mathrm{HD}}(t) = 2S(t)$$

Substituting these expressions for $S_D(t)$ etc into eq 1 gives

$$\frac{\mathrm{d}S(t)}{\mathrm{d}t} = \frac{k}{2}[(N_{\mathrm{T}}x - S(t))(N_{\mathrm{T}}(1 - x) - S(t)) - S^2(t)] \quad (2)$$

and thus

$$S(t) = N_{\mathrm{T}}x(1 - x)\left[1 - \exp\left(-\frac{k}{2}N_{\mathrm{T}}t\right)\right] \qquad (3)$$

Evidently each efficient scission and recombination increases the number of D and H blocks in the mixture by 1. Initially we have N_{D} deuterio repeat units located in m_{D} polyester molecules and the number-average degree of polymerization is then $X^{\mathrm{D}}_{\mathrm{n}}(0) = N_{\mathrm{D}}/m_{\mathrm{D}}$. After a reaction time t when there have been $S(t)$ efficient scissions, the number-average degree of polymerization for the deuterated sequences in the mixture is now

$$X^{\mathrm{D}}_{\mathrm{n}}(t) = \frac{N_{\mathrm{D}}}{m_{\mathrm{D}} + S(t)}$$

Similarly for the hydrogenous sequence we have

$$X^{\mathrm{H}}_{\mathrm{n}}(t) = \frac{N_{\mathrm{H}}}{m_{\mathrm{H}} + S(t)}$$

Assuming the polyester chains had a Gaussian configuration and applying the random phase approximation in conjunction with the asymptotic properties of the scattering laws for a Gaussian chain, BFZ were able to write down the SANS cross section for such a partially reacted system as

$$\frac{N_T(b_H - b_D)^2}{d\Sigma/d\Omega} = \frac{Q^2a^2}{12x(1-x)} + \frac{1}{2x(1-x)}\left[\frac{1}{X_n^D(t)} + \frac{1}{X_n^H(t)} - \frac{1}{X_n^{Av}}\right] - 2\chi \tag{4}$$

where **Q** is the scattering vector defined as $(4\pi/\lambda)\sin\theta$ for neutrons of wavelength λ and a scattering angle 2θ to the incident beam direction, X_n^{Av} the number-average degree of polymerization of the whole sample, i.e., $1/X_n^{Av} = x/X_D(0) + (1-x)/X_H(0)$, and χ is the interaction parameter between the D and H forms of the polyester. Replacing for $X_n^D(t)$ and $X_n^H(t)$

$$\begin{aligned}\frac{N_T(b_H - b_D)^2}{d\Sigma/d\Omega} &= \frac{Q^2a^2}{12x(1-x)} + \frac{1}{2x(1-x)} \times \left[\frac{m_D + S(t)}{N_D} + \frac{m_H + S(t)}{N_H} - \frac{1}{X_n^{Av}}\right] - 2\chi \\ &= \frac{Q^2a^2}{12x(1-x)} + \frac{1}{2x(1-x)} \times \left[\frac{m_D}{N_D} + \frac{S(t)}{N_D} + \frac{m_H}{N_H} + \frac{S(t)}{N_H} - \frac{1}{X_n^{Av}}\right] - 2\chi \end{aligned} \tag{5}$$

Before any transesterification, and on the assumption that the D and H polyesters are miscible at a molecular level, then

$$\frac{N_T({b_H}^2 - b_D)^2}{d\Sigma/d\Omega} = \frac{Q^2a^2}{12x(1-x)} + \frac{1}{2x(1-x)}\left[\frac{m_D}{N_D} + \frac{m_H}{N_H} - \frac{1}{X_n^{Av}}\right] - 2\chi$$

Consequently if the left-hand side is plotted as a function of Q^2 a linear plot should result with a slope $(a^2/12x(1-x))$ and an intercept at $Q = 0$ given by

$$Z(0) = \frac{1}{2x(1-x)}\left[\frac{1}{X_n^D} + \frac{1}{X_n^H} - \frac{1}{X_n^{Av}}\right] - 2\chi \tag{6}$$

where m_D/N_D and m_H/N_H have been replaced by $(X_n^D)^{-1}$ and $(X_n^H)^{-1}$ respectively.

After a reaction time t, the intercept at $Q = 0$ from the SANS data is (from eq 5)

$$Z(t) = \frac{1}{2x(1-x)}\left[\frac{1}{X_n^D} + \frac{1}{X_n^H} - \frac{1}{X_n^{Av}} + \frac{S(t)}{N_D} + \frac{S(t)}{N_H}\right] - 2\chi$$

but $N_D = N_T x$ and $N_H = N_T(1-x)$, and because molecular weights of polyesters are modest, then χ can be assumed to be zero.

$$\therefore Z(t) = Z(0) + \frac{1}{2x(1-x)}\left[\frac{S(t)}{x(1-x)N_T}\right]$$

Replacing for $S(t)$ given in eq 3

$$Z(t) = Z(0) + \frac{1}{2x(1-x)}[1 - \exp(-kN_Tt/2)] \tag{7}$$

A series of values for $Z(t)$ for different reaction times in conjunction with a single value before transesterification commences, $Z(0)$, can thus be manipulated to provide the rate constant k for the transesterification reaction.

In summary the application of SANS to transesterification in polyesters requires samples to be a mixture of deuterated and hydrogenous polyesters. At the outset the molecules composing the mixture are either fully deuterated or fully hydrogenous. The scattering cross section when plotted according to eq 5 should be linear, in the intermediate Q range, with a slope determined by the statistical segment length, a, and a finite intercept at $Q = 0$, which is symbolized by $Z(0)$. As transesterification takes place, the deuterated and hydrogenous repeat units become dispersed over all polymer molecules in the mixture. In the SANS data this produces a reduction in the scattered intensity as the extent of reaction increases. As the reaction proceeds the average degree of polymerization of the deuterated (or hydrogenous) sequences in the polyester molecules (which are now isotopic copolymers) decreases as the number of effective scissions increases. This decrease in sequence length produces an increase in the intercept, $Z(t)$, when data is plotted according to eq 5. This variation in $Z(t)$ can be used to provide the rate constant for the transesterification reaction.

In the initial mixture, the contrast between deuterio and hydrogenous polyester is large and the sequence length of each is also large since they are homopolymers. The reduction in the intensity of scattering in the initial stages of the reaction is large because the isotopic composition difference between molecules is still large but the scission and recombination with different isotopic species has a profound influence on the scattering. In these early stages of the reaction SANS is very sensitive to the kinetics. At later stages in the reaction two factors reduce the sensitivity quite markedly. First the sequence lengths of hydrogenous and deuterated repeat units become too short to have a sufficiently strong dependence on Q that is observable in the data. Second the composition of the molecules approach each other and the average scattering length density per repeat unit approaches a common value, i.e., in eqs 4 and 5, $b_H \approx b_D$, and there is no excess coherent scattering above incoherent background scattering.

Experimental Section

Materials. Hydrogenous Poly(ethylene terephthalate) (HPET). All HPETs used were supplied by ICI plc and were dissolved in a 1:1 (w/w) mixture of trichlorobenzene and phenol, precipitated in methanol, and recovered as powders. Subsequent X-ray fluorescence on the vacuum-dried PET showed that all traces of metallic catalyst residues were removed by this process. A portion of the HPET with the highest molecular weight (code A) was redissolved in the trichlorobenzene−phenol mixture and heptane added (with stirring) to precipitate the majority of the polymer. The residue remaining in solution was then precipitated in methanol and dried under vacuum at 313 K. This HPET was coded B. A third HPET, coded C, was an oligomeric polymer and, apart from the dissolution−precipitation procedure, was used as received. Viscosity average molecular weights were obtained for each of these polymers from dilute solution viscometry using hexafluoro2-propanol solutions and parameters of the Mark−Houwink−Sakurada equation from the literature.[27] The molecular weights of these polymers are given in Table 1.

A further three HPET samples were used to investigate the influence of end group balance (−COOH:−OH ratio) on the kinetics of the reaction; these all had approximately the same

Table 1. Molecular Weights and −COOH/−OH End Group Ratios in Poly(ethylene terephthalate)s

polyester	molecular weight/ 10^3 g mol^{-1}	mole ratio of end groups −COOH/−OH
A	34.4	1
B	4.5	1
C	1.9	1
11	19.6	0.36
40	21.9	0.62
22	20.6	0.88
DPET1	23.1	1
DPET2	13.6	1

molecular weight but with different levels of carboxylic acid end groups. In order of increasing level of acid end group these are coded 11HPET, 40HPET, and 22HPET, the values of the ratio were supplied by ICI and obtained using an IR spectroscopic method.

Deuterated Poly(ethylene terephthalate) (DPET). DPET was prepared according to the method previously published by Gümther and Zachmann[28] using dimethyl terephthalate prepared from deuterioterephthalic acid and deuterio ethylene glycol. The DPET obtained was examined by ^{1}H NMR for purity and its molecular weight obtained from intrinsic viscosity in hexafluoro-2-propanol solution. Two DPETs were used in this work, one with a high molecular weight, DPET1, which was used in mixtures with HPET A, B. and C. The lower molecular weight, DPET2 was used in mixtures with the HPETs prefaced by the codes 11, 40, and 22.

Transesterified Sample Preparation. Intimate mixtures of HPET and DPET were prepared by co-dissolving the two polymers in the trichlorobenzene−phenol mixed solvent followed by precipitation into methanol. The precipitates were Soxhlet extracted for 48 h with methanol before drying under vacuum at 413 K for 3 days. The temperature was then increased to 433 K for 2 h immediately before transesterification to remove final traces of water.

A sample of the mixture (which contained equal weights of D and HPET) was placed in an infrared sample preparation die and subjected to a load of 5 tons under vacuum for 30 s. The solid disk obtained was then quickly placed in a hole cut in a nickel plate (∼0.5 mm thick), and the top and bottom were covered with polyimide film. This assembly was placed between the previously heated platens of a laboratory press, and the platens were brought into contact with the nickel plate and polymer. The entire region where the platens were situated was suffused with a continuous flow of dry nitrogen. After a set time at the transesterification temperature, the mold platens were separated and the nickel plate plus partially transesterified polyester mixture rapidly plunged into ice water. The transparent polyester specimen was then recovered and dried under vacuum until required. A similar preparation method was used in our earlier work on transesterification of a main chain liquid crystal polymer,[22] and viscometry showed that no degradation had taken place. The range of temperature used is limited by the rate of reaction; below 543 K the reaction is too slow, and approaching 573 K the reaction becomes too fast and uniformity of reaction and temperature throughout the sample becomes questionable.

Small-Angle Neutron Scattering (SANS). All SANS data were collected at room temperature using the LOQ neutron diffractometer at the U.K. pulsed neutron source, ISIS, at the Rutherford Appleton Laboratory. Calibration of the scattered neutron intensity in terms of scattering cross section, $d\Sigma/d\Omega$ was made using the scattering from mixtures of deuterio and hydrogenous polystyrene of known molecular weight and composition. Data were normalized for variations in sample thickness and transmission and the background scattering subtracted. This background scattering was calculated as the volume fraction weighted sum of the scattered intensities of pure DPET and pure HPET that had been subjected to the same thermal treatment as the mixtures and were essentially amorphous. The range of scattering vector used was $0.01 \leq Q/\text{Å}^{-1} \leq 0.25$, and typical data collection times were on the order of 1−2 h, longer times being used for those specimens subjected to longer transesterification times and/or higher temperatures of transesterification.

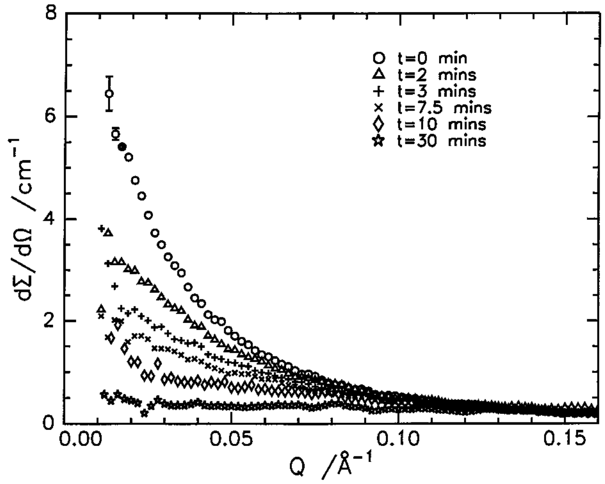

Figure 1. Coherent scattering cross section for mixtures of DPET1 with hydrogenous poly(ethylene terephthalate) A, weight fraction composition 0.5, heated at 553 K for the times indicated.

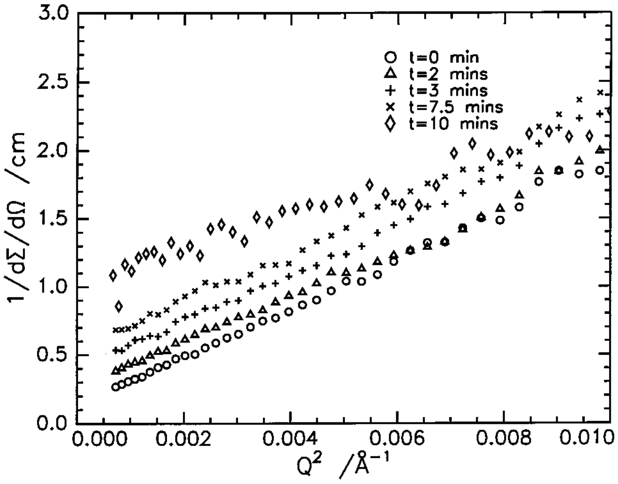

Figure 2. Data of Figure 1 plotted in the Zimm representation suggested by eq 5.

Results

Figure 1 shows the coherent scattering cross section obtained for mixtures of DPET1 with HPET A at a weight fraction of 0.5 held for various times at 553 K. Error bars are only shown on the data for the specimen with no transesterification, these are typical of the counting errors for all the specimens. Note that data for 30 min of transesterification has essentially no excess scattering above the incoherent background, the reaction has progressed sufficiently that the deuterated sequences are not long enough to generate excess scattering, and the contrast between the different PET molecules is insufficient. The BFZ interpretation and theory of transesterification suggests that these data when plotted in the Zimm plot manner, i.e., $d\Sigma(Q)/d\Omega$ as a function of Q^2, should produce a series of linear data sets all approximately parallel to each other. As transesterification proceeds, i.e., for increased times at 553 K, the intercept at $Q = 0$ should become larger. Figure 2 shows the data plotted in this manner and evidently the data sets for longer times have larger intercepts relative to that for no heat treatment. Except

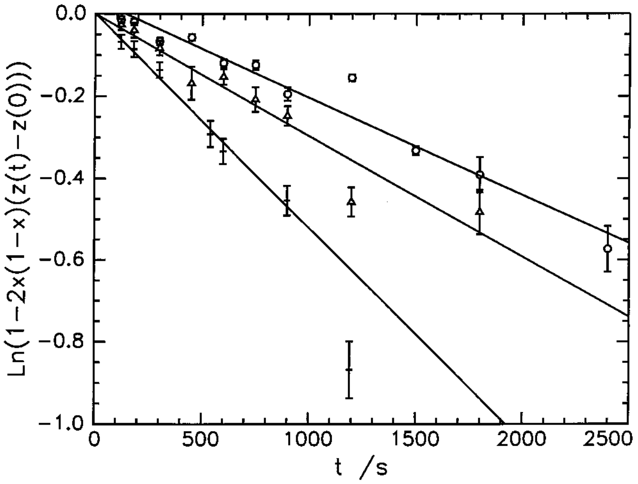

Figure 3. Intercepts from Zimm plots of scattering cross section plotted according to eq 8, for mixtures of DPET1 and PET A at temperatures of (○) 543 K, (△) 553 K, and (+) 563 K.

Table 2. Temperature Dependence of Rate Constants for Deuterio Poly(ethylene terephthalate)−Hydrogenous Poly(ethylene terephthalate) Mixtures

	k/cm^3 mol^{-1} s^{-1}			
T/K	DPET1/A	DPET2/11	DPET2/40	DPET2/22
543.15	0.054 ± 0.006	0.191 ± 0.03	0.137 ± 0.05	0.152 ± 0.04
553.15	0.081 ± 0.01	0.210 ± 0.03	0.227 ± 0.04	0.210 ± 0.07
563.15	0.189 ± 0.007	0.656 ± 0.04	0.518 ± 0.06	0.660 ± 0.09

for the longer times of holding at 553 K the data plotted in this way are approximately parallel to each other. The intercept at $Q = 0$ is the quantity $Z(t)$, and eq 7 relates $Z(t)$ at finite extents of transesterification (i.e., reaction time t) to the rate constant of the reaction. This equation can be rearranged to give

$$\ln[1 - 2x(1 - x)(Z(t) - Z(0))] = -t/\tau \tag{8}$$

where τ is the relaxation time of the reaction and $\tau = 2/(kN_T)$.

Consequently when plotting $Z(t) - Z(0)$ according to eq 8, we anticipate a series of straight lines with a negative slope from the value of which we can obtain the rate constants at each temperature. Figure 3 shows the intercepts of Figure 2 plotted according to eq 8 with linear least-squares fits to the data points. The rate constants obtained are given in Table 2, which includes rate constants obtained over the same temperature range for mixtures of deuterio PET with hydrogenous PET with differing ratios of carboxylic acid to hydroxyl ends. These latter data pertain to the lower molecular weight DPET2 mixed with the different hydrogenous PET polymers.

In a separate series of SANS experiments, DPET1 was mixed with two hydrogenous PET polymers with lower molecular weights than that of PET A. These mixtures were heated at one temperature only (543 K) for different times and from the SANS data on these heat treated mixtures, the rate constants in Table 3 were obtained.

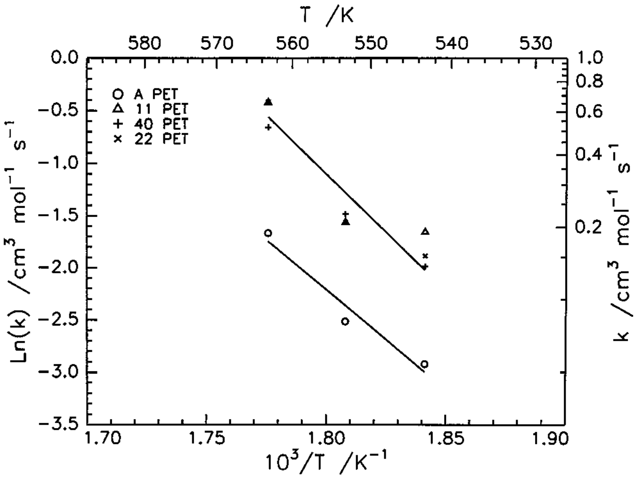

Figure 4. Arrhenius plot of rate constants obtained for all DPET and hydrogenous poly(ethylene terephthalate) mixtures at a weight fraction of 0.5. Solid lines are linear least-squares fits to the data.

Table 3. Molecular Weight Dependence of Rate Constants for Transesterification at 543.15 K

polyester mix	k/cm^3 mol^{-1} s^{-1}
DPET1/A	0.054 ± 0.006
DPET1/B	0.063 ± 0.008
DPET1/C	0.21 ± 0.01

Table 4. Parameters of the Arrhenius Equation for Transesterification of PET

PET mixture	E_a/kJ mol^{-1}	A/cm^3 mol^{-1} s^{-1}
DPET1/A	159 ± 30	9.6×10^{13}
DPET2/11	156 ± 75	1.6×10^{14}
DPET2/40	169 ± 25	2.1×10^{15}
DPET2/22	186 ± 62	1.1×10^{17}

Discussion

Referring to eq 5 which describes the Q dependence of the reciprocal scattering cross section as transesterification proceeds, there should be no change in slope during the course of the reaction. Each data set should be parallel to that for no transesterification but displaced vertically to higher reciprocal cross section because the scattering intensity decreases as the transesterification reaction increases its conversion. Figure 2 shows that this prediction prevails for much of the data, although at larger reaction times the slope of $N_T(b_H - b_D)^2/(d\Sigma(Q)/d\Omega)$ does seem to reduce somewhat. From the slope of the data plotted as in Figure 2, the statistical step length a for PET can be obtained, and this value should not vary whatever the extent of transesterification. (Some practical limitations to the use of SANS to follow transesterification have been noted earlier which will influence the possibility of obtaining the values of a.) From a total of 89 separate SANS data sets for mixtures of deuterio PET with hydrogenous PET at a weight fraction of 0.5, the average value of a obtained was 20 ± 3 Å over the range of temperatures and the extent of transesterification investigated.

Figure 4 is an Arrhenius plot of the rate constants given in Table 2. The activation energies and preexponential factors obtained for each combination of deuterio and hydrogenous PET are collected in Table 4. Because of the limited temperature range the activation energies obtained are within the errors of each individual value and the average activation energy is 168 ± 18 kJ mol^{-1}, we make no comments regarding the preexponential factors since they are subject to large uncertainties due to the extremely long extrapolation used and the limited range of temperatures for which we were able to obtain data. Although the activation energy is not influenced by the deuterio/hydrogenous combination, it is quite

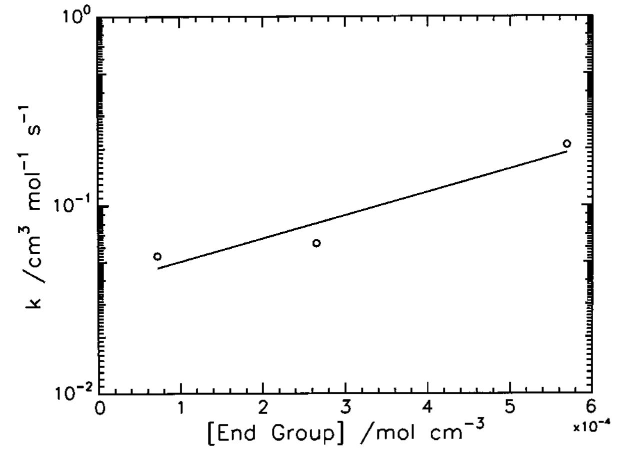

Figure 5. Second-order rate constants obtained for transesterification in mixtures of DPET2 with hydrogenous PETs 11, 40, and 22 at 543 K plotted as a function of the molar concentration of all end groups.

clear from Figure 4 that the values of the rate constant are affected by the nature of the PET. The major difference between DPET1/HPET A and the other combinations in Table 2 is the molecular weights of the polyesters concerned, HPET 11, 40, and 20 are all approximately the same molecular weight but much less than the molecular weight of HPET A. Furthermore, DPET2 is almost half the molecular weight of DPET1. The role of molecular weight in the transesterification reaction is made clear by the rate constants (at 543 K) given in Table 3 for mixtures of DPET1 with different molecular weights of hydrogenous PET. The ratio of −OH to −COOH end groups in these mixtures was the same at approximately unity. As the molecular weight of the hydrogenous PET is reduced, the concentration of end groups increases. Figure 5 shows the rate constants plotted as a function of the molar concentration of end groups in DPET1−hydrogenous poly(ethylene terephthalate) in the mixture. The linear least-squares fit to a semilogarithmic plot of these data gives the relation

$$\log k = -1.42 + 1235[\text{end group}]$$

and for infinite molecular weight polymer, i.e., [end group] = 0, this suggests that the rate constant for direct ester interchange is 0.038 cm^3 mol^{-1} s^{-1}. Evidently the overall concentration of end groups in the PET mixture has a significant influence on the rate of transesterification, and this accelerates rapidly as the end group concentration increases.

The question remains as to which end group is more effective at promoting the interchange reaction, carboxyl or hydroxyl? A priori, based on the results using low molecular weight carboxylic acids and alcohols,[1] we expect that the hydroxyl group to be more effective. Although the carboxyl to hydroxyl end group ratio for hydrogenous poly(ethylene terephthalate)s 11, 40, and 22 differ from each other, this is not reflected in the rate constants of Table 2, and the errors associated with the Arrhenius plots also mean that we cannot discern any dependence of the parameters on [COOH]/[OH] ratio. Although the level of carboxyl end groups varies over a 2-fold range in these mixtures, the hydroxyl end group level does not have the same range, that of sample 11 being ca. 1.4 times that of sample 40, which is approximately equal to the −OH end group level of sample 22. An explanation of the apparent absence of any influence of carboxyl groups could be that the rate of transesterification due to the hydroxyl groups is much greater than that due to the carboxyl groups, and hence the influence of these latter chain ends on the reaction kinetics is unobservable. This hypothesis is borne out by a separate NMR study of transesterification in mixtures of PET and polyethylene-2,6-naphthalene dicarboxylate.[29]

The rate constants and the relation for the effective number of scissions, $S(t)$, can be used to obtain some insight into aspects that may be of more direct relevance if two polyesters from different sources are being combined by melt mixing. These are the change in the number-average molecular weight of a sequence of like repeat units and the weight fractions of homopolymer and mid and end sequence blocks of like repeat units as a function of the reaction time. These aspects have been discussed by Kotliar[30] and applied to polyamides by Miller.[31] Strictly, for Kotliar's equations to be applicable, the reacting mixture should be one phase, the molecular weight distributions of each component should be the most probable, and the interchange reaction should be a random cleavage followed by random coupling of ends. Furthermore, although Kotliar's equations are quoted in terms of number-average molecular weights, he states they are equally applicable to all molecular weight averages when the most probable distribution prevails. The number of efficient scissions, $S(t)$, is calculated on the basis of all polyester molecules in the mixture. From these data we have calculated the average number of scissions per molecule, $\bar{S}_m(t)$ and the average molecular weight of a deuterio PET sequence has been calculated from

$$M_D(t) = M_D(0)/(1 + \bar{S}_m(t)) \tag{9}$$

This average molecular weight includes homopolymeric deuterio PET and sequences incorporated into isotopic copolymers either as end sequences or as mid sequences, i.e., flanked by hydrogenous PET.

The weight fraction of pure deuterio PET (which will be of reduced molecular weight because of transesterification) is given by

$$W(D) = [1/(1 + \bar{S}_m(t))]^2 \tag{10}$$

The weight fraction of end block deuterio PET sequences is

$$W(\text{D}-) = \frac{2\bar{S}_m(t)}{(1 + \bar{S}_m(t))^2} \tag{11}$$

i.e., as a result of one scission and recombination (with hydrogenous PET) of a deuterio PET molecule. Finally the weight fraction of middle block (two or more cleavages) deuterio PET sequence is

$$W(-\text{D}-) = \bar{S}_m{}^2(t)/(1 + \bar{S}_m(t))^2 \tag{12}$$

Figure 6 shows the average molecular weight calculated for DPET1/A mixtures using typical values of the rate constant over the temperature range explored. There is a rapid decrease in the average molecular weight in the first 400 s for the values of k used, followed by a continuous slow decline over the whole time scale used in the calculations. Discrimination between the different

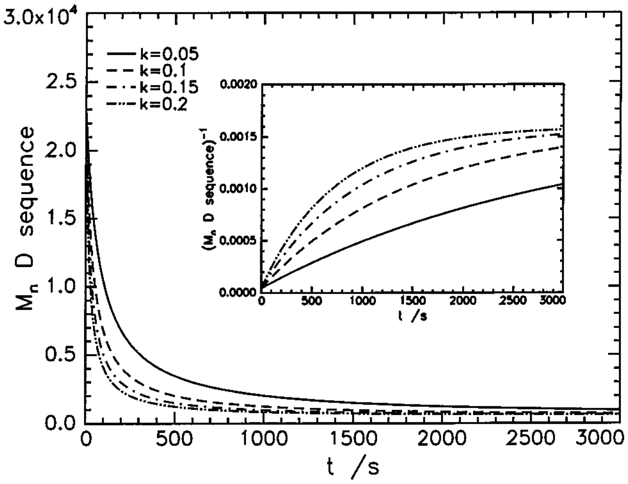

Figure 6. Average molecular weight of deuterio poly(ethylene terephthalate) sequences in DPET1/A mixtures as a function of transesterification time. Rate constants used are within the range obtained experimentally and values used are given. Inset: same data plotted in reciprocal form to clarify the influence of the rate constant.

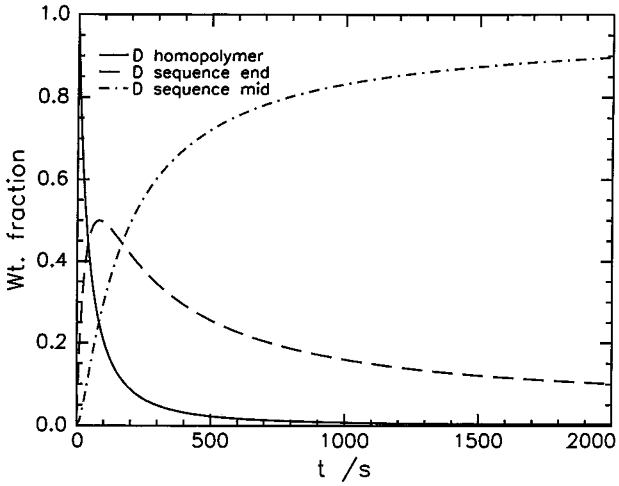

Figure 7. Weight fractions of homopolymeric DPET1 and end and mid DPET1 sequences calculated as a function of transesterification time and for a rate constant of 0.05 cm^3 mol^{-1} s^{-1}.

rates is made easier where the reciprocal of the average molecular weight is plotted as a function of reaction time as shown in the inset of Figure 6. The equilibrium average molecular weight obtained at long transesterification times and high temperatures suggests that on average a sequence of three consecutive D PET repeat units exists in the copolymers formed.

This rapid fall in average molecular weight of D sequences is reflected in the very rapid decrease in the weight fraction of homopolymeric D PET (Figure 7) even for the lowest rate constant used in the calculation. After ca. 2 min, the weight fraction of homopolymer is ca. 0.15. The weight fraction of deuterated sequences that are surrounded by hydrogenous material increases rapidly initially but slows down as transesterification proceeds. The end-deuterated sequence concentration passes through a maximum as the reaction goes to higher conversion but even at long reaction times there is still a finite weight fraction of end-deuterated sequences.

The curves in Figures 6 and 7 illustrate the reason that the sensitivity of SANS to transesterification becomes much reduced as reaction extent increases and which was alluded to earlier. These aspects are made clear by the SANS data obtained for DPET1/A mixtures held at 573 K. At this temperature, the reaction is extremely rapid, and after 5 min, there is essentially no excess scattering from which the rate constants can be derived. Because of the rapidity of reaction and the finite time required for uniformity of temperature to be obtained, shorter reaction times cannot be used without incurring considerable uncertainty, and consequently, we have not attempted to use SANS to obtain kinetic parameters for transesterification at 573 K.

Conclusions

Small-angle neutron scattering has been successfully used to establish second order rate constants for transesterification in poly(ethylene terephthalate). The rate of reaction is highly dependent on the concentration of end groups in the mixture (i.e., molecular weight of polymers). Although hydrogenous poly(ethylene terephthalate)s with differing ratios of carboxylic acid to hydroxyl end groups were used, no influence of this ratio could be discerned. This has been attributed to the hydroxyl group balance being little different in the hydrogenous polymers and the rate constant for alcoholysis being significantly higher than that for acidolysis. The activation energy of the transesterification reaction is not influenced either by the concentration of end groups or their nature and has a value of 168 ± 18 kJ mol^{-1}.

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