Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Functional Polymers. XLII. 4-Vinyl (or 4-Isopropenyl)-2,6-di-t-butylphenol: Synthesis and Copolymerization

Paul Grosso[a][b]; Otto Vogl[a]
[a] Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts [b] Dow Chemical Company, Midland, Michigan

To cite this Article Grosso, Paul and Vogl, Otto(1986) 'Functional Polymers. XLII. 4-Vinyl (or 4-Isopropenyl)-2,6-di-t-butylphenol: Synthesis and Copolymerization', Journal of Macromolecular Science, Part A, 23: 9, 1041 — 1056
To link to this Article: DOI: 10.1080/00222338608081111
URL: http://dx.doi.org/10.1080/00222338608081111

J. MACROMOL. SCI.–CHEM., A23(9), pp. 1041-1056 (1986)

Functional Polymers. XLII. 4-Vinyl (or 4-Isopropenyl)-2,6-di-t-butylphenol: Synthesis and Copolymerization*

PAUL GROSSO[†] and OTTO VOGL[‡]

Department of Polymer Science and Engineering
University of Massachusetts
Amherst, Massachusetts 01003

ABSTRACT

Polymerizable vinyl- and isopropenyl derivatives of 2,6-di-t-butylphenol have been synthesized, polymerized, and copolymerized. 2,6-Di-t-butyl-4-vinylphenol and O-acetyl-2,6-di-t-butylphenol were prepared in yields of 50 and 80%, respectively, starting from 2,6-di-t-butylphenol. 2,6-Di-t-butyl-4-isopropenylphenol was also synthesized in nearly 50% yield. The two hindered phenol monomers and some of their acetyl derivatives were copolymerized with styrene, methyl methacrylate, and n-butyl acrylate.

---

[*] This paper is dedicated to Professor Georg Manecke on the occasion of his 70th birthday with warmest personal wishes. For Part XLI of this series, see A. Gupta, M. N. Sarbolouki, A. L. Huston, G. W. Scott, W. Pradellok, and O. Vogl, J. Macromol. Sci.–Chem., A23(10), 1179 (1986).

[†] Present address: Dow Chemical Company, Midland, Michigan 48674

[‡] To whom correspondence should be addressed at Polytechnic University, Brooklyn, New York 11201.

0022-233X/86/2309-1041$3.50/0

INTRODUCTION

Hindered phenol antioxidants have been used for many years to protect plastic materials from thermal autoxidation [1-5], including compounds that have more than one phenol group in the molecule (vide infra).

High-molecular-weight nonfugitive, nonleachable stabilizers have received considerable attention in recent years [6]. In fact, polymer-bound antioxidants were probably the first polymer-bound stabilizer to be used [7].

We make a distinction between polymer-bound stabilizers, i.e., compounds that can be incorporated by virtue of a reactive group in already prepared polymers, such as $-CH_2Br$ or $-CH_2SH$ which might be incorporated into vulcanizing systems for rubbers, and polymerizable stabilizers, those having a polymerizable group such as a vinyl or epoxy group for incorporation into addition polymers, or dihydroxy, diamine, or dicarboxylic acid groups for incorporation into condensation polymers.

Antioxidants have been attached onto polymers (polymer bound) in various ways: by carbene insertion on polypropylene of 4-oxo-3,5-di-t-butyl-2,5-cyclohexadieneylidene followed by dehydrogenation [8]; by irradiation of polypropylene in the presence of 3,5-di-t-butylbenzyl methacrylate [9, 10]; by incorporation of 4-(4-hydroxy-3,5-di-t-butylphenyl)-2-butyl methacrylate into 67:33 butadiene-acrylonitrile copolymer during vulcanization [11, 12]; by endcapping of amino-terminated polydiene (MW 1 500) with 4-hydroxy-3,5-di-t-butylbenzyl bromide [13]; by reacting 2-(4-hydroxy-3,5-di-t-butylphenyl)propionic acid onto isocyanate-terminated polybutadiene or polyisoprene [14]; or by incorporating 4-hydroxy-3,5-di-t-butylbenzyl mercaptan into natural rubber [15]. Another method was used for the termination with 2,6-di-t-bytylphenol of a cationically produced styrene/isobutylene polymer. This group was attached as an end group to a polymer of about MW 1 500 in the para position [16].

Also, ethyl 3-(4-hydroxyphenyl-3,5-di-t-butylphenyl)propionate was attached to the hydroxy group of a propylene/10-undecene-1-ol copolymer, and poly(p-vinylphenol) was "tertiary-butylated" with isobutylene [17, 18].

Direct copolymerization of polymerizable antioxidants has led to a number of copolymers. Most are described in the patent literature and many have very specific and limited applications. A number of polymerizable monomers have been described, as well as some of their copolymers: 2-vinyloxyethyl-4-hydroxy-3,5-di-t-butylbenzoate with styrene and methyl methacrylate [19, 20]; N-(4-hydroxy-3,5-di-t-butylphenyl)methacrylamide with 1,3-butadiene and styrene [21]; 2,6-di-t-butyl-4-vinylphenol and 2,6-di-t-butyl-4-isopropenylphenyl phenol with styrene and 1,3-butadiene [22]. Other polymerizable antioxidants that were prepared were 3-(4-hydroxy-3,5-di-t-butylphenyl)-2,2-dimethylpropyl methacrylate [23], 4-(4-hydroxyphenyl-

3,5-di-t-butylphenyl)-2-butyl methacrylate [24, 25], and 3-(4-hydroxy-3,5-di-t-butylphenyl)-1-propene [26, 27], as well as 2-(4-hydroxy-3,5-di-t-butylphenyl)-1-t-alkylethylene [28].

During the 10 years since we started to work intensively in the area of polymerizable hindered and/or hydrogen-bonded phenolic stabilizers, work in our research group and in several other laboratories has centered on the use of 4-vinyl- (or 4-isopropenyl)-2,6-di-t-butylphenol.

The first good synthesis of 4-isopropenyl-2,6-di-t-butylphenol [29] and a method which is probably most suitable for larger-scale synthesis both are by base-catalyzed cleavage (75% yield) of 4,4'-isopropylidene-bis(2,6-di-t-butylphenol). The compound was also prepared by addition of methyl Grignard reagent to 4-hydroxy-3,5-di-t-butylacetophenone followed by dehydration or isomerization of 4-isopropylidene-2,6-di-t-butyl-2,5-cyclohexadienone [30, 31].

4-Vinyl-2,6-di-t-butylphenol was made initially from 3-(4-hydroxy-3,5-di-t-butylphenyl)acrylic acid by decarboxylation [32]. Often the O-acetyl compounds of 4-vinyl (or 4-isopropenyl)-2,6-di-t-butylphenol [31-34] were synthesized because it was believed that the vinyl or isopropenyl compounds could not polymerize with radical initiators [35, 36]. Indeed, some early and, at that time, very authoritative work seemed to confirm this presumption.

One route used methyl-(4-isopropenyl-2,6-di-t-butylphenyl) ether, another proceeded via O,4-diacetyl-2,6-di-t-butylphenol. This compound was either reduced, dehydrated, and deacetylated to 4-vinyl-2,6-di-t-butylphenol or allowed to react with methyl Grignard reagent followed by dehydration of the carbinol and deacetylation to 4-isopropenyl-2,6-di-t-butylphenol.

The patent literature [28] describes a process for preparing hindered alkenyl phenols which can be used for the synthesis of 4-vinyl and 4-isopropenyl derivatives; 2,6-di-t-butyl-4-acetoxyphenol as the starting material which was hydrogenated with copper chromite catalyst. The 4-(α-hydroxy)ethyl compound was treated with concentrated hydrochloric acid and gave the 4-(α-chloro)ethyl compound [2,6-di-t-butyl-4-(α-chloro)ethylphenol] which was dehydrochlorinated with pyridine. As the second route 2,6-di-t-butyl-4-ethylphenol was chlorinated directly to 2,6-di-t-butyl-4-(α-chloro)ethylphenol with elemental chlorine in carbon tetrachloride with a small amount of hydrogen bromide as the catalyst. The route to the 4-vinyl derivative of 2,6-di-t-butylphenol via the chlorine instead of the bromine substituent seems to avoid the necessity of protecting the free phenol hydroxyl group by acetylation and seems to be a potentially desirable method for large-scale preparations of this compound, possibly even of the 4-isopropyl derivative.

A detailed account of the background on polymer-bound antioxidants is given in Ref. 37.

It was the objective of this work to develop a good laboratory synthesis for 4-vinyl (or 4-isopropenyl)-2,6-di-t-butylphenol, to characterize the compounds well, and to study their polymerization and copolymerization with such resonance-stabilized monomers as styrene, methyl methacrylate, and n-butyl acrylate.

MATERIALS

Argon gas (Linde Division, Union Carbide Corp.) was purified by passing it through a column (40 cm long and 5 cm in diameter) packed with BTS catalyst which was heated to 150°C; this procedure yielded gas less than 1 ppm in oxygen. Argon thus purified is here referred to as "oxygen-free." Azobisisobutyronitrile (AIBN) (Aldrich Chemical Co.) was recrystallized twice from methanol and dried for 12 h at room temperature and 0.1 torr. Benzene (MCB Manufacturing Chemists) was heated to reflux over sodium-potassium amalgam and distilled. n-Butyl acrylate (Aldrich Chemical Co.) was washed with aqueous sodium hydroxide to remove inhibitors, dried, and distilled under nitrogen.

Cyclohexane (Aldrich Chemical Co.) was heated to reflux over calcium hydride for one day and distilled. To remove inhibitors, methyl methacrylate (Aldrich Chemical Co.) was distilled at 100°C at atmospheric pressure and stored under argon in the cold. Styrene (Aldrich Chemical Co.) was distilled at 44-45°C under aspirator vacuum to remove inhibitors, then stored under argon in the cold. Triethylamine (Ethyl Corporation) was heated to reflux over calcium hydride and distilled. All other reagents and solvents were used as received.

MEASUREMENTS

Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer. Low-molecular-weight crystalline samples were analyzed as potassium bromide pellets, while high-molecular-weight samples and low-molecular-weight oils were analyzed as films deposited from chloroform, cyclohexane, benzene, or o-xylene on a sodium chloride plate.

^{1}H-NMR spectra were recorded on a Varian T-60 60-MHz spectrometer and ^{13}C-NMR spectra on a Varian CFT-20 Fourier-transform spectrometer operating at 22.6 MHz. Sample concentrations were typically 20-40 w/v% in $CDCl_3$ or benzene-d_6. Several hundred transients were accumulated for low-molecular-weight samples, while polymer samples required at least 20 000 transients. Other parameters included a pulse delay of 0 to 15 s, a pulse width of 5 to 15 μs, and an acquisition time of 1.023 s.

Inherent viscosity measurements were made at 30°C using an Ubbelohde-type viscometer. Reported values are the averages of three runs. Solution concentrations were 0.5 g/dL in benzene.

Gel-permeation-chromatography measurements were performed on a Waters Associates Model 201 liquid chromatograph using tetrahydrofuran as solvent. The flow was 1.5 mL/min. The instrument was calibrated using a set of four narrow-distribution polystyrenes supplied by Pressure Chemicals and Waters Associates.

Melting points of low-molecular-weight samples were determined on a Melt-Temp capillary melting point apparatus and are uncorrected.

Microanalyses were performed by the Microanalytical Laboratory at the University of Massachusetts, Amherst, Massachusetts.

PREPARATION OF MONOMERS AND POLYMERIZATION OF O-ACETYL-2,6-DI-T-BUTYL-4-VINYLPHENOL

O-4-Diacetyl-2,6-di-t-butylphenol, O-acetyl-2,6-di-t-butyl-4-(1-hydroxyethyl)phenol, and O-acetyl-2,6-di-t-butyl-4-vinylphenol were prepared according to Hewgill [32]. The final product was purified by distillation through a very short column at reduced pressure; yield of O-acetyl-2,6-di-t-butyl-4-vinylphenol (collected at 138-140°C and 0.01 torr) was 90%. The colorless, viscous liquid slowly crystallized while stored at -5°C.

2,6-Di-t-butyl-4-vinylphenol. In a 500-mL round-bottom flask, O-acetyl-2,6-di-t-butyl-4-vinylphenol (41.0 g, 150 mmol) was dissolved in 250 mL of dry toluene, and lithium aluminum hydride (5.8 g, 15 mmol) was added. The gray solution was heated to reflux for several hours; excess lithium aluminum hydride was destroyed by adding 30 mL of ethyl acetate. The aluminum complex was then hydrolyzed by adding 100 mL of concentrated hydrochloric acid; the organic layer was separated and washed with three 70-mL portions of saturated aqueous sodium carbonate and then with water. The toluene solution was dried over magnesium sulfate, and the solvent was removed under reduced pressure; the yellow oil was distilled at 86-90°C and 0.4 torr and yielded 21.0 g (60%) of liquid 2,6-di-t-butyl-4-vinylphenol.

O-Acetyl-2,6-di-t-butyl-4(2-hydroxy-2-propyl)phenol. Into a 2-L, three-neck, round-bottom flask (fitted with a mechanical stirrer, a Claisen adapter carrying an argon inlet, a 1-L addition funnel, and a 25-mL septum-capped addition funnel) were placed magnesium turnings (5.60 g, 230 mmol) which had been ground in a mortar. The assembly was heated with a heat gun while under an argon atmosphere. Iodomethane (32.6 g, 230 mmol) was added in dry diethyl ether, and the methylmagnesium iodide Grignard reagent was prepared. After 30 min, after all the magnesium had dissolved, the 25-mL addition funnel was replaced by the argon inlet, and O-4-diacetyl-2,6-di-t-butylphenol (60.0 g, 210 mmol) dissolved in 1 L of dry ether was added. After the addition was complete, the reaction was heated to reflux and stirred for 4 h. The magnesium complex was hydrolyzed by dropwise addition of ammonium chloride (32 g in 100 mL water). The amber-colored organic layer was separated from the aqueous layer, and diethyl ether was removed on a rotary evaporator to yield a tan solid. The product was not purified further before dehydration to O-acetyl-2,6-di-t-butyl-4-isopropenylphenol. However, a ^1H-NMR ($CDCl_3$) of the crude product showed peaks at δ: 1.5 ppm ($C(C\underline{H}_3)_3$), 1.7 ppm ($HO\!-\!\overset{|}{C}(CH_3)_2$), 2.2 ppm ($COC\underline{H}_3$), 3.5 ppm ($O\underline{H}$), and 7.5 ppm (aromatic). The infrared spectrum (neat) showed peaks at 3 440 cm^{-1} (broad, hydrogen-bonded O–H stretch), 1 770 cm^{-1} (acetate C=O stretch), and 1 603 cm^{-1} (aromatic C=O stretch).

O-Acetyl-2,6-di-t-butyl-4-isopropenylphenol. Crude O-acetyl-2,6-di-t-butyl-4-(2-hydroxy-2-propyl)phenol (58 g) was placed in a 250-mL round-bottom flask; potassium hydrogen sulfate (1.5 g, freshly fused and ground) and powdered copper (0.1 g) were added as well as 60 mL of a mineral oil chaser. The mixture was stirred at 60°C and 0.2 torr until the end of dehydration was evident by the absence of violent bubbling in the reaction vessel. The dehydration product was then distilled from the same flask through a very short column. The product, a clear, viscous liquid, was collected between 130 and 140°C at 0.05 torr. The yield over two steps (Grignard reaction and dehydration) was 40 g (63%). The infrared spectrum (neat) showed peaks at: 1 770 cm^{-1} (acetate C=O stretch), 1 632 cm^{-1} (vinylidene C=C stretch), and 1 597 (aromatic C=C stretch). ^{13}C-NMR analysis ($CDCl_3$) showed peaks at: 21.90 ppm ($OCO\underline{C}H_3$); 22.47 ppm ($CH_2\!=\!\overset{|}{C}\!-\!\underline{C}H_3$); 31.45 ppm ($C(\underline{C}H_3)_3$); 35.37 ppm ($\underline{C}(CH_3)_3$); 112.12 ppm ($\underline{C}H_2\!=\!\overset{|}{C}\!-\!CH_3$); 123.59, 138.14, 143.37, and 147.46 ppm (aromatic); 141.85 ppm ($CH_2\underline{\overset{|}{C}}\!-\!CH_3$); and 170.69 ppm ($\underline{C}\!=\!O$). The ^1H-NMR ($CDCl_3$) spectrum displayed peaks at δ: 1.3 ppm ($C(C\underline{H}_3)$, 18H); 2.0 ppm ($CH_2\!=\!\overset{|}{C}\!-\!C\underline{H}_3$, 3H); 2.2 ppm ($COC\underline{H}_3$, 3H); 4.8 and 5.1 ppm ($C\underline{H}_2\!=\!\overset{|}{C}\!-\!CH_3$, 2H); and 7.2 ppm (aromatic, 2H).

Analysis: Calculated for $C_{19}H_{28}O_2$: C, 79.12; H, 9.78%. Found: C, 79.32; H, 10.74%.

2,6-Di-t-butyl-4-isopropenylphenol. O-Acetyl-2,6-di-t-butyl-4-isopropenylphenol (20.2 g, 70 mmol) was dissolved in 125 mL of dry toluene. The solution was added to a 500-mL round-bottom flask, followed by lithium aluminum hydride (2.7 g, 70 mmol). The gray solution was heated to reflux for several hours; after the normal workup, the toluene solution was evaporated to dryness under reduced pressure, leaving a light-yellow oil. Distillation of the oil at 92-94°C and 0.05 torr yielded 11.2 g (74%) of liquid 2,6-di-t-butyl-4-isopropenylphenol, which was stored under argon at -5°C where it slowly crystallized [5].

2,6-Di-t-butyl-4-acetylphenol. 2,6-Di-t-butylphenol (52 g, 250 mmol), acetic anhydride (30 mL, 300 mmol), and boron trifluoride etherate (40 mL) were kept at 5°C for 7 days. After work-up and recrystallization from EtOH/H_2O, a faintly orange material was obtained (19.4 g, 30%, mp 150-151.5°C). Infrared analysis (KBr) showed peaks at 3 595 cm^{-1} (hindered phenol O–H stretch) and 1 670 cm^{-1} (methyl phenyl ketone C=O stretch). The ^{13}C-NMR spectrum ($CDCl_3$) showed peaks at 26.27 ppm ($-CO\underline{C}H_3$); 30.15 ppm ($C(\underline{C}H_3)_3$); 34.37 ppm ($\underline{C}(CH_3)_3$); 126.09 ppm, 129.17 ppm, 135.82 ppm, and 158.43 ppm (aromatic), and 197.53 ppm ($-\underline{C}OCH_3$). ^{1}H-NMR analysis ($CDCl_3$) showed resonance at δ: 1.5 ppm ($C(C\underline{H}_3)_3$), 18H); 2.6 ppm ($COC\underline{H}_3$, 3H); 2.9 ppm (O$\underline{H}$, 1H); and 8.1 ppm (aromatic, 2H).

Analysis: Calculated for $C_{16}H_{24}O_2$; C, 77.38; H, 9.74%. Found: C, 77.21; H, 9.86%.

Polymerization of O-Acetyl-2,6-di-t-butyl-4-vinylphenol in Solution. A polymerization tube was charged with O-acetyl-2,6-di-t-butyl-4-vinylphenol (0.96 g, 3.5 mmol), dry benzene (3 mL), and AIBN (30 mg, 0.18 mmol, 5 mol%). The tube was degassed by the freeze-thaw technique and sealed at 0.01 torr. After 3 days at 70°C the polymer was precipitated by adding the tube contents to 250 mL methanol. The product was collected on a sintered-glass funnel and dried at 80°C and 0.025 torr to yield 0.89 g (93%) of a fine white powder. The inherent viscosity of the polymer (0.5% in benzene, 30°C) was 0.29 dL/g. The infrared spectrum (film) showed bands at 1 769 cm^{-1} (C=O stretch) and 1 596 cm^{-1} (aromatic C=C stretch). The ^{13}C-NMR spectrum ($CDCl_3$) showed peaks at: 22.63 ppm ($CO\underline{C}H_3$), 31.73 ppm ($C(\underline{C}H_3)_3$), 35.12 ppm ($\underline{C}(CH_3)_3$), 124.8 to 145.6 ppm (aromatic), and 170.10 ($O\underline{C}OCH_3$). ^{1}H-NMR showed peaks at δ: 1.1 ppm ($C(C\underline{H}_3)_3$), 2.2 ppm ($COC\underline{H}_3$), and 6.4 ppm (aromatic).

Analysis: Calculated for $(C_{18}H_{26}O_2)_n$: C, 78.79; H, 9.55%. Found: C, 78.25; H, 9.19%.

Copolymerization of O-Acetyl-2,6-di-t-butyl-4-vinylphenol with Methyl Methacrylate in Solution. A polymerization tube was charged with O-acetyl-2,6-di-t-butyl-4-vinylphenol (0.64 g, 2.3 mmol), methyl methacrylate (0.70 g, 7.0 mmol), dry benzene (4.8 mL), and AIBN (30 mg, 0.18 mmol, 2 mol%). The tube was degassed by the freeze-thaw technique and sealed at 0.01 torr. After 3 days at 70°C the contents of the tube had formed a solid plug. The plug was dissolved in benzene (20 mL), and the polymer was precipitated by slow addition of the solution to 250 mL methanol. The product was collected on a sintered-glass funnel and dried at 80°C (0.025 mm) for 12 h to yield 1.13 g (84%) of a white polymer. The inherent viscosity of the polymer (0.5% in benzene, 30°C) was 0.35 dL/g. The infrared spectrum (film) showed bands at 1 597 cm^{-1} (methacrylate C=O stretch), and 1 768 cm^{-1} (acetate C=O stretch). The ^{13}C-NMR spectrum (CDCl_3) showed peaks at: 17.99 ppm ($-\overset{\overset{\text{CO}}{|}}{\text{C}}-\underline{\text{C}}\text{H}_3$), 50.93 ppm ($-\text{O}\underline{\text{C}}\text{H}_3$), 126-145 ppm (aromatic), 171.3 ppm ($\text{O}\underline{\text{C}}\text{OCH}_3$), and 177.5 ppm ($\underline{\text{C}}\text{O}_2\text{CH}_3$).

The ^{1}H-NMR spectrum showed δ: 0.4-2.0 ppm (backbone $\text{C}\underline{\text{H}}_2$, $\text{C}\underline{\text{H}}$); 1.2 ppm ($\text{C}(\text{C}\underline{\text{H}}_3)_3$); 2.2 ppm ($\text{OCOC}\underline{\text{H}}_3$); 2.8 ppm ($\text{CH–C}\underline{\text{H}}_3$); 3.5 ($\text{OC}\underline{\text{H}}_3$); and 6.7 ppm (aromatic).

Analysis: Calculated for $-\!(\text{C}_{16}\text{H}_{26}\text{O}_2)_{\overline{0.46}}(\text{C}_5\text{H}_8\text{O}_2)_{\overline{0.54}}$: C, 68.63; H, 8.74%. Found: C, 68.82; H, 8.66%.

Copolymerization of 2,6-Di-t-butyl-4-isopropenylphenol with n-Butyl Acrylate in Solution. A polymerization tube was fitted with a high-vacuum three-way stopcock, and one take-off of the stopcock was capped with a septum. The tube was flushed with argon, and 2,6-di-t-butyl-4-isopropenylphenol (0.25 g, 1 mmol) dissolved in dry benzene (1.0 mL) was added by syringe. n-Butyl acrylate (1.30 g, 10 mmol) was added in the same manner, as was AIBN (3.2 mg, 0.02 mmol, 0.2 mol%) dissolved in benzene (1 mL), and the tube was sealed at 0.01 mm. It was placed in an oil bath at 70°C; after 3 days the polymer was isolated by pouring the contents of the tube into 250 mL methanol. The suspension which resulted was allowed to coalesce on the walls of the vessel. The supernatant liquid was decanted, and the sticky polymer was redissolved in benzene. Freeze-drying gave a tacky, water-white film of polymer, which was dried further at room temperature and 0.05 torr for 18 h; yield 0.62 g (40%). The inherent viscosity of the polymer (0.5% in benzene, 30°C) was 0.04 dL/g. The infrared spectrum (neat) displayed peaks at 3 450 cm^{-1} (O–H stretch) and 1 745 cm^{-1} (ester C=O stretch). ^{1}H-NMR (CHCl_3) showed peaks at δ: 0.8-1.6 ppm ($\text{O–CH}_2\text{–C}_3\underline{\text{H}}_7$ and backbone protons), 1.5 ppm ($\text{C}(\text{C}\underline{\text{H}}_3)_3$), 2.2 ppm ($-\text{C}\underline{\text{H}}_3$ pendant group), 4.1 ppm ($\text{O–C}\underline{\text{H}}_2-$), 5.0 ppm ($-\text{O}\underline{\text{H}}$), and 7.0 ppm (aromatic). Comparison of peak areas at 4.1 and 7.0 ppm indicated a copolymer composition of 40% 2,6-di-t-butyl-4-isopropenylphenol and 60% n-butyl acrylate.

Analysis: Calculated for $-\!(\text{C}_{17}\text{H}_{26}\text{O})_{\overline{0.48}}(\text{C}_7\text{H}_{12}\text{O}_2)_{\overline{0.52}}$: C, 73.89; H, 10.02%. Found: C, 73.84; H, 11.03%.

Copolymerization of 2,6-Di-t-butyl-4-isopropenylphenol with Styrene in Solution. A polymerization tube was charged with 2,6-di-t-butyl-4-isopropenylphenol (0.25 g, 1 mmol) dissolved in freshly distilled styrene (1.2 g, 10 mmol), AIBN (3.2 mg, 0.02 mmol, 0.2 mol%) in dry benzene (1.0 mL), and the tube was sealed at 0.01 torr. After 3 days in a 70°C oil bath the tube was opened and the polymer was precipitated in 200 mL methanol. The product was collected by filtration and dried for 12 h at 60°C and 0.1 torr to yield 0.32 g (22%). The inherent viscosity of the polymer (0.5%

in benzene, 30°C) was 0.23 gL/g. Infrared analysis of the copolymer (film) showed bands at 3 640 cm^{-1} (hindered phenol O–H stretch), 3 100-3 000 cm^{-1} (aromatic C–H stretch), 2 980-2 840 cm^{-1} (aliphatic C–H stretch), 1 950-1 740 cm^{-1} (styrene overtone and combination bands), 1 601 cm^{-1} (styrene C=C stretch), and 1 595 cm^{-1} (C=C stretch of 2,6-di-t-butylphenyl group). ^{1}H-NMR ($CDCl_2$) showed peaks at δ: 0.8-2.2 ppm (backbone protons), 1.4 ppm ($C(C\underline{H}_3)_3$), 5.0 ppm (–O$\underline{H}$), 7.1 ppm (aromatic protons of styrene), and 6.6 ppm (aromatic protons of 2,6-di-t-butyl-4-isopropenylphenol).

Analysis: Calculated for $-(C_{17}H_{26}O)_{0.18}(C_8H_8)_{0.82}$: C, 90.56; H, 8.26%. Found: C, 90.56; H, 8.23%.

Copolymerization of 2,6-Di-t-butyl-4-isopropenylphenol with Styrene in Emulsion. A polymerization tube was charged with distilled water (6 mL), polyethylene glycol (MW = 1 000) emulsifier (0.1 mL), sodium dodecyl sulfate emulsifier (10 mg), and sodium hydroxide (3 mg). Argon, deoxygenated through an Oxy-Trap, was bubbled through the solution for 30 min. The tube was then charged with 2,6-di-t-butyl-4-isopropenylphenol (0.25 g, 1 mmol) which had been dissolved in freshly distilled styrene (2.4 g, 20 mmol). Potassium persulfate initiator (70 mg, 0.2 mmol, 1 mol%) and a stirring bar were added, the tube was closed with a septum, and an argon atmosphere was maintained. The contents of the tube were stirred rapidly at 50°C for 48 h. The latex in the tube was coagulated by addition of 10% aqueous lithium chloride solution (1 mL) and concentrated hydrochloric acid (2 mL). On shaking the tube, clumps of polymer were formed which were collected by filtration. The polymer was reprecipitated from benzene into methanol and filtered; yield 0.12 g (5%).

Preparation of Polymers of 2,6-Di-t-butyl-4-isopropenylphenol. A solution copolymerization of 2,6-di-t-butyl-4-isopropenylphenol with styrene gave a yield of 22%, and the polymer had an inherent viscosity of 0.23 dL/g.

The IR and ^{1}H spectra showed that the 2,6-di-t-butyl-4-isopropenylphenol was incorporated in the copolymer. A feed ratio of 10:1 styrene: phenol gave a polymer composition of 82:18 styrene:phenol.

A comparison of copolymerizations of blocked and free hindered phenols appears in Table 1. These data clearly indicate that, while polymerization is able to proceed in the presence of the free hindered-phenol monomers when oxygen is excluded, the polymers produced are obtained in lower yield and are of lower molecular weight than polymers incorporating blocked hindered phenols.

RESULTS AND DISCUSSION

For the preparation of 2,6-di-t-butyl-4-vinylphenol and O-acetyl-2,6-di-t-butyl-4-vinylphenol, 2,6-di-t-butylphenol was subjected to simultaneous Friedel-Crafts O-acylation and C-acylation at the 4-

TABLE 1. Copolymerizations[a] of O-Acetyl-2,6-di-t-butyl-4-vinylphenol with Methyl Methacrylate

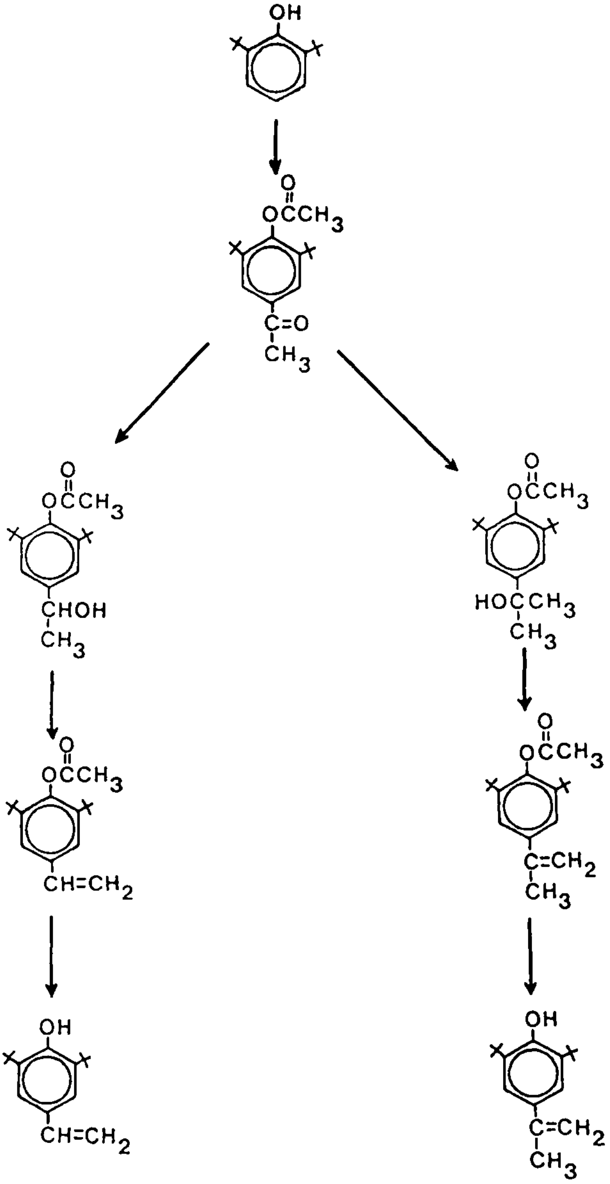
Methyl methacrylate		O-Acetyl-2,6-di-t-butyl-4-vinylphenol		
g	mmol	g	mmol	$\overline{M}_n$
0.80	8.0	0.55	2.0	46 900
0.60	6.0	0.10	4.0	36 200
0.40	4.0	1.64	6.0	37 400
0.20	2.0	2.19	8.0	28 200

[a] Polymerizations carried out at 70°C for 16 h, using 0.5 mol% AIBN.

position with 5 equiv aluminum chloride and excess acetyl chloride as solvent. Reduction of the methyl ketone with sodium borohydride in ethanol and dehydration of the resulting alcohol gave O-acetyl2,6-di-t-butyl-4-vinylphenol in about 80% yield. This compound could be most effectively isolated by vacuum distillation through a very short column (138-140°C and 0.01 torr); it crystallized slowly, especially when cooled to -5°C. Further purification of O-acetyl-2,6-di-t-butyl-4-vinylphenol prior to polymerization was achieved by distillation at 90-100°C and 0.025 torr.

Lithium aluminum hydride (LAH) was used to cleave the acetate ester. The reaction was carried out in toluene, a high-boiling solvent which readily dissolved O-acetyl-2,6-di-t-butyl-4-vinylphenol provided yields of up to 60%. The liquid product was collected at 86-90°C and 0.4 torr, and solidified when stored at -5°C.

2,6-Di-t-butyl-4-isopropenylphenol was synthesized in an overall yield of 43%. The key intermediate was O,4-diacetyl-2,6-di-t-butylphenol. Grignard reaction with methylmagnesium iodide gave the tertiary carbinol. It was thought that, by using two or more equivalents of Grignard reagent, the O-acetyl group might be cleaved while the methyl ketone was being reacted. However, the steric hindrance presented by the two ortho-t-butyl groups imposed a severe barrier to this cleavage. Even a fivefold excess of the Grignard reagent resulted in only a 10% cleavage of the O-acetate group as determined by ^{1}H-NMR. The crude propanol was dehydrated directly, without purification, over potassium hydrogen sulfate and then distilled to yield 63% (two steps) of O-acetyl-2,6-di-t-butyl-4-isopropenylphenol. The details of the reaction are the same as those for the vinyl compound. Cleavage of the ester group by LAH was used to obtain 2,6-di-t-butyl-4-isopropenylphenol in 74% yield:



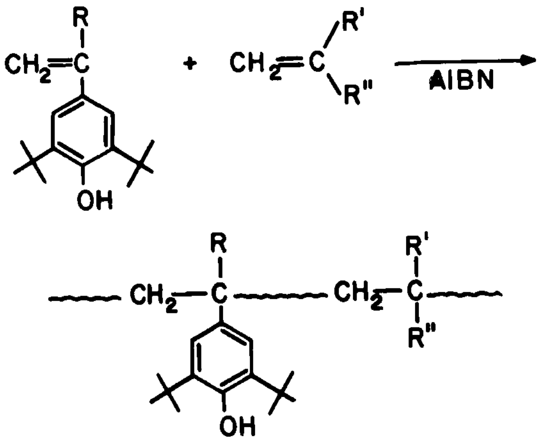
The monomer synthesis routes used in this work were chosen because the first intermediate, O,4-diacetyl-2,6-di-t-butylphenol, provided access to both the vinyl and the isopropenyl monomers. This route also provided both monomers in blocked, acetylated form, which was desirable for comparative studies of reactivity in emulsion polymerization and in the study of chain transfer reactions [37].

Monoacylation of 2,6-di-t-butylphenol in the 4-position was accomplished in 30% yield by reaction in an ether solution with acetic anhydride with boron trifluoride etherate catalyst at 5°C for several days. This product clearly could have provided both 2,6-di-t-butyl-4-vinylphenol and 2,6-di-t-butyl-4-isopropenylphenol by borohydride reduction and Grignard reaction, respectively, followed by dehydration, but overall yields were low.

As one of two methods potentially providing shorter routes to 2,6-di-t-butyl-4-isopropenylphenol, alkylation of 2,6-di-6-butylphenol with propylene oxide and aluminum trichloride was investigated, but the desired product, 2-(4-hydroxy-3,5-di-t-butylphenyl)-1-propanol, which would yield our monomer after dehydration, was not obtained. A short time after this investigation had been completed, an article by Layer [38] appeared which described the alkylation of 2,6-di-t-butylphenol with propylene oxide using basic catalysts at 220°C. Using this technique, 2,6-di-t-butyl-4-vinylphenol could be made in two steps (alkylation and dehydration) from 2,6-di-t-butylphenol, but a separation of the products of C- and O-alkylation (4:1 ratio) would be necessary, and yields of the proper products were expected to be low.

The polymerization of O-acetyl-2,6-di-t-butyl-4-vinylphenol proceeded at a reasonable rate and in good yield with AIBN as the generator for the initiating radicals. A series of copolymerizations with methyl methacrylate was carried out, and the yield of polymer was determined as a function of time. The results of the copolymerization experiments of O-acetyl-t-butyl-4-vinylphenol with methyl methacrylate are described in Table 1.

Homopolymerization of O-acetyl-2,6-di-t-butylphenol gave 93% conversion after 1.5 days at 70°C; the inherent viscosity of the polymer was 0.29 dL/g. Copolymerization of the same monomer with methyl methacrylate (1.5 days, 70°C) yielded the copolymer in 85% yield with an inherent viscosity of 0.35 dL/g:



R = H, CH_3
R' = H, CH_3
R'' = $COOCH_3$, C_6H_5

Polymerization and copolymerization of the free-phenol monomer 2,6-di-t-butyl-4-vinylphenol required the stringent elimination of oxygen during the entire polymerization reaction. Numerous methods of removing oxygen from the polymerization medium were explored before success was achieved. Repeated freeze-thaw cycles proved adequate for polymerizations in solution, because molecular oxygen or oxygen radicals which can react with a growing polymeric carbon radical or oxygen radicals are readily terminated with the hydrogen of the free hydroxyl group of the 2,6-di-t-butylated phenols monomer. When peroxy radicals of persulfate were used as initiator, they were found to react also with the phenolic hydroxyl groups of the hindered phenol monomer in the system, causing inhibition of the polymerization. To circumvent this problem in emulsion polymerizations (to be described in a subsequent publication), water-soluble azo initiators had to be chosen as generator for the initiating radicals.

2,6-Di-t-butyl-4-isopropenylphenol, as an α-methylstyrene derivative with a presumably low ceiling temperature of polymerization, as expected, did not homopolymerize. The copolymerization of 2,6-di-t-butyl-4-isopropenylphenol and n-butyl acrylate was studied in benzene solution using AIBN as initiator. The polymerization tube was flushed with prepurified argon gas, degassed by several freeze-thaw cycles, and sealed. After 3 days at 70°C the yield of polymer was 40% with an inherent viscosity of 0.04 dL/g. Since work-up of the n-butyl acrylate copolymers was difficult, further copolymerization studies of 2,6-di-t-butyl-4-isopropenylphenol were carried out with styrene as the comonomer.

Solution polymerization of 2,6-di-t-butyl-4-isopropenylphenol with styrene gave a 22% yield of a copolymer with an inherent viscosity of 0.23 dL/g. The infrared spectrum and the ^{1}H-NMR spectrum showed incorporation of the 2,6-di-t-butyl-4-isopropenylphenol into the copolymer. A feed ratio of 10:1 styrene:2,6-di-t-butyl-4-isopropenylphenol gave a copolymer composition of 82:18 styrene:2,6-di-t-butyl-4-isopropenylphenol. Copolymerization of styrene and 2,6-di-t-butyl-4-isopropenylphenol was also carried out by radical polymerization in emulsion. A mixture of a nonionic (PEG 1000) and an anionic (sodium dodecyl sulfate) emulsifier was used, and the tube was flushed free of oxygen with highly purified argon gas. Since persulfate radicals generated by thermal decomposition of potassium persulfate were used as initiators for the copolymerization, it was expected that the yield would be low, and indeed a yield of only 5% of copolymer was obtained. The results of polymerization experiments with O-acetylated and copolymerization experiments of free hydroxyl hindered phenol copolymers with styrene, methyl methacrylate, and n-butyl acrylate are shown in Table 2.

TABLE 2. Polymerizations of Blocked and Free Hindered-Phenol Monomers with Styrene, Methyl Methacrylate, and n-Butyl Acrylate

Hindered-phenol monomer	Amount		Comonomer	Amount		Reaction time, d	Temperature, °C	Medium[a]	Yield, %	η_{inh}, 30°C, dL/g
	g	mmol		g	mmol					
O-Acetyl-2,6-di-t-butyl-4-vinylphenol	0.96	3.5	-	-	-	1.5	70	S	93	0.29
O-Acetyl-2,6-di-t-butyl-4-vinylphenol	0.64	2.3	Methyl methacrylate	0.70	7.0	1.5	70	S	84	0.35
O-Acetyl-2,6-di-t-butyl-4-vinylphenol	0.55	2.0	Styrene	2.4	20.0	1.1	50	E	74	0.32
2,6-Di-t-butyl-4-isopropenylphenol	0.25	1.0	n-Butyl acrylate	1.3	10.0	3.0	70	S	40	0.04
2,6-Di-t-butyl-4-isopropenylphenol	0.25	1.0	Styrene	1.2	10.0	3.0	70	S	22	0.23
2,6-Di-t-butyl-4-isopropenylphenol	0.25	1.0	Styrene	2.4	20.0	2.0	50	E	5	-

[a] S = solution, E = emulsion.

ACKNOWLEDGMENT

The work presented in this paper was supported by the Dow Chemical Company, Midland, Michigan, and in part by funds from the National Science Foundation given to the Materials Research Laboratory of the University of Massachusetts, Amherst, Massachusetts. The content of this paper is part of the PhD thesis of P. Grosso, University of Massachusetts, 1983. We would like to express our appreciation to E. Cary for her assistance in preparing this manuscript.

REFERENCES

[1] J. Shelton, "Stabilization Against Thermal Oxidation," in Polymer Stabilization (W. L. Hawkins, ed.), Wiley-Interscience, New York, 1972.

[2] G. Scott, "New Developments in the Mechanistic Understanding of Antioxidant Behavior," in Long-Term Properties of Polymers and Polymeric Materials (B. Ranby and J. Rabek, eds.), Wiley, New York, 1979.

[3] K. Ingold, "The Inhibition of Autoxidation by Phenols," in Essays on Free-Radical Chemistry (R. Norman, ed.), Chemical Society, London, 1970.

[4] T. Ryan, R. Calvert, and N. Billingham, "The Distribution of Additives and Impurities in Isotactic Polypropylene," in Stabilization and Degradation of Polymers (D. Allara and W. L. Hawkins, eds.), American Chemical Society, Washington, D.C., 1978.

[5] G. Odian, Principles of Polymerization, 2nd ed., Wiley-Interscience, New York, 1981, p. 248.

[6] D. Bailey and O. Vogl, J. Macromol. Sci.–Rev. Macromol. Chem., C14(2), 267 (1976).

[7] M. E. Cain, G. T. Knight, P. M. Lewis, and B. Saville, J. Rubber Res. Inst., Malaya (1968).

[8] C. de Jonge, G. Hoentjen, V. Ershon, and G. Nikiforov, Makromol. Chem., 180, 1077 (1979).

[9] M. Gillies, Stabilizers for Synthetic Resins, Noyes, Park Ridge, New Jersey, 1981, pp. 245ff.

[10] G. Scott, U.S. Patent 4,213,892 (1980).

[11] M. Gillies, Stabilizers for Synthetic Resins, Noyes, Park Ridge, New Jersey, 1981, pp. 248ff.

[12] C. Parks, U.S. Patent 4,158,955 (1979).

[13] A. Spasskova and G. Egorova, Vestn. Leningr. Univ., Fiz. Khim., 2, 155 (1977); Chem. Abstr., 87, 153151w (1977).

[14] N. Domnina, L. Gorokhova, and V. Shagov, Zh. Prikl. Khim. (Leningrad), 55(4), 884 (1982); Chem. Abstr., 97, 183709h (1982).

[15] M. Fernando, G. Scott, and J. Stuckey, J. Rubber Res. Inst., Sri Lanka, 54(2), 531 (1977); Chem. Abstr., 91, 92718v (1979).

[16] K. Russell and L. Vail, U.S. Patent 4,107,144 (1978).

[17] T. Tomatsu, T. Iwata, and H. Furuta, Japanese Kokai 76 136,784; Chem. Abstr., 86, 12235n (1977).

[18] T. Tomatsu, H. Furuta, and T. Iwakuni, Japanese Kokai 76 136,781; Chem. Abstr., 86, 12235m (1977).

[19] M. Kato, Japanese Kokai 72 39,496; Chem Abstr., 78, 112141p (1973).

[20] Y. Tanaka, M. Kato, and N. Usami, Japanese Kokai 76 125,480; Chem. Abstr., 86, 73683k (1977).

[21] R. Kline, U.S. Patent 4,152,319 (1979).

[22] R. Kline, U.S. Patent 4,097,464 (1978).

[23] D. K. Parker, U.S. Patent 4,091,225 (1978).

[24] D. K. Parker, U.S. Patent 4,029,713 (1977).

[25] D. K. Parker, U.S. Patent 3,989,741 (1976).

[26] H. Yamada and Y. Taniide, Japanese Kokai 74 19,270 (1974); Chem. Abstr., 82, 139653b (1975).

[27] R. Layer and L. Tenney, European Patent Application 48,439 (1982); Chem. Abstr., 97, 24746b (1982).

[28] D. K. Parker, U.S. Patent 4,072,724 (1978).

[29] J. Kohovec, H. Pivcova, and J. Pospisil, Collect. Czech. Chem. Commun., 36, 1986 (1971).

[30] J. Pospisil, M. Pisova, M. Soucek, and O. Exner, Ibid., 40, 2093

[31] D. Braun and B. Meier, Angew. Chem., Int. Ed. Eng., 10, 566 (1971).

[32] F. Hewgill and W. Smith, J. Polym. Sci., Polym. Lett. Ed., 14, 463 (1976).

[33] D. Braun and W. Wittig, Makromol. Chem., 181, 557 (1980).

[34] H. Suda, S. Kanoh, H. Hasegawa, and M. Motoi, Kanagawa Daigaku Kogakubo Kiyu, 15(1), 71 (1982); Chem. Abstr., 97, 197910d (1982).

[35] D. Braun and B. Meier, Makromol. Chem., 167, 119 (1973).

[36] D. Braun and B. Meier, Ibid., 175, 791 (1974).

[37] P. Grosso, PhD Dissertation, University of Massachusetts, Amherst, Massachusetts, 1983.

[38] R. Layer, J. Org. Chem., 46, 5224 (1981).

Received August 9, 1985
Revision received October 15, 1985