DOI: 10.1002/masy.200850533

An FTIR Study on the Solid-State Copolymerization of bis(2-hydroxyethyl)terephthalate and Poly(butylene terephthalate) and the Resulting Copolymers

Maya Ziari,[1,2,3] *Otto van Asselen,*[2] *Martijn Jansen,*[2,3] *Han Goossens,**[2]
Peter Schoenmakers[1]

Summary: The first aim of this work was to study the solid-state copolymerization (SSP) of bis(2-hydroxyethyl)terephthalate (BHET) with poly(butylene terephthalate) (PBT) by FTIR spectroscopy. The development of the chemical microstructure during the SSP-reaction was examined as a function of the BHET content, showing the different regimes. The thermal behaviour of the resulting copolymers with different BHET contents was also investigated during cooling using infra-red dynamic spectra. For low BHET-concentrations, only crystallization of PBT-sequences was observed, while for high BHET-concentrations, only crystallization of PET-sequences was detectable with a cross-over behaviour for intermediate concentrations.

Keywords: FTIR spectroscopy; polyesters; solid-state modification

Introduction

Poly(butylene terephthalate) (PBT) and poly(ethylene terephthalate) (PET) are two semi-crystalline polymers that are used in many engineering applications. The main advantage of PBT is its high crystallization rate, making it suitable for injection molding applications with short molding cycle times,[1] while PET has a considerably lower crystallization rate and is therefore mainly used for fiber applications and packaging.[2] The glass transition temperature of PBT is rather low compared to PET ($T_g \approx 45\,^{\circ}C$ for PBT and $T_g \approx 80\,^{\circ}C$ for PET). To obtain a T_g higher than 45 °C, PBT and PET can be reactively blended in the melt. The concomitant ester-interchange reactions occurring in the melt first result in the formation of block copolymers, but as the reaction proceeds, random PBT-PET copolymers are obtained.[3–5] These random PBT-PET copolymers have a T_g in between that of PBT and PET homopolymer. However, the shorter and more irregular homopolymer sequences of these random copolymers consequently lead to a lower melting temperature, crystallization rate and crystallinity with respect to pure PBT. It is therefore desirable to synthesize PBT-PET copolymers having a T_g higher than PBT homopolymer, but with a crystallization behavior comparable to that of PBT. Therefore, a copolymerization method should be used, which enables to retain large crystallizable homopolymer PBT blocks with a non-random chemical microstructure.

In our previous work,[6] PBT-PET copolymers were made by copolymerization in the melt (MP) and the solid state (SSP) of bis(2-hydroxyethyl)terephthalate (BHET) with PBT. The chemical microstructure of the synthesized PBT-PET copolymers was examined by ^{13}C-NMR spectroscopy sequence distribution analysis. As expected, the chemical microstructure of the PBT-PET

---

[1] Polymer-Analysis group, Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

[2] Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands
E-mail: j.g.p.goossens@tue.nl

[3] Dutch Polymer Institute, PO Box 902, 5600 AX Eindhoven, The Netherlands

copolymers obtained by MP was fully random. However, when BHET was incorporated into PBT via SSP, a non-random blocky chemical microstructure was obtained. When the fraction of BHET used for incorporation in PBT was increased, the blocky character of the chemical microstructure became more pronounced, suggesting that BHET may react by self-condensation to form homopolymer PET blocks.[7,8] The ^{13}C-NMR sequence distribution analysis also showed that transesterification reactions occurred between BHET monomer and PBT. It was not clear if the formed homopolymer PET blocks are present as a separate phase or if these blocks reside in the amorphous phase of PBT.

In this paper, the incorporation of BHET into PBT via SSP is studied in more detail. The kinetics of the incorporation via SSP is studied under isothermal conditions by using FTIR spectroscopy. During the SSP process, a competition between annealing and dissolution of the PBT-crystals, incorporation of BHET in the amorphous PBT and BHET homopolymerization exists, of which the relative rates depend on the ratio of PBT/BHET. In a previous paper, the miscibility of the BHET with PBT and the thermal properties of the resultant BD_xEG_y-copolymers obtained via SSP were investigated using DSC.[9] BD_x denotes the mol% of PBT (expressed in 1,4-butanediol units), whereas EG_y denotes the mol% of BHET units. It was observed that BHET is partially miscible in the amorphous PBT, depending on the PBT/BHET ratio. The crystallization behaviour of the resultant BD_xEG_y copolymers, where BD_x represents the initial mol% PBT and EG_y the mol% of hydroxyl end groups per mole BHET, was studied by DSC and it was observed that when more BHET is incorporated the onset of crystallization shifts to lower temperatures, while the crystallization exotherm becomes broader.[9] However, the $(BD_{30}EG_{70})_{SSP}$ copolymer displayed a much sharper crystallisation exotherm with a slightly higher onset. A similar observation was made by Misra and al.[10] However, DSC lacks the possibility to investigate the crystallization behaviour of the individual components if the crystallization exotherms display a large overlap. In this respect, temperature-dependent FTIR spectroscopy is much more discriminating by following absorption bands, which can either be assigned to the crystalline or amorphous phase of PBT or PET.

The SSP kinetics was investigated under isothermal conditions using two compositions. In that way, the development of the chemical microstructure during the SSP reaction could be examined together with the miscibility of BHET and PBT. Temperature-dependent experiments were performed on three different BD_xEG_y copolymers and compared to PBT using the dynamic infra-red spectra obtained through the 2D IR correlation algorithm developed by Noda et al.[11,12]

Experimental Part

The BDEG copolymers were obtained by incorporation of BHET into PBT by using SSP.[6,9]

At first, the kinetics of the SSP reactions was investigated with attenuated total reflection (ATR)-FTIR spectroscopy. A BioRad FTS3000 spectrometer equipped with a MCT detector was used to record the spectra. The samples were pressed onto the diamond window of a SPECAC Golden Gate ATR accessory. Next, the sample was heated to 120 °C, where the initial spectrum was recorded. Upon starting the experiment, the sample was heated to 180 °C using a heating rate of 30 °C/min. Spectra were recorded during the reaction with a time interval of 60 seconds using a spectral resolution of 4 cm^{-1}, co-adding 62 scans. At 180 °C, the feed consists of a semi-crystalline fraction of PBT and a liquid fraction of BHET. During the initial stage of the SSP-reaction, the fraction of the liquid BHET in contact with the crystal increases, while the fraction of PBT decreases. It becomes then very difficult to monitor the reaction quantitatively.

Therefore, it was decided to perform all experiments in the transmission mode. Then, a more or less constant cross-section of the sample is monitored. These experiments were performed using a BioRad UMA500 IR microscope coupled to a BioRad FTS6000 spectrometer. A Linkam TMS600 hot stage was used for temperature control. To obtain a thin sample, the powder samples were cold pressed by a diamond anvil cell. Next, the sample was placed in between two zinc selenide (ZnSe)-windows and transferred to the Linkam hot stage. Spectra were recorded with a resolution of 2 cm^{-1} co-adding 250 scans.

The crystallization behaviour of three BDEG copolymers were also followed using the same set-up as described above with a cooling rate of 10 °C/min. The samples, however, were not covered with a second ZnSe window. For these experiments, spectra were recorded using a resolution of 2 cm^{-1} co-adding 100 scans. The 2D-Pocha software, developed at the Kwansei Gakuin University (Japan), was used for data treatment. The spectrum at 180 °C was taken as the mean spectrum for the dynamic spectra calculations.

Results and Discussion

Assignment of the Absorption Bands of the Pure Components

Table 1 shows the assignment of most relevant absorption bands of PBT, PET and BHET. For crystalline PBT, a band at 1454 cm^{-1} (CH_2 bending) is observed that for amorphous PBT shifts to 1468 cm^{-1} together with absorption bands at 1320 cm^{-1} (ring ester in plane) and 1389 cm^{-1} (CH_2 wagging). Crystalline PET shows characteristic absorption bands at 1471 cm^{-1} (CH_2 bending), 1342 cm^{-1} (CH_2 wagging), and at 990 cm^{-1}, of which the latter band is only observed if chain folding occurs. Typical bands of amorphous PET can be observed at 1371 cm^{-1} (CH_2 wagging), 1458 cm^{-1} (CH_2 bending). For BHET, a lot of absorption bands overlap with PBT or PET. To follow the copolymerization, the absorption band at 3550 cm^{-1} (OH stretching) can be used.

Kinetics of the SSP Reaction Studied by FTIR Spectroscopy

Since the spectra of PBT, BHET and PET show overlapping absorption bands, we decided to focus on the four following absorption bands: the crystalline PET absorption band at 1342 cm^{-1}, the absorption band at 1371 cm^{-1} of amorphous PET or BHET, the crystalline PBT band at 1454 cm^{-1} and the OH-stretch vibration band of BHET at 3550 cm^{-1}.

The SSP-kinetics at 180 °C was followed for the $(BD_{70}EG_{30})_{feed}$ and $(BD_{30}EG_{70})_{feed}$ systems. Figures 1a and 1b show the individual spectra before and after the SSP-reactions, while the kinetic results are shown in Figures 2a and 2b, respectively. The disappearance of the absorption band at 3550 cm^{-1} shows that in both cases the BHET is converted. For the $(BD_{70}EG_{30})_{feed}$ system (Figure 2a), the intensity decreases gradually and the behaviour is typical for a series of two irreversible consecutive first-order reactions. This was also observed for the incorporation of 2,2-bis[4-(2-hydroxyethoxy)phenyl]-propane (Dianol 220).[14] The $(BD_{30}EG_{70})_{feed}$ system (Figure 2b) shows a

Table 1.
Assignment of the absorption bands of the pure components.[13]

	PBT (cm^{-1})		PET (cm^{-1})		BHET (cm^{-1})
	amorphous	crystalline	amorphous	crystalline	
OH stretching					3550
CH_2 bending	1468	1458/1454	1458/1440	1471	1453
Ring-in-plane def	1408	1409	1409	1409	1407
Ring CH in-plane def				1380	
CH_2 wagging	1389	1389	1371	1342	1372
Ring CCH			1315		
Chain folding		1320		990	

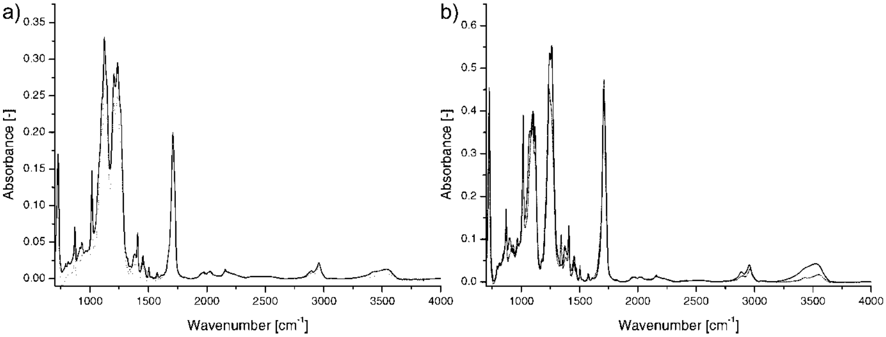

Figure 1.
Spectra before (-) and after (..) the SSP-reaction: a) $(BD_{70}EG_{30})_{feed}$ and b) $(BD_{30}EG_{70})_{feed}$.

different behaviour. After a similar gradual decrease of the intensity up to approx. 20 min, the reaction accelerates and finally reaches a plateau level after approx. 50 min. In both figures, the absorption band of the PET CH_2 wagging mode in the crystalline state is also depicted, although the band position changes from at 1340 to 1342 cm^{-1} on going from $(BD_{70}EG_{30})_{feed}$ to $(BD_{30}EG_{70})_{feed}$. Cole et al. studied the microstructure of PET homopolymer using reflection and transmission FTIR spectroscopy and showed that the ethylene glycol segments for PET in the crystalline phase are always in the mutual trans orientation (T), while in the amorphous phase a mutual gauche orientation predominantly exists (G).[13,15] They also observed that different conformation states can also exist for the C–O bond of the glycol group, which can likewise exist in a trans (t) or gauche (g) conformation as well as the terephthalic acid segment. If the latter is in a non-trans conformation and the ethylene glycol segment is in a trans (T) conformation, a "rigid" amorphous band will be observed at 1340–1338 cm^{-1}. X-ray diffraction measurements showed that all three groups adopt the trans conformation (T, t, T_b) in the crystalline phase. Then, an absorption band at 1342 cm^{-1} of the glycol C-C unit will appear. The change in peak position is a strong indication that for the $(BD_{70}EG_{30})_{feed}$ system the BHET is incorporated in the PBT chain, while for the $(BD_{30}EG_{70})_{feed}$ system separate PET crystals can be formed. The difference in behaviour is also found for the 1371 cm^{-1} band. For the $(BD_{30}EG_{70})_{feed}$ system, the same intensity profile is found as for the OH-stretching vibration band of BHET

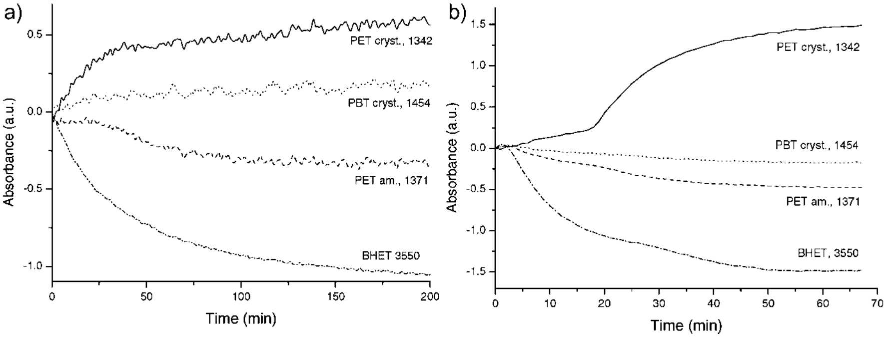

Figure 2.
Relative intensities of the indicated absorption bands of crystalline PET, amorphous PET, PBT and BHET during SSP of: a) $(BD_{70}EG_{30})_{feed}$ and b) $(BD_{30}EG_{70})_{feed}$.

($3550\ cm^{-1}$), but $(BD_{70}EG_{30})_{feed}$ system remains at the same absorption level for the first 30 min and then starts to decrease up to approx. 40 min followed by a plateau. This might indicate that during the first 30 min, the decrease of the intensity due to the conversion of BHET is compensated by the formation of amorphous PET, which also has an absorption band at that wavenumber.

For the $(BD_{30}EG_{70})_{feed}$ system, the crystalline PBT band at $1454\ cm^{-1}$ decreases, probably because of the decrease of the BHET that also has an absorption band at $1454\ cm^{-1}$, although this decrease may also be attributed to partial dissolution of the PBT-crystals that may occur because of the high mole fraction of BHET acting as a solvent for PBT. On the contrary, for the $(BD_{70}EG_{30})_{feed}$ system, the band at $1454\ cm^{-1}$ increases. This behaviour can only be explained by the occurrence of annealing and perfectioning of the PBT-crystals due to the high mobility during the SSP-reaction.

Temperature Dependent Experiments

Changes in the FTIR-spectra were monitored as a function of temperature. Figure 3 shows the dynamic spectra of BDEG copolymers with different PBT/BHET ratios cooled from the melt in a temperature range from 240 to 170 °C. For the PBT homopolymer, positive bands at 1454, 1386 and $1320\ cm^{-1}$ develop during cooling. These bands can be assigned to crystalline PBT (CH_2 bending and wagging modes). Also the positive band at $1408\ cm^{-1}$ can be assigned to amorphous PBT (See Table 1). In the spectra of the $(BD_{70}EG_{30})_{SSP}$ system, beside the positive bands of crystalline PBT, also a positive band is observed at $1338\ cm^{-1}$,

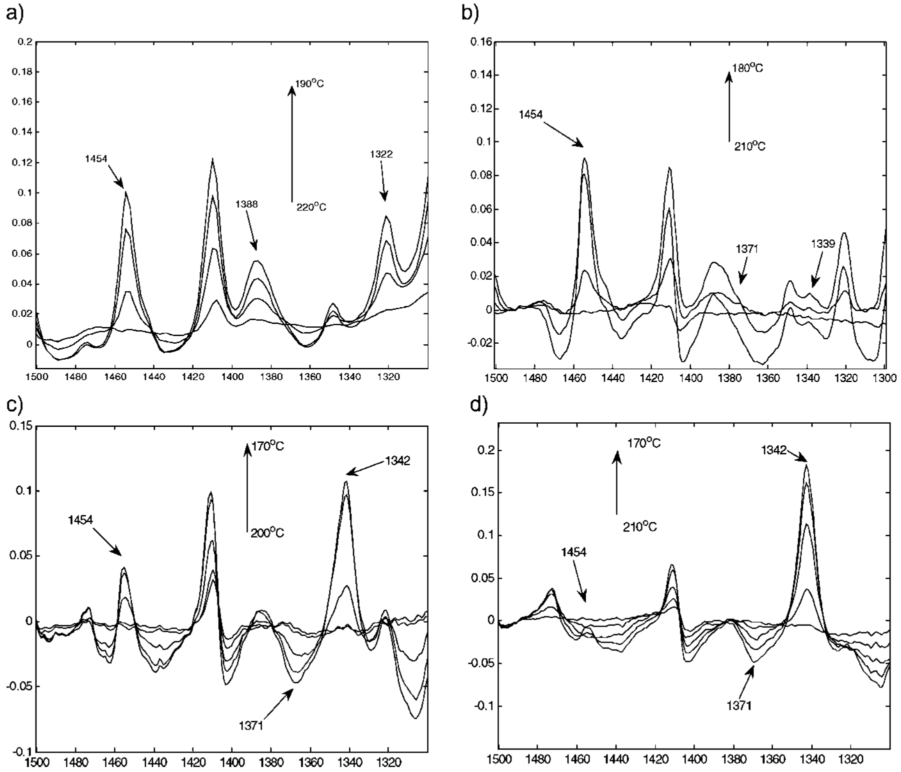

Figure 3.

Dynamic spectra as a function of temperature: 210–170 °C with 10 °C steps: a) PBT, b) $BD_{70}EG_{30}$, c) $BD_{50}EG_{50}$, and d) $BD_{30}EG_{70}$.

which can be assigned to CH_2 wagging of an ethylene segment (trans conformation) with the terephthalate segment in a non-trans configuration. This is an indication that ethylene segments are incorporated into the PBT chain.

In the spectra corresponding to sample $(BD_{50}EG_{50})_{SSP}$ the positive bands of PBT are weaker and positive bands at 1471 and 1342 cm^{-1} corresponding to crystalline PET appear. Negative bands can be observed at 1315 and 1371 cm^{-1}, which can be assigned to amorphous PET, as well as a band at 1465 cm^{-1}, which can be assigned to amorphous PBT. These spectral features clearly indicate that PET crystals are formed. Furthermore, the crystalline PBT and PET bands appear almost at the same time. The limited miscibility of BHET with PBT promotes the formation of separate PET-crystals. However, no visible absorption band at 990 cm^{-1} related to PET chain folding is found, suggesting that the crystalline PET chain segments are not long enough.

In the spectra corresponding to the $(BD_{30}EG_{70})_{SSP}$ system weak spectral features of crystalline PBT are present together with strong positive and negative features of PET. If we have a closer look at the bands at 1320 and 1454 cm^{-1} and the band at 1342 cm^{-1} it can be noticed that PET crystallizes much earlier, indicating that PBT and PET crystallize independently and are mostly like in a separate phase. This is confirmed by the presence of an absorption band at 990 cm^{-1} that can be assigned to chain folding of PET.

These observations are in line with the previously reported DSC-results.[9] When more BHET is incorporated, the onset of crystallization shifts to lower temperatures, while the crystallization exotherm becomes broader, mainly because the PBT crystallization is disturbed by the presence of short PET sequences in PBT. However, the exotherm of the $(BD_{30}EG_{70})_{SSP}$ copolymer, which is much sharper with a slightly higher onset, is due to crystallization of PET, while at lower temperatures only a small PBT crystalline fraction is formed. Most likely, because of the limited miscibility of BHET in the amorphous phase of PBT and the concomitant formation of PET homopolymer by self-condensation, the large interfacial area leads to a strong nucleation effect.

Conclusions

FTIR spectroscopy in transmission can be used to follow the kinetics of BHET-incorporation in PBT during SSP and to study the microstructure of the resulting BDEG copolymer. These results show that depending on the ratio of PBT/BHET, a competition exists between annealing of PBT, incorporation of BHET in amorphous PBT and BHET homopolymerization. For the $(BD_{70}EG_{30})_{feed}$ system, BHET is incorporated in PBT forming a non-random copolymer, while for high BHET concentrations a separate PET phase is found.

The dynamic spectra measured during cooling from the melt clearly showed that for low and intermediate BHET-concentrations, crystallization of PBT is responsible for the crystallization exotherm, as observed by DSC, while for high BHET-concentrations the DSC crystallization exotherm is caused by crystallization of PET.

Acknowledgements: This work is part of the research program of the Dutch Polymer Institute (DPI) under project numbers 143 and 337.

[1] H.-J. Radusch, in Handbook of Thermoplastic Polyesters, S. Fakirov, Ed., Wiley-VCH, Weinheim **2002**, Chapter 8, 389.
[2] V. B. Gupta, Z. Bashir, in Handbook of Thermoplastic Polyesters, S. Fakirov, Ed., Wiley-VCH, Weinheim **2002**, Chapter 7, 317.
[3] S. C. E. Backson, A. M. Kenwright, R. W. Richards, *Polymer* **1995**, *36*, 1991.
[4] B. Jacques, J. Devaux, R. Legras, E. Nield, *J. Polym. Sci., Polym. Chem. Ed.*, **1996**, *34*, 1189.
[5] J. H. Kim, W. S. Lyoo, W. S. Ha, *J. Appl. Polym. Sci.* **2001**, *82*, 159.
[6] M. A. G. Jansen, J. G. P. Goossens, G. de Wit, C. Bailly, C. E. Koning, *Anal. Chem. Acta* **2006**, *557*, 19.

[7] K. Tomita, *Polymer* **1973**, *14*, 50.

[8] C.-C. Lin, S. Baliga, *J. Appl. Polym. Sci.* **1986**, *31*, 2483.

[9] M. A. G. Jansen, L. H. Wu, J. G. P. Goossens, G. de Wit, C. Bailly, C. E. Koning, *J. Pol. Sci., Pol. Chem. Ed.*, **2007**, *45*, 882.

[10] A. Misra, S. N. Garg, *J. Pol. Sci., Pol. Phys. Ed.*, **1986**, *24*, 983.

[11] I. Noda, *Applied Spectroscopy* **1990**, *4*, 44.

[12] P. Harrington, A. Urbas, P. J. Tandler, *Chemometrics and Intelligent Laboratory Systems* **2000**, *50*, 149.

[13] K. C. Cole, A. Ajji, E. Pellerin, *Macromolecules* **2002**, *35*, 770.

[14] M. A. G. Jansen, J. G. P. Goossens, G. de Wit, C. Bailly, C. E. Koning, *Macromolecules* **2005**, *38*, 2659.

[15] K. C. Cole, A. Ajji, E. Pellerin, *Macromol. Symp.* **2002**, *184*, 1.