

## Pivalolactone, 3<sup>a)</sup>

### Reactive blending of polypivalolactone with polycarbonate

Edze Jan Tijsma\*, Leen van der Does, Adriaan Bantjes

Department of Chemical Technology, University of Twente, P. O. Box 217, 7500 AE Enschede, The Netherlands

Ivan Vulić, Gerard Hidde Werumeus Buning

DSM Research, P. O. Box 18, 6160 MD Geleen, The Netherlands

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#### SUMMARY:

The occurrence of interchange reactions during heating of polypivalolactone (PPVL) with three polymers and their influence on the blend properties were studied. Physical blends of PPVL and bisphenol-A polycarbonate (PC) were found to be immiscible. By heating of PPVL/PC blends in the melt at 280 °C, in diphenyl ether at 260 °C and in a twin-screw extruder (TSE) at 280 °C partial formation of copolymers was observed, provided that tetrabutyl orthotitanate (TnBT) was added. After heating of equimolar PPVL/PC blends in a TSE for 15 min, a PPVL-PC block copolymer could be isolated containing 25 mol-% pivalolactone (PVL) units. The results from thermal analyses indicated that PPVL/PC blends had become more miscible, due to the presence of copolymers formed by interchange reactions. After heating of equimolar mixtures of PPVL and a polyarylate (PAr) in a TSE for 15 min, PPVL-PAr copolymers with 5 mol-% PVL units could be isolated. Probably due to this low degree of interchange, no effect on the miscibility of the initially immiscible PPVL/PAr blends could be observed. PPVL/poly(butylene terephthalate) (PBT) blends, obtained after heating in a TSE, decomposed at a temperature between the melting temperatures of PPVL and PBT, indicating that interchange reactions may have occurred.

#### Introduction

Recent years have seen an increasing interest in reactive blending of polymers, for it opens a convenient route for preparing new copolymers starting from existing polymers. In general, the aim of reactive blending is that chemical reactions occur during heating of blends of a polymer with another polymer or a monomeric compound. Depending on the type of equipment used, reactive blending can be divided into reactive compounding (batch) and reactive extrusion (continuous). Examples of reactions<sup>1)</sup> which have been performed by reactive blending are grafting of monomer onto polymer, controlled degradation of high molecular weight polymers, introduction of functional groups or interchange reactions of polyesters with other polyesters or monomeric compounds.

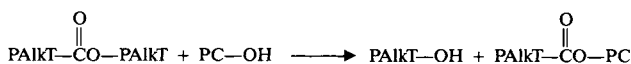
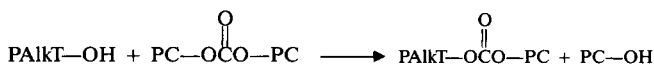
The reactions occurring during reactive blending can improve the compatibility between immiscible polymers<sup>2)</sup>. Furthermore, interchange reactions between two

a) Part 1: cf. ref. <sup>10)</sup>; part 2: cf. ref. <sup>11)</sup>.

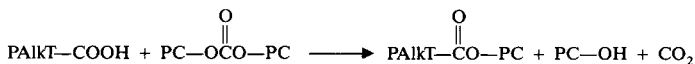
polymers or a polymer and a monomeric compound may result in the formation of copolymers. In the case of polyester/bisphenol-A polycarbonate (PC) blends, interchange reactions start between 250 and 300 °C in the presence of catalysts, finally resulting in the formation of copolymers<sup>3</sup>. The interchange reactions which may occur between poly(alkylene terephthalate)s and PC are assumed to be alcoholysis, acidolysis and ester interchange (see Scheme 1)<sup>4</sup>. These reactions, in particular ester interchange between ester and carbonate groups, take place at a relatively high rate in the presence of a suitable catalyst, e. g., tetrabutyl orthotitanate (TnBT)<sup>4,5</sup>. Recently, it was found that during melt-mixing of poly(ethylene terephthalate)/PC blends in the presence of TnBT intramolecular exchange occurred followed by decarboxylation, resulting in the formation of aliphatic aromatic ether bonds<sup>6</sup>. Copolymers have also been obtained via interchange reactions between poly(alkylene terephthalate)s and monomeric compounds<sup>7-9</sup>.

*Scheme 1.* Interchange reactions between poly(alkylene terephthalate)s (PAIKT)s and PC<sup>4</sup>

Alcoholysis:



Acidolysis:

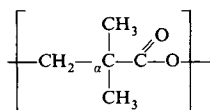


Ester interchange:



The aim of our investigations is to prepare copolymers containing the pivalolactone (PVL) unit, and in our previous papers interchange reactions between polypivalolactone (PPVL) and monomeric compounds were discussed<sup>10,11</sup>. With respect to interchange reactions between PPVL and polymers no reports are known, whereas, as far as blending of PPVL with polymers in general is concerned, only a limited amount of data is available<sup>12-16</sup>. Cruz et al. found that PPVL/PC blends were completely immiscible<sup>12,13</sup>, which was assumed to be caused by the shielding of the methyl

groups next to the carbonyl group in PPVL<sup>12</sup>). Furthermore, it was concluded that interchange reactions during melt-blending did not occur<sup>13</sup>).



Polypivalolactone (PPVL)

In this paper results are presented on the occurrence of interchange reactions during reactive blending of PPVL with other polymers. Apart from the PPVL/PC system, which was studied in detail by DSC, viscometry, NMR and IR, reactive blending was also investigated with blends of PPVL and two polyesters, i.e., poly(butylene terephthalate) and a copolyester of bisphenol-A with 50% isophthalate and 50% terephthalate.

## Experimental part

### Materials

Polypivalolactone (PPVL), with limiting viscosity number  $[\eta] = 0,62$  dL/g in trifluoroacetic acid (TFA) at 25 °C, was prepared as described elsewhere<sup>10</sup>. Bisphenol-A polycarbonate (PC) with a molecular weight ranging from 20 000 to 25 000 was obtained from Aldrich. Poly(tetramethylene terephthalate) [poly(butylene terephthalate) (Arnite® T/06-200)], with  $[\eta] = 1,01$  dL/g in TFA at 25 °C, was supplied by DSM. Polyarylate (PAr) was prepared by interfacial polycondensation of bisphenol-A and isophthaloyl dichloride and terephthaloyl dichloride (mole ratio 2 : 1 : 1)<sup>17</sup>. Polymers were dried thoroughly before use.

Tetrabutyl orthotitanate (TnBT, Merck), used as a catalyst during melt-blending, was used as received. Diphenyl ether (Aldrich), TFA (Janssen Chimica), chloroform and methylene chloride (both from Merck) were used without further purification. The ethanol used for washing and precipitation was of technical grade.

### Heating of PPVL/polymer blends

Mixtures of PPVL and polymers with and without TnBT (0,5 wt.-%) were introduced into 10-mL glass tubes equipped with a provision for either applying a vacuum or keeping a nitrogen atmosphere. After vacuating and flushing with nitrogen three times, the tubes were inserted in a temperature-controlled ( $\pm 2$  °C) salt bath (10 parts of potassium nitrate and 8,5 parts of sodium nitrite) and heated at 280 °C for 240 min. When diphenyl ether was used as an inert reaction medium (Tab. 1, exp. no. A-50/02), heating was carried out at 260 °C for 240 min.

In an alternative procedure, equimolar mixtures of PPVL and polymers with and without TnBT (0,5 wt.-%) were placed in a 50-mL two-necked reaction vessel equipped with a stainless steel stirrer, with an inlet for nitrogen and an outlet with a provision for applying a vacuum (Tab. 1, exp. no. A50/01). After the reaction vessel was evacuated and flushed with nitrogen for three times, it was inserted into the salt bath kept at 280 °C. While the contents were stirred under a slow stream of nitrogen, samples were removed at various times. Analogously, experiments were carried out in diphenyl ether at 260 °C.

Furthermore, blending was performed on a co-rotating twin screw mini-extruder, developed by DSM, with a screw length of 12 cm and a capacity of about 4 g polymer (Tab. 1, exp. nos. B-50/01,

B-50/02 and B-xx/01). The extruder temperature was 280 °C and the screw speed was 100 rpm. The extruder was provided with a heated channel through which the polymer could be fed back. After blending, the extruder valve was opened and the resulting polymer fibre was cooled in a water bath.

After drying overnight (vac. at 60 °C), the blends were studied by thermal analyses, NMR and IR.

#### *Selective extraction of polymers*

Samples of PPVL/PC and PPVL/PAr blends were extracted in a Soxhlet apparatus for 5 h with methylene chloride, which is a solvent for PC and PAr and a non-solvent for PPVL. Both the dissolved fraction (precipitated in ethanol) and the undissolved polymer were dried, weighed and characterized by IR, <sup>1</sup>H NMR and DSC. Experiments performed on (non-reacted) mixtures of PPVL and PC and of PPVL and PAr showed that PC and PAr were quantitatively separated from PPVL by this procedure.

#### *Measurements*

Viscometric measurements were carried out with solutions of 0,025 g polymer in 10 mL of TFA, using an Ubbelohde viscometer thermostated at 25 °C. <sup>1</sup>H NMR spectra were recorded on a Bruker AC 250F using deuterated solvents (trifluoroacetic acid or chloroform); chemical shifts are given in parts per million downfield from tetramethylsilane (TMS). IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrophotometer using KBr discs. Thermal analyses were performed at a heating rate of 20 °C/min using a Perkin-Elmer DSC 7, calibrated using gallium and indium; all DSC runs were carried out under a nitrogen atmosphere with samples of approximately 5 mg. Thermogravimetric measurements were carried out under a helium atmosphere at a heating rate of 20 °C/min using a Perkin-Elmer TGA 7.

## **Results and discussion**

### *Heating of PPVL/PC blends*

The occurrence of interchange reactions in polypivalolactone (PPVL)/bisphenol-A polycarbonate (PC) blends during heating at 260–280 °C was studied under various conditions (see Tab. 1). In a first series of experiments, the reaction products of equimolar PPVL/PC blends (i. e., with 28 wt.-% PPVL) were analyzed as a function of the reaction time, after heating at 280 °C in the melt in the presence of tetrabutyl orthotitanate (TnBT) (Tab. 1, exp. no. A50/01). In a second series (Tab. 1, exp. no. A-50/02), boiling diphenyl ether (260 °C) was used as an inert reaction medium<sup>18, 19</sup>. The reaction products were extracted with methylene chloride, in which PC is completely soluble, whereas PPVL was found to be insoluble in this solvent. The soluble fractions were analyzed by <sup>1</sup>H NMR and FT-IR spectroscopy. It appeared, according to the <sup>1</sup>H NMR spectra, that the soluble products contained significant amounts of PVL units, which strongly indicated that interchange reaction had taken place between PPVL and PC (Fig. 1).

Without TnBT as a transesterification catalyst, no interchange was observed. Similar results with respect to the use of a titanium catalyst have been observed in poly(ethylene terephthalate) (PET)/PC blends<sup>4, 5, 20</sup> and poly(butylene terephthalate) (PBT)/PC blends<sup>21, 22</sup>. The results of the <sup>1</sup>H NMR spectra were confirmed for both series by

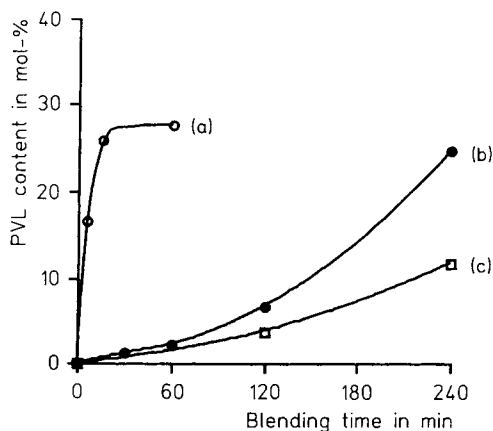
Tab. 1. Heating of PPVL/PC blends using various blending processes

Exp. No.	PPVL/PC		Catalyst <sup>a)</sup>	$t$ min	Blending <sup>b)</sup>
	(mol/mol)	(wt./wt.)			
A-50/01	50/50	28/72	TnBT	0–240	St
A-50/02	50/50	28/72	TnBT	0–240	SSt
B-50/01	50/50	28/72	—	0–30	TSE
B-50/02	50/50	28/72	TnBT	0–60	TSE
A-xx/01	80/20–20/80	61/39–9/91	TnBT	240	S
B-xx/01	60/40–20/80	37/63–9/91	TnBT	15	TSE

a) TnBT = tetrabutyl orthotitanate (0,5 wt.-%).

b) St = heating at 280 °C with stirring; SSt = heating in boiling diphenyl ether at 260 °C with stirring; TSE = heating in a twin screw extruder; S = heating in boiling diphenyl ether at 260 °C.

Fig. 1. The amount of PVL units in the soluble fractions of reaction products after methylene chloride extraction of PPVL/PC blends after heating vs. reaction time; (a) in a TSE with TnBT, (b) in diphenyl ether with TnBT and (c) in the melt with TnBT



data from FT-IR. As shown in Fig. 2 for the second series, absorptions from C=O groups of pivalolactone (PVL) units at  $1730\text{ cm}^{-1}$  as well as from C=O in PC at  $1780\text{ cm}^{-1}$  were present in the soluble fractions. Besides, an increase of the ester band with respect to the carbonate band with reaction time was observed. In addition, the C=O absorption from PC progressively appeared in the insoluble fractions. Furthermore, it was observed that the amount of soluble material increased steadily with reaction time. In the FT-IR spectra of these PPVL/PC blends no new infrared absorptions were observed, e.g., at  $1740\text{ cm}^{-1}$  corresponding with mixed aliphatic-aromatic structures<sup>11)</sup>, thus indicating that extensive randomization had not occurred. The lack of randomization in these blends illustrates the relatively high chemical stability of PPVL towards interchange reactions<sup>10)</sup>, for melt-blending of PBT/PC blends at  $253\text{ °C}$  resulted in random copolymers after 200 min<sup>23)</sup>.

The results from the extraction experiments showed that interchange occurred to a larger extent in diphenyl ether at  $260\text{ °C}$  than by heating in the melt at  $280\text{ °C}$  (curves

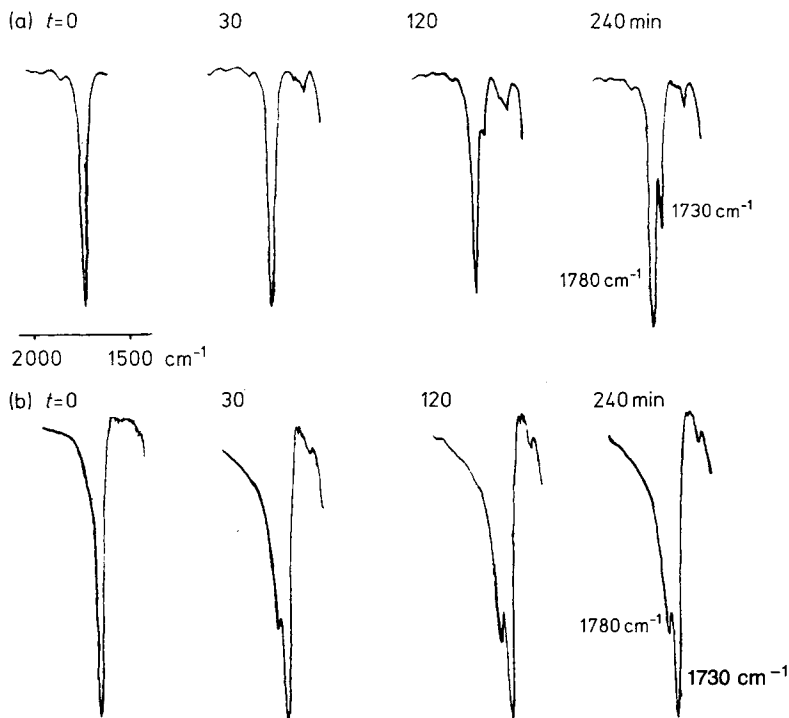


Fig. 2. C=O bands of methylene chloride-extracted PPVL/PC blends after heating in diphenyl ether (Tab. 1, exp. no. A-50/02) for (a) soluble and (b) insoluble fractions; characteristic absorptions: PPVL,  $1730 \text{ cm}^{-1}$  (s, C=O); PC,  $1780 \text{ cm}^{-1}$  (s; C=O)

(b) and (c) in Fig. 1), which may be explained by a more efficient mixing of PPVL with PC due to the presence of diphenyl ether<sup>18,19</sup>. However, relatively long reaction times (up to 240 min) were needed and also extensive washing was necessary to remove diphenyl ether from the reaction products.

Therefore, reactive blending of PPVL with PC was performed at  $280^\circ\text{C}$  in a twin-screw extruder (TSE). In general, the use of a TSE results in more interchange reactions than with a single-screw extruder, because of a larger interfacial area accessible for these reactions. In this study, blending was performed in a small-scale TSE provided with a heated channel through which the polymer blend could be fed back. Thus, the residence time of the blend in the extruder could be regulated without adjusting the screw speed.

The effect of blending time and of the addition of a catalyst (i. e.,  $\text{InBT}$ ) was evaluated using equimolar PPVL/PC blends. From analysis of the methylene chloride extracts of the reaction products it was shown that the soluble fractions of blends prepared without a catalyst (Tab. 1, exp. no. B-50/01) contained hardly any PVL units, i. e., 3 mol-% after 30 min blending. On the other hand, the amount of PVL units in

the soluble fractions of blends heated in the presence of TnBT (Tab. 1, exp. no B-50/02) increased rapidly with reaction time, and after 15 min blending this amount remained at a constant level of about 25–30 mol-% (curve (a) in Fig. 1). Furthermore, the amount of soluble material increased relatively fast from 72 wt.-% to 83 wt.-% after 60 min of heating in a TSE. By comparing the various blending processes (curves (a), (b) and (c) in Fig. 1), it is clear that heating in a TSE was the most efficient process with respect to the rate of interchange reactions, which is most likely due to a very efficient mixing of PPVL with PC in a TSE.

From the FT-IR spectra it was observed that the same structural changes had occurred as shown before for the blending in diphenyl ether, i.e., PVL units were present in the soluble fractions and PC blocks appeared in the insoluble fractions. Besides, the original ester carbonyl band of PPVL at  $1730\text{ cm}^{-1}$  was slightly shifted to  $1735\text{ cm}^{-1}$  in the soluble fractions. Although this shift was only small, it was found in all samples concerned. An explanation for this shift may be the occurrence of randomization during melt-blending, resulting in less blocky copolymers. It was shown earlier that during melt-blending of PPVL, PC and dimethyl terephthalate, resulting in the formation of random copolymers, this band shifted from  $1730$  to  $1740\text{ cm}^{-1}$  (11).

As shown above, interchange reactions occurred during heating of PPVL/PC blends in the melt. These reactions might have an effect on the properties, because the blends have been partially converted into copolymers. The (block) copolymers formed might act as compatibilizers, thus improving the compatibility of PPVL with PC. Therefore, additional experiments were conducted with various blend compositions in diphenyl ether (Tab. 1, exp. no. A-xx/01) and in a TSE (Tab. 1, exp. no. B-xx/01). The thermal properties of the reaction products were investigated in order to determine whether the compatibility of PPVL with PC was improved by the occurrence of interchange reactions.

#### *Glass temperatures of PPVL/PC blends before and after reactive blending*

The miscibility of PPVL/PC blends with various compositions was studied by DSC. In order to investigate the phase behaviour of physical PPVL/PC blends, i.e., in which no interchange had taken place, attempts were made to prepare films of these blends by solution-casting. However, films thus prepared were rather heterogeneous with respect to composition, possibly caused by the larger affinity of one of the polymers for the solvents used, i.e., the so-called  $\Delta\chi$  effect<sup>24</sup>). Therefore, physical PPVL/PC blends were studied by mixing PPVL and PC in various amounts and weighing these into DSC pans. Next, in the first DSC heating run the blend was heated to  $280\text{ }^\circ\text{C}$  during which the sample melted followed by a cooling and a second heating run; thermal transitions were determined from the later two curves. In this way long residence times in the melt were avoided, thus minimizing the occurrence of interchange reactions.

In Fig. 3 thermal transitions of the physical PPVL/PC blends are plotted. Several authors proposed that PPVL showed a glass temperature  $T_g$  at about  $-10\text{ }^\circ\text{C}$ <sup>25,26</sup>) or close to  $6\text{ }^\circ\text{C}$ <sup>27</sup>). This transition was also ascribed to a  $\gamma$ -relaxation process<sup>28,29</sup>), whereas  $T_g$  was determined at about  $100\text{ }^\circ\text{C}$  using dielectric relaxation measurements<sup>28–30</sup>). No transition corresponding with a  $T_g$  of PPVL in physical PPVL/PC

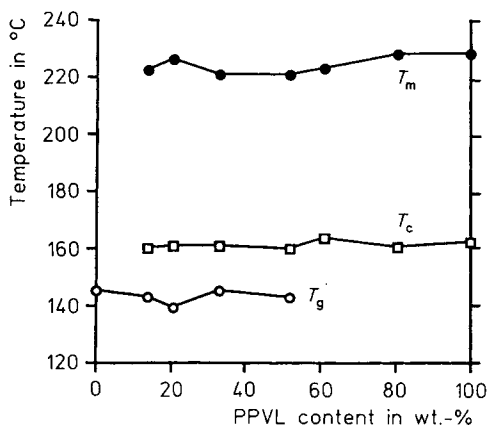


Fig. 3. Thermal properties of physical PPVL/PC blends

blends by DSC was detected, which was most likely due to the high degree of crystallinity and the rapid crystallization of PPVL, as has been reported by Cruz et al.<sup>13</sup>). As shown in Fig. 3, the physical blends of PPVL and PC showed one  $T_g$  for blend compositions of 0–50 wt.-% PPVL close to the  $T_g$  for PC ( $T_g = 145^\circ\text{C}$ ), thus indicating that PPVL and PC were immiscible.

In order to investigate whether the immiscibility of PPVL/PC blends was affected by the occurrence of interchange reactions, the thermal properties of equimolar PPVL/PC blends after reactive blending were determined. Fig. 4 shows the glass temperature  $T_g$  of the blends versus the reaction time.  $T_g$  decreased rapidly when the blending was performed in a TSE at  $280^\circ\text{C}$  in the presence of ThBT (Fig. 4, exp. no. B-50/02), resulting in a  $T_g$  of  $121^\circ\text{C}$  after 60 min heating. By blending in the melt at  $280^\circ\text{C}$  with ThBT,  $T_g$  decreased less rapidly (Fig. 4, exp. no. A-50/01), whereas by blending in a TSE without ThBT no depression of  $T_g$  was observed (Fig. 4, exp. no. B-50/01). Obviously, the occurrence of interchange reactions, as indicated by the results shown in Fig. 1, had a positive effect on the miscibility of PPVL/PC blends.

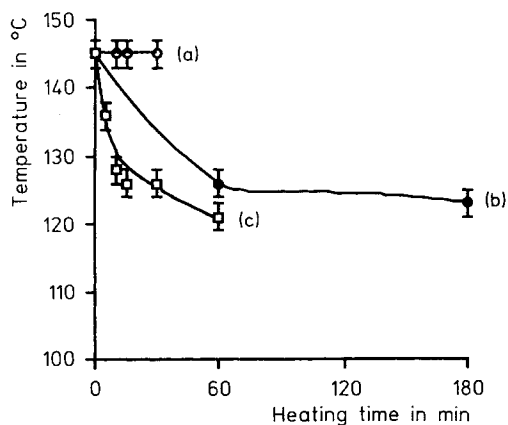


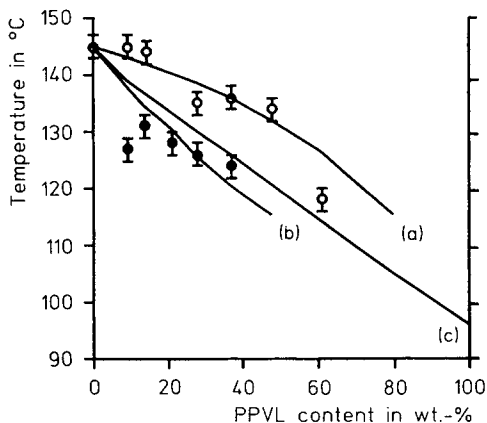
Fig. 4. Glass temperatures  $T_g$  of equimolar PPVL/PC blends after heating vs. reaction time; (a) in a TSE without ThBT, (b) in the melt with ThBT and (c) in a TSE with ThBT



Since blending of PPVL and PC in the presence of TnBT in diphenyl ether at 260 °C and in a TSE at 280 °C seemed to be an effective way to induce interchange reactions, thus resulting in an improved miscibility, blends of various compositions were studied after heating in diphenyl ether and in a TSE (Tab. 1, exp. nos. A-xx/01 and B-xx/01).

With respect to the glass temperatures of the reaction products, it appeared that the  $T_g$ 's for both series show a pattern quite different from the physical blends (Fig. 5, vs. Fig. 3). Only one  $T_g$  was observed and it is clear from Fig. 5 that the glass temperatures were not only significantly lower than the  $T_g$  for pure PC, but also

Fig. 5. Glass temperature  $T_g$  of PPVL/PC blends after heating vs. the amount of PPVL in the blends; (a) in diphenyl ether with TnBT, (b) in a TSE with TnBT, according to Eqs. (2) and (3); (c) according to Eqs. (2) and (3) for a miscible blend with  $k^* = 1$



showed a dependence on the PPVL content in the blend. Evidently, both blending in diphenyl ether at 260 °C and in a TSE at 280 °C resulted in more miscible blends. There are several equations known relating  $T_g$  to blend composition<sup>31-33</sup>. The  $T_g$  can be expressed by an equation derived by Utracki et al.<sup>33</sup>:

$$(\ln T_g)/T_g = \sum_i (w_i \cdot \ln T_{gi})/T_{gi} \quad (1)$$

in which  $w_i$  and  $T_{gi}$  represent the weight fraction and the glass temperature of component  $i$ , respectively. For two-component blends showing limited miscibility, an empirical parameter  $k$  was introduced:

$$w_1 \cdot \ln(T_g/T_{g1}) + k \cdot w_2 \cdot \ln(T_g/T_{g2}) = 0 \quad (2)$$

It should be noted that, since assignment of the subscript  $i$  is arbitrary, each value of  $k$  can be replicated in

$$k^* \equiv 1/k \quad (3)$$

For values of  $k^*$  much smaller than 1, blends are immiscible, whereas for values of  $k^*$  close to 1, blends are miscible. In Tab. 2 the values of  $k^*$  are presented for physical blends and for blends after heating in diphenyl ether (Tab. 1, exp. no. A-xx/01) and in

Tab. 2. Values of  $k^*$  for the Utracki equations (2) and (3) for PPVL/PC blends

PPVL content in wt.-%	Physical blends		Heated blends			
	$T_g$ °C	$k^*$	diphenyl ether <sup>a)</sup>		TSE <sup>b)</sup>	
			$T_g$ °C	$k^*$	$T_g$ °C	$k^*$
0	145	—	145	—	145	—
9	—	—	145	0	127	0,18
14	143	0,25	144	0,20	131	0,45
20	139	0,09	—	—	128	0,53
28	—	—	135	0,62	126	0,66
33	145	0	—	—	—	—
37	—	—	134	0,36	124	0,84
48	—	—	134	0,30	—	—
52	143	0,04	—	—	—	—
61	—	—	118	0,73	—	—

<sup>a)</sup> Tab. 1, exp. no. A-xx/01.

<sup>b)</sup> Tab. 1, exp. no. B-xx/01.

a TSE (Tab. 1, exp. no. B-xx/01). From this table it can be seen that, by heating in diphenyl ether,  $k^*$  values were obtained higher than those for the corresponding physical blends. Furthermore, heating in a TSE resulted in  $k^*$  values approaching 1, in particular with increasing amounts of PPVL in the blends, thus indicating the formation of more miscible blends.

#### *Melting and crystallization of PPVL/PC blends before and after reactive blending*

The  $T_m$  of PPVL, as determined by DSC, was 228 °C. As shown in Fig. 3, only small melting point depressions were observed for physical PPVL/PC blends, also indicating that these blends were immiscible. The exact determination of  $T_m$  appeared difficult for several samples due to the occurrence of double melting endotherms. This was probably caused by the presence of two crystalline forms of PPVL in the samples, as previously reported for PPVL<sup>27)</sup>. Furthermore, it appeared that a strong widening of the melting endotherm occurred already with blends containing small amounts of PPVL. In a typical DSC run PPVL started to melt at 213 °C and at 235 °C the melting was complete, whereas for a physical blend containing e. g. 33,2 wt.-% PPVL a melting traject of 190–239 °C was observed. On cooling, all blends exhibited an exothermic peak ( $T_c$ ) due to PPVL crystallization, and the crystallization enthalpies were as large as the melting enthalpies.

All blends obtained after heating showed evidence of melting of PPVL. The degree of miscibility of blends in which one component is semi-crystalline (PPVL) and the other amorphous (PC) can be determined by measurement of the melting point depression<sup>34)</sup>. The melting temperature, i. e., the peak of the melting endotherm, of PPVL/PC blends after blending in diphenyl ether in the presence of TnBT (Tab. 1 exp.

no. A-xx/01) is shown in Fig. 6 as a function of the amount of PPVL in the blends. All blends obtained demonstrated broad melting transitions as was observed for the physical PPVL/PC blends. Addition of PC decreased  $T_m$ , until at 70 wt.-% PC this reduction was about 10°C. Further addition resulted in blends with melting temperature close to that of pure PPVL, as shown in Fig. 6. Similar results were found for PPVL/PC blends after heating in a TSE, and, although some melting point depression was observed, the trend was even less clear than the one presented in Fig. 6. Thus, based on melting point depression data no conclusions concerning blend miscibility could be made.

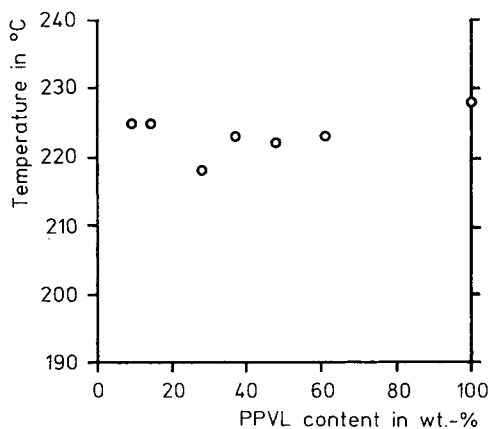


Fig. 6. Melting temperature  $T_m$  of heated PPVL/PC blends vs. the amount of PPVL in the blends (after blending in diphenyl ether (Tab. 1, exp. no. A-xx/01))

Fig. 7 shows that the melting enthalpy  $\Delta H_m$  of physical PPVL/PC blends, as determined by DSC, was a linear function of the amount of PPVL in the blend. This observation was in agreement with what would be expected for an immiscible system containing a separate crystalline PPVL phase, thus confirming the results from the  $T_g$  determinations. In Fig. 7 also the enthalpies of melting  $\Delta H_m$  are shown as a function

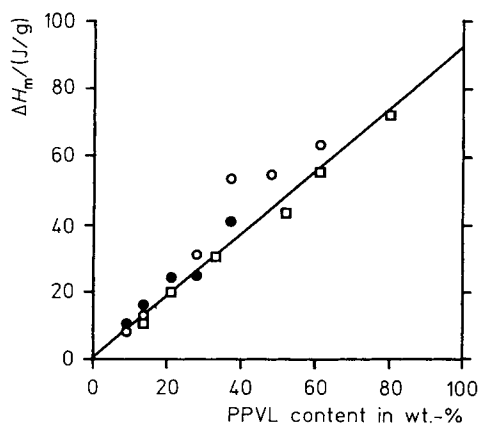


Fig. 7. Melting enthalpy  $\Delta H_m$  vs. the amount of PPVL in the blends; (○) after heating in diphenyl ether, (●) after heating in a TSE and (□) physical blends

of blend composition after heating in diphenyl ether (Tab. 1, exp. no. A-xx/01) and in a TSE (Tab. 1, exp. no. B-xx/01). The values of  $\Delta H_m$  for these blends deviated only to some extent from the straight line, suggesting that, although interchange reactions have occurred between PPVL and PC, no significant reduction in the degree of crystallinity had taken place.

Upon cooling all blends with various compositions obtained after heating in diphenyl ether (Tab. 1, exp. no. A-xx/01) showed crystallization exotherms, and up to 70 wt.-% PC addition these PPVL/PC blends showed crystallization in a temperature range close to that of pure PPVL. The blends with higher amounts of PC crystallized more slowly, resulting in multiple exotherms in the cooling curves. This would indicate that PPVL crystallization in these blends is seriously affected by the presence of PC. Although delay in crystallization occurred in some blends, no crystallization was observed on heating after cooling, thus preventing effects on the  $T_g$ 's measured.

Upon cooling after the first DSC heating run the blends with various compositions obtained after heating in a TSE (Tab. 1, exp. no. B-xx/01) showed multiple crystallization exotherms. The three blends with the highest amounts of PC (>80 wt.-%) appeared to have two  $T_c$ 's at  $T_{c,II} \approx 1100$  and  $T_{c,III} \approx 65^\circ\text{C}$ , whereas the blends with lower amounts of PC showed an additional peak at  $T_{c,I} \approx 160^\circ\text{C}$  (see Fig. 8(a)). Since the methylene chloride-soluble fractions of the latter blends showed only one  $T_c$ , i. e., at about  $160^\circ\text{C}$  (see Fig. 8(b)) it was assumed that exotherm I corresponded to (block) copolymers of PPVL and PC. Both other exotherms may be considered coming from crystallization of PPVL in the presence of PC, which can have a retarding effect on the crystallization process. Thus, exotherm II was assumed to represent PPVL crystallizing from a PC-poor phase, whereas exotherm III may be assigned coming from PPVL crystallizing from a PC-rich phase. Similar results have been reported on other systems, e. g., with PBT/PC blends<sup>35</sup>).

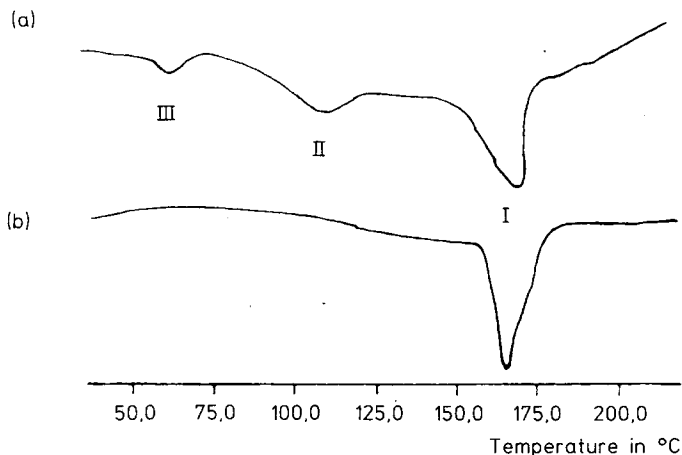


Fig. 8. Cooling curves of (a) a PPVL/PC blend after 15 min heating in a TSE at  $280^\circ\text{C}$  and of (b) the methylene chloride-soluble fraction of this reaction product

### *Blends of PPVL with other polyesters*

In addition, blends of PPVL with two other polyesters, i. e., with polyarylate (PAr) and with PBT, were also studied. PAr, soluble in methylene chloride, showed a  $T_g$  of 197 °C, which was close to the value of 194 °C reported in literature<sup>17)</sup>. Physical blends of PPVL and PAr showed  $T_g$ 's near 200 °C, no  $T_m$  depression and values for  $\Delta H_m$  near to the straight line connecting the extreme points. These results suggest that physical PPVL/PAr blends were immiscible.

Melt-blending of equimolar amounts of PPVL and PAr in the presence of TnBT was carried out in diphenyl ether at 260 °C and in a TSE at 280 °C. The amounts of PPVL units in the soluble fractions (in methylene chloride) of reaction products obtained after blending in diphenyl ether appeared to be very small (less than 0,5 mol-% after 180 min blending). Furthermore, no depression of  $T_m$ ,  $T_g$  nor  $T_c$  was observed. Blending in a TSE was more effective with respect to interchange reactions, for the soluble fraction in the reaction product obtained after 15 min blending in a TSE in the presence of TnBT contained 5 mol-% PVL units. Moreover, this blend appeared to have a  $T_g$  of 159 °C, whereas 30 min blending without TnBT in a TSE resulted in a blend with a  $T_g$  of 186 °C. The effect of TnBT on the blending process was also demonstrated by the appearance of the blends, for without catalyst the resulting products were extremely brittle, while with TnBT the products were less brittle. All blends obtained after melt-blending in a TSE showed evidence of PPVL melting and, upon cooling, crystallization. No  $T_m$  depression nor the occurrence of multiple crystallization exotherms was observed.

These results show that the degree of occurrence of interchange reactions between PPVL and PAr was much lower than for PPVL/PC blends. It has been reported that interchange reactions took place during melt-blending of PAr with PBT<sup>36)</sup>. However, only after reaction times > 100 min at 250 °C changes in the thermal properties were observed, indicating the occurrence of interchange reactions. Unlike PPVL/PAr and PBT/PAr blends, interchange reactions in PET/PAr blends have been reported to occur rapidly by melt-blending at 280 °C, resulting in a randomization of the block copolymers initially formed after 10 min<sup>37)</sup>.

Melt-blending of PPVL with PBT was carried out in diphenyl ether at 260 °C and in a TSE at 280 °C. In most experiments TnBT was added, but it should be noted that the PBT may have contained traces of titanium catalyst, which had been used for the synthesis of PBT. Both PPVL and PBT are not soluble in most common solvents, and therefore extraction procedures with the reaction products after blending proved not to be successful.

All blends prepared showed at least two melting peaks coming from PBT ( $T_m \approx 218$  °C) and from PPVL ( $T_m \approx 228$  °C). The blends obtained after blending in diphenyl ether at 260 °C showed upon cooling two crystallization exotherms at  $\approx 185$  °C and  $\approx 170$  °C, which were assigned to PBT and PPVL crystallization, respectively. A weak third exotherm between 140 and 160 °C was found for reaction products obtained after blending in a TSE, which may be assigned to interchange products. Although several of the latter products showed some indication of a  $T_g$  at  $\approx 80$  °C, i. e., between the  $T_g$  of PBT ( $T_g = 43$  °C) and of PPVL ( $T_g \approx 100$  °C), results

from DSC were sometimes erratic with respect to glass temperatures, which may be explained by the relatively high degree of crystallinity in the blends.

Due to the considerations mentioned above, no conclusions could be drawn whether interchange reactions had occurred to a significant extent during melt-blending of PPVL with PBT. Therefore, less common techniques, i. e., for demonstrating whether interchange reactions take place, were used to determine whether interchange reactions had occurred in PPVL/PBT blends. Recently, thermogravimetry (TG) was used to show that interchange reactions had taken place in PET/PC blends<sup>38)</sup> and in PBT/PC blends<sup>39)</sup>. The onset of thermal degradation in the latter blends appeared at lower temperatures than for the individual components, which was assumed to indicate that interchange reactions resulted in less stable products<sup>39)</sup>. The TG curves presented in Fig. 9(a) show that an equimolar PPVL/PC blend, obtained after heating in a TSE for

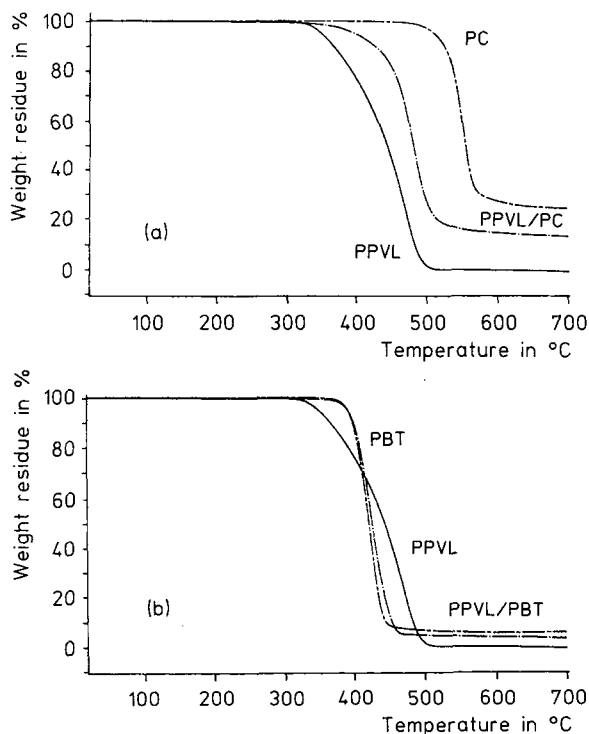


Fig. 9. TG curves of (a) PPVL, PC, and an equimolar PPVL/PC blend after reactive blending in a TSE and of (b) PPVL, PBT and an equimolar PPVL/PBT blend after reactive blending in a TSE

15 min, started to decompose at a temperature between those of the individual components, which has also been observed in PET/PC blends after reactive blending<sup>38)</sup>. The intermediate behaviour of PPVL/PC blends obtained after reactive blending may be considered indicative for the occurrence of interchange reactions. From the TG curves presented in Fig. 9(b) it appeared that, with respect to thermal degradation, an equimolar PPVL/PBT blend showed a comparable behaviour, which may indicate the occurrence of interchange reactions.

## Conclusions

The immiscibility of physical PPVL/PC blends was demonstrated by the absence of a melting point depression, because one  $T_g$  close to the  $T_g$  of PC was observed and because  $\Delta H_m$  was a linear function of the amount of PPVL in the blend. The fact that no  $T_g$  corresponding with a transition in PPVL was observed by DSC was attributed to the high degree of crystallinity of PPVL.

In order to study the extent of interchange reactions in PPVL/PC blends, mixtures of PPVL and PC were blended in the melt under various conditions. In general, it was found that without a catalyst added, no interchange was detected. Both heating in the melt at 280 °C and in diphenyl ether at 260 °C resulted in the partial formation of PPVL/PC copolymers containing significant amounts of PVL units (12 and 25 mol-% after 240 min, respectively), provided that TnBT was present during blending. Although only one  $T_g$  was observed for these blends, the value was clearly lower than the  $T_g$  for PC and depended on the composition of the blend. Based on the small melting point depression, the crystallization behaviour and the results from FT-IR, it was concluded that the extent of interchange reactions was not very great and no randomized copolymers were formed.

In order to improve the mixing during blending, equimolar PPVL/PC blends were heated in a TSE. Copolymers could be isolated without TnBT, containing 3 mol-% PVL units after 30 min blending, whereas this value was 25 mol-% after 15 min blending in the presence of TnBT. Based on the occurrence of multiple crystallization exotherms and the results from FT-IR, the conclusion was drawn that blending in a TSE was more efficient with respect to the occurrence of interchange reactions. Again the small melting point depression indicated that complete randomization had not occurred.

Melt-blending of PPVL with other polyesters, i. e., with PAr and PBT, was studied by blending in diphenyl ether and in a TSE. Although small amounts of PVL units were present in the PPVL/PAr copolymers isolated, no melting point depression nor the occurrence of multiple crystallization exotherms was observed. These results suggested that the degree of interchange reactions between PPVL and PAr was much lower than for PPVL/PC blends. The only indication for the occurrence of interchange reactions in PPVL/PBT blends after blending in a TSE in the presence of TnBT may be deduced from the results from TG. These blends showed the same decomposition behaviour as PPVL/PC blends, i. e., decomposition started at a temperature between those of the individual components.

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<sup>1)</sup> S. B. Brown, "Reactive Extrusion: A Survey of Chemical Reactions of Monomers and Polymers during Extrusion Processing", in: "Reactive Extrusion, Principles and Practice", M. Xanthos, Ed., Hanser Publishers, Munich 1992, p. 79

- 2) S. B. Brown, "Reactive Extrusion: A Survey of Chemical Reactions of Monomers and Polymers during Extrusion Processing", in: "Reactive Extrusion, Principles and Practice", M. Xanthos, Ed., Hanser Publishers, Munich 1992, p. 126
- 3) R. S. Porter, L.-H. Wang, *Polymer* **33**, 2019 (1992)
- 4) F. Pilati, E. Marianucci, C. Berti, *J. Appl. Polym. Sci.* **30**, 1267 (1985)
- 5) P. Godard, J. M. Dekoninck, V. Devlesaver, J. Devaux, *J. Polym. Sci., Part A: Polym. Chem.* **24**, 3315 (1986)
- 6) C. Berti, V. Bonora, F. Pilati, M. Fiorini, *Makromol. Chem.* **193**, 1665 (1992)
- 7) F. L. Hamb, *J. Polym. Sci., Polym. Chem. Ed.* **10**, 3217 (1972)
- 8) W. J. Jackson, Jr., H. F. Kuhfuss, *J. Polym. Sci., Polym. Chem. Ed.* **14**, 2043 (1976)
- 9) M. S. Chen, C. Lee, N. H. Chang, B. C. Chang, H. B. Tsai, *Polymer* **30**, 1472 (1989)
- 10) E. J. Tijsma, L. van der Does, A. Bantjes, I. Vulić, *Makromol. Chem.* **194**, 305 (1993)
- 11) E. J. Tijsma, L. van der Does, A. Bantjes, I. Vulić, G. H. Werumeus Buning, *Makromol. Chem.* **194**, 2807 (1993)
- 12) C. A. Cruz, J. W. Barlow, D. R. Paul, *Macromolecules* **12**, 726 (1979)
- 13) C. A. Cruz, J. W. Barlow, D. R. Paul, *J. Appl. Polym. Sci.* **24**, 2399 (1979)
- 14) M. Aubin, R. E. Prud'homme, *Macromolecules* **13**, 365 (1980)
- 15) US Pat. 4,201,703 (1980), Ethyl Corporation, invs.: P. A. Zorzi, J. D. Jones, M. E. Kucsma; *Chem. Abstr.* **93**, 73053 z (1980)
- 16) J. E. Harris, S. H. Goh, D. R. Paul, J. W. Barlow, *J. Appl. Polym. Sci.* **27**, 839 (1982)
- 17) W. M. Eareckson III, *J. Polym. Sci.* **40**, 399 (1959)
- 18) R. W. Stackman, *Ind. Eng. Chem. Prod. Res. Dev.* **20**, 336 (1981)
- 19) R. W. Stackman, *J. Macromol. Sci., Chem.* **A25**, 65 (1988)
- 20) T. R. Nassar, D. R. Paul, J. W. Barlow, *J. Appl. Polym. Sci.* **23**, 85 (1979)
- 21) J. Devaux, P. Godard, J. P. Mercier, *Polym. Eng. Sci.* **22**, 229 (1982)
- 22) J. Devaux, P. Godard, J. P. Mercier, *J. Polym. Sci., Polym. Phys. Ed.* **20**, 1901 (1982)
- 23) J. Devaux, P. Godard, J. P. Mercier, *J. Polym. Sci., Polym. Phys. Ed.* **20**, 1881 (1982)
- 24) A. Robard, D. Patterson, G. Delmas, *Macromolecules* **10**, 706 (1977)
- 25) H. A. Oosterhof, *Polymer* **15**, 49 (1974)
- 26) J. Grebowicz, M. Varma-Nair, B. Wunderlich, *Polym. Adv. Technol.* **3**, 51 (1992)
- 27) C. W. Paul, *J. Appl. Polym. Sci.* **36**, 675 (1988)
- 28) T. M. Malik, R. E. Prud'homme, *J. Macromol. Sci., Phys.* **B23**, 323 (1984)
- 29) R. Plesu, T. M. Malik, R. E. Prud'homme, *Polymer* **33**, 4463 (1992)
- 30) J. Noah, R. E. Prud'homme, *Macromolecules* **12**, 300 (1979)
- 31) T. G. Fox, *Bull. Am. Phys. Soc.* **1**, 123 (1956)
- 32) L. A. Wood, *J. Polym. Sci.* **28**, 318 (1958)
- 33) L. A. Utracki, J. A. Jukes, *J. Vinyl Technol.* **6**, 85 (1984)
- 34) T. Nishi, T. T. Wang, *Macromolecules* **8**, 909 (1975)
- 35) D. C. Währmund, D. R. Paul, J. W. Barlow, *J. Appl. Polym. Sci.* **22**, 2155 (1978)
- 36) M. Kimura, R. S. Porter, *J. Polym. Sci., Polym. Chem. Ed.* **21**, 367 (1983)
- 37) M. Kimura, G. Salee, R. S. Porter, *J. Appl. Polym. Sci.* **29**, 1629 (1984)
- 38) C. Berti, V. Bonora, M. Fiorini, F. Pilati, *Makromol. Chem.* **193**, 1679 (1992)
- 39) G. Montaudo, C. Puglisi, F. Samperi, *J. Polym. Sci., Part A: Polym. Chem.* **31**, 13 (1993)