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[54] **COPOLYESTER-ETHER POLYMERS**

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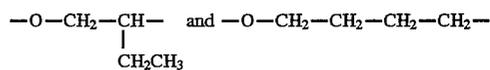
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[57] **ABSTRACT**

A segmented copolyester-ether polymer comprises 9.5 to 33 percent by weight hard segment residues of polybutylene terephthalate and 0.5 to 67 percent by weight soft segment residues of a polyether polyol comprised of n units of

residue (1) and m units of residue (2), wherein the total value of n+m is in the range 2 to 70, m/(n+m) is in the range 0.05 to 0.98, and residues (1) and (2) have the structures:



(1)

(2)

The polyether polyol is further characterized in that at least 95 percent of the hydroxyl groups are primary hydroxyl groups.

### 3 Claims, No Drawings

**A statutory invention registration is not a patent. It has the defensive attributes of a patent but does not have the enforceable attributes of a patent. No article or advertisement or the like may use the term patent, or any term suggestive of a patent, when referring to a statutory invention registration. For more specific information on the rights associated with a statutory invention registration see 35 U.S.C. 157.**





A 100-mL flask was charged with the following reagents: 11.2 g (0.0100 mole) of the polyether glycol prepared in Reference Example 1, 19.4 g (0.100 mole) dimethyl terephthalate, 12.62 g (0.140 mole) 1,4-butanediol, 33.7 mg Irganox-1010 (about 2000 ppm in final polymer) and 12 mg titanium tetraisopropoxide (about 50 ppm Ti in final polymer). The flask was equipped with a polymer head having an argon/vacuum inlet, a short distillation column and a metal stirrer. The flask was given an argon atmosphere by alternating vacuum and argon three times. The flask was then placed in a Belmont metal bath preheated to 200° C., and with stirring under dynamic argon atmosphere, the contents of the flask formed a melt solution. The contents of the flask were heated at 200° C. with stirring for about 2 hr to effect ester interchange and distill methanol from the flask. Then the temperature was increased to 245° C., and a vacuum of 0.2 mm was gradually applied over the next 10 min. Full vacuum was maintained for about 45 min while the temperature was maintained at 245° C. A high melt viscosity, semi-crystalline polymer was obtained having inherent viscosity of 1.12. Thermal analyses showed a DSC peak melting point at 197° C. and a TGA 10 percent mass loss in nitrogen at 371° C. A 120-mil thick disc pressed at 245° C. had D-scale shore hardness of 45 and a density of 1.20 g/ml. Tensile properties obtained from 10-mil thick films pressed at 245° C. showed Young's modulus of 176 MPa, yield stress of 17 MPa, yield strain of 26 percent, break stress of 27 MPa and break strain of 400 percent.

## Examples 2-5

These examples illustrate the preparation of the copolyester-ether polymers comprising poly(butylene terephthalate) residues and 9, 34, 45 and 60 percent by weight, respectively, residues of the polyether glycol prepared largely as described in Example 1 and are described in Table 1.

TABLE 1

Example	Analyses of Examples 3-6				
	2	3	4	5	6
Wt. % PPBG	9	34	36	45	60
Reaction Time					
Total (minutes)	153	167	120	162	149
Vacuum (minutes)	82	90	45	59	34
Inherent Viscosity (dL/g)	1.12	1.08	1.12	1.1	0.417
DSC					
Tm (°C.)	222	194	197	180	127
Tg (°C.)		-32	-26	-36	-42
DMA					
T (tanδmax) (°C.)	—	-18	-18	-27	—
tanδmax	—	0.195	0.185	0.342	—
TGA					
10% Mass Loss in Air (°C.)	360	347		321	314
Shore Hardness (D Scale)	47	44	44	39	13
Density (g/ml)	1.29	1.21	1.20	1.18	1.11
Young's Modulus (MPa)	768	165	157	84	—

## Comparative Example 1

This example illustrates the preparation of a comparative copolyester-ether comprising 67 percent by weight poly

(butylene terephthalate) residues and 33 percent by weight polytetramethylene glycol (PTMG) residues.

A 100-mL flask was charged with the following reagents: 10.6 g (0.0100 mole) of polytetramethylene glycol (MW 1000, Aldrich Cat. No. 34,529-6), 19.4 g (0.100 mole) dimethyl terephthalate, 12.62 g (0.140 mole) 1,4-butanediol, 33.7 mg Irganox-1010 (about 2000 ppm in final polymer) and 12 mg titanium tetraisopropoxide (about 50 ppm Ti in final polymer). The flask was equipped with a polymer head having an argon/vacuum inlet, a short distillation column and a metal stirrer. The flask was given an argon atmosphere by alternating vacuum and argon three times. The flask was then placed in a Belmont metal bath preheated to 200° C., and with stirring under dynamic argon atmosphere, the contents of the flask formed a melt solution. The contents of the flask were heated at 200° C. with stirring for about 2 hr to effect ester interchange and distill methanol from the flask. Then the temperature was increased to 245° C., and a vacuum of 0.2 mm was gradually applied over the next 10 min. Full vacuum was maintained for about 45 min while the temperature was maintained at 245° C. A high melt viscosity, semi-crystalline polymer was obtained having inherent viscosity of 1.17 g/dL. Thermal analyses showed a DSC peak melting point at 197° C. and TGA 10 percent mass loss in nitrogen at 371° C. A 120-mil thick disc pressed at 245° C. had D-scale shore hardness of 53 and a density of 1.20 g/ml. Tensile properties obtained from 10-mil thick films pressed at 245° C. showed Young's modulus of 194 MPa, yield stress of 18 MPa, yield strain of 31 percent, break stress of 38 MPa and break strain of 680 percent.

## Comparative Examples 2-5

These examples illustrate the preparation of comparative copolyester-ethers using polytetramethylene glycol. The polymers were prepared largely as described in Comparative Example 1 and are described in Table 2.

TABLE 2

Example	Analyses of Comparative Examples 2-5			
	2	3	4	5
Wt. % PTMG	9	29	44	66
Reaction Time				
Total (minutes)	132	146	150	142
Vacuum (minutes)	61	36	40	39
Inherent Viscosity (dL/g)	0.925	0.965	1.02	0.661
DSC				
Tm (°C.)	226	215	195	141
Tg (°C.)	—	-16	-19	—
DMA				
T (tanδmax) (°C.)	—	-26	-52	—
tanδmax	—	0.099	0.185	—
TGA				
10% Mass Loss in Air (°C.)	370	350	336	245
Shore Hardness (D Scale)	44	54	41	18
Density (g/ml)	1.25	1.21	1.16	1.09
Young's Modulus (MPa)	886	326	110	—

## Comparative Example 6

This example illustrates the preparation of a comparative copolyester-ether comprising 67 percent by weight poly

(butylene terephthalate) residues and 33 percent by weight polybutylene glycol (PBG) residues, wherein the polybutylene glycol contains only secondary hydroxyl groups.

A 100-mL flask was charged with the following reagents: 10.0 g (0.0100 mole) of polybutylene glycol (MW 1000, Dow Chemical Co. research sample of B100-1000, Lot No. TB920421-3936), 19.4 g (0.100 mole) dimethyl terephthalate, 12.6 g (0.140 mole) 1,4-butanediol, 33.7 mg Irganox-1010 (about 2000 ppm in final polymer) and 12 mg titanium tetrakisopropoxide (about 50 ppm Ti in final polymer). The flask was equipped with a polymer head having an argon/vacuum inlet, a short distillation column and a metal stirrer. The flask was given an argon atmosphere by alternating vacuum and argon three times. The flask was then placed in a Belmont metal bath preheated to 200° C., and with stirring under dynamic argon atmosphere, the contents of the flask formed a melt solution. The contents of the flask were heated at 200° C. with stirring for about 4.5 hr then heated at 220° C. with stirring for about 3 hr to effect ester interchange and distill methanol from the flask. Then the temperature was increased to 245° C., and a vacuum of 0.3 mm was gradually applied over the next 5 min. The melt viscosity increased slowly, and full vacuum was maintained for about 2.2 hr while the temperature was maintained at 245° C. A semi-crystalline polymer was obtained having inherent viscosity of 0.84 g/dL. Thermal analyses showed a DSC peak melting point at 213° C. and TGA 10 percent mass loss in nitrogen at 361° C.

The polymer product was ground to pass a 20 mesh (850 micron) screen, dried under vacuum at 100° C. and then subjected to solid state polymerization by slowly increasing the temperature from 160° to 200° C. over a period of 4 hr while maintaining vacuum of 0.1 mm Hg then holding at 200° C. for 2 hr while maintaining vacuum of 0.1 mm Hg, giving a high-molecular weight polymer having inherent viscosity of 1.05 g/dL. Thermal analyses showed a DSC peak melting point at 216° C. and TGA 10 percent mass loss in nitrogen at 356° C. A 120-mil thick disc pressed at 245°

C. had D-scale shore hardness of 52 and a density of 1.20 g/ml. Tensile properties obtained from 10-mil thick films pressed at 245° C. showed Young's modulus of 130 MPa, yield stress of 14 MPa, yield strain of 32 percent, break stress of 27 MPa and break strain of 400 percent.

The copolyester-ether polymers of the present invention have a cost advantage over similar materials of the prior art because (i) the polyether polyol used to prepare the copolyester-ether polymer are typically available at a cost below that of polytetramethylene glycol, which is the industry standard, and (ii) the copolyester-ether polymer of this invention may be prepared directly from the melt within rather short reaction times due to the primary hydroxyl groups of the polyether polyol used.

We claim:

1. A segmented copolyester-ether polymer comprising:

(a) 99.5 to 33 percent by weight hard segment residues of polybutylene terephthalate and

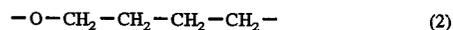
(b) 0.5 to 67 percent by weight soft segment residues of a polyether polyol comprising:

(i) n units of residue (1) having the formula:



and

(ii) m units of residue (2) having the formula:



wherein the total value of n+m is in the range 2 to 70, m/(n+m) is in the range 0.05 to 0.98.

2. The segmented copolyester-ether polymer of claim 1 wherein the polyether polyol has at least 95 percent primary terminal hydroxyl groups.

3. The segmented copolyester-ether polymer of claim 1 prepared by melt condensation polymerization.

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