

Pivalolactone, 2^{a)}

Copolyester synthesis via interchange reactions with polypivalolactone

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SUMMARY:

The synthesis of copolyesters via interchange reactions of polypivalolactone (PPVL) with several compounds was studied. The synthetical procedures are two-stage melt processes: in the first stage ester bonds in the polymer chain are cleaved and new groups are incorporated in the polymer chain, while in the second step condensation of the end-groups formed occurs. For the synthesis of copolymers, three procedures were used, with tetrabutyl orthotitanate as a catalyst. PPVL was heated with equimolar mixtures of bisphenol-A diacetate (BPAac) and terephthalic acid (TA), but no copolymers were formed; instead, polycondensation of BPAac with TA occurred, leaving the PPVL unaffected. From PPVL and mixtures of BPAac and dimethyl terephthalate (DMT) polymers were obtained which contained a significant amount of copolymeric sequences. However, most of the polymeric chains consisted of PPVL and poly(bisphenol-A terephthalate) blocks. Random copolymers with thermal stability were obtained after heating PPVL with bisphenol-A polycarbonate and DMT. The latter process was studied in detail by IR, DSC, and solubility and selective degradation tests. Based on the results of these studies, the reactions occurring during the three procedures were discussed.

Introduction

Polyester blends have been extensively studied both for industrial applications and academic interest¹⁾. An important characteristic of polyester blends is the potential for interchange reactions when heated in the melt. Interchange reactions between a polymer and another polymer or monomeric compounds can open a new route to prepare novel copolymers. The idea of using preformed polymers as starting compounds for the synthesis of copolyesters originates from several considerations. Apart from the fact that nowadays a large number of polyesters is available, the use of combinations of polyesters with different features makes it possible to influence the properties of the resulting materials. Moreover, the available knowledge how to process polyesters in general enables the production of these copolymers directly during

a) Part 1: cf. ref. 4)

processing. When it is possible to control the occurring interchange reactions, a wide variation in composition and microstructure, and thus in properties, can be realized within the processing equipment (e. g., reactive extrusion).

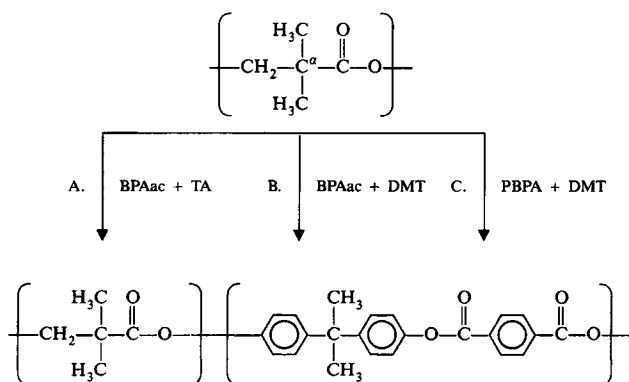
In 1972, Hamb reported on the synthesis of copolymers by interchange reactions between polymers and monomeric compounds^{2,3}. Hamb developed a general procedure to prepare copolyesters of glycols and bisphenols from a preformed polyester, a diacid, and a bisphenol diacetate. In the first stage of this process the monomers cleave the ester bonds in the polymer chain via interchange reactions. This initial cleavage is followed by condensation of the end-groups formed. A more detailed discussion concerning interchange reactions with polyesters is presented in a previous paper⁴.

Based on the study of Hamb, copolymers were prepared by melting a preformed polyester with an acetoxybenzoic acid⁵⁻⁷. Interchange reactions using this process appeared to be very interesting, for the reaction between poly(ethylene terephthalate) (PET) and *p*-acetoxybenzoic acid yielded liquid crystalline polymers when a certain amount of oxybenzoic groups is present in the polymer chains⁶. Also terephthalate copolyesters of ethylene glycol and other alkanediols were prepared by means of interchange reactions of PET with these diols^{8,9}.

The aim of our work is to develop copolymers containing the pivalolactone (PVL) unit, and as part of this study, this paper reports on the synthesis of copolymers via interchange reactions with poly(pivalolactone) (PPVL). Although PPVL shows a high chemical stability, due to the absence of hydrogen atoms at the α position with respect to the carboxyl group (see Scheme 1), it was found that it is possible to introduce other groups in the polymer chain of PPVL by means of interchange reactions⁴.

In this paper results are presented of interchange reactions with PPVL for the synthesis of copolymers by procedures as outlined in Scheme 1. The interest in copolymers consisting of PVL and bisphenol-A terephthalate units is based on the

Scheme 1. Procedures for the synthesis of copolymers via interchange reactions with PPVL



expected chemical stability and high-thermal properties of these materials, considering the properties of PPVL and poly(bisphenol-A terephthalate). Furthermore, introduction of other groups in the highly crystalline and poorly soluble PPVL might have an effect on the solubility, possibly making the copolymers suitable for processing from solutions.

Two procedures (A and B in Scheme 1) start from PPVL and mixtures of monomeric compounds, i. e., mixtures of terephthalic acid (TA) and bisphenol-A diacetate (BPAac), and of dimethyl terephthalate (DMT) and BPAac, respectively. In the third route, C, two polymers, i. e. PPVL and bisphenol-A polycarbonate (PBPA), and DMT are used. The latter procedure is based on a recently developed process for the synthesis of aromatic polyesters by means of interchange reactions between PBPA and DMT¹⁰.

Experimental part

Materials

Pivalolactone (PVL) was purified by distilling over calcium hydride, and was stored under nitrogen at -30°C . 4,4'-Isopropylidenediphenyl diacetate (bisphenol-A diacetate, BPAac) was prepared from bisphenol-A and acetic anhydride¹¹. Terephthalic acid (TA, Janssen Chimica) and dimethyl terephthalate (DMT, Merck) were used as received. Tetrabutyl orthotitanate (TNBT, Merck) used as a catalyst in the polymerization procedures, was added as a solution in dry toluene. Diphenyl ether (Aldrich), used as a solvent in several polymerization runs, trifluoroacetic acid (TFA, Janssen Chimica), and chloroform (Merck) were used without further purification. The chloroform used in the viscometric measurements was purified by standard procedures. The ethyl alcohol used for precipitation and the acetone and the diethyl ether used for washing were of technical grade. The piperidine used in selective degradation experiments was obtained from Aldrich; methylene chloride (Merck) was of analytical grade.

Polypivalolactone (PPVL), with $\eta_{\text{inh}} = 0,6$ dL/g in TFA, was prepared as described in a previous paper⁴. Bisphenol-A polycarbonate (PBPA) was bought from Aldrich and had a molecular weight ranging from 20000 to 25000.

Copolyester synthesis

Reactions were carried out by a two-stage process in a 30 (or 50)-mL reaction vessel, equipped with a stainless steel stirrer with an inlet for nitrogen. A condenser with a provision for applying a vacuum was attached through a sidearm. The glass reactor was heated using a temperature-controlled ($\pm 2^{\circ}\text{C}$) salt bath (10 parts of potassium nitrate and 8,5 parts of sodium nitrite).

Typical procedure for route A: PPVL (3,00 g; 30 mmol of repeating unit), TA (4,98 g; 30,0 mmol), BPAac (9,36 g; 30,0 mmol), and TNBT (0,5 wt.-%) were placed in the reaction vessel (Tab. 1, exp. no. A-3). After the vessel was evacuated and flushed with nitrogen three times to remove air, it was inserted into the salt bath kept at 250°C . While the reactants were stirred under a slow stream of dry nitrogen for 3 h, the acetic acid formed was distilled out of the glass reactor. During the second stage a vacuum ($P = 0,15$ mbar) was applied for 2 h, during which the reaction melt solidified. After grinding, washing overnight with acetone and drying overnight (vac. at 60°C), 10,27 g of a finely powdered pale yellow polymer was obtained.

Analogously, polymer syntheses were carried out in a high-boiling solvent, i. e., diphenyl ether (b. p. 259°C).

Typical procedure for route B: PPVL (2,00 g; 20,0 mmol of repeating unit), DMT (3,88 g; 20,0 mmol), BPAac (6,24 g; 20,0 mmol) and TNBT (0,5 wt.-%) were introduced in the reaction vessel (Tab. 2, exp. no. B-2). Following the same procedure as for route A, the reaction was carried out at 250°C , during which methyl acetate was distilled out of the reactor. After dissolving in

trifluoroacetic acid, precipitating in a large excess of ethyl alcohol and drying overnight (vac. at 60 °C), 4,80 g of a pale yellow polymer was obtained with $\eta_{inh} = 0,17$ dL/g in trifluoroacetic acid.

Typical procedure for route C: PPVL (2,00 g; 20,0 mmol of repeating unit), DMT (5,43 g; 28,0 mmol), PBPA (5,08 g; 20,0 mmol of repeating unit), and TNBT (0,1 wt.-%) were placed in the glass reactor (Tab. 4, exp. no. C-3). After evacuating and flushing with nitrogen, the reaction vessel was introduced in the salt bath at 280 °C. During the first stage the reactants were stirred under nitrogen for 3 h, and the dimethyl carbonate formed was distilled out of the reaction vessel. In the second stage (temperature 280 °C) a vacuum ($P = 0,1$ mbar) was applied for 2 h. The clear orange viscous melt was then cooled to room temperature, during which a glassy polymer was formed. After dissolving in chloroform, followed by precipitating in ethyl alcohol, thoroughly washing with diethyl ether and drying overnight (vac. at 60 °C), 7,40 g of an almost white glassy polymer was obtained with $\eta_{inh} = 0,22$ dL/g in chloroform.

When the second stage of the reaction was carried out at 300 °C (Tab 4, exp. no. C-4), 7,89 g of a polymer was obtained with $\eta_{inh} = 0,58$ dL/g in chloroform.

Study of copolyester synthesis via procedure C: Mixtures of PPVL (0,28 g; 2,8 mmol of repeating unit), DMT (0,82 g; 4,2 mmol), PBPA (0,72 g; 2,8 mmol of repeating unit), and TNBT (0,1 wt.-%) were placed in 10-mL polymerization tubes equipped with a provision for either applying a vacuum or keeping a nitrogen atmosphere. After evacuating and flushing with nitrogen three times, the tubes were introduced in the salt bath at 280 °C. After increasing reaction times the tubes were removed from the salt bath, cooled to room temperature, and after grinding and washing with diethyl ether (to remove non-reacted DMT) finely powdered materials were obtained.

After drying overnight (vac. at 60 °C) samples were studied by IR, DSC, and solubility and selective degradation tests.

Characterizations

Solubility: The dried samples were extracted in a Soxhlet apparatus with methylene chloride as a selective solvent for PBPA for 5 h. Both the dissolved fraction (precipitated in ethyl alcohol) and the undissolved polymer were dried, weighed and characterized by ^1H NMR.

Experiments performed on (non-reacted) mixtures of PPVL and PBPA showed that PBPA was quantitatively separated from PPVL by this procedure.

Selective degradation: The carbonate groups present in the samples were selectively degraded using a similar procedure as described by Pilati et al.¹²⁾ In a typical degradation experiment a sample (0,2 g; containing at most 0,6 mmol of carbonate groups) was treated with piperidine (0,5 mL; 5 mmol) in methylene chloride (12,5 mL) at room temperature for 5 h. After this treatment the non-soluble polymer was separated by filtration and characterized by NMR and viscometric measurements.

Tests performed on (non-reacted) blends of PPVL and PBPA showed that the carbonate groups had reacted completely, whereas the reaction had no effect on PPVL.

Measurements: Viscometric measurements were carried out either with solutions of 0,025 g polymer in 10 mL of trifluoroacetic acid or with solutions of 0,050 g polymer in 10 mL of chloroform, using an Ubbelohde viscometer thermostated at 25 °C. ^1H NMR spectra were recorded on a Bruker AC 250F using deuterated solvent (trifluoroacetic acid or chloroform); chemical shifts are given in parts per million downfield from TMS. IR spectra were recorded using KBr discs by means of a Bio-Rad FTS 60 FT-IR spectrometer. 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 (TG) 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

Copolyester synthesis via procedures A and B

It was shown in a previous study that it is possible to introduce other groups in the polymer chain of poly(pivalolactone (PPVL) by means of interchange reactions between PPVL and several monomeric compounds⁴⁾. In particular, ester interchange occurred readily in the presence of a titanium catalyst. Based on these results, the synthesis of copolyesters by mixing PPVL in the melt with equimolar mixtures of bisphenol-A diacetate (BPAac) and terephthalic acid (TA) (procedure A in Scheme 1) was studied. The reaction was carried out by heating PPVL, BPAac and TA under nitrogen at 250 °C in the presence of tetrabutyl orthotitanate (TNBT). During these experiments it was observed that no homogeneous reaction mixture was obtained, for the TA remained suspended in the melt. After applying a vacuum, during which acetic acid distilled from the heterogeneous melt, the reaction mixture completely solidified.

Tab. 1. Characteristics of polymers synthesized via procedure A (3 h, 250 °C, N₂; 2 h, 25 °C, 0,15 mbar)

Exp. No.	Composition in mol-%						T_m °C	ΔH_m J/g	Yield ^{a)} in %
	initial			final ^{b)}					
	PPVL	BPAac	TA	PVL	BPAac	TA			
A-1	67	17	17	99	< 1	< 1	228	63	63
A-2	54	23	23	84	9	7	218	41	86
A-3	33	33	33	52	26	22	225	16	84
A-4 ^{c)}	33	33	33	—	—	—	—	—	48
A-4-1 ^{d)}	—	—	—	59	22	19	225	24	12
A-4-2 ^{d)}	—	—	—	—	—	—	218	5	36
A-5 ^{e)}	33	33	33	—	—	—	—	—	60
A-5-1 ^{d)}	—	—	—	46	30	25	219	14	49
A-5-2 ^{d)}	—	—	—	—	—	—	218	5	10

a) Yield = (final weight/initial weight) · 100.

b) Determined from ¹H NMR spectra in deuterated TFA.

c) Reaction carried out in diphenyl ether; 3 h condensation.

d) Fractionated: 1 = TFA-soluble fraction; 2 = TFA-insoluble fraction.

e) Reaction carried out in diphenyl ether; 6 h condensation.

Data on the polymers obtained by procedure A are presented in Tab. 1. The materials appeared to be only partially soluble in trifluoroacetic acid (TFA), and consequently composition data derived from the ¹H NMR spectra relate only to the TFA-soluble parts of these polymers. It can be seen from Tab. 1 that the soluble parts contain BPAac as well as TA units. However, the ¹H NMR spectra of most of these materials did not indicate the presence of copolymeric structures, for only peaks could be detected which

are also present in the ^1H NMR spectrum of blends of PPVL and poly(bisphenol-A terephthalate). The results from DSC experiments also suggest that no (or little) interchange had occurred between PPVL, BPAac and TA. All polymers show a melting peak in the region where non-reacted PPVL ($T_m \approx 228^\circ\text{C}$) would give a melting peak. The presence of non-reacted PPVL in the reaction products was confirmed by the results of the TG measurements, showing considerable weight losses at $\approx 300^\circ\text{C}$, indicative of PPVL-degradation.

These results show that procedure A is unsuitable for the synthesis of copolymers containing pivalolactone and bisphenol-A terephthalate units. The reaction products consisted mainly of both homopolymers, i. e., PPVL and poly(bisphenol-A terephthalate), which may be caused by the high stability of PPVL towards acidolysis^{13,14}. It was shown in a previous study that ester interchange of PPVL with BPAac occurred readily, whereas acidolysis with TA did not occur⁴. Several attempts were made to enlarge the possibilities of interchange reactions by extending the first stage of the process (i. e., before condensation). However, during this stage, stirring of the heterogeneous melt became increasingly difficult, and when the first step was carried out for more than 2 h, stirring was no longer possible. Without stirring, the conversions of the monomeric compounds did not increase.

The fact that TA remained suspended in the melt may well have affected the results. Riecke et al. studied interchange reactions of several 2-methylisophthalate polyesters with 2-methylisophthalic acid, and they also reported low rates of acidolysis, which were suggested to be caused by the heterogeneity of the reaction mixtures¹⁵. Attempts were made to dissolve TA in the reaction mixture, and therefore diphenyl ether (b. p. 259°C) was used as a reaction medium^{16,17}. In one run (Tab. 1, exp. no. A-4) using the same reaction conditions as in the bulk, no significant improvement was achieved. In another experiment the first stage of the process was extended from 3 to 6 h (Tab. 1, exp. no. A-5), during which period stirring was possible due to the presence of the solvent. Most of the reaction product appeared to be soluble in TFA (80% against 20% for exp. no. A-4), and a higher amount of both monomeric compounds in the fraction of TFA-soluble polymer was found. These results, combined with the measured low value for the enthalpy of melting of the TFA-soluble fraction, may indicate the occurrence of interchange reactions. However, from the terephthalate region in the ^1H NMR spectrum of this polymer, it could be concluded that the interchange reactions had taken place only to a very small extent.

Another route to introduce bisphenol-A terephthalate groups via interchange reactions was studied starting from PPVL and mixtures of BPAac and dimethyl terephthalate (DMT) (Procedure B). Oishi et al. investigated the synthesis of aromatic copolyesters from dimethyl phthalates and bisphenol-A or BPAac¹⁸. Polycondensation of dimethyl phthalates with BPAac resulted in the formation of polyarylates having logarithmic viscosity numbers of 0,34 dL/g (in chloroform at 30°C , $c = 0,5\text{ g/dL}$), while starting with bisphenol-A instead of BPAac, products were obtained with logarithmic viscosity numbers not higher than 0,10 dL/g. Copolymer synthesis via procedure B, i. e., starting from PPVL and mixtures of BPAac and DMT, yielded clear homogeneous reaction mixtures, and after completion of the reaction under vacuum,

Tab. 2. Characteristics of polymers synthesized via procedure B (3 h, 250 °C, N₂; 2 h, 250 °C, 0,15 mbar)

Exp. No.	Composition in mol-%						$\eta_{inh}^a)$ dL/g	$r^b)$	Yield ^{c)} in %
	initial			final ^{d)}					
	PPVL	BPAac	DMT	PVL	BPAac	DMT			
B-1	54	23	23	65	19	16	0,16	0,16	37
B-2	33	33	33	40	33	27	0,17	0,06	52
B-3	25	38	38	30	37	34	0,17	0,11	77
B-4	18	41	41	26	40	35	0,17	0,10	72
B-5	15	34	51	16	41	42	0,17	0,12	87 ^{e)}

a) Inherent viscosity, determined in TFA at 25 °C ($c = 0,25$ g/dL).

b) Interchange ratio, calculated using Eq. (1).

c) Yield = (final weight/initial weight) · 100.

d) Determined from ¹H NMR spectra in deuterated TFA.

e) Corrected for the excess DMT used.

during which methyl acetate was removed and the melt solidified, TFA-soluble polymers were obtained.

From the results presented in Tab. 2 it is obvious that polymers with higher mole fractions of both monomeric compounds could be obtained, as compared with procedure A. The data also show that the fraction of DMT in the reaction products is always lower than the fraction of BPAac, which is probably caused by loss of DMT during the reaction due to sublimation. By using excess DMT (50 mol-% with respect to BPAac; Tab. 2, exp. no. B-5), it was possible to increase the fraction of DMT in the final polymer. It can be seen from Tab. 2, that the polymers had the same η_{inh} -values, i. e., 0,17 dL/g, irrespective of the initial composition. Several attempts were made to increase the molecular weight of the polymers by solid-state polycondensation. However, heating a sample of polymer B-2 for 7 h at 200 °C under vacuum ($P < 0,1$ mbar) resulted in a material with the same η_{inh} -value as the starting polymer.

In contrast to the ¹H NMR spectra of polymers prepared by procedure A, the terephthalate region of the spectra from polymers prepared by procedure B consisted of several distinct peaks indicating the presence of copolymeric structures (see Fig. 1). Based on a study of Gouinlock et al., concerning bisphenol-A/neopentyl glycol/terephthalate copolyesters¹⁹⁾, these peaks were assigned as noted in Tab. 3. Making such assignments, some remarks concerning the degree of interchange could be made using the peaks of the three sequences for the terephthalate unit, ITI, ITP and PTP (see Tab. 3). The interchange ratio r , as a measure for the degree of interchange, can be defined as

$$r \equiv (2a + b)/[2(a + b + c)] \quad (1)$$

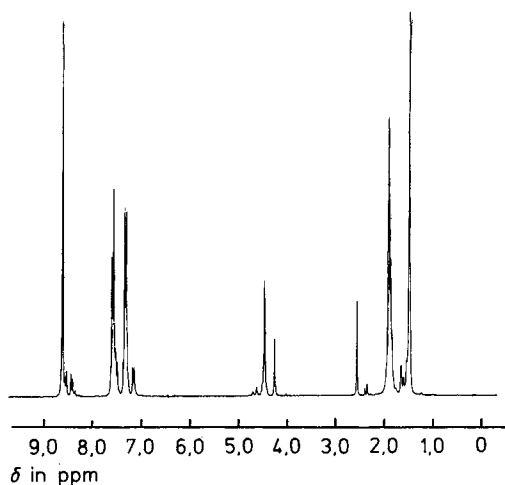
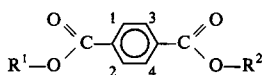


Fig. 1. ^1H NMR spectrum of a polymer prepared from PPVL, BPAac and DMT (Tab. 2, exp. no. B-3); solvent: deuterated TFA

Tab. 3. Chemical shifts for protons of the terephthalate unit (T) as a function of R^1 and R^2 ; solvent: deuterated TFA



Triad	Type of units		Protons	Chemical shift δ in ppm
	R^1	R^2		
ITI	Isopropylidene-di-1,4-phenylene (I)	Isopropylidene-di-1,4-phenylene (I)	H^{1-4}	8,65 (s)
ITP	Isopropylidene-di-1,4-phenylene (I)	2,2-Dimethyl-ethylene (P)	H^{1-2}	8,55 (q)
			H^{3-4}	8,45 (q)
PTP	2,2-Dimethyl-ethylene (P)	2,2-Dimethyl-ethylene (P)	H^{1-4}	8,35 (s)

in which a , b and c denote the integrals of the peaks of the triads PTP, ITP and ITI, respectively. For $r = 0$, no interchange has occurred, whereas for $r = 1$ interchange is considered to be complete.

For all polymers prepared by procedure B the interchange ratio is low (see Tab. 2), suggesting that the units are mainly present as ITI and PP blocks. Although these copolymers show more or less blocky character, the DSC curves do not display any peaks coming from non-reacted PPVL. On the other hand, the prepared polymers

showed (small) endotherms above 300 °C and appeared to be stable up to temperatures well above 300 °C. In the next section the thermal characteristics of these materials will be compared with those of the polymers prepared by procedure C.

Copolyester synthesis via procedure C

Copolyester synthesis via procedure C was carried out by heating PPVL, bisphenol-A polycarbonate (PBPA) and DMT under nitrogen at 280 °C in the presence of TNBT. After 3 h of reaction, during which the dimethyl carbonate formed was distilled from the reaction mixture, the second stage of the procedure was carried out under vacuum. After completion of the reaction, clear orange-coloured glassy polymers were formed upon cooling. Characteristics of polymers synthesized via procedure C are presented in Tab. 4. It appeared that when DMT and PBPA were used in equimolar amounts, the mole fraction of DMT in the reaction product was clearly lower than the fraction of bisphenol-A (BPA) (Tab. 4, exp. no. C-1), due to sublimation of DMT. In order to increase the amount of DMT in the polymers, excess DMT was added in the initial mixtures. The results presented in Tab. 4 show that the amount of DMT was increased by using 40 or 50 mol-% excess DMT (with respect to PBPA), but the mole fraction of DMT in the polymers remains lower than the fraction of BPA (Tab. 4, exp. nos. C-2 and 3).

Tab. 4. Characteristics of polymers synthesized via procedure C (3 h, 280 °C, N₂; 2 h, 280 °C, 0,1 mbar)

Exp. No.	Composition in mol-%						Content of end-groups ^{d)} in mol-%	$\frac{\eta_{inh}}{dL/g}$ ^{a)}	r ^{b)}	Yield ^{c)} in %
	initial			final ^{d)}						
	PPVL	PBPA	DMT	PVL	BPA	DMT				
C-1	33	33	33	37	37	26	6,7	0,19	0,21	86
C-2	28	28	43	33	37	31	4,7	0,23	0,36	93
C-3	29	29	41	38	36	26	4,5	0,22	0,28	81
C-4 ^{e)}	29	29	41	33	37	30	2,2	0,58	0,30	80
C-5	22	33	46	25	41	33	8,3	0,20	0,23	89
C-6 ^{e)}	22	33	46	25	42	33	4,2	0,31	0,24	81
C-7	56	19	26	61	21	19	5,2	—	0,52	65
C-8	50	21	29	59	27	14	3,7	—	0,43	60
C-9	37	25	38	41	32	28	8,4	0,18	0,50	67
C-2	28	28	43	33	37	31	4,7	0,23	0,36	93
C-5	22	33	46	25	41	33	8,3	0,20	0,23	89
C-10	16	35	49	16	45	39	5,2	0,30	0,19	95

a) Inherent viscosity, determined in chloroform at 25 °C ($c = 0,50$ g/dL).

b) Interchange ratio, calculated using Eq. (1).

c) Yield = (final weight/initial weight) · 100; corrected for the excess DMT used.

d) Determined from ¹H NMR spectra in deuterated chloroform.

e) Condensation carried out at 300 °C.

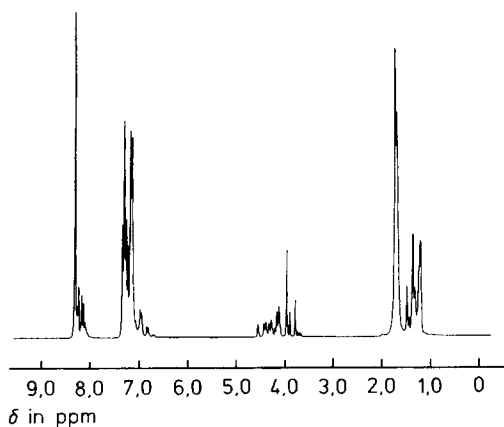
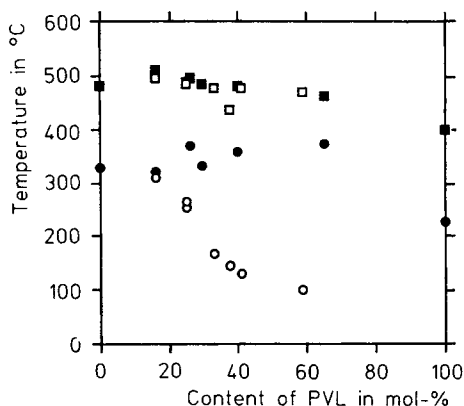


Fig. 2. ^1H NMR spectrum of a polymer prepared from PPVL, PBPA and DMT (Tab. 4, exp. no. C-5); solvent: deuterated chloroform

Fig. 2 shows a ^1H NMR spectrum of a copolymer prepared by procedure C. Comparing this spectrum with that of a polymer obtained by procedure B (Fig. 1), it is obvious that peaks are present at nearly the same positions (taking into account solvent effects), but also that the peaks in the spectrum of Fig. 2 are much more split into multiplets. It is also clear from the NMR spectra that the prepared materials contain peaks which can be assigned to methyl ester and methyl carbonate end-groups, according to the peaks in the region of 3,5 to 4,0 ppm. The origin of these end-groups will be discussed in the next section. Using the relative intensities of these peaks, the amount of methyl ester and carbonate end-groups could be calculated. From the data in Tab. 4 it can be seen that, for copolymers with comparable composition, increasing numbers of end-groups go with decreasing η_{inh} -values. E. g., for copolymers with PVL/BPA/DMT $\approx 25/41/33$ mol-%, the numbers of end-groups range from 4,2 to 8,2 mol-%, whereas the η_{inh} -values vary between 0,31 and 0,20 dL/g. The highest η_{inh} -values and the lowest number of end-groups were obtained by raising the temperature of the condensation step from 280 to 300 °C (Tab. 4, exp. nos. C-4 and 6).

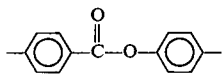
Apart from data about composition and end-groups also microstructural information could be obtained from the ^1H NMR spectra. The terephthalate region of the spectrum presented in Fig. 2 shows two singlets and a quartet, which indicate the presence of copolymeric sequences also found for polymers obtained by procedure B (see Tab. 3). From the relative peak intensities the interchange ratio r could be calculated using Eq. (1) (see Tab. 4). These values show that interchange had occurred to a larger extent as compared with the polymers obtained by procedure B, implying that the copolymers prepared by procedure C have a more random character. From Tab. 4 it can be seen that by decreasing the amount of PPVL in the initial mixture, not only the amount of PVL units in the reaction product decreases, but also that less random copolymers are obtained.

Fig. 3. Thermal transitions of copolymers obtained by procedure B and C vs. the mole fraction of PVL in the copolymers; T_m is melting temperature, and at T_{dec} the rate of weight loss is maximal. (●): T_m , B-series; (■): T_{dec} , B-series; (○): T_m , C-series; (□): T_{dec} , C-series



Copolymers prepared by procedure B and C were studied by DSC and TG. In Fig. 3 the thermal transitions of these copolymers are plotted vs. the mole fraction of PVL units in the materials. The DSC curves of the copolymers showed only very small endotherms, indicating low crystallinities. The melting temperatures of the copolymers obtained by procedure B were all above 300 °C. By increasing the amount of PVL up to 60 mol-% in the materials prepared by procedure C, the melting temperature decreased from 310 to 100 °C, which is illustrative of the more random character of the latter copolymers. TG measurements indicated that the copolymers obtained by procedure B and C are stable to temperatures well above 300 °C; the materials start to lose weight at temperatures ranging from 360 to 380 °C.

In order to obtain more insight into the interchange reactions occurring between PPVL, PBPA and DMT, reaction products were analyzed by IR, DSC, and solubility and selective degradation tests at various reaction times during the first stage of the process at 280 °C, i. e., before condensation. In all these experiments the initial composition was the same, i. e., PPVL/PBPA/DMT = 28/28/43 mol-%. IR spectra of samples obtained from these experiments are shown in Fig. 4. As shown in Fig. 4, the absorption at 1770 cm^{-1} , indicating the amount of BPA-carbonate groups, becomes smaller with increasing reaction time, finally resulting in a complete disappearance after a reaction time of 180 min. Along with the disappearance of the carbonate group, the original ester carbonyl band of PPVL at 1730 cm^{-1} shifts towards 1740 cm^{-1} and a new band appears at 1070 cm^{-1} . Both the 1740 and the 1070 cm^{-1} band were previously assigned to aromatic-aromatic ester groups²⁰, i. e.,



The shift of the 1730 cm^{-1} band can be explained by the occurrence of interchange reactions resulting in aliphatic-aromatic ester groups of the type

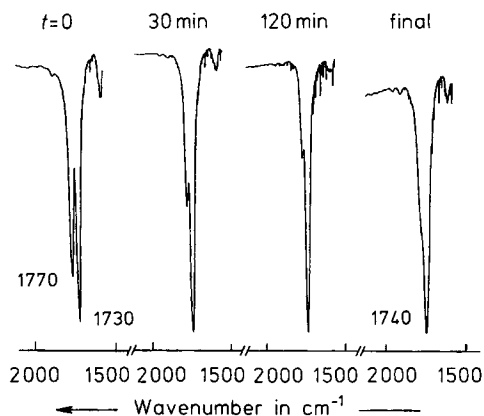
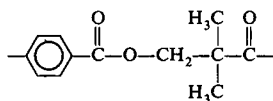


Fig. 4. Evolution of the C=O stretching bands of samples taken during the first stage of the reaction between PPVL, PBPA and DMT; characteristic IR absorptions: PPVL, 1730 cm^{-1} (s; C=O); PBPA, 1770 cm^{-1} (s; C=O); reaction products from procedure C, 1740 cm^{-1} (s; C=O)

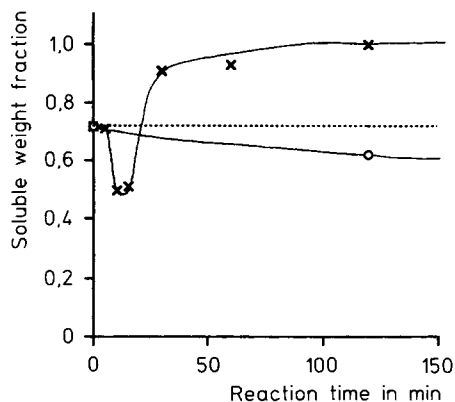


Probably due to a lack of resolution, this aliphatic-aromatic ester carbonyl band cannot be distinguished from the aromatic-aromatic ester carbonyl band, thus resulting in one (wide) band at 1740 cm^{-1} .

Solubility tests, on the other hand, yielded results strongly indicating the presence of aliphatic-aromatic ester structures. Reaction products were extracted with methylene chloride, in which PBPA is completely soluble, whereas PPVL was found to be insoluble in this solvent. In Fig. 5 the weight fraction of the reaction products soluble in methylene chloride is plotted vs. the reaction time for two runs carried out with and without TNBT as a catalyst. The fraction of polymeric material soluble in methylene chloride increased with reaction time in the presence of TNBT, which strongly indicates the occurrence of (interchange) reactions of PPVL and possibly formation of the above-mentioned aliphatic-aromatic ester groups. The initial sharp decrease of the soluble weight fraction may be due to interchange reactions between PPVL and PBPA resulting in macromolecules consisting of long blocks of PPVL and PBPA, which are no longer soluble in methylene chloride.

The soluble fractions were further analyzed by ^1H NMR spectroscopy, and both the composition and the amount of methyl ester and methyl carbonate end-groups are tabulated in Tab. 5. From the data in Tab. 5 it can be seen that the mole fractions of PVL and DMT in the soluble fraction increase with reaction time, thus confirming the formation of the above-mentioned aliphatic-aromatic ester linkages. The non-soluble fractions after 15 min (with catalyst) or after 2 h (without catalyst) appeared to consist of pure PPVL. From the results in Tab. 5 it is also clear that for the formation of copolymers the presence of TNBT is necessary. This is in agreement with the fact that

Fig. 5. Soluble weight fraction (in methylene chloride) vs. the reaction time of products obtained after reaction of PPVL, PBPA and DMT (PPVL/PBPA/DMT = 28/28/43 mol-%) with (×) and without (○) a catalyst ($\text{Ti}(\text{OBu})_4$)



Tab. 5. Composition and amount of methyl ester and methyl carbonate end-groups of soluble fractions (in methylene chloride) of reaction products obtained after reaction between PPVL, PBPA and DMT (PPVL/PBPA/DMT = 28/28/43 mol-%) with and without a catalyst

Reaction time in min	Composition ^{a)} in mol-%			Content of end-groups ^{a)} in mol-%
	PVL	BPA	DMT	
<i>With 0,1 wt.-% $\text{Ti}(\text{OBu})_4$:</i>				
5	1,7	98	0	0
10	2,5	98	0	0
15	7,2	92	0,1	4,3
30	30	65	5,7	9,4
45	32	44	25	14
60	33	44	23	12
120	23	38	39	17
Final ^{b)}	33	37	31	4,7
<i>Without a catalyst:</i>				
120	0,9	96	3,2	6,8

^{a)} Determined from ^1H NMR spectra in deuterated chloroform.

^{b)} After condensation (Tab. 4, exp. no. C-2).

TNBT was reported to accelerate significantly ester interchange reactions^{4, 10, 12, 21, 22}. Without catalyst no dimethyl carbonate was formed, and the amount of PVL units in the CH_2Cl_2 -soluble fraction after 2 h reaction is negligible (see Tab. 5).

The selective degradation of carbonate groups was achieved by reacting samples, obtained after various reaction times, with piperidine in methylene chloride¹²). Pilati et al. used this method, in which the reaction between piperidine and carbonate groups gives urethanes, to isolate poly(ethylene terephthalate) blocks from block copolymers of ethylene terephthalate and bisphenol-A carbonate. However, the conditions of the

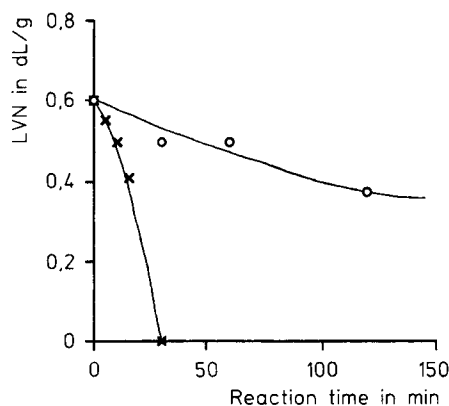


Fig. 6. Logarithmic viscosity number (LVN) in TFA of PPVL blocks isolated by selective degradation using piperidine from reaction products obtained after reaction of PPVL, PBPA and DMT (PPVL/PBPA/DMT = 28/28/43 mol-%) with (x) and without (o) a catalyst ($\text{Ti}(\text{O}i\text{Bu})_4$) as a function of reaction time

procedure suggested by Pilati et al., i.e., 0,01 mmol piperidine per 0,5 g PBPA (containing about 2 mmol carbonate groups), proved to be insufficient to degrade all carbonate groups present in our samples. By reacting the samples with a tenfold molar excess of piperidine with respect to the initial amount of carbonate groups, the reaction was found to be complete after 5 h. Since under these conditions no effect on PPVL was observed, this method was applied to study the presence of PPVL blocks in the products formed by the reaction of PPVL with PBPA and DMT with and without TNBT as a catalyst. In Fig. 6 the logarithmic viscosity number of the isolated PPVL in TFA is plotted vs. the reaction time for runs with and without TNBT. After reaction times longer than 15 min in the presence of TNBT the reaction products were completely soluble in methylene chloride after reaction with piperidine, indicating that no PPVL blocks were present in the samples. This result is in accordance with the calculated values for the interchange ratio (see Tab. 4). From the products obtained after reaction in the absence of TNBT, the logarithmic viscosity numbers of the PPVL, separated after selective degradation of the carbonate groups by piperidine, decreased slowly with reaction time (see Fig. 6).

The occurrence of interchange reactions between PPVL, PBPA and DMT in the presence of TNBT was also confirmed by DSC experiments. In Fig. 7 DSC curves of reaction products obtained at various times during the first stage of the process are shown. Both the decrease in melting temperature and in melting enthalpy support the assumption that interchange reactions had taken place.

Discussion of interchange reactions with polypivalolactone

Three types of interchange reactions involving polyesters can be distinguished in which either ester groups in the polymer chain or end-groups react^{23,24}. It was shown earlier that interchange of PPVL with diacetates (esterolysis) and with diols (alcoholysis) occurred readily, whereas reaction of PPVL with diacids (acidolysis) proved to be less effective⁴.

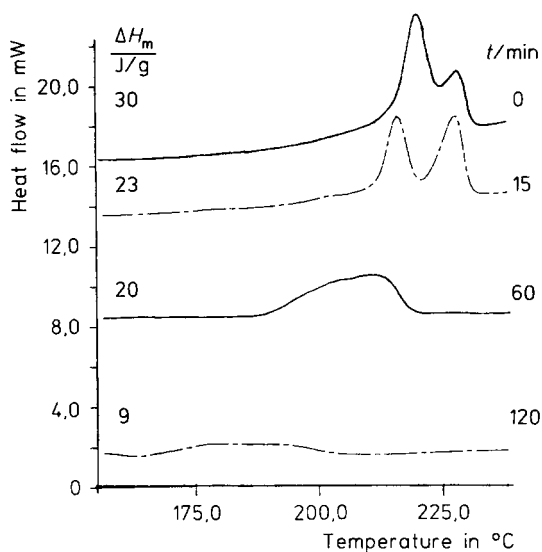
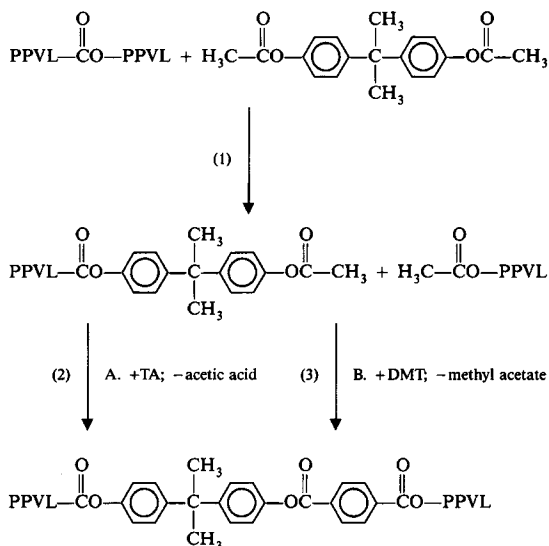


Fig. 7. DSC curves of samples taken during the first stage of the reaction between PPVL, PBPA and DMT with $\text{Ti}(\text{O}i\text{Bu})_4$ as a catalyst

Scheme 2 summarizes the interchange reactions which might have occurred using procedures A and B. Based on the results of a previous study⁴⁾, reaction (1) in Scheme 2 is assumed as a first step for procedures A and B, i. e., the esterolysis of PPVL by BPAac. Although interchange between ester groups in PPVL and TA or DMT could also take place, it was found that acidolysis of PPVL by TA did not occur⁴⁾. In addition, when PPVL was heated with DMT in the presence of TNBT, no incorporation of aromatic units in the polymer chain was found. Whether copolymers are formed depends also on the occurrence of the second step: the coupling of isopropylene-di-1,4-phenylene acetate- and 2,2-dimethylethylene acetate-terminated chains by reaction with TA (reaction (2)) or with DMT (reaction (3)). Apart from these interchange reactions, the competitive reaction between the monomeric compounds resulting in the formation of poly(bisphenol-A terephthalate) must be considered. If polymer cleavage followed by the coupling of the end-groups formed and polymerization of monomeric compounds are the main reactions, then the main question is which of these reactions is favoured.

The results from procedure A show that the reactions between PPVL and mixtures of BPAac and TA do not result in the formation of copolymers, indicating that polymerization of BPAac with TA is favoured above cleavage. Only by extending the first stage of the process, very few copolymeric (ITP-)sequences were found to be present in the reaction products. It is likely that these copolymeric structures do not origin from interchange reactions between PPVL and the monomeric compounds, but

Scheme 2. Interchange reactions for procedure A and B

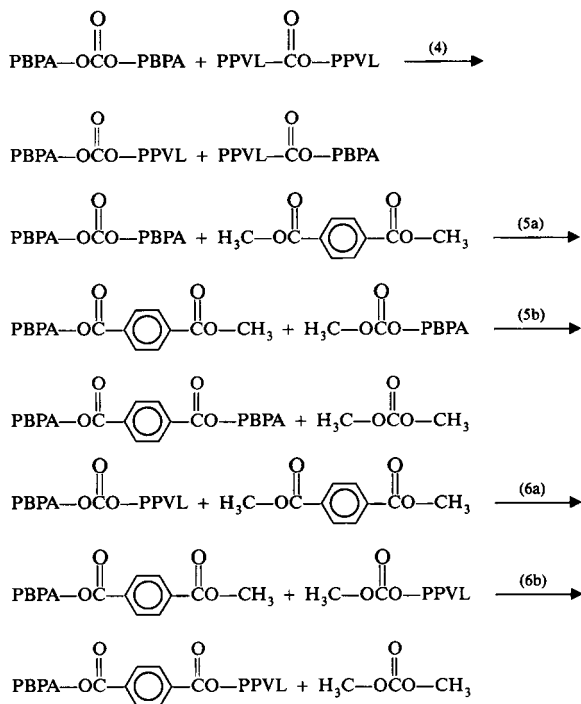


are formed by interchange reactions between PPVL and the poly(bisphenol-A terephthalate) formed. Hamb showed in a similar study that the reaction of PET, TA and BPAac was useful for the preparation of copolyesters²). In contrast to the results from Hambs study, it is clear that procedure A cannot be used for the synthesis of copolyesters from PPVL.

Copolymeric structures are formed by the interchange reaction of PPVL with mixtures of BPAac and DMT. Both ITP- and PTP-sequences could be determined in the ¹H NMR spectra, suggesting that interchange reactions had taken place. The occurrence of interchange reactions was also indicated by the presence of peaks in the ¹H NMR spectra corresponding to isopropylidenedi-1,4-phenylene acetate and methyl terephthalate end-groups (at $\delta = 2,40$ and $4,20$ ppm, respectively; see Fig. 1). Obviously, the use of DMT instead of TA resulted in an increase of the interchange/polymerization ratio. However, polymers prepared by this procedure consisted mainly of ITI and PP blocks, as pointed out by the values of the interchange ratio *r*.

Interchange reactions with PBPA and monomeric esters, resulting in the formation of polyesters, were described recently by Berti et al.¹⁰). It was suggested that this two-stage melt process proceeds by interchange reactions between carbonate and ester groups. In our experiments, a polycarbonate was reacted with a polyester and a monomeric ester. During the first stage of the process the amount of carbonate groups decreased until after 180 min reaction PBPA was completely degraded. The main interchange reactions which may have taken place in the reaction between PPVL, PBPA and DMT are presented in *Scheme 3*.

Scheme 3. Interchange reactions for procedure C



Reaction (4) represents the first step for procedure C, i. e., the interchange reaction between PPVL and PBPA. The melt-blending of PPVL with PBPA (without DMT and TNBT) has been studied by Cruz et al., but no interchange reactions could be detected, which was attributed to the fact that the two polymers were immiscible²⁵. However, we have found that the melt-blending of PPVL with PBPA (without DMT) in the presence of TNBT leads to interchange reactions²⁶. Heating these polymers in the melt at 280 °C for 4 h resulted in a CH₂Cl₂-soluble fraction which consisted of a copolymer containing 12 mol-% of PVL. Therefore, in the system used in procedure C the molten DMT can be considered as a plasticizer and reaction (4) is very likely to occur.

Apart from interchange reactions between the two polymers, it is assumed that also reactions between carbonate groups and DMT (reactions (5) and (6)) took place, as has been reported by Berti et al.¹⁰. It can be seen from Tab. 5 that in the early stages of procedure C mainly PVL units are incorporated into the polycarbonate chain, whereas the amount of DMT units increases only after longer reaction times. This suggests that the incorporation of DMT is accelerated after PVL units are built-in in the polymer chain; consequently, reaction (6) seems of more importance than reaction (5). Furthermore, the occurrence of reactions (5a) and (6a) is indicated by the presence in the

^1H NMR spectra of peaks corresponding to methyl ester and methyl carbonate end-groups in the region of 3,5 to 4,0 ppm (see Fig. 2 and Tab. 5). After applying a vacuum, the amount of end-groups decreased due to condensation (see Tab. 5, final).

Another reaction which may have its effect on the final product may be the interchange reaction between ester groups in PPVL and ester groups formed by reaction (4). However, for several systems in which PPVL was blended with other polyesters in the presence of TNBT, little or no interchange reactions took place²⁶. Therefore, we suggest that the copolymer synthesis by procedure C can be described by means of the reactions presented in Scheme 3.

Conclusions

In this study three procedures (A, B and C) were used for the synthesis of copolyesters via interchange reactions with PPVL. The procedures are two-stage melt processes: in the first stage new groups are incorporated in the polymer chain, whereas in the second step condensation of the end-groups formed takes place.

Heating PPVL with equimolar mixtures of BPAac and TA in the presence of TNBT did not result in the formation of copolymers, probably due to the high stability of PPVL towards acids (procedure A). From PPVL and mixtures of BPAac and DMT in the presence of TNBT, TFA-soluble polymers of relatively low molecular weight were obtained (procedure B). Although the materials contained a significant amount of copolymeric sequences, most of the polymeric chains consisted of PPVL and poly(bisphenol-A terephthalate) blocks (interchange ratio r close to 0). The prepared copolymers showed melting temperatures above 300 °C and appeared to be stable well above their melting temperature.

Heating PPVL with PBPA and DMT resulted in the formation of more random copolymers (r values ranging from 0,2 to 0,5) (procedure C). From the results of a more detailed study, it could be concluded that interchange between PPVL, PBPA and DMT occurred readily in the presence of TNBT. These reactions resulted in a complete disappearance of carbonate groups (within 180 min) and of PPVL blocks (within 15 min) and in the formation of aliphatic-aromatic ester groups. The prepared chloroform-soluble copolymers were of low crystallinity, showing melting transitions in the DSC curves between 100 and 310 °C, depending on the amount of PVL in the copolymers. Furthermore, these materials showed high thermal stabilities; the copolymers started to lose weight at temperatures ranging from 360 to 380 °C, whereas PPVL is known to decompose at 300 °C.

Concerning the reactions occurring using the different procedures, it is assumed that in all three systems two competitive processes are of importance during the first stage of the syntheses. Apart from cleavage of ester bonds in PPVL by the other compounds, resulting in the incorporation of these compounds in the polymer chain, reaction between the other compounds might also be possible. In the case of procedure A, the latter was dominant and the reaction products mainly consisted of non-reacted PPVL and poly(bisphenol-A terephthalate). The use of DMT instead of TA made cleavage somewhat more favourable, but still the units tended to cluster in blocks. Cleavage became dominant when PPVL, PBPA and DMT were heated in the melt, thus resulting

in the formation of random copolymers. The main reason for this phenomenon is suggested to be the relatively high reactivity of the carbonate groups in PBPA with respect to interchange reactions.

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