Chain Extension of Recycled Poly(ethylene terephthalate) with 2,2′-(1,4-phenylene)bis(2-oxazoline)

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ABSTRACT: The present work provides improved recycled high molecular weight poly-(ethylene terephthalate) (PET) by chain extension using 2,2′-(1,4-phenylene)bis(2-oxazoline) (PBO) as the chain extender. PBO is a very reactive compound toward macromolecules containing carboxyl end groups but not hydroxyl end groups. In the case of PET, where both species are present, for even better results, phthalic anhydride (PA) was added in the initial sample, before the addition of PBO. With this technique, we succeeded in increasing the carboxyl groups by reacting PA with the hydroxyl terminals of the starting polymer. From this modification of the initial PET sample, PBO was proved an even more effective chain extender. So, starting from a recycled PET with intrinsic viscosity $[\eta] = 0.78$, which would be $[\eta] = 0.69$ after the aforementioned treatment without a chain extender or $\bar{M}_n = 19,800$, we prepared a PET grade having $[\eta] = 0.85$ or $\bar{M}_n = 25,600$ within about 5 min. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 2206–2211, 2000

Key words: chain extender; poly(ethylene terephthalate) (PET); bisoxazolines; post-consumer soft-drink bottles; recycling

INTRODUCTION

Poly(ethylene terephthalate) (PET), a linear thermoplastic polyester, known as one of the major synthetic fibers, has become an important commercial material with many other applications, for example, soft-drink and mineral water bottles, photographic films, recording audio and video tapes, films for food packaging, and insulating material for capacitors. For each application, a certain number-average molecular weight ($\bar{M}_n$) is needed, for example, PET for audio or video tapes usually has an intrinsic viscosity $[\eta]$ of 0.55; as the requirements of mechanical properties become more stringent, higher molecular weight becomes necessary, for example, the PET for fibers has an $[\eta]$ of 0.65; for carbonated soft drink bottles, an $[\eta]$ of 0.78, and for industrial tire cords, an $[\eta]$ higher than 0.85.

This high number-average molecular weight PET is usually produced by "solid-state polycondensation" of a prepolymer and not by continuation of the melt polymerization, because the longer time in the melt state causes an excessive degradation of the final product with a significant increase in carboxyl end groups.[1] Solid-state polycondensation overcomes this problem, but is slow and requires special equipment for large-scale operation. For this reason, the use of the so-called chain extenders seems to be very attractive.[2–19] This coupling of macromolecules can take place during the last stage of the production of the polymer or even in an extruder.[18] The chain extenders generally are bifunctional compounds, easily preparable, thermally stable, nonvolatile in

PBO
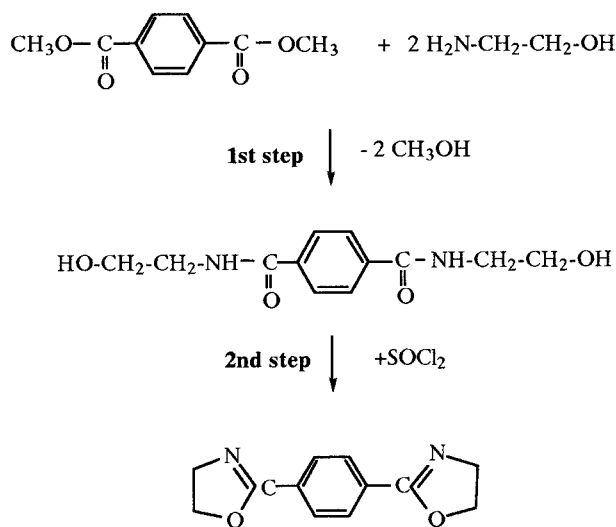
Scheme 1

the melt temperature of the polymer, and capable of a fast reaction with polymer chain ends in a nearly irreversibly manner with no volatile products, it is desirable for such reactions to be of addition or ring-opening type. The main chain extenders of this type which have been proposed[2–5] are bis(epoxides) or diepoxides, bis(cyclic carboxylic anhydride), and diisocyanates. Also, some active phenolic esters have been reported to be effective chain extenders[6,7]; however, the liberated phenol is an undesirable by-product. So, an addition-type chain extender without the generation of a by-product is preferable. But some of these compounds cause undesirable branching or introduce less thermally stable linkages in the polymer. Later on, some types of bis(oxazoline)s,[6–14] bis(benzoxazinone)s,[15–17] and bis(N-acyl-lactam)s[14,18,19] were claimed as effective chain extenders. In the present article, we prepared 2,2′-(1,4-phenylene)bis(2-oxazoline) (PBO; Scheme 1) and used it for the chain extension of a recycled postconsumer soft-drink bottle PET, which exhibited an increased viscosity without the need for postpolycondensation techniques and without forming unwanted by-products.

EXPERIMENTAL

Materials

Postconsumer PET bottles from Coca-Cola, free from polyethylene cups and polypropylene labels,

were washed with detergent, rinsed with hot water, and vacuum-dried at 120°C for 12 h. This material was cut in a mill into small pieces, (Φ = 2–3 mm), for easier melting and used after further drying as previously reported.

Preparation of PBO

PBO was prepared following a two-step method[20] with some minor changes:

First step: In a three-necked round-bottom flask fitted with an argon inlet and a Claisen condenser, 48.5 g of dimethyl terephthalate (0.25 mol) was mixed under stirring with 90 g of aminoethanol (1.5 mol). The mixture was heated at 120°C for 2 h until all released methanol was distilled away. This was confirmed by weighing again the reaction flask after the end of this period of time. After 4 h of further heating, the mixture was cooled at room temperature and the excess of 2-aminoethanol was evaporated under a vacuum. The prepared N,N'-bis(2-hydroxyethyl) terephthalamide was recrystallized from water/ethanol (5:2) and dried in a vacuum oven at 80°C to give 55.5 g of white needles (yield 88%). Mp = 231–233°C.

Second step: N,N'-Bis(2-hydroxyethyl)terephthalamide, 43.2 g (0.176 mol), and 400 mL of methylene chloride were introduced to a three-necked flask fitted with an argon inlet and a mechanical stirrer. To the above mixture, 68 mL (0.932 mol) of thionyl chloride was added dropwise at 0°C. After 24 h of stirring at room temperature, the product was filtered and cautiously added to a 5% NaHCO$_3$ aqueous solution under vigorous stirring. The precipitated product was repeatedly washed with water, recrystallized from ethanol, and dried in a vacuum oven to give 16.8 g of white powder (yield 44%) characterized by ^{1}H-NMR, mass spectrometry, and elemental analysis. Mp = 244–245°C (literature,[21] 246°C).

ANAL. Calcd for C$_{12}$H$_{12}$N$_2$O$_2$ (MW: 216.2): C, 66.65%; H, 5.59%; N, 12.95%. Found: C, 66.31%; H, 5.64%; N, 12.98%

Chain-Extending Reaction

In the first part of the study, to a 250 mL three-necked, round-bottom flask equipped with a mechanical stainless-steel stirrer, argon inlet, and outlet tube, 50 g of polyester chips were added and predried for 30 min at 120°C with the aid of a heated silicon oil bath under a flow of argon and stirring (60 rpm). Then, the flask was placed in a

salt (NaNO$_2$/KNO$_3$ 40:60 w/w) bath heated at 290 ± 1°C, and after 5 min of heating, complete melting of the chips was observed. At this point of time, a control sample was taken from the flask and 0.254 g (stoichiometric quantity) of the chain extender was added, while the speed of stirring increased to 200 rpm.

Samples of approximately 5 g were taken from the flask by increasing instantaneously the argon flow rate at certain time intervals (7.5, 10, 12.5, 15, 20, and 25 min) after the start of heating. The added amount of the chain extender was the theoretical required as well as the double one, assuming that the main reaction is that between carboxyl end groups of polyester and dioxazoline.

In the second part of the study, 0.473 g of phthalic anhydride was added to the PET chips, and when this mixture was completely melted (5 min), the control sample was taken from the flask and 1.2 g of PBO was added. The procedure that followed was carried out as before.

Measurements

All viscosity measurements were conducted at 25.0 ± 0.1°C in an Ubbelohde-type viscometer on solutions in 60/40% w/w phenol/tetrachloroethane at a polymer concentration of 0.25%. The intrinsic viscosity of each sample was calculated using the Solomon–Ciuta[22] equation of a single-point measurement:

$$[\eta] = [2(\eta_{sp} - \ln \eta_{rel})]^{0.5}/c$$

The number-average molecular weight ($\bar{M}_n$) of the samples was calculated from $[\eta]$ values using the Berkowitz[23] equation:

$$\bar{M}_n = 3.29 \times 10^4 \times [\eta]^{1.54}$$

The carboxyl end-group content was determined according to Pohl's method.[24]

The hydroxyl end-group content was determined according to the method proposed by Zimmermann and Tryonadt.[25] This method is based on the reaction of the hydroxyl end groups of PET with a known quantity of 3,5-dinitrobenzoyl chloride followed by titration of the excess hydrolyzed acid chloride.

The theoretical amount (stoichiometric quantity) of the chain extender to be added in the polyester was calculated from the following equation[9]:

$$W \% = \frac{MW \times CC_0}{2 \times 10^4}$$

where MW is the molecular weight of PBO, and CC_0, the carboxyl content of the initial recycled PET sample.

RESULTS AND DISCUSSION

The recycled PET sample, in this work, was first analyzed by the methods previously described and showed the following characteristics: $[\eta]$ = 0.78, CC = 47 equiv/10^6 g, and hydroxyl content (HC) = 64 equiv/10^6 g. From the aforementioned end-group values, we can estimate the $\bar{M}_n$ of the sample as ≈18,000, while from intrinsic viscosity, as ≈19,800. This is a satisfactory approximation, given that from the two methods only the first is an absolute one.

Among the problems met in the reprocessing of recycled PET are the hydrolytic degradation caused by the retained moisture[26–29] (Reaction 1), catalyzed by hydrochloric acid and derived from PVC,[30,31] and the carboxyl groups of PET[32] itself, as well as the thermal decomposition[33,34] due to the high temperature of the process (Reaction 2) are of main importance:
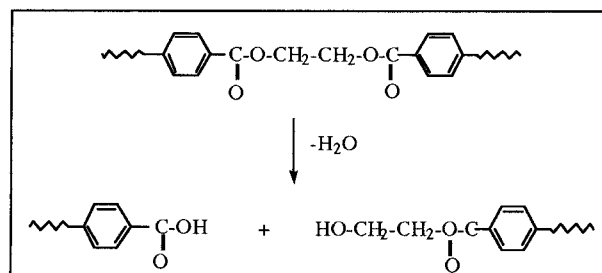
Reaction 1
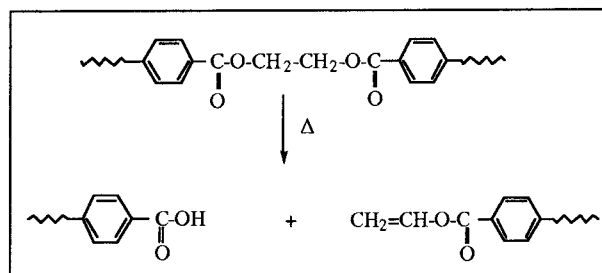
Reaction 2

PET usually contains about 0.45% w/w moisture, which is difficult to get rid of; consequently, a catastrophic degradation takes place during extrusion of recycled PET.
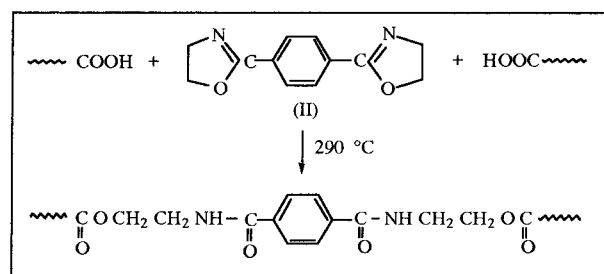
Chain Extension with Only PBO

To compare our chain-extension results in this research, first, a blank run (control) was performed with recycled PET alone. Seven samples were drawn from the reaction flask in this run at certain time intervals (5, 7.5, 10, 12.5, 15, 20, and 25 min) after the starting of the heating (290°C). An increase of carboxylic end groups ($47–55$ equiv/10^6g) is caused by this processing (see Table I) due to hydrolytic degradation in the first 5 min provoked by the retained moisture and to thermal decomposition during the rest of the time.

The intrinsic viscosity measurements of the control samples [see Table I and Fig. 1(curve 1)] reveal the decreasing molecular weight of the polyester. When the processing is carried out in the presence of the theoretical amount of PBO, the intrinsic viscosity for the samples of this series shows a different behavior. During the first 5 min (melting stage), the two curves coincide, that is, the same hydrolytic degradation takes place. After that, $[\eta]$ increases, but not significantly [Fig. 1(curve 2)]. According to a successful work of Cardi et al.,[11] the stoichiometric quantity of the chain extender is not sufficient to react with additional carboxylic groups formed during processing as a consequence of Reactions 1 and 2. In our case, another probable reason must be the inefficient stirring into a glass reactor of a so viscous melt material. To override this problem, we decided to select as the chain-extension temperature 290°C instead of the most usual 270–280°C, resulting in a more intensive thermal decomposition. Cardi et al.[11] suggested, also, that when the oxazoline concentration exceeds twice the carboxyl content most likely its reaction is incomplete and the unreacted chain extender may act as an internal lubricant.

When the double stoichiometric quantity of PBO was used, an even better result was obtained (curve 3, Fig. 1) and the carboxyl content decreased, suggesting that reaction 3 took place. From the literature,[35] we find that oxazolines react easily with carboxylic compounds, forming esteramide groups.
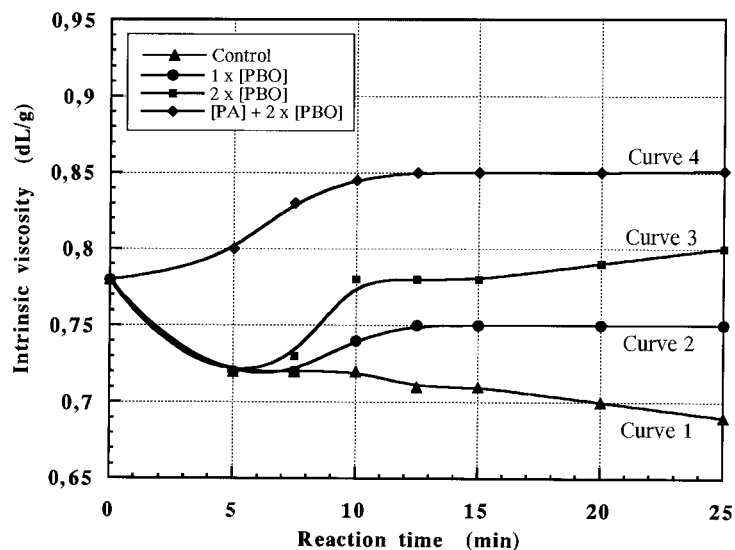

Reaction 3

Chain Extension with PBO and PA

According to the above results, this initial recycled polyester having a higher carboxyl content can result in a polymer of higher molecular weight using PBO, when both samples are of similar intrinsic viscosity. As mentioned before, the initial PET sample of this work has $CC_0 = 47$ and $HC_0 = 64$, so we can increase the carboxyl end groups by reacting PA (**II**) with the hydroxyl terminals of the starting polyester as shown in Reaction 4. When we added PA at the same time as PBO in the melt (5 min), the anhydride sublimed and the experiment failed. Therefore, we decided

Table I   Intrinsic Viscosity and Carboxyl Content of Unmodified and Modified PET Samples

Reaction Time (min)	Control		2 × [PBO]		[PA] + 2 × [PBO]	
	$[\eta]$ (dL/g)	Carboxyl Content (equiv/10^6 g)	$[\eta]$ (dL/g)	Carboxyl Content (equiv/10^6 g)	$[\eta]$ (dL/g)	Carboxyl Content (equiv/10^6 g)
0	0.78	47	0.78	47	0.78	47
5	0.72	53	0.72	53	0.80	105
7.5	0.72	53	0.73	35	0.83	97
10	0.72	54	0.78	30	0.85	74
12.5	0.71	54	0.78	22	0.85	69
15	0.71	54	0.78	20	0.85	65
20	0.70	55	0.78	21	0.85	60
25	0.69	55	0.80	21	0.85	56

Figure 1 Variation of intrinsic viscosity with reaction time of unmodified and modified PET samples.

to add PA at the same time as PET (0 min), and after 5 min, when this mixture was completely melted, PBO was added. This technique is in accordance with that of Inata and Matsumura,[9] when they used 2,2′-bis(2-oxazoline) as a chain extender:
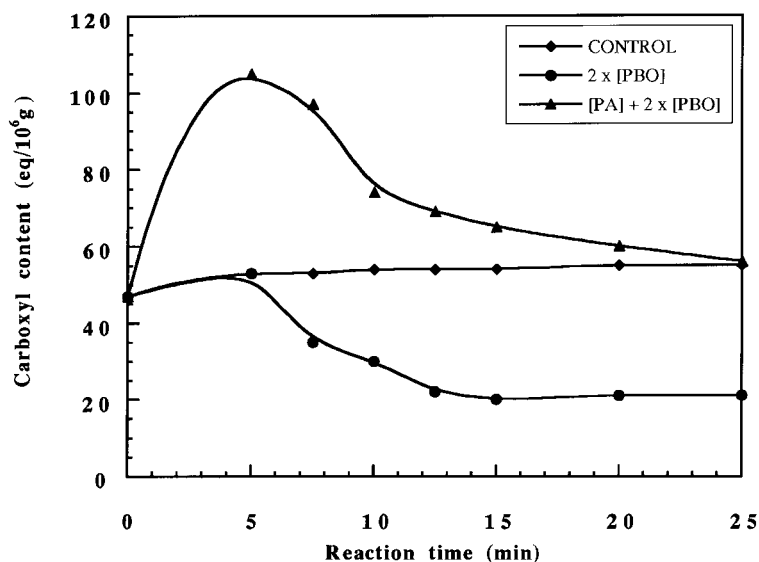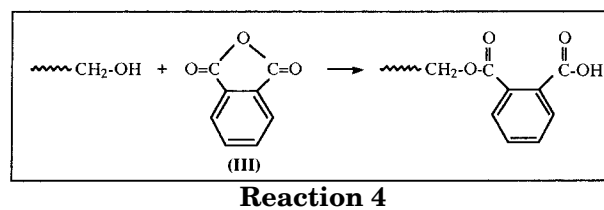
Reaction 4

Figure 2 Variation of carboxyl content with reaction time of unmodified and modified PET samples.

It is worthwhile noting that after the complete melting of the mixture (PET + PA), which was achieved after 5 min of heating, a reaction of PET hydroxyl end groups with PA took place, which resulted in a sample showing a $CC = 105$ equiv/10^6 g. This is another good proof that Reaction 3 takes place to a very high extent, because when this sample was analyzed for hydroxyl groups, it gave an $HC = 9$ equiv/10^6 g.

As shown in curve 4 (Fig. 1) during the first 5 min of reaction, PA counteracted the hydrolysis effect and gave some kind of chain extension. After the addition of PBO, a further increase in $[\eta]$ occurred during the first 5 min and this value of 0.85 remained unchanged the rest of the time.

Carboxylic end-group content as a function of time is reported in Figure 2. One can see the gradual small increase of the CC of the control sample during the time of 25 min. The curve of modified PET with a double amount of PBO lies well below the corresponding unmodified one. The curve representing the data of PET samples with PA seems to be parallel to the previous one, except this part of the time, that is, the first 5 min when PA reacted with PET hydroxyl end groups, resulted in an abrupt increase of carboxyl content.

CONCLUSIONS

From the above chain-extension experiments of the recycled PET sample, PBO has been proved to be an effective chain extender. Starting from the recycled PET with $[\eta] = 0.78$, which would be $[\eta] = 0.69$ after the aforementioned treatment without the chain extender or $\bar{M}_n = 19{,}800$, we prepared a PET grade having $[\eta] = 0.85$ or $\bar{M}_n = 25{,}600$ within about 5 min.

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