Controlled Polymerization in Unsaturated Polyesters. II. B-Staging*

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Synopsis

Addition of substituted quinones to unsaturated polyesters in a stoichiometric ratio with a low temperature initiator gives rapid polymerization to a stable, partially polymerized or B-staged unsaturated polyester. A stable, high temperature peroxide can be incorporated which is unaffected by the first-stage polymerization but which will initiate polymerization to the C-stage when the sample is heated. This process appears possible because of a low rate of reaction of substituted quinones with growing free radical chains in polyester polymerization. In general, the rate of reaction of the quinone seems to decrease with size and number of substituents. Alkyl-substituted quinones yield a stable product upon reaction with growing radical chain, whereas chloroquinone does not.

Thermosetting resins by their nature require polymerization be carried out in a mold whose shape is that of the final object desired. Further forming of the polymerized three-dimensional structure is generally impossible. Fabrication of objects is facilitated if polymerization can be carried out in stages. An intermediate stage of polymerization may have the advantage of handling a solid rather than a liquid, shorter polymerization cycle in a mold, and lower heat given off in exothermic reactions. Baekeland[2] obtained three-stage polymerization with the first synthetic thermosetting plastic, the phenol–formaldehyde resins. He termed these three stages A-stage (a soluble liquid or solid which can be melted), B-stage (a less soluble material which is softened by heat and can be molded under pressure), and C-stage (an insoluble, infusible solid which cannot be molded). This stagewise polymerization of phenol and formaldehyde he called the Bakelite Process. Stagewise polymerizations have been achieved in other major thermosetting condensation polymers, urea or melamine–formaldehyde[3] and epoxy.[4,5]

We have achieved stagewise vinyl polymerization of the fourth major thermosetting plastic, an unsaturated polyester–styrene solution, by use of certain quinones in a certain stoichiometry with certain peroxides as described. The polymerization proceeds rapidly at low temperature to

* Paper I of this series[1] covers the use of 2,5-diphenyl-*p*-benzoquinone for hot dilution of unsaturated polyesters without affecting the low temperature polymerization properties.

a solid, stable intermediate B-stage which can subsequently be further polymerized by heat to an infusible C-stage.

EXPERIMENTAL

Materials

Unsaturated polyester was 1:1 isophthalic acid:maleic anhydride propylene glycol polyester prepared by the two-step process described previously.[6] Polyester for runs in Table I had 150 ppm (based on polyester + styrene) hydroquinone added at the beginning of the second step and 200 ppm of *tert*-butyl catechol added with the styrene. Polyester for runs in Tables II and III had no hydroquinone added and 150 ppm *tert*-butyl catechol added with styrene. The final polyester had an acid number of 15 and a number-average molecular weight of 3500. The weight-average molecular weight was approximately 7000. The solid polyester was ground and dissolved at room temperature in rubber-grade styrene which contained 10 ppm-*tert*-butyl catechol to give a 40% styrene–60% unsaturated polyester solution.

The following quinones were obtained from Eastman Kodak Company and used without further purification: 2,5-di-*tert*-butyl-*p*-benzoquinone, 2,5-di-*tert*-octyl-*p*-benzoquinone, *p*-benzoquinone, 2,5-dichloro-*p*-benzoquinone, and 2,5-dimethyl-*p*-benzoquinone. The 1,2-naphthoquinone and 1,4-naphthoquinone were obtained from Eastman Kodak Company and were recrystallized from benzene and from aqueous ethanol, respectively. The methyl-*p*-benzoquinone was obtained from Eastman Kodak Company and was sublimed before use. The 2,5-di-*tert*-amyl-*p*-benzoquinone, m.p. 110–112°C., was obtained by oxidation of Eastman Kodak Company 2,5-di-*tert*-amylhydroquinone with chromium trioxide in acetic acid followed by recrystallization from aqueous methanol. The 2,5-diiso-propyl-*p*-benzoquinone, m.p. 40–42°C., was obtained by oxidation of Eastman Kodak Company 2,5-diisopropylhydroquinone with chromium trioxide in acetic acid followed by recrystallization from aqueous methanol. The 2-methyl-5-isopropyl-*p*-benzoquinone, m.p. 44–45°C., was prepared as described previously.[7] The *tert*-butyl catechol was supplied by Dow Chemical Company.

Methyl ethyl ketone peroxide was Wallace and Tiernan 60% methyl ethyl ketone peroxide in dimethyl phthalate. Cobalt naphthenate, 6% cobalt metal, was supplied by California Chemical Company. Dicumyl peroxide was Di-Cup (Hercules Powder Company).

Determination of Extent of Reaction

Polymerization exotherm was chosen as a rapid method of determining the extent of reaction of a B-staged or partially polymerized polyester. The polymerization reaction between styrene and fumarate ester is exothermic. The heat of reaction can be approximated by placing a catalyzed unsaturated polyester sample in a bath warm enough to decompose the

TABLE I

Comparison of 2,5-Di-tert-butyl-p-quinone (DBQ) and tert-Butyl Catechol (TBC) in Stagewise Unsaturated Polyester Polymerization

	Run no.										
	1	2	3	4	5	6	7	8	9	10	11
Initiator[a]											
MEKP, %	1.0	1.0	1.0	1.0	1.0	0.5	0.5	0.1	0.1	1.0	1.0
Cobalt naphthenate, %	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Dicumyl peroxide, %	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Modifier added	None	DBQ	TBC	DBQ	TBC	DBQ	TBC	DBQ	TBC	DBQ	TBC
Modifier concn., ppm		5000	3800	500	380	500	380	500	380	5000	3800
Molar ratio modifier to low temperature initiator		1:1.5	1:1.5	1:15	1:15	1:7.5	1:7.5	1:1.5	1:1.5	1:1.5	1:1.5
Temperature of initial polymerization, °C.	25	25	25	25	25	25	25	25	25	49	49
Solidification or gel time, min.	16	30	>43,000	23	106	84	900	86,000	>139,000	7	20,000
% Polymerized 1 hr. after solidification	100	20		37	30					40	
% Polymerized various times after initiator addition											
1 day		30	<10	100	100	36	84			40	
1 week		30	<10			52	100			40	
1 month		30	<10			100				40	
2 months		40								40	100[b]

[a] MEKP as percentage of 60% solution of methyl ethyl ketone peroxide in dimethyl phthalate; cobalt naphthenate reported as percentage of 6% cobalt solution.

[b] Sample polymerized from bottom to top and when total sample was gelled, total sample was 100% polymerized.

TABLE II
Comparison of Various Quinones in Stagewise Unsaturated Polyester Polymerization

Run no.	Modifier added[a]	Molar ratio modifier to low temperature initiator[a]	Time to polymerize to solid or gel, min.	% Polymerization 1 hr. after solidification	% Polymerized various times after initiator addition		
					1 Week	1 Month	2 Months
1	p-Benzoquinone	1:1.5	>475,000	<10	<10	<10	<10
2	Methyl-p-benzoquinone	1:1.5	129,000	<10	<10	<10	<10
3	2,5-Dimethyl-p-benzoquinone	1:1.5	570	20	25	40	85
4	2,5-Dichloro-p-benzoquinone	1:1.5	3,600	30	100	100	100
5	2-Methyl-5-isopropyl-p-benzoquinone	1:1.5	840	<10	20	25	30
6	2,5-diisopropyl-p-benzoquinone	1:1.5	570	20	20	30	—
7	2,5-di-tert-butyl-p-benzoquinone	1:1.5	23	20	30	30	40
8	2,5-di-tert-amyl-p-benzoquinone	1:1.5	24	20	30	40	40
9	2,5-di-tert-octyl-p-benzoquinone	1:1.5	13	40	40	40	50
10	1,4-Naphthoquinone	1:1.5	167	20	30	40	70
11	1,2-Naphthoquinone	1:1.5	>259,000				

[a] Initiator system is the same as Table I, run 2, except modifier added in place of 2,5-di-tert-butyl-p-benzoquinone.

TABLE III

Comparison of Various Ratios of Quinones to Low Temperature Initiator in Stagewise Unsaturated Polyester Polymerization

Run no.	Modifier	Molar ratio modifier to low temperature initiator[a]	Time to polymerize to solid or gel, min.	% Polymerization 1 hr. after solidification	% Polymerized various times after initiator addition		
					1 Week	1 Month	2 Months
1	DBQ	4:1	>43,000	<10	<10	<10	—
2	DBQ	3:1	>43,000	<10	<10	<10	—
3	DBQ	2:1	540	20	20	30	—
4	DBQ	1:1.5	23	20	30	30	40
5	DBQ	1:2	20	50	50	50	50
6	DBQ	1:3	15	50	50	60	60
7	DBQ	1:4	10	60	60	60	—
8	DBQ	1:15	8	—	100[b]	100	100
9	Q	1:1.5	>172,000	<10	<10	<10	<10
10	Q	1:3	3,000	—	36	100	100

[a] Initiator system is the same as Table I, run 2, except the amount or type modifier is varied to give the ratio shown.
[b] After one day.

peroxide and observing the heat rise. A high heat rise shows low polymerization prior to immersion in the warm bath, while no heat rise shows complete polymerization. Quantitatively, the extent of partial polymerization can be approximated by comparison of the peak temperature reached in the polymerization of samples which have been previously partially polymerized with those which have not. If polymerization were adiabatic and heat capacity and heat transfer were constant over the temperature range, then partial polymerization could be calculated by the equation:

$$100 - \left[\frac{\Delta H_{\text{polymerization (B-staged sample)}}}{\Delta H_{\text{polymerization (unpolymerized sample)}}} \times 100 \right]$$

$$= 100 - \left[\frac{C_p(PE - T_0)}{C_p(PE_0 - T_0)} \times 100 \right] = \% \text{ polymerization of B-staged sample}$$

where PE = peak exotherm temperature of B-staged sample, T_0 = bath temperature, and PE_0 = peak exotherm of previously unpolymerized sample. Using this equation and ignoring heat loss and change in C_p gives an answer of the correct order of magnitude. Duplicate runs with the same polyester agree within $\pm 5\%$. An additional error is added to the data in Tables I–III due to use of different polyester preparations which had aged for different lengths of time. This error is $\pm 5\%$.

The peak exotherm was measured by placing a 50-g. sample of unsaturated polyester in a 150-ml. corked beaker with a thermocouple in a glass rod centered in the sample. The sample was placed in a bath at 114°C. and the temperature rise recorded. B-staged samples were stored in the dark prior to exotherm measurement. The gel time of the sample was observed by dropping 6-mm. glass beads into a sample of polyester in a 6-in. test tube until the beads no longer sank in the sample.

RESULTS

Substitution of 2,5-di-*tert*-butyl-*p*-benzoquinone (DBQ) for the usual inhibitor for the unsaturated polyesters *tert*-butyl catechol (TBC) is shown in Table I. Two initiators are present: a room temperature system of methyl ethyl ketone peroxide and cobalt naphthenate and a high temperature initiator, dicumyl peroxide.
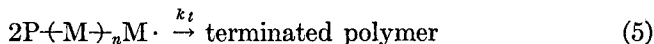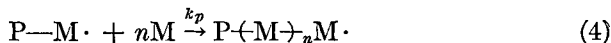
Substitution of various quinones for the DBQ in the above unsaturated polyester system is shown in Table II.

Variation in the ratio of DBQ to methyl ethyl ketone peroxide in the above unsaturated polyester system is shown in Table III. Data for *p*-benzoquinone (Q) are also given.

DISCUSSION

The mechanism of vinyl copolymerization of unsaturated polyesters initiated by peroxide may be written as shown in eqs. (1)–(5):

$$P + A \xrightarrow{k_d} 2fP\cdot \tag{1}$$

$$P \xrightarrow{k_h} 2fP\cdot \qquad (2)$$

$$P\cdot + M \xrightarrow{k_a} P\text{---}M\cdot \qquad (3)$$

$$P\text{---}M\cdot + nM \xrightarrow{k_p} P(M)_nM\cdot \qquad (4)$$

$$2P(M)_nM\cdot \xrightarrow{k_t} \text{terminated polymer} \qquad (5)$$

where P = peroxide, $P\cdot$ = free radical from peroxide, f = fraction of theoretical radicals which start polymerization (efficiency), A = activator, M = unsaturation in styrene or fumarate ester, $M\cdot$ = styryl or fumaryl radical. Peroxide is decomposed by either an activator [eq. (1)] or heat [eq. (2)] to give peroxide radicals, some of which initiate polymerization [eq. (3)]. Polymerization is propagated [eq. (4)] and terminated [eq. (5)]. If the termination reaction (5) were absent, polymerization would proceed to completion with a very small amount of peroxide. Addition of 0.6% methyl ethyl ketone peroxide is sufficient to overcome reaction (5) and to carry the reaction essentially to completion at room temperature.
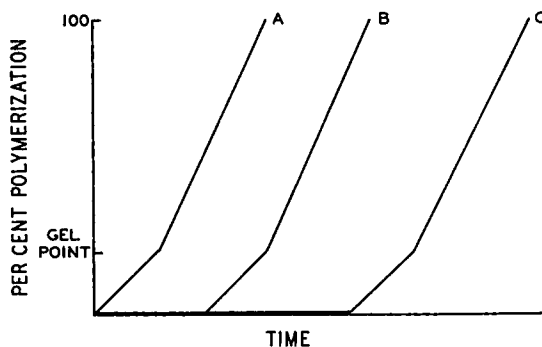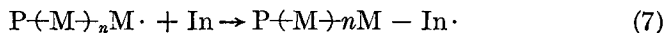

Fig. 1. Unsaturated polyester polymerization in the presence of added inhibitor: (A) no inhibitor; (B) 0.02% inhibitor; (C) 0.05% inhibitor. This figure is an idealization and does not represent actual experimental data.

An inhibitor, In, can be added to give a second termination reaction [eq. (6) or (7)]:

$$P\cdot + In \xrightarrow{k_{In}} P_{In}\cdot \qquad (6)$$

$$P(M)_nM\cdot + In \rightarrow P(M)nM - In\cdot \qquad (7)$$

If reaction (6) or (7) is very fast and the product is inactive, then these reactions will predominate over reactions (3), (4), or (5). Addition of an ideal inhibitor will stop polymerization completely until all inhibitor is consumed. Reaction will then proceed as in an uninhibited case if initiator is still present. The polymerization accelerates after gelation due to a
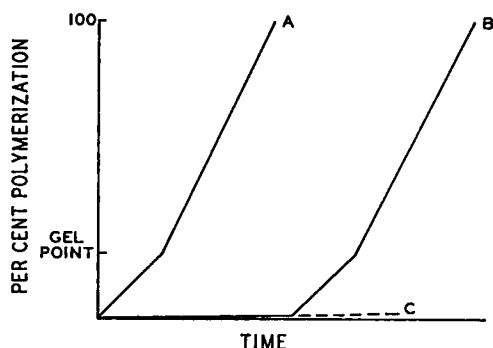
Fig. 2. Unsaturated polyester polymerization in the presence of conventional inhibitor, TBC: (A) no inhibitor; (B) added TBC plus excess initiator; (C) added TBC equivalent to initiator. This figure is an idealization and does not represent actual experimental data.
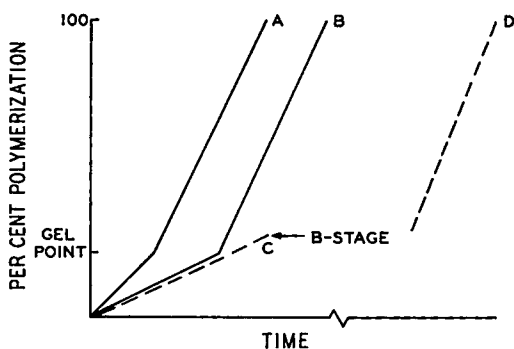

Fig. 3. Stagewise polymerization of unsaturated polyester: (A) no modifier added; (B) added DBQ plus excess initiator; (C) addedDBQ equivalent to initiator; (D) polymerization (C) continued by addition of a high temperature peroxide. This figure is an idealization and does not represent actual experimental data.

decrease in reaction (5), the Tromsdorff-Norrish effect.[8,9] The effect of adding an ideal inhibitor is illustrated in Figure 1.

Addition of increasing amounts of a conventional unsaturated polyester inhibitor, tert-butyl catechol, is illustrated in Table I (runs 1, 3, and 5). A small amount (run 5) appears to stop reaction until it is consumed, after which reaction proceeds normally. If amounts of inhibitor equivalent to the low temperature initiator are added, then reaction is stopped completely (run 3). This type action is illustrated in Figure 2. A similar result is seen with p-benzoquinone as the inhibitor (Table III, runs 9 and 10).

However, if substituted quinones such as 2,5-di-tert-butyl-p-benzoquinone (DBQ) are added instead of the conventional inhibitors, a quite different result is obtained. Table I (runs 1, 2, and 4) shows that addition of DBQ slows the time to react to the gel stage only slightly. If amounts

of DBQ equivalent to the initiator are added (run 2), the reaction stops at a stable intermediate stage of polymerization or B-stage. A stable, high temperature peroxide such as dicumyl peroxide can be present during this reaction, and when the sample is heated at a later date the peroxide decomposes to carry the reaction to completion or C-stage. This process of addition of a substituted quinone in approximately stoichiometric quantity with the initiator to produce a stable B-stage is illustrated in Figure 3. This action of substituted quinones can be explained if it is assumed these substituted quinones have a low vale of k_{In} in reactions (6) and (7) but produce a stable product. The low value of k_{In} is probably a result of the steric effect of substituents on the quinone upon the reaction with free radicals. A very similar effect has been observed by Waters[10] when measuring the redox potential of DBQ. Reaction proceeds at a reasonable rate in the presence of the modifier, but chains are eventually terminated by DBQ and the product is stable. Cohen[11] has shown styrene polymerizes initially half as fast in the presence of DBQ as in its absence.

The difference between equal molar amounts of DBQ and TBC is illustrated in Table I. The DBQ sample always gels faster but the reaction stops and the intermediate product is more stable. This difference is magnified at higher additive concentrations (runs 2 and 3, compared to runs 4 and 5). At low concentrations, reaction (5), which does not involve inhibitor, becomes an important part of the termination reaction.

Raising the temperature with TBC does not result in a B-stage, as is illustrated in runs 10 and 11. DBQ samples gel faster at higher temperature, and the gel is a stable, partially polymerized or B-stage material. The TBC sample was polymerized from the bottom of sample to the top, and when the sample was completely gelled it was completely polymerized.

The difference between the action of substituted quinones and materials usually called retarders should be pointed out. In a classical retarder, the rate in reaction (6) or (7) is of the same order of magnitude as k_p, but the reaction product is reactive and reacts at a rate less than k_p. The overall rate is decreased but the reaction is not stopped.

The effect of varying ratios of quinones to low temperature peroxide is illustrated in Table III. If it is assumed that the efficiency, f, in reaction (1) is 0.6,[12] then in run 4 the DBQ and low temperature initiator are in approximately 1:1 molar ratio. This appears close to optimum for obtaining a rapid conversion to the B-stage and stability of the product at a low conversion. A large excess of quinone leads to long gel times (runs 1, 2, and 3). As the excess of initiator over modifier increases (runs 5, 6, and 7), the conversion in the stable B-stage is increased. At large excess of initiator (run 8), no stable B-stage is obtained.

Various substituted quinones are compared in B-staging unsaturated polyesters in Table II. The larger substituents appear to give a lower k_{In} and a more rapid polymerization to the gel stage. The dichloroquinone (run 4) is interesting in the reaction product must be unstable and capable of further polymerization.

Tobolsky[12] has shown that if very low amounts of initiator are used in styrene polymerization, termination, [eq. (5)] stops polymerization short of completion in what he terms dead-end radical polymerization. Stability of the partially polymerized sample was not reported, but it is probably low. This type polymerization may be more difficult to achieve in unsaturated polyesters due to the Tromsdorff-Norrish effect.[8,9]

Other peroxides, such as cyclohexanone peroxide and benzoyl peroxide, have been used instead of methyl ethyl ketone peroxide for low temperature initiation, and di-*tert*-butyl peroxide has been used instead of dicumyl peroxide for high temperature initiation with equivalent results.

SUMMARY

Addition of substituted quinones to an unsaturated polyester in stoichiometric ratio with a low temperature initiator gives a rapid polymerization to a stable, partially polymerized or B-staged unsaturated polyester.

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Résumé

L'addition dans un rapport stoéchiométrique de quinones substituées aux polyesters non-saturés en présence d'initiateurs, actifs à basse température permet une polymérisation rapide et partielle avec formation d'un polyester insaturé d'étape-B. Un peroxyde stable, actif à des températures élevées peut être incorporé et reste inchangé par la premièr étape de polymérisation, mais peut initier une polymérisation lors de la troiisème étape lorsque l'échantillon est chauffé Ce procédé pourrait être possible à cause de la faible vitesse de réaction de la quinone substituée avec la chaîne en croissance portant le radical libre dans la polymérisation du polyester. En général la vitesse de réaction semble diminuer avec la grandeur et le nombre des substituants. Les quinones portant des substituants alcoyles donnent un produit stable ap ès réaction avec la chaîne en croissance radiocalaire contrairement à la chloroquinone.

Zusammenfassung

Der Zusatz substituierter Chinone zu ungesättigten Polyestern in stöchiometrischem Verhältnis zu einem Tieftemperaturstarter führt zu rascher Polymerisation unter Bildung eines teilweise polymerisierten oder im B-Zustand vorliegenden ungesättigten Polyesters. Ausserdem kann ein stabiles Hochtemperaturperoxyd zugesetzt werden, das zwar in der ersten Polymerisationsstufe nicht reagiert, jedoch beim Erhitzen der Probe die Polymerisation zur C-Stufe startet. Dieser Prozess wird anscheinend durch die niedrige Geschwindigkeit der Reaktion des substituierten Chinons mit wachsenden Radikalketten bei der Polyesterpolymerisation ermöglicht. Allgemein nimmt die Geschwindigkeit der Reaktion des Chinons mit Grösse und Zahl der Substituenten ab. Während alkylsubstituierte Chinone bei der Reaktion mit der wachsenden Radikalkette ein stabiles Produkt ergeben, ist dies bei Chlorchinon nicht der Fall.