

# Ordered structures and progressive transesterification in PC/PBT melt blends studied by FTi.r. spectroscopy combined with d.s.c. and n.m.r.

I. Hopfe, G. Pompe\* and K.-J. Eichhorn

Institute of Polymer Research Dresden, PO Box 120411, Dresden 01069, Germany  
 (Received 19 February 1996; revised 4 June 1996)

Melt blends of polycarbonate (PC) and poly(butylene terephthalate) (PBT) were characterized by their transesterification and crystallization behaviour using Fourier transform infrared spectroscopy (FTi.r.) as well as nuclear magnetic resonance (n.m.r.) spectroscopy and differential scanning calorimetry (d.s.c.). The transesterification can be analysed by FTi.r. spectroscopy using two different spectral features. The appearance of new bands is used for the direct proof, and changes of i.r. bands correlated with structural order for the indirect proof. The results from the PC-rich blend show that the indirect proof is very sensitive, but a detailed knowledge of the crystallinity is necessary for a correct analysis. The improvement of the compatibility of both components due to the formed copolymers has been observed in the blend PC/PBT 50/50 by i.r. microscopy. Furthermore, a splitting of the PBT carbonyl band was found and discussed. The changes of the observed two peaks correlate directly with the changes in the conformation of the tetramethylene sequences of PBT. © 1997 Elsevier Science Ltd.

(Keywords: infrared spectroscopy; PC/PBT blend; transesterification)

## INTRODUCTION

FTi.r. is a useful tool to study the conformations and conformation regularities of polymers, intra- and intermolecular interactions of polymer chains (e.g. by hydrogen bonds) and chemical reactions<sup>1–3</sup>. Additionally, semicrystalline polymers show i.r. bands which correlate to the crystallinity, as inferred by, for example, d.s.c. The existence of regular ordered sequences (conformation) promotes the crystallizability. With the FTi.r. method alone it is difficult to distinguish between the influence of conformation and crystallinity on i.r. bands. An assignment of the i.r. bands is possible only by knowledge of the obtained crystallinity, as measured, for example, by d.s.c.

The melt blend of semicrystalline poly(butylene terephthalate) (PBT) and amorphous polycarbonate (PC)—a technologically interesting blend<sup>4</sup>—is a system with many possible influences on the vibrational behaviour of its components by chemical reactions and morphological changes. It is known that exchange reactions take place between PC and PBT during thermal treatment<sup>5–8</sup>. Devaux *et al.*<sup>6</sup> have postulated transesterification to be the most important exchange reaction, resulting in the new chemical structure of copolymers with i.r. bands of the aromatic ester at 1740 and 1070 cm<sup>-1</sup> and of the aromatic–aliphatic carbonate at 1770 cm<sup>-1</sup>. The i.r. band of the formed aliphatic–aliphatic carbonate at 1763 cm<sup>-1</sup> was assigned according to Berti *et al.*<sup>9</sup>.

In addition, the progressive transesterification causes a

transition from homopolymers via block copolymers to random copolymers. Due to the diminishing of the molecular chain length the crystallizable content of PBT decreases. Therefore, the crystallized part of PBT or poly(ethylene terephthalate) (PET), as measured by d.s.c., was also used as a convenient tool for examining the degree of transesterification<sup>10–12</sup>.

Both FTi.r. and d.s.c. have limitations concerning the calculation of the degree of transesterification:

- Since the new copolymer bands at 1070 and 1740 cm<sup>-1</sup> arise close to the intensive bands of pure PC and PBT, respectively, the detection of a low copolyester content by FTi.r. is limited. The lowest concentration for direct detection using the i.r. band at 1070 cm<sup>-1</sup> was found to be  $c_{\text{cop}} = 3.5 \text{ mol}\%$ , as determined by n.m.r.
- The melting heat is determined by the content of the crystallizable molecular chains. Since the crystallization rate is markedly decreased by both the increasing content of PC<sup>13–15</sup> and the progressive transesterification<sup>16</sup>, the measured melting heat is influenced by the applied crystallization conditions. Klee<sup>17</sup> used FTi.r. and d.s.c. results for a qualitative estimation of the degree of transesterification. In the blend PC/PBT 80/20 (wt%), annealed for a short time at 543 K and subsequently crystallized isothermally at 473 K for 20 min, Klee did not observe a measurable PBT crystallinity during reheating from 473 up to 543 K. His interpretation was that a non-crystallizable random copolyester was formed by transesterification. From our point of view, Klee did not use the optimal crystallization regime, and the observed behaviour of the reheating

\* To whom correspondence should be addressed

scan does not unconditionally correspond to the random copolyester.

The transesterification also influences the behaviour of the amorphous phases. Wang *et al.*<sup>7</sup>, Suzuki *et al.*<sup>10</sup> and Murff *et al.*<sup>11</sup> have investigated a blend consisting of PC and PET. The products of transesterification act as compatibilizers between both blend components. The homogenization can be analysed by the behaviour of the glass transition temperature using d.s.c. Analogous results were also found for other polyester blends<sup>18,19</sup>, and are thus also expected for PC/PBT.

In this article the influence of progressive transesterification on selected i.r. bands is described in correlation to structural (e.g. conformation and crystallinity) and chemical changes. The crystallinity, the glass transition behaviour and the crystallization rate have been investigated by d.s.c. The copolyester content ( $c_{\text{cop}}$ ) was determined by n.m.r. spectroscopy. The combination of FTi.r., d.s.c. and n.m.r. is very useful for a conclusive interpretation of the spectra, obtained with blends treated in different ways.

Additionally, the behaviour of the PBT- and PC-rich phases in dependence on the progressive transesterification was investigated. At the start of annealing a marked phase dispersity was observed in the blend PC/PBT 50/50, sufficient for such an investigation by FTi.r. microscopy with a lateral resolution of 20  $\mu\text{m}$ .

Furthermore, linear temperature programmed FTi.r. spectroscopy was carried out on selected samples to support the band assignments to the semicrystalline, the amorphous solid and the amorphous liquid states.

## EXPERIMENTAL

The semicrystalline PBT was a commercial product (Grisuplast U, CFW Premnitz, FRG), synthesized with  $1.4 \times 10^{-4}$  mol% tetra(isopropyl) titanate as the catalyst<sup>20</sup>. After isothermal crystallization at 468 K the glass transition temperature was determined to be 314 K, the melting peak temperature 498 K, and the crystallinity 38%. The second component was a commercial amorphous PC (Lexan 161) from General Electric Plastics, The Netherlands, with a glass transition temperature of 421 K. Blends with the compositions PC/PBT 70/30, 50/50 and 30/70 were produced without additives and inhibitors by melt mixing in an extruder<sup>21</sup>.

For an unambiguous interpretation of the results of the different methods, the preparation of well-defined samples is necessary. The samples (pieces from injection mouldings with the size  $2 \times 2 \times 1$  mm) were annealed within the Perkin Elmer DSC 2 device by  $n$  cycles ( $n$  is the number of cycles per measuring series) between 277 and 533 K. The heating rate was  $10 \text{ K min}^{-1}$  and the annealing time  $t_{v,i}$  at 533 K was about 2 min. The value  $\sum t_{v,i}(533 \text{ K}) = nt_{v,i}(533 \text{ K}) \equiv \sum t_{v,i}$  was used as a measure of the thermal history.

Additionally, the crystallinity was varied by three different cooling regimes (Table 1) applied to each blend composition.

All d.s.c. heating scans of the measuring series with  $n$  cycles were recorded. The PBT crystallinity at room temperature<sup>22</sup> and a possible change in crystallinity due to cold crystallization during the heating scan could be calculated.

The <sup>1</sup>H n.m.r. spectra were recorded with a Bruker AC

250 NMR spectrometer<sup>22</sup>. The copolyester content  $c_{\text{cop}}$  was determined from signal intensities of the terephthalate-centred triads in the <sup>1</sup>H n.m.r. spectrum.

Generally, the FTi.r. investigations were carried out on microtome cuts (thickness 2–3  $\mu\text{m}$ ) of the annealed samples with a Bruker FTIR microscope. The lateral resolution was 20 and 200  $\mu\text{m}$ , respectively. The thermal dependence of the vibrational behaviour of the initial materials and some blends in the range 298–528 K has been studied *in situ* with a modified SPECAC temperature cell in a Bruker IFS 66 spectrometer<sup>23</sup>. The spectral resolution was  $2 \text{ cm}^{-1}$ , and 200 scans were co-added.

## I.r. SPECTRA OF THE PURE COMPONENTS

In the following, the behaviour of the most important i.r. bands and their assignment according to Klee<sup>17</sup> and Stach<sup>24</sup> will be discussed. This is necessary for the interpretation of the band behaviour in the blend system. Table 2 gives an overview. According to Klee the out-of-plane ring deformation bands of PC and PBT at 833 and 872  $\text{cm}^{-1}$ , respectively, exist up to the polymer degradation temperature ( $T \leq 630 \text{ K}$ ). In the PBT component this band does not show a dependence on crystallinity. For the analysis of structural changes in the blends the carbonyl bands  $\nu\text{C}=\text{O}$  of both components, the C–O–C vibration, and also the band at 728  $\text{cm}^{-1}$  of PBT are interesting. I.r. bands caused by the bending and wagging vibrations of the tetramethylene sequences of PBT also need to be taken into consideration for an estimation of the influence of the blend composition and the progressive transesterification. These bands were investigated using pure PBT by Stach<sup>24</sup> and are described in Table 3. According to Stach the *trans-trans-trans* ( $t-t-t$ )

Table 1 Different crystallization regimes

Crystallization regime		
I	II	III
Rapid cooling to 468 K and isothermal crystallization, $t_{c,\text{iso}} = 30 \text{ min}$	Non-isothermal crystallization with a cooling rate of:	
	10 $\text{K min}^{-1}$	80 $\text{K min}^{-1}$

Table 2 Assignment of the most important bands of PBT and PC at room temperature<sup>17,24</sup>

Band assignment	Wavenumber ( $\text{cm}^{-1}$ )	
	PC	PBT
Coupled vibration of carbonyl and ring out of plane (oop)		728
oop ring deformation	833	872
Combination of skeleton and, rocking vibrations		Range 811–970 <sup>a</sup>
$\nu_s\text{O}-\text{C}-\text{O}$	1010	
In-plane (ip) ring deformation		1018
ip ring		1108
$\nu_{\text{as}}\text{O}-\text{C}-\text{O}$	1165–1235	
$\nu_{\text{as}}\text{C}-\text{O}-\text{C}$		1260
Correlated with ordered structure <sup>25</sup>		1320
ip ring	1410	1410
$\text{CH}_2$ bending and wagging		Range 1386–1470 <sup>a</sup>
ip ring	1504	1504 <sup>a</sup>
$\nu\text{C}=\text{O}$	1775	1720

<sup>a</sup> Influenced by ordered structures

conformation is energetically higher, and consequently the corresponding bands appear at higher wavenumbers than the bands associated with the *gauche-trans-gauche* (*g-t-g*) conformation. In the melt the intensity of all these bands is diminished and only a broad band with a maximum at  $1470\text{ cm}^{-1}$  was observed. This maximum has been correlated with a dominant *trans* part in the amorphous liquid state.

The exact observation of the  $\text{CH}_2$  bending and wagging vibrations of PBT in the blends is not simple because some absorbances of PC also appear in this range (see Figure 1).

The spectral region of the carbonyl bands  $\nu\text{C}=\text{O}$  of PC and PBT was chosen for the estimation of the composition (PC/PBT ratio). Birley and Chen<sup>26</sup> used the ratio of maximum absorbances, whereas in this article the ratio of integrated absorbances was calculated to include the amorphous and crystalline parts of PBT.

## RESULTS AND DISCUSSION OF D.S.C. AND N.M.R. OF THE ANNEALED BLENDS

At the beginning ( $\sum t_{v,i} \approx 1.6$  min) the PBT crystallinity of the isothermally crystallized blends was independent of the blend composition and was about 38%. The amorphous phases of the blends are characterized by two glass transitions, one due to the PBT-rich phase and one due to the PC-rich phase<sup>16</sup>. The influence of the increasing annealing time on the d.s.c. heating scans of the blend PC/PBT 50/50 (crystallization regime I) is shown in Figure 2. The glass transition temperatures of the amorphous PBT- and PC-rich phases shift to higher and lower temperatures, respectively. In the final state, one glass transition was observed. This behaviour is caused by the compatibilizing effect of the formed copolyester. With increasing annealing time the heat of fusion and the peak temperature decrease<sup>16</sup>. Of note is the change in intensity of the so-called cold crystallization, which occurred during the heating scan at  $T > T_g(\text{PC})$ . Knowledge of the cold crystallization is important for the interpretation of i.r. bands of PBT related to structural order in the blends and their relation to the degree of transesterification. The dependence of the  $^1\text{H}$  n.m.r. results on annealing time are given in Figure 3 for all blends. At the beginning,  $c_{\text{cop}}$  is zero within the detection limit of the n.m.r. method. The copolyester content increases with increasing annealing time and PBT content. A double logarithmic representation of the  $c_{\text{cop}}$  values at constant annealing time  $\sum t_{v,i}$  versus the initial PBT content gives a straight line with a slope of 2.5. This result confirms the relation by Devaux *et al.*<sup>6</sup>. They found that the transesterification rate is proportional to the catalyst content  $c(\text{titanate})^{2.5}$ , whereby the value of the catalyst is proportional to the PBT content. Consequently, the transesterification in the blends of different composition should follow the same reaction scheme but with different reaction rates.

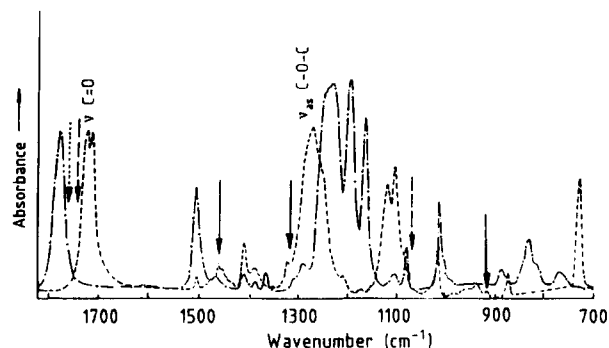
## RESULTS AND DISCUSSION OF THE FT.I.R. INVESTIGATIONS

### Temperature dependence of the i.r. spectra of pure PBT and PC

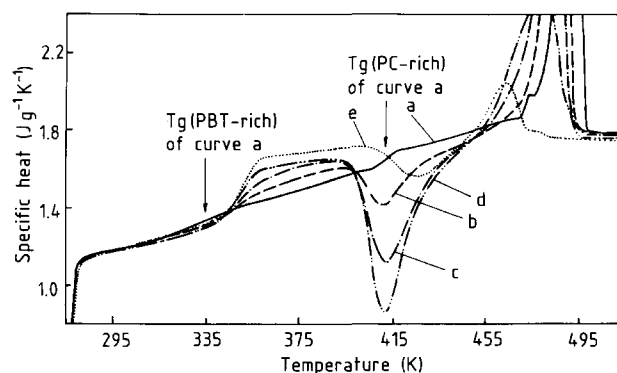
The changes in the PBT spectra during heating from room temperature to 505 K are connected with the phase

**Table 3** Conformation-dependent vibrations in PBT determined at room temperature (see Stach<sup>24</sup>)

Vibration unit	Wavenumber ( $\text{cm}^{-1}$ )	
	<i>g-t-g</i> conformation ( $\Rightarrow \alpha$ -crystallite)	<i>t-t-t</i> conformation (produced under stress) ( $\Rightarrow \beta$ -crystallite)
$\text{CH}_2$ bending	1452, 1460	1470, 1485
$\text{CH}_2$ wagging	1173, 1386	1208, 1393
Combination of skeleton and, rocking vibrations	811, 918	842, 960



**Figure 1** I.r. spectra of the pure components PC (---) and PBT (—), known conformation bands ( $\uparrow$ ), expected range of formed copolyester ( $\downarrow$ ) and expected range of formed aliphatic carbonate ( $\downarrow$ )



**Figure 2** Influence of the annealing time on the d.s.c. heating scans of the blend PC/PBT 50/50.  $\sum t_{v,i}$  (min): 1.6, curve a (—); 7, curve b (---); 13, curve c (-.-.); 20, curve d (-·-·); 44, curve e (·-·-·)

transition from the semicrystalline to the liquid amorphous state (Figure 4). At room temperature the bands of the *g-t-g* conformation can be observed, which diminish in the melt. In this way the correlation of the *g-t-g* conformation with the crystallinity was confirmed. For most bands (for example  $870\text{ cm}^{-1}$ ), normal thermal behaviour was observed. The wavenumber and the intensity decrease with increasing temperature. An exception is the behaviour of the carbonyl vibration  $\nu\text{C}=\text{O}$  and the band at  $728\text{ cm}^{-1}$ . In the semicrystalline state up to about 465 K a splitting of the  $\nu\text{C}=\text{O}$  band was observed with two maxima at  $1714$  and  $1720\text{ cm}^{-1}$ . The peak intensity at  $1714\text{ cm}^{-1}$  has been little diminished in relation to that at  $1720\text{ cm}^{-1}$  with increasing temperature. This could be caused by a low degree of partial melting. A strong qualitative change can be seen as a consequence of the

melting process. In the amorphous liquid state only one band at  $1721\text{ cm}^{-1}$  was observed, and the integral absorbance of the  $\nu\text{C=O}$  band is hardly changed. These changes apparently correlate with the conformation of the tetramethylene sequences. During the melting process the band at  $1714\text{ cm}^{-1}$  diminishes as well as the band of the  $g-t-g$  conformation at  $1458\text{ cm}^{-1}$ . In the melt only the band at  $1721\text{ cm}^{-1}$  exists, and in the range of the  $\text{CH}_2$  bending vibrations an absorption maximum was observed at  $1470\text{ cm}^{-1}$ , which indicated a dominance of *trans* states. Therefore, the split  $\nu\text{C=O}$  band at room temperature reflects the existence of the amorphous phase with a dominant *trans* part and the crystalline phase with the  $g-t-g$  conformation in the semicrystalline PBT. A smaller but similar tendency with respect to the change in wavenumber during the melting process was observed for the coupled vibration at  $728\text{ cm}^{-1}$ . Apparently, an indirect influence of the conformations on this vibration also exists, which is smaller than the influence on the  $\nu\text{C=O}$  vibration. This can be understood by considering the molecular structure of PBT. To our knowledge an influence of the conformation on the  $\nu\text{C=O}$  band and the coupled vibration at  $728\text{ cm}^{-1}$  in PBT has not been reported in the literature.

The investigated PC samples are amorphous as measured by d.s.c. The bands shift as expected with increasing temperature, and the typical shape of the i.r. spectra (Figure 1) remains about the same.

#### Blend PC/PBT 70/30—influence of crystallization regimes and increasing annealing time on i.r. spectra

The high PC content in this blend system reduces the PBT crystallization rate. Therefore, it is possible to produce melt films at room temperature realizing a completely amorphous state A (crystallization regime III), and a state B in which PBT is partially crystallized

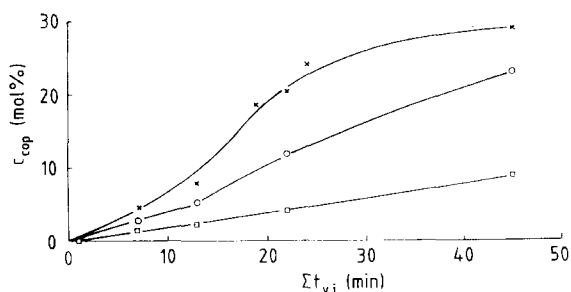


Figure 3 Dependence of the copolyester content  $c_{\text{cop}}$  on the annealing time  $\sum t_{v,j}$  of PC/PBT blends: 30/70 ( $\times$ ), 50/50 ( $\text{O}$ ) and 70/30 ( $\square$ )

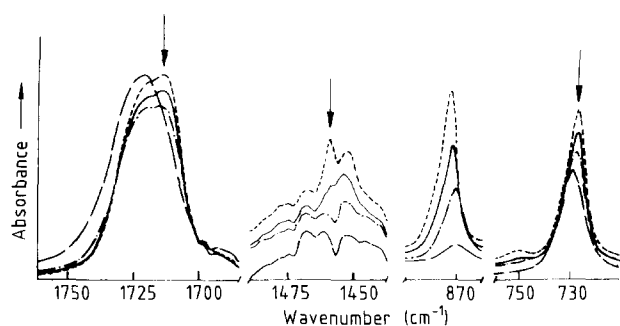


Figure 4 I.r. spectra of pure PBT at different temperatures: room temperature (---), 360 K (—), 465 K (···) and 505 K (-·-·)

(crystallization regime I). The d.s.c. measurements confirm both of these states and show that PBT of the amorphous sample A crystallizes during the d.s.c. heating scan  $T > T_g(\text{PC}) = 420\text{ K}$  by cold crystallization. In Figure 5 the i.r. spectra of PC/PBT 70/30 after  $\sum t_{v,j} \approx 1.6\text{ min}$  in the amorphous state A and the semicrystalline state B are shown in selected ranges. The i.r. spectra of pure PBT and PC are also provided, for a direct comparison. A marked difference between the i.r. spectra of both blend states can be observed at room temperature (Figure 5a). The spectra of the crystallized state B can be obtained by superposition of the spectra of both pure components. The difference between both spectra of the

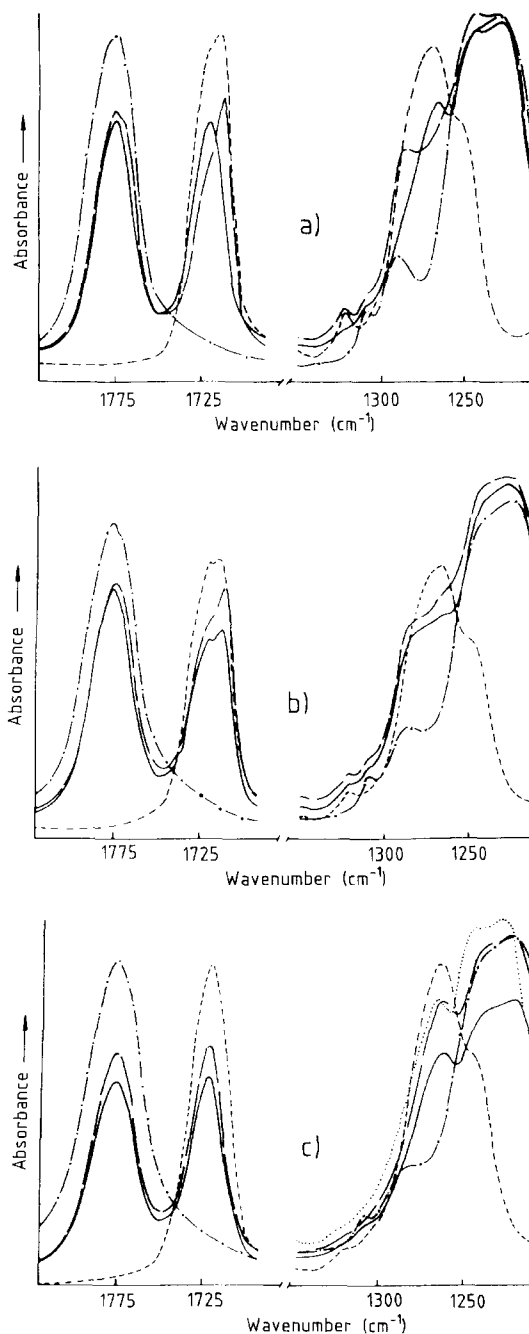


Figure 5 Selected regions of i.r. spectra of pure PC (---), pure PBT (-·-·), blend PC/PBT 70/30: state A, amorphous (—), state B, crystallized (···) at (a) room temperature, (b) 432 K and (c) 505 K (with the range of  $\nu_{\text{as}}\text{C-O-C}$  of the blend in amorphous state A measured at room temperature (·····))

different blend states disappears at  $T = 433 \text{ K} > T_g(\text{PC})$  (Figure 5b). As a consequence of the higher mobility of the amorphous liquid PC matrix at  $T > T_g(\text{PC})$  the tetramethylene sequences of PBT are able to arrange in the energetically favourable  $g-t-g$  conformation. The cold crystallization of PBT can take place in blend state A. In Figure 5c the PBT content of both blend states is in the molten state. The blend spectra are about the same. The blend spectra in Figures 5b and 5c can be obtained by a superposition of the spectra of PC and PBT at the respective temperature. In Figure 5c the blend spectrum of the amorphous state A measured at room temperature (see Figure 5a) is additionally plotted in the range of  $\nu_{\text{as}}\text{C}-\text{O}-\text{C}$ . The expected similarity of this spectrum to those in the amorphous liquid state is evident. The higher wavenumber of the bands in the amorphous solid state is caused by the lower measuring temperature in comparison to the temperature of the amorphous liquid state.

These results are important for the discussion of the influence of copolyester content on the crystallizable part. The spectrum after  $\sum t_{v,i} \approx 7 \text{ min}$ , using the crystallization regime I, is identical to the spectrum of the amorphous state A. The transesterification rate of the PC-rich blend is low, and only a copolyester content of about 0.4 mol% is formed after  $\sum t_{v,i} \approx 7 \text{ min}$ . This low copolyester content, acting additionally to the PC content, reduces strongly the crystallization rate, and the crystallization is completely suppressed during the crystallization regime I. Another crystallization condition<sup>16</sup> has to be chosen to make the PBT crystallization possible. In this way it can be shown that the existence of the observed amorphous state after a short annealing time is not caused by the non-crystallizable random copolyester.

The attained copolyester content of the PC-rich blend was 2.9 mol%, determined by n.m.r. This value is too low for a distinct detection in the i.r. spectra. So, the determination of  $c_{\text{cop}}$  with n.m.r. and the results of the d.s.c. are very helpful to understand the observed changes of the FTi.r. spectra.

#### Blend PC/PBT 50/50—observation of the homogenization due to progressive transesterification

The change in dispersity of the blend PC/PBT 50/50 can be shown by polarizing light microscopy (Figure 6). At the beginning, two regions can be clearly separated: a birefringent spherulitic crystalline and a homogeneous one with a diameter of about  $20 \mu\text{m}$ . The lateral resolution of i.r. microscopy permits the investigation of the microscopically different phases.

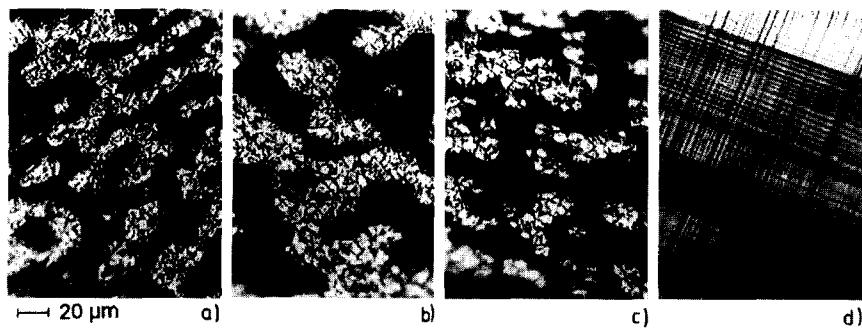


Figure 6 Morphology of blend PC/PBT 50/50 by polarizing light microscopy (crossed polarizers) at different annealing times  $\sum t_{v,i}$  (min): (a) 1.6, (b) 7, (c) 13 and (d) 20. In (d) the superstructure was formed due to the cutting technique

Figure 7 shows the  $\nu\text{C}=\text{O}$  ranges of i.r. spectra with different lateral resolutions. The spectra of the PC-rich and PBT-rich regions were measured with a lateral resolution of  $20 \mu\text{m}$ . The average spectrum of the microscopically different regions was measured with a lateral resolution of  $200 \mu\text{m}$ . The qualitative estimation of the absorbance ratio of PC to PBT confirms the expectation that the PC content of the homogeneous phase is higher, and this ratio of the birefringent spherulitic phase is lower than the average value.

It is remarkable that the homogeneous region is opaque at the beginning ( $\sum t_{v,i} = 1.6 \text{ min}$ ) and dark at  $\sum t_{v,i} = 7 \text{ min}$ . This observation correlates with the d.s.c. and FTi.r. results. At  $\sum t_{v,i} = 1.6 \text{ min}$  the PBT content is maximally crystallized both in the PBT- and PC-rich phases. With increasing annealing time the crystallization rate is decreased by the increasing copolyester content. In the PC-rich phase the additional copolyester content suppresses the crystallization of PBT so strongly that the PC-rich phase after  $\sum t_{v,i} = 7 \text{ min}$  contains only amorphous PBT, and appears dark on polarized light microscopy. The splitting of the  $\nu\text{C}=\text{O}$  band of PBT reflects this behaviour also, as described above for pure PBT. After  $\sum t_{v,i} \geq 20 \text{ min}$  ( $c_{\text{cop}} \geq 6 \text{ mol}\%$ ), one homogeneous phase was obtained and the  $\nu\text{C}=\text{O}$  band shows one maximum. The conclusions from light microscopy, the results of the d.s.c. heating scans, and the behaviour of the i.r. bands at  $1720$ ,  $1450$  and  $728 \text{ cm}^{-1}$  agree with each other in relation to the discussed behaviour of i.r. bands of pure PBT in dependence on the crystallinity.

An exception is the final state, which is homogeneous and completely amorphous at  $298 \text{ K}$ . In contradiction to the expectation, a splitting of the  $\nu\text{C}=\text{O}$  band of both PBT and PC was observed. The behaviour of the PBT bands indicates a strong increase of the amorphous content with a dominant *trans* part. A certain amount of the  $g-t-g$  conformation still exists, but is not correlated with a measurable crystallinity. The structure of the  $\nu\text{C}=\text{O}$  band of PC at  $1775 \text{ cm}^{-1}$  was found also in other states, as in the blend PC/PBT 70/30 and in solution-cast foils of pure PC. The structuring in the blends is more enhanced than in pure PC. Radusch *et al.*<sup>27</sup> and also Wings and Trafara<sup>28</sup> found by wide-angle X-ray scattering (WAXS) that PC was crystallized after a long annealing time of the blends PC/PBT. Measurements by d.s.c. and WAXS did not give any indications of PC crystallinity in our samples. An explanation of the splitting of the  $\nu\text{C}=\text{O}$  band of PC is that the PC molecules have a higher probability for a conformation change due to the

higher mobility of the neighbouring PBT molecules. The chain conformation is only a precondition for PC crystallinity. A measurable PC crystallinity was not realized by the used crystallization condition. I.r. measurements of semicrystalline PC were carried out by Schmidt *et al.*<sup>29</sup> The authors did not observe a splitting of the carbonyl band. More investigations are necessary for an explanation of the observed splitting.

Figure 8a shows the double logarithmic representation of the ratio of the integrated absorbances of  $\nu\text{C}=\text{O}$  (PC/PBT) versus the mass ratio of PC to PBT in the initial state. For the calculation of the integrated absorbance of all three blends, i.r. spectra obtained with a lateral resolution of  $200\ \mu\text{m}$  were used. Within the accuracy of the method the values give a straight line.

In Figure 8b the ratio of the integrated absorbance of the microscopically different regions ( $20\ \mu\text{m}$ ) in the blend PC/PBT 50/50 is represented in dependence on the copolyester content. The strongest difference between both regions was observed at  $c_{\text{cop}} = 1.5\ \text{mol}\%$  ( $\sum t_{v,i} \approx 7\ \text{min}$ ). In the spherulitic region a PC/PBT composition of  $\leq 30/70$  and in the microscopically homogeneous region a composition of  $\geq 70/30$  have been estimated with the help of the relation in Figure 8a. In this annealing state a coarser dispersion was found with polarizing microscopy than at shorter  $\sum t_{v,i}$ . With increasing copolyester content the heterogeneity disappears, and the absorbance ratio will be constant. The d.s.c. analysis (Figure 2) also shows a homogenization of the amorphous phases with one glass transition in the final state. Within the limits of the methods used the final state is morphologically and compositionally nearly homogeneous.

It should be mentioned that direct proof of transesterification by the band  $1070\ \text{cm}^{-1}$  is possible at  $c_{\text{cop}} \geq 6\ \text{mol}\%$  in this blend.

#### Blend PC/PBT 30/70—direct proof of all new i.r. bands of formed transesterification products

The PBT-rich blend is the blend with the highest transesterification rate. At the high transesterification degree of  $c_{\text{cop}} \approx 23\ \text{mol}\%$  the band  $1760\ \text{cm}^{-1}$  of the formed aliphatic-aliphatic carbonate is clearly detectable and the  $\nu\text{C}=\text{O}$  band of PC disappears (Figure 9).

With increasing transesterification, the i.r. bands of PBT correlated with conformation show changes at room temperature analogous to the changes of i.r. bands of pure PBT during the melting process. In the initial state the skeleton vibrations at  $811$  and  $918\ \text{cm}^{-1}$  caused by the *g-t-g* conformation have been observed. The

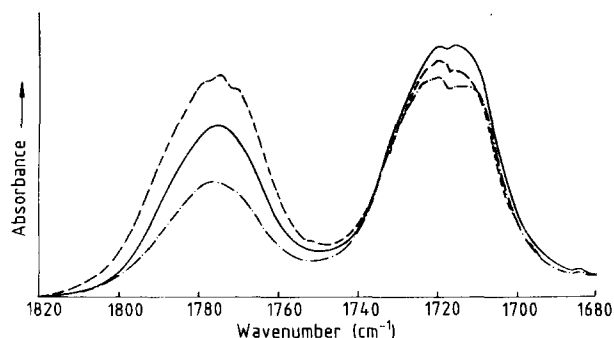


Figure 7 I.r. spectra of the  $\nu\text{C}=\text{O}$  vibration of the blend PC/PBT 50/50 with different lateral resolutions:  $20\ \mu\text{m}$ —PC-rich region (---), PBT-rich region (-.-);  $200\ \mu\text{m}$ —average spectra (—)

intensity of these bands measured at room temperature decreases with progressive transesterification. The influence of changed conformation on the  $\nu\text{C}=\text{O}$  band and the band at  $728\ \text{cm}^{-1}$  appears also as discussed for pure PBT.

These changes agree with the d.s.c. results in dependence on the increasing transesterification. The crystallinity of PBT at room temperature shifts to zero, and in the following heating scan a cold crystallization with decreasing intensity appears. In the final state the  $\nu\text{C}=\text{O}$  band of PBT has a shoulder at lower wavenumbers. This

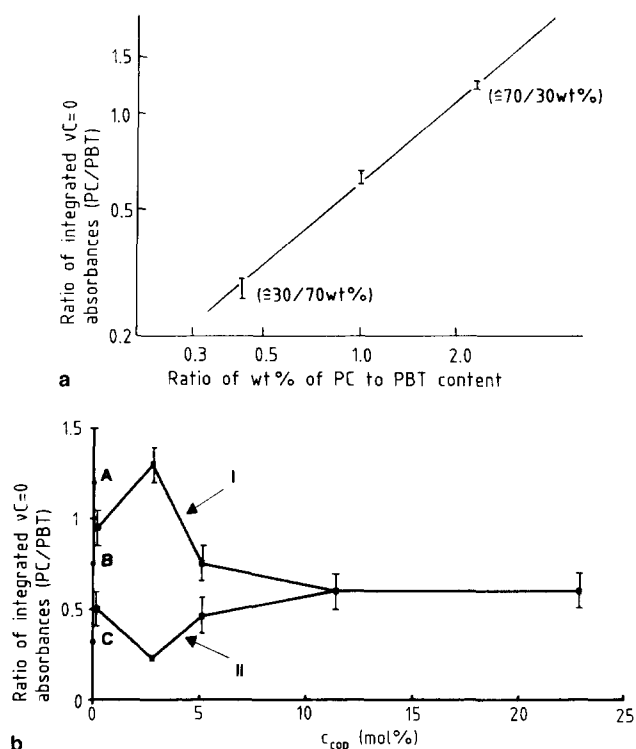


Figure 8 (a) Double logarithmic representation of the dependence of the ratio of the integrated  $\nu\text{C}=\text{O}$  absorbances (PC/PBT) on the mass ratio of PC to PBT, measured in the initial states and with a lateral resolution of  $200\ \mu\text{m}$ . (b) Ratio of the integrated  $\nu\text{C}=\text{O}$  absorbances (PC/PBT) of the optical different regions of blend PC/PBT 50/50 (measured with a lateral resolution of  $20\ \mu\text{m}$ ) in dependence on  $c_{\text{cop}}$ . I, Homogeneous region; II, spherulitic region; ■, measured data within the limits of error; A, B, C (●), values from Figure 8a

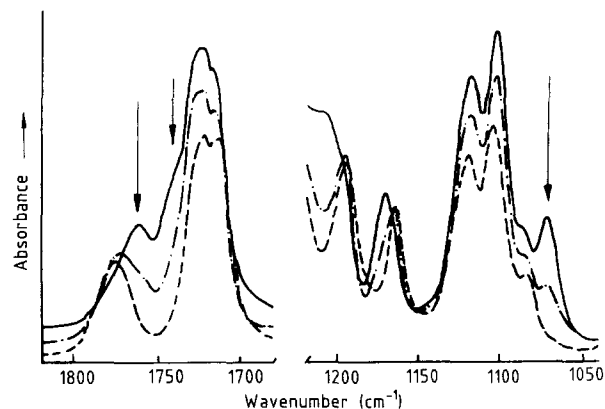


Figure 9 I.r. spectra of the blend PC/PBT 30/70 at different copolyester contents  $c_{\text{cop}} \geq 0$  (---),  $15\ \text{mol}\%$  (-.-) and  $23\ \text{mol}\%$  (—). ↓, I.r. bands of formed aromatic ester and aliphatic-aliphatic carbonate

shoulder is caused by the small amount of PBT with the  $g-t-g$  conformation, which is not crystallized at room temperature. This part can crystallize at  $T > T_g(\text{PC})$  by cold crystallization.

## CONCLUSIONS

PC/PBT melt blends were characterized by their reaction and crystallization behaviour using FTIR as well as n.m.r. spectroscopy and d.s.c. Samples of the pure components and of the blends PC/PBT 70/30, 50/50 and 30/70 prepared within the DSC 2 device were investigated. Temperature-dependent i.r. measurements were carried out to guarantee a correct assignment of the bands.

The n.m.r. results confirm the dependence of the transesterification rate on the catalyst content used in the PBT synthesis. The maximum attained copolyester content was 23 mol% in the PBT-rich blend.

A new aspect of the interpretation of the i.r. spectra of pure PBT was found. The carbonyl band  $\nu_{\text{C=O}}$  shows a splitting into two maxima of 1720 and 1714  $\text{cm}^{-1}$  that correlates to the conformation of the tetramethylene sequences. The splitting disappears in the melt. A similar but weaker correlation also exists between the conformation and the band at 728  $\text{cm}^{-1}$ , which shifts to 731  $\text{cm}^{-1}$  in the amorphous state.

The values of the PBT crystallinity measured by d.s.c. and the n.m.r. results permit a clear interpretation of the i.r. spectra. The crystallization rate of the blends decreases with increasing PC and copolyester content. The existence of the crystallizable PBT part was proved by cold crystallization. In particular, the PC-rich blend shows that the i.r. bands of different blend states can be only correctly interpreted with knowledge of the PBT crystallinity.

In the blend PC/PBT 50/50 the homogenization of both components in dependence on the progressive transesterification can be analysed by i.r. microscopy with a lateral resolution of 20  $\mu\text{m}$ . The dispersity of the observed PC-rich and PBT-rich phases disappeared at  $c_{\text{cop}} \geq 6 \text{ mol}\%$ .

In some blend states a splitting of the carbonyl vibration of PC appears. This splitting is presumably caused by changes in conformation, which are possible by better mobility of PC molecules in the PBT environment. These ordered structures do not yet lead to a PC crystallinity under the applied experimental conditions.

After a long annealing time ( $\sum t_{v,i} \geq 20 \text{ min}$ ) the carbonyl band of the formed aliphatic-aliphatic carbonate linkage at 1760  $\text{cm}^{-1}$  was observed in the PBT-rich blend.

In summary, we conclude that the indirect proof of the transesterification by the i.r. bands correlated to the ordered structures of PBT is more sensitive than the direct proof by the separation of the new bands of the formed copolyester. For an unambiguous interpretation of the indirect influence of the transesterification on the special i.r. bands, knowledge of the crystallinity is necessary.

## ACKNOWLEDGEMENTS

Financial help from the Deutsche Forschungsgesellschaft is gratefully acknowledged. We thank Dr H. Komber for the n.m.r. measurements and L. Häussler for the d.s.c. investigations, whose results are very important for our work.

## REFERENCES

- Hummel, D. O., *I.r.-Spektrometrie von Polymeren*. (eds W. Fresenius, H. Günzler, W. Huber, I. Lüderwald, G. Tölg and H. Wisser). *Analytiker-Taschenbuch*, Vol. 6, Springer-Verlag, Berlin, 1985.
- D'Esposito, L. and Koenig, J. L., *J. Polym. Sci., Polym. Phys.* 1976, **14**, 1731.
- Coleman, M. M. and Painter, P. C., *Appl. Spectrosc. Rev.* 1984, **20**, 255.
- Becker, G. and Braun, D. (ed.) *Kunststoff-Handbuch*, Vol. 3/2: 'Technische Polymer-Blends' (ed. L. Bottenbruch), Carl Hauser, München, 1993.
- Porter, R. S. and Wang, L. H., *Polymer* 1992, **33**, 2019.
- Devaux, J., Godard, P. and Mercier, J. P., *J. Polym. Sci., Polym. Phys.* 1982, **20**, 1875.
- Wang, L. H., Huang, Z., Hong, T. and Porter, R. S., *J. Macromol. Sci.-Phys.* 1990, **B29**, 155.
- Huang, Z. and Wang, L. H., *Makromol. Chem., Rapid Commun.* 1986, **7**, 255.
- Berti, C., Bonora, V. and Pilati, F., *Makromol. Chem.* 1992, **193**, 1665.
- Suzuki, T., Tanaka, H. and Nishi, T., *Polymer* 1989, **30**, 1287.
- Murff, S. R., Barlow, J. W. and Paul, D. R., *J. Appl. Polym. Sci.* 1984, **29**, 3232.
- Eguiazabal, J. I., Cortazar, M., Iruiñ, J. J. and Guzman, G. M., *J. Macromol. Sci.-Phys.* 1988, **B27**, 19.
- Delimoy, D., Bailly, Chr., Devaux, J. and Legras, R., *Polym. Eng. Sci.* 1988, **28**, 104.
- Radusch, H.-J. and Androsch, R., *Angew. Makromol. Chem.* 1994, **214**, 179.
- Halder, R. S., Joshi, M. and Misra, A., *J. Appl. Polym. Sci.* 1990, **39**, 1251.
- Pompe, G., Häußler, L., Hopfe, I. and Komber, H., *Proc. Polymer-werkstoffe '94*, Merseburg, September 1994; Pompe, G. and Häußler, L., *J. Polym. Sci., Polym. Phys.* (submitted).
- Klee, W. Dissertation, University of Köln, 1991.
- Porter, R. S., Jonza, J. M., Kimura, M., Desper, C. R. and George, E. R., *Polym. Eng. Sci.* 1989, **29**, 55.
- Zhang, R., Luo, X. and Ma, D., *J. Appl. Polym. Sci.* 1995, **55**, 455.
- Androsch, R. Dissertation, TU Merseburg, 1993.
- Pompe, G., Häussler, L. and Winter, W., *J. Polym. Sci., Polym. Phys.* 1996, **34**, 211.
- Pompe, G., Meyer, E., Komber, H. and Haman, H., *Thermochim. Acta* 1991, **187**, 185.
- Hopfe, I., Pompe, G., Eichhorn, K.-J. and Häussler, L., *J. Mol. Structure* 1995, **349**, 443.
- Stach, W. Dissertation, University of Köln, 1982.
- Gillette, P. C., Dirlikov, S. D., Koenig, J. L. and Lando, J. B., *Polymer* 1982, **23**, 1759.
- Birley, A. W. and Chen, X. Y., *Br. Polym. J.* 1984, **16**, 77.
- Radusch, H.-J., Androsch, R., Vogel, J., Trempler, J. and Fakirov, S., *Angew. Makromol. Chem.* 1992, **198**, 135.
- Wings, N. and Trafara, G., *Makromol. Chem., Macromol. Symp.* 1991, **52**, 253.
- Schmidt, P., Dybal, J., Turska, E. and Kulczycki, A., *Polymer* 1991, **32**, 1862.