

**United States Patent** [19]**Hergenrother et al.**[11] **Patent Number:** **4,567,240**[45] **Date of Patent:** **Jan. 28, 1986**[54] **ETHYNYL TERMINATED ESTER  
OLIGOMERS AND POLYMERS  
THEREFROM**[75] **Inventors:** **Paul M. Hergenrother, Yorktown;  
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represented by the Administrator of  
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Administration, Washington, D.C.**[21] **Appl. No.:** **613,138**[22] **Filed:** **May 23, 1984**[51] **Int. Cl.<sup>4</sup> .....** **C08G 63/76**[52] **U.S. Cl. ....** **525/328.1; 525/328.5;  
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526/285; 528/173; 528/176; 528/182; 528/192;  
528/272; 528/274; 528/293; 528/294; 528/304;  
528/306; 528/308**[58] **Field of Search .....** **528/173, 176, 182, 192,  
528/272, 274, 293, 294, 304, 306, 308; 526/285;  
525/328.1, 328.5, 328.9, 329.5, 437, 445**[56] **References Cited****U.S. PATENT DOCUMENTS**

3,666,023	5/1972	Kehr et al. ....	260/858
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[57] **ABSTRACT**

A new class of ethynyl-terminated oligomers and the process for preparing same are disclosed. Upon the application of heat, with or without a catalyst, the ethynyl groups react to provide crosslinking and chain extension to increase the polymer use temperature and improve the polymer solvent resistance. These improved polyesters are potentially useful in packaging, magnetic tapes, capacitors, industrial belting, protective coatings, structural adhesives and composite matrices.

**14 Claims, No Drawings**

## ETHYNYL TERMINATED ESTER OLIGOMERS AND POLYMERS THEREFROM

### ORIGIN OF THE INVENTION

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 85-568 (72 Stat. 435; 42 USC 2457).

### BACKGROUND OF THE INVENTION

Polyesters are commercially available and are widely used in a variety of applications such as magnetic tapes, packaging, capacitors, industrial belting, protective coatings, structural adhesives and composite matrices. There are basically three classes of polyester: amorphous thermoplastics, crystalline or semi-crystalline materials, and unsaturated or crosslinked polymers. Each class of polyesters has a unique set of properties. The synthesis of polyesters is amenable to tailor a material for a particular application. A tremendous amount of work has been reported on polyesters and excellent reviews are available, e.g., I. Goodman "Polyesters," in *Encyclopedia of Polymer Science and Technology* Vol. 11, p. 62 (1969), edited by H. F. Mark and N. G. Gaylord; H. V. Boenig "Unsaturated Polyesters," *Ibid.*, Vol. 11, p. 129 (1969); and P. W. Morgan "Condensation Polymers," Chapter on Polyesters, p. 325, Interscience Publishers, New York (1965).

The amorphous polyesters of the prior art are sensitive to certain solvents especially in a stressed condition and, upon exposure, undergo solvent induced stress crazing and cracking. The crystalline polyesters have better solvent resistance than the amorphous materials but are generally more difficult to process. In addition, the degree of crystallinity in the polymer influences the properties and in many instance, the degree of crystallinity cannot be controlled, especially when processed as adhesives or composite matrices. The crosslinked polyesters undergo pronounced shrinkage upon cure which results in built-in stresses. In addition, these crosslinked polyesters are generally brittle materials and cannot be thermoformed. The materials of this invention exhibit improved solvent resistance, higher use temperature, good toughness, and thermoformability and thereby overcome the disadvantages of the prior art.

It is therefore an object of the present invention to provide a novel method for preparing ethynyl-terminated polyesters.

Another object of the present invention is to provide a new composition of matter comprised of ethynyl-terminated ester oligomers and polymers.

A further object of the present invention is to provide novel cured resins in the form of films, coatings, adhesives and composite matrices produced from cured ethynyl-terminated polyesters.

An additional object of the present invention is to provide polymers having improved solvent resistance and use temperature properties.

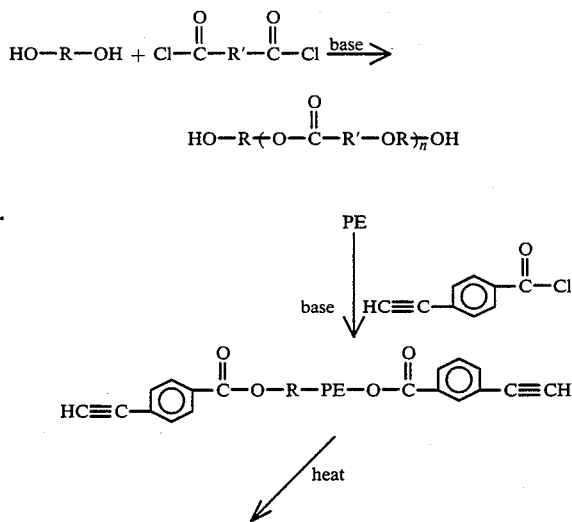
Another object of the present invention is to provide a process for preparing thermoplastic polyesters having improved solvent resistance and use temperatures without compromising the advantageous thermoformability and toughness property characteristics thereof.

A further object of the present invention is a process for preparing controlled density thermoplastic poly-

esters to thereby influence the physical properties of the cured material.

### BRIEF DESCRIPTION OF THE INVENTION

According to the present invention, the foregoing and additional objects are attained by synthesizing hydroxy-terminated polyarylates (HTPA) with number average molecular weights of approximately 2500, 5000, 7500 and 10,000 and converting these to the corresponding 4-ethynylbenzoyloxy-terminated polyarylates (ETPA) by reaction with 4-ethynylbenzoyl chloride. The terminal ethynyl groups on the resulting ethynyl-terminated ester oligomers or polymers were thermally reacted to provide chain-extension and crosslinking. The cured ETPA exhibited higher glass transition temperatures and better solvent resistance than a high molecular weight linear polyarylate. Solvent resistance was further improved by curing 2,2-bis(4-ethynylbenzoyloxy-4'-phenyl) propane, a coreactant, with the ETPA at concentrations of approximately 10-30% (w/w). The general reaction for reacting hydroxy-terminated oligomers or polymers with ethynyl benzoyl chloride to yield ethynyl-terminated ester oligomers or polymers is illustrated by the general equation:

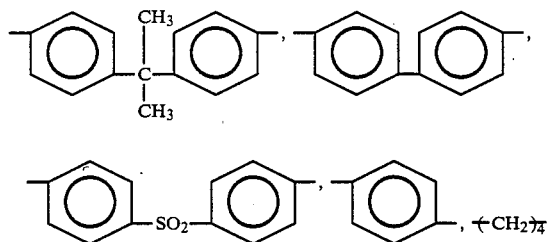


Cured Polymer (via chain extension and crosslinking) where:

PE refers to the polyester radical portion

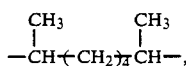
n is an integer from 4 to 100 repeat units, base is an organic base selected from the group consisting of triethylamine, pyridine, quinoline, diethylamine, and piperidine,

R is selected from the group of radicals consisting of

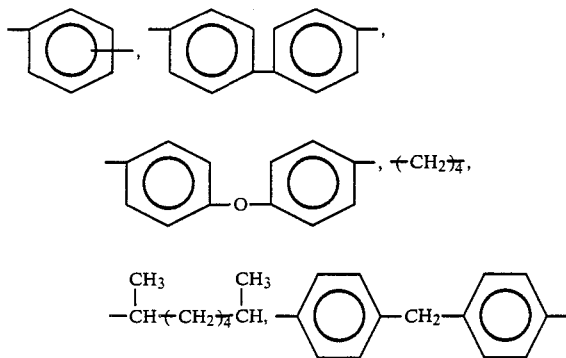


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-continued



and mixtures thereof  
and R' is selected from the group of radicals consisting of



and mixtures thereof.

The molecular weight of the ester oligomer or polymer can be readily controlled which, accordingly, controls the amount of ethynyl groups and, therefore, the crosslink density. High crosslink density provides better solvent resistance, less thermoformability, poorer processability as adhesives or composite matrices, and lower toughness. The synthesis of ethynyl-terminated polyesters can be readily controlled to provide tailored materials for specific applications.

The use of the ethynyl group on the ends of oligomers or polymers to chain extend and crosslink can be readily extended to virtually any polyester to improve the solvent resistance and increase the use temperature. Another advantage derived from this invention is less shrinkage during the cure relative to the more conventional crosslinked polymers.

The crosslink density of the resins obtained from the above reaction can be readily controlled which, accordingly, influences the properties of the cured material. Uncured polyesters terminated with ethynyl groups are soluble in a variety of solvents such as chloroform, N,N-dimethylacetamide, and m-cresol. Solutions thereof can be conveniently used to form coatings, films, adhesive tapes and laminating prepreps and subsequently cured to provide components with better solvent resistance and higher use temperature than comparable conventional polyesters. Also, the cured solvent resistant materials obtained in the above reaction, depending on the molecular weight, are thermoformable and relatively tough unlike the crosslinked solvent resistant conventional polyesters.

The use of 4-ethynylbenzoyl chloride as an end-capping agent for hydroxy-terminated polysulfones is described in Hergenrother's U.S. Pat. No. 4,431,761, issued Feb. 14, 1984. 4-Ethynyl benzoyl chloride is potentially useful for end-capping any polymer having terminal groups that react with acid chlorides, such as hy-

4

droxyl, amine, amide and similar groups. The present invention extends this concept to include polyesters.

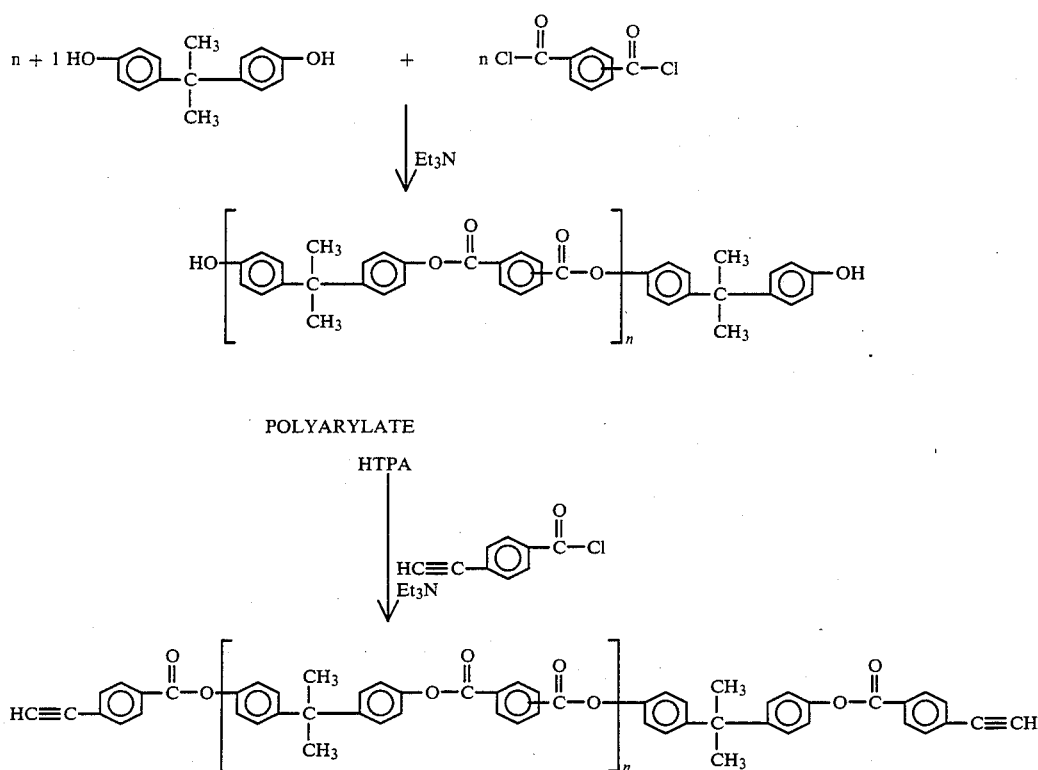
Aromatic polyesters (polyarylate) engineering thermoplastic, such as ARDEL<sup>®</sup> D-100, a Union Carbide Corporation product, generally exhibit good mechanical properties. This material, unlike the polysulfones, has good retention of physical properties after exposure to UV radiation. However, ARDEL<sup>®</sup> D-100 is also solvent sensitive, undergoing solvent induced stress crazing and cracking. In the present invention, to increase the solvent resistance of polyarylates, while retaining their desirable chemical and mechanical properties, ethynyl-terminated polyarylates of various molecular weights were synthesized. These materials were subsequently "cured" by exposure to heat at a sufficiently high temperature to cause crosslinking and/or chain extension.

The starting materials employed in the specific Examples herein were obtained as follows. Methyl 4-bromobenzoate was prepared by refluxing 4-bromobenzoic acid (Aldrich Chemical Company) with an excess of methanol containing a catalytic amount of sulfuric acid. Ethynyltrimethylsilane was purchased from Silar Laboratories, Inc. ARDEL<sup>®</sup> D-100 was obtained from Union Carbide Corporation. Methyl 4-[(trimethylsilyl)ethynyl] benzoate and methyl 4-ethynylbenzoate were prepared using procedures similar to those described by W. B. Austin et al in the *Journal of Organic Chemistry* Vol. 46, p. 2280 (1981).

A detailed description for the preparation of all the starting materials is found in an article to appear in the *Journal of Polymer Science, Polymer Chemistry Edition*, Vol.22, p.3011 (1984), which is incorporated herein by reference.

Hydroxy-terminated polyarylate (HTPA) polymer synthesis was performed by the reaction of a calculated excess of 2,2-bis(4-hydroxyphenyl) propane with 50/50 1,3-benzenedicarbonyl chloride/1,4-benzenedicarbonyl chloride in ethanol-free chloroform containing a 10% excess of an organic base, e.g., triethylamine. Additional solvents equally applicable to the present invention are methylene chloride and N,N-dimethylacetamide. Also, additional organic bases equally applicable to the present invention include the group consisting of pyridine, quinoline, diethylamine, and piperidine. The reaction was conducted over a period of three hours on a 50 mmol scale at a concentration of 12% (w/v). The chloroform solution was poured into acetone in a blender to precipitate a white solid. The solid was successively washed three times with water, once with methanol, and dried under vacuum at 60° C. for four hours. To convert the recovered HTPA to 4-ethynylbenzoyloxy-terminated polyarylate (ETPA), the HTPA (10 g) was dissolved in chloroform (90 mL) containing a 50% excess of triethylamine. Under a nitrogen atmosphere, a solution of 4-ethynylbenzoyl chloride (50% excess) in chloroform (10 mL) was added to the stirred polymer solution. Stirring was continued for three hours and the workup was the same as for the HTPA described above.

The following equation chemically illustrates the described preparation of ETPA.



where  $n$  is a integer of 4 to 100

ETPA

## SPECIFIC EXAMPLES

### EXAMPLE I

Synthesis of a Hydroxy-Terminated Polyarylate with a Molecular Weight of 2500 ( $2500\text{-}\bar{M}_n$  HTPA)

2,2-Bis(4-hydroxyphenyl) propane (Bisphenol A) (13.7383 g, 0.06018 mole) was dissolved in 150 mL of ethanol-free chloroform containing 16.0 mL (0.1147 mole) of triethylamine. Under a nitrogen atmosphere, a solution of 1,3-benzenedicarbonyl chloride (5.2902 g, 0.02606 mole) and 1,4-benzenedicarbonyl chloride (5.2902 g, 0.02606 mole) dissolved in 50 mL of chloroform was added to the magnetically stirred 2,2-bis(4-hydroxyphenyl) propane solution over a period of ten minutes. The mixture was then stirred at room temperature for three hours and approximately 100 mL of the solvent removed by distillation. The polymer solution was slowly poured into 500 mL of acetone in a blender to precipitate the polymer. The polymer was successively washed three times with water, once with methanol, and dried under vacuum at  $60^\circ\text{C}$ . for four hours. Yield of  $2500\text{-}\bar{M}_n$  HTPA was 16.06 g (82%).

### EXAMPLE II

Synthesis of a Hydroxy-terminated Polyarylate with a Molecular Weight of 7500 ( $7500\text{-}\bar{M}_n$  HTPA)

2,2-Bis(4-hydroxyphenyl) propane (Bisphenol A) (14.4038 g, 0.06310 mole) was dissolved in 150 mL of ethanol-free chloroform containing 18.4 mL (0.1320 mole) of triethylamine. Under a nitrogen atmosphere, a solution of 1,3-benzenedicarbonyl chloride (6.1057 g, 0.03007 mole) and 1,4-benzenedicarbonyl chloride

(6.1057 g, 0.03007 mole) dissolved in 50 mL of chloroform was added to the magnetically stirred 2,2-bis(4-hydroxyphenyl) propane solution over a period of ten minutes. The mixture was then stirred at room temperature for three hours and approximately 100 mL of the solvent removed by distillation. The polymer solution was slowly poured into 500 mL of acetone in a blender to precipitate the polymer. The polymer was successively washed three times with water, once with methanol, and dried under vacuum at  $60^\circ\text{C}$ . for four hours. Yield of  $7500\text{-}\bar{M}_n$  HTPA was 20.51 g (92%).

**EXAMPLE III** Synthesis of a 4-Ethynylbenzoyloxy-Terminated Polyarylate with a Molecular Weight of 2500 ( $2500\text{-}\bar{M}_n$  ETPA)

The 2500-molecular weight hydroxy-terminated polyarylate ( $2500\text{-}\bar{M}_n$  HTPA) (10.00 g, 0.0040 mole) was dissolved in 90 mL of ethanol-free chloroform containing 1.67 mL (0.012 mole) of triethylamine. Under a nitrogen atmosphere, a solution of 4-ethynylbenzoyl chloride (1.98 g, 0.012 mole) dissolved in 10 mL of chloroform was added to the stirred  $2500\text{-}\bar{M}_n$  HTPA solution over a period of five minutes. The mixture was then stirred at room temperature for three hours. The polymer solution was slowly poured into 500 mL of acetone in a blender to precipitate the polymer. The polymer was successively washed with 5% sodium bicarbonate solution, twice with water, once with methanol, and dried under vacuum at  $60^\circ\text{C}$ . for four hours. Yield of  $2500\text{-}\bar{M}_n$  ETPA was 9.66 g (88%).

the ETPA due to C≡C-H stretching was not seen in the thermally reacted material.

CHARACTERIZATION OF HYDROXY-TERMINATED POLYARYLATES, 4-ETHYNYLBENZOYLOXY-TERMINATED POLYARYLATES, AND ARDEL® D-100

Approximate $\bar{M}_n$ (g/mol)	Substituent	$\eta_{inh}^b$ (dL/g)	GPC <sup>c</sup> Peak Retention Time (min)	T <sub>g</sub> of Cured Polyarylates (°C.)			Cured Films		
				DSC <sup>d</sup>	Heat-Up	Cool-Down	T <sub>g</sub> (°C.)	TMA <sup>f</sup>	Chloroform Solubility
2500	—OH	0.24	18.68	178	177	203	184	—	Soluble
2500	HC≡C—C <sub>6</sub> H <sub>4</sub> CO <sub>2</sub>	0.30	18.53	218	181	237	214	212	Very Slight Swelling
5000	—OH	0.33	18.26	191	190	205	185	—	Soluble
5000	HC≡C—C <sub>6</sub> H <sub>4</sub> CO <sub>2</sub>	0.34	18.23	215	190	230	208	212	Slight Swelling
7500	—OH	0.41	17.86	197	196	210	190	194	Soluble
7500	HC≡C—C <sub>6</sub> H <sub>4</sub> CO <sub>2</sub>	0.42	17.86	207	195	230	205	210	Swelling
10,000	—OH	0.43	17.45	197	196	210	191	196	Soluble
10,000	HC≡C—C <sub>6</sub> H <sub>4</sub> CO <sub>2</sub>	0.47	17.45	203	196	227	196	206	Swelling
24,000 <sup>g</sup>	—	0.59	17.21	197	196	208	193	196	Soluble

(ARDEL®)  
D-100

<sup>a</sup>Information provided by Union Carbide Corporation, Bound Brook, New Jersey (H. Gardner).

<sup>b</sup>Inherent viscosity, 0.5% solution in chloroform at 25° C.

<sup>c</sup>Gel permeation chromatography using  $\mu$ -Styragel (10<sup>6</sup>, 10<sup>5</sup>, 10<sup>4</sup>, 10<sup>3</sup> Å), chloroform as solvent.

<sup>d</sup>Differential scanning calorimetry at heating rate of 20° C./min.

<sup>e</sup>Torsional braid analysis at heating rate of 3° C./min.

<sup>f</sup>Thermal mechanical analysis at heating rate of 5° C./min.

#### Synthesis of a 4-Ethynylbenzoyloxy-Terminated Polyarylate with a Molecular Weight of 7500 (7500- $\bar{M}_n$ ETPA)

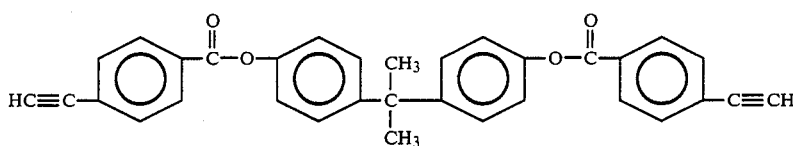
The 7500-molecular weight hydroxy-terminated polyarylate (7500- $\bar{M}_n$  HTPA) (10.00 g, 0.00133 mole) was dissolved in 90 mL of ethanol-free chloroform containing 0.56 mL (0.0040 mole) of triethylamine. Under a nitrogen atmosphere, a solution of 4-ethynylbenzoyl chloride (0.66 g, 0.0040 mole) dissolved in 10 mL of chloroform was added to the stirred 7500- $\bar{M}_n$  HTPA solution over a period of five minutes. The mixture was then stirred at room temperature for three hours. The polymer solution was slowly poured into 500 mL of acetone in a blender to precipitate the polymer. The polymer was successively washed with 5% sodium bicarbonate solution, twice with water, once with methanol, and dried under vacuum at 60° C. for four hours. Yield of 7500- $\bar{M}_n$  ETPA was 9.83 g (95%).

Additional Examples included the preparation of HTPA with a calculated  $\bar{M}_n$  of 5000 and 10,000, prepared as shown in the equation above and subsequently converted to ETPA by reaction with 4-ethynylbenzoyl chloride. Characterization of the HTPA, the ETPA and ARDEL® D-100 is given in the Table below. As shown therein, GPC peak retention times continuously decreased with increasing  $\bar{M}_n$ .  $\bar{M}_n$  of ARDEL® D-100 is approximately 24,000.

T<sub>g</sub>s determined by DSC and TBA differed somewhat although the basic trends are the same. The T<sub>g</sub>s of the HTPA initially increased with increasing molecular weight, then leveled off at  $\bar{M}_n = 7500$ . The T<sub>g</sub>s of the thermally reacted ETPA decreased with increasing molecular weight due to lower crosslink density. A small peak at 3280–3290 cm<sup>-1</sup> in the infrared spectra of

All the uncured polyarylates in the Table were soluble at concentrations of 20% (w/v) in chloroform and in m-cresol. Films were cast from m-cresol solution and cured to a final temperature of 250° C. in flowing air. Higher cure temperatures were not used due to the possibility of degrading the polymer. The 2500 and 5000- $\bar{M}_n$  HTPA did not form usable films. The film obtained from the 2500- $\bar{M}_n$  ETPA was too badly cracked for mechanical test specimens to be cut, but smaller specimens for TMA and solvent testing could be obtained. Reaction of the ethynyl group has provided chain-extension and/or crosslinking during the cure thereby increasing its effective molecular weight. Film specimens of the cured ETPA and ARDEL® were tested with a variety of solvents. All samples were resistant to ethylene glycol (deicing fluid) and to JP-4 (jet fuel) after 24 hours immersion under stress. Stress was applied to a film specimen by bending the small strip back upon itself. ARDEL® failed almost immediately on immersion in tricresyl phosphate (hydraulic fluid) and the 10,000- $\bar{M}_n$  ETPA failed after several minutes, but the lower molecular weight ETPA specimens were intact after 24 hours. In chloroform, ARDEL® dissolved and the higher molecular weight ETPA were swollen after ten minutes. Under the same conditions only very slight swelling was observed in the cured 2500- $\bar{M}_n$  ETPA.

It is desirable to incorporate into one material the good mechanical properties of ARDEL® and the higher molecular weight ETPA and the good solvent resistance of the lower molecular weight ETPA with its high crosslink density. One approach is through the use of a reactive plasticizer. A material thought to be compatible with the ETPA was synthesized by reaction of 4-ethynylbenzoyl chloride with 2,2-bis(4-hydroxyphenyl) propane to obtain



2,2-Bis(4-ethynylbenzoyloxy-4'-phenyl) propane 10

4-Ethynylbenzoyl chloride (2.72 g, 16.5 mmol) was added to a stirred solution of 2,2-bis(4-hydroxyphenyl) propane (1.71 g, 7.5 mmol) in 15 mL of dry pyridine. After stirring overnight, the mixture was added to 500 mL of 5% hydrochloric acid to precipitate a solid. The solid was stirred with 10% sodium bicarbonate solution, collected by filtration, and allowed to air dry. Recrystallization from an 80/20 ethanol/chloroform mixture provided 2,2-bis(4-ethynylbenzoyloxy-4'-phenyl) propane (2.39 g, 66% yield) as light yellow needles, mp 182°-183° C.; IR(KBr) 3280 and 3245 (m, sharp, C≡CH), 2110 (vw, C≡CH), 1730 (vs, ester C=O) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.70 (s, 6, CH<sub>3</sub>), 3.25 (s, 2, C≡CH), 7.1-8.5 (m, 16, aromatic).

Anal, Calcd for C<sub>33</sub>H<sub>24</sub>O<sub>4</sub>: C, 81.80; H, 4.99. Found: C, 81.97; H, 5.07.

The DSC curve of this 2,2-bis(4-ethynylbenzoyloxy-4'-phenyl) propane showed a sharp exotherm at 219° C. due to reaction of ethynyl groups that occurred soon after melting. A DSC curve of the reacted material showed no melting endotherm, indicating essentially complete reaction of the ethynyl groups. The melting point of this material is slightly below the T<sub>g</sub>s of the uncured ETPA and should be miscible with the polymers. A thermally reacted mixture of 10% 2,2-bis(4-ethynylbenzoyloxy-4'-phenyl) propane with an ETPA (M<sub>n</sub> = 7500) produced a material with a T<sub>g</sub> of 214° C., 7° C. higher than for the cured ETPA alone. A cured film of the same composition was tough and highly flexible yet swelled only very slightly on exposure to chloroform for 10 minutes.

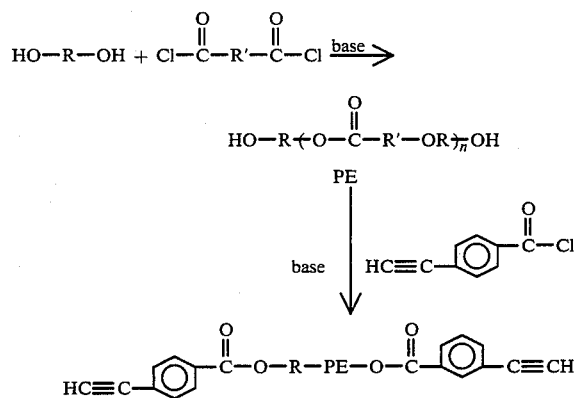
The thermally induced reaction of the ethynyl group on ester oligomers or polymers begins at about 200° C. and reaches a maximum rate in the 250°-350° C. range. The reaction only proceeds at a moderate or fast rate at a temperature above the glass transition temperature of the oligomer or polymer. At a temperature less than the T<sub>g</sub>, the material is in the glassy state where there is essentially no segmental molecular mobility. ETPA films cured for 0.5 hour at 250° C. in circulating air showed no residual ethynyl groups by Fournier transform infrared spectroscopy indicating complete reaction.

Thus, the synthesis of various molecular weight ethynylbenzoyloxy-terminated polyarylates and the improved characteristics thereof for use as composite matrices and the like has been clearly demonstrated. The thermally induced reaction of the ethynyl groups results in modified crosslinked polyarylates having higher T<sub>g</sub>s and improved solvent resistance when compared with exemplary uncrosslinked polyarylates, e.g., ARDEL® D-100. Although the molding properties of the ETPA were good only when the T<sub>m</sub> of the uncured ETPA was relatively low, the mechanical properties of cured films of the ETPA were essentially equal to that of ARDEL® D-100. Also, the thermal stabilities as determined by TGA were similar to ETPA and ARDEL® D-100.

Although the invention has been described relative to specific examples, it is not so limited, and numerous variations and modifications thereof will be readily apparent to those skilled in the art without departing from the spirit or scope of the invention as set forth in the appended claims. It is therefore to be understood that the invention may be practiced otherwise than as specifically described.

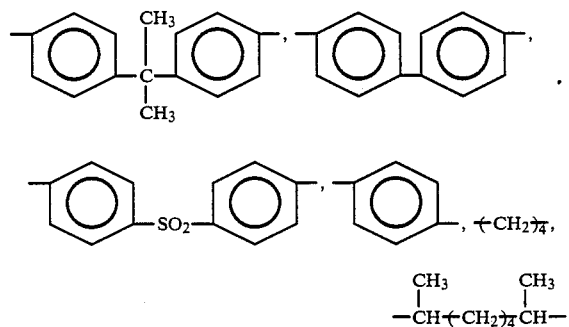
What is claimed as new and desired to be secured by Letters Patent of the United States is:

1. An ethynyl terminated ester oligomer for producing a cured polymer having improved solvent resistance, higher use temperature and synthesized according to the general reaction

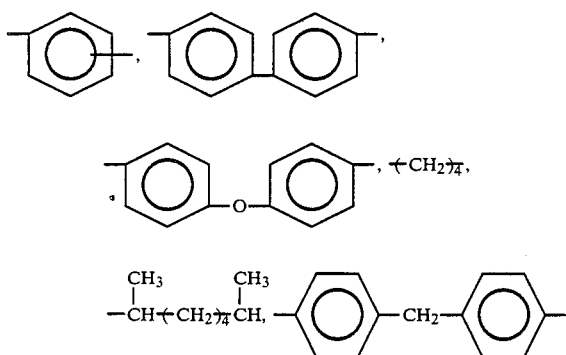


where

PE refers to the polyester radical portion,  
n is an integer and represents 4 to 100 repeat units,  
base refers to an organic base selected from the group consisting of triethylamine, pyridine, quinoline, diethylamine and piperidine,  
R is selected from the group of radicals consisting of



and mixtures thereof, and  
R' is selected from the group of radicals consisting of



and mixtures thereof.

2. A cured polymer formed from the ethynyl terminated ester oligomer of claim 1 by casting the oligomer into a film and heating the cast film in the temperature range of approximately 250° for thirty minutes.

3. A method for preparing an ethynyl-terminated polyarylate comprising:

(a) dissolving a quantity of an hydroxy-terminated polyarylate in a solvent selected from the group consisting of ethonol-free chloroform, methylene chloride and N,N-dimethylacetamide and containing at least an equimolar quantity of an organic base selected from the group consisting of triethylamine, pyridine, quinoline, diethylamine, and piperidine,

(b) dissolving at least an equimolar quantity of an ethynylbenzoyl chloride in a solvent also selected from the group of solvents listed above and adding the resultant to the stirred solution of hydroxy-terminated polyarylate obtained in step (a) over a period of five minutes and continuing stirring for approximately three hours,

(c) precipitating a polymer from the stirred solution,

(d) washing the precipitate, and

(e) drying the washed precipitate to recover a yield of ethynylbenzoyloxy-terminated polyarylate.

4. The method of preparing the ethynyl-terminated polyarylate of claim 3 wherein the hydroxy-terminated polyarylate has a number average molecular weight of approximately 2500 and the ethynylbenzoyl chloride is 4-ethynylbenzoyl chloride.

5. The method of preparing the ethynyl-terminated polyarylate of claim 3 wherein the recovered product has a number average molecular weight in the range of approximately 2500 to approximately 10,000.

6. The method of preparing the ethynyl-terminated polyarylate of claim 3 wherein the step of washing the precipitate includes washing the precipitate

- (a) once with a 5% sodium bicarbonate solution,  
 (b) twice with distilled water, and  
 (c) once with methanol.

7. The method of preparing the ethynyl-terminated polyarylate of claim 3 wherein the molar ratio of raw ingredients comprise:

- 0.0040 mole hydroxy-terminated polyarylate (2500- $\bar{M}_n$ ),  
 0.012 mole triethylamine, and  
 0.012 mole 4 ethynylbenzoyl chloride to yield an approximately 88% yield recovery of 2500- $\bar{M}_n$  ethynyl-terminate polyarylate.

8. The method of preparing the ethynyl-terminated polyarylate of claim 3 wherein the molar ratio of raw ingredients comprise:

- 0.00133 mole (7500- $\bar{M}_n$ ) hydroxy-terminated polyarylate,  
 0.0040 mole triethylamine, and  
 0.0040 mole 4-ethynylbenzoyl chloride to yield an approximately 95% yield recovery of 7500- $\bar{M}_n$  ethynyl-terminated polyarylate.

9. An ethynyl-terminated ester oligomer formed as the reaction product of an hydroxy-terminated ester oligomer and 4-ethynylbenzoyl chloride.

10. The ethynyl-terminated ester oligomer of claim 9 having a number average molecular weight in the range of 2500-10,000.

11. A polymer film formed from the ethynyl-terminated ester oligomer of claim 10 by casting the oligomer into a film and heating the cast film at approximately 250° C. for thirty minutes to effect crosslinking and oligomer chain extension.

12. A method of increasing the solvent resistance and  $T_g$  of 4-ethynylbenzoyloxy-terminated polyarylate (ETPA) by thermally reacting 70-90% by weight thereof with 10-30% by weight of 2,2-bis(4-ethynylbenzoyloxy-4-phenyl) propane to yield a material having improved solvent resistance and a higher  $T_g$  than that of the ETPA alone.

13. The method of claim 12 wherein the 4-ethynylbenzoyloxy-terminated polyarylate has a g/mole molecular weight in the range of 2500-10,000.

14. The method of claim 12 wherein the 2,2-bis(4-ethynylbenzoyloxy-4'-phenyl) propane and 4-ethynylbenzoyloxy-terminated polyarylate thermal reaction product is made into a m-cresol solution comprising 15% solids content (weight/volume),

doctored onto plate glass as a film and stage dried in air at increasing temperature intervals to reach 250° C. in approximately 30 minutes to yield a flexible, transparent, insoluble yellow film.

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