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A Neutron Scattering Investigation of the Transesterification of a Main-Chain Aromatic Polyester

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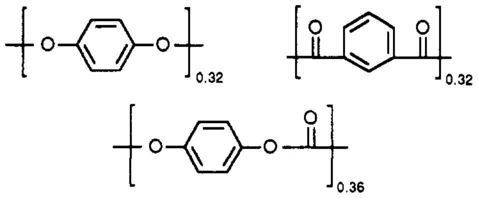
ABSTRACT: The kinetics of transesterification of a main-chain aromatic polyester have been investigated by small-angle neutron scattering. Data were analyzed by a recently proposed procedure to provide rate constants per monomer unit. From the temperature dependence of this rate constant, an activation energy of ca. 157 kJ mol^{-1} was evaluated. This value is essentially identical to that obtained for poly(ethylene terephthalate). From a comparison of rate constants obtained for two different initial molecular weights of the main-chain aromatic polyester, it appears that the mechanism of the reaction proceeds via an active chain end route.

Introduction

Interchange reactions between polymers have often been used to prepare multiblock copolymers in a rather uncontrolled way.[1] Additionally, such reactions may also be used to produce a more uniform molecular weight distribution for homopolymers with an initially very broad distribution, since the most probable distribution eventually results from such interchange reactions but the average molecular weight is unaltered.[2] One such interchange reaction which occurs in polyesters is transesterification. This is the random scission and recombination of molecules induced by heating, where recombination does not necessarily take place between the same fragments which together made up the initial molecule. If the two polyesters are chemically different, copolyesters are produced. Transesterification reactions have been sporadically studied over a 50-year period beginning with the work of Flory.[3] Despite this duration of study, kinetic data are still somewhat sparse and the nature of the mechanism of the reaction is also unclear.

Recently,[4-7] this position with regard to poly(ethylene terephthalate) (PET) has been improved by the application of small-angle neutron scattering (SANS). SANS responds to the deuterium-labeled molecules in a polymer system composed of hydrogenous and deuterated molecules; consequently, if transesterification takes place, the SANS-determined molecular weight of the labeled molecules will appear to decrease because the deuterated segments become distributed over an increasing number of molecules as the reaction proceeds and isotopic block copolyesters are formed. Early applications of SANS to PET transesterification utilized a knowledge of the molecular weight obtained by light scattering to evaluate the kinetics of transesterification. Benoit et al.[8,9] have shown that all the kinetic information can be gained from the SANS spectrum in the *intermediate* Q range (Q is the scattering vector = $(4\pi/\lambda)\sin\theta$). The scattering in this range is determined by the *number*-average molecular weight of the polymer. Moreover, using data in this region of Q avoids the necessity of extrapolation with low-Q data. Low-Q scattering tends to be contaminated by scattering from microvoids and can lead to artifacts being obtained on the analysis of such data. Microvoids can generally be removed by annealing the polymer at temperatures well above T_g for a sufficiently long time. Since transesterification in polyesters has been observed at temperatures *below* the melting point, it is clearly impractical to anneal polyesters and be confident that no transesterification has taken place.

We report here the use of SANS to establish the kinetics of transesterification of an aromatic main-chain random terpolyester which we designate LCP. This polymer has the stoichiometric formula



and we have discussed its dilute solution properties in an earlier publication.[10] Clearly, it is of relevance to ascertain whether the increased backbone rigidity influences the transesterification kinetics.

Theory

The interpretation of the SANS data from mixtures of deuterated and hydrogenous polyesters has been theoretically described by Benoit et al.[8] By use of the random-phase approximation and noting that, at intermediate scattering vector ranges, extrapolation of Zimm plot data for polydisperse polymers to $Q = 0$ yields the *number*-average molecular weight,[11] eq 1 was obtained where x is

$$\frac{1}{I'(Q)} = \frac{Q^2b^2}{12x(1-x)} + \frac{1}{2x(1-x)}\left(\frac{1}{n_D(t)} + \frac{1}{n_H(t)} - \frac{1}{n^\circ_T}\right) - 2\chi \qquad (1)$$

the number fraction of deuterated monomer units in the sample and $n_D(t)$ and $n_H(t)$ are the number-average degrees of polymerization of the deuterated and hydrogenated polymer, respectively, at time t after the commencement of transesterification. The statistical step length of the

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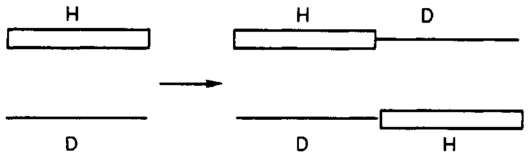
Scheme I



polymer is denoted by b, and χ is the Flory–Huggins interaction parameter between the deuterated and hydrogenous polymers. Consequently at $Q = 0$ and assuming $\chi = 0$ (generally true as long as the molecular weight of the polymers is not too high) then

$$\frac{1}{I'(0)} = Z(t) = \frac{1}{2x(1-x)}\left(\frac{1}{n_D(t)} + \frac{1}{n_H(t)} - \frac{1}{n^\circ_T}\right) \qquad (2)$$

with n°_T being the number-average degree of polymerization of the total sample

$$\frac{1}{n^\circ_T} = \frac{x}{n_D(t=0)} + \frac{(1-x)}{n_H(t=0)} \qquad (3)$$

As defined by Benoit et al.[8] and in terms of absolute scattering, $I'(0)$ is the number-average degree of polymerization of the scattering species. A relation between the intercept, $Z(t)$, of a Zimm plot of $1/I'(Q)$ as a function of Q^2 was obtained on the basis of the idealized reaction of Scheme I (where scission takes place at random along the H and D chains) and noting the influence of the number of effective scissions at time t, $S(t)$, on the values of n_H and n_D. By this means eq 4 was obtained and N_T is the

$$Z(t) = Z_0 + \frac{1}{2x^2(1-x)^2}\frac{S(t)}{N_T} \qquad (4)$$

total number of monomer units in the specimen.

Since

$$S(t) = N_T x(1-x)[1 - \exp(-t/\tau)]$$

with τ being the relaxation time for the approach to equilibrium monomer distribution, then replacement into eq 4

$$Z(t) - Z_0 = \frac{1}{2x(1-x)}[1 - \exp(-t/\tau)] \qquad (5)$$

rearranging

$$\ln\,[1 - 2x(1-x)(Z(t) - Z_0)] = -(t/\tau) \qquad (6)$$

and a plot of the left-hand side as a function of transesterification time t should be linear with slope $-1/\tau$. Consequently, the data required are the average degree of polymerization of the deuterated sequences before any transesterification reaction and as a function of reaction time thereafter.

Experimental Section

Preparation of Deuterated Polymer. The partially deuterated LCP was prepared from deuteriohydroquinone and deuteriohydroxybenzoic acid. Deuteriohydroquinone was prepared by repeated refluxing of hydroquinone in a 1% (v/v) D_2SO_4 solution in heavy water. Deuteriohydroxybenzoic acid was prepared using the inclusion catalyst β-cyclodextrin hydrate and the procedure described by Komiyama and Hirai.[12] The third monomer, isophthalic acid, could not be prepared in a deuterated form, and consequently the polymer contained hydrogenous isophthalic acid residues. Both fully hydrogenous and deuterated versions of LCP were prepared by a nonaqueous dispersion polymerization[13] utilizing the acetate derivatives of the hydroquinone and the hydroxybenzoic acid. After polymerization, both polymers were separately dissolved in a mixture of trifluoroacetic acid and dichloromethane, centrifuged and precipitated by pouring into a large excess of butan-2-one, filtered, and dried under vacuum at 313 K to constant weight. This procedure removes the suspension agent and catalyst from the polymerization procedure. The polymerization procedure used results in the majority of the end groups being acetate functionalized, but no attempts were made to quantify this aspect here.

Small-Angle Neutron Scattering. Mixtures of deuterated and hydrogenous LCP were prepared by dissolving the two polymers at an approximately 50:50 weight ratio in a mixture of trifluoroacetic acid and dichloromethane (20:80 (v/v)). The solution (ca. 3% (w/v) polymer) was poured into Teflon dishes and the solvent allowed to evaporate at ambient pressure and temperature until a coherent, but still flexible, film was obtained. At this stage disk specimens were cut from the sheet, placed between glass plates, and dried under vacuum for 1 week. During this period the temperature was raised to 373 K (T_g = 403 K). The specimens, ca. 0.2 mm thick, were then annealed at selected temperatures by placing each specimen in a previously heated compression mold for a predetermined time. After this time the specimens were quickly removed and immediately quenched in ice water and dried under vacuum at 300 K for 1 week. Several specimens so prepared were stacked together to give a total thickness of 1 mm. The majority of neutron scattering data were obtained using the LOQ small-angle diffractometer[14] at the pulsed neutron source, ISIS, located at the Rutherford Appleton Laboratory, Oxon, U.K. The instrument was calibrated for absolute scattering by reference to a deuteriopolystyrene–hydrogenous polystyrene mixture whose absolute scattering cross section was known. Each scattering spectrum had a background subtracted and was corrected for variations in transmission and sample thickness. The background scattering was a composition weighted sum of the scattering from hydrogenous LCP and deuterated LCP. The molecular weight of the deuterated polymer was calculated using eq 7 where $I(0)$ is the observed intensity at

$$M = N_A I(0)\, K/[(\rho_D - \rho_H)^2 c_D(1 - c_D)] \qquad (7)$$

$Q = 0$ after correction for background scattering, transmission, and thickness, c_D is the concentration of deuterated polymer (in g mL^{-1}), K is the calibration constant converting $I(0)$ to the absolute cross section, N_A is Avogadro's number, and ρ_D and ρ_H are the scattering length densities of the deuterated and hydrogenous polymers. Since the deuterium-labeled polymer was not perdeuterated, ρ_D was calculated on the basis of the average degree of deuteration over the three monomer units. Some results were also obtained using the D17 diffractometer at the Institut Laue–Langevin, Grenoble, France, as well as on LOQ. Within experimental error, the molecular weights were identical.

Results

Two different molecular weight samples of LCP were investigated. The lower molecular weight (MW = 71 400) was transesterified at five different temperatures (533–603 K) for a range of times from 5 to 180 s. (The melting point of LCP is 545 K.) Longer times were needed at the lowest temperature to be able to observe the decrease in molecular weight due to transesterification since the process was slow at this temperature. Zimm plots ($1/I(Q)$ $f(Q^2)$) in the intermediate Q range for some of these specimens are shown in Figure 1 and show the behavior predicted by Benoit et al.;[8] i.e., the different specimens have roughly parallel values of $1/I(Q)$ which extrapolate to different intercepts. Extraction of the correct values of $Z(t)$ from such intercepts was not as straightforward as the theoretical analysis of Benoit et al. implies. Values of $Z(t)$ are obtained by extrapolation of SANS data plotted in the Zimm representation in the region where $R_g^{-1} < Q < b^{-1}$, where R_g is the radius of gyration of the polymer molecule. For LCP the definition in practical terms of this range was problematic. Other SANS data from a very much lower Q range than that used here[15] have shown that the configuration of the molecule becomes increasingly rodlike as the sample is annealed in the temperature range $T_g \leq T \leq T_m$; the values of both R_g and the persistence

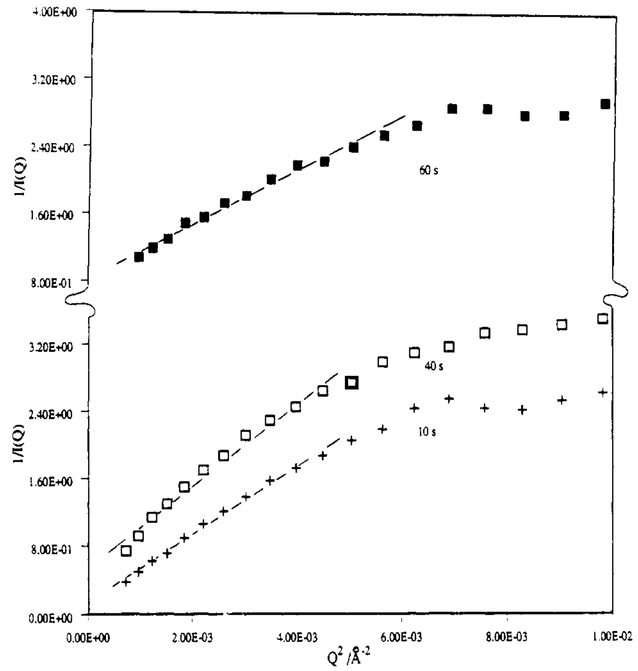


Figure 1. Zimm plots ($I^{-1}(Q)$ $f(Q^2)$) for LCP specimens transesterified at 563 K for the times indicated.

length (and thus b) increase as the annealing temperature increases. Due to the rapid transesterification above T_m, we have no *direct* evidence that this process continues in the melt; however, indirect evidence suggests this is so. From these data, the radius of gyration of the LCP used here is initially (at 448 K) ca. 57 Å; at 523 K this increases to 69 Å. The increase in b over this range is also not large, increasing from ca. 10 to 45 Å on prolonged annealing. With this knowledge in mind, the range of Q values we have used to extract $Z(t)$ was from 3×10^{-2} Å^{-1} as the lower limit to 0.1 Å^{-1} as the upper limit. Strictly, the lower limit is slightly higher than that defined by Benoit et al. based on the radii of gyration given above. However, these values were calculated from the weight-average molecular weights and do not pertain to the lowest molecular weight species present. Moreover, during transesterification, the molecular weight distribution should become increasingly more probable; i.e., there will be an increasing amount of lower molecular weight species, and therefore because of these reasons the lower Q limit can be relaxed. Confidence in the choice of the correct Q range can be obtained by calculating the value of b, the statistical step length, from the slope of the linear least-squares line drawn through the data points over the selected Q range. The values of b so obtained were in the range of 7–14 Å, in reasonable agreement with that of 10 Å obtained from a Murakami plot[15] for data of several different molecular weights annealed at 448 K for 1 h. This value suggests that, for the short transesterification times used here, the LCP molecules have not undergone significant configurational changes even though transesterification is considerably advanced at the highest temperature and longest times. However, we should point out that, because of the form of eq 1 wherein b appears as a squared term, the slope can vary markedly but the change in b is not so great. Hence, the value of b obtained is perhaps not too sensitive a test for the correctness of the Q range used unless it is wildly wrong.

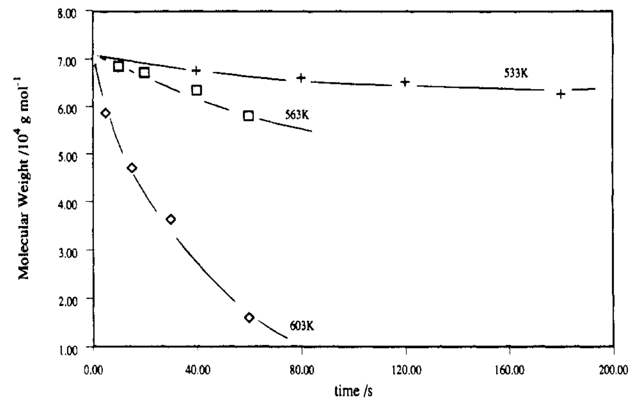


Figure 2. Dependence of the molecular weight of LCP on transesterification time at the temperatures indicated. Lines are guides to the eye.

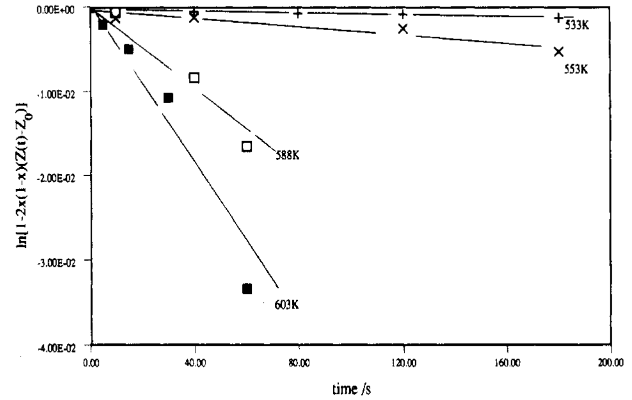


Figure 3. Data plotted according to eq 5 for the temperatures indicated. Lines are least-squares fits to the data.

Table I
Relaxation Times (τ) and Rate Constants per Monomer Unit (k) for the Transesterification of LCP

T/K	$\tau/10^4$ s	$k^a/10^{-3}$ s^{-1}
533	14.9	1.62
553	4.0_5	5.93
563	2.8_9	8.36
588	0.36	66.8
603	0.18	132.76

[a] Rate constant per monomer unit.

The dependence of the molecular weight of the deuterated LCP on transesterification time at each temperature is shown in Figure 2. Lines through the data are merely guides to the eye, although an exponential line can be fitted to these data with reasonable correlation coefficients (ca. 0.95–0.99). These data show the exponential dependence of molecular weight on transesterification time predicted by eq 4 on replacing for $S(t)$. Weight-average molecular weights were determined by light scattering before transesterification and on a sample annealed at 603 K for 60 s. No change in M_w (within experimental error) was observed. Figure 3 shows the data of Figure 2 plotted according to eq 6, the lines through the data points being least-squares fits. Table I presents the relaxation times obtained from the slopes of these plots. Since the relaxation time, τ, is related to the rate constant per monomer unit for transesterification by

$$\tau = 2/kN_T$$

and N_T was known from the sample preparation, the calculated values of k calculated are given in Table I. Figure 4 is a plot of these rate constants as a function of reciprocal temperature; the line is a least-squares fit of an exponential power law to the data and gives an activation energy of 173.8 kJ mol^{-1} (correlation coefficient 0.994). This value of the activation energy is in the same region as that obtained by Kugler et al.[7] for poly(ethylene terephthalate) by SANS. The reaction scheme used (Scheme I) could be criticized as being idealized. However, Benoit et

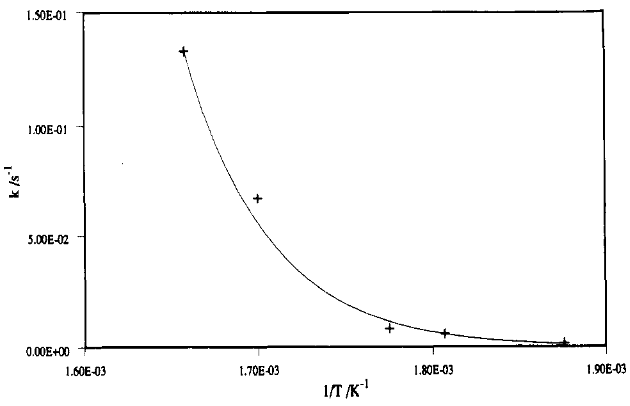
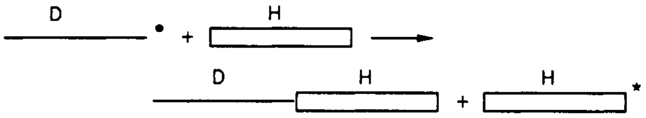


Figure 4. Rate constant per monomer unit, k, as a function of the reciprocal transesterification temperature for the LCP original molecular weight 71 400. The line is a nonlinear least-squares fit of the equation $k = A \exp(-B/T)$ to the data.

Scheme II



al.[8] also discussed a reaction scheme where transesterification was initiated by active chain ends, as shown in Scheme II, with the active chain end being transferred to the other sequence which reacts further. This model for the reaction leads to the same kinetic equations, but the rate constant clearly depends on the concentration of chain ends. Consequently, as the molecular weight of the starting polymer increases and the concentration of chain ends decreases, the rate constant at a particular temperature should decrease but the activation energy should be approximately constant whatever the molecular weight as long as it is not too low. To ascertain whether this mechanism prevailed, some additional experiments were made on a different fraction of deuterated LCP with an initial molecular weight of 104 000. Samples were transesterified in the manner described above at temperatures of 523, 553, 573, and 603 K. At 523 K no change in molecular weight of the deuterated LCP was noted for transesterification times as long as 150 s; for the three higher temperatures the dependence of the experimentally determined rate constant per monomer unit on $(1/T)$ is described by the relation

$$k = 1.49_9 \times 10^{10} \exp(-17.06 \times 10^3/T) \tag{8}$$

with a correlation coefficient of 0.97. The activation energy calculated from this relation is 141.9 kJ mol^{-1}, in fair agreement with that obtained for the lower molecular weight polymer. From the data for the lower molecular weight polymer reported here, we obtained

$$k = 1.48 \times 10^{14} \exp(-20.90 \times 10^3/T) \tag{9}$$

Evidently, the rate constant for the transesterification reaction of the higher molecular weight LCP is considerably smaller than that for the low molecular weight polymer. The dependence of the two rate constants on the reaction temperature calculated from eqs 8 and 9 is shown in Figure 5. We also note here that the rate constants for transesterification for these two molecular weights are considerably less than that quoted by Kugler et al. for a PET of initial molecular weight 23 000. This is the expected result if the active chain end mechanism prevails. However, the presence of the more flexible ethylene glycol residues in PET may also have some influence on the value of k.

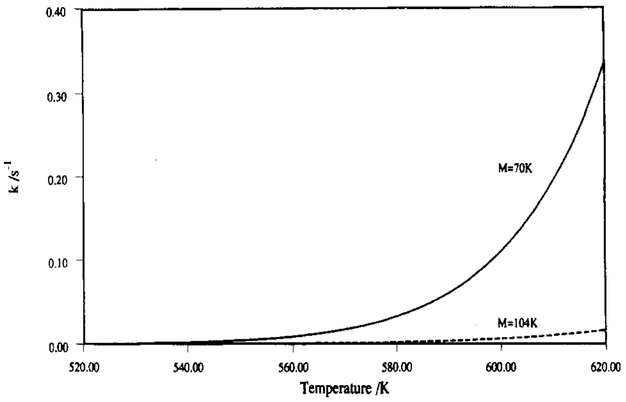


Figure 5. Dependence of the rate constant on the temperatures calculated from Arrhenius parameters for high and low molecular weight LCP specimens.

Conclusions

Small-angle neutron scattering can be used to evaluate accurately the kinetics of transesterification reactions for a main-chain aromatic polyester. The activation energy obtained by noting the influence of temperature on the rate constant (per monomer unit) is 157 ± 16 kJ mol^{-1}. From observations of the value of the rate constant for two different initial molecular weights, it appears that the reaction proceeds by an active chain end mechanism. The similarity of the activation energies of transesterification for LCP (rigid backbone) and PET (less rigid) suggests that the same mechanism may be evident in both polymers.

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Registry No. (Hydroquinone)(hydroxybenzoic acid)(isophthalic acid) (copolymer), 31072-57-8.