Macromolecules **2005,** *38,* 2659−2664

Reaction Kinetics of the Incorporation of 2,2-Bis[4-(2-hydroxyethoxy)phenyl]propane in Poly(butylene terephthalate) via Solid-State Polymerization

M. A. G. Jansen,[†] J. G. P. Goossens,*[,†] G. de Wit,[†] C. Bailly,[§] and C. E. Koning[‡]

Dutch Polymer Institute, Laboratory of Polymer Technology, Faculty of Chemical Engineering and Chemistry, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands, Dutch Polymer Institute, Laboratory of Polymer Chemistry, Faculty of Chemical Engineering and Chemistry, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands, and Laboratoire de Chemie et de Physique des Hauts Polymères, Université Catholique de Louvain, Place Croix du Sud, 1 B-1348 Louvain-la-Neuve, Belgium

Received August 5, 2004; Revised Manuscript Received January 14, 2005

ABSTRACT: The kinetics of the incorporation of an aromatic diol in poly(butylene terephthalate) (PBT) via solid-state polymerization (SSP) was studied. The selected diol was 2,2-bis[4-(2-hydroxyethoxy)phenyl]-propane (Dianol 220). Mixtures consisting of 85 mol % PBT and 15 mol % Dianol were isothermally polymerized in the solid-state at 180 °C while the polymerization time was varied. Combining HPLC and ^{1}H NMR spectroscopy results showed that Dianol monomer reacts with PBT via two consecutive first-order reactions, the Dianol monoester being an intermediate and fully incorporated Dianol as the final product. The two corresponding reaction rate constants were determined by fitting the first-order equations with experimental data, revealing that free Dianol monomer is more reactive toward transesterification with PBT than its monoester. Dianol was fully incorporated in PBT after a reaction time of 4 h. This result was confirmed by ^{13}C NMR sequence distribution analysis. SEC measurements showed that the molecular weight and polydispersity first decrease during the SSP reaction due to chain scission of PBT. The subsequent recombination of polymer chains after complete incorporation of all Dianol monomer leads to a buildup of the molecular weight resulting in high molecular weight copolymers.

Introduction

Poly(butylene terephthalate) (PBT) is an aromatic semicrystalline polyester with a high crystallization rate. It is generally known that properties of polycondensates such as PBT can be easily modified by reactive blending in the melt with other polycondensates.[1] The transesterification reactions occurring in the melt convert the blends first into blocky copolymers and, as the reaction proceeds, a random copolymer will eventually be obtained.[2−7] This randomization process results in decreased homopolymer block lengths and may therefore have a large influence on the melting temperature, crystallization behavior, and degree of crystallinity of the resulting copolymers. It would thus be desirable to develop a modification method that retains large crystallizable PBT blocks and concomitantly a high crystallization rate, whereas other material properties (e.g., increase of glass transition temperature and impact strength, compatibility with other polymers) can be enhanced. A method that recently has gained attention to prepare polyester copolymers is solid-state polymerization (SSP). SSP is a traditionally used technique to increase the molecular weight of polycondensates by heating the polymer just below its melting temperature in the presence of a nitrogen flow or vacuum.[8] At this temperature, the mobility of the polymer chains in the amorphous phase is sufficiently high for transesterification reactions to occur. In this way, it is possible to obtain copolymers from blends of polycondensates via SSP. Sivaram and co-workers[9,10] prepared copolymers via SSP using semicrystalline oligomer blends from poly(ethylene terephthalate) (PET) and poly(ethylene naphthalate) (PEN) as starting material. They showed that transesterification occurred predominantly during the first 2 h of the SSP reaction, whereas the molecular weight of the resulting copolymers still continued to increase for longer reaction times. Sequence distribution analysis via ^{1}H NMR spectroscopy confirmed that the PET/PEN copolymers were nonrandom and hence homopolymer blocks were still present after SSP.

To our knowledge, no studies have been performed on the incorporation of monomers in a semicrystalline homopolymer polycondensate via SSP. A different molecular microstructure might be obtained compared to copolymers obtained via SSP of oligomer blends.

In this study, a diol monomer was incorporated in the amorphous phase of PBT via SSP, leaving relatively long, crystallizable PBT sequences unchanged. A mixture consisting of 85 mol % PBT and 15 mol % 2,2-bis-[4-(2-hydroxyethoxy)phenyl]propane (Dianol 220) was used as starting material. The kinetics of the incorporation via SSP was studied by variation of the reaction time under isothermal conditions. A reaction mechanism was proposed and the corresponding reaction rate constants were determined by fitting theoretical calculated values with experimentally obtained data using a least-squares method. The incorporation was also studied by sequence distribution analysis using quantitative ^{13}C NMR spectroscopy. Finally, the change in molecular weight and molecular weight distribution were determined as a function of reaction time. In subsequent papers, a detailed description will be given of the chemical microstructure of these PBT−Dianol

---

* Corresponding author: E-mail J.G.P.Goossens@tue.nl, Telephone: +31 40 2475029. Fax: +31 40 2436999.

[†] Dutch Polymer Institute, Laboratory of Polymer Technology, Faculty of Chemical Engineering and Chemistry, Eindhoven University of Technology.

[‡] Dutch Polymer Institute, Laboratory of Polymer Chemistry, Faculty of Chemical Engineering and Chemistry, Eindhoven University of Technology.

[§] Laboratoire de Chemie et de Physique des Hauts Polymères, Université Catholique de Louvain.

10.1021/ma0483773 CCC: $30.25

copolymers made by SSP as a function of composition. Also the thermal properties will be discussed and compared to PBT−Dianol copolymers obtained via traditional melt copolymerization.

Experimental Section

Materials. Poly(butylene terephthalate) (PBT) pellets ($\bar{M}_n$ = 16 kg/mol, $\bar{M}_w$ = 37 kg/mol) were provided by GE Plastics (Bergen op Zoom, The Netherlands) and used as received. 2,2-Bis[4-(2-hydroxyethoxy)phenyl]propane (Dianol 220) was provided by Air Liquide (Paris, France) and was recrystallized twice from acetone prior to use. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP, 99%) obtained from Biosolve (Valkenswaard, The Netherlands), was used for solution mixing of PBT with Dianol. For NMR measurements, deuterated trifluoroacetic acid (TFA-d, 99% deuterated) was obtained from Aldrich and deuterated chloroform ($CDCl_3$, 99% deuterated) was obtained from Merck.

Solution Preparation of a PBT—Dianol Mixture from HFIP. First, PBT pellets were ground into powder by a mill (Retsch type ZM 100) after cooling with liquid nitrogen. The PBT powder was subsequently dried in a vacuum oven at 70 °C for 48 h. Then 19.944 g of PBT (0.0906 mol) and 5.057 g of Dianol (0.0160 mol) were dissolved in 50 mL of HFIP at a temperature of approximately 55 °C. After complete dissolution, the temperature was raised to 65 °C and the HFIP was distilled off. As soon as the material started to precipitate, a vacuum of 80−100 mBar was applied to enhance the removal of HFIP. Finally, the obtained lump of material was dried in an oven for 24 h and was then cooled in liquid nitrogen and subsequently ground into powder using an analytical laboratory mill (Waring, type 32BL80). This powder was subsequently dried in a vacuum oven for a period of 48 h prior to further analysis. The PBT/Dianol powder mixture, obtained via dissolution in HFIP, will be abbreviated in this article as $(BD_{85}Di_{15})_{HFIP}$ where BD_{85} denotes the mol percentage (mol %) of butanediol (BD) units and Di_{15} the mol % of Dianol (Di) units in the mixture.

Solid-State Polymerization (SSP). The experimental setup for SSP consisted of a vessel with a heating element. A salt mixture of KNO_3 (53 wt %), $NaNO_2$ (40 wt %), and $NaNO_3$ (7 wt %) was used as heating medium.[11] The reactor comprised a glass tube (inner diameter = 2.4 cm) and a sintered glass plate at the bottom. A small heat exchange glass coil (inner diameter = 5 mm) surrounded the reactor and entered the inner glass tube at the bottom just below the glass plate. Nitrogen gas was heated by passing through this coil prior to entering the reactor. The gas flow was controlled by a flow meter.

For the SSP reactions as described in this article,[12] 3 g of $(BD_{85}Di_{15})_{HFIP}$ powder (mixed via dissolution in HFIP as described above) were placed on the sintered glass plate. The powder was fixed by addition of 18 g of glass pearls (d = 2 mm) on top of the powder. A nitrogen flow of 3 L/min was applied and the SSP temperature was kept at 180 °C. SSP reaction times (t_{ssp}) were varied between 0 and 24 h. For each t_{ssp}, a new SSP reaction mixture was prepared. After elapsing of t_{ssp}, the reactor was removed from the salt bath and quenched for 5 min in water of 80 °C and then further cooled in water of ambient temperature. The synthesized SSP copolymers will be abbreviated in this article as $(BD_{85}Di_{15})_{ssp}$ where BD_{85} and Di_{15} are respectively the mol % butanediol (BD) units and Dianol (Di) units as present in the initial $(BD_{85}Di_{15})_{HFIP}$ mixture being used for SSP.

Nuclear Magnetic Resonance Spectroscopy (NMR). All solution ^1H NMR spectra were recorded on a Varian 400 MHz spectrometer at 25 °C and at a resonance frequency of 400.164 MHz. For the ^1H NMR measurements, 15 mg of polymer was dissolved in 0.8 mL of a 80:20 vol % $CDCl_3$:TFA-d mixture. All chemical shifts are reported in ppm downfield from tetramethylsilane (TMS), used as the internal standard. The spectra were acquired using 32 scans, a delay time (d_1) of 5 s and a total number of data points of 64k.

Quantitative proton-decoupled solution ^{13}C NMR spectra were recorded on a Varian 300 MHz spectrometer, operated at a resonance frequency of 75.462 MHz. For ^{13}C NMR measurements, 50 mg of polymer was dissolved in 0.8 mL of pure TFA-d. TMS was used as internal standard. Then 3000−4000 scans were acquired with 64k data points, a d_1 of 12 s, a 90° pulse, and a spectral width of 18.8 kHz. For the sequence distribution analysis, overlapping peaks were integrated after Lorentzian deconvolution of the spectra using the deconvolution option implemented in the Varian NMR software.

Size Exclusion Chromatography (SEC). The number-average molecular weight ($\bar{M}_n$) and the polydispersity index (PDI) of the synthesized $(BD_{85}Di_{15})_{ssp}$ copolymers and the $(BD_{85}Di_{15})_{HFIP}$ mixture were determined by SEC. The system was equipped with a Waters type 710B injector (injection volume = 50 μL) and two PFG linear XL columns from PSS (8 × 300 mm in size, 7 μm particles) thermostated by a Spark Holland Mistral thermostat at 30 °C. HFIP containing 0.4 wt % ammonium acetate was used as eluent. A Waters type 510 pump provided a flow rate of 0.4 mL/min. For detection, a Waters model 490 UV-detector (λ = 265 nm) was used. Prior to using HFIP as eluent, the SEC system was calibrated with polystyrene (PS) standards using THF as eluent. The remaining measuring conditions were kept equal. The obtained PS calibration curve was used to determine the relative $\bar{M}_n$ of the synthesized $(BD_{85}Di_{15})_{ssp}$ copolymers and $(BD_{85}Di_{15})_{HFIP}$ mixture. In addition, PBT homopolymer samples with known $\bar{M}_n$ values (determined by end group titration) were measured by the same SEC system. A fitting curve was made using the $\bar{M}_n$ values obtained by end group titration and the $\bar{M}_n$ obtained via the PS calibration curve. The measured $\bar{M}_n$ of the $(BD_{85}Di_{15})_{HFIP}$ mixture and the $(BD_{85}Di_{15})_{ssp}$ copolymers were fitted using this calibration curve and corrected to obtain an absolute value. No correction was made for possible differences in hydrodynamic volumes for the $(BD_{85}Di_{15})_{ssp}$ copolymers vs pure PBT.

High Performance Liquid Chromatography (HPLC). The fraction of unreacted Dianol in $(BD_{85}Di_{15})_{HFIP}$ in each $(BD_{85}Di_{15})_{ssp}$ sample was determined via HPLC. The system was equipped with a Hewlett-Packard 1100 series injector (injection volume = 25 μL), a Chrompack column (Chromsep 150 × 4.6 mm Intersil 5 ODS-3) thermostated at 35 °C. An Agilent diode array detector (λ = 240 nm) was used for detection. A solvent mixture consisting of acetonitrile (20 vol %) and water (80 vol %) was used as eluent. A HP 1100 series HPLC pump provided a flow of 1.0 mL/min.

Prior to measuring, a weighed amount of each $(BD_{85}Di_{15})_{ssp}$ sample was dissolved in HFIP and subsequently precipitated in acetonitrile. The HFIP/acetonitrile solution was filtered over a 0.45 μm filter and subsequently injected into the HPLC system. A calibration curve was used in order to determine the amount of free Dianol in each sample. Calibration samples were prepared by dissolution of a known amount of Dianol in a mixture of HFIP:acetonitrile (5:95 vol %) of known volume. The area of the peak corresponding to free Dianol in the $(BD_{85}Di_{15})_{ssp}$ samples was fitted with the calibration curve and converted into a weight fraction of free Dianol.

Differential Scanning Calorimetry (DSC). The crystallinity ($\chi_{heating}$) of the synthesized $(BD_{85}Di_{15})_{ssp}$ copolymers was measured by a TA Instruments Q1000 DSC equipped with an autosampler and refrigerated cooling system (RCS). The DSC cell was purged with a nitrogen flow of 50 mL/min. The temperature was calibrated using the onset of melting for indium. The enthalpy was calibrated with the heat of fusion for indium. Samples of 5−7 mg were prepared in hermetically closed aluminum pans. Samples were measured in the temperature range from at 0 to 250 °C using a heating rate at 10 °C/min and isothermal periods of 3 min at 0 and 250 °C, respectively.

Results and Discussion

To study the kinetics of the incorporation of Dianol into PBT, a $(BD_{85}Di_{15})_{HFIP}$ mixture was polymerized in the solid-state while the polymerization time (t_{ssp}) was varied between 0 and 24 h. The overall chemical structure of the resulting $(BD_{85}Di_{15})_{ssp}$ copolymer, con-

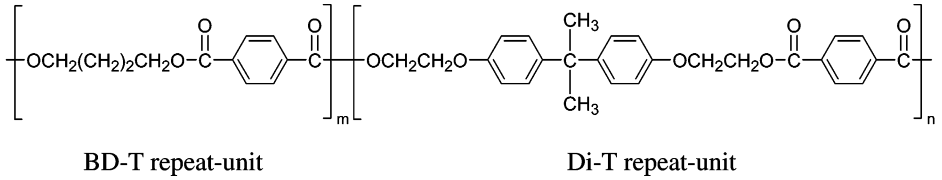

Figure 1. Overall chemical structure of a $(BD_xDi_y)_{ssp}$ copolymer with BD−T and Di−T repeat units.

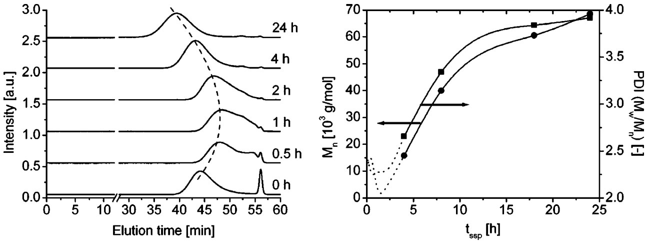

Figure 2. (a) SEC chromatograms of $(BD_{85}Di_{15})_{ssp}$ samples with different t_{ssp} and (b) development of $\bar{M}_n$ and PDI as a function of t_{ssp}.

sisting of BD−T and Di−T repeat units, is shown in Figure 1.

During SSP, transesterification reactions occur between the Dianol monomer and the PBT chains present in the amorphous phase. Hence it can be expected that the molecular weight will change. The number-average molecular weight ($\bar{M}_n$) and the polydispersity index (PDI) of the $(BD_{85}Di_{15})_{ssp}$ copolymers were determined by size exclusion chromatography (SEC). The change in molecular weight distribution as a function of reaction time (t_{ssp}) is shown in Figure 2a. The SEC chromatogram of $(BD_{85}Di_{15})_{HFIP}$ mixture ($t_{ssp} = 0$ h) shows the Dianol monomer as a sharp peak at an elution time of 56 min. The broad peak, starting at a lower elution time, represents the PBT homopolymer. Already after 0.5 h of transesterification, the Dianol monomer peak becomes significantly smaller, while the peak originating from PBT shifts to higher elution times. This shift indicates that PBT chains are cleaved due to the transesterification reaction with one hydroxyl end group of free Dianol monomer. As a consequence, oligomers are formed which can be derived from the broadening of the polymer peak in the initial stage of the SSP reaction. At $t_{ssp} = 1$ h, the polymer peak has its maximum broadness and highest elution time. After $t_{ssp} = 2$ h, the polymer peak becomes less broad and shifts back to lower elution times. Hence, recombination of polymer chains takes place resulting in higher $\bar{M}_n$ values.

In the SEC chromatogram corresponding to $t_{ssp} = 4$ h, the Dianol monomer peak has almost completely disappeared, but some small traces of cyclic dimers and oligomers might still be present. This result is in agreement with the ^{1}H NMR analysis of the sample with $t_{ssp} = 4$ h (Figure 4) and the HPLC measurements (F_F in Figure 5), which will be discussed in the next section. The $\bar{M}_n$ and PDI of each chromatogram, as shown in Figure 2a, are plotted as a function of t_{ssp} in Figure 2b. Because of overlap of the Dianol monomer peak with the broad PBT peak (Figure 2a), it was not possible to obtain an accurate $\bar{M}_n$ and PDI for $(BD_{85}Di_{15})_{ssp}$ samples with t_{ssp} less than 2 h. Therefore, the $\bar{M}_n$ and PDI curve for $t_{ssp} \leq 2$ h were plotted in Figure 2b as dotted lines. Figure 2b also shows that after completion of the Dianol incorporation around $t_{ssp} = 4$ h, the $\bar{M}_n$ of the $(BD_{85}Di_{15})_{ssp}$ copolymer steadily increases. Hydroxybutyl chain end groups are still present in high concentration and react with each other via alcoholysis upon releasing 1,4-butanediol. After ca. 20 h of SSP, the $\bar{M}_n$ levels off. Obviously, the hydroxybutyl end group concentration has become too low at this stage. After $t_{ssp} = 24$ h, $\bar{M}_n$ becomes close to 70 kg/mol. The PDI increases from 2.3 ($t_{ssp} = 0$ h) to 3.8 ($t_{ssp} = 24$ h). The increase in PDI can be explained by the absence of a Flory distribution[13] for SSP. The crystalline fraction of the $(BD_{85}Di_{15})_{ssp}$ copolymers cannot participate in the polycondensation reaction. However, this part does participate in the SEC analysis.

The chemical microstructure of the $(BD_{85}Di_{15})_{ssp}$ copolymers will have a blocky character consisting of unmodified homopolymer PBT blocks (only BD−T repeat units) which are predominantly present in the crystalline domains and amorphous parts consisting of both BD−T and Di−T repeat units. The Dianol monomer has two hydroxyl end groups which both can react with PBT. Consequently, Dianol can be present in three forms during the SSP reaction, Dianol can be present in three forms: (1) as free monomer containing two hydroxyl end groups (=free Dianol, represented as F), (2) as Dianol containing one free hydroxyl end group (=monoester, represented as M), and (3) as fully incorporated Dianol (=diester, represented as D). The three forms of Dianol are schematically depicted in Figure 3.

Figure 4 shows the 4−5 ppm region of a ^{1}H NMR spectrum of the $(BD_{85}Di_{15})_{ssp}$ copolymers with different solid-state polymerization times (t_{ssp}). It can be observed that the multiplet peak intensities of (a^*) and (b^*) gradually decrease as the SSP reaction proceeds, while two new peaks appear more downfield at 4.43 (b) and 4.77 (a) ppm. Peaks (a^*) and (b^*) originate from the two protons in the $-CH_2-$ groups next to the free hydroxyl end groups of free Dianol (F) (see Figure 3). However, the protons in the $-CH_2-$ group next to the free hydroxyl end group of the Dianol monoester (M) have an identical chemical shift as those in the $-CH_2-$ groups of free Dianol. Hence, both free Dianol (F) and the Dianol monoester (M) contribute to peaks (a^*) and (b^*).

When the free hydroxyl end groups of free Dianol or Dianol monoester react via transesterification with PBT, a carbonyl group is formed close to the $-CH_2-$ groups (Figure 3). The presence of the electron withdrawing carbonyl group close to the $-CH_2-$ groups results in the formation of two new peaks, a and b, having a chemical shift more downfield with respect to peaks a^* and b^*. Also here, the chemical shift of the protons in the $-CH_2-$ groups close to a carbonyl bond is identical for Dianol monoester and Dianol diester. Consequently, both Dianol monoester and Dianol diester contribute to peaks a and b. The small peaks at 4.35 and 4.70 ppm (s_1 and s_2) are the result from the ester formation between a small fraction of free hydroxyl end groups from F or M and deuterated trifluoroacetic acid,[14] used as NMR-solvent.

When the fraction of free Dianol (F_F) is known as a function of t_{ssp}, the integrals of the peaks in the 4−5 ppm region can be used to obtain the fraction of Dianol monoester (F_M) and Dianol diester (F_D) as a function of

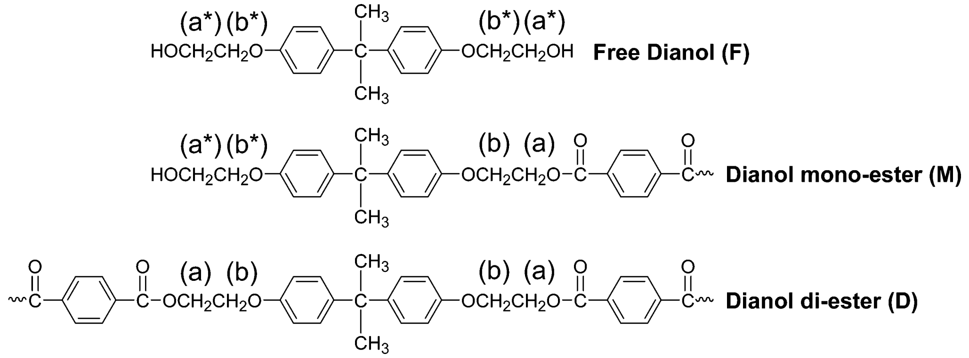

Figure 3. Three forms of Dianol that can be present during the SSP reaction: free Dianol monomer (F), Dianol monoester (M), and fully incorporated Dianol diester (D).

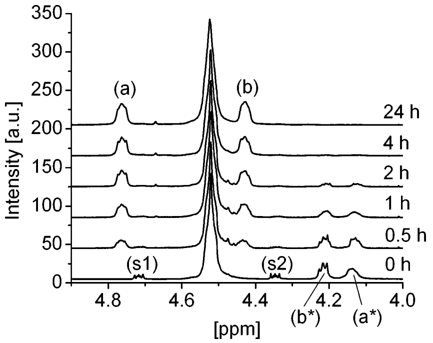

Figure 4. ^{1}H NMR spectra: 4−5 ppm region shown at different t_{ssp} (see Figure 3 for the identification of peaks).

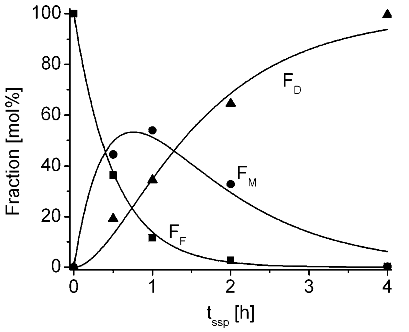

Figure 5. Experimentally determined values for F_F (■), F_M (●), and F_D (▲) using HPLC and ^{1}H NMR spectroscopy measurements as a function of t_{ssp} and calculated values for F_F, F_M and F_D using $k_1^f = 2.0$ h^{-1} and $k_2^f = 0.83$ h^{-1} (−).

t_{ssp}. The mole fraction of free Dianol (F_F) in (BD_{85}-Di_{15})$_{HFIP}$ ($t_{ssp} = 0$ h) and each ($BD_{85}Di_{15}$)$_{ssp}$ sample was determined via HPLC. The obtained value for F_F of the ($BD_{85}Di_{15}$)$_{HFIP}$ mixture was 15.1 mol % and is thus in agreement with the mole fraction of Dianol used for the mixture (≈15 mol %, see Experimental Section). Subsequently, F_F was set at 1 and the F_F values for the samples after SSP were proportionally adjusted. Prior to calculation of the fractions F_M and F_D, the integrals in the 4−5 ppm region were used to express the total amount of Dianol (sum of F_F, F_M, and F_D) as an integral value:

$$I(\text{total Dianol}) = I\left(\frac{(a^*) + (b^*) + (s_1 + s_2)}{2}\right) + I(a) \quad (1)$$

where

$$I\left(\frac{(a^*) + (b^*) + (s_1 + s_2)}{2}\right) = F + 0.5\text{ M} \quad \text{and}$$

$$I(a) = D + 0.5\text{ M}$$

The chemical shift of peak a^* is closely positioned to that of peak b^* making an accurate determination of the integral value of peak a^* impossible. However, peaks a^* and b^* should have equal integral values and therefore the integral was taken over both a^* and b^* and subsequently divided by 2 (see eq 1). Peak s_2 was also taken into account because this peak originates from F or M. The integral values of peaks s_2 are very small and were therefore added to the peak integral values of s_1 and subsequently averaged (see eq 1). It was already mentioned that, based on the number of protons, Dianol monoester (M) equally contributes to both peaks a and a^* (2 protons for M vs 4 protons for F and D, see Figure 3). Now, the amounts of F, M, and D have to be expressed as an integral value. The following eqs were used:

$$F = F_F I(\text{total Dianol}) \quad (2)$$

$$^1/_2M = I(\text{total Dianol}) - (a) - F \quad (3)$$

$$D = (a) - M \quad (4)$$

The fractions of free Dianol (F_F), Dianol monoester (F_M), and Dianol diester (F_D) can now be calculated by

$$F_M = \frac{M}{I(\text{total Dianol})} \quad (5)$$

$$F_D = \frac{D}{I(\text{total Dianol})} \quad (6)$$

The fractions F_F, F_M, and F_D, calculated via eqs 2, 5, and 6, are plotted as a function of t_{ssp} in Figure 5. F_F, obtained from HPLC measurements, rapidly decreases. Already after $t_{ssp} = 1$ h, 90% of free Dianol monomer (F_F) has reacted with PBT via alcoholysis reactions. At $t_{ssp} = 4$ h, no free Dianol monomer is left. The fraction of Dianol monoester (F_M) increases to a maximum at $t_{ssp} = 1$ h. This maximum clearly indicates that Dianol monoester (M) is an intermediate product that reacts with PBT via a consecutive alcoholysis reaction. At $t_{ssp} = 4$ h, all Dianol monoester has been fully incorporated ($F_D = 100$).

Consequently, the distribution of F_F, F_M, and F_D as a function of t_{ssp} is typical for a series of two irreversible consecutive first-order reactions.[15] The corresponding reaction scheme is schematically given in eq 7a

$$\text{F} \xrightarrow{k_1^f} \text{M} \xrightarrow{k_2^f} \text{D} \quad (7a)$$

where k_1^f and k_2^f are the reaction rate constants of the two consecutive reactions. F, M, and D represent free Dianol, Dianol monoester, and Dianol diester, respectively.

The reaction rate eqs can be described by

$$-\frac{\mathrm{d}F_\mathrm{F}}{\mathrm{d}t} = k_1^f F_\mathrm{F} \tag{7b}$$

$$\frac{\mathrm{d}F_\mathrm{M}}{\mathrm{d}t} = k_1^f F_\mathrm{F} - k_2^f F_\mathrm{M} \tag{7c}$$

$$\frac{\mathrm{d}F_\mathrm{D}}{\mathrm{d}t} = k_2^f F_\mathrm{M} \tag{7d}$$

Solving the set of differential equations, eqs 7b−7d, results in

$$F_\mathrm{F}(t) = F_{\mathrm{F},t=0}\mathrm{e}^{-k_1^f t} \tag{8}$$

$$F_\mathrm{M}(t) = \frac{k_1^f}{k_2^f - k_1^f}(\mathrm{e}^{-k_1^f t} - \mathrm{e}^{-k_2^f t})\cdot F_{\mathrm{F},t=0} \tag{9}$$

$$F_\mathrm{D}(t) = \left(1 - \frac{k_2^f}{k_2^f - k_1^f}\mathrm{e}^{-k_1^f t} + \frac{k_1^f}{k_2^f - k_1^f}\mathrm{e}^{-k_2^f t}\right)F_{\mathrm{F},t=0} \tag{10}$$

where it is assumed that at $t_\mathrm{ssp} = 0$ h, $F_\mathrm{M} = 0$ and $F_\mathrm{D} = 0$. Furthermore, eqs 7−10 are only valid when the reaction volume remains unchanged during the reaction and the Dianol monomer is homogeneously distributed in the amorphous phase. To verify whether the amorphous phase does significantly change during the SSP reaction, the crystallinity (χ_heating) of each $(\mathrm{BD}_{85}\mathrm{Di}_{15})_\mathrm{ssp}$ sample was determined by DSC using the first heating run. The obtained values for χ_heating were corrected in such a way that only the crystallizable BD−T repeat units were taken into account. The results are shown in Figure 6. It can be seen that the variation in χ_heating is ±5% for $0 \leq t_\mathrm{ssp} \leq 4$ h and consequently the reaction volume can considered to be constant. When $t_\mathrm{ssp} > 4$ h, all Dianol is fully incorporated (see Figure 5) and χ_heating only increases due to annealing. In addition, unpublished results show that Dianol acts as a solvent for PBT and therefore Dianol should be homogeneously distributed in the amorphous phase of PBT, once the Dianol monomer is molten.

Reaction rate constants k_1^f and k_2^f were obtained via a least-squares fitting method. The fractions F_F, F_M, and F_D were calculated for different t_ssp (0, 0.5, 1, 2, and 4 h) using eqs 8−10 with initial arbitrary values for k_1^f and k_2^f. A minimum total square error value was found for $k_1^f = 2.0\ \mathrm{h}^{-1}$ and $k_2^f = 0.83\ \mathrm{h}^{-1}$. To validate the integrity of the values found, the fractions F_F, F_M, F_D were calculated as a function of t_ssp, using eqs 8−10. These calculated values for fractions F_F, F_M, and F_D are also plotted in Figure 5. It can be seen that the calculated fractions, based on k_1^f and k_2^f, are in good agreement with the experimentally obtained fractions (obtained via eqs 2, 5, and 6).

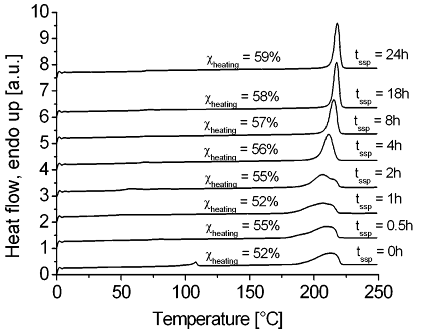

Figure 6. DSC traces (first heating run) of the synthesized $(\mathrm{BD}_{85}\mathrm{Di}_{15})_\mathrm{ssp}$ copolymers as a function of t_ssp. Values for χ_heating are corrected for the weight fraction of crystallizable BD−T repeat units present in each sample.

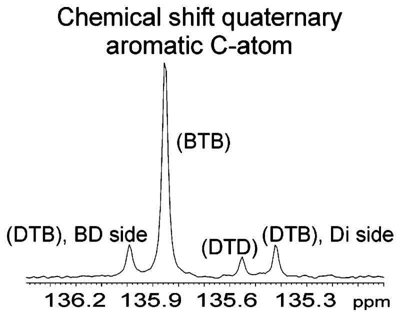

Figure 7. ^{13}C NMR spectrum (135−137 ppm region) of a $(\mathrm{BD}_{85}\mathrm{Di}_{15})_\mathrm{ssp}$ copolymer at $t_\mathrm{ssp} = 4$ h: splitting of the quaternary carbon atom into four peaks with different chemical shifts and integral size.

Sequence	Chemical shift [ppm]
DTB, BD side	136.0
BTB	135.9
DTD	135.6
DTB, Di side	135.4

Schematic representation sequence
BTD, BD-side

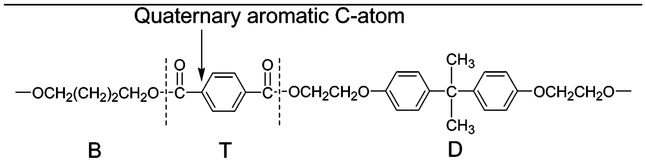

Figure 8. Four possible dyad sequences and corresponding chemical shifts. For convenience, a schematic representation of a BTD dyad sequence is included.

Because $(k_1^f/k_2^f) > 2$, it can be concluded that the presence of a PBT chain on one side of Dianol (i.e., Dianol monoester) results in a decreased hydroxyl end group reactivity compared to the end groups of free Dianol. Flory[16] postulated that reactivity of functional end groups remains independent of molecular weight of the corresponding polymers. However, he remarked that for small molecules a higher end group reactivity is possible. This effect is clearly observed from the results described above.

Besides ^{1}H NMR spectroscopy, also ^{13}C NMR spectroscopy was used to study the incorporation of Dianol in PBT via SSP. Kricheldorf[17] already showed in the early seventies that the ^{13}C NMR shift of carbonyl carbon atoms present in terephthalate based polyesters is determined by adjacent monomeric units. Later, Newmark[18] used the same method for PBT−PET copolymers and found that the signal of the quaternary carbon atom of the terephthalate unit, i.e., the carbon atom next to the carbonyl group, splits up into a total of four peaks. Each of these peaks represents a dyad sequence. In Figure 7, the 135−137 ppm region of the ^{13}C NMR spectrum is shown for a $(\mathrm{BD}_{85}\mathrm{Di}_{15})_\mathrm{ssp}$ copolymer with $t_\mathrm{ssp} = 4$ h. Also for this copolymer, the signal

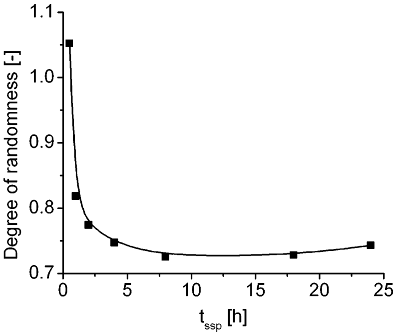

Figure 9. Degree of randomness (R) as a function of t_{ssp} obtained via quantitative ^{13}C NMR spectroscopy measurements.

of the quaternary carbon atom, adjacent to the carbonyl group, splits into four peaks. The four corresponding dyad sequences, including chemical shifts, are shown in Figure 8. A schematic representation of a BTD sequence is shown for convenience.

The peaks as shown in Figure 7 were integrated and the corresponding integral values were normalized to a total value of 1. It will be shown in a subsequent article that the four peak signals in Figure 7, corresponding to the four dyad sequences, can be used in a quantitative way. The normalized integral values can be used to determine the degree of randomness (R) as a function of t_{ssp}. R is defined by[19]

$$R = \frac{F_{\mathrm{DTB,tot}}}{2\cdot(F_{\mathrm{BD-T}}F_{\mathrm{Di-T}})} \tag{11a}$$

where

$$F_{\mathrm{BD-T}} = (F_{\mathrm{DTB,tot}}/2 + F_{\mathrm{BTB}}) \tag{11b}$$

$$\mathrm{F}_{\mathrm{Di-T}} = (F_{\mathrm{DTB,tot}}/2 + F_{\mathrm{DTD}}) \tag{11c}$$

$$F_{\mathrm{DTB,tot}} = F_{\mathrm{DTB,BD\ side}} + F_{\mathrm{DTB,Di\ side}} \tag{11d}$$

where F_i denotes the normalized fraction of each sequence (i = DTB, BD side; BTB; DTD; DTB, Di side).

R should be 1 for a fully random copolymer[19,20] in which the repeat units (in this study: BD−T and Di−T; see Figure 1) are randomly distributed over the copolymer. A value for R smaller than 1 indicates that similar repeat units tend to form blocks.

In Figure 9, the calculated degree of randomness is shown as a function of t_{ssp}. It was already mentioned that with SSP only the amorphous phase of PBT should be accessible for incorporation of Dianol, while the crystalline fraction should remain unchanged. As a consequence, the preserved crystallizable PBT homopolymer blocks result in a value for R below unity, which can clearly be observed in Figure 9. The degree of randomness rapidly decreases during the first hour and remains constant after $t_{ssp} = 4$ h. This stabilization of R implies that the final chemical microstructure of the $(BD_{85}Di_{15})_{ssp}$ copolymer does not change anymore. Hence, all Dianol should be fully incorporated around $t_{ssp} = 4$ h, which is in agreement with the results plotted in Figure 5.

Conclusions

Dianol was successfully incorporated in PBT via SSP using a reaction temperature of 180 °C. HPLC measurements in combination with ^{1}H NMR spectroscopy showed that the incorporation of Dianol in PBT occurs via a series of two consecutive first-order transesterification reactions. The Dianol monomer first forms an intermediate species (Dianol monoester) where PBT is attached on one side of the Dianol monomer. A second transesterification reaction results in Dianol diester. The reaction rate constants k_1^f and k_2^f were determined via a least-squares fitting method which resulted in $k_1^f = 2.0\ \mathrm{h}^{-1}$ and $k_2^f = 0.83\ \mathrm{h}^{-1}$. The fraction of amorphous phase did not considerably change during the SSP reaction. Hence, the obtained values for k_1^f and k_2^f are within experimental error. Because $(k_1^f/k_2^f) > 2$, it can be concluded that Dianol attached to a PBT chain (Dianol monoester) becomes less reactive toward transesterification compared to free Dianol monomer. Apparently, the hydroxyl end groups of Dianol monoester have a reduced reactivity compared to hydroxyl end groups of free Dianol monomer. It was also shown that the Dianol monomer was fully incorporated around $t_{ssp} = 4$ h. In agreement, ^{13}C NMR sequence distribution analysis showed that the degree of transesterification did not significantly change after $t_{ssp} = 4$ h. SEC measurements showed that oligomers are formed in the initial stage of the SSP reaction. Alcoholysis results subsequently in an increase of the molecular weight. The broadening of the molecular weight distribution as a function of t_{ssp} can be explained by the absence of a Flory distribution during SSP.

References and Notes

(1) Denchev, Z. In *Handbook of Thermoplastic Polyesters*; Fakirov, S., Ed.; Wiley-VCH: Weinheim, Germany, 2002; Chapter 17, p 757−813.
(2) Devaux, J.; Godard, P.; Mercier, J. P. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1881−1894.
(3) Fakirov, S.; Sarkissova, M.; Denchev, Z. *Macromol. Chem. Phys.* **1996**, *197*, 2837−2867.
(4) Denchev, Z.; Sarkissova, M.; Fakirov, S.; Yilmaz, F. *Macromol. Chem. Phys.* **1996**, *197*, 2869−2887.
(5) Fakirov, S.; Sarkissova, M.; Denchev, Z. *Macromol. Chem. Phys.* **1996**, *197*, 2889−2907.
(6) Montaudo, G.; Montaudo, M. S.; Scamporrino, E.; Valatini, D. *Macromolecules* **1992**, *25*, 5099−5107.
(7) Fernandez-Berridi, M. J.; Iruin, J. J.; Maiza, I. *Polymer* **1995**, *36*, 1357−1361.
(8) Fakirov, S. In *Solid State Behavior of Linear Polyesters and Polyamides*, Schultz, J. M., Fakirov, S., Eds.; Prentice Hall: Englewood Cliffs, NJ, 1990; Chapter 2, p 19−43.
(9) James, N. R.; Ramesh, C.; Sivaram, S. *Macromol. Chem. Phys.* **2001**, *202*, 1200−1206.
(10) James, N. R.; Ramesh, C.; Sivaram, S. *Macromol. Chem. Phys.* **2001**, *202*, 2267−2274.
(11) Kirk, R. E.; Othmer, D. F. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed.; Kroschwitz, J. I., Howe-Grant, M., Eds.; Wiley-Interscience: New York, 1997; Vol. 22, p 400.
(12) The PBT as received already contained residuals of tetra-*n*-butyl titanate ($Ti(OBu)_4$) catalyst, so promoting the transesterification reaction by additional catalyst was not necessary.
(13) Flory, P. J. In *Principles of Polymer Chemistry*; Cornell University Press: London, 1953; Chapter 8, p 317−326.
(14) Kenwright, A. M.; Peace, S. K.; Richards, R. W.; Bunn, A.; MacDonald, W. A. *Polymer* **1999**, *40*, 2035−2040.
(15) Santen van, R. A.; Niemantsverdriet, J. W. In *Chemical Kinetics and Catalysis*; Twigg, M. V., Spencer, M. S., Eds.; Plenum Press: New York, 1995; Chapter 2, p 38−41.
(16) Flory, P. J. In *Principles of Polymer Chemistry*; Cornell University Press: London, 1953; Chapter 3, pp 69−105.
(17) Kricheldorf, H. R. *Makromol. Chem.* **1978**, *179*, 2133−2143.
(18) Newmark, R. A. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 559−563.
(19) Yamadera, R.; Murano, M. *J. Polym. Sci., Part A-1* **1967**, *5*, 2259−2268.
(20) Devaux, J.; Godard, P.; Mercier, J. P. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1875−1881.

MA0483773