

## Linear Polymers of 4,4'-(2,2-Butylidene)dibenzoic Acid

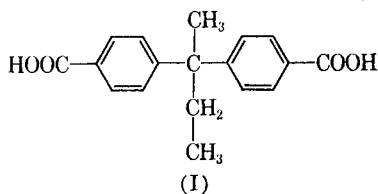
ARTHUR M. SCHILLER, JOHN C. PETROPOULOS,  
and CATHERINE S. HSIA CHEN, *Stamford Research Unit, Plastics  
and Resins Division, American Cyanamid Company, Stamford,  
Connecticut*

### Synopsis

Polyesters and polyamides have been prepared and characterized from 4,4'-(2,2-butylidene)dibenzoic acid. The polymers are amorphous with the exception of the piperazine polyamide. This novel diacid yields hard, tough polymers. The properties of the ethylene glycol and bisphenol A polyesters have been thoroughly investigated and are reported.

Polyesters and polyamides have continually increased in use since the pioneering work of Carothers and co-workers.<sup>1</sup> With the advent of aromatic polycarbonates, tough and strong polymers with high glass transition temperatures became available. However, the polycarbonates are partially crystalline in nature and this contributes to their strength properties. It was of interest to study the properties of polymers with high glass transition temperatures that are amorphous in nature.

We would like to report on our work with 4,4'-(2,2-butylidene)dibenzoic acid (I) in the preparation of polyesters and polyamides. Preparation of this diacid has been described,<sup>2</sup> and its use as an alkyd resin intermediate has been reported.<sup>3</sup>



### EXPERIMENTAL

#### Preparation of 4,4'-(2,2-Butylidene)dibenzoyl Chloride

The diacid dichloride was prepared in better than 90% yield via reaction of the acid with excess thionyl chloride under reflux, followed by vacuum distillation. The fraction boiling at 239°C./1 mm. Hg was collected. The diacid dichloride gradually crystallized to a solid, m.p. 54°C.

### Preparation of Polyesters

**A. Based on Aliphatic Diols.** The bis- $\beta$ -hydroxyethyl ester of 4,4'-(2,2-butyldiene)dibenzoic acid was prepared by reaction of 6-8 moles of ethylene glycol with 1 mole of the diacid to an acid number of 0.05-0.10 mg. KOH/g. sample. The excess glycol was stripped off until the product was a nontacky solid at room temperature. A solution polymerization method was developed<sup>4</sup> for conversion of the bisester to a high molecular weight polyester. The bisester was diluted to 50% solids in tetralin and zinc acetate added as transesterification catalyst. Ethylene glycol was azeotroped from the reaction mixture under nitrogen until about 95% of the calculated amount was collected. A modified Dean-Stark trap with a bottom return was then placed between the reactor and condenser. The trap was filled with Linde Molecular Sieves No. 5A and azeotroping continued. The Linde Molecular Sieves acted as a very efficient glycol scavenger. The polymer was recovered by devolatilizing on steam-heated rolls or through the use of a devolatilizer-extruder (Compex machine).

The usual melt polymerization method<sup>5</sup> could be used, but only for preparation of small amounts of polymer because of the extremely high melt viscosities of the polymers. The polyesters based on aliphatic diols, other than ethylene glycol, were prepared by melt polymerization.

**B. Based on Bisphenol A.** The most efficient method for the preparation of the bisphenol A polyester of 4,4'-(2,2-butyldiene)dibenzoic acid in sufficient quantities was interfacial polycondensation<sup>5</sup> involving the diacid chloride and bisphenol A. The polymer was soluble in the methylene

TABLE I  
Thermal Properties of Polymers of 4,4'-(2,2-Butyldiene)dibenzoic Acid

Coreactant <sup>a</sup>	Softening temp. $T_s$ , °C. <sup>b</sup>	$T_m$ , °C. <sup>c</sup>	$T_s - T_m$ , °C.
Ethylene glycol	160-170	105-109	~55
Trimethylene glycol	110-120		
1,4-Butanediol	80-90		
1,5-Pentanediol	80		
Ethylenediamine	249-261		
Trimethylenediamine	233-240		
Tetramethylenediamine	221-230	173-182	~50
Hexamethylenediamine	210-219	154-164	~55
4,4'-(2,2-Propyldiene)-dianiline	327-335		
Bisphenol A	290-310	204-211	~100
Bisphenol A/ 1,5-pentanediol (80:20)	210-235	125	~100
Piperazine	272-281	219-232	~50

<sup>a</sup> Intrinsic viscosities in dioxane at 30°C. for polyesters and in dimethylformamide at 30°C. for polyamides were >0.40 dl./g. in all cases.

<sup>b</sup> Carried out on melting point block.

<sup>c</sup> By differential thermal analysis.

TABLE II  
Physical Properties of 4,4'-(2,2-Butylidene)dibenzoic Acid Polyesters

Property	ASTM test method	Molded Specimen			Bisphenol A polycarbonate
		Ethylene glycol polyester	Bisphenol A polyester	Bisphenol A	
Mechanical					
Tensile yield strength, psi	D638	10,000	10,000	9,000	
Tensile modulus $\times 10^5$ , psi	D638	3.3	2.7	2.8-3.2	
Elongation at yield, %	D638	5-6	8-11	5-7	
Elongation at break, %	D638	50	—	60	
Flexural yield strength (apparent), psi <sup>a</sup>	D790	16,000	15,000	11-13,000	
Flexural modulus $\times 10^5$ , psi	D790	3.6	2.7	3.2	
Izod impact, fppi	D256				
Notched		0.5	2-3	2	
Unnotched		27	24	>65	
Tensile Impact, fppsi					
Long specimen		500	120	600	
Short specimen		250	60-90	200	
Rockwell hardness	D785	75-85M	90-100M	60M	
		124R	123R	119R	
Abrasion resistance (Armstrong), cc./100 cycles	D1242	0.13	0.11	0.09	

(continued)

TABLE II (continued)

Property	ASTM test method	Ethylene glycol polyester	Bisphenol A polyester	Bisphenol A polycarbonate
Thermal				
$T_g$ , °C.		105-109	204-211	149
Thermal coefficient of expansion, $10^{-5}$ in./in./°F.	D696	4.3	3.7	3.7
Heat distortion temperature (264 psi), °F.	D648	210-220	390-420	280-290
Flammability ( $1/8 \times 1/2 \times 5$ in. specimens), in./min.	D635 D757	Self-extinguishing 0.62	Self-extinguishing 0.29	Self-extinguishing 0.34
General				
Specific gravity		1.2	1.14	1.2
Moisture absorption (24 hr.), %		0.2	0.2	0.2
Intrinsic viscosity, dl./g.		0.5	0.6	—
		Additional Properties of Film		
Gas and vapor permeability, standard cc./100 in. <sup>2</sup> -24 hr. atm. (4-mil basis)	D1434	190	1540	1215
Dry gases: O <sub>2</sub>		23	198	186
N <sub>2</sub>		332	2190	3160
CO <sub>2</sub>		26	144	214
CH <sub>4</sub>		155	1400	1100
Wet gases: O <sub>2</sub>		22	169	229
N <sub>2</sub>				

<sup>a</sup> Yield strength is termed apparent since yielding occurs at flexural yield strains in excess of 5%, which is the normal limit for ASTM D790.

chloride that was used as the organic phase. This necessitated a precipitation step for recovery of the polymer. Methanol was used as the precipitating medium. The variables involved in this system have recently been studied by Morgan and Kwolek.<sup>6</sup>

The polymer was also prepared via melt polymerization of bisphenol A diacetate and the diacid.<sup>5</sup> Solution polymerization of the diacetate and diacid was used in a similar manner to the preparation of the ethylene glycol polyester.

### Preparation of Polyamides

Polyamides were prepared from 4,4'-(2,2-butyldiene)dibenzoic acid by both interfacial polymerization<sup>5</sup> and melt polymerization of the stoichiometric diamine-diacid salt.<sup>1,7</sup> As with the polyesters, melt polymerization methods are difficult to carry out on large scale because of high melt viscosities.

### DATA AND RESULTS

Many polyesters and polyamides of 4,4'-(2,2-butyldiene)dibenzoic acid were prepared and evaluated with respect to thermal properties. These are listed in Table I.

Following down a homologous series, the softening temperature decreases with increasing separation of the diacid moieties in the polymer as would be expected. An interesting relation appears to exist between the softening temperature  $T_s$  and the glass transition temperature  $T_g$ . For the aliphatic coreactants the difference is about 50–60°C. and it is about 100°C. for the aromatic polymers. The ethylene glycol, hexamethylenediamine, and bisphenol A polymers give a convenient range of thermal properties. The physical properties of these polymers are presented in Tables II and III. Bisphenol A polycarbonate is included for comparison.

TABLE III  
Physical Properties of Polyhexamethylene Butyldiene Dibenzamide

Property	
Flexural strength, psi	18,000–20,000
Flexural modulus $\times 10^6$ , psi	0.35–0.36
Izod impact, notched, fppi	0.7–0.9
Heat distortion temperature (264 psi), °F.	295–300
Rockwell hardness	104M
$T_g$ , °C.	154–164
Intrinsic viscosity (dimethylformamide at 30°C.), dl./g.	0.45

The ethylene glycol and bisphenol A polyesters were investigated in greater detail than the other polymers because of their interesting properties. Further properties measured are given in Tables IV and V.

TABLE IV  
Electrical Properties of 4,4'-(Butylidene)dibenzoic Acid Polyesters

Property	ASTM test method	Ethylene glycol polyester	Bisphenol A polyester	Bisphenol A polycarbonate
Dielectric constant	D150			
At 23°C.				
10 <sup>2</sup> cycles/sec.		3.4	3.4	3.0
10 <sup>3</sup> cycles/sec.		3.2	3.2	3.0
10 <sup>6</sup> cycles/sec.		3.0	2.6	2.9
At 80°C.,				
10 <sup>6</sup> cycles/sec.		3.2	3.1	—
At 125°C., 10 <sup>6</sup> cycles/sec.		—	3.1	—
Dissipation factor	D150			
At 23°C.				
10 <sup>2</sup> cycles/sec.		0.0034	0.0047	0.0014
10 <sup>3</sup> cycles/sec.		0.0049	0.0057	0.0020
10 <sup>6</sup> cycles/sec.		0.0250	0.0310	0.0110
At 80°C.,				
10 <sup>6</sup> cycles/sec.		0.019	0.022	—
At 125°C.,				
10 <sup>6</sup> cycles/sec.		—	0.0080	—
Dielectric loss factor at 23°C., 50% R.H.				
10 <sup>2</sup> cycles/sec.		0.012	0.016	0.004
10 <sup>3</sup> cycles/sec.		0.016	0.018	0.006
10 <sup>6</sup> cycles/sec.		0.075	0.081	0.032
Dielectric strength (short-time), v./mil	D149			
At 23°C.		400	440	400
At 80°C. (1 hr.)		460	530-620	—
At 100°C.		—	—	600
At 125°C. (1 hr.)		—	430-520	—
Dielectric strength (2 mil film, short-time, v./mil:	D149			
		4,000	5,000	5,000
Surface resistivity (after 4 days), ohms	D257			
At 23°C., 50% R.H.		$1.2 \times 10^{15}$	$5.5 \times 10^{15}$	$1.7 \times 10^{15}$
At 35°C., 90% R.H.		$9 \times 10^{11}$	$3 \times 10^{14}$	$2 \times 10^{14}$
Volume resistivity (after 4 days), ohm.-cm.	D257			
At 23°C., 50% R.H.		$4.1 \times 10^{15}$	$9.3 \times 10^{15}$	$8.1 \times 10^{15}$
At 35°C., 90% R.H.		$2 \times 10^{15}$	$3 \times 10^{15}$	$3 \times 10^{15}$

The thermal decomposition behavior of various of the polymers was determined by thermogravimetric analysis at a heating rate of 10°C./min. The results are summarized in Table VI.

TABLE VA  
Chemical Resistance Properties of 4,4'-(Butylidene)dibenzoic Acid-Ethylene Glycol Polyester, Three Months at Room Temperature

Reagent	Weight change, %	Appearance
Gasoline	+0.03	Slight discoloration
<i>n</i> -Heptane	-0.08	Good
Ethanol	+0.24	Good
10% NaOH	+0.16	Good
10% HCl	+0.32	Good
10% Lactic acid	+0.38	Good
Ink	+0.38	Stained
Acetone		Dissolves
Ethyl acrylate		Dissolves

TABLE VB  
Chemical Resistance Properties of 4,4'-(Butylidene)dibenzoic Acid-Bisphenol A Polyester, Ten Days at 23 and 95°C.

Reagent	Weight change, %	
	At 23°C.	At 95°C.
10% Acetic acid	+0.42	+1.1
10% H <sub>2</sub> SO <sub>4</sub>	+0.32	+0.60
10% NaOH	+0.36	-7.8 <sup>a</sup>
10% NaCl	+0.33	+0.60
Gasoline	+0.42	—
Ethanol	+0.31	—

<sup>a</sup> Sample faded.

TABLE VI  
Decomposition Temperatures of 4,4'-(2,2-Butylidene)dibenzoic Acid Polymers

Polymer	N <sub>2</sub>		Air	
	<i>T</i> <sub>i</sub> , °C. <sup>a</sup>	<i>T</i> <sub>10</sub> , °C. <sup>b</sup>	<i>T</i> <sub>i</sub> , °C. <sup>a</sup>	<i>T</i> <sub>10</sub> , °C. <sup>b</sup>
Hexamethylenediamine	359	437	353	435
4,4'-(2,2-Isopropylidene) bisaniline	425	486	374	451
Piperazine	425	465	297	426
Bisphenol A	430	475	348	413
Bisphenol A polycarbonate	426	494	367	469

<sup>a</sup> *T*<sub>i</sub> = temperature at which decomposition initiates.

<sup>b</sup> *T*<sub>10</sub> = temperature at which 10% weight loss occurs.

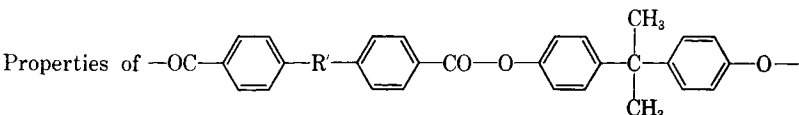
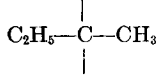
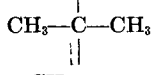


## DISCUSSION

If we look again at the structure (I) of 4,4'-(2,2-butylidene)dibenzoic acid we see that the essential features are: (a) high degree of aromaticity, (b) *p*-phenylene linkage, (c) nonplanarity of the molecule, and (d) unsymmetrical substitution of the central C atom. The high aromatic content imparts rigidity in the glassy state and a high melt viscosity in the liquid state. The *para* substitution enhances the rigidity of the polymer

molecule and imparts a degree of toughness greater than *ortho* or *meta* substitution.<sup>8</sup> The nonplanarity of the molecule decreases the ability of the polymer segments to pack and limits the intermolecular bonding of the carbonyl functions and aromatic rings. The unsymmetrical substitution on the central carbon atom also hinders intermolecular packing. Therefore, we expect the polymers to be rigid, somewhat tough, and mainly amorphous. If any of the polymers are capable of crystallizing, we expect difficulty in achieving a high degree of crystallinity. The polymers should also exhibit high softening points. The data presented substantiate the predicted properties. The only polymer prepared in this work that was found to be crystalline was the piperazine polyamide. The other polymers did not crystallize even after prolonged annealing.

Polyesters based on bisphenols and aromatic acids have been described by Conix.<sup>9</sup> The polymers exhibited exceptionally high glass transition temperatures and high melt viscosity. Direct comparisons with the data presented are difficult because of the different techniques used for measurement of glass transition and the crystalline nature of many of the polymers produced. However, the data on the bisphenol A polyester of 4,4'-(2,2-butylidene)dibenzoic acid fits very well with the data presented by Conix as shown in Table VII.

TABLE VII

Properties of 	$T_m$ , °C.
R	
	204-211 <sup>a</sup>
	225-230 <sup>b</sup>
	170-205 <sup>b</sup>
	190-220 <sup>b</sup>

<sup>a</sup> By differential thermal analysis.

<sup>b</sup> By elongation vs. temperature.

The decomposition temperatures of the polymers (Table VI) indicate the high thermal stability that can be expected from aromatic polyesters and polyamides.

The physical and mechanical properties of 4,4'-(2,2-butylidene) dibenzoic acid polymers, as shown in Tables I-VI, cover the range of medium to high impact materials. The ethylene glycol polyester falls in the area presently served by impact polystyrenes and methacrylates and the ABS polymers. However, it has the advantages of clarity, hardness, heat resistance



and chemical resistance. The polyester based on bisphenol A compares very favorably with bisphenol A polycarbonate in all properties, with the added advantages of higher heat resistance and lack of latent crystallinity—a factor which may cause the polycarbonate to gradually embrittle in use.

### References

1. Mark, H., and C. S. Whitby, Eds., *Collected Papers of W. H. Carothers on Polymeric Substances*, Interscience, New York, 1940.
2. Petropoulos J. C. (to American Cyanamid Co.), U. S. Pat. 2,848,486 (1958).
3. Petropoulos, J. C., *Offic. Dig. Feder. Soc. Paint Technol.*, **34**, 994 (1962).
4. Schiller, A. M., and W. F. Oliver (to American Cyanamid Co.), U. S. Pat. 3,066,116 (1962).
5. Sorenson, W. R., and T. W. Campbell, *Preparative Methods of Polymer Chemistry*, Interscience, New York-London, 1961.
6. Morgan, P. W., and S. L. Kwolek, *J. Polymer Sci.*, **62**, 33 (1962).
7. Carothers, W. H. (to du Pont Co.), U. S. Pat. 2,071,253 (1937); U. S. Pat. 2,130,947 (1938).
8. Edgar, O. B., and R. Hill, *J. Polymer Sci.*, **8**, 1 (1951).
9. Conix, A., *Ind. Eng. Chem.*, **51**, 147 (1959).

### Résumé

On a préparé et caractérisé des polyesters et des polyamides à partir de l'acide 4,4'-(2,2-butyldène) dibenzoïque. Les polymères sont amorphes à l'exception du polyamide de pipérazine. Ce nouveau diacide donne des polymères durs. Les propriétés des polyesters d'éthylène glycol et de bisphénol A ont été étudiées complètement et décrites.

### Zusammenfassung

Aus 4,4'-(2,2-Butylden)-dibenzoesäure wurden Polyester und Polyamide hergestellt und charakterisiert. Die Polymeren sind mit Ausnahme des Piperazinpolyamides amorph. Die genannte neue Disäure liefert harte Polymere. Die Eigenschaften der Äthylenglykol- und Bisphenol-A-Polyester wurden eingehend untersucht und beschrieben.

Received August 29, 1963