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Transesterification in Mixtures of Poly(ethylene terephthalate) and Poly(ethylene naphthalene-2,6-dicarboxylate): An NMR Study of Kinetics and End Group Effects

Stephen Collins, Alan M. Kenwright, Catherine Pawson, Stella K. Peace,[†] and Randal W. Richards*

Interdisciplinary Research Centre in Polymer Science and Technology, University of Durham, DURHAM, DH1 3LE, UK

W. A. MacDonald[‡] and P. Mills

ICI plc, Wilton, Teesside, TS6 8JE, UK

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ABSTRACT: Mixtures of poly(ethylene terephthalate) and poly(ethylene naphthalene-2,6-dicarboxylate) have been transesterified at temperatures between 553 and 573 K. The partially transesterified polymers were analyzed using ^{1}H NMR, and the rate constants for transesterification were obtained using a kinetic expression based on a second-order reversible reaction mechanism. The hydroxyl end groups have been shown to have a significant effect on the kinetics of the reaction by comparing rate constants obtained for the same polyester mixture but with hydroxyl end groups quantitatively esterified by trifluoroacetic acid. Carboxyl end groups do not have such a significant role in transesterification, and from the variation of rate constant at one temperature for a series of PET polymers with differing carboxyl to hydroxyl end groups, it appears that transesterification by direct ester−ester interchange is very small. The NMR data have also been used to calculate the randomness factor and number-average sequence length of the terephthalate sequences in the copolymer as transesterification progresses. The initially immiscible polyester mixture becomes miscible after a critical amount of transesterification takes place; no matter what reaction temperature is used, this homogenization takes place when the randomness factor has a value of 0.5. This does not correspond to completely random copolymer formation but suggests that the number-average sequence length of the terephthalate units in the copolyester is ca. 4−8.

Introduction

Transesterification reactions between polyesters have been investigated for a number of years,[1−3] but a coherent assembly of kinetic data has been notably absent. For much of the reported data details of the nature of the end groups and the molecular weights of the polyesters used are absent. Furthermore, the incorporation or absence of any catalyst is frequently obscure particularly when polymers of commercial origin have been used. Earlier work by us indicated clearly the importance of the nature of the end group in influencing the kinetics of the reaction.[4,5] The accompanying paper on a small-angle neutron scattering investigation of transesterification in poly(ethylene terephthalate) (PET) also demonstrates the importance of the role of end groups via the effect of molecular weight on the values of the rate constant.

In the earlier NMR investigation[5] of the melt transesterification between PET and poly(ethylene naphthalene−2,6-dicarboxylate) (PEN), we demonstrated that the mechanism follows reversible second-order kinetics and that the rate of the reaction is severely reduced when the hydroxyl end group is quantitatively esterified by trifluoroacetic acid. We report here a further NMR study of this reaction with the aims of (i) obtaining the activation energy, (ii) quantifying the role of carboxylic acid end groups in the transesterification, and (iii) assessing the extent of direct ester−ester exchange. In concert with these aims we have been able to establish the critical value of the randomness factor associated with the formation of a single homogeneous phase and the average sequence length of PET units at this point.

NMR Theory

The basis of the use of NMR in following the transesterification reaction was fully discussed in our earlier paper[5] where the second-order reversible kinetics of the reaction were established.[6] Consequently, we do no more here than provide a précis. As PET and PEN react, an increasing number of terephthalate−ethylene−naphthalate (TEN) residues form in the polymer system. The ^{1}H NMR signal from these units is at 4.85 ppm and can easily be differentiated from the resonance of TET (4.80 ppm) and NEN (4.90 ppm) sequences. The amplitude of this TEN signal, x say, is directly proportional to the mole fraction of TEN sequences in the polymer. Likewise, the amplitudes of the signals for TET (a) and NEN (b) sequences in the original unreacted mixtures are direct measures of their mole fraction composition in the polyester mixture. The rate equation for the reaction between the two polyesters is

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

where r, the transesterification ratio, is x/a. Consequently, determination of x as a function of reaction time of the polyesters at a fixed temperature allows the evaluation of the second-order rate constant k.

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* To whom correspondence should be addressed.

[†] Current address: Unilever plc, Colworth Laboratory, Sharnbrook, Bedfordshire MK44 1LQ, UK.

[‡] Current address: DuPont Teijin Films Ltd, Wilton, Middlesbrough TS90 8JF, UK.

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Table 1. Molecular Weights and Ratio of −OH to −COOH End Groups for All Polyesters

polymer	mol wt/10^3 g mol^{-1}	mole ratio of end groups −COOH/−OH
PET A	34.4	1
PET 11	19.6	0.36
PET 40	21.9	0.62
PET 22	20.6	0.88
PEN	27.3	

Experimental Section

Polyesters. PET and PEN polymers were supplied by ICI, and molecular weights were obtained by dilute solution viscometry using either hexafluoro-2-propanol or 2-chlorophenol as solvent at 298 K. For PEN intrinsic viscosity data in hexafluoro-2-propanol were used together with the Mark−Houwink parameters for PET in the absence of any available values for PEN. Consequently, the molecular weight obtained for PEN can only be an approximate value. All the molecular weights so obtained and the ratio of −COOH to −OH end groups (data supplied by ICI) in the polyesters used here are given in Table 1.

Preparation of Polyester Mixtures. Mixtures of each PET with the single PEN used were prepared after each polyester had been dried at 433 K under vacuum for 3 h. Equal weights of each polyester were dissolved in 2-chlorophenol at 353 K followed by precipitation in methanol. The polymer mixture was then Soxhlet extracted for 2 days with dry methanol and finally dried under vacuum at 313 K to constant weight. Polyesters treated in this way retain their original unmodified chain ends.

A second set of PET/PEN mixtures was prepared by dissolving equal weights of the polymer in a 1:4 v/v mixture of trifluoroacetic acid and dichloromethane and stirring for 5 days, before precipitating in methanol followed by Soxhlet extraction and drying. This procedure esterifies the original −OH end groups to produce $-O-CO-CF_3$ ends.[4] The extent of this conversion is sufficiently high that no residual −OH ends were identifiable within the accuracy of the NMR spectrometer used.

Transesterification. Samples of each mixture were encapsulated in DSC pans and placed in the furnace of a Perkin-Elmer Pyris 1 DSC. The sample was then rapidly heated (200 K min^{-1}) to the desired transesterification temperature, at which point the sample was held for known times before being rapidly quenched to room temperature. The DSC pan was then opened and the "button" of partially transesterified polymer placed in an NMR tube to which was added a 1:4 v/v mixture of deuteriotrifluoroacetic acid and deuteriodichloromethane before sealing the tube.

Analysis of Transesterified Mixtures. All mixtures before and after heating were analyzed by ^{1}H NMR using a 400 MHz Varian VXR-S spectrometer and tetramethylsilane as the internal standard. Additionally, separate PETA/PEN mixtures in both unmodified and end fluoro-esterified forms were analyzed by DSC. For this purpose the partially transesterified mixture after quenching to room temperature was reheated at 20 K min^{-1} in the DSC, and the heat capacity changes were recorded. The high heating rate of 20 K min^{-1} was used to reduce the occurrence of further transesterification during thermal analysis.

Results

Thermal Analysis. Figure 1 shows a series of DSC thermograms for the PEN/PETA mixture with unmodified hydroxyl end groups obtained after transesterification at 573 K (the highest reaction temperature used) for increasing times. Clearly evident at the lowest transesterification time are two glass transition temperatures (T_g) that converge to a single value as the reaction time increases. At this reaction temperature only a single crystallization exotherm and melting endotherm are observed due to PET. The amplitudes of both endotherm and exotherm decrease as reaction time increases, and after 5 min reaction no melting endotherm is apparent. For the two lower transesterification temperatures used, the melting endotherm of the PEN is discernible at short reaction times, i.e., before transesterification has progressed to a significant extent. Figure 2 shows the T_g values of PET and PEN in the partially transesterified mixtures as a function of the reaction time at each temperature. At 573 and 563 K the T_g for PET increases rapidly with reaction time, and there is a concomitant decrease in the T_g of PEN. After ~400 s at 573 K only one T_g is evident; for a single T_g to be observed at 563 K a slightly longer reaction time is needed. For a transesterification temperature of 553 K at least 1200 s reaction time is required before a single T_g is observed.

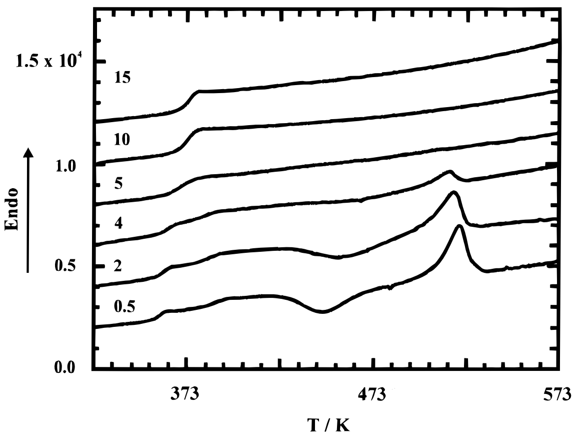

Figure 1. DSC thermograms for PEN/PETA mixtures transesterified at 573 K for the times indicated on each curve. The weight fraction composition was 0.5, and hydroxyl groups were unmodified.

Melting points showed the same dependence on reaction time and temperature. The higher the reaction temperature, the shorter the time needed before the melting points disappeared, and the partially transesterified specimens become amorphous. At the lowest temperature used (553 K), although there was a convergence of the melting points, there were always two melting endotherms observable in the DSC thermogram.

Figure 3 compares the T_g values of the PEN and PET components of the mixture for mixtures wherein the hydroxyl groups have been esterified by trifluoroacetic acid with the values for polyesters with unmodified end groups. Clearly the change in T_g is considerably slowed on esterifying the hydroxyl end groups with trifluoroacetic acid. For reaction temperatures of 553 and 563 K, over the whole range of reaction times used, two glass transition temperatures are always observable, and convergence to a single T_g is now very slow.

NMR Analysis. The NMR resonances in the region 4.8−4.9 ppm were analyzed in exactly the same manner as set out in our earlier paper using the second-order reversible kinetic scheme proposed by Devaux.[5,6] As obtained by this procedure, the rate constants are pseudo-first-order because the abscissa values, $\ln[b/(b - r)]$ (see eq 1), are dimensionless. To convert these rate constant values to more conventional units (concentration$^{(1-n)}$ time^{-1}, where n is the order of the reaction), enabling comparison with rate constants for transesterification in PET alone, we have multiplied the rate

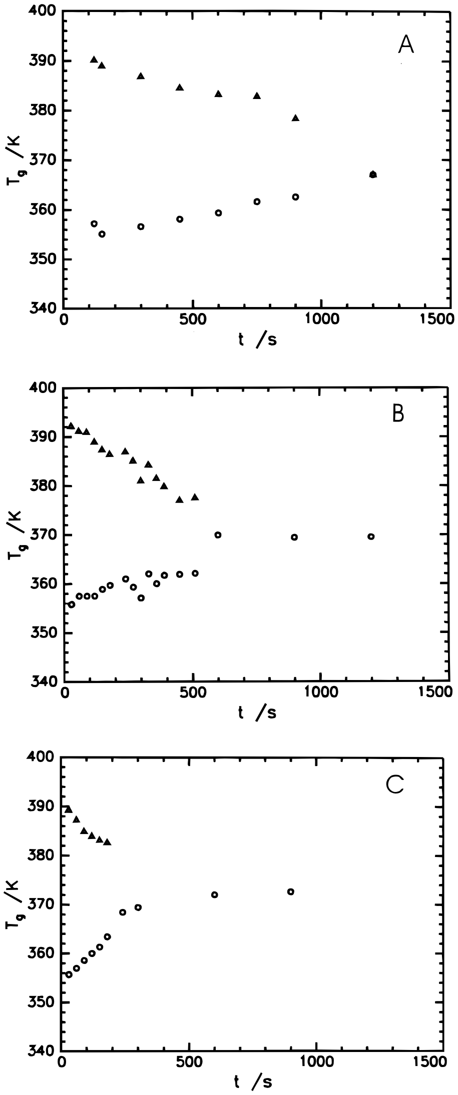

Figure 2. T_g values recorded as a function of reaction time for PEN/PETA mixtures (weight fraction 0.5) with unmodified hydroxyl groups at reaction temperatures of (A) 553, (B) 563 K, and (C) 573 K.

constants by the repeat unit molecular weight of PET divided by the density of molten PET (1.15 g cm^{-3}). We accept that this procedure introduces some inaccuracy, but in the absence of a value for the density of molten PEN it appears to be the most reasonable manner to produce rate constants in conventional units. The values obtained are set out in Table 2.

Discussion

Notwithstanding the coprecipitation of the PET/PEN mixtures, it is evident from the thermal analysis data that the PET and PEN exist as separate phases until there has been a critical extent of reaction between them and thereafter a single T_g is observed. For −OH-terminated PETA in a 50:50 mixture with PEN, the final value of the T_g is 369 ± 1 K. The reaction time needed to achieve this is highly dependent on the transesterification temperature used.

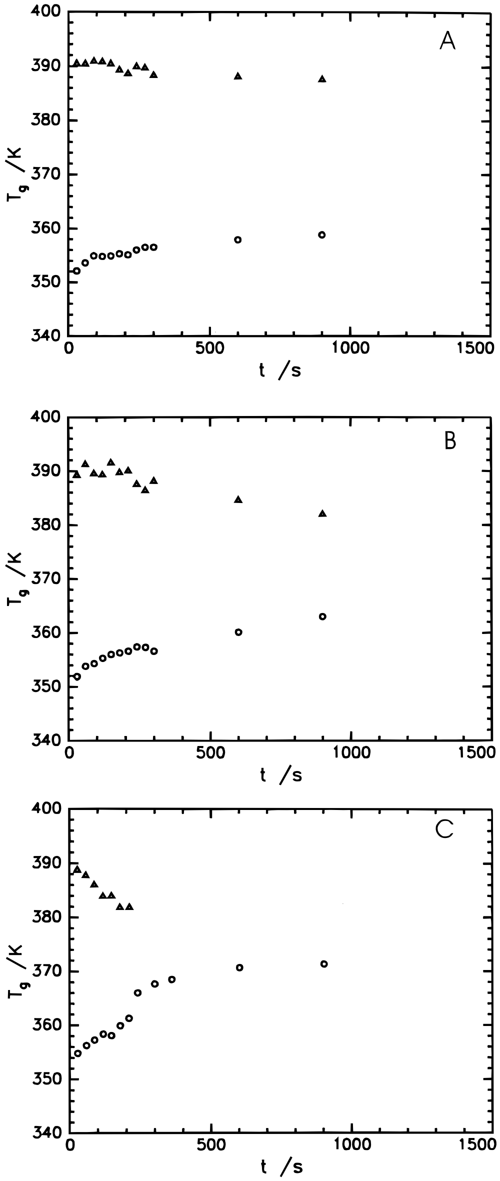

Figure 3. T_g values recorded for partially transesterified mixtures of PEN and PETA with hydroxyl ends esterified with trifluoroacetic acid. Reaction temperatures: (A) 553, (B) 563, and (C) 573 K.

Table 2. Second-Order Rate Constants for Transesterification in PET/PEN Mixture

A. Influence of Temperature

	PETA−OH ends	PETA TFA esterified
T/K	k/cm^3 mol^{-1} s^{-1}	k/cm^3 mol^{-1} s^{-1}
553	(8.0 ± 0.7) × 10^{-2}	(2.2 ± 0.1) × 10^{-2}
563	(17.5 ± 2.2) × 10^{-2}	(6.5 ± 0.5) × 10^{-2}
573	(24.2 ± 2.5) × 10^{-2}	(7.7 ± 0.3) × 10^{-2}

B. Influence of −COOH End Groups at 563 K

PET code	mol of COOH/ mol of PET repeat units	−OH ends	TFA esterified ends
		k/cm^3 mol^{-1} s^{-1}	k/cm^3 mol^{-1} s^{-1}
11	4.91 × 10^{-3}	(8.68 ± 0.5) × 10^{-2}	(0.25 ± 0.06) × 10^{-2}
40	6.22 × 10^{-3}	(10.1 ± 0.4) × 10^{-2}	(2.47 ± 0.2) × 10^{-2}
22	8.20 × 10^{-3}	(20.9 ± 0.4) × 10^{-2}	(12.4 ± 2.3) × 10^{-2}

When the hydroxyl end groups are esterified completely with trifluoroacetic acid, there appears to be little affect on the time to achieve a single T_g value when the reaction temperature is 573 K. However, for the two lower reaction temperatures (553 and 563 K) over the reaction times investigated a single T_g was not obtained. Hence, for all of the reaction times investigated for these

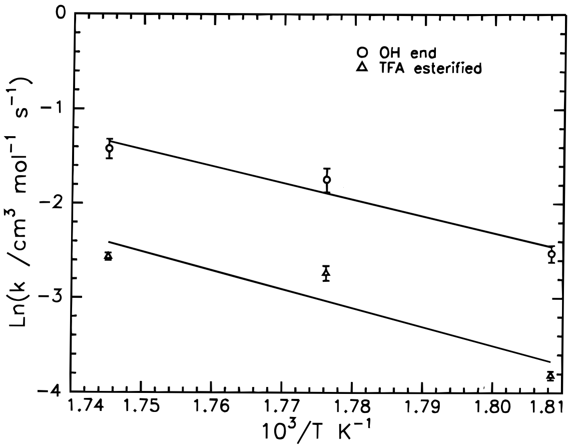

Figure 4. Arrhenius plots of second-order rate constants for transesterification in PEN/PETA mixtures with weight fraction composition 0.5.

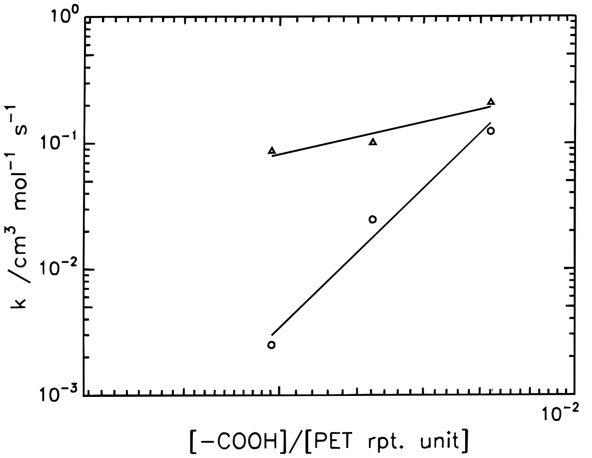

Figure 5. Rate constants for transesterification at 563 K as a function of the carboxylic end group content of PET in PEN/PET mixtures with hydroxyl end groups esterified with trifluoroacetic acid (○) and with unmodified ends (△).

two lower temperatures for the end esterified polyesters and for a considerable proportion of the time for all other mixtures, the reacting system is not a single phase. This could render the subsequent kinetic and sequence distribution analysis questionable. However, this separation into two phases may be consequent on the subsequent cooling from the melt phase after transesterification and may not reflect the degree of mixing of the two polyesters in the melt state where the reactions take place. Second, we note that Kotliar[2] remarked that analysis of interchange reactions on the basis of one uniform thermodynamic phase is valid for the interfacial region between immiscible polymers. Third, our earlier work showed that the kinetic data followed the anticipated reversible second-order kinetics very well. Therefore, there is sufficient support to treat the kinetic data and the subsequent sequence distribution data using the methods derived for reactions in a homogeneous phase. The rate constants for PETA with both types of end groups (i.e., unmodified and esterified with TFA) mixed with PEN are plotted in Arrhenius form in Figure 4 together with the linear least-squares fit to the data points. We are aware that the range of temperature explored is only 30 K. At temperatures less than 553 K the rate of reaction is very slow because of the proximity of the reaction temperature to the polyester melting points, especially that of PEN. For temperatures greater than 573 K, the rate of reaction is very rapid, and uncertainties in the reaction time make reliable evaluation of the rate constant difficult. Additionally, higher temperatures induce other undefined reactions as well as transesterification, and thus the data may contain artifacts. From the least-squares fits in Figure 4 the activation energy, E_a, and preexponential factor, A, obtained for PETA with hydroxyl ends are 146 ± 33 kJ mol^{-1} and 5.5×10^{12} cm^3 mol^{-1} s^{-1}, respectively. For PETA with TFA esterified ends the equivalent values are 165 ± 60 kJ mol^{-1} and 11.4×10^{13} cm^3 mol^{-1} s^{-1}. These parameters, when used in the Arrhenius rate constant equation, accurately reproduce the observed rate constants from the NMR data. Evidently the blocking of the hydroxyl ends reduces the transesterification rate considerably, the rate constants being a factor of 3 smaller than those obtained when the hydroxyl groups are unaltered. The hydroxyl end groups clearly play a significant role in the transesterification. These rate constants should be compared to those obtained by small-angle neutron scattering for mixtures of deuterated and hydrogenous PET. When hydroxyl end groups are left unaltered, these rate constants are of the same magnitude with activation energies and preexponential factors for each polyester system also having very similar values.

We remarked above that the hydroxyl end appears to play an important role in determining the overall rate of transesterification. Attempts were made to esterify the carboxylic acid ends of the polyesters, but either was not successful, or we could not ensure that all carboxyl residues had reacted quantitatively. Therefore, an indirect method was attempted using PET samples with different ratios of carboxyl to hydroxyl ends but similar molecular weights. The hydroxyl ends of each polyester were quantitatively esterified with trifluoroacetic acid, and the rate constants for transesterification at 563 K were obtained as described above. These values are reproduced in Table 2b together with the values for the mixtures where the hydroxyl end groups are unmodified, and both sets are plotted as a function of the ratio of −COOH groups to PET repeat units in the double-logarithmic plot of Figure 5. Linear least-squares fits to these data sets give the following relations:

$$k = 14.9([\mathrm{COOH}]/[\mathrm{PET\ rpt\ unit}])^{7.6}\qquad \text{TFA esterified}$$

$$k = 2.9([\mathrm{COOH}]/[\mathrm{PET\ rpt\ unit}])^{1.75}\qquad \text{unmodified end groups}$$

For end TFA-esterified polyesters the rate constant becomes very small when [COOH]/[PET rpt unit] is of the order of 2×10^{-3}. This result suggests that direct ester interchange at this temperature (563 K) is a negligibly small component of the transesterification reactions.

In addition to using the NMR spectra to obtain kinetic data, the resonances between 4.8 and 4.9 ppm can also be used to gain some insight into the number-average sequence length and nature of the copolymer produced in the transesterification reaction.[7,8] From the intensities of the resonances associated with the TET, NEN, and TEN sequences the mole fraction of terephthalate, T, and naphthalene dicarboxylate, sequences are

$$M_{\mathrm{T}} = \frac{I_{\mathrm{TEN}}}{2} + I_{\mathrm{TET}}$$

$$M_{\mathrm{N}} = \frac{I_{\mathrm{TEN}}}{2} + I_{\mathrm{NEN}}$$

respectively. Hence, the probability of finding a TEN sequence in a copolymer is

$$P_{\mathrm{TEN}} = \frac{I_{\mathrm{TEN}}}{2M_{\mathrm{T}}}$$

and the probability of finding an NET sequences is

$$P_{\mathrm{NET}} = \frac{I_{\mathrm{TEN}}}{2M_{\mathrm{N}}}$$

The degree of randomness, *B*, of the copolymer is defined as[9]

$$B = P_{\mathrm{TEN}} + P_{\mathrm{NET}}$$

For $B = 0$, a mixture of two homopolymers is indicated, $B = 1$ is characteristic of a random distribution of TET and NEN sequences in the copolymer, and an alternating copolymer, i.e., a chain made wholly of TEN sequences, gives a *B* value of 2.

Figure 6 shows the degrees of randomness obtained from the NMR data for PETA with unmodified and TFA transesterified hydroxyl ends. At 573 K (Figure 3C) the *B* value approaches that for a statistically random copolymer in ca. 2500 s for PET with hydroxyl ends. At 553 K even after 4000 s there is clearly some blockiness remaining in the polyester chains. The slowing down effect of transesterifying the hydroxyl ends is abundantly evident in Figure 6. For reaction at 553 K even after an hour at this temperature the copolymer formed must have characteristics more akin to a block copolymer.

Although the *B* values give an indication of the nature of the copolymer formed and we know that the number-average molecular weight of the whole mixture does not alter (in the absence of any other reactions, e.g., thermal degradation), it is useful to know the number-average sequence length of TET or NEN units. These values can then define the onset of a homogeneous mixture (i.e., with a single T_{g}) at a particular number-average sequence length. The number-average sequence lengths and *B* are algebraically related (see below), but they cannot be extracted from *B* values alone. They are obtainable from the ^{1}H NMR data, the number-average sequences of TET and NEN units, N_{TET} and N_{NEN}, respectively, being given by

$$N_{\mathrm{TET}} = 1/P_{\mathrm{TEN}}$$

$$N_{\mathrm{NEN}} = 1/P_{\mathrm{NET}}$$

For a mixture of homopolymers the number-average sequence lengths have a value of infinity; if the number-average sequence length of the minor component present (on a molar basis) is 1, then a strictly alternating copolymer is indicated. A number-average sequence length of 2 is characteristic of a random distribution of the minor component repeat units over all molecules in the system.

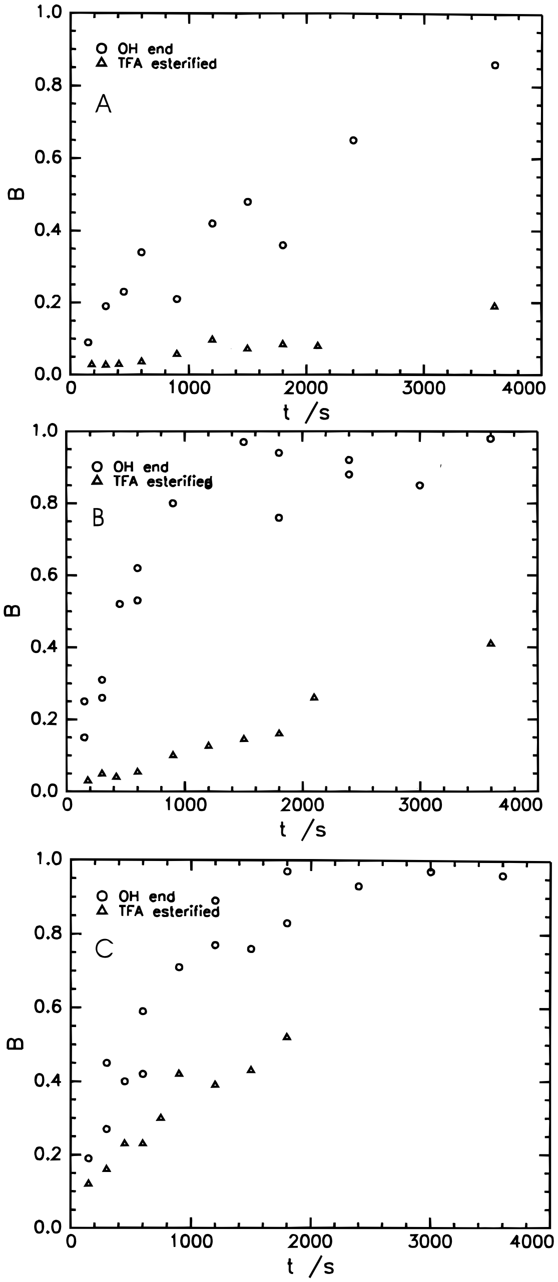

Figure 6. Values of the degree of randomness, *B*, as a function of reaction time of PEN/PETA mixtures (0.5 weight fraction) at temperatures of (A) 553, (B) 563, and (C) 573 K.

Figure 7 shows values of N_{TET} calculated, and the influence of both temperature and end group blocking is clearly evident on the dispersal of the TET units over all molecules in the mixture. For unmodified hydroxyl groups, N_{TET} rapidly approaches the value of 2 for a random distribution particularly at temperatures of 563 and 573 K. Notably, the N_{TET} value of 2 is obtained more quickly than the *B* values of 1 in Figure 7. It is also evident that there is a considerable fall in the number-average sequence length of TET sequences in the early stages of the transesterification reaction. Esterifying the hydroxyl ends by trifluoroacetic acid clearly slows this randomization process, especially in the early stages of the reaction. However, it is evident that the asymptotic limit of the value of N_{TET} will also be 2; i.e., the blocking

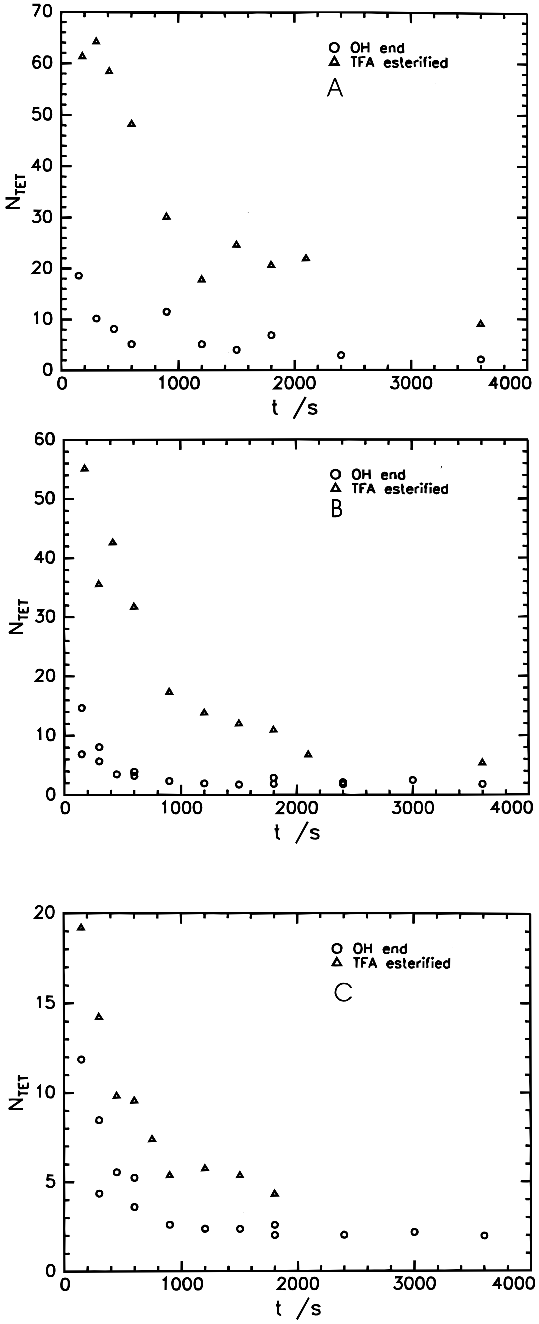

Figure 7. Number-average sequence length of PET repeat units in the copolymer mixtures obtained as a function of reaction times at (A) 553, (B) 563, and (C) 573 K.

of the hydroxyl group has no effect on the final nature of the copolymer.

Clearly the transesterification reaction takes place primarily through the action of the end groups. Using the hypothesis put forward to Kotliar,[2,3] i.e., that end group facilitated reactions lead to the same statistics as random interchange reactions, we can calculate the weight fractions of various species as a function of reaction time. Figure 8 shows the weight fraction of the initial PET content in the mixture that appears as homopolymer (i.e., unreacted), as an end sequence (once reacted), or as sequences flanked by PEN (twice and more times reacted). In calculating these weight fractions, the range of rate constants we have used spans those encountered in the transesterification reactions investigated here. As the rate constant increases, the more rapid is the incorporation of PET repeat units as midunits in the block copolymer, i.e., the more rapidly is a random chain structure obtained. Slowing the reaction by blocking the end groups leads to a finite region of reaction time where the weight fraction of PET as end sequences exceeds that as mid- and homopolymer (Figure 8A). Correlating this observation with the data in Figure 7A for TFA end esterified polyesters, it appears that on average the copolymer produced under these conditions will have characteristics that are mainly blocklike because the sequence length values, N_{TET}, are also large in this region. The weight fractions of Figure 8 were calculated using Kotliar's expressions based on the number of scissions per number-average molecule of PET initially present in the mixture, i.e.,

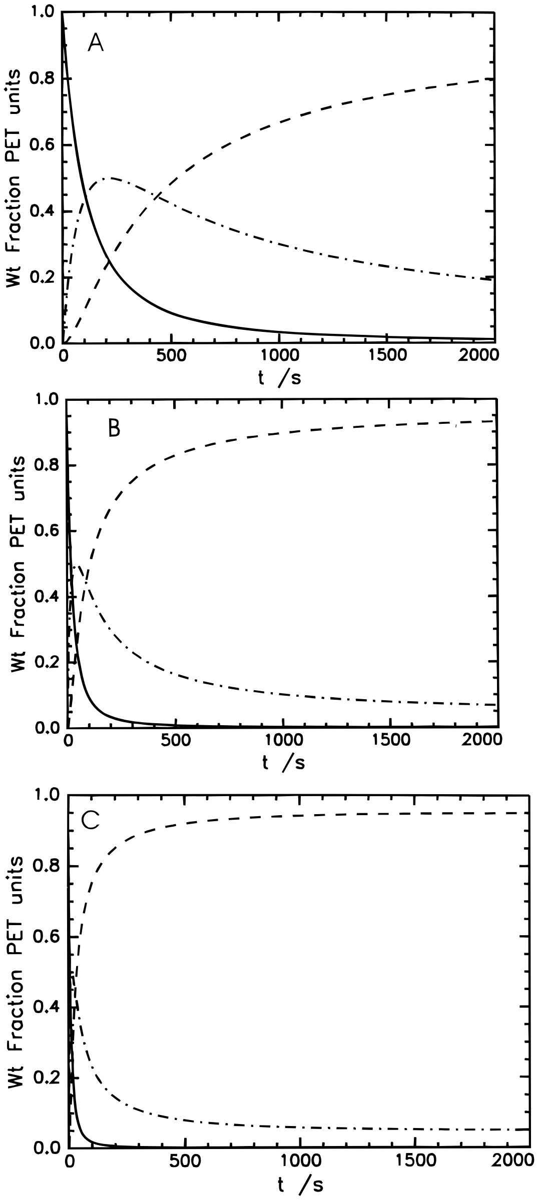

Figure 8. Weight fraction of PET repeat units present as homopolymer (solid line), end units (dot−dash line), or mid units (dashed line) as a function of reaction time for rate constants of (A) 0.02, (B) 0.1, and (C) 0.2 cm^3 mol^{-1} s^{-1}. The weight fraction values are calculated with respect to the original mass of PET in the PEN/PETA mixtures.

$$W\,(\text{PET homopolymer}) = \frac{1}{(1+S)^2}$$

$$W\,(\text{PET as end units}) = \frac{2S}{(1+S)^2}$$

$$W\,(\text{PET as mid units}) = \frac{S^2}{(1+S)^2}$$

where S is the number of effective scissions and has been calculated using the relation derived by Benoit, Fischer, and Zachmann[10] with the rate constants specified in the legend to Figure 8.

Finally, we return to the observation of the occurrence of a single T_g value at differing reaction times dependent on the temperature of the reaction. It appears that this is associated with a particular value of B, the degree of randomness, being achieved. Figure 9 plots all the T_g values for PETA/PEN mixtures (unmodified hydroxyl ends) as a function of the B values calculated from the NMR data. From this plot it appears that a single T_g, and thus a single homogeneous phase in the polyester mixture, is associated with a B value of 0.5, i.e., when the copolyester still has a blocklike nature. By correlating this B value of 0.5 with the number-average sequence length, N_{TET}, the number-average sequence length of PET repeat units in the copolymer that are commensurate with the formation of a single homogeneous phase is ca. 4−8 units.

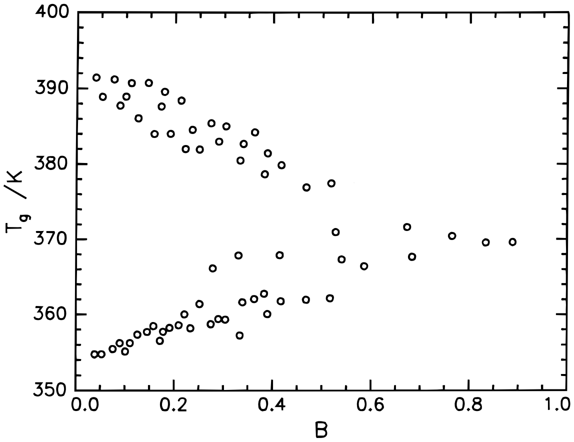

Figure 9. T_g values obtained in PEN/PETA mixtures with unmodified hydroxyl ends as a function of the degree of randomness, B.

Conclusions

The extent of transesterification between PET and PEN has been followed using ^{1}H NMR and second-order rate constants evaluated using a kinetic scheme proposed by Devaux. For the mixtures with a weight fraction composition of 0.5 investigated here rate constants were in the region of 0.2×10^{-2} to 25×10^{-2} cm^3 mol^{-1} s^{-1}. Low values of the rate constant are symptomatic of low reaction temperatures or when the hydroxyl end groups of both polyesters had been esterified with trifluoroacetic acid. Modifying the hydroxyl end groups in this way slows the reaction rate severely. Activation energies obtained from rate constant values in the temperature range from 553 to 573 K were 146 ± 33 kJ mol^{-1} for polyesters with unmodified hydroxyl groups and 165 ± 60 kJ mol^{-1} for polymers with esterified end groups. The randomness factors and number-average sequence lengths have also been calculated from the NMR data, and these indicate that the final product is a statistically random copolymer of the two polyesters. At higher reaction temperatures the extent of block copolymer formation is extremely transient due to the rapidity of the reaction. Esterifying the hydroxyl ends slows this reaction sufficiently that there is a finite time where the majority of the copolymer in the mixture has block copolymer characteristics. The two polyesters are immiscible, but after a sufficient extent of reaction, a single T_g is obtained. A single T_g in the mixture correlates with a degree of randomness of 0.5 and an average PET repeat unit sequence length of ca. 4−8 in the copolyester formed on transesterification.

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