Poly(butylene terephthalate) Copolymers Obtained via Solid-State Polymerization and Melt Polymerization. A Study on the Microstructure via ^{13}C NMR Sequence Distribution

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ABSTRACT: The chemical microstructure of poly(butylene terephthalate) (PBT) copolymers obtained by incorporation of a rigid diol, 2,2-bis[4-(2-hydroxyethoxy)phenyl]propane (Dianol 220), into PBT using solid-state polymerization (SSP) and melt polymerization (MP) was analyzed. ^{13}C NMR sequence distribution analysis showed that Dianol was randomly incorporated in the PBT−Dianol copolymers obtained by MP. However, the used ^{13}C NMR sequence distribution analysis method was based on solution NMR. As a consequence, the obtained chemical microstructure reflects both the crystalline and amorphous part. For PBT−Dianol copolymers obtained by SSP, the modification only took place in the amorphous phase of PBT. Hence, knowledge of the chemical microstructure of the amorphous phase is important for tailoring the final properties of these copolymers obtained by SSP. Therefore, a calculation method was developed to adjust the solution ^{13}C NMR peak integral values of the dyad sequences in such a way that only the amorphous fraction, which participates in the transesterification process, was taken into consideration for calculating the degree of randomness. The semicrystalline PBT−Dianol copolymers as obtained by SSP were initially represented by the often-used two-phase (crystalline/amorphous) model. The resulting chemical microstructure of the amorphous phase gave a strong indication that part of the amorphous phase was not accessible for incorporation of Dianol by SSP. Therefore, a three-phase (crystalline, rigid amorphous and mobile amorphous) model was used to represent the morphology of the PBT−Dianol copolymers. Crystalline, mobile amorphous, and rigid amorphous fractions were determined by DSC. Using this three-phase model, the calculation method showed that only the mobile amorphous fraction was accessible for incorporation of Dianol by SSP. At the used solid-state polymerization temperature of 180 °C, the PBT chains in the rigid amorphous and crystalline phase are not mobile enough to participate in the transesterification reaction. Furthermore, determination of the chemical microstructure of the mobile amorphous fraction showed that Dianol was fully randomly incorporated in this fraction.

Introduction

Poly(butylene terephthalate) (PBT) is a semicrystalline aromatic polyester with a high crystallization rate in combination with good mechanical properties.[1] However, its relatively low glass transition temperature makes unfilled PBT less suitable for use at elevated temperatures. It is generally known that the material properties of PBT can be modified by reactive melt blending with other polycondensates.[2] Transesterification reactions in the melt first result in the formation of block copolymers, and with proceeding reaction times, copolymers with a random microstructure are obtained.[3−9] Random copolymers have shorter and more irregular homopolymer sequences and may therefore exhibit a decreased melting temperature, crystallization rate, and crystallinity compared to pure PBT.

Synthesis of copolymers with a predetermined, nonrandom microstructure may also be obtained using monomers either with unsymmetrically located functional groups or with groups of varying chemical nature. This approach was extensively discussed by Vasnev and Kuchanov in their review in 1986.[10] A method suitable for preparation of copolymers from polycondensates with retention of long homopolymer blocks is solid-state polymerization (SSP).[11] With SSP, the PBT homopolymer is heated just below its melting temperature (T_m) but far above its glass transition temperature (T_g) so that the crystalline fraction, consisting of homopolymer PBT blocks, will be retained. As a result of the high reaction temperature close to T_m, the amorphous fraction will become mobile enough for transesterification reactions to occur. Polymer chain ends present in the amorphous phase will react with each other by transesterification, resulting in a recombination of polymer chains. Similarly, when a mixture of different semicrystalline homopolymer polycondensates is heated below the T_m of the lowest melting homopolymer, a copolymer

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will be obtained. In this way, Sivaram and co-workers prepared several copolymers.[11−13] In addition, our previous work[14,15] showed that SSP can also be used to incorporate diol monomers into semicrystalline polycondensates. 2,2-Bis[4-(2-hydroxyethoxy)phenyl]propane (Dianol 220) was successfully incorporated into PBT via SSP. Copolymers of different compositions were obtained using different PBT/diol ratios. Quantitative ^{13}C NMR sequence distribution analysis[16−21] was used to study the difference in chemical microstructure between PBT−Dianol copolymers obtained via SSP and via MP.[15] A clear difference in chemical microstructure was observed: the copolymers obtained by MP have a fully random microstructure, whereas the SSP copolymers have a nonrandom microstructure. The latter result is due to the presence of homopolymer PBT blocks. For tailoring the overall properties of copolymers obtained by SSP, it is important to know how the diol is incorporated and distributed in the amorphous phase. However, the total chemical microstructure as obtained by quantitative ^{13}C NMR sequence distribution analysis includes both the crystalline and amorphous phase and hence does not give exclusive information about the chemical microstructure of the amorphous phase only.

In the present paper, a calculation method is discussed which reveals the chemical microstructure of the amorphous phase using the peak integral values of the dyad sequences as obtained from the quantitative ^{13}C NMR sequence distribution analysis. Initially, a two-phase model (based on a crystalline and an amorphous phase) will be used to describe the morphology of the semicrystalline PBT−Dianol copolymers obtained by SSP. Crystallinity measurements were done by DSC and implemented in the calculation method to determine the chemical microstructure of the amorphous phase. In the second part, the morphology of the semicrystalline PBT−Dianol copolymers will be described by a three-phase model (crystalline, rigid amorphous and mobile amorphous fraction) and the calculation method will be accordingly adjusted to exclusively determine the chemical microstructure of the mobile amorphous fraction.

Experimental Section

Materials. Poly(butylene terephthalate) (PBT) pellets ($\bar{M}_n$ = 15 kg/mol and $\bar{M}_w$ = 34 kg/mol, determined by size exclusion chromatography) 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. 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.

Synthesis of PBT—Dianol Copolymers: Solid-State Polymerization (SSP) and Melt Polymerization (MP). The synthesis of PBT−Dianol copolymers by SSP and MP was described in detail in previous work.[15] Powder mixtures of different PBT/Dianol ratios were used as feed for the SSP and MP reactions in order to obtain copolymers of different compositions. For the SSP reactions, the PBT and Dianol powder were mixed by dissolution in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) prior to SSP. After complete dissolution, the HFIP was evaporated and the obtained lump of material was ground into powder. The PBT/Dianol mixtures used for MP or SSP are abbreviated as $(BD_xDi_y)_{feed}$. BD_x denotes the mole percentage (mol %) of PBT (expressed in 1,4-butanediol units), whereas Di_y denotes the mole percentage of Dianol (expressed in Di units) in the $(BD_xDi_y)_{feed}$ mixtures. Solid-state polymerized (BD_xDi_y) copolymers are indicated as $(BD_xDi_y)_{ssp}$ copolymers, where BD_x and Di_y represent the initial mol % PBT and Dianol present in the $(BD_xDi_y)_{feed}$ mixture being used for SSP. The actual mole fractions of BD and Di units after SSP differ only slightly from the initial fractions present in the $(BD_xDi_y)_{feed}$ mixtures. These differences can be attributed to the evaporation of 1,4-butanediol during the SSP reaction. For all $(BD_xDi_y)_{ssp}$ copolymers, a solid-state polymerization temperature (T_{ssp}) of 180 °C was used in combination with a solid-state polymerization time (t_{ssp}) of 9 h. This time proved to be long enough for complete incorporation of the Dianol into the PBT. Furthermore, after this reaction time, it was shown that the molecular weight of the resulting $(BD_xDi_y)_{ssp}$ copolymers did not significantly increase anymore.[14] Melt polymerized (BD_xDi_y) copolymers are denoted as $(BD_xDi_y)_{mp}$, where BD_x and Di_y respectively represent the initial mol % PBT and Dianol present in the $(BD_xDi_y)_{feed}$ powder mixture being used for MP. Also here, the mole fractions of BD and Di units after MP slightly differ from the reactions initially present in the $(BD_xDi_y)_{feed}$ mixtures.

Nuclear Magnetic Resonance (NMR) Spectroscopy. All solution ^{1}H NMR spectra were recorded on a Varian 400 MHz spectrometer at 25 °C at a resonance frequency of 400.164 MHz. For the ^{1}H 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 copolymers with less than 10 mol % of incorporated Dianol, an Oxford 500 MHz spectrometer was used, operated at a resonance frequency of 125.685 MHz. For ^{13}C NMR measurements, 50 mg of polymer was dissolved in 0.8 mL of pure TFA-*d*. TMS was used as the internal standard.

For spectra recorded with the 300 MHz spectrometer, 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 spectra recorded with the 500 MHz spectrometer, 4000−5000 scans were acquired with 75k data points, a d_1 of 12 s, a 90° pulse, and a spectral width of 25 kHz. Spinning was not used for the spectra recorded with the 500 MHz spectrometer.

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.

Differential Scanning Calorimetry (DSC). Specific heat capacity measurements were done on a Perkin Elmer Pyris Diamond DSC equipped with an Intracooler II. Nitrogen was used as purge gas. $(BD_xDi_y)_{ssp}$ copolymer samples of 18−20 mg were wrapped in approximately 5 mg of aluminum foil where the aluminum weights of the sample and reference were closely matched. Crystallinity was estimated from the heat of fusion from scan measurements at 20 K/min from 0 to 260 °C. The peak area was obtained using a linear baseline for integration. Heat of fusion of the infinite crystal was assumed to be 145 J/g (32 kJ/mol).[22−24] Specific heat capacity in the vicinity of the glass transition was calculated from StepScan DSC measurements with steps of 1 K and isothermal waiting times of 1 min. The mobile amorphous fraction was determined as the ratio of the increase of heat capacity at the glass transition for the sample under investigation and that for 100% amorphous PBT [0.35 J/(g K)].[22,25] The step in heat capacity for the semicrystalline samples was obtained using tangents to the measured curves below and above the glass transition. The tangents above T_g were constructed as linear superposition of the heat capacities for crystalline and liquid PBT according to ATHAS database.[22] The crystalline heat capacity was used as the tangent below T_g. Details about the calculation of the crystallinity, as well as mobile and rigid amorphous fractions, are given below.

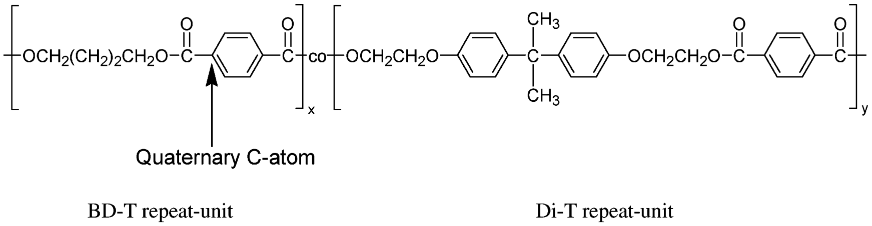

Figure 1. Chemical structure of a (BD_xDi_y) copolymer, consisting of BD−T and Di−T repeat units. The arrow marks the quaternary carbon atom which ^{13}C NMR signal is used in the sequence distribution analysis.

Table 1. Overview of the Used $(BD_xDi_y)_{feed}$ Mixtures and the Resulting $(BD_xDi_y)_{ssp}$ and $(BD_xDi_y)_{mp}$ Copolymers

composition feed[a] $(BD_xDi_y)_{feed}$		composition after SSP[b] $(BD_xDi_y)_{ssp}$		degree of randomness[c]	crystallinity[d]	
$x = F_{BD-T,feed}$ (mol %)	$y = F_{Di,feed}$ (mol %)	$F_{BD-T,total}$ (mol %)	$F_{Di-T,total}$ (mol %)	$R_{ssp,\ total}$	$\chi_{heating,total}$ (%)	$\chi_{heating,PBT\ only}$ (%)
100	0	100	0		54.5	54.5
95	5	96	4	0.82	51.8	55.8
90	10	90	10	0.76	46.6	57.3
85	15	84	16	0.73	41.1	57.4
80	20	76	24	0.73	33.4	54.7
75	25	69	31	0.76	25.6	48.8
70	30	61	39	0.82	15.5	35.7
65	35	54	46	0.89	5.7	15.7

composition feed[a] $(BD_xDi_y)_{feed}$		composition after MP[b] $(BD_xDi_y)_{mp}$		degree of randomness[c]
$x = F_{BD-T,feed}$ (mol %)	$y = F_{Di,feed}$ (mol %)	$F_{BD-T,total}$ (mol %)	$F_{Di-T,total}$ (mol %)	$R_{mp,total}$
95	5	96	4	1.04
90	10	90	10	0.93
85	15	81	19	0.99
80	20	74	26	0.98
75	25	70	30	0.99

[a] Composition of the feed mixtures used for SSP (amounts of PBT and Dianol were weighed so that a specific mole ratio PBT:Dianol was obtained. [b] Compositions of the $(BD_xDi_y)_{ssp}$ and $(BD_xDi_y)_{mp}$ copolymers were determined by ^1H NMR spectroscopy. [c] $R_{ssp,total}$ and $R_{mp,total}$ were obtained by quantitative ^{13}C NMR spectroscopy. [d] $\chi_{heating,total}$ is the total crystallinity, based on $\Delta H_{melting}$. $\chi_{heating,PBT\ only}$ was obtained by dividing $\chi_{heating,total}$ by the present weight fraction of BD−T repeat units.

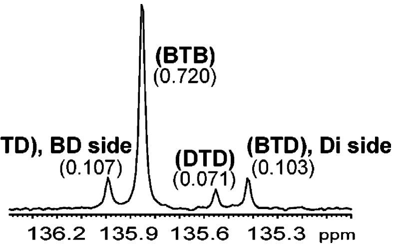

Figure 2. ^{13}C NMR spectrum (135−136 ppm) of a $(BD_{85}Di_{15})_{ssp}$ copolymer: splitting of the quaternary carbon atom (marked by the arrow in Figure 1) into four peaks. Peak integral values are also listed.

Results and Discussion

$(BD_xDi_y)_{ssp}$ and $(BD_xDi_y)_{mp}$ copolymers were synthesized using different PBT/Dianol ratios. The procedures to synthesize these copolymers were explained in previous work.[15] The general chemical structure of the (BD_xDi_y) copolymer is shown in Figure 1. For both $(BD_xDi_y)_{ssp}$ and $(BD_xDi_y)_{mp}$ copolymers, the overall chemical compositions obtained from ^1H NMR measurements are listed in Table 1.

In previous work,[15] the chemical microstructure of the synthesized $(BD_xDi_y)_{ssp}$ and $(BD_xDi_y)_{mp}$ copolymers was studied by ^{13}C NMR dyad sequence distribution using the chemical shift of the aromatic quaternary carbon atom (marked with the arrow in Figure 1). This peak, positioned in the 135−136 ppm region of the ^{13}C NMR spectrum, splits up into four different peaks as is shown in Figure 2 for a $(BD_{85}Di_{15})_{ssp}$ copolymer. Each peak originates from a different dyad sequence. Because the four peaks shown in Figure 2 are slightly overlapping, a Gaussian deconvolution procedure was applied for a clear peak separation. Subsequently, the integral value of each peak was determined. The obtained integral values were normalized to a total value of 1. These values are also listed in Figure 2.

The normalized peak integral values can be used to calculate the composition and the degree of randomness (R) of each (BD_xDi_y) copolymer. The latter parameter represents the sequence distribution of a copolymer. The following equations[15] were used:

$$F_{BTD,total} = F_{BTD,BD-side} + F_{BTD,Di-side} \tag{1}$$

$$F_{BD-T,total} = (F_{BTD,total}/2 + F_{BTB}) \tag{2}$$

$$F_{Di-T,total} = (F_{BTD,total}/2 + F_{DTD}) \tag{3}$$

$$R_{total} = \frac{F_{BTD,total}}{2 \cdot (F_{BD-T,total} \cdot F_{Di-T,total})} \tag{4}$$

where $F_{BTD,BD-side}$, F_{BTB}, F_{DTD}, and $F_{BTD,Di-side}$ represent the integral values of the dyad sequences. $F_{BD-T,total}$ and $F_{Di-T,total}$ denote the total mole fractions of BD−T and Di−T repeat units, respectively. For a fully random copolyester, the distribution of the two different BD−T and Di−T repeat units should obey Bernoullian statistics.[16,26] The degree of randomness (R_{total}) as calculated using eq 4 should then be equal to 1. If R_{total} is smaller than 1, the repeat units tend to be arranged in blocklike structures. Schematic representations of copolymers obtained by MP (random: $R_{mp,total}$ = 1) and by SSP

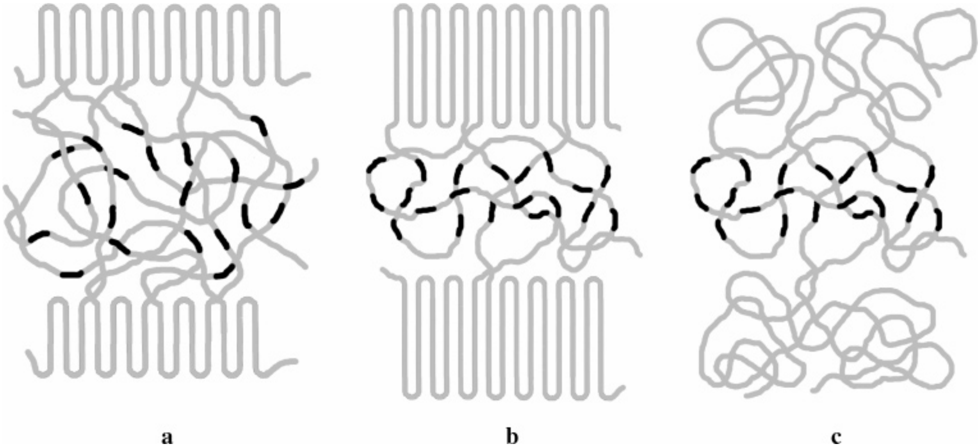

Figure 3. Schematic representation of the chemical microstructures: (a) $(BD_xDi_y)_{mp}$ random distribution of BD−T and Di−T repeat units, $R_{mp,total} = 1$; (b) $(BD_xDi_y)_{ssp}$ nonrandom distribution of Di−T repeat units, $R_{ssp,total} < 1$; (c) after dissolution of a $(BD_xDi_y)_{ssp}$ copolymer in TFA-*d*.

(nonrandom: $R_{ssp,total} < 1$) are shown in Figures 3a and b, respectively.

The values for $R_{ssp,total}$ and $R_{mp,total}$ for all synthesized $(BD_xDi_y)_{ssp}$ copolymers and $(BD_xDi_y)_{mp}$ copolymers, respectively, are also listed in Table 1. It can be seen that all synthesized $(BD_xDi_y)_{mp}$ copolymers have a fully random distribution ($R_{mp,total} = 1$) for the whole composition range. Only for the $(BD_{95}Di_5)_{mp}$ and $(BD_{90}Di_{10})_{mp}$ copolymers, the obtained values for $R_{mp,total}$ slightly deviate from unity. This deviation is due to the low peak signal intensity of the DTD dyad sequence for these low Dianol concentrations.

The microstructure of the $(BD_xDi_y)_{ssp}$ copolymers, represented by $R_{ssp,total}$, depends on the mole fraction of incorporated Dianol. $R_{ssp,total}$ decreases to a minimum value of 0.73 at $F_{BD-T,total} \approx 83$ mol % and then gradually increases to unity with increasing Dianol content. DSC measurements showed that the total crystallinity ($\chi_{heating}$) of the $(BD_xDi_y)_{ssp}$ copolymers decreased for increasing fractions of incorporated Dianol. Finelli et al.[27] synthesized a $(BD_0Di_{100})_{mp}$ copolymer (i.e., a homopolymer only consisting of Di−T repeat units) and observed that this homopolymer was fully amorphous. Hence, Di−T repeat units are not able to crystallize. To obtain the crystallinity of the PBT-segments only, $\chi_{heating}$ was divided by the weight fraction of BD−T repeat units ($W_{BD-T,total}$). Both $\chi_{heating}$ and $\chi_{heating,PBT\ only}$ are listed in Table 1 for the $(BD_xDi_y)_{ssp}$ copolymers. It can be seen that $\chi_{heating,PBT\ only}$ initially shows a small increase for $(BD_xDi_y)_{ssp}$ copolymers with $F_{BD-T,total} > 90$ mol % compared to $\chi_{heating,PBT\ only}$ of a $(BD_{100}Di_0)_{ssp}$ homopolymer (i.e., a PBT homopolymer after HFIP treatment and subsequent SSP). For $F_{BD-T,total} < 63$ mol %, $\chi_{heating,PBT\ only}$ decreases to a value which is even below $\chi_{heating}$ of a $(BD_{100}Di_0)_{feed}$ homopolymer (i.e., a PBT homopolymer after HFIP treatment; $\chi_{heating} = \chi_{heating,PBT\ only} = 38.3$). This result is remarkable because it was assumed that the crystalline fraction is preserved during SSP and that modifications only take place in the amorphous phase. This decrease of $\chi_{heating,PBT\ only}$ for increasing fractions of Dianol monomer might already occur during the preparation of the $(BD_xDi_y)_{feed}$ mixtures. Another possibility is that $\chi_{heating,PBT\ only}$ decreases during the SSP reaction. The small increase of $\chi_{heating,PBT\ only}$ for $F_{BD-T,total} > 90$ mol % with respect to $(BD_{100}Di_0)_{ssp}$ homopolymer may be the result of the solvent-induced crystallization effect of Dianol, when present in small amounts during the SSP reaction. The increased mobility will favor the crystallization, simultaneously occurring with SSP over the dissolution of the crystalline PBT fraction. Once the crystalline PBT blocks are dissolved, all polymer chain segments will have sufficient mobility to participate in the transesterification reactions. Hence, the degree of randomness of the $(BD_xDi_y)_{ssp}$ copolymers will gradually increase for $(BD_xDi_y)_{feed}$ mixtures with higher Dianol content (Table 1).

Because the ^{13}C NMR sequence distribution analysis is based on solution NMR, the $(BD_xDi_y)_{ssp}$ copolymers have to be completely dissolved prior to measuring. The microstructure of a dissolved $(BD_xDi_y)_{ssp}$ copolymer is schematically depicted in Figure 3c. For clarity, the homopolymer blocks of the former crystalline part and the modified former amorphous part are drawn separately, although realizing that this conformation is unlikely. In this way, however, it can be clearly seen that the obtained degree of randomness for the $(BD_xDi_y)_{ssp}$ copolymers ($R_{ssp,total}$) is an *overall* degree of randomness, in which both the former crystalline and former amorphous parts contribute to the total signal intensity. Therefore, $R_{ssp,total}$ does not give exclusive information on the chemical microstructure of the amorphous phase, the only part of the material that can participate in the transesterification process during SSP. Knowledge about the chemical microstructure of the amorphous phase is important because it influences the thermal properties of the corresponding copolymer. To reveal the chemical microstructure of the amorphous phase after SSP, it is necessary to correct the obtained peak integral values of the different dyad sequences in such a way that only the amorphous part is taken into consideration. Hence, the relationship between crystallinity of the $(BD_xDi_y)_{ssp}$ copolymers and the peak integral values of the dyad sequences has to be established in order to proportionally adjust these values. The corrected peak integral values should then represent the microstructure of the amorphous phase. A method to correct the peak integral values of the dyad sequences will be discussed below. The morphology of the semicrystalline $(BD_xDi_y)_{ssp}$ copolymers will first be represented by a two-phase (crystalline/amorphous) model.

A. Chemical Microstructure Based on the Two-Phase Model. The calculation method described below consists of three steps. First, the ratio of BD−T and Di−T repeat units in the amorphous phase is calculated. Subsequently, a mole balance is made with respect to the total copolymer. Finally, the peak integral values are corrected by taking previous calculations into account. The data for a $(BD_{85}Di_{15})_{ssp}$ copolymer are used to illustrate the calculation method.

1. Mole Ratio of BD—T and Di—T Repeat Units in the Amorphous Phase. The degree of randomness ($R_{ssp,total}$), calculated using eq 4, is based on the overall mole fractions of BD−T and Di−T repeat units in the copolymer. When this equation is used to calculate the degree of randomness of the amorphous phase only, then the mole fractions of BD−T and Di−T repeat units present in the amorphous phase have to be considered. Therefore, the crystallinity of the $(BD_{85}Di_{15})_{ssp}$ copolymer should be known. The crystallinity (denoted as $\chi_{heating}$) was determined by dividing the melting enthalpy ($\Delta H_{melting}$) of the first heating run (obtained via DSC) by the melting enthalpy (ΔH^0_{fuse}) for 100% crystalline PBT. For ΔH^0_{fuse}, values of 145[22-24] J/g (32 kJ/mol) and 140[28] J/g (31 kJ/mol) are reported in the literature. In this study, a value of 145 J/g was used for ΔH^0_{fuse}. For $(BD_{85}Di_{15})_{ssp}$, $\Delta H_{melting}$ has a value of 59.4 J/g which corresponds to $\chi_{heating} = 41.0\%$, and hence, $\alpha_{heating} = 59.0\%$. It has to be mentioned that during the SSP reaction annealing may occur which results in PBT crystals with a larger lamellar thickness and an increased crystallinity. Furthermore, the DSC traces of the first heating run of the SSP samples gave sharp melting peaks and did not show any reorganization upon heating. Hence, $\chi_{heating}$ as obtained from the first DSC heating run should represent the crystallinity of the $(BD_xDi_y)_{ssp}$ copolymers directly after SSP. Now, a BD−T mass balance with respect to the total $(BD_{85}Di_{15})_{ssp}$ copolymer can be made:

$$\chi_{heating}W_{BD-T,\chi} + \alpha_{heating}W_{BD-T,\alpha} = W_{BD-T,total} \quad (5)$$

where $\chi_{heating}$ and $\alpha_{heating}$ represent the fractions of the crystalline and amorphous phase based upon $\Delta H_{melting}$ of the first heating run. $W_{BD-T,\chi}$ and $W_{BD-T,\alpha}$ are the weight fractions of BD−T repeat units in the crystalline phase and amorphous phase, respectively, whereas $W_{BD-T,total}$ is the total weight fraction of BD−T repeat units based on the entire copolymer. $W_{BD-T,total}$ was calculated using $F_{BD-T,total}$ (obtained via ^{1}H NMR measurements; values are shown in Table 1):

$$F_{BD-T,total} = 0.836 \cong W_{BD-T,total} = 0.716 \text{ BD−T } (M_{BD-T} = 220.2 \text{ g/mol})$$

$$F_{Di-T,total} = 0.164 \cong W_{Di-T,total} = 0.284 \text{ Di−T } (M_{Di-T} = 446 \text{ g/mol})$$

It is assumed that the crystalline fraction only consists of PBT homopolymer segments (BD−T repeat units) and thus for this fraction $W_{BD-T,\chi} = 1$. This assumption also implies that Dianol is only incorporated into the amorphous phase (present as Di−T repeat units). Using $W_{BD-T,\chi} = 1$, together with $\chi_{heating} = 0.411$, $\alpha_{heating} = 0.589$, and $W_{BD-T,total} = 0.716$, gives $W_{BD-T,\alpha} = 0.518$; i.e., the amorphous phase of the $(BD_{89}Di_{15})_{ssp}$ copolyester consists of 51.8 wt % BD−T repeat units and thus of 48.2 wt % Di−T repeat units. Recalculation into mole fractions gives

$$W_{BD-T,\alpha} = 0.518 \cong F_{BD-T,\alpha} = 0.685 \text{ BD−T}$$

$$W_{Di-T,\alpha} = 0.482 \cong F_{Di-T,\alpha} = 0.315 \text{ Di−T}$$

Consequently, for the $(BD_{85}Di_{15})_{ssp}$ copolyester, the mole ratio in the amorphous phase is $(F_{BD-T,\alpha}/F_{Di-T,\alpha}) = 2.18$.

2. Total Mole Fraction of BD—T and Di—T Repeat Units Based on the Total Copolymer (Crystalline and Amorphous Fraction). The next step is to calculate the overall mole fractions of BD−T and Di−T repeat units in the total copolymer. It was already mentioned that Di−T repeat units are assumed to be present only in the amorphous phase, whereas the BD−T repeat units are distributed over both the amorphous and crystalline phase. A composition balance based on the total $(BD_{85}Di_{15})_{ssp}$ copolymer can be made:

$$F_{Di-T,\alpha(total)} + F_{BD-T,\alpha(total)} + F_{BD-T,\chi(total)} = 1 \quad (6)$$

where $F_{Di-T,\alpha(total)}$ and $F_{BD-T,\alpha(total)}$ are the mole fractions of Di−T and BD−T repeat units in the amorphous phase, respectively, and $F_{BD-T,\chi(total)}$ is the mole fraction of BD−T repeat units in the crystalline phase. All fractions mentioned in eq 6 are based on the total copolymer composition. From the earlier mentioned assumption that all Di−T repeat units are exclusively present in the amorphous phase, it follows that $F_{Di-T,\alpha(total)} = 0.164 = F_{Di-T,total}$. By using the earlier calculated mole ratio $(F_{BD-T,\alpha}/F_{Di-T,\alpha}) = 2.18$, a value of $F_{BD-T,\alpha(total)} = 0.357$ is found. This latter mentioned value will be used to determine the degree of randomness of the amorphous phase as will be shown in the next part. Using $F_{BD-T,\alpha(total)} = 0.357$ in eq 6, results in $F_{BD-T,\chi(total)} = 0.480$.

3. Correction of ^{13}C NMR Peak Integral Values of Dyad Sequences Used To Obtain the Chemical Microstructure of the Amorphous Phase. The peak integral values of the four dyad sequences (as shown in Figure 2) have to be corrected in such a way that these values only give information about the distribution of BD−T and Di−T repeat units in the amorphous phase. Therefore, the fraction of each sequence in the amorphous phase has to be known. On the basis of the assumption that all Di−T repeat units are present in the amorphous phase and by definition of eqs 1 and 3, sequences (DTD), (BTD,Di-side), and (BTD,BD-side), determining the degree of randomness, should be present in the amorphous phase. For simplicity, all DTD and BTD sequences present at the boundary of the crystalline and amorphous phase are in this calculation method added to the amorphous phase. Consequently, the peak integrals of the previously mentioned dyad sequences remain unchanged, and hence the mole fractions of sequences in the amorphous phase are as follows: $F_{DTD,\alpha} = 0.071$, $F_{BTD,BD-side,\alpha} = 0.107$, and $F_{BTD,Di-side,\alpha} = 0.103$ (see Figure 2). The only unknown parameter is the mole fraction of (BTB) sequences in the amorphous phase ($F_{BTB,\alpha}$). This value can be obtained using the earlier calculated value for the total mole fraction of BD−T repeat units in the amorphous phase, $F_{BD-T,\alpha(total)}$, together with eq 2 applied to the amorphous phase:

$$F_{BD-T,\alpha(total)} = ((F_{BTD,BD-side,\alpha} + F_{BDT,Di-side,\alpha})/2 + F_{BTB,\alpha}) \quad (7)$$

where $F_{BD-T,\alpha(total)} = 0.357$, $F_{BTD,\ BD-side,\alpha} = 0.107$, and $F_{BTD,Di-side,\alpha} = 0.103$. Using these values in eq 7 results in $F_{BTB,\alpha} = 0.252$.

Table 2. Calculated Parameters and the Resulting Degree of Randomness of the Amorphous Phase Using the Two-Phase Model for the $(BD_{85}Di_{15})_{ssp}$ Copolymer

sequences total copolymer	$F_{BTD,BD-side}$	F_{BTB}	F_{DTD}	$F_{BTD,Di-side}$
normalized peak integral values by ^{13}C NMR	0.107	0.720	0.071	0.103
total composition by ^{13}C NMR	$F_{BD-T,\ total} = 0.825$		$F_{Di-T,total} = 0.175$	
crystalline fraction, total	$F_{BD-T,\chi(total)} = 0.480$			
amorphous fraction, total	$F_{BD-T,\alpha(total)} = 0.357$		$F_{Di-T,\alpha(total)} = 0.164$	
amorphous fraction only	$F_{BD-T,\alpha} = 0.685$		$F_{Di-T,\alpha} = 0.315$	
sequences amorphous phase	$F_{BTD,\ BD-side,\alpha}$	$F_{BTB,\alpha}$	$F_{DTD,\alpha}$	$F_{BTD,Di-side,\alpha}$
corrected peak integral values	0.107	0.252	0.071	0.103
normalized corrected peak integral values	20.1	47.3	13.3	19.3
degree of randomness before correction		$R_{ssp,total} = 0.73$		
degree of randomness after correction (two-phase model)		$R_{ssp,\alpha} = 0.89$		

4. Calculation of Corrected Degree of Randomness ($R_{ssp,\alpha}$). The final step is to normalize the corrected integral values of the four dyad sequences to a total value of 1. The thus obtained integral values can subsequently be used with eq 4 to give the degree of randomness of the amorphous phase ($R_{ssp,\alpha}$), which results in $R_{ssp,\alpha} = 0.89$. Because during SSP the crystalline fraction is no longer participating, the value of $R_{ssp,\alpha}$ is larger than $R_{ssp,total}$, which has a value of 0.73. The results of the described calculations are summarized in Table 2.

The previously described calculation method was also applied to the other synthesized $(BD_xDi_y)_{ssp}$ copolymers given in Table 1. The uncorrected values of $R_{ssp,total}$ and the values obtained after application of the correction method, $R_{ssp,\alpha}$, are plotted in Figure 4 as a function of $F_{BD-T,total}$. The degree of randomness of the mobile amorphous fraction ($R_{ssp,mobile\ \alpha}$), which will be discussed later, is also shown.

It can be seen that the values for $R_{ssp,\alpha}$ are higher compared to the original values of $R_{ssp,total}$. These higher values are expected because the PBT segments, present in the crystalline phase and hence not participating in the transesterification reactions during SSP, are no longer taken into account. Furthermore, like $R_{ssp,total}$, $R_{ssp,\alpha}$ is dependent on the fraction of incorporated Dianol. It can be seen that the values for $R_{ssp,\alpha}$ are still below unity over a large composition range. Only when the crystallinity $\chi_{heating} = 0$ (and hence $F_{BD-T,\alpha} = F_{BD-T,total}$), $R_{ssp,\alpha} = R_{ssp,total} \approx 1$. Apparently, the values of $R_{ssp,\alpha}$ are only below unity when the $(BD_xDi_y)_{ssp}$ copolymers have a crystalline fraction. A possible explanation is that a small fraction of the amorphous phase, close to the crystal surface, is not accessible for the transesterification reactions. Wunderlich and coworkers[29−33] proposed a model in which the amorphous phase in several semicrystalline polymers, including PBT, is divided into a mobile amorphous fraction (α_{mobile}) and a rigid amorphous fraction (α_{rigid}). Two models are often used to describe this rigid amorphous fraction.[33] One model is based on adjacent reentry folds of polymer chains, whereas the other model is based on fringed micelles. It is assumed for PBT that the rigid amorphous fraction does not become mobile until fusion.[25] Consequently, it might be possible that the PBT parts in this rigid amorphous fraction are still not mobile enough for participation in the transesterification process at the applied SSP temperature (T_{ssp}) of 180 °C. The values for the amorphous fraction ($\alpha_{heating}$) as used in eq 5 may therefore be overestimated. In that case, an additional correction for $R_{ssp,\alpha}$ is necessary.

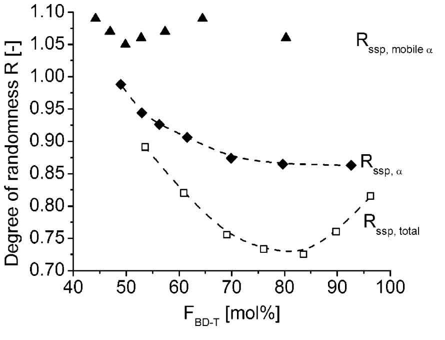

Figure 4. Sequence distribution analysis of $(BD_xDi_y)_{ssp}$ copolymers: total degree of randomness $R_{ssp,total}$ (□, based on the total microstructure), corrected degree of randomness $R_{ssp,\alpha}$ (◆, based on the two-phase model) and $R_{ssp,mobile\ \alpha}$ (▲, based on the three-phase model) as a function of $F_{BD-T,total}$.

The mobile amorphous fraction (α_{mobile}) can be calculated by eq 8a. In this equation, the Δc_p is the heat capacity increase at T_g and $\Delta c_p{}^0{}_\alpha$ is the Δc_p increase for 100% amorphous PBT at T_g. The literature value for $\Delta c_p{}^0{}_\alpha$ is 77 J/mol·K (0.35 J/g·K) at $T_g = 320$ K.[22,25] The rigid amorphous fraction α_{rigid} does not contribute to the increase of Δc_p at the T_g. The crystallinity can be obtained by eq 8b, where $\Delta H^0{}_{fuse} = 145$ J/g.[22−24]

$$\alpha_{mobile} = \Delta c_p / \Delta c_p{}^0{}_\alpha \tag{8a}$$

$$\chi_{heating} = \Delta H_{melting} / \Delta H^0{}_{fuse} \tag{8b}$$

Hence, α_{rigid} can be described by

$$\alpha_{rigid} = 1 - \chi_{heating} - \alpha_{mobile} \tag{8c}$$

Figure 5 shows the obtained values for the fractions α_{mobile}, $\chi_{heating}$, and α_{rigid} as a function of $F_{BD-T,total}$ for the $(BD_xDi_y)_{ssp}$ copolymers. The curves are guides to the eye only and were obtained after polynomial fitting of the obtained data points. It can be seen that α_{rigid} increases with increasing $F_{BD-T,total}$, whereas, according to Figure 4, $R_{ssp,\alpha}$ decreases with increasing $F_{BD-T,total}$. Hence, correction of $R_{ssp,\alpha}$ by subtracting the contribution of the rigid amorphous fraction α_{rigid}, presumably

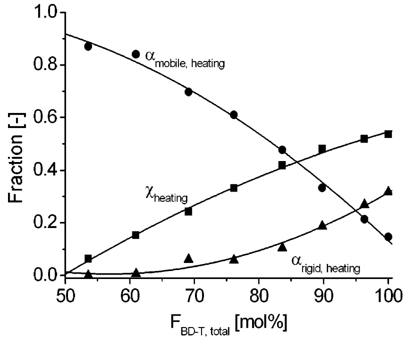

Figure 5. Crystalline ($\chi_{heating}$, ■), rigid amorphous ($\alpha_{rigid,heating}$, ▲) and mobile amorphous ($\alpha_{mobile,heating}$, ●) fractions as a function of $F_{BD-T,total}$.

Table 3. Calculated Parameters and the Resulting Degree of Randomness of the Accessible Amorphous Fraction Using the Three-Phase Model for the $(BD_{85}Di_{15})_{ssp}$ Copolymer

sequences total copolymer	$F_{\text{BTD,BD-side}}$	F_{BTB}	F_{DTD}	$F_{\text{BTD,Di-side}}$
normalized peak integral values by ^{13}C NMR	0.107	0.720	0.071	0.103
total composition by ^{13}C NMR	$F_{\text{BD-T,total}} = 0.825$		$F_{\text{Di-T,total}} = 0.175$	
crystalline fraction	$F_{\text{BD-T},\chi} = 1$		$F_{\text{Di-T},\chi} = 0$ (assumed)	
rigid amorphous fraction	$F_{\text{BD-T},\alpha_{\text{rigid}}} = 1$		$F_{\text{Di-T},\alpha_{\text{rigid}}} = 0$ (assumed)	
mobile amorphous fraction	$F_{\text{BD-T},\alpha_{\text{mobile}}} = 0.574$		$F_{\text{Di-T},\alpha_{\text{mobile}}} = 0.426$	
mobile amorphous fraction, total	$F_{\text{BD-T},\alpha_{\text{mobile}}(\text{total})} = 0.221$		$F_{\text{Di-T},\alpha_{\text{mobile}}(\text{total})} = 0.164$	
rigid amorphous fraction, total	$F_{\text{BD-T},\alpha_{\text{rigid}}(\text{total})} = 0.136$		$F_{\text{Di-T},\alpha_{\text{rigid}}(\text{total})} = 0$	
crystalline fraction, total	$F_{\text{BD-T},\chi(\text{total})} = 0.480$		$F_{\text{Di-T},\chi(\text{total})} = 0$	
sequences mobile amorphous fraction	$F_{\text{BTD,BD-side},\alpha_{\text{mobile}}}$	$F_{\text{BTB},\alpha_{\text{mobile}}}$	$F_{\text{DTD},\alpha_{\text{mobile}}}$	$F_{\text{BTD,Di-side},\alpha_{\text{mobile}}}$
corrected peak integral values	0.107	0.116	0.071	0.103
normalized corrected peak integral values	0.270	0.292	0.178	0.257
degree of randomness before correction		$R_{\text{ssp,total}} = 0.73$		
degree of randomness after correction (three-phase model)		$R_{\text{ssp},\alpha\ \text{mobile}} = 1.07$		

not participating in the transesterification process, should give the degree of randomness of the mobile amorphous fraction which is independent of composition. Of course, the required correction gets smaller with increasing mol % of incorporated Dianol (decreasing FBD−T, total).

B. Chemical Microstructure Based on the Three-Phase Model. Now that all fractions (χ_{heating}, α_{mobile}, and α_{rigid}; Figure 5) are known as a function of the $(BD_x\text{-}Di_y)_{ssp}$ copolymer composition, the correction method for the integral values of the quaternary carbon atom can be adjusted for the three-phase model. Also here, the $(BD_{85}Di_{15})_{ssp}$ copolyester is used to illustrate the calculation model. The first step is to adjust the BD−T mass balance as previously described by eq 5. The term α_{heating} in eq 5 has to be replaced by a rigid amorphous component and a mobile amorphous component:

$$\chi_{\text{heating}}\cdot W_{\text{BD-T},\chi} + \alpha_{\text{rigid}}\cdot W_{\text{BD-T},\alpha_{\text{rigid}}} + \alpha_{\text{mobile}}\cdot W_{\text{BD-T},\alpha_{\text{mobile}}} = W_{\text{BD-T,total}} \qquad (9a)$$

where χ_{heating} is the crystalline fraction and α_{mobile} and α_{rigid} are the mobile and rigid amorphous fractions. $W_{\text{BD-T},\chi}$, $W_{\text{BD-T},\alpha_{\text{rigid}}}$, and $W_{\text{BD-T},\alpha_{\text{mobile}}}$ are the weight fractions of BD−T repeat units in the crystalline, rigid amorphous, and mobile amorphous fraction, respectively. $W_{\text{BD-T,total}}$ is the total weight fraction of BD−T repeat units based on the whole copolymer. The remaining crystalline fraction (χ_{heating}) after SSP should only consist of BD−T repeat units and hence $W_{\text{BD-T},\chi} = 1$. When $R_{\text{ssp},\alpha}$ was calculated, it was assumed that the polymer chains in the rigid amorphous fraction α_{rigid} are still not mobile enough at $T_{\text{ssp}} = 180$ °C to participate in the transesterification reactions. Hence, α_{rigid} should also only consist of BD−T repeat units and consequently $W_{\text{BD-T},\alpha_{\text{rigid}}} = 1$. All Dianol should be present in α_{mobile}, and thus eq 9a can be simplified to

$$\chi_{\text{heating}} + \alpha_{\text{rigid}} + \alpha_{\text{mobile}}\cdot W_{\text{BD-T},\alpha_{\text{mobile}}} = W_{\text{BD-T,total}} \qquad (9b)$$

According to Figure 5, for the $(BD_{85}Di_{15})_{ssp}$ copolymer $\chi_{\text{heating}} = 0.411$, $\alpha_{\text{mobile}} = 0.473$, and $\alpha_{\text{rigid}} = 0.116$. Using these values together with $W_{\text{BD-T,total}} = 0.716$ (see earlier) in eq 9b yields $W_{\text{BD-T},\alpha_{\text{mobile}}} = 0.399$. Hence, α_{mobile} consists of ca. 40 wt % BD−T and ca. 60 wt % Di−T repeat units. Recalculation into mole fractions results in $F_{\text{BD-T},\alpha_{\text{mobile}}} = 0.574$ and $F_{\text{Di-T},\alpha_{\text{mobile}}} = 0.426$. The mole ratio $(F_{\text{BD-T},\alpha_{\text{mobile}}})/(F_{\text{Di-T},\alpha_{\text{mobile}}})$ is equal to 1.35.

The assumption that Dianol is only incorporated in the mobile amorphous fraction implies that $F_{\text{Di-T},\chi(\text{total})} = 0$ and $F_{\text{Di-T},\alpha_{\text{rigid}}(\text{total})} = 0$ and $F_{\text{Di-T},\alpha_{\text{mobile}}(\text{total})} = F_{\text{Di-T,total}} = 0.164$. Using this latter mentioned value in the previously calculated mole ratio $(F_{\text{BD-T},\alpha_{\text{mobile}}})/(F_{\text{Di-T},\alpha_{\text{mobile}}}) = 1.35$ results in $F_{\text{BD-T},\alpha_{\text{mobile}}(\text{total})} = 0.221$. The latter value will be used to calculate the degree of randomness for the mobile amorphous fraction. Furthermore, $F_{\text{BD-T},\alpha_{\text{rigid mobile}}(\text{total})}$ and $F_{\text{BD-T},\chi(\text{total})}$ can be calculated by combining a total BD−T composition balance with the ratio between α_{rigid} and χ_{heating}:

$$F_{\text{BD-T},\alpha_{\text{mobile}}(\text{total})} + F_{\text{BD-T},\alpha_{\text{rigid}}(\text{total})} + F_{\text{BD-T},\chi(\text{total})} = F_{\text{BD-T,total}} \qquad (10a)$$

$$\frac{\alpha_{\text{rigid}}}{\chi_{\text{heating}}} = \frac{F_{\text{BD-T},\alpha_{\text{rigid}}(\text{total})}}{F_{\text{BD-T},\chi(\text{total})}} \qquad (10b)$$

where $F_{\text{BD-T},\alpha_{\text{mobile}}(\text{total})} = 0.221$, $F_{\text{BD-T,(total)}} = 0.836$, $\alpha_{\text{rigid}} = 0.116$ and $\chi_{\text{heating}} = 0.411$. Hence, for the $(BD_{85}Di_{15})_{ssp}$ copolymer $F_{\text{BD-T},\alpha_{\text{rigid}}(\text{total})} = 0.480$ and $F_{\text{BD-T},\chi(\text{total})} = 0.136$.

The last step is to correct the integral values of the dyad sequences in such a way that they represent the sequence distribution of the mobile amorphous fraction ($R_{\text{ssp},\alpha_{\text{mobile}}}$).

Because $F_{\text{Di-T},\alpha_{\text{mobile}}(\text{total})} = F_{\text{Di-T,total}}$, the integral values F_{DTD}, $F_{\text{BTD,Di-side}}$, and $F_{\text{BTD,BD-side}}$ remain unchanged. The only integral value that needs to be corrected is $F_{\text{BTB},\alpha_{\text{mobile}}}$. This value can be obtained by applying eq 2 to the following mobile amorphous fraction:

$$F_{\text{BD-T},\alpha_{\text{mobile}}(\text{total})} = (F_{\text{BTD,total}}/2 + F_{\text{BTB},\alpha_{\text{mobile}}}) \qquad (11)$$

Using $F_{\text{BD-T},\alpha_{\text{mobile}}(\text{total})} = 0.221$ and $F_{\text{BTD,total}} = 0.210$ in eq 11 results in $F_{\text{BTB},\alpha_{\text{mobile}}} = 0.116$.

The values found for $F_{\text{DTD},\alpha_{\text{mobile}}}$ (0.071), $F_{\text{BTD,Di-side},\alpha_{\text{mobile}}}$ (0.103), $F_{\text{BTD,BD-side},\alpha_{\text{mobile}}}$ (0.107), and $F_{\text{BTB},\alpha_{\text{mobile}}}$ (0.12) are normalized and subsequently used in eq 4 to give the degree of randomness of the mobile amorphous fraction: $R_{\text{ssp},\alpha_{\text{mobile}}} = 1.07$. The calculated parameters are summarized in Table 3.

Similar calculations were done for the remaining $(BD_xDi_y)_{ssp}$ copolymers. The distribution of BD−T and Di−T repeat units over the crystalline, rigid amorphous and mobile amorphous fraction as a function of $F_{\text{BD-T,total}}$ is shown in Figure 6. $F_{\text{Di-T},\alpha_{\text{mobile}}(\text{total})}$ linearly decreases with increasing fraction $F_{\text{BD-T,total}}$ because $F_{\text{Di-T},\alpha_{\text{mobile}}(\text{total})} = F_{\text{Di-T,total}}$ and $F_{\text{Di-T,total}} + F_{\text{BD-T,total}} = 1$. Also fraction $F_{\text{BD-T},\alpha_{\text{mobile}}(\text{total})}$ linearly decreases with increasing $F_{\text{BD-T,total}}$, but the linearity is lost when $F_{\text{BD-T,total}} < 75$ mol %. For these values of $F_{\text{BD-T,total}}$, a leveling off is observed. Dianol will not evaporate at $T_{\text{ssp}} = 180$ °C, and hence, the fraction of polymer chain segments end-capped with Dianol gradually increases when the frac-

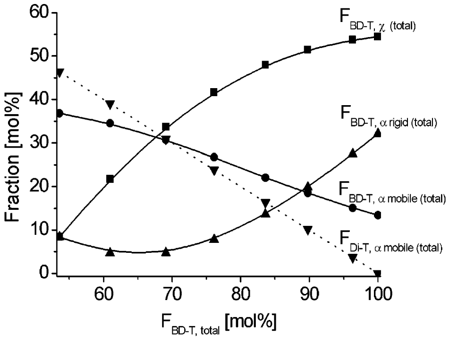

Figure 6. Distribution of BD−T and Di−T repeat units in $(BD_xDi_y)_{ssp}$ copolymer based on the three-phase model: mole fraction of BD−T repeat-units in the crystalline fraction ($F_{BD-T,\chi(total)}$, ■), mobile amorphous fraction ($F_{BD-T,\alpha_{mobile}(total)}$, ●) and rigid amorphous fraction ($F_{BD-T,\alpha_{rigid}(total)}$, ▲) as a function of $F_{BD-T,total}$ and mole fraction of Di−T repeat units in the mobile amorphous fraction ($F_{Di-T,\alpha_{mobile}(total)}$, ▼) as a function of $F_{BD-T,total}$. $F_{Di-T,\alpha_{rigid}(total)}$ and $F_{Di-T,\chi(total)}$ are assumed to be 0.

tion of Dianol present in the initial $(BD_xDi_y)_{feed}$ mixtures increases. As a consequence, the polymer chain segments in the amorphous phase cannot efficiently recombine anymore because the elimination of the condensation product (i.e., Dianol) is stagnating. Hence, the molecular weight will decrease. Previous work[15] showed that for $F_{BD-T,total} \leq 75$ mol % the number-average molecular weight ($\bar{M}_n$) indeed decreases. The polymer chains present in the mobile amorphous fraction become end-capped with Dianol and recombination of polymer chains with elimination of Dianol is no longer possible. Furthermore, it can be seen that for values of $F_{BD-T,total} < 75$ mol %, a large fraction of BD−T is still present in the crystalline phase, whereas rigid amorphous BD−T is almost absent. This result is an indication that Dianol dissolves the rigid amorphous fraction during the SSP reaction so that the BD−T repeat units in this rigid amorphous fraction become sufficiently mobile to participate in the transesterification reactions. Further research by DSC and small-angle X-ray scattering (SAXS) experiments have to be done to verify this hypothesis.

In Figure 4, the calculated values for $R_{ssp,\alpha_{mobile}}$ are shown as a function of $F_{BD-T,total}$. These degrees of randomness have now been corrected for the crystalline and the rigid amorphous fraction, both not participating in the transesterification reactions. It can be seen that all values for $R_{ssp,\alpha_{mobile}}$ are very close to one, pointing to a fully random copolyester structure in the mobile amorphous fraction, which is comparable to the results obtained for the $(BD_xDi_y)_{mp}$ copolyesters. The observation that these values for $R_{ssp,\alpha_{mobile}}$ are slightly higher than unity is probably not the result of errors in our measurements. It might be possible that at the interface between mobile and rigid amorphous fraction, which is not strictly defined, some Di−T repeat units are present. With the calculation method as previously described, these Di−T repeat units were all assumed to be part of the mobile amorphous fraction. This consequent error might result in values for $R_{ssp,\alpha_{mobile}}$ slightly larger than unity.

Conclusions

The calculation method presented in this paper shows that it is possible to determine the chemical microstructure of the amorphous phase using the peak integral values from the ^{13}C NMR dyad sequences originating from the quaternary carbon atom. When the morphology of the $(BD_xDi_y)_{ssp}$ copolymers is represented by the traditional two-phase (crystalline/amorphous) model, the values of $R_{ssp,\alpha}$ are still below unity for a large composition range. Only when the $(BD_xDi_y)_{ssp}$ copolymers are fully amorphous ($\chi_{heating} = 0$), $R_{ssp,\alpha} = R_{ssp,total} = 1$. Hence, the presence of a crystalline fraction ($\chi_{heating} > 0$) results in a decrease of $R_{ssp,\alpha}$. Heat capacity measurements showed that, in the presence of a crystalline fraction, the amorphous phase consists of a mobile amorphous fraction and a rigid amorphous fraction. The calculation method based on the two-phase model was extended by taking the mobile and rigid amorphous fraction into account. The degree of randomness of the mobile amorphous fraction ($R_{ssp,\alpha_{mobile}}$) was calculated with the assumption that the PBT chains in the rigid amorphous fraction are not mobile enough to participate in the transesterification reactions and thus all Dianol is only incorporated into the mobile amorphous fraction. This assumption results in values for $R_{ssp,\alpha_{mobile}}$ between 1.05 and 1.09. These values show that the chemical microstructure of the mobile amorphous fraction is fully random. Hence, Dianol is incorporated in a similar way as with melt polymerization although with SSP only the most mobile chain segments are participating in the transesterification reaction.

The slightly larger values found for $R_{ssp,\alpha_{mobile}}$ are possibly the result of a consequent error during the calculation. Most likely, the interface between mobile and rigid amorphous fraction is not so well-defined. In the calculation method as described in this article, all Di−T repeat units were assumed to be present in the mobile amorphous fraction. This assumption results therefore values for $R_{ssp,\alpha_{mobile}}$ slightly larger than unity.

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