Pivalolactone, 1

Interchange reactions with polypivalolactone

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SUMMARY:

Ester interchange, alcoholysis, and acidolysis of polypivalolactone (PPVL) were studied by melting PPVL with bisphenol diacetates, 1,4-butanediol, or aromatic diacids. Interchange of PPVL with the diacetates and the diol occurred readily, in particular in the presence of a titanium catalyst. Melting PPVL with 10 mol-% of bisphenol-A diacetate in the presence of 0,5 wt.-% tetrabutylorthotitanate resulted in an incorporation of 33% of the diacetate in the polymer chains, whereas the logarithmic viscosity number decreased by 81%. The ester interchange was suggested to proceed by an initial cleavage of ester bonds in the polymer chain of PPVL, resulting in the formation of shorter chains, followed by a reaction between the newly formed ester end-groups and initially present hydroxyl chain ends. The acidolysis of PPVL with the diacids proved to be less effective; in the case of the acidolysis of PPVL with 10 mol-% isophthalic acid, less than 1% of the diacid was incorporated in the polymer chains and a decrease in the logarithmic viscosity number of only 22% was found. Both the high stability of the ester bond in PPVL towards acids in general and the heterogeneity of these systems were supposed to cause the behaviour of PPVL with respect to acidolysis. The results concerning the interchange reactions with PPVL were compared with studies on other polyesters.

Introduction

Interchange reactions involving condensation polymers are of significant industrial importance, since they are essential for the manufacture of many polyesters (e.g., poly(alkylene terephthalate)s), whereas they also occur in the preparation of block copolymers in melt-blending processes. The copolyesters formed by melt-blending of bisphenol-A polycarbonate and poly(alkylene terephthalate)s are typical examples of reaction products of interchange reactions during melt-blending^{1–3}. When it is possible to control the interchange reactions during melt-blending of two polymers, a wide variation in composition and microstructure can be realized directly within the processing equipment.

Interchange reactions which might occur with (poly)esters are shown in Scheme 1. Three types of interchange reactions involving polyesters can be distinguished, in which either ester groups in the polymer chain or end-groups react^{4,5}. It was shown already by Flory that alcoholysis occurs by the reaction of a diol with a linear polyester of 1,10-decanediol and adipic acid⁶. The exchange reaction between carboxyl and ester

groups (acidolysis) was first described by Korshak et al. based on the reaction of poly(ethylene adipate) and adipic acid⁷. It was found that the rate of acidolysis is generally much lower as compared to the rate of alcoholysis⁸.

1. Alcoholysis

2. Acidolysis

3. Ester interchange

Scheme 1. Interchange reactions with (poly)esters

Ester interchange, double ester interchange, or esterolysis is the third type of interchange reactions, indicating reaction between two ester groups. Although Flory has described ester interchange with polyesters as being very slow, or not occurring at all⁸, it was shown by a study involving the reaction between poly(ethylene terephthalate) (PETP) and a bisphenol diacetate that esterolysis occurs readily⁹. Difficulties in separating the contribution of ester interchange from the other two types of interchange reactions made its study sometimes problematic. Some authors claimed the occurrence of ester interchange with ester groups in the polymer chain without considering the possibility of interchange reactions with hydroxyl and carboxyl end-groups of the polymer^{10, 11}. Reaction products could thus also have been formed from consecutive alcoholysis and acidolysis involving these end-groups. Ester interchange was also investigated by Ramjit, who postulated an "associative reaction mechanism" for the ester interchange reactions in polyesters of adipic acid and linear and branched glycols (Scheme 2)¹².

Although ester interchange has not found any practical application in the preparation of polyesters, it plays an important role during the melt-blending of polyesters. On mixing bisphenol-A polycarbonate and poly(butylene terephthalate) (PBT) in the melt, copolymers were formed, and an ester interchange reaction catalyzed by titanium residues present in commercial PBT was suggested to explain the formation of these copolymers¹³. The same reaction was assumed to be the main source of randomization during melt-blending of PETP and bisphenol-A polycarbonate in the

Scheme 2. "Associative reaction mechanism" for the ester interchange of polyesters¹²⁾

presence of titanium alkoxides^{2,3)}. Ester interchange was also reported in analogous systems, such as PBT with a copolyester of bisphenol-A with 50% terephthalate/50% isophthalate¹⁴⁾.

Interchange reactions between polymers and monomeric compounds were studied by Hamb, who developed a process for the preparation of copolyesters of glycols and bisphenols, employing a preformed polyester, a diacid, and a bisphenol diacetate^{9,15)}. Based on this study, copolymers with interesting properties (i.e., liquid-crystalline behaviour) were prepared by melting a preformed polyester with an acetoxycarboxylic acid¹⁶⁻¹⁸⁾. It was reported by Riecke et al. that the reaction between poly(ethylene 2-methylisophthalate), 2-methylisophthalic acid, and bisphenol-A diacetate proceeded through acidolysis of the polyester by the diacid, whereas ester interchange occurred only to a small degree¹⁹⁾. This result is in contrast with that obtained for the system consisting of PETP, terephthalic acid, and bisphenol-A diacetate, in which both ester interchange and acidolysis were reported to be of importance⁹⁾. Recently a process was developed for the synthesis of aromatic polyesters based on bisphenol-A polycarbonate and esters of phthalic acids, which was suggested to proceed by interchange reactions between carbonate and ester groups²⁰⁾.

The aim of our work is to develop copolymers containing the pivalolactone unit. As part of this study, we were interested in interchange reactions with polypivalolactone (PPVL). Since the pivalolactone unit does not have hydrogen atoms at the α -position with respect to the carboxyl group, PPVL shows a high thermal and hydrolytic stability. PPVL is a highly crystalline polyester with a melting temperature of about 230 °C. Because of the fact that its mechanical properties are comparable with those of polymers such as PETP and nylon-6, PPVL was long considered as a potential engineering plastic. PPVL was reported to have a higher resistance towards chemical attack as compared to the resistance of PETP and nylon-6, especially with respect to acid and alkali²¹⁻²³⁾. As far as interchange reactions are concerned, only melt-blending of PPVL with bisphenol-A polycarbonate has been studied, but no inter-

change reactions could be detected, which was attributed to the fact that the two polymers are immiscible²⁴).

PPVL

BPac

BPAac

This paper deals with interchange reactions between PPVL and several monomeric compounds, especially diacetates, diols, and diacids, since these reactions may be the first step in a convenient route to make copolymers containing the pivalolactone unit. Next to ester interchange reactions of PPVL with two bisphenol diacetates (i.e., 4,4'-biphenyldiol diacetate (BPac) or bisphenol-A diacetate (BPAac)), also the alcoholysis of PPVL with 1,4-butanediol, and the acidolysis with two aromatic diacids (terephthalic or isophthalic acid) were investigated.

Experimental part

Materials

Pivalolactone was purified by distilling over calcium hydride, and was stored under nitrogen at -30°C . Both 4,4'-biphenyldiol diacetate (4,4'-biphenyldiol diacetate, BPac) and 4,4'-isopropylidenediphenyl diacetate (bisphenol-A diacetate, BPAac) were prepared by refluxing the corresponding phenols in acetic anhydride²⁵. 1,4-Butanediol, terephthalic acid and isophthalic acid (Merck) were used without further purification. Tetrabutyl orthotitanate (Merck), sodium pivalate (Aldrich), and zinc acetate (Merck), used as catalysts in the interchange reactions, were used as received. All solvents used were of analytical grade. Poly(ethylene terephthalate) used in this study was bought from Aldrich, and a 0,25 wt.-% solution in trifluoroacetic acid at 25°C had a logarithmic viscosity number of 0,70 dL/g.

Polypivalolactone

Distilled pivalolactone, 20,2 mL (0,2 mol), 200 mL of hexane, and tetrabutylammonium hydroxide (0,4 mmol; added as a 12,5 wt.-% solution in methanol from Merck) as an initiator, were added to a three-necked flask equipped with a mechanical stirrer and a reflux condensor, under a slow nitrogen purge. The solution was heated to reflux, and within 5 min a fine, white suspension of polypivalolactone (PPVL) started to appear. The suspension was filtered after refluxing for 2 h. The residue was washed thoroughly with hexane and dried overnight i. vac. at

60 °C. The yield of polymer in various runs always exceeded 90 wt.-%. The logarithmic viscosity numbers of 0,25 wt.-% solutions of the resulting PPVL in trifluoroacetic acid at 25 °C ranged from 0,55 to 0,64 dL/g. ¹H NMR (trifluoroacetic acid): δ = 1,35 (s; methyl) and δ = 4,35 (s; methylene). Intensity ratio: 3 : 1.

Interchange reactions with polypivalolactone and with poly(ethylene terephthalate)

A mixture of PPVL and either a diacetate, a diol, or a diacid, and a catalyst was 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. The stoichiometries used for ester interchange are given in Tab. 1, those for alcoholysis and acidolysis, in Fig. 6. In a typical procedure PPVL, 4,00 g (40 mmol), BPac, 1,08 g (4 mmol), and tetrabutyl orthotitanate (0,5 wt.-% with respect to PPVL) were placed in the reaction vessel. After the reaction vessel was evacuated and flushed with nitrogen three times to remove air, it was inserted into a Wood's metal bath kept at 250 °C. While the contents were stirred under a slow stream of dry nitrogen for at least 3 h, samples were removed at various times. These samples were ground, washed by stirring overnight in a solvent (acetone or ethyl alcohol) to remove non-reacted monomeric compounds, filtered, and finally dried overnight i. vac. at 60 °C.

Analogously, the ester interchange of PETP with bisphenol-A diacetate was studied.

Methods

Viscometric measurements were carried out with solutions of 0,025 g of polymer in 10 mL of trifluoroacetic acid (Janssen Chimica), using an Ubbelohde-type viscometer at 25 °C.

Compositions of the polymers were determined from the ¹H NMR spectra measured on a Bruker AC 250 F using deuterated trifluoroacetic acid (Aldrich) as a solvent; chemical shifts are in parts per million downfield from tetramethylsilane.

Results and discussion

Ester interchange of polypivalolactone

Interchange reactions might occur when PPVL is heated in the melt with suitable monomeric compounds, resulting in an incorporation of these compounds according to the reactions in Scheme 1. In addition, the molecular weight might decrease if ester groups in the polymer chain are involved. The ester interchange of PPVL with diacetates was studied with respect to the catalyst used, the amount of the catalyst, and the quantity of diacetate (10 or 20 mol.-% with respect to PPVL). The reactions with both 4,4'-biphenyldiol diacetate (BPac) and bisphenol-A diacetate (BPAac) were characterized by a decrease in the logarithmic viscosity number (LVN) until a constant value, LVN_{∞} , was reached after 180 min, while ¹H NMR measurements indicated the incorporation of the diacetates in the polymers. Both the decrease in the LVN, ΔLVN , defined as

$$\Delta LVN \text{ (in \%)} \equiv \{(LVN_0 - LVN_{\infty})/LVN_0\} \cdot 100$$

in which LVN_0 corresponds to the LVN of the starting polymer, and the conversion of diacetate are presented in Tab. 1. A higher value of ΔLVN was generally accompanied by a higher amount of incorporated diacetate.

The results presented in Tab. 1 indicate that ester interchange of PPVL with the diacetates did occur, although the ester bonds in PPVL show a high chemical

Tab. 1. Ester interchange of PPVL and of PETP with 4,4'-biphenyldiol diacetate (BPac) and with bisphenol-A diacetate (BPAac)

Exp. No.	Diacetate		Catalyst ^{a)}		Δ LVN ^{b)} in %	Conversion of diacetate ^{c)} in %
	type	content in mol-%	type	content in wt.-%		
1	None	—	None	—	0	—
2	BPac	10	None	—	22	< 1
3	BPac	10	Zn(OAc) ₂	0,5	32	< 1
4	BPac	10	Ti(Obu) ₄	0,5	76	25
5	BPac	10	NaPiv	0,5	68	18
6	BPac	10	Ti(Obu) ₄	5	81	26
7	BPAac	10	Ti(Obu) ₄	0,1	59	< 1
8	BPAac	10	Ti(Obu) ₄	0,5	81	33
9	BPAac	10	Ti(Obu) ₄	1,0	84	40
10	BPAac	20	Ti(Obu) ₄	0,5	79	34
11 ^{d)}	BPAac	10	Ti(Obu) ₄	0,5	77	60

a) Zn(OAc)₂ = zinc acetate; Ti(Obu)₄ = tetrabutyl orthotitanate; NaPiv = sodium pivalate (amount with respect to polymer).

b) Decrease in logarithmic viscosity number based on viscosity determinations in trifluoroacetic acid ($c = 2,5$ mg/mL) at 25 °C.

c) Determined by ¹H NMR.

d) Using PETP instead of PPVL.

resistance^{21–23}). Fig. 1 illustrates the effect of the used catalyst on the LVN vs. reaction time during the ester interchange of PPVL with BPac. It should be noted that heating of PPVL at 250 °C without diacetate (Tab. 1, exp. no. 1) did not result in any decrease of the LVN. After heating of PPVL with BPac without a catalyst, or using zinc acetate, a Δ LVN of 22% and 32% was observed, respectively. Although the corresponding ¹H NMR spectra showed some diacetate present in the polymer, the amount of incorporated diacetate appeared to be too small to be determined

Fig. 1. Logarithmic viscosity number (LVN) vs. reaction time for the ester interchange of PPVL with BPac (10 mol-%) using different catalysts (0,5 wt.-%); (a): exp. no. 2, no catalyst; (b): exp. no. 3; Zn(OAc)₂; (c): exp. no. 5, sodium pivalate; (d): exp. no. 4, Ti(Obu)₄

quantitatively from these spectra. On the other hand, the experiments with catalysts such as tetrabutyl orthotitanate and sodium pivalate indicated more pronounced the occurrence of ester interchange reactions. It was observed that tetrabutyl orthotitanate was the most powerful catalyst in terms of both the decrease in the LVN and the amount of BPac present in the polymer. This is in agreement with the fact that this catalyst was reported to accelerate significantly ester interchange reactions with other polyesters^{2, 3, 13}. When using tetrabutyl orthotitanate as a catalyst in the experiments with PPVL (and PETP), colouration took place from white to light-brown upon addition of the catalyst. This phenomenon is probably due to the semiconducting properties of the metal species²⁶. Although sodium salts are not generally known for their capacity as interchange catalysts²⁷, it has been reported that sodium pivalate is a good catalyst for the conversion of PPVL into its monomer²⁸.

It appeared from the experiments with the two diacetate types that the Δ LVN and the conversion of diacetate depended on the diacetate used, both values being always higher with BPAac than with BPac (Tab. 1). It was expected that the higher melting temperature of BPac as compared to that of BPAac (159 vs. 83 °C) would result in a higher rate of sublimation. During the reactions a rather high loss of BPac was observed due to this sublimation, thus contributing to lower amounts of BPac incorporated in the polymers.

The ester interchange depended upon the amount of catalyst, as shown by the data in Fig. 2, which were obtained by reacting PPVL with BPAac in the presence of different amounts of tetrabutyl orthotitanate as a catalyst. Increasing the amount of

Fig. 2. Logarithmic viscosity number (LVN) vs. reaction time for the ester interchange of PPVL with BPAac (10 mol.-%) using varying amounts of tetrabutyl orthotitanate as a catalyst;

(a): exp. no. 7, 0,1 wt.-%;
(b): exp. no. 8, 0,5 wt.-%;
(c): exp. no. 9, 1 wt.-%

catalyst from 0,1 to 0,5 wt.-% had an apparent effect, while in the presence of 1,0 wt.-% catalyst there was no significant difference when using 0,5 wt.-% tetrabutyl orthotitanate. A similar effect of the catalyst concentration was observed with BPac (Tab. 1, exp. nos. 4 and 6).

Reaction mechanism of the ester interchange

As indicated from the data shown in Tab. 1, BPAac was incorporated in PPVL and in PETP (exp. no. 11) by reaction in the molten state, in both cases showing a rapid

decrease in the LVN (Fig. 3). In the case of PETP, this decrease has been explained by ester interchange reactions giving shorter chains of PETP with equal amounts of isopropylidenediphenylene acetate and ethylene acetate end-groups (Scheme 3)⁹. Although Hamb reported that this mechanism was not generally accepted for polyesters, since hydroxyl (or carboxyl) chain ends were held responsible for ester interchange⁸, it appeared to be a suitable mechanism to explain his results.

Scheme 3. Mechanism for the interchange reaction of PETP with BPAac⁹

Fig. 3. Logarithmic viscosity number (LVN) vs. reaction time for the ester interchange of PPVL and PETP with diacetates (10 mol-%) using tetrabutyl orthotitanate (0.5 wt.-%) as a catalyst; (a): exp. no. 4, PPVL with BPac; (b): exp. no. 11, PETP with BPAac; (c): exp. no. 8, PPVL with BPAac

Typical ¹H NMR spectra of PPVL after reaction with BPAac are presented in Fig. 4. Apart from the peaks assigned to the polymeric backbone, i.e., at $\delta = 1.35$ (methyl) and at $\delta = 4.35$ (methylene), the ¹H NMR spectra showed a number of smaller peaks on positions in accordance with incorporated diacetate groups.

Ester interchange reactions with PPVL apparently resulted in the formation of shorter chains, as indicated by the decrease in the LVN, with both isopropylidenediphenylene acetate and 2,2-dimethylethylene acetate end-groups (as shown from the ¹H NMR spectra). During the early stages of the reaction (Fig. 4A) an equal number of both end-groups was present. In the course of time (Fig. 4B), however, the peak

Fig. 4. ^1H NMR spectra of PPVL after reaction with BPAac (Tab. 1, exp. no. 8). (A): after 30 min; (B): after 180 min

corresponding with the isopropylidenediphenylene acetate end-groups (4a in Fig. 4) vanished, while the peak assigned to the 2,2-dimethylethylene acetate end-groups (4 in Fig. 4) increased. This phenomenon was found in all the experiments and could not be explained by Hamb's mechanism for the ester interchange of PETP, suggesting equal numbers of isopropylidenediphenylene acetate and ethylene acetate end-groups⁹.

However, from our experiment in which PETP was used as a preformed polyester (Tab. 1, exp. no. 11), it appeared that already in an early stage of the reaction (Fig. 5A) the amount of isopropylidenediphenylene acetate end-groups (2a in Fig. 5) was smaller than the number of ethylene acetate end-groups (2 in Fig. 5). After a long reaction time

($t > 180$ min; see Fig. 5 B) this amount could even be neglected in comparison with the number of ethylene acetate end-groups.

It is obvious that there were reasons to reconsider Hamb's mechanism for the interchange of polyesters with bisphenol diacetates as presented in Scheme 3, and based on our results we therefore suggest the mechanism as shown in Scheme 4. The first step in the reaction is supposed to be ester interchange, resulting in a decrease in the LVN and an introduction of the monomeric compound in the polyester. We assume that in the course of time a second reaction occurred, because after reaction times longer than 120 min the amount of 2,2-dimethylethylene acetate end-groups (ethylene acetate end-groups in the case of PETP) still increased, while the total number of diphenylene groups and the LVN remained constant. In order to explain these results, we suppose that alcoholysis took place between diphenylene acetate end-groups and hydroxyl end-groups in the preformed polyester, as visualized in the second step in Scheme 4. Flory already described such a process being responsible for the interchange and equilibration of two polyesters in the melt⁸⁾. Although proof for the formation of phenol end-groups could not be derived from the ^1H NMR spectra, since only one hydrogen atom was involved, it appears that the mechanism presented in Scheme 4 can explain the results fairly well. The occurrence of a second step involving interchange reactions of chain ends accounts for both the fact that the LVN decreased to a certain level, and for the observation that the total amount of diphenylene residues in the polymer chains remained constant after longer reaction times.

Scheme 4. Proposed mechanism for the interchange reaction of PPVL with BPAac

Hamb's mechanism for the ester interchange of PETP with BPAac differs from the one presented in this work concerning the role of chain ends. Since Hamb also did not use end-capped PETP, it is thus more likely that his observation of an equal number of both chain ends was based on the interchange reaction of PETP with equimolar

amounts of monomeric compounds. In that case the number of hydroxyl end-groups present in the preformed polyester would be very small as compared to the number of chain ends formed by interchange reactions, and consequently too small to have any significant effect.

Fig. 5. ¹H NMR spectra of PETP after reaction with BPAac (Tab. 1, exp. no. 11). (A): after 30 min; (B): after 180 min

Alcoholysis and acidolysis of polypivalolactone

Besides the ester interchange of PPVL with diacetates also the alcoholysis with 1,4-butanediol and the acidolysis with two aromatic diacids were studied in the

presence of 0,5 wt.-% of tetrabutyl orthotitanate. The results of the three types of interchange reactions are shown in Fig. 6. The reaction of PPVL with 1,4-butanediol was characterized by an initial rapid decrease of the LVN resulting in a Δ LVN of 71%, whereas 20% of the diol was incorporated in the polymer chain.

During the experiment in which PPVL was mixed in the melt with terephthalic acid, the diacid did not dissolve and remained suspended in the polymer melt throughout the reaction. Probably due to this heterogeneity, no reaction could be detected. In the case of the reaction of PPVL with isophthalic acid, it was also observed that the reaction mixture remained partly heterogeneous. From Fig. 6 it can be concluded that chain cleavage of PPVL had occurred, although the acidolysis resulted in less chain scission than in the case of the ester interchange with BPAac: Δ LVN was 22% for the acidolysis versus 81% for the ester interchange. This relatively low decrease was in accordance with the ^1H NMR spectra, for only a very small amount of aromatic groups was present in the polymeric backbone.

Fig. 6. Logarithmic viscosity number (LVN) vs. reaction time for the ester interchange of PPVL with BPAac (Tab. 1, exp. no. 8) (c), for the alcoholysis with 1,4-butanediol (b), and for the acidolysis with isophthalic acid (a), using tetrabutyl orthotitanate (0,5 wt.-%) as a catalyst and 10 mol.-% monomeric compound

Comparison with interchange reactions of other polyesters

In Tab. 2 some data concerning interchange reactions with polyesters from literature^{9, 17-19} and from our study are summarized. Using PETP as the starting polymer, Hamb found that the effects on the change of the viscosity in the case of acidolysis by 10 mol.-% terephthalic acid and for the ester interchange by 10 mol.-% BPAac were comparable: Δ LVN values were 64% and 79%, respectively⁹. A similar result was obtained for the decrease in the LVN in our ester interchange with PETP, i. e., 77% (Tab. 1; exp. no. 11).

Riecke et al. found, in contrast with the study of Hamb concerning PETP, that by heating equimolar amounts of poly(ethylene 2-methylisophthalate) and BPAac no decrease in the molecular weight of the polymer was found, and thus it was concluded that ester interchange had not taken place¹⁹. Riecke et al. also observed that acidolysis of poly(ethylene 2-methylisophthalate) with an equimolar amount of 2-methylisophthalic acid resulted in a conversion of 45,9% of the diacid, while the rates of acidolysis of 2-methylisophthalate polyesters of 1,4-butanediol, 2,2-dimethyl-1,3-propanediol, and 1,4-cyclohexylenedimethanol were substantially lower.

Tab. 2. Data on interchange reactions of polyesters with different monomeric compounds

Starting polymer	Type of interchange ^{a)}	Result ^{b)}	Ref.
PETP	B, C	+	9, 17)
PBT	B, C	+	18)
PEMeI ^{c)}	B	+	19)
PEMeI ^{c)}	C	—	19)
Other PMeIs ^{d)}	B	—	19)
PPVL	A, C	+	This study
PPVL	B	—	This study

^{a)} A = alcoholysis; B = acidolysis; C = ester interchange (see Scheme 1).

^{b)} (+) = interchange occurred readily; (—) = little or no interchange.

^{c)} PEMeI = poly(ethylene 2-methylisophthalate).

^{d)} 2-Methylisophthalate polyesters of 1,4-butanediol, 2,2-dimethyl-1,3-propanediol, and 1,4-cyclohexylenediphenol.

Although care should be taken when comparing these results with those of our study (especially with respect to the use of catalysts), some remarks about interchange reactions with PPVL can be made. Mechanisms have been reported in literature concerning ester interchange ¹²⁾ and alcoholysis ⁸⁾, and we assume that the interchange reactions with PPVL occur in a similar way by cleavage of ester bonds in the polymer chain. Comparing our study on PPVL with studies on other polyesters (Tab. 2), it appeared that, with respect to ester interchange and alcoholysis, PPVL is comparable with other polyesters (e. g., PETP).

The relatively low rate of acidolysis of PPVL with the two aromatic diacids may be caused by the high stability of PPVL towards acids in general ^{21, 22)}. Also the fact that (part of) the diacids remained suspended in the melt may well have affected the rate of acidolysis. Riecke et al. also reported low rates of acidolysis in the case of several 2-methylisophthalate polyesters with 2-methylisophthalic acid, which were suggested to be caused by the heterogeneity of the reaction mixtures ¹⁹⁾.

Based on the above-mentioned results we made a preliminary study to prepare copolyesters by mixing PPVL in the melt with a mixture of a diacetate and an equimolar amount of diacid. However, in most experiments the reaction mixtures became solid, and only homopolymers (or highly blocked copolymers) could be detected. A modification of this method to prepare copolymers, avoiding the use of diacids, is under investigation ²⁹⁾.

Conclusions

The results of the present work show that, in spite of the high chemical resistance of PPVL, it is possible to introduce new groups into the polymer by means of interchange reactions. In particular the ester interchange of PPVL with diacetates, using a suitable catalyst, appeared to be rather effective. Melting PPVL with 10 mol.-% BPAac in the presence of 0,5 wt.-% tetrabutyl orthotitanate resulted in an incorporation of 33% of the diacetate, whereas a decrease in the LVN of 81% was found. Based

on an end-group analysis using ^1H NMR spectroscopy, a reaction mechanism for the interchange of PPVL with diacetates was suggested. The first step was assumed to be an ester interchange between PPVL and the diacetate, resulting in shorter chains. Subsequently, alcoholysis of the formed isopropylidenediphenylene acetate end-groups with initially present hydroxyl chain ends was supposed to result in a redistribution of acetate end-groups. Since similar results were found using PETP as a starting polymer, the proposed mechanism by Hamb concerning the ester interchange of PETP had to be adjusted, in particular with regard to the role of chain ends. Although in ester interchange of polyesters with monomeric compounds the main reaction step is the ester interchange reaction, in which the polyester chain is cleaved by the monomeric compound, it can be concluded from this study that also chain ends are of importance.

The behaviour of PPVL towards alcoholysis with 1,4-butanediol appeared to be comparable with its behaviour towards ester interchange. The alcoholysis of PPVL resulted in an incorporation of 20% of the diol and a decrease of the LVN of 71%, whereas the acidolysis of PPVL with the aromatic diacids was less effective. Only in the case of isophthalic acid some interchange could be detected. Both the stability of PPVL towards acids in general and the heterogeneity in these systems were proposed to contribute to the behaviour of PPVL towards acidolysis.

Considering both the results of this study and investigations concerning interchange reactions on the other polyesters, it can be postulated that, with regard to ester interchange and alcoholysis, PPVL is comparable with, e.g., PETP and PBT. Towards acidolysis, however, PPVL appeared to be much more stable than most other polyesters.

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