

Synthesis and Characterization of a New Block Copolymer: Poly(butylene terephthalate-co-olefin) Application on PP/PBT Blend and PBT Homopolymer

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SYNOPSIS

The synthesis of a new block copolymer was investigated by the condensation of terephthaloyl chloride, hydrogenated α,ω -dihydroxy polybutadiene and butanediol. The resulting (PBT) product is termed as the hard segment, and the hydrogenated α,ω -dihydroxy polybutadiene is termed as the corresponding soft segment. This block copolymer was characterized by FTIR, ^1H and ^{13}C -NMR, DSC, and SEC. Quantitative estimations of the contents of block segments have been carried out by NMR. The product was used either to increase the properties of PBT/PP blends or the impact strength of PBT. In both cases the mechanical properties are described. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Thermoplastic elastomers are materials composed of segregated microphase domains. They are block copolymers containing rigid blocks such as polystyrene,^{1,2} polyurethanes,^{3,4} polyamides,^{5,6} and polyesters⁷⁻¹¹ linked by flexible blocks such as polyethers or polydienes. The mutual incompatibility of the hard and soft segments results in the formation of semicrystalline hard domains interdispersed in the continuous matrix.¹²⁻¹⁴ Thus, they offer a variety of mechanical properties higher than those of traditional elastomers. Generally the Young's modulus and the yield stress increase with increasing concentrations of hard segments.¹⁵ The soft segments contribute to improve both the flexibility and the extensibility of the elastomer.

Our interest has been focused on the preparation of multiblock copolymers based on poly(butylene terephthalate), PBT, constituting the hard segments. The polyethers representing the soft segments are the subject of numerous works.^{7,8,16} How-

ever, the polyolefins (soft segments) are less well known.

This article reports on the synthesis and characterization of a new block copolymer by the reaction of hydrogenated α,ω -dihydroxy polybutadiene with PBT monomers prepared from terephthaloyl chloride and butanediol. The effect of the addition of small amounts of this block copolymer (as a compatibilizer) in the binary polypropylene (PP)/PBT mixture was studied. The block copolymer was also inserted into the homopolymer PBT in order to determine whether an increase in impact properties is observed.

EXPERIMENTAL

Synthesis of Block Copolymer

Materials

Terephthaloyl chloride, dimethyl terephthalate, butanediol, and all solvents were reagent grade products and were used as supplied by Aldrich. Toluene was kept over sodium for 24 h. Pyridine was freshly distilled. Hydrogenated α,ω -dihydroxy polybutadiene was obtained from Nippon Soda company and

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used without further treatment. It has the following specifications:

- molecular weight: $\bar{M}_n = 2000 \pm 100$.
- functionality: 1.8.
- microstructure exhibits 18% of 1,4 units and 82% of 1,2 units.

It was prepared by hydrogenation of α,ω -dihydroxy polybutadiene that was obtained by the anionic method. After hydrogenation with palladium, no insaturation remained and the functionality was 1.8 as for α,ω -dihydroxy polybutadiene.

Synthesis of Block Copolymer by Transesterification

The block copolymer was prepared by reacting dimethyl terephthalate, butanediol, and hydrogenated α,ω -dihydroxy polybutadiene in a 10 : 10 : 1 molar ratio. The two stage synthesis was performed according to the method described by Hoechele.¹⁷ In a flask adapted for melt polycondensation, the first stage was performed by the transesterification of dimethyl terephthalate with butanediol and hydrogenated α,ω -dihydroxy polybutadiene. The catalyst was $\text{Ti}(\text{OiPr})_4$ (0.2% wt based on dimethyl terephthalate). The reaction was controlled by the amount of the distilled methanol at 180°C. In the second stage, polycondensation was carried out. A thermal stabilizer was added (400 ppm of 50/50 Irganox1076/Irgafos168) and the temperature was raised to 250–260°C. The pressure was maintained at 100–200 Pa for 2 h.

Synthesis of Block Copolymer by Condensation

The block copolymers were prepared by reacting terephthaloyl chloride, butanediol, and hydrogenated α,ω -dihydroxy polybutadiene in 5 : 5 : 1, 10 : 10 : 1, and 20 : 20 : 1 molar ratios. The polycondensations were carried out in the usual two step way. The synthesis of a typical block copolymer is described in the following section.

In a three-necked round-bottom flask (equipped with a magnetic stirrer, a thermometer, and a dropping funnel) 50 g hydrogenated α,ω -dihydroxy polybutadiene (0.025 mol) and 40 g pyridine (0.5 mol) in toluene were introduced. Terephthaloyl chloride, 50.9 g, (0.25 mol) in anhydrous toluene was added. Stirring was performed for 24 h at 100°C.

In the second step, 22.5 g of butanediol (0.25 mol) was added, and the temperature was maintained for 24 h. After reaction, the mixture was dissolved into

chloroform. The pyridine and pyridinium chloride were separated from the reaction mixture by washing with water, after which the solvent was evaporated off. The mixture was dissolved into tetrahydrofuran (THF) to isolate the PBT homopolymer. The solvent was evaporated and the copolymer was washed with ether to eliminate the unreacted hydrogenated α,ω -dihydroxy polybutadiene, and to stop the block copolymer from having a poor polyester content.

The pure copolymer was obtained by fractional precipitation in THF/methanol (5/2 volume ratio).

Characterization

The structure of the block copolymer was determined by FTIR, ^1H , ^{13}C -NMR spectroscopy, and size exclusion chromatography (SEC). FTIR spectra were conducted with a Nicolet apparatus. The accuracy of the bands was given with an error $\pm 2 \text{ cm}^{-1}$. ^1H and ^{13}C -NMR spectra were recorded on a Bruker AC 200 apparatus using deuterated chloroform as both internal reference and solvent. SEC investigations were monitored with a Waters Associates Apparatus equipped with microstyrogel columns; the diameters of the pores were 10000, 1000, 500, and 100 Å. The detection was performed by a refractometer model BD 40. THF was used as the eluent (flow 1.5 mL/min at 27°C). DSC analyses of the samples were performed on a Perkin-Elmer DSC4 at a heating rate of 20°C/min over two temperature ranges of –100–100°C and 50–250°C. The cooling rate was 320°C/min.

Blends and Mechanical Tests

Blend of PP/PBT

The blends were prepared using a Brabender cell kneader at 250°C. The twinning speed of the rollers was 48 rpm. The materials coming from the mixer were compression molded in a heated press, at a temperature of 250°C and a pressure of 20 bars. The mold size used was cut in ISO 1/2 (ISO being a unit of size). The specimens were tested with a Instron 1195. A crosshead speed of 2 mm/min was needed to measure the breaking strength and elongation at break.

SEM (scanning electron microscopy) was used to analyze surface fractures. The test bar was cooled in liquid nitrogen and then broken. The surface was observed by SEM with a Cambridge Stereoscan 100.

Blend of PBT and Block Copolymer

The homopolymer PBT/block copolymer blend, having a 90/10 weight ratio was prepared under the

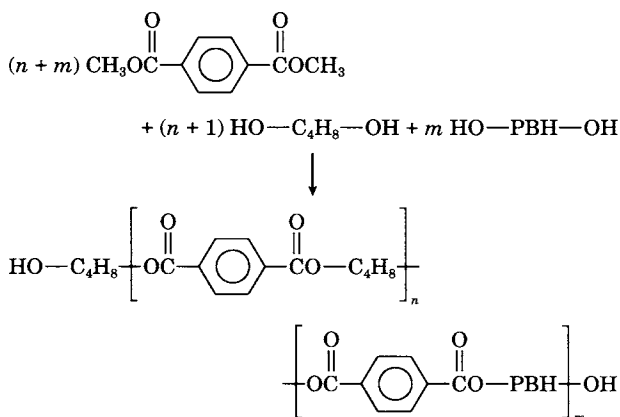
same conditions as above. The material coming from the mixer was molded by compression in a heated press, at 240°C and 20 bars, in order to obtain 4 mm thick sheets. From these sheets, parallel pipe-shaped samples (60 × 10 × 4 mm³) were cut to perform Charpy impact tests. The conditions were:

- impact speed of 2.9 m/s;
- axe length/hammer of 23 cm;
- start angle: 150°C;
- developed energy: 4 J;
- hammer weight: 950 g;
- test span: 40 mm.

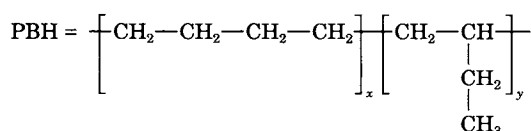
RESULTS AND DISCUSSION

Synthesis and Characterization of Multiblock Copolymers

The synthesis of the multiblock copolymer was carried out by transesterification, which is used in industry for synthesizing PBT.^{18,19} The reaction scheme is:



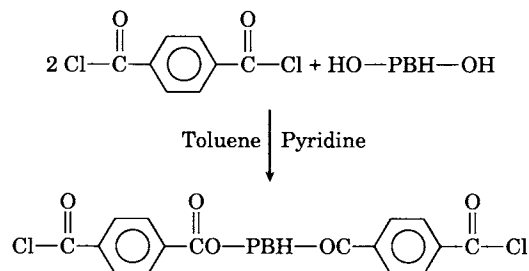
with



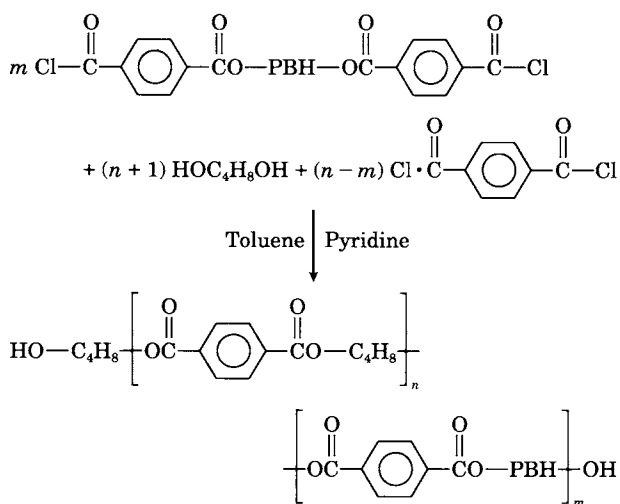
The ¹H-NMR spectra of the product show a very low signal at 8 ppm assigned to aromatic protons incorporated in the copolymer (10%). This is due to the difference in reactivity between the butanediol and hydrogenated α,ω -dihydroxy polybutadiene. The reactants condense to yield the PBT homopolymer. Moreover the poor compatibility between the hydrogenated α,ω -dihydroxy polybutadiene and the

PBT oligomers does not favor the polycondensation process. So another method was investigated: the block copolymer was synthesized by condensation. Pyridine was used as an acid acceptor and the reaction was as follows:

Step 1:



Step 2:



The differences in solubility of hydrogenated α,ω -dihydroxy polybutadiene and PBT were used for the purification of block copolymer (Fig. 1).

The purification method was monitored by SEC and ¹H-NMR. The PBT homopolymer was separated from the mixture by filtration using THF (PBT is insoluble in THF). The solvent was evaporated and the block copolymer rich in PBT was washed with ether to eliminate the unreacted hydrogenated α,ω -dihydroxy polybutadiene as well as the block copolymer, which is poor in polyester.

The block copolymer exhibiting a high polyester content was isolated by fractional precipitation in a THF/methanol mixture in volume ratio 5/2. In this reaction, the concentration of starting materials is an important parameter, and experiments were carried out with different (terephthaloyl chloride)/(hydrogenated α,ω -dihydroxy polybutadiene) molar ratios. In these reactions the amounts of PBT in

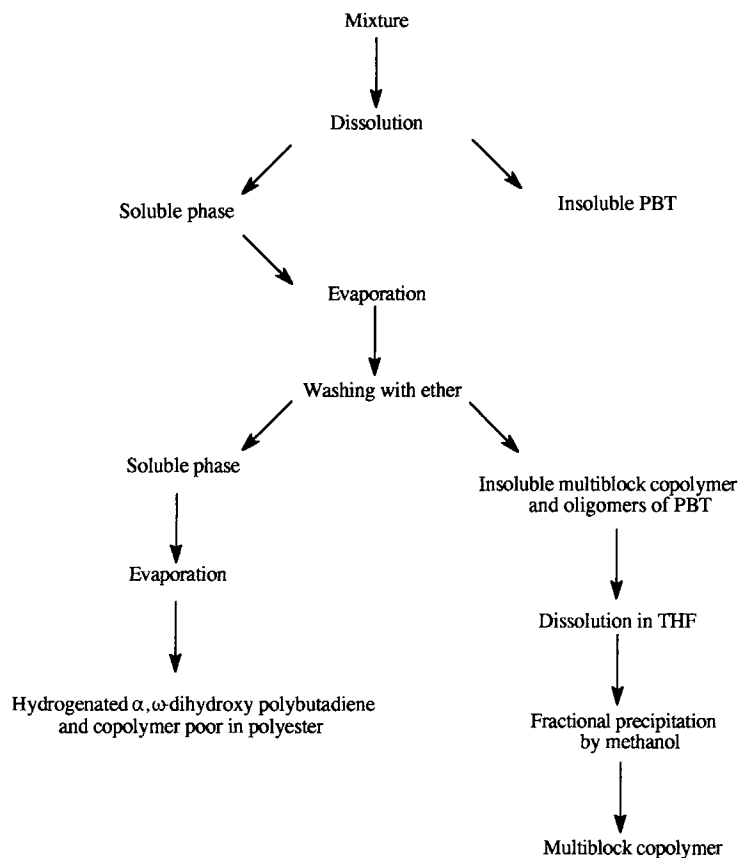
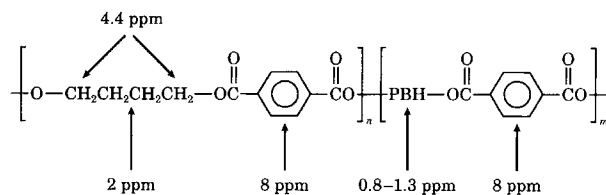


Figure 1 Purification of block copolymer.

the copolymer were constant when the ratio was greater than 5. The results of these different experiments are summarized in Table I.

A typical $^1\text{H-NMR}$ spectrum of a multiblock copolymer is given in Figure 2 and the assignments of peaks are as follows:



The PBT content in the copolymer was calculated by measuring the peak areas of the aromatic protons and the hydrogenated polybutadiene protons.

Actually every hydrogenated polybutadiene segment represents 281 protons by mole ($\bar{M}_n = 2000$) and every aromatic ring represents $4n + 4m$ protons:

$$4 H_n + 4 H_m = A$$

$$281 H_m = B$$

where A represents the area of aromatic protons and B represents the area of all protons coming from

Table I Results of Copolycondensation

Experiment	Butanediol (mol)	Hydrogenated α,ω -Dihydroxy Polybutadiene (mol)	Terephthaloyl Chloride (mol)	PBT wt Fraction (%)	Yield of Block Copolymer (wt %)	Homopolymer (wt %)
1	5	1	5	18.3	60	10
2	10	1	10	26.8	35	39
3	20	1	20	26.8	20	59

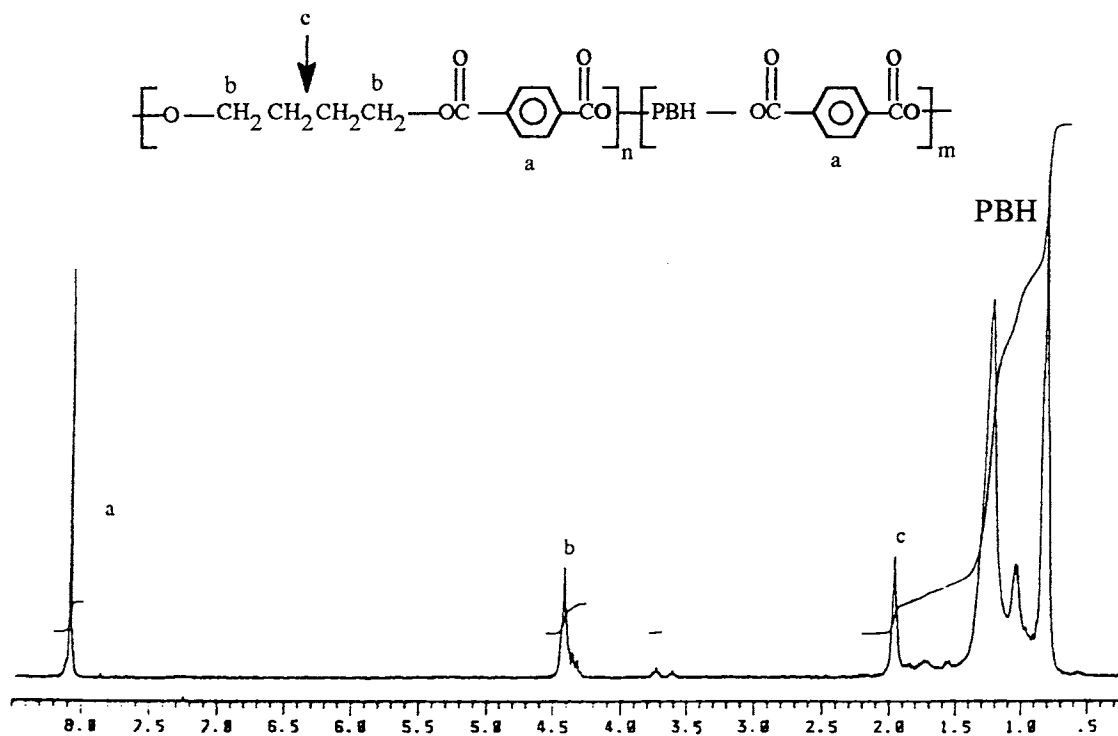


Figure 2 $^1\text{H-NMR}$ spectrum of the block copolymer $(\text{PBT})_n-(\text{PBH})_m$.

hydrogenated polybutadiene. The molar ratios of hard segment (X_n) and soft segment (X_m) are given by the following formulae:

$$X_n = \frac{n}{n+m} = 1 - \frac{B}{70A}$$

$$X_m = \frac{m}{n+m} = \frac{B}{70A}$$

The weight of PBT in copolymer is given by the following formula:

$$\% \text{PBT} = [220X_n / (220X_n + 2132X_m)] * 100.$$

For example, Experiment 2 gives 26.8%.

This value is confirmed by elemental analysis of C, H, and O elements, which permits one to calculate

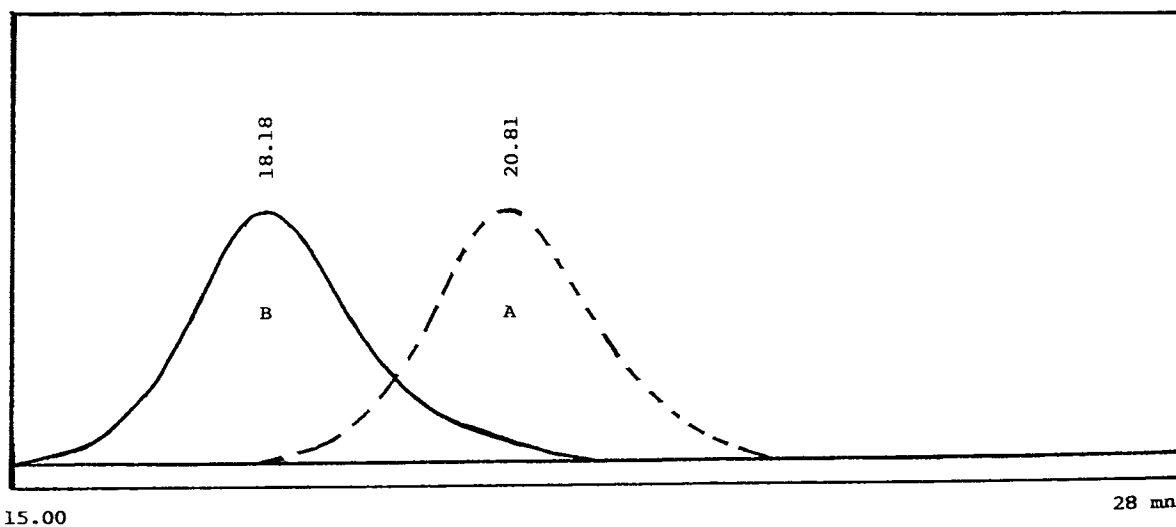


Figure 3 SEC curves of (A) hydrogenated α,ω -dihydroxy polybutadiene (PBH) and (B) of the multiblock copolymer $(\text{PBT})_n-(\text{PBH})_m$.

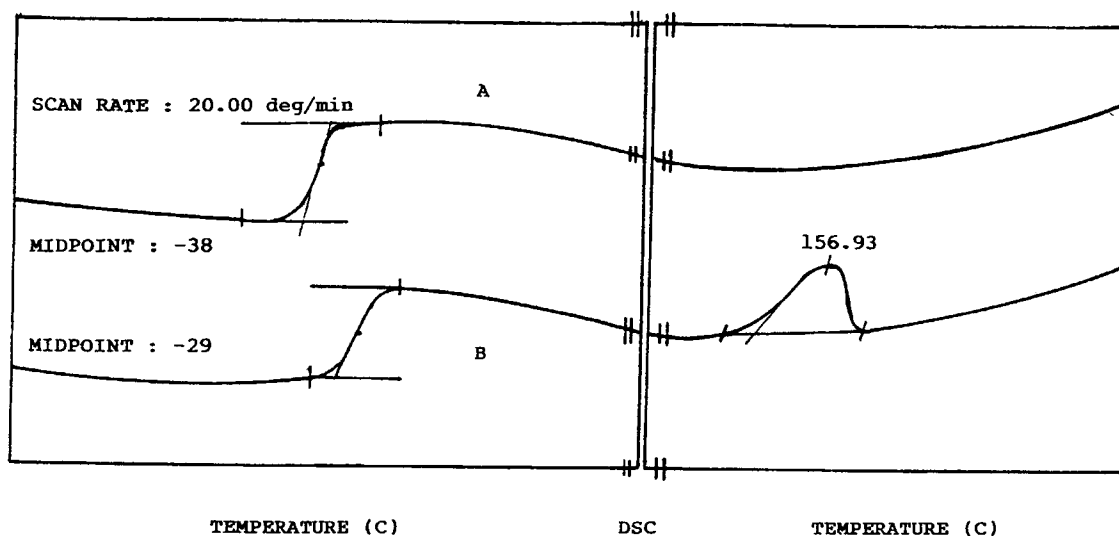


Figure 4 DSC traces of (A) hydrogenated α,ω -dihydroxy polybutadiene (PBH) and (B) of the multiblock copolymer $(PBT)_n-(PBH)_m$.

the wt % of PBT in the copolymer from the equations:

$$\%(O) = (64n + 64m)/(220n + 2132m)$$

$$\%(C) = (144n + 1782m)/(220n + 2132m).$$

For the same example the elemental analysis gives 28 wt % of PBT in the copolymer, which is in good agreement with the NMR result.

The ^{13}C -NMR spectrum of the multiblock copolymer shows the expected signals of the C-atom of PBT. The chemical shifts at 129 and 133 ppm are characteristic for aromatic carbons and at 165 ppm for ester carbons.

Finally, FTIR analysis indicates the presence of an intense carbonyl band at 1718 cm^{-1} and an aromatic band at 1018 cm^{-1} .

SEC analyses of the starting hydrogenated α,ω -dihydroxy polybutadiene and the resulting copolymer show an important increase in molecular weight (Fig. 3), due to polycondensation of the hydrogenated α,ω -dihydroxy polybutadiene with polyester PBT.

The copolymer was studied by differential scanning calorimetry (DSC). The DSC endotherm curve (Fig. 4) exhibits a glass transition temperature (T_g) at -29°C corresponding to hydrogenated polybutadiene (soft segment), which is 8°C higher than that of pure hydrogenated polybutadiene ($T_g = -38^\circ\text{C}$). This result could be explained by the formation of a block copolymer. The T_g of segments of PBT was not detected. This fact is related to the low degree of polymerization of these segments. In

the literature, the T_g of PBT homopolymer is in the 17°C and 80°C range.²⁰⁻²² However, the melting point of the copolymer is 157°C corresponding to the PBT (hard segment). This temperature can be used to determine the approximate degree of polymerization " n ".

According to Flory²³ the melting point T_m of an oligomer is a function of the degree of polymerization n according to the following equation:

$$\frac{1}{T_m} = \frac{1}{T_m^o} + \frac{2R}{\Delta H_m^o} \times \frac{1}{n}$$

where T_m^o is the melting point of an infinitely large polymer, ΔH_m^o is the enthalpy of melting butylene terephthalate units, and R is the ideal gas constant. The melting points of the individual oligomers were determined by DSC. The results are summarized in Table II.

The details of synthesis of individual oligomers were previously reported.²⁴

Figure 5 represents the variation of the reciprocal of the melting point T_m against the reciprocal of n

Table II Melting Points of PBT Oligomers

n	T_m ($^\circ\text{C}$)
1	71
2	137
3	169
5	187

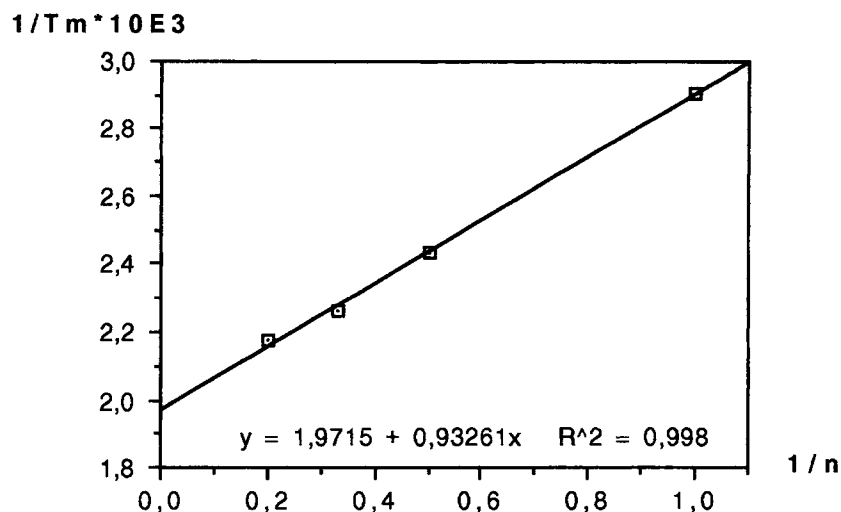


Figure 5 Melting point of oligomers as a function of the degree of polymerization, n .

(n being the number of butylene terephthalate units in the oligomers).

Treatment of such data according to this theory is in excellent agreement with the literature.²⁵ Thus, T_m° is determined as 235°C; it is also the melting point of the PBT homopolymer.²⁶ The value of ΔH_m° is 17.5 kJ/mol.

We find $n = 2.5$ that conforms to 21% of PBT in the copolymer instead of 26.8% (as determined by ¹H-NMR). It is normal to find this difference because we assimilated the structure of oligomers to PBT segments incorporated in the multiblock copolymer.

Study of Compatibilizing in PP/PBT Blends

Morphology

Figures 6 and 7 show the morphology of the PP/PBT 60/40 blend and the effect of the added block copolymer by SEM micrographs. The blend (Fig. 6) is characteristic of an incompatible blend, with nodules (particle size 138 μm) inserted in a continuous phase.

A significant reduction in size of the dispersed phase (particle size 18 μm) was evident when 5% of the block copolymer was added (Fig. 7).

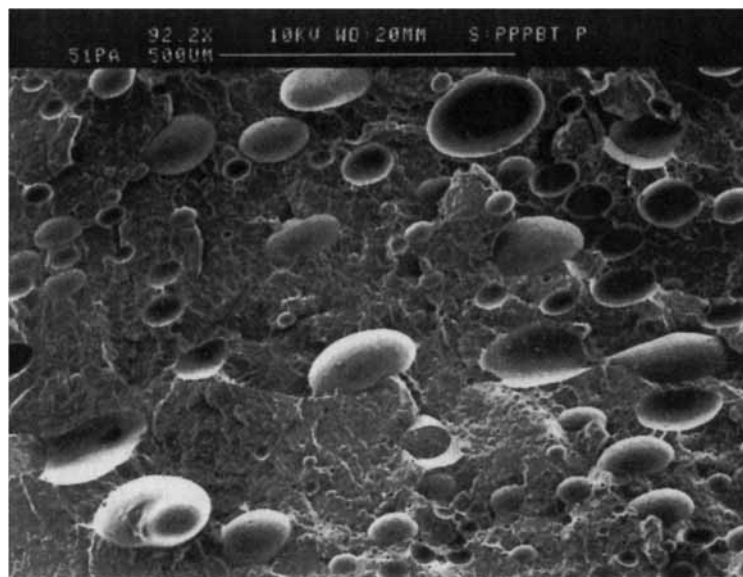


Figure 6 TEM photograph of PP/PBT without the multiblock copolymer.

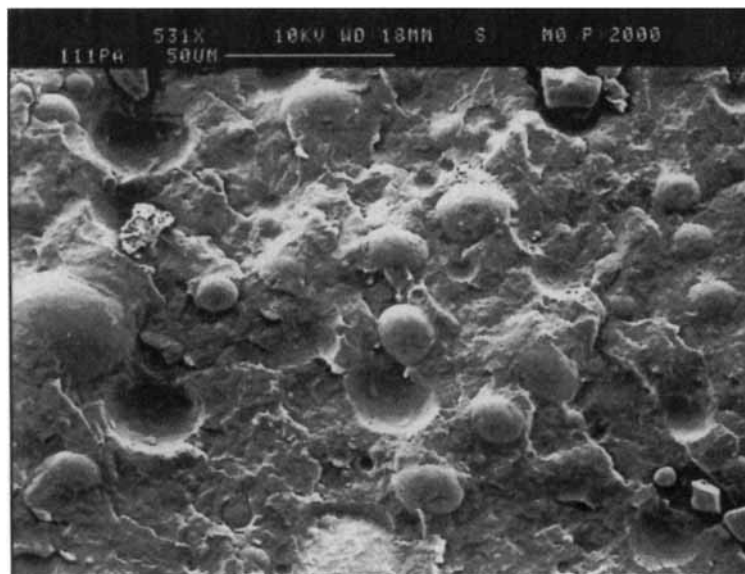


Figure 7 TEM photograph of PP/PBT with the multiblock copolymer.

Stress-Strain

Stress-strain tests were performed at room temperature at 2 mm/min crosshead speed. Maximum stress and elongation at break were recorded. The results were based on 10 samples of PP/PBT (60/40) blends and blends with 5% block copolymer. The results are shown in Table III. Addition of the block copolymer in the PP/PBT blend reduces the maximum stress level whereas the elongation at break is doubled. These results indicate that the multiblock copolymer is not a good compatibilizer.

Impact Tests

The impact strength was obtained by Charpy tests executed at room temperature. The results were based on 13 samples of a PBT/multiblock copolymer (90/10) blend and pure PBT. The stress-strain tests were run in the same conditions as above. The results are listed in Table IV. The incorporation of 10% of the block copolymer in PBT improved the

impact strength 170%, and the elongation at break was slightly increased.

CONCLUSION

The synthesis of the polyester/polyolefin block copolymer was investigated by the condensation of terephthaloyl chloride and butanediol in presence of hydrogenated α,ω -dihydroxy polybutadiene. The hard segment (PBT) content of the copolymer is about 28% in weight and is more important than that of the copolymer obtained by transesterification [using dimethyl terephthalate as the generator of polyester segment (10%)]. The thermal analysis of the copolymer shows a glassy phase at -29°C corresponding to hydrogenated polybutadiene and a crystalline phase at 157°C corresponding to PBT.

It was found that the addition of this block copolymer affects the size and the adhesion of the dis-

Table III Mechanical Tests of Blends with and without Block Copolymer

PP/PBT	Breaking Strength (MPa)	Elongation at Break (%)
Without copolymer	17.2	3.3
With copolymer	12.0	7.0

Table IV Effect of Block Copolymer in PBT

PBT	Elongation at Break (%)	Breaking Strength (MPa)	Impact Strength (KJ/m ²)
Without copolymer	4.1	37.4	7.8
With copolymer	8.2	38.9	21.1

persed phase with the continuous phase in the PBT/PP blend as observed by SEM. However, the stress-strain tests were not improved except for elongation at break.

Finally, addition of the block copolymer to the PBT homopolymer increased its impact strength by 170%, thus showing a good compatibility with the mixture. In conclusion, this copolymer demonstrates good antishock properties.

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