The Stability of Solutions in Reactive Monomers of Crosslinkable Polyesters Containing Bisacid A2

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Synopsis

Earlier papers[1-6] have dealt with the synthesis and purification of bisacid A2; the preparation of unsaturated polyesters by cocondensing bisacid A2 with maleic anhydride in varying proportions in the presence or absence of phthalic anhydride as a further modifying acid, using propylene glycol as the polyesterification diol; the hardness and the thermal and mechanical properties of cast, cured resins and glass fiber-reinforced laminates; and the water and chemical resistance of the cured resins. This paper deals with the solution stability of the liquid resins prior to cure and, in particular, with the observed fact that solutions containing esters of bisacid A2 in sufficient quantity do not require the addition of stabilizers commonly needed for commercial polyesters in order to impart an acceptable shelf life to the liquid resins.

INTRODUCTION

Theory of Stabilization. Gel Inhibition in Commercial Polyester Systems

Vinyl monomers such as styrene and methylmethacrylate contain stabilizers to prevent spontaneous polymerization as a result of free-radical initiation and propagation. These stabilizers act as hydrogen donors, see reaction (A), and owe their efficiency to the resonance-stabilized free radical produced which does not continue the propagation upon collision with other molecules. Resonance stabilization depends on the existence of a number of canonical forms having energy levels which are low enough for the system to remain permanently in its hydrogen-abstracted form. A typical and highly efficient stabilizer is hydroquinone which has the canonical forms as given in reaction (B) below:


$$\text{(A)}$$

1847

(B)
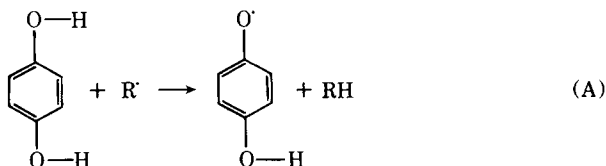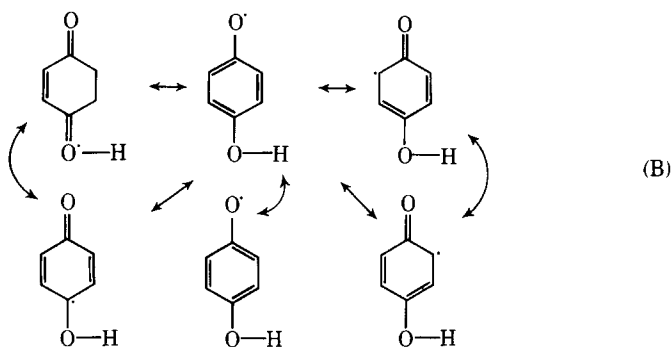
Crosslinkable polyester solutions in which the solvent is also a reactive vinyl-type monomer (usually styrene) require stabilization just as much as the vinyl monomer on its own, and it is therefore common practice to stabilize these solutions by the addition of about 150 ppm of hydroquinone. When the system is eventually ready to be cured, the stabilizing influence of the hydroquinone is overruled by generating suitably large quantities of hydrogen-abstracting propagating radicals, for instance, from ketone hydroperoxides (MEK hydroperoxide, cyclohexanone hydroperoxide) which have been split thermally or by the action of an activator such as cobalt naphthenate:

MEK hydroperoxide   free radical
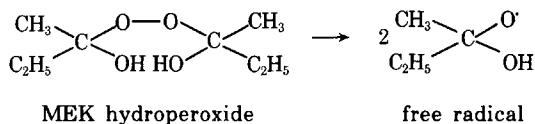
In order to guarantee an acceptable shelf life of polyester resins in styrene, it has therefore been general practice to include "external stabilizers" such as hydroquinone. The polyesters, however, are usually maleic/phthalic cocondensates with propylene glycol.

One cannot expect facile hydrogen atom abstraction from the ordinary carboxyl esters of phthalic and maleic esters, but some similar effect might quite conceivably be present in acids in which the carboxyl group is attached to an aromatic nucleus through a methylene bridge. This can be represented by reactions (C) and (D):

(C)
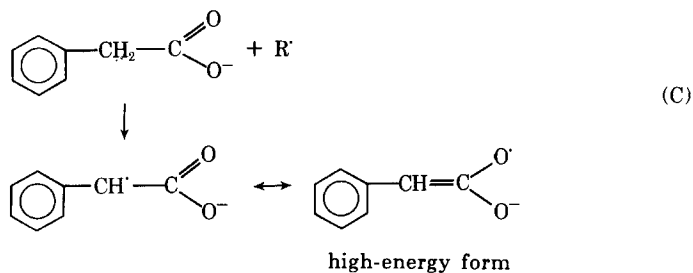
high-energy form

and, more likely, by the benzylic free radical canonical forms:

(D)
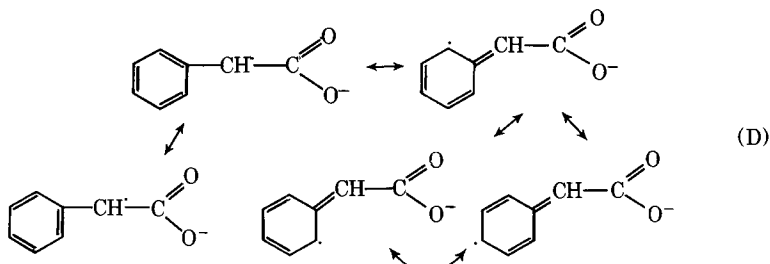
Because of the high-energy nature of the alternative structure of mode (C), mode (D) would doubtlessly dominate in a structure like
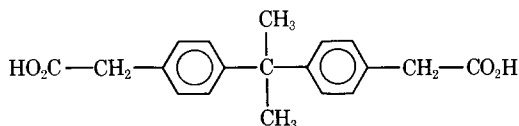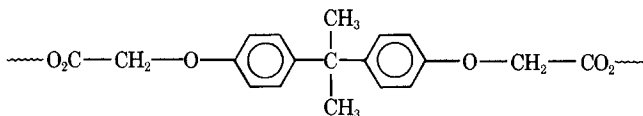

but this acid is not readily available. If it were, it might be an effective internal stabilizer. (Subsequent work described in the following, has shown that the ethyl ester of the simple analogue of the above acid (phenyl-acetic acid) has stabilizing activity, but that this is limited in time.)

Bisacid A2 has obvious structural similarities with the acid molecule depicted above, but the interpolation of an ether bond between the methyl-ene group and the aromatic nucleus has significant effects on the relative importance of the two potential modes of stabilization analogous to (C) and (D). The desired electron drift is now able to occur owing to the oxygen's I effect (E), resulting in a reduced-energy species (F) of the high-energy canonical form of (C) and making internal stabilization feasible by that mode, while a mode analogous to (D) is ruled out owing to the electron barrier which the oxygen atom imposes at the entrance to the aromatic nucleus:

(E) (F)

reduced-energy form
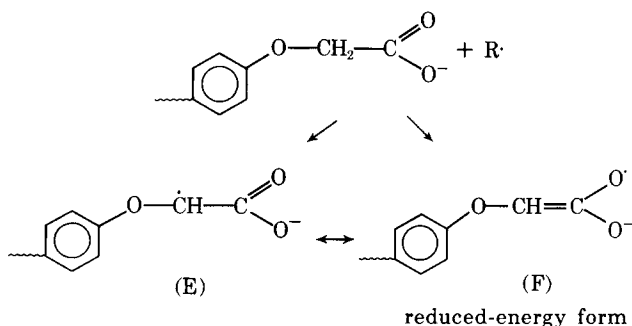
Since there exists an abundance of such entities, even quite a low degree of resonance stabilization in the ether bridge system may produce the over-all stabilizing activity found in polyesters containing bisacid A2 units.

If evidence is found for a high degree of stabilization of the structure

$$\sim\!\!O_2C\!-\!CH_2\!-\!O\!-\!\!\!\langle\bigcirc\rangle\!\!-\!\!\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\!-\!\!\langle\bigcirc\rangle\!\!-\!O\!-\!CH_2\!-\!CO_2\!\sim$$

then it may well be found also that crosslinkage with vinyl monomers becomes exceedingly difficult and that bisacid A2 affords an ideal system of stabilization, that is to say, a system which is not *excessively* effective and therefore does not prevent cure when cure is *intended* to take place, i.e., after addition of catalyst and accelerator.

Stability of Solutions of Copolyesters of Bisacid A2. Concept of "Internal Stabilization"

The question arises whether one could not build a stabilizing entity into the polymer chain itself to act as an "internal stabilizer" giving an acceptably long shelf life. If this additionally reduces the reactivity, this may also be helpful, since it would give better control over the cure of the system and lower peak exotherms. This would make larger moldings possible.

One of the most interesting features of polyester solutions in styrene which contain bisacid A2 in the polyester chain in suitable quantities is the observed fact that they do not require any hydroquinone stabilizer at all and yet remain essentially unchanged in viscosity over at least six months (see later). This is strongly indicative that internal stabilization has been accomplished.

External Stabilization

If the propane unit of the bisphenol A skeleton effectively blocks para effects such as are observed in hydroquinone, then certain simple model substances are worth investigating for their possible efficacy in producing gel inhibition when added to solutions of a 1:1 maleic/phthalic polyester containing 45% styrene. The following model substances suggest themselves: (1) phenoxyacetic acid and its ethyl and *tert*-butyl esters; (2) anisole; (3) phenylacetic acid and its ethyl ester; (4) furthermore, bisacid A2 itself and its ethyl ester.

If the methylene groups of bisacid A2 are responsible for *internal* stabilization, then the first should likewise provide *external* stabilization by the same mode, anisole should be inactive as a stabilizer, and phenylacetic acid might be such a good inhibitor as to prevent cure even in the presence of curing catalysts.

EXPERIMENTAL

Preliminary Experiments

A straight maleic/phthalic (1:1 mole) polyester was made (resin 6.3); yield: 99.4%, acid value: 11.6; 45% styrene solutions were made by

shaking 27.5 g of powdered resin with 22.5 g of destabilized styrene in Red Devil shaker at room temperature (23°C).   To each was added, at the time of weighing out, putative stabilizers as follows: (a) 0.25 g (0.5%) anisole;   (b) 0.25 g (0.5%) bisester A22 (ethyl ester of bisacid A2);   (c) 0.25 g (0.5%) bisacid A2;   (d) 0.25 g (0.5%) phenylacetic ester (ethyl); (e) 0.25 g (0.5%) phenoxyacetic acid (prepared according to Vogel);   (f) 0.25 g (0.5%) phenylacetic acid;   (g) 5 g (10%) bisester A22;   (h) 0.25 g (0.5%) phenoxyacetic ester (ethyl).   (All esters were specially prepared, and NMR spectra were run for structural verification.)

The time to gelling was as follows: (a) <4 days;   (b) about 4 days; (c) <4 days;   (d) 17 days;   (e) <4 days;   (f) <4days;   (g) >200 days; (h) 70 days.   All the solutions (including the ungelled portions of a, c, e, and f) could be readily cured by MEKP/cobalt naphthenate catalysis and postcured at 80°C for 3 hr to give brittle solids, so that the stabilizer did not cause subsequent curing problems.

It was seen that the simple aromatic ether and the acids were inactive (bisacid A2 was not soluble in the system anyway), but the ethyl esters of all three acids were effective stabilizers.   At 0.5% addition, however, none of them seemed to achieve a minimum gel-free shelf life of three months.

The internally stabilized polyesters of series I (which were found to be so remarkably stable even in the absence of external stabilizer) all contained from 11% upward of bisacetate.   It was for this reason that experiment g was set up with 10% of bisester A22, and this did indeed prove to be very stable.

Main Experiments

Although it cannot be finally stated that the various putative stabilizers might not *yet* prove to be effective if added in sufficiently large amounts, it was clear that the esters of bisacid A2, phenoxyacetic acid, and phenylacetic acid were the only ones that merited further investigation at this stage on the grounds of prima facie practicality.   Phenylacetic ester, however, was excluded, because its odor is so unpleasant that it would not find favor with processors or end users even if it proved to be an excellent stabilizer at addition levels of, say, 1% or so.

The main experiments were designed to determine the time to gelling (in days) of resin solutions to which bisester A22, ethyl phenoxyacetate, and *tert*-butyl phenoxyacetate were added in amounts ranging from 0.25% to 14% on the liquid resin.   The results (days to gelling) are shown in Table I.

The results shown in Table I revealed some remarkable facts: (1) The phenoxyacetic esters were about as effective at a 0.5% addition level as they were at 14%.   (2) There was no difference in the performance of the ethyl ester on the one hand and the *tert*-butyl ester on the other.   (3) Bisester A22, as distinct from the phenoxyacetic esters, increased its effi-

TABLE I
Time to Gelling of Resin Solutions with Additives

Additive, %	Time to gelling, days		
	Ethyl phenoxyacetate	*tert*-Butyl phenoxyacetate	Bisester A22
0.25	—	—	11
0.5	24	24	16
1	24	24	16
2	30	29	17
4	27	36	21
7	24	24	21
10	24	24	122
14	30	24	122

ciency gradually, giving limited protection at levels of up to 7%, but imparted longer-term stability when present in amounts of 10% or more.

DISCUSSION AND CONCLUSIONS

On the basis of the stability experiments described above, one may conclude that stabilization can occur by *either* of the two mechanisms indicated in the introduction, that is, by the mechanism outlined in structures C and D on the one hand and structures E and F on the other. The first is operative when an alkylated carboxyl group is attached to an aromatic nucleus via a methylene bridge, and the second, when the same group is attached to an aromatic nucleus via an oxymethylene bridge. The ester group is essential, since the analogous acids and the ether anisole fail to show the stabilizing effect. If a methylene or oxymethylene bridge were not essential, then phthalates, too, would be active and the problem of stabilization in the common commercial maleic/phthalic copolyesters would not have arisen in the first place.

A diligent search of thousands of potential stabilizing compounds other than (i) copper naphthenate in amounts of less than 10 ppm, (ii) certain quaternary ammonium, phosphonium, and sulfonium compounds at a level of about 0.1%, and (iii) hydroquinone and other phenols has been conducted by polyester researchers in industry for decades, and esters were generally discarded as ineffective.[7] The esters of aryl and aryloxyacetic acids have never, to the writer's knowledge, been examined in this context before. However, it is claimed that the propylene oxide adduct of bisphenol A (free from phenol) also has considerable activity.[8] This seems to indicate that aromatic oxymethylene-bridged alkylol compounds share the property of stabilization activity with aromatic oxymethylene-bridged alkylcarboxylic esters. Bisphenol glycol polyesters of maleic anhydride should therefore not require the addition of hydroquinone to impart stability. However, a spokesman of one leading company in the polyester field who also includes bisphenol glycol polyesters in their range of commercial

products[7] maintains that hydroquinone is essential for the long-term stability of this type of liquid resin. It follows that while *internal* stabilization can be imparted by including bisacid A2, internal stabilization cannot be achieved by simply using bisphenol glycols as the esterification diols. The stabilization activity of bisphenol A adducts of propylene oxide as observed by others[8] is therefore only of the *external* kind.

The question of a stabilization mechanism cannot yet be regarded as conclusively settled. However, the synthesis of further model compounds —which is outside the scope of the present investigation—should provide an interesting field. For practical purposes, however, one may dismiss stabilization by esters which are linked to an aromatic nucleus through a methylene bridge, because it does not afford protection *for a sufficiently long period of time.*

In retrospect, it is not surprising to find that copolyesters of bisacid A2 containing more than 10% of bisacetate should be as stable as those compositions to which similar amounts of bisacetate were externally added in the form of a simple bisester of the same acid. It remained to be seen whether the former, representing internal stabilization, were not perhaps ipso facto more efficient than the external stabilization in the latter. For this reason, one more resin was specially prepared as follows:

Resin 18 (belonging to series I), a 1:1 saturated/unsaturated molar ratio polyester in which the molar ratio of the saturated acids was bisacid A2:- phthalic 21:19. This represented the following composition in the final resin: bisacetate, 4.6 wt-%, phthalate, 42.1 wt-%, -propylene-, 22.6 wt-%, maleate, 30.7 wt-%. Final acid value: 11.7; yield: 96.8% theoretical.

If this resin, when made into a solution containing 45% styrene, were to gel within 21 days, then it could be said that internal stabilization with 4.6% or so of bisacetate is no more efficient than external stabilization with bisester A22 which, at addition levels of 4% and 7%, reached just this shelf life. If, on the other hand, the shelf life of the liquid resin made from resin 18 exceeded 21 days significantly or perhaps even reached three months or more, then it could be said that internal stabilization is more efficient than external stabilization with bisester A22 and that the level necessary to afford such protection may lie around or below 5% of bis- acetate.

In the event the latter proved to be the case, gelling occurred in the liquid resin 18 only after 128 days.

SUMMARY

Polyester solutions of resins containing bisacid A2 esters in reactive monomers show remarkable stability even in the absence of hydroquinone. Hydroquinone is normally employed to impart stability and provide an acceptable shelf life for liquid resins in commercial production. An explanation of this observation on the basis of chemical resonance structures

was sought. It was found that neither of two stabilization mechanisms can as yet be dismissed, and the indications are that both may contribute. These findings were based on (1) experiments involving "external stabilization" with simple esters of bisacid A2 as well as other model substances, these compounds being added to solutions of standard maleic/phthalic polyesters in styrene (45% styrene); and (2) on stability observations on resins of maleic/phthalic/bisacid A2 cocondensates at a constant molar ratio of total saturated acids to maleic acid of 1:1, but with weight percentages of bisacetate from about 5% upward.

It was seen that simple esters of bisacid A2 *did* act as external stabilizers as did esters of phenylacetic and phenoxyacetic acids, but in the latter two·the stabilizing activity was short lived even in the presence of quite large percentage additions. The longer-term stabilizing activity of simple esters of bisacid A2 depended on their being present in amounts upward of about 7%.

Comparing "external stabilization" as implicit in the preceding paragraph ·with "internal stabilization" (cocondensation of bisacid A2 into the ·polyester main chain), it was seen that the latter was more efficient and that about 5% bisacetate was sufficient to provide a shelf life of about four months to the liquid resin.

The fact that only moderate amounts of bisacetate are able to impart solution stability in the absence of stabilizers required for conventional ·polyester solutions is likely to be of interest to polyester manufacturers.

References

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