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(72) Inventeurs/Inventors:
MANG, MICHAEL N., US;
WHITE, JERRY E., US

(73) Propriétaire/Owner:
DOW GLOBAL TECHNOLOGIES INC., US

(74) Agent: SMART & BIGGAR

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(54) Title: HYDROXY-FUNCTIONAL POLYESTERS AS THERMOPLASTIC BARRIER RESINS

(57) **Abrégé/Abstract:**

Polyesters having improved barrier to oxygen are normally solid, thermoplastic methylol polyesters having backbone repeating units containing pendant hydroxyl and methylol moieties and divalent organic moieties such as m-phenylene, p-phenylene, and isopropylidene diphenylene. Such polyesters are prepared by reacting diglycidyl esters of aromatic diacids such as diglycidyl terephthalate or diglycidyl ethers of dihydric phenols with diacids such as isophthalic acid.



ABSTRACT

5

Polyesters having improved barrier to oxygen are normally solid, thermoplastic methylol polyesters having backbone repeating units containing pendant hydroxyl and methylol moieties and divalent organic moieties such as m-phenylene, p-phenylene, and isopropylidene diphenylene. Such polyesters are prepared by reacting diglycidyl esters of aromatic diacids such as diglycidyl terephthalate or diglycidyl ethers of dihydric phenols with diacids such as isophthalic acid.

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HYDROXY-FUNCTIONAL POLYESTERS
AS THERMOPLASTIC BARRIER RESINS

5 This invention relates to thermoplastic
polyesters and to articles prepared from such
polyesters.

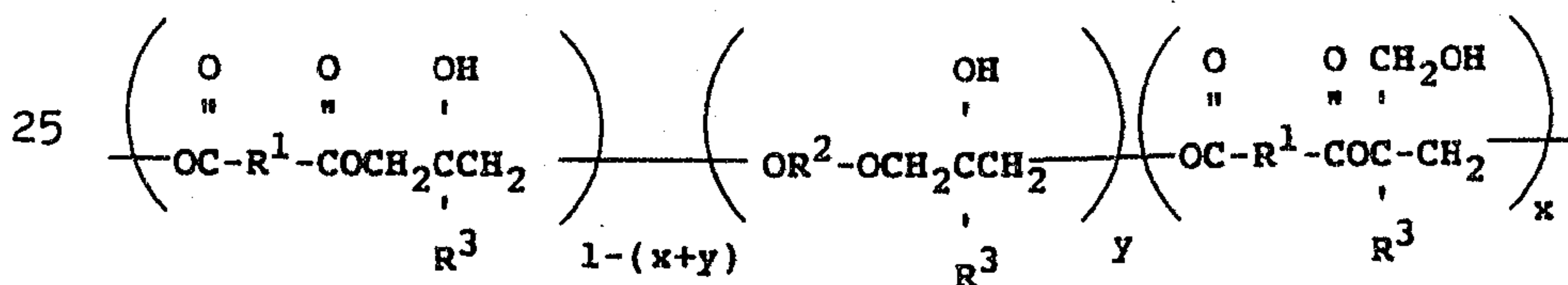
10 Polyesters such as polyethylene terephthalate
are used commercially in the packaging of various
materials such as seasonings, carbonated beverages,
detergents, cosmetics, etc. See, "Thermoplastic
Polyester Resins for Containers" D.P. Callander, *Polym.*
Sci., 25(8), 453-457 (1985). While polyethylene
15 terephthalate exhibits adequate gas barrier properties
for containing some materials, it is inadequate for
containing and storing such materials as beer, wine and
low-acid foods such as meats or vegetables.

20 In order to improve the barrier properties of
these polyesters, it has been recently learned to use
hydroxyphenoxyether polyalkylene terephthalates and
other hydroxyphenoxyether esters in packaging
25 applications requiring improved barrier. See, for

example, Japanese Patent Shutsugan Kokai No. 62-25151. While such polymers exhibit improved barrier properties, they are generally used in blends with other polymers because, in neat form, they undergo crosslinking when extruded or otherwise processed at temperatures above their glass transition temperatures.

In view of the limited barrier properties of the polyethylene terephthalates and the poor thermal processability of polyesters having pendant hydroxyl moieties and phenoxyether moieties, it would be highly desirable to provide a polymer having good thermal processability and a genuinely high barrier less than 2.0 cm³-mil/100 in²-atm-day (7.9 x 10⁻¹ cm³-mm/m²-atm-day) to oxygen. Polymers that retain such high barrier in both dry and moist environments would be especially desirable.

The present invention is, in one aspect, a normally solid, thermoplastic methylol polyester having repeating units represented by the formula:



Formula I

wherein each of R^1 and R^2 is individually a divalent organic moiety which is predominantly hydrocarbon, each R^3 is individually hydrogen or lower alkyl, y is a fraction from 0 to 0.5, and x is a fraction from 0.05 to 0.4.

5

In another aspect, this invention is a process for preparing the methylol polyester which comprises contacting a dicarboxylic acid or a mixture of two or
10 more dicarboxylic acids with a diglycidyl ether, a diglycidyl ester or a combination thereof in the presence of an onium catalyst in an ether solvent under conditions sufficient to form the polyester. Surprisingly, this process employing an onium catalyst
15 in an ether solvent yields in thermoplastic polymer which is in contrast to the prior art processes which employ a base catalyst in an amide solvent and yield a substantially crosslinked polymer which is not
20 thermoplastic.

20

In another aspect, this invention is an article suitable for packaging oxygen-sensitive materials such as foodstuffs and medicines wherein the article is
25 fabricated of the methylol polyester. This article can be in the form of a molded container, an impermeable film or a coating or an interlayer of a laminate or a coextruded container.

30

In addition to their use as barrier containers and films, the polymers of this invention are also useful as molding, extrusion and casting resins.

The methylol polyesters of this invention are processible as thermoplastics. For the purposes of this invention, a thermoplastic is defined as a material which flows at temperatures above its glass transition temperature and in which crosslinking or network formation does not occur. Thermoplastic processing is defined as heating a material to a temperature sufficient for flow to occur, with subsequent or concurrent forming into a shaped article. The article can be reheated and reformed any desired number of times, and the polymer does not undergo significant crosslinking or network formation during this handling. A test for crosslinking can be made by attempting to dissolve the polymeric material in an organic solvent, especially after exposure to the temperatures normally encountered during thermoplastic processing. Crosslinked polymers will not dissolve, while uncrosslinked polymers will dissolve in solvents for organic polymers. Thermoplastic polymers may be extruded at temperatures above their glass transition temperatures or they can be compression molded into films and plaques. Such polymers remain both soluble and processible after such thermal treatment.

In the preferred methylol polyesters of this invention as defined by the aforementioned Formula I, each of R^1 and R^2 is individually a divalent aromatic moiety such as arylene, alkylenearylene, dialkylenearylene, diaryleneketone, diarylenesulfone, diarylenesulfoxide, alkylidene-diarylene, diarylene oxide, diarylene sulfide and diarylenecyanomethane. Examples of divalent aromatic moieties include p-phenylene, m-phenylene and naphthalene, diphenylene-isopropylidene, 3,3'-dialkyldiphenylene-isopropylidene,

diphenylenemethane, 3,3',4,4'-tetraalkyldiphenylene-
-isopropylidene, and the corresponding alkyl-substituted
derivatives of the other named divalent aromatic
moieties. Of these divalent aromatic moieties,
5 p-phenylene, m-phenylene and diphenylene-isopropylidene
are more preferred, with p-phenylene being most
preferred. Alternatively, each of R^1 and R^2 is
individually (1) an aliphatic, hydrocarbon, divalent
moiety such as alkylene, cycloalkylene and alkenylene,
10 advantageously those having from 2 to 10 carbons or (2).
an aliphatic heteroatomic moiety having an alkylene or
cycloalkylene groups which are interrupted by a
heteroatomic moiety such as oxygen, sulfur, imino,
sulfonyl, carboxyl, carbonyl and sulfoxyl. Of these
15 aliphatic divalent moieties, the alkynes, such as
ethylene, propylene and butylene, are more preferred.

In Formula I, x is preferably a number from
0.05 to 0.4, most preferably from 0.1 to 0.3, and y is
20 preferably from 0 to 0.5. Each R^3 is individually
hydrogen or a hydrocarbyl or substituted hydrocarbyl
wherein hydrocarbyl is a monovalent hydrocarbon such as
alkyl, cycloalkyl, aralkyl, or aryl and the
substituent(s) is a monovalent moiety which is inert in
25 the reactions used to prepare the methylol polyester.
The polyesters are most preferably those represented by
the formula:

30



15

25

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mixtures of different diacids can be suitably employed. Of these diacids, terephthalic acid is most preferred.

5 Examples of suitable dihydric phenols include
4,4'-isopropylidene bisphenol (bisphenol A), 4,4'-dihydroxydiphenylethylmethane, 3,3'-dihydroxydiphenyldiethylmethane, 3,4'-dihydroxydiphenylmethylpropylmethane, bisphenol, 4,4'-dihydroxydiphenyloxide, 4,4'-dihydroxydiphenylcyanomethane, 4,4'-dihydroxybiphenyl,
10 4,4'-dihydroxybenzophenone, 4,4'-dihydroxydiphenyl sulfide, 4,4'-dihydroxydiphenyl sulfone, 2,6-dihydroxynaphthalene, 1,4'-dihydroxynaphthalene, catechol, resorcinol, hydroquinone and other dihydric phenols listed in U.S. Patents 3,395,118; 4,438,254 and
15 4,480,082. In addition, mixtures of different dihydric phenols can be employed. Of these other dihydric phenols, bisphenol A, hydroquinone and mixtures thereof are most preferred.

20 Examples of preferred onium catalysts include tetrahydrocarbyl quaternary ammonium halides wherein hydrocarbyl is a monovalent hydrocarbon radical such as alkyl, aryl, cycloalkyl, aralkyl and alkaryl, preferably having from 1 to 16 carbons. Examples of such preferred
25 onium catalysts include tetrakis(n-butyl)ammonium bromide and the corresponding chloride, iodide and fluoride, with tetrakis(n-butyl)ammonium bromide being most preferred. Other suitable onium catalysts include
30 tetrahydrocarbyl phosphonium halides such as ethyltriphenylphosphonium iodide and tetraphenylphosphonium bromide.

The polyesters are suitably prepared at temperatures in the range from 60°C to 160°C under an inert atmosphere. Preferred conditions for preparing

such polyesters are set forth in the following working examples.

5 The barrier articles, for example, containers, films and coatings, of this invention are fabricated from the polyesters using conventional fabricating techniques for normally solid, thermoplastic polymers such as extrusion, compression molding, injection molding, blow molding and similar fabrication techniques commonly employed to produce such articles.

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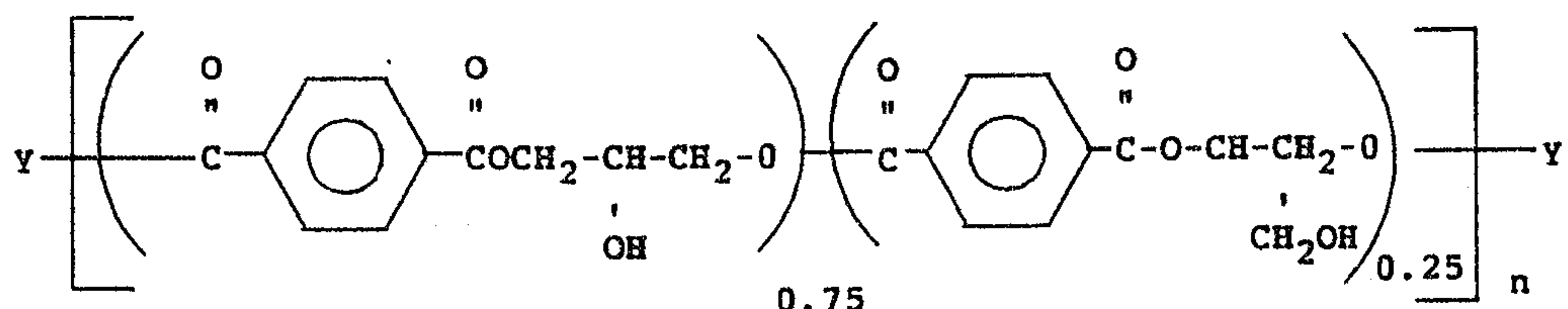
15 The following examples are given to illustrate the invention and should not be interpreted as limiting it in any way. Unless stated otherwise, all parts and percentages are given by weight.

Example 1

20 A. Preparation of the Polyester

In a 100-millileter (mL) resin kettle equipped with stirrer, condenser and nitrogen sparge, a mechanically stirred mixture of 9.35 g (33.6 mmol) of diglycidyl terephthalate, 5.57 g (33.6 mmol) of terephthalic acid and 4.01 g (12.5 mmol) of tetrakis(n-butyl)ammonium bromide was charged with 35 mL of dioxane and then heated under nitrogen to a temperature of 100°C for 42 hours. The hot reaction product was then poured into 500 mL of water in a blender. The precipitated product was filtered, redissolved in dimethylformamide (DMF) (100 mL) and reprecipitated by pouring into 500 mL of water. The resulting product was then collected by suction filtration and dried at 85°C. The polyester is represented by the formula:

30



Formula III


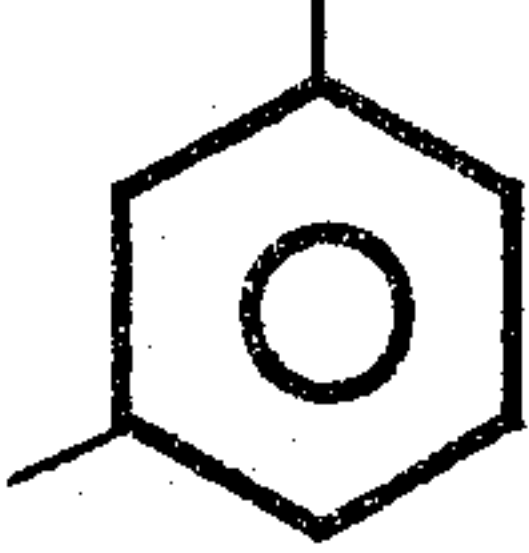
wherein Y and Y' are as previously defined.

15 Following the foregoing procedure, several additional polyesters were prepared using different diacids and diglycidyl esters as reported in Table I. In each of these polyesters, R³ was hydrogen.

20 B. Polyester Testing

Each polyester was tested for intrinsic viscosity and T_g. Polyester specimens (10 cm x 10 cm x 0.013 cm) for oxygen barrier evaluations were prepared by compression molding samples (3.5 g) of the polymer
 25 between Teflon™ sheets in a brass template at 200°C to 230°C at 13.8 mPa for 10 to 30 minutes, then at 1380 to 2750 mPa for 2 to 4 minutes and then cooled at 1380 to 2750 kPa for 10 minutes. Oxygen transmission rates were
 30 then measured for the samples. The results of these tests are reported in Table I.

TABLE I

Sample No.	$R^{1\oplus}$	η_{inh}^{\oplus} (dL/g)	T_g^{\oplus} (°C)	$OTR^{\oplus,\oplus}$ (RH [⊕])
1		0.47	102	0.8 (3.15 x 10 ⁻¹) (60%)
2		0.40	97	0.8 (3.15 x 10 ⁻¹) (60%)

⊕From Formula I
⊕ η_{inh} - inherent viscosity in DMF at 0.5 g/dL and 25°C
⊕ T_g - glass transition temperature
⊕ASTM Method D-3985 measured for compression molded films (23°C to 24°C)
⊕Oxygen transmission rate (OTR) measured in cc-mil/100 in²-atm-day (cm³-mm/m²-atm-day)
⊕Relative humidity of the oxygen stream

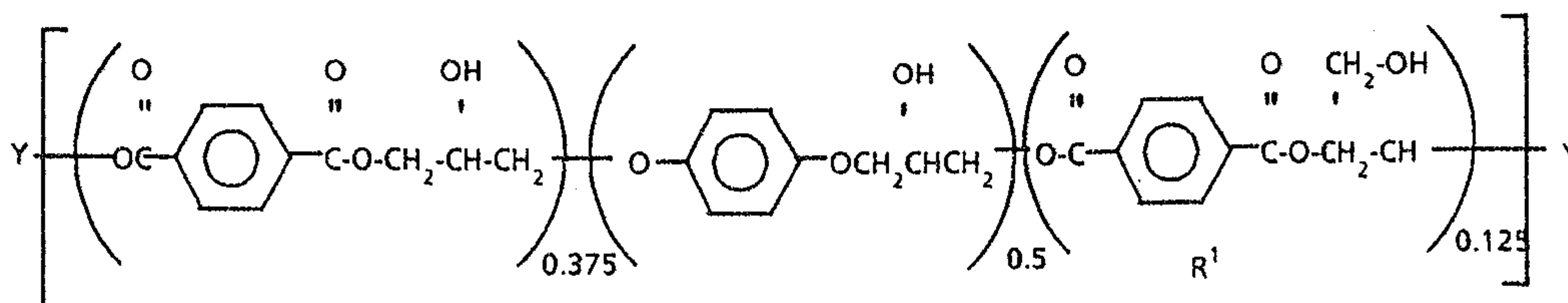
As evidenced by the data of Table I, the thermoplastic polyesters of this invention exhibited excellent barrier to oxygen permeation.

Example 2

5

A 100-mL minireactor equipped with a stirrer, two nitrogen inlets and a thermometer was charged with the diglycidyl ether of hydroquinone (8.12 g, 36.4 mmol, epoxy equivalent weight - 111.67 g/equivalent epoxide),
10 terephthalic acid (5.99 g, 36.0 mmol) and tetrakis(n-butyl)ammonium bromide (4.01 g, 12.5 mmol). The mixture was stirred while flowing nitrogen into the reactor and adding 50 mL of diglyme and then heated to 155°C for 6 hours. The resulting two-phase product was
15 poured into 500 mL of water in a blender and the precipitated product was collected by filtration and dried in a vacuum oven at 60°C overnight. The filtered product was dissolved in DMF (100 mL), and the solution
20 was poured into 500 mL of water. The reprecipitated product was collected by filtration and dried at 60°C for 18 hours. The resulting polyester was compression molded into a film under the conditions described in Part B of Example 1. The film was soluble in dimethyl
25 formamide and was thus not crosslinked to any significant degree. The polyester product was a hydroxy/methylol poly(ester/ether) represented by the formula:

30



Formula IV

wherein Y and Y' are as defined hereinbefore is tested for intrinsic viscosity, T_g and oxygen permeability and the results (Sample No. 1) are reported in Table II.

15

Example 3

A 500-mL flask equipped with a stirrer, condenser, and nitrogen inlet is charged with the diglycidyl ether of bisphenol-A (85.0 g, 0.245 mmol), isophthalic acid (40.9 g, 0.246 mmol) and tetrakis(n-butyl)ammonium bromide (20.00 g, 62 mmol). The flask was purged with nitrogen and 250 mL of dioxane was added. The resulting mixture was heated to reflux for 3.5 hours and 5 mL of glacial acetic acid was added. The mixture was stirred at reflux for an additional hour and allowed to cool to 25°C. The solution of product was poured into 2 L of water and the resulting precipitate is collected by filtration and dried under vacuum at 70°C overnight. The product was then dissolved in dioxane (550 mL) and reprecipitated by pouring into 2 L of water. The product was collected by filtration and dried under vacuum. This polyester was

30

tested for inherent viscosity, T_g and oxygen permeability and the results are reported in Table II.

Several additional hydroxy/methylol poly(ether/esters) are similarly prepared using different diacids and diglycidyl ethers of dihydric phenols as reported in Table II and tested for intrinsic viscosity, T_g and oxygen permeability. The results (Sample Nos. 2-9) are reported in Table II. In all of these hydroxy/methylol poly(ether/esters), R^3 was hydrogen.

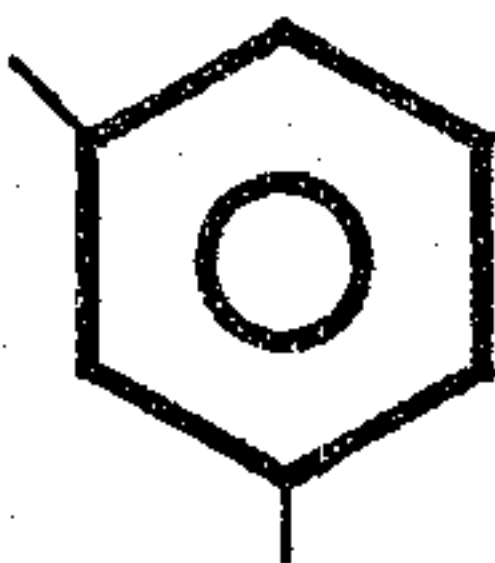
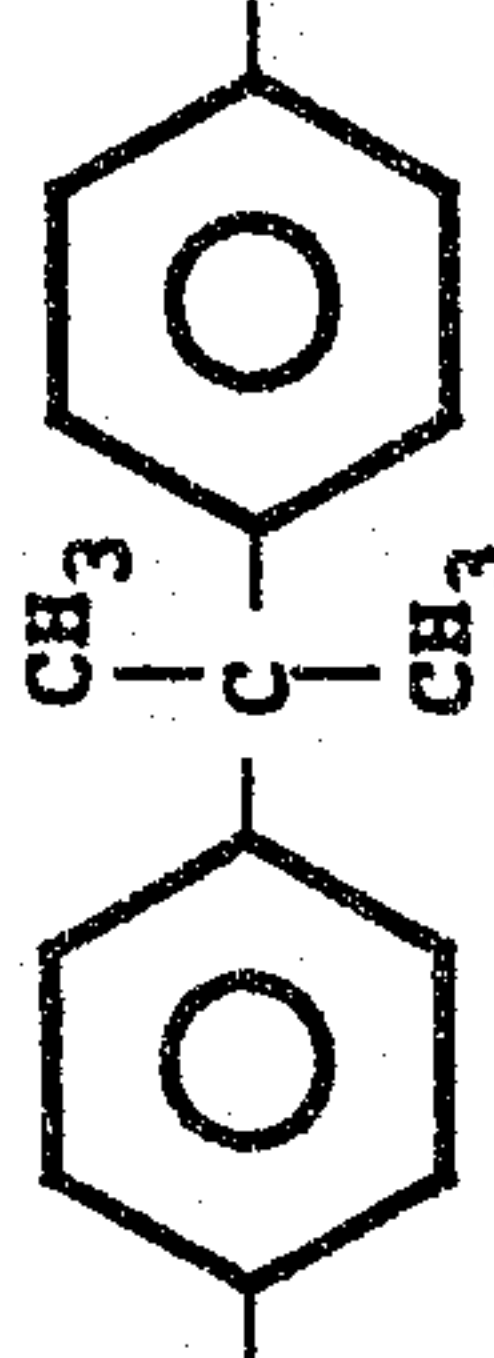
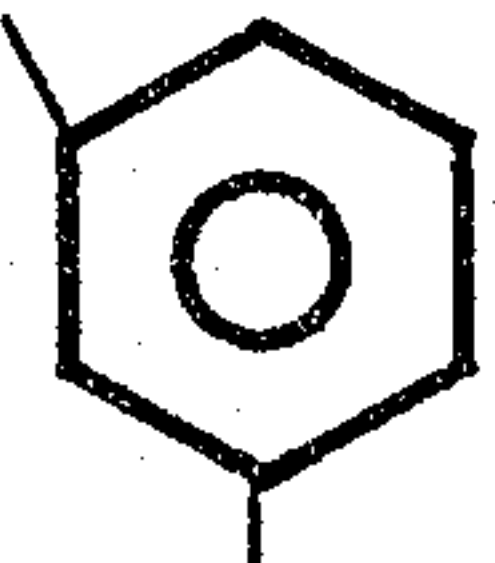
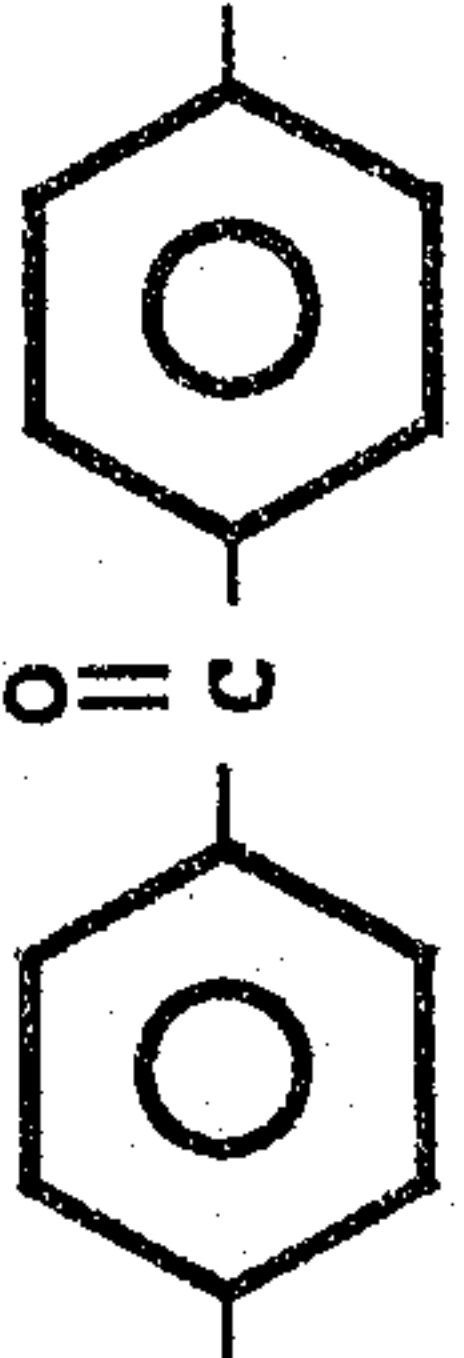
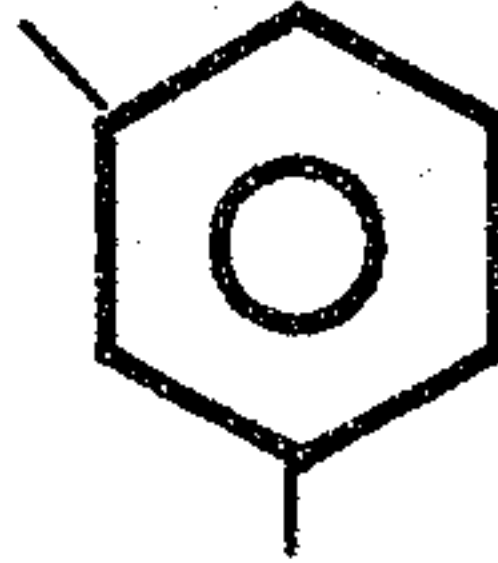
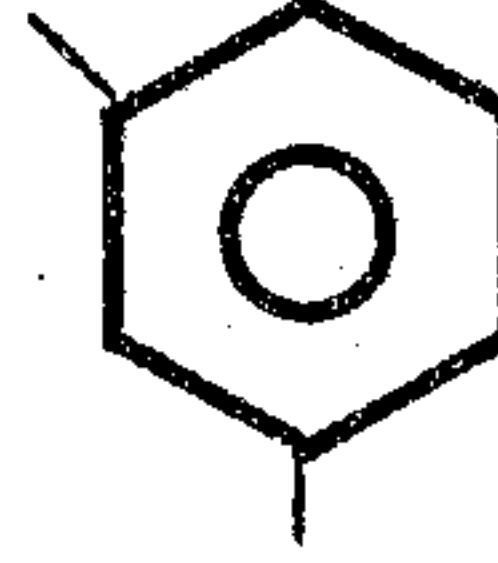
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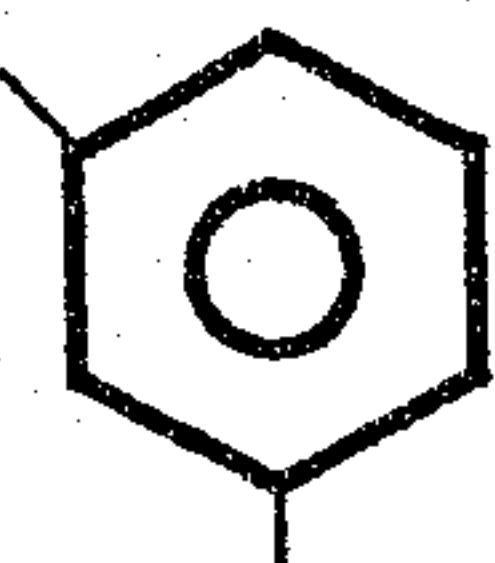

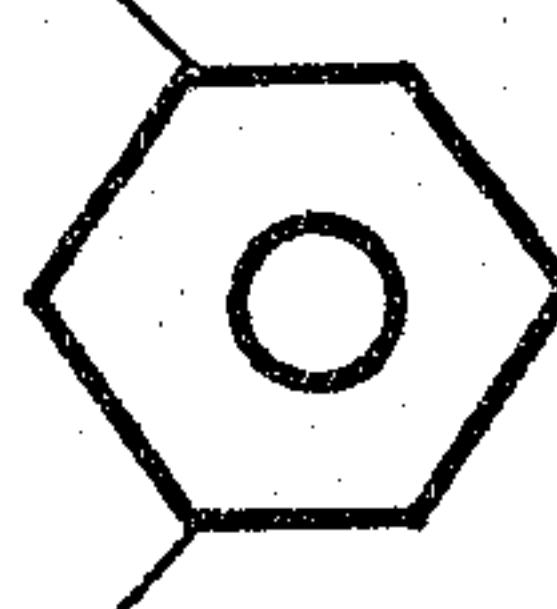
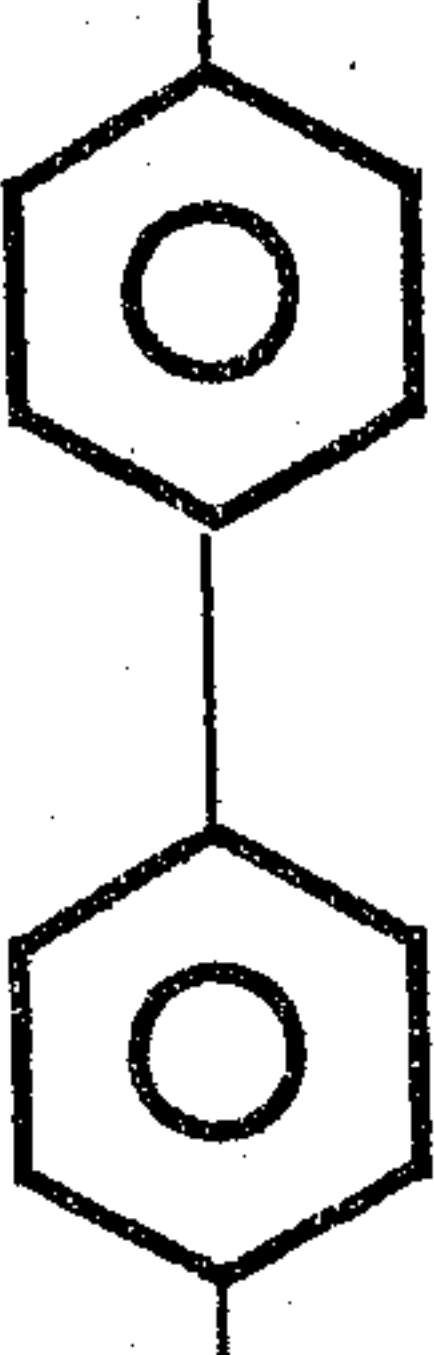
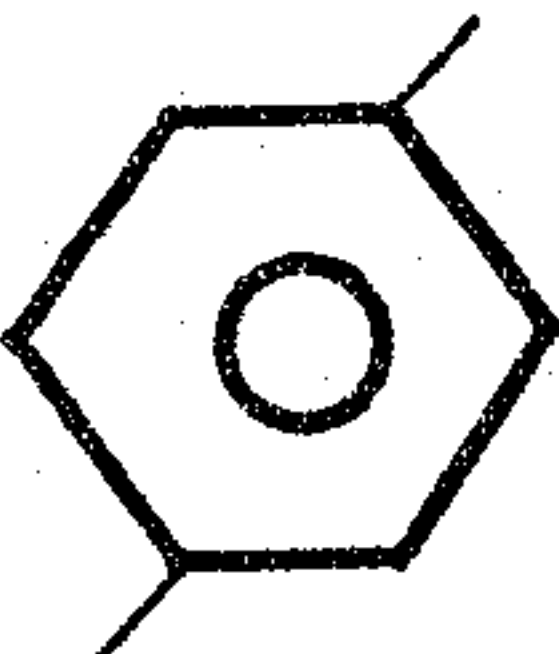
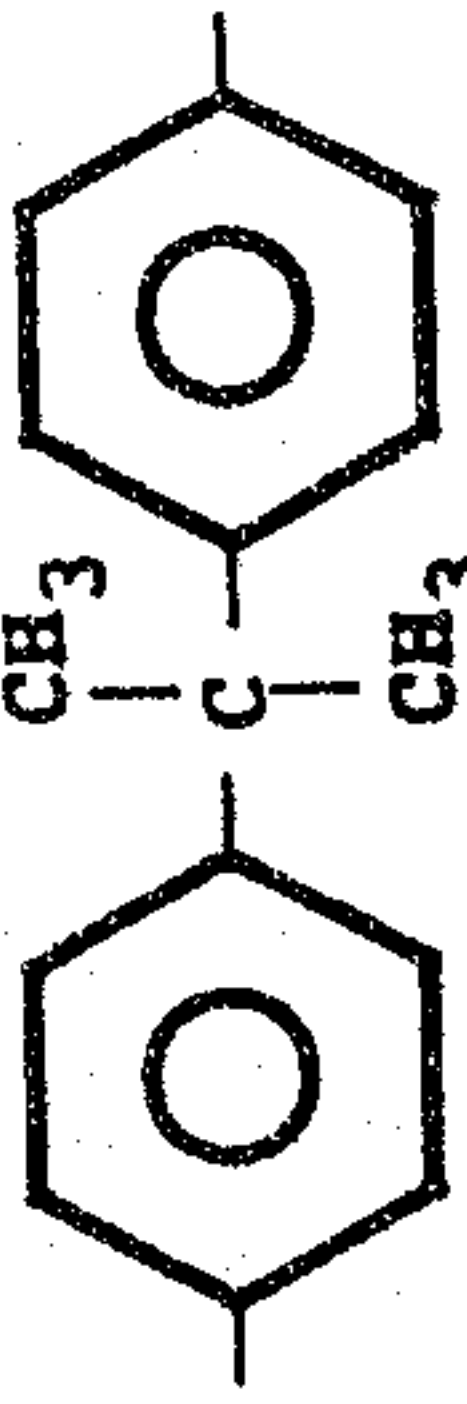
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TABLE II

Sam- ple No.	Composition		$\eta_{inh}^{\textcircled{3}}$ (dL/g)	$T_g^{\textcircled{4}}$ (°C)	$OTR^{\textcircled{5},\textcircled{6}}$ (RH $^{\textcircled{6}}$)
	R^1	R^2			
1			0.48	97	1.9 (7.5 x 10 ⁻¹) (60-65)
2			0.50	111	1.61 (6.3 x 10 ⁻¹) (80-90)
3			0.39	78	0.55 (2.2 x 10 ⁻¹) (70-80)

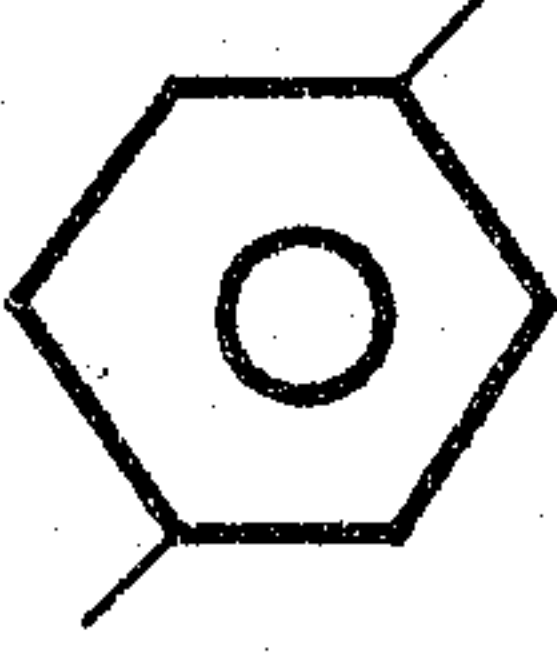
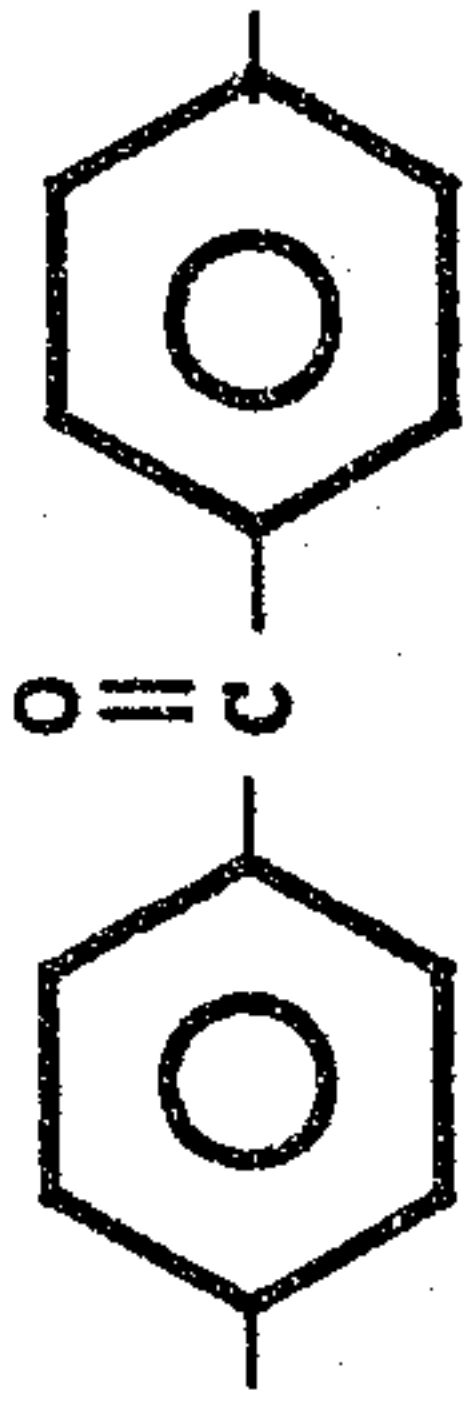

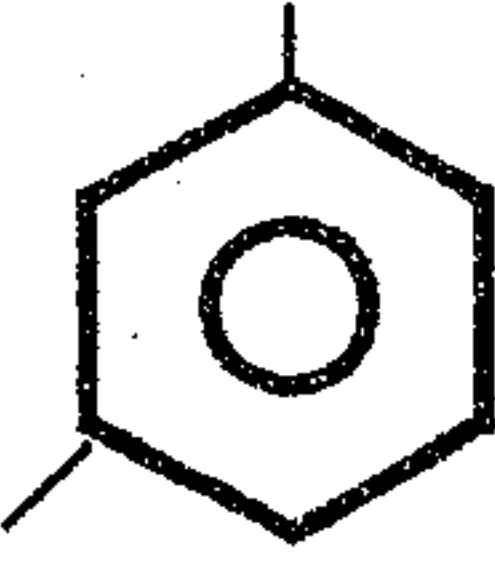


^①See Formula I
^② η_{inh} - inherent viscosity in DMF at 0.5 g/dL and 25°C
^③ T_g - glass transition temperature
^④ASTM Method D-3985 measured for compression molded films (23°C to 24°C)
^⑤Oxygen transmission rate (OTR) measured in cc-mil/100 in²-atm-day (cm³-mm/m²-atp-
^⑥Relative humidity of the oxygen stream (%)

TABLE II (cont'd)

Sample No.	Composition		η_{inh}° (dL/g)	T_g° (°C)	$OTR^{\circ, \circ}$ (RH) [⊙]
	R1 [⊙]	R2 [⊙]			
4			0.53	79	0.42 (1.6×10^{-1}) (47-50)
5			0.57	108	0.56 (2.2×10^{-1}) (70-80)
6			0.56	100	3.24 (12.7×10^{-1})

⊙ See Formula I
⊙ η_{inh} - inherent viscosity in DMF at 0.5 g/dL and 25°C
⊙ T_g - glass transition temperature
⊙ ASTM Method D-3985 measured for compression molded films (23°C to 24°C)
⊙ Oxygen transmission rate (OTR) measured in cc-mil/100 in²-atm-day (cm³-mm/m²-atm-day)
⊙ Relative humidity of the oxygen stream (%)

TABLE II (cont'd)

Sam ple No.	R^1 ^①	Composition R^2 ^②	η_{inh} ^③ (dL/g)	T_g ^④ (°C)	OTR ^⑤ (RH) ^⑥
7			0.35	108	1.31 (5.2×10^{-1}) (47-50)
8			0.41	78	0.83 (3.3×10^{-1}) (85-95)
9			0.37	76	0.52 (2.0×10^{-1}) (80-90)

① See Formula I

② η_{inh} - inherent viscosity in DMF at 0.5 g/dL and 25°C③ T_g - glass transition temperature

④ ASTM Method D-3985 measured for compression molded films (23°C to 24°C)

⑤ Oxygen transmission rate (OTR) measured in cc-mil/100in²-atm-day (cm³-mm/m²-atm-day)

⑥ Relative humidity of the oxygen stream (8)

As evidenced by the data in Table II, the thermoplastic hydroxy/methylol poly(ether/esters) of the invention exhibit excellent barrier to oxygen permeation.

Comparative Example 1

5 A 100-mL minireactor equipped with a stirrer, two nitrogen inlets and a thermometer under nitrogen was charged with the diglycidyl ether of hydroquinone (4.73 g, 21.0 mmol, epoxy equivalent weight of 112.54 g/equivalent epoxide), terephthalic acid (3.49 g, 21.0 mmol), N-methylpyrrolidinone (NMP)(9.8 mL) and benzyldimethyl amine (46 μ L). The resulting mixture was heated to 130°C for 30 minutes. An additional 15.6 mL of NMP was added and the mixture was heated at 130°C for an additional 4 hours. The mixture was allowed to cool to room temperature and then was poured into 500 mL of water. The precipitate was collected, washed with water and methanol and dried at 40°C overnight. The resulting polymer had an inherent viscosity of 0.43 dL/g in DMF.

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20 When the polymer was compression molded at 220°C for 14 minutes the resulting film was not soluble in DMF. Further, the melt flow rate of the polymer was measured according to ASTM Method 1286-89, Condition 200/5.0 and, after the initial equilibration period of 6 minutes

25 specified in the method, the polymer did not flow from the apparatus. These results indicated substantial crosslinking of the polymer had occurred.

Comparative Example 2

30 The minireactor used in Comparative Example 1 was charged with the diglycidyl ether of bisphenol-A (13.737 g, 40.0 mmol) and isophthalic acid (6.643 g,

40.0 mmol). N-methylpyrrolidone (NMP, 25.8 mL) and N,N-dimethyl-benzylamine 89 μ L) were added to the minireactor with stirring under nitrogen, and the mixture was heated to 130°C for 30 minutes. Additional NMP (41 mL) was added and heating was continued at 130°C for 4 hours. The mixture was allowed to cool to room temperature and was poured into water (500 mL) and mixed in a Waring blender. The precipitated product was collected by suction filtration and dried in a vacuum oven at 50°C for 24 hours. The resulting product had an inherent viscosity of 0.24 dL/g in DMF at 25°C. The product was then compression molded at 200°C for 14 minutes to give a brittle film. A piece of the film was shaken with DMF, but the film did not dissolve. Comparative Examples 1 and 2 show that both high and low molecular weight polyesters prepared using basic catalysts in amide solvents crosslink upon exposure to thermal conditions typically used to fabricate or otherwise thermally process barrier thermoplastic polymers.

Example 4

A 100-mL minireactor, equipped with stirrer, condenser and nitrogen inlet was charged with the diglycidyl ether of bisphenol-A (12.502 g, 36.4 mmol), isophthalic acid (5.984 g, 36.0 mmol) and tetra-n-butylammonium bromide (4.015 g, 12.5 mmol). Dioxane (35 mL) was added under a flow of nitrogen and the mixture was heated to reflux for 4 hours. The mixture was diluted with additional dioxane (50 mL) and poured into water (500 mL) in a Waring blender. The resulting precipitated product was dried under vacuum at 80°C for 16 hours and was redissolved in tetrahydrofuran (100 mL). The product was reprecipitated into water and

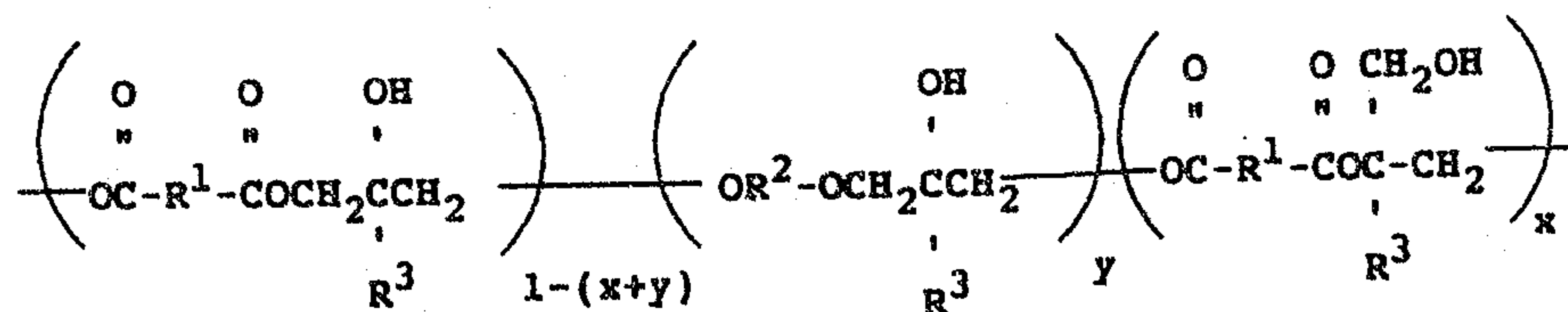
redried as described above. The resulting
poly(ether/ester) had an inherent viscosity of 0.44 dL/g
in dimethylformamide at 25°C. The poly(ether/ester) was
compression molded into films at 220°C in the manner
described in Part B of Example 1. The resulting film
5 was soluble in tetrahydrofuran. The poly(ether/ester)
was tested for melt flow rate according to ASTM Method
1286-89, Condition 200/5.0 and, after the prescribed 6
minute equilibration period, found to have a melt flow
rate of 7.72 g/10 minutes. After experiencing 30
10 minutes in the cylinder of the melt flow apparatus at
200°C, the poly(ether/ester) exhibits a melt flow rate
of 6.90 g/10 minutes. The extruded strands of the
polymer exiting the melt flow apparatus are soluble in
dimethyl-formamide, thus exhibiting little or no
15 crosslinking had occurred.

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1. A normally solid, thermoplastic methylol polyester having repeating units represented by the formula:



Formula I

wherein each of R^1 and R^2 is individually a divalent organic moiety which is predominantly hydrocarbon, each R^3 is individually hydrogen or lower alkyl, y is a fraction from 0 to 0.5 and x is a fraction from 0.05 to 0.4.

2. The polyester of Claim 1 wherein each of R^1 and R^2 is individually a divalent aromatic moiety selected from arylene, alkylenearylene, dialkylenearylene, diaryleneketone, diarylenesulfone, diarylenesulfoxide, alkylencarbonylarylene, alkylenesulfonylarylene, alkylidene-diarylene, diarylene

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oxide, alkyleneoxyarylene, alkyleneethioarylene, diarylene sulfide and diarylenecyanomethane.

3. The polyester of Claim 2 wherein each of R^1 and R^2 is individually a divalent aromatic moiety selected from
5 m-phenylene, p-phenylene, isopropylidene diphenylene, biphenylene, biphenylene oxide, methylenediphenylene, biphenylene sulfide, naphthylene, biphenylenecyanomethane, 3,3'-dialkyldiphenylene-isopropylidene and 3,3',4,4'-tetraalkyldiphenylene-isopropylidene.

10 4. The polyester of Claim 3 wherein each of R^1 and R^2 is individually m-phenylene, p-phenylene and isopropylidene diphenylene.

5. The polyester of Claim 1 wherein each of R^1 and R^2 is individually a divalent aliphatic moiety selected from
15 alkylene, dialkyleneketone, dialkylenesulfone, dialkylenesulfoxide, dialkeneoxide and dialkylenesulfide.

6. The polyester of Claim 5 wherein each of R^1 and R^2 is individually a divalent aliphatic moiety selected from ethylene, propylene and butylene.

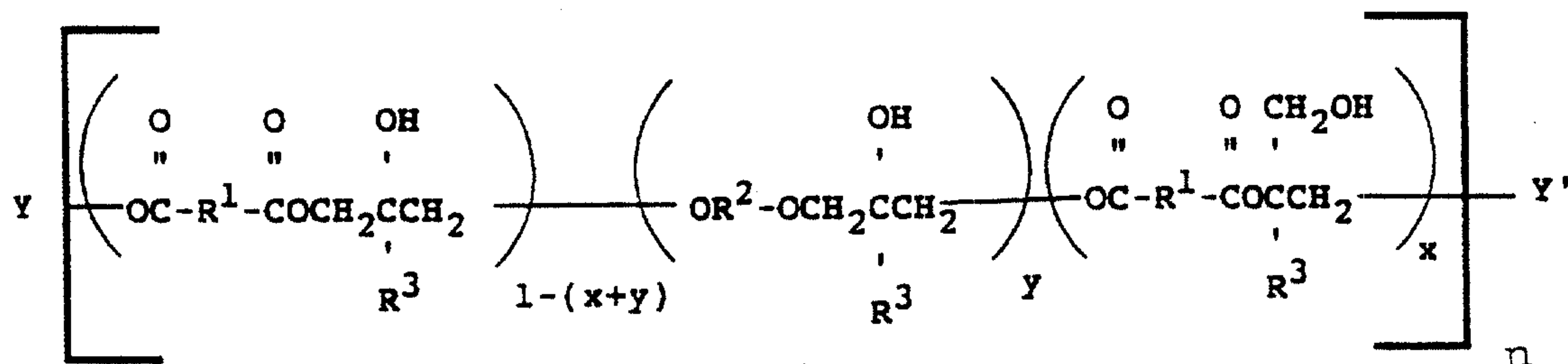
20 7. The polyester of Claim 1 wherein x is a number from 0.1 to 0.3.

8. The polyester of Claim 7 wherein x is a number from 0.1 to 0.2.

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9. The polyester of Claim 8 which is represented by the formula:



Formula II

wherein each Y and Y' is individually hydrogen or a monovalent organic terminating group, and n is a whole number from 10 to 1000.

10. The polymer of Claim 9 wherein R¹ is m-phenylene, R² is isopropylidenediphenylene, x is 0.2, and n is 200 to 800.

11. The polymer of Claim 9 wherein R¹ is p-phenylene, y is 0, x is 0.2 and n is a number from 200 to 800.

12. The polymer of Claim 9 wherein R¹ is m-phenylene or p-phenylene; R² is isopropylidene-diphenylene, diphenylenecarbonyl, m-phenylene, p-phenylene and biphenylene; R³ is hydrogen; y is 0.5; x is 0.125 and n is a number from 200 to 800.

13. The polymer of Claim 1 in the form of a barrier container.

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14. The polymer of Claim 2 in the form of a barrier film.

15. The polymer of Claim 1 in the form of a barrier coating.

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16. The polymer of Claim 1 in the form of a foamed article.

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