

Chain Extension of Polyesters PET and PBT with Two New Diimidodiepoxides. II

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SYNOPSIS

Two new diglycidyl ester compounds containing preformed imide rings for better thermal stability were prepared to be used as chain extenders for PET and PBT. The preparation of these compounds was carried out in two steps. In the first step, diimidodiacids were prepared from pyromellitic anhydride and 3-aminopropanoic acid or 4-(aminomethyl)benzoic acid. From these diimidoacids, in a second step, diimidodiepoxides were obtained by reaction with epichlorohydrin. The aforementioned diimidodiepoxides were used as chain extenders for poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) with satisfactory results. The polyester samples obtained from various residence times in the reactor, were characterized by solution viscosity measurements, carboxyl, and hydroxyl end-group determination. Starting from a PET having intrinsic viscosity ($[\eta]$) of 0.60 dL/g and carboxyl content (CC) of 42 equiv/10⁶ g, one could obtain PET with $[\eta]$ of 1.16 and CC below 5 equiv/10⁶ g. The typical reaction condition for the coupling of PET was its heating with the chain extender under argon atmosphere above its melting temperature (280°C) for several minutes. Analogous results were obtained for PBT. The hydroxyl content in all cases was increased. © 1996 John Wiley & Sons, Inc.

Keywords: chain extender • *N,N'*-bis(glycidylester)pyromellitimide • diimidodiepoxide • poly(ethylene terephthalate) (PET) • poly(butylene terephthalate) (PBT)

INTRODUCTION

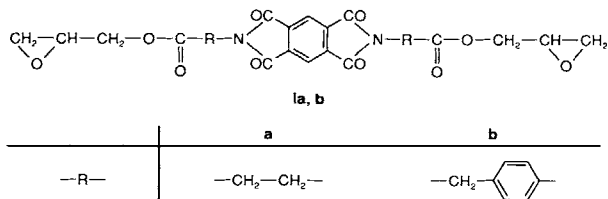
Poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) are well known as commercially polymeric materials with numerous applications. However, their molecular weight M_n which is strongly related to their mechanical properties is relatively low, and their carboxyl content is high enough, because of the vigorous conditions used during their preparation by melt polycondensation technique.¹ A higher molecular weight with a low carboxyl content gives to both polymers improved mechanical and chemical properties such as toughness and hydrolytic stability. To achieve this combination various technologies were proposed in the past, such as the solid-state post-polyconden-

sation, and the chain extension with suitable bifunctional compounds known as "chain extenders."²⁻¹⁴ The latter can react within a few minutes with PET or PBT end groups, under melt conditions at an atmospheric pressure, so that in practice they can easily be applied during the ordinary melt processing such as spinning, extruding, and injection molding. Among the chain extenders used, the most effective are those which react with the carboxyl end groups without liberating a byproduct (addition type) such as diepoxides. These react with both carboxyl and hydroxyl end groups. From this reaction, however new hydroxyl groups are formed which can lead to branching or even crosslinking.

Recently it was reported, that a limited degree of branching gives to PET melt the ability to be molded in a very fine closed cell foam.¹⁵ For this reason in our previous article¹⁴ we have prepared three diepoxides and we used them as chain extenders for PET and PBT with very satisfactory results. In the

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present article we have prepared two new diepoxides (**Ia**, **Ib**) and we used them as chain extenders for the above polyesters:



EXPERIMENTAL

Synthesis of Diepoxides

N,N'-bis[2(carbo-2'3'-epoxypropoxy)ethyl]pyromellitimide (**Ia**)

Pyromellitic anhydride was first reacted with 3-aminopropionic acid according to the method described in the literature^{16,17} to give the *N,N'*-bis(2-carboxyethyl)pyromellitimide. The latter reacted then with epichlorohydrin at reflux for 40 min in presence of benzyltrimethylammonium chloride as catalyst as described in the literature¹⁸ to give the epoxide **Ia** as white powder (yield 72%). This showed a mp at 164°C (determined by DSC) or 162–165°C (by hot-stage microscopy). The epoxy content of **Ia** was found to be 289 g/equiv (theor. value 236 g/equiv).

IR (KBr): 1785 cm⁻¹ [imide carbonyl (symmetric stretching)], 1720 cm⁻¹ [ester carbonyl and imide carbonyl (asymmetric stretching)], 915 cm⁻¹ [oxirane deformation], and 725 cm⁻¹ [imide ring].

ANAL. Calcd for C₂₂H₂₀O₁₀N₂: C, 55.93%; H, 4.27%; N, 5.94%. Found: C, 56.12%; H, 4.04%; N, 6.33%.

N,N'-bis[4(carbo-2,3'-epoxypropoxy)benzyl]pyromellitimide (**Ib**)

The reaction of pyromellitic anhydride with 4-(aminomethyl)benzoic acid gave the *N,N'*-bis(4-carboxybenzyl) pyromellitimide which after heating with epichlorohydrin for 90 min gave **Ib** as pale yellow powder (yield 89%). This showed a mp at 290°C (by DSC) or 285–288°C (by hot stage microscopy). The epoxy content of **Ib** was 310 g/equiv (theor. value 298 g/equiv). The IR spectrum showed the characteristics peaks mentioned above.

ANAL. Calcd for C₃₂H₂₄O₁₀N₂: C, 64.43%; H, 4.06%; N, 4.63%. Found: C, 64.26%; H, 4.00%; N, 4.71%.

Chain Extending Reaction

To a 250 mL three-necked, round-bottom flask, equipped with a mechanical stainless steel stirrer, argon inlet and outlet tube, 30 g of well-dried polyester chips and a certain amount of chain extender were added. The mixture was stirred (60 rpm) at room temperature for 30 min under a flow of argon and then the flask was placed in a salt bath (NaNO₂/KNO₃ 40 : 60 w/w) heated at 280 ± 1°C in the case of PET and at 250 ± 1°C in the case of PBT. After 4–5 min of heating the complete melting of the chips was observed and the speed of stirring increased to 200 rpm. Samples of approximately 5 g were taken from the flask at certain time intervals (5, 10, 15, 20, 30, and 60 min after the complete melting).

Measurements

Melting points were determined on a Perkin-Elmer Differential Scanning Calorimeter DSC-2. Elemental analyses were carried out with a Perkin-Elmer model no. 240 instrument. The IR absorption spectra were recorded on a Perkin-Elmer model 281-B spectrophotometer on KBr discs.

Viscosity measurements were conducted at 25 ± 0.1°C in a Ubbelohde-type viscometer on solutions in 60 : 40 w/w phenol/tetrachloroethane, at a polymer concentration of 1.0%. The intrinsic viscosity of each sample was calculated by using the Solomon-Ciuta¹⁹ equation of a single point measurement:

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

Some samples were partially insoluble in the above solvent mixture at the concentration of 1%. In this case the insoluble part of the sample was removed by filtration and determined, so the concentration of the solution was calculated and used in the Solomon-Ciuta equation.

The carboxyl end group content (CC) was determined according to Pohl's method.²⁰ The hydroxyl end group content (HC) was determined according to the method proposed by Zimmermann and Kolbig²¹ reported also by Weisskopf.²² The latter is based on the reaction of the hydroxyl end groups on PET with *o*-sulfobenzoic acid cyclic anhydride.

The epoxy content (EC) of compounds **Ia** and **Ib** was determined by the pyridinium chloride-pyridine method as described in literature.²³ Compound **Ia** was insoluble in pyridine and was not subjected to this determination. The EC is expressed in terms of epoxide equivalent or epoxy equivalent weight and

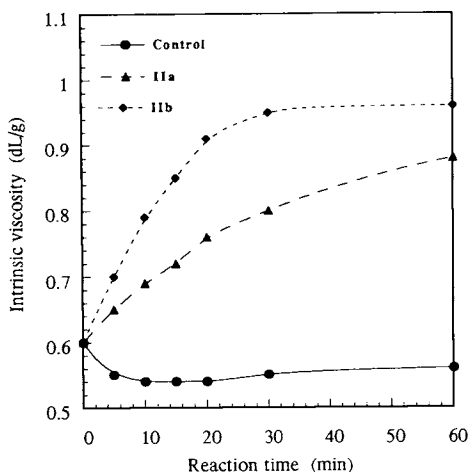


Figure 1. PET: Variation of $[\eta]$ with reaction time.

is defined as the weight of compound in grams which contain 1 g-equiv of epoxy.

The degree of crosslinking²⁴ (DC) defined as the percentage of the insoluble gel was determined as follows: 250 mg of polyester was dissolved in 25 mL of solvent phenol/tetrachloroethane (60 : 40) at 120°C for 1 h. After removal of the soluble portion by filtration, the insoluble gel was washed with acetone, and dried to constant weight by heating under vacuum.

RESULTS AND DISCUSSION

The diepoxides prepared in the present work are new compounds and their structure was well characterized by determination of melting point, epoxy content, elemental analysis and IR spectra. To check if they can be added to polyester melts we studied their thermal stability by DSC. The DSC thermogram of **Ia** showed an exotherm at 302°C and **Ib** at 347°C. Analogous exotherms were also detected in the DSC thermograms of diepoxides prepared in our previous work¹⁴ (**Ic–Ie**): **Ic** ($R = p$ -phenylene) at 328°C, **Id** ($R = m$ -phenylene) at 335°C and **Ie** ($R =$ methylene) at 353°C. These exotherms must be due to the epoxy groups of compounds, because they were also observed by other investigators in diepoxides with quite different structure than ours and were attributed to decomposition, isomerization and polymerization of epoxy groups.^{25,26}

Diepoxide **Ia** or **Ib** was added in PET melt with intrinsic viscosity 0.60 dL/g, carboxyl content 42 equiv/ 10^6 g and hydroxyl content 91 equiv/ 10^6 g or in PBT melt with $[\eta] = 0.84$ dL/g, CC = 44 equiv/

10^6 g and HC = 60 equiv/ 10^6 g. The theoretical amount of the chain extender to be added in the polyester melt was calculated from the equation:⁶

$$w \% = \frac{MW \times CC_o}{2 \times 10^4}$$

where MW is the molecular weight of the chain extender and CC_o the carboxyl content of the initial polyester. As theoretical amount we mean the quantity of chain extender which is needed so that 1 mol of chain extender reacts with 2 mol of polyester, assuming that only the carboxyl groups will react in this process. The latter is not quite true because as it is known both carboxyl and hydroxyl groups can react with epoxy groups. However it is reported

that the reaction of an epoxide $\begin{matrix} \diagdown & & / \\ & O & \end{matrix}$ with an acid (R_1COOH) in an absence of catalyst preferably gives hydroxy ester (R_1COOCH_2CHROH or $R_1COOCHRCH_2OH$) than ether ($R_1COOCH_2CHROCH_2CHROH$) which is the product of reaction of the above hydroxy ester with the epoxide.²⁷ Also it is reported that carboxyl groups react more preferentially than hydroxyl groups with electrophilic groups such as epoxy groups.^{2,5} The chain extending reaction was monitored by viscometry (Figs. 1–3), carboxyl end group content (Fig. 4 and 5) and hydroxyl content (Fig. 6 and 7).

While the heating of thoroughly predried PET or PBT melt is accompanied with a decrease of viscosity, an opposite effect was observed in the presence of the diepoxide **Ia** or **Ib**. From Figure 1, one may note that diepoxide **Ib** is more efficient as chain

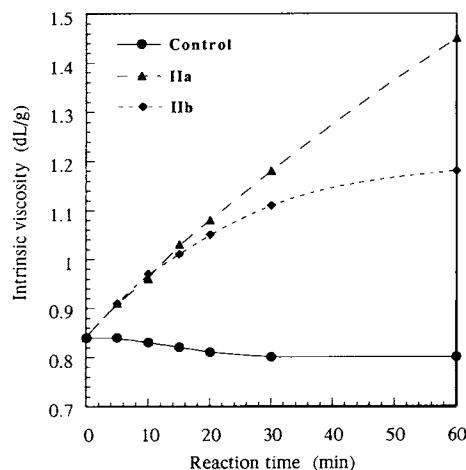


Figure 2. PBT: Variation of $[\eta]$ with reaction time.

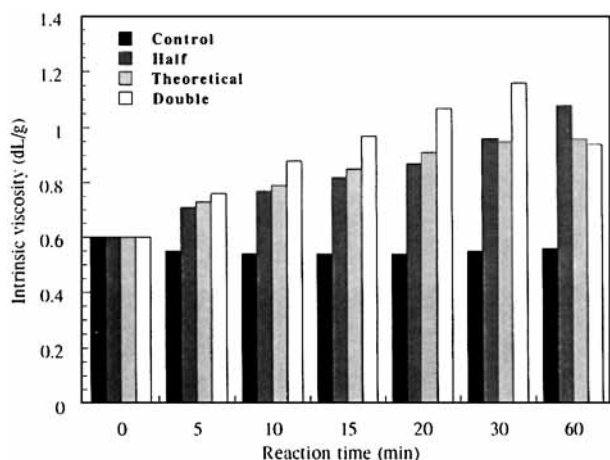


Figure 3. PET: Variation of $[\eta]$ with reaction time at three different added amounts of chain extender **Ib**.

extender than **Ia** in the case of PET. This behavior is inverted however in the case of PBT (Fig. 2). This behavior may be due to the different temperature of application which is 280°C for PET and 250°C for PBT. The temperature of 280°C seems to be very high for compound **Ia** which melts at 165°C. When the double quantity of theoretical amount of chain extender **Ib** was added to PET melt a decrease of viscosity was observed after 30 min of reaction (Fig. 3) due most probably to the concurrent formation of branching through the reaction of pendant hydroxyl groups of macromolecules with the excess of diepoxide.

The results obtained from the determination of the carboxyl end groups content of PET and PBT

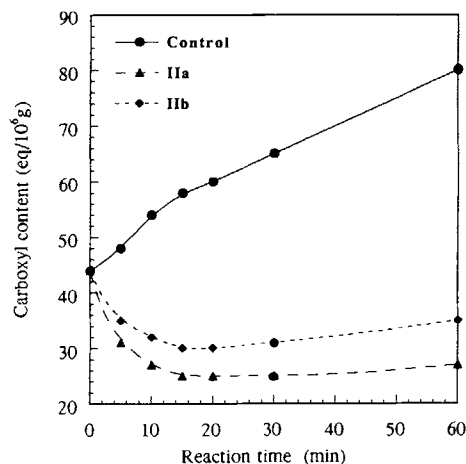


Figure 5. PBT: Variation of CC with reaction time.

samples obtained after heating with **Ia** or **Ib** for a certain time (Figs. 4 and 5) confirmed that diepoxide **Ib** is a better chain extender than **Ia** for PET and the inverse happens for PBT.

As far as the hydroxyl content of the samples is concerned, this remained about the same in the blank experiment for both polyesters during the first 20 min of reaction (Figs. 6 and 7). After that, a decrease took place which was more pronounced in the case of PET and is attributed to the continuation of polycondensation. However in presence of a chain extender during the first 20 min a considerable increase of hydroxyl content was observed in both polyesters. This is a clear indication that carboxyl groups react with diepoxide, because this reaction is accompanied by the generation of hydroxyl groups.

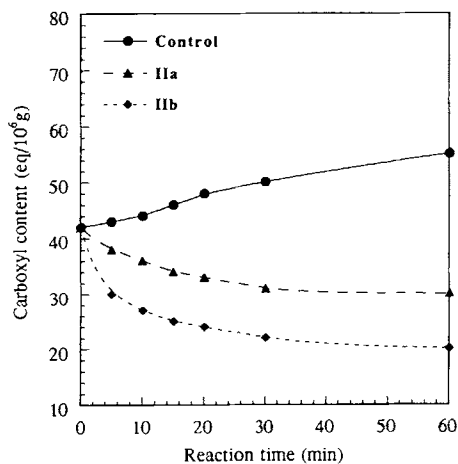


Figure 4. PET: Variation of CC with reaction time.

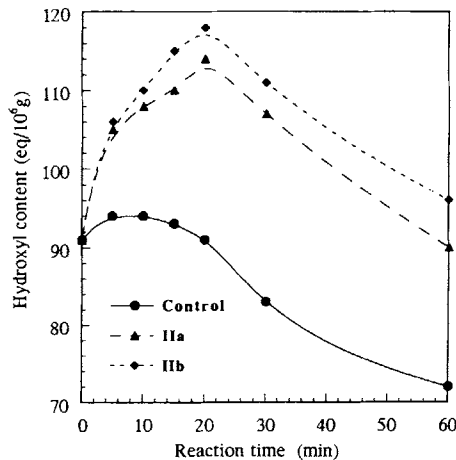


Figure 6. PET: Variation of HC with reaction time.

However we can not exclude the occurrence of the reaction between hydroxyl end groups with diepoxide, because this leads to the formation of a new hydroxyl group. Since the reaction of the hydroxyl group with the epoxy group can not affect the hydroxyl content, the observed decrease of hydroxyl content after 20 min must be attributed to the decomposition of the hydroxyethylester end group into carboxylic acid and acetaldehyde.¹⁴

In the chain extended polyester samples an insoluble residue was detected from viscometric solutions and determined gravimetrically in the case of PET chain extended by diepoxide **Ib** (Fig. 8). In all other cases, i.e., for compound **Ia** or for both compounds in the case of PBT, this residue was negligible and it appeared after 30 min or even more time of reaction. This residue most probably due to crosslinked polymer the amount of which depends on the reaction time and the added amount of chain extender.

Taking into account the results of our previous work¹⁴ as well as those of the present we can arrive at the following conclusions. Diimidodiepoxides are compounds with satisfactory chain extension ability for saturated thermoplastic polyesters providing that their melting point is lower than that of application temperature. By selecting the appropriate chain extender for a given polyester, controlling its amount and the reaction time, it is possible to obtain polyesters with predetermined properties as for example with a specified limited degree of crosslinking.

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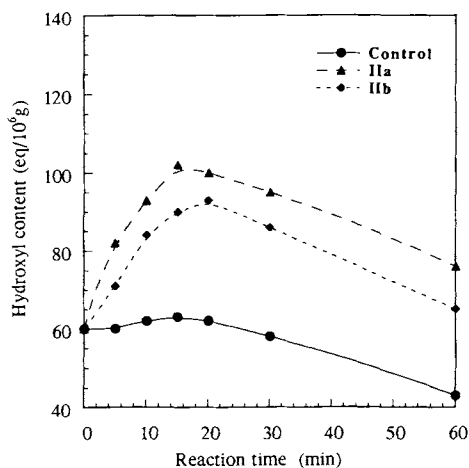


Figure 7. PBT: Variation of HC with reaction time.

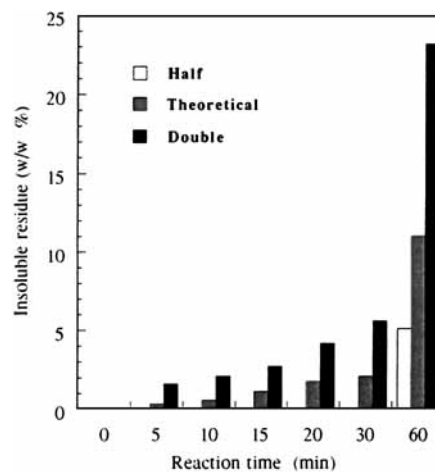


Figure 8. PET: Variation of insoluble residue with reaction time at three different added amounts of chain extender **Ib**.

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