

Fig. 1. Dynamic mechanical properties of cotton-filler polystyrene.

constructed. Such plots are found to resemble those of the dynamic mechanical behavior of thermoplastic polymers at various temperatures. For example, a specific solvent concentration range is reached where the modulus curve goes through an inflection while the damping curve passes through a maximum.

By analogy with the glass transition temperature, we call this critical concentration the "glass transition concentration," and give it the symbol C_g . We have made preliminary measurements of polystyrene-benzene, -chloroform, and -ethyl acetate systems, and on poly(methacrylate)-benzene systems. A typical plot is shown in Figure 1. With it, for comparison, is a corresponding plot of dynamic mechanical properties versus temperature. A more complete report, including a discussion of the relation between glass transition concentration and glass transition temperature, will be made later.

References

1. Lewis, A. F., and J. K. Gillham, *J. Appl. Polymer Sci.*, **6**, 422 (1962).
2. Lewis, A. F., and M. C. Tobin, *SPE Trans.*, **1**, 177 (October, 1961).

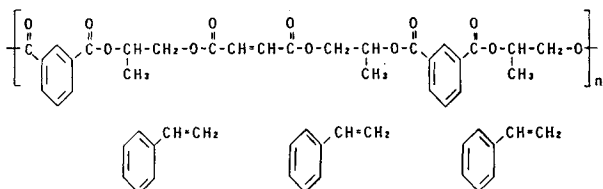
ARMAND F. LEWIS
MARVIN C. TOBIN

American Cyanamid Company
Central Research Division
Stamford, Connecticut

Received August 15, 1961

Control of Free-Radical Inhibitor Action in Unsaturated Polyesters

Substituted quinones show quite different relative free-radical inhibitor activities when tested under various polymerization conditions used in unsaturated polyester production and fabrication. In the preparation of unsaturated polyester solutions, such as shown below, it is desirable to produce a solution which is quite stable (does not polymerize) until the material is shaped in a mold. Polymerization should then proceed rapidly to give a solid product which can be removed from the mold. Prior to molding, it is desirable to have a stable solution at elevated temperature (114°C.), such that mixing of high-melting polyesters and vinyl monomers can be done rapidly. A stable solution is also desirable at ambient temperature, so that the solution may be stored prior to use. The advantage of rapid polymerization in the mold is that maximum production from a mold is allowed.



Short polymerization time is usually obtained by means of decomposition of a free-radical initiator such as a peroxide.

TABLE I. Relative Inhibitor Effectiveness in Unsaturated Polyesters under Various Conditions^a

A. Uninitiated polymerization at 114°C.:	DPQ > Q > DCQ > HQ > TBC
B. Initiated with benzoyl peroxide at 82°C.:	Q > DCQ > HQ ≅ TBC ≅ DPQ
C. Initiated with methyl ethyl ketone peroxide and cobalt naphthenate at 25°C.:	HQ ≅ Q > TBC > DCQ ≅ DPQ

^a Inhibitor abbreviations: DPQ, 2,5-diphenyl-*p*-benzoquinone, Q, *p*-benzoquinone, DCQ, 2,6-dichloro-*p*-benzoquinone, HQ, hydroquinone, TBC, *tert*-butyl catechol.

We find that the relative effectiveness of substituted benzoquinones and hydroquinones changes when measured under polymerization conditions used in unsaturated polyester manufacture and fabrication, as is shown in Table I. Polymerization and stability data are given in Table II.

The exact reason for the changes in relative effectiveness under the different conditions is not clear from these data. The changes may be due to a change in the primary radical formed, as different primary radicals are formed in each of these cases. The rate of radical production per se or the influence of inhibitor on the radical-forming process are also possible causes.

Regardless of the reason for the change in relative inhibitor effectiveness, a wide variety of control of inhibitor

TABLE II. Effects of Various Inhibitors on Stability of Unsaturated Polyesters

	Inhibitor added ^a					
	None	2,5-Diphenyl- <i>p</i> -benzoquinone	<i>p</i> -Benzoquinone	2,6-Dichloro- <i>p</i> -benzoquinone	Hydroquinone	<i>tert</i> -Butyl catechol
Moles inhibitor added per million parts resin	0	0.7	1.8	1.1	1.8	1.2
Stability, ^b uninitiated at 114°C., hr.	0.2	4.2	3.5	2.5	1.2	0.4
Cure at 82°C. ^c						
Gel time (66–88°C.), min.	2.3	6.0	15.0	10.0	4.6	4.7
Propagation (88°C. to peak exotherm), min.	3.5	5.5	5.0	5.2	6.1	4.8
Time to peak exotherm (66°C. to peak exotherm), min.	5.8	11.5	20.0	15.2	10.7	9.5
Peak exotherm, °C.	212	211	211	211	204	217
Cure at 25°C. ^d						
Gel time ^d (time to solidify), min.	4	8	26	7	31	17
Propagation (gel time to peak exotherm), min.	12	11	31	10	38	25
Time to peak exotherm, ^d min.	16	19	57	17	69	42
Peak exotherm, °C.	154	154	41	158	39	106

^a Inhibitor concentration: 200 ppm in a 40% styrene solution of an unsaturated polyester prepared from 2:1:3.15 mole ratio isophthalic/maleic anhydride/propylene glycol.

^b Stability: time required for a sample to solidify at given temperature.

^c Initiator: 1% benzoyl peroxide. Method is standard method of Society of Plastics Industry as described in *Proceedings*, Sixth Annual Technical Section, Reinforced Plastics Division, Society of Plastics Industry, February 28, 1951, Section 1, pages 1–4.

^d Initiator: 0.6% methyl ethyl ketone peroxide and 0.6% cobalt naphthenate solution (6% cobalt metal). A 50-g. sample was placed in a 150-ml. beaker in a water bath with a thermocouple centered in the resin for measuring the peak exotherm. Gel time: time from catalyst addition until the resin solidifies. Time to peak exotherm: time from catalyst addition to peak exotherm.

The peroxide is decomposed by heat in a mold or by accelerators such as cobalt naphthenate or tertiary amines in an unheated mold. A stability of polyester solutions is usually obtained by adding free-radical inhibitors such as hydroquinone, *tert*-butyl catechol, or benzoquinone. However, these materials usually have not only the desired ability to increase the stability in the absence of initiator but also the undesirable effect of increasing polymerization time in the presence of initiator.

Szwarc^{1,2} has shown that the reactivity of quinones with methyl or styryl radicals varies with the substituents on the quinone. The effectiveness of benzoquinones as inhibitors can be controlled by these substituents. However, the relative effectiveness of the various substituted benzoquinones appears to be the same whether the attacking radical is methyl or styryl.

action appears possible in unsaturated polyesters through variation of the substituents on quinone inhibitors. In the present case, diphenyl quinone shows good inhibitor activity in the absence of initiator and poor inhibitor activity in the presence of initiator. This is exactly what is desired technologically.

References

1. Szwarc, M., *J. Polymer Sci.*, **16**, 367 (1955).
2. Rembaum, A., and M. Szwarc, *J. Am. Chem. Soc.*, **77**, 4468 (1955).

P. HAROLD PARKER, JR.

California Research Corporation
Richmond, California

Received March 26, 1962