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Small angle neutron scattering investigation of transesterification in Poly(ethylene terephthalate)-poly(Butylene terephthalate) mixtures

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Abstract

The transesterification reaction between polyethylene terephthalate and polybutylene terephthalate (PBT) was investigated by small-angle neutron scattering. For this purpose deuterio polyethylene terephthalate (dPET) was synthesised and fractionated to produce three samples whose molecular weight ranged from circa 14 000 g mol^{-1} to 63 400 g mol^{-1}. Mixtures of these two polymers containing 10% of the deuterio polymer were transesterified to varying extents by heating for known times at different temperatures. The apparent molecular weight of the deuterio polymer decreases as the extent of reaction increases and this is observed in the small-angle scattering data. From these data second order rate constants were obtained, the values are somewhat larger than those obtained for main-chain mesomorphic polyesters but of the same order of magnitude for transesterification in polyethylene terephthalate alone. No influence of the large difference in molecular weight of the dPET on the rate constants was observed. The activation energy obtained from these data was 61 ± 7 kJ mol^{-1}, a value which is less than half that reported for other polyester transesterifications. The reaction appears to be dominated by the scission of the PBT component of the mixture. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Transesterification; Polyester; Kinetics

1. Introduction

Transesterification is a generic term applied to a collection of intermolecular reactions between polyester, which include alcoholysis, acidolysis and ester interchange. These reactions take place readily not only between polyesters but also such polymer combinations as polymethacrylate and polycarbonate [1], polyester and polycarbonate [2–16] and polymethacrylate with polyester. The reaction of similar characteristics between polyamides is termed transamidation [17]. Although fundamental aspects of transesterification reactions were set out over 50 years ago by Flory [18] the kinetic and mechanistic data available for such reactions between two polymers is very small.

Until recently, the work reported by Devaux [2–5] probably constituted the most concentrated analysis of the transesterification reaction. NMR was used as the analytical method, and was successful because two chemically distinct polymers were used. The progress in reaction was followed by the growth in amplitude of a new resonance owing to the adjacency of different units in the co-polyester molecule resulting from transesterification. This method has more recently been applied to transesterification in polyethylene terephthalate and polyethylene-1,6-naphthalene dicorboxylate mixtures [19] but only one study extracts rate constants for the overall transesterification reaction from these NMR data (A. Bunn, A.M. Kenwright, S.K. Peace, and R.W. Richards, unpublished results).

NMR as a diagnostic method to follow the extent of reaction becomes more restricted when the two reacting polymers are chemically identical since no change in environment of the functional groups occurs on reaction. As we set out in more detail later, the transesterification reaction is a dynamic equilibrium reaction during which the sequence length of units, which originated from a particular starting chain become shorter and shorter. The number of polymer chains in the reacting system does not decrease (if the system is sealed and no thermal degradation takes place) and, therefore, the average molar mass does not change. However, if the molecules of one type were uniquely observable it would appear as if their molecular weight decreased as the transesterification reaction progressed as a result of the distribution of segments over all macromolecules in the reacting system.

Deuterating one of the reacting polymers makes it observable by small angle neutron scattering (SANS) and this was

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capitalised on by Kugler et al. [21] over 10 years ago in a study of the transesterification kinetics of polyethylene terephthalate. The analysis of these data was not rigorously correct, but an appropriate way of analysing the data was developed by Benoit et al. [22,23] and first applied to a main-chain aromatic terpolyester by MacDonald et al. [24]. Since then a small number of other polyesters examined by SANS [25,26] and one report of its application to the transamidation reaction [17], however, in the majority of reports values of rate constants are not given and there are no speculations about the mechanism of the reaction.

In an earlier paper [27] we discussed the use of ^{13}C NMR to determine the sequence length distribution as transesterification proceeds in PET–polybutylene terephthalate (PBT) mixtures. We report here the use of SANS to evaluate kinetic parameters and subsequent mechanistic insight into the transesterification reaction between PET and PBT. Our aims were to establish rate constants and activation energies for the reaction and secondly, by noting the influence of molecular weight on the rate constant, to determine the relative importance of end group driven reactions (alcoholysis, acidolysis) vis a vis ester exchange. An outline of the salient aspects of the theory developed by Benoit et al. [22] is given followed by the experimental procedure used. The data obtained and the kinetic parameters evaluated are set out, and we close with a comparison of the various constants obtained and some speculations about the reaction mechanism.

2. Theory of small angle neutron scattering from transesterifying systems

The relevant equation to be applied to SANS data for transesterifying polymers was obtained by Benoit et al. [22] by generalising the random phase approximation expression derived by de Gennes and applying this to copolymers. In the range of intermediate scattering vector, Q, defined by $1/R_g \le Q \le b$, the scattering law is simplified by the absence of cross-term contributions and the coherent scattering cross-section $\mathrm{d}\sigma(Q)/\mathrm{d}\Omega$, is related to the molecular parameters by Eq. (1)

$$\frac{N_T(a_D - a_H)^2}{\mathrm{d}\sigma(Q)/\mathrm{d}\Omega} = \frac{Q^2b^2}{12x(1-x)} + \frac{1}{2x(1-x)}\left[\frac{1}{n_D(t)} + \frac{1}{n_H(t)} - \frac{1}{n_T^o}\right] - 2\chi. \tag{1}$$

The scattering vector is defined by the neutron beam wavelength, λ, and scattering angle 2θ via the relation

$$Q = \frac{4\pi}{\lambda}\sin\theta.$$

Radius of gyration and statistical step length of the polymer are denoted by R_g and b respectively and x is the number fraction of deutero repeat units which at a time t after reaction has begun has a degree of polymerisation $n_D(t)$. The number average degree of polymerisation of hydrogenous sequences is $n_H(t)$, and n_T^o is the number average degree of polymerisation of the mixture, which is assumed to be constant. (This last assumption was verified experimentally [21].) The coherent scattering lengths of the hydrogenous and deutero monomers are a_H and a_D, respectively and there are N_T monomer units of all types per unit volume. Inspecting Eq. (1), the Q independent part, denoted by z is

$$z = \frac{1}{2x(1-x)}\left[\frac{1}{n_D(t)} + \frac{1}{n_H(t)} - \frac{1}{n_T^o}\right] - 2\chi, \tag{2}$$

which will be the intercept if the left-hand side of Eq. (1) is plotted as a function of Q^2. Evidently as the reaction proceeds and $n_D(t)$ and $a_H(t)$ decrease then z increases in magnitude. From a consideration of the number of efficient scissions and recombination, i.e. those that lead to the bonding of hydrogenous and deuterated sequences, Benoit et al. obtained

$$z(t) - z(0) = \frac{1}{2x(1-x)}[1 - \exp(-t/\tau)], \tag{3}$$

where τ is the relaxation time of the second order reaction between molecules with a rate constant k, i.e.

$$\tau = 2/kN_T. \tag{4}$$

There are two points to make about the use of Eqs.(1)–(4). Firstly, if the reacting species differ only in the deuterium labelling and the molecular weight is not large then $\chi = 0$. If the two polyesters are miscible and the value of χ is finite, as long as the value of χ does not change with extent of transesterification, its value is immaterial because the subtraction in Eq. (3) removes it. If χ is sufficiently large that the polymers are immiscible, then reaction may only take place at the interface between them and the value of k obtained may be an artefact. In such cases transesterification generally causes the polymers to become miscible but this may be at a fairly advanced state of the reaction.

Secondly the ability to observe the reaction by SANS relies on there being sufficient contrast between the deuterium labelled molecules and the matrix. Clearly as reaction proceeds, the molecules become more and more compositionally alike and consequently the scattering signal decreases in amplitude, the signal to noise ratio becomes larger and eventually the excess scattering above the flat incoherent background becomes negligible.

3. Experimental

3.1. Polyesters

PBT was obtained from Polysciences and dissolved in dichloroacetic acid followed by precipitation into dry methanol. The polymer was Soxhlet extracted overnight

Table 1
Weight average molecular weights of PBT and dPET fractions obtained form intrinsic viscosities

Polymer	$\overline{M}_w/10^3$ g mol^{-1}
PBT	31
DPETF1	14.1
DPETF2	31.6
DPETF3	63.4

with dry methanol to remove trace amounts of dichloroacetic acid, followed by drying to constant weight under vacuum at 313 K.

Deuterio polyethylene terephthalate (dPET) was prepared from deuterio dimethyl terephthalate using the method described by Gumther and Zachmann. The reaction mixture obtained after cooling was treated in the same way as the PBT previously. From ^{13}C NMR the deuteration of this polymer was at least 95 at.% based on H/D exchange. The melting point of the dPET obtained by differential scanning calorimetry was 525.4 K when a heating rate of 10 K min^{-1} was used. A 3% w/v solution of dPET in dichloroacetic acid was prepared and heptane slowly added whilst it was vigorously stirred. When a permanent cloudiness in the solution was obtained no further heptane was added but stirring continued for an additional 2 h to ensure completion of precipitation–dissolution processes. Stirring was then stopped and the precipitate allowed to settle before being filtered off, washed and dried. The procedure was repeated to obtain three fractions of dPET weighing between 3 and 5 g each.

Molecular weights of dPET fractions and the PBT were obtained by dilute solution viscometry. For PBT the solvent used was a 40:60 w/w mixture of 1,1,2,2-tetrachloroethane and phenol, the Mark–Houwink coefficients of which (K and α) are 9.31×10^{-2} ml g^{-1}and 0.87 at 303 K [28]. Dry trifluoroacetic acid was used as the viscometry solvent for dPET, at 303 K the Mark–Houwink coefficients are 43.3×10^{-2} ml g^{-1}and 0.68[29]. Table 1 reports the molecular weights obtained for all polymers.

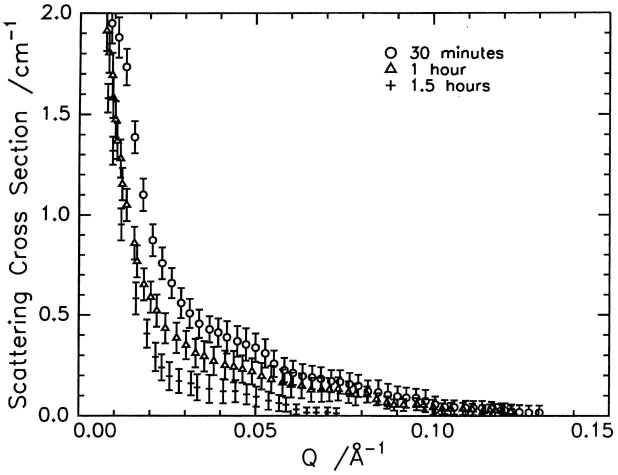

Fig. 1. Scattering cross-sections as a function of scattering vector for the 10% mixture of deutero polyethylene terephthalate (dPETF3) and polybutylene terephthalate after heating at 523 K for the times indicated.

3.2. Small angle neutron scattering

Mixtures of PBT and each fraction of dPET containing circa 10% w/w of dPET were prepared by co-dissolution in dichloroacetic acid and precipitation in methanol, followed by Soxhlet extraction and drying. Samples from each mixture were placed in small glass tubes, which were evacuated and sealed before being placed in an oil bath at a known temperature for a defined time. The temperatures used were 476, 523 and 573 K and the maximum times at each of these temperature were 6 h, 3 h, and 30 min, respectively. These temperatures were selected on the basis of differential scanning calorimetry data on PET–PBT mixtures [30] that showed the existence of a melting point at 472 K after minimal heat treatment at 476 K. The two higher temperatures were selected to provide sufficient range to allow evaluation of activation energy but minimising the possibility of degradation. Following heat treatment the mixtures were compression moulded into plaques approximately 1 mm thick. Each blend was first compressed at 300 K in a mould with polyimid film between polyester and compressing plates. The temperature of the plates was then raised to 530 K at 100 K min^{-1} and the applied pressure increased to 30×10^5 N m^{-2}, the specimen was held under these conditions for 90 s. Following release of pressure the polyester specimen was rapidly withdrawn, quenched in ice water and finally dried under vacuum.

SANS data on each sample were obtained using the LOQ diffractometer at the ISIS pulsed neutron source at the Rutherford Appleton Laboratory, Oxfordshire, UK. The useable Q range was $0.01 \leq Q/\text{Å}^{-1} \leq 0.2$ and the incident beam was defined by a 10 mm diaphragm immediately before the sample. Scattered intensities were normalised and corrected for thickness and transmission effects and the incoherent background subtracted was calculated as the weight fraction weighted sum of the scattered intensity from pure PBT and pure dPET. Finally the scattered intensity was converted to absolute coherent neutron scattering cross section using the scattering from a mixture of hydrogenous and deuterated polystyrene of known scattering cross section.

4. Results and discussion

Typical SANS profiles obtained for partially transesterified mixtures are shown in Fig. 1. A notable feature is the small scattering cross-sections observed owing to the low deuterio polymer content in the mixtures. At these small scattering cross-sections the differences in detector response at the different values of Q become evident. It is this aspect which is responsible for the oscillations in the scattering

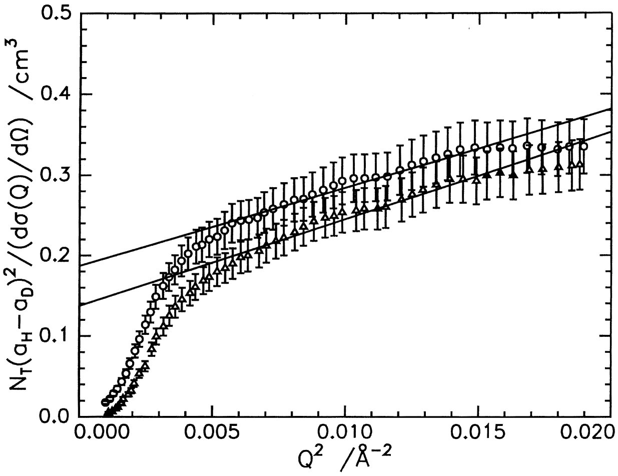

Fig. 2. Scattering cross-sections for 10% mixture of dPETF1 with PBT plotted in the Zimm form suggested by equation 1. The solid lines are linear least-squares fits to the data over the range $0.006 \le Q^2$/Å$^{-2} \le 0.015$. Both sets of data pertain to transesterification at 523 K for 2 hours (○) and 2.5 hours (△).

cross section at higher Q values. At low Q there is a steep increase in the scattering cross-section and for the different specimens we note that the curves coalesce at low Q. This very intense scattering at low Q is attributed to long period scattering from crystalline regions of PBT. PBT crystallises very rapidly on cooling and it could not be completely suppressed no matter how quickly the samples were quenched on removal from the press during the preparation of plaques of the partially transesterified PET–PBT mixture. We stress at this point that this crystallisation takes place after the transesterification reactions were carried out and therefore this crystallinity has no bearing on the kinetics of the reaction. A similar coalescence in scattering cross section is also noted at high Q, where the scattering is determined by the intrinsic incoherent scattering cross-section of the specimens. Since the composition of each specimen is approximately identical in terms of D and H content, the high Q scattering is expected to be more or less the same for all samples. In the Q range between these two extremes the scattering cross section depends on the duration of the transesterification reaction, becoming smaller as the reaction proceeds. The data were also plotted in Zimm plot form suggested by Eq. (1) and linear least square lines fitted to the data between $0.005 \le Q^2$/Å$^{-2} \le 0.017$, typical examples of which are given in Fig. 2. The influence of the excess long period scattering owing to the crystalline regions is evident in Fig. 2 as abrupt decrease in the reciprocal scattering cross section for Q^2 less than circa 0.003 Å^{-2}. From these plots values of $z(t)$ were obtained as the intercept at $Q^2 = 0$ and values of b, the statistical step length of the dPET obtained from the slope. For the lower temperature of transesterification (476 K), the average value of b obtained from all data was 10 ± 1 Å. For the highest temperature (and hence greatest extent of transesterification), 573 K, the value of b was slightly smaller at 8 ± 1 Å.

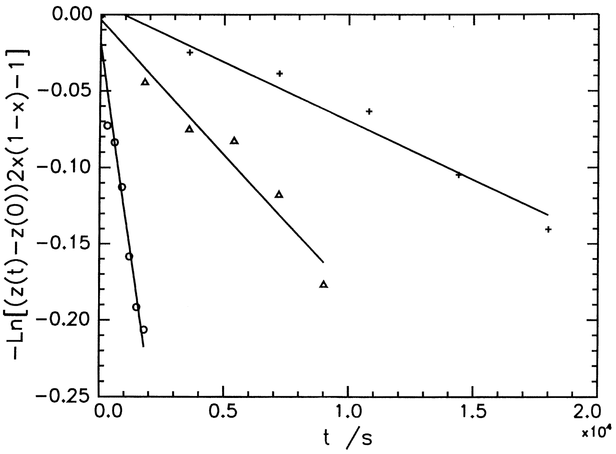

Fig. 3. Intercepts for dPETF3 at $Q = 0$ from Zimm type plots of figure 2 after subtraction of the intercept for zero transesterification plotted according to equation 3. The solid lines are linear least-squares fits to the data. ○ 573 K, △ 523 K, + 476 K.

Fig. 3 shows the values of $z(t)$ plotted in a manner suggested by Eq. (3), and linear least squares fit to the data for dPETF3 at each of the temperatures investigated. Table 2 reports the relaxation times, τ, obtained from the slopes and the rate constants obtained per mole of repeat unit per unit volume evaluated from the values of τ. For dPETF1, a value of τ could not be obtained for the highest transesterification temperature because the reaction was so rapid that no SANS intensity above background was observable. The extent of dispersion of the deuterated segments in these samples was so great that insufficient contrast was generated between ‘labelled’ molecules and matrix. An Arrhenius plot of all the rate constants is given in Fig. 4 and a single line was drawn through all the data because there appears to be no evidence from these data that the activation energy is molecular weight dependent. From the linear least squares fit to all the data the activation energy for the reaction was calculated to be 61 ± 7 kJ mol^{-1}.

The values of the statistical step length obtained from the scattering data are of the same order as reported for other polyesters. MacDonald et al. [24] reported values of b from 9 to 40 Å as the transesterification temperature increased of a main-chain aromatic liquid crystal polymer. This stiffening was attributed to the higher temperatures approaching the nematic region of the terpolymer investigated. Li et al. [31] report a value of 26 Å for b of a mesormorphic polyester with a flexible spacer group of 10 methylene units in the chain. Arrighi et al. [26] did not directly extract values of statistical step length for a similar co-polyester as that used by Li et al., but estimated a value between 60 and 120 Å in comparison to the theoretical expressions for the dependence of the radius of gyration on polymer molecular weight. Most synthetic polymers have statistical step lengths in the range 6–20 Å [32], consequently the value

Table 2
Relaxation times and rate constants obtained from SANS data

dPET Fraction	476 K		523 K		573 K	
	τ/10^5 s	k/10^{-3} s^{-1} mol cm^{-3}	τ/10^5 s	k/10^{-3} s^{-1} mol cm^{-3}	τ/10^5 s	k/10^{-3} s^{-1} mol cm^{-3}
dPET F1	8.54 ± 0.30	0.39 ± 0.01	3.15 ± 0.16	1.1 ± 0.1	—	—
dPET F2	5.6 ± 1	0.60 ± 0.09	2.3 ± 0.2	1.48 ± 0.13	0.48 ± 0.04	7.1 ± 0.5
dPET F3	5.3 ± 0.4	0.63 ± 0.04	2.4 ± 0.2	1.4 ± 0.1	0.38 ± 0.03	8.9 ± 0.6

of 10 Å obtained here for the lowest extent of transesterification is in the anticipated range. The slightly smaller values at the highest extent of transesterification studied are just outside the estimated error in the values of *b*. The longer methylene groups sequence in PBT would be expected to reduce the value of *b* to some extent as a result of the increased flexibility from the ‘dilution’ of phenylene rings in the backbone. Thus incorporation of PBT units will lead to a reduction in *b*. However, it should be noted that the extent of transesterification observable by SANS is not large because of the reduction in contrast as reaction proceeds. Thus a significant reduction in statistical step length may require considerably longer reaction times with consequent loss of contrast and no measurable scattering. For dPETF3 evaluating the intercept of the Zimm plot as a molecular weight of the PET block, then after 30 min at 573 K, the average block molecular weight was circa 7000. This corresponds to an average sequence length of circa 35, i.e. considerably more reaction is needed before individual dPET units are spread over all molecules. The SANS signal will have become a featureless constant value at all *Q* long before this complete transesterification point is reached.

We now turn to the rate constants obtained for the second order reaction, Table 2, and compare them with values in the literature for other polyester combinations. The most direct comparison is with the data of Li et al. [25] for mesomorphic polyester and that of MacDonald et al. [24] for mesomorphic terpolyester. PET–PBT transesterification has rate constants which are of the same order of magnitude as those observed by Li et al. [25], the highest value observed by us being some 5 times the largest noted by Li et al. [25]. The rate constants reported here are about the same magnitude as those reported by MacDonald et al. The rate constants are considerably smaller than those obtained by Kugler et al. [21] (after approximately correcting their reported rate constants to the same basis as those obtained for dPET–PBT transesterification) for PET alone. However, S.K.Peace, R.W. Richards (unpublished data) have recently redetermined the rate constants for transesterification in PET and their values of *k* are of the same magnitude as those for the PET–PBT mixtures discussed here. It appears that the rate constants reported by Kugler are anomalously large, an aspect also commented on by Li et al. [25]. This disparity in rate constant values may be attributable to the role of end groups in the transesterification process. If the reaction is mainly driven by the end groups, then the lower molecular weights of polyester will lead to an increased transesterification rate, yielding higher apparent rate constants. There is some evidence to suggest that transesterification is an end group driven reaction [24] and the use of dPET fractions here was deliberately chosen to explore this aspect. However, the variation in rate constant with molecular weight observed is not sufficiently consistent at each temperature for us to make definitive statements about this. At the lowest reaction temperature used (476 K), the rate constants increase as the molecular weight of the dPET increases. This is also true for the two rate constants obtained at 573 K, but the values of *k* at 523 K for each PET fraction are essentially all identical. Consequently the evidence for the role of end groups in the reaction is not strong. What data we have suggests that the end groups are not the reaction foci for transesterification in PET–PBT, i.e. ester interchange is the dominant reaction. However, since the molecular weight of the PBT was not varied there is the possibility that the PBT end groups may be the rate determining units.

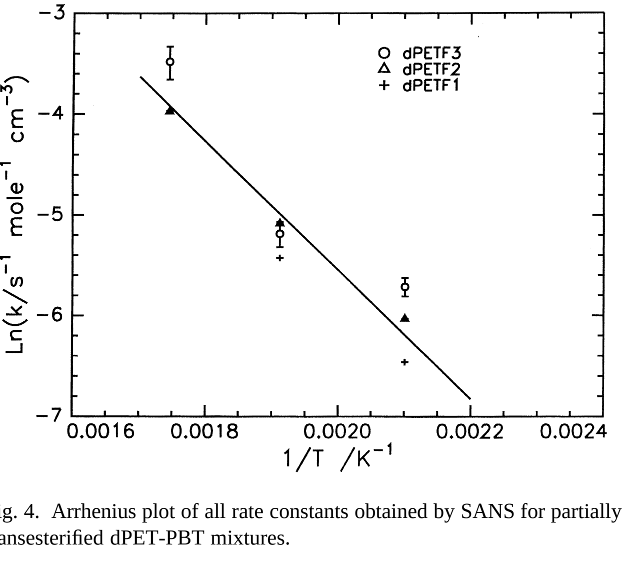

Fig. 4. Arrhenius plot of all rate constants obtained by SANS for partially transesterified dPET-PBT mixtures.

Rate constants are fundamental kinetic parameters of any reaction, but for transesterification reactions in polyesters the germane information is the average length of a sequence of identical monomer units, and how this varies with time and reaction conditions. To obtain this we require the number of efficient scissions (i.e. those that are not followed by a re-combination of the same two species formed) as a function of time. For reaction times much less than the relaxation time and for equal degree of polymerisation of

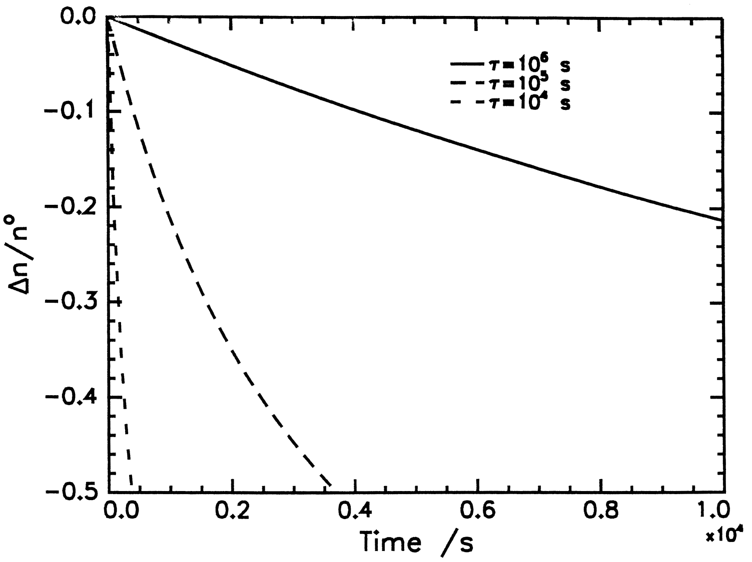

Fig. 5. Relative change in degree of polymerisation for a polyester undergoing transesterification with relaxation times for the reaction in the range determined from the SANS analyses presented here.

hydrogenous and deuterated polyester, the number of efficient scissions per polymer molecule is given by

$$S(t) = 2x(1 - x)n_D^o t/\tau.$$

For the purpose of using transesterification reactions to obtain block co-polyesters with defined properties, it is the relative changes in the degree of polymerisation, i.e. how much the apparent degree of polymerisation of the labelled block has decreased relative to the starting degree of polymerisation, that is of importance.

$$\frac{\Delta n_D(t)}{n_D^o} = \frac{-S(t)}{1 + S(t)}.$$

The variation of $\Delta n_D(t)/n_D^o$ for the range of τ values encountered here is shown in Fig. 5 for a typical polyester degree of polymerisation of 150. From this figure at the highest temperature investigated $\Delta n_D(t)/n_D^o$ is -0.5 after circa 1000 s, i.e. the average degree of polymerisation is 50% of the original degree of polymerisation, a figure which is commensurate with the approximate molecular weights reported earlier obtained from the SANS data. It is appropriate here to point out that SANS, like all scattering techniques, is most sensitive to the larger species present and thus the parameter obtained from SANS may be biased by this sensitivity to longer sequences. There may be smaller sequences of dPET distributed over all molecules, but which are of insufficient length to contribute to the observable Q dependent scattering and thus they play no role in determining the value of $d\sigma(Q)/d\Omega$, consequently the rate constants obtained may be smaller than the true values. Additionally the extent of transesterification observable by SANS is much smaller than that accessible to NMR when chemically distinct polyesters are used and this may further limit the accuracy of the rate constants.

Lastly we comment on the value of the activation energy obtained. At 61 kJ mol^{-1} this is less than half the value reported for other polyesters of circa 150 kJ mol^{-1} and smaller than the activation energies reported for transesterification reactions between polyesters and polycarbonate (100–130 kJ mol^{-1}). Since the rate constants observed are not altered significantly from those for other polyesters, the pre-exponential factor is important in bringing the rate constants into the range observed for all polyesters. Transesterification of PET alone has an activation energy of -150 kJ mol^{-1}, it seems that it must be some feature of the PBT which reduces the activation energy and gives a smaller pre-exponential factor. There is some evidence that ester exchange is the dominant mechanism here and this may be owing to the easier scission of PBT relative to that of PET as a result of the tetramethylene sequence in PBT. There is a rapid acceleration in the scissions in the polyester mixture as the reaction temperature increases (see Fig. 5), this can be rationalised by noting where the reaction temperature is relative to the melting point. PBT crystallises rapidly and readily and at 476 K the temperature is some 20° below the melting point and thus the competition between crystallisation and transesterification will favour crystallisation and the apparent rate of transesterification will be small. At 523 K this competition between the two processes is just in favour of the transesterification reaction. At 573 K the driving force for crystallisation of PBT is effectively zero and a significantly enhanced rate of transesterification is observed and thus the number of effective scissions is increased.

5. Conclusions

SANS on partially transesterified mixtures of PET and PBT has demonstrated that transesterification reactions take place and the data were analysed to provide rate constants. The rate constants were of the same magnitude as those for other polyesters but the activation energy was considerably less than for these other reactions. For the lowest temperature studied here, the reduced rate was attributed to the competition between crystallisation and transesterification. For all three temperatures, the reduced activation energy indicates that PBT undergoes scission more easily than PET. Although the variation of rate constant with dPET molecular weight was not absolutely definitive, the changes in rate constant suggest ester exchange being the predominant transesterification mechanism and this support the notion that the PBT undergoes scission more easily than PET.

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