Ester interchange reactions in poly(ethylene terephthalate): Observation using small-angle neutron scattering*

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Ester interchange reactions have been studied in poly(ethylene terephthalate) (PET) by means of small-angle neutron scattering (SANS). Cast film PET samples containing 20 wt% deuterated PET chains were prepared at low temperature. The SANS molecular weight of the as-prepared specimen agrees with the g.p.c. value and the molecular dimensions are close to the unperturbed value. Samples were then annealed at temperatures of 150°C–300°C at times from 10–600 min. If ester interchange occurs in a blend sample, block copolymer chains are formed with the blocks consisting of protonated and deuterated sequences. The SANS M_w obtained from these samples is an apparent M_w, the M_w of the blocks, and is lower than the g.p.c. value. Ester interchange is shown to be rapid in the melt and also to take place at a slower rate at temperatures 15°C below T_m, in general agreement with previous studies. An apparent clustering effect at elevated temperatures is also reported.

INTRODUCTION

Many condensation polymers undergo interchange reactions at elevated temperatures. These reactions involve a redistribution of chain segments with no change in the number-average molecular weight. This redistribution, however, tends to produce the equilibrium molecular weight distribution consistent with the degree of polymerization and consequently the weight-average molecular weight can change. Indeed, the occurrence of ester interchange was first demonstrated by Flory[1] by mixing high and low molecular weight decamethylene adipate polyesters and measuring the decrease in viscosity with time. In addition to producing a more uniform molecular weight polymer, interchange reactions may also be used to form a block copolymer of two different species. A summary of the available information on interchange reactions in both polyesters and polyamides up to 1981 can be found in a review article by Kotliar[2].

Ester interchange reactions are known to occur in poly(ethylene terephthalate) (PET) both at melt temperatures and at elevated temperatures in the solid state. Recently, Dröscher and Schmidt[3] measured the kinetics of ester interchange in PET by means of a model reaction between normal PET chains and a di(oxyethylene) oxy-containing oligoester. They found that significant ester interchange takes place in minutes at melt temperatures. In the solid state, the reaction occurs at temperatures 20°C below the melting temperature, although at a much slower rate.

In this paper, ester interchange reactions in PET are examined by means of small-angle neutron scattering (SANS). The success of this technique is based on the difference in coherent scattering length between hydrogen and deuterium. Deuterium-labelled molecules are randomly dispersed in a normal (protonated) polymer matrix; small-angle scattering is observed as a result of contrast between the two types of chains. The z-average radius of gyration, R_g^z, and the weight-average molecular weight, M_w, can be evaluated from the data. If ester interchange reactions occur in a blend sample, random block copolymer chains, in which the blocks are protonated, and deuterated sequences are formed. This is shown schematically in *Figure 1*. As a result, a SANS M_w (the M_w of the blocks) which is much less than the g.p.c. M_w is obtained. Such a SANS observation of ester interchange in polycarbonate has previously been demonstrated[4]. Our purpose in performing these experiments was not to perform a detailed kinetic study of ester interchange, but more simply to examine the stability of protonated/deuterated blend samples at temperatures where these reactions occur and to determine the extent to which SANS investigations of annealing and processing of blend samples, without ester interchange effects, is possible at these temperatures.
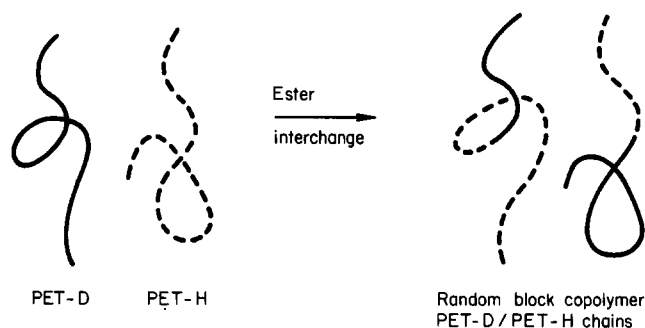
Figure 1 Ester interchange in a blend sample results in the formation of block copolymer chains, with the blocks consisting of protonated and deuterated sequences

SANS experiments on PET are relatively difficult to perform because of poor contrast between the deuterated and protonated chains and a large contribution of background scattering due to voids and other inhomogeneities. However, especially low-background samples have recently been prepared in this laboratory[5]. In these specimens, scattering is sufficiently low that single chain dimensions can be reliably obtained. Such samples are prepared at low temperature, where no ester interchange occurs.

SAMPLE PREPARATION AND CHARACTERIZATION

Deuterated PET (PET-D) was synthesized by E I du Pont de Nemours and Company from deuterated ethylene glycol and terephthalic acid. G.p.c. analysis showed $M_w = 60\,500$ and $M_w/M_n = 3.6$. The protonated material (PET-H) was commercial PET (Goodyear Cleartuff) with $M_w = 89\,800$ and $M_w/M_n = 3.1$. It should be noted that the commercial PET presumably contains transesterification catalysts used in its manufacture. Details of the sample preparation are described elsewhere[5]. Briefly, thin films are cast from solution at 60°C and then pressed under vacuum for 15 min at 100°C to reduce their void content. There is no evidence for ester interchange reactions at temperatures below 200°C. All blend samples contained 20 wt% PET-D. The as-prepared films were annealed in an oven under vacuum at temperatures from 150 to 300°C. The molecular weight of every annealed specimen was checked by g.p.c. to determine the extent to which degradation had taken place. The annealing process often produces voids. Therefore, heat-treated samples were re-pressed at 100°C before neutron scattering measurements were made.

EXPERIMENTAL

The neutron measurements were performed at the National Center for Small Angle Scattering Research (Oak Ridge National Laboratory) on the 10-m SANS instrument located at the Oak Ridge Research Reactor (ORR). For this instrument an area detector ($64 \times 64\,cm^2$) with $1\,cm^2$ element size is positioned at a fixed sample to detector distance of 4.5 m. The range of scattering vector $Q = 4\pi\lambda^{-1}\sin\theta$ sampled with this geometry is $0.007 \leqslant Q \leqslant 0.125\,Å^{-1}$ where $\lambda = 4.75\,Å$ is the incident wavelength and 2θ is the angle of scatter. The scattering patterns were corrected on a cell-by-cell basis for instrumental background and detector efficiency

variation, divided by the sample transmission (T) and thickness and normalized to a constant incident flux. Correction for the spatial variation of detector efficiency was accomplished by dividing all measured scattering patterns by the background-connected scattering from an isotropic scatterer (water or polyethylene). Blank samples of pure PET-D and PET-H were also measured to check for the presence of scattering from voids and other inhomogeneities and to provide a basis for substraction of the angular independent incoherent scattering arising principally from ^1H nuclei.

The corrected scattering patterns all exhibited cylindrical symmetry about the incident beam and the measured intensities were therefore radially averaged and converted to an absolute differential scattering cross section $d\Sigma/d\Omega\,(Q)$ per unit solid angle, per unit volume of material (in units of cm^{-1}) by comparison with the scattering of secondary standards of monodisperse polystyrenes.

RESULTS AND DISCUSSION

Figure 2 shows the scattering cross sections for completely protonated (PET-H) and completely deuterated (PET-D) samples. The scattering in the PET-H sample is very small and consists mainly of angular-independent incoherent scattering. There is a small amount of coherent scattering in the PET-D sample at low Q, presumably due to voids. This scattering is an order of magnitude less than we had previously experienced[5], however, so that the newly synthesized PET-D appears to be impurity free. The void scattering forms only a small correction to the partially labelled specimens in the Q range examined here.

A plot of $(d\Sigma/d\Omega)^{-1}\,(Q)$, the reciprocal of the absolute intensity, against Q^2 for a 20 wt% PET-D sample after appropriate background corrections is shown in *Figure 3*. The radius of gyration and molecular weight were obtained by fitting the data to the equation

$$(d\Sigma/d\Omega)^{-1}(Q) = \frac{1}{C_N M_{WD}}\left(1 + \frac{Q^2 R_g^{z2}}{3}\right) \tag{1}$$

with C_N a constant given by:

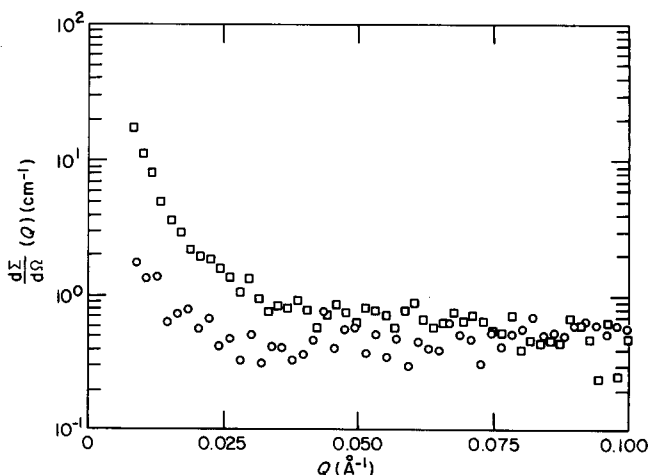$$C_N = (a_H - a_D)^2 N_A X(1-X)\rho/m_D^2 \tag{2}$$

Figure 2 $d\Sigma/d\Omega\,(Q)$ vs. Q for a protonated blank (100% PET-H, (□)) and a deuterated blank (100% PET-D, (○))
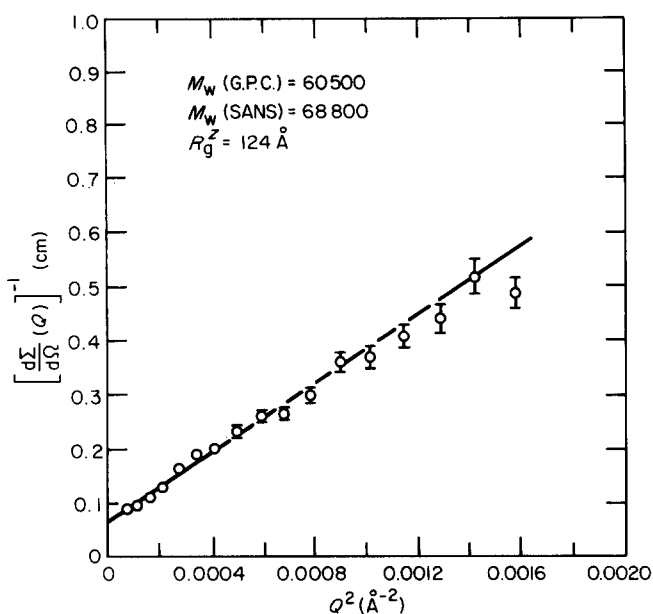
Figure 3 $(d\Sigma/d\Omega)^{-1}$ (Q) vs. Q^2 for radially averaged scattering from 20wt% PET-D $M_w = 60\,500$) in a PET-H matrix $(M_w = 89\,900)$ (as-prepared specimen)

annealed samples were re-dissolved in solution and films re-cast at 60°C. Since the as-prepared films show no evidence of clustering, the dissolution and re-casting process should allow the true SANS M_w to be determined. These samples are listed in the 'Re-cast sample' column of *Table 1*. The g.p.c. and SANS molecular weights are now in agreement at 240°C, 10 min. A Zimm plot of the sample annealed at 240°C for 10 min and its re-cast counterpart is shown in *Figure 6*. After 120 min and 600 min, the SANS M_w's (Re-cast column) are clearly less than the g.p.c. values, indicating that ester interchange has occurred at these times. At 210°C the clustering is again apparent after 120 and 600 min but there is no evidence of ester interchange, as can be seen by the agreement between g.p.c. molecular weights and SANS molecular weights in the 'Re-cast' column. At 150°C there is no evidence of clustering or ester interchange after 600 min.

The ester interchange results shown here are in at least qualitative agreement with those of Dröscher and
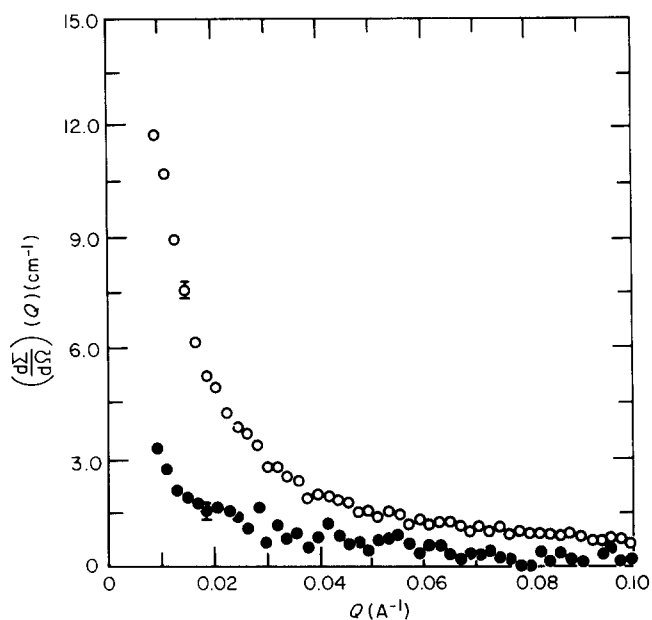
where a_H and a_D are the coherent scattering lengths of the labelled and unlabelled repeat units, m_D is the mass of the PET-D repeat unit, N_A is Avagadro's number, ρ is the density of the PET-D, M_{WD} is the molecular weight of the PET-D and R_g^z is the z-average radius of gyration. Where the molecular weight distributions are approximately matched, the volume fraction X may be replaced by the mole fraction[6]. Corrections for the mismatch in molecular weight between the H and D species were ignored as they are small ($\sim 5\%$), and the goal of the study was not the precise determination of molecular parameters. The SANS M_w of 68 800 is within 15% of the g.p.c. value (60 500). The z-average radius of gyration was converted to a weight-average radius of gyration via the known polydispersity[7] and the value of $R_g^w/M_w^{1/2}$ was calculated to be 0.376, almost identical to the value of 0.373 previously reported[5].

Ester interchange reactions were first studied in the melt ($T_m = 255°C$) at temperatures of 270 and 300°C. The scattering curves for samples annealed at these two temperatures for 10 minutes are shown in *Figures 4* and *5* with the as-prepared scattering curves plotted for comparison. At 270°C, the SANS apparent M_w is 15 400, a factor of almost 4 smaller than the g.p.c. value, implying that each of the PET-D chains has undergone on the average three interchange reactions in this time. At 300°C, the SANS apparent M_w is < 5000 after 10 min reaction time. There is a small amount of degradation ($\sim 15\%$) in the samples, but this cannot account for the rapid SANS M_w decrease observed. In this way, it is concluded that SANS does demonstrate rapid ester interchange in PET at melt temperatures.

Below the melting point the results require more discussion. At 240°C after 10 min, the SANS M_w is 103 800 compared with the g.p.c. M_w of 40 700. With increasing annealing time at 240°C the SANS M_w decreases as shown in *Table 1*. The high SANS M_w is apparently due to a clustering artifact such as has been found in other polymers, most notably polyethylene[8-10]. To separate the clustering artifact from ester interchange,

Figure 4 $d\Sigma/d\Omega$ (Q) vs. Q for a 20wt% PET-D sample annealed for 10 min ($\bullet$) at 270°C (as-prepared sample plotted for comparison ($\circ$))
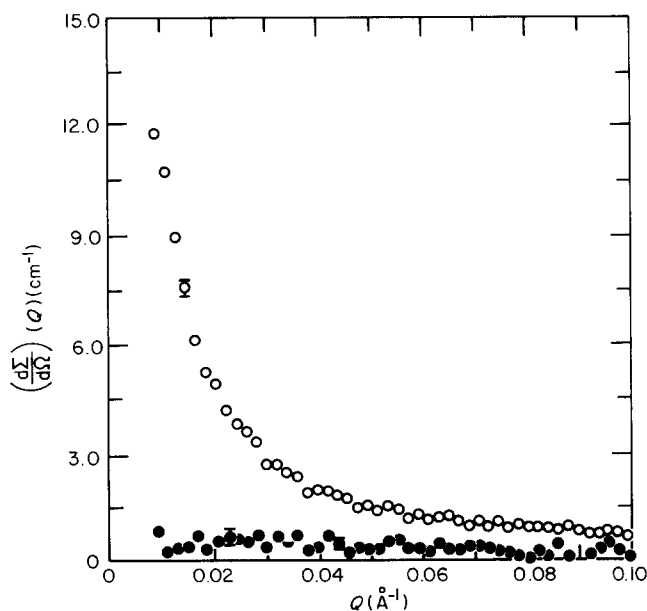

Figure 5 $d\Sigma/d\Omega$ (Q) vs. Q for a 20wt% PET-D sample annealed for 10 min ($\bullet$) at 300°C (as-prepared sample plotted for comparison ($\circ$))

Table 1 Ester interchange in the solid state

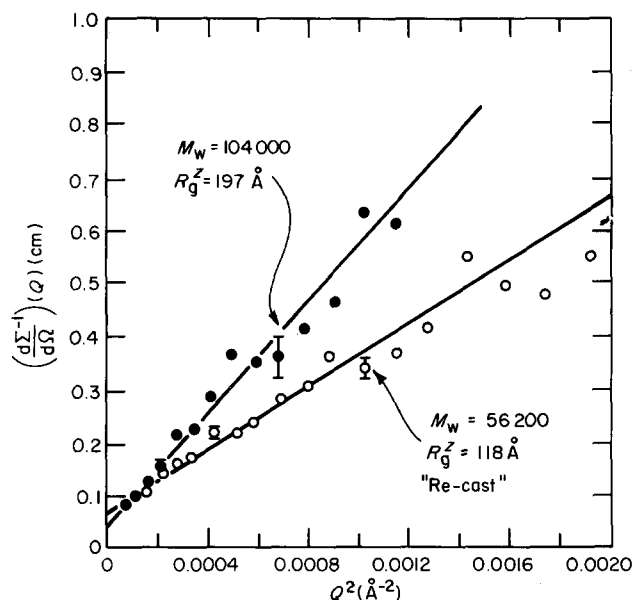| Temperature (°C)	Time (min)	M_w (SANS) $\times 10^{-3}$	R_g^z (Å)	M_w (g.p.c.) $\times 10^{-3}$	Re-cast samples M_w (SANS) $\times 10^{-3}$	R_g^z (Å)
240	10	103.8	197	42.4	56.2	101
	30	57.5	126	41.1	35.2	72
	120	55.8	126	51.2	21.4	58
	600	19.7	59	55.3	13.7	50
210	10	56.6	128	66.1	–	–
	30	48.9	116	54.5	–	–
	120	106.8	190	53.2	49.3	121
	600	60.9	133	38.8	44.6	102
150	600	58.8	111	48.1	54.5	125

Figure 6 $(d\Sigma/d\Omega)^{-1}$ (Q) vs. Q^2 for a 20 wt% PET-D sample annealed for 10 min at 240°C. Also plotted is its 're-cast' counterpart

crystallized at 240°C for 3 h. The melting points of the two materials are within 1°C. Thus, there appears to be no evidence of a melting point difference in PET.

Wu *et at.*[11] recently reported seeing severe segregation as well as ester interchange in PET samples melt-pressed at 270°C for 5 min. These samples were amorphous, further evidence that the clustering is unrelated to a melting point difference. The low temperature cast film preparation scheme used in the series of experiments reported here has the advantage that effects of ester interchange and clustering are absent in the as-prepared films. These effects clearly complicate the interpretation of PET SANS data.

ACKNOWLEDGEMENT

Schmidt; that is, ester interchange is rapid in the melt and becomes significant in the solid state at temperatures above 225°C. As mentioned earlier, the present results may be influenced by the presence of transesterification catalysts in the PET-H and so perhaps it might be possible to anneal for longer times without ester interchange with catalyst-free PET. The results clearly demonstrate, however, that it is possible to anneal for long times at temperatures below 210°C without ester interchange occurring.

The clustering artifact is somewhat surprising given the scarcity of hydrogens in PET. Clustering in polyethylene has been explained by a 6°C difference in the crystallization temperatures of PE-H and PE-D. To test whether a similar effect operates in PET, samples of PET-D and PET-H were melted at 280°C for 5 min in a differential scanning calorimeter and then isothermally

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