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# Controlled Synthesis of Block Polyesters by Reactive Extrusion

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**Summary:** The synthesis of block copolyesters by combining transesterification resistant oligoesters with poly(ethylene terephthalate) is described. Critical factors in the synthesis include processing conditions (temperature), end groups and catalysts used in oligoester synthesis. It is necessary to achieve a balance between ease of incorporation/synthesis and transesterification resistance. The process is discussed with reference to poly(neopentyl isophthalate) as a representative transesterification resistant oligoester. The primary motivation for the work has been the development of higher barrier poly(ethylene terephthalate) useful for making monolayer beverage containers.

**Keywords:** block copolyester; oligoester synthesis; PET; poly(ethylene terephthalate); poly(neopentyl isophthalate); reactive extrusion; transesterification resistance

## Introduction

Conventional single layer poly(ethylene terephthalate) (PET) bottles do not have sufficient gas ($CO_2$, $O_2$) barrier for many applications (*e.g.* beer bottles, baby food containers). Other properties (*e.g.* heat distortion temperature) may also be less than optimal.

PET is a semicrystalline polymer with barrier properties that are largely determined by the rate of gas transmission through the amorphous phase.[1,2] PET copolymers may have markedly improved barrier performance and a large number of patents and papers relate to this area.[1,3,4] Other properties (*e.g.* % crystallinity, $T_g$, and $T_m$) are strongly influenced by the length of PET homopolymer segments.[5] The incorporation of comonomers into PET, which necessarily reduces the PET segment length, is therefore anticipated to have a strong influence over both these properties and the materials properties that depend on these parameters. These factors limit both the type and level of comonomer than can be introduced in an effort to reduce gas barrier.

It is also known that various properties (*e.g.* barrier properties, impact, heat distortion temperature) for block copolyesters or polyester blends can be superior to those of random copolyesters of the same nominal composition.[6] However, block copolyester and polyester

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blends have a propensity to undergo rapid transesterification during processing (*e.g.* extrusion, solid stating, injection molding) leading to a deterioration of the abovementioned properties. To address this, various approaches have been described and applied to reduce the extent of transesterification; these include using the use of mild processing conditions and transesterification inhibitors.[7,8] Much of this effort is described in the patent literature.

The main thrust of our work has been to design and synthesize block polyesters that have both desirable properties (in particular, high gas barrier and PET-like processing) and a reduced tendency to undergo structural randomization and consequent property degradation by transesterification. This has been achieved though the use of blocks made from transesterification resistant segments.[9] In designing the transesterification resistant segment, it is necessary to achieve a balance between ease of incorporation/synthesis and transesterification resistance.

In this paper, we examine the synthesis of polyesters containing segments based on neopentyl glycol (NPG) by reactive extrusion and determine their resistance of the segments to transesterification during extrusion and subsequent solid stating.

## Experimental Part

$^1$H NMR spectra were obtained with a Bruker Avance DRX500 on samples dissolved in 1:1 deuterochloroform:deuterotrifluroacetic acid. Chemical shifts are reported in ppm from tetramethylsilane. Spectra were recorded immediately after sample preparation to avoid unwanted trifluoroacetylation.[10]

Oligoester molecular weights quoted were determined on a Waters Associates GPC with THF as eluent at 1 mL/min at 22 °C. The columns were calibrated with narrow polydispersity polystyrene standards (Polymer Laboratories) and molecular weights are reported as polystyrene equivalents. PET molecular weights were determined by GPC on a Hewlett Packard 1090 high performance liquid chromatograph equipped with a diode array detector (270 nm) and four Waters Ultrastyragel columns with 10% HFIP in chloroform containing 1% tetrabutylammonium acetate as eluent at 1 mL/min at 30 °C.

Differential Scanning Calorimetry was carried out with a Metler Toledo DSC 821 equipped with a TSO801RO sample robot under nitrogen. For $T_m$ measurements samples were weighed into 40μL aluminum sample pans, crimp sealed and pierced. A heating rate of 20 °C/min was used.

The PET used was Eastman 9663; a PET homopolymer with an intrinsic viscosity of 0.82. Two samples of oligo (NPG-IPA) were obtained from UCB: Crylcoat 2988 had $M_n$ = 7900 (acid value from data sheet of 30 mg KOH/g), Crylcoat 690 had $M_n$ = 8100 (hydroxyl value from data sheet of 30 mg KOH/g). The PET was dried in a desiccant drier system to give a moisture level of 40 ppm. The oligoester was cryoground to a powder and dried in a vacuum oven at 50 °C for 16 h.

## Oligoester Synthesis

Oligoesters were prepared by polycondensation and end group functionality controlled by adjusting the stoichiometry of the reaction and confirmed by $^1$H NMR. The following procedure is typical.

NPG (380 g) and catalyst (butylhydroxyoxostannane) (2.5 g) were heated to 80°C under nitrogen in a 500 mL flanged flask equipped with mechanical stirrer, insulated fractionating column and stillhead, and thermocouple. Isophthalic acid (251 g) was added portionwise with stirring (approximately 150 rpm). The temperature of the mixture was slowly ramped up to 240°C. After 1 h. the temperature had risen to about 170°C and the condensate had started to distil (b.p. 100°C). When 56 ml of condensate had distilled and the temperature at the stillhead had begun to fall (*ca* 6 h), the molten polyester was poured from the reaction flask and allowed to cool. The polyester had $M_n$ = 4200.

## Reactive Extrusion

Experiments were performed on a JSW TEX 30 twin screw extruder having a 30 mm screw diameter and an overall L/D of 42 [comprising ten temperature controlled barrel sections of L/D 3.5, three unheated sampling monitoring blocks of L/D 1.167 and a cooled feed block of L/D 3.5]. The PET and the oligoester were fed into the extruder using a JSW TTF20 gravimetric feeder and a K-Tron KQX gravimetric feeder respectively. The extruder was operated in co-rotating (intermeshing self wiping) modes with throughputs of between 1 and 5 kg/h. The screw design consisted of kneading, conveying and reversing elements as shown in Fig. 1. The screw speed was routinely set at 155 rpm (40% of motor output). The residence times were 37 minutes for a throughput rate of 1 kg/h, 17 minutes for 2 kg/h and 5 minutes for 5 kg/h. The barrel temperature profile was as shown in Fig. 1. The melt temperatures and pressures were monitored at three points along the barrel as well as in the die. The extrudate was air-cooled by passage along a conveyor belt and pelletized.

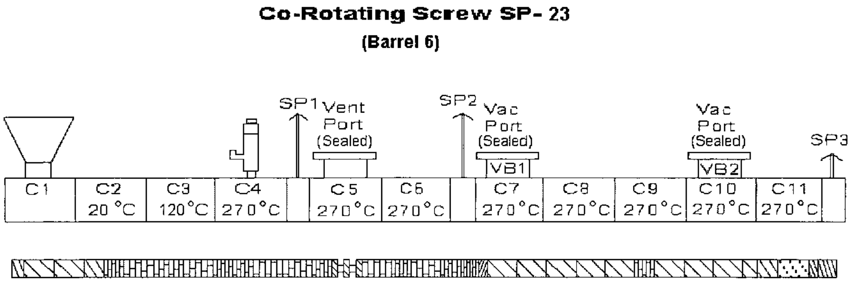


Fig. 1. Screw and barrel profile employed in processing oligomeric polyesters with Eastman 9663 PET homopolymer on JSW Tex 30 twin-screw extruder.

A selection of the extrudate samples were taken, cryoground and extracted in a Soxhlet extractor with chloroform for 2 days. The extract was evaporated to dryness, the residue weighed and then analyzed by $^1$H NMR. The results of this analysis indicated that, in the case of the IPA-end capped oligoester, all of the oligoester (>95%) was chemically incorporated since no oligoester was identified in the extract by $^1$H NMR analysis.

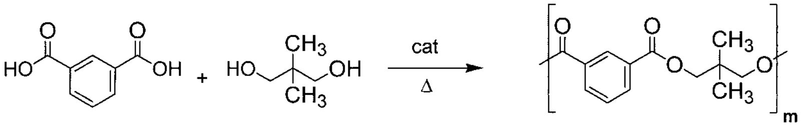
## Solid Stating

A Buchi GKR-50 flash distillation apparatus was used to heat samples *in vacuo*. A sample of the block polyester was crystallized by heating to *ca* 70°C/30 mmHg for 16 h. The apparatus was then attached to a vacuum pump equipped with a liquid nitrogen trap. After 0.5 hours the vacuum was stabilized to 0.35-0.5 mmHg. and the temperature was raised to 220°C and maintained for 6.5 h.

The product was characterized by GPC, which showed that the molecular weight had increased (from number average molecular weight *ca* 16000 to 25000) the 'H NMR (Fig. 2) was unchanged showing that the polymer had not undergone transesterification during solid stating.

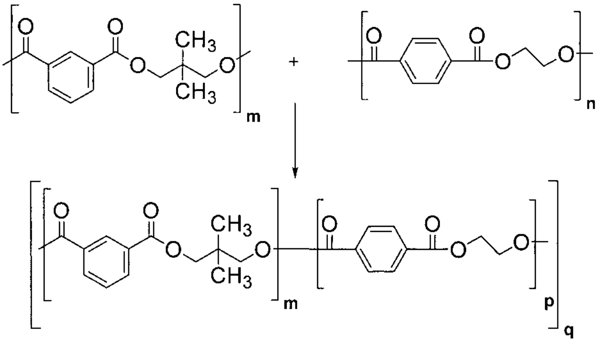
## Results and Discussion

Oligoesters of the desired block length were prepared by conventional polycondensation (Scheme 1). End group control was achieved by adjusting the stoichiometry of the reaction. Oligo(neopentyl isophthalate) can also be obtained commercially with predominantly -OH or $CO_2H$ chain ends. The oligoesters were melt blended at levels of 5-20 mole% of repeat units with PET, ideally to produce segmented block copolymers according to Scheme 2, where the segment length of the transesterification resistant block *m* is retained. Processing was carried out in a twin-screw extruder. The average melt temperature was 270 °C and residence times between 5-37 minutes (corresponding to throughput rates of between 5 and 1 kg/h) were explored.



Scheme 1

Evidence for oligoester incorporation came from Soxhlet extraction (amount of residual oligomer), GPC (the expected MW decrease, disappearance of oligomer) and NMR (disappearance of end group signals). Evidence for retention of block integrity was provided by DSC (similar $T_m$, % crystallinity to PET) and NMR (number of EG-IPA-NPG sequences = block junctures).



Scheme 2

This block copolyester was subsequently also subjected to solid stating (6 h at 220 °C/1 mm Hg) to increase the molecular weight of the copolyester and again the product examined by $^1H$ NMR to establish the block integrity.

The $^1H$ NMR spectra shown in Fig. 2 provide evidence for the retention of block integrity during processing and subsequent solid stating. The spectrum (a) of the oligoester shows signals due to H2 (refer Fig. 3) of the repeat unit (NPG-IPA-NPG sequence) at 8.70 ppm and a smaller signal, which we attribute to the H2 of NPG-IPA-H chain ends, at 8.73 ppm. This region is almost unchanged in spectrum (b) of the oligoester processed with PET and (c) of the solid stated polyester. In spectra (b) and (c) the signal at 8.72 ppm is due to the H2 of the NPG-IPA-EG sequence of the block juncture. In the spectrum (d) of random poly(ethylene isophthalate-*co*-ethylene terephthalate) the H2 signal for the repeat unit (attributable to a EG-IPA-EG sequence) appears significantly shifted at 8.77 ppm. That no signal at 8.77 ppm appears in spectra b and c shows that there are no EG-IPA-EG sequences and thus no substantial structural randomization during melt processing or solid stating.

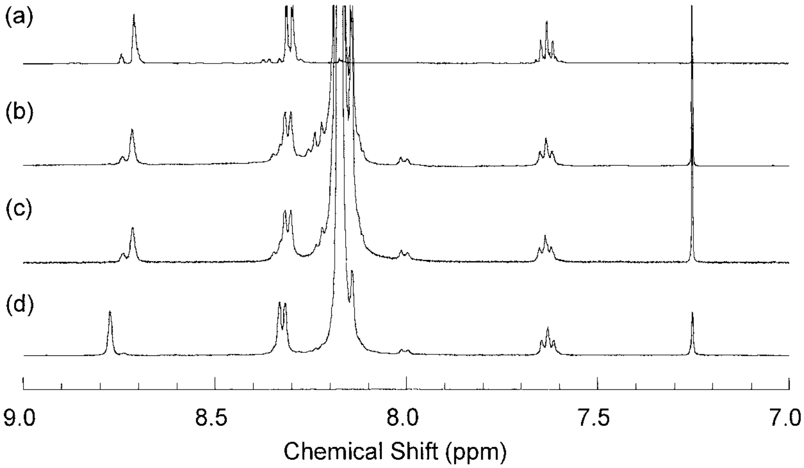


Fig. 2. Region 7-9 ppm of $^1$H NMR spectra ($CF_3COOH/CDCl_3$ solvent) of (a) IPA capped oligo(neopentyl isophthalate) (Crylcoat 2988, **1**), (b) this oligoester (10% wt%) processed with PET (270 °C, 37 min), (c) this product solid stated (220 °C/1 mmHg, 6 h), (d) conventional poly(ethylene isophthalate-co-ethylene terephthalate).

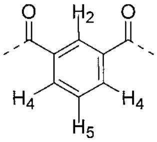
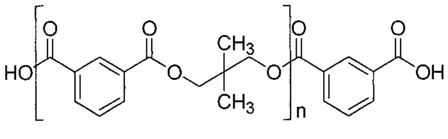
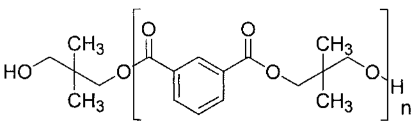


Fig. 3. Designation of isophthalate hydrogens.

As a control, analogous ethylene glycol (EG) based oligomers were prepared and processed with PET under similar conditions. The extent of transesterification of oligo(ethylene isophthalate) poly(ethylene terephthalate) blends was also determined by $^1$H NMR by determining triad fractions (ratio TPA-EG-IPA-EG-TPA : IPA-EG-IPA-EG-TPA : IPA-EG-IPA-EG-IPA) from the appearance of the triplet(s) at 7.62 ppm due to the H4 of the isophthalate repeat unit as described by Ha *et al.*[11] This analysis showed that there was substantial loss of block integrity during extrusion under conditions where poly(ethylene isophthalate-*co*-ethylene terephthalate) remains unchanged.



**1**



**2**

In the synthesis of transesterification resistant segments, attention must be paid to end groups since factors that increase resistance to transesterification can also create a resistance to incorporation. We found that the oligoester with IPA groups (**1**) showed a greater level of incorporation (>95%) than that with NPG chain ends (**2**) (*ca* 80% for an extrusion experiment with 30 min residence time). It is also known that end groups can have a significant effect on the rate of transesterification of PET polyester blends and that, for example, EG end capped PET is more prone to transesterification than TPA end capped PET.[12,13] It is also possible to facilitate incorporation of transesterification resistant segments either through the use of chain coupling agents (*e.g.* pyromellitic dianhydride) or through the use of an oligoester with reactive chain ends.[2]

Further evidence for resistance of oligomer (1) to transesterification comes from measurement of the melting transition ($T_m$) and % crystallinity of the polyester products by DSC (Fig. 4). Incorporation of up to 10 mole% of IPA-NPG repeat units from NPG or IPA end capped oligo(NPG-IPA) ($M_n$~8000) left the $T_m$ and % crystallinity (36% after crystallization) unchanged. PET processed with IPA end capped oligo(EG-IPA) of similar molecular weight ($M_n$~7000) had substantially lower ($T_m$) and % crystallinity. It is known[5,14,15] that random PET-PEI copolyesters have markedly reduced crystallinity and $T_m$ ( for PET $T_m$=257 °C, with 10% IPA $T_m$=226 °C, with 20% IPA $T_m$=204 °C).[15]

Reasons for the transesterification resistance of NPG based polyester segments still need to be defined. NPG based polyesters are well known to be more resistant to hydrolysis than analogous EG based copolymers and are widely used in the coatings industry for this property.[16] The hydrolysis resistance is often attributed to steric factors but other factors such as relative hydrophobicity must also be considered. It is also known that the rate of alcoholisis of polyesters by neopentyl glycol is slow relative to that by ethylene glycol or propylene glycol.[17] However, a number of factors will influence the rate of transesterification including the ester group reactivity, end group reactivity, miscibility of the polyester segments, and the presence of residual polycondensation catalysts. The extent of miscibility of poly(IPA-NPG) and PET is not established. Qualitative evidence for miscibility is the finding that films with up to 20% poly(IPA-NPG) are highly transparent and that multiple $T_g$'s are not evident in the DSC thermograms. More detailed kinetic studies on transesterification involving these and other oligoesters are in progress.

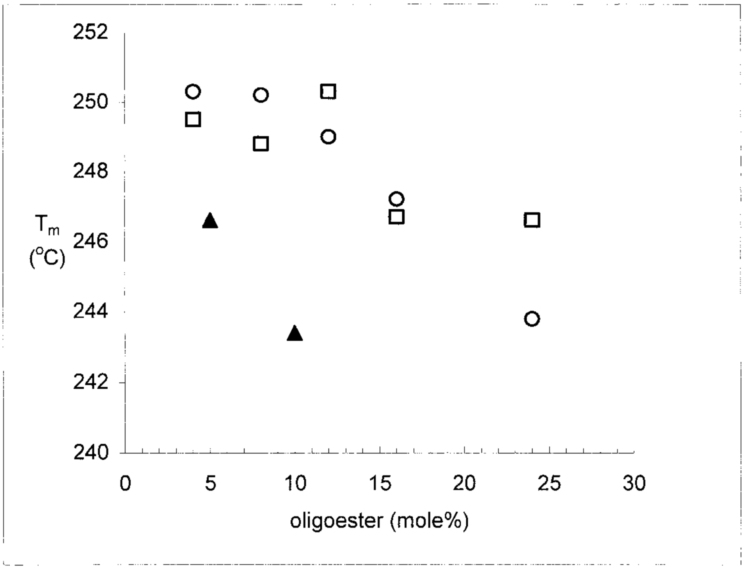


Fig. 4. Variation of $T_m$ with on incorporation of (a) NPG end capped oligo(NPG-IPA) = □, (b) IPA end capped oligo(NPG-IPA) = ○ and (c) oligo(EG-IPA) = ▲ incorporated by reactive extrusion (set temperature 270 °C, throughput rate of 1 kg/h, residence time 37 minutes - see Experimental). X axis is mole % of oligoester repeat units *vs* PET repeat units.

The barrier properties of amorphous films prepared from copolyesters containing NPG based blocks appear similar or better than those of EG based copolyesters of similar overall composition.[9] Those prepared from the poly(IPA-NPG) based block copolyesters had oxygen barrier slightly better than random PET-PEI copolyesters of similar IPA content. The replacement of EG by NPG does not cause deterioration of barrier properties. Barrier properties are anticipated to improve on biaxial orientation of the films.

## Conclusions

The controlled synthesis of block copolyesters by reactive extrusion has been achieved. Oligoester segments based on NPG, in particular Oligo(IPA-NPG), have been demonstrated to have resistance to transesterification such that the block integrity can be maintained during melt processing with PET and subsequent solid stating allowing the synthesis of block copolyester products with defined structure. This has enabled the synthesis of block polyesters with crystallinity, melting point and processing properties similar to those of PET but with significantly improved barrier properties.

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