

# Peroxy Radical Activated Addition of *tert*-Butylcatechol to 2,6-Di-*tert*-butyl-7-Substituted Quinone Methide Polymerization Retarders

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## Supporting Information

**ABSTRACT:** Peroxy radicals formed by the autoxidation of styrene react with 4-*tert*-butylcatechol (TBC) to give a *tert*-butyl-semiquinone radical. When the TBC radical is generated in the presence of a 2,6-di-*tert*-butyl-7-substituted quinone methide (QM), the result is *o*-TBC addition at the 7-position of the QM. The effects of TBC/QM addition are observed during styrene polymerization retarder testing under aerobic conditions for 2-(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)acetonitrile (QM-CN), 2,6-di-*tert*-butyl-4-(methoxymethylene)cyclohexa-2,5-dienone (QM-OMe), and 4-benzylidene-2,6-di-*tert*-butylcyclohexa-2,5-dienone (QM-Ph). Increasing the concentrations of QM-Ph and TBC during aerobic batch styrene polymerization allowed for silica gel chromatography isolation of 5-(*tert*-butyl)-3-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(phenyl)methyl)benzene-1,2-diol, a novel compound. Radicals generated by the autoxidation of cumene and by homolysis of dicumylperoxide also activate TBC/QM addition. TBC/QM interaction causes a reduction in the performance of QMs as styrene polymerization retarders under aerobic conditions. Under anaerobic test conditions, a better simulation of industrial styrene purification, the TBC/QM interaction leads to only minimal reduction in retarder performance.

## INTRODUCTION

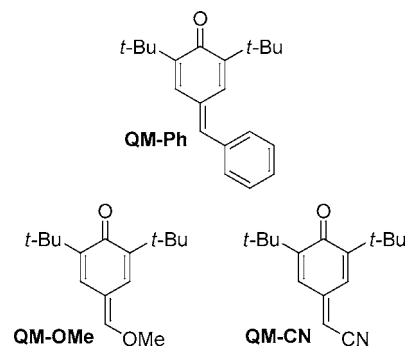
Thermal self-initiation of styrene polymerization<sup>1–3</sup> creates physical and economic complications for styrene production, because styrene, whether prepared from ethylbenzene dehydrogenation or methylbenzylalcohol dehydration, is purified by distillation at temperatures of 70–120 °C.<sup>4,5</sup> In order to mitigate in-process polymerization, producers add inhibitors and retarders to the distillation train. Industrial inhibition practices have evolved from the use of elemental sulfur<sup>4,5</sup> to hydroxylamine<sup>6</sup> or nitroxide<sup>7</sup> inhibitors in combination with nitrophenol retarders.<sup>8,9</sup> While it is possible to operate using only inhibitors, nearly all producers prefer to also add a retarder for protection in areas of low flow and during unexpected plant shutdowns. Toxic nitrophenol polymerization retarders, such as the current commodity of choice, 2,6-dinitro-4-*sec*-butylphenol (DNBP), are candidates for government restrictions on production, importation, and use.<sup>10,11</sup> These restrictions have created a need for a new environmentally compatible and economically viable polymerization retarder for the styrene industry.

2,6-Di-*tert*-butyl-7-substituted quinone methides (QMs) have endured extensive research because of their antipolymerant and antioxidant characteristics,<sup>12–15</sup> and they are the leading candidates to replace DNBP. While QM chemistry has been applied successfully in field trials, there remain concerns over how the chemistry interacts with other styrene additives.<sup>16</sup> In addition to the inhibition chemicals added to the bottoms of the distillation towers, 4-*tert*-butylcatechol (TBC) is added into the overhead of the styrene finishing tower, where it continues on with the styrene product for polymerization protection during transportation and storage.<sup>4</sup> If the styrene tower overhead is designed with a partial recycle or the need arises to rework off specification styrene, some of this TBC may be recycled back into the tower where the QM retarder is present. Here we report the polymerization testing of three quinone methide polymerization

retarders in the presence of TBC, identify a mechanism of QM/TBC addition, and describe how conditions required for QM/TBC addition are not present in styrene production.

## RESULTS AND DISCUSSION

Merrill<sup>16</sup> reported that 15 ppm of TBC renders 100 ppm of a 7-aryl quinone methide ineffective towards preventing styrene polymerization during a 120 °C test, under conditions described as “in the absence of oxygen.” In order to determine the validity of these claims, ensure the safety and performance of QMs in styrene production, and better understand potential QM/TBC interaction mechanisms, similar testing was performed on a series of QMs (Figure 1). QM-Ph, QM-OMe, and QM-CN were chosen because of their reported effectiveness as styrene polymerization retarders, and to determine if previously reported



**Figure 1.** Retarder performance testing was carried out on the above three 7-substituted quinone methides.

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differences in reactivity caused by varying the 7-substituent change the interaction with TBC.<sup>13,17</sup>

While all three compounds were prepared according to published synthetic routes,<sup>18–21</sup> the hydrolytic instability of QM-OMe required recrystallization prior to each test. We observed a 10% conversion to 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde when crystalline QM-OMe is stored for 24 h under nitrogen. It is common industry practice to test antipolymerants on the basis of equal weight fractions, because that is how they are dosed into a production facility.<sup>17</sup> However, the polymerization testing described within contains equimolar retarder concentrations to eliminate performance differences from variations in initial molar concentration (Table 1). The concentration of TBC (15 ppm) was chosen because it represents the highest levels of TBC present in any portion of the styrene plant. The results of the retarder testing are shown in Figure 2.

QM/TBC retarder testing was carried out under anaerobic conditions by sparging the solutions with nitrogen prior to heating (Figure 2d). While the presence of TBC caused a minor decrease in retarder performance compared to the results without TBC (Figure 2c), a complete loss of performance as reported by Merrill<sup>16</sup> was not observed. To probe the effect that oxygen has on QM performance in the presence of TBC, the polymerization experiments were repeated without sparging the solutions with nitrogen (Figure 2a,b). Without TBC, the QM retarders maintain their performance despite the increased polymerization rate caused by the dissolved oxygen. However, the loss of performance when TBC and dissolved oxygen are present is consistent with the results reported by Merrill.<sup>16</sup> This indicates that in order for interaction to take place between TBC and a QM, the system must contain dissolved oxygen. The small loss of QM performance and the small performance improvement of the blank observed under anaerobic conditions (Figure 2d) are likely due to the presence of styrene autoxidation products present in the system prior to sparging.

To better understand the nature of QM/TBC interaction, the concentration of the inhibitors was increased from ppm levels to percent levels, and instead of relying on dissolved oxygen already present in the styrene, the reactions were sparged continuously

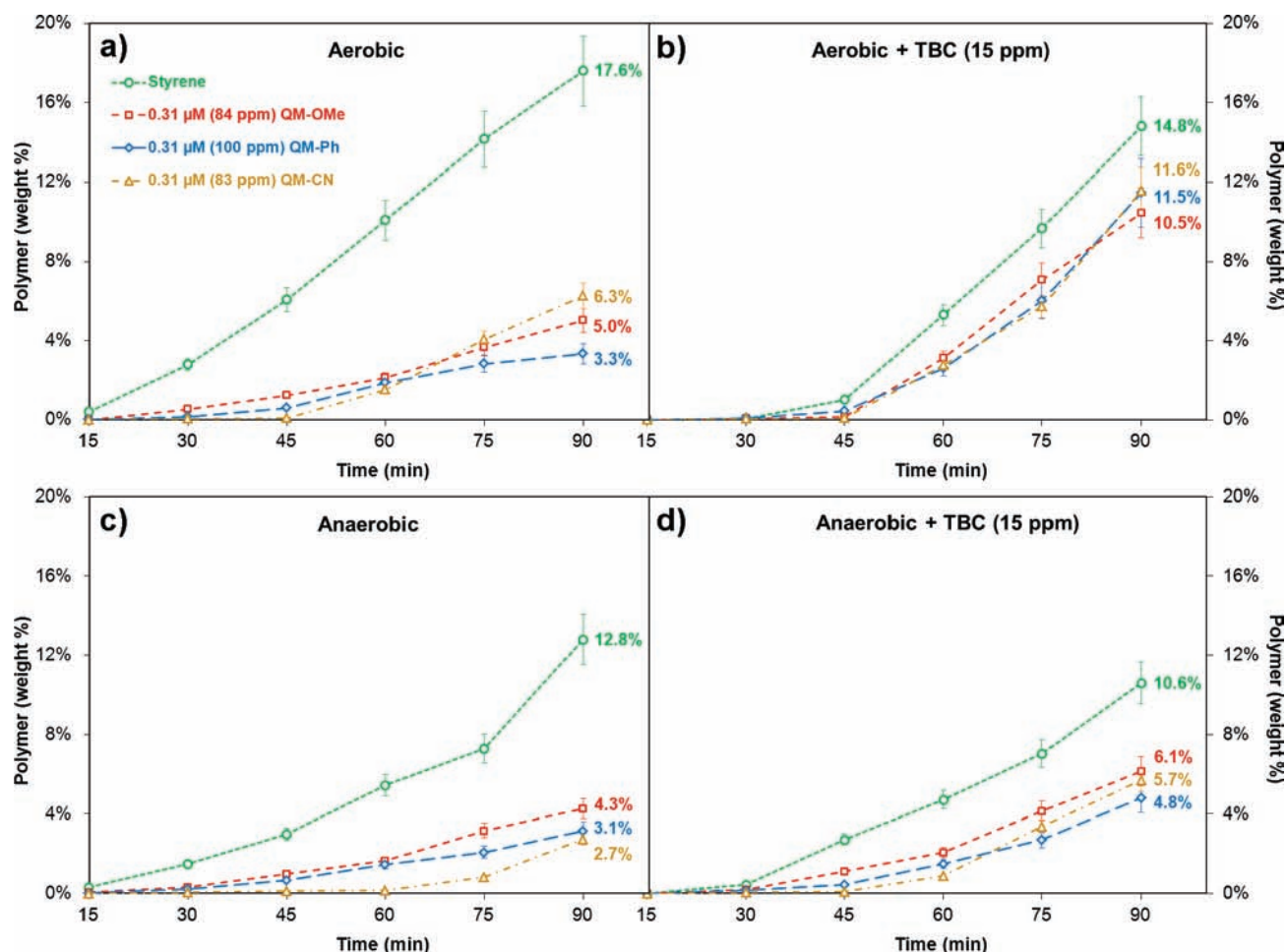
with oxygen. When equimolar amounts of TBC and QM-Ph are dissolved in a minimal amount of styrene, and the mixture is heated to 80 °C while sparging with oxygen, 44% conversion to an adduct is observed by GC. Silica gel chromatography allows for the isolation of 5-(*tert*-butyl)-3-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(phenyl)-methyl)benzene-1,2-diol (**1**), a compound that has not previously been reported. TBC addition products for QM-OMe and QM-CN were observed by GC–MS as the elimination product: 2,6-di-*tert*-butyl-4-(5-(*tert*-butyl)-2,3-dihydroxybenzylidene)cyclohexa-2,5-dienone. However, because the yields of adduct were too low to allow for isolation and further characterization, it was not possible to determine if the elimination occurs also during retarder testing or if it is a function of ionization in the mass spectrometer. Under the same conditions described above, if styrene is replaced with ethylbenzene, no reaction is observed. When the solvent is changed to cumene, which readily undergoes autoxidation,<sup>22</sup> adduct yields comparable to those in styrene are obtained. This is consistent with proposed TBC antioxidant mechanisms where TBC reacts with the autoxidation product of a hydrocarbon, not with oxygen.<sup>23</sup> Further evidence for peroxide-induced TBC activation causing adduct formation is observed when dicumylperoxide is added to equimolar TBC/QM solution in ethylbenzene at 80 °C to give a 23% yield of compound **1**. On the basis of these results a proposed mechanism for TBC/QM addition is shown in Figure 3. The first step is the reaction of TBC with a peroxy radical to generate a semiquinone radical intermediate. Quinone methides preferentially react with carbon radicals, which accounts for the addition to the unhindered carbon ortho to the semiquinone. Hydrogen abstraction by the hindered phenoxy radical, followed by rearomatization of the TBC ring, affords compound **1**.

While the peroxide-induced TBC addition explains the results obtained by Merrill,<sup>16</sup> it will have little effect on the performance of QMs as retarders for styrene production. Styrene is distilled at high vacuum, which greatly reduces the solubility of oxygen in hydrocarbons. Published experimental data for toluene indicates that at 50 °C and 0.33 atm the saturation limit for oxygen is less than 0.11 ppm.<sup>24</sup> The absence of soluble oxygen in the styrene purification train is demonstrated by the

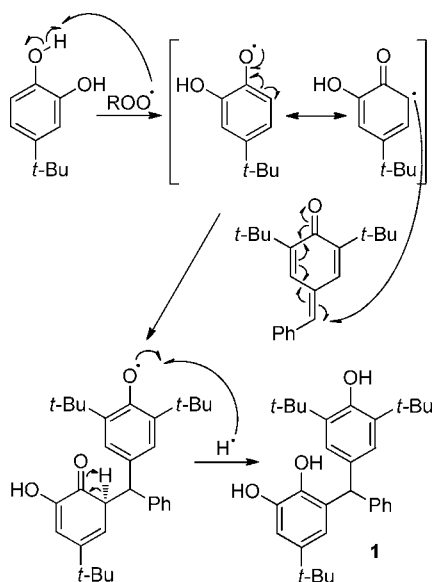
Table 1. Styrene polymerization retarder test results

retarder <sup>a</sup>	TBC (ppm)	O <sub>2</sub> <sup>b</sup>	polymer concentration (wt %) <sup>c</sup> at time (min) <sup>d</sup>					
			15	30	45	60	75	90
QM-Ph	–	–	0.03	0.23	0.66	1.45	2.07	3.14
QM-Ph	15	–	0.01	0.16	0.44	1.48	2.69	4.80
QM-Ph	–	yes	0.02	0.17	0.60	1.88	2.84	3.34
QM-Ph	15	yes	0.01	0.08	0.43	2.62	6.03	11.45
QM-CN	–	–	0.00	0.07	0.13	0.16	0.84	2.73
QM-CN	15	–	0.00	0.06	0.09	0.88	3.36	5.69
QM-CN	–	yes	0.00	0.05	0.08	1.53	4.07	6.26
QM-CN	15	yes	0.00	0.06	0.09	2.77	5.72	11.57
QM-OMe	–	–	0.05	0.32	0.98	1.65	3.16	4.27
QM-OMe	15	–	0.00	0.19	1.11	2.06	4.15	6.14
QM-OMe	–	yes	0.00	0.52	1.23	2.14	3.67	5.02
QM-OMe	15	yes	0.00	0.06	0.16	3.10	7.06	10.45
–	–	–	0.31	1.50	2.97	5.45	7.30	12.80
–	15	–	0.00	0.44	2.71	4.72	7.02	10.59
–	–	yes	0.41	2.80	6.07	10.08	14.16	17.59
–	15	yes	0.00	0.05	1.00	5.30	9.66	14.81

<sup>a</sup>Retarder concentration was kept constant at 0.31 μM, a typical plant dosage. <sup>b</sup>Dissolved oxygen: all reactions were carried out under nitrogen atmosphere; soluble oxygen was removed by sparging with N<sub>2</sub>. <sup>c</sup>Polymer concentrations were determined by methanol precipitation/absorbance (ASTM D2121). <sup>d</sup>Results are displayed as an average of four separate reactions.



**Figure 2.** Equimolar QM retarder testing at 120 °C. (a) Nitrogen atmosphere only, dissolved oxygen levels not consistent with plant operation: QM retarder performance is maintained. (b) Retarder performance is decreased substantially in the presence of dissolved oxygen and TBC. (c) Anaerobic conditions, no TBC: dissolved oxygen levels consistent with plant operation. (d) Anaerobic conditions with 15 ppm of TBC: maximum potential TBC concentration in styrene production.



**Figure 3.** Proposed mechanism for TBC addition to QMs.

ineffectiveness of phenolic antioxidants like TBC as in-process inhibitors without constant oxygen injection into the system.<sup>5</sup> The pressure tube retarder testing performed without nitrogen

sparging contains much higher soluble oxygen than is present in the plant. Styrene saturated with air contains 50 ppm of oxygen,<sup>25</sup> and heating the tubes increases the pressure inhibiting oxygen diffusion into the gas phase. Styrene inhibitor testing must be carried out in a rigorously maintained anaerobic environment if the goal is to recreate plant conditions.

## CONCLUSIONS

The styrene polymerization retarder performance of three 2,6-di-*tert*-butyl-7-substituted quinone methides, leading candidates to replace DNBP, was measured in the presence of TBC at varying levels of dissolved oxygen. In the presence of dissolved oxygen, TBC has a negative effect on QM styrene polymerization retarder performance. Autoxidation products of styrene react with TBC, forming a semiquinone radical that adds to the 7-position of the QM to form an adduct that does not inhibit styrene polymerization. Evidence for the mechanism of addition was found by preparing 5-(*tert*-butyl)-3-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(phenyl)methyl)benzene-1,2-diol with both styrene and cumene as solvents, and through reaction with dicumylperoxide. TBC does not affect QM retarder performance under anaerobic conditions found in styrene production.



## EXPERIMENTAL SECTION

**Materials.** Prior to use, styrene was passed over alumina to remove the TBC that is packaged with the product. 2-(3,5-Di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)acetonitrile (**QM-CN**),<sup>18</sup> 2,6-di-*tert*-butyl-4-(methoxymethylene)cyclohexa-2,5-dienone (**QM-OMe**),<sup>19,20</sup> and 4-benzylidene-2,6-di-*tert*-butylcyclohexa-2,5-dienone (**QM-Ph**)<sup>21</sup> were prepared according to previous literature reports. Due to its hydrolytic instability, **QM-OMe** had to be recrystallized from hexanes immediately prior to each use to remove 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde generated during storage.<sup>26</sup>

**Instrumentation.** Gas chromatography (GC) was carried out on a Hewlett-Packard 5890 with a Hewlett-Packard 3396 series II. GC measurements were quantified using 2,6-di-*tert*-butyl-4-methylphenol as an internal standard. Absorbance measurements for ASTM D2121<sup>27</sup> were performed using a Hach DR/2010 UV-vis spectrophotometer. <sup>1</sup>H and <sup>13</sup>C spectra were recorded on a Varian Oxford 300 NMR in CDCl<sub>3</sub> with a TMS standard. GC-MS was completed using an Agilent 6890 GC with a 5973 mass detector. Midwest Microlab, LLC performed carbon and hydrogen combustion analysis with an Exeter Analytical, Inc. CE440 elemental analyzer.

**Anaerobic Retarder Test.** **QM-Ph** (0.100 g, 0.34 mmol) and styrene (1.000 g, 9.6 mmol) were weighed into a 20-mL scintillation vial. **TBC** (0.250 g, 1.5 mmol) and styrene (10.0 g, 96 mmol) were weighed into a different 20-mL scintillation vial; 0.250 g of the **QM-Ph** solution, 0.375 g of the **TBC** solution, and 250 g of styrene were added to a 400-mL glass jar to give a 0.31 μM (100 ppm) **QM-Ph** and a 0.08 μM (15 ppm) **TBC** solution. Twenty-four Ace Glass #15 threaded pressure tubes equipped with PTFE screw caps and fluoroelastomer (FETFE) O-rings were filled with 8.0 g of 0.31 μM (100 ppm) **QM-Ph** styrene solution. Each tube was sparged with nitrogen for 2 min using a gas dispersion tube and then sealed under nitrogen. The 24 tubes were loaded into a test tube heating block preheated to 120 °C. At 15-min intervals, four tubes were removed from the block, cooled in an ice bath, and placed into a freezer (−17 °C) to quench the reaction. Methanol precipitation and absorbance spectroscopy (ASTM D2121) were used to measure the polymer concentrations in each of the tubes, and the four data points for each time were averaged.

**Aerobic Retarder Test.** **QM-Ph** (0.100 g, 0.34 mmol) and styrene (1.000 g, 9.6 mmol) were weighed into a 20-mL scintillation vial. **TBC** (0.250 g, 1.5 mmol) and styrene (10.0 g, 96 mmol) were weighed into a different 20 mL scintillation vial. 0.250 g of the **QM-Ph** solution, 0.375 g of the **TBC** solution and styrene (250 g) were added to a 400 mL glass jar to give a 0.31 μM (100 ppm) **QM-Ph** and a 0.08 μM (15 ppm) **TBC** solution. Twenty-four Ace Glass #15 threaded pressure tubes equipped with PTFE screw caps and fluoroelastomer (FETFE) O-rings were filled with 8.0 g of 0.31 μM (100 ppm) **QM-Ph** styrene solution. The vapor space of each tube was swept with nitrogen for 2 min and then sealed under nitrogen. The 24 tubes were loaded into a test tube heating block preheated to 120 °C. At 15-min intervals, four tubes were removed from the block, cooled in an ice bath, and placed into a freezer (−17 °C). Methanol precipitation and absorbance spectroscopy (ASTM D2121) were used to measure the polymer concentrations in each of the tubes, and the four data points for each time were averaged.

**Synthesis of 5-(*tert*-Butyl)-3-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(phenyl)-methyl)benzene-1,2-diol (**1**).** To a three-neck 100-mL round-bottom flask, equipped with a

reflux condenser, gas inlet, magnetic stirbar, and rubber septa, was added **QM-Ph** (20 g, 0.068 mol), **TBC** (11.25 g, 0.068 mol), and styrene (30 g, 0.288 mol). The mixture was heated to 80 °C while sparging continuously with oxygen. The reaction was monitored by GC, and after 2 h a new peak was observed at 15.8 min. After 24 h of continuous heating/sparging/stirring, the yield of the new peak was 21%. The reaction stalled after 36 h at a final GC yield of 44%. Silica gel chromatography (1% MeOH in CH<sub>2</sub>Cl<sub>2</sub>) followed by rotary evaporation on 10 g of the reaction mixture gave 5-(*tert*-butyl)-3-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(phenyl)-methyl)benzene-1,2-diol (**1**) as a sticky yellow solid (1.68 g, 3.6 mmol, 32% isolated yield). Mp 78–80 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.29–7.21 (m, 3H), 7.19 (t, *J* = 7.3 Hz, 2H) 6.95 (s, 2H), 6.82 (s, 1H), 6.42 (s, 1H), 5.57 (s, 1H), 5.12, (b, 1H), 4.73 (b, 2H), 1.35 (s, 18H), 1.14 (s, 9H). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ: 152.39, 143.89, 143.68, 143.09, 138.71, 135.83, 132.48, 131.03, 129.13, 128.44, 126.51, 125.91, 119.01, 110.78, 51.39, 34.33, 34.17, 31.34, 30.26. Anal. Calcd for C<sub>31</sub>H<sub>40</sub>O<sub>3</sub>: C, 80.83; H, 8.75; O, 10.42. Found: C, 80.54; H, 8.65.

## ASSOCIATED CONTENT

### Supporting Information

Experimental details for all polymerization retarder tests, dicumylperoxide activated synthesis of 5-(*tert*-butyl)-3-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(phenyl)-methyl)benzene-1,2-diol (**1**), GC-MS of 2,6-di-*tert*-butyl-4-(5-(*tert*-butyl)-2,3-dihydroxybenzylidene)cyclohexa-2,5-dienone, and NMR characterization of compound **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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