

## **Bisacid A2 (2,2-Diphenylolpropane dioxyacetic acid) as a Constituent of Crosslinked Polyesters**

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### **Synopsis**

The preparation of polyester resins using Bisacid A2 as the modifying acid in systems containing maleic unsaturation is briefly described. The detailed compositions of the various resins, the yields, final acid values, and capillary melting ranges are tabulated. The preparation of resin solutions in reactive monomers (principally styrene) and the viscosities of the resulting liquid resins at various monomer contents are given. The casting of unfilled standard sheet for subsequent testing is described. The range of Barcol hardnesses of the cast cured sheets is reported.

### **INTRODUCTION**

The preparation and purification of Bisacid A2 was described in two earlier communications.<sup>1,2</sup>

In the commercial production of crosslinkable polyesters for subsequent conversion to reinforced laminates, there exists a choice of various acids and anhydrides for cocondensation with the acid or acid anhydride carrying the unsaturation. There also exists a choice of reactive monomers for subsequent crosslinkage. Since the ingredients (including the diols used for polycondensation) may be used in greatly variable combinations, a wide range of products is obtainable. Each will possess the properties common to the class as a whole, but subtle differences will exist in such parameters as, for example, stiffness, heat resistance, and chemical resistance, which enables manufacturers to "tailor" resins to specific end use requirements.

The most commonly used "modifying acid," that is to say, the saturated acid with which maleic or fumaric acids are coesterified, is phthalic acid (phthalic anhydride), mainly because it is least expensive.

However, glass-reinforced (and indeed unreinforced cast) epoxy resins are competing with glass-reinforced polyesters in that they possess similar physical properties to a higher degree, albeit at substantially higher cost. Since epoxy resins are based on bisphenol-A, it was thought that polyesters containing similar structural units in the polymer chains before crosslinkage, such as those provided by Bisacid A2, might afford products which are comparable in at least some aspects of performance (especially chemical resistance and a reduced tendency toward brittle failure) to epoxy materials.

The preparation of two series of resins and of cast crosslinked and unreinforced sheet using Bisacid A2 is reported.

## EXPERIMENTAL

### Preparation of Polyesters

Polyesters containing Bisacid A2 were prepared in the usual laboratory manner, using propylene glycol as the diol, with azeotropic removal of water in the presence of xylol until all theoretical water was removed, followed by recovery of the solvent and continued heating in a stream of nitrogen until the desired acid value was obtained. Although commercial resins are reacted to acid value 30–25, the Bisacid A2 resins were taken to acid value 10, because this is likely to improve chemical resistance, although the longer reaction time produced a darker product and one which gave higher solution viscosities in the reactive monomer. However, no gelling troubles were ever encountered.

Two series of resins were prepared:

(i) Series I contains nine resins in which the molar ratio of saturated to unsaturated acids was maintained constant at 1:1, but in which the saturated acids consisted of mixtures of Bisacid A2 and phthalic anhydride in molar proportions of from infinity to zero in  $1/8$ -mole steps. The mole-% and weight-% compositions and other data are given in Table I.

(ii) Series II consisted of eleven resins in which Bisacid A2 was the sole saturated modifying acid, but in which the mole ratio of Bisacid A2 to maleic ranged from 0.25 to 1.0. The mole-% and the weight-% compositions and other data are given in Table II.

### Preparation of Cast Crosslinked Unfilled Polyester Sheet

#### *Solutions*

All the resins in series I and II were readily soluble in styrene, in methyl methacrylate, and in mixtures of these reactive monomers, with the sole exception of the one containing maleic and phthalic anhydride only which gelled before fully dissolving in styrene and required the addition of the usual inhibitors (150 ppm hydroquinone) to prevent gelation. None of the resins containing Bisacid A2 (irrespective of the amount of the latter) required inhibitor, and the resulting solutions were stable for several months. The continued stability of these solutions will be monitored and reported after one year. The solutions were prepared by tumbling the powdered resin with the appropriate amounts of monomeric solvent at room temperature.

As for the subsequent curing of the liquid resins, a methyl ethyl ketone peroxide-cobalt naphthenate catalyst system was used, and all styrene-based solutions cured readily, although it would appear that the standard maleic-phthalic polyester solutions were more reactive than those contain-

TABLE I

Molar ratio of Bisacid A2 to phthalic anhydride	Composition of polyester, wt-%			Number of unsaturations per 1000 mol. wt.	Final AV <sup>a</sup>	Yield, %	Capillary melting range (sinter point to clear point), °C
	Bisacetate	Phthalate	Maleate/ fumarate				
∞	63.7	0	20.8	15.6	10.0	96.3	53-64
0.875:0.125	58.0	4.0	21.7	16.3	8.6	99.2	54-64
0.75:0.25	51.9	8.3	22.7	17.0	10.5	100	51-67
0.625:0.375	45.4	13.1	23.8	17.8	10.7	96.1	49-58
0.5:0.5	38.1	18.3	24.9	18.7	10.2	96	38-48
0.375:0.625	30.9	21.7	27.0	20.3	10.9	100	45-51
0.25:0.75	21.2	30.4	27.7	20.8	9.6	100	44-52
0.125:0.875	11.2	37.6	29.3	22.0	7.7	97.6	42-52
0	0	45.5	31.1	23.3	9.9, 9.0, 9.5	99.1, 97.2, 99.4	35-45, 42-56, 45-54

<sup>a</sup> AV = acid value (mg KOH per g of compound).

TABLE II

Molar ratio of Bisacid maleic anhydride	Composition of polyester, wt-%			Final AV	Yield, %	Number of unsaturations per 1000 mol. wt.	Capillary melting range (sinter point to clear point), °C
	Bisacetate	Maleate/ fumarate	Propylene				
0.2:0.8	33.9	45.1	20.9	12.6	97.5	3.97	46-56
0.25:0.75	40.2	40.2	19.6	10-12	98.1	3.52	46-53
0.25:0.75	40.2	40.2	19.6	23.5	103.6	3.52	53-63
0.333:0.667	49.4	32.4	18.2	12.1	100	2.85	55-61
				9.7	98.8		
0.364:0.636	52.3	30.0	17.7	8.2	100	2.54	44-55
0.4:0.6	55.6	27.3	17.1	9.9	98.4	2.44	47-55
0.428:0.572	58.1	25.3	16.6	10.4	97.6	2.26	—
0.444:0.556	59.3	24.3	16.4	10.9	99.1	2.17	65-70
0.462:0.538	60.7	23.2	16.1	9.3	97.9	2.07	57-63
0.48:0.52	62.1	22.0	15.9	12.0	97.7	1.97	56-65
0.5:0.5	63.7	20.8	15.6	10.1	97.4	1.86	52-60
				8.4	97.0		(Sl. over- cooked)
				8.7	99.0		—
				13.3	98.0		—

ing even small amounts of Bisacid A2. Solutions based on methyl methacrylate could not be made to cure satisfactorily if the resin contained any Bisacid A2, but it was possible to achieve cure with an equimolar mixture of styrene and methyl methacrylate, although the resins took substantially longer to gel than with styrene alone.

Solutions were made to reactive monomer contents ranging from 30% to 55% and the viscosities determined at 23°C on a Ferranti-Shirley cone-and-plate viscometer. Most of the solutions showed only very slight pseudo-plasticity and could therefore be regarded as effectively constant in viscosity over shear rates relevant to reinforced polyester lamination.

The viscosities of the liquid resins are given in Tables III and IV. It is seen that, compared to the straight maleic-phthalic polyester (bottom of Table III), the solution viscosities of the Bisacid-A2-containing resins are considerably higher at comparable concentrations. This may be a cost advantage in laminating resins, which, when made up to a desired viscosity with styrene, result in a higher content of styrene in the cured product, this may help to partly offset the cost of Bisacid A2 which will no doubt be very much more expensive than phthalic even if Bisacid A2 were made on a commercial scale.

TABLE III  
Viscosities of Solutions of Series I Resins\*

Molar ratio of Bisacid A2 to phthalic anhydride	Viscosity of solutions at 23°C in styrene, poises					Viscosity of solutions at 23°C in methyl methacryl- ate (30% MMA), poises
	30% st	35% st	45% st	50% st	55% st	
—	694	48.5	13.2	4.8	2.6	55
0.875:0.125	274	18.3	—	—	—	—
0.75:0.25	187	—	—	—	—	—
0.625:0.375	90	—	—	—	—	—
0.5:0.5	32	—	—	—	—	—
0.375:0.625	41	—	—	—	—	29
0.25:0.75	30	—	—	—	—	27
0.125:0.875	56	—	—	—	—	43
0	43	—	2.3	—	—	55

\* The maleic content of these polyesters is equimolar with the combined saturated acids.

It should also be noted that the lower the acid value to which a given composition is reacted, the higher becomes the solution viscosity as befits the increased molecular weight.

#### Casting

Castings were prepared by making a U-shaped gasket from 1/8-in.-thick polypropylene sheet and using red Hermetite gasket cement between the

TABLE IV  
Viscosities of Solutions of Series II Resins<sup>a</sup>

Molar ratio of Bisacid A2 to maleic anhydride	Viscosity of solutions at 23°C in styrene, poises					Viscosity of solutions at 23°C in equimolar methyl methacrylate-styrene		
	30% st	35% st			55% st	45% reactive monomers	50% reactive monomers	50% reactive monomers
		45% st	50% st	55% st				
0.2:0.8	—	—	9.3	3.8	2.2	—	—	—
0.25:0.75 (to AV 10-12)	—	—	16.5	7.1	3.4	—	—	—
0.25:0.75 (to AV 23.5	—	—	6.0	2.5	1.2	—	—	—
0.333:0.667	215	135	12.6	5.1	1.9	—	—	—
0.364:0.636	172	22	4.3	2.0	—	4.3	1.9	—
0.4:0.6	258	45	—	—	—	—	—	—
0.428:0.592	383	36	—	—	—	—	—	—
0.444:0.556	445	28	—	—	—	—	—	—
0.462:0.538	226	20	—	—	—	—	—	—
0.48:0.52	289	15	—	—	—	—	—	—
0.5:0.5	694	78	17 <sup>b</sup>	6.8 <sup>b</sup>	3.1 <sup>b</sup>	—	—	—
			13.2	4.8	2.6	—	—	—

<sup>a</sup> Bisacid A2 the sole saturated acid, molar ratios of Bisacid/maleic ranging from 0.25 to 1.

<sup>b</sup> Two different batches.

gasket and the release coated glass plates. The cells were clamped using suitably strong spring clips.

The resins were catalyzed by adding to 96 parts of the solution (a) 2 parts of 50% solution of MEK peroxide in dimethylphthalate and (b) 2 parts of a solution of Cobalt Naphthenate (1% cobalt) which had been received at 10% cobalt content in white spirit and which had then be diluted to 1% with styrene. After room-temperature curing for 16–24 hr, the casting was postcured at 80°C for 3 hr, the cell was opened, and the resulting heets were edge trimmed.

### Properties of Cast Sheets

These will be the subject of further communications. The chemical resistance, dynamic mechanical properties, and heat distortion points are being investigated at present, and a report on the stiffness and strength of glass-reinforced laminates will be made in due course. In the meantime, the Barcol hardness of the cast sheets has been determined. It was found that the Barcol hardness was consistently between 35 and 45, which is the usual range for commercial polyesters. Within that range it was not possible to observe any significant correlation with the known composition of the polyesters or with the amount of reactive monomer present in the original casting liquid.

### SUMMARY

Crosslinkable unsaturated polyester resins containing Bisacid A2 were prepared in two series, one with and one without phthalic anhydride as a second modifying acid. In the second series, various amounts of maleic anhydride were cocondensed with Bisacid A2 only, while in the first series the molar proportions of maleic to saturated acids were kept constant. Solutions were prepared in suitable reactive monomers at various concentrations and their viscosities were determined. The liquid resins were catalyzed, cast, and postcured. The resulting sheets of  $\frac{1}{8}$  in. thick were tested for Barcol hardness and are being examined for other properties of interest.

### References

1. R. S. Lenk, *J. Appl. Polym. Sci.*, **15**, 311 (1971).
2. R. S. Lenk, *J. Appl. Polym. Sci.*, **15**, 1753 (1971).

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