Chain Extension of Poly(ethylene terephthalate) by Reactive Blending Using Diepoxides

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ABSTRACT: Molecular weight increase via chain extension reactions of poly(ethylene terephthalate) with commercially available diepoxides was studied in a custom-made laboratory scale reactor and a Brabender rheomixer under reactive blending conditions. The products were characterized by carboxylic end group analysis, intrinsic viscosity, and differential scanning calorimetry. PET was effectively modified in the laboratoryscale reactor using cyclic diepoxides because the resulting polymers show intrinsic viscosities that are comparable to virgin PET (0.68-0.75 dL/g vs. 0.74 dL/g) and much higher than processed PET (0.55), while carboxyl contents were reduced to a third of that of the virgin PET. Diglycidyl ethers produced polymers displaying decreased viscosity values, increased carboxyl content, and lower melting points. Low concentrations of extender and short reaction times generally favored chain extension. In addition, purging with nitrogen resulted in chain extended polymers having the highest values of intrinsic viscosity ($[\eta] = 0.79, 0.82$). Similar trends were observed with modified products in the rheomixer having somewhat smaller viscosity values, larger carboxyl contents, and increased melting points. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2121-2127, 1999

Keywords: chain extension; poly(ethylene terephthalate); diepoxides; reactive blending

INTRODUCTION

The mechanical and chemical properties displayed by poly(ethylene terephthalate) (PET)^{1,2} have rendered it a useful polymer for significant practical applications. However, its production through polycondensation leads to low molecularweight polymers together with an increased number of terminal carboxyl group content. Moreover, during processing at high temperatures, thermal and/or hydrolytic processes occur, which produce additional carboxylic end groups and also decrease the molecular weight of the polyester.^{3–5} Research should, therefore, be directed to the production of polymers with increased molecular

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weights (or increased intrinsic viscosity) and low carboxyl content.

The problem was initially approached by adding bifunctional acid derivatives during polycondensation,⁶ which although resulted in improved polyester products, was associated with volatile formation and lack of reaction control. This work, however, triggered the use of bifunctional compounds of various chemical structures, known as chain extenders. These compounds increased the molecular weight of the polymer and they simultaneously eliminated the carboxylic end groups. A diversity of compounds has been used as chain extenders for poly(ethylene terephthalate). In two patent disclosures isocyanates, anhydrides, and epoxides were used^{7,8} in molding formulations. Triphenyl phosphite was used for chain extension, affording polymers with increased intrinsic viscosity accompanied by decreasing hydroxyl

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and slightly decreased carboxyl content.⁹ Much work has been carried out by Inata et al. with carboxyl^{10,11,14,15} and hydroxyl^{12,13} addition-type heterocyclic bifunctional compounds such as oxazolines, oxazines, or oxazinones. These compounds reacted with the carboxyl or hydroxyl end groups of PET and resulted in improved chainextended polymers with very low carboxyl content. Oxazolines were very effective in additiontype reactions, and were used extensively in reactive extrusion processes for the modification of a wide variety of industrial polymers^{16,17} including PET. Recently, a new family of diepoxides (N,N'-Bis(glycidyl ester) pyromellitimides), was synthesized and employed under controlled conditions for the chain extension of PET and PBT leading to enhanced intrinsic viscosity and reduced carboxyl content.¹⁸⁻²⁰ When the epoxide ring opens during the reaction, a new hydroxyl group is created that can branch to a limited extent. This is reportedly considered advantageous for polymer melts used in molding compositions.²¹

In this work, chain-extending reactions of PET were performed using commercially available diepoxides widely employed in the epoxy resin industry. Reactive blending or reactive extrusion is the preferred methods for simultaneous modification and processing of a large number of industrially important polymers.^{22,23} For this reason a custom-made laboratory-scale mixer^{24,25} and a Brabender rheomixer were used for reactions in the melt.

EXPERIMENTAL

Materials

PET grade 9236 of intrinsic viscosity $[\eta] = 0.74$ g/dL was supplied by Akzo Chemie. Bis(3,4-epoxycyclohexylmethyl)adipate (I) and 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexyl carboxylate (II) are products of Union Carbide; 1,4-cyclohexanedimethanol diglycidyl ether (III) and 1,4-butanediol diglycidyl ether (IV) were purchased from Aldrich; diglycidyl ether of bisphenol A (V) is a Dow Chemical product. All epoxides were used as received. The structures of the chain extending reagents are shown in Scheme 1.

Chain Extension Reaction

The chain extension reactions were performed in a stainless steel custom-made laboratory-scale re-



actor described elsewhere,²⁴ and a medium-scale Brabender rheomixer. For reactions performed in the laboratory-scale reactor the virgin PET granules were finely ground and exhaustively dried under vacuum for 24 h at 120°C. The chain extender was dissolved in 2 mL of dry methylene chloride, the solution was added to the dry PET powder, and the solvent was removed under vacuum, leaving the polymer evenly coated with the extender. Extender quantities ranged from one to eight times the theoretical amount based on the carboxyl content of virgin PET (0.5–4 wt % of the polymer). The mixture was allowed to react under stirring at 270°C, with a speed of 80 rpm and reaction times of 5 and 10 min.

In the reactions performed in the Brabender rheomixer, equipped with a Plasticorder PL 2000-6 and a mixer head type W50E with three heating zones, dried PET pellets (50-60 g) were mixed with one and two times the theoretical amount of the extender (0.5-1 wt %), at 270°C and 50 rpm for 2.5 or 5 min.

For simplifying reaction conditions nitrogen atmosphere was not used in most of the experiments except in three cases for comparative purposes. The processed polymers were powdered, washed thoroughly with acetone to remove the unreacted diepoxides, dried, and used for characterization.

Characterization

Carboxyl content of polyesters was determined by the titration method described by Pohl.²⁶ Solution viscosity measurements were carried out in a Cannon-Ubbelohlde dilution viscometer at 35 \pm 0.1°C in *o*-chlorophenol solutions of approximate 0.6 dL/g initial concentration. The intrinsic viscosity, [η], was determined by extrapolation using the Huggins equation. The limits of error in these solution viscosity experiments were calculated as $\pm 5\%$.

Thermal transitions of virgin and modified PET were determined on a TA Instruments DSC 10 calorimeter, coupled with a 2010 Controller. Both T_g and T_m were obtained at the second heating according to ASTM D3418-82 at a heating rate of 15°C/min. Thermal stabilities were determined on a TA Instruments TGA 2050 thermogravimetric analyzer at a heating rate of 15°C/min. The experiments were performed under inert atmosphere.

RESULTS AND DISCUSSION

Reactive Blending Methods

The diepoxides used in this work were low-cost, industrially produced materials. Their high boiling points well exceeded the reaction temperature of 270°C, therefore permitting their use in the reactive blending process. Structurally, two classes of epoxides were employed: the first (compounds I and II) with the epoxide group condensed on cyclohexyl groups, and the second (compounds III, IV and V) with epoxide group at both ends of aliphatic diethers.

Virgin polyester was ground and coated with the diepoxide before hand to facilitate processing. The theoretical amount, that is, the quantity of diepoxides needed for 1 mol of the extender to react with 2 mol equivalents of carboxy-terminated PET, was calculated⁸ to be about 0.5 wt % of the polymer, taking into account the molecular weight of the extender and the carboxyl content of the virgin polyester used (42 eq/ 10^6 g). In our experiments multiples of the theoretical quantity (0.5, 1, 2, 3, and 4 wt %) were employed for investigating the effect of added extender on the outcome of the reaction with the assumption that only carboxyl groups react with epoxides. In fact, carboxylic groups are more reactive towards electrophilic groups²⁷ compared to hydroxy groups,

which is the other reactive end group in the PET molecule.

Intrinsic Viscosity and Carboxyl Content

The property that characterizes chain-extended polyesters is their intrinsic viscosity $[\eta]$, which is a direct measure of the molecular weight of the polymer and which is very sensitive to small variations of the polymer chains. Carboxyl content is a significant quantity because the carboxylic group is participating in the extension reaction and is also formed by thermal and hydrolytic degradation. Monitoring carboxylic end groups therefore provides information on the course of the reaction, which, combined with intrinsic viscosity values give an estimate of the type of chain extended polymer, i.e., linear or branched. Branching could occur, at high temperatures, between an epoxide and a hydroxyl group that is formed by the reaction of a carboxylic group with an epoxide. In general, linear chain extension is probed by high viscosity and low carboxyl content, while branching is evidenced by intermediate viscosity and low carboxyl content.²⁸

Tables I–V display the results of the reactions of PET with the various chain extenders under various conditions. Modified PET polymers in the laboratory scale reactor obtained after 5 min show increased intrinsic viscosity values and decreased carboxyl content with respect to the processed PET-1 and a strong dependence on the type of extender. Compared to virgin PET-V, intrinsic viscosity values are equal (Tables I and II) for extenders I, II, or smaller, but carboxyl contents are still favorably low. In general, the best chain extending capability is displayed by the cycloaliphatic diepoxide II followed by cycloepoxide I with the longer spacer. Among the diglycidyl ethers, extender III gives to PET higher intrinsic viscosity and lower carboxyl content than processed PET (Table III). In the presence of theoretical amount (0.5 wt %) of V (Table V), PET displays a high $[\eta]$ value that decreases sharply with larger amounts. At the same concentration, extender II results in polymers having a relatively low intrinsic viscosity. However, at a concentration that is twice the theoretical amount of II, modified PET displays its highest intrinsic viscosity value and the lower carboxyl content among all the chain extended polyesters (entry II-1, Table II). Extenders I and III, on the other hand, are effective at higher concentrations (3 wt %, Tables I and III). In this case, the intrinsic viscosity curves show maximum values.

Reaction Product	Added Chain Extender (% wt)	Reaction Time/Reactor (min)	$\mathop{T_g}_{(^\circ\mathrm{C})}$	T_m (°C)	$[\eta]$ (dL/g)	Carboxyl Content (eq/10 ⁶ g)
PET-1	_	Virgin	81	249.6	0.73	42
PET-2	_	5	78	251.7	0.55	67
PET-3	_	10	78	251.0	0.52	70
PET-4	_	$5(N_2)$	79	251.4	0.60	59
PET-5	_	4 (Brab)	80	254.5	0.59	56
I-1	0.5	5	75	249.4	0.70	12
I-2	1	5	70	247.2	0.68	16
I-3	2	5	68	246.4	0.65	19
I-4	3	5	70	246.5	0.72	16
I-5	4	5	53	243.6	0.68	17
I-6	1	$5(N_2)$	72	247.5	0.79	26
I-7	0.5	10	74	248.3	0.64	25
I-B1	0.5	2.5 (Brab)	73	252.0	0.68	30
I-B2	0.5	5 (Brab)	75	253.6	0.64	37

Table I Thermal Transitions, Intrinsic Viscosity, and Carboxyl Content of Virgin, Processed, and Chain-Extended PET with Extender I in the Lab-Scale Reactor and the Brabender Rheomixer at 270°C

Enhanced reaction times normally lead to the completion of the chain extension. However, the degradation reactions¹ that are responsible for low intrinsic viscosity and high carboxyl content are also operating. Thus, virgin PET processed for 10 min (Table I, PET-3) shows a very low intrinsic viscosity (0.52 dL/g) and a large carboxyl content (70 eq/10⁶ g). The decreasing intrinsic viscosities and increasing carboxyl contents of the 10-min

reaction products in the laboratory scale reactor (Tables I–V; entries I-7, II-7 to II-10, III-6, IV-6, V-6) indicate less effective chain coupling reactions that must be mainly attributed to thermal degradation due to prolonged heating. The larger $[\eta]$ decrease is displayed by extender V, which may be attributed to branching via reaction with the hydroxyl groups. It should be noted that this extender bears phenyl groups that are known to

 Table II
 Thermal Transitions, Intrinsic Viscosity, and Carboxyl Content of Chain-Extended PET

 with Extender II
 II

Reaction Product	Added Chain Extender (% wt)	Reaction Time (min)	$\mathop{T_g}_{(^\circ\mathrm{C})}$	T_m (°C)	[η] (dL/g)	Carboxyl Content (eq/10 ⁶ g)
II-1	0.5	5	78	249.2	0.71	16
II-2	1	5	74	249.2	0.75	6
II-3	2	5	68	246.5	0.71	15
II-4	3	5	71	248.5	0.73	11
II-5	4	5	56	244.7	0.70	10
II-6	1	$5(N_2)$	74	248.5	0.82	24
II-7	0.5	10	77	248	0.62	27
II-8	1	10	77	247.7	0.67	22
II-9	2	10	70	247.7	0.67	17
II-10	3	10	67	246.1	0.68	16
II-B1	0.5	2.5 (Brab)	78	251.4	0.71	26
II-B2	0.75	2.5 (Brab)	75	252	0.68	29
II-B3	1	2.5 (Brab)	76	252	0.68	30
II-B4	0.5	5 (Brab)	80	253	0.66	24
II-B5	1	5 (Brab)	78	253	0.64	29

Reaction Product	Added Chain Extender (% wt)	Reaction Time (min)	T_{g} (°C)	T_m (°C)	[η] (dL/g)	Carboxyl Content (eq/10 ⁶ g)
III-1	0.5	5	74	250.3	0.65	28
III-2	1	5	69	249.1	0.65	32.3
III-3	2	5	66	249.2	0.63	34
III-4	3	5	62	249.6	0.66	29
III-5	4	5	58	248.0	0.54	27.1
III-6	0.5	10	78	249.3	0.59	36

 Table III
 Thermal Transitions, Intrinsic Viscosity, and Carboxyl Content of Chain-Extended PET

 with Extender III at Two Different Reaction Times

accelerate the reaction of epoxide groups with hydroxyl moieties.²⁴ The formation of carboxylic groups due to degradation can be offset by the presence of larger quantities of added extender. This is shown when increasing amounts of extender II were employed (Table II; II-7, II-8, II-9, II-10) in 10-min reactions. The greater number of epoxide groups react further with the carboxyl groups, created by degradation with concurrent increase in intrinsic viscosity and decrease in the carboxylic content of polyesters. For the reasons mentioned above, a reaction duration of 5 min was chosen for most of the experiments.

For establishing that moisture has a negative effect on the chain extension of PET, two experiments were carried with extenders I and II at twice the theoretical amount (1 wt %) in nitrogen atmosphere. The modified polyesters exhibited intrinsic viscosities of 0.79 and 0.82, respectively, which are the largest obtained in our experiments (Table I, I-6; Table II, II-6). In addition, the carboxyl contents for these two modified polyesters were higher compared to the ones performed under open atmosphere conditions (26 and 27 eq/10⁶) compared to 6 and 15). Therefore, chain extension is enhanced while decarboxylation is reduced.

The use of the Brabender rheomixer for the modification of PET was expected to result in improved modified polyesters by providing efficient mixing and better control of temperature and mixing speed compared to laboratory reactor. However, the soobtained chain-extended polymers exhibited comparable behavior to the modified polymers obtained in the laboratory scale reactor. This is shown from the intrinsic viscosity and carboxyl content values listed in Tables I–V. The experiments were run at the theoretical or twice the theoretical concentration of extenders I, II, and V and for periods of 2.5 and 5 min. The shorter reaction times were chosen because after 5 min the torque in the mixer was getting equal to that of processed PET without the extender. In general, 5-min reaction experiments provided lower molecular weight polyesters compared to products of 2.5-min experiments, as is shown by the lower values of viscosity and the higher carboxyl contents (IB-1, IB-2; IIB-1, IIB-4, IIB-3, IIB-5; VB-1, VB-2). These results indicate that the reaction proceeds fast and further heating

Reaction Product	Added Chain Extender (% wt)	Reaction Time (min)	T_{g} (°C)	T_m (°C)	[η] (dL/g)	Carboxyl Content (eq/10 ⁶ g)
IV-1	0.5	5	80	251.2	0.62	35.3
IV-2	1	5	78	250.4	0.55	41.4
IV-3	2	5	71	249.3	0.61	40.2
IV-4	3	5	68	248.3	0.58	32.3
IV-5	4	5	68	248.0	0.55	30
IV-6	0.5	10	77	249.6	0.54	41

 Table IV
 Thermal Transitions, Intrinsic Viscosity, and Carboxyl Content of Chain-Extended PET

 with Extender IV at Two Different Reaction Times

Reaction Product	Added Chain Extender (% wt)	Reaction Time (min)	T_{g} (°C)	T_m (°C)	[η] (g/dL)	Carboxyl Content (eq/10 ⁶ g)
V-1	0.5	5	77	249.6	0.67	20
V-2	1	5	68	248.2	0.50	27
V-3	2	5	68	247.7	0.55	28
V-4	3	5	67	245.9	0.58	26
V-5	4	5	56	245.7	0.44	31
V-6	0.5	10	77	249.5	0.55	33
V-B1	0.5	2.5(Brab)	78	251.9	0.69	36
V-B2	0.5	5 (Brab)	79	252.5	0.65	39

Table V Thermal Transitions, Intrinsic Viscosity, and Carboxyl Content of Chain-Extended PET with Extender V at Two Different Reaction Times

leads to degradation of the products. Among the three extenders tested, extender V displayed a rather significant improvement in $[\eta]$ for both reaction times used ($[\eta] = 0.69$ and 0.65 for 2 and 4 min reaction time, respectively). This is in agreement with the results obtained in the laboratory mixer mentioned previously in this article (Table I, V-1), which established the satisfactory behavior of extender V at low concentrations.

Comparing the intrinsic viscosities and carboxyl contents of the products of this work with those obtained with custom-made diepoxides^{18,19} or heterocyclic bifunctional compounds,^{10–15} it is seen that the diepoxides employed in this study are less effective in chain-extending reactions. However, our results were obtained employing low-cost commercially available materials, which was the major scope of this work.

Thermal Studies

The thermal transitions of chain-extended polymers obtained in the laboratory scale reactor display a decreasing trend with increasing concentration of an extender and longer reaction time. This behavior is in agreement with increasing the chain length, modifying polymers from linear to branched. In any case, the introduction in the polymer chains of new segments and new linkages due to the reaction with the extenders is expected to affect the crystallization behavior, leading to lower melting ranges. When the extension creates branching, which usually occurs at higher concentrations and longer reaction times, the melting points of the polymers decrease even further. The amorphous regions of the chain-extended polyesters increase as a consequence of the presence of extender molecules deliberately linked with polymer chain ends. These irregularities in the polymer molecules create increased segmental mobility leading, in turn, to depressed T_{g} .

Modified polymers produced in the rheomixer display somewhat higher transitions than polymers modified in the laboratory reactor. It may be suggested that the type of mixing achieved in this equipment is responsible for the observed transitions. These differentiations can be attributed to the low levels of branching in these polyesters, as shown by the combination of medium values of $[\eta]$ and carboxyl content in conjunction with high values of T_m .

CONCLUSIONS

The modified polyesters obtained by chain extension reactions with the diepoxides in question in the molten phase exhibited intrinsic viscosities higher than the processed PET, and in some cases, equal or higher than virgin, unprocessed PET. In addition, carboxyl contents were reduced to values well below that of virgin PET. Cyclic diepoxides proved to be more effective chain extenders than diglycidyl ethers. The reaction is fast and the theoretical amount of the extender is sufficient for effective chain extension. Short reaction times and a decrease of moisture promoted effective chain extension by suppressing thermal and hydrolytic degradation, respectively.

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